AN ABSTRACT OF THE THESIS OF

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Abstract approved: Redacted for privacy
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The primary objective of this research was to evaluate the effect of soil pH and salts on phytotoxicity of 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine (atrazine), 2-chloro-4,6-bis(ethylamino)-*s*-triazine (simazine), 2-(*tert*-butylamino)-4-(ethylamino)-6-(methylthio)-*s*-triazine (terbutryn), and 2-(*sec*-butylamino)-4-(ethylamino)-6-methoxy-*s*-triazine (GS-14254).

Experiments were conducted to determine the s-triazine adsorption and phytotoxicity on soils ranging in pH from pH 5.2 to 9.6. To evaluate the effect of salts on interactions between terbutryn and plants, barley (*Hordeum vulgare* L., var. Firlsbeck III) was grown in nutrient solutions with different pH and salt (Na and Ca) stresses. In addition, a field trial was established to evaluate toxicity to alfalfa (*Medicago sativa* L.) from application of s-triazines on selected high pH soils in central Oregon.

The average adsorption of the three ^{14}C ring-labeled s-triazines

on the soils was in the order terbutryn > GS-14254 > atrazine. Adsorption of all chemicals decreased on natural and lime-amended soils as pH increased except for two soils. The magnitude of decreased adsorption was greater for GS-14254 than for terbutryn and atrazine. It was postulated that the greater decrease in GS-14254 adsorption was due to the methoxy-s-triazine having less affinity for the clay and organic constituents in the soil and the possible greater expression of chemical solubility with increased soil pH. Subsequent growth chamber studies using lime-amended Chehalis sandy loam (pH 7.0) showed increased toxicity from GS-14254 to barley in proportion to the amount of decreased adsorption of GS-14254. Adsorption-desorption studies with Chehalis sandy loam indicated that the extent and strength of chemical adsorption was equivalent for GS-14254 (pKa 4.36) and terbutryn (pKa 4.32) at the soil suspension pH of 5.2. Two Oregon soils, Crooked silt loam (pH 8.5) and Boyce silt loam (pH 9.6) adsorbed large amounts of the three s-triazines, with Crooked silt loam adsorbing nearly 100% of the GS-14254 and terbutryn and 90% of the atrazine. The ED_{50} values obtained for the Crooked silt loam, 10.2 and 13.2 kg ai/ha for atrazine and terbutryn, substantiated the large adsorption values.

Barley plants grown under different pH stresses did now show increased toxicity from terbutryn. Also, adjusting the pH of terbutryn solutions from pH 4 to pH 10 for short periods of time did not alter the phytotoxic effects of the chemical in the absence of soil.

Sodium (Cl^-, $SO_4^=$, and $CO_3^=$) salt solutions in which barley was grown did not increase terbutryn toxicity. Barley grown in calcium salt solutions, particularly in the $CaCO_3$ solutions, did show slightly increased toxicity from terbutryn. Subsequent calcium carbonate nutrient solution studies showed approximately a 15% increase in toxicity to barley at the lowest concentration of terbutryn (0.03 ppm) with the highest concentration of calcium carbonate (10 meq/l). It was suggested that this increased phytotoxicity may be a result of a more efficient and rapid uptake of the terbutryn due to increased root growth with a resultant increase in barley transpiration.

The s-triazine applications to established alfalfa on soils of pH 7.1 to 8.5 showed toxicity from simazine to be greater than GS-14254, with no injury noted from terbutryn. The order of phytotoxicity was in accord with the amount of chemical adsorbed to the soils. With simazine, the toxicity to alfalfa appeared to be more closely correlated with organic matter content of the soils than pH, whereas pH of the soils was more closely correlated to phytotoxicity of GS-14254.

Sorption and Phytotoxicity of Triazine Herbicides in Neutral and Calcareous Soils

by

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DEDICATED TO BECKY

Because of her support and unselfishness
through ten years of studies, I dedicate
this thesis to my wife.

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SORPTION AND PHYTOTOXICITY OF TRIAZINE HERBICIDES IN NEUTRAL AND CALCAREOUS SOILS

INTRODUCTION

The s-triazines, since their introduction in the 1950's, have proven to be effective weed control chemicals for many crops grown under various conditions. Extensive research on their mode of action, uptake phenomena, and adsorption and movement in soil systems has been accomplished to assure that the s-triazines are correctly and effectively used.

The s-triazines are introduced into the environment primarily through the soil for subsequent uptake by plants; consequently, an understanding of the reactions between the chemical and the soil becomes vital to the effective management of the chemical and its resultant phytotoxicity. Some soil parameters investigated which influence s-triazine efficacy include: clay mineral type, organic matter, pH, cation-exchange capacity, ion saturation, texture, and moisture.

Several instances of toxicity to crops grown in the western United States have been observed after application of s-triazines.[1] Injury to corn (*Zea mays* L.) has been reported after application of

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[1] Personal communication from Dr. Eugene Hill, Geigy Chemical Corporation, New York.

2-chloro-4-(ethylamino)-6-(isopropylamino)-_s_-triazine (atrazine) on high pH soils in Kansas and Nebraska. In Arizona, after 2-(_sec_-butylamino)-4-(ethylamino)-6-methoxy-_s_-triazine (GS-14254) was applied to a high pH soil, phytotoxicity to alfalfa (_Medicago sativa_ L.) was noted. Application rates of the herbicides were in accord with those recommended for the organic matter and clay content of the soils, which suggests that the high pH level or conditions associated with a high pH might be factors in the observed phytotoxicity. Since most research on the s-triazines had been accomplished on soils under higher rainfall conditions, very little information was available to explain the observed phytotoxicity of s-triazines under conditions of low rainfall and high pH soils.

The primary objective of this research was to further evaluate the chemical reactivity of atrazine (a chloro-s-triazine) and two new compounds, 2-(_tert_-butylamino)-4-(ethylamino)-6-(methylthio)-_s_-triazine (terbutryn), and GS-14254 (a methoxy-s-triazine) on high pH soils. The research was designed to ascertain possible reasons for enhanced phytotoxicity of atrazine, terbutryn, and GS-14254 on natural and lime-amended soils. In addition to adsorption and desorption studies, interactions between terbutryn and barley (_Hordeum vulgare_ L., var. Firlsbeck III) grown in the growth chamber in nutrient solutions at different pH and salt (Na and Ca) levels were studied. A field trial was also established to investigate toxicity to established alfalfa from application of 2-chloro-4, 6-bis(ethylamino)-s-triazine (simazine), terbutryn, and GS-14254 on selected high pH soils.

SORPTION OF THREE s-TRIAZINES ON NATURAL AND LIME-AMENDED SOILS

Introduction

Organic matter (11) and certain clay minerals, e.g., montmorillonite and illite (9), have been shown to adsorb s-triazines. However, the pH of the soil system can greatly influence the amount of s-triazine adsorbed to the above mentioned soil fractions. Reduced adsorption of 13 methylthio ($-SCH_3$), methoxy ($-OCH_3$), and chloro (-Cl)-s-triazines resulted when a clay system of pH 6 was adjusted from 6 to 10 with sodium hydroxide. To explain the decreased adsorption it has been postulated that less protonation of s-triazines occurs with an increase in pH (28).

The structures of s-triazines have been shown to affect adsorption (28). Adsorption of three s-triazines on a montmorillonite clay system at pH levels between 2 and 7 was determined to be in the order 2, 4-bis(isopropylamino)-6-(methylthio)-s-triazine (prometryne) > 2, 4-bis(isopropylamino)-6-methoxy-s-triazine (prometone) > 2-chloro-4, 6-bis(isopropylamino)-s-triazine (propazine) with maximum adsorption occurring in the vicinity of the pKa value of the respective compound (28). Other workers observed that the magnitude of adsorption of the same compounds as measured by Kd values, the ratio of the amount of herbicide adsorbed to the amount in the equilibrium solution, for 25 Missouri soils, pH range 4.3 to 7.1, was prometryne 9.1, prometone 7.8, and propazine 2.0 (22). The order of adsorption was partially explained by the basicity of the compounds. The pKa values for prometryne, prometone, and propazine are 3.05, 4.30, and 1.85, respectively. The pKa values range, dependent upon additional side groups, from 4.15 to 4.76 for OCH_3-, 3.05 to 4.32 for SCH_3-, and 1.0 to 1.85 for Cl-s-triazines. Indicative of their dissociation constants methoxy and methylthio-s-triazines are generally adsorbed in greater amounts than the chloro-s-triazines (29). Additionally, studies show that as the pH of a clay system increased from 4 to 8, adsorption decreased more for the methoxy and methylthio than for the chloro-s-triazine (28).

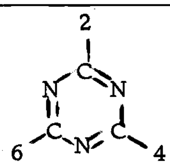
Consistent with the reported decreased s-triazine adsorption with increased pH, several authors have observed increased phytotoxicity to crops. Strawberries (*Fragaria* sp.) showed increased injury from 2-chloro-4,6-bis(ethylamino)-*s*-triazine (simazine) when soils were limed from pH 4.2 to pH 6.5 (18). Similarly, increased toxicity to corn (*Zea mays* L.) has been noted with prometryne on Yolo loam amended with lime from pH 6.6 to 7.9 (26).

The objective of this research was to relate adsorption of 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine (atrazine), 2-(*tert*-butylamino)-4-(ethylamino)-6-(methylthio)-*s*-triazine (terbutryn), and 2-(*sec*-butylamino)-4-(ethylamino)-6-methoxy-*s*-triazine (GS-14254) on natural and lime-amended soils to phytotoxicity.

Material and Methods

Chemicals. Chemical structures and some properties of atrazine, terbutryn, and GS-14254 are presented below.

Table 1. Chemical properties of three s-triazine compounds.[a]

Common name or designation	s-Triazine: Basic ring	Groups on ring: 2	4	6	Solubility ppm at 20 to 25 C	pKa
Atrazine		Cl	NHC_2H_5	$NH_iC_3H_7$	33	1.68
Terbutryn		SCH_3	NHC_2H_5	$NH_tC_4H_9$	58	4.32
GS-14254		OCH_3	NHC_2H_5	$NH_sC_4H_9$	620	4.36

[a]Data supplied by manufacturer.

Preparation of lime-amended soils. Analytical grade calcium carbonate was added to three screened and air-dried soils, Deschutes sandy loam (pH 5.9), Chehalis sandy loam (pH 5.2), and Woodburn silt loam (pH 5.2) to raise the natural soil pH. The Deschutes sandy loam and Chehalis sandy loam were adjusted to pH 7.0, 7.5, and 7.75 while Woodburn silt loam was adjusted to pH 7.0, 7.35, and 7.5. The soils were thoroughly mixed, moistened to field capacity, and incubated in a growth chamber for 21 days. The incubated samples were air-dried, ground, and rescreened for subsequent adsorption and growth chamber studies.

Adsorption of atrazine, terbutryn, and GS-14254. Duplicate 5 g air-dried samples of 10 natural soils and three lime-amended soils were equilibrated in glass centrifuge tubes for 12 hr in a water shaker bath at 25 C with 10 ml of 20 ppm ^{14}C ring-labeled atrazine, terbutryn, and GS-14254. Preliminary studies indicated that maximum adsorption of the chemical was essentially complete within 1 hr. The specific activities of atrazine, terbutryn, and GS-14254 were 10.1, 5.4, and 32.4 μc/mg, respectively. The soil suspension was centrifuged at 15000 rpm for 5 min and the supernatant decanted. One ml of the supernatant was combined with 10 ml of a prepared scintillation fluor and ^{14}C activity assayed in a liquid scintillation counter. The scintillation fluor consisted of toluene and Triton X-100[2] in 2:1 v/v ratio, PPO (4 g/l) as the primary fluor, and POPOP (0.1 g/l) as the secondary fluor. Counting efficiency was determined by a spiking technique with an internal toluene standard. The herbicide adsorption to the soil was calculated by the difference between initial and final herbicide concentration in solution.

Desorption of atrazine, terbutryn, and GS-14254. Duplicate 10 ml samples of 20 ppm ^{14}C ring-labeled atrazine, terbutryn, and GS-14254 were added to 5 g Chehalis sandy loam in a glass tube and equilibrated for 12 hr. A 1 ml portion of the supernatant was assayed for ^{14}C as previously described. The resultant moist soils were

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[2] A non-ionic surfactant supplied by Rohm & Haas Co.

extracted for 2 hr in the water shaker bath at 25 C with a 10 ml aliquot of distilled water, 0.1S[3], 1.0S, or 10.0S of a $CaCl_2$ solution. The soil samples were centrifuged and a 1 ml portion decanted from the supernatant and assayed for ^{14}C activity. The extraction procedure was repeated five times with the amount of labeled compound remaining in the liquid phase of the moist soil subtracted from the total after each extraction. The pH of the distilled water, 0.1, 1.0, and 10.0S $CaCl_2$ solutions was 5.45, 5.60, 6.80, and 8.90, respectively.

GS-14254 toxicity to barley. Unlimed and limed Chehalis sandy loam soil samples, 230 g, were treated with 80% wettable powder formulations of GS-14254 at rates of 0, 0.34, 0.67, and 1.34 kg ai/ha by surface spray followed by a 30 sec mix in a glass container. The herbicide-treated soils were placed in plastic pots and eight presoaked (two days) barley (*Hordeum vulgare* L., var. Firlsbeck III) seeds were placed on the soil surface and covered with 1.27 cm of white quartz sand. The pots were subirrigated and placed in the growth chamber. Treatments were replicated four times. The growth chamber conditions were: air temperatures 27 C day and 15.5 C night, day length 16 hr (10,800 lux).

After four days the emerged barley plants were thinned to five uniform plants per pot. The moisture level was maintained at field

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[3] One symmetry equals the meq $CaCl_2$ to satisfy the CEC, 16.9 meq/100 g.

capacity throughout the duration of the trial by subirrigation. The plant foliage was harvested after 12 days, dried at 90 C for 24 hr, and dry weights were recorded.

ED_{50} determination. Crooked silt loam soil, 230 g, was treated with 80% wettable powder formulations of atrazine or terbutryn at rates of 0, 1.12, 2.24, 3.36, 4.48, 5.60, 6.72, and 7.84 kg ai/ha. Procedures and growth chamber conditions were as described for the GS-14254 phytotoxicity study. The experiment was repeated twice with three replicates per treatment. Foliage dry weights were determined. The amount of herbicide required to reduce barley growth by 50%, ED_{50}, was ascertained by extrapolating the dosage response curve.

Results and Discussion

Adsorption of atrazine, terbutryn, and GS-14254. The average adsorption of three s-triazines on the 10 soils studied was 31.0, 25.5, and 14.4 μg/g soil for terbutryn (SCH_3), GS-14254 (OCH_3) and atrazine (Cl), respectively (Table 2). The adsorption order for the three triazines agreed with previous reports which showed the order was methylthio- > methoxy- > chloro-s-triazines (22, 28).

Adsorption of atrazine, terbutryn, and GS-14254 decreased as soil pH increased from 5.2 to 8.0 (Figure 1). Simple correlation values for soils of ≤ pH 8 (Table 2) indicated adsorption at various

Table 2. The chemical and physical properties of ten soils and related adsorption values of atrazine, terbutryn, and GS-14254.

		Ca	Mg	Na	CEC	OM	Clay	Adsorption		
								Atrazine	Terbutryn	GS-14254
Soil types[a]	pH	meq/100 g soil				percent		μg chemical/g soil		
Chehalis sl	5.2	8.6	5.2	nd[b]	16.9	1.7	18	11.7	36.6	36.3
Woodburn sil	5.2	7.1	1.3	0.6	12.8	2.3	19	16.8	35.2	33.4
Deschutes sl	5.9	6.5	4.9	0.4	12.9	0.9	12	10.1	30.1	26.6
Metolius sl	7.1	11.1	4.8	0.5	18.5	1.4	14	9.4	28.2	23.0
Powder sil	7.7	25.2	9.0	1.7	31.9	2.9	21	15.0	31.3	22.7
Boyce l	8.0	16.7	7.4	0.7	20.0	2.2	11	11.2	29.7	19.5
Gila sic	8.0	46.8	13.5	8.4	29.1	1.1	53	9.8	26.5	12.1
Quincy sl	8.0	25.2	2.9	0.3	11.0	0.5	7	4.6	18.2	7.6
Crooked sil	8.5	38.4	20.6	1.4	34.1	0.8	21	36.4	39.2	39.5
Boyce sil	9.6	30.4	7.0	16.7	27.8	0.7	12	28.7	34.9	35.0
Average								14.4	31.0	25.5
pH correlation coefficients (r)[c]								- .47	- .73	- .90

[a] All soils from Oregon except Gila sic (Arizona) and Quincy sl (Washington).

[b] Not determined.

[c] Correlation coefficient of ± .71 at 5 percent level and ± .83 at 1 percent level required for significance.

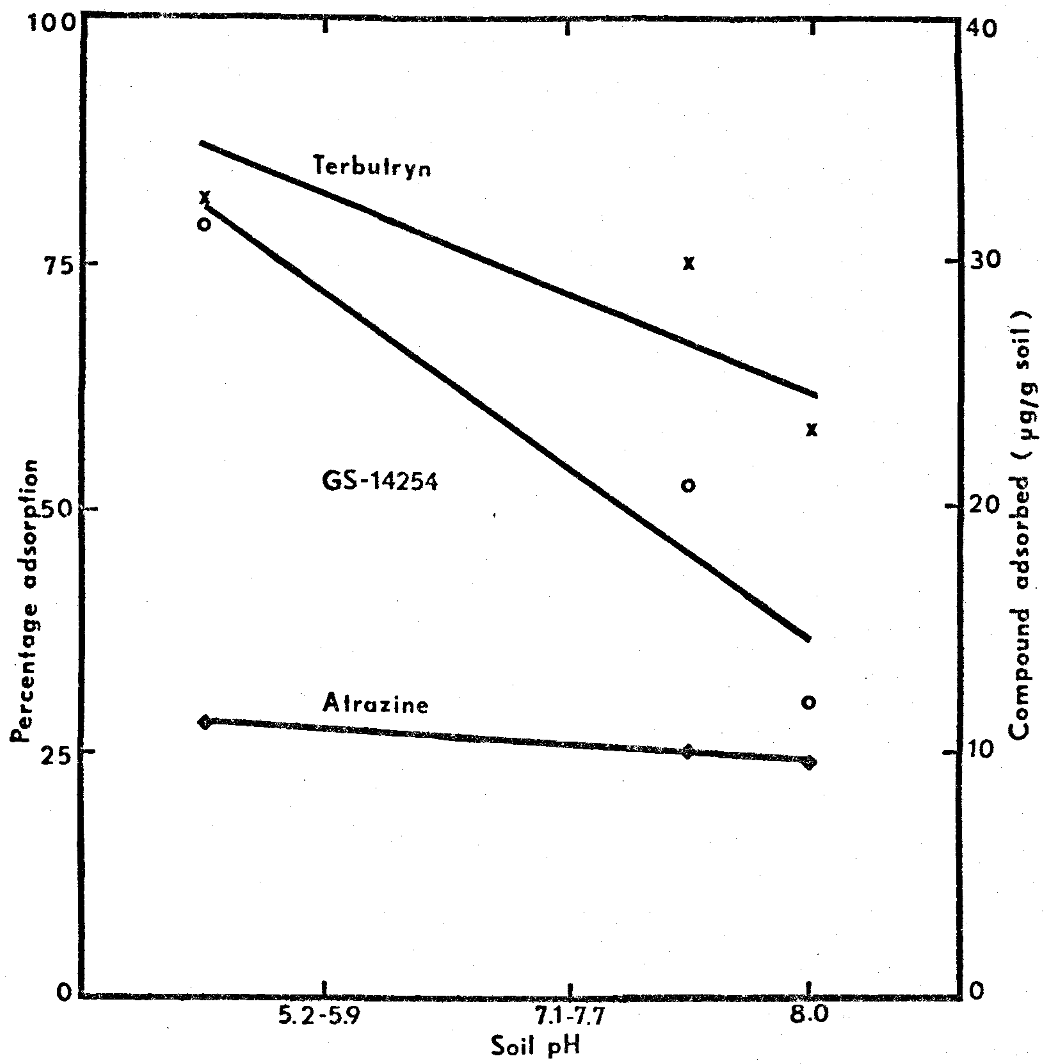

Figure 1. Average adsorption values for atrazine, terbutryn, and GS-14254 on soils of $\leq$ pH 8.

soil pH levels was significantly different at the 1 percent level for GS-14254 adsorption and at the 5 percent level for terbutryn adsorption. The observed decrease in atrazine adsorption was not significantly different with increased soil pH values. The adsorption of GS-14254 (a methoxy-s-triazine) decreased with increased pH regardless of other chemical or physical properties of the soil (Table 2), whereas, atrazine showed much less adsorption change with difference in pH and terbutryn showed intermediate adsorption response to pH changes. The decreased sorption with increased pH was consistent with results obtained by Weber (28), who showed that adsorption of prometryne (SCH_3) and prometone (OCH_3) declined sharply as pH increased by small increments from pH 4.5 to 8 in a Na-montmorillonite system. Additionally, propazine (Cl) adsorption was less extreme and decreased more slowly over the same pH range. Analysis of Weber's data (29) revealed that as pH of the Na-montmorillonite system increased from 5.0 to 6.0, prometryne and prometone adsorption decreased by 105 and 175 mole/g, respectively, possibly indicating a greater influence of pH on methoxy- than on methylthio-s-triazines. Similar results were evident with the s-triazine series 2-methylthio-4-(diethylamino)-6-(isopropylamino)-_s_-triazine (ipatryne), 2-methoxy-4-(diethylamino)-6-(isopropylamino)-_s_-triazine (ipatone), and 2-chloro-4-(diethylamino)-6-(isopropylamino)-_s_-triazine (ipazine) (28).

Organic matter, rather than clay content, was the most important factor affecting adsorption of atrazine, terbutryn, and GS-14254 on soils with similar pH (Table 2). The Boyce loam soil (organic matter 2.2% and clay 11%) adsorbed 11.2, 29.7, and 19.5 μg/g soil of atrazine, terbutryn, and GS-14254, respectively, whereas Gila silty clay (organic matter 1.1% and clay 53%) adsorbed 9.8, 26.5, and 12.1 μg/g soil of the compounds. Based on ED_{50} values, relative adsorption of prometryne and simazine was greater on sphagnum moss, fibrous peat, and muck soils than on bentonite clay (6). The pH of the four growth media differed only by 0.2 units, i.e., 7.2 to 7.4.

The Boyce silt loam, pH 9.6, and Crooked silt loam, pH 8.5, consistently adsorbed large quantities of the three s-triazines studied (Table 2). Nearly 100% of the terbutryn and GS-14254 and 90% of the atrazine were adsorbed to the Crooked silt loam. The greater amount of terbutryn than atrazine adsorbed to Crooked silt loam was reflected in the ED_{50} values which increased from 10.2 for atrazine to 13.2 kg ai/ha for terbutryn. The high adsorption of the three s-triazines on the Boyce silt loam and the Crooked silt loam soils can not be attributed to high organic matter or clay content since Crooked silt loam soil contained only 0.8% organic matter and 21% clay and Boycesilt loam soil contained 0.7% organic matter and 12% clay. These soils did, however, contain excessive amounts of Ca and/or

Mg and Na (Table 2). Because of the high soil pH, excess salts, and the near uniform adsorption of all three s-triazines, it is suggested that hydrolysis of the compounds studied occurred at the 2 position on the triazine ring. Hydrolysis of chloro-s-triazine has been shown to take place in alkaline solutions (14). After hydrolysis the chemical structures of the three compounds used in this study would be the same except for the alkylamino group on the 6 position of the triazine ring. The alkylamino groups would be C_4H_9t for terbutryn, C_4H_9s for GS-14254, and C_3H_7i for atrazine. The difference in alkylamino groups may account for the slightly less "atrazine" adsorbed. Sorption of s-triazines with the same group on the 2 position is influenced by the length of the alkylamino groups on the 4 and 6 positions, adsorption decreasing in the order $C_4H_9t > C_4H_9s > C_2H_5 > C_3H_7i$ (28). Further, it is suggested that the high salt content of these soils will reduce the solubility of the three triazine derivatives and cause a "salting out" effect, enhancing adsorption. Adsorption of dinitrophenols was increased on montmorillonite clay in 1 N NaCl concentrations (9). It has been postulated that an increase in atrazine and simazine adsorption with 0.3 ionic strength KCl, NH_4Cl, and $CaCl_2$ solutions compared to water was due to effects on solubility.[4]

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[4] Hurle, K. B. and V. H. Freed, unpublished data, 1970. Oregon State University, Corvallis.

<u>Adsorption of three s-triazines on unlimed and limed soils.</u> Chemical adsorption on unlimed Deschutes sandy loam (pH 5.9), Chehalis sandy loam (pH 5.2), and Woodburn silt loam (pH 5.2) was in the order terbutryn > GS-14254 > atrazine (Figure 2).

The average amount of chemical adsorbed was 71.2, 70.5, and 55.7% on the unlimed Woodburn silt loam, Chehalis sandy loam, and Deschutes sandy loam, respectively (Table 3). The difference in original soil pH (Deschutes pH 5.9 and Woodburn and Chehalis 5.2), would partially account for less chemical being adsorbed by the Deschutes sandy loam.

Table 3. Average adsorption of three s-triazines on three unlimed and lime-amended soils.

Soil series	Adsorption[a]			
	Unlimed	Limed		Difference between unlimed and pH 7.5
		7.0	7.5	
	%	%	%	%
Deschutes sl	55.7	44.2	35.4	20.3
Chehalis sl	70.5	40.3	30.0	40.5
Woodburn sil	71.2	51.9	42.7	28.5

[a] Average adsorption value for atrazine, terbutryn, and GS-14254.

When the soil pH was increased to 7.0 and 7.5, adsorption of the chemical was in the order Woodburn silt loam > Deschutes sandy loam > Chehalis sandy loam. The organic matter content of the

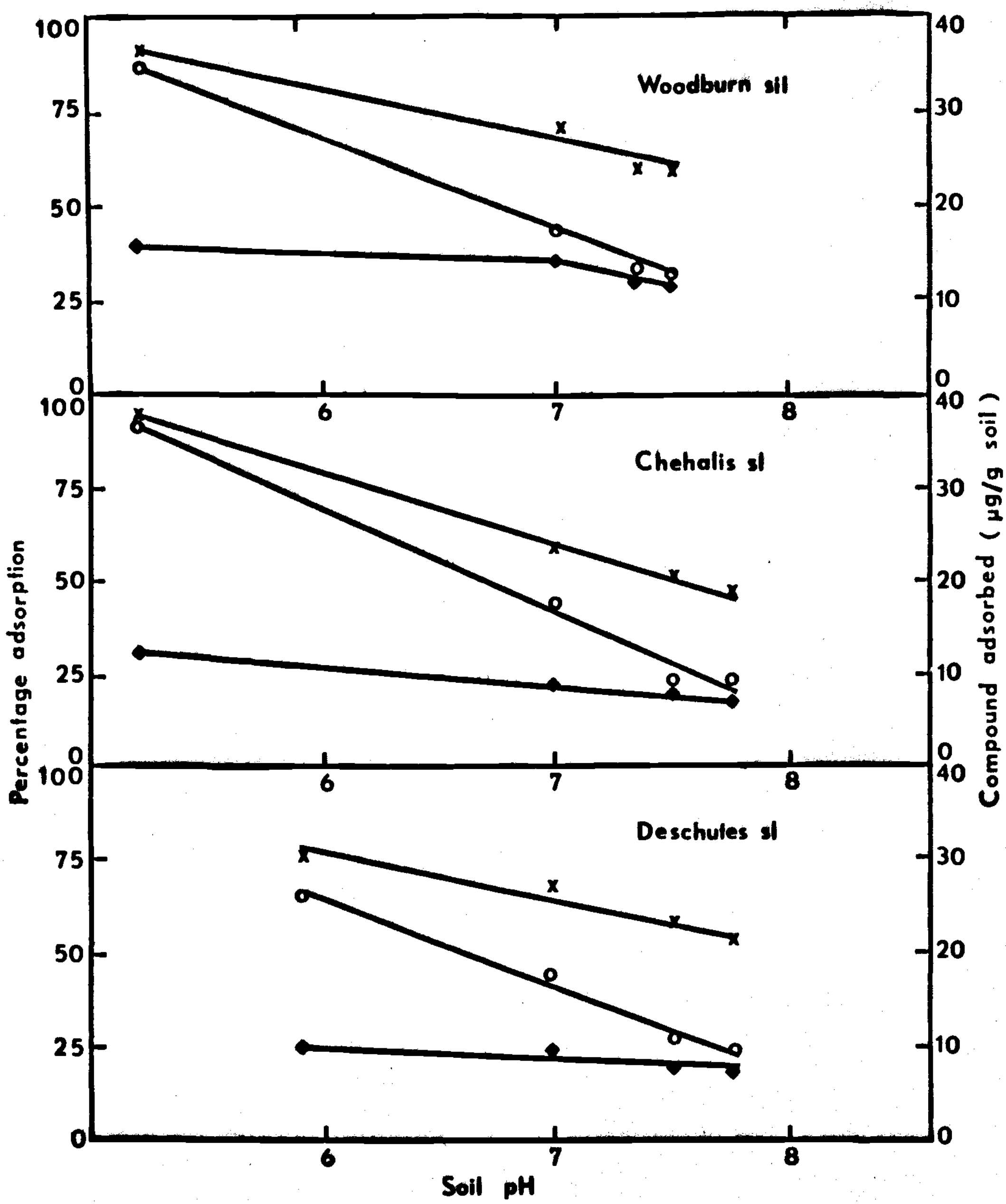

Figure 2. Adsorption of three s-triazines on unlimed and limed soils.

Legend: Terbutryn (x—x), GS-14254 (o—o), and atrazine (◆—◆).

Woodburn silt loam (2.3%) as opposed to Chehalis sandy loam (1.7%) probably accounted for the majority of the adsorption differential at pH 7.0 and 7.5. However, Deschutes sandy loam, which has the lowest clay (12%) and organic matter (0.9%) content of the three soils, adsorbed more chemical than Chehalis sandy loam when limed to pH 7.0 and 7.5. This increased adsorption probably was due to the porous nature of Deschutes sandy loam soil which may have allowed some absorption of the chemical (2).

Adsorption of the chemicals on the limed soils decreased as soil pH increased. As was evident for the soils of pH 5.2 to 8.0 (Table 2), the magnitude of reduced adsorption for each compound as pH increased was in the order GS-14254 > terbutryn > atrazine (Figure 2). The average decrease in adsorption across the three soils, from the unlimed to the pH 7.5, was 53.0, 27.1, and 9.3% for GS-14254, terbutryn, and atrazine, respectively. The decreased adsorption ratio of 1:2.9:5.7 (atrazine = 1) was fairly consistent for the three soils. The same ratios were obtained for the natural soils of pH $\leq$ 8 (Figure 1).

A partial explanation of the greater adsorption reduction of GS-14254 (620 ppm) than terbutryn (58 ppm) could be that a high pH level may have less effect on the solubility of methoxy- than on methylthio-s-triazines. Prometone (OCH_3) was 1.4 times as soluble as prometryne (SCH_3) at pH 2, and five times as soluble at pH 3, but at pH 5 to 10 prometone was 15 times more soluble (27). Another possible reason for the greater reduced adsorption of GS-14254 than terbutryn could be that methoxy-s-triazines generally have less affinity for colloidal surfaces, clay and organic matter, than the methylthio-s-triazines (25, 28).

Desorption of atrazine, terbutryn, and GS-14254. The order of chemical desorption from Chehalis sandy loam, pH 5.2, was atrazine > GS-14254 > terbutryn, as determined from the average amount of compound desorbed by the water and three $CaCl_2$ solution treatments (Table 4). Of the amount initially adsorbed on the soil, 50.0, 27.6, and 25.3% of the atrazine, GS-14254, and terbutryn was desorbed, respectively. The greater desorption of atrazine probably can be explained from a study of the chemical structures of the compounds. Terbutryn (pKa 4.32) and GS-14254 (pKa 4.36) may protonate more readily at pH 5.2 than atrazine (pKa 1.68). Hence the protonated chemical may compete for available exchange sites on the soil surface which would result in a stronger bonded compound than the unprotonated atrazine.

All $CaCl_2$ concentrations desorbed more of the three chemicals from Chehalis sandy loam than water alone. The increased desorption by $CaCl_2$ solutions over water probably was partially due to an exchange of the herbicide by the Ca^{++} ions for the adsorption sites on the soil surface. Weber (28) found that approximately 7.1% of the prometone adsorbed on montmorillonite clay (pH 6), was desorbed with water while 17.4% was desorbed with 0.1 M $BaCl_2$. He postulated that $BaCl_2$ displaced prometone primarily through cation exchange of protonated prometone by Ba^{++} ions. Also, adsorption of prometone (pKa 4.3) on montmorillonite clay at pH 4 and 6 was attributed to a combination of coulombic (cation-exchange) forces, direct association with hydrogen on the clay surface, and molecular adsorption.

Table 4. Adsorption-desorption of three s-triazines from Chehalis sandy loam.

	Adsorbed					
	Initial		After 5 extractions		Amount desorbed	
Chemical	μg/5 g	%	μg/5 g	%	μg/5 g	%
Atrazine						
H_2O	67.9	33.9	43.4	21.7	24.5	36.1
0.1S $CaCl_2$	63.3	31.6	25.1	12.5	38.2	60.3
1.0	69.8	34.9	30.6	15.3	39.2	56.2
10.0	66.4	33.2	34.9	17.4	31.5	47.5
Terbutryn						
H_2O	174.6	87.3	138.9	69.4	35.7	20.6
0.1S $CaCl_2$	178.7	89.3	131.6	65.8	47.1	26.3
1.0	177.6	88.8	125.6	62.7	52.1	29.4
10.0	178.0	89.0	133.8	66.9	44.2	24.9
GS-14254						
H_2O	174.2	87.1	133.1	66.5	41.1	23.6
0.1S $CaCl_2$	174.7	87.3	126.3	63.1	48.4	27.7
1.0	175.7	87.8	121.9	60.9	53.8	30.6
10.0	174.6	87.3	125.3	62.6	49.3	28.2

The 1.0S concentration of the $CaCl_2$ solution desorbed the compounds most efficiently. After five extractions, 1.0S $CaCl_2$ desorbed 39.2, 52.1, and 53.8 µg/5 g soil of atrazine, terbutryn, and GS-14254, respectively. The 0.1 and 10.0S $CaCl_2$ solutions desorbed slightly less chemical than the 1.0S $CaCl_2$ solution. The 0.1S $CaCl_2$ solution probably did not contain sufficient exchangeable calcium for maximum exchange while the 10.0S concentration may have reduced solubility of the herbicides. Atrazine, 2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine (ametryne), and 2-(ethylamino)-4-(isopropylamino)-6-methoxy-s-triazine (atratone) solubility decreased with increased concentrations of $CaCl_2$ as compared to water.[4] In water, the solubility of atrazine, ametryne, and atratone was 30, 209, and 1670 ppm, respectively, whereas in a 0.2 M $CaCl_2$ solution solubility was reduced to 26, 165, and 1300 ppm. The 10.0S $CaCl_2$ (approximately 0.9 M $CaCl_2$) used in this desorption study could effectively lower the solubility of the three s-triazines, thereby reducing the amount of chemical released. Decreased aqueous solubility of prometone was the suggested reason for less desorption of the chemical by 1 M $BaCl_2$ solution than by water (29).

This study would indicate that the difference in solubility of GS-14254 (620 ppm) and terbutryn (58 ppm) would not be a major factor in their desorption at the soil pH of Chehalis sandy loam, 5.2, as water desorbed approximately the same amount of both compounds.

The strength of bonding for GS-14254 and terbutryn appears to be similar as the 1.0S $CaCl_2$ solution displaced the compounds similarly.

<u>GS-14254 toxicity to barley on limed Chehalis sandy loam</u>. GS-14254 was more toxic to barley as soil pH levels increased (Figure 3). When the GS-14254 was applied at a rate of 0.34 kg ai/ha, barley growth was reduced by 53% at pH 7.0 as compared to barley growth in treatments on unlimed Chehalis sandy loam. Similar growth reductions were obtained on the Chehalis soil limed to pH 7.5 and 7.75. Increased prometryne phototoxicity reduced corn yield on Yolo loam (pH 6.6) when the soil was limed to 7.9 at a 2.3 kg/ha rate (26).

The increased GS-14254 toxicity to barley grown on limed soils in the growth chamber study confirms the decreased adsorption of the chemical on soils as pH increased. Adsorption of GS-14254 on unlimed Chehalis sandy loam, pH 5.2, was 48% more than on limed Chehalis sandy loam, pH 7.0, which corresponds closely with the 53% barley growth reduction on the limed soil. These results would indicate that the amount of chemical not adsorbed with increasing pH would be available for uptake by the plant. Lavy (17), using three chloro-s-triazines, has shown increased uptake of ^{14}C by corn plants as pH increased.

The bioactivity of s-triazines may be significantly altered by cultural practices which tend to affect the soil pH levels in the vicinity

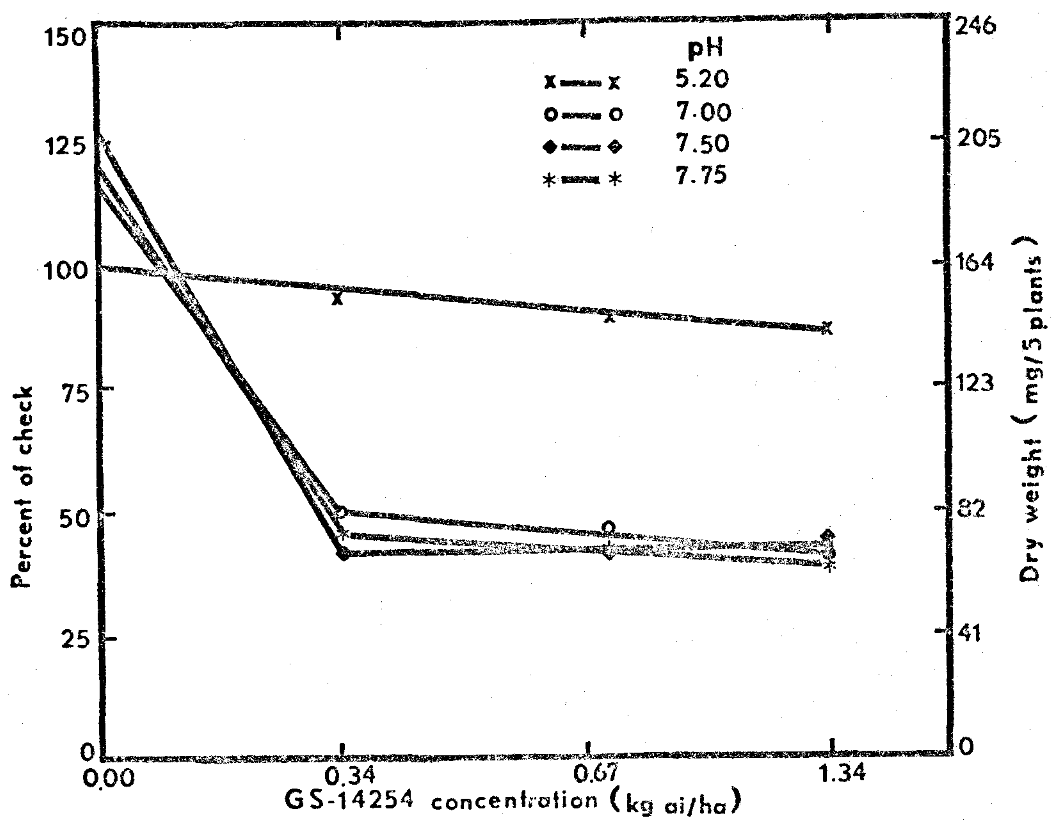

Figure 3. Phytotoxicity of GS-14254 on barley growth in Chehalis sl limed to given pH levels.

of the applied herbicide. Such cultural practices include fertilization, pH of the irrigation water, and addition of lime or sulfur amendments. This study would suggest that activity of methoxy-s-triazines would probably be more affected by changes in pH than methylthio- or chloro-s-triazines.

TERBUTRYN TOXICITY TO BARLEY GROWN UNDER STRESS FROM SALTS AND HIGH pH CONDITIONS

Introduction

Approximately one-third of the earth's surface is comprised of arid or semi-arid land which contains substantial amounts of sodium, calcium, and magnesium salts (16). These salts can have a pronounced effect on soil pH, nutrient and water availability, and herbicide phytotoxicity.

Research with s-triazines has focused on factors which influence adsorption since these herbicides are introduced primarily into the soil system. Two soil constituents, organic matter and clay types, have been investigated extensively in relation to magnitude of s-triazine adsorption (6, 12, 29, 31). Additionally, the soil pH and salt concentration have been shown to influence the amount of s-triazine chemicals adsorbed. Adsorption of 13 s-triazines on montmorillonite clay decreased with increasing pH, with a greater adsorption reduction occurring for the methylthio- and methoxy- than for the chloro-s-triazine compounds (29). Both montmorillonite clay and a soil of high organic matter content added to a sand and nutrient solution growth media showed greater toxicity of 2, 4-bis(isopropylamino)-6-(methylthio)-*s*-triazine (prometryne) to wheat (*Triticum aestivum* L. em. Thell.) at pH 6.4 than at pH 4.5 (30). Under field conditions, increased injury to corn (*Zea mays* L.) from prometryne application was noted when Yolo loam soil (pH 6.6) was limed to pH 7.9 (26). Hurle and Freed[4] showed reduced solubility of 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine (atrazine) in 0.3 ionic strength $CaCl_2$ solutions resulted in a 17% increased adsorption of the compound on Woodburn silt loam. No attempt was made by the authors to correlate the increased adsorption under the high salt conditions with phytotoxicity of the chemical.

High pH conditions and salt concentrations can alter both plant growth and the chemical applied. Reduced solubility of atrazine, 2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-*s*-triazine (ametryne), and 2-(ethylamino)-4-(isopropylamino)-6-methoxy-*s*-triazine (atratone) was shown with increasing ionic strength of KCl, NH_4Cl, and $CaCl_2$ solutions.[4] Further, hydrolysis of chloro-s-triazines has been shown to occur with increasing pH above neutral (14). The adverse effect of high salt levels on plant growth has been attributed to reduced water uptake as a result of high soil solution osmotic pressure. Inhibition of kidney bean (*Phaseolus vulgaris* L.) growth was similar for equivalent osmotic solutions of NaCl, Na_2SO_4, or $CaCl_2$ nutrient solutions (10). On the other hand, Thorup (23) observed a reduction in water uptake for tomatoes growing in $NaCO_3$ solutions but did not observe a decrease when NaCl was added to the nutrient solution in equivalent osmotic concentrations. Nutrient solutions above pH 8 reduced root growth of tomato (*Lycopersicon esculentum* L.), lettuce (*Lactuca* *sativa* L.), and bermudagrass (*Cynodon dactylon* (L.) Pres.) (4). Additionally, Thorup (23) found solutions of > pH 8 restricted both the growth of tomato adventitious roots and water uptake by the plant. The roots resumed growth when the pH of the nutrient solution was adjusted to < pH 8.

The accumulation of certain ions in high salt soils can have an adverse effect on plant growth. Ions common in high salt soils, i.e., sodium, calcium, magnesium, chloride, sulfate and bicarbonate (1) have been shown to be toxic or restrictive to plant growth at high concentrations, and others, i.e., boron and lithium, may be phytotoxic at very low concentrations (13). High concentrations of sodium have reduced the availability of calcium for plant uptake (7), while high concentrations of calcium may restrict potassium absorption (15).

The objective of this research was to investigate the phytotoxicity of 2-(*tert*-butylamino)-4-(ethylamino)-6-(methylthio)-*s*-triazine (terbutryn) to barley (*Hordeum vulgare* L., var. Firlsbeck III) grown under different pH and salt (Na and Ca) stress conditions.

Materials and Methods

Terbutryn toxicity to barley grown in pH 4, 6, and 8 solutions. Eight pre-soaked (two days) barley seeds were planted in pots which contained 300 g white quartz sand rinsed with distilled water. The barley plants were grown for eight days with fresh 0.1 strength

Hoagland's solution added daily. On the eighth day the barley was thinned to six uniform plants per pot. The nutrient solution which remained in the pots was removed by addition of 100 ml of distilled water and subsequent suction application at the bottom of the pot. The bottom of each pot was sealed and 50 ml of either water or 1 ppm terbutryn solution added. Prior to addition, the water and terbutryn solutions (technical chemical of 97.8%) were adjusted to pH 4, 6, and 8 with either 0.05 N HCl or 0.05 N NaOH. The treatment solutions remained in the pots for two days, and then were displaced with 400 ml of distilled water and the suction application. Hoagland's solution was then added to sustain plant growth. The barley was grown for ten more days, harvested, and foliage and root dry weight determined. The roots were washed with tap water to remove adhering sand particles.

A complete randomized block design was used with four replicates per treatment. The plants were grown under continuous light in the greenhouse with temperatures varying from a maximum of 27 C during the day to a minimum of 18.5 C at night.

Barley response to terbutryn solutions of pH 6, adjusted from pH 4, 8, and 10. Materials and procedures used in this study were as described for the previous experiment, with the exception that all water and terbutryn solutions were adjusted to pH 6. Prior to application to the barley, the water and terbutryn solutions were adjusted to pH 4, 6, 8, and 10 with 0.05 N HCl or 0.05 N NaOH for one hour and subsequently readjusted to pH 6.

Terbutryn toxicity to barley grown in sodium or calcium salt solutions. Parafilm was stretched over a quart jar lid drilled with four holes. Four pre-soaked (two days) barley seeds were inserted into the parafilm over the holes. The lids containing the germinated seeds were floated on one-half strength Hoagland's solution for three days. At the end of the third day the seedlings were thinned to three uniform plants per lid and transferred to quart jars containing 900 ml of 0.5 strength Hoagland's solution. Duplicate samples of sodium or calcium salts (Cl, SO_4, and CO_3) at rates of 5 meq/l were added to the Hoagland's solution. Appropriate checks with no salts added were included. After the addition of the salts, 5 ml of a 9 ppm terbutryn solution were added to each quart jar to make a .05 ppm terbutryn solution. Air was bubbled through the nutrient solution in each quart jar. All salts added were totally dissolved except for the $CaSO_4$, $CaCO_3$, and Na_2CO_3. The nutrient solutions which contained precipitates were stirred twice a day to minimize sedimentation. The nutrient solutions were replenished to the 900 ml level with 0.5 strength Hoagland's solution on the second and sixth day. The barley was grown for ten days in the salt-amended Hoagland's solution and foliage and roots were harvested separately and dry weight recorded. The roots were water rinsed to remove all foreign material. The initial pH of each solution and the pH on the second, sixth and tenth days was determined with a combination calomel-glass electrode.

Plants were maintained in a growth chamber during the three day establishment period and during the ten day exposure to herbicide-salt treatments. Growth chamber conditions were as follows: air temperature 27 C day and 15.5 C night, day length 16 hr (10,800 lux).

Terbutryn toxicity to barley grown in calcium carbonate amended nutrient solutions. The barley seedlings were prepared as for the previous salt nutrient solution study. Sufficient $CaCO_3$ was added to each quart jar so that the final concentrations in the 0.5 strength Hoagland's solution were 0, 2.5, 5.0, and 10.0 meq/l. Likewise, sufficient quantities of a 9 ppm terbutryn solution were added so that the final concentrations in the nutrient solution were 0, .03, .06, .09, and .12 ppm. All $CaCO_3$ amended nutrient solutions contained precipitates which were stirred twice a day to minimize sedimentation. The amount of transpiration by the barley was determined by measuring the 0.5 strength Hoagland's solution required to replenish the solution in the quart jar to the original level. Evaporation was ascertained by averaging the loss of nutrient solution from two jars which contained no plants. The barley seedlings were grown for ten days in the nutrient solutions. Roots and foliage dry weights were then determined. All treatments were run in duplicate.

Results and Discussion

Terbutryn toxicity to barley grown in various pH and salt solutions. Barley growth was similar in pH solutions adjusted to pH 4, 6, and 8 without terbutryn (Table 5).

Table 5. Terbutryn toxicity to barley grown in pH 4, 6, and 8 solutions.

Solution pH	Terbutryn ppmw	Yield mg dry wt/6 plants
pH 4	0.14	925.1
pH 4	0	1236.8
pH 6	0.14	965.3
pH 6	0	1302.7
pH 8	0.14	853.6
pH 8	0	1248.4
LSD (.05) mg		132.3

The addition of terbutryn resulted in a significant reduction of barley growth at all pH levels. Growth was reduced by 25.2, 25.9, and 31.6% for pH solutions of 4, 6, and 8, respectively. No significant differences in yield were observed among terbutryn treatments at the three pH levels. Weber (30) also found no difference in wheat plant height after prometryne was added to sand culture adjusted to pH 4.3 and 6.4.

Barley growth was reduced by approximately 30% as compared to the check when the terbutryn solutions which had been previously adjusted to pH 4, 6, 8, and 10 were included with the 0.5 strength Hoagland's solution (Table 6).

Table 6. Barley response to terbutryn solutions of pH 6, adjusted from pH 4, 8, and 10.

Solution pH	Previous terbutryn pH	Terbutryn ppmw	Foliage and root yield mg dry wt/6 plants
pH 6	4	0.14	852.5
pH 6	6	0.14	965.3
pH 6	8	0.14	907.7
pH 6	10	0.14	899.4
pH 6	6	0	1302.7
LSD (.05) mg			233.9

No significant differences in barley growth occurred as a result of the pretreatment of the terbutryn solution. However, there was a slight trend for increased toxicity to barley from terbutryn solutions which had been acid pretreated to pH 4, and basic pretreated at pH 8 and 10 as compared to the pH 6 treatment.

The pH of the system did not appear to directly influence the response of barley to terbutryn. Further, within the limits of pH 4 to 10, the pH of the herbicide solution applied would not significantly affect the phytotoxicity when applied to a soil of neutral reaction. However, one must recognize that the terbutryn solutions were exposed to the pH 4 and pH 10 solutions for a relatively short time. A hydrolysis reaction possibly could occur with longer exposure to the more basic or acidic solutions. Armstrong (3) found significant atrazine hydrolyzed in aqueous solution in ten days at pH 2 and 12, in 100 days at pH 4 and 11, and in 1,000 days at pH 6 and 10. Further, the reaction of terbutryn in a soil of pH 4 may be quite different than in a solution of pH 4 because of the increased acid ion concentrations which may occur in the vicinity of the soil colloids (29).

The additions of sodium and calcium salts (Cl, SO_4, and CO_3), except Na_2CO_3, increased barley growth as compared to Hoagland's solution (Table 7). Shourbagy and Wallace (20) found an average growth increase of 32.5% for Firlsbeck III and four other barley varieties when 5 and 10 meq/l sodium salts were added to nutrient solutions. Likewise, soybeans (_Glycine_ _max_ L. var. Jackson) grown in sand culture with nutrient solutions containing 0, 0.1, 1.0, and 10.0 meq/l $CaCl_2$ resulted in total plant dry weights of 180, 191, 199, and 230 mg/plant, respectively (15).

With the addition of terbutryn to the solutions containing the calcium salts total barley growth was reduced by approximately 66%. Barley growth was reduced approximately 60% when terbutryn was added to the solution which contained the sodium salts (Table 7). Barley growth tended to be reduced most by calcium carbonate plus terbutryn treatments in this experiment as well as in another preliminary salt study (Appendix Table 5).

Table 7. Barley growth and solution pH for sodium and calcium salts added to 0.5 strength Hoagland's solution.

Salt added	Terbutryn ppm	pH 2nd day	pH 6th day	pH 10th day	Yield mg dry wt/3 plants	% of check
0	0	6.20	6.10	5.60	439.7	100.0
0	0.05	5.90	6.25	6.15	174.8	39.8
NaCl	0	6.20	6.00	5.30	495.5	100.0
NaCl	0.05	5.90	6.20	6.00	197.3	39.8
Na_2SO_4	0	6.45	6.20	5.50	550.1	100.0
Na_2SO_4	0.05	6.05	6.30	6.15	220.1	40.0
Na_2CO_3	0	7.00	6.40	5.70	398.5	100.0
Na_2CO_3	0.05	6.50	6.30	5.95	176.6	44.3
$CaCl_2$	0	6.00	5.85	5.20	548.3	100.0
$CaCl_2$	0.05	5.80	6.20	6.10	201.4	36.7
$CaSO_4$	0	6.10	5.95	5.40	478.1	100.0
$CaSO_4$	0.05	5.80	6.20	6.15	165.6	34.6
$CaCO_3$	0	7.10	6.90	7.20	459.7	100.0
$CaCO_3$	0.05	7.30	6.98	7.20	148.7	32.3

Terbutryn toxicity to barley grown in calcium carbonate amended nutrient solutions. Barley growth did not differ from the check when 2.5 and 5.0 meq/l $CaCO_3$ was added to the nutrient solution; however, barley growth did increase by 18% for the 10 meq/l rate (Table 8). Foliage growth was reduced by approximately 15% for all levels of $CaCO_3$ as compared to the control; however, root growth was increased by 16, 25, and 76% for the 2.5, 5.0, and 10 meq/l $CaCO_3$ levels, respectively (Table 8). The reduced availability of certain ions for plant uptake or use may partially account for the reduced foliage growth observed for the three $CaCO_3$ levels used in this study. Biddulph (5) showed in nutrient solutions that large amounts of precipitated iron on the root surfaces inhibited the uptake of additional iron. The composition of the precipitate on the root surface was shown to be predominantly ferric phosphate at pH's below 6.0 while at pH 7.0 calcium was an important constituent along with the iron and phosphorous. He further showed that phosphorous precipitation could occur in the leaves. The precipitated phosphorous could explain the similar foliage growth reduction noted in this study for the three $CaCO_3$ levels (Table 8). Additionally Wadleigh and Bower (24) measured potassium and magnesium in the foliage of kidney beans grown in increasing $CaCl_2$ concentration solutions and found a decreased quantity of these ions in the foliage with increasing $CaCl_2$ added to water culture.

Table 8. Barley growth at four $CaCO_3$ amended nutrient solution levels with and without terbutryn.

Terbutryn ppm	$CaCO_3$ Levels 0.0	2.5	5.0	10.0
	mg dry wt/3 plants[a]			
0				
Foliage	308	257	268	277
Roots	149	173	186	262
Total	457	430	454	539
0.03				
Foliage	189	172	198	131
Roots	70	72	91	58
Total	259	244	289	189
0.06				
Foliage	98	115	112	93
Roots	31	40	37	35
Total	129	155	149	128
0.09				
Foliage	101	85	92	69
Roots	34	30	31	25
Total	135	115	123	94
0.12				
Foliage	70	70	77	82
Roots	25	31	28	32
Total	95	101	105	114

[a]Average of duplicate samples.

Several reports in the literature have indicated the importance of calcium for proper root growth (4, 15). This would not fully explain the greater root growth obtained for the 10 meq/l as compared to the 2.5 and 5.0 levels of $CaCO_3$. Comparable amounts of Ca^{++} should be dissolved in the nutrient solutions at all rates of $CaCO_3$ used in this study as the solubility of $CaCO_3$ in a pure solution is about 1 meq/l. However, more $CaCO_3$ precipitate would be present in the 10 meq/l rate than the lower rates. In this study increased $CaCO_3$ precipitate was more evident on the root surface for the 10 meq/l rate than for the lower $CaCO_3$ rates. It is suggested that the close contact of the $CaCO_3$ with the roots allowed exchange of calcium and/or other ions more rapidly than at the lower $CaCO_3$ rates, thus increasing root growth. This $CaCO_3$-plant reaction requires more study to elucidate the above postulation.

With the addition of 0.03 ppm terbutryn there was no difference in barley growth among the 0, 2.5, and 5.0 meq/l $CaCO_3$ rates (Table 8). However, total plant growth at the 10 meq/l level was approximately 15% less than for the other $CaCO_3$ levels. The 0.03 ppm terbutryn solution reduced barley growth by 76% in the 10 meq/l $CaCO_3$ series but by only 43% in the 0 meq/l $CaCO_3$ series. Terbutryn rates greater than .03 ppm were equally toxic to barley at all levels of $CaCO_3$.

The increased terbutryn toxicity (.03 ppm) to barley grown in the nutrient solution amended with 10 meq/l $CaCO_3$ did not appear to be related to changes in nutrient solution pH. The control, which contained no additional $CaCO_3$, remained essentially unchanged in pH for the duration of the experiment (Table 9). Although the initial pH of all solutions was 6.9, the nutrient solutions which contained the added $CaCO_3$ increased to pH 7.5 within two days. Subsequent increase in solution pH was minimal for the duration of the growing period. Further, the pH of the 2.5 and 5.0 meq/l treatments did not differ significantly from the 10.0 meq/l $CaCO_3$ treatments. Since no yield difference occurred between the control and the 2.5 or 5.0 meq/l $CaCO_3$, one would thus discount pH as a significant factor in the growth reduction at 10 meq/l $CaCO_3$. Also, investigators (4, 23) have shown pH values less than 8 did not reduce plant growth.

Table 9. Nutrient solution pH values recorded during the experiment.

$CaCO_3$ meq/l	Terbutryn concentration	Day 0	Day 2	Day 6	Day 10
0.0	0	6.80	6.55	6.70	6.85
	a	6.85	6.90	6.80	6.80
2.5	0	6.80	7.20	7.60	7.55
	a	6.90	7.35	7.60	7.65
5.0	0	6.85	7.30	7.65	7.70
	a	6.90	7.45	7.70	7.70
10.0	0	6.90	7.40	7.60	7.60
	a	6.90	7.60	7.75	7.75

a Average of .03, .06, .09, and .12 ppm terbutryn concentrations.

The increased root growth (Table 8) and greater transpiration rate of barley at the 10 meq/l $CaCO_3$ level (Table 10) may partially explain the increased terbutryn toxicity to the barley. The increased root growth would give added surface area for increased uptake of the chemical and nutrient solution. The increased uptake of terbutryn could explain the greater reduced transpiration rate for the 10 meq/l $CaCO_3$ concentration with the addition of terbutryn as compared to the other levels of $CaCO_3$ (Table 10). Smith and Buchholtz (21) found that a 24 hr treatment with 20 ppm atrazine reduced corn and soybean transpiration by about 45 and 70%, respectively. In addition, certain ions have been shown to influence uptake of triazines. Nitrogen in the form of urea was found to increase the concentration of four s-triazines in collected stem exudate as compared to water control plants (19) and Figuerola (8) found high nitrogen content in Hoagland's solution added to sand growth media increased terbutryn toxicity to wheat. The experiments on the addition of $CaCO_3$ to nutrient solutions have indicated the possibility of increased phytotoxicity of terbutryn. The enhanced transpiration rate of plants which occurred with the addition of the high level of $CaCO_3$ in relation to the increased root growth appeared to be responsible for the increased terbutryn phytotoxicity.

Table 10. Amount of transpiration for barley at the four levels of $CaCO_3$ with and without terbutryn.

$CaCO_3$ meq/l	Terbutryn concentration	Day 2	Day 6	Day 10	Total
			ml[b]		
0.0	0	58	228	235	521
	a	68	185	191	444
2.5	0	60	280	185	530
	a	55	194	173	422
5.0	0	63	158	240	461
	a	46	214	207	487
10.0	0	120	300	260	680
	a	39	160	201	400

a Average of .03, .06, .09, and .12 ppm terbutryn concentrations.
b Values corrected for evaporation loss.

TOXICITY OF THREE s-TRIAZINES TO ESTABLISHED ALFALFA ON HIGH pH OREGON SOILS

Introduction

Toxicity of s-triazines to crops grown on high pH soils has been reported in several states.[1] Under controlled conditions, Wallace *et al.*, (26) found that corn (*Zea mays* L.) showed increased 2, 4-bis (isopropylamino)-6-(methylthio)-*s*-triazine (prometryne) toxicity when grown on Yolo loam soil limed to pH 7.9 than on natural Yolo loam soil, pH 6.6. As a partial explanation for the increased phytotoxicity, Weber (28) has shown decreased adsorption of 13 s-triazines with increasing pH on montmorillonite clay. With the decreased adsorption more chemical would be found in the solution phase, thus leading to increased phytotoxicity. Additionally, Weber (28) noticed that adsorption decreased more for the methylthio- and methoxy- than for the chloro-s-triazines when pH increased from 4 to 8. Since most of the s-triazine toxicity at high pH values problems have been observed in routine farming practices, a program was developed to show the problems under field research conditions.

Crop production areas of central Oregon were screened as potential sites for the field trials. Four site locations were selected near Prineville, Oregon. The soil pH levels in the area are near neutral to pH 10 and toxicity to alfalfa (*Medicago sativa* L.) had been reported after applications of 2-chloro-4, 6-bis(ethylamino)-s-triazine (simazine).[5]

The purpose of this study was to observe and measure weed control effectiveness and alfalfa reaction to applications of simazine, 2-(tert-butylamino)-4-(ethylamino)-6-(methylthio)-s-triazine (terbutryn), and 2-(sec-butylamino)-4-(ethylamino)-6-methoxy-s-triazine (GS-14254) on high pH soils. The field trials were established to augment the s-triazine adsorption and phytotoxicity studies.

Material and Methods

Four trial sites were selected from commercially established alfalfa fields in the fall of 1969. Prior to establishment of the herbicide trials, each site was characterized as to location and crop conditions (Table 11). Soil samples were collected from 0 to 15.2 cm and analyzed for physical and chemical characteristics by the Soil Testing Laboratory, Oregon State University (Table 12).[6]

Experimental plots were 3.05 m by 6.1 m and arranged in a randomized complete block design with four replications. Simazine,

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[5] Personal communication from Mr. E. Wood, former Crook County Extension Agent.

[6] Additional information concerning conditions at time of herbicide application, other agricultural chemicals applied to the trial area, type and amount of irrigation, rainfall, and soil profile descriptions are presented in the 1970 Weed Control Research Report, Farm Crops Department, Oregon State University.

terbutryn, and GS-14254 were applied to dormant alfalfa in November, 1969. Rates of 0.45, 0.90, 1.80, and 3.60 kg ai/ha were applied in 450 L of water per ha with a bicycle-plot sprayer.

The effects of the herbicides on weed control and toxicity to alfalfa were evaluated visually and by forage yields. The density and distribution of the principal weeds in the trial sites were determined in April, 1970 (Table 13). Independent visual evaluations of alfalfa injury and weed control were made in April and June by two individuals and averaged. The first cutting of the alfalfa was harvested in late June, 1970, when maturity of the crop was approximately two percent alfalfa bloom at all sites. An area of 0.76 m by 4.57 m was harvested from each plot with a mechanical plot harvester and fresh weights were recorded. A subsample, approximately 1 kg, was collected from the harvested plot to ascertain the ratio of weeds to alfalfa and for moisture determinations.

Results and Discussion

Site descriptions. All trial sites were located within 8.0 kilometers of Prineville, Oregon. The alfalfa was well established at each location (Table 11).

The sites ranged in soil pH from 7.1 to 8.5 with calcium and magnesium the predominant cations (Table 12). Organic matter content ranged from 0.8 to 2.9% while clay content was 11.2 to 21.6%.

Table 11. Location and crop characteristics of weed control sites.

Location	Soil type	Age of stand yr	Alfalfa Variety	Stand condition
Sigman Ranch	Metolius sl	6	NK 919	Good
Boston Ranch				
Cain 3	Powder sil	1	Vernal	Very good
Barrett	Boyce l	10	Unknown	Good
Cain 1	Crooked sil	1	Vernal	Fair

Essentially the only weed species present at the Metolius sandy loam soil site was downy brome which was uniformly distributed throughout the trial area (Table 13). The Crooked silt loam soil site contained very few weeds, probably due to the soil pH of 8.5. Mallow, the principal weed present, is classified taxonomically in the Malvaceae family and is fairly tolerant to high soil pH and salt conditions (32). Kentucky bluegrass was the predominant weed species at the Boyce loam site but it was not uniformly distributed. A fairly dense but very irregular infestation of tansymustard was present at the Powder soil site. Additionally, this site contained light stands of blue mustard (*Chorispora tenella* DC.), field pennycress (*Thlaspi arvense* L.), and common dandelion (*Taraxacum officinale* Weber).

Table 12. Chemical and physical characterization of soils for s-triazine trial sites.

											Particle size distribution		
			P	B	CEC	K	Ca	Mg	Na	OM	Sand	Silt	Clay
Location	Soil type	pH	ppm		meq/100 g					%			
Sigman Ranch	Metolius sl	7.1	4.3	0.8	14.5	2.4	11.1	4.8	0.5	1.4	56.4	29.5	14.1
Boston Ranch													
Cain 3	Powder sil	7.7	11.2	1.1	31.9	2.0	25.2	9.0	1.7	2.9	24.6	53.8	21.5
Barrett	Boyce 1	8.0	17.3	1.3	20.0	2.0	16.7	7.4	0.7	2.2	43.4	45.4	11.2
Cain 1	Crooked sil	8.5	20.7	2.4	34.1	5.0	38.4	20.6	1.4	0.8	24.6	53.8	21.6

Table 13. Density and distribution of principal weeds for alfalfa trials.

Soil type	pH	Principal weeds	Density plants/0.092 m^2	Distribution
Metolius sl	7.1	Downy brome (*Bromus tectorum* L.)	14.7	Very uniform
Powder sil	7.7	Tansymustard (*Descurainia pinnata* (Walt.) Britt.)	1.5	Very patchy
Boyce l	8.0	Kentucky bluegrass (*Poa pratensis* L.)	7.5	Irregular
Crooked sil	8.5	Mallow (*Malva* sp.)	Very light stand	Uniform

Weed control. Visual weed control evaluations and weed forage yield results were comparable for sites with high weed densities and uniform distribution. Poorer correlations between visual weed control and weed yields occurred with decreasing weed densities and irregular weed stands (Table 14). The lack of correlation between visual and weed forage yields was particularly apparent at the lower herbicide rates or where the herbicide resulted in poor weed control, i.e., terbutryn. Because of the irregular weed density of the control plots (range from 0.78 to 2.55 metric ton/ha) at the Boyce loam soil site, the visual evaluations are probably closer to the actual Kentucky bluegrass weed control than the weed yield for the terbutryn-treated plots. The difference between visual weed evaluations and weed yield at the Powder site was probably due to the presence of common dandelion which was not controlled and was harvested, but was not included in the visual evaluations.

Good to excellent control of downy brome, tansymustard, and Kentucky bluegrass resulted from the 0.90 to 3.60 kg ai/ha rates of simazine (Table 14). The experimental herbicide, GS-14254, gave good control of tansymustard at all application rates, downy brome at 0.90, and Kentucky bluegrass at 1.80 kg ai/ha. Poor weed control, less than 50%, resulted from the use of terbutryn at all rates and for all weed species present.

Alfalfa injury from three s-triazines. Visual toxicity on the alfalfa from the chemicals applied was most apparent at the first evaluation in April (Table 15). Minor simazine injury symptoms were evident at the 0.90 kg ai/ha rate while at the 3.60 kg rate, alfalfa injury was as high as 28% for Boyce loam soil. By the second evaluation in June, only simazine applied at 3.60 kg rate showed any visual signs of alfalfa injury.

Alfalfa injury resulting from GS-14254 applications occurred at the 3.60 kg rate for the first evaluation on all soils except the Crooked silt loam. Essentially no alfalfa toxicity was apparent by the second evaluation for GS-14254 applications on any of the soils.

There was no visual phytotoxicity or effect on alfalfa growth from terbutryn at any herbicide rate, location or time of evaluation.

Toxicity to alfalfa from the simazine application was in the order Boyce loam (pH 8.0) > Metolius sandy loam (pH 7.1) > Powder silt

Table 14. Visual and weed forage yield evaluations.

Treatment	kg ai/ha	Metolius sl: Visual Evaluation[a] 1	Metolius sl: Visual Evaluation[a] 2	Metolius sl: Weed control[b]	Powder sil: Visual Evaluation 1	Powder sil: Visual Evaluation 2	Powder sil: Weed control	Boyce l: Visual Evaluation 1	Boyce l: Visual Evaluation 2	Boyce l: Weed control	Crooked sil: Visual Evaluation 1	Crooked sil: Visual Evaluation 2
Simazine	0.45	22	22	38	25	5	-6	35	38	65	0	0
	0.90	80	86	66	94	92	80	85	79	95	0	0
	1.80	95	100	100	98	99	78	90	91	100	0	0
	3.60	100	100	100	100	100	100	100	98	100	0	0
Terbutryn	0.45	8	5	15	2	0	-8	10	0	37	0	0
	0.90	16	5	8	18	18	88	0	2	34	0	0
	1.80	18	21	22	18	15	48	10	10	40	0	0
	3.60	40	47	52	28	22	50	10	17	38	0	0
GS-14254	0.45	25	25	12	81	85	99	30	38	62	0	0
	0.90	80	84	86	99	95	94	40	58	57	0	0
	1.80	95	96	100	99	100	100	70	80	92	0	0
	3.60	100	100	100	100	100	100	100	96	100	0	0

[a] Visual evaluation 0% = no control, 100% = complete control.

[b] Based on weed forage yields with yields of the check being 0% weed control.

loam (pH 7.7) > Crooked silt loam (pH 8.5) (Table 15). The Powder silt loam soil contained higher amounts of organic matter (2.9%) and clay (21.5%) than the Boyce and Metolius soils, probably accounting for the reduced alfalfa toxicity (Table 12). Increased adsorption of atrazine (a chloro-s-triazine) was shown for the Powder soil as compared to the Metolius and Boyce soils (Chap. I, Table 2).

Table 15. Visual evaluations of alfalfa injury.

		Metolius sl		Powder sil		Boyce 1		Crooked sil	
		Evaluation[a]		Evaluation		Evaluation		Evaluation	
Treatment	kg ai/ha	1	2	1	2	1	2	1	2
					(percent)[b]				
Simazine	0.45	0	0	0	0	0	0	0	0
	0.90	1	0	1	0	5	0	0	0
	1.80	3	0	2	0	10	0	0	0
	3.60	25	7	12	6	28	10	0	0
Terbutryn	0.45	0	0	0	0	0	0	0	0
	0.90	0	0	0	0	0	0	0	0
	1.80	0	0	0	0	0	0	0	0
	3.60	0	0	0	0	0	0	0	0
GS-14254	0.45	0	0	0	0	0	0	0	0
	0.90	0	0	0	0	0	0	0	0
	1.80	<1	0	<1	0	0	0	0	0
	3.60	4	1	5	0	12	0	0	0
Check	0.0	0	0	0	0	0	0	0	0

[a]Average value for four replications.

[b]0% = no effect, 100% = complete kill.

The toxicity of GS-14254 on the alfalfa was Boyce loam > Powder silt loam = Metolius sandy loam > Crooked silt loam. The toxicity observed for GS-14254 on the alfalfa grown in these four soils agreed with the adsorption values of the s-triazines on the same soils (Chap. I, Table 2). In other words, the higher the adsorption, the lower the toxicity. If only pH is considered the expected toxicity to alfalfa from GS-14254 would be in the order Metolius sandy loam < Powder silt loam < Boyce loam. The GS-14254 applied to the Metolius and Powder soils, however, displayed equal alfalfa toxicity. The effect of organic matter in the Powder silt loam reduced alfalfa toxicity from the GS-14254 and simazine. The reduced toxicity was more apparent for the simazine than for the GS-14254 even though the absolute toxicity of the GS-14254 was lower. Boyce loam (pH 8.0) contained a higher organic matter content than did the Metolius soil (pH 7.1) but more visual GS-14254 injury to alfalfa was noted for Boyce than for Metolius. At the higher pH, irregardless of the organic matter, more phytotoxicity was observed.

No phytotoxicity was observed from any of the herbicides, at any rate, applied on the Crooked silt loam. Sorption studies showed nearly 100% adsorption of terbutryn and GS-14254 and 90% of atrazine on Crooked silt loam (Chap. I, Table 2). Adsorption of s-triazines to Crooked silt loam has been discussed earlier.

Alfalfa yields. The yields of alfalfa grown on the Metolius sandy loam soil were significantly increased by both simazine and GS-14254 at rates of 0.90 to 3.60 kg (Table 16). The lowest rate, 0.45 kg, achieved only 20% downy brome control for both compounds and

Table 16. Herbicide effect on alfalfa and weed yields.

		Metolius sl pH 7.1		Powder sil pH 7.7		Boyce l pH 8.0		Crooked sil pH 8.5	
Treatment	kg ai/ha	Weeds	Alfalfa	Weeds	Alfalfa	Weeds	Alfalfa	Weeds	Alfalfa
		metric ton/ha[a]							
Simazine	0.45	1.63	3.36	1.19	5.26	0.52	5.20	0	3.78
	0.90	0.90	4.10	0.22	6.00	0.07	5.91	0	4.46
	1.80	0.00	5.02	0.25	6.18	0.00	5.76	0	4.21
	3.60	0.00	4.25	0.00	5.51	0.00	4.79	0	3.70
Terbutryn	0.45	2.24	3.52	1.21	5.00	0.92	4.90	0	4.05
	0.90	2.42	3.05	0.13	5.62	0.96	5.13	0	3.96
	1.80	2.06	3.47	0.58	5.35	0.87	4.61	0	4.46
	3.60	1.28	3.43	0.56	5.46	0.90	5.00	0	4.39
GS-14254	0.45	2.33	3.16	0.02	5.89	0.56	5.22	0	4.17
	0.90	0.36	4.23	0.07	5.91	0.63	5.24	0	5.37
	1.80	0.00	4.64	0.00	5.46	0.11	5.82	0	3.83
	3.60	0.00	4.70	0.00	5.46	0.00	5.31	0	3.72
Check	0	2.64	3.02	1.12	5.31	1.46	4.64	0	3.99
LSD metric ton/ha 5% level			.60		N.S.[b]		.83		N.S.
CV %			11.4		11.9		11.2		13.8

[a] Average value of four replications, for first cutting only.

[b] Nonsignificant.

resultant alfalfa yields were only slightly higher than the check. Alfalfa yields were increased by approximately 60% over the check for the 1.80 kg rate for both simazine and GS-14254. Simazine, at the 3.60 kg rate, reduced alfalfa yields by 25% when compared to alfalfa yields on the plots treated with the 1.80 kg rate. This yield reduction was due to phytotoxicity of simazine. However, alfalfa yield for the 3.60 kg rate of simazine was still significantly higher than the check. Alfalfa yield was not reduced at the 3.60 kg rate of GS-14254 at the Metolius site. The application of terbutryn to the alfalfa grown on the Metolius sandy loam soil site did not increase alfalfa yields.

Alfalfa yields for the Powder soil site were not significantly increased for any herbicide (Table 16). This failure to increase alfalfa yield was probably due to the poor weed stand, irregular weed distribution, and the excellent stand of alfalfa in the trial area.

At the Boyce soil site the alfalfa yields were significantly higher than the check at the 0.90 and 1.80 kg rates of simazine (Table 16). The 3.60 kg rate of simazine reduced alfalfa yield by 20% when compared to the 1.80 kg rate. A significant yield increase was obtained only for the 1.80 kg rate of GS-14254. Because of poor Kentucky bluegrass control alfalfa yield was not significantly increased at the 0.90 kg rate of GS-14254. As with the two prior soil locations terbutryn did not significantly increase alfalfa yields.

No alfalfa yield increase was obtained with the application of any of the three s-triazines at the Crooked silt loam soil site.

In retrospect, simazine and GS-14254 applied at the rate of 1.80 kg ai/ha provided good control of the weed species present in three of the four trial locations. Terbutryn did not provide adequate weed control nor did it increase alfalfa yields for any site.

Toxicity from GS-14254 to alfalfa appeared to increase with increasing soil pH; however, alfalfa yields were not significantly reduced. Simazine injury to alfalfa was evident at three of the four high pH soil sites with the extent of injury more closely correlated to the organic matter content than to soil pH.

SUMMARY

The amount of chemical adsorbed on the natural and lime-amended soils was found to be in the order terbutryn > GS-14254 > atrazine. With increased soil pH, terbutryn and GS-14254 adsorption decreased more rapidly than did atrazine. Since the GS-14254 (pKa 4.32) showed even more of an adsorption reduction with increased soil pH than the terbutryn (pKa 4.36) and since the pKa values for the two compounds are quite similar, it is suggested that the greater difference in solubility and less affinity of GS-14254 for organic and clay surfaces accounts for the difference in reduced adsorption. Additional research is required to determine the influence of organic matter and clay content greater than 3% on the adsorption of GS-14254 with soils of pH between 7 and 8.

The toxicity of GS-14254 to barley increased with the addition of lime to Chehalis sandy loam soil. The toxicity was in proportion to the reduced adsorption between the unlimed and limed soil. Further, toxicity to alfalfa observed in the field occurred in the reversed order of adsorption, that is, simazine > GS-14254 > terbutryn. In other words, the less adsorption, the greater the toxicity.

Terbutryn toxicity to barley grown in the absence of soil was not enhanced when the barley was grown at different pH stresses. Only calcium carbonate at high levels appeared to influence phytotoxicity for the sodium and calcium salts tested. These data would indicate that high pH or salts present in calcareous or saline soils probably will not significantly influence plant response to the addition of s-triazines in the soil system. However, higher pH and salt levels will have a direct effect on the s-triazine chemical, especially with respect to decreased adsorption and solubility. The methoxy-s-triazines appear to be the most affected by pH and salt concentration. Selective use of these compounds may have to be restricted on some soils of pH 7 to 8. On the other hand, some agricultural soils which contain high salt levels, did have a high affinity for the s-triazines.

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APPENDIX

Appendix Table 1. Chemical and physical properties of selected soils.

Soil type	P	K	Sand	Silt
	ppm	meq/100 g soil	%	
Chehalis sl	18.0	0.9	50	32
Woodburn sil	69.0	0.8	18	63
Deschutes sl	22.0	0.4	65	23
Metolius sl	4.3	2.4	56	30
Powder sil	11.2	2.0	25	54
Boyce l	17.3	2.0	43	46
Gila sic	14.2	1.5	3	44
Quincy sl	37.0	1.2	61	32
Crooked sil	20.7	5.0	25	54
Boyce sil	30.7	3.8	28	60

Appendix Table 2. Calcium carbonate added to unlimed soils.

Soil type	Initial pH	pH			
		7.0	7.35	7.5	7.75
		$CaCO_3$ meq/100 g soil			
Chehalis sl	5.2	3.0		7.0	60.0
Woodburn sil	5.2	5.0	12.0	70.0	
Deschutes sl	5.9	1.5		3.0	36.0

Appendix Table 3. Yield of barley grown in the growth chamber on lime-amended Chehalis sandy loam with GS-14254 application.

Chehalis sl		Barley yield mg dry wt/5 plants			
		GS-14254 kg ai/ha			
pH	Rep.	0	0.34	0.67	1.34
5.20	I	165.8	160.1	150.7	157.3
	II	188.2	159.2	143.9	124.8
	III	153.9	147.0	151.8	148.3
	IV	155.0	171.8	146.7	138.9
Average		165.7	155.5	147.4	143.2
7.00	I	183.7	73.6	73.6	72.6
	II	206.7	92.9	75.7	66.4
	III	166.3	79.0	58.1	69.7
	IV	199.2	81.4	83.7	65.0
Average		189.0	81.7	76.4	68.4
7.50	I	183.2	71.1	83.4	80.6
	II	196.3	73.3	67.8	67.7
	III	192.0	76.7	55.6	64.6
	IV	188.9	68.4	64.4	71.8
Average		190.1	72.4	67.8	71.2
7.75	I	235.6	67.8	82.9	70.3
	II	184.9	66.5	61.6	67.6
	III	197.5	77.3	83.5	72.9
	IV	221.4	72.3	79.4	57.8
Average		209.8	71.0	76.8	67.2

Appendix Table 4. Barley yield for Crooked silt loam with atrazine and terbutryn applications.

Treatment	kg ai/ha	Trial I Rep I	Trial I Rep II	Trial I Rep III	Trial I Ave.	Trial II Rep I	Trial II Rep II	Trial II Rep III	Trial II Ave.
		mg dry wt/5 plants							
Terbutryn	1.12	88.2	89.5	76.9	84.9	96.0	118.3	90.5	101.6
	2.24	75.3	85.8	89.9	83.7	115.2	119.0	100.3	111.5
	3.36	81.9	81.3	94.5	85.9	99.9	100.6	88.0	96.2
	4.48	76.0	92.7	71.2	80.0	88.4	98.0	110.3	98.9
	5.60	71.6	89.6	81.0	80.9	90.4	68.2	94.6	84.4
	6.72	65.9	71.1	80.9	72.6	92.2	94.8	89.7	92.2
	7.84	83.1	68.5	78.1	76.6	90.4	102.6	100.7	97.9
Atrazine	1.12	73.8	83.2	67.5	74.8	121.1	177.7	112.2	117.6
	2.24	82.5	78.1	62.7	74.4	104.3	109.2	94.7	102.4
	3.36	62.9	70.2	69.3	67.5	119.0	87.5	105.1	103.9
	4.48	69.8	71.4	61.3	67.5	113.6	73.5	98.0	94.7
	5.60	57.3	64.1	83.8	68.5	100.1	88.0	91.6	93.2
	6.72	61.8	71.9	63.5	65.7	90.0	77.3	91.3	86.3
	7.84	62.4	55.2	61.0	59.5	77.8	88.6	89.4	85.3
Control	0	96.4	118.0	104.4	106.3	104.2	126.8	132.4	121.1

Appendix Table 5. Barley growth and solution pH for sodium and calcium salts added to 0.5 strength modified Hoagland's solution.

Salt added	Terbutryn ppm	pH 5 days	pH 10 days	Yield mg dry wt/3 plants	Percent of check
Regular Hoagland's	0	6.9	6.9	727.5	117.1
Regular Hoagland's	0.05	7.1	6.9	408.5	65.8
Modified Hoagland's[a]	0	6.5	5.7	621.0	100
Modified Hoagland's	0.05	6.5	5.7	484.9	78.1
NaCl	0	6.6	6.0	946.9	152.5
NaCl	0.05	6.7	6.4	528.6	85.1
$CaCl_2$	0	6.8	6.0	640.9	103.2
$CaCl_2$	0.05	6.6+	6.4	434.6	70.0
Na_2CO_3	0	7.2+	7.1	301.9	48.6
Na_2CO_3	0.05	7.1-	7.0	342.9	55.2
$CaCO_3$	0	6.8	6.7	811.6	130.7
$CaCO_3$	0.05	6.9	6.8	231.7	37.3

[a]$CaCl_2$ substituted for $Ca(NO_3)_2$ and NH_4NO_3 added for source of N.

Appendix Table 6. ED_{50} values for terbutryn and atrazine on three Prineville soils.

		Barley yield mg dry wt/5 plants							
		terbutryn kg ai/ha							
Soil type	Rep	0.0	0.34	0.67	1.08	1.34	1.68	2.02	ED_{50} value
Metolius sl	1	127.1	90.1	80.3	68.8	67.9	70.3	67.8	2.80
	2	114.1	82.6	77.1	91.8	72.0	67.0	61.9	
Powder sil	1	172.4	123.4	115.2	85.4	92.4	72.4	74.8	2.24
	2	144.1	113.8	85.8	101.2	97.5	81.6	86.4	
Boyce l	1	204.7	99.0	92.9	93.3	75.2	80.3	69.3	0.34
	2	196.4	95.5	89.0	83.8	84.3	91.4	79.0	
		atrazine kg ai/ha							
Metolius sl	1	127.1	74.0	72.9	67.5	70.4	70.2	62.4	2.30
	2	114.1	67.3	64.2	73.0	69.1	60.2	61.0	
Powder sil	1	172.4	80.1	87.9	65.9	73.5	72.0	47.4	0.56
	2	144.1	89.5	75.6	74.4	74.9	73.4	44.3	
Boyce l	1	204.7	98.5	78.2	79.7	82.9	77.9	74.3	0.28
	2	196.4	87.2	76.7	78.1	75.9	73.7	72.8	

Appendix Table 7. Adsorption of terbutryn and atrazine on $CaCO_3$.

Chemical	Adsorption[a] $\mu g/0.5\ g\ CaCO_3$
Terbutryn	21.5
Atrazine	1.0

[a]Ten ml of 20 ppm terbutryn and atrazine added to 0.5 g of $CaCO_3$.

Appendix Table 8. Terbutryn adsorbed on polypropylene test tubes and caps or Metolius sandy loam.

	Terbutryn adsorbed[a]						
	hr						
Treatment	0.5	1.0	2.0	4.0	8.0	16.0	32.0
				μg			
Metolius sl[b]	140.0	136.4	139.2	140.0	142.8	142.6	145.8
Without soil	18.6	-	-	-	86.0	-	108.2

[a]Ten mls of 20 ppm terbutryn added.

[b]5 g soil

Appendix Table 9. Terbutryn adsorption on various cap covers or Metolius sandy loam with glass test tubes.[a]

Treatment	Terbutryn ^{14}C [b]			
	Supernatant µg	Cap[c] µg	Total µg	Remainder µg
No cap[d]	185.8	-	185.8	14.2[e]
No cap + 5 g soil	60.6	-	60.6	139.4
Polypropylene cap	97.8	92.2	190.0	10.0
Polypropylene cap + 5 g soil	62.2	1.2	63.4	136.6
Saran Wrap	104.0	81.6	185.6	14.4
Saran Wrap + 5 g soil	60.0	1.2	61.2	138.8
Parafilm	84.4	110.2	194.6	5.4
Parafilm + 5 g soil	61.0	0.4	61.4	138.6
Glad Bag	110.4	88.2	198.6	1.4
Glad Bag + 5 g soil	62.2	2.0	64.2	135.8
Aluminum foil	181.2	0.0	181.2	18.8
Aluminum foil + 5 g soil	43.0	0.0	43.0	157.0

[a] Equilibration time 2 hr at 25 C.

[b] Ten ml of 20 ppm terbutryn added.

[c] Desorbed with absolute methanol.

[d] Shaken on wrist-action shaker at room temperature without cover on tube.

[e] Preliminary experiment indicated approximately 5% of ^{14}C terbutryn was lost at 25 C in open system after 2 hr.