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Goswami, K.P.; Green, R.E.

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Simultaneous Extraction of Hydroxyatrazine, Atrazine, and Ametryne from Some Hawaiian Soils

KISHORE P. GOSWAMI AND RICHARD E. GREEN

Simultaneous Extraction of Hydroxyatrazine, Atrazine, and Ametryne from Some Hawaiian Soils[1]

KISHORE P. GOSWAMI AND RICHARD E. GREEN[2]

ABSTRACT

A simple procedure is described for simultaneous extraction from soil of 2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine (atrazine), 2-methylthio-4-ethylamino-6-isopropylamino-*s*-triazine (ametryne) and their common hydrolysate (hydroxyatrazine = HA). The procedure involves extraction by shaking in acidified methanol, centrifugation, and subsequent quantitative separation of HA from the parent triazines by liquid-liquid partitioning. The pH of methanol was adjusted with 4*N* HCl to obtain a final pH of 2.5 in the soil extract, using a 1:10 soil/solvent ratio. HA recovery with one extraction was 94% for both Molokai (Typic Torrox) and Hilo (Hydrandept) soils having soil extract pH values of 2.4 and 3.4, respectively. In all cases atrazine and ametryne were quantitatively recovered in soil extracts. After protonation HA was quantitatively separated from the mixture of HA and atrazine or ametryne by partitioning in an aqueous methanolic soil-extract/chloroform system when the water/methanol extract ratio was 1.25. HA extraction from soil was extremely pH dependent. Dissolution of calcium chloride in acidified methanol decreased recovery of added HA from 94% to 76% for Hilo soil but had no effect on % HA recovery from Molokai soil; the electrolyte was found to increase the pH of Hilo soil extract, a result of the net positive charge of this soil at low pH. The recovery of added HA from Ca-montmorillonite was 33%, suggesting that the procedure may be less suitable for soils with high permanent negative charge.

Additional Index Words: triazine extraction, herbicide extraction, triazine metabolite, soil extraction, extraction.

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[2] Junior Soil Scientist and Professor, respectively, Dep. of Agronomy and Soil Science, Univ. of Hawaii, Honolulu.

Extraction from Soils

AN IMPORTANT PATHWAY of degradation and detoxication of *s*-triazine herbicides in soil is their nonbiological conversion to corresponding hydroxyanalogs (Adams,

1966; Armstrong and Chesters, 1968; Armstrong, Chesters, and Harris, 1967; Russell et al., 1968; Skipper, Gilmore, and Furtick, 1967; Obien, 1970; Obien and Green, 1969).

A quantitative extraction of *s*-triazines and their degradation products is essential to studies of their fate and interactions in soil. Numerous references could be cited reporting procedures for extraction of 2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine (atrazine) from soil, but little has been published on the recovery of 2-methylthio-4-ethylamino-6-isopropylamino-*s*-triazine (ametryne) and their common hydrolysate: 2-hydroxy-4-ethylamino-6-isopropylamino-*s*-triazine (hydroxyatrazine, hereafter called HA). Although *s*-triazine herbicides are soluble in most organic solvents, methanol has been preferred by many workers for extraction either by shaking or by use of the Soxhlet apparatus. The 2-hydroxy products of *s*-triazines are much less soluble than the parent compounds, and being more polar are expected to be adsorbed on soil to a greater extent.

HA is readily dissolved in water or methanol by acidifying with dilute HCl to protonate the HA molecule. The pK_a of HA has not been reported, but measurements on hydroxy analogs of other triazines suggest pK_a 5. Ward and Weber (1968) reported that aqueous solubilities of hydroxysimazine and HA were 44 and 38 times higher, respectively, at pH 3 than at pH 7. Solubility of ametryne was doubled at pH 3.

Protonation of HA on the surface of soil colloids results in the formation of a keto form of the protonated hydroxy species (Russell et al., 1968). Adsorption of HA associated with protonation increases the difficulty of recovering HA from soil. Dealkylated hydroxy-*s*-triazines are among the possible degradation products which are even more polar than HA and are likely to pose a more severe extraction problem. Skipper et al. (1967) recovered only 25% of the applied ^{14}C-atrazine in methanol extracts of sterile and nonsterile soils, 2 to 4 weeks after ^{14}C-atrazine treatment. The low recovery of ^{14}C was probably due to adsorption of HA, the principal product of atrazine degradation in soils. Harris (1965) studied simazine hydrolysis in soils and found that Soxhlet extraction with methanol recovered most of the simazine but less than half of the hydroxysimazine. He recovered additional amounts of hydroxysimazine with 0.5*N* sodium hydroxide in the subsequent extraction. Alkali extraction from soil requires considerable cleanup before the extract can be used for chromatographic and other analyses (Harris, 1967). Obien (1970) obtained slightly higher recovery of applied HA from Kapaa soil (pH 4.9) during adsorption measurements when 0.05*N* calcium chloride solution in methanol was employed as the extractant. Hance and Chesters (1970) reported 89.5% recovery of ^{14}C-labeled HA from a fortified soil in three successive extractions: (i) with 0.1*N* HCl; (ii) refluxing with methyl cyanide-water (9:1), and (iii) refluxing with methyl cyanide-water ammonia (90:9:1). This procedure possibly cannot be employed when the parent compounds are also present in the soil due to the likelihood of hydrolyzing the parent compounds in the acid extraction.

Separation of Hydroxy-Product from Parent Compounds

Partitioning of HA from atrazine in aqueous soil perfusate was achieved by Armstrong et al. (1967) in 5-ml aliquots by adding sufficient HCl to obtain pH 3, followed by three successive extractions with 3-ml portions of chloroform in a separatory funnel. Atrazine was thus removed in chloroform, leaving HA in the aqueous pthase; HA was estimated by ultraviolet spectrophotometry with 89–99% efficiency of separation in standard solution. This process was modified by Obien (1970) to allow analysis of a large number of samples at one time. He placed a 2-ml methanolic or aqueous soil-extract sample in a test tube, acidified it with 0.5 ml of 0.5*N* hydrochloric acid and extracted with 8 ml chloroform. HA was estimated in 1 ml of the aqueous phase by scintillation counting. The partitioned HA was 48.3% of the applied quantity in methanol.

Research on the degradation of atrazine and ametryne in our laboratory required improved procedures for extacting these compounds along with their degradation products from soil for quantitative determinations on a large number of samples. Since it was known that the parent triazines could be quantitatively desorbed in methanol (Obien, 1970), efforts were concentrated mainly on the recovery of HA while keeping the pH high enough to prevent any acid hydrolysis of the parent compounds, if present. The optimized procedures were then tested for the simultaneous extraction of HA and the parent compounds.

MATERIALS AND METHODS

Extraction of HA from Soil

Molokai, Hilo, or Kapaa surface soil samples (2.0 g oven dry weight) were placed in 50-ml polyethylene centrifuge tubes. The soil properties are given in Table 1. Soil samples were treated with aqueous solutions of ^{14}C-ring labeled compounds to give 12.75 $\mu g/g$ concentration (total) of HA alone or HA mixed with half the amount of ametryne or atrazine. Water content of the soil was established at a value corresponding to zero moisture tension. The tubes were then closed with rubber stoppers, shaken to mix the contents, and stored at room temperature (24.0 ± 1°C). An equal number of soil samples were stored with the same water content but without any ^{14}C-labeled triazine compounds added. After 40 hours of storage, all soil samples were extracted in duplicate with 20-ml portions of methanol containing different amounts of 4*N* HCl (100 ml volume with or without addition of calcium chloride (0.05*N* with respect to the extractant)). The tubes were shaken for 3 hours in an end-to-end shaker and centrifuged at 17,300 *xG* for 15 min. One milliliter of the clear supernatant extract was transferred to a counting vial and mixed with 15 ml of scintillation solution containing 7.0 g PPO, 0.3 g dimethyl-POPOP and 100.0 g naphthalene in 1 liter of dioxane. Estimations of the recovered radioactivity were made by counting on a liquid scintillation spectrometer.

Table 1.—Soil properties

Soil series	Subgroup	Soil depth	pH (1:1 paste)	Water	Organic matter	Total N	CEC	Fe_2O_3[2]
		cm		% wt	%	%	meq/100 g	
Hilo	Typic Hydrandept	0–30	5.2	171.1	8.9	0.25	59.5[1]	27.6
Kapaa	Typic Gibbsithumox	0–10	4.7	18.5	10.5	0.38	18.5	32.7
Molokai	Typic Torrox	0–40	5.8	16.2	3.1	0.13	17.8	14.1

[1] From Y. Kanehiro and A. T. Chang, 1956. Tech. Bull. 31, Hawaii Agr. Exp. Sta., Univ. of Hawaii.
[2] Soil Data Bank, Dep. of Agronomy and Soils, Univ. of Hawaii.

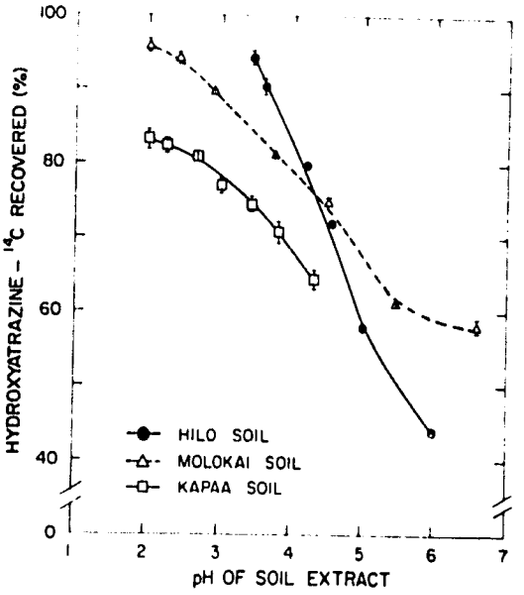

Fig. 1—Effect of pH on the recovery of added hydroxyatrazine from soil with methanol.

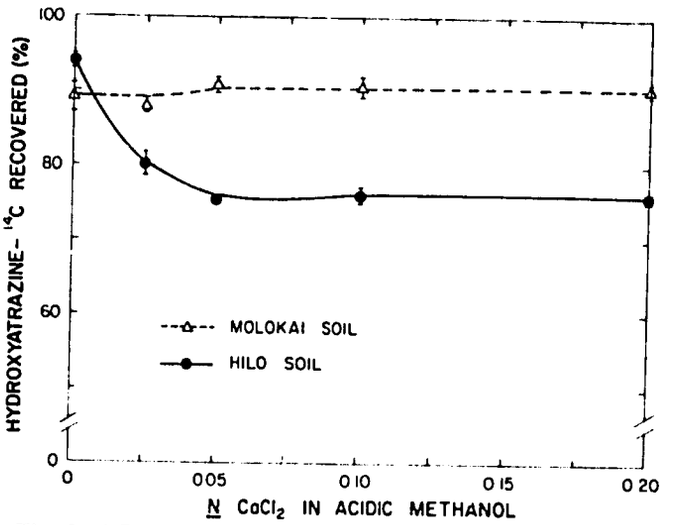

Fig. 2—Effect of calcium chloride in acidic methanol on the recovery of added hydroxyatrazine from soil. Extract pH values are shown in Table 2.

Standard counts were obtained by adding the same ^{14}C-ring labeled compounds to methanolic extracts from the untreated but similarly incubated soils. Different standard counts were obtained for each pH level. The water scintillation liquid ratio in the counting vial was maintained constant to avoid further corrections in counting efficiency due to water quenching.

A separate test was conducted to determine if addition of calcium chloride to the acidified methanol would further improve the efficiency of HA extraction from soil. This study was conducted in duplicate with two soils using calcium chloride concentrations of nil, 0.025*N*, 0.05*N*, 0.10*N*, and 0.20*N* in acidified methanol (0.5 ml of 4*N* HCl 100 ml methanol).

Measurement of HA

Partition of HA from atrazine or ametryne and subsequent estimation of HA in the acidified methanolic extracts were achieved by the chloroform extraction procedure initially used by Armstrong et al. (1967) on aqueous solutions. This procedure was simplified by Obien (1970), but with an attendant decrease in efficiency of HA separation. We have improved Obien's simplified process to obtain a quantitative partition. A 2-ml aliquot of methanolic soil extract or methanol containing equal amounts of HA alone and HA plus ametryne or atrazine was treated with 0.5 ml of 0.25*N* HCl in a 25 ml test tube with ground glass stopper. The contents were shaken and allowed to stand for 1 min. Different amounts (0, 1, 2, 3, 4, and 6 ml) of distilled water were then added to duplicate tubes, followed by addition of 10 ml of chloroform. The contents were mixed thoroughly by shaking the test tubes end-to-end several times. Similar mixing was repeated three times with a half-min interval between the two mixings. The tube was opened after 10–15 min when the aqueous phase was clear, and tapped gently to let any chloroform from the sides return to the lower phase. If the aqueous phase was turbid, additional time was allowed for clearing. A 500 μl aliquot of the aqueous phase was pipetted into a counting vial and mixed with 15-ml scintillation solution for estimation of the recovered HA radioactivity.

Calculation of the percent HA radioactivity in a 2.0-ml aliquot of the original methanol extract was based on the total volume of the aqueous-methanol phase (2 ml methanol extract + 0.5 ml HCl + ml water added). The process was repeated with 2 ml aliquots of methanolic solutions of ^{14}C-labeled ametryne or atrazine to allow corrections for any radioactivity from these sources present in the aqueous phase used for hydroxy-product assay.

RESULTS AND DISCUSSION

Extraction of HA from Soil

The results shown in Fig. 1 clearly demonstrate the large pH-dependence of HA desorption from soil by methanol. The pH-dependence is more striking in the Hydrandept (Hilo soil) than in the two Oxisols (Molokai and Kapaa soils). The recovery of HA was 84% from Kapaa and 96% from Molokai soil when the pH of the soil methanol extract reached 2.0, whereas 94% HA was desorbed from Hilo soil when the pH of the methanol extract was only 3.4. Thus the extent of HA desorption may vary from soil to soil at any given pH value. All our results are based on a single-step shaking procedure. In case of low recoveries, a second or third extraction should help recover the remaining HA. Also, our soils were incubated for only 40 hours prior to the extraction. Lower recoveries could be expected from soils incubated for several weeks or longer.

Obien (1970) measured an increase in the efficiency of extracting HA when $CaCl_2$ was added to nonacidified methanol. The possible enhancement of HA extraction by addition of $CaCl_2$ to acidified methanol (0.5% of 4*N* HCl in methanol) was evaluated in the present study with Molokai and Hilo soils (Fig. 2). The recovery of HA from Molokai soil remained unaffected by the presence of calcium chloride in acidified methanol, but the recovery of HA from Hilo soil was decreased by increasing concentration up to 0.05*N* $CaCl_2$. A comparison of the pH values of methanolic soil extracts for these soils (Table 2) shows that in the Hilo soil extract, pH increased with increasing concentration of $CaCl_2$ whereas no pH change occurred in extracts of the Kapaa and Molokai soils. This pH change in the Hilo extract, and the evidence of pH-dependence of HA extraction (Fig. 1), suggest that the results for Hilo soil in Fig. 2 were due to the effect of $CaCl_2$ on pH in this soil. This effect is not surprising considering the mineralogy of the soil (amorphous hydrated alumino-silicates and oxides of iron and aluminum) and the known effects of electrolyte concentration on pH. Whereas most soils

Table 2—Effect of calcium chloride concentration on the pH of acidified methanolic soil extract

Normality of $CaCl_2$ in acidic methanol	pH of soil extract		
	Hilo	Kapaa	Molokai
0.000	3.44	2.40	2.94
0.025	3.90	2.63	3.01
0.050	4.15	2.56	2.94
0.100	4.23	2.64	2.94
0.200	4.26	2.58	2.68

Table 3—Recovery of *s*-triazines from Molokai soil (pH of extract = 3.0) and partition of hydroxyatrazine from ametryne or atrazine by liquid-liquid extraction with chloroform in soil extract or standard methanolic solution

^{14}C compound *s* applied	Soil extract	Partition of HA from atrazine or ametryne in aqueous-methanol phase	
	Total ^{14}C recovered	Soil extract	Standard methanol solution
		of applied HA recovered*	
HA and ametryne	96.9	72.0	100.9
HA and atrazine	95.4	90.8	99.4
HA	90.6	91.4	99.3
Ametryne	100.4	0.56 ± 0.04†	0.27 ± 0.04†
Atrazine	99.7	0.71 ± 0.01†	0.56 ± 0.01†
Mean deviation	±0.7	±0.9	±1.0

* When ametryne or atrazine was added without HA, the recovery in the aqueous-methanol phase was calculated as percent of the applied compound.

† Value not included in calculation of mean deviation due to difference in order of magnitude.

contain clay minerals which have a net negative charge throughout the pH range used in this study, the amorphous minerals in Hydrandepts of Hawaii have a net positive charge at low pH; soils with a net negative charge manifest a pH *decrease* in the presence of an electrolyte such as $CaCl_2$, but soils with a net positive charge show a pH *increase* (Mekaru and Uehara, 1972). Thus in the Hilo soil, the $CaCl_2$ increased the pH and caused a concomitant decrease in HA recovery.

To determine the correct acid methanol ratio for maximum recovery of hydroxy-*s*-triazines for a particular soil, we prepared 100 ml volumes of acidic methanol in separate flasks containing 100 to 1,000 μl volumes of 4*N* HCl. After soil extraction with the acidic methanol, the pH of the soil extracts was measured. It was considered undesirable to establish the pH of the soil extract below pH 2.0 for fear of hydrolyzing the parent triazine compounds when present. The extracts could be stored, if necessary, after neutralizing the acidity with dilute alkali. The acidified methanol extracts of the three soils were clear and had very little coloration. No organic matter was extracted in the system. A brownish colloidal precipitate appeared in some extracts from Molokai soil on neutralization. The neutral supernatent extracts were concentrated 25–50 times by evaporation under vacuum and were utilized for thin-layer chromatographic analysis without cleanup.

Partitioning of HA

After extraction of HA and parent triazine compounds from soil in acidified methanol, the HA was separated by liquid-liquid partition for quantitative determination. The efficiency of partitioning HA with different water methanol ratios is shown in Fig. 3. A water/methanol ratio of 1.25 provided quantitative partitioning of HA in the chloroform-methanol system. This was achieved by adding 2.0 ml water to an aliquot of 2.0 ml methanol solution or soil extract to which 0.5 ml of 0.25*N* HCl had been added.

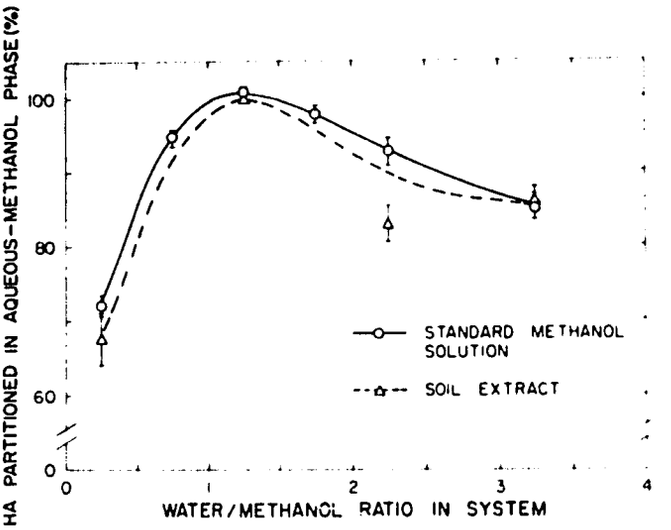

Fig. 3—Effect of water on the partitioning of hydroxyatrazine from ametryne in soil extract of methanol in a chloroform-methanol system.

The results obtained with Molokai soil extracts were not statistically different than those obtained with a pure methanolic solution of HA. Only 72% of the added HA was partitioned into the aqueous-methanol phase when only 0.5 ml water was added to the system (i.e. 0.5 ml of 0.25*N* HCl) giving a water/methanol ratio of 0.25. The decline in the efficiency of partitioning of HA with increasing amounts of water for ratios greater than 1.25 is hard to explain, but was probably due to an increase in the pH which affected protonation of HA, and in addition due to the quenching effect of emulsified chloroform in water. Increasing water/methanol ratios were found to result in increasing pH values (Goswami, 1972). It is recommended that the liquid-liquid partition of HA be carried out in ground-glass stoppered test tubes since rubber stoppers absorb chloroform and appeared to cause errors in the HA determination.

The presence of 0.5 ml of 0.25*N* HCl in the $CHCl_3$-CH_3OH-H_2O system (pH = 1.7) probably protonated both ametryne (pK_a = 4.0) and atrazine (pK_a = 1.7) but did not alter appreciably their solubility in chloroform or hydrolyze them in a 4-hour period. Acidified methanolic soil extract (pH = 3.0) with an equal volume of water but without additional HCl, partitioned only about 50% of HA in the aqueous phase. This indicates that approximately half of the HA molecules were not protonated in the acidic methanol soil extract and that the additional amount of HCl was necessary for quantitative protonation and partitioning of the HA.

Extraction and Partition of Soil Applied HA and Its Parent Compounds

The optimized procedure developed for the determination of HA was evaluated further by extraction of a 1:1 mixture of HA and ametryne or atrazine from soil. The results of total recoveries of HA alone or HA mixed (1:1) with ametryne or atrazine from soil are summarized in Table 3. Also summarized in Table 3 are the results of

partitioning of HA from ametryne or atrazine in the soil extracts or in standard methanol solutions. The recoveries of the soil-applied ametryne or atrazine were nearly 100%, whereas 90.6% of the applied HA was recovered from the Molokai soil. Out of the 1:1 mixture of HA and ametryne or atrazine applied to soil, the respective recoveries were 96.9% and 95.4%. It would be expected that these recovery figures include all the parent compound and about 90% of the HA applied to soil.

The total recoveries were based on the measurement of combined ^{14}C recovered in the methanol extracts. Subsequent analysis of these soil extracts for percent HA by the modified liquid-liquid partitioning procedure confirmed that negligible amounts of parent compounds were partitioned in the aqueous phase (Table 3). The apparent recovery of HA in soil treated with ametryne or atrazine (0.56 and 0.71%) was due in part to polar impurities in the original parent compound (about 1%). Partitioning of HA from the mixture (with ametryne or atrazine) in the soil extract was nearly quantitative.

A possible problem associated with the acidified-methanol extraction is the chemical hydrolysis of atrazine and ametryne during extraction. The quantitative recovery of these compounds (Table 3) confirmed that hydrolysis was not a problem. As long as the pH of the system is maintained above 2.0, no measurable triazine hydrolysis is likely to occur during the brief extraction period. The "half life" of atrazine has been shown to be nearly 2 weeks in a sterilized soil system buffered at pH 2.0 (Armstrong et al., 1967), and more than 11 weeks for ametryne in Molokai soil buffered at pH 3.5 (Obien, 1970).

The following conclusions are based on the results presented in Table 3.

1. HA and ametryne or atrazine were simultaneously recovered from soil in a one step (shaking) extraction procedure using acidified methanol (soil solvent = 1:10).
2. Atrazine and ametryne were recovered quantitatively without any detectable hydrolysis of these compounds when soil extract pH = 3.
3. Recovery of the applied HA from soil was > 90% in acidified methanol.
4. Partitioning of the soil-applied and recovered HA in the aqueous phase of chloroform-methanol-water system was quantitative when the water methanol ratio was 1:25.

ADDENDUM

The three soils included in the HA extraction experiments were part of a more comprehensive study concerned with s-triazine herbicide degradation in Hawaiian soils. It is likely that the cation exchange capacity of these soils can be attributed principally to the pH-dependent negative charge associated with amorphous alumino-silicates, iron and aluminum oxides and organic matter; this negative charge would diminish with decreasing pH. The Hilo soil has a net positive charge below pH 4.5 (Mekaru and Uehara, 1972), and the other two soils would also lose capacity to hold cations or protonated HA at pH 3, the pH maintained during methanol extraction. Thus, in these soils the low pH facilitates HA extraction by methanol in two ways: (1) HA is protonated at low pH increasing its solubility in methanol; and (2) the pH-dependent negative charges of these soils are diminished at low pH reducing the likelihood of protonated HA being held by the negative sites.

If the mechanism described above is operating, then one might expect a lower extraction efficiency on soils having a high permanent negative charge in contrast to the pH-dependent charge characteristic of the soils used in this study. This thought occurred to us after completion of the study reported above and submission of the manuscript for review. A subsequent test of extraction efficiency showed that only 33% of the applied HA was recovered from Ca-saturated montmorillonite and 74% from Ca-saturated halloysite. Apparently protonated HA molecules are held on negatively charged sites on montmorillonite and halloysite at low pH and resist desorption by methanol. An increase in HA adsorption on montmorillonite with decreased pH is consistent with results obtained for other triazines (Weber, 1966, Yamane and Green, 1972).

Thus, we conclude that the one-step shaking procedure proposed herein is highly efficient on soils of low permanent negative charge but is expected to be less efficient in removing HA from soils containing a high percentage of montmorillonite or other clays having a high permanent negative charge.

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