AN ABSTRACT OF THE THESIS OF

___JOHN DONALD GAYNOR___ for the ___Doctor of Philosophy___
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Title: ATRAZINE, TERBUTRYN AND GS-14254 ADSORPTION,

DESORPTION AND SOLUBILITY IN SALT SOLUTIONS AND

MOVEMENT IN SOIL MATERIALS

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Dr. V. V. Volk

The solubility of 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine (atrazine), 2-(tert-butylamino)-4-(ethylamino)-6-(methyl-thio)-s-triazine (terbutryn) and 2-(sec-butylamino)-4-ethyl-amino)-6-methoxy-s-triazine (GS-14254) was determined in 0.005 to 2.5 ionic strength (μ) Na, K and Ca chloride salt solutions. The adsorption and desorption of the s-triazines by Cloquato soil was investigated in 0.05 to 2.5 μ Na and Ca chloride salt concentrations.

The effect of pH on the adsorption of the s-triazines by soils with a range in carbon content and the contribution to s-triazine adsorption by soil organic matter, aluminum and iron oxides, and amorphous components was investigated with oxidation and chemical dissolution treatments.

Surface transport and leaching of atrazine and terbutryn from

unlimed and limed Peavine soil was studied under simulated rainfall conditions.

The solubility of the three s-triazines in aqueous solution decreased in the order GS-14254 > atrazine $\geq$ terbutryn. The strongly hydrated Ca cation reduced solubility less than the weakly hydrated Na or K cations. Salt concentrations < 0.1 μ had little effect on solubility but 2.5 μ salt concentration reduced solubility 85% for Na and K and 58% for Ca chloride. It was postulated that strongly hydrated cations orient water molecules about themselves such that protons interact with the basic s-triazines thereby reducing the salt effect. Strongly hydrated cations also destabilize the bonds in the water molecule permitting proton association with anions which reduce the free ions in solution and cause a smaller increase in the activity coefficient of the s-triazines.

S-triazine adsorption by the salt amended soils and the chemically extracted soils increased in the order atrazine $<$ GS-14254 $<$ terbutryn. Salt concentrations < 1.0 μ decreased s-triazine adsorption by Cloquato soil with the Na and Ca cations reacting similarly. In the presence of salts GS-14254 and terbutryn adsorption decreased more than atrazine adsorption. It was suggested that atrazine with its lower pKa value acted as a neutral molecule and would not be affected by salt levels while GS-14254 and terbutryn with higher pKa values underwent cation competition for adsorption sites. Salt

concentrations $> 1.0 \mu$ increased s-triazine adsorption through the phenomenon of salting out.

GS-14254 and terbutryn were adsorbed by hydrogen bonding through coordination with hydrated cations. Atrazine with a more negative chlorine atom and lower pKa value did not appear to be coordinated with hydrated cations. More s-triazine was desorbed from the systems initially equilibrated in $> 1.0 \mu$ salt solutions to indicate herbicide salting out in the double layer.

Atrazine adsorption could not be reliably predicted by pH changes in soil systems. Adsorption appeared to occur on non-specific sites in the hydrophobic carbon fraction. GS-14254 and ter-butryn adsorption always decreased as pH increased; however, the pH effect was reduced with soils high in carbon. GS-14254 adsorption was reduced more by a pH increase than terbutryn, possibly because of higher solubility and a lower affinity for clay surfaces.

Removal of organic matter from soils by hydrogen peroxide oxidation had little effect on GS-14254 and terbutryn adsorption by Kinney and Jory soils indicating an equal affinity for organic and clay surfaces. Atrazine adsorption on Jory soil decreased after hydrogen peroxide oxidation.

Aged hydrous oxide surfaces in the Parkdale C soil did not contribute greatly to s-triazine adsorption. S-triazine adsorption increased with activation of gel hydrous oxide surfaces in the

Parkdale C soil by ammonium oxalate and sodium pyrophosphate extraction. The high s-triazine adsorption by the alkaline Boyce and Crooked soils was attributed to gel hydrous oxides removed by ammonium oxalate. Only a slight reduction in terbutryn and GS-14254 adsorption occurred after ammonium oxalate extraction suggesting these compounds have a high affinity for clay surfaces exposed after the removal of the amorphous gel constituents.

Unlimed Peavine soil adsorbed 60% and 98% of the added atrazine and terbutryn; however, adsorption of both chemicals was reduced 10% after the addition of lime. After application of 12 cm to 15 cm of simulated rainfall the upper horizon of the Peavine soil contained 85% and 87% of the chemically extracted atrazine and terbutryn in the unlimed soil and 67% and 83% in the limed soil.

Atrazine degradation occurred to a greater extent in unlimed than limed Peavine soil since chemical extraction of the soil recovered 26% and 79%, respectively, of the added atrazine. Terbutryn degradation was not catalyzed by the acid soil environment as 82% and 103% was recovered from the respective plots.

Lime greatly reduced the amount of surface water runoff and associated s-triazine losses. Atrazine and terbutryn losses in the runoff water and transported sediment from the limed plots were 0.02% and 0.01% respectively. Surface water and transported sediment removed 1.7% and 3.7% of the total amount of atrazine

and terbutryn recovered from the unlimed plots. Losses were higher when rainfall was applied soon after s-triazine application. S-triazine concentrations were higher on transported sediment than in runoff water due to adsorption; however, greater amounts of the chemicals were lost in the runoff water.

In conclusion, salt concentrations in the soil solution would not be high enough to reduce s-triazine solubility. Low salt concentrations would reduce GS-14254 and terbutryn adsorption, thus increasing phytotoxicity.

GS-14254 and terbutryn adsorption always decreased when the soil pH increased upon addition of base whereas atrazine adsorption increased in some soils. Soils high in clay and carbon content greatly reduced the effect of pH on s-triazine adsorption. Atrazine adsorption occurred in the soil carbon fraction whereas GS-14254 and terbutryn showed equal affinity for organic and clay mineral surfaces.

Atrazine and terbutryn losses in transported sediment and runoff water from herbicide treated areas are not great enough to create a threat to nontarget organisms or surrounding crops. Because of high adsorption, atrazine and terbutryn leaching in unlimed and limed soil was restricted to the top 23 cm of soil after addition of 15 cm of rainfall.

Atrazine, Terbutryn and GS-14254 Adsorption,
Desorption and Solubility in Salt Solutions
and Movement in Soil Materials

by

John Donald Gaynor

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Head of Department of Soil Science

Dean of Graduate School

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INTRODUCTION

The family of s-triazine herbicides constitute one of the most useful and widely employed agricultural chemicals since the discovery of herbicides. The s-triazine herbicides, since their introduction in 1952, have been extensively studied with respect to soil adsorption, crop selectivity, plant absorption, degradation, volatilization and mammalian toxicity.

Root uptake is the primary mechanism whereby the s-triazine herbicides enter the plant. The s-triazines are employed over a wide geographical area; hence, many climatic and edaphic parameters must be investigated to establish proper management practices to achieve the desired phytotoxic effect. An extensive literature has been accumulated which indicates that the s-triazines are adsorbed by organic matter and clay minerals and that phytotoxicity is correlated with pH, exchange capacity, solubility and ion saturation. Little research has been reported on the effect of salt solutions on s-triazine solubility or adsorption-desorption reactions.

Increased toxicity of 2-chloro-4,6-bis(ethylamino)-$\underline{s}$-triazine (simazine) to alfalfa has been reported on sandy soils in Eastern

Oregon.[1] Under irrigated conditions the effective time period of

weed control has been considerably shortened. The rate of applica-

tion of the simazine was in accord with that recommended for the

soil physical and chemical properties. Preliminary studies under

similar conditions indicated good weed control and no injury in alfalfa

and fruit orchards for two growing seasons was possible with 2-(sec-

butylamino)-4-(ethylamino)-6-methoxy-s-triazine (GS-14254) indicat-

ing the methoxy-s-triazine was less susceptible to leaching because

of greater adsorption. In arid regions of the Western United States

injury to corn from s-triazine herbicides applied to alkaline soils

has also been noted. Increased phytotoxicity has been attributed to

decreased s-triazine adsorption and enhanced leaching by irrigation;

however, in some high pH soils high adsorption of 2-chloro-4-(ethyl-

amino)-6-(isopropylamino)-s-triazine (atrazine), 2-(tert-butylamino)-

4-(ethylamino)-6-(methylthio)-s-triazine (terbutryn) and GS-14254

has been measured.

A knowledge of the reactions of the s-triazines in soils is

necessary for their efficient use. Of equal importance is the quan-

tification of s-triazine losses by volatilization, degradation, sediment

transport, surface runoff and leaching to prevent environmental

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[1]Personal communication from Mr. William Anliker, Research
and Development Representative, Ciba-Geigy Corporation.

contamination. Recent evidence indicates that s-triazine losses by surface overwash and leaching are not sufficient to cause environmental problems; however, the need for sound agricultural practices was stressed. The addition of agricultural lime to soils may greatly influence the magnitude of losses by surface overwash and leaching.

The primary objective of this research was to evaluate the effect of salt solutions and amorphous components on the soil reactions of atrazine, terbutryn and GS-14254. Studies were initiated to evaluate the effect of salts on the solubility of the s-triazines and to investigate the influence of salt solutions on adsorption and desorption reactions by soil. In addition, an attempt was made to determine the effect of pH on the adsorption of these compounds by soils with a wide range in carbon content and to determine the effect of carbon content and amorphous soil components on s-triazine adsorption. A field trial was initiated to quantitatively determine the magnitude of lateral losses and leaching of atrazine and terbutryn from limed and unlimed soil.

S-TRIAZINE SOLUBILITY IN CHLORIDE
SALT SOLUTIONS

Introduction

Under low rainfall conditions the phytotoxic activity of the soil active s-triazine herbicides could be greatly affected by salt accumulations. High levels of salt in irrigation water, fertilizer bands or deposited in rows by water evaporation could change s-triazine solubility and resultant phytotoxicity.

S-triazine solubility has been extensively studied as a function of pH and molecular structure (Ward and Weber, 1968). For mono-alkyl substituted s-triazines which differed only in the methoxy, chloro, methylthio or hydroxy group of the ring structure, the solubility at pH 3 decreased in the order $OCH_3 > SCH_3 > OH > Cl$. As the N-alkylamino complexity of the two side chain functional groups increased $[NHC_2H_5-NHC_2H_5; NHC_2H_5-N(C_2H_5)_2]$ the solubility of the compounds at pH 3 changed from the above to $OH > OCH_3 > Cl > SCH_3$ (Ward and Weber, 1968; Ward and Holly, 1966). The solubility significantly increased below pH 3 as the s-triazine basicity increased (solubility and basicity order: $OH > OCH_3 > SCH_3 \gg Cl$) and the size and steric hindrance of the N-alkylamino substituent decreased [bis(ethylamino) > bis(isopropylamino)] (Ward and Weber, 1968).

To explain the solubility changes, Ward and Weber (1968)

suggested protonation of the ring nitrogen atom at the one and/or three position with subsequent cation formation.

The solubility of polar basic nonelectrolytes may be reduced (salted out) or increased (salted in) by electrolyte solutions (Long and McDevit, 1952; Harned and Owen, 1968). The hydration of the cations and anions, the orientation of the water molecules in the hydration sphere, and the polarity of the nonelectrolyte influence solute solubility.

The general trend for the salting out of basic polar nonelectrolytes by cations with a common anion is $K > Na > Ca$. For a common cation the anion order for salting out is $OH > SO_4 > Cl$. Cations which strongly orient water molecules, such as Li, will release protons to hydrophilic anions, such as OH or acetate, causing a reduction in the number of free ions in solution and hence a smaller change in the activity coefficient (increased solubility) of the nonelectrolyte. Also, with an increase in the basicity of the nonelectrolyte, the protons from water will orient more readily around the highly hydrated cations and increase the solubility relative to less hydrated cations. Very few results have been published for salt effects on s-triazine solubilities; however, one would expect salting out with a common anion to follow the cation order $K > Na > Li$ and for a common cation to follow the anion order $OH > SO_4 > Cl$.

The solubility of 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine (atrazine), 2-(ethylamino)-4-(isopropylamino)-6-methoxy-s-triazine (atratone) and 2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine (ametryne) was reduced by addition of 0.3 and 0.6 ionic strength (μ) NH_4, K and Ca chloride salts.[2] S-triazine solubility decreased in the expected cation order Ca $< NH_4 <$ K.

Research was initiated to determine the effect of temperature and K, Na and Ca chloride salts on the solubility of atrazine, 2-(tert-butylamino)-4-(ethylamino)-6-(methylthio)-s-triazine (terbutryn) and 2-(sec-butylamino)-4-(ethylamino)-6-methoxy-s-triazine (GS-14254) in aqueous solution.

Materials and Methods

Solubility-temperature relationships

Atrazine (0.05 g), terbutryn (0.05 g) and GS-14254 (0.10 g) were added to 100 ml of deionized water and adjusted to pH 6 with N NaOH after equilibration for six hours. All pH measurements were made with a Corning, Model 7 pH meter with a calibrated calomel-glass combination electrode. The pH adjusted herbicide solutions were shaken in 250 ml Erlenmeyer flasks at room

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

temperature (> 20 C) for 92, 116, 140, 164 and 188 hours. A five ml

aliquot from each system was filtered (Whatman No. 5) and analyzed

on a Cary, Model 11 double beam ultraviolet spectrophotometer at

219 nm, 222 nm and 224 nm for GS-14254, atrazine and terbutryn

respectively. Preliminary studies showed no s-triazine was adsorbed

by the filter paper. Samples of the herbicide solutions were diluted

with deionized water to a range of one to five ppm. Absorbance

measurements (A) were made at 206 nm and 255 nm for background

correction of samples and standards according to the equation:

$$E = A_{unk} - \frac{A_{206} + A_{255}}{2} \qquad (1)$$

where E is the corrected absorbance and A_{unk} is the absorbance

at the analytical wavelength of the s-triazine compound.

Atrazine (0.05 g), terbutryn (0.05 g) and GS-14254 (0.10 g)

were added to 100 ml of deionized water, adjusted to pH 6 with N

NaOH and equilibrated six days at room temperature in 250 ml

Erlenmeyer flasks. After equilibration the samples were placed

in a constant temperature room at 1 C, 8 C, 20 C and 29 C. After

three days equilibration at a constant temperature, the samples were

filtered and analyzed on a Cary ultraviolet spectrophotometer. Dilu-

tions, absorbance and background corrections were made as de-

scribed previously. The GS-14254 compound at one C was tempera-

ture equilibrated 14 days because of its higher solubility.

Solubility in Na, K and Ca chloride

Sufficient Na, K and Ca chloride salts and atrazine (0.05 g), terbutryn (0.05 g) and GS-14254 (0.10 g) were added to 100 ml volumetric flasks to give final salt concentrations of 0.005, 0.05, 0.1, 0.5, 1.0 and 2.5 ionic strength (μ) after dilution with deionized water. The equation, $\mu = \frac{1}{2} \Sigma MZ^2$ where M is the molarity of the ion species (moles/l) and Z is the valence of the cation or anion, was used to calculate the ionic strength. After an initial equilibration of six hours the pH of the salt systems which were greater than 6 was adjusted with 0.2 $\underline{N}$ HCl. The Na and Ca systems at pH less than 6 were adjusted with $\underline{N}$ NaOH and the K systems with $\underline{N}$ KOH. In all systems <0.2 ml was required for the pH adjustment. The Ca systems were adjusted with NaOH because of the low solubility (0.05 $\underline{N}$) of Ca(OH)$_2$. After the pH adjustment the samples were transferred to 250 ml Erlenmeyer flasks and shaken for six days at room temperature. Upon removal from the shaker, the samples were placed in a constant temperature room at 20 C for three days without shaking, filtered and analyzed on the Cary recording spectrophotometer. The herbicide concentration was calculated by equation (1). Blank solutions of salt concentration similar to the herbicide systems were used for background correction.

Results and Discussion

Solubility-temperature relationships
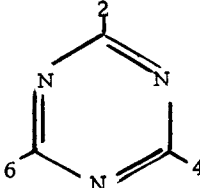
S-triazine solubility remained essentially constant after 116 hours (Table 1). The variation in solubility at times > 116 hours probably resulted from small temperature variations. After equilibration for 188 hours, the solubility of atrazine and GS-14254 equilibrated at room temperature was greater than at 20 C. Terbutryn solubility was greater at 20 C than after equilibration at room temperature.

Structurally the three chemicals investigated differ at the two and six positions of the s-triazine ring with a common ethylamino group at the four position (Table 2). The solubility of the s-triazines investigated increased in the order methylthio < chloro < methoxy (Table 3). For structurally related compounds with similar side chain alkylamino functional groups, Ward and Weber (1968) and Ward and Holly (1966) observed increasing solubility in the order chloro < methylthio < methoxy. Weber (1967) established the same order for basicity of the chemical compounds. He also indicated that the methoxy, methylthio, chloro and hydroxy group had a greater effect on basicity (pKa range 1.85-4.76) than the side chain alkylamino functional groups at the two positions of the ring structure (pKa range 4.15-4.76).

Table 1. Solubility of atrazine, terbutryn and GS-14254.

Time Hr.	Chemical solubility					
	Atrazine		Terbutryn		GS-14254	
	ppm	$Mx10^{-4}$	ppm	$Mx10^{-4}$	ppm	$Mx10^{-4}$
92	35.5	1.65	21.5	0.89	669	29.73
116	39.0	1.81	24.5	1.02	702	31.20
140	31.0	1.44	24.0	1.00	705	31.33
164	39.5	1.83	25.8	1.07	712	31.64
188	36.5	1.69	24.4	1.01	725	32.22
188 @ 20 C	34.1	1.58	35.2	1.46	690	30.70

Table 2. Chemical properties of three s-triazine compounds.

Common name or designation	Basic ring	S-triazine			
		Groups on ring			pKa
		2	4	6	
Atrazine		Cl	NHC_2H_5	NHC_3H_{7i}	1.68
Terbutryn		NHC_4H_{9t}	NHC_2H_5	SCH_3	4.10
GS-14254		NHC_4H_{9s}	NHC_2H_5	OCH_3	4.36

Ward and Weber (1968) observed that within a given s-triazine

structure, increased complexity of the N-alkylamino functional groups

decreased solubility and reversed the trend with basicity. For the

methoxy s-triazines, 2-methoxy-4, 6-bis(ethylamino)-s-triazine

(simatone; pKa = 4.15) and 2-methoxy-4-ethylamino-6-diethylamino-

s-triazine (trietatone; pKa = 4.51), solubility was 132×10^{-4} M and

10.6×10^{-4} M respectively. For the s-triazines studied, the pKa

and basicity increased in the order chloro (1.68) < methylthio (4.10) <

methoxy (4.36) indicating, as Ward and Weber (1968) found, that fac-

tors other than s-triazine basicity were responsible for solubility

differences.

The lower solubility of terbutryn relative to atrazine may be

accounted for by the higher hydrophobicity of the tert-butylamino

group. The complexity of one alkylamino functional group for two

s-triazines with similar functional groups at the two positions of

the ring structure may have a large effect on solubility. Ametryne [4-

(isopropylamino) group] and terbutryn [2-(tert-butylamino) group]

solubilities of 8.5×10^{-4} M (Ward and Weber, 1968) and 1.46 x

10^{-4} M, respectively, demonstrate the importance of complexity

of one functional group on solubility. If the methylthio group and

basicity were the only factors governing solubility, terbutryn (pKa=

4.1) would display equal or greater solubility than ametryne (pKa = 4.0).

For terbutryn, steric hindrance of the amido bonding sites between

molecules in the solid phase would result in higher solubility; however, the <u>tert</u>-butylamino group is more hydrophobic than the isopropylamino group.

The much greater solubility of GS-14254 (30. 7 x 10^{-4} M) primarily results from the methoxy group which would circumvent a decrease in solubility brought about by the 2-(<u>sec</u>-butylamino) group.

Within each of the s-triazines studied, the solubility increased as temperature increased from 1 C to 29 C (Table 3). A 29 fold increase in temperature increased solubility 52. 3%, 41. 6% and 11. 2% for terbutryn, atrazine and GS-14254 respectively.

The relatively small increase in GS-14254 solubility relates to the methoxy functional group. If the functional group at the two position of the s-triazine ring were important in solubility, terbutryn and GS-14254 would be expected to have similar solubilities and solubility change with temperature. The <u>tert</u>-butylamino group at the two position in terbutryn would be expected to cause greater steric hindrance of amido bonding sites in the solid phase which would give terbutryn a greater solubility than GS-14254 and a lower solubility change with temperature.

The work of Finkel'shtein and Boitsov (1962) indicates that the ring nitrogen atoms carry a partial negative charge while the two, four and six functional groups on the ring retain a partial positive charge. The oxygen atom of the methoxy group could be

more negative than the sulfur atom of the methylthio group, thus, the

overall more negative polarity of the methoxy s-triazine would result

in less molecular attraction in the solid phase. The attractive forces

in the solid phase are greater for the methylthio and chloro-s-

triazines as inferred from their lower solubilities. An increase in

temperature would reduce these attractive forces to a greater extent

as manifested by a greater relative increase in solubility. This

same analogy, i.e., the weaker the bonds the less the effect of

temperature, has also been observed for temperature effects on

adsorption (Hamaker and Thompson, 1972).

Solubility in Na, K and Ca chloride

At equivalent ionic strengths (μ) the s-triazine solubility

increased in the order methylthio < chloro < methoxy (Tables 4, 5

and 6), as observed for the electrolyte free systems. No salt-s-

triazine complexes were detectable from the ultraviolet spectra.

Salt concentrations <0.1 μ had only minimal effects on solubil-

ity. At salt concentrations > 0.1 μ, the s-triazine solubility

decreased at the same rate within each salt type. At the 2.5 μ salt

concentration Ca reduced s-triazine solubility 58% whereas Na

and K reduced solubility 85%. Long and McDevit (1952) also

observed that monovalent cations suppressed solubility more than

divalent cations for polar basic nonelectrolytes.

Table 3. Temperature effects on s-triazine solubility.

Temperature C	S-triazine solubility					
	Atrazine		Terbutryn		GS-14254	
	$Mx10^{-4}$	ppm	$Mx10^{-4}$	ppm	$Mx10^{-4}$	ppm
1	1.39	30.0	1.09	26.2	29.3	660
8	1.41	30.4	1.10	26.5	32.5	732
20	1.58	34.1	1.46	35.2	30.7	690
29	1.97	42.5	1.66	40.0	33.0	744

Table 4. Atrazine solubility in chloride salts.

Salt conc.	Cation					
	Na^+		K^+		Ca^{++}	
	Atrazine concentration					
μ	$Mx10^{-4}$	ppm	$Mx10^{-4}$	ppm	$Mx10^{-4}$	ppm
0	1.58	34.1	1.58	34.1	1.58	34.1
0.005	1.67	35.9	1.69	36.5	1.61	34.7
0.05	1.59	34.3	1.63	35.1	1.61	34.7
0.1	1.60	34.5	1.65	35.5	1.67	35.9
0.5	1.11	24.0	1.17	25.2	1.30	28.0
1.0	0.79	17.0	0.81	17.5	1.23	26.6
2.5	0.28	6.1	0.24	5.3	0.67	14.4

Table 5. Terbutryn solubility in chloride salts.

Salt conc.	Cation					
	Na$^+$		K$^+$		Ca^{++}	
	Terbutryn concentration					
μ	Mx10^{-4}	ppm	Mx10^{-4}	ppm	Mx10^{-4}	ppm
0	1.46	35.2	1.46	35.2	1.46	35.2
0.005	1.54	37.2	1.40	33.8	1.56	37.5
0.05	1.37	33.0	1.37	33.0	1.45	35.0
0.1	1.32	31.9	1.27	30.6	1.43	34.5
0.5	0.96	23.2	0.95	23.0	1.20	28.8
1.0	0.67	16.2	0.68	16.4	0.99	23.9
2.5	0.24	5.7	0.22	5.3	0.61	14.8

Table 6. GS-14254 solubility in chloride salts.

Salt conc.	Cation					
	Na$^+$		K$^+$		Ca^{++}	
	GS-14254 concentration					
μ	Mx10^{-4}	ppm	Mx10^{-4}	ppm	Mx10^{-4}	ppm
0	30.7	690	30.7	690	30.7	690
0.005	31.3	705	30.8	694	31.0	698
0.05	29.3	659	29.2	658	30.3	682
0.1	26.7	600	26.9	606	29.7	668
0.5	20.9	470	20.6	464	25.6	575
1.0	13.7	308	14.5	327	22.0	495
2.5	3.9	89	4.3	97	13.1	294

Several qualitative and quantitative approaches have been proposed to explain the effect of electrolytes on polar nonelectrolyte solubility. To account for the observed order of cation and anion effects Kruyt and Robinson (1926) suggested the concept of preferred orientation of the water molecules in the hydration sphere of an ion.

The preferred orientation concept suggests that strongly hydrated cations, such as Li and Ca, orient water molecules about themselves with protons exposed to the solute. Basic nonelectrolytes will be attracted to the protons thereby reducing the salting out effect. The effect of salt type will be dependent upon their hydration energies. Hydration energies for Na, K, Ca and Cl are 101, 81, 389 and 86 kcal/mole (Pauling, 1970). The s-triazine herbicides accept protons and by the Lowry-Bronsted definition are considered bases. The Ca ions due to their high hydration energy orient the water dipoles and the s-triazines to reduce the salting out effect. Na and K cations would have a lesser effect on water orientation and thus reduce s-triazine solubility more than the Ca salt. S-triazine solubility was reduced similarly by Na and K salts because of their similar hydration energies (101 and 81 kcal/mole).

The reduced s-triazine solubility in the presence of Na, K and Ca is also partly attributed to the chloride anion. Strongly hydrated anions, e.g., SO_4, have an affinity for protons which reduces the solubility of the s-triazines. The preferred orientation concept

agrees with the conclusions of Ward and Weber (1968). They sug-
gested s-triazine solubility increased at low pH through protonation
of the one and/or three ring nitrogen atoms.

An empirical expression which graphically describes non-
electrolyte-salt solubility and permits direct calculation of non-
electrolyte activity coefficients is the Setschenow equation (Long and
McDevit, 1952):

$$\log \frac{f}{f^o} = \log \frac{S^o}{S} = KC_s \tag{1}$$

This expression is the simplified form of the more exact and
complex expression:

$$\log \frac{f}{f^o} = \log \frac{S^o}{S} = K_s C_s + K_i(S-S^o) \tag{2}$$

where f^o and f are the activity coefficients of the nonelectrolyte
in the standard state and salt solution; S^o and S are the corres-
ponding solubilities; K, K_s and K_i are the Setschenow constant, salt
and solute interaction parameters respectively and C_s is the electro-
lyte concentration. Equation (2) reduces to equation (1) if S and S^o
are small. The salt parameter K_s in equation (2) is not the same
as the Setschenow parameter which includes ion-solute as well as
solute-molecule interactions (self-interactions), i.e., a combination
of K_i and K_s. The self-interaction term, K_i, may be as large as
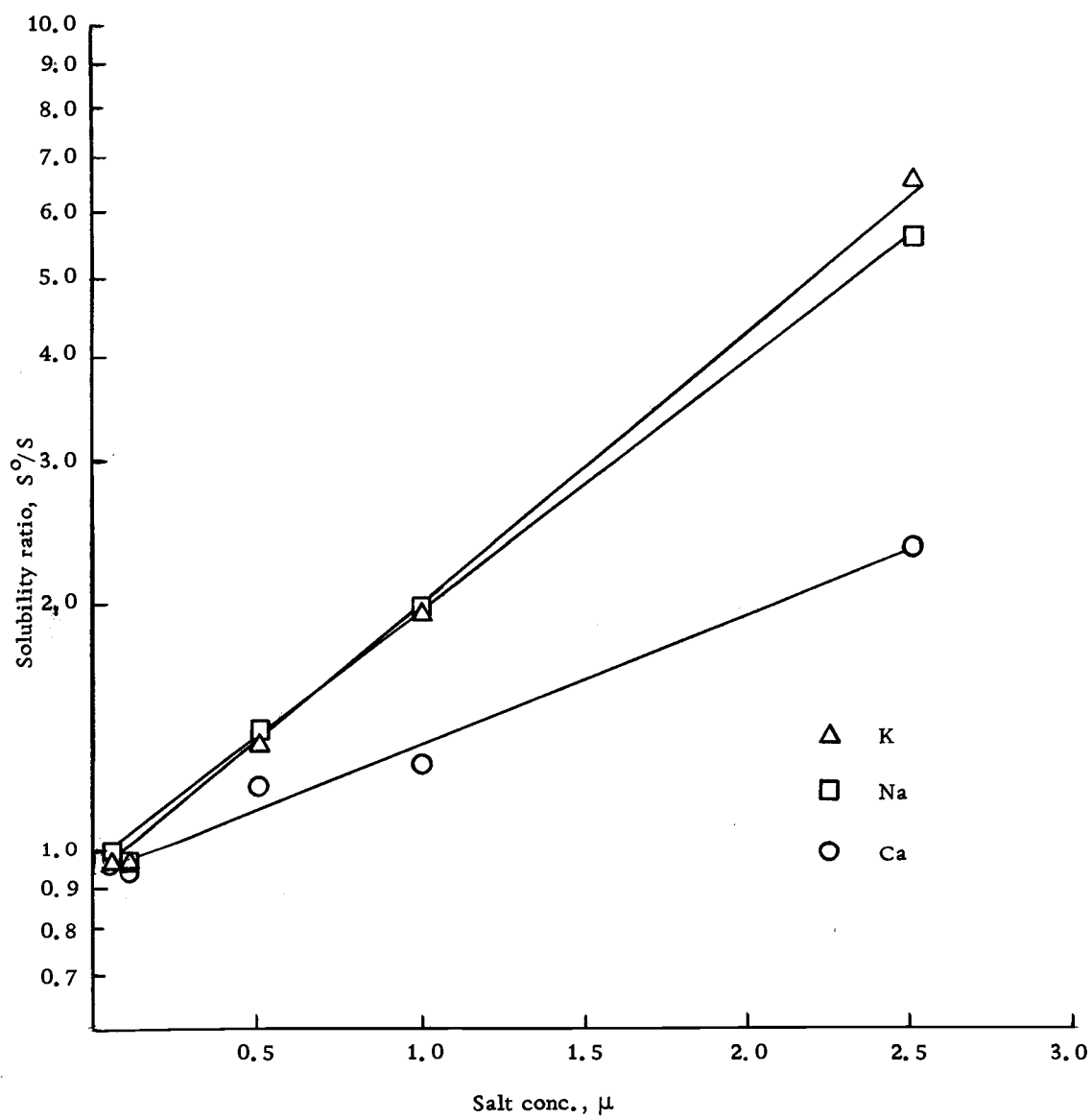
Figure 1. Atrazine solubility in chloride salts.
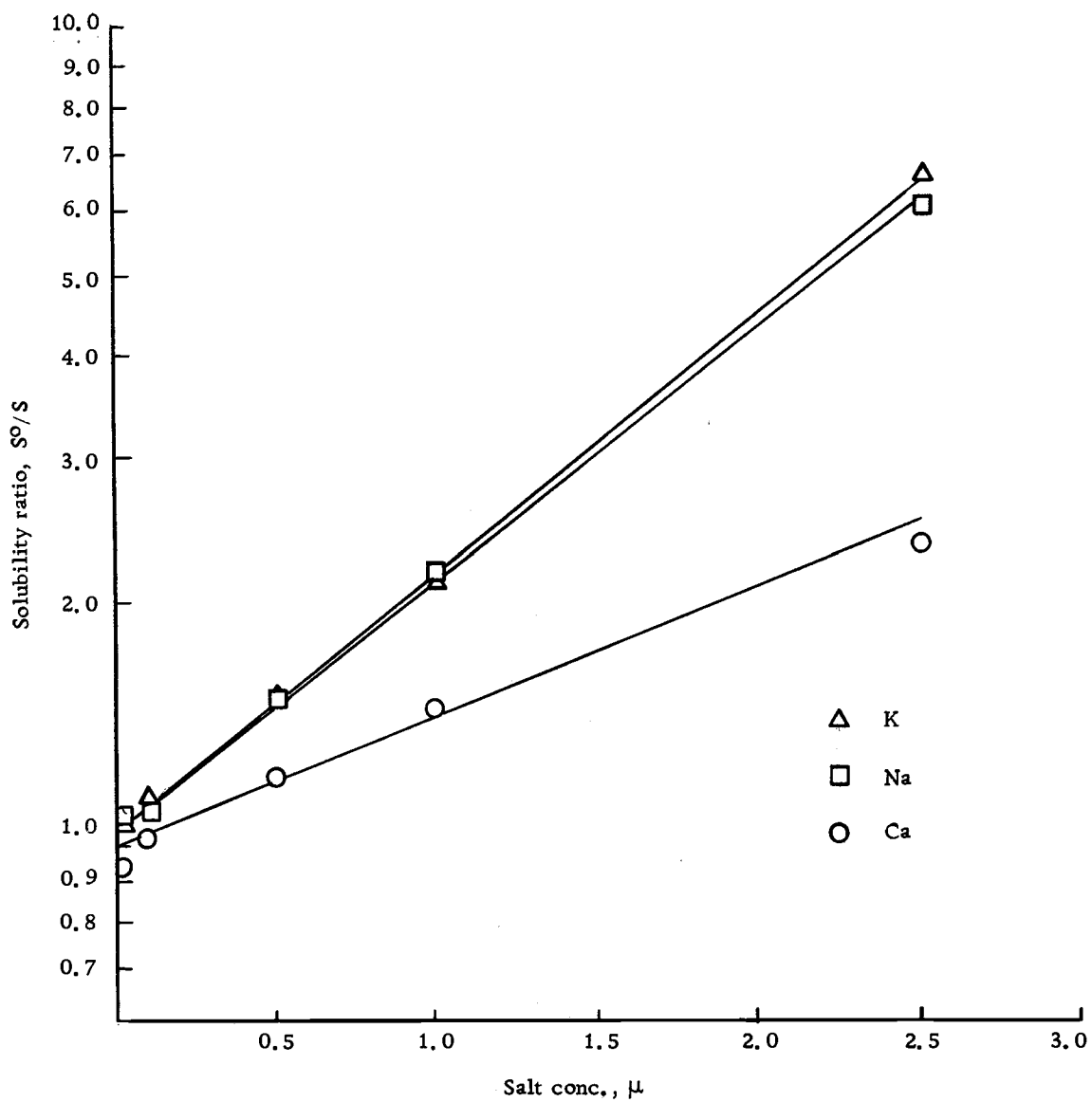
Figure 2. Terbutryn solubility in chloride salts.
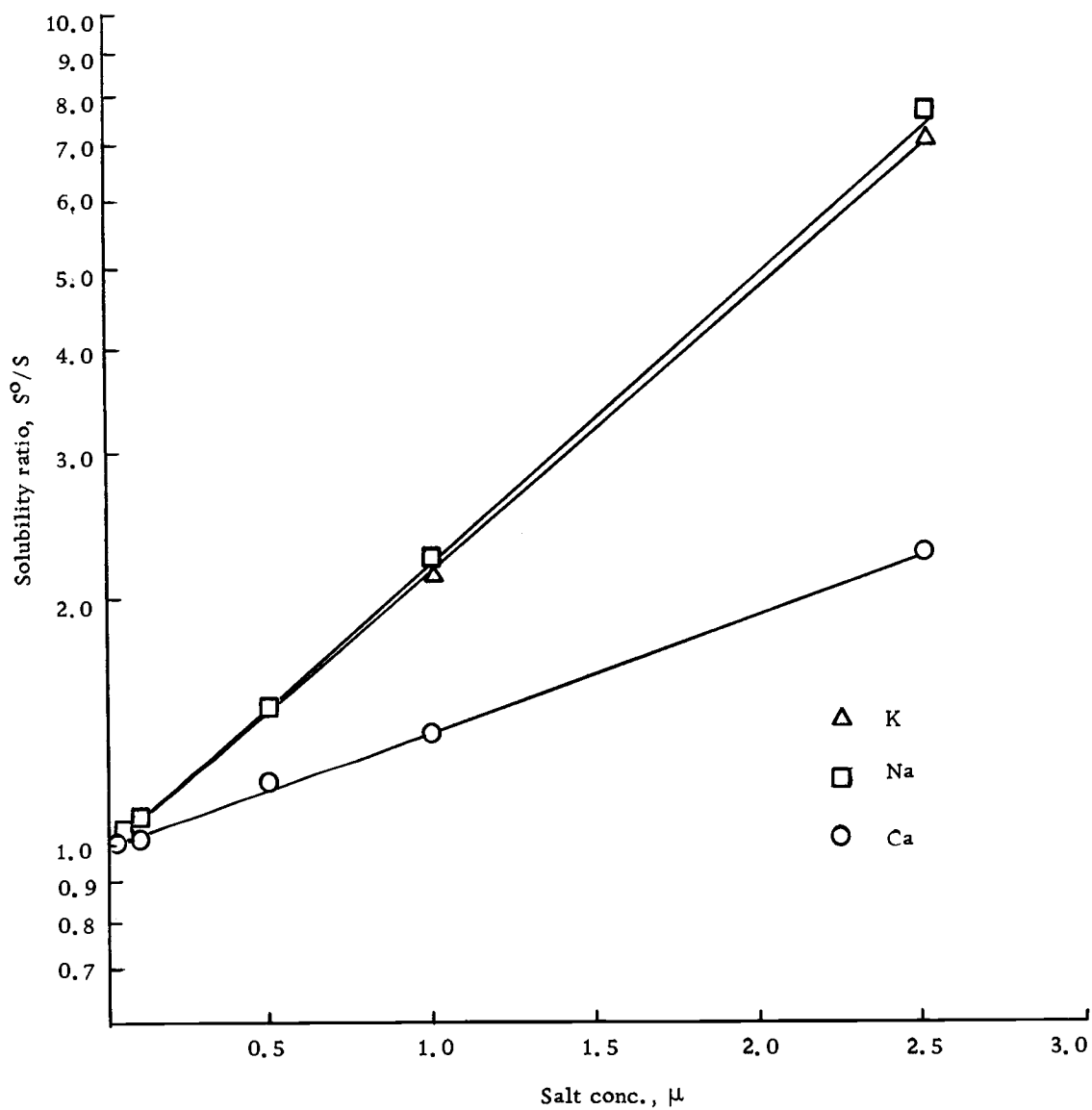
Figure 3. GS -14254 solubility in chloride salts.

the salt parameter term, K_s, and becomes more significant as solute polarity increases. Relative values for the Setschenow constant, K, can be compared for different salts within each s-triazine compound because the interaction term K_i is constant and independent of salt (Long and McDevit, 1952).

Bearing in mind the limitations of the Setschenow equation, the parameter K was graphically determined for the s-triazine data (Figures 1, 2 and 3; Table 7). The K values for Na and K chloride are similar for each of the s-triazines (0.310-0.354) and are significantly higher than those for Ca (0.149-0.156) (Table 7). The higher K values for Na and K chloride indicate these cations more effectively salt out s-triazines than Ca chloride.

Table 7. Salt coefficients (K) for s-triazines.[a]

Salt	Atrazine	Terbutryn	GS-14254
NaCl	0.310a	0.317a	0.354a
KCl	0.339a	0.320a	0.337a
CaCl$_2$	0.155b	0.156b	0.149b

[a]Coefficients followed by the same letter are not significantly different at the 1% level.

The increased activity coefficients ($\frac{f}{f^O} > 1$) of the s-triazines by

salts is explained by the "localized hydrolysis" concept proposed by

Harned and Owen (1958). The "localized hydrolysis" concept is

similar to the preferred orientation concept with respect to water

orientation about cations but differs in that anions are attracted to

the protons. Anions which have a high affinity for protons will have

a lesser effect on the activity coefficient of the solute (higher solu-

bility) due to a reduction in the number of free ions in solution.

Salting out of polar basic nonelectrolytes, then, would be expected to

conform to the lyotropic series for cations and anions, namely,

solubility increases in the order Cs < Rb < K < Na < Li and OH <

SO_4 < Cl < Br < NO_3 < I. Thus the highest solubility for polar basic

nonelectrolytes would occur in LiI solutions. Since the Ca cation

has a greater hydration energy than Li (127 kcal/mole) more anions

would be attracted to protons oriented about Ca than for Na or K

leaving fewer ions in solution. The activity coefficient of the

s-triazines, as reflected by the K value, increased less for Ca

than for Na or K chloride hence a higher solubility.

It is recognized that the hydration concept only explains rela-

tive salt effects on nonelectrolyte solubility. Other treatments to

explain observed effects of salts on polar nonelectrolyte solubility

have considered expressions for changes in dielectric constant of

the solution, i. e., a decrease in dielectric constant results in salting

out; dipole moment and polarizability of the nonelectrolyte, i.e.,
increased solubility as dipole moment increases; and van der Waals
forces.

Although anion and cation combinations may have different
effects on s-triazine salting out, the solubility values obtained with
the chloride salts indicate that salts in the soil solution ($\sim$0.02 $\underline{N}$)
would have an insignificant effect on solubility. Richards (1954)
reported that saturated saline soils do not exceed 0.1 $\underline{N}$ salt concen-
tration and that most agricultural soils have salt levels below 0.02 $\underline{N}$.

It may be possible; however, that under the right management
conditions, i.e., band application of fertilizers with herbicides and
low moisture conditions, salt levels may become high enough to
precipitate the s-triazines. This condition would probably be re-
lieved upon application of water.

Summary and Conclusions

The aqueous solubility of the s-triazines increased in the order
terbutryn $\leq$ atrazine < GS-14254. As the ambient temperature
increased from 1 C to 29 C s-triazine solubility increased for the
three chemicals but GS-14254 solubility increased less (11%) than
terbutryn (52%) and atrazine (42%). The relatively small increase
in solubility of the methoxy-s-triazine is primarily due to the
methoxy functional group which imparts a more overall negative

polarity to the s-triazine, thus, there is less intermolecular attraction in the solid phase.

Salt concentrations $<0.1\mu$ did not greatly affect s-triazine solubility. Salt concentrations $>0.1\mu$ reduced s-triazine solubility and in 2.5μ salt concentration Na and K chloride reduced s-triazine solubility 85% whereas Ca chloride reduced solubility 58%. It was postulated that the s-triazine molecules were attracted to the water protons strongly oriented about the highly hydrated Ca cations, thus producing a smaller reduction in solubility. The Na and K cations had a lesser effect on the orientation of the water molecules because of their lower hydration energy, thus s-triazine solubility would be reduced to a greater extent because of unfavorable interaction with water protons. The higher solubility of the s-triazines in Ca relative to the Na and K salt solutions was also attributed to the attraction of the chloride anion to the oriented water protons about the Ca cation which reduced the number of free ions in solution. The reduction of free ions in solution would manifest a higher s-triazine solubility relative to the weakly hydrated Na and K cations.

The data show that the solubility of atrazine, terbutryn and GS-14254 is not reduced until salt concentrations are greater than 0.1μ. Salts in the soil solution rarely attain such high levels; however, salt concentrations may be greater than 0.1μ in banded

fertilizer rows. Under normal agricultural practices s-triazine solubility would not be affected by salts in the soil solution.

S-TRIAZINE ADSORPTION AND DESORPTION BY
CLOQUATO SANDY LOAM

Introduction

Arid and semiarid lands which contain substantial amounts of
Na, Ca and Mg salts comprise approximately one-third of the earth's
surface (Kelly, 1951). The presence of these salts can have a pro-
nounced influence on plant growth, nutrient uptake, water and soil
management and herbicide reactions. Because the s-triazine herbi-
cides are widely used under varied climatic conditions and are pre-
dominantly active through the soil phase, the influence of salts on
their reactions in the soil are of primary interest.

S-triazines are adsorbed to organic matter (Hayes, 1970) and
clay minerals, i.e., montmorillonite and kaolinite (Frissel and Bolt,
1962; Weber and Weed, 1968) through hydrogen bonding and cation
exchange mechanisms (Weber, 1970b). Adsorption of s-triazines
by montmorillonite and organic matter was pH dependent with max-
imum adsorption occurring at the pKa of the compound (Weber,
1970a; Weber, Weed and Ward, 1969). Structure and basicity ap-
peared to have an interrelated effect on adsorption (Weber, 1966;
Hance, 1969). The methoxy, methylthio, hydroxy and chloro func-
tional groups determined the primary mechanism of adsorption
while the alkylamino groups present on the ring structure determined

magnitude (Weber, 1966). For s-triazines which differed only in the methoxy, methylthio, hydroxy or chloro functional groups adsorption decreased in the order $SCH_3 > OCH_3 > OH > Cl$. Adsorption for s-triazines with a common methoxy, methylthio, hydroxy or chloro functional group increased with N-alkylamino complexity.

Reduced solubility of the s-triazines by salts in solution has been suggested to explain reduced mobility (Helling, 1971), increased soil adsorption (Frissel and Bolt, 1962; Colbert, 1972) and decreased desorption (Weber, 1970b).

Adsorption of 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine (atrazine) and 2-chloro-4, 6-bis(ethylamino)-s-triazine (simazine) by Woodburn soil increased 12% to 115% when 0.3 ionic strength (μ) NH_4, K and Ca chloride salt was present.[2] A greater increase in adsorption occurred in the presence of K and NH_4 than for the Ca chloride salt of equivalent ionic strength. The aqueous solubility for atrazine was 29.9, 25.3, 27.4 and 28.4 ppm in the absence of salt and 0.3μ K, NH_4 and Ca chloride salts respectively. The increased adsorption was attributed to reduced s-triazine solubility; however, the pH of the salt amended soils was 1.0 unit lower than the check system because of salt displacement of acidic cations from the soil. Fusi and Corsi (1969) measured a reduction in atrazine adsorption of 20% or less by several soils in the presence of 0.01 $\underline{N}$ to 0.5 $\underline{N}$ NaCl. Atrazine adsorption in the presence of

dilute salt solutions was reduced more by acid soils than for neutral soils. Atrazine adsorption increased in all soils at salt concentrations > 3 $\underline{N}$. Several investigators have assumed no change in adsorption when small amounts of salt were used to flocculate soil suspensions (Williams, 1968; Hance, 1965; Nearpass, 1967).

S-triazine desorption from montmorillonite, anion and cation exchange resins, nylon and cellulose triacetate was reversible with deionized water (Ward and Holly, 1966; Weber, 1970b). Moyer, McKercher and Hance (1972) observed no differences between distilled water and 0.01 $\underline{N}$ $CaCl_2$ solvents in the desorption of atrazine and 2,4-bis(isopropylamino)-6-(methylthio)-$\underline{s}$-triazine (prometryne) from dried montmorillonite systems. Atrazine and simazine were desorbed by deionized water from muck soil and calcium saturated bentonite (Harris and Warren, 1963). Although each desorption from the muck soil was less than from the bentonite, reversibility was observed for both adsorbents.

Desorption of 2,4-bis(isopropylamino)-6-methoxy-$\underline{s}$-triazine (prometone) from montmorillonite adjusted to pH values from 1 to 8.5 occurred similarly with 0.1 M $BaCl_2$ (Weber, 1966). Weber (1966) concluded that barium exchanged with protonated prometone since desorption with deionized water removed lesser amounts (1%-7%) of the prometone at pH < 6 than at pH 8.5 (25%). The displacement of 24.6 meq Na/100 g by prometone at pH 6 further supported the

concept of cation exchange.

The lack of information on salt effects on s-triazine reactions in soil encouraged research on the effect of chloride salts on the adsorption and desorption of atrazine, 2-(tert-butylamino)-4-(ethylamino)-6-(methylthio)-s-triazine (terbutryn) and 2-(sec-butylamino)-4-(ethylamino)-6-methoxy-s-triazine (GS-14254) on Cloquato sandy loam soil.

Materials and Methods

Soil characterization

Cloquato sl soil was air dried and screened to pass a 2 mm sieve.

The soil past pH was determined with a Model 7, Corning pH meter fitted with a glass-calomel combination electrode.

Carbon content was measured by dry combustion (Young and Lindbeck, 1964) using a Leco induction carbon analyzer and a wet oxidation method (Walkley and Black, 1934).

After removal of soluble salts with deionized water, duplicate five gram soil samples were extracted by four washings with 0.5 $\underline{N}$ $BaCl_2$. The exchangeable bases, K, Ca, Mg and Na, were determined on a Perkin Elmer 306 atomic absorption spectrophotometer.

Adsorption from salt solutions

Stock solutions of five ppm ^{14}C-ring labeled atrazine, terbutryn and GS-14254 were prepared. Sufficient Na or Ca chloride salt was added by weight to duplicate five gram soil samples to give 0.05, 0.1, 0.5, 1.0 or 2.5 ionic strength (μ) salt concentrations when 10 ml of the herbicide solution were added to each system. The ionic strength was calculated by $\mu = \frac{1}{2} \Sigma MZ^2$ where M is the molarity of the ion species (moles/l) and Z is the valence of the cation or anion. All systems were adjusted to pH 6 with not more than 0.15 ml $\underline{N}$ NaOH. The systems were equilibtated at 25 C for 12 hours. After equilibration, the samples were centrifuged for 20 minutes at 14,000 rpm, decanted and the weight of solution remaining in the test tube gravimetrically assayed.

Desorption from salt amended soils

Six 2-hour desorptions with ten ml of 0.01 $\underline{N}$ CaCl$_2$ followed the initial equilibration. After each desorption the solution volume and the occluded solution was determined gravimetrically. Correction for occluded s-triazine in the equilibrium soil solution was made after adsorption and each desorption. The soil pH was measured after adsorption and desorption on blank samples containing non-labeled s-triazine.

S-triazine assay

The s-triazine adsorbed was determined by difference in ^{14}C activity of the herbicide solution before and after equilibrium with the soil. One ml of each supernatant aliquot removed from the soil after adsorption and desorption was added to a scintillation fluor which consisted of toluene: Triton X-100 (2:1 v/v), PPO (2, 5-diphenyloxazole, 4 g/l), and POPOP [1, 4-bis-2-(5-phenyloxazolyn)-benzene, 0. 1 g/l]. Because the toluene: Triton X-100 fluor has a low salt solubility, 15 ml of a gel fluor containing toluene (500 ml), glycerol (5 ml), Tween 80:Span 80 (polyoxyethylene sorbitan mono-oleate:sorbitan monooleate; 1:9; 4 ml), PPO (3 g), POPOP (50 mg) and thixin (20 g) was used for the herbicide solutions which contained 1 μ and 2. 5 μ salt concentrations. Adsorption and desorption was calculated by equation (1) and (2) respectively.

$$\left[\frac{A - (\frac{C-B}{SA \times CE}) V}{A} \right] 100 = \% \text{ adsorbed} \qquad (1)$$

$$\left[\frac{(\frac{C-B}{SA \times CE}) V - E}{D} \right] 100 = \% \text{ desorbed} \qquad (2)$$

where A = herbicide added (μg), B = background (cpm), C = aliquot activity (cpm/ml), V = total volume (ml), CE = count efficiency (cpm/dpm, determined by internal spiking), SA = stock herbicide specific

activity (dpm/μg), D = herbicide adsorbed or left on the soil after each desorption (μg) and E = herbicide occluded in the soil solution from the previous adsorption or desorption (μg).

Results and Discussion

Adsorption from salt solutions

Cloquato sl soil adsorbed 94.8%, 94.5% and 34.7% of the added terbutryn, GS-14254 and atrazine (Table 1). S-triazine adsorption by the Cloquato sl soil decreased in the order methylthio > methoxy > chloro in agreement with the observation by Weber (1970a) for s-triazine adsorption by montmorillonite. As also presented by others (Weber, 1966; Weber et al., 1969) the adsorption of these compounds increased with complexity of the alkylamino group, i.e., $C_3H_{7i} < C_4H_{9s} < C_4H_{9t}$ but the primary mechanism for adsorption was determined by the methoxy, methylthio or chloro functional group.

Compared to the salt free system, adsorption of terbutryn and GS-14254 by the Cloquato sl soil was reduced at all salt levels (Table 1). The Na and Ca chloride salts reduced adsorption similarly. At salt concentrations < 1.0 μ the reduction in terbutryn and GS-14254 adsorption (28.3% and 12.5%) may result from competition for adsorption sites by salt cations; however, Hamaker and Thompson

Table 1. S-triazine adsorption by Cloquato sl as affected by salt concentration.

Salt	\	\	\	Salt concentration, μ	\	\	LSD	\
	0	0.05	0.1	0.5	1.0	2.5	.05	.01
				Atrazine adsorbed, %				
NaCl	34.7	29.9	30.4	34.8	37.9	55.5	5.1	7.8
$CaCl_2$	34.7	28.8	29.0	37.3	33.6	39.3	1.5	2.3
				Terbutryn adsorbed, %				
NaCl	94.8	81.6	87.7	85.9	82.8	92.8	5.2	8.1
$CaCl_2$	94.8	84.9	84.3	86.1	81.0	83.4	1.7	2.6
				GS-14254 adsorbed, %				
NaCl	94.5				67.3			
$CaCl_2$	94.5		80.1		68.0			

Table 2. Chemical properties of Cloquato sl soil.

Salt type and conc., μ	pH	Carbon %	Exchangeable bases				Sum of bases
			Ca^{++}	Mg^{++}	Na^+	K^+	
			---------- meq/100 g -------------				
0	5.8	0.72	7.51	2.70	0.16	0.31	10.8
NaCl							
0.05			7.00	2.11	0.20	0.31	9.8
0.1			6.05	2.50	3.00	0.28	11.8
0.5			3.62	1.36	6.96	0.22	12.2
1.0			2.88	1.14	9.56	0.20	13.8
2.5			2.18	0.62	10.90	nd*	13.6
$CaCl_2$							
0.05			9.20	1.15	0.20	0.22	10.8
0.1			10.50	1.23	0.16	0.22	12.2
0.5			11.65	0.52	0.14	0.18	12.4
1.0			12.50	0.30	0.16	0.16	13.1
2.5			13.50	0.16	nd	nd	13.6

* not determined

(1972) suggested that adsorption of neutral molecules would show little effect from salts. Atrazine with its lower pKa (1.68) would respond as a neutral molecule and not be affected by salt, whereas terbutryn and GS-14254 with higher pKa values (4.10 and 4.36) may be subject to cation competition if they react as protonated species. Although these studies were conducted at pH 6 the soil surface may be more acidic (Harter and Ahlrichs, 1969) but surface and solution acidity would be similar at higher salt concentrations. As expected, the suite of exchangeable bases changed with the concentration of salt in the equilibrating solution (Table 2).

Cation competition for adsorption sites between terbutryn and GS-14254 and added salt may be implied by the similar herbicide adsorption reduction caused by Na and Ca chloride (Table 1). Solubility studies (Chapter 1) showed that Na more effectively reduces s-triazine solubility than Ca; hence, a greater reduction in adsorption should occur with Na salt which was not observed. Using a mass action equation to describe the equilibrium condition, more cations would be found in the double layer than s-triazine molecules which, through competition for exchange sites, would reduce adsorption.

Armstrong and Chesters (1968) found that 0.1 μ NaCl reduced atrazine adsorption by a carboxylic cation exchange resin (pH 4.5) from 39% (no salt) to 34%. Atrazine adsorption by several acidic

soils was reduced in the presence of 0.01 $\underline{N}$ to 0.5 $\underline{N}$ salt concen-

trations of NH_4Cl, $(NH_4)_2SO_4$, NaCl, $MgSO_4$ or KCl salts but

increased at a salt concentration of 3 $\underline{N}$ (Fusi and Corsi, 1969).

Adsorption of atrazine by neutral or calcareous soils was not

affected by the above salts at concentrations from 0.01 $\underline{N}$ to 0.5 $\underline{N}$

but increased at higher salt concentrations. These results suggest

that in low pH systems protonated atrazine and cations in solution

compete for adsorption sites while at higher pH values adsorption

of atrazine by H-bonding is unaffected by the presence of salts. The

increase in atrazine adsorption at salt concentrations > 0.5 $\underline{N}$ may

reflect salting out.

Contrary to this study and those reported earlier (Armstrong

and Chesters, 1968; Fusi and Corsi, 1969), Abernathy and Davidson

(1971) observed an increase in the Freundlich K value for prometryne

adsorbed by Ca-Eufaula and Norge soils from 0.364 to 0.465 ml/g

and 0.712 to 0.962 ml/g, respectively, when the $CaCl_2$ concentra-

tion of the equilibrating solution increased from 0.015 μ to 0.75 μ.

These authors suggested that the cation may serve as a salt link

between the soil surface and s-triazine as described by Sullivan and

Felbeck (1968) between s-triazines and humic acid, thus increasing

prometryne adsorption. One would expect the adsorption of terbutryn

and prometryne (pKa = 4.05) to respond similarly to additions of salt.

Terbutryn and prometryne have similar solubilities (1.46 x 10^{-4} M

and 1.67×10^{-4} M respectively) and the alkylamino functional

groups, 2-(tert-butylamino)-4-(ethylamino) and 4,6-bis(isopropyl-

amino), respectively, do not differ greatly. At a solution pH > 7

Hance (1969) observed slightly higher adsorption of five s-triazines

by Ca and Mg montmorillonite than for Na montmorillonite. Adsorp-

tion at pH <5 followed the order of ion displacement (Na > Ca > Mg)

which suggested coulombic forces were involved while above pH 7

salt linking was postulated.

Salt linking, i.e., the formation of an ionic bond between

adsorbed cation and s-triazine, does not occur to any great extent

as suggested (Hance, 1969; Sullivan and Felbeck, 1968; Abernathy

and Davidson, 1971) since such a mechanism would require consid-

erable energy to break the water-salt bond [Hydration energy for

Ca = 389 kcal/mole (Pauling, 1970)] and to form an s-triazine-salt

ionic bond. Since desorption was possible with deionized water,

bond energies of this magnitude could not be involved. Nearpass

(1967) indicated that the adsorption of atrazine and simazine by

Bayboro clay soil was independent of the predominating cation but

dependent upon exchange acidity.

As reflected by the increase in atrazine adsorption in $2.5\,\mu$

salt solutions, the concentration of salt and herbicide in the double

layer is sufficiently high to cause salting out. Solubility data

(Chapter 1) showed that NaCl reduced s-triazine solubility more

than $CaCl_2$. In agreement with the solubility data, s-triazine

adsorption increased more in NaCl than $CaCl_2$ at salt concentra-

tions $> 1 \mu$. Salting out may also account for the increased terbutryn

adsorption at salt concentrations $> 1 \mu$ although adsorption was still

below the check systems.

S-triazine desorbed

Preliminary studies at pH 6 showed that 0.01 $\underline{N}$ $CaCl_2$ or

deionized water desorbed s-triazine compounds similarly from

Cloquato sl soil. Thus, cation exchange mechanisms for the adsorp-

tion of protonated s-triazine molecules would not appear to be a

significant mechanism. On the other hand s-triazine adsorption by

cation exchange mechanisms could occur and not be elucidated

under the experimental conditions. Salt retained in the occluded

solution after the initial equilibration with herbicide and added salts

may be sufficiently high to displace protonated s-triazine cations in

the desorption equilibration. Although no salts were added to the

check system, free salts were not previously removed by leaching

the soils. To prevent dispersion and hydrolysis of the soil, 0.01 $\underline{N}$

$CaCl_2$ was selected for desorption.

Atrazine, terbutryn and GS-14254 desorption was not greatly

influenced by salt type or initial salt concentrations $< 1 \mu$ (Figures 1,

2, 3, 4 and 5). However, terbutryn and GS-14254 desorption from
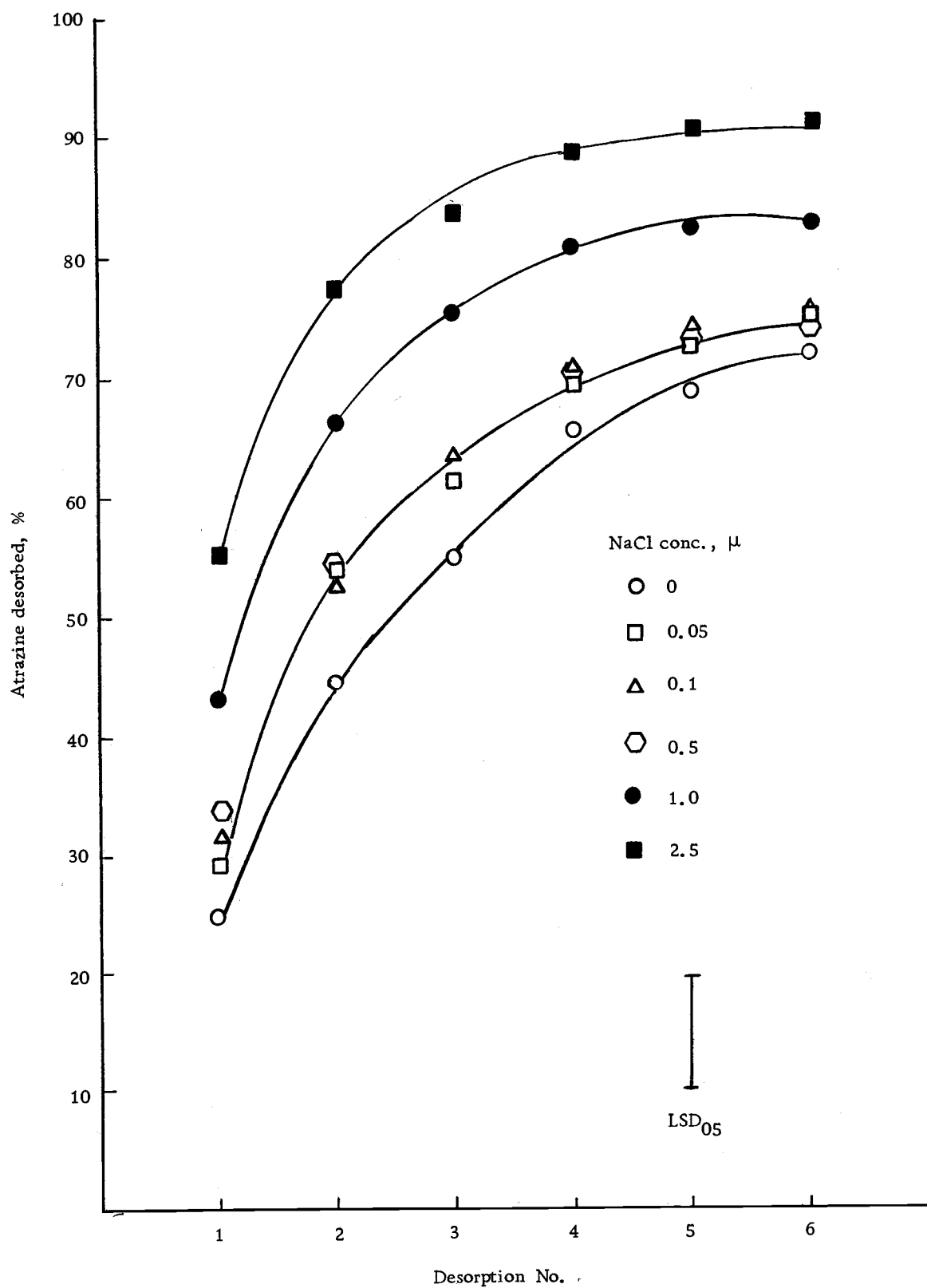
Figure 1. Cumulative atrazine desorption from NaCl amended Cloquato sl.
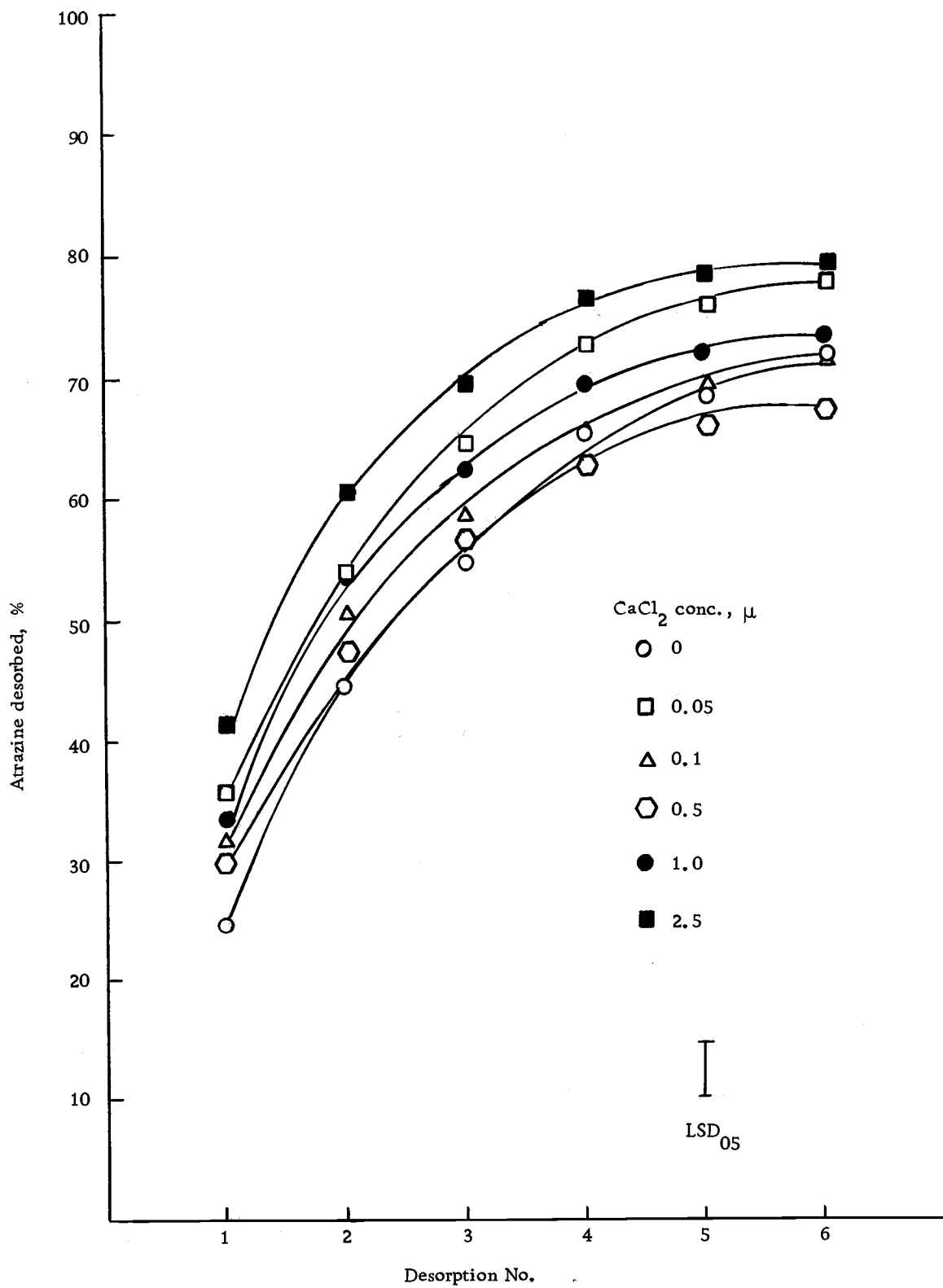
Figure 2. Cumulative atrazine desorption from CaCl$_2$ amended Cloquato sl.
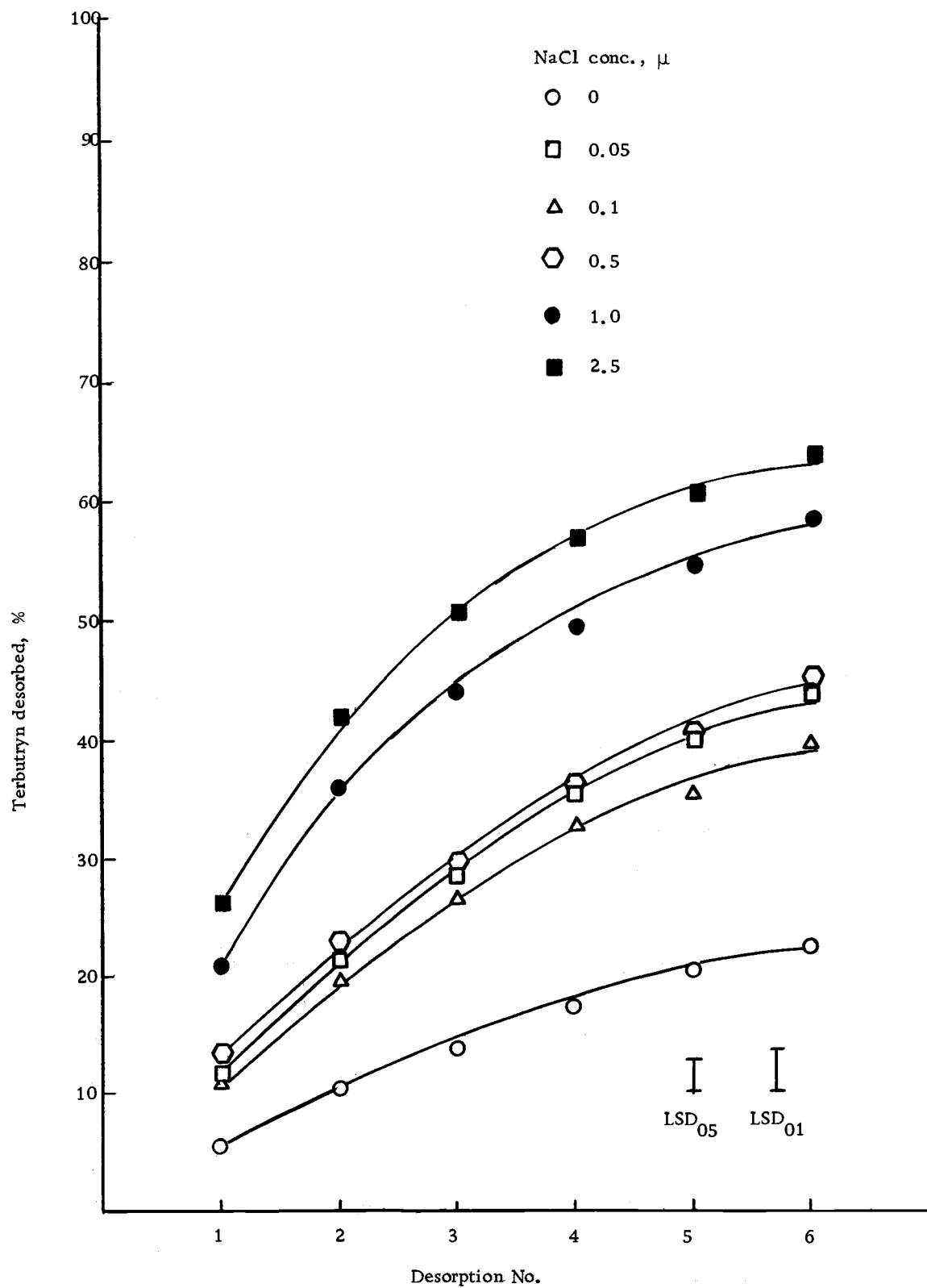
Figure 3. Cumulative terbutryn desorption from NaCl amended Cloquato sl.
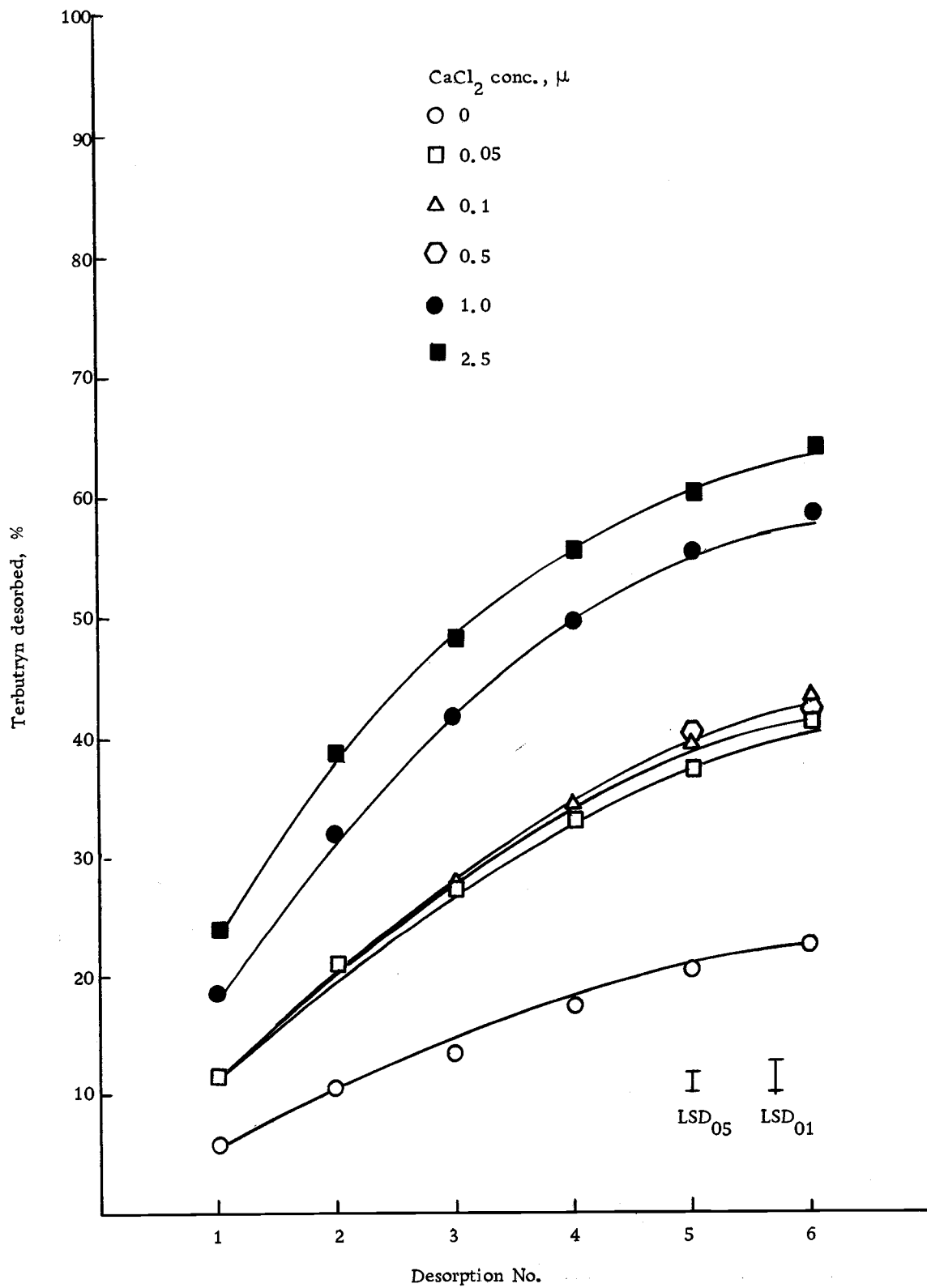
Figure 4. Cumulative terbutryn desorption from $CaCl_2$ amended Cloquato sl.
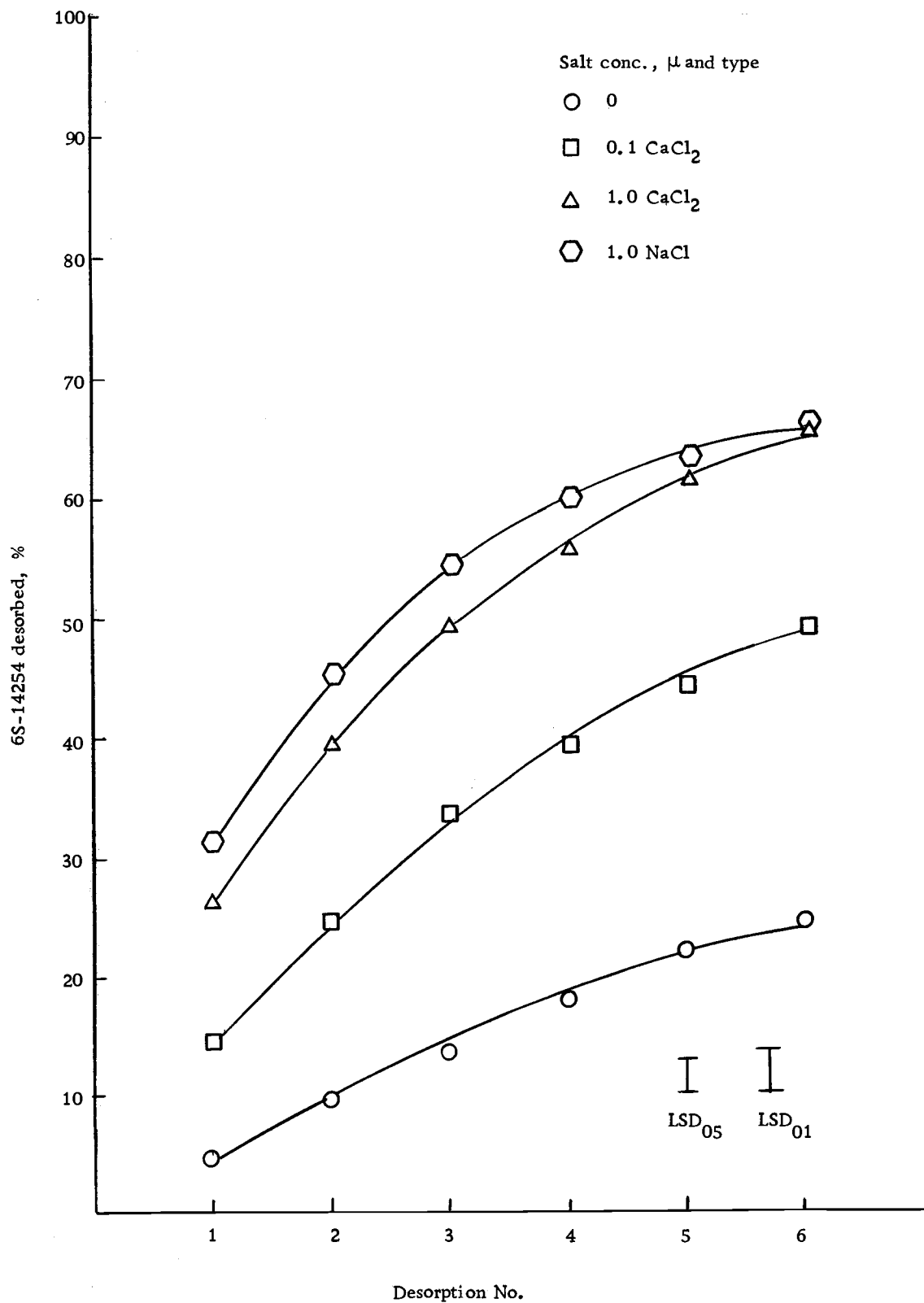
Figure 5. Cumulative GS-14254 desorption from Cloquato sl.

the soil initially equilibrated with <1 μ salt concentration was twice that desorbed from the soil system which received no salt (Figures 3, 4 and 5). Six 0.01 $\underline{N}$ CaCl$_2$ extractions desorbed approximately 23% and 45% of the adsorbed terbutryn and GS-14254 from the check soil and soil treated initially with <1 μ salt solution. Atrazine desorption on the other hand, was not affected by salt concentrations <1 μ. Approximately 72% of the adsorbed atrazine was extracted from the Cloquato soil initially amended with <1 μ salt solutions after six 0.01 $\underline{N}$ CaCl$_2$ desorptions (Figures 1 and 2).

The larger quantities of terbutryn and GS-14254 desorbed by the systems initially equilibrated with <1 μ salt concentration compared to the system without added salt may reflect readsorption of the two desorbed s-triazines by the check soil. The check soil showed a slight decrease in pH (0.3 units) upon addition of 0.01 $\underline{N}$ CaCl$_2$ solvent. A decrease in soil pH would reduce the amount of terbutryn and GS-14254 desorbed by the salt free system relative to those with salt added. The salt treated soils had previously been adjusted to pH 6 to reduce the effect of salt induced pH changes on adsorption. The readsorption of terbutryn and GS-14254 may also account for the lack of a difference in desorption between deionized water and the 0.01 $\underline{N}$ CaCl$_2$ solvents. Readsorption of atrazine by the small pH change in the check soil would not be expected because of a lower pKa value for the atrazine.

At salt concentrations <1.0 μ terbutryn and GS-14254 precipitation in the double layer and subsequent solubilization upon addition of 0.01 $\underline{N}$ $CaCl_2$ does not account for the increased desorption of these compounds when compared to the check soils since atrazine would be expected to react similarly. In a previous study (Chapter 1) atrazine and terbutryn solubility at 20 C and pH 6 was 34.1 ppm and 35.2 ppm. The solubility of these two compounds decreased at the same rate as salt concentration increased. A more plausible explanation is coordination of the s-triazines through the adsorbed water molecules associated with the salt-soil system. Hydrogen bonding between the ring nitrogen atoms at the one and/or three position of the atrazine molecule and water adsorbed to the salt would occur to a lesser extent than for terbutryn and GS-14254 because of the lower pKa value of atrazine and greater electron withdrawing power of the chlorine atom at the two position.

Earlier it was noted that s-triazine adsorption increased at salt concentrations >1 μ and that this increase was greater for NaCl than for $CaCl_2$. Significantly more atrazine, terbutryn and GS-14254 was desorbed from the soils which had >1 μ salt in the initial equilibrating solution. In compliance with the solubility data (Chapter 1) 1 μ NaCl salt solutions enhanced desorption more than equivalent $CaCl_2$ solutions supporting the concept that the s-triazines were salted out. Frissel (as cited by Abernathy and Davidson, 1971)

reported similar increases for s-triazine adsorption at salt concentrations > 1 $\underline{N}$. It was postulated that high salt concentrations increased the activity coefficient of the s-triazines in solution without affecting the clay surface. The increase in the activity coefficient would reduce s-triazine solubility and increase apparent adsorption through precipitation of the s-triazine.

After the third desorption, subsequent extractions removed each s-triazine from all treatments at similar rates regardless of the initial salt concentration. This indicates that the initial enhanced desorption at salt concentrations > 1.0 μ was due to salting out and that the precipitated s-triazine was soluble in the desorption solution. Terbutryn and GS-14254 adsorption appeared to be reversible as approximately 5% of the chemical was removed by each desorption after the third desorption. In the initial adsorption equilibrium 95% of the added terbutryn and GS-14254 was adsorbed, thus, 5% remained in the equilibrium solution. The amount of atrazine desorbed from each soil system decreased from 30% to 10% per extraction as the number of extractions increased indicating desorption was not strictly reversible according to the adsorption isotherm. Since each extraction was performed for two hours, equilibrium may not have been reached for the atrazine system. In preliminary studies, adsorption equilibrium was reached after 12 hours but the desorption equilibrium rate was not determined. Desorption with deionized

water of various s-triazines from charcoal, anion and cation exchange

resins and Na-montmorillonite was quantitative indicating weak physi-

cal forces were involved (Weber, 1970b). Ward and Holly (1966) also

found that desorption of six s-triazines was reversible from nylon

and cellulose triacetate. Hysteresis was not observed in the desorp-

tion isotherms.

The much greater desorption of atrazine from the Cloquato sl

soil reflects its greater mobility in the soil compared to the methoxy

and methylthio compounds (Helling, 1970). These differences in

mobility have been attributed to higher adsorption of the methylthio

and methoxy-s-triazines relative to the chloro analog and a higher

distribution coefficient between s-triazine adsorbed and in solution

(Helling, 1970; and Weber, 1970b).

To extrapolate from these experiments; one would not expect

s-triazine solubility in soils to be significantly altered by salts

under normal agricultural practices. Further, in the presence of

high levels of fertilizers, the s-triazine herbicides in the soil system

could be precipitated and upon addition of water solubilization would

result in increased phytotoxicity. Greater phytotoxicity could occur

for methoxy and methylthio-s-triazines than chloro-s-triazines

because of a greater reduction in adsorption in the presence of low

salt concentrations.

Summary and Conclusions

For all salt amendments, the adsorption of the s-triazines

increased in the order atrazine < GS-14254 < terbutryn. Salt concen-

trations < 1.0 µ reduced s-triazine adsorption compared to the

unamended soils. At equivalent salt concentrations Na or Ca

chloride reduced adsorption of each s-triazine to the same extent.

GS-14254 and terbutryn adsorption was reduced more than atrazine

adsorption because of their higher pKa values and resultant competi-

tion for exchange sites between s-triazine and salt cations. At salt

concentrations > 1.0 µ atrazine and terbutryn adsorption increased

relative to lower salt concentrations by s-triazine salting out in the

double layer. In agreement with solubility data s-triazine adsorption

increased more for Na than Ca chloride salts.

Equivalent amounts of atrazine (75%) were desorbed from

Cloquato soil amended with <1.0 µ salt concentrations irrespective

of the type of salt in the initial equilibrium system. Desorption of

more terbutryn and GS-14254 occurred from salt amended soils (43.7%)

at salt concentrations <1.0 µ than from unamended soils (23.7%).

Terbutryn and GS-14254 were postulated to be adsorbed by H-bonding

with water molecules adsorbed to the cations on the exchange complex,

whereas atrazine with a more electronegative chlorine atom and

lower pKa value did not undergo significant H-bonding by coordination

through adsorbed water molecules.

Desorption of more s-triazine occurred from Cloquato soil initially equilibrated with soil concentrations $> 1.0 \mu$ than at lower salt concentrations. The initial enhanced s-triazine desorption from the soil systems initially equilibrated with $> 1.0 \mu$ salt concentrations occurred through the solubilization of the precipitated s-triazine by the high salt concentration in the double layer. After three extractions with 0.01 $\underline{N}$ CaCl$_2$, similar quantities of s-triazine were desorbed from all treated soils irrespective of the initial equilibrium salt concentration.

Salt levels in the soil solution would not affect the solubility of the s-triazine herbicides. Low salt concentrations in the soil solution would reduce the adsorption of GS-14254 and terbutryn and increase their phytotoxicity to plants. Concentrated fertilizer bands would precipitate the s-triazine herbicides in the soil solution and increase desorption and phytotoxicity under improved moisture conditions.

S-TRIAZINE ADSORPTION AS AFFECTED
BY SOIL CONSTITUENTS

Introduction

The s-triazine herbicides enter the plant system primarily

through the soil environment, hence, selectivity and uptake are

directly linked to their reaction with soil. The s-triazine herbicides

are used on a variety of crops with wide geographical distribution.

The diversity of soils formed under different environments necessi-

tates the investigation of many soil constituents on s-triazine adsorp-

tion to ensure wise and intelligent use of these compounds.

S-triazine phytotoxicity is inversely correlated with clay con-

tent, organic matter, cation exchange capacity and exchangeable

bases (Day, Jordan and Jolliffe, 1968). Adsorption of the chemicals

occurs readily on montmorillonite, illite (Frissel and Bolt, 1962)

and to a lesser extent on kaolinite (Weber and Ward, 1968). Several

investigators have determined that organic matter contributes more

to s-triazine adsorption than clay or cation exchange capacity (Talbert

and Fletchall, 1965; Walker and Crawford, 1968). Highly decomposed

organic material was more reactive to s-triazine adsorption than

fresh plant material because of the decrease in hydrophilic oxygen

groups and increased carbon content (Walker and Crawford, 1968).

In agreement with these results, adsorption takes place on the humic

acid and humin fractions rather than with fulvic acid or polysaccharides (Hayes, 1970).

Nearpass (1967) investigated the effect of pH and exchange acidity on 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine (atrazine) and 2-chloro-4,6-bis(ethylamino)-s-triazine (simazine) adsorption by Bayboro clay. Adsorption was reduced similarly when Mg, Ca, Na or K hydroxide was added at 1/3, 2/3, 1 and 1-1/3 times the KCl exchange acidity of the soil. The equilibrium s-triazine concentration was negatively correlated with the equilibrium solution pH (simazine r = -0.997; atrazine r = -0.960). Equilibrium constants calculated from equilibrium data for s-triazine adsorbed by Bayboro soil neutralized with Ca, Mg, Na or K hydroxide showed that reserve acidity was involved in adsorption.

Model clay minerals and organic preparations have been extensively studied to determine the influence of pH on s-triazine adsorption. The adsorption of several s-triazines by Na-montmorillonite reached a maximum at the ionization constant (pKa) of the s-triazine (Weber, 1970a). Reduced adsorption at pH values below the pKa value was attributed to proton displacement of s-triazine cations. The authors attributed the reduced adsorption at pH values above the pKa to reduced protonation of the chemical. The quantity of s-triazine adsorbed increased with basicity and complexity of the alkylamino functional groups. The order of adsorption for the methoxy,

methylthio and chloro functional groups was SCH_3 > OCH_3 > Cl

and for the alkylamino functional groups NHC_2H_5 - NHC_4H_{9t} >

NHC_2H_5 ~ NHC_4H_{9s} > NHC_2H_5 - NHC_3H_{7i}.

Organic preparations at different pH values produced the same

trends for s-triazine adsorption as observed for montmorillonite

(Weber, Weed and Ward, 1969). Methylthio and methoxy-s-triazines

displayed maximum adsorption at their pKa values (~4) while chloro-

s-triazines had maximum adsorption at pH 2 (pKa ~2) and were less

affected by higher pH.

As the pH of montmorillonite suspensions increased from four

to eight methoxy-s-triazine adsorption was reduced more than

methylthio-s-triazine adsorption. The greater adsorption of methyl-

thio-s-triazines relative to the methoxy analogs has been partly

attributed to lower solubility. The solubility of 2, 4-bis(isopropyl-

amino)-6-methoxy-s-triazine (prometone) was 1.4 times greater

than 2, 4-bis(isopropylamino)-6-(methylthio)-s-triazine (prometryne)

at pH 2 and 18 times greater at pH 7. The larger atomic size of

sulfur may also allow better orientation of methylthio-s-triazine

cations on clay surfaces. The ketotautomer, oxy-methyl isomer

of the methoxy analog would further reduce adsorption by clays due

to the slightly negative charge of the oxygen in the carbonyl group.

Since s-triazine adsorption related closely to acidity and

organic matter an investigation of the reserve acidic groups and

organic matter in soils is warranted. Reserve acidity arises

through the dissociation of hydronium ions from hydrous aluminum

and iron oxides and carboxyl and phenolic groups associated with

organic matter (Jackson, 1963). Acid strength of hydrous oxides

is dependent upon their degree of crystallinity which affects hydronium

dissociation (pKa), i. e. , greater crystallinity produces stronger

Al-OH bonds which are less susceptible to dissociation. It is con-

ceivable that reserve acid sites could play a significant role in s-tri-

azine adsorption.

Recently much effort has centered on a quantitative definition

of the forms of extractable hydrous oxides, i. e. , organic bound,

amorphous (gel and aged) hydrous oxides and crystalline oxides.

The classification of amorphous materials includes discrete colloidal

hydrous oxides of iron, aluminum and silicon and the various solid

solutions of silica, alumina and water referred to as 'allophane'.

Various extraction reagents for the amorphous hydrous oxides permit

a relatively useful but imprecise differentiation of the forms of

amorphous hydrous oxides found in soil materials without greatly

altering the crystalline mineral fraction (McKeague, Brydon and

Miles, 1971; Dudas and Harward, 1971). Extractants and the relative

forms of amorphous hydrous oxides extracted include: 1) 0. 1 M

sodium pyrophosphate - organically bound Fe and Al salts and

amorphous (gel) hydrous oxides, 2) acid ammonium oxalate -

organically bound Fe and Al salts, amorphous (gel and aged) hydrous

oxides and some crystalline forms, i.e., magnetite and 3) boiling

KOH dissolution - amorphous (gel and aged) hydrous oxides and

soluble Al-hydroxy interlayers.

The objectives of this study were to: 1) evaluate the effect of

soil pH on atrazine, 2-(tert-butylamino)-4-(ethylamino)-6-(methyl-

thio)-s-triazine (terbutryn) and 2-(sec-butylamino)-4-(ethylamino)-6

methoxy-s-triazine (GS-14254) adsorption by soils of varied organic

matter and clay content, 2) determine the effect of hydrous oxides,

organically bound Fe and Al salts, and organic matter on atrazine,

terbutryn and GS-14254 adsorption and 3) determine the soil fraction

responsible for enhanced s-triazine adsorption by the high pH Boyce

and Crooked soils.

Materials and Methods

Chemical characterization of selected soils

The Kinney series, Woodcock series, Jory, Parkdale C

horizon, Boyce and Crooked soils were air dried and ground to pass

a 2 mm sieve.

The pH of the soils was measured in a soil paste with a Corning,

Model 7 pH meter. A calibrated glass-calomel combination electrode

was employed.

The carbon content of the soils was determined by dry combustion (Young and Lindbeck, 1964) using a Leco induction carbon analyzer and by wet oxidation with $\underline{N}$ $K_2Cr_2C_7$ and concentrated H_2SO_4 (1:2) (Walkley and Black, 1934).

Cation exchange capacity (CEC) was determined on duplicate soil samples saturated with 0.5 $\underline{N}$ $CaCl_2$. Calcium displacement was accomplished with 0.5 $\underline{N}$ $MgCl_2$ after removal of excess saturating ions with distilled water. The displaced calcium was measured by atomic absorption spectrophotometry.

pH adjustment of soils

The pH of Kinney series, Woodcock series, Jory and Parkdale C horizon soil was adjusted by addition of sufficient $\underline{N}$ NaOH so that 10 or 20 meq base/100 g was present in each system. The soil paste pH was determined with a Corning, Model 7 pH meter after equilibration with s-triazine herbicide solution.

Chemical treatment of soils

Separate samples of Kinney (C= 6.48%), Jory, Parkdale C horizon, Boyce and Crooked soils were treated with: i) acid ammonium oxalate, ii) hydrogen peroxide, iii) sodium pyrophosphate, iv) hydrogen peroxide followed by acid ammonium oxalate, and v) sequential acid ammonium oxalate, boiling potassium hydroxide and acid

ammonium oxalate.

Acid ammonium oxalate extraction. Soil samples (soil:

solution ratio = 1:40) were extracted in darkness four hours with

0.2 M $(NH_4)_2C_2O_4$ (pH 3) (McKeague and Day, 1966).

Sodium pyrophosphate extraction. The soil samples were

extracted 16 hours in 250 ml centrifuge bottles with 0.1 M $Na_4P_2O_7$

(soil:solution ratio = 1:40) (Aleksandrova, 1960).

Hydrogen peroxide oxidation. The soil samples (100 g) were

weighed into one liter beakers and reacted with 30% hydrogen peroxide

diluted to 6% during the reaction time. The oxidation process was

conducted in a water bath at 60-70 C and continued until no further

reaction was observed with addition of 30% hydrogen peroxide.

Potassium hydroxide dissolution. The soil samples were

boiled 2.5 minutes in 0.5 $\underline{N}$ KOH (soil:solution ratio = 1:1000) after

which the samples were cooled and separated from the soil by sedi-

mentation and centrifugation. The procedure was similar to that of

Hashimoto and Jackson (1960) except KOH was used to minimize

destruction of micaceous minerals.

Ammonium acetate extraction. The Boyce and Crooked soils

were extracted eight times with 0.5 $\underline{N}$ CH_3COONH_4 (pH 4.8; soil:

solution ratio = 1:4). Excess CH_3COONH_4 was removed with four

20 ml portions of distilled water.

Water leached. Three liters of distilled water were leached

through 50 grams of Boyce and Crooked soils.

Acid leached. Two hundred grams of Boyce and Crooked soils were leached with two liters of 0.1 $\underline{N}$ HCl followed by one liter of 0.1 $\underline{N}$ NaCl. Excess ions were removed with distilled water.

Preparation of chemically extracted soils

Ten meq NaOH/100 g were added to separate subsamples from each of the acid and water leached, ammonium acetate and one-half hour acid ammonium oxalate extracted Boyce and Crooked soils.

After extraction of the various soils, the excess acid ammonium oxalate, sodium pyrophosphate and ammonium acetate extractant was removed by centrifugation. Two to six 100 ml washes with distilled water removed the occluded extractant. Upon removal of excess extractant, the soil samples were sodium saturated with four portions of 0.5 $\underline{N}$ NaCl followed by two to five 100 ml washes with distilled water until a constant pH was maintained. The soils were then dried at 70 C, ground and used for chemical characterization (carbon content and CEC) and herbicide adsorption studies.

The acid ammonium oxalate, sodium pyrophosphate and potassium hydroxide extracts were analyzed for iron, aluminum and silica by atomic absorption spectrophotometry. Cation exchange capacity and carbon were determined as stated previously.

S-triazine adsorption by soils after selected treatments

Stock solutions of five ppm ^{14}C-ring labeled atrazine, terbutryn and GS-14254 were prepared in distilled water. One or five gram

soil samples which had been subjected to the previously mentioned treatments were equilibrated > 12 hours with the s-triazine solutions (soil:solution ratio = 1:2). The five gram samples were equilibrated at 25 C in a constant temperature shaking water bath. The one gram samples were equilibrated with a Burrell wrist action shaker at room temperature. Adsorbent and solution were separated by centrifugation for 20 minutes at 14,000 rpm.

S-triazine analysis

A one ml aliquot of the supernatant solutions was analyzed by liquid scintillation spectrophotometry and herbicide adsorption determined by difference in activity before and after equilibration with the soil. The scintillation fluor consisted of toluene: Triton X-100 (2:1 v/v), PPO (2,5-diphenyloxazol, 4 g/l) and POPOP [1,4-bis-2-(5-phenyloxazolyn)-benzene, 0.10 g/l].

A one-half ml aliquot from highly color quenched samples was digested three hours at 75 C in two-tenths ml perchloric acid and one-half ml of 30% hydrogen peroxide. After digestion to a clear solution and cooling, six ml of cellusolve (ethylene glycol monoethyl ether) and ten ml toluene phosphor containing PPO (6 g/l) were added to each vial. Recovery of s-triazine added to one-half ml unlabeled extracts was approximately 100% after digestion. Adsorption was calculated by the equation:

$$\left[\frac{A - (\frac{C - B}{SA \times CE})V}{A} \right]100 = \% \text{ adsorbed}$$

where A = s-triazine added (μg), C = activity of aliquot (cpm/ml),

B = background (cpm), V = total volume (ml), CE = count efficiency

(cpm/dpm, determined by internal spiking) and SA = herbicide spe-

cific activity (dpm/μg).

Results and Discussion

Influence of pH on s-triazine adsorption

S-triazine adsorption increased in the order chloro < methoxy <

methylthio for the soils investigated (Table 1). A similar order was

determined for s-triazine adsorption by montmorillonite and organic

matter (Weber, 1970a; Weber et al., 1969).

The addition of 10 or 20 meq NaOH/100 g generally decreased

the adsorption of the three s-triazines investigated. Correlation

coefficients between the s-triazine adsorbed and pH were highly sig-

nificant for all chemicals; however, a much higher correlation

coefficient was calculated for GS-14254 (r = -0.88) and terbutryn

(r = -0.71) than for atrazine (r = -0.55) (Table 1).

The addition of base to the soils always decreased GS-14254

and terbutryn adsorption. Atrazine adsorption was much less

predictable upon addition of base since increased adsorption (3.2%

Table 1. Chemical and physical properties of selected soils and related s-triazine adsorption.

| Soil series | Carbon | Clay | CEC | Exchange Acidity | pH | S-triazine adsorbed, % | | |
	------%--------		----meq/100 g------			Atrazine	Terbutryn	GS-14254
Kinney	6.48	36.0	6.5	42.6	5.6	74.6	98.9	99.2
			nd*	32.6	6.7	71.8	98.4	98.3
			nd	22.6	7.2	68.6	97.5	94.3
Kinney	2.08	41.5	8.9	31.1	5.7	80.5	99.4	99.8
			nd	21.1	6.4	61.4	97.5	98.6
			nd	11.1	7.2	38.7	90.6	85.7
Kinney	0.74	31.0	16.1	27.9	5.4	76.3	99.7	99.7
			nd	17.9	6.2	71.0	98.9	99.4
			nd	7.9	6.8	26.1	90.1	91.8
Woodcock	6.00	16.5	12.9	31.1	6.3	65.7	96.6	96.6
			nd	21.1	7.4	71.7	94.7	83.7
			nd	11.1	8.0	70.3	93.8	74.2
Woodcock	3.18	13.0	3.6	28.3	5.8	57.7	95.2	96.5
			nd	18.3	7.6	49.5	90.6	73.1
			nd	8.3	8.3	50.2	89.7	64.1
Woodcock	1.21	8.0	3.2	22.4	6.0	61.4	96.3	98.1
			nd	12.4	7.6	28.5	76.5	61.1
			nd	2.4	8.5	21.0	68.2	34.5
Jory	2.36	33.6	10.5	21.9	5.9	51.9	95.6	93.6
			nd	11.9	7.6	57.0	84.4	61.6
			nd	1.9	9.0	55.1	80.0	54.7
Parkdale C	0.78	9.4	4.0	nd	7.2	18.2	63.7	59.7
			nd	nd	9.1	18.1	44.2	23.1
pH correlation coefficients (r)						-0.55**	-0.71**	-0.88**

*not determined

and 6. 0%) occurred by Jory and Woodcock (C = 6.00%) soils and

decreased adsorption occurred with the Kinney, Woodcock (C = 3.18%

and 1.21%) and Parkdale C soils. Atrazine, terbutryn and GS-14254

adsorption decreased more markedly for the soils with lower carbon

contents.

The effect of pH on methoxy and methythio-s-triazine adsorp-

tion by soils is consistent with studies by Weber (1970a) and Weber

et al. (1969), who observed a decrease in s-triazine adsorption by

Na-montmorillonite and soil organic matter preparations over the

pH range four to seven. Colbert (1972) and Weber (1970b) also

determined that adsorption of methoxy analogs was reduced more

than methylthio analogs over a similar pH range. Weber (1970a)

suggested that for a pH range from five to ten the solubility of

methylthio-s-triazines was reduced less than for methoxy-s-triazines.

He further indicated that the methoxy analog had a lower affinity for

clay surfaces than the methylthio analog. Hance (1969) questioned

the contribution of the clay surface to s-triazine adsorption in soil

systems since 78% of the atrazine adsorbed by a synthetic Ca-humate:

Ca-montmorillonite (humate = 14.5%) mixture was accounted for by

the organic fraction. Organic matter is adsorbed to clay minerals

interlamellarly (Kodama and Schnitzer, 1971) as well as externally

(Greenland, 1965b) but whether it is uniformly coated over the

particles or adsorbed in discrete islands is not fully understood.

The terbutryn and GS-14254 herbicides were readily adsorbed by the Kinney soil series and were relatively unaffected by addition of base (Table 1). The high adsorption of terbutryn (90% to 99%) and GS-14254 (86% to 99%) by the Kinney soil series indicates adsorption may take place in the hydrophobic fraction of the organic matter or by the clay fraction. The pH change (5.6 to 7.2) which occurred in these soils (Table 1) would certainly have an effect on carboxyl groups of the organic fraction and hence adsorption.

Ward and Holly (1966) established a linear relationship between s-triazine adsorption and partitioning between water and cyclohexane. This relationship and the fact that the s-triazines are relatively nonpolar would indicate an affinity for hydrophobic surfaces. Their studies on nylon and cellulose triacetate and the research of Armstrong and Chesters (1968) with carboxyl and phenolic resins suggests the importance of COOH and OH functional groups in adsorption. Walker and Crawford (1968) suggested that the $-(CH_2)_6-$ groups in nylon and the blocking of the hydrophilic groups by acetate groups in cellulose triacetate could produce a hydrophobic nature to these adsorbents which would be responsible for adsorption. Because of the organic nature of exchange resins the same argument could apply to the results of Armstrong and Chesters (1968) although the importance of the carboxyl groups in catalyzing hydrolysis was emphasized. The explanation of Walker and Crawford (1968) seems more

compatible with the observed correlation between adsorption and hydrophobicity of the s-triazines.

Greenland (1965a) reviewed the mechanisms proposed for binding humic substances to clay minerals. The bonds most commonly postulated involved coulombic attraction and H-bonding between the more polar hydrophilic groups of the molecules leaving the more hydrophobic molecules available for s-triazine adsorption. The presence of sesquioxides or amorphous components also could replace adsorption sites lost by the neutralization of the organic fraction.

The decreased s-triazine adsorption by the Woodcock series and Parkdale C soils (clay < 20%) upon addition of NaOH indicate pH dependent organic functional groups are significantly involved in adsorption by these soils (Table 1). The low clay content and high availability of hydrophilic COOH groups for s-triazine adsorption could account for the decrease in adsorption as pH increased.

Atrazine adsorption appeared to be interrelated with pH, organic matter and sesquioxide or mineral content. Small responses to pH changes were measured for 2-chloro-4, 6-bis(isopropylamino)-s-triazine (propazine) and prometryne adsorption on an organic soil (C = 13.6%) while soils low in carbon (1.5%) and a bentonite clay displayed the expected reduction in adsorption as the pH increased (Walker and Crawford, 1968). These authors indicated different

mechanisms were responsible for adsorption on the two surfaces,
viz., minerals: ion-induced dipoles, organic soils: nonspecific
reactions with hydrophobic groups.

The neutralization of 91% and 72% respectively of the exchange
acidity in the Jory (C = 2.36%) and Kinney (C = 2.08%) soils changed
atrazine adsorption +3.2% and -41.8% respectively. Nearpass (1967)
showed that atrazine and simazine adsorption by Bayboro soil
decreased as exchange acidity decreased upon the addition of base;
however, in this study atrazine adsorption by soils high in carbon
and clay content was not correlated with exchange acidity.

In summary, terbutryn and GS-14254 adsorption always
decreased upon addition of base, whereas atrazine adsorption could
not reliably be predicted by changes in pH. The decreased terbutryn
and GS-14254 adsorption upon addition of base appeared to relate to
hydrophilic carbon sites, clay content, s-triazine solubility and
differences in the methylthio and methoxy functional groups. Atra-
zine, terbutryn and GS-14254 adsorption occurred on nonspecific,
hydrophobic carbon sites when the clay and carbon content of the
soils were high.

Adsorption by Kinney, Jory and Parkdale C soils

Exclusive of the reduced adsorption of terbutryn and GS-14254
by a pH increase upon addition of NaOH and with sodium pyrophosphate

extraction, all extraction treatments increased s-triazine adsorption by the Parkdale C horizon, Jory and Kinney (C = 6.48%) soil series (Table 2). S-triazine adsorption before and after all treatments followed the order atrazine < GS-14254 < terbutryn.

Chemical extractions or hydrogen peroxide oxidation of the Kinney and Jory soils had little effect on terbutryn and GS-14254 adsorption (Table 2). Extraction of the organically complexed sesquioxides by sodium pyrophosphate reduced terbutryn and GS-14254 adsorption by the same magnitude as the addition of 10 meq NaOH/100 g. The accompanying rise in pH from 5.4 to 9.5 (Table 3) brought about by the alkaline sodium pyrophosphate extractant makes it difficult to determine if the reduction in adsorption is due solely to a pH change or to the removal of Fe and Al constituents. Adsorption may occur at the organically complexed Fe and Al acid sites which may be neutralized by base.

The acid ammonium oxalate extraction before and after hydrogen peroxide oxidation produced a slight increase in terbutryn and GS-14254 adsorption by the Kinney and Jory soils (0,4% to 6.5%) (Table 2). Adsorption sites altered or removed by the hydrogen peroxide oxidation treatment and acid ammonium oxalate extraction were probably compensated for by the residual carbon and sesquioxides remaining in the soils and the exposed clay surfaces. Further removal of amorphous components by the KOH dissolution sequence

Table 2. Atrazine, terbutryn and GS-14254 adsorption by Kinney, Jory and Parkdale C soils.

	S-triazine adsorbed, %								
	Atrazine			Terbutryn			GS-14254		
				Soil series					
Treatment	Kinney	Jory	Parkdale C	Kinney	Jory	Parkdale C	Kinney	Jory	Parkdale C
None	74.5	51.8	18.2	98.8	95.6	63.7	99.2	93.6	59.7
10 meq NaOH/100 g	73.2	57.0	18.1	98.4	84.4	44.2	98.3	61.6	23.1
$(NH_4)_2C_2O_4$	96.4	79.6	58.1	100.0	99.5	96.0	100.0	99.7	96.7
$Na_4P_2O_7$	94.5	67.9	27.3	98.5	87.9	68.5	97.2	70.5	29.0
H_2O_2	85.5	36.7	21.4	99.5	97.1	74.7	99.7	97.8	84.9
$H_2O_2 + (NH_4)_2C_2O_4$	91.2	56.2	59.3	99.2	98.3	97.5	99.6	99.1	98.8
$H_2O_2 + (NH_4)_2C_2O_4$ +KOH + $(NH_4)_2C_2O_4$	93.8	75.6	48.1	98.9	98.7	95.1	98.4	99.5	98.6

LSD_{05} = 4.7%, LSD_{01} = 7.1% for atrazine adsorption by Kinney, Jory and Parkdale C soils.

Table 3. Chemical properties of Kinney, Jory and Parkdale C soils after chemical extraction.

Soil series	Treatment	pH	Carbon %	CEC meq/100g	Fe_2O_3 ----- %	Al_2O_3 -----	$\frac{SiO_2}{Al_2O_3}$
Kinney	None	5.6	6.48	6.5	nd*	nd	nd
	$(NH_4)_2C_2O_4$	6.1	6.11	26.3	1.37	4.06	0.15
	$Na_4P_2O_7$	9.3	4.40	33.8	0.93	2.09	0.05
	H_2O_2	7.0	1.36	11.0	nd	nd	nd
	$H_2O_2+(NH_4)_2C_2O_4$	6.1	1.25	15.0	1.60	3.45	0.17
	$H_2O_2+(NH_4)_2C_2O_4+$ KOH+$(NH_4)_2C_2O_4$	5.9	1.23	20.0	2.98	11.2	0.95
Jory	None	5.4	2.36	10.5	nd	nd	nd
	$(NH_4)_2C_2O_4$	6.2	2.12	11.3	1.52	1.26	0.16
	$Na_4P_2O_7$	9.5	1.27	13.1	0.14	0.31	0.23
	H_2O_2	7.0	0.55	8.5	nd	nd	nd
	$H_2O_2+(NH_4)_2C_2O_4$	6.2	0.54	9.0	1.82	1.30	0.13
	$H_2O_2+(NH_4)_2C_2O_4+$ KOH+$(NH_4)_2C_2O_4$	6.0	0.64	12.3	3.70	7.98	0.98
Parkdale C	None	7.2	0.78	4.0	nd	nd	nd
	$(NH_4)_2C_2O_4$	6.5	0.61	5.3	1.49	5.10	0.67
	$Na_4P_2O_7$	9.5	0.48	10.2	0.02	0.19	0.10
	H_2O_2	7.1	0.26	4.0	nd	nd	nd
	$H_2O_2+(NH_4)_2C_2O_4$	6.1	0.23	4.9	1.49	4.90	0.68
	$H_2O_2+(NH_4)_2C_2O_4+$ KOH+$(NH_4)_2C_2O_4$	6.1	0.16	4.3	2.49	6.37	0.98

* not determined

did not produce any further changes in adsorption although twice as much Fe and Al oxides (Table 3) were removed by this treatment.

The negligible effect of hydrogen peroxide oxidation of organic matter and removal of amorphous components from Kinney and Jory soils on terbutryn and GS-14254 adsorption suggests these chemicals have an equal affinity for mineral and carbon surfaces. Walker and Crawford (1968) observed a strong dependence of prometone for adsorption to mineral surfaces while prometryne showed equal affinity for both surfaces.

Atrazine adsorption was much more affected by the chemical extractions of the Jory and Kinney soils (Table 2). Acid ammonium oxalate and sodium pyrophosphate extractions increased atrazine adsorption markedly (20% to 30%). These extractants remove Fe and Al associated with the organic and mineral fractions (McKeague et al., 1971) thereby releasing organic functional groups. Atrazine adsorption may be strongly dependent upon organic surfaces (Walker and Crawford, 1968). Further support that atrazine adsorption occurs by the organic fraction is indicated by the large decrease (15.1%) in adsorption by the Jory soil following hydrogen peroxide oxidation of the organic matter. The increased adsorption by Kinney soil (11%) following hydrogen peroxide oxidation may be associated with reprecipitation of organically released Fe and Al components to form highly reactive gel hydrous oxides (Table 3). The increase

in atrazine adsorption by the Kinney and Jory soils after the acid ammonium oxalate extraction and the KOH dissolution sequence may reflect further liberation of residual organic sites or activation of residual amorphous components through the removal of aged hydrous oxide surfaces and interlayer aluminum hydroxide polymers. The pH of these soils is high enough (pH 6) to exclude coulombic attractive forces between the clay mineral and atrazine (pKa = 1.68); however, H-bonding between hydroxyls of the amorphous components and the chloro or 4,6-N-alkylamino functional groups is possible.

The Parkdale C horizon soil responded quite differently to s-triazine adsorption following the different treatments. Except for the pH effect from the addition of base and after sodium pyrophosphate extraction which reduced GS-14254 and terbutryn absorption, all treatments on the Parkdale C soil increased s-triazine adsorption equally (30% to 40%) (Table 2). Although significant quantities of amorphous components were removed (15%) by the KOH dissolution sequence, such removal only served to expose more reactive sites. Skipper (1970) had determined that 49.1% of the clay fraction of the Parkdale C soil was amorphous. S-triazine adsorption by the organic fraction in the Parkdale C soil (C = 0.78%) would be negligible. The low adsorption of atrazine (18%), terbutryn (64%) and GS-14254 (60%) by the untreated Parkdale C soil indicate that the aged hydrous oxides are less reactive than the gel hydrous

oxides exposed by the extractants.

No studies on the effect of amorphous components on s-triazine adsorption have been reported; however, silica gel (SiO_2), Florisil (a magnesium silicate) and alumina (Al_2O_3) have been used to selectively partition s-triazines for removal of impurities prior to s-triazine identification (Delley et al., 1967; Mattson, Kahrs and Murphy, 1970). Differential adsorption of the s-triazines by these adsorbents is controlled by adsorbent pH and water content and solvent polarity. The low adsorption by the Parkdale C untreated soil could indicate that aged hydrous oxide surfaces and coatings are less reactive to s-triazines because of their more crystalline nature. Also, allophanic materials contain a large number of hydroxyl groups (Wada, 1966) that may participate in H-bonding with s-triazines.

The adsorption of the s-triazines by the Parkdale C soil also demonstrates that CEC sites are not responsible for adsorption as this property did not change with treatment (CEC = 4 meq/100 g) (Table 3) but pH dependent CEC sites were not measured.

Adsorption by Boyce and Crooked soils

Abnormally high adsorption of atrazine (84% and 92%), terbutryn (94% and 99%) and GS-14254 (94% and 99%) by Boyce and Crooked soils respectively has been attributed to s-triazine salting out and/or

Table 4. Chemical properties of Boyce and Crooked soils after chemical extraction.

Soil series	Treatment	pH	Carbon %	CEC meq/100 g	Fe_2O_3 %	Al_2O_3 %	$\dfrac{SiO_2}{Al_2O_3}$
Boyce	None	8.7	1.30	42.5	nd*	nd	nd
	$(NH_4)_2C_2O_4$ (4 hr)	7.4	1.77	71.3	0.14	0.28	0.86
	$Na_4P_2O_7$	9.1	0.58	57.4	0.01	0.01	22.2
	H_2O_2	8.1	0.37	38.8	nd	nd	nd
	$H_2O_2+(NH_4)_2C_2O_4$	7.6	0.67	50.0	0.19	0.41	0.81
	$H_2O_2+(NH_4)_2C_2O_4+$ KOH+$(NH_4)_2C_2O_4$	6.9	0.43	23.8	0.78	0.67	7.55
	$(NH_4)_2C_2O_4$ (1/2 hr)	8.7	nd	nd	0.06	0.21	0.24
Crooked	None	8.0	0.91	66.3	nd	nd	nd
	$(NH_4)_2C_2O_4$ (4 hr)	7.5	1.19	76.3	0.20	0.35	1.03
	$Na_4P_2O_7$	9.3	0.29	61.1	0.01	0.01	31.7
	H_2O_2	7.9	0.28	50.0	nd	nd	nd
	$H_2O_2+(NH_4)_2C_2O_4$	7.4	0.56	51.3	0.22	0.43	0.79
	$H_2O_2+(NH_4)_2C_2O_4+$ KOH +$(NH_4)_2C_2O_4$	6.9	0.43	68.0	0.86	0.76	7.78
	$(NH_4)_2C_2O_4$ (1/2 hr)	8.6	nd	nd	0.08	0.24	0.22

* not determined

hydrolysis of the methylthio, methoxy or chloro functional group
(Colbert, 1972).

The contribution of carbon contained by the Boyce (1.30%) and
Crooked (0.91%) soils (Table 4) was insignificant in s-triazine adsorp-
tion as reflected by no change after oxidation of the soils with hydro-
gen peroxide (Tables 5 and 6).

Leaching with water had no significant effect on atrazine adsorp-
tion by Crooked soil even when ten meq NaOH/100 g was added (pH
9.6) to the soil prior to equilibration with atrazine (Table 5). Adsorp-
tion by Boyce soil was reduced 4.6% for the same treatment. These
results and the uniform low adsorption of atrazine (38%) by Cloquato
soil amended with <1 ionic strength salt concentrations (Chapter 2,
Table 1) preclude the possibility of increased adsorption due to salting
out.

Excessive leaching of Boyce and Crooked soils with HCl and ex-
haustive extraction with CH_3COONH_4 (pH 4.8) produced minor
changes in atrazine adsorption (Table 5). Leaching with HCl and
extraction with CH_3COONH_4 increased atrazine adsorption from
84% to 100% partly because of the reduced pH (4.6 and 5.7). The
addition of ten meq NaOH/100 g to the Boyce and Crooked soils
after these treatments raised the pH to 9.5 and decreased adsorption
by Boyce soil 11.6% and 1%. Atrazine adsorption decreased 3.5%
by the pH adjusted, HCl leached Crooked soil but adsorption remained
at 100% after the addition of base to the ammonium acetate extracted

Table 5. Atrazine adsorption by Boyce and Crooked soils after chemical extraction.

Treatment	Atrazine adsorbed, %	
	Boyce	Crooked
None	84. 1	91. 6
10 meq NaOH/100 g (2)	77. 8	92. 3
CH_3COONH_4	99. 3	100. 0
(2) + CH_3COONH_4	83. 1	100. 0
H_2O	79. 5	89. 5
(2) + H_2O	79. 2	91. 0
HCl	99. 8	99. 9
(2) + HCl	72. 5	88. 1
$(NH_4)_2C_2O_4$ (1/2 hr)	65. 0	79. 1
(2) + $(NH_4)_2C_2O_4$ (1/2 hr)	57. 4	73. 6
$(NH_4)_2C_2O_4$ (4 hr)	38. 7	52. 4
$Na_4P_2O_7$	65. 1	81. 4
H_2O_2	83. 3	92. 6
$H_2O_2 + (NH_4)_2C_2O_4$ (4 hr)	35. 5	50. 8
$H_2O_2 + (NH_4)_2C_2O_4 +$ KOH $+ (NH_4)_2C_2O_4$	17. 8	21. 4

LSD_{05} = 3.6%, LSD_{01} = 4.9%

Table 6. Terbutryn and GS-14254 adsorption by Boyce and Crooked soils after chemical extraction.

Treatment	Terbutryn adsorbed, %		GS-14254 adsorbed, %	
	Boyce	Crooked	Boyce	Crooked
None	96.0	99.2	94.2	99.3
$(NH_4)_2C_2O_4$	80.7	87.2	86.9	92.7
$Na_4P_2O_7$	88.0	93.7	71.3	87.6
H_2O_2	93.5	97.5	94.1	96.1
$H_2O_2 + (NH_4)_2C_2O_4$	89.8	94.2	94.0	97.4
$H_2O_2 + (NH_4)_2C_2O_4 +$ KOH $+ (NH_4)_2C_2O_4$	68.1	68.6	63.8	69.6

Terbutryn LSD_{05} = 5.9%, LSD_{01} = 9.8%

GS-14254 LSD_{05} = 1.6%, LSD_{01} = 2.6%

soil. The acid leaching treatments would dissolve carbonates; however, this fraction does not appear to have a significant effect on adsorption.

The small but significant reduction in atrazine adsorption by Boyce soil after acid leaching and pH adjustment with base suggested a relationship with amorphous components. The acid ammonium oxalate extraction before and after hydrogen peroxide oxidation of organic matter reduced atrazine adsorption 46.9% and 39.6% respectively by the Boyce and Crooked soils (Table 5). Smaller but significant changes in terbutryn and GS-14254 adsorption also accompanied the acid ammonium oxalate extraction (Table 6). Sodium pyrophosphate extraction reduced s-triazine adsorption 6% to 23%.

Further removal of amorphous components with the KOH dissolution sequence reduced atrazine adsorption (Boyce = 17.8%; Crooked = 21.4%) to levels predicted by pH and chemical properties. Terbutryn and GS-14254 adsorption was reduced 30% by the corresponding treatment.

The reduction of adsorption brought about by the removal of amorphous Fe and Al components indicates the importance of this fraction towards adsorption by the Boyce and Crooked soils. Although considerably less amorphous material was removed from the Boyce and Crooked soils relative to the Kinney, Jory and Parkdale C soils (Tables 3 and 4), its contribution to adsorption may be greater

because of the low carbon and clay content, and the high pH.

The sodic Boyce and calcareous Crooked soils occur under low rainfall conditions and are frequently subject to flooding (Anonymous, 1966). The poorly drained condition, low rainfall and high pH have combined to keep weathered alumina and silica in the environment (SiO_2/Al_2O_3 for the KOH dissolution sequence of the Boyce and Crooked soils = 7.6 and 7.8 respectively). Corresponding SiO_2/Al_2O_3 ratios for the Kinney, Jory and Parkdale C soils subjected to the same treatment were 0.95, 0.98 and 0.98 respectively. The Kinney, Jory and Parkdale C soils occur under high rainfall and have undergone extensive leaching and weathering.

Hydroxy aluminum polymers precipitate on clay surfaces in soils of pH > 7 (Hsu and Bates, 1964) and in the presence of silica, amorphous or allophanic alumino-silicate minerals could be formed (Chichester, 1967). H-bonding between oxygen or hydroxyl groups and s-triazine ring nitrogen atoms at the one and/or three position or methylthio, methoxy or chloro functional groups could take place on these surfaces. The importance of these sites in s-triazine adsorption was inferred from the high adsorption by Parkdale C soil after removal of aged outer coatings of amorphous components.

In summary, s-triazine adsorption is reduced less with lime applications to soils high in carbon content (> 2.5%) and clay minerals (> 31%). In mineral soils GS-14254 adsorption decreased more than

terbutryn adsorption as pH increased. Atrazine adsorption could not reliably be predicted by changes in pH. Terbutryn and GS-14254 adsorption occurred to the same extent on organic, mineral and/or sesquioxide surfaces while atrazine adsorption occurred on amorphous materials and organic surfaces.

The high s-triazine adsorption by the Boyce and Crooked soils occurred on the amorphous iron and aluminum hydroxy component. Chemical extraction of the Boyce and Crooked soils with sodium pyrophosphate, acid ammonium oxalate and the potassium hydroxide dissolution sequence reduced s-triazine adsorption. Leaching the soils with acid ammonium acetate, HCl and water did not greatly influence adsorption.

Summary and Conclusions

S-triazine adsorption by the soils studied increased in the order atrazine <GS-14254 <terbutryn. Upon addition of each increment of base, terbutryn and GS-14254 adsorption always decreased, whereas atrazine adsorption increased 6% and 5% in Woodcock and Jory soil. A greater reduction in GS-14254 adsorption by soils relative to terbutryn, occurred with equivalent increases in soil pH because the solubility of the methoxy-s-triazine increased more rapidly as pH increased and the larger sulfur atom bonds more readily to clay mineral surfaces than the oxygen atom. S-triazine adsorption occurred in nonspecific hydrophobic sites in carbon since soils with > 2. 5% carbon and > 31% clay greatly reduced the reduction

in s-triazine adsorption relative to soils lower in carbon and clay minerals upon addition of base.

Extraction of the amorphous hydrous oxides with ammonium oxalate and the potassium hydroxide dissolution sequence did not greatly affect terbutryn and GS-14254 adsorption by Kinney and Jory soils. Oxidation of the soil carbon with hydrogen peroxide produced a similar effect, thus, terbutryn and GS-14254 appeared to have an equal affinity for mineral and organic surfaces. Hydrogen peroxide oxidation of organic matter reduced the atrazine adsorption 15% by Jory soil which suggested chloro-s-triazine adsorption occurred to a greater extent in the hydrophobic than mineral surfaces relative to the methoxy and methylthio analogs. Extraction of the Kinney and Jory soils with ammonium oxalate, sodium pyrophosphate and the potassium hydroxide dissolution sequence increased atrazine adsorption through the liberation of hydrophilic carbon sites and synthesis of gel hydrous oxide surfaces.

S-triazine adsorption by Parkdale C horizon soil increased 30% to 40% after chemical extraction of the hydrous oxides but smaller increases in s-triazine adsorption were observed after hydrogen peroxide oxidation. The increased adsorption after chemical extraction occurred after removal of less reactive, aged hydrous oxide surfaces and exposure or synthesis of more reactive, gel hydrous oxide surfaces.

Atrazine (84% and 92%), terbutryn (96% and 99%) and GS-14254

(94% and 99%) were highly adsorbed by the high pH Boyce and Crooked

soils. Removal of soluble salts, inorganic and organic carbon by

leaching with water, hydrochloric acid and hydrogen peroxide oxida-

tion did not greatly change s-triazine adsorption. Chemical extrac-

tion of the hydrous oxides with ammonium oxalate before and after

the hydrogen peroxide treatment reduced atrazine adsorption 40%

to 45%. The potassium hydroxide dissolution treatment removed

additional hydrous oxide components and further reduced s-triazine

adsorption, thus, this fraction appeared to be responsible for the

enhanced adsorption by the Boyce and Crooked soils. The results

suggest that weathered silica and alumina remained in the poorly

drained soil profile to form gel hydrous oxide components which

provided a suitable surface for s-triazine adsorption.

S-TRIAZINE SURFACE AND SUBSURFACE MOVEMENT IN SOILS

Introduction

The soil active s-triazine herbicides constitute one of the most widely used and useful families of herbicides. Because of their wide and diversified use under many different soil conditions, s-triazine movement to adjacent fields and waterways by surface runoff could occur. Also, the s-triazine herbicides could leach through coarse textured soils and contaminate ground water thereby causing an adverse effect on nontarget organisms. Recently the literature concerned with subsurface and lateral movement of the s-triazine compounds has been extensively reviewed (Helling, 1970).

Losses of atrazine[3] applied at 3.4 kg/ha to Cecil sl soil (slope = 6.5%) by lateral movement were 7.3% after a one hour application of 6.4 cm of simulated rainfall (White et al., 1967). A simulated rainfall of 1.2 cm for one hour, which more approximated a normal storm, induced surface losses by runoff and sediment transport of 2%. Proximity of rainfall to herbicide application date greatly affected runoff losses. Simulated rainfall applications of 3.1 cm one and 96 hours after the atrazine application, resulted in losses by surface runoff and sediment transport of 12.0% and 5.3%

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[3] Common and chemical names of s-triazines reported herein are listed in Table 1.

respectively. Under natural rainfall conditions annual losses

by surface runoff and sediment transport of atrazine applied at

rates from 0. 6 to 9. 0 kg/ha to Hagerstown sicl soil (slope = 14%)

averaged 2. 6% (Hall, Pawlus and Higgins, 1972). Most of the

herbicide loss by surface runoff occurred during the first month after

herbicide application. The percentage lost in the surface waters and

transported sediment ranged from 1. 7% to 3. 7% and was independent

of atrazine application rate. Approximately 53% and 15% of the

applied atrazine was extracted from the soil at the 0-10 cm and 10-20

cm depth within one month of application. From these studies it was

concluded that the magnitude of atrazine losses by lateral movement

was dependent upon storm intensity and frequency, storm proximity

to herbicide application date, crop cover and density, rate and

formulation of herbicide, topography and soil characteristics.

Leaching of s-triazine herbicides is related to herbicide solu-

bility, formulation and application rate, adsorption characteristics

and water application rates. Helling (1970) compiled data from

many sources and established the order of increasing s-triazine

mobility with texture as clay loam < loam < silt loam < sandy loam.

The high adsorption and low solubility of the s-triazine herbicides

has generally prevented leaching to depths greater than 15. 2 cm

(Helling, 1970). Leaching in fine textured soils to depths greater

than the plow layer has been observed when rainfall averaged 28

Table 1. Chemical designation of s-triazines mentioned in text.

Common name	Chemical name
Ametryne	2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine
Atratone	2-(ethylamino)-4-(isopropylamino)-6-methoxy-s-triazine
Atrazine	2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine
GS-14254	2-(sec-butylamino)-4-(ethylamino)-6-methoxy-s-triazine
Terbutryn	2-(tert-butylamino)-4-(ethylamino)-6-(methylthio)-s-triazine
Prometone	2,4-bis(isopropylamino)-6-methoxy-s-triazine
Prometryne	2,4-bis(isopropylamino)-6-(methylthio)-s-triazine
Propazine	2-chloro-4,6-bis(isopropylamino)-s-triazine
Simazine	2-chloro-4,6-bis(ethylamino)-s-triazine

inches and high rates (> 4 kg/ha) of simazine or atrazine were

applied (Helling, 1970). Leaching up to 20 cm has been reported

in coarse textured soils at rates < 4 kg/ha. Usually the highest

concentrations of s-triazine are found in the top 7. 6 cm.

The tendency for s-triazines to leach in soils is directly

correlated to adsorption (Helling, 1970). Weber (1970a) and Weber,

Weed and Ward (1969) measured maximum adsorption of several

s-triazines by montmorillonite and soil organic matter at the respec-

tive pKa values of the s-triazine. At pH values below the pKa of the

s-triazines adsorption took place via coulombic forces while H-bond-

ing was postulated at pH values above the pKa value. Desorption of

prometone (pKa = 4. 28) from montmorillonite was irreversible with

deionized water at a suspension pH < 6 (Weber, 1966) indicating

leaching in acid soils would be greatly reduced. Nearpass (1965)

observed greater leaching of simazine in limed soil and suggested

decreased adsorption occurred at the higher pH.

This research was conducted to determine the 1) effect of

rainfall on atrazine and terbutryn losses by runoff and sediment

transport from unlimed and limed soil; 2) leaching of the atrazine

and terbutryn and 3) relation of atrazine and terbutryn adsorption

to the leaching and runoff observations.

Materials and Methods

Site location and soil characterization

The runoff and leaching trial was located 15 miles north of Corvallis and one mile west of Suver, Oregon at the USDA-SCS Plant Materials Testing farm. The trial was located on a Peavine soil series with a 3-5% north facing slope. The soil is well drained with an average depth to bedrock of one and one-half feet.

Soil samples were collected for chemical analysis in 7.6 cm increments to a total depth of 45.7 cm before and after liming the test plots. The soils were air dried and ground and pH, carbon content, exchangeable bases, extractable aluminum and cation exchange capacity measured.

The soil paste pH was determined with a Corning, Model 7 pH meter. A single combination glass-calomel electrode was used.

Carbon content was determined by oxidizing duplicate soil samples with $\underline{N}$ $K_2Cr_2O_7$ and concentrated H_2SO_4 (1:2, v/v) (Walkley and Black, 1934). After cooling, the samples were diluted with distilled water and the excess $Cr_2O_7^=$ was determined by titration in the presence of 'Ferroin' indicator with 0.35 $\underline{N}$ $Fe(NH_4)_2(SO_4)_2$.

Duplicate ten gram soil samples were extracted for exchangeable bases with four, 20 ml aliquots of neutral 0.5 $\underline{N}$ CH_3COONH_4.

The extracted Ca, Mg, Na and K were determined by atomic absorption spectrophotometry.

Aluminum was extracted from duplicate ten gram soil samples by four washings with 0.5 $\underline{N}$ CH_3COONH_4 (pH 4.8; soil:solution ratio = 1:2). Aluminum in the combined extracts was determined by atomic absorption spectrophotometry in a nitrous oxide-acetylene flame.

Cation exchange capacity was determined by saturating duplicate soil samples four times with 0.5 $\underline{N}$ $CaCl_2$ (soil:solution ratio = 1:4). After removal of excess ions with distilled water, the calcium on the exchange sites was displaced by four, 20 ml extractions with 0.5 $\underline{N}$ $MgCl_2$. Calcium in the combined extracts was determined by atomic absorption spectrophotometry.

Field trial preparation

Four adjacent plots of approximately 3.04 m by 9.15 m were rototilled to an average depth of 15.2 cm. Excess plant material was removed from the plots and the plots were leveled to a uniform slope ($\sim$3%) and rolled with a waterfilled roller (15 gal capacity). Lime (11.2 metric tons/ha) was uniformly rototilled into two of the four plot areas.

To stabilize the soil surface, water (22.9 cm total) was applied to the unlimed plots over a one week period at the rate of 3.1 cm/hr through a single, centrally located irrigation sprinkler (1/4 inch

nozzle; 40 psi). Water (38. 1 cm total) was applied over a two week period to the limed plots.

Approximately one week after the last water application 3. 60 kg ai/ha atrazine or terbutryn were applied in 425 1/ha water to the limed and unlimed plot with a bicycle-plot sprayer.

Immediately after chemical application, three plot frames (1. 16 m square by 20. 3 cm high) were equally spaced in each plot and set to a depth of 10. 2 cm at a radius of 3. 8 m from the sprinkler head (Figure 1). The plot frames were constructed of 1/8 inch galvanized steel with four 7/8 inch holes on the downslope side to facilitate runoff collection (Dixon and Peterson, 1964). Rubber hoses were connected to the runoff holes to channel surface water and sediment to 15 1 calibrated collection cans. The three plot frames on each main plot constituted replications for runoff collection. Only two plot frames were installed on the unlimed plot which was treated with atrazine.

Water applications (7 cm) were made 12 hours and one week respectively after the chemical was applied to the plots. Because water had to be transported to the site a 30 minute refill period was required midway through each application. The water applied to each area was calculated from calibrated collection cans placed along an arc 3. 1, 3. 8 and 4. 6 m from the sprinkler head. Five cans were placed along each arc.

N

0.9 m ← 1.16 m → ← 0.9 m

1.16 m

Runoff
collection
can

3.8 m

Irrigation sprinkler

Water supply

▲ Soil profile sample locations

O Calibrated rainfall collection cans
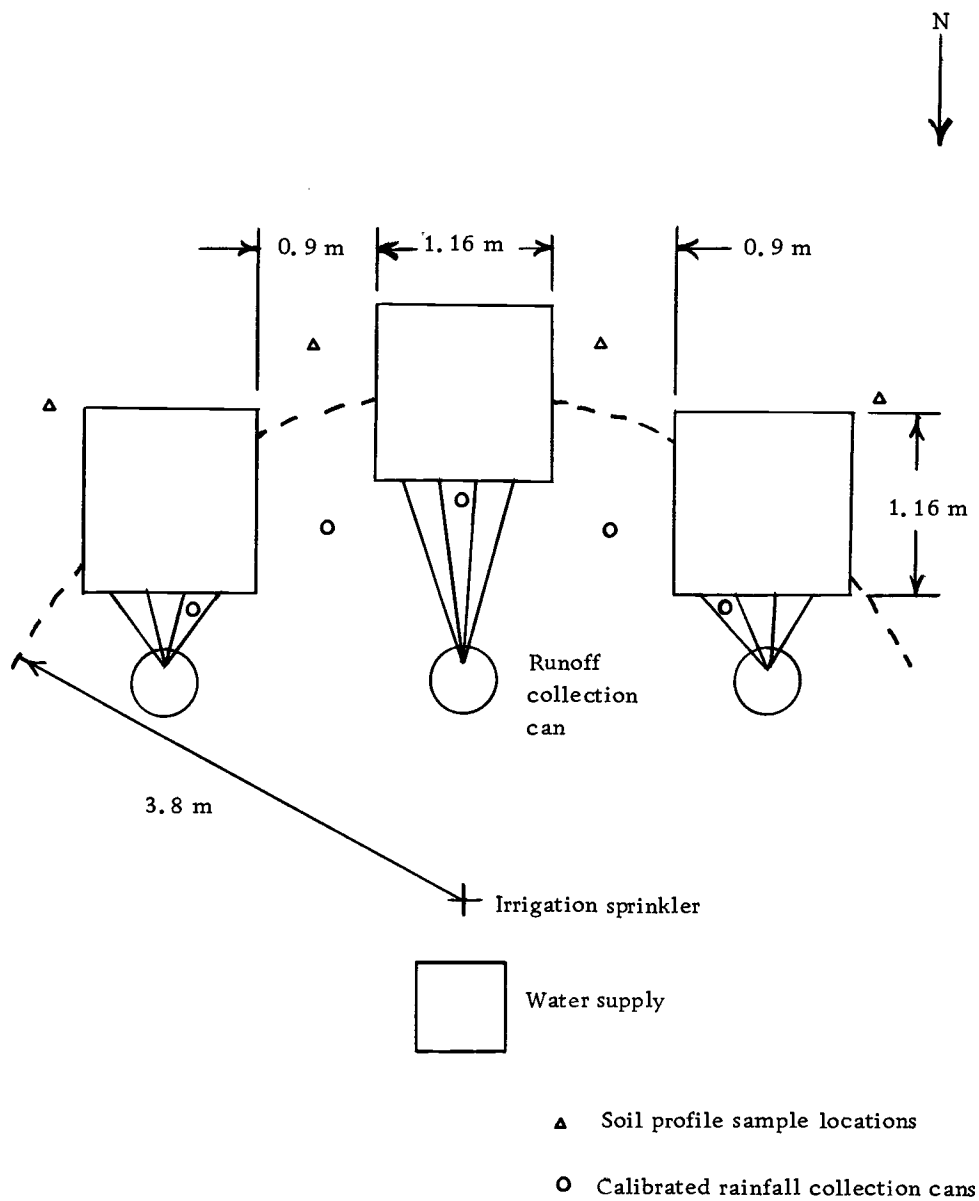
Figure 1. Location of plot frames and sprinkler apparatus for atrazine and terbutryn
runoff and sediment collection.

Runoff and sediment collection

The amount of runoff collected after each water application
was determined volumetrically in the calibrated runoff collection
cans. Sediment in the runoff was determined gravimetrically on a
50 ml aliquot. The total amount of sediment was also weighed after
separation of the runoff sample by sedimentation and filtration.

S-triazine assay of water samples

The terbutryn and atrazine content of the water samples was
conducted by two methods: i) flash evaporation of the total water
runoff or a one liter aliquot (where sample size permitted) and ii) liq-
uid extraction of the water runoff with chloroform.

Flash evaporation. A one liter aliquot of the runoff water was
reduced to dryness with a Buchler portable flash evaporator unit
(Model PF9GN and FE-2). The residue was transferred to 50 ml
beakers with 100% reagent grade methanol and dried under a hood.
The residue was transferred from the beakers with two ml reagent
grade benzene followed by rinsing with n-hexane (85%) to 180 mm by
20 mm chromatographic columns containing 12.5 g basic alumina
(Activity V) (Mattson, Kahrs and Murphy, 1970). The columns were
leached with 75 ml n-hexane (85%) followed by elution of the s-tri-
azines with 150 ml benzene:n-hexane (1:1, v/v). The

benzene:n-hexane eluate was dried under a hood and the residue

redissolved with 100% methanol. The samples were diluted with

distilled water to a 40% methanol content prior to analysis by

ultraviolet spectrophotometry. Atrazine and terbutryn absorbance

was determined at 222 nm and 224 nm respectively on a Cary, Model

11 spectrophotometer. Net absorbance (E) was calculated by the

equation:

$$E = A_{unk} - \frac{A_{206} + A_{255}}{2} \tag{1}$$

where A_{unk} = absorbance at the maximum absorption band for

terbutryn or atrazine and A_{206} and A_{255} are the absorbance values

at 206 nm and 255 nm for background correction. Water samples

which contained no s-triazine were treated similarly and used in the

reference beam. The concentration of s-triazine was determined

from a graph of net absorbance versus herbicide concentration.

Chloroform extraction. A second one liter aliquot of runoff

water from the plots which were treated with atrazine was extracted

twice with reagent grade chloroform (1:1, water:chloroform) in a

one liter separatory funnel. Water samples from the plots treated

with terbutryn were made basic with one ml of aqueous ammonia

before the chloroform extraction (8 :1, water:chloroform)(Abbott,

Bunting and Thomson, 1965). The chloroform extracts were dried

and the residue transferred to a basic alumina column with two ml

of reagent grade benzene followed by rinsing with n-hexane. The columns were leached with 75 ml n-hexane (85%) followed by elution of the s-triazines with 150 ml benzene:n-hexane (1:1, v/v).

Following the alumina clean-up the benzene:n-hexane eluate was dried under a hood and the residue was transferred with acetone to 25 ml glass stoppered Erlenmeyer flasks. After the samples were dried under a hood, ten ml of H_2SO_4 ($\underline{N}$ and 2 $\underline{N}$ for terbutryn and atrazine respectively) were added and the samples were hydrolyzed in a water bath at 90 C for three hours. After cooling, the acid hydrolyzate was extracted with 50 ml reagent grade chloroform and the hydroxy-s-triazine in the acid media was analyzed by ultraviolet spectrophotometry (Cary, Model 11) at 240 nm, 225 nm and 255 nm. The measurements at 225 nm and 255 nm were made for background correction and net absorbance was calculated from equation (1).

Soil and sediment assay

Thirty six hours after the application of water to each plot, soil samples at 7.6 cm increments to a total depth of 45.7 cm were removed from four locations across each main plot. The samples were stored moist at one C to reduce losses by volatilization. Immediately after sampling, the soils collected at each increment were uniformly mixed and moisture content determined gravimetrically by drying an aliquot for 24 hours at 105 C.

Sufficient moist soil to give 50 grams of oven dry soil was adjusted to 30% moisture content (w/w) and extracted for 24 hours with 100 ml of reagent grade methanol on a shaker. One ml of aqueous ammonia was added to the terbutryn samples. The soil sediments which were recovered from the water samples were dried at 70 C and extracted similarly. After extraction the samples were suction filtered (Whatman No. 40) and leached with an additional 100 ml of methanol. Clean-up with basic alumina and analysis of the hydrolyzate was performed as described in the water assay procedure for chloroform extraction.

Water and soil samples which contained 100 μg and 50 μg respectively of atrazine and terbutryn were assayed to calculate terbutryn and atrazine recovery factors. After addition of the chemicals, the soil samples were incubated at room temperature (30% moisture content) one month before extraction. S-triazine hydrolysis to hydroxy-s-triazine which could occur on the soil during incubation, would be removed by the basic alumina clean-up and would give a lower recovery factor.

To quantitatively determine the amount of s-triazine recovered from the plots, undisturbed soil cores (71.6 cm^3) were removed for bulk density determination at each sampling depth. The actual quantity of chemical at each soil depth could be calculated by multiplying the concentration of atrazine or terbutryn on the soil

by the total weight of soil at each depth. The bulk densities and corresponding soil weights per plot frame at each 7.6 cm increment are 1.03 (106 kg), 1.18 (121 kg) and 1.24 (127 kg).

Adsorption by unlimed and limed Peavine sil soil

Five grams of air dry soil from each sampling depth in the unlimed and limed plots was equilibrated for 12 hours with five ppm ^{14}C-ring labeled atrazine or terbutryn (soil:solution ratio = 1:2) at 25 C in a shaking water bath.

The adsorbent and solution phases were separated by centrifugation for 20 minutes at 14,000 rpm. The soil paste pH was measured after centrifugation. A one ml aliquot of the supernatant was analyzed for s-triazine in solution by liquid scintillation spectrophotometry. The fluor consisted of 2:1 (v/v) toluene: Triton X-100, PPO (2, 5-diphenyloxazol, 4 g/l) and POPOP [1, 4-bis-2-(5-phenyloxazolyn)-benzene, 0.1 g/l]. Adsorption was calculated by the equation:

$$\left[\frac{A - (\frac{C - B}{SA \times CE})V}{A} \right] 100 = \% \text{ adsorbed}$$

where A = herbicide added (μg), C = activity of aliquot (cpm/ml), B = background (cpm), SA = specific activity of stock (dpm/μg), CE = count efficiency (cpm/dpm, determined by internal spiking) and V = total volume (ml).

Results and Discussion

Adsorption by Peavine sil soil

Terbutryn was adsorbed (98%) to a greater extent by Peavine soil than was atrazine (60%) (Table 2). The addition of lime reduced terbutryn and atrazine adsorption; however, adsorption was reduced more for terbutryn than for atrazine. With lime application, terbutryn adsorption was reduced 12.0%, 5.1% and 1.3%, respectively, by soil from increasing 7.6 cm increments while atrazine adsorption was reduced 8.4% and 2.9% for the top two soil increments and increased 10.6% by soil from the 15.2 cm to 22.8 cm increment. These results support the conclusion reported earlier (Chapter 3) in that atrazine adsorption could not be reliably predicted from pH changes whereas terbutryn adsorption always decreased as pH increased. Terbutryn with a higher pKa value (4.10) would logically be more affected by pH changes than atrazine (pKa = 1.68).

The lower adsorption of atrazine indicates a greater probability for leaching relative to terbutryn. The addition of lime may increase both terbutryn and atrazine leaching. Larger amounts of terbutryn than atrazine could be lost by surface transport of eroded particles because of greater adsorption.

Table 2. Chemical properties and s-triazine adsorption on Peavine soil.

| Depth | pH | Carbon | Extractable cations | | | | | CEC | Base | S-triazine adsorbed, % | |
| | | | Ca | Mg | K | Na | Al | | Ex- | | |
cm		%	-------- meq/100 g ------------						change	Atrazine	Terbutryn
					Unlimed soil						
0-7.6	5.4	2.62	9.70	2.25	0.77	0.14	2.07	11.90	12.9	64.9	98.3
7.6-15.2	5.6	2.50	11.31	1.71	0.65	0.10	1.56	12.59	13.8	58.7	96.5
15.2-22.8	5.6	1.12	11.47	1.39	0.53	0.08	1.13	15.04	12.5	57.4	98.3
					Limed soil						
0-7.6	7.2	2.62	20.52	2.27	0.99	0.11	0.63	25.03	23.9	56.5	86.3
7.6-15.2	6.9	2.50	13.27	2.56	0.69	0.06	1.14	17.60	16.7	55.8	91.4
15.2-22.8	6.4	1.12	11.31	3.21	0.80	0.08	1.39	15.87	15.4	68.0	97.0

Runoff and sediment losses

Liming the Peavine soil reduced surface runoff and sediment erosion (Table 3). During the first water application period, water runoff for the unlimed and limed plots which were treated with atrazine was 1.45% and 0% of that applied. Corresponding values for the terbutryn treated plots were 10.0% and 0%. Similar results were obtained during the second water application period except that some runoff did occur from the limed plots (Table 3).

Sediment losses from the atrazine and terbutryn treated unlimed plots were 5.6 and 25.5 kg/ha after 5.54 cm and 7.60 cm respectively of water were applied (Table 3). The application of an additional 6.95 cm and 7.70 cm of water one week later removed 32.1 and 40.8 kg/ha sediment from the respective plots. Sediment losses from the atrazine and terbutryn treated limed plots for the second water application period were 26.3 and 0 kg/ha during application of 7.34 cm and 7.00 cm of water. The absence or low runoff from the limed plots may be due to improved soil micro-structure by $CaCO_3$ addition (Pettry and Rich, 1971). Calcium flocculates soil particles through exchange with cations on the clay exchange sites. Also, stabilization could occur through formation of calcium-silicate hydrates which could bond to adjacent particles.

Table 3. Water applied, surface runoff and sediment losses from unlimed and limed Peavine soil.

		Atrazine treated plots	Terbutryn treated plots
		Unlimed soil	
Water applied, cm	(1)	5.54	7.60
	(2)	6.95	7.70
Runoff, cm	(1)	0.08	0.76
	(2)	0.53	1.08
Sediment transported, kg/ha	(1)	5.6	25.5
	(2)	32.1	40.8
		Limed soil	
Water applied, cm	(1)	7.45	8.34
	(2)	7.34	7.00
Runoff, cm	(1)	0	0
	(2)	0.24	0.01
Sediment transported, kg/ha	(1)	0	0
	(2)	26.3	0.4

(1) and (2), water applied 12 hours and one week after herbicide application

S-triazine in runoff and sediment

The concentration of atrazine and terbutryn in the runoff water was higher for the first than for the second runoff period (Tables 4 and 5). Atrazine concentrations were 0.59 and 0.35 ppm respectively. Although atrazine concentration decreased during the second runoff period, 8 g/ha (Table 4) more atrazine was removed due to the greater amount of runoff.

No measurable atrazine was associated with the sediment for the first runoff period (<3 ppm) because of the small amount of sediment collected (5.6 kg/ha) and inherent analytical difficulties. The atrazine concentration associated with the sediment from the second runoff period was 21.0 ppm indicating large quantities could be lost by sediment transport. However, because the total amount of sediment removed was small (32.1 kg/ha) only 0.5 g/ha total atrazine was lost by this pathway compared to 6.7 and 14.7 g/ha removed by the water from the first and second simulated rainfall.

Terbutryn losses by runoff and sediment transport showed a similar trend to atrazine losses (Table 5). Terbutryn concentrations in the runoff water were 1.48 and 0.25 ppm for the first and second runoff periods. Quantitative losses were 116.4 g/ha and 26.7 g/ha respectively (Table 5). Terbutryn concentrations associated with the sediment were greater (44.4 ppm and 9.0 ppm respectively) than

Table 4. Atrazine losses in runoff water and sediment from unlimed and limed Peavine soil.

	Water application period	Water		Soil Amount and conc.		Sum	Water	Soil	Sum
		g/ha	ppm	g/ha	ppm	g/ha	----------- % -----------		
Unlimed	1	6.7	0.59	0	0	6.7	0.31	0	0.31
	2	14.7	0.35	0.5	21.0	15.2	1.63	0.05	1.68
Limed	1	0	0	0	0	0	0	0	0
	2	1.5	0.16	0.1	0.9	1.6	0.02	0.01	0.02

Table 5. Terbutryn losses in runoff water and sediment from unlimed and limed Peavine soil.

	Water application period	Water		Soil Amount and conc.		Sum	Water	Soil	Sum
		g/ha	ppm	g/ha	ppm	g/ha	----------- % -----------		
Unlimed	1	116.4	1.48	1.1	44.4	117.5	3.69	0.03	3.72
	2	26.7	0.25	0.4	9.0	27.1	0.95	0.01	0.97
Limed	1	0	0	0	0	0	0	0	0
	2	0.3	0.16	0	0	0.3	0.01	0	0.01

those for runoff but total amounts of terbutryn lost were small

(1.1 g/ha and 0.4 g/ha) because of the low sediment loads.

As expected by the low runoff , very small amounts of atrazine

(1.6 g/ha) and terbutryn (0.3 g/ha) were lost during the second runoff

period from the limed plots.

S-triazine distribution in the soil profile

Atrazine recovered from the unlimed and limed soil reflected

the great influence of pH on degradation (Table 6). After the first

and second water application periods atrazine recovered from the

unlimed soil profile by chemical extraction was 63.7% and 26.3%

and 77.4% and 78.7% from the limed plot. The great differences in

atrazine recovered from the unlimed plot for the two water applica-

tion periods indicates enhanced degradation at the lower pH. Degrada-

tion during storage at one C would be minimal. Greater degradation

of atrazine to the nonphytotoxic hydroxy form increased as pH de-

creased and when the soils were well mixed with atrazine (Obien and

Green, 1969; Armstrong, Chesters and Harris, 1967).

Of the atrazine recovered from the unlimed plot, 95.0% and

84.8% was found in the top 7.6 cm of the soil profile after application

of 5.54 cm and 12.49 cm of water. No atrazine was found below

15.2 cm. Upon addition of lime 74.7% and 67.4% of the chemically

extracted atrazine was found in the top 7.6 cm increment after

Table 6. Atrazine concentrations and percent recovered from unlimed and limed Peavine soil.

Depth cm	Unlimed Water application period				Limed Water application period			
	1 ppm	1 %	2 ppm	2 %	1 ppm	1 %	2 ppm	2 %
0-7.6	2.60	95.0	0.96	84.8	2.48	74.7	2.28	67.4
7.6-15.2	0.12	5.0	0.15	15.2	0.62	21.4	0.98	22.0
15.2-22.8	0		0		0.11	3.9	0.30	10.6
Percent recovered		63.7		26.3		77.4		78.7

Statistical analysis	F
Depth (D)	**
D x Lime	NS

Table 7. Terbutryn concentrations and percent recovered from unlimed and limed Peavine soil.

Depth cm	Unlimed Water application period				Limed Water application period			
	1 ppm	1 %	2 ppm	2 %	1 ppm	1 %	2 ppm	2 %
0-7.6	3.19	82.6	3.07	87.0	3.25	85.0	3.64	82.7
7.6-15.2	0.59	17.4	0.27	8.7	0.38	11.1	0.49	12.8
15.2-22.8	0		0.13	4.3	0.12	3.8	0.17	4.6
Percent recovered		89.9		82.3		89.1		102.6

Statistical analysis	F
Depth (D)	*
D x Lime	NS

application of 7. 45 cm and 14. 79 cm of water. Greater mobility of

atrazine in the soil profile upon lime application was suggested by

the trace amounts (3. 9% and 10. 6%) recovered at the 15. 2 cm and

22. 8 cm depth after the two water applications. The distribution of

atrazine in the profile was highly significant with depth but the

depth X lime interaction was significant only at the 25% probability

level. Atrazine concentrations in Cecil sl soil after 6. 4 cm rainfall

for one hour were 3. 6 ppm and 0. 1 ppm in the top 7. 6 cm and 7. 6 cm

to 15. 2 cm depths (White et al. , 1967).

Chemical extraction of terbutryn from the unlimed soil after

application of 7. 60 cm and 15. 30 cm of water was 89. 9% and 82. 3%

(Table 7). The top 7. 6 cm of the soil profile contained 82. 6% and

87. 0% of the chemically extracted terbutryn. No terbutryn was

recovered below 15. 2 cm after the first water application period but

4. 3% was recovered from this depth after the second water applica-

tion period. Compared to the unlimed plot, liming had little effect

on the distribution of terbutryn in the soil. The top horizon contained

85. 0% and 82. 7% of the chemically extracted terbutryn and 3. 8% and

4. 6% was recovered from the 15. 2 cm to 22. 8 cm horizon after the

addition of 8. 34 cm and 15. 34 cm of water. Total terbutryn chem-

ically extracted from the soil profile of the limed plot was 89. 1%

and 102. 6% of that applied after the two water applications.

The higher concentrations (> 3 ppm) of terbutryn in the top

horizons of the soil profile could be anticipated from the adsorption

data (Table 2). Although atrazine and terbutryn adsorption in the

0-7.6 cm horizon was reduced (8.4% and 12.0%) similarly by addition

of lime, leaching appeared to occur to a greater extent with atrazine

because of its lower adsorption (65% and 98% respectively).

Of the total amount of atrazine recovered from the soil and by

surface runoff, 0.31% and 1.70% was accounted for in the water and

sediment in the two runoff periods (Table 4) from the unlimed plots.

Terbutryn losses from the unlimed soil for the corresponding periods

were 3.72% and 0.97% respectively (Table 5). Since s-triazine

recovery from the plots was less than 100% of that applied (Tables 6

and 7) the percentage lost by lateral movement would be less if

expressed on initial application rate (3.60 kg/ha).

These results support the conclusions of others in that many

interrelated factors govern the magnitude of s-triazine losses from

soil. Most of the surface loss of the s-triazines occurs when rainfall

is received immediately or soon after application of the s-triazines

to soil. A 50% reduction in atrazine loss by lateral transport was

observed when rainfall was applied 96 hours as compared to one

hour after atrazine application (White et al., 1967). Surface soil

temperatures in excess of 100 C were measured indicating volatiliza-

tion was the prime factor for the reduction. Losses of prometone and

atrazine by volatilization increased as sand content increased and

organic matter and clay content decreased (Jordan et al., 1970).
Atrazine losses from Cecil sl soil increased approximately 20% as
temperature increased from 35 C to 45 C. The quantity of s-triazine
volatilized was greater from moist than from dry soil and increased
as vapor pressure of the s-triazine increased.

In a similar study on Hagerstown sicl (14% slope) the mean
total loss by runoff and sediment transport of atrazine applied at
rates from 0. 6 kg/ha to 9. 0 kg/ha was 2. 6% for the growing season
(Hall et al., 1972). The amounts of atrazine lost increased with
rate from 10. 2 g/ha to 264.9 g/ha. Greater amounts were lost in
the water fraction (2. 4 % versus 0. 16% for sediment) but concentra-
tions were higher on eroded sediment. Losses by runoff and sedi-
ment transport were greatest after initial application of atrazine
to the soil and decreased during the growing season.

In this study, the small amount of atrazine (0. 01 kg/ha) and
terbutryn (0. 10 g/ha) lost by lateral movement would not be expected
to be detrimental to sensitive crops. Sublethal rates (1. 1 kg/ha to
2. 2 kg/ha) of atrazine and simazine increased dry forage yields
140% and 550% (Kay, 1971). The increased yields were accompanied
by increased protein and nitrate content. Filare (Erodium circu-
tarium (L) L'Her) seeds harvested from atrazine treated plots (2. 2
kg/ha) were heavier and more vigorous than those from untreated
plots. An increase in protein content of seeds has been shown to

increase growth and yield (Schweizer and Ries, 1969).

Atrazine and terbutryn concentrations (0.59 ppm and 1.48 ppm) in the runoff water could provide a potential threat to organisms in nearby waterways; however, studies have indicated that the toxicity of the s-triazines is low for mammals and fish. Mammalian studies indicate chloro-s-triazines are least toxic (i.e., atrazine LD_{50} mouse = 1750 mg/kg) while methoxy-s-triazines (i.e., atratone LD_{50} mouse = 905 mg/kg) are most toxic (Knusli, 1964). Rats fed 100 mg propazine, atrazine, ametryne, prometryne or prometone for 90 days were comparative in behavior and habits with control animals. High atrazine concentrations of 10 ppm and 5 ppm were lethal to minnows 6 and 25 hours after exposure (Vivier and Nisbet, 1965). Toxicity was greatly reduced when plants and soil were introduced into the aquarium.

Losses of atrazine and terbutryn by lateral movement or soil leaching would not be hazardous to plants or organisms. Because of the high adsorption of the s-triazines to soil particles, the potential does exist for environmental contamination if excessive soil erosion were allowed to occur. S-triazines are reversibly desorbed from soil materials (Chapter 2, Figures 1 thru 5; Harris and Warren, 1963) with chloro-s-triazines being desorbed more readily than methoxy or methylthio analogs. Readsorption of

desorbed s-triazines by soil particles in water ways would occur

according to the new equilibrium conditions.

Summary and Conclusions

Terbutryn (97. 7%) adsorbed more readily onto unlimed Peavine

soil than atrazine (60. 3%). Addition of lime, 11 metric tons/ha,

to the soil reduced terbutryn adsorption. Atrazine adsorption on the

limed soil decreased for only the upper soil horizons.

The addition of lime to the Peavine soil improved the soil struc-

ture and increased the infiltration rate so that no runoff occurred

from the atrazine or terbutryn treated plots after application of 7 cm

to 8 cm of water. Of the total amount of water applied during the

first application period 1. 5% and 10. 0% was collected as runoff

from the atrazine and terbutryn treated unlimed plots. After appli-

cation of an additional 7 cm of water one week later 9. 6% and 14. 0%

of that applied to the respective plots was collected as runoff.

Analysis of the runoff water and transported sediment from the first

water application period contained 0. 31% and 3. 72% of the total amount

of atrazine and terbutryn recovered from the plots. Analysis of the

runoff water and transported sediment from the second runoff period

contained 1. 68% and 0. 97% of the total recovered atrazine and

terbutryn. Atrazine and terbutryn concentrations in the runoff water

from the first application period were 0. 59 ppm and 1. 48 ppm while

lesser concentrations (0.35 ppm and 0.25 ppm) were found after the second runoff period. Terbutryn and atrazine concentrations associated with the sediment for the first runoff period were 44.4 ppm and 0 ppm while concentrations of 9.0 ppm and 21.0 ppm were found after the second runoff period. The high concentrations of s-triazine associated with the sediment reflect the high adsorptive capacity of the soil; however, because of the low sediment loads only 0.01% to 0.05% of the s-triazine recovered from runoff was associated with the sediment.

Atrazine chemically extracted from the soil in the unlimed plot underwent chemical hydrolysis to the nonphytotoxic hydroxyatrazine form since only 64% and 26% of the total atrazine applied could be recovered after the first and second water application periods. The addition of lime greatly reduced the hydrolysis of atrazine as 77.4% and 78.7% of the total atrazine applied was recovered from the plots. Terbutryn did not hydrolyze or chemically degrade in the soil as 89.9% and 82.3% of the total terbutryn applied was recovered from the unlimed plot and 89.1% and 102.6% was recovered from the limed plot after the first and second additions of water.

The addition of lime promoted atrazine leaching in the Peavine soil since the top 7.6 cm of the unlimed and limed soil contained 95% and 75%, respectively, of the chemically extracted atrazine after the first application of water. Liming did not increase terbutryn leaching

as the top 7. 6 cm of unlimed and limed soil contained 83% and 85% of the chemically extracted herbicide. Logically, the greater adsorption of terbutryn relative to atrazine would prevent leaching in the unlimed and limed soil. No atrazine or terbutryn leached further than 22. 8 cm in the plots after the addition of 15 cm of water.

Contamination from atrazine and terbutryn treated soil of adjacent fields and waterways by runoff water or transported sediment and by leaching would not be expected because of the high adsorption of these chemicals. However, the results indicate the potential for contamination of surrounding fields and waterways does exist if sound management practices are not followed.

SUMMARY AND CONCLUSIONS

The solubility of atrazine, terbutryn and GS-14254 was rela-tively unaffected by salt concentrations <0.1 μ (ionic strength). Intensely hydrated cations, i.e., Ca, reduced solubility less than weakly hydrated cations, i.e., Na and K. Proton orientation about strongly hydrated cations favored solubilization of the basic s-tri-azines, thus a lesser reduction in solubility was observed for the Ca salt than with Na or K salt. Also, it was postulated that protons oriented about highly hydrated cations could interact with anions and thereby reduce the number of ions in solution and produce a smaller change in the activity coefficient of the s-triazines.

S-triazine adsorption by the salt amended Cloquato soil and the chemically extracted soils increased in the order atrazine < GS-14254 < terbutryn. Salt concentrations < 1.0 μ decreased GS-14254 and terbutryn adsorption more than atrazine. It was postulated that reduced adsorption occurred by cation competition for adsorption sites with protonated GS-14254 or terbutryn cations. Although con-clusive evidence of s-triazine adsorption by cation exchange mech-anisms was lacking, GS-14254 (pKa = 4.36) and terbutryn (pKa = 4.10) could be adsorbed by this means because of their higher pKa values, whereas hydrogen bonding was probably the main mechanism for atrazine adsorption (pKa = 1.68) by the Cloquato sl soil (pH 6).

Salt concentrations <1.0 μ enhanced GS-14254 and terbutryn desorption from salt amended Cloquato soil, whereas equal amounts of atrazine were desorbed from the salt amended and check soils. Hydrogen bonding between GS-14254 or terbutryn and the hydrated cations at the exchange sites was postulated, whereas atrazine with a more electronegative chlorine atom at the two position and lower pKa value would not undergo extensive adsorption by coordination through hydrated cations.

At salt concentrations > 1 μ enhanced desorption of the s-triazines from Cloquato soil was attributed to salting out due to higher salt levels in the double layer. One would not expect salt levels to be high enough in agricultural soils to influence s-triazine solubility. However, low salt levels may decrease GS-14254 and terbutryn adsorption and increase phytotoxicity.

Atrazine adsorption was not consistently decreased by an increase in pH as was the adsorption of GS-14254 and terbutryn. For the same increase in pH the adsorption of GS-14254 was reduced more than terbutryn; however, in soils with a high carbon content the pH effect on atrazine, terbutryn and GS-14254 adsorption was reduced.

Hydrogen peroxide oxidation of soil organic matter did not greatly affect GS-14254 or terbutryn adsorption by Kinney and Jory soils but reduced atrazine adsorption on Jory soil . GS-14254 and

terbutryn appeared to have an equal affinity for organic and clay mineral surfaces while atrazine had an affinity for organic surfaces only.

Enhanced s-triazine adsorption by Boyce, Crooked and chemically extracted Parkdale C soil was attributed to gel amorphous hydrous oxides. Removal of amorphous components from the high pH Boyce and Crooked soils reduced atrazine adsorption 40% to 50% but GS-14254 and terbutryn adsorption appeared to occur with equal affinity on the exposed clay mineral surfaces. Aged amorphous hydrous oxides in the Parkdale C soil did not appear to contribute significantly to s-triazine adsorption; however, adsorption of GS-14254, terbutryn and atrazine increased 30% to 40% after extraction with acid ammonium oxalate.

Unlimed Peavine soil contained 95% and 83% of the chemically extracted atrazine and terbutryn in the top 7.6 cm of soil after the addition of 5.5 cm and 7.6 cm of water. Liming enhanced atrazine leaching but had little effect on terbutryn movement.

Atrazine recovery from the unlimed and limed soil approximated 26% and 79% indicating acid catalyzed degradation at the lower pH. Chemical extraction of the terbutryn added to the unlimed and limed soil recovered 90% to 100% of that applied.

The addition of lime to the Peavine soil greatly reduced surface runoff. Losses of atrazine and terbutryn by surface overwash from

unlimed soil were 1. 7% and 3. 7% of the total amount recovered from the plots. Higher losses occurred when herbicide application shortly preceded rainfall but intensity of runoff determined the amount lost. Herbicide concentrations were higher on transported sediment but quantitative losses were greatest in the water fraction. Contamination of waterways or nearby fields by surface transport of s-triazines would not appear to be a problem; however, because of the high adsorption of terbutryn by sediments, management practices which minimize erosion should be practiced.

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APPENDIX

Table 1. Chemical properties and atrazine adsorption by Cloquato sl soil as affected by salt concentration.

Salt type	Salt concentration, μ	pH	Conductivity mm hos/cm	Atrazine adsorbed %
NaCl	0	5.8	0.16	35.1
	0.005	5.7	0.81	35.0
	0.05	5.3	5.0	36.3
	0.5	5.0	>15	39.5
	5.0	4.2	>15	93.5
$CaCl_2$	0	5.8	0.16	35.1
	0.005	5.6	0.50	36.5
	0.05	5.2	2.45	37.5
	0.5	4.8	>15	38.8
	5.0	4.2	>15	70.1

Table 2. Chemical properties and atrazine adsorption-desorption from Na-Cloquato sl soil as affected by salt concentration.

Salt type	Salt concentration, μ	pH	Cation saturation Na	Cation saturation Ca	Atrazine adsorbed	Atrazine desorbed**
			---- meq/100 g ----		-------%--------	
NaCl	0	6.6	9.0	nd*	31.6	93.5
	0.05	5.8	9.0	nd	32.3	73.5
	0.5	5.1	9.0	nd	45.9	67.9
	5.0	4.3	9.0	nd	94.3	83.0
$CaCl_2$	0	6.6	9.0	nd	31.6	93.5
	0.05	5.8	4.0	5.8	40.5	65.4
	0.5	4.8	0.7	8.0	45.3	66.8
	5.0	4.2	0.2	8.4	73.7	73.6

* not determined   **Desorbed with distilled water (4x) and 0.08 $\underline{N}$ $MgCl_2$ (4x)

Table 3. S-triazine desorbed with distilled water or 0.01 $\underline{N}$ CaCl$_2$ from Cloquato sl.

	S-triazine desorbed, % *					
	Atrazine		Terbutryn		GS-14254	
Desorption			Salt .conc., μ**			
solvent	0	0.1	0	0.1	0	0.1
Water	83.9	86.9	26.5	52.4	19.2	41.5
0.01 $\underline{N}$ CaCl$_2$	88.8	92.0	22.8	44.3	24.8	49.5

* Sum of six desorptions   ** Initial equilibrium salt concentration

Table 4. Atrazine and hydroxyatrazine adsorption and desorption from Boyce and Crooked soils.

Soil	Adsorbed, %		Desorbed, %	
series	Atrazine	Hydroxyatrazine	Atrazine	Hydroxyatrazine
Boyce	83.5	96.1	103(0.80)	78.2
Crooked	95.2	98.9	92.4(0.46)	41.6

( ) Hydroxyatrazine in desorption extract (100% methanol, 2x + distilled water, 5x)

Table 5. Chemical properties of selected soils extracted with ammonium acetate (pH 4.8) and related atrazine adsorption.

Soil	Carbon	Extractable	pH	Atrazine	
series		Al		Adsorbed	Desorbed**
	%	meq/100 g		%	%
Kinney	6.48	18.2	5.4	78.0	95.1
		18.2	6.5*	92.5	78.1
Kinney	0.74	22.7	5.2	92.0	109.4
		22.7	7.5	44.0	135.2
Woodcock	6.00	2.0	6.2	78.3	98.4
		2.0	7.2	91.9	71.9
Woodcock	1.21	12.2	5.4	62.3	177.0
		12.2	7.4	32.1	167.9
Jory	2.36	1.2	5.4	66.8	92.9
		1.2	7.8	87.5	59.0
Boyce	1.30	0.04	7.6	90.0	111.4
		0.04	9.9	92.3	97.9
Crooked	0.91	0.05	7.6	97.1	104.5
		0.05	9.7	97.6	100.5

*pH adjusted with NaOH.

**Desorbed with distilled water (2x) and 100% methanol (2x). Not corrected for occluded atrazine after adsorption. Hydroxyatrazine in the water and methanol desorption solution <4 %

Table 6. Water applied to atrazine treated unlimed Peavine soil.

Distance from sprinkler, m	Time elapsed, minutes	Water applied, cm Collection can No.					Average
		1	2	3	4	5	
				Application period 1			
3.1	120	5.77	6.53	5.97	5.54	5.26	5.54
3.8		6.07	6.22	5.87	5.44	4.90	
4.6		5.94	5.64	5.44	5.16	4.93	
				Application period 2			
3.1	120	7.62	7.82	7.65	7.06	5.61	6.96
3.8		7.42	7.98	7.87	7.04	5.28	
4.6		7.49	7.47	7.19	6.15	4.39	

Table 7. Water applied to atrazine treated limed Peavine soil.

Distance from sprinkler, m	Time elapsed, minutes	Water applied, cm Collection can No.					Average
		1	2	3	4	5	
				Application period 1			
3.1	160	5.46	7.56	9.75	9.86	8.33	7.45
3.8		5.16	6.63	7.37	9.25	8.69	
4.6		4.88	5.59	6.91	8.43	7.77	
				Application period 2			
3.1	190	7.14	10.59	10.08	10.36	8.10	7.34
3.8		5.79	8.00	8.26	8.00	6.22	
4.6		4.17	5.21	5.64	6.15	5.87	

Table 8. Water applied to terbutryn treated unlimed Peavine soil.

Distance from sprinkler, m	Time elapsed, minutes	Water applied, cm Collection can No.					Average
		1	2	3	4	5	
		Application period 1					
3.1	135	6.71	8.13	7.87	8.81	7.75	7.26
3.8		6.38	7.16	6.86	7.95	7.70	
4.6		6.76	6.60	6.22	6.99	7.06	
		Application period 2					
3.1	167	6.50	7.98	9.02	9.55	9.27	7.70
3.8		5.59	6.83	7.16	8.92	8.64	
4.6		5.64	6.17	6.68	7.92	9.19	

Table 9. Water applied to terbutryn treated limed Peavine soil.

Distance from sprinkler, m	Time elapsed, minutes	Water applied, cm Collection can No.					Average
		1	2	3	4	5	
		Application period 1					
3.1	165	6.78	8.08	7.54	10.52	9.35	8.34
3.8		6.07	8.10	8.59	9.83	9.02	
4.6		6.22	6.22	8.13	10.29	9.91	
		Application period 2					
3.1	187	7.92	10.24	9.32	8.94	7.37	6.99
3.8		5.61	6.50	6.55	7.82	6.35	
4.6		5.28	4.52	4.65	6.63	6.86	

Table 10. Chemical and physical properties and related s-triazine adsorption by Peavine soil.

Depth cm	Carbon %	pH	Bulk density	S-triazine adsorbed, % Atrazine	Terbutryn
			Unlimed soil		
22. 8-30. 4	0. 94	5. 6	1. 39(143)	55. 6	98. 4
30. 4-45. 7	0. 64	5. 6	1. 39(286)	56. 3	98. 8
			Limed soil		
22. 8-30. 4	0. 94	6. 4	1. 39(143)	72. 3	97. 0
30. 4-45. 7	0. 64	6. 4	1. 39(286)	58. 6	97. 8

( ) Weight of soil per plot (kg) at indicated depth

Table 11. Atrazine and terbutryn recovery from unlimed and limed Peavine soil.

Depth cm	S-triazine recovered, % Atrazine	Terbutryn	Standard error, % Atrazine	Terbutryn
		Unlimed soil		
0-7. 6	53. 0	69. 1	0. 4	9. 9
7. 6-15. 2	56. 6	80. 8	2. 2	9. 6
15. 2-22. 8	40. 2	75. 8	7. 6	5. 5
22. 8-30. 4	32. 4	72. 0	10. 7	3. 0
30. 4-45. 7	26. 8	nd*	2. 8	nd
		Limed soil		
0-7. 6	51. 6	83. 1	3. 6	2. 3
7. 6-15. 2	53. 0	68. 5	1. 6	3. 5

* not determined   50 µg added to 50 g soil

Table 12. Atrazine and terbutryn recovery from water samples.

Method	S-triazine recovered, % Atrazine	Terbutryn	Standard error, % Atrazine	Terbutryn
Flash evaporated	32. 0	16. 3	nd*	3. 7
CHCl₃:Water (1:1)	66. 5	10. 0	9. 5	nd
CHCl₃:Water (1:4) acidic**	nd	16. 3	nd	nd
CHCl₃:Water (1:8) basic	nd	24. 0	nd	7. 7

* not determined   ** 0. 1 N HCl final concentration   100 ug added to one liter water
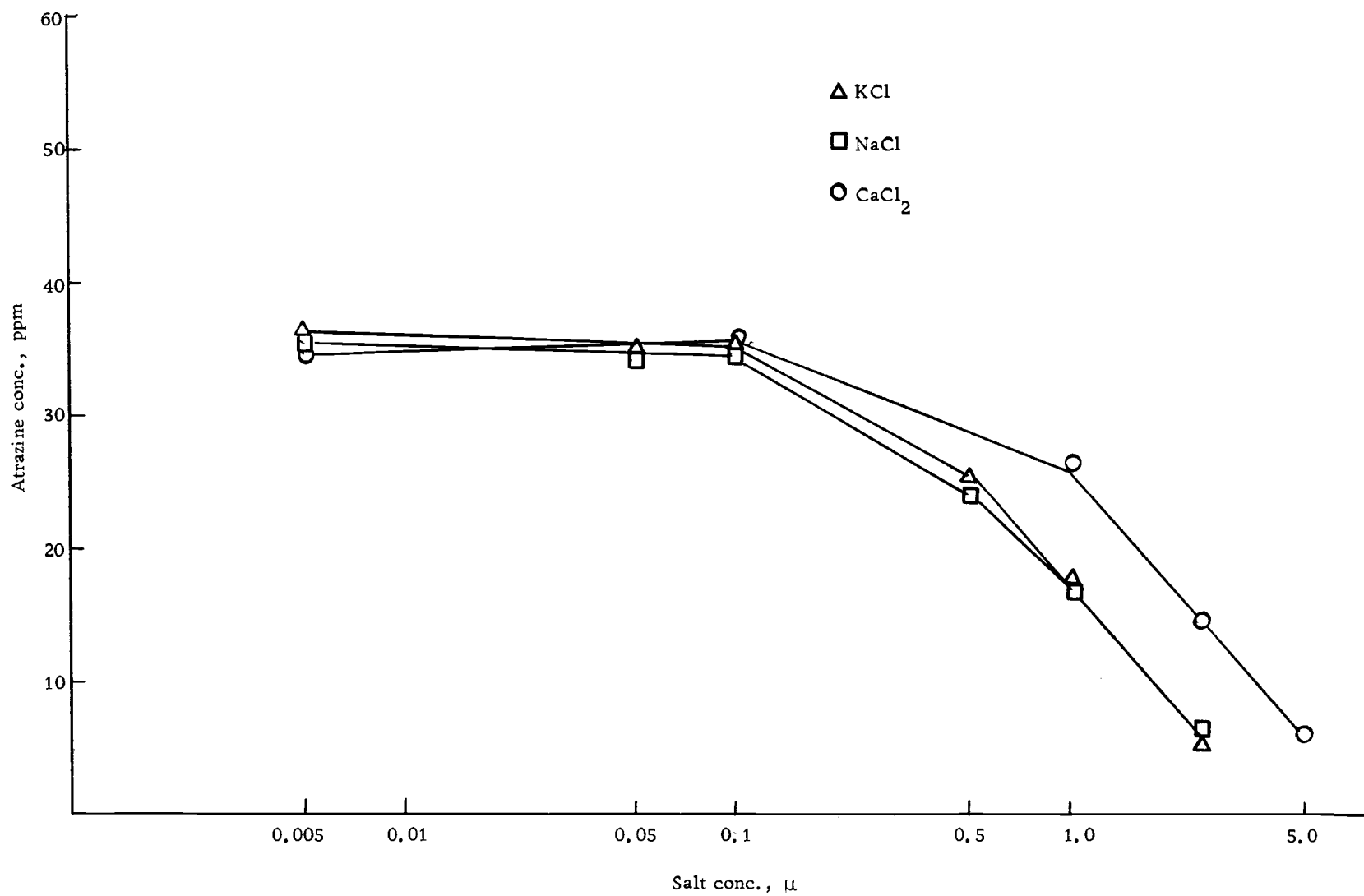
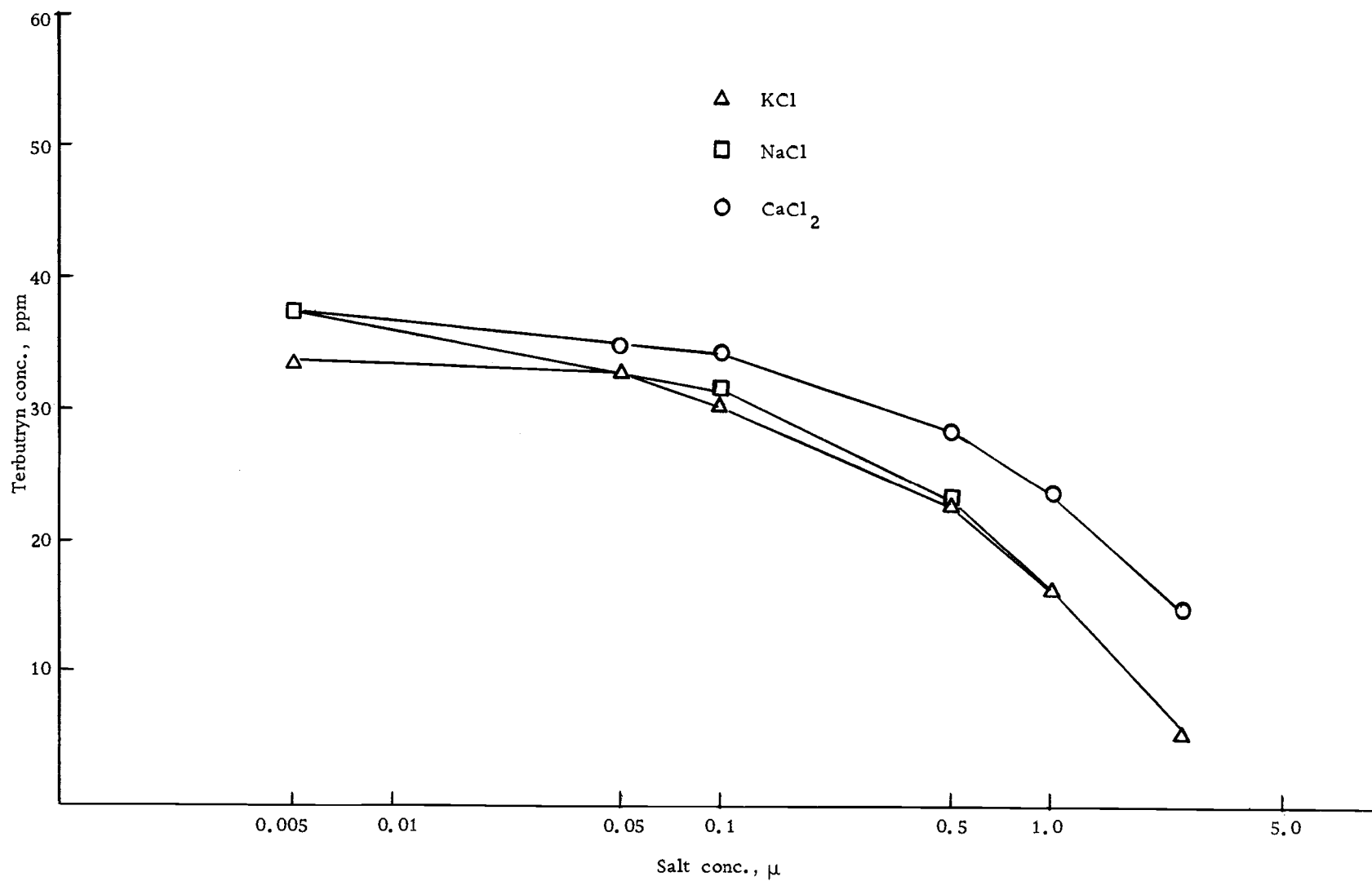Figure 1. Atrazine solubility in Na, K and Ca chloride salt.

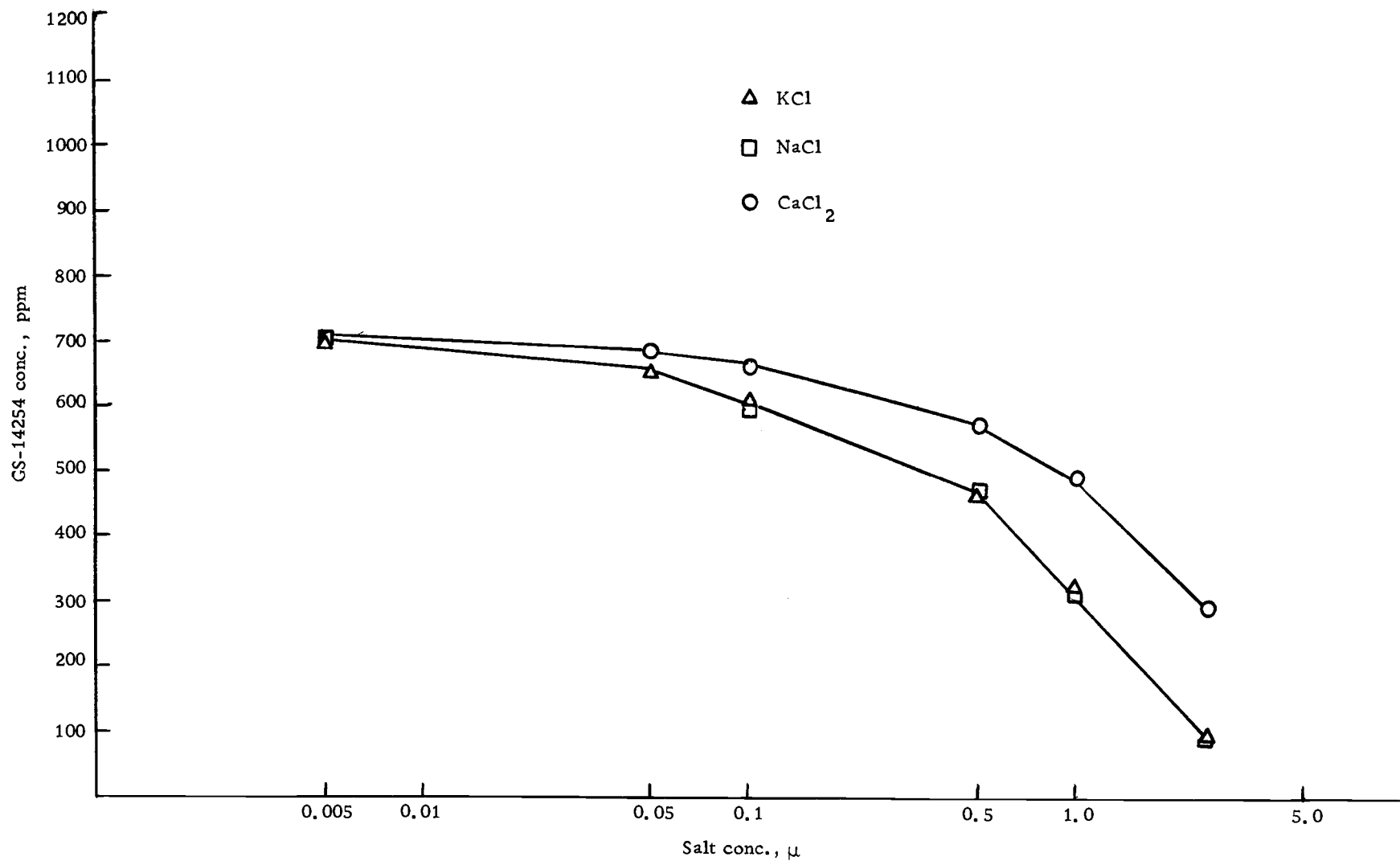Figure 2. Terbutryn solubility in Na, K and Ca chloride salt.

Figure 3.   GS-14254 solubility in Na, K and Ca chloride salt.