ABSTRACT

MORROW, KAREN STEELE. Atrazine Efficacy and Interactions With Poultry Litter. (Under the direction of Richard Allen McLaughlin.)

The purpose of this study has been to investigate interactions between soil, poultry litter and atrazine (2-chloro-4-ehtylamino-6-isopropylamino-1,3,5-triazine). Consideration was given to atrazine efficacy, leaching and sorption when applied in conjunction with poultry litter. Application of recommended amounts of poultry litter increased the average mass of oats and soybeans and the application of atrazine increased soybean chlorosis and oat fatality. Leachate from pots that had atrazine applied in conjunction with composted and weathered poultry litter was collected and analyzed for atrazine, DIA (2-chloro-4-ethylamino-6-amino-1,3,5-triazine) and desethylatrazine or DEA (2-chloro-4-amino-6-isopropyl-amino-1,3,5-triazine), using solid phase extraction and GC-MS. Greater amounts of poultry litter significantly increased the amount of leachate from the pots and the amount of leached atrazine was dependent on leachate volume. The sorption of atrazine onto soil and poultry litter was measured through a batch adsorption experiment and Freundlich (K_f) adsorption constants were calculated. Stockpiled litter at the recommended rate (1X) had the lowest Kf (0.68) followed by soil (1.06), 3X stockpiled litter and soil (1.17), 1X weathered litter and soil (1.20), 3X weathered litter and soil (1.93), stockpiled litter (17.65), and weathered litter (33.76).

ATRAZINE EFFICACY AND INTERACTIONS WITH POULTRY LITTER

by

KAREN STEELE MORROW

A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Master of Science

SOIL SCIENCE

Raleigh

2002

APPROVED BY:

BIOGRAPHY

Karen Steele Morrow is the daughter of Jeffry J. Steele, a high school science teacher, and Dr. Susan H. Steele, a veterinarian. She was born in Framingham, Massachusetts on August 26, 1973. Karen grew up in Massachusetts with visits to both sets of grandparents in New York City and on a farm in Indiana. Her involvement in the Girl Scouts and encouragement in science propelled her to study ways that she might make a difference in the environment. Karen graduated from Framingham North High School in 1991 and pursued a Bachelor of Science in Natural Resources and Environmental Sciences at Purdue University in West Lafayette, Indiana and graduated with honors in 1995. During her four years at Purdue Karen was involved with the band program, and many of the School of Agriculture's outreach and recruiting programs. Karen began her studies at North Carolina State University in July of 1995. Karen was married to Jeffrey Carlton Morrow in 1999.

ACKNOWLEDGEMENTS

I would like to thank the lab and field technicians that helped me to complete the research; Byron Johnson, Craig Baird, Mark Hughes, and Holly Taj. Thank you to my committee for allowing me to defend and finish despite the length of time; Dr. McLaughlin, Dr. Mikkelsen, and Dr. York.

I would like to thank my family for their continuous support especially my parents Susan and Jeffry Steele.

Lastly I want to thank my husband Jeffrey Morrow, without whose encouragement, confidence and unending patience I would have given up long ago. His never ending support allowed me to continue to finishing writing my thesis without worry, he patiently read for grammar and spelling mistakes, listened to me work my way through problems out loud and was always there to hold me up.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Corn fields receiving poultry litter have been reported to have more severe weed problems than fields not receiving litter. This has caused concern among farmers about the efficacy of herbicides used in conjunction with poultry litter. This study was intended to determine if atrazine efficacy was affected by poultry litter applications through accelerated degradation and enhanced adsorption.

Characteristics of Poultry Litter

The poultry industry in North Carolina is rapidly growing, and as the production of birds increases so does the amount of waste that must be disposed. North Carolina consistently ranks within the top five poultry-producing states adding approximately 1,000,000 birds from 1994 to 1995 (NCDA 1995). North Carolina is currently the largest turkey producing state (NCDA 1996). In 1994 poultry production contributed 28.3% of the 6.4 billion dollars of revenue to North Carolina agriculture (NCDA 1996). This tremendous amount of poultry production leads to the increasing problem of where to dispose of the poultry litter, made up of bedding; typically wood chips or peanut hulls, and manure from the birds. In 1990 North Carolina produced $1.496*10^6$ Mg (12% of the manure in the United States) of poultry manure and ranked second in total amount of poultry manure produced (Moore *et al.* 1995). The current best management practice for disposing of poultry litter is using litter as a fertilizer source for crops (Zublena *et al.* 1993). Ninety percent of the poultry litter produced is land-applied with application rates based on the nutrient requirements for the crop and the nutrient availability of the litter (Moore *et al.* 1995). Poultry litter is generally applied within 6 to 12 miles of production sites (Moore *et al.* 1995).

Poultry litter contains the macronutrients nitrogen, phosphorus, and potassium as well as the micronutrients: Ca, Mg, S, Na, Fe, Mn, B, Mo, Zn, and Cu. Nitrogen is available in several forms from the litter; the primary being ammonium (NH_4^+) that is derived from the uric acid in the litter (Zublena *et al.* 1993). An accumulation of potassium, phosphorus, calcium and magnesium was found in soils that received long-term applications of poultry litter (Kingery *et al.* 1993).

Originally, an explanation for the increased weed pressure was that weed seeds were present in the poultry litter. Zublena *et al.* (1995) studied the effects of broiler litter, urea, and urea and diammonium phosphate and a control on weed germination. Pots were filled with sterile soil (fritted clay) and poultry litter (equivalent to 14.5 and 29 Mg ha^{-1}), then half were inoculated with spiny amaranth (*Amaranthus spinosa*), pitted morning-glory (*Ipomoea* *lacunosa L.*), sicklepod (*Cassia obtusifola*), and large crabgrass (*Digitaria sanguinalis*). No weeds emerged in the non-inoculated pots after 6 weeks of incubation. Crabgrass and spiny amaranth germination and growth were inhibited by some sources of litter, and litter actually killed or prevented germination at a high rate of 32 grams per kilogram of soil. This litter toxicity was attributed to free ammonia.

No difference in the populations of any weed species were found when poultry litter, litter by-products, commercial fertilizers, and a control were compared (Parsons *et al.* 1992). Poultry litter treatments were applied to soils that had been fumigated to destroy weed seeds and to non-fumigated controls. Weed species were counted and identified after three weeks of growth.

Possible Effects of Poultry Litter on Soil

Poultry litter added to fields can greatly alter physical and chemical soil properties, including microbial content, organic matter content, and pH.

Poultry litter can increase the amount of soil organic matter which in turn increases soil water-holding capacity, water infiltration rates, cation exchange capacity, and structural stability (Moore *et al.* 1995). Long-term application of poultry litter to fescue (*Festuca arundinacea*) pastures increased organic matter content from 1.84 to 2.36% (Kingery *et al.* 1993). Organic fertilizer treatments can increase soil microbial activity that would lead to an increased degradation of herbicides (Rouchard *et al.* 1996). Litter increased the pH by approximately 0.5 unit in fescue pastures (Kingery *et al.* 1993). Chicken manure was shown to be as effective as $Ca(OH)_2$ in increasing soil pH for a highly weathered ultisol (Hue 1992).

Characteristics of Atrazine

Atrazine (2-chloro-4-ehtylamino-6-isopropylamino-1,3,5-triazine) is a weakly basic triazine herbicide (Aherns 1994). The degradation products of atrazine include hydroxyatrazine (2-hydroxy-4-ethylamino-6-isopropylamino-1,3,5-triazine), desisopropylatrazine (2-chloro-4-ethylamino-6-amino-1,3,5-triazine; DIA) and desethylatrazine (2-chloro-4-amino-6-isopropyl-amino-1,3,5-triazine; DEA) (Aherns 1994).

Atrazine is commonly applied as a suspension using a mechanical sprayer. Application rates are based on the crop and soil texture. Recommended rates for coarse sandy soils are 1.78 kg a.i. ha^{-1}. Recommended rates for fine and medium textured soils are 2.67 kg a.i.ha^{-1} and 2.11 kg a.i. ha^{-1}. The highest recommended rate for atrazine application is on organic soils including peat, muck and high organic clay at 2.67 kg a.i. ha^{-1} . It is recommended that on organic soils only post-emergent applications are used (Syngenta 2001).

Factors affecting atrazine degradation are pH, soil type, addition of organic amendments, soil moisture, and pesticide concentration. Atrazine hydrolysis, or transformation to hydroxyatrazine, is chiefly a surface-catalyzed reaction. Atrazine degradation is dominated by chemical degradation at both moderately acidic and neutral pH, but microbial decomposition is more significant at soil pH near neutral (Blumhorst *et al.* 1994).

Detection of atrazine in groundwater has been well documented nationwide (Fleming *et. al.* 1992; Wietersen *et. al.* 1993). Pesticide leaching potential (PLP) for many different herbicides and soil leaching potentials (SLP) for a variety of North Carolina soils have been developed (Weber 1991). The leaching potentials are normalized to 0 to 100%. For atrazine, the leaching potential is pH dependent. When surface applied on crops, the PLP for atrazine is 60% at pH 7 and 52% at pH 5. The pesticide leaching potential is a function of the half-life, rate of application, and the affinity of the pesticide for soil organic matter. Application of litter may raise the soil pH, increasing the potential for atrazine leaching into ground water. SLPs are dependent on soil organic matter content, soil texture, and pH. The sandy Coastal Plain soils such as Lakeland sand (SLP 88) and Norfolk sands (SLP 74) have very high leaching potentials, because of their coarse textures and low organic matter. The PLP and SLP indices, when used together, can help one predict the risk factor for groundwater contamination from pesticides. Since both the PLP and SLP are high (60-79) to very high (80-100) for atrazine and the sandy Costal Plain soils, the risk for groundwater contamination of atrazine in Lakeland sand and Norfolk sand is considered very high (McLaughlin *et al.* 1994; Weber 1991).

Possible Interactions of Atrazine, Soil, and Poultry Litter

Herbicide efficacy is the measurement of the amount of weed control for a given herbicide at a specific application rate. Weed control by weakly basic herbicides, like atrazine, is inversely related to the amount of organic carbon in the soil (Weber *et al.* 1993).

Atrazine has a moderate affinity for soil with an average K_{oc} of 100 mg L^{-1} (Aherns 1994). Adsorption increases at lower pHs (Aherns 1994). K_{oc} for atrazine added to sandy soils ranged from 56.8 when animal manure was added at 2.1 total Carbon ha^{-1} to 106.0 when manure was applied at 8.4 total Carbon ha^{-1}, compared to a K_{oc} of 25.3 when the sandy soil is not amended (Guo *et al.* 1991).

Organic fertilizer treatments resulted in an increase in both adsorption and persistence for five insecticides (Rouchard *et al.* 1996). Insecticide biodegradation was also slowed during the first cropping period as a result of the increased adsorption.

Microbial decomposition results in the dealkalyated metabolites DIA and DEA. Atrazine hydrolysis is in part surface-catalyzed, hence an increase in surface area would increase the amount of atrazine degradation through hydrolysis (Schoen *et al.* 1987). Optimum conditions for atrazine degradation are low atrazine concentrations, high organic matter content, acid conditions (pH 4), and moist soil conditions (Schoen *et al.* 1987). Moist soil conditions could be associated with the addition of organic matter by improving water retention (McBride 1994).

Atrazine degradation has been shown to be greater when applied on fields receiving poultry litter (Gupta *et al.* 1996). When atrazine was applied on fields receiving untreated poultry litter the atrazine was 86% degraded after 30 days. The atrazine degradation was almost twice as fast as soil and atrazine alone, and only a small amount of atrazine was lost when applied on fields receiving sterile poultry litter, indicating that microbial degradation was increased with the litter application.

Soil pH is an important factor in atrazine degradation. Hydrogen ion concentration controls atrazine adsorption between the solution and the soil (Nearpass 1967). Adsorption of atrazine decreases as pH increases when organic matter content is held constant (Harris and Warren 1964, Talbert and Fletchall 1965). In soils treated with atrazine at concentrations of 100 mg atrazine l^{-1}, the half-life of atrazine in the soil dropped from 938 days at pH 7.2 to 693 days at pH 10, at pH 4.0 the half-life was 324 days (Schoen *et al.* 1986). Hydrolysis of atrazine into hydroxy atrazine occurs ad pH levels below 6 (Aherns 1994).

Bioassays were used to study atrazine efficacy as affected by tillage method (conventional vs. no-till), lime rate, atrazine rate, and acid forming vs. nonacid-forming nitrogen fertilizers (Lowder and Weber 1982). Neither tillage method affected atrazine efficacy alone, but liming from pH 5.5 to 6.3 significantly increased the efficacy and the length of time the atrazine remained in the soil. Increasing the application rate of atrazine also increased the efficacy and persistence of atrazine in the soil.

Experiments

The effects of poultry litter on atrazine efficacy were studied in three experiments. Atrazine efficacy was measured with an oat (*Avena sativa*) and soybean (*Glycine max*) bioassay. Leachate from the bioassay study was used to determine the amount and type of degradation and the amount of atrazine available for weed uptake. Atrazine sorption was studied on soil, poultry litter and soil/litter combinations to examine absorption rates and degradation.

References

Ahrens, William H. ed. (1994) “Atrazine” in Herbicide Handbook, Seventh Edition. Weed Science Society of America. p. 20-23.

Blumhorst, Michael R. and Jerome B. Weber. (1994) Chemical Versus Microbial Degradation of Cyanazine and Atrazine in Soils. Pesticide Science 42:79-84.

Fleming, Gwen F., F. William Simmons, Loyd M. Wax, Robert E. Wind, and Merle E. Carr (1992). “Atrazine Movement In Soil Columns as Influenced by Starch-Encapsulation and Acrylic Polymer Additives,” Weed Science 40:465-470.

Guo, Lei, Thomas J. Bicki, and Thomas D. Hinesly (1991). “Effect of Carbon-rich Waste Materials on Movement and Sorption of Atrazine In a Sandy, Coarse-Textured Soil,” Environmental Toxicology and Chemistry 10:1273-1282.

Gupta, Gian, and John Baummer III. (1996). “Biodegradation of atrazine In soil using poultry litter,” Journal of Hazardous Materials 45:185-192.

Harris , C.I., and G. F. Warren. (1964) “Adsorption and desorption of herbicides by soil,” Weeds 12: 120.

Hue, N.V. (1992). “Correcting soil acidity of a highly weathered ultisol with chicken manure and sewage sludge,” Communications in Soil Science and Plant Analysis 23:241-264.

Kingery, W.L., C.W. Wood, D.P. Delany, J.C.Williams, G.L. Mullins, E. van Santen (1993). “Implications of long-term Land Application of Poultry Litter on Tall Fescue Pastures,” Journal of Production Agriculture 6(3)390-395.

Lowder, Steve, and Jerome B. Weber (1982). “Atrazine Efficacy and Longevity as Affected by Tillage Liming and Fertilizer Type,” Weed Science 30:273-280.

McBride, Murray B. (1994) “Composition and Structure of Soil Solids” in Environmental Chemistry of Soils. Oxford University Press. p. 31-62.

McLaughlin, R.A., J.B. Weber, R.L Warren. (1994). Soil Facts - Protecting Groundwater in North Carolina. North Carolina Cooperative Extension Service, AG-439-31.

Moore, P.A. Jr., T.C. Daniel, A.N. Sharpley and C.W. Wood (1995). “Poultry manure management: Environmentally sound options," Journal of Soil and Water Conservation. 50:321-327.

Nearpass, D.C. (1967). "Effects of soil acidity on the adsorption of simazine and atrazine in Bayboro clay soil," Soil Science 103: 177.

Syngenta Crop Protection, Agricultural Division (2001). "Pesticide Label for AATREX 4L", Greensboro, NC.

North Carolina Division of Agriculture Statistics (1996) http://www.agr.state.nc.us/stats/

Parsons, J.T., J.P. Zublena, and T.A. Carter (1992). "Viability of Weed Seed In Poultry Manure and Mortality Compost," In Proceedings of the National Poultry Waste Management Symposium.

Rouchard, J., A. Thiron, D. Callens, R. Bulcke (1996). "Soil dissipation of the post-emergence herbicide sulcotrione In maize crops treated with organic fertilizers," Bulletin of Environmental Contamination and Toxicology 57:398-405.

Schoen, Sarah R., Wray L. Winterlin (1987). "The Effects of Various Soil Factors and Amendments on the Degradation of Pesticide Mixtures," Marcel Dekker, Inc. p. 347-377.

Talbert, R. E., and O.H. Fletchall. (1965) "The absorption of soil s-triazines in soils," Weeds 13:46.

US Department of Agriculture, (1998). Agricultural resources: Situation and outlook Report. U. S. Government Printing Office, Washington DC.

Weber, J.B. (1991). Potential for Groundwater Contamination From Selected Herbicides: A Herbicide/Soil Ranking System. In Proceedings of the Southern Weed Science Society 44:45-56.

Weber, Jerome B., Jack A. Best, and Jane U. Gonese (1993). "Bioavailability and Bioactivity of Sorbed Organic Chemicals," In Sorption and Degradation of Pesticides and Organic Chemicals in Soils SSSA Special Publication No. 32:153-196.

Wietersen, R.C., T.C. Daniel, K.J. Fermanich, B.D. Girard, K. McSweeney, and B. Lowery (1993). "Atrazine Alachlor and Metolachlor Mobility Through Two Sandy Wisconsin Soils," Journal of Environmental Quality 22:811-818.

Zublena, J.P., C.C. Mitchell, J.T. Parsons, R.H. Walker, T.A. Carter and D.A. Crouse (1995). "Viability of Weed Seed In Poultry Manure and Mortality Compost," In Proceedings of the 7th International Symposium on Agricultural and Food Processing Wasters (ISAFPW95) p. 1-7.

Zublena, J.P., J.C. Barker, and T.A. Carter. (1993). Soil Facts - Poultry Manure as a Fertilizer Source. North Carolina Cooperative Extension Service, AG-439-5.

ATRAZINE EFFICACY WHEN APPLIED TO SOIL AMENDED WITH POULTRY LITTER

Abstract

The effectiveness of atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) applied in conjunction with poultry litter was measured through an oat (*Avena sativa*) and soybean (*Glycine max*) bioassay. Poultry litter application rates were based on nitrogen recommendations for corn (*Zea mays*) and applied at the recommended rate, 3 times (3X), and 5 times (5X) the recommended rate. Emergence of oat and soybean was inhibited at the 5X stockpiled litter application rate. Stockpiled and weathered litter applied at 1X and 3X rates increased the average mass of oat and soybean. Application of atrazine, despite rate, to the bioassay pots increased soybean chlorosis and oat mortality. Weathered litter application rates did not inhibit soybean emergence as the 5X application rate.

Introduction

North Carolina ranked second in the United States in overall poultry production in 1990 producing 611 million birds (broilers, layers, turkeys) and 1.496 $* 10^6$ Mg of dry manure (Moore *et al.* 1995). It also ranked first in turkey production (NCDA 1996). In 1994 poultry production contributed 28.3% of the $6.4 billion of revenue to North Carolina agriculture (NCDA 1996). This tremendous amount of poultry production leads to the increasing problem of where to dispose of the poultry litter, which is typically bedding materials like wood chips or peanut (*Arachis hypogaea*) hulls mixed with manure from the birds. The current best management practice for disposing of poultry litter is land application as a fertilizer source for crops (Zublena *et al.* 1993). The majority of poultry litter (> 90%) is land applied. Land application rates are typically based on the nitrogen needs of the crop to decrease the risk of nitrate leaching into the groundwater. In some instances, applications based on nitrogen needs result in an excess of phosphorus in the soil (Moore *et al.* 1995). The amount of phosphorus in fields receiving litter can exceed the total amount needed for the crop (Sims 1992; Wood 1992).

Herbicide efficacy is the measurement of the amount of weed control for a given herbicide application. Rouchard *et al.* (1996) did field degradation studies on five insecticides in soil amended with organic fertilizers and planted to vegetable crops. Recent applications of organic fertilizer treatments (cow manure, pig slurry, compost or green manure) resulted in an increase in both insecticide adsorption and persistence. Insecticide biodegradation was slowed during the first cropping period as a result of the increased adsorption. Lowder and Weber (1982) used bioassays to study atrazine efficacy as affected by tillage method (conventional vs. no-till), lime rate, atrazine rate, and acid forming vs. nonacid-forming nitrogen fertilizers. Neither tillage method affected atrazine efficacy alone, but liming significantly increased efficacy and persistence of atrazine remained. Increasing the application rate of atrazine also increased the efficacy and persistence. Weed control by weakly basic herbicides, like atrazine, is inversely related to the amount of organic carbon in the soil (Weber *et al.* 1993).

Increased weed pressure in fields where litter is applied had been thought to be the result of the introduction of viable weed seed in the litter (Parsons *et al.* 1992; Zublena *et al.* 1992). One study done in Duplin, Sampson and Wayne Counties of North Carolina found that there was no difference between populations of weeds and weed species with the addition of either litter or conventional fertilizers (Parsons *et al.* 1992). Zublena *et al.* (1995) studied the effects of broiler litter, urea, urea and diammonium phosphate and a control on weed germination. Pots were filled with sterile soil (fritted clay) and poultry litter (equivalent to 14.5 and 29 Mg ha^{-1}), then half were inoculated with spiny amaranth (*Amaranthus spinosa*), pitted morningglory (*Ipomoea lacunosa*), sicklepod (*Cassia obtusifola*), and large crabgrass (*Digitaria sanguinalis*). No weeds emerged in the non-inoculated pots after 6 weeks of incubation, indicating that viable weed seeds were not present in the broiler house litter or that weed seeds may have been dormant. Large crabgrass and spiny amaranth germination and growth were inhibited by some sources of litter, and litter actually killed or prevented germination at a high rate of 32 g Kg^{-1} of soil. This litter toxicity was attributed to free ammonia.

Since litter is apparently not a source of weed seed, other explanations for the reported increase in weed pressure in fields receiving litter are needed. Litter applied to the soil surface may act as a physical barrier, preventing the herbicide from reaching the soil and therefore preventing contact with germinating weed seeds. Litter, especially when applied at very high application rates, could also interfere with herbicidal activity on the weeds through adsorption. With the addition of litter, the organic matter of the soil is at least temporarily increased and herbicide adsorption may prevent plant uptake. Finally, decomposition of the herbicide could be enhanced due to increased microbial populations.

Materials and Methods

A bioassay with oat and Pioneer 9442 soybean was conducted to measure atrazine efficacy as affected by poultry litter.

Oat and soybean were selected for their sensitivity to atrazine (Horowitz and Hulin 1971; Kratky and Warren 1971; Marriage 1975; Lavy and Santelmann ,1986; Lowder and Weber 1982; Weber 1986). Foliar chlorosis of both oat and soybean seedlings followed by necrosis will occur as atrazine rates increase (Ashton *et al.* 1973). In oat, chlorosis begins at the tip of the blade and then continues down to the base. In soybean, and other broadleaf species, triazine chlorosis begins on the outer edges of the leaves and then covers the entire leaf area.

Much of the land application of poultry litter in North Carolina occurs on sandy Coastal Plain soils. Lakeland sand (siliceous, thermic, coated Typic Quartzipsamments) from the Sandhills Research Station, Jackson Springs, NC was selected due to its low organic matter content, which minimizes the interactions between atrazine and the native soil organic matter.

Stockpiled poultry litter was obtained from North Carolina State University's Unit 9 poultry house, Raleigh NC and analyzed by the North Carolina State University Soil Science Service Lab (see Table 2.1). The stockpiled litter had been cleaned from production houses, piled, and left uncovered.

Application rates of litter were based on nitrogen recommendations for corn (Zublena *et al.* 1993). Litter was applied to the surface of pots at 0X, 1X, 3X, and 5X the recommended nitrogen rate for a 120 bu ac^{-1} corn crop using a 50% availability factor assuming no residual nitrogen and no pre-plant fertilizer (see Table 2.2). The corresponding rates used in the experiments are given in Table 2.3. The pots were plastic drinking cups, 10 cm in diameter with small holes in the bottom for drainage. The amount of litter per pot was calculated using the diameter of the pot to calculate the area of the soil that would be exposed.

BIOASSAY:

Oat Bioassay:

Pots were 10 cm diameter plastic drinking cups with small holes burned in the bottom. Each pot was filled with 350 ml (approximately 650 g) of Lakeland sand and completely saturated with water. The pots were allowed to drain for 1 hour and the seeds were planted. The oat seeds were pre-germinated in moist paper towels for 3 days. Five pre-germinated oat seeds were planted in each pot approximately 1 cm into the soil, with five replicates of each litter rate and atrazine rate (see Table 2.3, 2.4). The poultry litter was weighed out for each pot and surface applied. After litter application the pots were watered with 50 ml of water and left to sit for 2 hours. Atrazine was applied as AATREX 4L (Syngenta Crop Protection, Inc., Greensboro, NC) at five rates (see Table 2.4) using a spray table to insure uniform coverage (Figure 2.1). To ensure complete surface coverage of the atrazine application, measurements were taken and solutions were made based on spraying 123 l water ha^{-1} of the AATREX water solution. After the atrazine was applied, the pots were moved to the greenhouse. All pots received the same amount of water daily. To determine water amounts, several pots were selected and watered in 15 ml increments until leaching occurred, the remaining pots were then watered with the same volume to minimize leaching receiving between 15 ml to 30 ml water daily. This experiment was done in June 1996 during which the greenhouse was often very hot and pots would be watered twice a day. After 14 days of growth, the plants were visually assessed for herbicide damage and it was determined if oat grew and were healthy, grew and then died or did not grow. Oat was then harvested and fresh weights of all plant material were recorded for each pot. This study was not repeated.

Soybean Bioassay:

Both stockpiled and weathered litter was used in this bioassay. Stockpiled litter was from the same source as the oat bioassay and kept in an airtight container not exposed to the elements in the greenhouse. The weathered litter pots were filled with 350 ml (approximately 650 g) of Lakeland sand and the stockpiled litter was applied as in Table 2.3. The weathered litter pots were periodically watered weekly for 110 days. Both litter treatments were subject to the same temperature variations in the greenhouse. Stockpiled litter was applied at the same rate as weathered litter to pots containing 350 ml of Lakeland sand (see Table 2.3). Five soybean seeds were planted in each pot approximately 2 cm into the soil, with five replicates of each litter and atrazine treatment. Atrazine was applied as AATREX 4L (Syngenta Crop Protection, Inc., Greensboro, NC) at four rates; 0, 1/10, ½, and the recommended rate (see Table 2.4) on a spray table to insure uniform coverage. To ensure complete surface coverage of the atrazine application, the atrazine was applied in the same manner as it was in the oat bioassay. After the atrazine treatment was applied, the pots were moved to the greenhouse. All pots received the same amount of water daily. The amount of water ranged between 15 ml to 30 ml to minimize leaching. The experiment was done in January 1997. After 15 days of growth, the soybean seedlings were visually assessed for herbicide damage. It was determined if the soybean grew and was healthy, grew and had damage or did not grow. The soybean was then harvested and fresh weights were recorded for each pot. This experiment was not repeated.

All of the statistical analyses were done using the SAS System for Windows, v6.12 (SAS Institute, Inc. Cary, NC, USA). A Type III Sum of Squares model was used because it allows for missing values (pots that did not have plant growth).

Results and Discussion

OAT BIOASSAY:

The average mass of all the oat plants in each pot was dependent on the amount of litter applied (p=0.001) (See Figure 2.2, Table 2.5). As the rate of litter increased the average mass of oat in all of the pots increased, except at the highest rate of litter. In pots where stockpiled litter was applied at 67 Mg ha^{-1}, no growth of the oat occurred so this rate of litter was dropped from the statistical analysis. Ammonia toxicity could have affected the germination of the seeds at the highest rate of litter. Measurements taken during a previous study found that free ammonia in soils treated with litter could possibly be responsible for concentrations of 2.7 to 5.2 mmol NH_3 gas per 100 g of soil (Zublena 1995). Ammonia levels exceeding 0.2 mmol per 100 g of soil can be toxic to some plants (Zublena 1995).

The amount of atrazine applied to the pots did not significantly affect the average mass of oat (p= 0.1760, Table 2.5). There was no significant interaction between litter and atrazine (p=0.3558, Table 2.5). The effect of litter and atrazine apparently counteracted each other, litter providing nutrients for the plant to grow and atrazine acting to decrease photosynthesis and ultimately cause necrosis.

The frequency of whether a plant grew and was alive, grew and died, or did not grow was also evaluated. The frequency was analyzed to investigate the effects of litter and atrazine on whether or not the plants grew and what kind of damage they sustained. This allowed for analysis independent of the weight of the plants, so that healthy plants that grew would not negate the weight of plants that did not grow. This information is summarized in Figures 2.3 to 2.6 and in Table 2.6. As the rate of litter increased from 0 to 40 Mg kg^{-1} the average mass of the plants increased but the number of plants did not, indicating that the plants that grew were healthier and more robust.

Comparing the ratio of the number of plants that died versus the number of plants that grew isolated the effects of both atrazine and litter. Of the litter rates, except for 67 Mg ha^{-1}, the amount of applied atrazine had a significant negative effect on the number of plants that died compared to the number that grew. Application of 2.2 kg a.i. ha^{-1} of atrazine (p=0.0018, Table 2.6) and at 1.1 kg a.i. ha^{-1} (p=0.0292, Table 2.6) significantly decreased the number of plants that died as compared to the number of plants that emerged. As the rate of atrazine increased, the number of plants that grew and were healthy decreased. The two lowest rates of atrazine, 0.22 and 0.022 kg a.i. ha^{-1}, did not affect the growth of the oat plants (p=0.1447, p=0.5697, Table 2.6).

Overall, atrazine had a significant effect on the percentage of plants that died (p=0.0016, Table 2.6), while litter did not (p=0.2632, Table 2.6).

To analyze for the effect of atrazine rates only the ratio of the total number of plants that grew versus the number of plants that were planted is used. Only the atrazine rate of 2.2 kg a.i. ha^{-1} compared to the untreated control had a significant effect on the number of plants that grew ($p=0.0001$, Table 2.7). Both the litter and the atrazine had significant effects on the total number of plants that grew ($p=0.0057$, $p=0.0001$, Table 2.7). Litter had less impact on the growth of the plants than the amount of atrazine applied. As litter application increased from 13 Mg ha^{-1} to 66.7 Mg ha^{-1}, fewer plants grew. As atrazine concentrations increased, fewer plants also grew.

SOYBEAN BIOASSAY:

The average mass of soybean per pot was dependent on the amount of litter applied ($p=0.0010$) and on the amount of atrazine applied ($p=0.0005$) (See Figure 2.7 and 2.8, Table 2.8). Within weathered litter, the rate of litter increased the average mass of soybean shoots regardless of atrazine application. For the stockpiled litter the mass of soybean increased slightly for all of the litter rates except for 67 Mg ha^{-1}. Since the 67 Mg ha^{-1} rate of litter was toxic to the soybean, this treatment was eliminated from statistical analyses. While studying the viability of weed seeds in poultry litter, it was found that free ammonia could be responsible for toxicities resulting in no growth of weeds (Zublena *et al*. 1995). There was no significant interaction between litter and atrazine for soybean mass (p=0.7352, Table 2.8). Aging the litter did not affect soybean seedling mass (p=0.5160, Table 2.8). No interactions between age and all of the other variables were evident.

For the stockpiled litter application only, the application of atrazine significantly increased soybean mass at all rates except for the 67 Mg ha^{-1} (p = 0.0296, Table 2.9, Figure 2.8). Again, the highest litter rate was dropped from this analysis due to its complete toxicity. There were no effects of either increasing litter application rates or interactions between treatments. A possible explanation for this is that the plants that grew were more robust, causing the average mass to be skewed. This is addressed when looking at the frequency of plants that grew, died, and suffered chlorosis.

Another assessment of treatment effects is the ratio of healthy (green plants with no chlorosis) and plants with chlorosis to total plants seeded. This allows for analysis independent of the weight of plants, so that healthy plants that grew will not negate the weight of plants that did not grow.

In the unamended atrazine control, the number of plants that grew and were healthy in weathered litter was significantly higher than the number of plants that grew and were healthy in the stockpiled litter (p=0.0255, Table 2.10, Figure 2.9). The addition of litter, either stockpiled or weathered, had a significant effect on the total number of plants that grew (p=0.0205,Table 2.10,

Figure 2.9, 2.10. 2.11, 2.12). The weathered litter was frequently watered and exposed to the atmosphere for 110 days before planting the soybean. This would allow for the nitrification of the ammonium. The ammonium is converted to nitrite through *Nitrosomonas* and *Nitrosococcus*, equation 1 and then to nitrate through *Nitrobacter*, equation 2 (Ludwick 1995). The nitrate is then able to leach through the soil.

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ + \text{energy} \quad [1]$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- + \text{energy} \quad [2]$$

The ammonium can also be lost to the atmosphere through volatilization after conversion to ammonia gas, equation 3. The ammonium concentrations would thereby be much lower in weathered litter compared to stockpiled litter, resulting in lower toxicities to the plants.

$$NH_3 + H^+ \leftrightarrow NH_4^+ \quad pK_a = 9.3 \quad [3]$$

Statistical analysis for the parameter estimates for the ratio of the total number of plants emerged (all plants that grew) to the number of planted seeds can help explain the effect of litter on the growth of plants (See Table 2.11). The litter rates of zero (p=0.0001) and 13 Mg ha^{-1} (p=0.0001) had a significant effect on emergence compared to the litter rate of 67 Mg ha^{-1} for stockpiled litter since there was no emergence at this rate. The higher rates of stockpiled litter (40 and 67 Mg ha^{-1}) had lower amounts of emergence than did the lower rates of litter for the stockpiled litter (see Figures 2.9, 2.10. 2.11, 2.12).

Litter rates and age had a significant effect on whether plants emerged (p=0.0001 and p=0.0001, Table 2.11), but atrazine did not (p = 0.0523). This was expected since atrazine must be taken up by the plant to inhibit photosynthesis and it does not inhibit emergence (Ashton *et al.* 1973).

Within the weathered litter, both litter and atrazine rate had an effect on the average mass of the plants (Figure 2.7 and Table 2.12). As the amount of litter increased within a rate of atrazine, the weight of the plants also increased (p=0.0062). Applying atrazine also increased the weight of the soybean (p=0.0001), but the effect was not rate dependent, only that atrazine was applied or not applied.

Within stockpiled litter, the application of atrazine had a positive effect on the average mass of plants (p = 0.0296) (Table 2.13, Figure 2.8). At the highest rate of litter no plant growth was observed.

Both the age of the litter (p=0.0001) and the rate of litter (p=0.0001) had a significant negative effect on soybean survival (Table 2.14 and Figures 2.13 to 2.16). Stockpiled litter reduced the emergence rate of soybean more than weathered litter. At the litter application rate of 67 Mg ha^{-1} soybean emergence was completely inhibited in stockpiled litter while in weathered litter emergence was not inhibited. The combination of litter rate and litter weathering had a significant effect on plant emergence ($p = 0.0001$).

The proportion of plants with chlorosis was used to estimate the amount of atrazine damage (Figure 2.17). The rate of litter, weathering of litter and the application of atrazine all had a significant impact on chlorosis occurrence (Table 2.15). At the zero and 0.22 kg a.i. ha^{-1} of atrazine no chlorosis was observed. At application rates of 1.1 and 2.2 kg a.i. ha^{-1}, plants in the weathered litter showed chlorosis (Figure 2.11, Figure 2.12), but plants in the stockpiled litter did not show chlorosis. This is reverse of what was expected for several reasons. Stockpiled litter was expected to show more chlorosis than weathered litter because weathering the litter allowed for more stable organic compounds (humus) that the atrazine could bind too, preventing plant uptake and therefore chlorosis. Weathering the litter allowed for the dissipation of ammonium as well as dissolved organic matter to be leached out the system. This may have allowed for more organic matter compounds to bond with atrazine in the stockpiled litter as opposed to the weathered litter and leaching the atrazine out of the system bound to the dissolved organic matter.

Conclusion

Ammonium toxicity appeared to prohibit the emergence of both oat and soybean at 67 Mg ha^{-1} application rate (5X recommended rate) for litter that was stockpiled as opposed to weathered *in situ*. The weathered litter did not appear to produce ammonium toxicity. The application of stockpiled litter increased the average mass of oat and soybean until it appeared that ammonium toxicity occurred at the highest rate. Zublena *et. al* (1995) found that some litter sources killed or prevented germination in weeds (crabgrass and spiny amaranth). Levels of ammonium-N from these soil and litter mixtures were measured from 380 to 730 mg kg^{-1}. These high levels of ammonium-N found when excessive amounts of poultry litter are applied could also damage crop seeds. When poultry litter is applied in excess of the crop's nutrient requirements NO_3 may move into ground water systems (Heathman et al 1995). Increased loss of NO_3-N and P in runoff may contaminate surface waters (Heathman et al 1995). Also affected is the timing of application. If stockpiled or fresh litter is allowed to weather insitu then the chance of ammonium toxicity to both weeds and crops is decreased. Long-term applications of poultry litter at high levels can lead to leaching and runoff of nutrients, and a build up of nutrients in the soil (Kingery et al 1993).

Stockpiled litter significantly reduced oat mortality when atrazine was applied at the 1.1 and 2.2 kg a.i ha^{-1} rates. Increased rates of stockpiled litter increased average fresh soybean mass, until ammonium toxicity occurred. The application of atrazine, at all rates, increased the average weight of soybean when applied with weathered litter.

At the control and lowest rate of atrazine no soybean chlorosis is present. The application of atrazine at the recommended rate in conjunction with the application of weathered litter resulted in soybean chlorosis, but plants in the stockpiled litter did not show chlorosis. It appeared that the stockpiled litter deactivated atrazine more readily than weathered litter. Further study of this is needed. This will affect timing of application of poultry litter when weed control is important.

Typically litter applied to fields is composted or weathered litter. Field application of stockpiled and weathered litter at recommended rates may slightly elevate the amount of weed emergence and the vigor of weed growth, but this study does not show conclusive evidence that litter should not be used as a fertilizer source. Litter application rates of stockpiled litter exceeding the recommended rates of application could damage crops with ammonium toxicity as well as inhibit weed emergence and should not be used. Allowing poultry litter to weather *insitu* or to compost before application will allow for the dissipation of ammonium as well as better weed control. Atrazine application rates applied at the recommended amount will best serve the grower for weed control when applied on fields with weathered litter.

References

Ashton, Floyd M. and Alden S. Crafts (1973). “Triazines,” In Mode of Action of Herbicides. New York, NY: John Wiley and Sons.

Esser, Herbert O, Gerard Dupuis, Edith Ebert, Christian Vogel, and Gino J. Marco (1975). “s-Triazines,” Kearney, P.C. and D.D. Kaufman. (Ed.), In Herbicides: Chemistry, Degradation, and Mode of Action, 2nd Edition, Reviewed and Expanded. Vol. 1, New York, NY: Marcel Dekker, Inc.

Heathman, G.C., A.N. Sharpley, S.J. Smith, and J.S. Robinson (1995). “Land application of poultry litter and water quality In Oklahoma, USA,” Fertilizer Research. 40:165-173.

Horowitz, M., and Nira Hulin (1971). “A Rapid Bioassay for Diphenamid and Its Application In Soil Studies,” Weed Research. 11:143-149.

Kingery, W.L., C.W. Wood, D.P. Delany, J.C.Williams, G.L. Mullins, E. van Santen (1993). “Implications of long-term Land Application of Poultry Litter on Tall Fescue Pastures,” Journal of Production Agriculture. 6(3)390-395.

Kratky, B.A., G.F. Warren (1971). “The Use of Three Simple Rapid Bioassays on forty-two Herbicides,” Weed Research. 11:257-262.

Lavy, T.L. and P.W. Santelmann (1986). “Herbicide Bioassay as a Research Tool,” in Research Methods in Weed Science - Third Edition, Southern Weed Science Society, 201-218.

Lowder, Steve, and Jerome B. Weber (1982). “Atrazine Efficacy and Longevity as Affected by Tillage Liming, and Fertilizer Type,” Weed Science. 30:273-280.

Ludwick, Albert E. ed. (1995). “Essential Plant Nutrients” in Western Fertilizer Handbook, Eight Edition. California Fertilizer Association. Interstate Publishers. p 87-107.

Marriage, P.B. (1975). “Detection of Triazine and Urea Herbicide Residues by Various Characteristics of Oat Seedlings In Bioassays,” Weed Research. 15:291-298.

Moore, P.A. Jr., T.C. Daniel, A.N. Sharpley and C.W. Wood (1995). “Poultry manure management: Environmentally sound options,” Journal of Soil and Water Conservation. 50:321-327.

North Carolina Division of Agriculture Statistics -
http//www/agr.state.nc.us/stats/ (1996).

Parsons, J.T., J.P. Zublena, T.A. Carter (1992). "Viability of Weed Seeds In Poultry Manure and Mortality Compost," In Proceedings of the National Poultry Waste Management Symposium. .

Rouchard, J., A. Thirion, A. Wauters, F. Van de Steene, F. Benoit, N. Ceustermans, J. Gillet, S. Marchand, L. Vanparys (1996). "Effects of Fertilizer on Insecticides Adsorption and Biodegradation In Crop Soils," Archives of Environmental Contamination and Toxicology. 31:98-106.

Sims, J.T. (1992). "Environmental management of phosphorus in agriculture and municipal wastes," F.J. Sikora (ed.) in Future Directions for Agricultural Phosphorus Research. 959-64. National Fertilizer and Environmental Research Center, TVA, Muscle Shoals, AL.

Weber, J.B. (1986). "Soils, Herbicide Sorption and Model Plant-Soil Systems," Research Methods in Weed Science Third Edition. 155-188. Southern Weed Science Society.

Weber, Jerome B., Jack A. Best, Jane U. Gonese (1993). "Bioavailability and Bioactivity of Sorbed Organic Chemicals," In Sorption and Degradation of Pesticides and Organic Chemicals in Soils SSSA Special Publication no. 32:153-196.

Wood, C.W. (1992) "Broiler litter as a fertilizers: Benefits and environmental concerns," p 304-312. In: Proceedings of the National Poultry Waste Management Symposium, Birmingham, AL. Auburn University, AL.

Zublena, J.P., J.C. Barker, T.A. Carter (1993). "Soil Facts - Poultry Manure as a Fertilizer Source," North Carolina Cooperative Extension Service, AG-439-5.

Zublena, J.P., T.A. Carter , D.A. Crouse , C.C. Mitchell, J.T.Parsons, and R.H. Walker (1995). "Viability of Weed Seed In Poultry Manure and Mortality Compost," In Proceedings of the 7th International Symposium on Agricultural and Food Processing Wasters (ISAFPW95) p. 1-7.

Table 2.1: Total elemental analysis of stockpiled poultry litter.

Nutrient	Elemental Analysis ($g\ kg^{-1}$)
Total Carbon	273.7
Total Nitrogen	25.2
Total Phosphorus	30.5
Total Potassium	24.5
Total Calcium	4.0
Total Magnesium	7.5

Table 2.2: Calculation of litter application rate.

1. Crop to be grown	Corn
2. Total N (lb. $acre^{-1}$) required	150
3. Pounds of starter or pre-plant N (lb. $acre^{-1}$)	0
4. Residual N credit from legumes (lb. $acre^{-1}$)	0
5. Net N needs of crop (lb. $acre^{-1}$)	150
6. N concentration of litter (lb. ton^{-1})	50.4
7. N available to crop (lb. ton^{-1}) assuming 50% availability factor	25.2
8. Application rate of litter (ton $acre^{-1}$)	5.95

Adapted from Poultry Manure as a Fertilizer Source (Zublena et al. 1993)

Table 2.3: Poultry litter application rates.

Litter Rates	Field Rate Mg ha^{-1}	Stockpiled Litter Amount for Pots g
0 Recommended rate	0	0
1X Recommended rate	13	6
3X Recommended rate	40	18
5X Recommended rate	67	30

Table 2.4: Atrazine application rates.

Atrazine Rates	Field Atrazine Rate kg a.i. ha^{-1}
0 Recommended rate	0.0
1/100 Recommended rate	0.022
1/10 Recommended rate	0.22
1/2 Recommended rate	1.1
Recommended rate	2.2

Table 2.5. Analysis of variance table for the average fresh weight of oat plants.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	2	2.46	1.23	8.87	0.001
ATRAZINE RATE	4	0.94	0.24	1.70	0.176
LITTER RATE * ATRAZINE RATE	7	1.12	0.16	1.16	0.3558

Table 2.6. Analysis of parameter estimates for litter and atrazine for the ratio of the number of oat plants that died to the total number of plants that grew.

Parameter	DF	Estimate	Std Error	Chi-square	Pr>Chi
INTERCEPT	1	-1.58	0.66	5.68	0.0171
LITTER RATE 13	1	-0.88	0.59	2.20	0.138
LITTER RATE 40	1	0.05	0.70	0.01	0.939
LITTER RATE 0	0	0.00	0.00	.	.
ATRAZINE RATE 0.022	1	0.46	0.80	0.32	0.5697
ATRAZINE RATE 0.22	1	1.13	0.78	2.10	0.1477
ATRAZINE RATE 1.1	1	1.76	0.81	4.76	0.0292
ATRAZINE RATE 2.2	1	3.68	1.18	9.76	0.0018
ATRAZINE RATE 0	0	0.00	0.00	.	.
SCALE	0	1.27	0.00		

NOTE: The scale parameter was estimated by the square root of Pearson's Chi-Squared/DOF.

LR Statistics For Type 3 Analysis

Source	NDF	DDF	F	Pr>F	Chi-square	Pr>Chi
LITTER RATE	2	52	1.33	0.272	2.67	0.2632
ATRAZINE RATE	4	52	4.35	0.004	17.38	0.0016

Table 2.7: Analysis of parameter estimates for the ratios of the total number of oat that grew to the total number of oat that were planted.

Parameter	DF	Estimate	Std Error	Chi-Square	Pr>Chi
ATRAZINE RATE 0.022	1	0.10	0.42	0.0545	0.8154
ATRAZINE RATE 0.22	1	-0.31	0.40	0.5856	0.4441
ATRAZINE RATE 1.1	1	-0.75	0.42	3.176	0.0747
ATRAZINE RATE 2.2	1	-1.81	0.46	15.5596	0.0001
ATRAZINE RATE 0	0	0.00	0.00	.	.
SCALE	0	1.08	0.00	.	.

NOTE: The scale parameter was estimated by the square root of Pearson's Chi-Squared/DOF.

LR Statistics For Type 3 Analysis

Source	NDF	DDF	F	Pr>F	Chi-Square	Pr>Chi
LITTER RATE	3	52	4.19	0.0099	12.57	0.0057
ATRAZINE RATE	4	52	6.23	0.0004	24.90	0.0001

Table 2.8. Analysis of variance for the average mass of soybean seedlings.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	0.41	0.14	5.85	0.001
ATRAZINE RATE	3	0.46	0.15	6.51	0.0005
LITTER RATE * ATRAZINE RATE	9	0.14	0.02	0.67	0.7352
WEATHERING	1	0.01	0.01	0.42	0.516
LITTER RATE * WEATHERING	2	0.01	0.00	0.18	0.8327
ATRAZINE RATE * WEATHERING	3	0.04	0.01	0.52	0.6712
LITTER RATE * ATRAZINE RATE * WEATHERING	5	0.11	0.02	0.97	0.4423

Table 2.9. Analysis of variance for average mass of soybean shoots due to litter and atrazine application.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	2	0.01	0.00	0.11	0.895
ATRAZINE RATE	3	0.23	0.08	2.90	0.0481
LITTER RATE * ATRAZINE RATE	5	0.13	0.03	1.04	0.4098
Contrast	**DF**	**Contrast SS**	**Mean Square**	**F Value**	**Pr > F**
Atrazine control vs. all other atrazine applications	1	0.13	0.13	5.14	0.0296

Table 2.10. Analysis of parameter estimates for the ratio of the total number of soybean plants that grew and were healthy to the number of plants that did not grow.

Parameter	DF	Estimate	Std Error	Chi-Square	Pr>Chi
INTERCEPT	1	-1.95	0.83	5.52	0.0188
LITTER RATE 0	1	1.44	0.95	2.31	0.1286
LITTER RATE 13	1	1.47	1.01	2.14	0.1436
LITTER RATE 40	1	1.02	0.80	1.61	0.2045
LITTER RATE 67	0	0.00	0.00 .	.	
ATRAZINE RATE 0	1	-1.58	1.21	1.71	0.1914
ATRAZINE RATE 0.22	1	0.09	1.19	0.01	0.9422
ATRAZINE RATE 1.1	1	-0.50	0.61	0.66	0.4167
ATRAZINE RATE 2.2	0	0.00	0.00 .	.	
WEATHERED	1	1.79	0.80	4.99	0.0255
STOCKPILED	0	0.00	0.00 .	.	
SCALE	0	1.06	0.00 .	.	

NOTE: The scale parameter was estimated by the square root of Pearson's Chi-Squared/DOF.

LR Statistics For Type 3 Analysis

Source	NDF	DDF	F	Pr>F	Chi-Square	Pr>Chi
LITTER RATE	3	21	1.48	0.25	4.44	0.218
ATRAZINE RATE	3	21	0.85	0.48	2.54	0.4681
WEATHERING	1	21	5.37	0.03	5.37	0.0205

Table 2.11. Analysis of parameter estimates for the ratio of the total number of plants that grew to the number of seeds that were planted.

Parameter	DF	Estimate	Std Error	Chi-Square	Pr>Chi
INTERCEPT	1	-0.91	0.38	5.65	0.0174
LITTER RATE 0	1	1.56	0.36	18.61	0.0001
LITTER RATE 13	1	1.66	0.36	20.74	0.0001
LITTER RATE 40	1	0.52	0.34	2.32	0.128
LITTER RATE 67	0	0.00	0.00 .	.	
ATRAZINE RATE 0	1	0.40	0.34	1.43	0.2323
ATRAZINE RATE 0.22	1	0.51	0.36	2.02	0.1556
ATRAZINE RATE 1.1	1	-0.31	0.30	1.11	0.2929
ATRAZINE RATE 2.2	0	0.00	0.00 .	.	
WEATHERED	1	1.16	0.26	20.35	0.0001
STOCKPILED	0	0.00	0.00 .	.	
SCALE	0	1.28	0.00 .	.	

NOTE: The scale parameter was estimated by the square root of Pearson's Chi-Squared/DOF.

LR Statistics For Type 3 Analysis

Source	NDF	DDF	F	Pr>F	Chi-Square	Pr>Chi
LITTER RATE	3	126	10.39	0.0001	31.18	0.0001
ATRAZINE RATE	3	126	2.57	0.0571	7.71	0.0523
WEATHERING	1	126	21.69	0.0001	21.69	0.0001

Table 2.12. Analysis of variance for fresh soybean weight for weathered litter.

Source	DF	Type III SS	Mean Square	F Value	Pr>F
LITTER RATE	3	0.46	0.15	6.94	0.00
ATRAZINE RATE	3	0.40	0.13	5.97	0.0012
LITTER RATE * ATRAZINE RATE	9	0.14	0.02	0.68	0.7283

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
Litter 0 vs. others	1	0.18	0.18	8.01	0.0062
Atrazine 0 vs. others	1	0.39	0.39	17.35	0.0001

Table 2.13. Analysis of variance for fresh soybean weight for stockpiled litter.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	2	0.01	0.00	0.11	0.895
ATRAZINE RATE	3	0.23	0.08	2.90	0.0481
LITTER RATE * ATRAZINE RATE	5	0.13	0.03	1.04	0.4098

Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
Atrazine 0 vs. other	1	0.13	0.132887	5.14	0.0296

Table 2.14. Analysis of variance for the proportion of plants that did not germinate, to analyze litter effect for soybean bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
WEATHERING	1	5.04	5.04	133.77	0.0001
LITTER RATE	3	6.53	2.18	57.75	0.0001
WEATHERING * LITTER RATE	3	4.14	1.38	36.63	0.0001

Table 2.15. Analysis of variance for the proportion of plants with chlorosis as influenced by litter age, litter rate and atrazine rate for soybean bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
WEATHERING	1	4.95	4.95	61.16	0.0001
LITTER RATE	3	20.66	6.89	85.04	0.0001
WEATHERING * LITTER RATE	2	8.64	4.32	53.32	0.0001
ATRAZINE RATE	3	0.72	0.24	2.96	0.0518
WEATHERING * ATRAZINE RATE	1	0.06	0.06	0.78	0.3861
LITTER RATE * ATRAZINE RATE	7	0.57	0.08	1.00	0.4561
WEATHERING * LITTER RATE * ATRAZINE RATE	1	2.34	2.34	28.87	0.0001

Figure 2.1. Atrazine application to pots on the spray table.

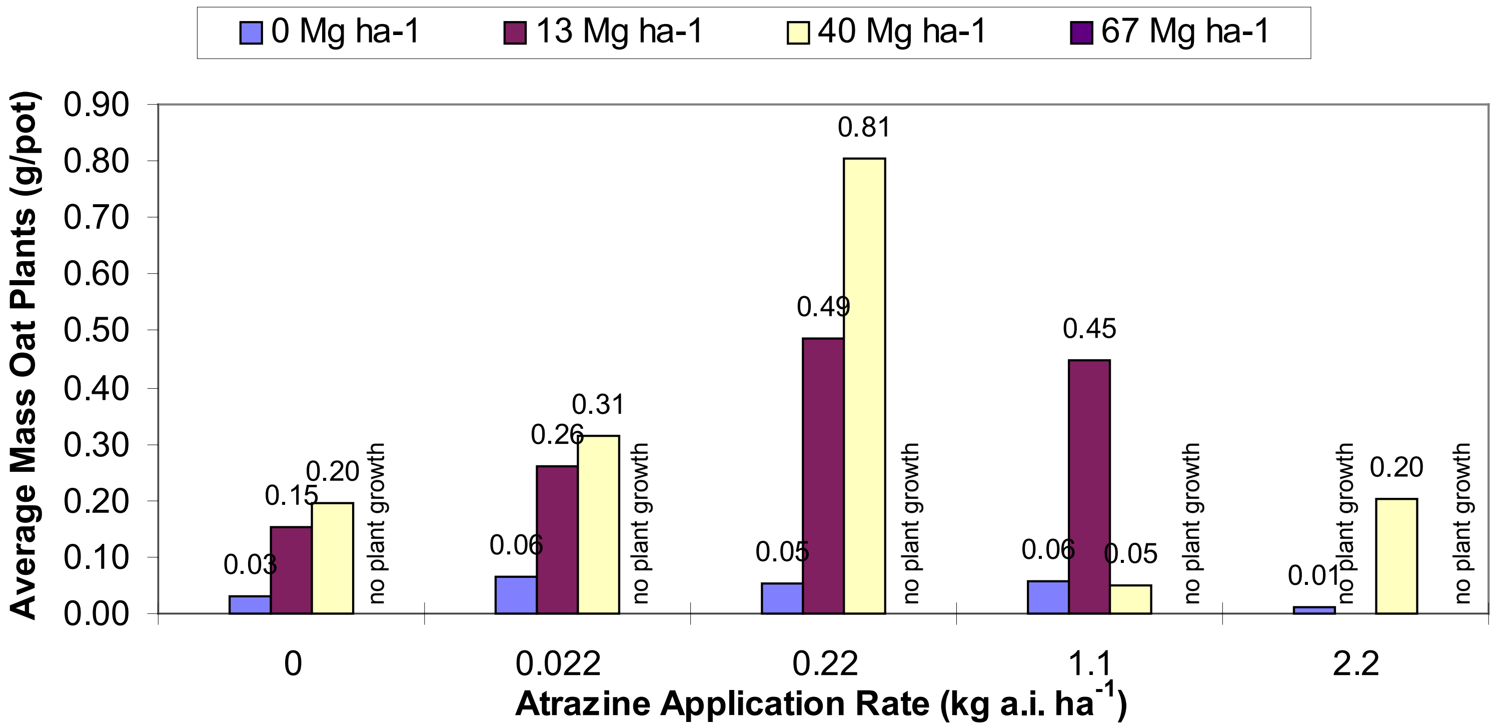


Figure 2.2. Average mass of oats per pot for stockpiled litter applied at four rates and atrazine applied at five rates.

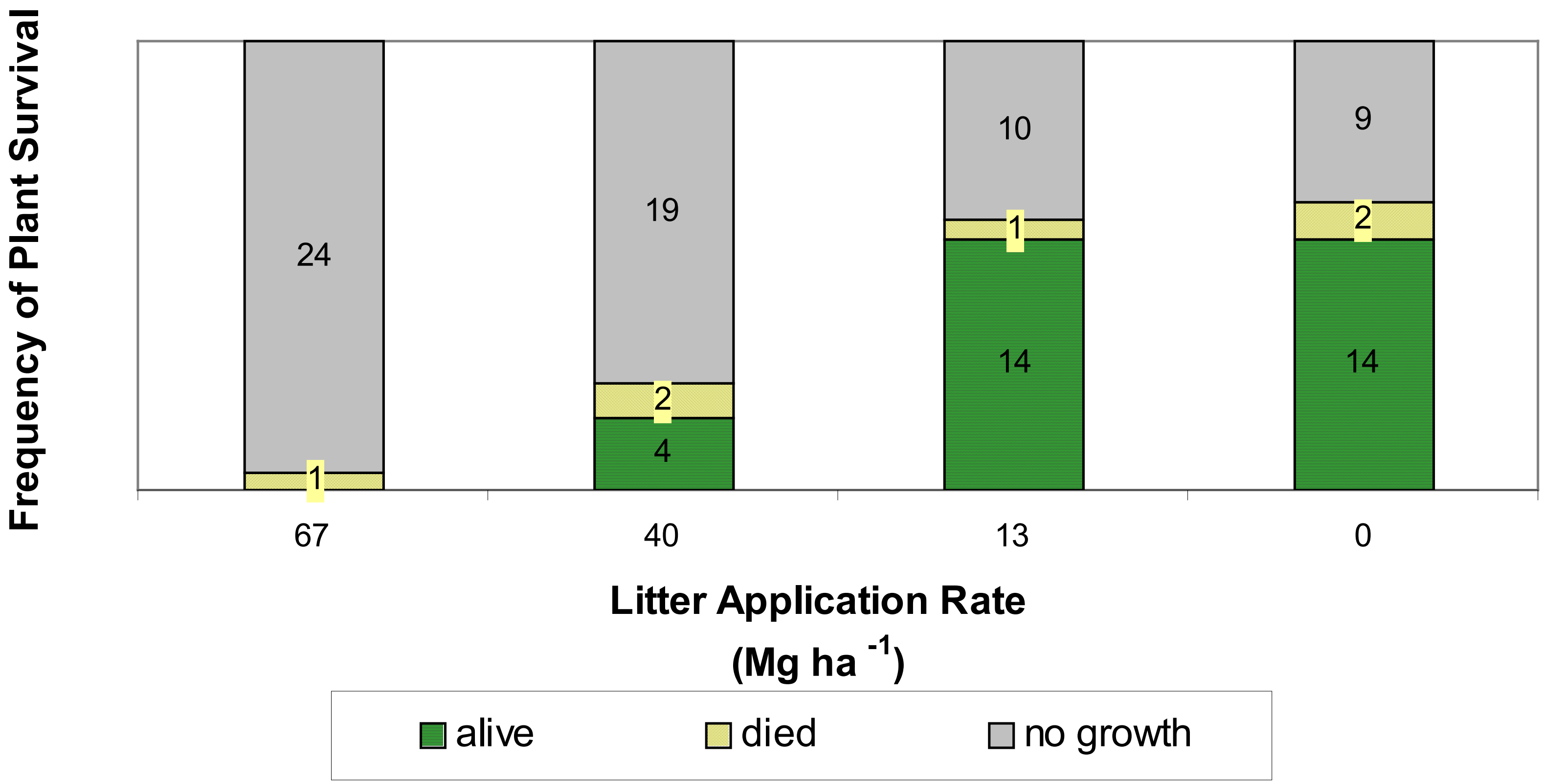


Figure 2.3. Frequency of Oat Plant Survival 14 Days After Exposure to 0 kg a.i. ha^{-1} Atrazine.

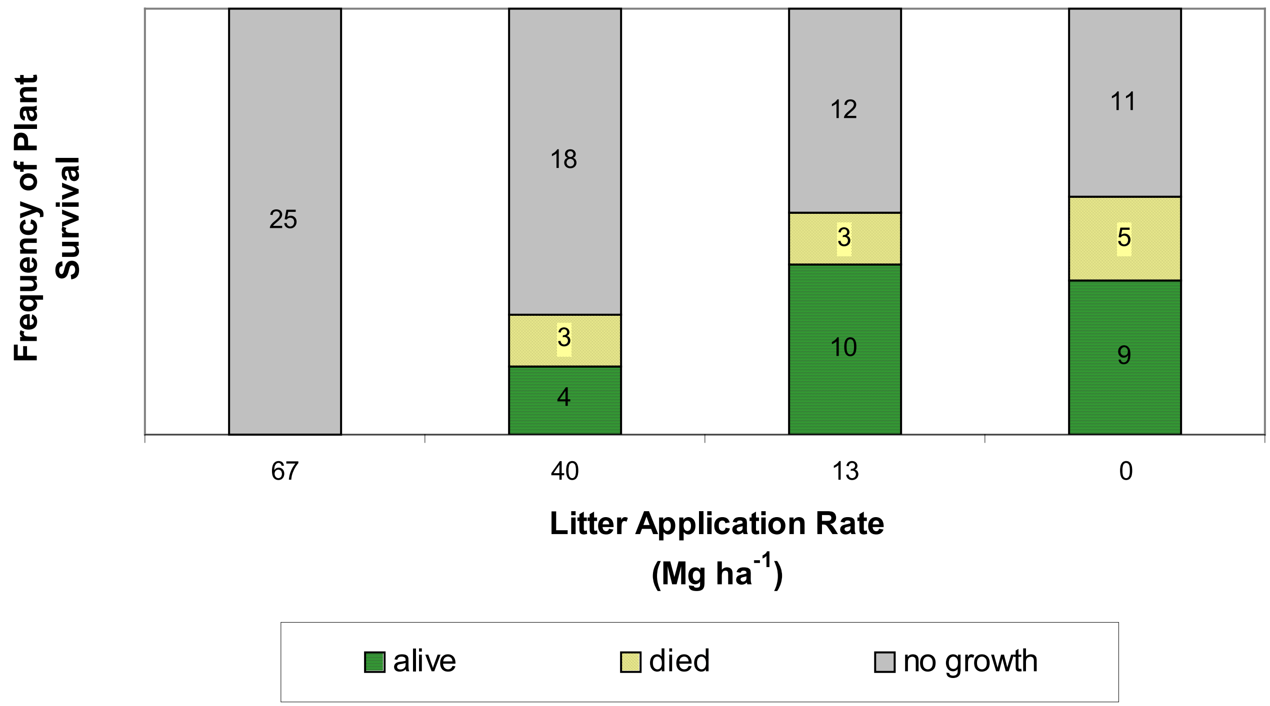


Figure 2.4. Frequency of oat plant survival 14 days after exposure to 0.22 kg a.i. ha^{-1} atrazine.

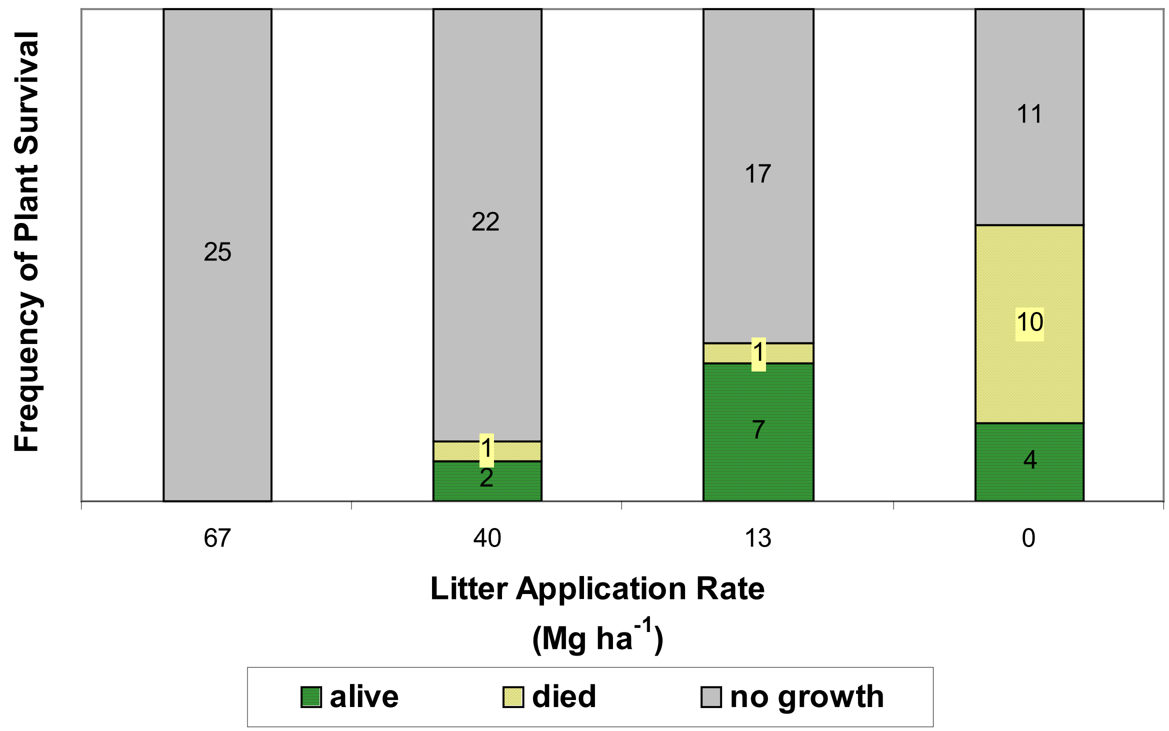


Figure 2.5. Frequency of Oat Plant Survival 14 Days After Exposure to 1.1 kg a.i. ha^{-1} Atrazine.

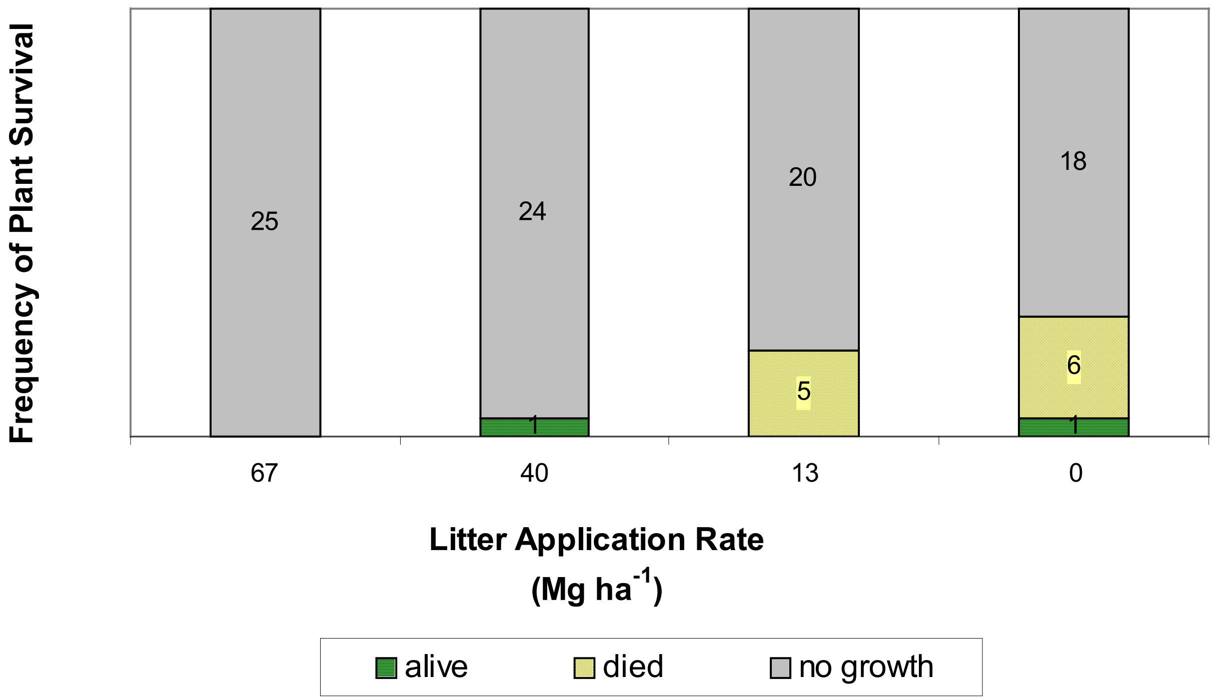


Figure 2.6. Frequency of Oat Plant Survival 14 Days After Exposure to 2.2 kg a.i. ha^{-1} Atrazine.

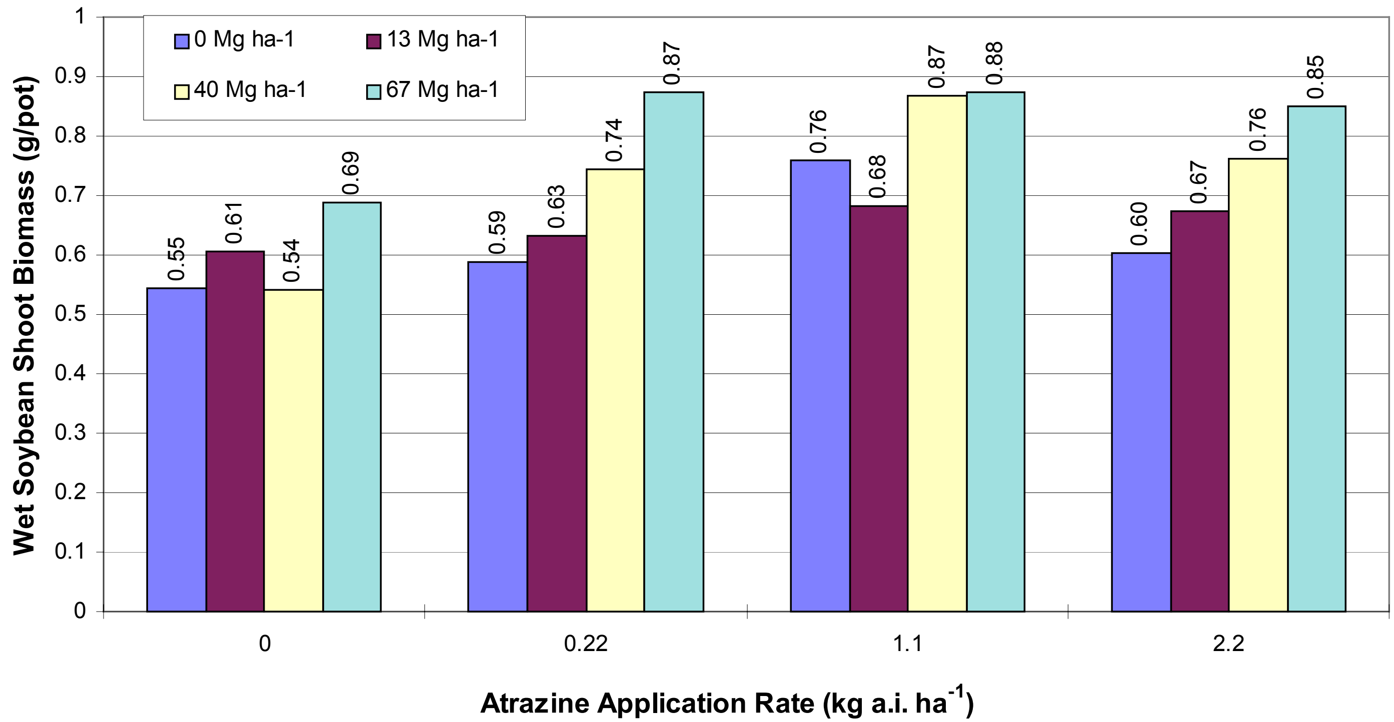


Figure 2.7. Fresh soybean shoot biomass grown in four rates of weathered poultry litter with four application rates of atrazine after 14 days of growth.

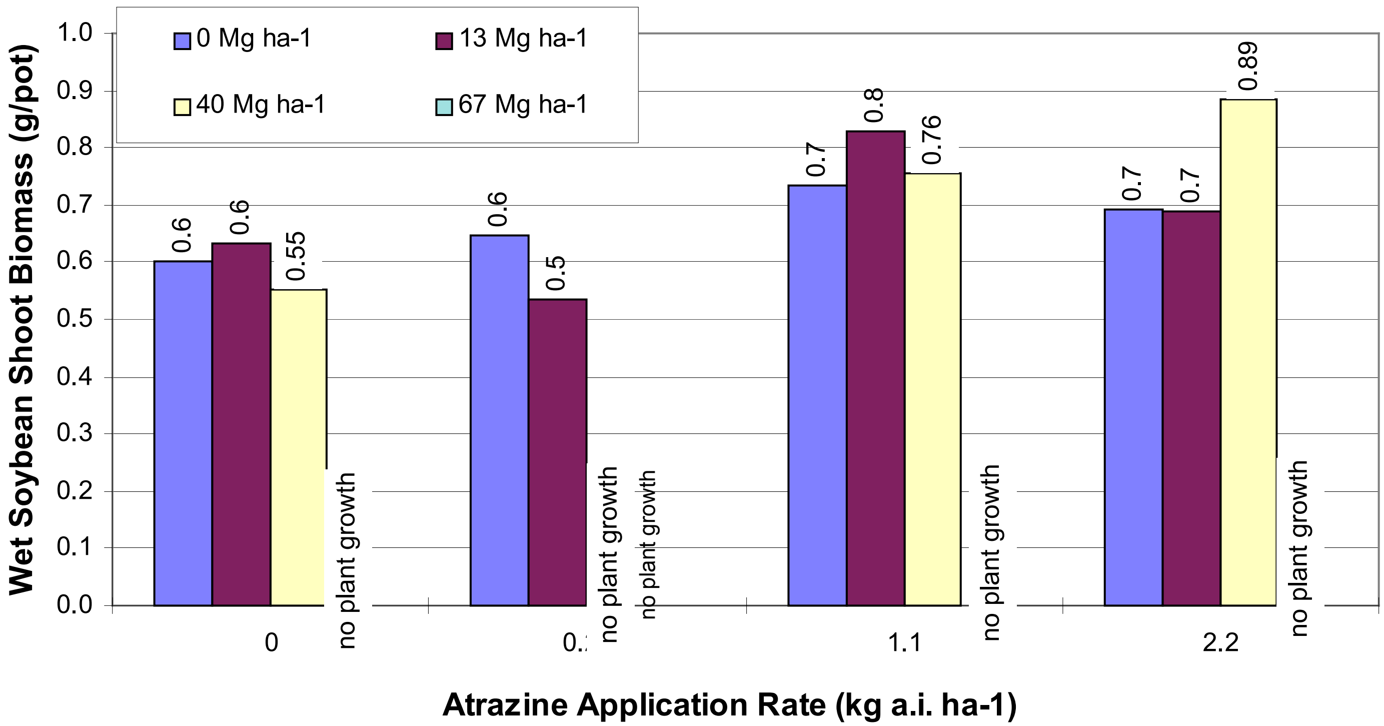


Figure 2.8. Fresh soybean shoot biomass grown in four rates of stockpiled poultry litter with four application rates of atrazine after 14 days of growth.

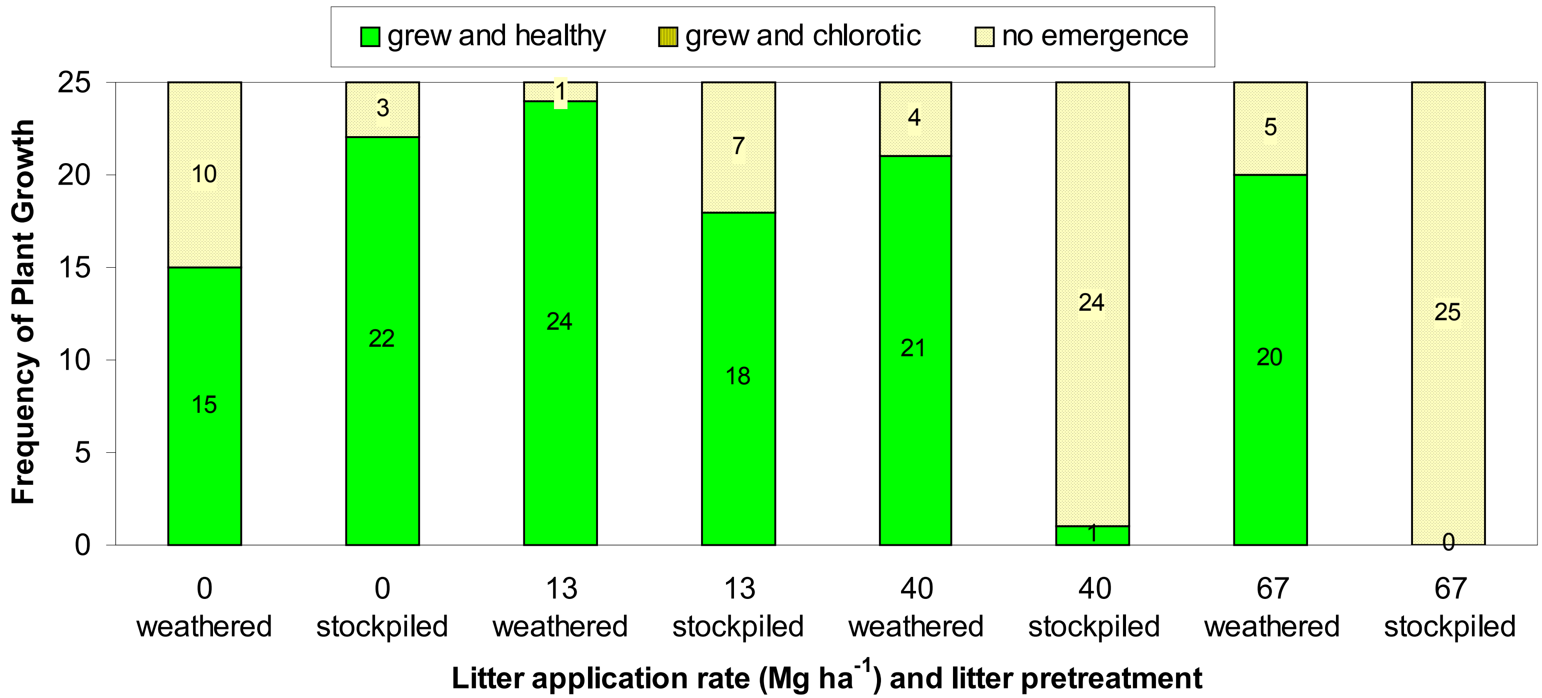


Figure 2.9. Frequency of Soybean Plant Growth for Weathered of Composted Litter and 0 kg a.i. ha^{-1} Atrazine.

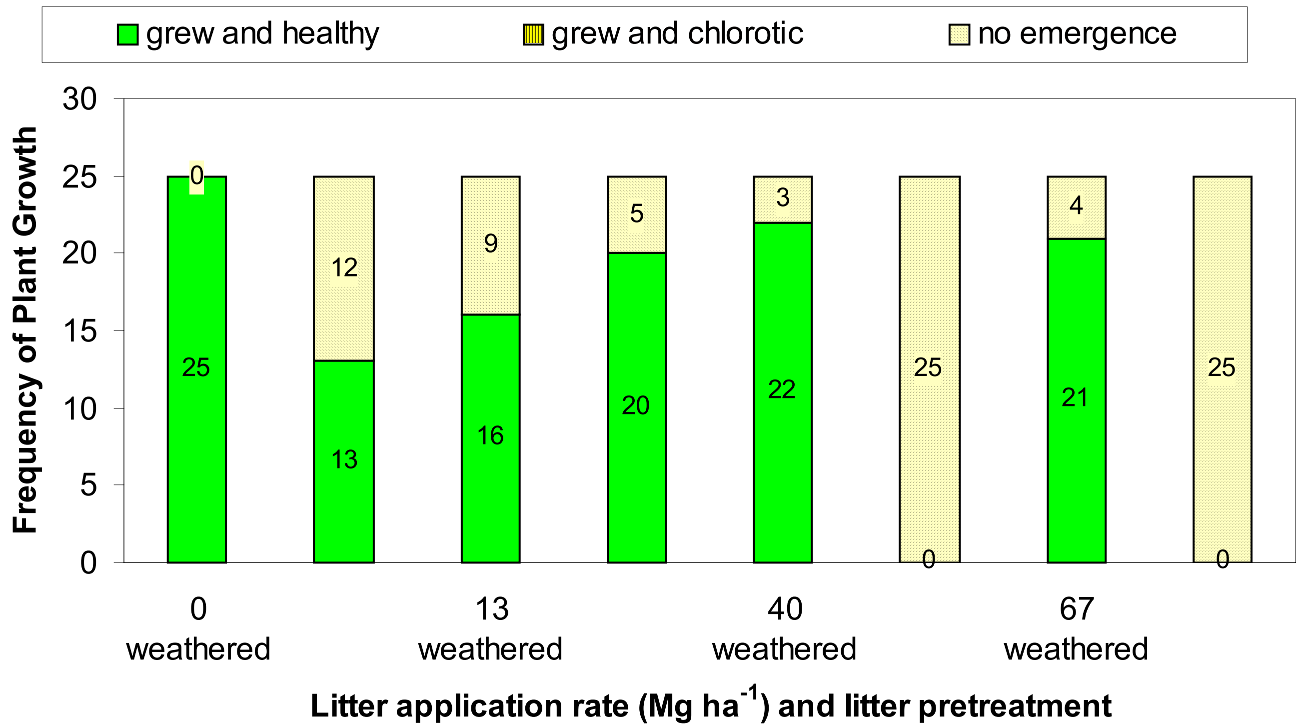


Figure 2.10. Frequency of Soybean Plant Growth for Weathered and Stockpiled Litter and 0.22 kg a.i. ha^{-1} Atrazine.

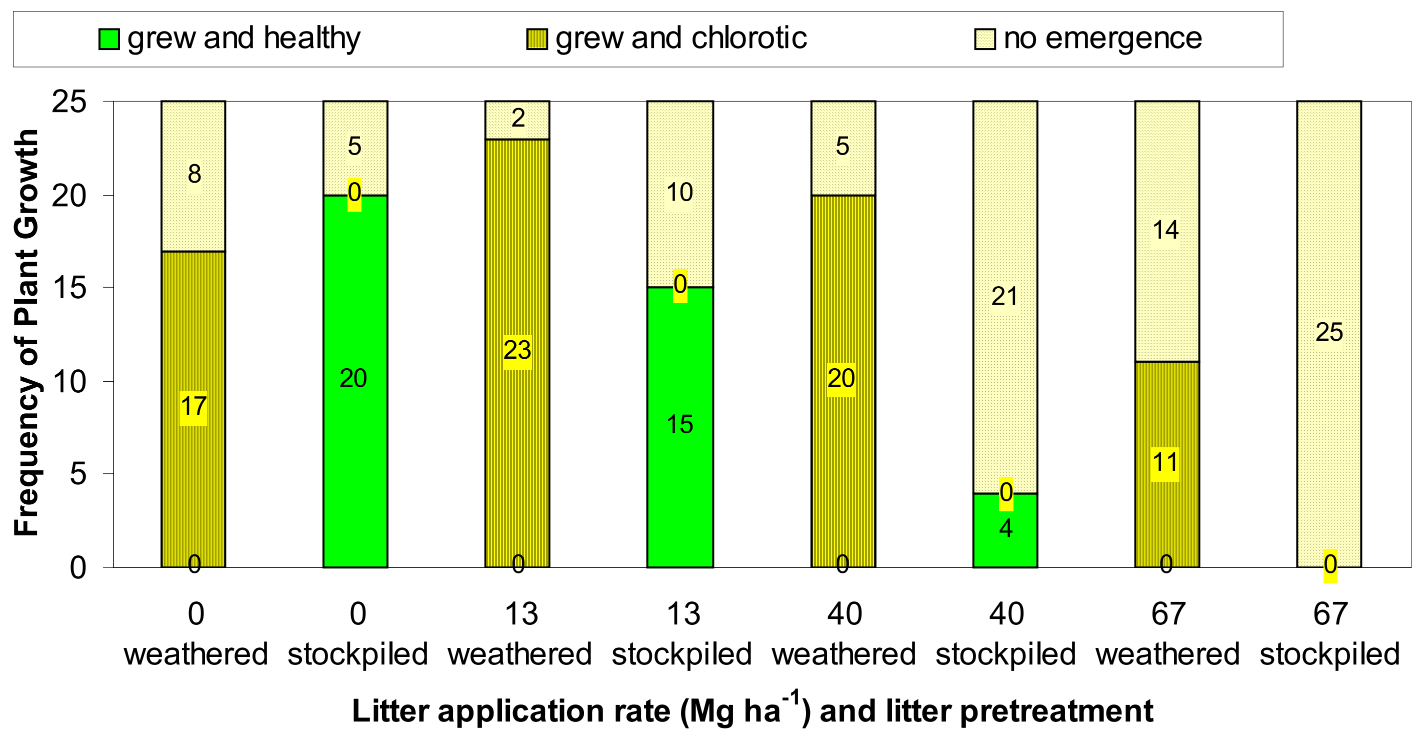


Figure 2.11. Frequency of Soybean Plant Growth for Weathered and Stockpiled Litter and 1.1 kg a.i. ha^{-1} Atrazine.

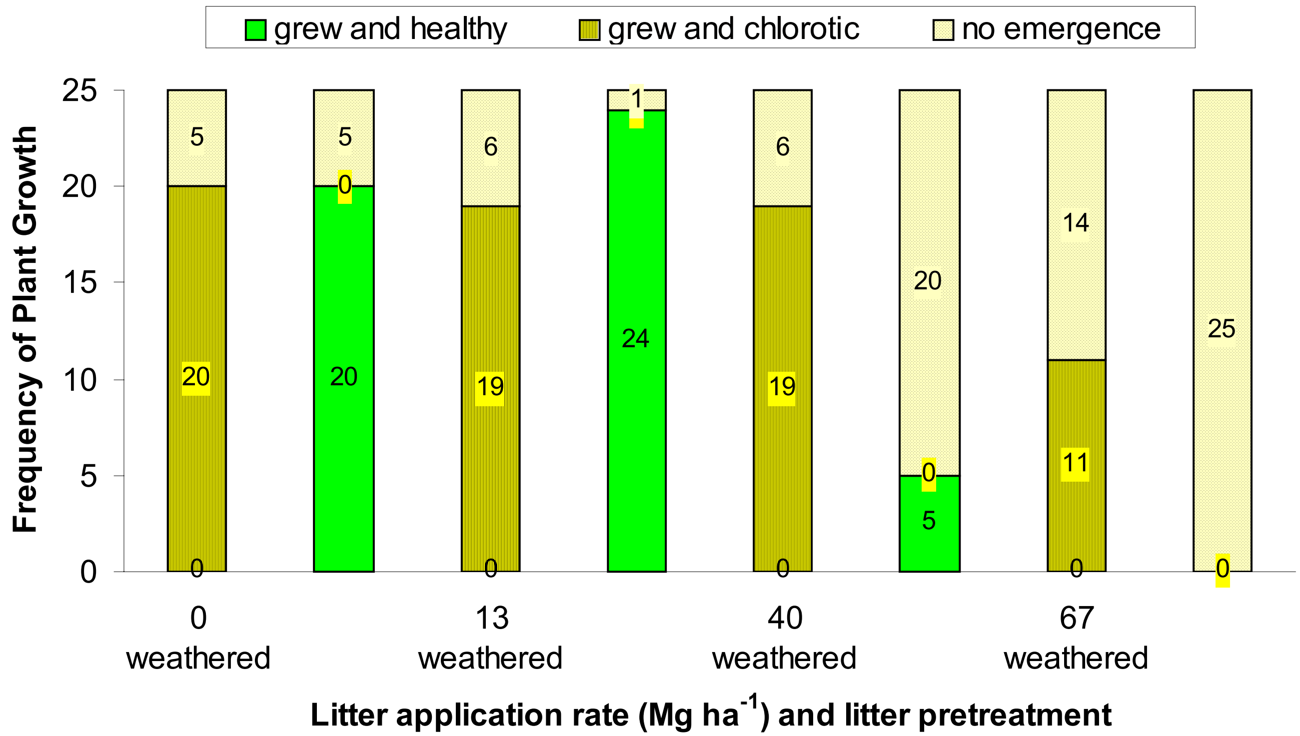


Figure 2.12. Frequency of Soybean Plant Growth for Weathered and Stockpiled Litter and 2.2 kg a.i. ha^{-1} Atrazine.

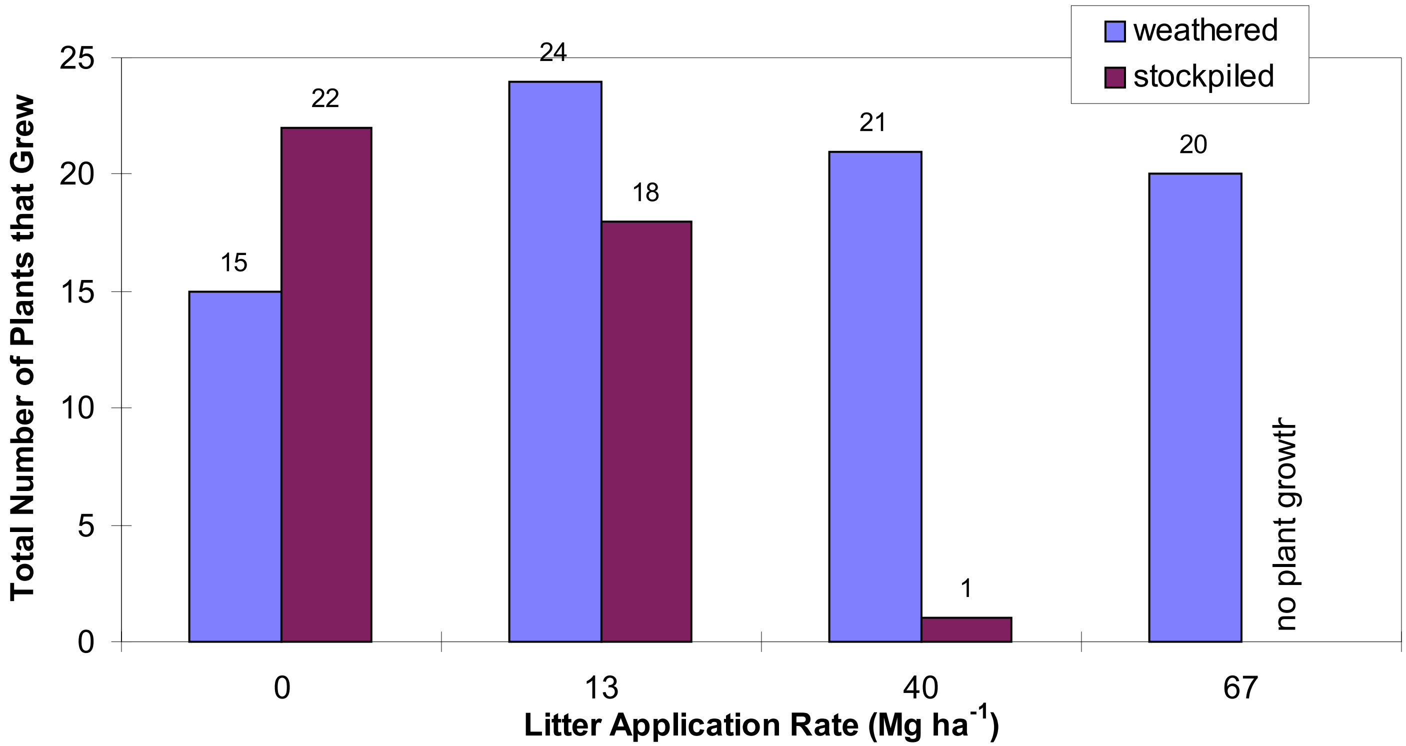


Figure 2.13. Total Number of Soybean Plants for Weathered and Stockpiled Litter Applied at Four Rates with Addition of 0.00 kg a.i. ha^{-1}.

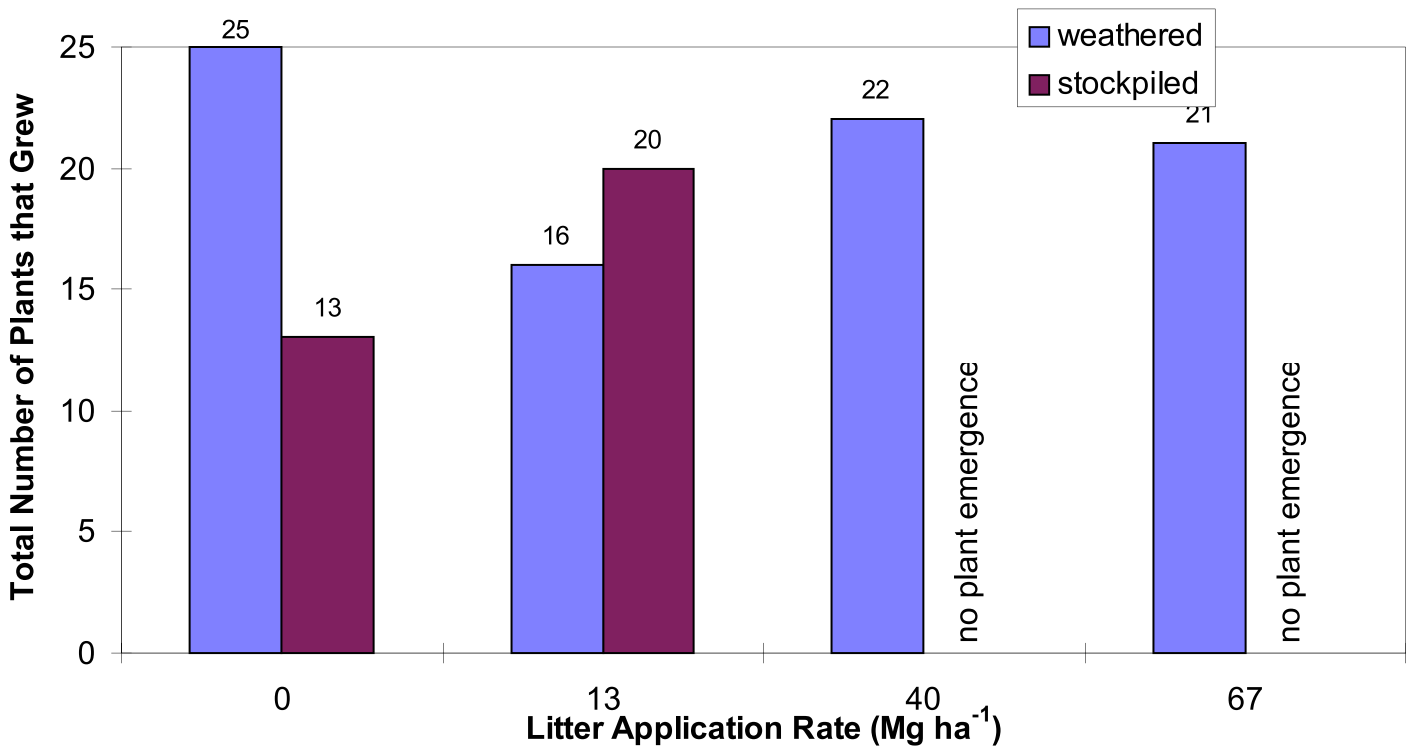


Figure 2.14. Total Number of Soybean Plants for Weathered and Stockpiled Litter Applied at Four Rates with Addition of 0.22 kg a.i. ha^{-1} atrazine.

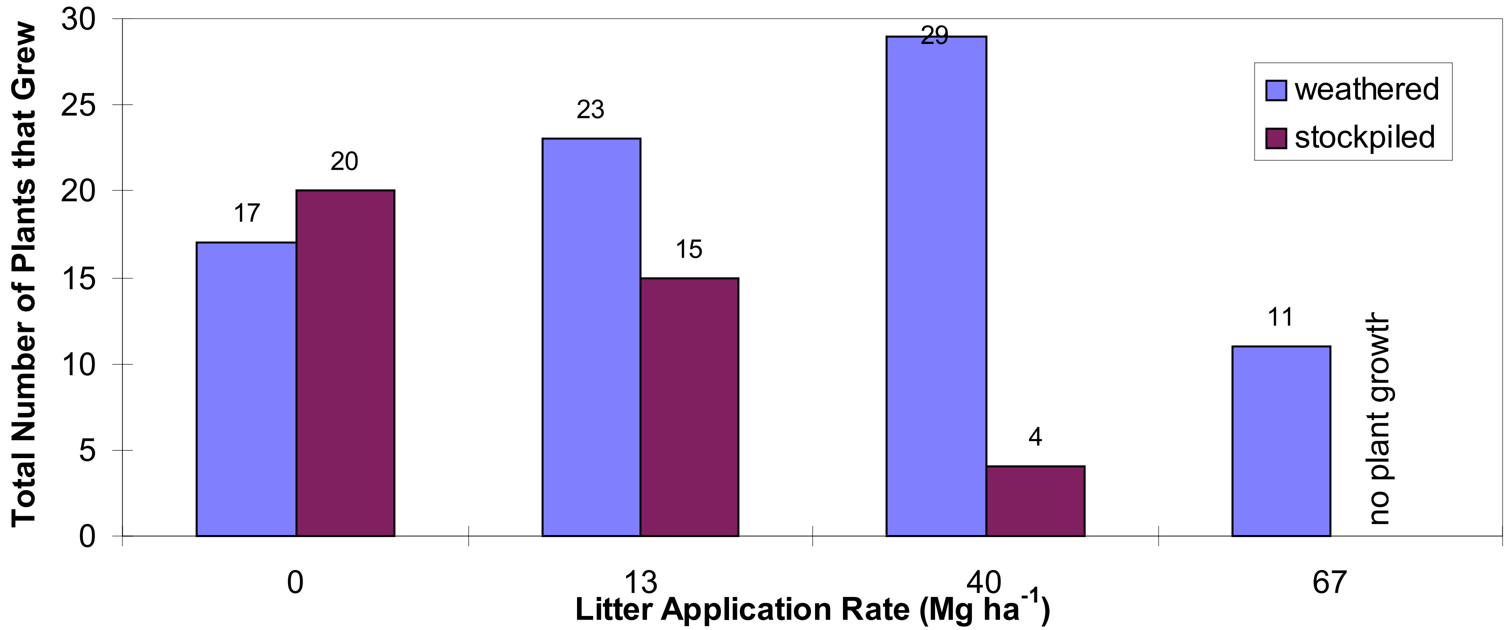


Figure 2.15. Total Number of Soybean Plants for Weathered and Stockpiled Litter Applied at Four Rates with Addition of 1.1 kg a.i. ha^{-1}.

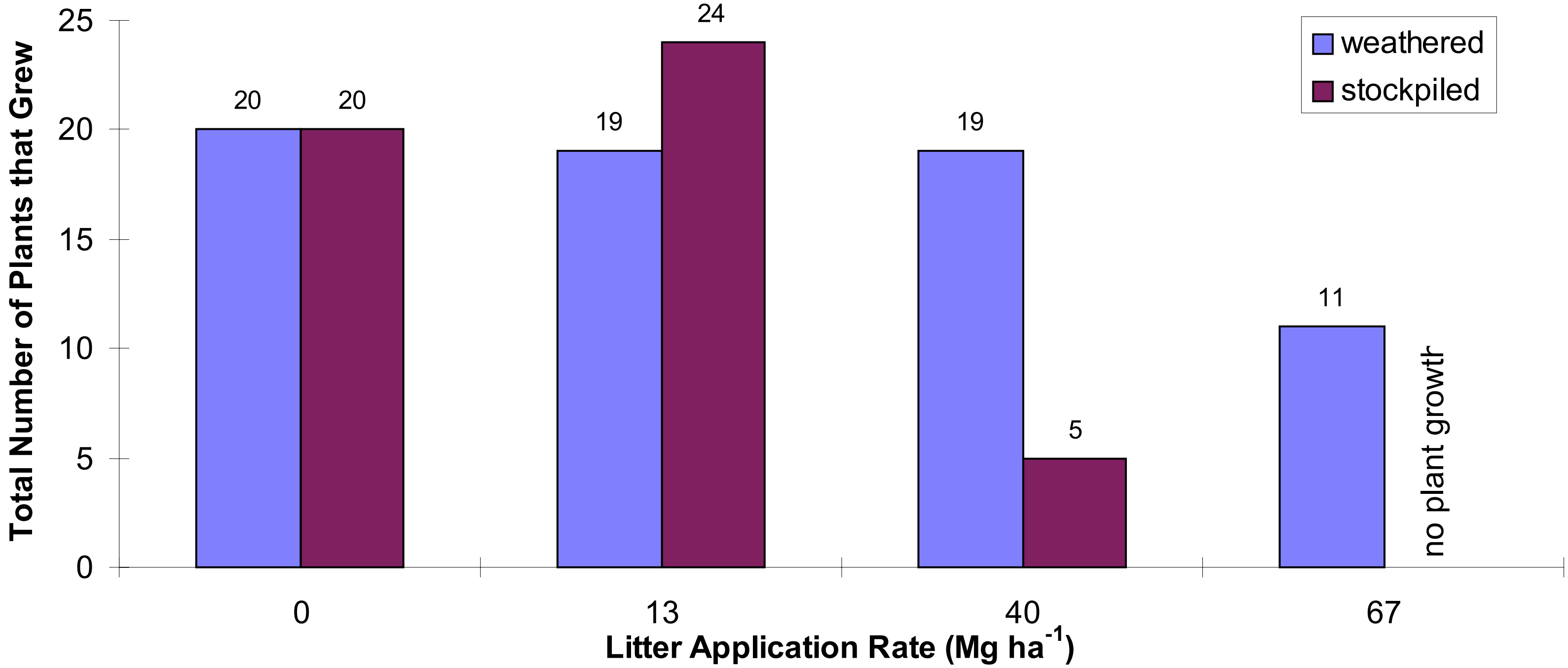


Figure 2.16. Total Number of Soybean Plants for Weathered and Stockpiled Litter Applied at Four Rates with Addition of 2.2 kg a.i. ha^{-1}.

Figure 2.17. Soybean plants with chlorosis.

POULTRY LITTER EFFECTS ON ATRAZINE LEACHING

Abstract

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is subject to degradation in the environment into hydroxyatrazine (2-hydroxy-4-ethylamino-6-isopropylamino-1,3,5-triazine), desisopropylatrazine or DIA (2-chloro-4-ethylamino-6-amino-1,3,5-triazine), and desethylatrazine or DEA (2-chloro-4-amino-6-isopropyl-amino-1,3,5-triazine). Soil type and organic amendments have been found to affect the amount of degradation and adsorption of atrazine. Leachate can be used to determine the amount of atrazine degradation and adsorption onto the soil. Leachate from pots that had atrazine applied in conjunction with either stockpiled or weathered poultry litter was collected and analyzed for atrazine, DIA and DEA, using solid phase extraction and GC-MS. Greater application rates of poultry litter significantly increased the amount of leachate from the pots. Total amount of atrazine leaching was dependent on the amount of leachate drained from each pot. The experiment, done in conjunction with an oat bioassay, showed that the amount of atrazine leached decreased for stockpiled poultry litter. When a similar experiment was done in conjunction with a soybean bioassay no significant difference between the amounts of atrazine leached for stockpiled ($p=0.06$) and weathered ($p=0.05$) litter. The greatest application rate of litter significantly increased the amount of atrazine leaching.

Introduction

Atrazine is subject to chemical and microbiological degradation in soils. The degradation products of atrazine include hydroxyatrazine, desisopropylatrazine (DIA) and desethylatrazine (DEA) (Ahrens 1994, Figure 3.1). Atrazine is a weakly basic s-triazine, and the sorption of atrazine is highly correlated with clay type and amount, organic matter content, and pH (Weber *et al.* 1993). Chemical degradation of atrazine is inversely related to soil pH (Weber *et al.* 1993). Soil type and organic amendments are important in affecting the rate of the microbial degradation of atrazine. Schoen *et al.* (1987) found that atrazine degradation increased as the organic matter content of soils increased. Both DEA and DIA are formed through biological degradation (Ahrens 1994). Atrazine is susceptible to photo-degradation to hydroxyatrazine and DEA, with a half-life of 15 days (Ahrens 1994).

Atrazine is absorbed through the roots of plants and translocated to the leaves. Atrazine has been shown to be absorbed by the roots of intact soybeans from an aqueous solution (Ashton and Crafts 1973). As a result, leachate can represent the amount of atrazine readily available in aqueous solution for plant uptake (Ahrens 1994).

Gupta *et al.* (1996) found that when poultry litter and soil were mixed, only 14% of applied atrazine remained after 30 days of incubation. After 60 days, 96% of the atrazine was degraded. These atrazine degradation rates in the presence of litter were almost twice as fast than with soil alone. Schoen *et al.* (1987) determined that water saturated soils provide optimal conditions for atrazine degradation.

Guo *et al.* (1991) consistently found lower amounts of atrazine in leachates from soils with organic amendments than from soils that were not amended. Soils were treated with waste-activated carbon (activated carbon used in corn sweetener filtration), digested municipal sewage sludge and animal manure. They found that the activated carbon was much more effective than the sewage sludge, and the animal manure at decreasing the amount of atrazine leached from the system. They assumed that the atrazine that did not leach was sorbed to the organic particles.

Atrazine sorption and movement was studied in soils amended with poultry manure, sewage sludge, mushroom compost, peat, and pig manure (Baskaran 1996). Sorption of atrazine was found to be dependent on the organic matter content of the soil, therefore the addition of organic waste reduced the leaching loses of atrazine. Sorption increased when dissolved organic carbon was combined with the soil before the addition of atrazine. Incubation of the soil with poultry manure for 24 hours resulted in 30.6% of the carbon added by the poultry litter remaining in the soil.

Volatilization of atrazine was found to be greater initially for atrazine applied to mulch compared to bare soil (Gish *et al.* 1995). However, the amount of volatilization decreased after irrigation which washed the herbicide into the mulch. After 35 days, about 4 to 9% of the applied atrazine to bare soil volatilized under temperatures ranging from 25°C to 35°C. Under mulched conditions, the range was from 2 to 6% of the applied atrazine.

When atrazine was applied to soil that has been previously treated with pig slurry containing dissolved organic matter, there was a larger retention capability than when applied to untreated soil (Businelli 1997). This was attributed to increased amount of organic carbon.

The purpose of this experiment was to determine if atrazine adsorption is affected by poultry litter through analysis of leachate from pots that were treated with poultry litter and atrazine. The composition of the leachate was used as an indicator of atrazine adsorption and degradation by measuring atrazine metabolites.

Materials and Methods

Much of the land application of poultry litter in North Carolina occurs on sandy Coastal Plain soils. A Lakeland sand (siliceous, thermic, coated Typic Quartzipsamments) collected at the Sandhills Research Station, Jackson

Springs, NC was selected due to its low organic matter content, which minimizes the interactions between atrazine and the native soil organic matter.

Litter:

Stockpiled poultry litter was obtained from North Carolina State University's Unit 9 poultry house, Raleigh, NC, and analyzed by the North Carolina State University Soil Science Service Lab (Table 3.1).

Application rates of litter were based on nitrogen recommendations for corn. Litter was applied to the surface of pots at 0X, 1X, 3X, and 5X the recommended nitrogen rate for a 120 bu ac^{-1} corn crop using a 50% availability factor. The recommended litter application rate was based on Zublena *et al.* (1993), assuming no residual nitrogen and no pre-plant fertilizer (see Table 3.2). The corresponding rates used in the experiments are given in Table 3.3. The pots were plastic drinking cups, 10 cm in diameter with small holes in the bottom for drainage. The surface area of soil in the pot determined the amount of litter per pot.

The pore volume of the Lakeland sandy soil was determined by weighing 50 cm^3 sand in a pot and then saturating the soil with water estimated the pore volume of the soil. The pot was allowed to drain for 30 minutes before weighing again. The pore volume was estimated as the difference between the two weights.

The pots, 10 cm diameter drinking cups, were prepared for an oat bioassay and then leachate from the pots was analyzed. Each pot was filled with 350 cm^3 (approximately 650 g) of Lakeland sand and completely saturated with water. The pots were allowed to drain for 1 hour. Litter was weighed out and applied to the surface of the pots (Figure 3.2). Five pre-germinated oat seeds were planted in each pot approximately 1 to 2 cm into the soil, with five replicates of each litter rate and atrazine rate (see Table 3.3). After litter application, the pots were watered with 50 ml of water and left to sit for 2 hours. Atrazine was applied as AATREX 4L (Syngenta Crop Protection, Inc., Greensboro, NC) at five rates (see Table 3.4) using a spray table to ensure uniform coverage. The atrazine was applied using the equivalent of 123 l water ha^{-1}, a volume large enough to obtain even coverage over the pots. Pots were moved to the greenhouse after atrazine application. All pots received the same amount of water daily. All pots received the same amount of water daily. To determine water amounts, several pots were selected and watered in 15 ml increments until leaching occurred, the remaining pots were then watered with the same volume to minimize leaching receiving between 15 ml to 30 ml water daily. This experiment was done in June 1996 during which the greenhouse was often very hot and pots would be watered twice a day.

After 14 days of growth the bioassay information was recorded and the plants were harvested.

The pots were placed onto plastic beakers and 130 ml (pore volume plus 30 ml) of water was added to each pot. The pots were allowed to drain freely for 2 hours. The beakers were then weighed to determine the amount of leachate. Multiplying the weight of leachate by 1 ml g-1 of water approximated the volume of leachate. Four ml of leachate was transferred into a capped polystyrene test tube, capped, and stored frozen until analysis.

Stockpiled and Weathered Litter Leachate (from soybean bioassay):

Weathered and stockpiled litters were used for this bioassay and leaching experiment. The weathered litter pots were the pots used from the previous bioassay and leaching experiments; see previous section. The stockpiled litter was kept in an airtight container in the greenhouse. Both litter treatments were subject to the same temperature variations in the greenhouse during that period. The pots were set up in the same way as the stockpiled litter leachate experiment, using soybean seeds. After 15 days of growth, the seedlings were visually assessed for herbicide damage. The soybean plants were then harvested and fresh weights were recorded for each pot (Weber 1986). Leachate was collected using the same procedure as for the stockpiled litter leachate.

Atrazine and metabolites in the leachate were determined by solid phase extraction (McLaughlin and Johnson 1997). Atrazine was extracted from the leachate on 1000 mg (BAKERBOND spe * Polar Plus) C_{18} (octadecyl) extraction columns (JT Baker, Phillipsburg, NJ). One ml of 10 μg L^{-1} TBA (terbuthylazine; 2-(tert-butylamino)-4-chlor-6(ethylamino)-2-triazine) was added to each sample before extraction to determine recovery rates. One ml of leachate for the 2.2 kg a.i. ha^{-1} rate of atrazine and the control samples from 0.0 kg a.i. ha^{-1} from each litter rate were diluted with 50 ml of deionized water and pulled through the SPE column using a vacuum manifold (Waters Milford, MA, USA). After extraction, the SPE columns were placed into the freezer until they were dried and eluted.

The SPE columns were dried by pulling air through using a vacuum manifold for approximately 1.5 hours. After drying, the columns were eluted with a total of 10 ml of pesticide-grade ethyl acetate. Five ml of ethyl acetate was added to the column and 1 ml was drawn through. The remaining 4 ml were allowed to soak for one minute and then pulled through the column. This was repeated with the next 5 ml of ethyl acetate. The collected samples were capped and stored in the refrigerator.

The eluted samples were placed in a warm water bath and concentrated under a gentle stream of nitrogen until just under 4 ml. Samples were brought to a final volume of 5 ml with pesticide-grade ethyl acetate. One ml of concentrated sample was placed in a sealed amber vial for analysis by GC-MS.

The amount of atrazine, DIA, DEA and TBA was determined with a Hewlett-Packard Model G1800A GCD (Palo Alto, CA). The operating parameters outlined by McLaughlin and Johnson (1997) were used. Separate injections were used for DIA and atrazine and for DEA due to overlapping peaks.

Results and Discussion

The average pore volume for the Lakeland sand was 28.9% at saturation, which translates to 101 ml for each pot. For the leachate collected during the oat bioassay, the amount of litter applied significantly increased the amount of leachate coming out of the pots (Figure 3.3, p=0.0001, Table 3.5). The volume of leachate from litter treatments applied at 40 and 67 Mg ha^{-1} the recommended rates were not significantly different but had significantly greater volume than both the control and the recommended rate of litter application.

A visual inspection of the coverage of the soil surface of each stockpiled litter application is shown in Figure 3.2. Total surface coverage was achieved with litter at the highest rate of application. Heavier litter application increased leachate volume in both weathered and stockpiled treatments compared with the recommended rate of litter application. Weathered litter had significantly less leachate than stockpiled litter (p=0.0001, Figure 3.4, Table 3.6). Within the weathered litter application rates, the rate has a significant effect (p=0.0003, Table 3.7) on the amount of leachate. The unamended control is only minimally significantly different from the other litter application rates (p=0.0585, Figure 3.5). For stockpiled litter, the control and lowest rate had significantly less leachate than the higher rates (p=0.0001, Figure 3.6, Table 3.8). Water uptake by plants could contribute to less water being in the soil at the time of leaching and hence more water leaching from pots receiving more litter since this experiment was performed on pots used for the bioassays.

When leachate samples were collected the leachate was visually assessed before solid phase extraction. As the litter application rate increased, the color of the leachate also changed from clear to dark brown. This is most likely due to an increase in dissolved organic matter content. During solid phase extraction the dissolved organic matter bound to the C-18 cartridges and was leached out when eluted with pesticide-grade ethyl acetate.

Atrazine and DEA were present in leachate 14 days after herbicide application for the oat bioassay, while DIA was only detected in one stockpiled litter treatment (Figure 3.7). As the amount of litter applied increased, the concentration of atrazine in the leachate decreased until it was comparable to the pots that did not receive litter. It is possible that those pots not receiving litter were subject to some atrazine loss by plant uptake. The effect of increasing litter application on the total amount of atrazine in the leachate (Figure 3.8) was not significant (p=0.1103, Table 3.9). The unamended litter control pots had significantly less atrazine in the leachate (p=0.0307, Table 3.9).

The atrazine concentration in the leachate (Figure 3.7) is not statistically different among litter treatments (p=0.2204, Table 3.10). The same is true for DEA, but not DIA. DIA was detectable only in the 13 Mg ha^{-1} treatment. Differences in DEA are not statistically different for either concentration or total leached (p=0.8362, Table 3.11, p=0.4897, Table 3.12).

Neither DEA nor DIA were detected in the leachate from the soybean bioassay. Age of litter, litter application rate, and their interaction all had a statistical influence on the concentration of atrazine in the leachate (p=0.0001, p=0.0001, p=0.0001, Table 3.13, Figure 3.9). As the rate of litter application increased, for both weathered and stockpiled litter, the atrazine concentration in the leachate decreased (p=0.0001). Litter weathering and rate also combined to decrease atrazine concentrations (p=0.0001).

DEA and DIA are formed through biological degradation (Ahrens 1994). The first experiment was done in June during warm months with stockpiled litter that had recently been obtained. These warm and moist conditions are conducive to microbial decomposition and help explain why DEA and DIA were not found during the soybean bioassay, which was performed in January during cooler months with stockpiled litter that had been stored covered in the greenhouse since June.

Atrazine concentrations in the leachate were not affected by any rate of weathered litter compared to the unamended control (p=0.2596; Figure 3.10, Table 3.14). The atrazine concentration was significantly lower for pots receiving stockpiled litter compared to the control (p=0.0001; Figure 3.11, Table 3.15). Since leachate volumes play a roll in atrazine concentrations it is best to look at total atrazine leached.

The total amount of atrazine that leached from the pots was significantly influenced by the interaction of litter age and the amount of litter applied (p=0.0140, Table 3.16, Figure 3.12). Within the weathered litter application rate, the amount of litter did significantly increased the total amount of atrazine leached from the litter application of 0 Mg ha^{-1} to 67 Mg ha^{-1} (p=0.0610; Figure 3.13, Table 3.17). The stockpiled litter has only a slightly significant impact on the total amount of atrazine leached (p=0.0543; Figure 3.14, Table 3.18). Stockpiled litter reduced total atrazine leached but the effect was only significant at the lowest litter rate (Figure 3.14).

Conclusions

Greater amounts of poultry litter significantly increased the amount of leachate draining from pots. Since the soil, litter and plant system was not closed; litter may have had a mulching effect and reduced evaporation from the soil surface. Plant uptake of water also contributed to the amount of water in the soil. Application of weathered litter produced less leaching than application of stockpiled litter. At the highest litter application rate (67 Mg ha^{-1}), weathered litter had less leaching (19% of the applied water) than stockpiled litter (39.3% of the applied water). Lesser litter application rates had a smaller impact on leaching volumes.

As the rate of stockpiled litter application increased from 13 to 67 Mg ha^{-1}, the concentration of atrazine in solution decreased. This was due to the increased amount of leachate as the litter application rate increased. A better comparison of atrazine leaching is to compare the total amount of atrazine leached as opposed to the atrazine concentration.

For the oat bioassay, the total amount of atrazine leached decreased as the amount of litter increased. However, all litter rates increased total atrazine leached compared to bare soil. The oat bioassay was done during June with freshly collected litter creating optimum conditions (warm and moist) for rapid microbial decomposition as shown with the appearance of DEA and DIA.

For the soybean bioassay the total amount of atrazine leached increased for both the weathered and stockpiled litter as the litter application increased. The soybean bioassay was done in the winter with cooler greenhouse conditions and litter that had been stockpiled longer than the litter used for the oat bioassay. Stockpiled litter had more atrazine leaching than weathered which may be due to higher amounts of dissolved organic matter in stockpiled litter. The atrazine measurement obtained in this experiment included atrazine attached to dissolved organic matter, and water-soluble atrazine. Weathered litter had more stable solid organic matter that would allow the atrazine to bond, as well as larger surface area for hydrolysis.

Litter applications could affect the potential for ground water contamination. Since the two leaching experiments contradict each other a more careful experiment needs to be done. If stockpiled litter is applied in warm summer months larger amounts of atrazine could be leached attached to dissolved organic matter than if no litter was applied. Conclusive recommendations cannot be made based on this experiment and it is recommended that the experiment be repeated under more careful guidelines in a closed system so that all aspects of atrazine loss can be determined.

References

Ahrens, William H. ed. (1994).“Atrazine” in Herbicide Handbook, Seventh Edition. Weed Science Society of America. p20-23

Ashton, Floyd M. and Alden S. Crafts (1973). “Triazines,” In Mode of Action of Herbicides. New York, NY: John Wiley and Sons.

Baskaran, S, N.S. Bolan, A. Rahman, and R.W. Tillman (1996). “Effect of exogenous carbon on the sorption and movement of atrazine and 24-D by soils,” Australian Journal of Soil Science Research. 34:609-622.

Businelli, Daniela (1997). “Pig Slurry Amendment and herbicide Coapplication Effects on s-Triazine Mobility In Soil - An Adsorption-Desorption Study,” Journal of Environmental Quality. 26:102-108.

Gish, Timothy J., Ali Sadeghi, and Brian J. Wienhold (1995). “Volatilization of Alachlor and Atrazine as Influenced by Surface Litter,” Chemosphere. 31:2971-2982.

Guo, Lei, Thomas J. Bicki, and Thomas D. Hinesly (1991). “Effect of Carbon-rich Waste Materials on Movement and Sorption of Atrazine In a Sandy, Coarse-Textured Soil,” Environmental Toxicology and Chemistry. 10:1273-1282.

Gupta, Gian, and John Baummer III. (1996). “Biodegradation of atrazine In soil using poultry litter,” Journal of Hazardous Materials. 45:185-192.

McLaughlin R.A. and B.S. Johnson (1997). “Optimizing recoveries of two cholorotriazine herbicide metabolites and 11 pesticides from aqueous samples using solid-phase extraction and gas chromatography-mass spectrometry,” Journal of Chromatography A. 790:161-167.

Moore, P.A. Jr., T.C. Daniel, A.N. Sharpley and C.W. Wood (1995). “Poultry manure management: Environmentally sound options,” Journal of Soil and Water Conservation. 50:321-327.

Schoen, Sarah R., Wray L. Winterlin (1987). “The Effects of Various Soil Factors and Amendments on the Degradation of Pesticide Mixtures,” . 347-377.

Weber, J.B. (1986). “Soils, Herbicide Sorption and Model Plant-Soil Systems,” Research Methods in Weed Science Third Edition. 155-188. Southern Weed Science Society.

Weber, Jerome B., Jack A. Best, Jane U. Gonese (1993). “Bioavailability and Bioactivity of Sorbed Organic Chemicals,” In Sorption and Degradation of Pesticides and Organic Chemicals in Soils. SSSA Special Publication no. 32:153-196.

Zublena, J.P., J.C. Barker, T.A. Carter (1993). “Soil Facts - Poultry Manure as a Fertilizer Source,” North Carolina Cooperative Extension Service, AG-439-5.

Table 3.1 : Total elemental analysis of poultry litter.

Nutrient	Elemental Analysis ($g\ kg^{-1}$)
Total Carbon	273.7
Total Nitrogen	25.2
Total Phosphorus	30.5
Total Potassium	24.5
Total Calcium	4.0
Total Magnesium	7.5

Table 3.2: Calculation of Litter Application (adaptation of Worksheet in Poultry Manure as a Fertilizer Source (Zublena, Barker, Carter 1993)).

1. Crop to be grown	corn
2. Total N (lb. $acre^{-1}$) required	150
3. Pounds of starter or pre-plant N (lb. $acre^{-1}$)	0
4. Residual N credit from legumes (lb. $acre^{-1}$)	0
5. Net N needs of crop (lb. $acre^{-1}$)	150
6. N totals of litter (lb. ton^{-1})	50.4
7. N available to crop (lb. ton^{-1}) assuming 50% availability factor	25.2
8. Application rate of litter (ton $acre^{-1}$)	5.95

Table 3.3: Poultry Litter Application Rates.

Litter Rates	**Field Rate Mg ha^{-1}**	**Stockpiled Litter Amount for Pots g**
0 Recommended rate	0	0
1X Recommended rate	13	6
3X Recommended rate	40	18
5X Recommended rate	67	30

Table 3.4: Atrazine Application Rates.

Atrazine Rates	Field Atrazine Rate kg a.i. ha^{-1}	Total Atrazine per Pot mg
0 RR	0.0	0
1/100 RR	0.022	9.37
1/10 RR	0.22	93.7
1/2 RR	1.1	36.8
RR	2.2	937

Table 3.5. Analysis of variance table for average leachate volume for oat bioassay.

Source	**DF**	**Type III SS**	**Mean Square**	**F Value**	**Pr > F**
LITTER RATE	3	24532.47	8177.49	59.78	0.0001
Contrast	**DF**	**Contrast SS**	**Mean Square**	**F Value**	**Pr > F**
0 litter rate vs. others	1	20209.49	20209.49	147.73	0.0001

Table 3.6. Analysis of variance for the volume of leachate from weathered litter compared to stockpiled litter for soybean bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	16141.39	5380.46	52.14	0.0001
WEATHERING	1	9909.07	9909.07	96.03	0.0001
LITTER RATE * WEATHERING	3	5769.92	1923.31	18.64	0.0001
Contrast	DF	Contrast SS	Mean Square	F Value	Pr > F
0 vs. others	1	4875.84	4875.84	47.25	0.0001

Table 3.7. Analysis of variance for the volume of leachate from weathered litter for soybean bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	2118.57	706.19	7.08	0.0003
Contrast	**DF**	**Contrast SS**	**Mean Square**	**F Value**	**Pr > F**
0 vs. others	1	368.20	368.20	3.69	0.0585

Table 3.8. Analysis of variance for average atrazine concentration in leachate from stockpiled litter for soybean bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	19792.74	6597.58	61.89	0.0001
Contrast	**DF**	**Contrast SS**	**Mean Square**	**F Value**	**Pr > F**
0 vs. others	1.00	6330.12	6330.12	59.38	0.0001

Table 3.9. Analysis of variance of total amount of atrazine leaching from oat bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	6217097.80	2072365.93	2.38	0.1103
Contrast	**DF**	**Contrast SS**	**Mean Square**	**F Value**	**Pr > F**
control vs. other	1	4946785.46	4946785.46	5.69	0.0307

Table 3.10. Analysis of variance of atrazine concentration from oat bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	424.93	141.64	1.65	0.2204

Table 3.11. Analysis of variance of DEA concentration from oat bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	67.17	22.39	0.29	0.8326

Table 3.12. Analysis of variance of total DEA leaching from oat bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	354210.32	118070.11	0.97	0.4897

Table 3.13. Analysis of variance of atrazine concentration in all of the leachate for weathered and stockpiled litter from the soybean bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	16141.39	5380.46	52.14	0.0001
WEATHERING	1	9909.07	9909.07	96.03	0.0001
LITTER RATE * WEATHERING	3	5769.92	1923.31	18.64	0.0001

Table 3.14. Analysis of variance of atrazine concentration for weathered litter from the soybean bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	156940.09	52313.36	1.47	0.2596
Contrast	**DF**	**Contrast SS**	**Mean Square**	**F Value**	**Pr > F**
0 vs. others	1.00	2673.74	2673.74	0.08	0.7873

Table 3.15. Analysis of variance of atrazine concentration for stockpiled litter from soybean bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	5094312.83	1698104.28	44.30	0.0001
Contrast	**DF**	**Contrast SS**	**Mean Square**	**F Value**	**Pr > F**
0 vs. others	1.00	5050826.75	5050826.75	131.78	0.0001

Table 3.16. Analysis of variance of the total amount of atrazine leaching from weathered and stockpiled litter from the soybean bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	495249068.22	165083022.74	2.11	0.1186
WEATHERING	1	123543227.23	123543227.23	1.58	0.2181
LITTER RATE * WEATHERING	3	967622865.80	322540955.27	4.12	0.014

Table 3.17. Analysis of variance of the total amount of atrazine leaching from weathered litter for the soybean bioassay.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	307786763	102595588	3.01	0.061

Table 3.18. Analysis of variance of the total amount of atrazine leaching from stockpiled litter.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
LITTER RATE	3	1155085171	385028390	3.14	0.0543

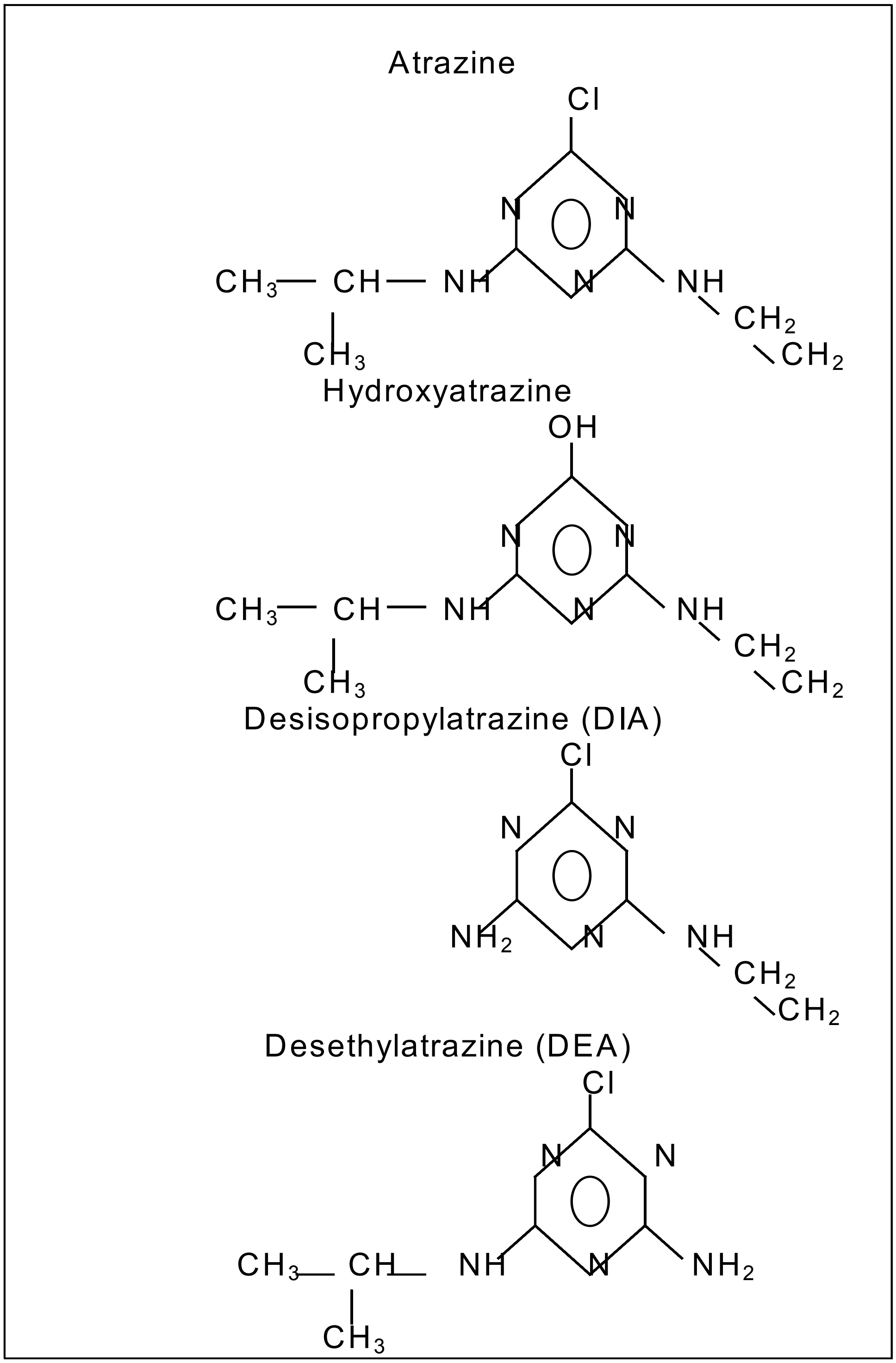
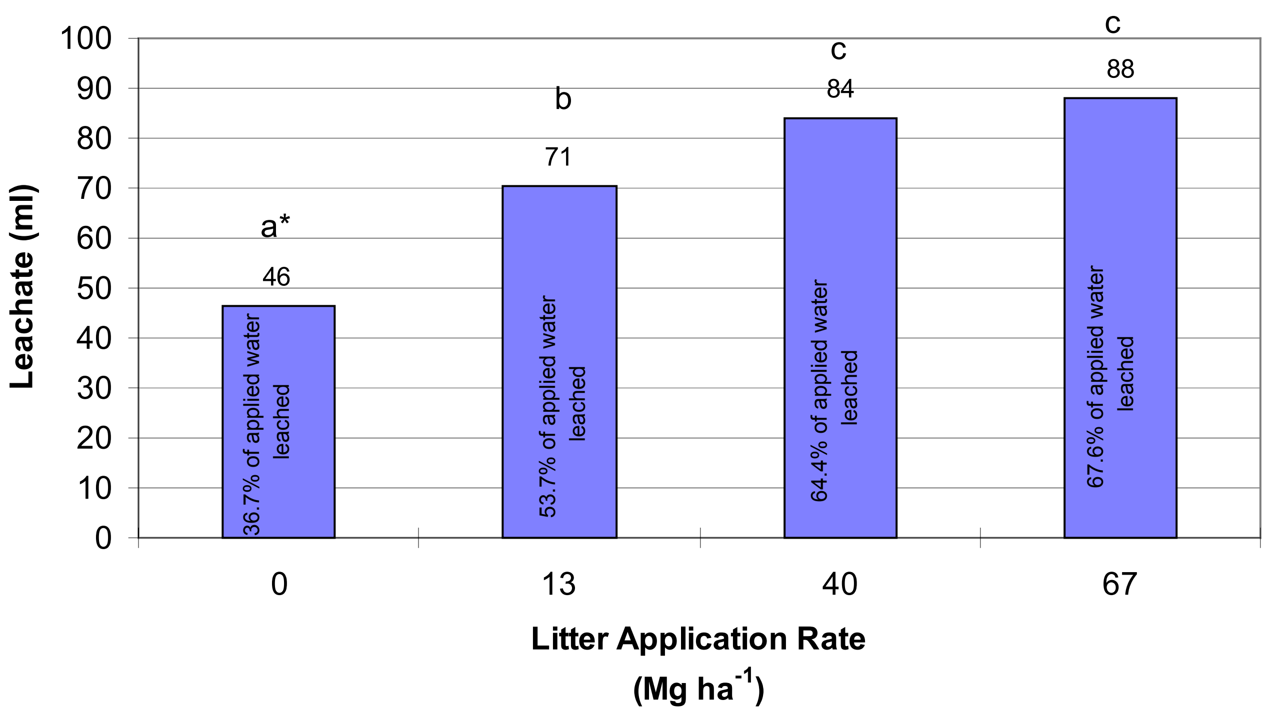


Figure 3.1. Atrazine and Metabolites.

Figure 3.2: Visual assessment of litter application rates and surface coverage.



*Values with the same letter and not significantly different (p≤0.05)

Figure 3.3. Average volume of leachate for each pot for composted litter from oat bioassay receiving 130 ml of water.

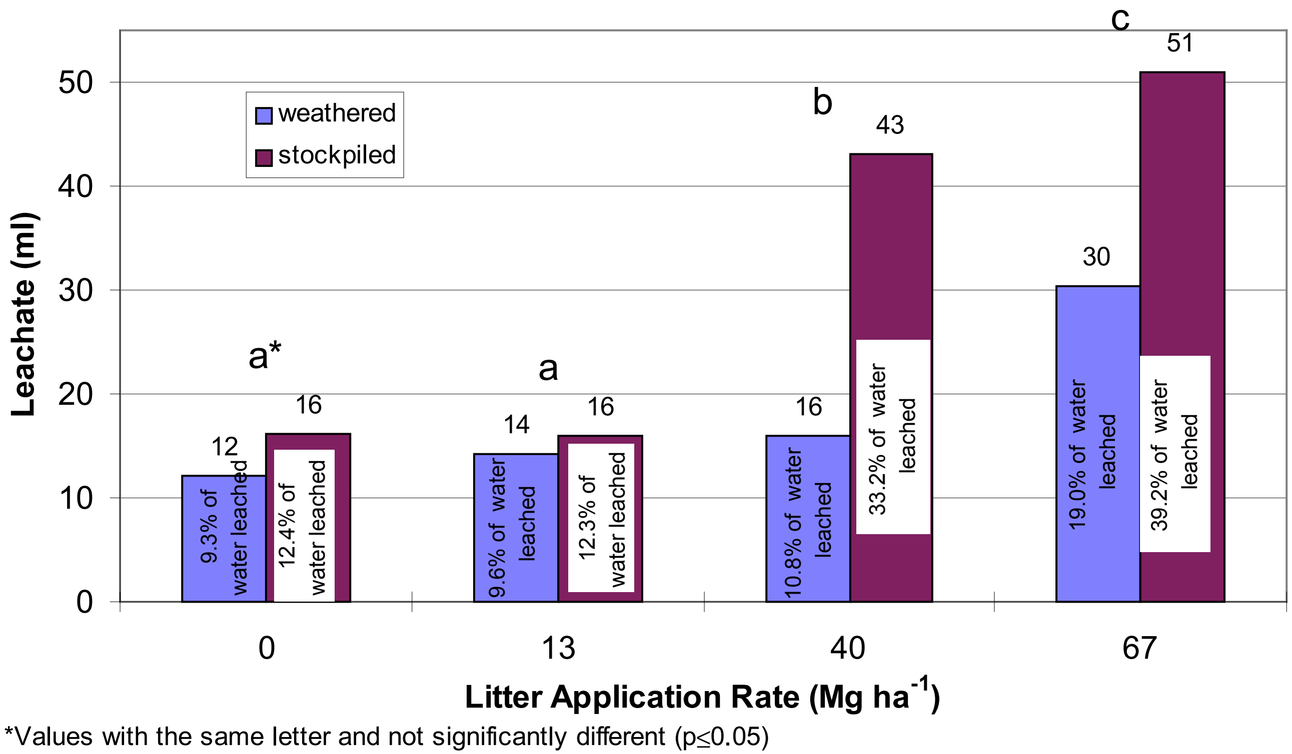


Figure 3.4. Average volume of leachate from weathered and stockpiled litter for the soybean bioassay receiving 130 ml of water.

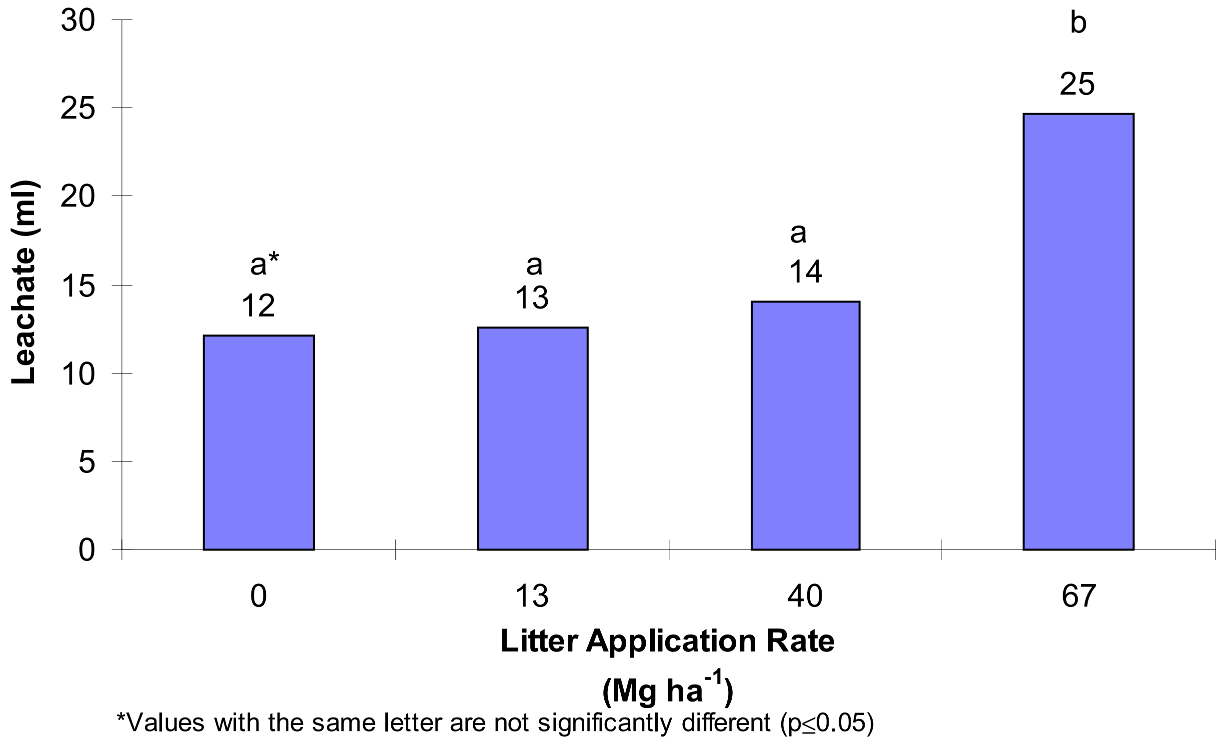


Figure 3.5. Average volume of leachate for pots with weathered litter from soybean bioassay.

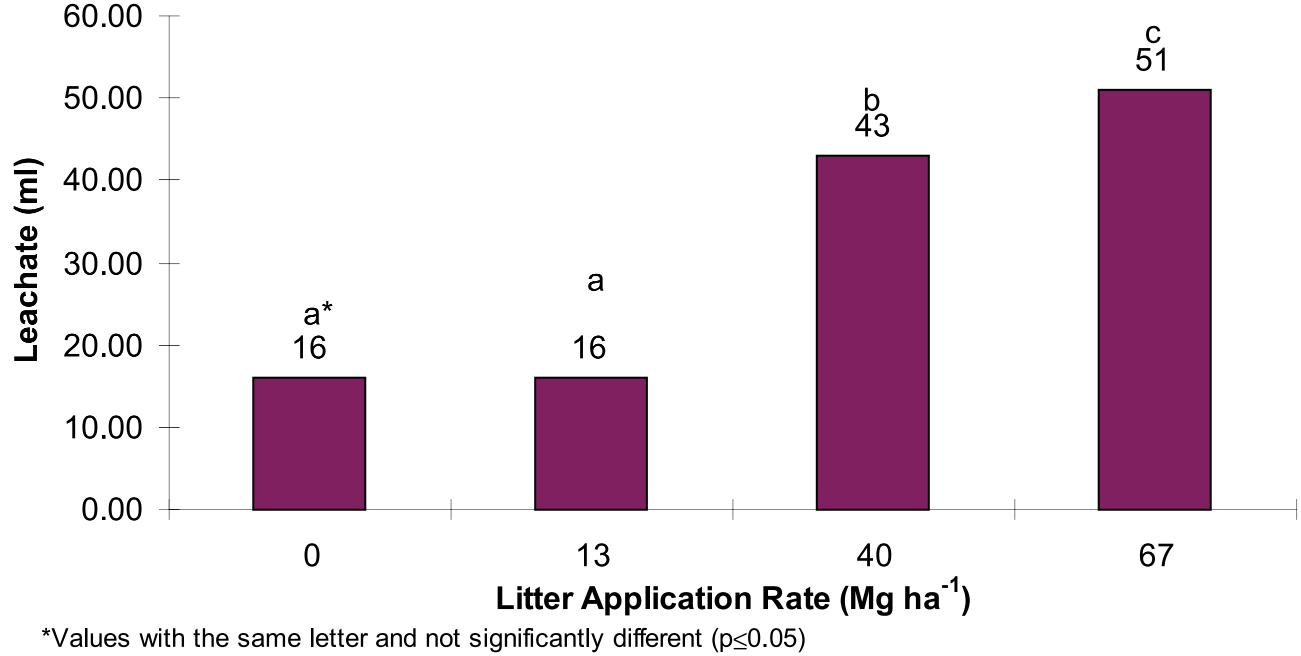


Figure 3.6. Average volume of leachate for pots with stockpiled litter from soybean bioassay.

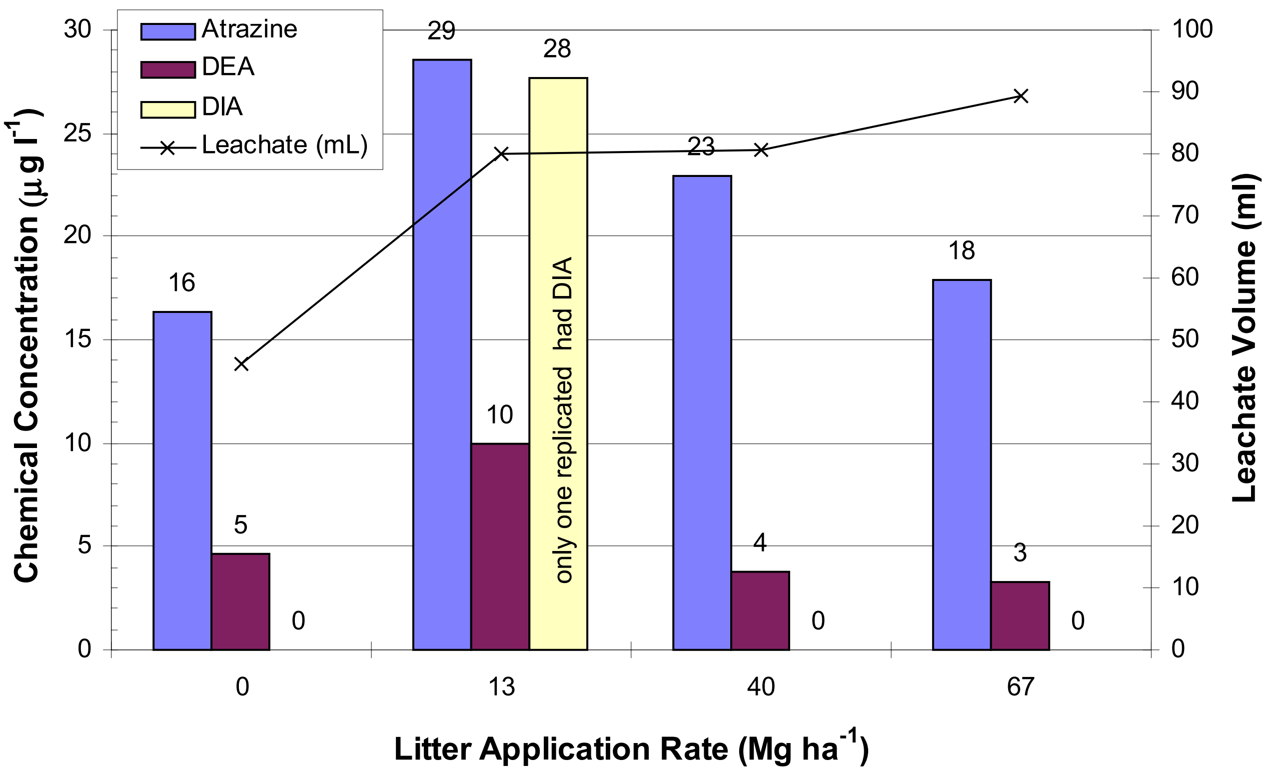


Figure 3.7. Average concentration of atrazine, DEA, and DIA in leachate for each stockpiled litter application and atrazine at 2.2 kg a.i. ha^{-1} for oat bioassay.

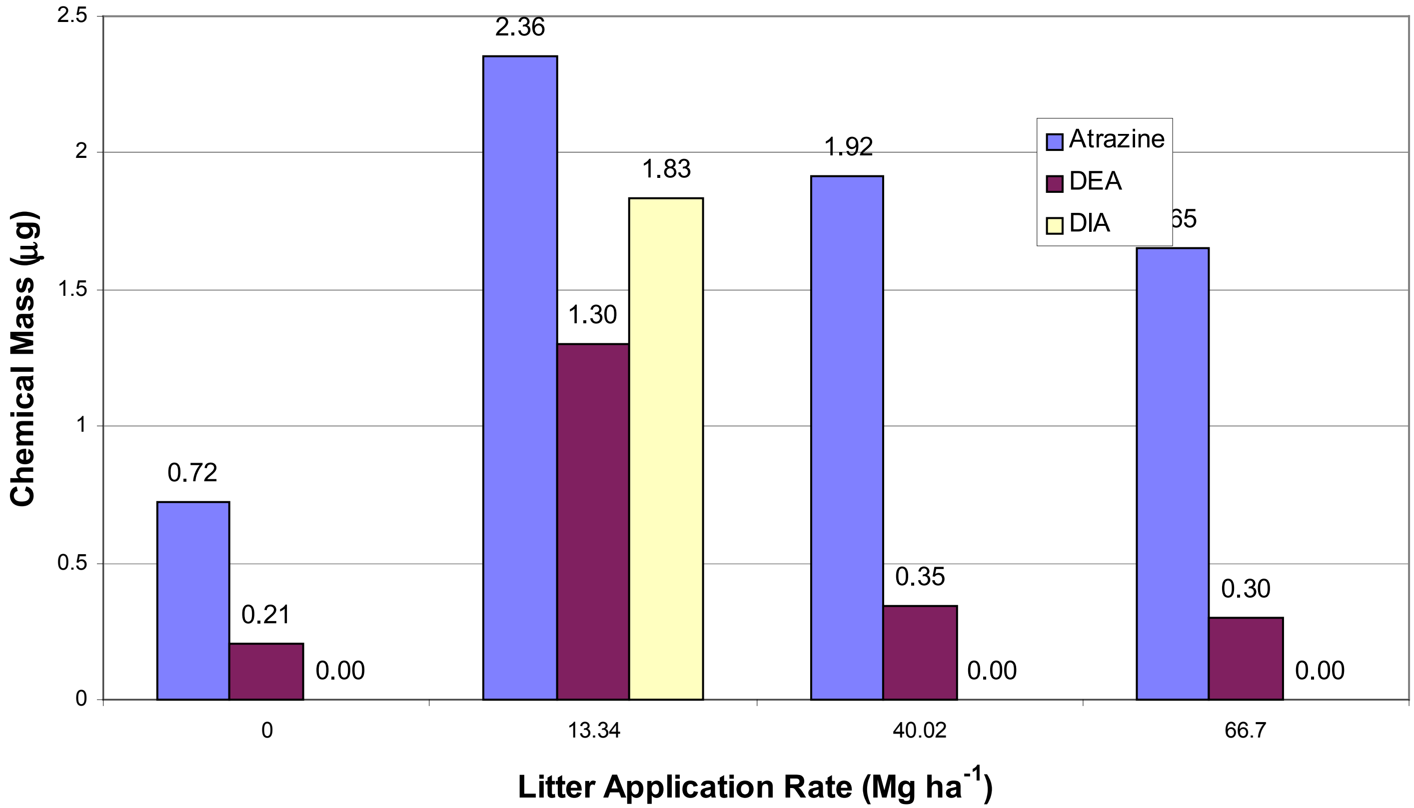


Figure 3.8. Total amount of atrazine, DEA, and DIA in leachate for each stockpiled litter application and atrazine at 2.2 kg a.i. ha^{-1} for oat bioassay.

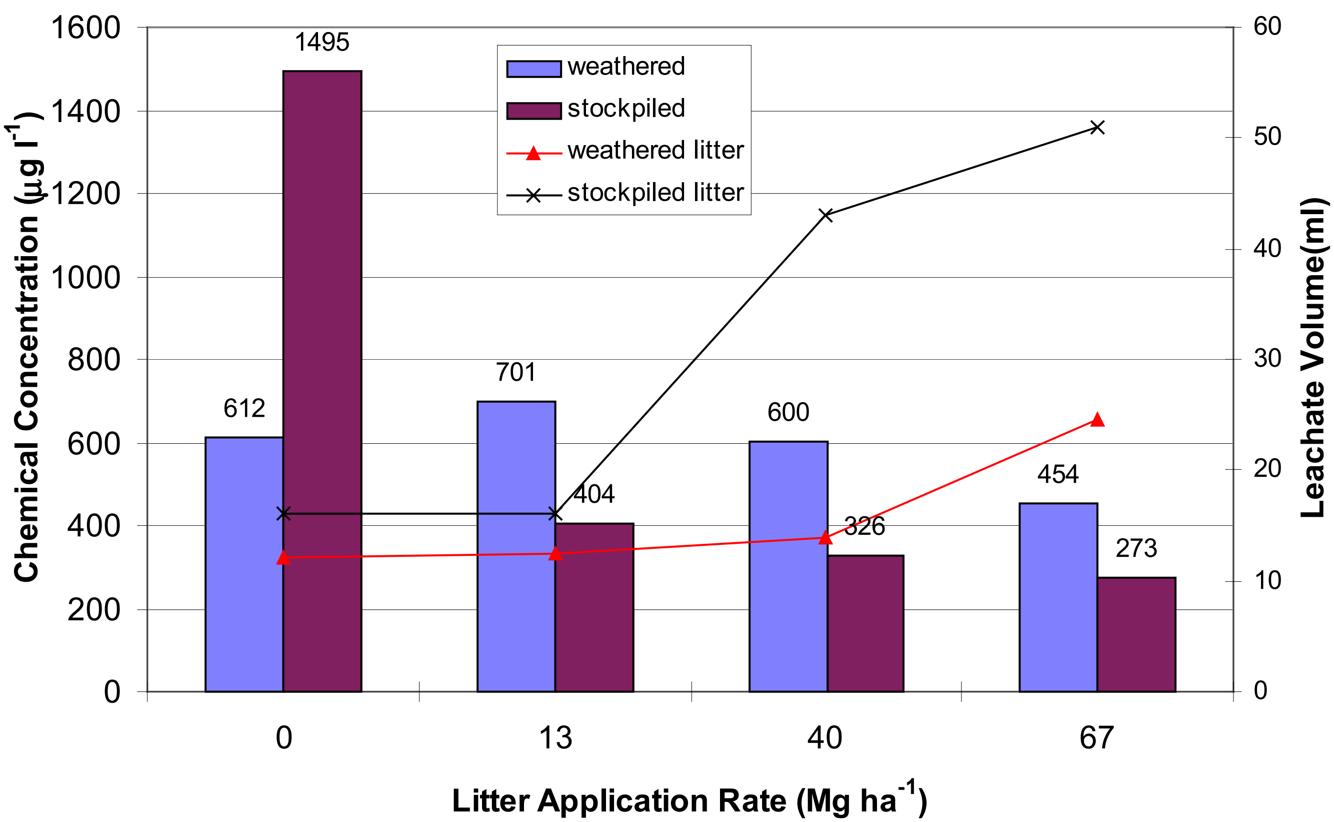
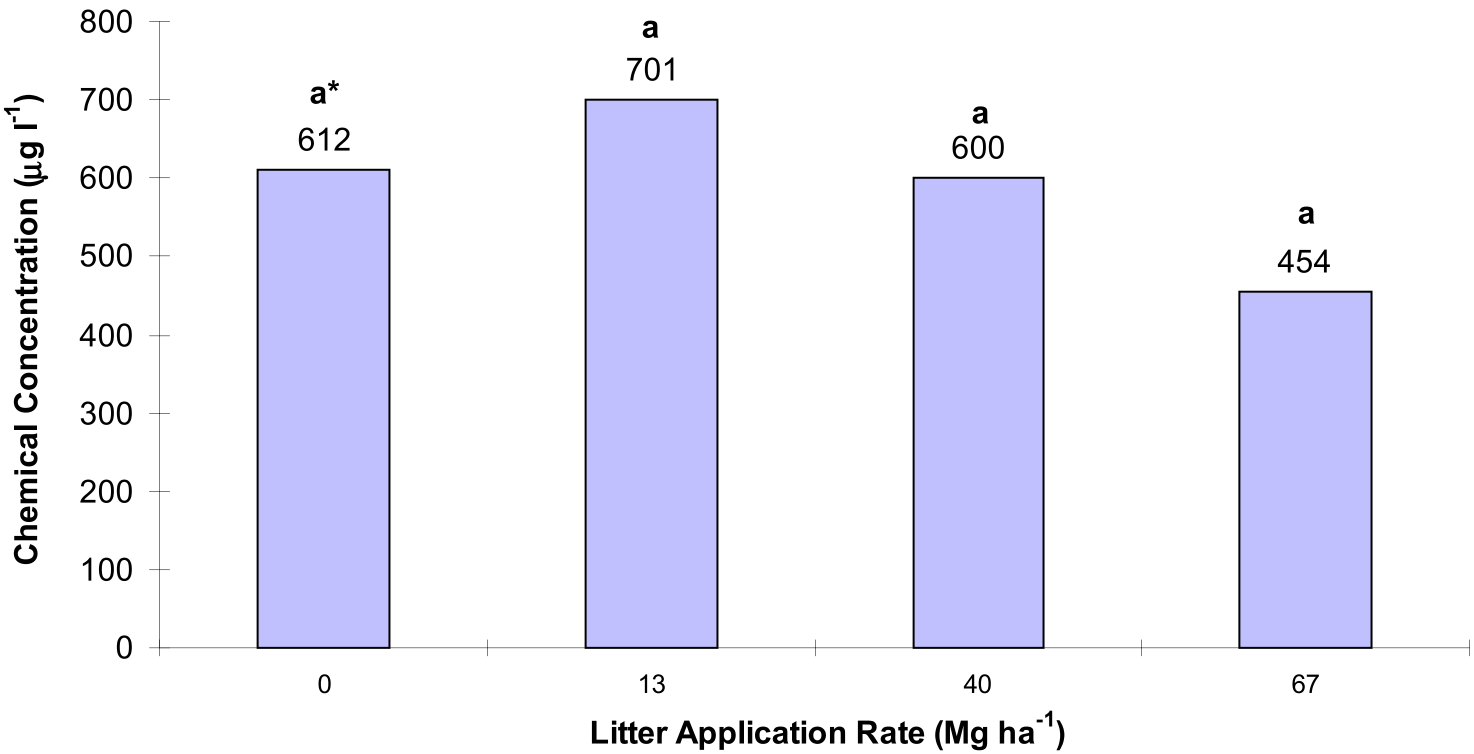


Figure 3.9. Comparison of atrazine concentration in leachate atrazine for weathered and stockpiled litter treatments for soybean bioassay.



*Values with the same letter are not significantly different ($p \leq 0.05$)

Figure 3.10. Average atrazine concentration in leachate for each weathered litter application and atrazine at 2.2 kg a.i. ha^{-1}.

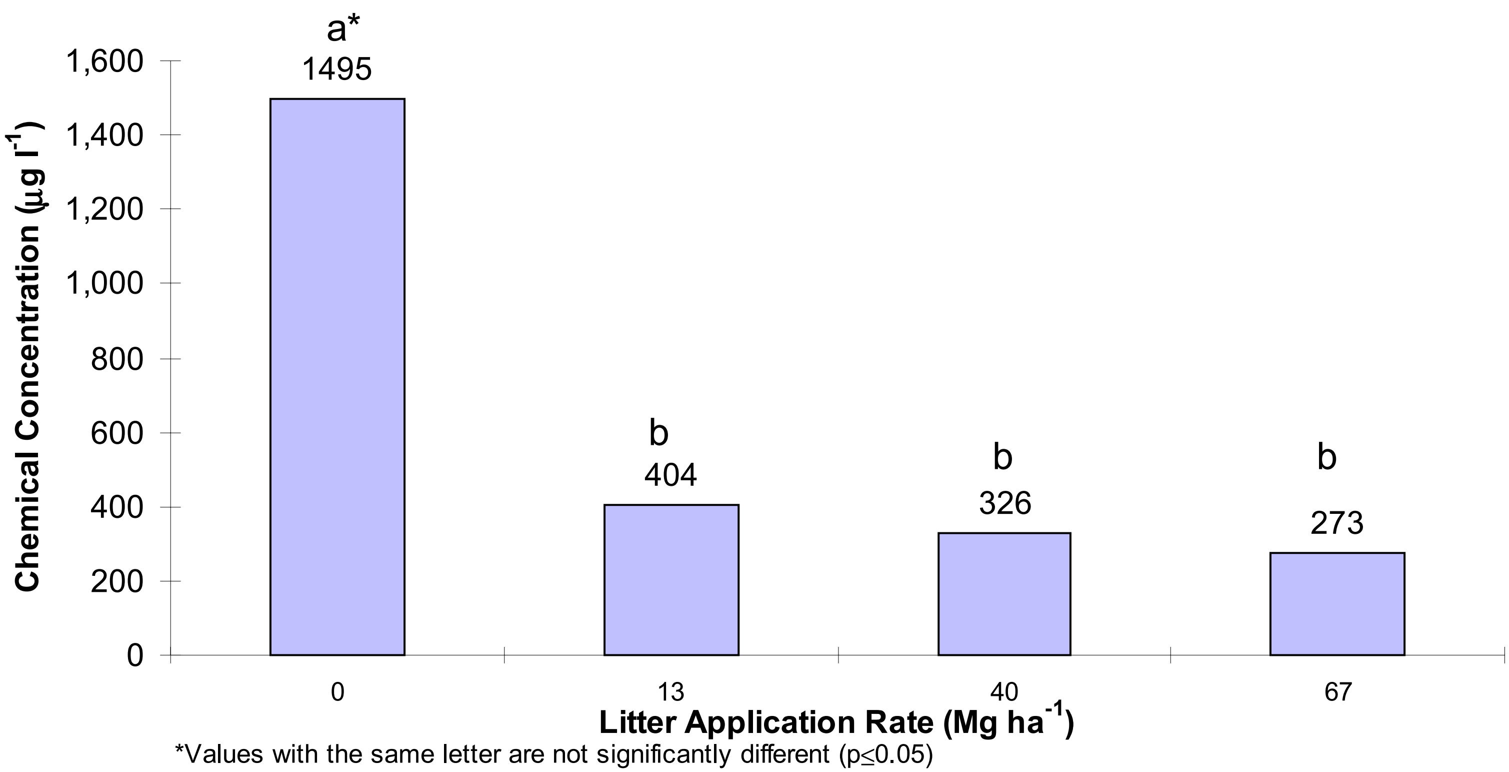


Figure 3.11. Average atrazine concentration in each stockpiled litter application and atrazine at 2.2 kg a.i. ha^{-1}.

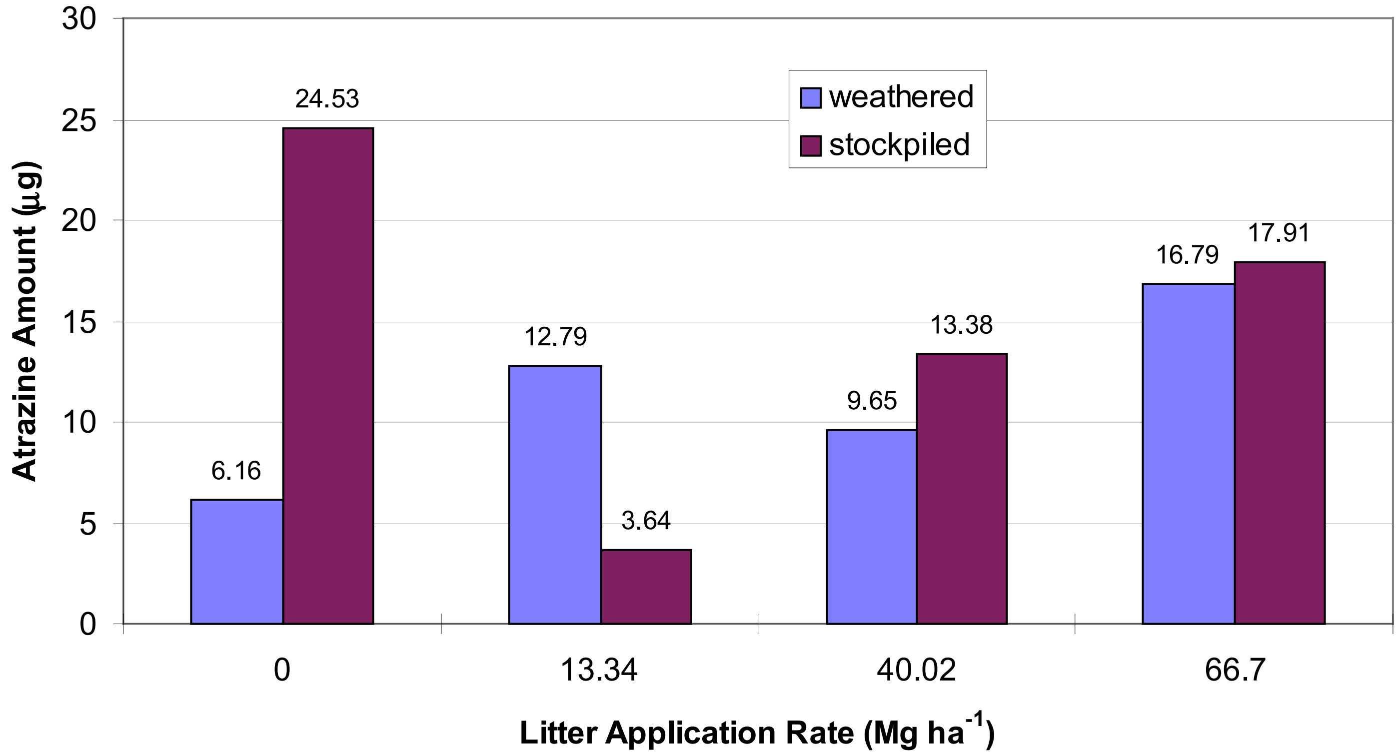
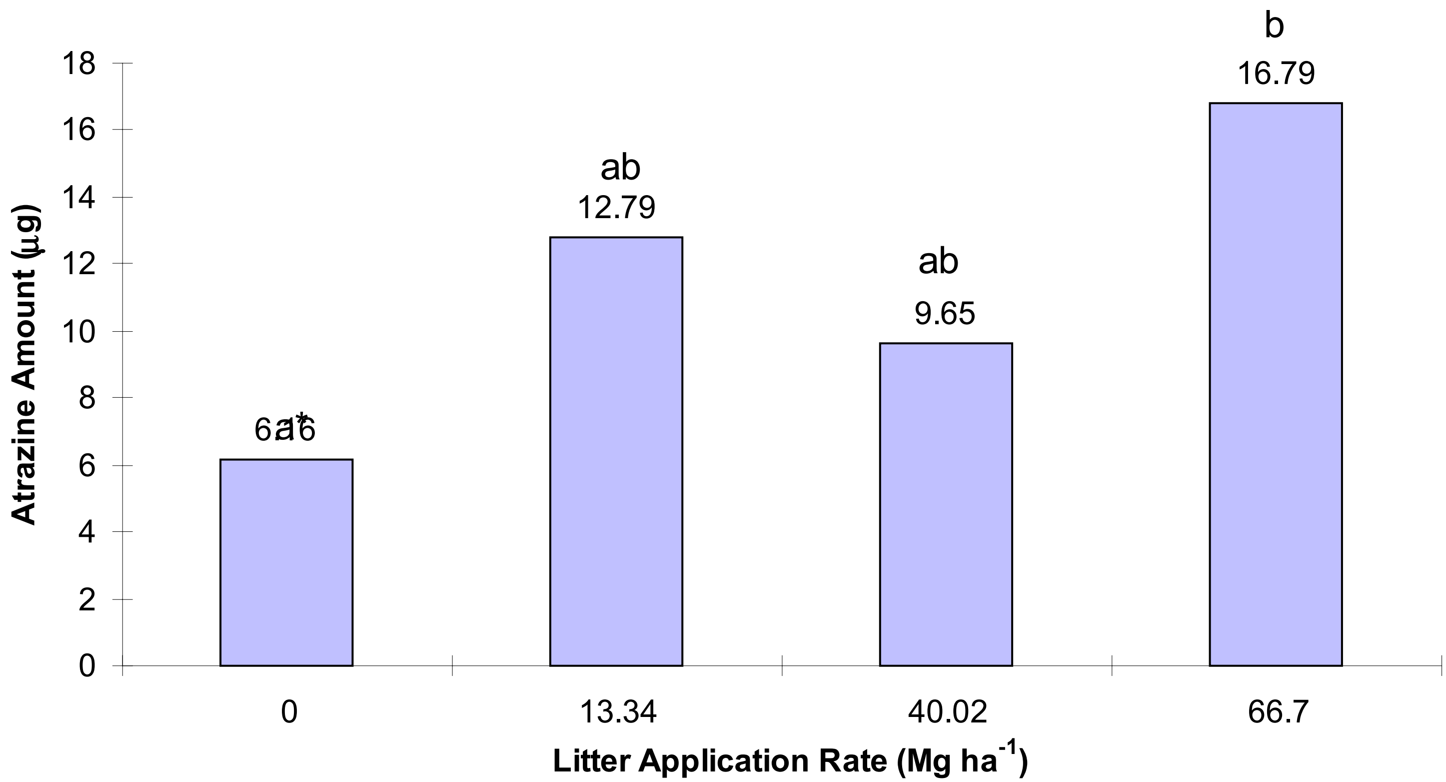
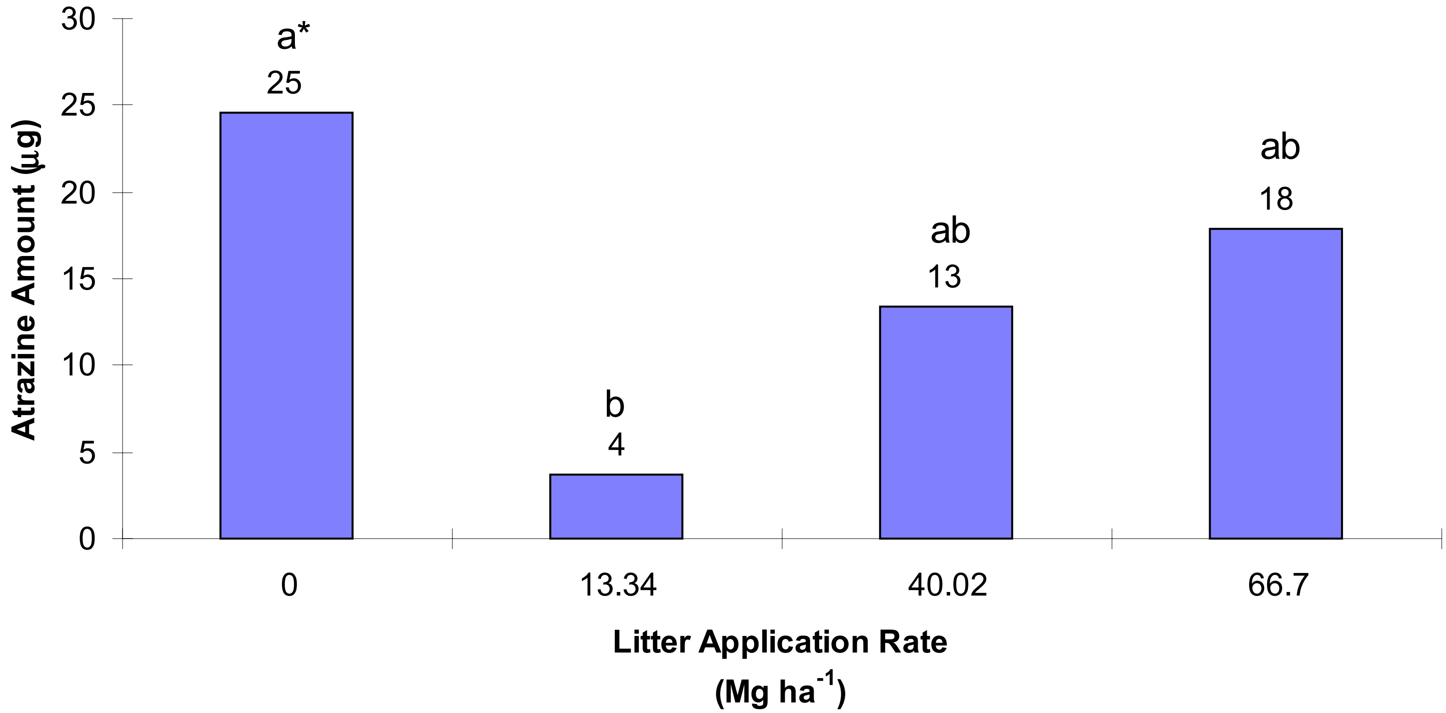


Figure 3.12. Comparison of total amount of atrazine leached for weathered and stockpiled litter rates.



*Values with the same letter are not significantly different ($p \leq 0.05$)

Figure 3.13. Total amount of atrazine in leachate for weathered litter application and atrazine at 2.2 kg a.i. ha^{-1}.



*Values with the same letter are not significantly different ($p \leq 0.05$)

Figure 3.14. Total amount of atrazine in leachate for stockpiled litter application and atrazine at 2.2 kg a.i. ha^{-1}.

ATRAZINE SORPTION ON POULTRY LITTER AND SOIL

Abstract

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is subject to degradation in the environment into hydroxyatrazine (2-hydroxy-4-ethylamino-6-isopropylamino-1,3,5-triazine), desisopropylatrazine (DIA, 2-chloro-4-ethylamino-6-amino-1,3,5-triazine) and desethylatrazine (DEA, 2-chloro-4-amino-6-isopropyl-amino-1,3,5-triazine). Soil type and organic amendments have been found to affect the amount of degradation and adsorption of atrazine. Sorption of atrazine onto soil and poultry litter was measured through a batch adsorption experiment. Stockpiled or weathered poultry litter were combined with a Lakeland sand (siliceous, thermic, coated Typic Quartzipsamments) based on the nitrogen recommendations for corn at 1X and 3X the recommended rate. The soil and litter combinations were shaken with atrazine and the amount of atrazine, DIA and DEA were measured in the solution. Freundlich adsorption constants (K_f) were calculated. Weathered litter had the highest affinity (K_f = 33.76) followed by stockpiled litter (17.65) 3X weathered litter and soil (1.93), 1X weathered litter and soil (1.20), 3X stockpiled litter and soil (1.17), soil (1.06), and 1X stockpiled litter and soil (0.68).

Introduction

Soil properties affecting efficacy of herbicides include soil organic matter content, clay content, pH, water holding capacity, cation exchange capacity, and specific surface area. Organic matter content has been highly correlated with atrazine efficacy (Blumhorst *et. al*. 1990). They estimated that for every 1% increase in organic matter content, an additional 0.94 kg ha^{-1} atrazine was necessary to maintain effective velvetleaf control.

Herbicide adsorption on soil can be quantified through adsorption isotherms. These isotherms are often used to model the behavior of the herbicide in soils based on organic matter or organic carbon content of the soil. Linear adsorption isotherms can be characterized using the linear adsorption partition, and are commonly used in simple chemical movement modeling programs.

Atrazine is subject to degradation through metabolism in plants, soil microbes, and other living organisms. The most common degradation products of atrazine include hydroxyatrazine, DIA and DEA. Chemical structures are provided in Figure 4.1 (Ahrens 1994).

Management of soil organic matter can impact herbicide adsorption. Compared to conventional farming, low-input farms (only organic fertilizer, and use of limited herbicides) resulted in both higher organic matter and greater herbicide adsorption (Mallawatantri *et al.* 1992). Chlorenvinphos concentrations were found to remain higher in soils amended with organic fertilizers, particularly when incorporated (Rouchard *et al.* 1982). This was attributed to reduced bioavailabilty to soil organisms capable of biodegrading the pesticide.

Since soil organic matter decreases the phytotoxicity of many herbicides by adsorption onto organic colloids, herbicide activity also may be decreased by the addition of animal manure (Quakenbush *et al.* 1981). Soluble organic compounds can influence the adsorption of herbicides onto soil through interaction with soil or interaction with the herbicide in solution (Lee *et al.* 1990).

Studies have determined the influence of organic wastes on the adsorption and desorption of pesticides on soils. The mobility of alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamdie) and atrazine was reduced the most with waste-activated carbon (activated carbon used in corn sweetener filtration), followed by digested municipal sludge and then animal manure (Guo *et al.* 1991, 1993). Lower amounts of atrazine were consistently found in leachates from soils with organic amendments than from soils that were not amended. They found that the activated carbon was much more effective than either the sewage sludge or the animal manure at decreasing the amount of atrazine leached from the system. They assumed that the atrazine that did not leach was sorbed to the organic particles.

Atrazine adsorption onto soil increased when the soil had been pretreated with dissolved organic matter (Barriuso *et al.* 1992). When the atrazine was preincubated with a dissolved organic matter solution prior to adsorption, adsorption onto the soil was dramatically decreased.

Animal waste and herbicide may be applied to fields at nearly the same time. When atrazine was applied after pig slurry the adsorption capability of the soil was increased by four times compared to the adsorption capability of untreated soil (Businelli 1997).

ADSORPTION CHARACTERIZATION:

The linear adsorption isotherm is illustrated in equation 1, where S = adsorbed concentration (mg kg^{-1}), C = solution concentration (mg l^{-1}) and K_d is the linear adsorption partition coefficient (l kg^{-1}) (Green *et al.* 1980; Koskinen and Cheng 1983; Rao and Davidson 1980).

$$S = K_d C \quad [1]$$

The affinity of a pesticide for soil organic matter is reported as the organic carbon partitioning coefficient, K_{oc}, which can be derived from the K_d (McBride 1994).

$$K_d = S/C \quad [2]$$

The K_{oc} is derived from the amount of organic carbon in the soil and the K_d, or the measure of interaction between the herbicide and the soil (Wagenet and Rao, 1995; Jury, *et al.* 1987). Where %OC is the percent of organic carbon

$$K_{oc} = K_d/\%OC * 100 \qquad [3]$$

The Freundlich equation is also used to characterize sorption onto soil particles for non-linear absorption. K and n are constants (Barriso *et al.* 1992, Businelli 1997, Guo *et al.* 1993, Rao *et al.* 1996, Weber 1986).

$$S = KC^{1/n} \qquad [4]$$

For herbicides in soil systems where the herbicide has a higher initial affinity for the soil and a lesser affinity at high equilibrium concentrations, a straight line is plotted when the logs of both sides of the Freundlich equation are taken.

$$\log(S) = \log(K) + 1/n(\log(C)) \qquad [5]$$

Atrazine adsorption for earthworm middens (containing earthworm cast and decomposing crop residue) followed the Freundlich equation, with K values ranging from 3.09 to 4.08 (Akhouri *et al.* 1996).

Materials and Methods

A batch adsorption experiment was done using the procedure outlined by Weber (1986).

A Lakeland sand, collected from the Sandhills Research Station, Jackson Springs, NC was selected due to its low organic matter content, which minimizes the interactions between atrazine and the native soil organic matter.

Stockpiled poultry litter (mixed and allowed to sit covered for one year) was obtained from North Carolina State University's Unit 9 poultry house, Raleigh NC. Application rates for the stockpiled litter were based on nitrogen recommendations for corn. Stockpiled litter was incorporated into 13.2 cm of soil at 0X, 1X, and 3X the recommended nitrogen rate for a 1.7 m^3 ha^{-1} corn crop using 50% availability factor. Litter application rates were based on calculations and recommendations for corn from Zublena *et al.*, (1993), assuming no residual nitrogen and no pre-plant fertilizer. Litter nutrient analysis is given in Table 4.1. Stockpiled litter was weathered in 10 cm plastic pots. Each pot was filled with 350 cm^3 (approximately 650 g) of Lakeland sand, then the stockpiled poultry litter was applied at 1X and 3X the recommended rate to the field-moist soil and mixed. The litter and soil in the pots was allowed to weather in a greenhouse, and weekly watered, with 15 to

30 ml for 110 days. After weathering the soil and litter mixtures were stored in the freezer to prevent any further microbial changes.

The soil, stockpiled litter, weathered litter and soil and litter mixtures were analyzed gravimetrically for moisture content. Gravimetric moisture samples were taken at the same time as the soils used for the adsorption experiment. The solids were weighed out in pre-weighed weigh boats and put in an 110°C oven for 24 hours and weighed on a Mettler-Toledo Model PB303 scale. Gravimetric moisture content was calculated using the formulas given by Weber (1986).

$$\theta = \text{water (dry-weight basis)} = \frac{\text{mass wet soil - mass dry soil}}{\text{mass of dry soil}} \quad [6]$$

$$\%\ \text{water}_{(\text{weight})} = \theta * 100 \quad [7]$$

To determine the pH in the soil and litter, 20 grams of soil and litter were placed in a 100 ml plastic beaker and 20 ml of 0.01 M $CaCl_2$ was added. The suspension was stirred and allowed to equilibrate for 5 minutes. The pH was also determined using 20 g of soil/liter in 20 ml of deionized water. An Orion Reset Model 601/A pH meter was standardized using buffer solutions of 4 and 7. A glass electrode was used to measure the pH for the soil and litter combinations (Weber 1986). Three measurements were taken form each sample for each pH.

Atrazine solutions were prepared in 0.01 M CaCl2 (Barriuso *et al*. 1992, Businelli 1997, Guo *et al.* 1993, Rouchard *et al.* 1996). A 10 mg l^{-1} stock atrazine solution was prepared by weighing out 22.29 mg of 98.7% purity analytical standard atrazine (Syngenta Crop Protection, Inc., Greensboro, NC). This was dissolved in 5 ml of pesticide grade ethyl acetate (Fisher Scientific, Chicago, IL) and then brought to 2.2 l with 0.01 M $CaCl_2$ prepared in distilled de-ionized water. The other concentrations of atrazine solution were prepared by diluting the 10 mg l^{-1} atrazine solution in 0.01 M $CaCl_2$. The solutions were stored at 4□C throughout the experiment.

The atrazine adsorption study was conducted by adding 50 ml of the atrazine solution to 10 g of premixed soil and litter material, except the litter samples, Table 4.2. To assure that some solution would be left to analyze after the litter absorbed the liquid 2g of stockpiled litter was added to 50 ml of atrazine solution and 1 g of weathered litter was added to 50 ml of atrazine solution. The stockpiled and weathered litters alone were bulky and when 10 g of the litter was combined with 50 ml of solution, all of the solution was absorbed into the litter particles. Controls were run using 50 ml of solution and were treated identically to the adsorption study. Three replicates were done for each sample. The flasks were shaken for 24 hours at 25 °C. After shaking, the flasks were allowed to settle for 1 hour and an aliquot was removed for solid phase extraction. When necessary the solutions were filtered using syringe filters. The adsorption isotherm parameters were determined using the guidelines given by Weber (1986) (Table 4.3). The study was not repeated.

ANALYTICAL METHODS:

Atrazine, DIA and DEA were analyzed by loading a specific aliquot (see Table 4.4) onto an EnviCarb cartridge (Supleco, Bellefonte, PA). The cartridges were activated with 2 ml of methanol and washed with water. The samples were spiked with 0.01 μg TBA (terbuthylazine; 6-chloro-N-(1,1-dimethylethyl)-N'-ethyl-1,3,5-triazine-2,4-diamine) as an internal check. The cartridges were air dried under vacuum and then eluted with 10 ml of pesticide grade ethyl acetate. The samples were evaporated and brought to volume with pesticide grade ethyl acetate (Fisher Scientific, Chicago, IL) and vortexed for 1 minute to ensure a homogeneous solution.

The concentrations of atrazine, DIA, DEA and TBA were determined with a Hewlett-Packard Model G1800A GCD (Palo Alto, CA). The operating parameters outlined in McLaughlin and Johnson (1997) was used. One injection was used for DIA and atrazine and another injection was used for DEA because of overlapping retention times.

The adsorption was calculated based on atrazine only and based on the total amount of herbicide (atrazine, DIA and DEA) found in the solution. To find the K value for the isotherm, the log of both sides was taken and a line plotted (see equations 4 and 5).

Results and Discussion

Gravimetric moisture content was calculated and is found in Table 4.5. The weathered litter had been air dried in the greenhouse during the weathering process. The stockpiled litter had a gravimetric moisture content that was 5.6 times greater than the weathered litter.

Measurement in 0.01M $CaCl_2$ consistently reduced the measured pH for all soil and litter combinations compared with water (Table 4.6, Figure 4.2). There was a significant difference between the pH measured with $CaCl_2$ and H_2O, $t < 0.0005$. Stockpiled litter had the highest pH (8.1) and adding it to the soil raised the pH by more than two units. The weathering process modified the litter pH to 6.2 but weathered litter slightly raised soil pH. The addition of weathered litter increased the pH the least from 4.1 to 5.9 for the mixture of soil and litter at the recommended rate (13 Mg ha^{-1}).

Both pH measurements in water and $CaCl_2$ are common practices. $CaCl_2$ more closely simulates salt concentrations that may be found in the field (Harper 1987; Weber 1986). Since the atrazine stock solution was in $CaCl_2$, both sets of measurements were taken.

$CaCl_2$ acts as a buffer and slightly regulates the pH change when litter is added. Though the trend, increasing pH with addition of litter, remains the same the change in pH is not as dramatic while measured with $CaCl_2$ instead of water.

Soil pH is an important factor in atrazine degradation, especially with hydrolysis. At low pHs (5.5-6.5) hydroxy atrazine is the major metabolite while at higher pHs (7.5-8) there are low hydrolysis rates (Aherns 1994). Hydroxyatrazine cannot be analyzed using gas chromatography as outlined in McLaughlin and Johnson (1997) so there was no attempt to determine its concentration.

Litter application increased the pH by approximately 0.5 units in fescue pastures (Kingery *et al.* 1993). Chicken manure was shown to be as effective as $Ca(OH)_2$ in increasing soil pH for a highly weathered ultisol (Hue 1992).

Hydrogen ion concentration controls atrazine adsorption between the solution and the soil (Nearpass 1967). Adsorption of atrazine decreases as pH increases, and organic matter content is kept the same (Harris and Warren 1964; Talbert and Fletchall 1965). If the organic matter content is the same it is assumed that the adsorption will decrease as pH increases.

ADSORPTION:

Atrazine and DEA were present in the liquid phase, but DIA was not found in any of the samples (Table 4.7). This indicated that some degradation of atrazine occurred during the 24 hours of shaking. The samples were processed immediately after shaking so degradation would not occur in storage. The equilibrium concentration (for the sum of atrazine and DEA) and the initial concentration are shown in Figure 4.3. A 1:1 line is also shown in Figure 4.3, this line shows no adsorption (the initial concentration and the equilibrium concentration would be the same). Since some adsorption did take place all points are below the 1:1 line.

Dissolved organic matter was captured on the solid phase extraction columns. As the samples were being passed through the columns the dissolved organic matter was visually observed bonding to the C-18 cartridges. When the columns were eluted the atrazine and metabolites that were bound to the dissolved organic matter were eluted. The measurement of atrazine and its metabolites in solution includes that which was bound to the dissolved organic matter, therefore the adsorption curve represents atrazine that is bound to the solid substrate only.

The adsorption isotherm was plotted for atrazine only (Figure 4.4) and the sum of atrazine and its metabolites (Figure 4.5). The amount absorbed was calculated using the formulas shown in Table 4.4 and is shown in Table 4.8 and Figure 4.4. To find the K value the log of both sides were plotted (Figure 4.6 shows for atrazine data only, Figure 4.7 for atrazine and its metabolites). The equation of the line was determined and then the K value was calculated by converting from the log K (see Table 4.9 and Table 4.10).

The higher the K_f the more adsorption will occur. Weathered litter had the largest K_f (33.76) followed by stockpiled litter (17.65). As expected, the weathered litter K_f was greater than that of the stockpiled litter. The process of weathering the litter decreased the amount of dissolved organic matter present as well as degrading the organic matter into more stable smaller compounds such as humus. The degradation of organic matter and decrease in dissolved organic matter would increase the amount of atrazine that could be sorbed to the substrate.

Stockpiled litter at the recommended rate had the lowest K_f this was not expected. It was expected that un-amended soil would have the lowest affinity for atrazine since it contained the least amount of organic matter. An increase in organic matter increases adsorption and an increase in pH decreases adsorption (Blumhorst *et. al.* 1990; Harris and Warren 1964; Talbert and Fletchall 1965). The addition of the litter at the recommended rate increased the pH by more than two units, which apparently reduced adsorption proportionately greater than the increase expected with the additional organic matter.

The K_f values for the Lakeland sand (1.06) are similar to values found in literature for other sandy soils, ranging from 1.7 for a Norfolk sand, to 0.78 for a soil containing 10.5% sand and 0.75% organic matter (Weber 1993, Harper 1988). As the organic matter content increases the K_f also increases, Drummer silt loam with 4.2% OM has a K_f of 4.7 (Weber 1988). Increases have not been as dramatic as the K_f for weathered litter at 32.58.

DEA was present after 24 hours in some of the samples and the results are summarized in Table 4.11 and Figure 4.8. The addition of organic matter will increase the micro-organisms in the soil and therefore increase the amount of DEA that is present. The soil, 1X stockpiled, stockpiled, 1X weathered and 3X weathered samples produced about the same concentration of DEA. Weathered litter alone did not produce more DEA than the soil alone. No DEA was present in the 3X stockpiled sample. The greatest amount of DEA measured was only 4% of the initial amount of atrazine applied. Since each sample did not produce DEA, no conclusions can be drawn, and this did not have any significant impact on the K_f.

Conclusions

As has been demonstrated in other studies, poultry litter raised the pH of the Lakeland sand. Stockpiled litter raised the pH more than the weathered material of the same source. The pH was raised 2-3 units above the pH 4 measured in the unamended soil.

The addition of litter to the soil generally increased the amount of atrazine adsorbed. The exception was stockpiled litter added to the soil at the recommended rate of 13 Mg ha^{-1}, which actually decreased adsorption due to pH increases. Compared to the soil alone, the 3X rate of stockpiled litter increased adsorption 10%, the 1X weathered litter increased adsorption 13%, and the 3X weathered litter increased adsorption 82%. Stockpiled litter alone was nearly 17 times as adsorptive as the soil and the weathered litter was more than 32 times as adsorptive.

The K_f values determined in this experiment also help to explain the leaching patterns for atrazine in the leaching experiment. The greater K_f values found in the litter amended soil would result in less atrazine leaching. The weathered litter had a much higher K_f and decreased the amount of atrazine leaching the greatest. As litter rates increased the amount of atrazine leached decreased, as expected from the higher K_f values in those amended soils. The 1X stockpiled litter treatment resulted in more atrazine leached than for soil alone, and in fact that treatment also resulted in lower K_f than soil alone.

The effect of poultry litter on atrazine adsorption may help explain some of the weed responses suggested by growers. Stockpiled litter has less adsorption capacity than weathered litter, and is more likely to increase pH. This suggests that adding fresh or stockpiled litter may increase atrazine leaching below the root zone, reducing its activity. The addition of higher rates of stockpiled litter seemed to offset the pH effects by increasing adsorption capacity of the soil. Weathered litter has less of an effect on pH or adsorption except at the highest rate. At high rates it is possible that the increased adsorption could reduce atrazine availability for weed uptake. These results may be less dramatic on soils with higher clay or organic matter content.

References

Ahrens, William H. ed. "Atrazine" in Herbicide Handbook, Seventh Edition. Weed Science Society of America. p20-23 (1994).

Akhouri, Neela M., Eileen J. Kladivko and Ronald F. Turco (1997). "Sorption and Degradation of Atrazine In Middens Formed by Lumbricus Terrestris," Soil Biology and Biochemistry. 293/4:663-666.

Barriuso, E., U. Baer, and R. Calvet (1992). "Dissolved Organic Matter and Adsorption-Desorption of Dimefuron, Atrazine and Carbetamide by Soils," Journal of Environmental Quality. 21:359-367.

Blumhorst, Michael R. and Jerome B. Weber (1994). "Chemical Versus Microbial Decomposition of Cyanazine and Atrazine In Soils," Pesticide Science. 42:79-84.

Blumhorst, Michael R., Jerome B. Weber, Len R. Swain (1990). "Efficacy of Selected Herbicides as Influenced by Soil Properties," Weed Technology. 4:279-283.

Businelli, Daniela (1997). "Pig Slurry Amendment and herbicide Coapplication Effects on s-Triazine Mobility In Soil - An Adsorption-Desorption Study," Journal of Environmental Quality. 26:102-108.

Green, R.E., J.M Davidson, J.W. Biggar (1980). "An Assessment of Methods Of Determining Adsorption-Desorption of Organic Chemicals," A. Banin and V. Kafkafi (ed.), In Agrochemicals in Soils. Pergamon Press, New York. p 73-82.

Guo, Lei, Thomas J. Bicki, Allan S. Felsot, and Thomas D. Hinesly (1993). "Sorption and Movement of Alachlor In Soil Modified by Carbon-Rich Wastes," Journal of Environmental Quality. 22:186-194.

Guo, Lei, Thomas J. Bicki, and Thomas D. Hinesly (1991). "Effect of Carbon-rich Waste Materials on Movement and Sorption of Atrazine In a Sandy, Coarse-Textured Soil," Environmental Toxicology and Chemistry. 10:1273-1282.

Harper, Sidney S. (1988). "Sorption of Metribuzin In Surface and Subsurface Soils of the Mississippi Delta Region," Weed Science. 36:84-89.

Harris , C.I., and G. F. Warren. (1964) "Adsorption and desorption of herbicides by soil," Weeds. 12: 120.

Hue, N.V. (1992). “Correcting soil acidity of a highly weathered ultisol with chicken manure and sewage sludge,” Communications in Soil Science and Plant Analysis 23:241-264.

Jury, W. A., D.D. Focht, and W.J. Farmer (1987). “Evaluation of Pesticide Ground Water Pollution Potential From Standard Indices of Soil-Chemical Adsorption and Biodegradation.” Journal of Environmental Quality 16:422-428.

Kingery, W.L., C.W. Wood, D.P. Delany, J.C.Williams, G.L. Mullins, E. van Santen (1993). “Implications of long-term Land Application of Poultry Litter on Tall Fescue Pastures,” Journal of Production Agriculture. 6(3)390-395.

Koskinen, William C. and Sidney S. Harper (1990). “The Retention Process: Mechanisms,” H.H. Cheng (Ed.), in Pesticides in the Soil Environment. (No. 2). Madison: Soil Science Society of America 51-77.

Lee, D.Y., W.J. Farmer, and Y. Aochi (1990). “Sorption of napropamide clay and soil in the presence of dissolved organic matter,” Journal of Environmental Quality. 19:567-573.

Mallawatantiri, A.P., D.J. Mulla (1992). “Herbicide Adsorption and Organic Carbon Contents on Adjacent Low-Input Versus Conventional Farms,” Journal of Environmental Quality. 21:546-551.

McBride, Murray (1994). Environmental Chemistry of Soils. Oxford University Press. 342-393.

McLaughlin, R.A. and B.S. Johnson (1997). “Optimizing recoveries of two chlorotriazine herbicide metabolites and 11 pesticides from aqueous samples using solid-phase extraction and gas chromatography-mass spectrometry,” Journal of Chromatography A. 161-167.

Nearpass, D.C. (1967). “Effects of soil acidity on the adsorption of simazine and atrazine in Bayboro clay soil,” Soil Science. 103: 177.

Quakenbush, Laura S., and Robert G. Wilson (1981). “Effect of Herbicide and Manure Applications on Soil Chemistry and Growth of Fieldbeans (Phaseolus vulgaris),” Weed Science. 29:508-512.

Rao, R.S.C., and J.M. Davidson (1980). “Estimation of Pesticide Retention and Transport Parameters Required in Non Point Source Pollution Models,” M.R. Overcash and J.M. Davidson (Ed.) in Environmental Impact of Non Source Point Pollution. Ann Arbor Science Publ., Ann Arbor, MI. p 23-67.

Rouchard, J., A. Thirion, A. Wauters, F. Van de Steene, F. Benoit, N. Ceustermans, J. Gillet, S. Marchand, L. Vanparys (1996). “Effects of Fertilizer on Insecticides Adsorption and Biodegredation In Crop Soils,” Archives of Environmental Contamination and Toxicology. 31:98-106.

Schoen, Sarah R., Wray L. Winterlin (1987). “The Effects of Various Soil Factors and Amendments on the Degradation of Pesticide Mixtures,” . 347-377.

Talbert, R. E., and O.H. Fletchall. (1965) “The absorption of soil s-triazines in soils,” Weeds. 13:46.

Wagenet, R.J. and R.S.C. Rao (1985). “Basic Concepts of Modeling Pesticide Fate in The Crop Root Zone”. Weed Science. 33:25-32.

Weber, J.B. (1986). “Soils, Herbicide Sorption and Model Plant-Soil Systems,” Research Methods in Weed Science Third Edition. 155-188. Southern Weed Science Society.

Weber, Jerome B. (1993). “Ionization and Sorption of Fomesafen and Atrazine by Soils and Soil Constituents,” Pesticide Science. 39:31-38.

Zublena, J.P., J.C. Barker, T.A. Carter (1993). “Soil Facts - Poultry Manure as a Fertilizer Source,” North Carolina Cooperative Extension Service, AG-439-5.

Table 4.1: Total elemental analysis of poultry litter used in atrazine adsorption experiment.

Nutrient	Elemental Analysis ($g\ kg^{-1}$)
Total Carbon	273.7
Total Nitrogen	25.2
Total Phosphorus	30.5
Total Potassium	24.5
Total Calcium	4.0
Total Magnesium	7.5

Table 4.2: Adsorbents used in atrazine sorption study.

Rate of Litter	Amount of Adsorbent (g)
Air dried soil	10
Stockpiled Litter	2
Recommended Rate of stockpiled Litter and Soil	10
3X stockpiled Litter and Soil	10
Weathered Litter	1
Recommended Rate of Weathered Litter and Soil	10
3X Weathered Litter and Soil	10
No Litter	0

Table 4.3: Adsorption isotherm parameters.

	Units	Calculation
Concentration added	$\mu g\ l^{-1}$	Given
Equilibrium concentration	$\mu g\ l^{-1}$	Measured
Concentration adsorbed	$\mu g\ l^{-1}$	(Concentration Added) - (Equilibrium Concentration)
Amount of solvent	l	0.05 l
Amount of sorbent	g	See Table 4.2
Water by weight		$\frac{\text{grams of water}}{\text{oven dry weight}}$
Mass of dry sorbent	g	$\frac{\text{Amount of sorbent}}{(1 + \text{Water by weight})}$
Total herbicide adsorbed	μg	(Concentration absorbed) * (amount of solvent)
Amount adsorbed	$\mu g\ g^{-1}$	$\frac{\text{total herbicide adsorbed}}{\text{mass of dry sorbent}}$

Table 4.4: Concentration Factors for Atrazine Analysis.

Atrazine Concentration ($mg\ l^{-1}$)	Aliquot for Extraction (ml)	Evaporated to (ml)	Concentration Factor
10	0.5	5	20
5	2	2	10
1	5	10	2
0.5	2	1	0.5
0.1	1	10	0.1
0			

Table 4.5: Gravimetric moisture content of soils and litter mixtures used in adsorption experiment.

	% moisture by weight
Air dried soil	1.88
Stockpiled Litter	45.49
3X Stockpiled Litter and Soil	3.01
Recommended Rate of Stockpiled Litter and Soil	2.99
Weathered Litter	8.03
3X Weathered Litter and Soil	0.56
Recommended Rate of Weathered Litter and Soil	0.69

Table 4.6: Average pH Measurements Taken with H_2O and $CaCl_2$.

	Ratio of solution to dry weight	pH in H_2O	Standard Deviation	pH in 0.01M $CaCl_2$	Standard Deviation	Student's t-test H_2O □ $CaCl_2$
Soil	20/20	4.1	0.03	3.9	0.01	0.0001
1X Stockpiled Litter and soil	20/20	6.6	0.00	6.2	0.01	0.0000
3X Stockpiled Litter and soil	20/20	7.0	0.02	6.8	0.04	0.0003
Stockpiled Litter	50/10	8.1	0.01	7.7	0.00	0.0000
1X Weathered Litter and soil	20/20	5.9	0.02	5.2	0.01	0.0000
3X Weathered Litter and soil	20/20	6.4	0.00	5.8	0.01	0.0000
Weathered Litter	50/10	6.2	0.02	6.0	0.02	0.0000

Table 4.7: Average of Three Measured Equilibrium concentrations (µg l-1) for Atrazine plus DEA found in extract.

Equilibrium Atrazine Concentration ($\mu g\ l^{-1}$)					
Calculated Initial Concentration	9934	4967	993	497	99
Equilibrium Concentration for Soil	6790	4406	871	472	64
Equilibrium Concentration for 1X Stockpiled Litter and soil	7575	4285	868	473	93
Equilibrium Concentration for 3X Stockpiled Litter and soil	8077	3847	728	495	89
Equilibrium Concentration for Stockpiled Litter	7880	2947	534	369	71
Equilibrium Concentration for 1X Weathered Litter and soil	8243	3701	740	451	83
Equilibrium Concentration for 3X Weathered Litter and soil	8613	3383	646	345	73
Equilibrium Concentration for Weathered Litter	8056	2440	517	321	52

Table 4.8: Average amount ($\mu g\ g^{-1}$) of atrazine sorbed to soil and litter mixtures.

Atrazine Sorbed to Soil and Soil Mixtures ($\mu g\ g^{-1}$)					
Calculated Initial Concentration ($\mu g\ l^{-1}$)	**9934**	**4967**	**993**	**497**	**99**
Soil	17.86	2.86	0.62	0.17	0.18
1X Stockpiled Litter and soil	14.12	3.51	0.64	0.17	0.03
3X Stockpiled Litter and soil	9.57	5.77	1.37	0.01	0.05
Stockpiled Litter	88.46	73.49	16.71	4.64	1.05
1X Weathered Litter and soil	10.40	6.37	1.28	0.27	0.08
3X Weathered Litter and soil	8.55	7.96	1.75	0.81	0.13
Weathered Litter	113.54	136.52	25.71	9.51	2.56

Table 4.9: Freundlich Constants for atrazine only.

	Freundlich Constants		
Litter/Soil Mixture	K_f	1/n	r^2
1X Stockpiled Litter and soil	0.68	1.35	0.98
Soil	1.06	0.94	0.78
3X Stockpiled Litter and soil	1.17	1.14	0.97
1X Weathered Litter and soil	1.20	1.12	0.97
3X Weathered Litter and soil	1.93	0.91	0.96
Stockpiled Litter	17.65	1.00	0.95
Weathered Litter	33.76	0.84	0.92

Table 4.10: Freundlich Constants for atrazine and DEA.

	Freundlich Constants		
Litter/Soil Mixture	K_f	1/n	r^2
1X Stockpiled Litter and soil	0.61	1.34	0.97
Soil	0.96	0.94	0.77
1X Weathered Litter and soil	1.10	1.09	0.94
3X Stockpiled Litter and soil	1.17	1.14	0.97
3X Weathered Litter and soil	1.78	0.87	0.93
Stockpiled Litter	16.75	0.96	0.93
Weathered Litter	32.59	0.82	0.91

Table 4.11: DEA concentration found in solution after 24 hours of shaking substrate with atrazine solution .

	($\mu g\ l^{-1}$)				
Initial Amount of atrazine	9934	4656	689	472	99
Soil	369.84	0	0	8.48	0
1X Stockpiled	382.48	0	0	9.16	0
3X Stockpiled	0	0	0	0	0
Stockpiled	377.68	0	0	0	0
1X Weathered	374.17	0	0	8.66	0
3X Weathered	380.25	0	0	8.44	0
Weathered	224.08	0	0	0	0

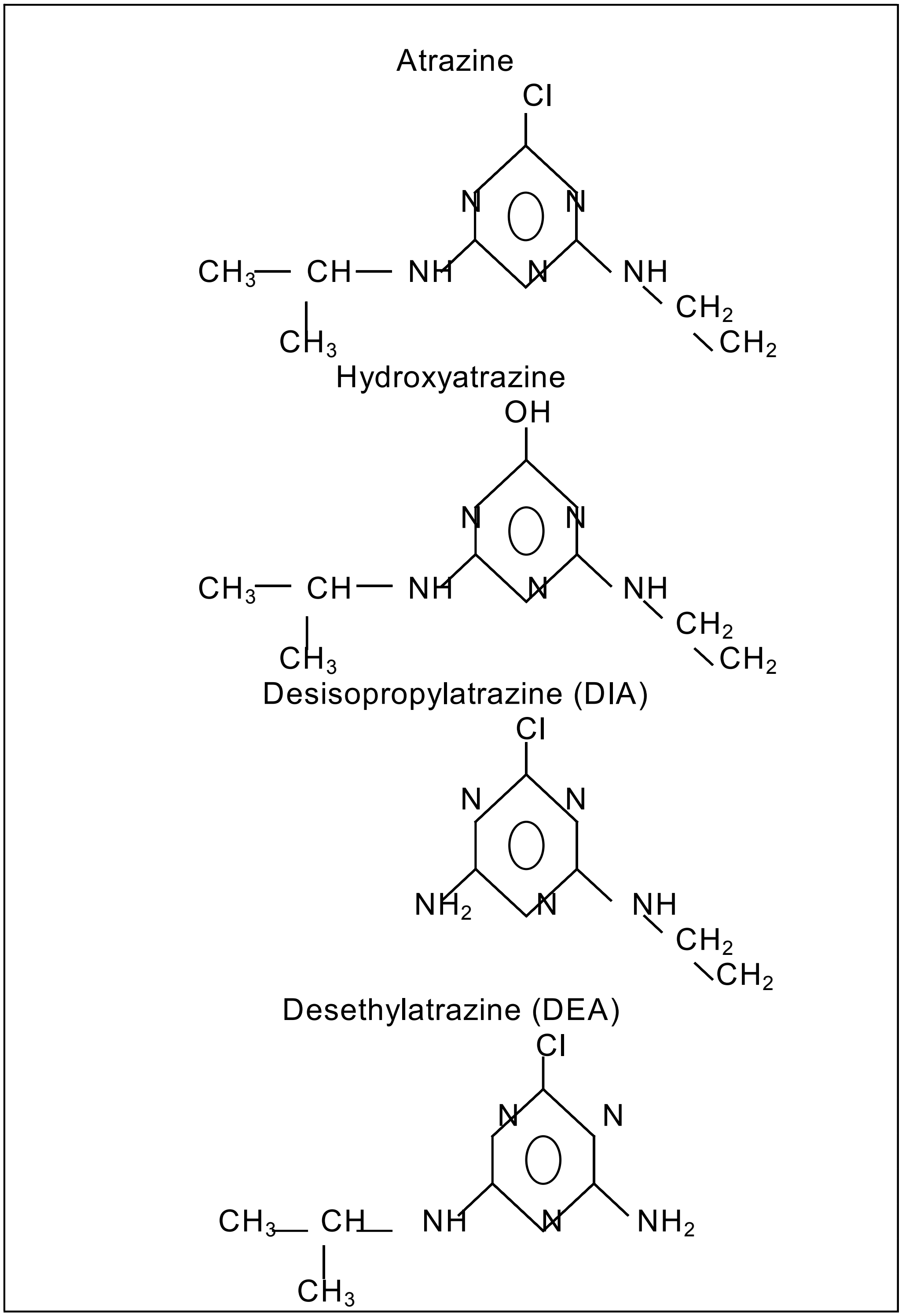


Figure 4.1: Atrazine and Metabolites.

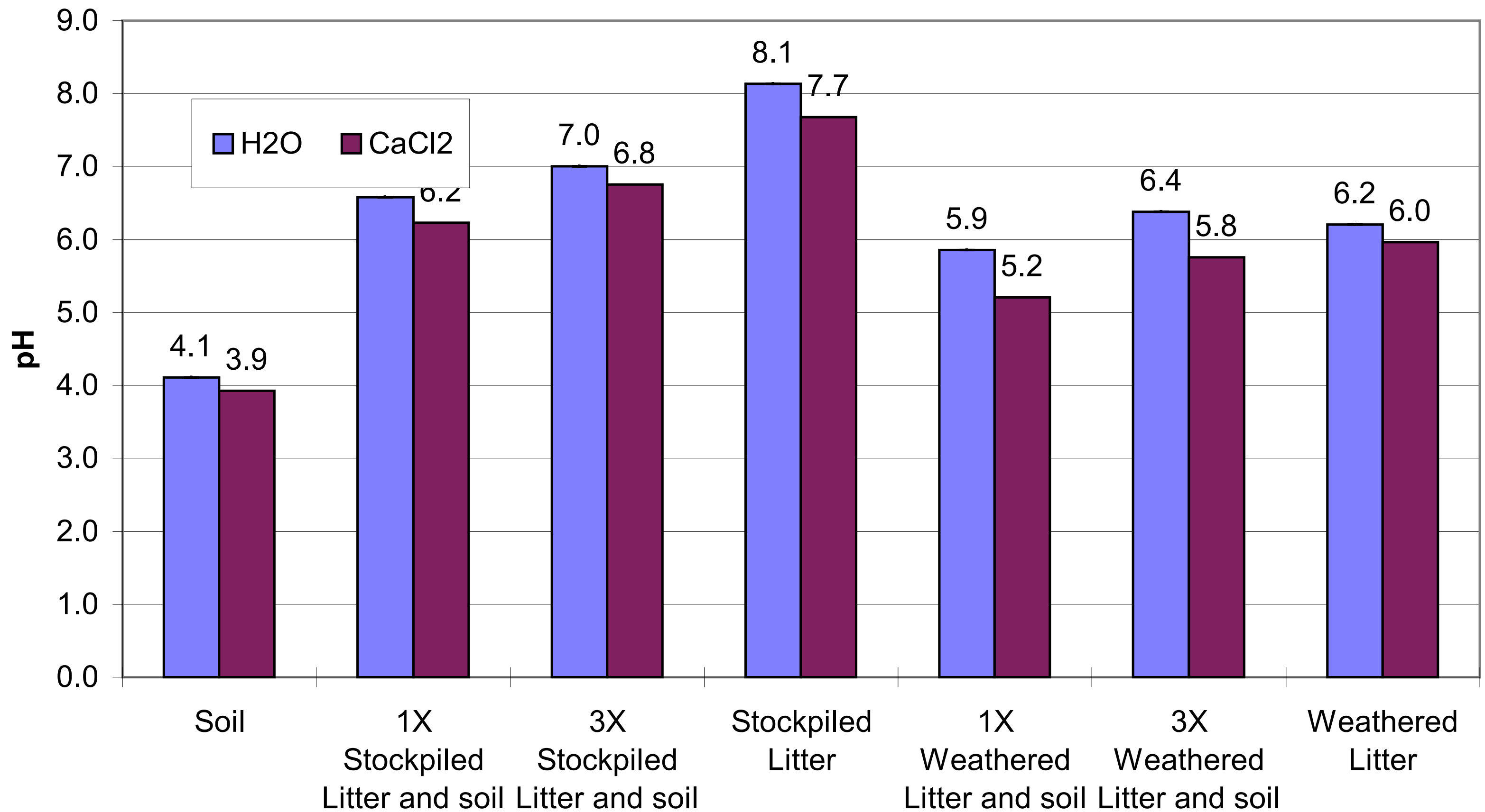


Figure 4.2: The pH of soil and litter mixtures measured in water of 0.01M $CaCl_2$.

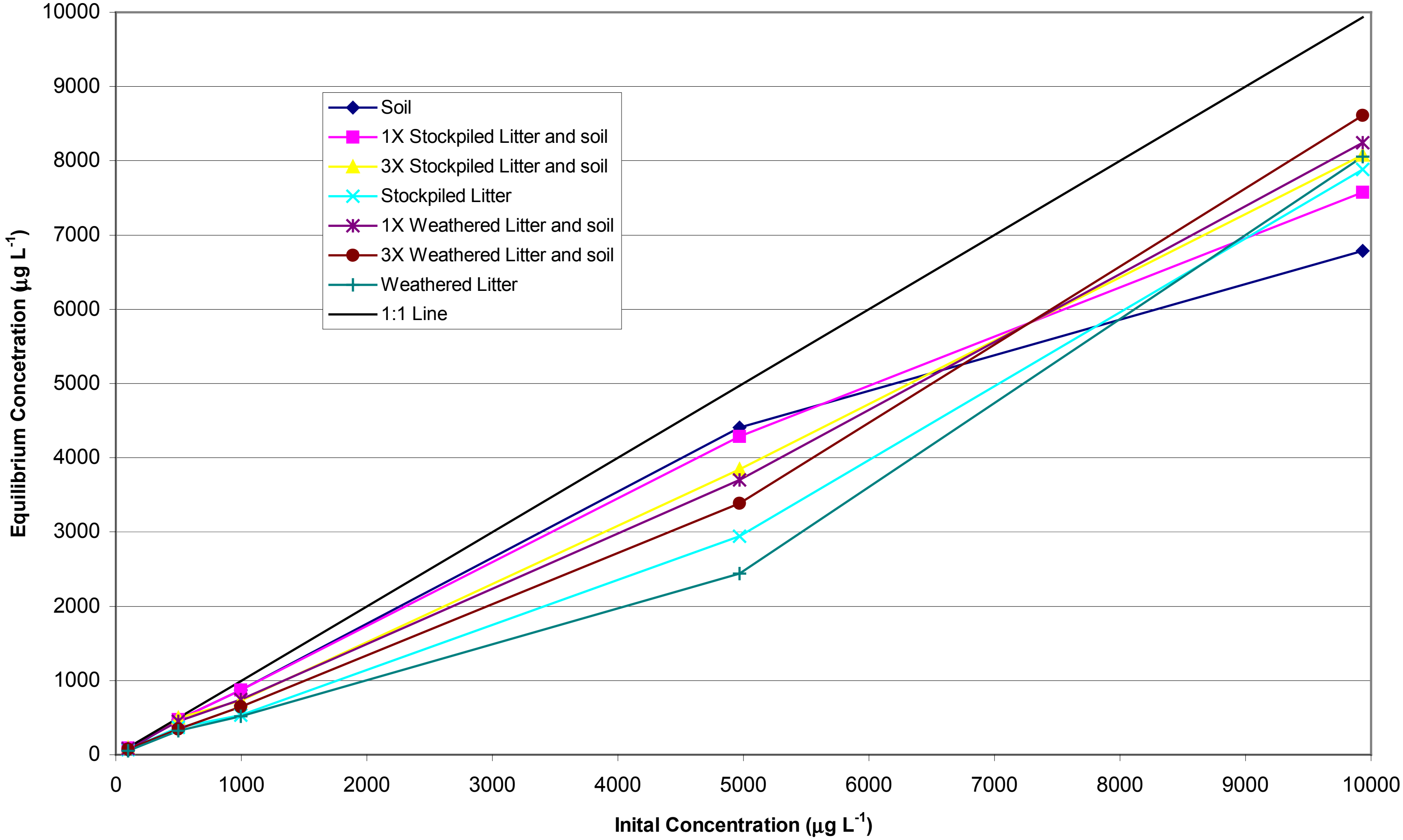


Figure 4.3: Equilibrium Concentration vs. Initial Concentration for Atrazine and DEA found in Solvent.

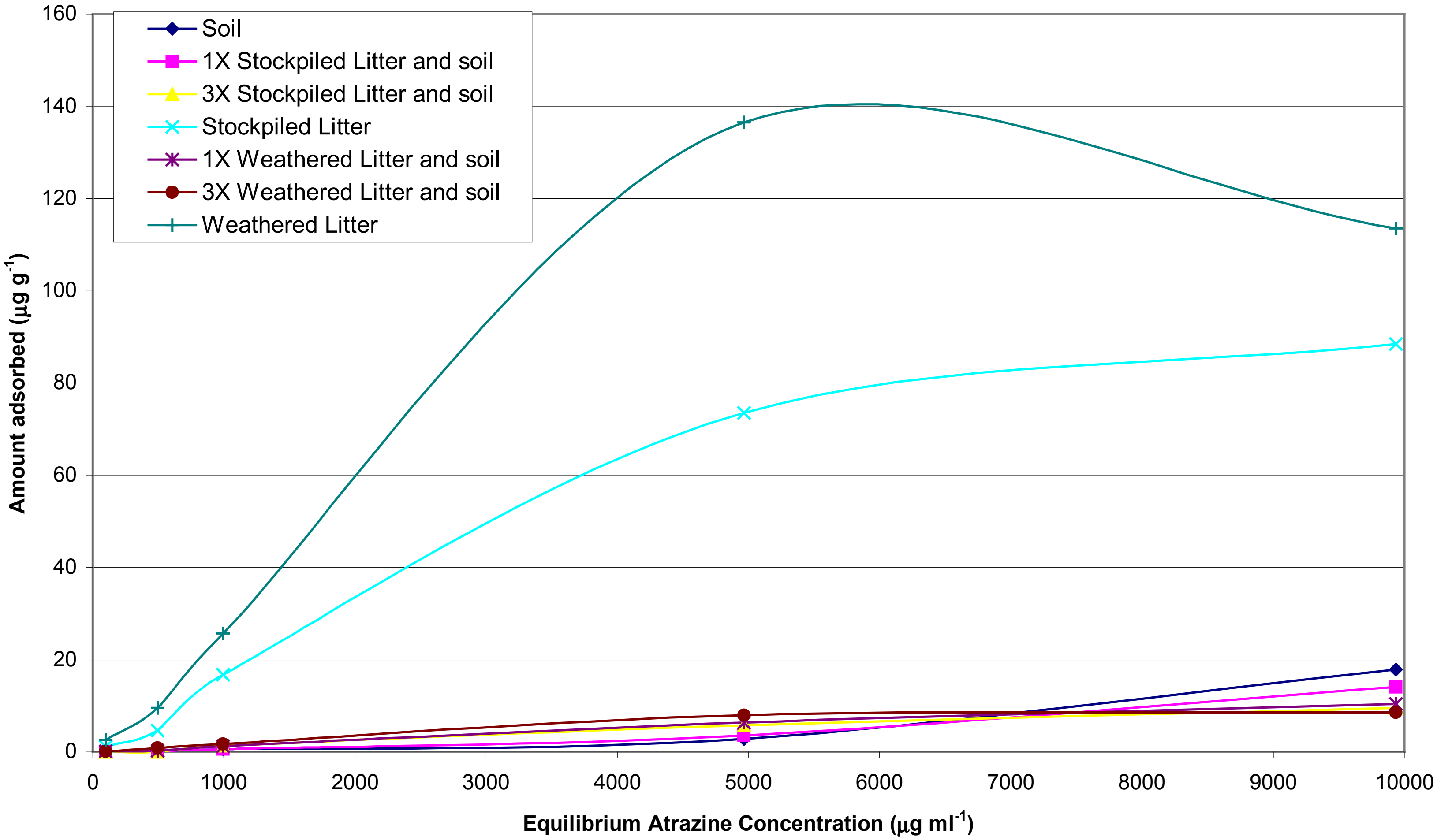


Figure 4.4 Absorption of Atrazine added to Lakeland soil and soil and poultry litter mixtures.

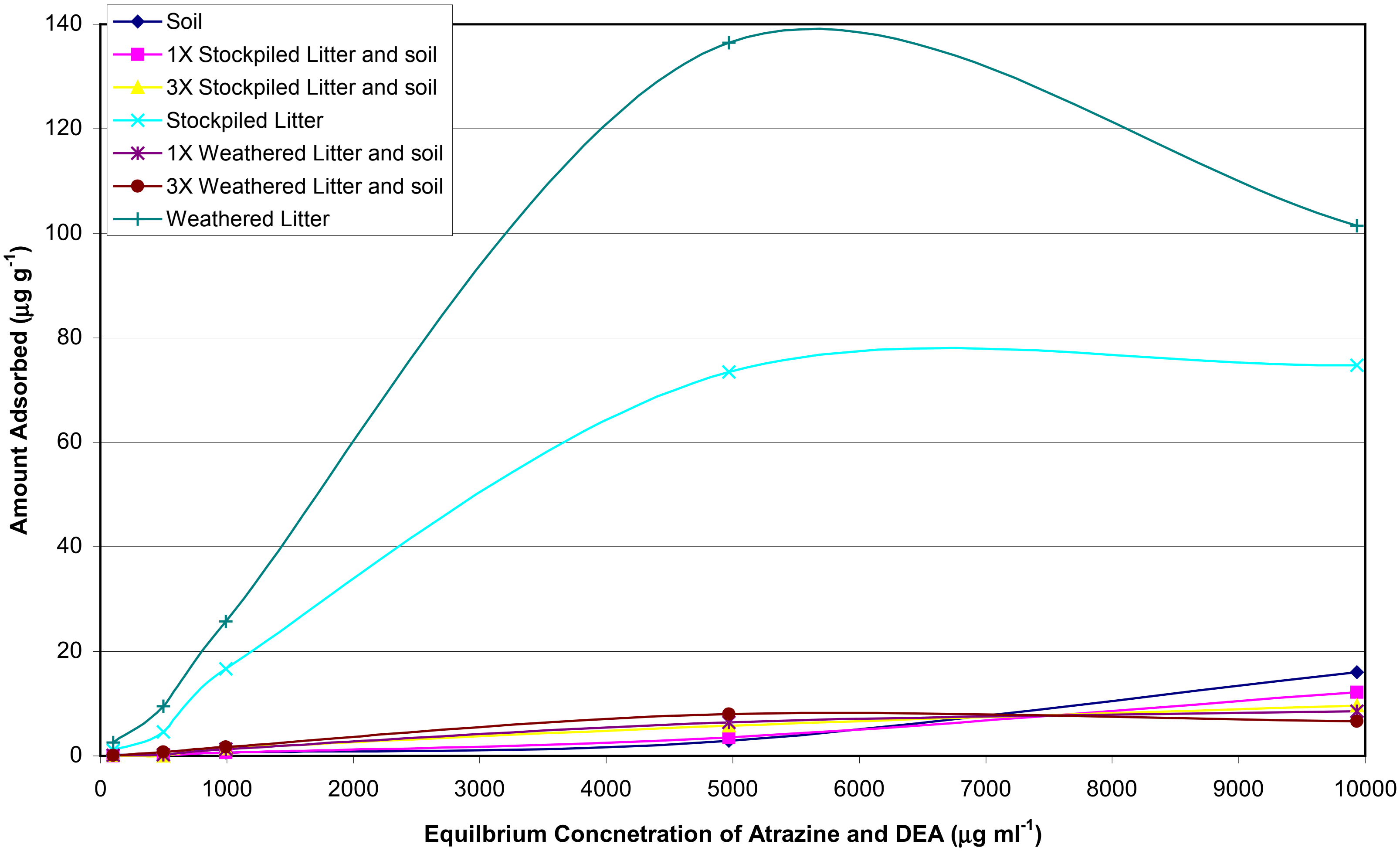


Figure 4.5: Adsorption of atrazine and DEA added to Lakeland soil or soil and poultry litter mixtures.

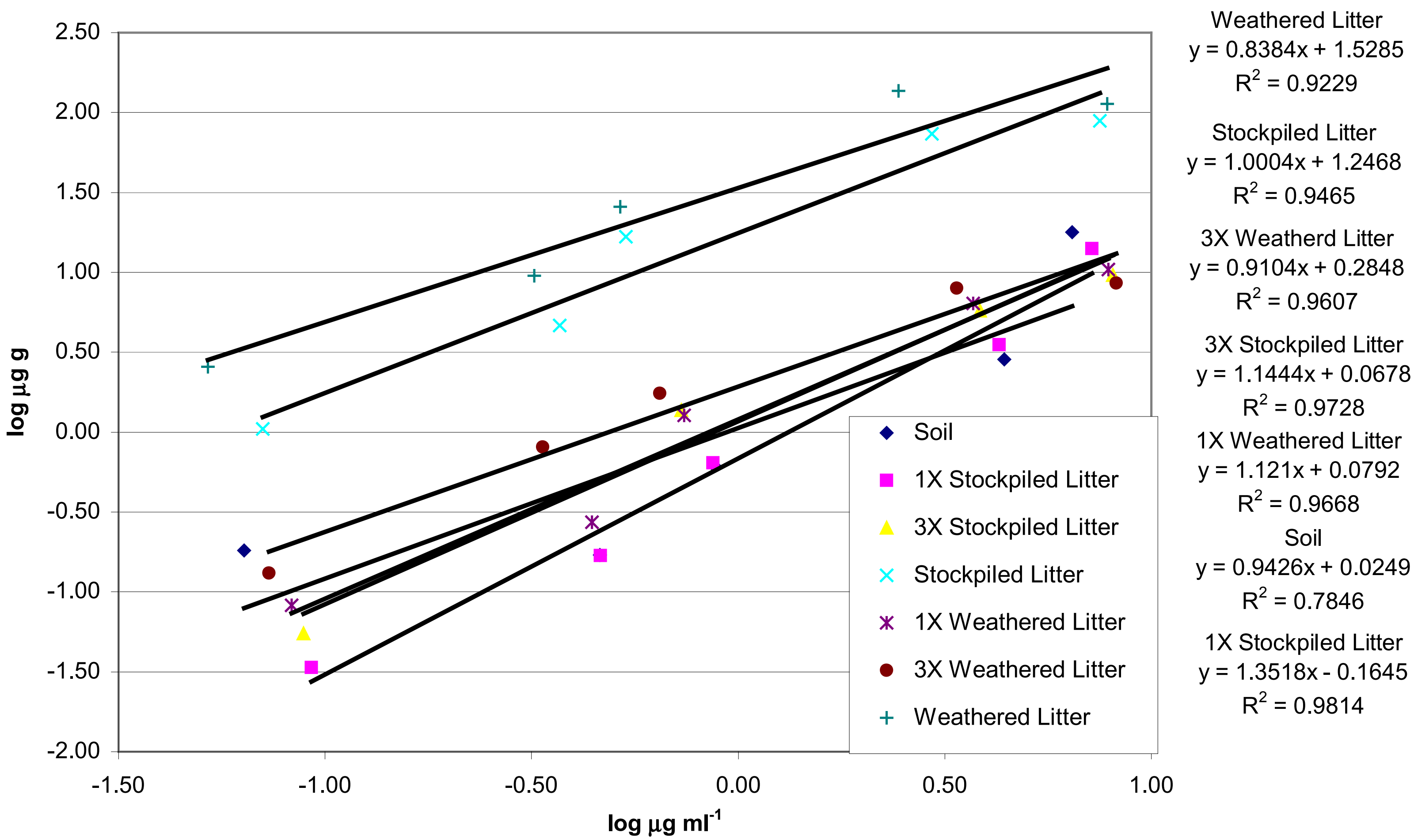


Figure 4.6: Freundlich isotherms for Atrazine added to Lakeland sand or soil and litter mixtures.

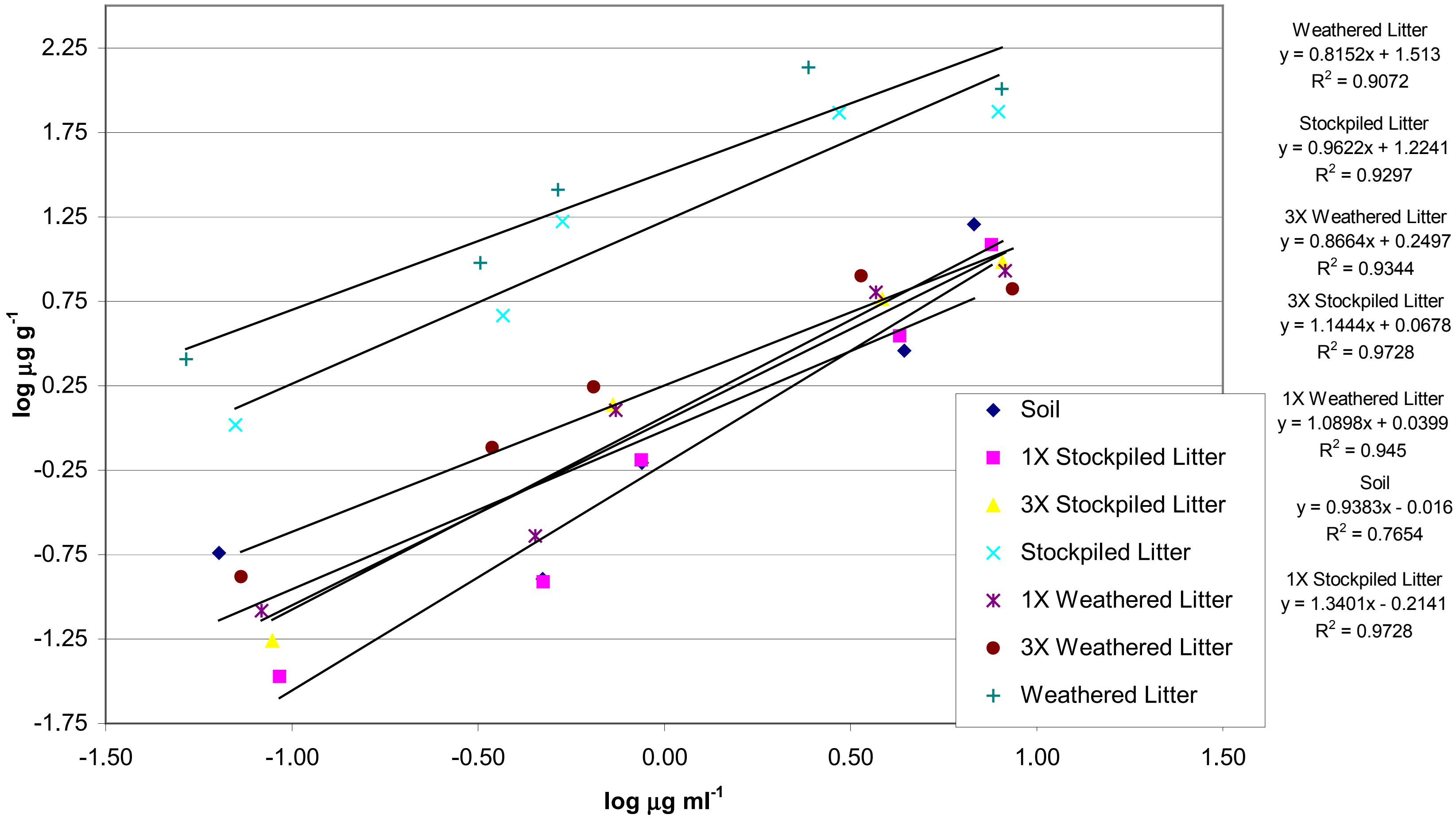


Figure 4.7: Freundlich isotherms for atrazine, and DEA on Lakeland soil or a soil and litter mixture.

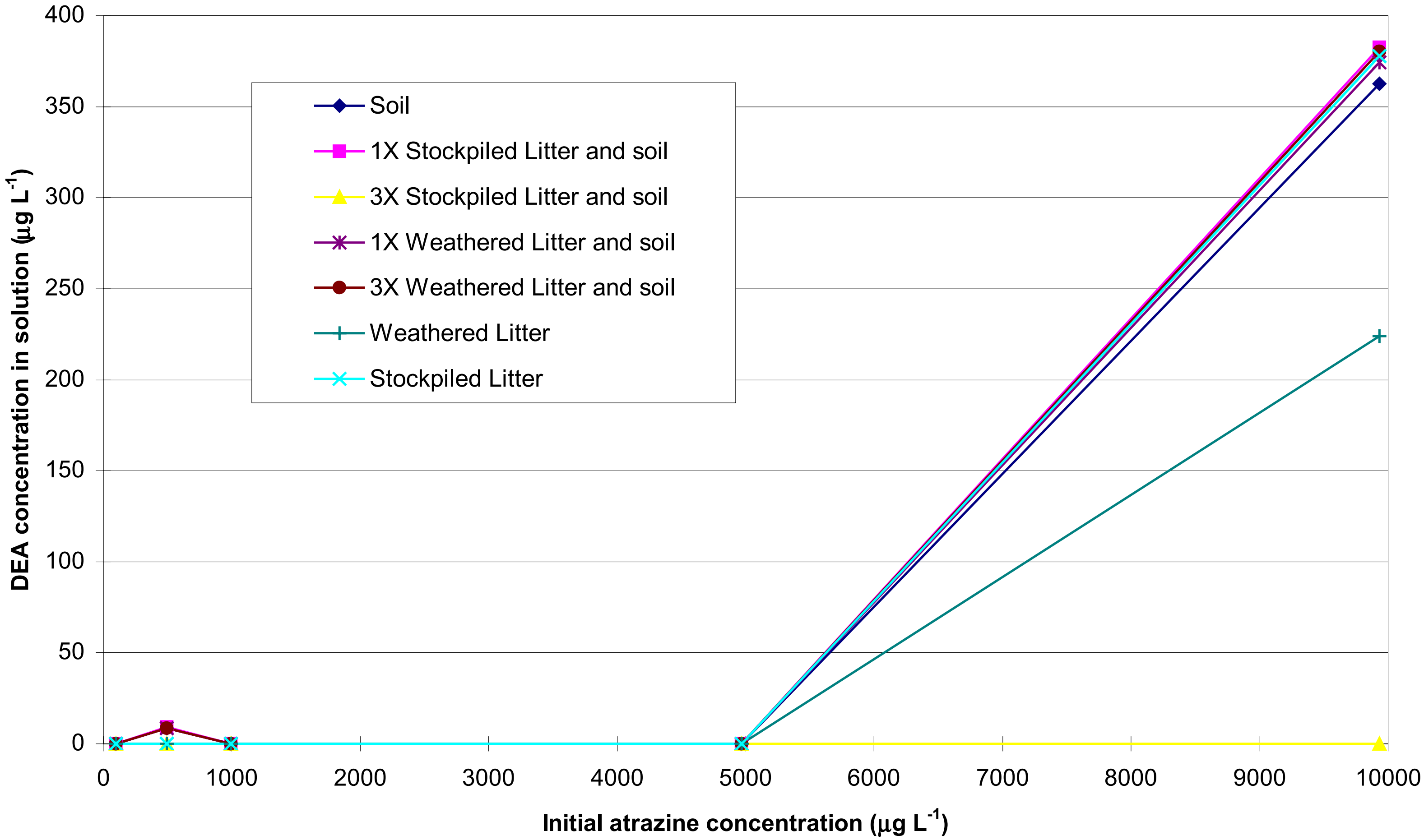


Figure 4.8: DEA concentration found in solution after 24 hours of shaking atrazine solution with soil, and soil and litter mixtures