The Fate of 3-Amino-1,2,4-triazole in Soils

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Laboratory investigations showed that the rate of recovery of 3-amino-1,2,4-triazole from Hagerstown silt loam soil is a function of temperature, pH, soil moisture, and microbiological activity. Evidence of complex formation between soil clay and this herbicide was obtained by x-ray defraction measurements. The fate of 3-amino-1,2,4-triazole in soil appears to be governed by the presence and activity of soil microorganisms, adsorption by normal constituents of the soil, and chemical reaction of the herbicide with soil matter.

Because of its unique physiological responses in plants, 3-amino-1,2,4-triazole (amitrole) is a herbicide of considerable usefulness. However, because of its lack of selectivity towards plants, a clear understanding about the fate, persistence, and behavior of this chemical in the soil is essential for its proper use.

With any given herbicidal agent, any two or more of the following factors which reduce effective concentration may operate simultaneously. These factors are adsorption, leaching, volatilization, microbiological breakdown, chemical breakdown, and removal by plants. Often one factor may affect another. Such is particularly true in the case of adsorption, which appears to play a dominant role in connection with leaching and vaporization. However, our knowledge of this field is not yet sufficiently sophisticated to enable us to examine more than one influencing process factor at a time.

Investigations by Sund have shown that the disappearance of amitrole in soil is dependent upon soil type (*11*). His unsuccessful attempt to recover all of the applied amitrole from a Maury loam soil by using 0.1*N* hydrochloric acid, 0.1*N* sodium hydroxide, 5% potassium sulfate, or distilled water indicated that the compound was being adsorbed on the soil particles in the same manner as ammonium ion. Further attempts by Sund to extract all of the amitrole from Maury loam soil by using solutions of various salts according to Harper's procedure (*8*) for recovering ammonia from soil were unsuccessful. These results led Sund to postulate that the herbicide was very strongly adsorbed on the soil particles and/or was held in some other chemical combination.

Since amitrole can be completely removed from solution by synthetic cation exchange resins, Sund conducted further studies to determine the rate of disappearance of amitrole from a number of different types of soils. His findings are presented in Figure 1.

At the end of 9 weeks, practically all of the amitrole had disappeared from the muck soil. The Yolo and Raub soils had only 4 and 6 p.p.m., respectively. The Cecil and Maury soils were next with 17 and 19 p.p.m. of amitrole, while Croton and Duke soils contained 23 and 26 p.p.m.

When the remaining percentage of original chemical was calculated for each soil, a strong correlation was found between amitrole disappearance and base exchange capacity. As indicated in Table I, the soil types may be separated into four groups according to their exchange capacities and clay content. The disappearance of amitrole from these soils is almost in direct proportion to the magnitude of the base exchange capacity and clay content of the respective soils. The muck soil, which has the highest exchange capacity, was the soil from which the chemical disappeared fastest, next were Yolo, Raub, Cecil, Maury, Croton, and finally Duke's sand.

Soils with a high base exchange capacity but a low degree of cation saturation would be expected to adsorb rapidly relatively large amounts of amitrole. The variances obtained in the initial analyses of the various soil types are probably due to different degrees of cation saturation and base exchange capacity among the soils.

Laboratory studies have shown that amitrole possesses the ability to form stable complexes with several metals, including cobalt, copper, nickel, iron, and magnesium (*1*, *11*). Thus, metal complexing may enter into the soil exchange system. Since the Yolo soil is high in calcium and magnesium, the disappearance of amitrole from this soil type is probably due to a combination of complexing and adsorption effects.

Following the work of Sund, studies were initiated at the Pennsylvania State University to determine whether or not corn grown in amitrole-treated soils adsorbed and stored the compound (*6*). The corn was grown in fields composed of Hagerstown silt loam. This soil is high in clay and silt content, and is native to the Middle Atlantic area of the United States.

No amitrole could be detected in corn plants of any age when grown in plots treated with rates of amitrole as high as 8 pounds per acre one day before the corn seeds were planted. The analytical procedure used was sensitive to at least 0.1 p.p.m. The analytical evidence was amply supported by the fact that there was no indication of any impairment of growth or other physiological process in these corn plants, for they appeared normal in every respect. They grew well throughout the season, and yielded a normal crop of grain at harvest.

When the same sensitive procedure of analysis was used, no amitrole could be detected in tissues of bean, spinach, and radishes grown in soils treated with 2, 4, and 5 pounds of the herbicide per acre 50 days before planting.

Since amitrole is readily absorbed by both roots and aerial parts of many plant species (*2*, *9*), and may be translocated freely inside the plant, the authors speculated that the amitrole rapidly became unavailable in Hagerstown silt loam. It then became of interest to determine the fate of this herbicide in the soil.

Difficulty was encountered in obtaining water extracts of the Hagerstown silt loam samples suitable for the colorimetric determination of amitrole as described by Sund (*11*). Materials of humic origin always present in the water extracts reacted with the nitroprusside reagent and absorbed strongly at the wave lengths most suitable for determining amitrole.

After lengthy investigations, saturated barium hydroxide solution proved to be

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an effective extractant for amitrole in soils containing excessive amounts of this interfering matter. Its merit arises from the fact that it yields an extract free of such interfering materials. Inasmuch as barium hydroxide solution does not release greater amounts of amitrole from the soil than does distilled water, there is no advantage to be gained by using it on soils that will yield colorless extracts with water. Attempts to replace saturated barium hydroxide with solutions of barium chloride, barium nitrate, or baryta were unsuccessful.

Water saturated with barium hydroxide was used in the analysis of all the soil samples. After the barium ion was removed from the soil extract by employing techniques normally used for barium sulfate determination, amitrole was determined by the nitroprusside method described by Sund (*11*).

Freed and Furtick recently used an extracting solution containing 0.5% calcium chloride and 0.5% ammonium chloride to remove amitrole from several Oregon soils (*7*). They found that recoveries were at least twice as high when this solution was used in place of distilled water.

No residual amounts of amitrole were found in any of the soil samples collected at intervals of 1, 2, 3, 5, 9, and 13 weeks after the last day of application of the herbicide from plots receiving 2, 4, and 8 pounds per acre. Therefore, laboratory studies were undertaken to study several factors which might affect its persistence in this soil. The factors studied were pH, soil moisture, microbial activity, and temperature.

The effect of soil pH on the disappearance of amitrole from Hagerstown silt loam was studied over a limited range, between pH 6.2 and pH 8.0. Figure 2 shows that a change in soil pH from 7.0 affected the persistence of amitrole. Either an increase or decrease in pH from neutrality hastened the disappearance of amitrole under the conditions of this test.

A direct correlation between soil moisture and the persistence of amitrole was found (Figure 3). At the end of 6 days, 58% of the added amitrole was recovered from air-dry soil; after the same length of time, only 8% was recovered from soil containing 15% moisture, and none from soil containing 30% moisture.

With the standard techniques used, it was not possible to demonstrate that a mixed population of soil microorganisms could use amitrole as a source of carbon or nitrogen, or that the compound was degraded by soil microorganisms in nutritionally adequate media, although in the latter case microbial growth was abundant. To determine more thoroughly the effects of soil microorganisms on amitrole, recovery tests were conducted with soil subject to steam sterilization and methyl bromide fumigation. Figure 4 indicates that the disappearance of the compound was much more rapid from nonsterile soil than from steam-sterilized soil. The same was not true for soil sterilized by fumigation with methyl bromide.

X-ray defraction measurements of the

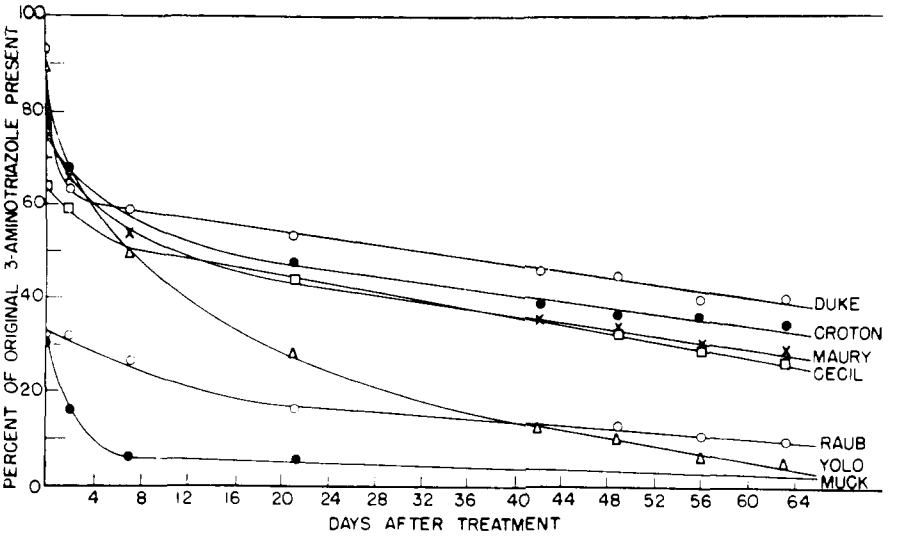

Figure 1. Decomposition of 3-amino-1,2,4-triazole in various soil types

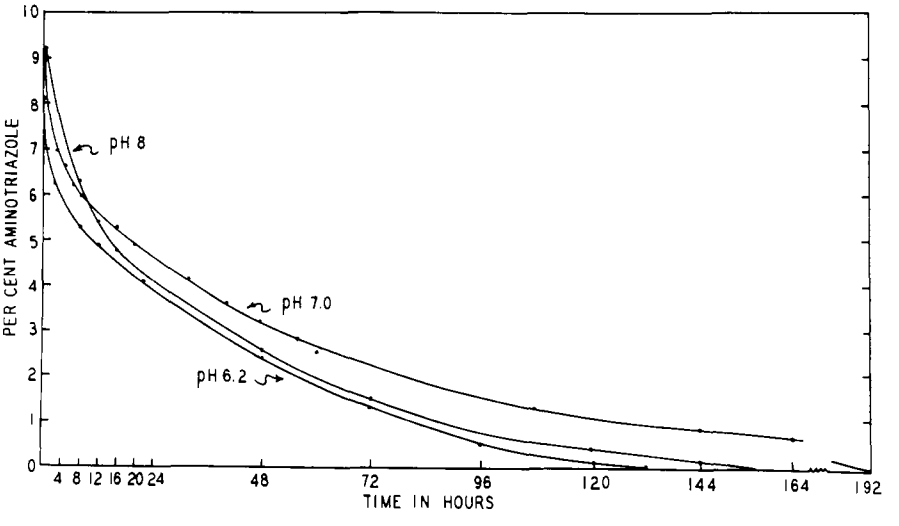

Figure 2. The effect of pH on the recovery of aminotriazole from Hagerstown silt loam soil

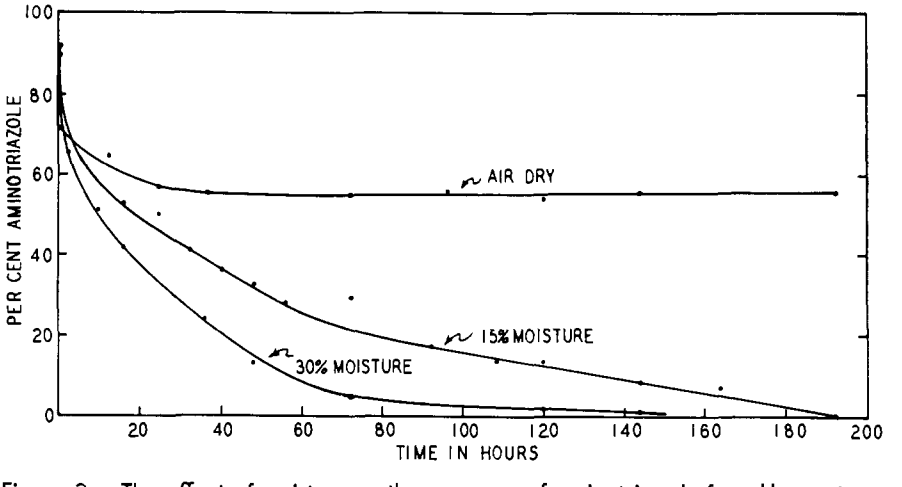

Figure 3. The effect of moisture on the recovery of aminotriazole from Hagerstown silt loam soil

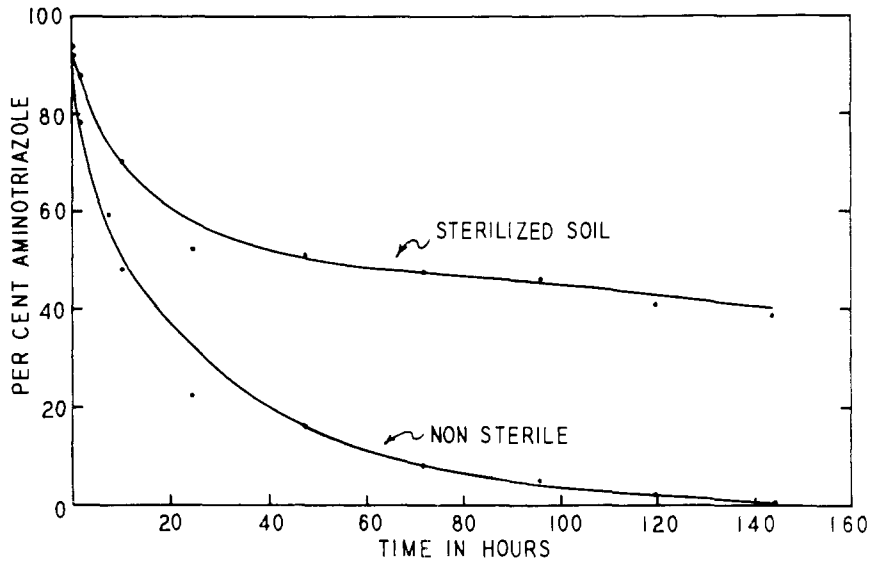

Figure 4. The effects of sterilization on the recovery of aminotriazole from Hagerstown silt loam soil

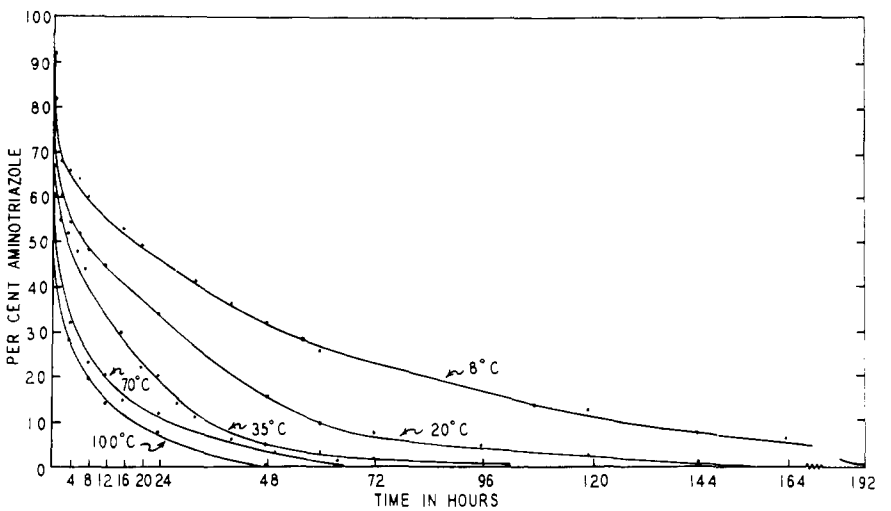

Figure 5. The effect of temperature on the recovery of aminotriazole from Hagerstown silt loam soil

clay fractions separated from Hagerstown silt loam soil treated with amitrole showed that the layers in the clay particles were more widely spaced than were the layers in the clay fraction separated from the untreated soil. The exact nature of the complexes formed were not studied further.

Figure 5 shows that the disappearance of amitrole from Hagerstown silt loam soil was directly related to soil temperature. Day *et al.* (*5*) found a high degree of variability in the persistence of amitrole among the 55 California soils they investigated. After 2 weeks, residues were entirely absent in 26 of the 55 soils, present in only trace amounts in six others, and present in substantial quantities in the remaining 23.

Day and coworkers studied in detail a number of factors which influenced the persistence of amitrole in five of the representative soils from the 55 mentioned above. Among these factors were soil type, time, mixtures of soils, steam sterilization, temperature, soil moisture, leaching, adsorptive capacities of the soil, and base exchange capacity. They found that the disappearance of amitrole was not closely related to soil classification, texture, base exchange capacity, or adsorption capacity, although there was some correlation with all of these factors. The compound was generally less persistent in the more highly evolved soils having finer texture and more highly developed colloidal particles. These workers concluded that soil microorganisms were the main agency of depletion of amitrole in their soils because the chemical was recovered for a longer period of time from sterile soil and from soils kept under conditions unfavorable to microbial growth.

Bondarenko studied the fate of C^{14}-amitrole in two silt loam soils of Ohio (*3*). The tests were carried out under no-leaching conditions. Considerable $C^{14}O_2$ was evolved from each soil within 24 hours after treatment. The rate of $C^{14}O_2$ evolution decreased rapidly until the 42nd day, then gradually until the experiment was terminated on the 240th day when extremely small amounts of $C^{14}O_2$ were evolved. These studies with radiolabeled amitrole demonstrated that with application rates as high as 10 pounds per acre, approximately 80% of the compound is completely metabolized within 30 days, and that this metabolism continues.

In another experiment, Bondarenko studied the fate of an application rate of 8 pounds per acre of amitrole, incorporated in the top 6 inches of soil under natural field conditions and immediately planted to soybeans. Fourteen months later, only a trace of C^{14} activity was detected in the top 1 inch of the soil; no C^{14} was detected at depths of 3, 6, or 12 inches. In a simultaneous experiment, 1 pound of amitrole was watered into field soils in which young corn plants were growing. Only a detectable trace of C^{14} activity was found in the top inch of the soil, whereas no activity was observed in the next 12 inches of this field trial at the end of the 14-month period.

Bondarenko concluded that a tenfold decrease in amitrole can normally be expected in the Ohio soils used for corn and soybean production 1 to 2 weeks after application and that the loss of amitrole is markedly accelerated by elevated soil temperatures, relatively high soil moisture, and conditions favoring microbiological activity.

The effects of temperature and concentration on behavior of amitrole in soil were investigated by Burschel and Freed (*1*), who used a sandy loam soil containing 2.8% organic matter and having a pH of 6.9. Increasing soil temperature from 15° to 29° C. or doubling the concentration of the compound caused the herbicide to disappear from the soil at a faster rate. They concluded that the decomposition process behaves as a first-order reaction.

In laboratory studies on the fate of amitrole-5-C^{14} in sterile and unsterile Yolo sandy loam, Ashton (*1*) found the compound to be rapidly and extensively degraded by microbiological activity. $C^{14}O_2$ was the major metabolic product formed, but at least 13 additional radiolabeled compounds were detected. One or more of these metabolic products was tenaciously bound to the soil and appeared to resist further degradation.

Riepma found that the rate of decomposition of amitrole varied in different soil of the Netherlands (*10*). Decomposition was more rapid in soils of high organic matter content, while

variation in clay content exerted little influence. Decomposition of amitrole was inhibited by preliminary soil sterilization, and more convincingly by addition of biological toxicants—e.g., hydroxylamine, sodium azide, and sodium arsenite. From these observations, Riepma concluded that decomposition of amitrole in soil is a microbiological process.

Apparently a number of factors influence the persistence of this compound in soil. Soils are complex, dynamic systems, and the composition and reactivity of soils vary greatly. The fate of a chemical in soil is influenced by the physical, chemical, and biological properties of the soil and of the herbicide, and the interaction of environmental variables and soil processes.

The effects of adsorption, leaching, evaporation, photochemical degradation, and chemical and microbiological breakdown cannot be sorted out in the field; therefore, it is nearly impossible to isolate and to study these factors separately in vivo. Laboratory studies tend to be unreliable as they disturb the natural soil system and introduce artifacts such as abnormal packing, unrealistic water application and movement, disturbance of the gaseous phase of the soil system, alteration of conditions for microbial growth, and sometimes, interference with the cation exchange capacity.

The investigations which have been briefly discussed represent the bulk of the known studies concerning the fate of amitrole in soil. They have demonstrated that soil type and texture, soil temperature, soil moisture, and soil pH were all factors which affected the persistence of amitrole in soil. $C^{14}O_2$ recovery from soil treated with C^{14}-amitrole illustrates that the compound is degraded in the soil. That amitrole is recovered for longer period of time from sterilized soil (*5, 6, 10*) supports the conclusion of both Bondarenko and Ashton that the compound is rapidly metabolized in the soil by microorganisms.

Sund's observation of positive correlation between the rate of depletion of amitrole from soils and base exchange capacity of the soil were not substantiated to a high degree by Day *et al.* They could not show a high degree of correlation between the persistence of amitrole in 55 soils to soil classification, texture, and base exchange capacity of adsorption capacity, although there was some correlation with all of these factors. The x-ray studies support Sund's conclusions on adsorption and suggest that the presence of specific soil constituents, namely montmorillonite clays, primarily contribute to the deactivation of amitrole via the adsorption mechanism.

The demonstration that the disappearance of amitrole from Hagerstown soil was a direct function of temperature indicates that factors other than microbial action are operative. By the same token, the increase in the rate of disappearance as the temperature is elevated lends little support to the idea that the disappearance is due to simple physical adsorption. Normally, adsorption of a compound from solution by an active adsorbent decreases as the temperature of the system is raised. It is, therefore, suggested that chemical reaction between amitrole and substances in the soil occur and constitute the third mechanism of deactivation of the compound in soil.

Since most of the major studies reported here were conducted under conditions which prevented volatilization, leaching, and photodecomposition, it is beyond the scope of this paper to ascribe their role in deactivating amitrole in soil. However, the vapor pressure of this compound is extremely low; therefore the authors assumed that it would not volatilize readily from soil. Also, amitrole is not known to be adversely affected by sunlight except in the presence of riboflavin. It is doubtful, therefore, that photodecomposition contributes significantly toward its deactivation in soil.

Day *et al.* showed that amitrole moves readily with the leaching water but with distribution patterns that vary appreciably among soils. The downward movement of amitrole was retarded in proportion to the capacity of the soil to adsorb the compound. Bondarenko's studies with the radioactive compound suggest that after prolonged periods of time the compound would be metabolized in at least the top 12 inches of soil.

The authors conclude that the fate of amitrole in soil is governed by the presence and activity of soil microorganisms, adsorption by normal constituents of the soil, and chemical reaction in the soil.

Table I. Base Exchange Capacity, Clay Content, and Organic Matter of Several Soil Types

Soil	Base Exchange, Meg. per 100 Grams	Per Cent Clay Content	Per Cent Organic Matter
Duke sand	3.6	2.0	1.5
Croton silt loam	11.0	9.0	3.9
Maury loam	10.2	9.7	3.1
Cecil sandy loam	5.8	8.8	2.5
Raub loam	20.6	15.8	4.1
Yolo sandy loam	29.5	15.2	4.5
Muck	99.1	---	---

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