ADSORPTION OF S-TRIAZINE HERBICIDES ON SOILS

AS AFFECTED BY ADSORBENT-pH INTERACTIONS

A THESIS SUBMITTED TO THE GRADUATE DIVISION

OF THE UNIVERSITY OF HAWAII

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE
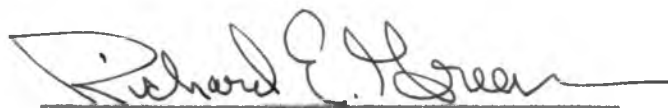
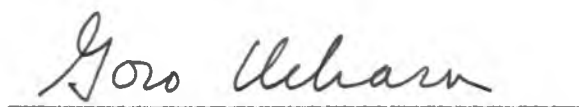IN SOIL SCIENCE

SEPTEMBER 1968

By
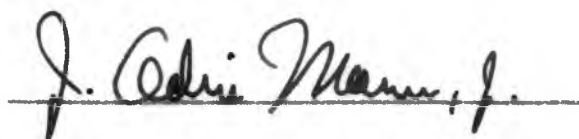
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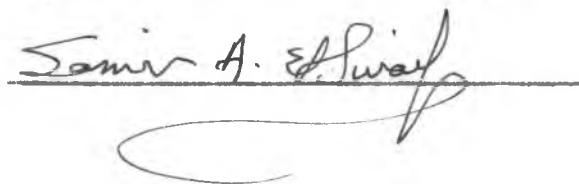Dr. Samir A. El-Swaify
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ACKNOWLEDGMENTS

I wish to express my appreciation and thanks to Dr. Richard E. Green for his sincere guidance towards the completion of my graduate program and for his help in <u>many</u> ways other than those which were normally required of an advisor. Also, my thanks to Mr. Santiago R. Obien, my friend and colleague, for helping me in the thin layer analysis of my samples. He introduced me and encouraged my interest into the field of pesticides, giving me insights into various aspects of pesticide research.

I am indebted to Miss Susan Abe for her help in the preparation of my experimental materials and especially in organizing some of my data during the crucial weeks of the preparation of my thesis. Also, my special thanks go to Miss Stella Honda for typing the final manuscript.

I would also like to thank my friends from foreign lands with whom I shared very rewarding experiences. Together with the faculty and staff of the Department of Agronomy and Soil Science, they made my two years of graduate work very memorable and my future more challenging.

The work was facilitated by the support of the Geigy Chemical Company which supplied the radioactive atrazine and ametryne. This research was financed by the Hawaii Agricultural Experiment Station Project 141.

Finally, my sincere thanks to my friends, especially Mr. Ken Shimoji, whose very presence has been a <u>source</u> of encouragement.

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INTRODUCTION

Soil-applied organic pesticides are used extensively in modern agriculture. Their efficiency in pest control is important to successful crop production, and their persistance and mobility in soils concern the general public.

The fate of pesticides in soils is governed by the several factors shown in Figure 1. Adsorption is the most important factor controlling the behavior of pesticides over short periods of time. Organic chemicals applied to the soil in solution equilibrate rapidly with the soil in an adsorption-desorption equilibrium that determines the extent of volatilization, degradation, leaching, etc.

Soil properties such as pH, organic matter and clay contents, cation and anion exchange capacities, and surface area control the adsorption of organic solutes. The mechanism of adsorption for a particular pesticide-soil combination depends entirely on the unique chemical properties of both the pesticide and the soil. The extreme variability of Hawaiian soils results in variable pesticide behavior in the field. Since an understanding of the nature of adsorption leads to efficient and safe use of pesticides, studies of adsorption in relation to the physical-chemical properties of pesticides and soils are needed.

In 1965 over 760 million pounds of synthetic organic pesticides were used in the United States. Herbicides comprised about 24 per cent of the total and were used to treat 120 million acres of U. S. cropland. In Hawaii alone about 500,000 pounds each of atrazine and ametryne are used yearly on sugarcane and pineapple fields for preemergence and postemergence weed control.
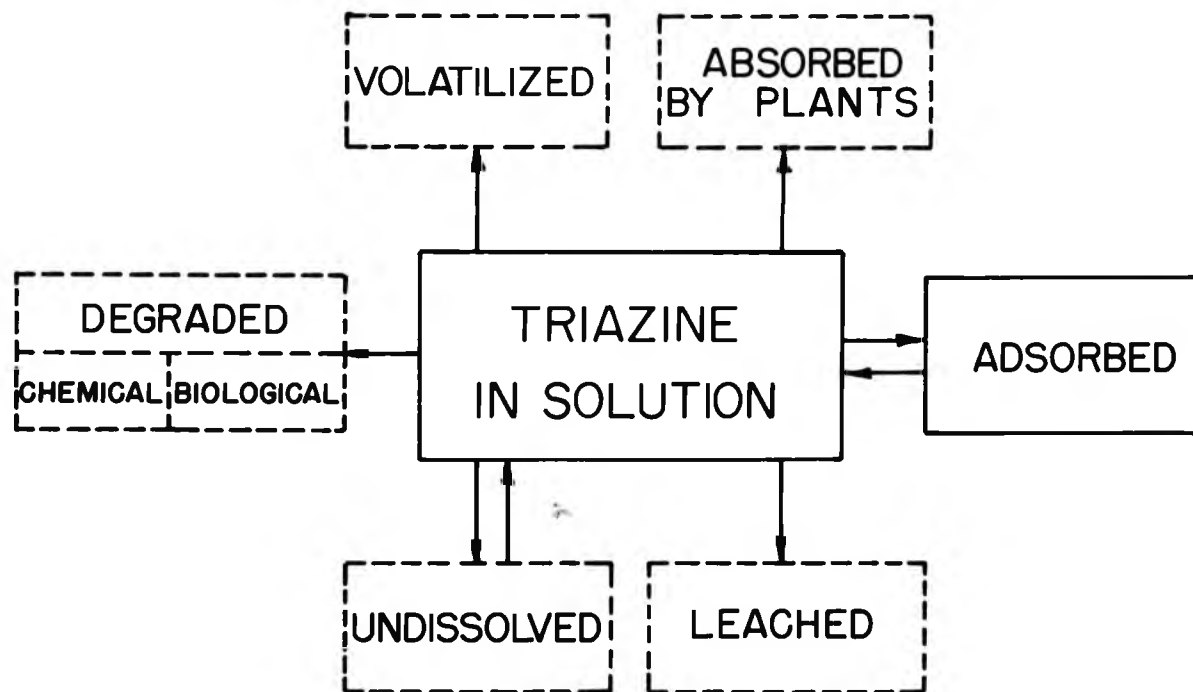
FIGURE 1. Behavior of the s-Triazines in Soils.

Adsorption of atrazine(2-chloro-4-ethylamino-6-isopropyl-amino-s-triazine) was shown by Hilton and Yuen (1963) to vary by as much as 50-fold on different Hawaiian sugarcane soils. Adsorption of ametryne (2-methylthio-4-ethylamino-6-isopropylamino-s-triazine) was shown by Barba (1967) to exceed that of atrazine; this result explained why ametryne was not toxic to bananas in cases where atrazine phytotoxicity occurred. In general, ametryne has been too phytotoxic for use in temperate region soils. Its excellent performance in Hawaii is apparently related to reversible adsorption.

The s-triazine herbicides are weakly dissociated bases; thus their behavior is somewhat determined by pH. In the present study the adsorption of atrazine and ametryne on several selected adsorbents was investigated with pH and temperature variables in order to better understand the nature of s-triazine adsorption. The pH variable allowed an assessment of the effect of protonation on adsorption, while the temperature variable was expected to provide experimental data for thermodynamic calculations.

The objectives of the study were to:

1. Relate the adsorption of atrazine and ametryne to the fundamental properties of the two chemicals and selected adsorbents.

2. Investigate the dependence of triazine adsorption on solubility as affected by temperature and pH.

3. Determine the enthalpy of adsorption for atrazine and ametryne as a means of expressing the differential affinity with which these herbicides are held on the soil.

REVIEW OF LITERATURE

1. Nature of Pesticide Adsorption

Adsorption can be defined as the accumulation of an adsorbate on the surface of an adsorbent. There are two types of adsorption--chemical and physical. Chemical adsorption occurs when there is a chemical bond formed between the adsorbent and adsorbate. Physical adsorption is a general term covering a number of bonding mechanisms which may or may not be electrostatic in nature (Adamson, 1967). Heats of physical adsorption are usually lower than 5 kcal/mole while heats of chemisorption often greatly exceed this value. Coulombic attractions occur between two species of net opposite charge and are inversely related to the square of the distance separating the charges. Van der Waal attractions, which are also non-chemical and therefore reversible, are short-range forces. They are directly related to the molecule's dipole moment and polarizability. It has been generally agreed that the adsorption of herbicides in soil is physical, as indicated by evidence for reversibility and multilayer adsorption.

2. Nature of the Adsorbent

Studies by many workers (Sheets, 1962; Talbert and Fletchall, 1963; Nearpass, 1965; McGlamery, 1966) have shown that certain soil properties greatly affect adsorption, especially organic matter, total clay content, cation exchange capacity, carbon content, and soil acidity. These properties affect surface area and the nature and source of the charge in soils.

The nature of clays in the soil greatly affects the surface area.

Montmorillonite and vermiculite have large specific surface areas (600-800 square meters per gram) while kaolinite and illite have smaller specific surface areas (7-30 and 65-100 square meters per gram, respectively). Many Hawaiian soils consist of amorphous oxides and hydroxides of iron and aluminum, the surface areas of which are difficult to measure; but probably range from 100-800 square meters per gram.

Organic matter in Hawaiian soils plays a great part in the adsorption of many herbicides from aqueous solutions. Hawaiian soils are generally higher in organic matter than most temperate climate soils (Blomberg and Holmes, 1959). In addition the abundance of organic residues and decomposition products from sugarcane roots and leaf trash contribute to the total surface area (Hilton and Yuen, 1966).

Since physical adsorption consists mainly of van der Waal attractions and those which may be electrostatic in nature, the source and nature of the charges must be considered.

Charges in the inorganic fraction occur in part because of isomorphous substitution in the tetrahedral and octahedral layer of the crystalline clay mineral, i.e., substititution of Al^{+3} for Si^{+4}, or Mg^{+2} or Fe^{+2} for Al^{+3}. Any one of these substitutions results in a permanent negative charge. Negative charges also occur when there is an ionization of hydroxyl groups in the broken edges of the silica layer, viz. $SiOH + H_2O \rightleftharpoons SiO^- + H_3O^+$, or a substitution for the H of the exposed OH by other exchangeable cations. Both negative and positive charges occur in the organic fraction. The negative charges occur because of the dissociation of phenolic, carboxylic and enolic hydroxylic groups. Depending on the pH and the isoelectric point of the

amino acid, a positive or negative charge or both can exist (Broadbent, 1952).

Thus, depending on the distribution and type of clay minerals, organic matter, and amorphous material, great changes in the cation and anion exchange capacities (milliequivalents/100 g) can be observed with changes in pH (Wada, 1958; Bear, 1965).

3. Nature of the Adsorbate

Among the many ways of classifying herbicides, it is most meaningful for the purpose of this discussion to classify them according to their behavior in water. The classes proposed herein are as follows: (1) permanently charged herbicides, e.g., paraquat and diquat (divalent cations); (2) dissociable herbicides; and (3) nondissociable herbicides, e.g., chlorinated benzenes. The dissociable herbicides can be further subdivided into the weak acids, e.g., 2,4-D, and the weak bases, e.g., the s-triazines.

The triazines are a class of compounds which behave as weak bases in aqueous solution. Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and prometryne (2-methylmercapto-4, 6-bis(isopropylamino)-s-triazine), a close analogue of ametryne, have pK_b values of 12.32 and 7.95, respectively, at 22 C (Zweig, 1964). Like all weak bases, they hydrolyze in water (Skoog, 1963). The hydrolysis of atrazine in water can be likened to that of ammonia.

$$NH_3 + H_2O \xrightleftharpoons[]{K_b} NH_4^+ + OH^- \qquad \text{where}$$
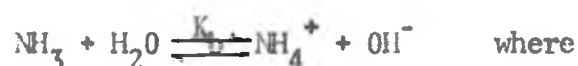
$$K_{b,NH_3} = \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]} \, , \qquad \text{and}$$

$$pK_{b,NH_3} = - \log K_{b,NH_3} = 4.76$$

$$\text{atrazine} + H_2O \xrightleftharpoons{K_b} \text{atrazine } H^+ + OH \qquad\qquad [1]$$

$$K_{b,\text{atrazine}} = \frac{[\text{Atrazine } H^+][OH^-]}{[\text{Atrazine}][H_2O]} \, , \qquad \text{and} \qquad [2]$$

$$pK_{b,\text{atrazine}} = - \log K_{b,\text{atrazine}} = 12.32$$

Thus, the K_b describes the position of the equilibrium in the above reaction. The amount protonated can also be calculated from the pK_a, which describes the equilibrium,

$$\text{atrazine } H^+ \xrightleftharpoons{K_a} \text{atrazine} + H^+. \qquad\qquad [3]$$

Then, $$K_{a,\text{atrazine}} = \frac{[\text{Atrazine}][H^+]}{[\text{Atrazine } H^+]} \, , \qquad \text{and} \qquad [4]$$

$$pK_{a,\text{atrazine}} = - \log K_{a,\text{atrazine}} = 1.68.$$

The relationship of the pK_a and pK_b for atrazine to the ionization constant of water is shown by the combination of expression [2] and [4]:

$$K_{b,atrazine} \cdot K_{a,atrazine} = K_{H_2O} \, ,$$

$$\frac{[Atrazine\ H^+][OH^-]}{[Atrazine][H_2O]} \cdot \frac{[Atrazine][H^+]}{[Atrazine\ H^+]} = \frac{[H^+][OH^-]}{[H_2O]}$$

Thus, $\quad pK_{b,atrazine} + pK_{a,atrazine} = pK_{H_2O} = 14$

In the subsequent discussion of the triazines, the pK_a will be used since it can be related directly to pH. Basicity is here defined as the ability of the base to react with water. As the reaction shown in equation [1] proceeds in the forward direction the K_b for different s-triazines becomes larger, making the value of their pK_b smaller. Therefore, the larger the pK_a, the more basic is the compound.

The structure together with their chemical and physical properties of some of the most used s-triazines are shown in Table 1. Basicity is affected by the substituents in the 2,4, and 6 positions (Weber, 1967). For changes in only the 2-position, the pK_a decreases as follows: $-OH(5.20)$, $-OCH_3(4.28)$, $-SCH_3(4.05)$, and $-Cl(1.85)$. Increasing complexity of substitution in the 4 and 6 positions with alkylamino groups increases the pK_a slightly. One can see in Table 1 that the solubility of the s-triazines are affected mainly by substitution in the 2-position. The order of decreasing solubility is $-OCH_3$, $-SCH_3$, $-Cl$, and $-OH$ (Ward and Holly, 1966). Another factor which affects solubility is the pH of the system. The total solubility of any ionizable compound is equal

TABLE 1. Chemical and Physical Properties of s-Triazines [a (Weber, 1966), b (Bailey and White, 1965), c (solubility data from Geigy), and d (Ward and Holly, 1966)].

CHEMICAL AND PHYSICAL PROPERTIES OF S-TRIAZINES

SUBSTITUTION

	PROPERTY	Y = -NHC$_2$H$_5$, Z = -NHC$_2$H$_5$	Y = -NHC$_2$H$_5$, Z = -NHC$_3$H$_7$	Y = -NHC$_3$H$_7$, Z = -NHC$_3$H$_7$
-Cl	NAME	SIMAZINE	ATRAZINE	PROPAZINE
	pK$_a$	1.65 (16) b	1.68 (22) b	1.85 a
	SOL	5 (20) b	70 (27) b	8.6 (20-22) b
	MW	201.7 b	215.7 b	229.7 b
	SA	55.3 b	64.8 b	68.7 b
	MP	225-227 b	173-175 b	212-214 b
-SCH$_3$	NAME	SIMETRYNE	AMETRYNE	PROMETRYNE
	pK$_a$	----	----	4.05 a
	SOL	516.2 (25) d	185 (20-22) c	48 (20) b
	MW	213.3 b	227.3 b	241.4 b
	SA	60.0 b	69.5 b	73.4 b
	MP	----	----	118-120 b
-OCH$_3$	NAME	SIMATONE	ATRATONE	PROMETONE
	pK$_a$	4.17 b	4.20 a	4.28 a
	SOL	3200 (20-22) b	1800 (20-22) b	750 b
	MW	197.2 b	211.3 b	225.3 b
	SA	58.4 b	67.9 b	71.8 b
	MP	----	----	----
-OH	NAME	HYDROXYANALOGUE	HYDROXYANALOGUE	HYDROXYANALOGUE
	pK$_a$	----	----	5.20 a
	SOL	----	6.9 (25) d	----
	MW	----	----	----
	SA	----	----	----
	MP	----	----	----

INCREASING BASICITY →

INCREASING BASICITY →

S-TRIAZINE STRUCTURE

TABLE LEGEND

pK$_a$ (°C)
SOL : SOLUBILITY IN WATER in μg/ml (°C)
MW : MOLECULAR WEIGHT
SA : SURFACE AREA IN Å^2
MP : MELTING POINT IN °C
a,b,c,d : SOURCE OF DATA

to the sum of the solubilities of the neutral molecule (at saturation) and of the ion (Albert, 1962).

4. pH Effects on Adsorption, Ionizability and Solubility

Charcoal has been used extensively in solute adsorption studies because of its large surface area and corresponding high adsorption. Leapold (1960) found that the adsorption of 2,4-D (weak acid) on charcoal was independent of pH (2.2 - 8.0). Adsorption of various herbicides on charcoal was highest for those herbicides which had the least dissociation. Kipling (1948) found that adsorption of acetic acid and n-butylamine on charcoal took place only in the undissociated molecular forms. Anderson (1947) summarized his finding on the adsorption of weak bases (alkaloid base nicotine) and weak acids (phenol, diethyl barbituric acid, salicylic acid) on charcoal by saying "Changes in pH which decrease the dissociation of the adsorbendum (adsorbate) increase adsorption."

Frissel and Bolt (1962), Talbert and Fletchall (1963), and Weber (1966) found that those minerals with the higher cation exchange capacities adsorbed more herbicide. For those herbicides which were weak bases, adsorption increased with decreasing pH, and with those which were weak acids the reverse was found. Talbert (1963) erroneously concluded that there was little difference between triazine adsorption on montmorillonite and illite despite a four-fold difference in CEC. However, as we shall observe later, very little protonation of atrazine or simazine occurs at the pH levels (5 and 7) used in Talbert's studies, and only the protonated form would be sensitive to changes in CEC. For valid comparisons of adsorbents, the pH must be chosen to specify the

extent of protonation.

Bailey (1968), studying the adsorption of organic herbicides by montmorillonite, also concluded that "the major factor governing the magnitude of adsorption by different chemical families basic in character is the dissociation constant of the adsorbate." He found that although the pH of the suspension (3.35) was not low enough to allow complete protonation to occur, all six triazines were adsorbed completely on H-montmorillonite. This suggests that the surface acidity also must be considered as a key factor affecting triazine adsorption.

The same factors which influence herbicide adsorption on pure clay minerals and carbon are important for soils. Of the four soil factors, organic matter content, total clay content, cation exchange capacity, and pH, Sheets (1962) found that organic matter content gave the highest correlation with ED_{50} (effective dosage giving a 50 per cent reduction in plant growth) for simazine. No attention was given to the possible interaction of pH and adsorbent characteristics for adsorption of ionizable herbicides.

The effect of pH on protonation ot the s-triazine in water can be calculated as shown by Albert (1962):

$$\text{per cent ionized} = \frac{100}{1 + \text{antilog}(pH - pK_a)} \qquad [5]$$

Weber (1966) showed that the amount of triazine adsorbed on montmorillonite clay increased with increasing protonation (decreasing pH) up to 50 per cent protonation, then decreased with decreasing pH.

Solubilities of the s-triazines range from 5 μg/ml for simazine to

3,200 µg/ml for simetone. The two herbicide properties which affect solubility at a given pH are intrinsic solubility and pK_a. The total solubility for any ionizable herbicide can be calculated for any set of conditions if the pK_a, pH, and the intrinsic solubility are known. Albert (1962) has given the following equation for bases:

$$S_T = S_i [1 + antilog(pK_a - pH)] \qquad [6]$$

where S_T is the total solubility, S_i the intrinsic solubility, and pK_a the negative log of the acid dissociation constant.

5. Temperature Effects on Adsorption, Ionizability, and Solubility

Harris (1964) determined adsorption isotherms for the herbicides, CIPC, monuron, DNBP, diquat, and atrazine at 0 and 50 C on bentonite. An increase in adsorption with decrease in temperature was observed for CIPC, monuron, DNBP, and atrazine, chemicals having solubilities < 200 µg/ml at 20 C. For diquat, having a solubility of 67g/100 ml or 670,000 µg/ml (20 C), there was no difference in adsorption. Harris attributed this lack of temperature dependence to the fact that exchange mechanisms are temperature independent. He further stated that the observed differences in adsorption were related to the indirect influence of temperature on solubility. Talbert and Fletchall (1963) found that the adsorption of simazine and atrazine increased with decreasing temperature. Weber (1965) studied the effect of temperature on adsorption of paraquat, diquat, and prometone (molecular form) on clays and charcoal (pH 6). Paraquat and diquat, which had equal adsorption at 10 and 55 C, were completely adsorbed from solutions containing amounts (in equivalents) less than the CEC of montmorillonite; however, at concentrations above the CEC flocculation of montmorillonite took place. The same behavior was

observed for kaolinite. On charcoal (Darco G-60) there were noticeable differences in adsorption due to temperature. At 55 C both diquat and paraquat were adsorbed considerably more than at 10 C, indicating an endothermic reaction.

On the other hand, the behavior of the prometone in the molecular form (pH 6) in response to temperature variation was the reverse of diquat and paraquat. Adsorption of prometone on montmorillonite increased with decreasing temperature. On kaolinite there was no detectable adsorption of prometone at either temperature. The adsorption of prometone on charcoal was the same at both temperatures. The pK_a which is used to calculate the per cent protonated and the solubility at any given pH is also affected by changes in temperature. These effects can be corrected by adding or subtracting selected temperature coefficients (Albert, 1962).

In general the solubility of most compounds increase with increasing temperature, though for some compounds such as butyl alcohol and certain thiocarbamates (Freed, 1967) the reverse is found. An increase in solubility with increasing temperature decreases adsorption. This suggests that compounds such as those previously mentioned with solubilities less than 200 µg/ml would show changes in adsorption on selected adsorbents with changes in temperature.

In exothermic reactions two things are happening when the temperature is increased in an adsorbate-adsorbent-solvent equilibrium. The attractive forces between the adsorbate and the surface of the adsorbent are weakened by the increase in kinetic energy and the solvent-adsorbate affinity is increased (Kipling, 1965). For adsorbates with low

solubilities, each molecule may have one or more hydration shells
(Freed, 1967). These hydration shells could have quite an effect on
adsorption by van der Waal forces. It is interesting to know that the
important features of a solvent are the same properties which affect
adsorption due to van der Waal forces, namely dipole moment, polarity,
and molecular size and structure (Parker, 1965). Because of this,
water becomes a competitor for adsorption sites.

6. Thermodynamics of Pesticide Adsorption

The amount of herbicide adsorbed does not necessarily describe the
energy with which it is held. This bonding energy can be obtained by
calculating thermodynamic constants. The only extensive work on the
thermodynamics of pesticide adsorption is that by Mills (1967), who
calculated the thermodynamic constants for the adsorption on soils of
1, 2, 3, 4, 5, 6, hexachlorohexane (a nondissociated pesticide).

In order to have a common basis in which to compare adsorption at
two temperatures, he recalculated the thermodynamic constants using a
reduced concentration, as discussed by Kipling (1965). The reduced
concentration (C_e/C_o), a measure of the activity or escaping tendency
of the solute, can be calculated by dividing the equilibrium concen-
tration by the solubility of the solute at the isotherm temperature.
Mills found that adsorption isotherms plotted with the reduced concen-
trations were the same at 20 and 30 C on some adsorbents, indicating a
zero heat of adsorption. On other adsorbents there was an apparent
increase in adsorption with an increase in temperature ($\Delta H > 0$), suggest-
ing that adsorption of the pesticide was endothermic.

The change in enthalpy ΔH for our particular case, is the heat

given off or taken up during adsorption. This heat of adsorption is a function of temperature, concentration, pressure, and other variables.

The true enthalpy, a state function, is an extensive variable which cannot be measured directly. But the change in enthalpy can be added or subtracted from other quantities. By the proper equations the change in enthalpy can be related to other thermodynamic quantities such as ΔG. The following equations can be derived for the adsorption equilibrium (Mills, 1967):

$$aA_{solute} + bA_{solvent}^{surface} \xrightleftharpoons{K_{eq}} cA_{solute}^{surface} + dA_{solvent} \text{ , or}$$

$$\text{herbicide (in solution)} \xrightleftharpoons{K_{eq}} \text{herbicide (adsorbed)}$$
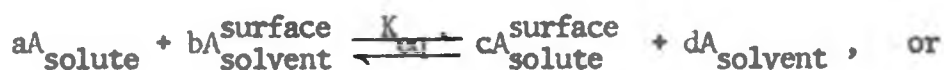
where a, b, c, and d are the stoichiometrical coefficients for the reaction. $A_{solvent}^{surface}$ and $A_{solvent}$ are the activities of the solvent on the surface and in solution, respectively. $A_{solute}^{surface}$ and A_{solute} are the activities of the solute adsorbed and in solution, respectively. The former two activities can be incorporated in the equilibrium constant, i.e., $K_{eq} = A_{solute}^{surface}/A_{solute}$. At low concentrations $A_{solute}^{surface}/A_{solute}$ is equal to $C_{solute}^{surface}/C_{solute}$ where $C_{solute}^{surface}$ and C_{solute} are in moles of solute per 1,000 grams of solvent in their respective phases. The thermodynamic functions and associated definitions pertinent to herbicide adsorption are given below:

$$\Delta G^{\circ} = - RT \ln \frac{\text{herbicide adsorbed}}{\text{herbicide in solution}} = - RT \ln K_{eq}$$

where ΔG° is the change in free energy, R is the gas constant, and T is temperature in °K.

$$\Delta H^{\circ} = \frac{RT_1 T_2}{T_2 - T_1} \ln K_{T_1}/K_{T_2}$$

where K_{T_1} and K_{T_2} are the equilibrium constants at the two experimental temperatures (°K). ΔH° is change in partial molal enthalpy at standard conditions.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

where ΔS° is the change in entropy at standard conditions. Thus, if one has isotherms or knows the equilibrium concentrations at different temperatures, ΔG°, ΔH°, and ΔS° can be calculated for different adsorbent-adsorbate combinations.

Weber (1966) also calculated some thermodynamic constants for the adsorption of organic solutes on charcoal. He used equation [3] and calculated the heats of adsorption (ΔH) for 2,4,D (4,160 cal/gram-mole) and DNOSBP (4.190 cal/gram-mole) a weak acid and phenol, respectively. These values would indicate that adsorption was due to physical bonding.

MATERIALS AND METHODS

1. Adsorbents and Other Variables

Rationale for selecting adsorbents

The importance of the interaction of pH (as it affects triazine protonation) and adsorbent properties was stressed in the Review of Literature. Adsorbents for this study were chosen to provide an evaluation of adsorbate-adsorbent bonding for the protonated and molecular forms of atrazine and ametryne. A description of the adsorbents and the reasons for their selection are given below.

The Molokai soil is probably the most extensive soil series planted to sugarcane in Hawaii. It is a Low Humic Latosol (Oxisol) characterized by a weak A_1 horizon overlying a weathered B horizon containing as much as 55 to 88 per cent kaolin clay (Sherman and Alexander, 1959). The mineralogical composition of Low Humic Latosols is predominantly kaolinite and/or halloysite and hydrated oxides of iron and aluminum. The organic carbon contents of four Molokai soils were found to range from 1.16 to 1.71 per cent (Blomberg and Holmes, 1959). The pH of soils in the Molokai family is generally above 6.0 (Fernandez, 1963). Cation exchange capacity (CEC) on one series was shown by Kanehiro and Chang (1956) to vary from about 20 meq/100g in the surface 8 inches to about 10 meq/100g at the 48-inch depth.

The adsorption of phenylurea herbicides was shown by Hilton and Yuen (1963) to be about six times higher in the surface soil of a Molokai profile than adsorption on soil from 24 inches. Suehisa (1968) found that atrazine adsorption on the Molokai surface soil was

extremely sensitive to pH.

Due to its importance in Hawaiian agriculture, the Molokai soil has
also been the subject of studies concerning soil structure (Cagauan
and Uehara, 1965), soil water adsorption and movement (Sharma and Uehara,
1968), and physical response to saline water (El-Swaify and Swindale,
1968).

The soil samples for this study were obtained from a road cut on
land belonging to the Oahu Sugar Company. The sampling site is located
about one mile above the H-1 defense highway and about 50 yards to the
left of Kunia road as one proceeds up the hill. The A_1 horizon (0 - 12
inches) and B_1 (12 - 34 inches) were sampled to allow a comparison of
adsorption on soils having different organic matter contents and CEC
values but similar mineralogy. The samples used in this study came from
the depth intervals 0 to 2 inches and 17 to 23 inches. The organic
carbon contents obtained by dry combustion were found to be 2.0 per cent
and 1.1 per cent for the surface and subsurface, respectively (Suehisa,
unpublished research report).

Kaolinite was chosen as a clay adsorbent because it is a principal
crystalline aluminosilicate clay mineral in the Molokai and many other
Hawaiian soils. A study of herbicide adsorption on this clay would
provide a measure of its contribution to adsorption by such soils.
Standard kaolinite #7 from the Dixie Rubber Pit Bath, South Carolina,
was obtained from Ward Natural Science Establishment.

Montmorillonite has been used in previous herbicide adsorption
studies because of its prevalence in temperate region soils and its
high CEC and surface area. Increased adsorption of triazine herbicides

on montmorillonite with decreasing pH has been clearly demonstrated by Frissel and Bolt (1962), Weber (1966), and Bailey, et al. (1968). Montmorillonite, a swelling clay, provides a striking contrast with kaolinite to evaluate the effect of CEC and specific surface on the relative adsorption of the protonated and molecular forms of atrazine and ametryne. Montmorillonite #26 from Clay Spur, Wyoming, was obtained from Ward Natural Science Establishment.

Charcoal was included in this study because it has an extremely high adsorption capacity for non-polar, slightly polar, and even ionic molecules. In addition, carbon is an important adsorbing component of Hawaiian sugarcane soils (Hilton and Yuen, 1963). Sugarcane fields are burned just prior to harvest to remove leaf trash. In dry areas the burns are relatively complete, but leave some carbonized particulate matter which has an extremely high adsorption capacity. Apart from the practical implications, the charcoal Darco G-60 (Matheson, Coleman, and Bell) used in this study was expected to provide a much different adsorption response to pH changes than the negatively charged clay minerals.

Adsorbent, adsorbate, pH, and temperature combinations

Adsorption measurements were made with several combinations of adsorbates and adsorbents under different pH and temperature conditions. The combination of variables are summarized in Table 2. The experiments were numbered for convenient reference. Isotherms were measured in most cases; in a few experiments only two concentrations were used.

Atrazine and ametryne adsorption were compared on the two Molokai samples and montmorillonite (experiments 1, 2, 3, 4, 6, and 7).

TABLE 2. Adsorbent, Adsorbate, pH, and Temperature Combinations for Adsorption Experiments.

| ADSORBENTS | ADSORBATES | | | | | | | |
| | Atrazine | | | | Ametryne | | | |
	Expt. No.	T(°C)	pH	C_o(μg/ml)	Expt. No.	T (°C)	pH	C_o(μg/ml)
Molokai (0 - 2) 2.5g	1	25	3.0 7.0	1 - 24	2	25	4.1 7.0	1 - 40
		10	7.0	2, 12		10	7.0	5, 20
Molokai (17 - 23) 2.5g	3	25	3.0 6.9	1 - 24	4	25	4.0 6.7	1 - 40
Kaolinite 0.5000g	5	25	3.2 5.1	1 - 24				
Montmorillonite 0.2500g	6	25	2.9 8.4	1 - 24	7	25	4.2 8.4	1 - 40
		10	8.4	2, 12		10	8.4	5, 20
Charcoal .050, .025g	8	25	7.0	1 - 24				
(17 - 23) Charcoal + Molokai .005g + 2.5g					9	24	4.2 6.4	15,20,40,80

The effect of pH on adsorption was determined on the above adsorbents plus kaolinite (experiment 5) and on the charcoal-soil mixture (experiment 9).

The temperature variable (10 and 25 C) was used on only Molokai (0 - 2) and montmorillonite with both atrazine and ametryne in the molecular form as adsorbates (experiments 1, 2, 6. 7).

2. Preparation of Adsorbents and Solutions

Preparation of soils and crystalline clay minerals

Samples of Molokai (0 - 2) and Molokai (17 - 23) which had been sieved through a 5-mesh sieve (3.962 mm) were saturated with 1 N $CaCl_2$ (to provide a nearly homoionic surface) overnight with occasional stirring. The soils (about 150 g each) were then put on a buchner funnel and successively leached with a 0.1N $CaCl_2$, 0.01N $CaCl_2$, and then with distilled water (approx. 1 liter). The samples were then air dried, ground with a mortar and pestle, and passed through a 32-mesh sieve (0.495 mm).

Samples of kaolinite and montmorillonite were ground with a mortar and pestle and passed through a 16-mesh sieve (0.991 mm). The samples were saturated with a 1N $CaCl_2$ solution overnight with occasional stirring, leached with a 0.1N $CaCl_2$ solution, and subsequently washed with reagent grade methanol. The samples were then air dried, ground, and passed through a 100-mesh sieve (0.147 mm).

Preliminary studies showed that the adsorption of atrazine on 25 and 50 mg charcoal was too high to obtain a measurable equilibrium concentration. Because the weighing of anything less than 25 mg charcoal presented difficulties in precision, a preliminary experiment with

atrazine was run on a mixture of Molokai (17 - 23) and charcoal.

The results of the above experiment showed that a 500:1 mixture was suitable for these studies. A bulk sample of this mixture was prepared by weighing 75.00 g of Molokai (17 - 23) and adding 150 mg of charcoal. Thus, each sample of the mixture (2.5 g) had 5 mg of charcoal.

Preparation of standard solutions of C^{14}-tagged atrazine and ametryne

A stock solution of C^{14}-tagged atrazine was made by adding 163.9 mg ring-labeled (2,4, and 6-position) atrazine (1.0 millicurie) to 50 ml reagent grade methanol and diluting to 4,098 ml with distilled water. This solution was 40.00 µg/ml (541,680 dpm/ml) with respect to C^{14}-atrazine.

Standard solutions of mixed C^{12}- and C^{14}-atrazine were made from the stock solutions. Technical grade atrazine (0.0612 g of a 97.6% purity) was dissolved in 25 ml reagent grade methanol and added to 500 ml of the above 40.00 µg/ml C^{14}-atrazine solution. Water was added to bring the volume to 2 liters. The resulting 40.00 µg/ml atrazine solution had a 3:1 $C^{12}:C^{14}$ ratio and contained 1.25% methanol.

Solutions having atrazine concentrations of 5.00, 10.00, and 30.00 µg/ml were made from dilutions of the 40.00 µg/ml solution.

A stock solution of C^{14}-ametryne was made by adding 69.4 mg ring-labeled (2, 4, and 6-position) ametryne (0.50 millicurie) to 25 ml of reagent grade methanol and diluting the contents to 500 ml with water. This solutions was 138.8 µg/ml (2,220,000 dpm/ml) with respect to C^{14}-ametryne.

Standard solutions of mixed C^{12}- and C^{14}-ametryne were made from the stock solutions by adding 22.4 mg technical grade ametryne (99.98) to a 500 ml volumetric flask. The content was dissolved in 10 ml reagent grade methanol. From the above stock solution 200 ml was taken and added with enough distilled water to make the desired volume. This solution was 100.00 µg/ml (88,800 dpm/ml).

Preparation of scintillation solution

The solution used for the liquid scintillation counting of the equilibrium solution was made by adding 7.0 g/liter PPO (2, 5-Diphenyloxazole) (scintillation grade from Packard), 0.300 g/liter Dimethyl POPOP [1, 4-bis- 2-(4-Methyl-5-Phenyloxazoyl)-Benzene], (scintillation grade from Packard), 100.0 g napthalene (recryst. from alc. from Eastman Organic Chemicals), and enough reagent dioxane (Matheson, Coleman, and Bell) to make a liter.

3. Adsorption Measurements

All adsorption measurements were made at two pH values for each adsorbate-adsorbent combination. The pH values were chosen to obtain the pH closest to pK_a of the adsorbate.

For some of the adsorption measurements, adsorption at two precisely controlled temperatures were made to allow the use of thermodynamic quantities to describe adsorption.

Adsorption measurements were obtained as follows: a known mass of the adsorbent, volume of acid, and the required volumes of herbicide solution of a given concentration and water were added to a 125 ml erlenmeyer flask to bring the total volume to 25 ml. The initial concentrations were calculated by dividing the amount of herbicide

added by the dilution volume. Adjustment of pH and equilibration under controlled temperatures required considerable preliminary work before adsorption measurements could be made.

pH adjustment of the suspension

Since the different adsorbents had different buffering capacities the pH of the suspension for 25 ml had to be obtained by preliminary trials of adding different volumes of 0.1N HCl.

Temperature control during equilibration

Temperature control for measurements made at the different temperatures was maintained to within ± .05 C by a Neslab T45 thermostatic controlled water bath. Measurements at ambient room temperature (24 ± 1 C) were run on a Burrel wrist shaker. Magnetic air driven stirrers were used to provide rapid equilibrium in the bath. A suspended platform was designed and fabricated of plexiglass to support both flasks and stirrers. The air driven magnetic stirrers (Bronwell Mag-jet) were connected in series and attached to a water supply by rubber tubing. To remove heat generated by the circulating pump and to bring the baths to temperatures below ambient, a Neslab portable cooler (PBC-4) was run continuously during adsorption measurements. The temperature of the bath and also of the flask was measured with a Beckman 5 degree differential thermometer ± .01 C and a standard mercury thermometer ± 0.1 C. The measurements were made at 10 and 25 C with a temperature variation of only ± .05 C.

Initial studies on the time required for temperature equilibrium, showed that within 10 minutes the temperature difference between the bath and the suspension in the flask and the stirrer was within 1 C

compared to an initial difference of 7 C), and final equilibrium took place within 40 minutes.

Since the flasks were almost submerged in the bath the problem of buoyancy and leakage of water into the flasks required sealing the tops of the flask with polyethylene squares (held in place with rubber bands) and weighing the flasks down with lead sinkers (suspended from the outside of the flask).

Centrifugation and measurements of equilibrium concentrations

To allow separation of the adsorbent from equilibrium solution, 5 ml of equilibrated suspension was centrifuged in a Servall RC2-automatic superspeed refrigerated centrifuge for 10 minutes at 10,000 rpm. Two ml aliquots in duplicate were removed and placed in the scintillation vial along with 15 ml of the scintillation solution. These vials were then counted on a Packard TRI-CARB liquid scintillation spectrometer. The settings on the TRI-CARB were determined at various intervals to achieve the maximum per cent efficiency. Blanks and the final standard solutions were run with samples.

Determination of equilibration time

Adsorption of the s-triazines in this study was determined by the change in solution concentration upon equilibration with an adsorbent. The time necessary for various adsorbate-adsorbent combinations to attain equilibrium is extremely variable (Hance, 1967). A preliminary study in our laboratory on adsorption of atrazine on Kapaa soil showed that the solution reached an apparent equilibrium after two to three hours of constant agitation. When suspensions were allowed to equilibrate for periods in excess of 24 hours, there was evidence of a further increase in

adsorption. This has since been recognized as the result of chemical hydrolysis, the hydroxyanalogue of atrazine being more highly adsorbed than atrazine (Green, et al., 1968). The concern in the work reported here was that adsorption equilibrium should be approached as closely as possible with a minimum of hydrolysis for low pH treatments.

The time required for adsorption equilibrium was determined by the following experiment: Five grams (oven dried) Kapaa (0 - 4)[1] was put into a 125 ml flask and 10 ml of a 40.00 μg/ml solution 3:1 atrazine solution were added. The volume was brought to 25 ml. The flask was stoppered and sealed and put into a previously equilibrated water bath at 25.1 ± 0.05 C. At 3, 6, and 8 hours the samples were removed and analyzed. The 3- and 6-hour equilibrations were measured in triplicate while the 8-hour samples were duplicated. Thin layer chromatograms were developed for the extracts at 3 and 6 hours to determine the extent of atrazine hydrolysis during equilibration for the low pH treatment. Chromatograms were analyzed on a radio chromatogram scanner.

Adsorption of atrazine on Kapaa soil at 25 C for 3, 6, and 8 hours is shown in Table 3. There was a slight increase in calculated adsorption for equilibration periods up to eight hours. However, considering the possibility of hydrolysis of atrazine and the experimental problems associated with longer equilibration, a three-hour equilibration period was chosen.

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[1] Kapaa (0 - 4) was initially selected as one of the adsorbents to be studied but was later eliminated when the number of adsorbents had to be reduced.

TABLE 3. Adsorption of Atrazine on Kapaa Soil with Time
(using initial concentrations of 16 μg/ml)

	Equilibration Time		
	3 hours	6 hours	8 hours
Equil. conc. (μg/ml)	10.86 ± 0.08	10.45 ± 0.13	10.31 ± 0.28
Amt. adsorbed (μg/g)	25.70 ± 0.38	27.71 ± 0.65	28.46 ± 1.40

Precision of Adsorption Measurements

The average deviations shown in Table 3 reflect random counting errors in addition to other experimental errors. The dilutions used in the making of the standard solutions in these studies were made with transfer pipets. Though many such dilutions were made, the error contribution from each dilution did not exceed 0.2%. Counting errors, estimated from error curves calculated from the Poisson distribution for the 99% confidence level (Nuclear-Chicago, 1963), ranged from 0.6% for the high count samples to 2.0% for the low count samples. Counting errors exceeded the cumulative dilution errors in most cases. In general, precision appeared poor if the equilibrium solution concentration was less than 1 µg/ml and adsorption was less than 1 µg/g at these concentrations.

Adsorption calculations

To calculate the equilibrium concentrations a simple ratio was used because of the linear relationship of concentration vs. counts per minute of the standard curve.

The amount adsorbed was assumed to be equal to the amount lost from solution. Thus, the calculation for the amount adsorbed was as follows:

$$x/m = V_t (C_o - C_e)/M$$

where V_t is the total volume of the solution, C_o the initial concentration, C_e the equilibrium concentration, M the mass of the adsorbent, and x/m the amount adsorbed in micrograms herbicide per gram oven-dry adsorbent. The data were then plotted on log-log paper to give the linear form of the Freundlich equation, i.e., $\log x/m = (1/n)\log C + \log K$.

The parameters of the Freundlich equation, thought to have physical meaning in some cases of adsorption (Adamson, 1967), were obtained from the curve drawn through the data points (visually determined best fit).

4. Solubility Measurements

Saturated solutions of atrazine and ametryne were prepared as follows: Atrazine and ametryne were weighed in excess of that required for saturation and put in 125 ml flasks. To this was added 10 ml of 0.001 N NaOH (to allow such a pH value that only the molecular form could exist) and enough 1% methanol (stock solutions were made up in 1 - 2% methanol) to bring the final volume to about 100 ml. The flasks were stoppered and allowed to equilibrate at room temperature 24 ± 1 C on the shaker and at 10 ± 1 C in the refrigerator. The equilibrating supernate was decanted into centrifuge tubes and centrifuged at 15,000 rpm for 20 minutes at the specified temperature. Aliquots were taken, diluted, and analyzed on the DK2 at 222 mμ. Measurements were made until equilibrium was reached (a modified method after Ward and Holly, 1966).

RESULTS AND DISCUSSION

1. pH Effects on Adsorption of Atrazine and Ametryne on Different
   Adsorbents

Comparisons of atrazine and ametryne adsorption on each adsorbent

The importance of the interaction of pH, triazine pK_a, and adsorbent properties was stressed in the Review of Literature (section entitled "pH Effects on Adsorption, Ionizability, and Solubility"). The pH - pK_a relationship determines the percentage protonation of a given triazine. Equation [5] was used to calculate the amount of protonation expected for three s-triazines in aqueous solution with pH varying from 0.5 - 7.0. Figure 2 shows the pH-protonation curves for atrazine, prometryne, and 2-hydroxy-4,6-bis(isopropylamino)-s-triazine. The lack of a published pK_a value for ametryne (the 2-position analogue of atrazine) and its hydroxyanalogue necessitated the use of the published pK_a values for prometryne and its hydroxyanalogue for comparison with atrazine (see Table 1). As stated earlier, the pK_a's change very little for the 4 and 6 position substitutions. Figure 2 shows the wide difference in pK_a values associated with particular 2-position groups. The way in which protonation varies with pH for compounds having different pK_a values is apparent. For example, it is clear that ametryne, with a pK_a near that of prometryne (pK_a 4.05), would be largely in the proto-nated form at pH 3.5, while atrazine (pK_a 1.68) would be only slightly protonated at the same pH.

The adsorption of atrazine and ametryne on Molokai (0 - 2) is shown in Figure 3. At pH 7 ametryne is more highly adsorbed than atrazine.
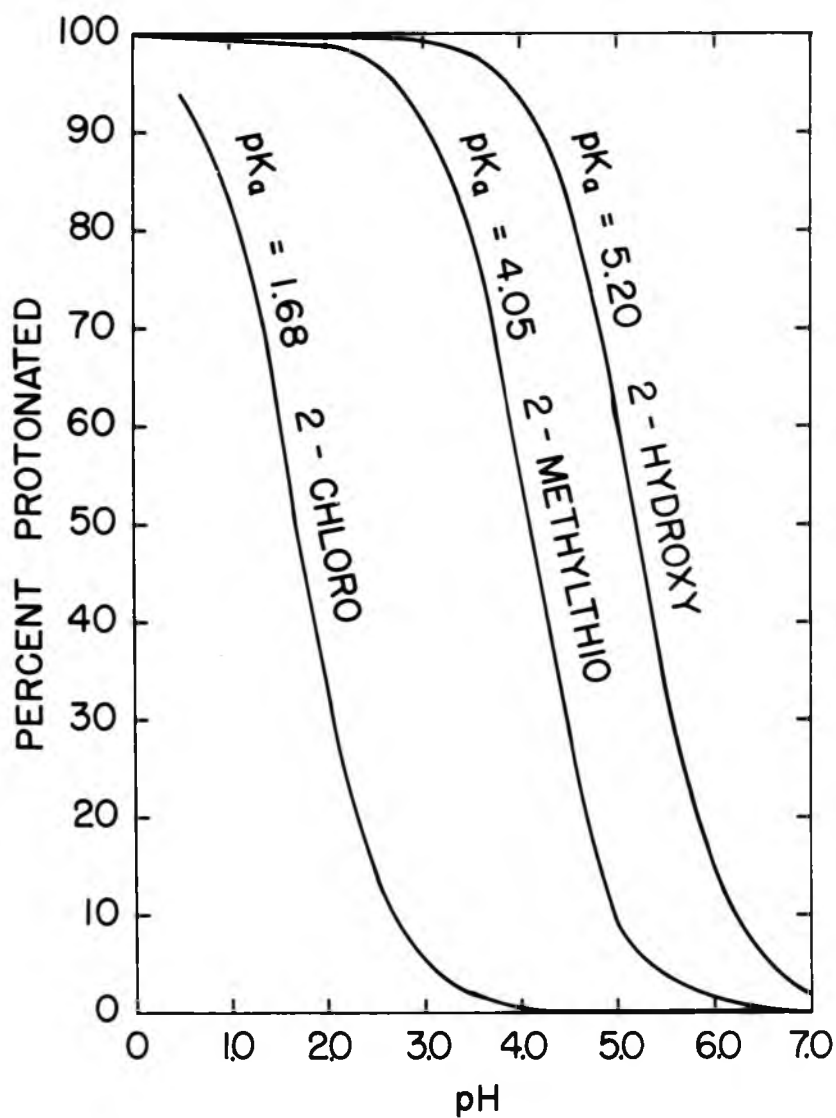
FIGURE 2. Calculated Protonation of Selected s-Triazines [2-chloro-
4-ethylamino-6-isopropylamino-s-triazine, 2-methylthio-4,
6-bis(isopropylamino)-s-triazine, and 2-hydroxy-4,6-bis
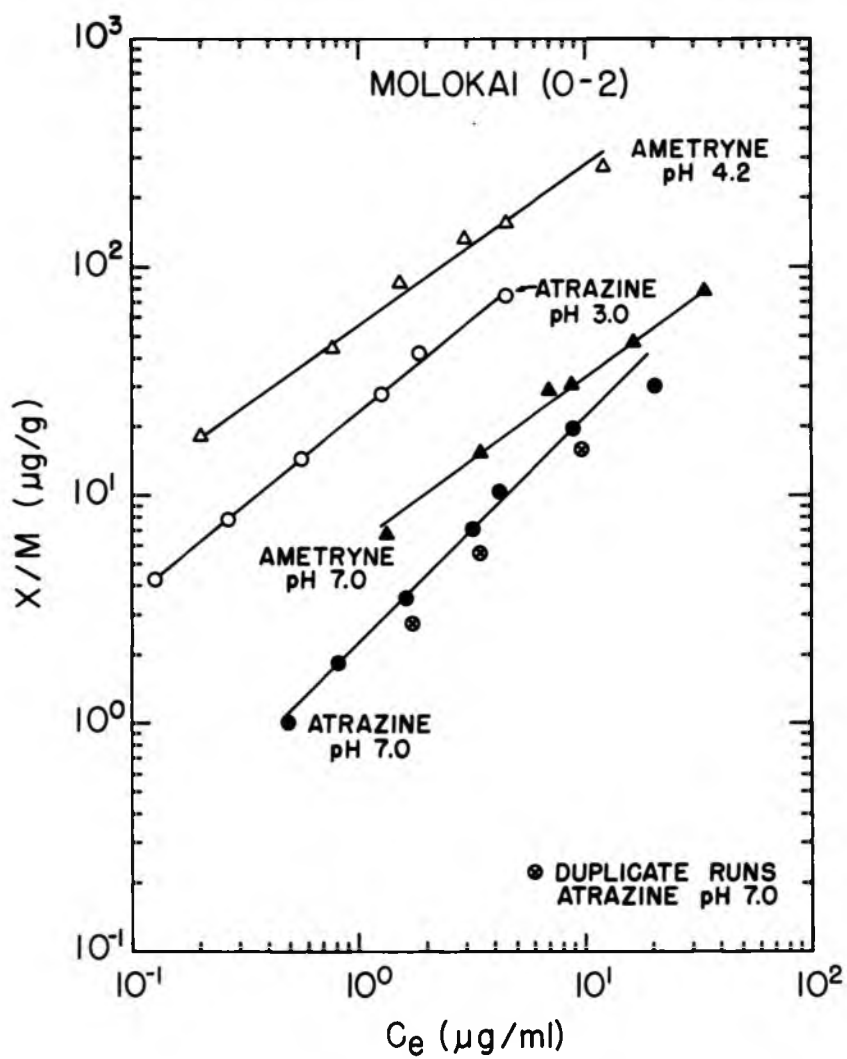(isopropylamino)-s-triazine] as Functions of pH.

FIGURE 3. Adsorption of Atrazine and Ametryne on Molokai (0 - 2).

Since both are in the molecular form at this pH, the difference in adsorption appears to be associated with the - SCH_3 and - Cl substitutions in the 2-positions. The adsorption isotherm of atrazine at pH 3 is lower than that of ametryne at pH 4. To understand what is happening one must look at the per cent protonated for each compound at the pH values of interest. Figure 2 shows that atrazine is 5% protonated at pH 3, whereas prometryne is 50% protonated at pH 4. For 50% of the protonated form to exist in solution, the pH of the atrazine suspension must be brought to 1.68, the pK_a of atrazine. For these experiments, a minimum pH of about 3.0 was used to avoid hydrolysis of the adsorbate (Armstrong, et al., 1967) and acid dissolution of the adsorbents.

The adsorption of atrazine and ametryne on Molokai (17 - 23), a dominantly kaolinitic subsurface horizon, is shown in Figure 4. Ametryne and atrazine have the same magnitude of adsorption in the molecular form (high pH). There is a decrease in the CEC (from 20 meq/100g in the surface soil to 10 meq/100g at 17 - 23 inches) and organic matter (2.0 vs. 1.1%), but only the decrease in organic matter content would reduce adsorption of the molecular form. The adsorption response to pH for both atrazine and ametryne is less pronounced on the subsurface Molokai than on Molokai (0 - 2), probably due to the limited CEC of the former adsorbent.

The data points for atrazine and ametryne at the low pH on Molokai (17 - 23) are scattered. This is due to the fact that adsorption (x/m) is not measured directly but is calculated from the change in solution concentration. When adsorption is low, the change in the concentration is small. Earlier work(Green and Yamane, 1968) has shown that the
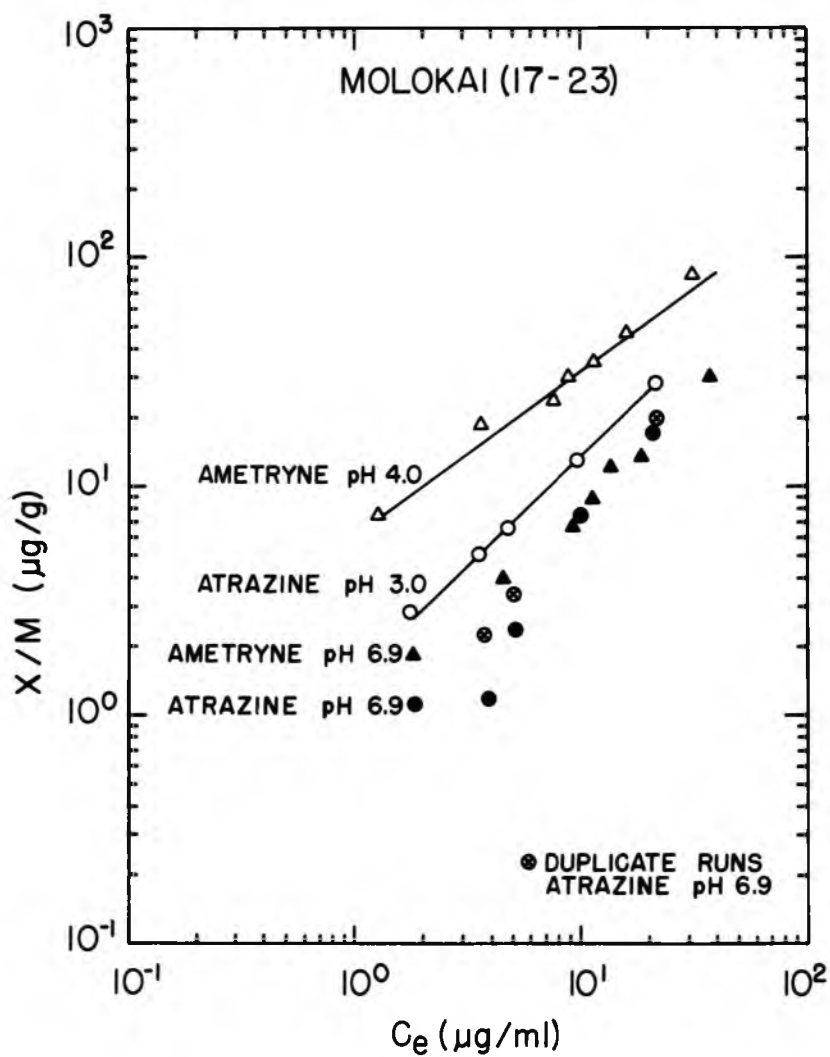
FIGURE 4. Adsorption of Atrazine and Ametryne on Molokai (17 - 23).

coefficient of variation for adsorption is much larger for subsurface horizons where the concentration change is small.

The adsorption of atrazine at both pH's on kaolinite was too low to be measured with any precision. The raw data are shown in Appendix Table A-1.

On montmorillonite, ametryne adsorption was again higher than atrazine at the high pH (Figure 5). At the lower pH, differential adsorption of ametryne and atrazine is apparent, demonstrating the importance of the relative protonation of these two compounds on adsorbents having a high CEC.

Comparison of adsorbents

The isotherms shown in Figures 3, 4, and 5 are presented again in Figures 6 and 7 to allow comparisons of three adsorbents. The adsorption of atrazine on all adsorbents is lower at the higher pH (Figure 6). This shows that the protonated form is preferred on these adsorbents. The surface area of the adsorbents decreases in the following order: montmorillonite, Molokai (0 - 2), and Molokai (17 - 23). This decrease in surface area is probably responsible for the decrease in adsorption of atrazine in the molecular form.

Despite the small amount of protonation of atrazine (5 %) at the low pH, the adsorption response on the three adsorbents due to a change in pH is clearly related to their CEC values.

Figure 7 shows that the general adsorption trends for atrazine are also applicable for ametryne, but the response of ametryne adsorption to a reduction in pH far exceeds that of atrazine. The relative protonation of ametryne (about 50% protonated) and atrazine (5%) at the low pH values

FIGURE 5. Adsorption of Atrazine and Ametryne on Montmorillonite.

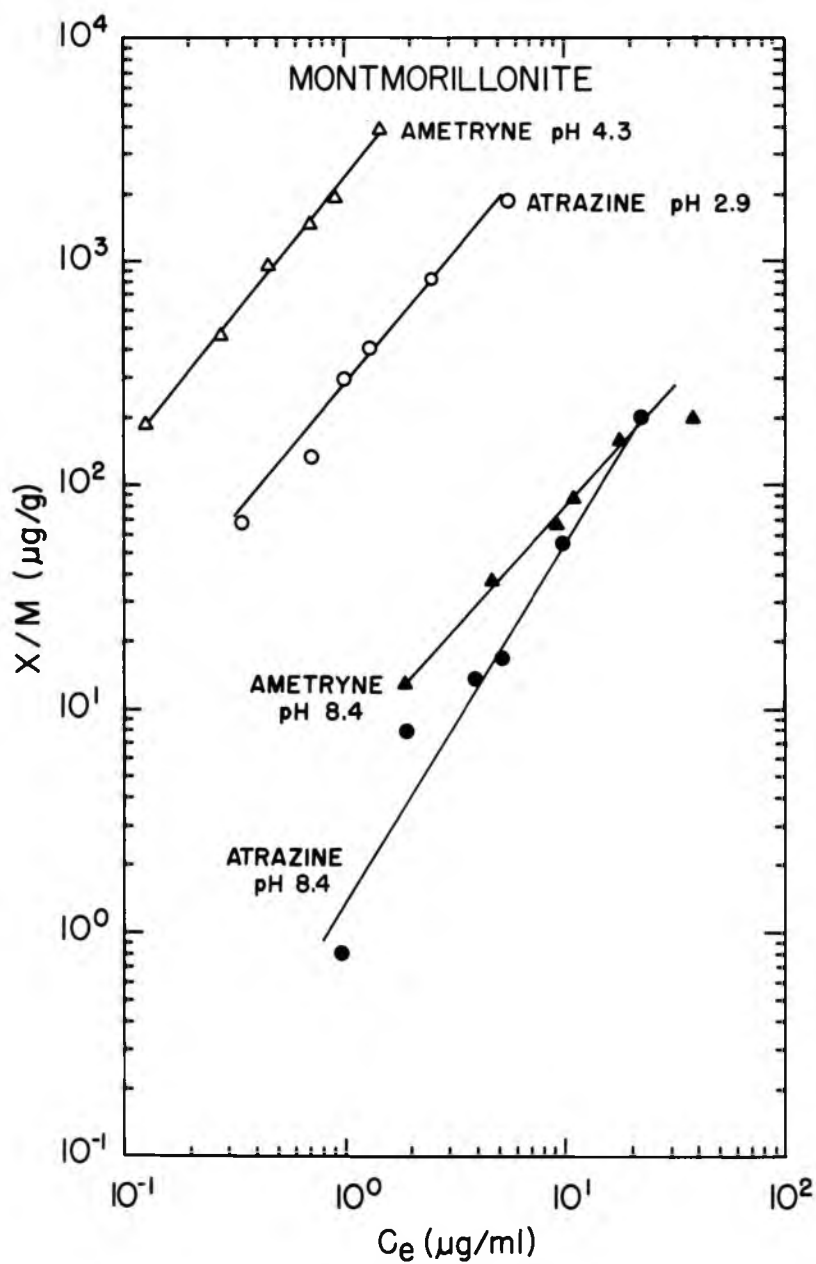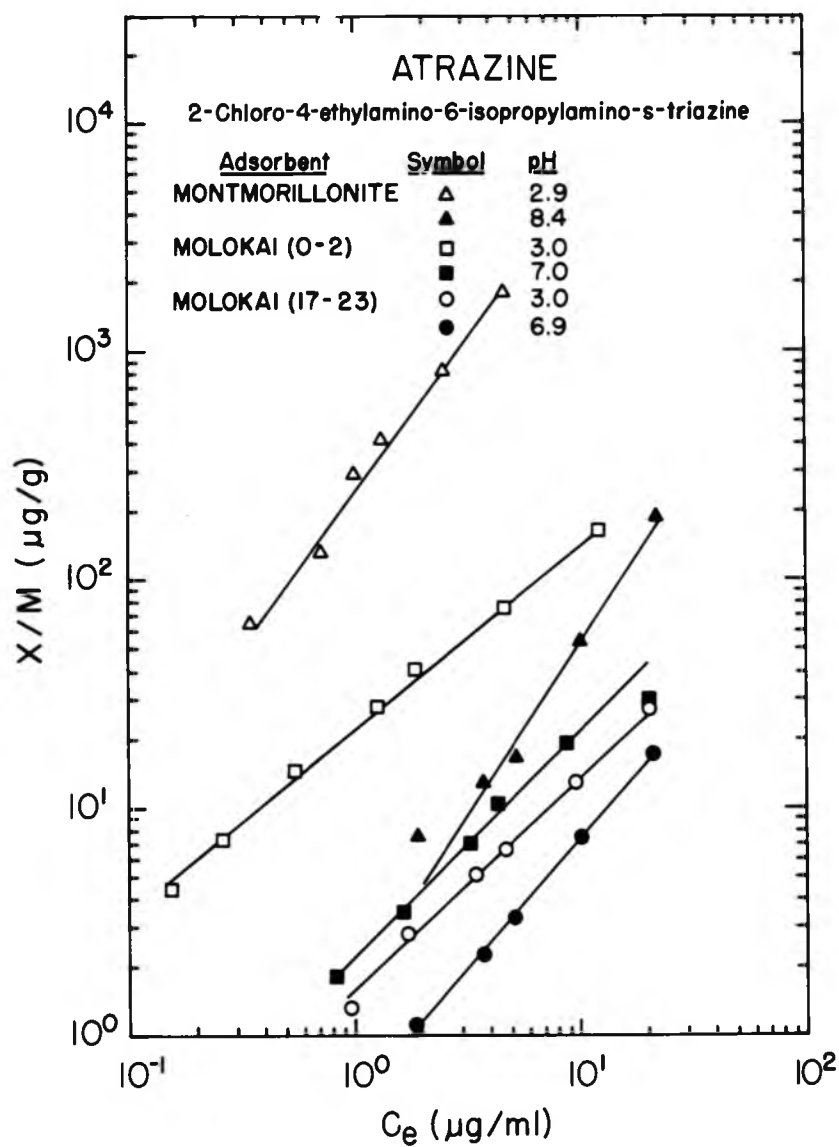FIGURE 6. Adsorption of Atrazine on Molokai (0 - 2), Molokai (17 - 23), and Montmorillonite in the Molecular (high pH) and Protonated (low pH) Forms.
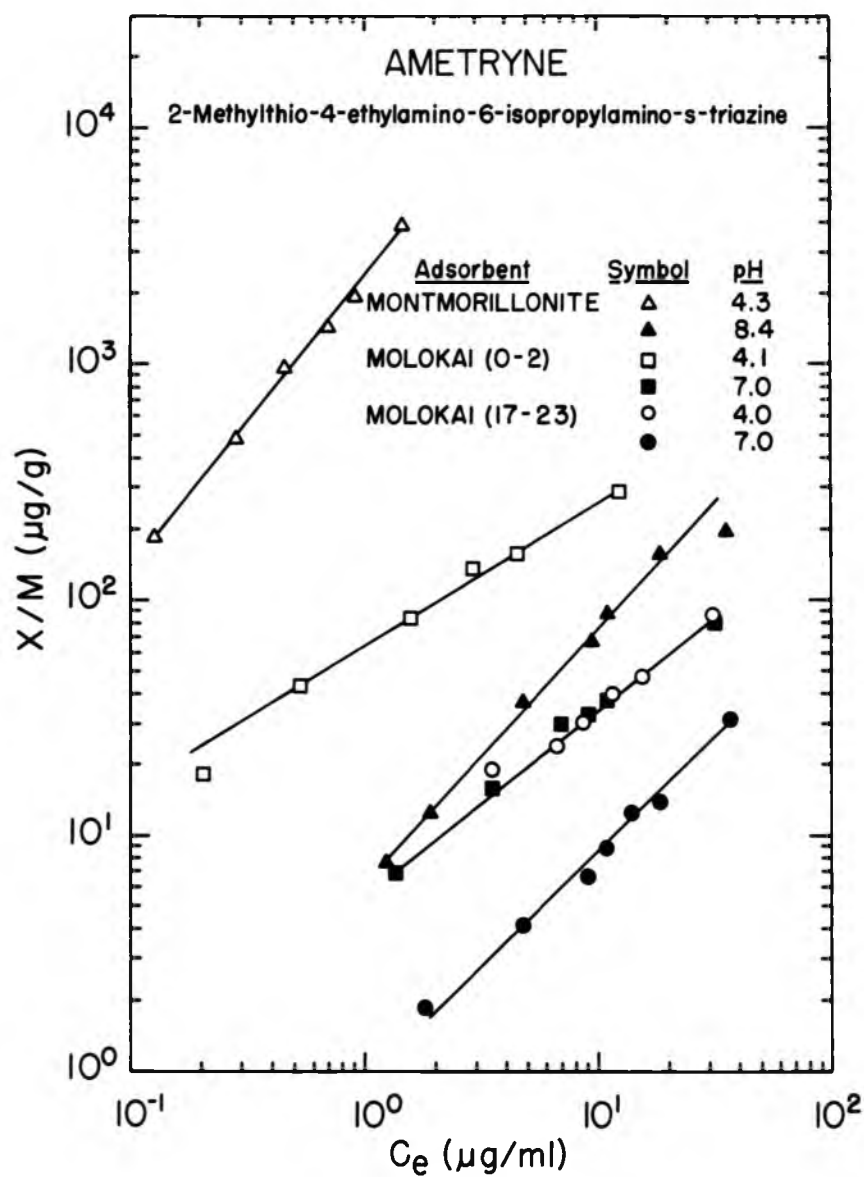
FIGURE 7. Adsorption of Ametryne on Molokai (0 - 2), Molokai (17 - 23), and Montmorillonite in the Molecular (high pH) and Protonated (low pH) Forms.

explains this difference between compounds.

The Freundlich equation, $x/m = KC$, $1/n$, though empirical in nature, can provide rough estimates of the adsorbent capacities and the intensity of adsorption (Adamson, 1967). The parameter K, the intercept at unit concentration on a log-log plot, estimates the capacity while $1/n$, the slope of a log-log plot, estimates the intensity.

The K and $1/n$ values obtained from isotherms in Figures 6 and 7 are shown in Table 4. The K for atrazine and ametryne at the low pH increases with increasing CEC of the adsorbents. Between different pH's, K is higher for the lower pH. The K for ametryne is almost always higher than the K for atrazine. Thus, the K is directly related to the CEC of the adsorbents and the per cent protonated, the latter of which is a function of both the pK_a of the adsorbate and the pH of the system. Valid interpretations of adsorption require knowledge of both CEC and the extent of protonation. Values of $1/n$ vary considerably between adsorbent-adsorbate-pH combinations but do not appear to give meaningful information on the intensity of adsorption in relation to the variables. The $1/n$ values were highest on montmorillonite, exceeding 1.0 in every case. These values exceed the maximum for the Freundlich equation. The nature of the curve (concave to the concentration axis) does not permit values of n greater than unity (Adamson, 1967).

Attempted measurements of atrazine adsorption on charcoal (experiment 8, Table 2) gave no results due to nearly complete adsorption of the solute. Subsequent measurements of ametryne adsorption on a 500:1 mixture of Molokai (17 - 23) and charcoal gave the results shown in Figure 8. The many-fold increase in adsorption due to the added carbon

TABLE 4. Freundlich Adsorption Parameters* for Atrazine and Ametryne on Three Adsorbents.

ADSORBENTS	ADSORBENT PROPERTIES		ADSORBATES							
	CEC m.e./100g	O.M. %	Atrazine				Ametryne			
			low pH		high pH		low pH		high pH	
			K	1/n	K	1/n	K	1/n	K	1/n
Montmorillonite	99	0.0	240	1.3	1.6	1.5	2,300	1.2	6.2	1.1
Molokai (0 - 2)	20	2.0	22	0.8	2.2	1.0	64	0.6	5.6	0.8
Molokai (17 - 23)	10	1.1	1.6	0.9	0.5	1.2	5.6	0.8	0.9	1.0

* From the equation $x/m = KC^{1/n}$.
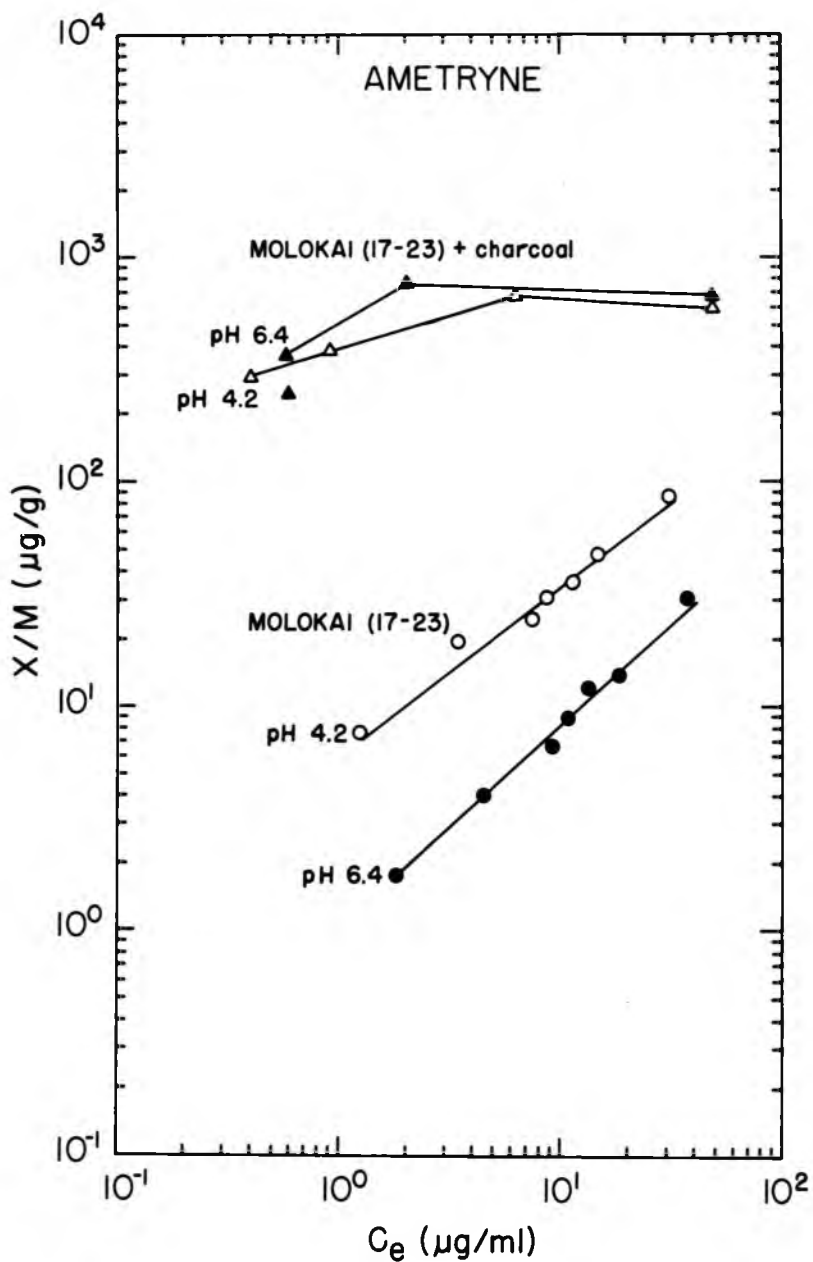
FIGURE 8. Adsorption of Ametryne on Molokai (17 - 23) and on the 500:1
Mixture of Molokai (17 - 23) and Charcoal in the Molecular
and Protonated Forms.

demonstrates the tremendous adsorption capacity of carbon for organic pesticides. As anticipated, the adsorption response to pH was much different for the charcoal-soil mixture.

With the exception of the one apparently erratic data point for pH 6.4, adsorption was higher for the molecular form than for the protonated form.

As stated previously, there was little confidence in adsorption data obtained for concentrations < 1 µg/ml. For the data points > 1 µg/ml, mean values of x/m for the two pH's were three standard deviations apart, indicating that the differences were probably real. Final conclusions concerning the pH effect on triazine adsorption on uncharged surfaces awaits further research.

2. Temperature Effect on Adsorption

As discussed in the Review of Literature (in section on "Temperature Effects on Adsorption, Ionizability, and Solubility"), the response of herbicide adsorption to temperature varies depending on the type of herbicide (i.e., permanent charge, nondissociable and dissociable) and the nature of the adsorbent, Weber, et al., (1965) showed that prometone (a methoxy 2-position analogue of prometryne) in the molecular form exhibited a difference in response with respect to temperature. Since little work had been done on the effect of temperature upon the adsorption of atrazine and ametryne in both the molecular and protonated forms, an experiment was set up to accomplish this. The adsorbents montmorillonite and Molokai (0 - 2) were chosen because past work on some s-triazines in the molecular form showed decreases in adsorption with increasing temperature. The data for the adsorption of atrazine and

ametryne in the molecular form on montmorillonite and Molokai (17 - 23) at 10 and 25 C are shown in Table 6.

It was expected that adsorption at 10 C would be higher than at 25 C. However, a comparison of adsorption of atrazine and ametryne at 25 C and 10 C on both adsorbents shows that the variation of C_e between duplicates is equal to or greater than the average deviation between mean C_e values at different temperatures. Thus, there was no detected temperature effect on adsorption.

The lack of differences in adsorption between 10 and 25 C will be discussed further in the section "Adsorption Isotherms with 'Reduced' Concentrations."

3. Triazine Solubility in Relation to Temperature and pH
Temperature effect on solubility

The solubility of atrazine and ametryne at 10 and 24 C was determined because there were no published data on the solubility of atrazine and ametryne for the experimental conditions used in this adsorption study (i.e., 10 and 24 C, 1 - 2% methanol, and an unbuffered solution at pH 7 - 8). The data are presented in Table 5 as mean ± the standard deviation for three replicates. The time required for equilibrium was about four days. The difference in solubility of ametryne at 24 C at three and four days is due to the large dilution required to make a reading on the Beckman DK-2.

The solubilities obtained in this study for atrazine shown in Table 6 are plotted in Figure 9 along with solubility data reported by other investigators. Although the measured solubilities are much lower than those of other investigators', the experimental conditions are also

TABLE 5. The Adsorption of Ametryne on Molokai (0 - 2) and Montmorillonite at 10 and 25 C.

	25 C		10 C		$(C_{e_{10}} - C_{e_{25}})/2$
ADSORBENT	C_o (µg/ml)	C_e ± Av. Dev. (µg/ml)	C_o (µg/ml)	C_e ± Av. Dev. (µg/ml)	
		Atrazine			
Molokai (0 - 2)	5.00	3.48 ± 0.04	5.00	3.44 ± 0.02	0.02
pH = 7	20.00	15.33	20.00	15.19 ± 0.11	0.07
Montmorillonite	5.00	4.63 ± 0.02	5.00	4.46 ± 0.01	0.08
pH = 8.4	20.00	18.44	20.00	18.21 ± 0.10	0.11
		Ametryne			
Molokai (0 - 2)	2.00	1.72 ± 0.00	2.00	1.65 ± 0.01	0.04
pH = 7	10.90	8.96 ± 0.17	10.90	9.16 ± 0.17	0.10
Montmorillonite	2.00	1.91	2.00	2.00 ± 0.01	0.04
pH = 8.45	10.90	10.36 ± 0.11	10.90	10.51 ± 0.00	0.12

TABLE 6. Water Solubility of Atrazine and Ametryne at 10 and 24 C

| | 24 ± 1 C | | | 10 ± 1 C | |
| | Atrazine | Ametryne | | Atrazine | Ametryne |
Equilibration Time	Mean ± S.D.* (µg/ml)	Mean ± S.D. (µg/ml)	Equilibration Time	Mean ± S.D. (µg/ml)	Mean ± S.D. (µg/ml)
3 days	42.0 ± 0.9	235 ± 11.8	3 days	28.5 ± 1.2	193.3 ± 1.5
4 days	44.0 ± 3.5	250 ± 11.8	4.5 days	28.3 ± 1.8	187.5 ± 2.9

* Estimated from the range of duplicate or triplicate measurements.
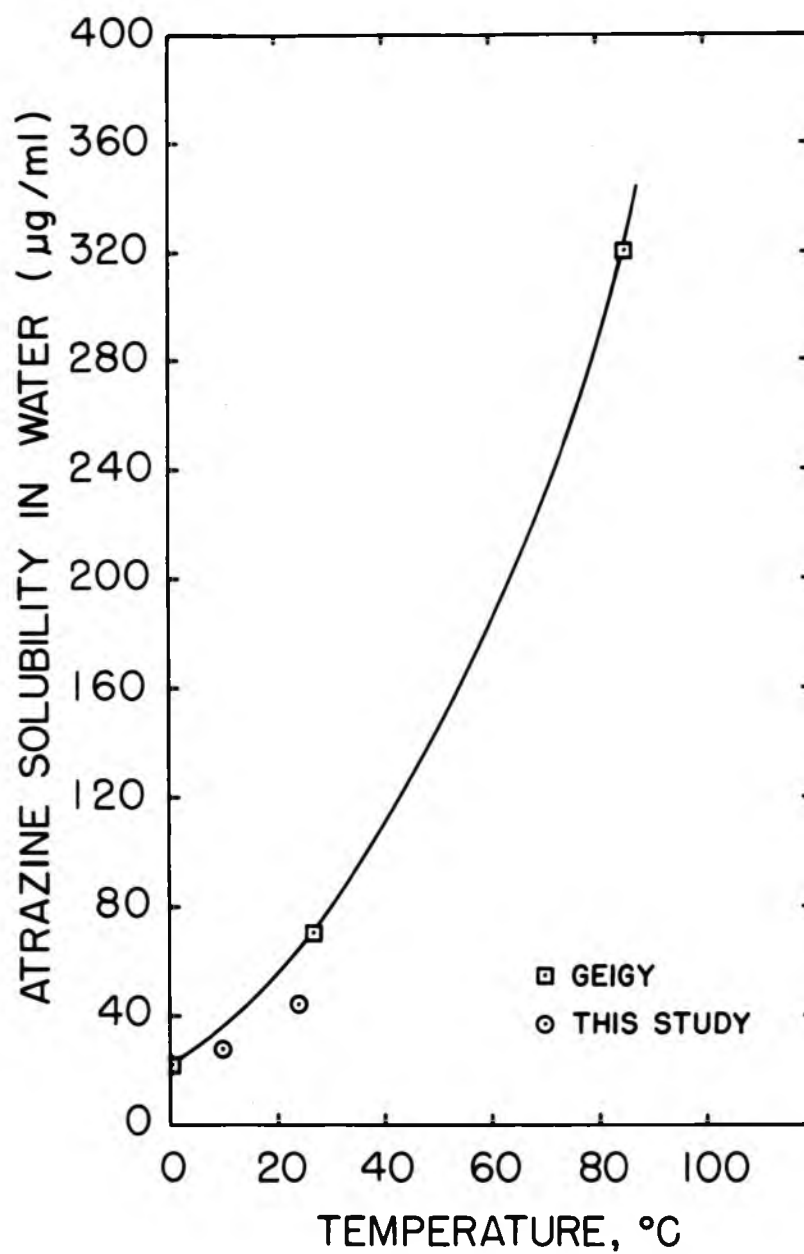
FIGURE 9. Solubility of Atrazine in Water as a Function of Temperature.

different. Swanson[2] showed that increasing salt concentrations decreased the atrazine solubility.

pH effect on solubility

In the previous discussion it was shown that an increase in temperature increases the intrinsic solubilities of the s-triazines. Another factor which also affects solubility as well as adsorption is the pH of the suspension. Figure 10 shows the calculated solubility curves for atrazine, ametryne, and their hydroxyanalogue. Because the pK_a values for ametryne and its hydroxyanalogue were not available, the pK_a values of prometryne (4.05) and its hydroxyanalogue (5.20) were used. The equation used to calculate the data points was given by Albert (1962):

$$S_T = S_1[1 + antilog(pK_a - pH)]$$

There are three variables in this equation: S_1 (the intrinsic solubility), pK_a, and pH. From Table 1 one can see that the intrinsic solubility and pK_a are physical and chemical properties of the s-triazines which vary mainly with substitution in the two position. At pH values from 7 to 5 for ametryne and 7 to 3 for atrazine, the intrinsic solubility is the property which determines total solubility. The importance of their pK_a's becomes apparent below a pH value of 5 for ametryne and 3 for atrazine. Although the intrinsic solubility of the hydroxyanalogue is lower than that of either ametryne or atrazine, the net solubility quickly approaches that of ametryne with decreasing pH.

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[2] Roger A. Swanson, University of Arizona. Personal communication, June 13, 1968.

FIGURE 10. Calculated Triazine Solubility as a Function of pH.

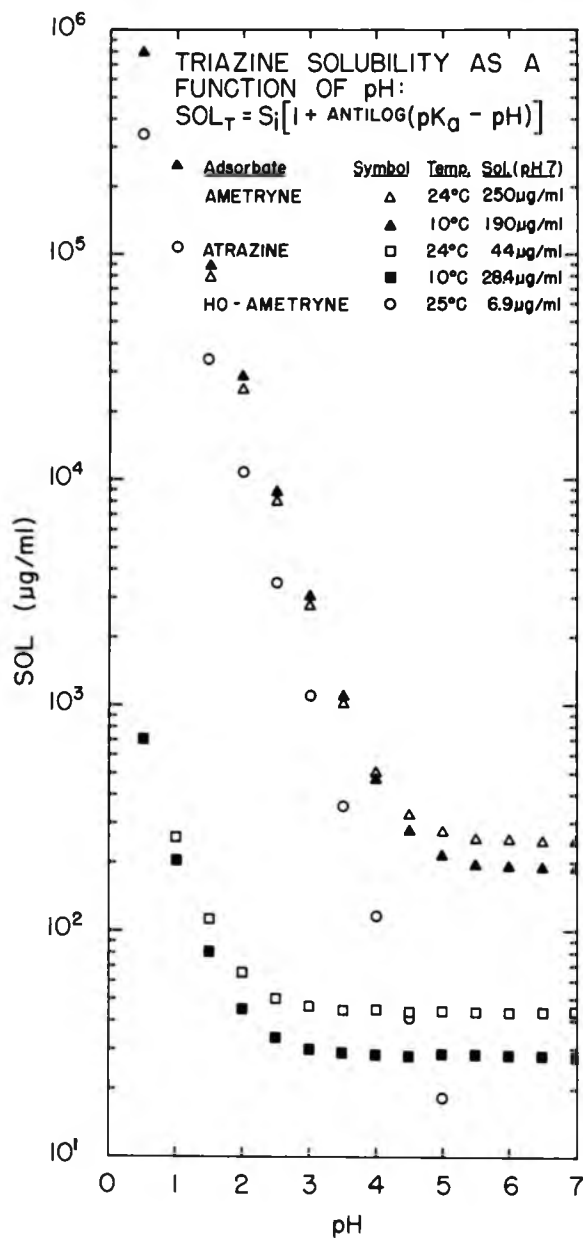The effect that temperature has on the total solubility decreases with intrinsic solubility. The differences between the total solubilities at two temperatures soon disappear as the pH is decreased.

4. Adsorption Isotherms with "Reduced" Concentration C_e/C_o based on temperature effects on solubility

Because of the complex adsorption-temperature-solubility relationship, isotherms at two temperatures cannot be compared directly. Mills (1967) used a "reduced" concentration in place of the equilibrium concentration as it had been discussed earlier, by Kipling (1965). The "reduced" concentration is obtained by dividing the equilibrium concentration (C_e) by the intrinsic solubility (C_o) at the working temperature (see Table 6 for the intrinsic solubilities of atrazine and ametryne at 10 and 24 C).

The calculated adsorption (x/m) of atrazine and ametryne on Molokai (0 - 2) at 10 and 25 C corresponding to data in Table 5 are plotted in Figure 11(A). The same x/m values are then replotted against the concentration ratio, C_e/C_o, by dividing the equilibrium concentration by the corresponding solubility, in Figure 11(B). Figure 11(A) shows that the adsorption of atrazine and ametryne on Molokai (0 - 2) at both temperatures was about equal. It was mentioned in the Review of Literature (in the section entitled "Temperature Effects on Adsorption, Ionizability, and Solubility") that when temperature is increased, the solvent-adsorbate affinity is increased (Kipling, 1965). One can see in Figure 9 that at 10 and 25 C the solubility of atrazine changes very little, 28.3 versus 44.0 µg/ml. Because the heat of adsorption due to physical bonding is low, the differences in adsorption for the triazines
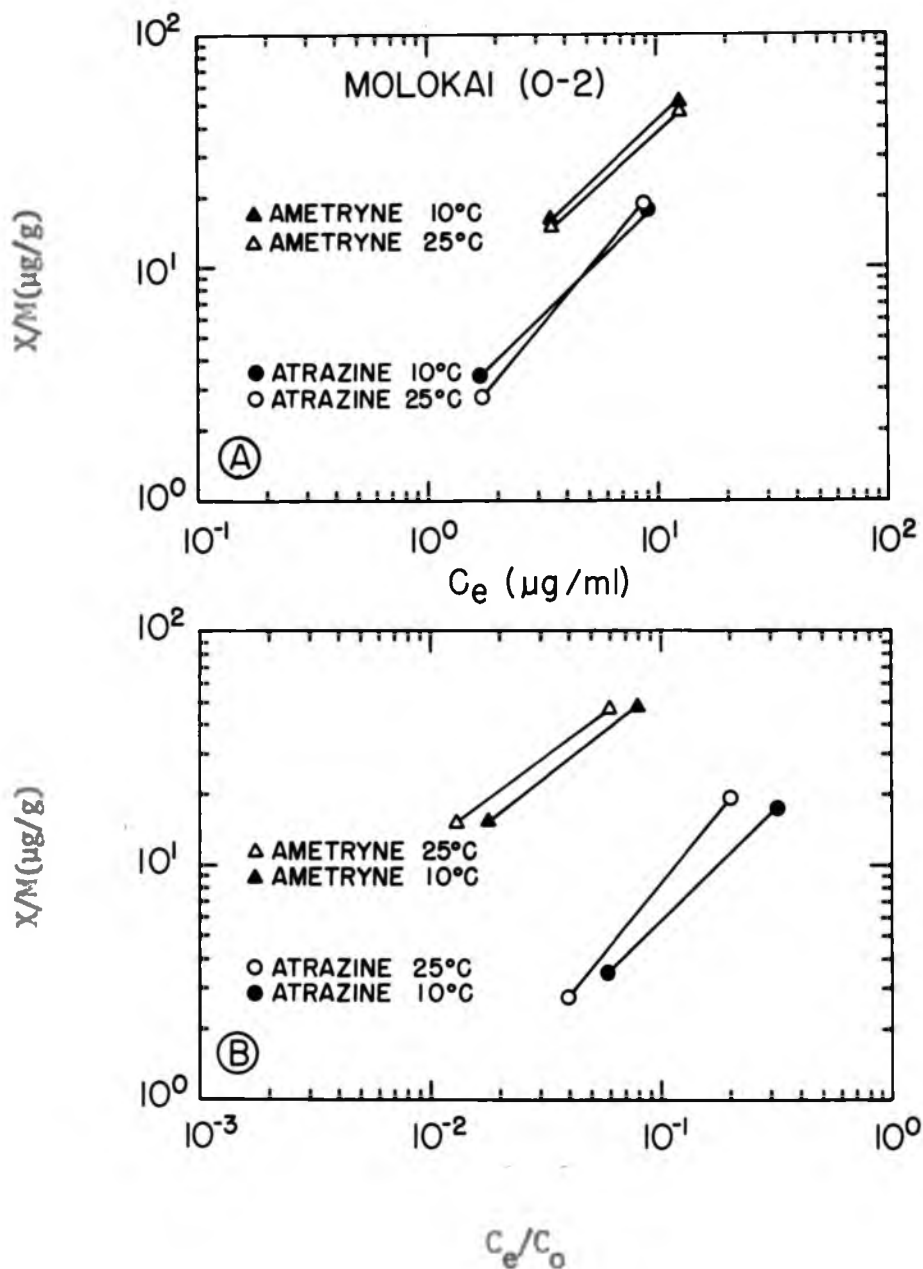
FIGURE 11. Adsorption Isotherms for Molokai (0 - 2) with "Reduced" Concentrations with Respect to Temperature.

at 10 and 25 C should be correspondingly small.

Since the difference in adsorption would be low for small ΔH° values, and the change in solubilities of atrazine and ametryne have been shown to be small, little change in adsorption at 10 and 25 C would be expected.

The adsorption of atrazine and ametryne on the "reduced" plot shows an unexpected effect of temperature on adsorption. Mills (1967) found similar results for hexachlorohexane. On the other hand, Weber, et al. (1965), Talbert and Fletchall (1963), and Harris and Warren (1964), working with the triazines, used larger temperature differences than those used in this study and found an inverse relationship between temperature and adsorption. However, considering the temperature range in which they were working and the effect of temperature on solubility, one wonders if the observed differences might be due only to solubility effects.

This discussion has been based upon the temperature-solubility behavior of most compounds. Deviations from the normal involve situations in which there is a wide departure from Raoult's law.

The scarcity of published solubility data for the triazines at various temperatures prompted a search in the literature for an equation that would allow calculation of the temperature-solubility relationship based on the properties of an ideal solution. Hildebrand and Scott (1950) presented such an equation, derived from thermodynamic considerations: it is shown in Figure 12. This theoretical curve is based on Raoult's law. The y axis is the log of the mole fraction of the solute while the x axis is the reciprocal of the absolute temperature. The equation requires only the melting point of the solute and its solubility at one
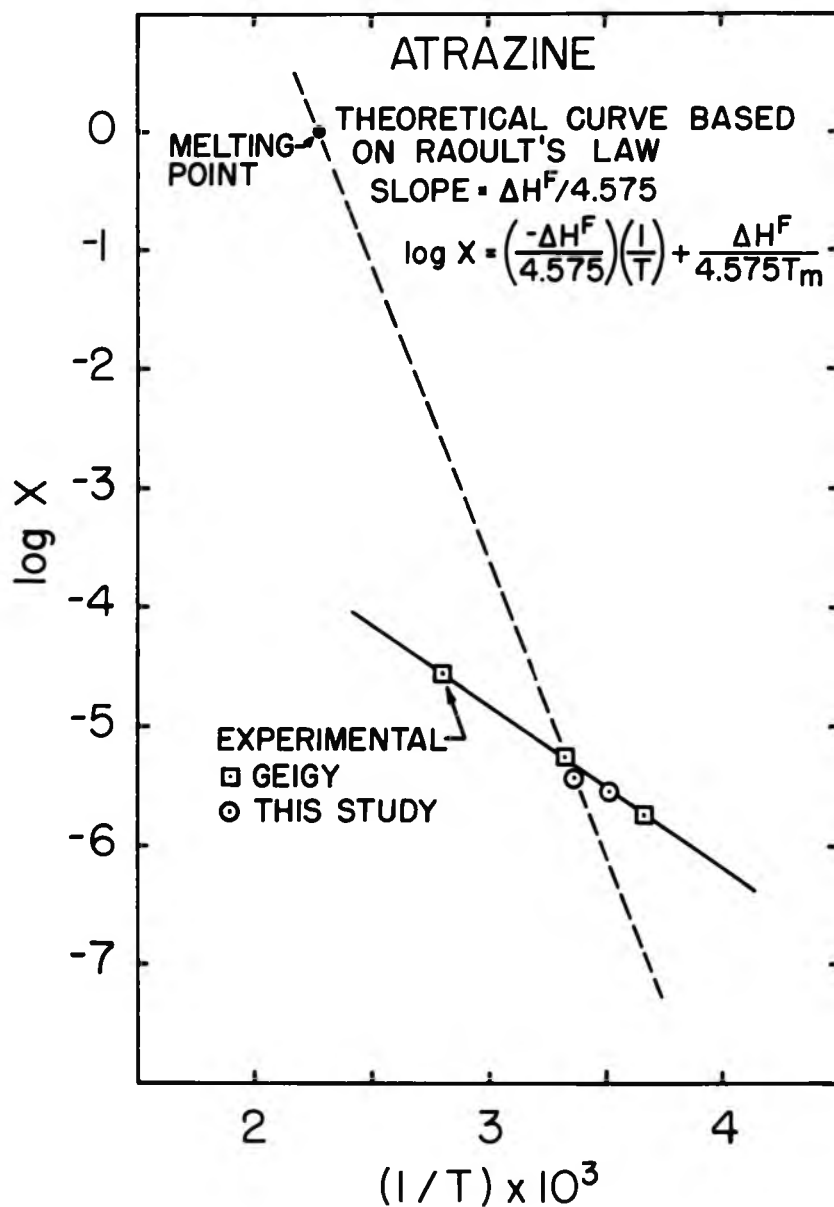
FIGURE 12. Theoretical Solubility Curve for Atrazine Based on Raoult's (X is the mole fraction of solute, T is the temperature in degrees Kelvin).

temperature. Figure 12 shows that experimental points deviate widely
from the theoretical curve. Some deviation is to be expected since
the curve is based upon the assumption that the solution is ideal, but
the discrepancy evident in Figure 12 is too great to allow further use
of the theoretical curve.

Despite the failure of an ideal-solution prediction of temperature
effects, the experimental data give a near-linear plot on the log X
versus 1/T relation shown in Figure 12. It seems that better estimates
of the solubilities at different temperatures might be made by extra-
polating the curve for two or more experimental points to obtain
solubilities at other desired temperatures.

C_e/C_o based on pH effects on solubility
_____

The parameter "reduced" concentration, as discussed above, was
used to compare adsorption at different temperatures. Like temperature,
pH also affects solubility (Figure 10). Increasing solubility with
decreasing pH does not decrease adsorption on all adsorbents, as is
clearly demonstrated in Figures 3 through 8. On adsorbents with nega-
tively charged surfaces adsorption is increased with decreasing pH
because of an increase in protonation. But on adsorbents which adsorb
the protonated and molecular form nonpreferentially, adsorption would be
expected to decrease with decreasing pH. This decrease in pH would
increase solubility and also the number of hydration shells surrounding
the adsorbate. As an increase in temperature increases the triazine's
affinity for water, so does a decrease in the pH.

The data used to plot Figure 13 was calculated from Figure 8.
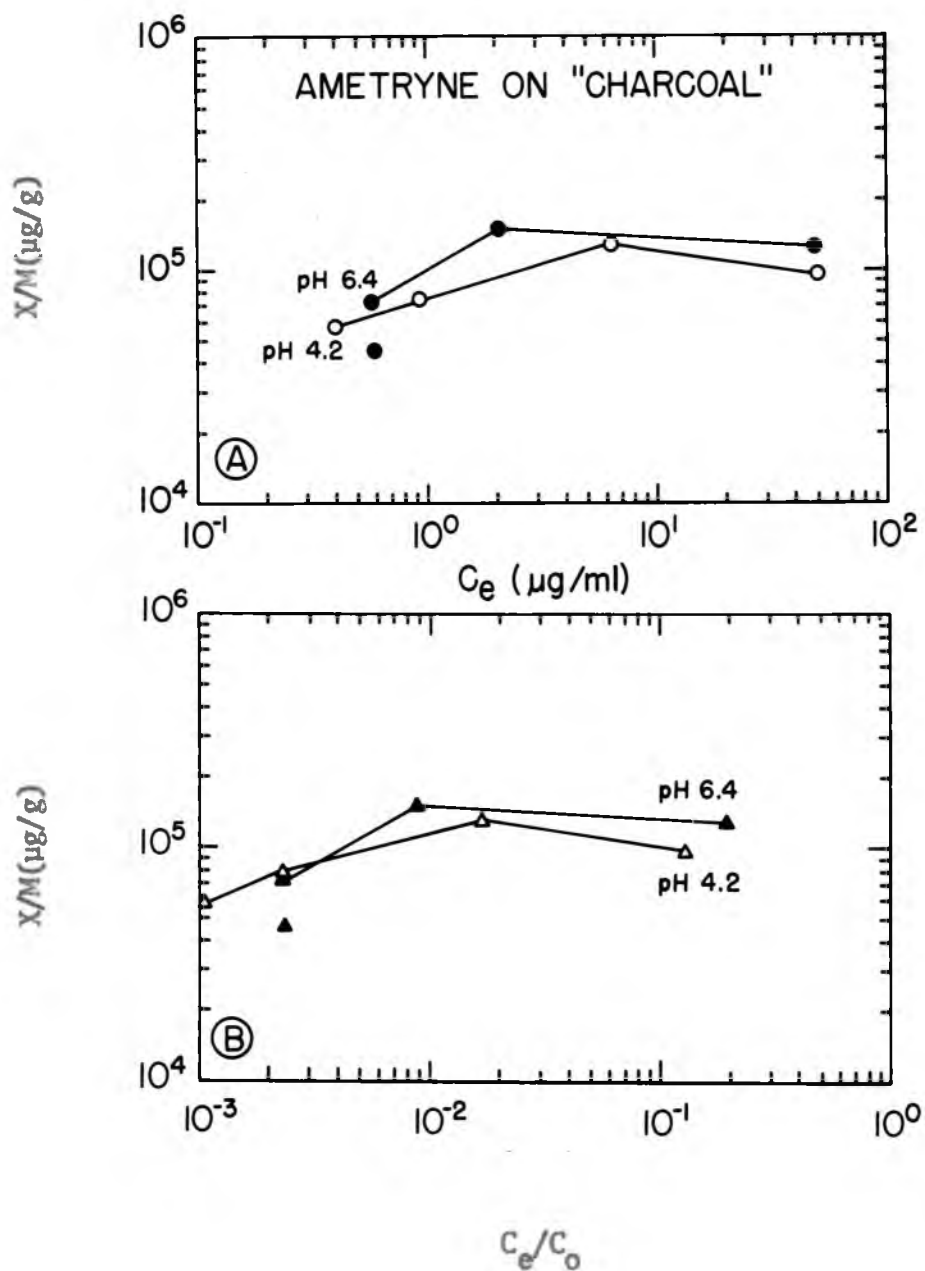
FIGURE 13.   Apparent Adsorption Isotherms for Ametryne on "Charcoal" with "Reduced" Concentrations with Respect to pH.

The concentrations corresponding to the eight points of the charcoal mixture were dropped vertically to the Molokai (17 - 23) curve. The x/m values of the Molokai (17 - 23) were then subtracted from x/m values for the charcoal-Molokai (17 - 23) mixture and replotted in Figure 13(A).

In the subsequent discussions, it should be remembered that the adsorbent-adsorbent interactions and other possible interactions have not been completely removed from the apparent adsorption due to charcoal. In Figure 13(A) the adsorption of the protonated form is higher than that of the molecular form. If we can now assume that the adsorbent (charcoal) cannot differentiate between the molecular form and the protonated form, the following discussion may explain the reversed behavior with respect to pH. Since decreasing pH increases solubility and thus the triazine's affinity for water, adsorption would decrease with decreasing pH (increasing total solubility). If this explanation is correct, a plot of reduced concentrations with respect to pH would bring the curves together or even switch their positions. The reduced concentrations were calculated and replotted in Figure 13(B). The curves have been brought closer together, though adsorption is still slightly higher at the lower pH.

The one data point at pH 6.4 which appears out of place is perhaps the result of poor duplication (see Appendix Table A-2). These adsorption measurements on charcoal, though preliminary in nature, indicate the possibility of an interesting relationship between pH, solubility, and adsorption on non-polar adsorbents.

SUMMARY AND CONCLUSIONS

The purpose of this study was to gain an understanding of the nature of adsorption in relationship to the basic physical-chemical properties of pesticides and soils. To do this, atrazine and ametryne, two widely used s-triazines in Hawaii, were selected as adsorbates. The adsorbents used were Molokai (0 - 2), Molokai (17 - 23), standard kaolinite, standard montmorillonite, and Darco G-60 charcoal. Isotherms at 25 C of atrazine and ametryne were determined on the different adsorbents at pH values allowing a comparison of adsorption in the molecular and partly protonated forms. Adsorption was also measured on Molokai (0 - 2) and montmorillonite at 10 C. The solubilities of atrazine and ametryne were determined for 10 and 24 C. The conclusions resulting from this study are listed below for each of the three previously stated objectives.

Objective 1. To relate the adsorption of atrazine and ametryne to
fundamental properties of the two chemicals and selected adsorbents.

   a. Ametryne adsorption on Molokai (0 - 2), Molokai (17 - 23),
and montmorillonite was equal or higher than that of atrazine
when both were in the molecular form. The difference in
adsorption of the molecular forms seems to be related to the
substitution in the 2-position ($-SCH_3$ versus $-Cl$).

   b. Ametryne adsorption on Molokai (0 - 2), Molokai (17 - 23),
and montmorillonite was also higher than atrazine at the
lower pH's. The difference between atrazine and ametryne
adsorption on all adsorbents was largest when the triazines
were in the protonated form. Adsorption with a triazine

having a constant per cent protonation increased with increasing CEC. Adsorption on a given adsorbent (relatively constant CEC) increased with increasing protonation.

c. The addition of 5 mg of charcoal to the subsurface Molokai increased the adsorption of ametryne more than ten-fold. In contrast to adsorption on soils and montmorillonite, adsorption of ametryne on charcoal was found to be slightly higher at the higher pH (molecular form).

d. The adsorption of atrazine on kaolinite at both pH's was too low to be measured with adequate precision.

Objective 2. To investigate the dependence of triazine adsorption on solubility as a function of temperature and pH.

a. The effect of solubility as related to temperature upon the adsorption of ametryne on soils could not be established from the measurements at 10 and 25 C. Further studies must be done with a larger temperature differential allowing for greater differences in solubility. However, replotting the data with "reduced" concentrations had the net effect of separating the isotherms for the two temperatures, indicating that ametryne adsorption was higher with the high temperature.

b. The effect of solubility as related to pH upon the adsorption of ametryne on adsorbents with high CEC could not be isolated due to the increase in adsorption with increasing protonation. On "charcoal," decreasing the pH (i.e., increasing solubility) appeared to decrease adsorption slightly, but the results were too variable to be conclusive. Use of "reduced" concentrations

(with respect to total solubility) appeared to bring the two
isotherms closer together. This shows that there probably
is no difference in adsorption of the protonated and molecular
form of ametryne on "charcoal."

Objective 3. To determine the enthalpy of adsorption for atrazine and
ametryne as a means of expressing the differential affinity with
which these herbicides are held on the soils.

a. For the temperatures used in these studies there appeared to
be no difference in the adsorption of atrazine and ametryne
on Molokai (0 - 2) and montmorillonite. The apparent lack of
response of adsorption with respect to temperature is perhaps
due to the small heat of adsorption for these compounds and
the small change of solubility of the compounds at 10 and 25
C. This lack of difference in adsorption at 10 and 25 C
prevented calculations of the heats of adsorption.

The adsorption responses of the two triazine compounds to different
pH's on different adsorbents emphasize that the conditions under which
adsorption is taking place must be stated before interpretations or
predictions can be made.

For the two s-triazines studied, the most important property
affecting adsorption on soils is their pK_a for it designates the amount
protonated at a given pH. Since adsorption is an adsorbent-adsorbate
interaction the above-mentioned properties must be related to the soil
properties which affect adsorption. The importance of the triazine's
pK_a becomes apparent only at low pH where protonation occurs and on
adsorbents which have reasonably high CEC's. At higher pH's the effect

on adsorption due to differences in the CEC of the adsorbents decreases. At the higher pH's adsorption of atrazine and ametryne is affected by the substituent in the 2-position on adsorbents which have high organic matter content and high surface area.

As mentioned in the Introduction, ametryne is too phytotoxic for general use in the continental United States, while both atrazine and ametryne are used in large quantities in Hawaii. The reason for this difference in phytotoxicity is the difference in soil properties. In Hawaii the high native organic matter content plus carbon residues from the burning of sugarcane fields increase the adsorption of ametryne and thus decrease phytotoxicity. Also, the low pH of Hawaiian soils causes ametryne to be protonated. A soil having a relatively low organic matter content must have a relatively high CEC and a pH < 6.0 to have appreciable adsorption of ametryne. Although the cation exchange capacities of many mainland United States soils may be relatively high, a high pH value tends to keep the triazines in the molecular, resulting in low adsorption if the organic matter content is low.

Though the conclusions reached in this study are based upon atrazine and ametryne interaction with selected adsorbents, the approach can be used on all pesticide-adsorbent combinations.

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APPENDIX

TABLE A-1. Detailed Adsorption Data for Atrazine on Several Adsorbents (25 C).

	C_o(µg/ml)	C_{eq}(µg/ml)	x/m(µg/g)		C_o(µg/ml)	C_{eq}(µg/ml)	x/m(µg/g)
Atrazine				Atrazine			
Molokai	0.60	0.49	1.1	Molokai	0.60	0.56	0.5
(0 - 2)	1.00	0.82	1.8	(17 - 23)	1.00	0.89	0.1
pH = 7.0	2.00	1.65	3.5	pH = 6.9	2.00	1.89	1.1
2.5g	4.00	3.44	5.6	2.5g	4.00	3.88	1.2
	10.90	9.76	11.4		5.45	5.31	2.4
1st run	24.00	21.06 ± 0.28	29.4 ± 2.8	1st run	10.90	10.35	7.5
					24.00	22.28	17.2
	1.00	1.00	0.0		1.00	0.94	0.1
	2.00	1.73 ± 0.00	2.7 ± 0.0		2.00	1.89 ± 0.02	1.1 ± 0.2
2nd run	4.00	3.29	7.1	2nd run	4.00	3.77	2.3
	5.41	4.34	10.6		5.45	5.11	3.3
	10.90	8.96 ± 0.17	19.4 ± 1.7		10.90	10.04 ± 0.04	8.3 ± 0.0
	24.00	13.85	10.1		24.00	22.03	19.7
	0.60	0.16	4.4		1.00	0.97	0.3
Atrazine	1.00	0.26	7.4	Atrazine	2.00	1.72 ± 0.04	2.8 ± 0.4
Molokai	2.00	0.55	14.5	Molokai	4.00	3.49	5.1
(0 - 2)	4.00	1.27	27.3	(17 - 23)	5.45	4.78	6.7
pH = 3.0	5.45	1.86	41.9	pH = 2.95	10.90	9.61 ± 0.00	12.9 ± 0.0
2.5g	10.90	4.57	74.3	2.5g	24.00	21.16	28.4
	24.00	12.37	116.3				
	1.00	0.99	0.8		1.00	0.34	65.8
Atrazine	2.00	1.92 ± 0.01	7.7 ± 1.3	Atrazine	2.00	0.71 ± 0.07	132.7 ± 11.1
Mont.	4.00	3.87	13.1	Mont.	4.00	1.10	290.3
pH = 8.45	5.45	5.28	16.9	pH = 2.90	5.45	1.32	412.8
0.25g	10.90	10.36 ± 0.10	54.6 ± 10.6	0.25g	10.90	2.58 ± 0.03	832.7 ± 3.4
	24.00	22.04	195.7		24.00	5.65	1835.4

TABLE A-1 (Continued). Detailed Adsorption Data for Atrazine on Several Adsorbents (25 C).

	C_o(g/ml)	C_{eq}(g/ml)	x/m(g/g)		C_o(g/ml)	C_{eq}(g/ml)	x/m(g/g)
	0.60	0.52	21.0		0.60	0.58	0.9
Atrazine	1.00	0.83	42.5	Atrazine	1.00	0.97	1.7
Mont.	2.00	1.69	78.5	Kaolinite	2.00	2.01	- 0.6
pH = 3.25	4.00	3.41	97.5	pH = 5.10	4.00	3.88	6.1
0.10g	5.45	4.59	216.3	0.50g	5.45	4.37	54.8
	10.90	9.29	4128.3		10.90	10.81	4.6
	24.00	20.22	944.0		24.00	22.81	6.0
	1.00	0.34	65.8		0.60	0.51	4.5
Atrazine	2.00	0.72	132.7	Atrazine	1.00	0.90	5.0
Mont.	4.00	1.10	290.3	Kaolinite	2.00	1.86	6.9
pH = 7.25	5.45	1.32	412.8	pH = 3.25	4.00	3.65	17.7
0.10g	10.90	2.58	832.7	0.50g	10.90	10.46	22.3
	24.00	5.65	1835.4		24.00	22.71	64.7

TABLE A-2. Detailed Adsorption Data for Ametryne on Several Adsorbents (25 C).

	C_o(μg/ml)	C_e(μg/ml)	x/m(μg/g)		C_o(μg/ml)	C_e(μg/ml)	x/m(μg/g)
	2.00	1.33	6.7		2.00	1.24	7.6
Ametryne	5.00	3.48 ± 0.03	15.2 ± 0.4	Ametryne	5.00	3.52 ± 0.02	18.8 ± 0.2
Molokai	10.00	7.08	29.2	Molokai	10.00	7.60	24.0
(0 - 2)	12.00	8.89	31.1	(17 - 23)	12.00	8.96	30.4
pH = 7.0	15.00	11.33	36.7	pH = 4.0	15.00	11.52	34.8
2.5g	20.00	15.34	46.7	2.5g	20.00	15.27	47.3
	40.00	32.02	79.8		40.00	31.46	85.4
	2.00	0.20	18.0		2.00	1.87	12.8
Ametryne	5.00	0.63	43.8	Ametryne	5.00	4.63 ± 0.02	37.8 ± 2.0
Molokai	10.00	1.58	84.2	Mont.	10.00	9.35	65.4
(0 - 2)	15.00	2.92	130.8	pH = 8.45	12.00	11.13	86.9
pH = 4.1	20.00	4.56	154.4	0.2500g	15.00	11.65	33.6
2.5g	40.00	12.32	286.8		20.00	18.44	156.3
					40.00	38.05	196.4
	2.00	1.82	1.8		2.00	0.13	187.3
Ametryne	5.00	4.59 ± 0.02	4.1 ± 0.2	Ametryne	5.00	0.28 ± 0.01	471.6 ± 0.8
Molokai	10.00	9.34	6.6	Mont.	10.00	0.45	954.8
(17 - 23)	12.00	13.77	12.3	pH = 4.3	15.00	0.72	1428.1
pH - 7.0	15.00	11.10	9.0	0.2500g	20.00	0.92 ± 0.03	1908.9 ± 3.7
	20.00	18.63	13.7		40.00	1.49	3851.4
	40.00	36.91	30.9				

TABLE A-2 (Continued). Detailed Adsorption Data for Ametryne on Several Adsorbents (25 C).

|	C_o (µg/ml)	C_e (µg/ml)	Total (µg) in 50 ml sol	C_o (µg/ml)	C_e (µg/ml)	Total (µg) in 50 ml sol
Ametryne	15.00	0.81	709.5	15.00	0.59	720.4
Molokai	15.00	0.37	731.3			
(17 - 23)	20.00	0.54	972.9	20.00	0.58	971.2
charcoal	20.00	0.61	969.5			
mixture	40.00	1.17	1941.6	40.00	2.19	1890.5
pH = 6.4	40.00	3.21	1839.5			
2.5g and	80.00	47.57	1671.4	80.00	48.01	1649.5
0.0050g	80.00	48.44	1628.0			
Ametryne	15.00	0.49	725.4	15.00	0.40	729.9
Molokai	15.00	0.31	734.5			
(17 - 23)	20.00	1.02	948.9	20.00	0.91	954.7
charcoal	20.00	0.80	960.1			
mixture	40.00	6.65	1662.1	40.00	6.41	1677.0
pH = 4.2	40.00	6.16	1692.0			
2.5g and	80.00	50.23	1488.5	80.00	50.60	1470.0
0.0050g	80.00	50.97	1451.6			
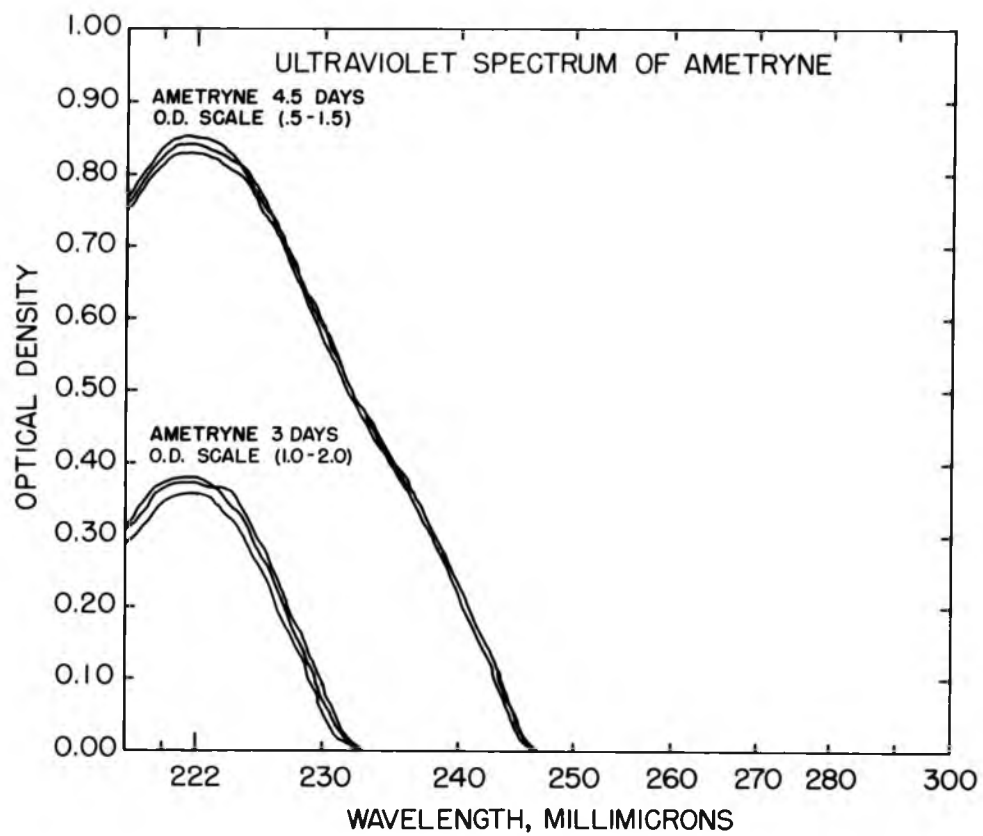
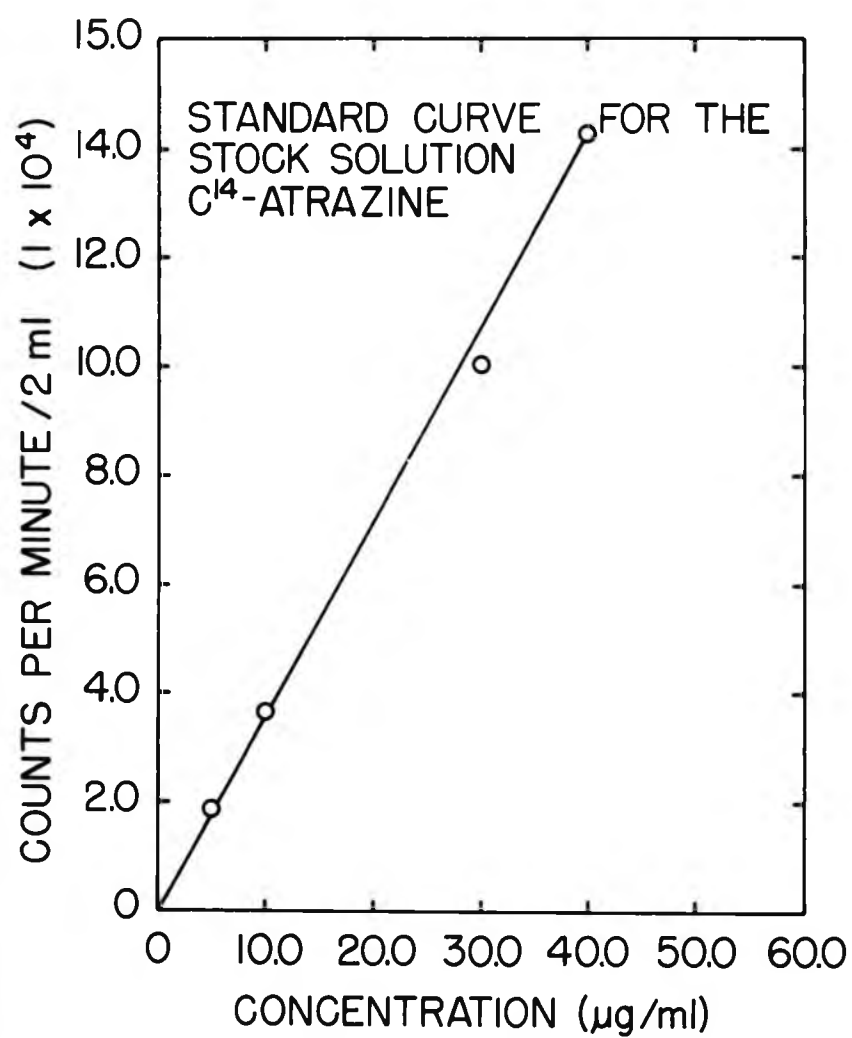FIGURE A-1. Ultraviolet Spectrum of "Saturated" Solutions of Ametryne (in triplicate) at 10 C.

FIGURE A-2. Standard Curve for C^{14}-Atrazine.