# The Persistence of Atrazine, Ametryne, Prometryne, and Diuron in Soils Under Greenhouse Conditions

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## INTRODUCTION

Although the persistence of triazine and urea herbicides in the soil has been studied extensively in temperate areas of the United States, insufficient data exists concerning the persistence of these herbicides under tropical conditions.

The behavior of herbicides in the soil is often affected by climatic and edaphic factors. Information obtained on the persistence of herbicides in the temperate area may not be entirely applicable in Puerto Rico considering that this island is provided with a great diversity of soil types under the influence of a tropical monsoonal climate.

The present studies were undertaken to gather much needed information on the persistence in 13 Puerto Rican soil types of 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (Atrazine), 2-ethylamino-4-isopropylamino-6-methylthio-s-triazine (Ametryne), 2,4-bis(isopropylamino)-6-methylthio-s-triazine (Prometryne), and 3,4-dichlorophenyl-1,1-dimethylurea (Diuron). A better understanding of the persistence characteristics of these compounds in our soils will contribute to the safe, effective, and efficient use of soil-applied herbicides in Puerto Rico and in other tropical areas.

## REVIEW OF LITERATURE

The first comprehensive review of the literature on the behavior of herbicides in the soil was made by Ennis (*4*).[2] More exhaustive and up-to-date reviews were provided by Upchurch (*19*) and Sheets and Harris (*6*). The present review is limited to locally accomplished research. Loustalot and Ferrer (*8*) showed that sodium pentachlorophenate when applied to heavy clay persisted for a longer period of time than when applied to sandy soil or sand-clay mixture. One month after application no appreciable reduction of toxicity was found to occur in clay soil. Toxicity in the sand-clay mixture was more or less the same as in the sandy soil. It was shown by these same investigators (*9*) that TCA persisted in a heavy soil for a longer period of time than in a light soil or in a mixture of both. In an experiment conducted under controlled conditions in the greenhouse,

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[2] Italic numbers in parentheses refer to Literature Cited, pp. 638.

Loustalot and Cruzado (*10*) demonstrated that sandy soil retained Monuron longer than did the heavier soil with a high clay content. Toxicity, at all levels of application, had practically disappeared in clay soil within 10 weeks, while it still persisted in the sandy soil at the end of that time. Loustalot and Cruzado (*11*) also studied the persistence of Monuron under field conditions. They found that corn planted immediately after treatment with Monuron at the rate of 1 pound per acre was not injured but velvet beans were affected thenceforth until the third planting which was made 2 weeks after treatment. Plots treated with 5 pounds per acre remained toxic for 4 months to both crops while those treated with 10 pounds remained toxic for 6 months to corn and for 8 months to velvet beans. Soil treated with Monuron at a rate of 20 pounds per acre remained toxic for 8 months to both test crops. After 12 months the soil treated with 80 pounds per acre of Monuron was no longer toxic to corn but remained toxic to velvet beans as evidenced by stunting and other symptoms of injury. The data obtained in this particular experiment by the two mentioned workers shows that Monuron persists in the soil for a long period even when applied at relatively low rates. The persistence of important herbicides, such as Simazine, Atrazine and Diuron, was studied locally by Cibes and González (*2*) in a Toa soil. Of these Atrazine was the first to disappear from the soil, followed in turn by Simazine and Diuron.

## MATERIALS AND METHODS

The procedure followed in these experiments was essentially the same as that used previously (*7*) except for minor details.

The experiments were conducted in a greenhouse at the Agricultural Experiment Station from 1966 to 1967. The bioassay method described by A. S. Crafts (*3*) was followed. Kanota oat (*Avena sativa* L.) was used as an indicator plant throughout these studies. The plants were grown in unperforated No. 2 tin cans. Each can received 500 g. of soil on an oven-dry weight basis. The soil in each unit was treated with the specific herbicide (Atrazine, Ametryne, Prometryne, and Diuron) at concentrations of 0, 0.5, 1, 2, 4, 8, 16, and 32 p.p.m. with the exception of Caño Tiburones soil. In the case of this soil, which is high in organic matter, two additional concentrations, 64 and 128 p.p.m., were added to the series. Thirty days after planting, 10 oat plants in each can were cut off at ground level. Their fresh weights were recorded and used afterward for calculating the $ED_{50}$ value (dosage of herbicide to reduce fresh weights of oats by 50 percent). After a period of 30 days, the dried soil from each can was pulverized. Plant tops from previous harvests were returned to the bottom of the original can and the soil poured in. Cultures were watered to bring the soil back to field capacity and again 13 oat seeds were sown and the resulting plants grown, as before, for 30 days. Six successive crops of oats were evaluated for each soil type during the course of these studies. The physical and chemical properties of the 13 soils used in these experiments are given in table 1. The $ED_{50}$ values were calculated for each replication of the various treatments and for each successive crop. The $ED_{50}$ values obtained for the various herbicides were subjected to analyses of variance and least significant difference tests, and the data thus derived served as a guide for evaluating each herbicide in the various soils.

TABLE 1.—*Chemical and physical properties of 13 Puerto Rican soils used in persistence studies of Atrazine, Ametryne, Diuron and Prometryne herbicides*

| Soil type | Organic matter | Cation exchange capacity | Exchange bases | | | Soluble phosphorus | pH | Texture | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Ca | Mg | K | | | Sand (2-0.05 mm.) | Silt (0.05-0.002 mm.) | Clay (0.002 mm.) |
| | *Percent* | *Meq./100g.* | *Meq./100g.* | *Meq./100g.* | *Meq./100g.* | *P.p.m.* | | *Percent* | *Percent* | *Percent* |
| Alonso | 3.2 | 13.8 | 5.4 | 2.0 | 0.91 | 4.0 | 5.1 | 14.9 | 39.3 | 45.8 |
| Bayamón | 1.7 | 5.0 | 2.7 | 1.5 | 0.19 | 6.0 | 4.7 | 68.1 | 4.4 | 27.5 |
| Caño Tiburones | 36.0 | 86.0 | 61.9 | 14.0 | 0.80 | 6.0 | 5.5 | 36.0 | 36.0 | 28.0 |
| Coloso | 3.7 | 23.0 | 14.9 | 5.8 | 0.15 | 8.0 | 5.7 | 22.7 | 37.4 | 39.9 |
| Coto | 3.2 | 14.0 | 16.6 | 0.7 | 0.35 | 13.0 | 7.7 | 23.4 | 24.8 | 51.8 |
| Fraternidad | 2.1 | 36.0 | 24.0 | 10.4 | 0.46 | 15.0 | 6.3 | 15.5 | 32.5 | 52.0 |
| Humata | 1.7 | 10.1 | 2.2 | 0.9 | 0.27 | 4.0 | 4.5 | 10.1 | 50.9 | 39.0 |
| Mabí | 4.9 | 26.5 | 11.5 | 14.2 | 0.56 | 3.0 | 5.7 | 22.7 | 40.7 | 36.6 |
| Moca | 3.8 | 31.0 | 23.4 | 4.7 | 0.22 | 6.0 | 5.8 | 26.3 | 27.7 | 46.0 |
| Múcara | 3.3 | 19.6 | 13.6 | 7.8 | 0.14 | 6.0 | 5.8 | 28.0 | 47.0 | 25.0 |
| Pandura | 2.0 | 7.7 | 5.5 | 2.4 | 0.13 | 5.0 | 5.7 | 59.4 | 28.2 | 12.4 |
| San Antón | 2.7 | 26.1 | 23.8 | 5.9 | 0.58 | 16.0 | 6.7 | 24.3 | 49.7 | 26.0 |
| Toa | 0.6 | 8.0 | 6.2 | 1.4 | 0.17 | 7.7 | 6.0 | 60.9 | 25.1 | 14.0 |

## RESULTS

The $ED_{50}$ values presented in table 2 show the effect of Atrazine, Ametryne, Prometryne, and Diuron on the fresh weight of oat plants produced during a series of six successive 30-day crops. A considerable increase in the $ED_{50}$ values of each herbicide existed throughout this period for the different soil types studied.

Prometryne showed the highest increases in $ED_{50}$ values of all the chemicals and was the first to become inactive in the soil. Further evidence of this is that the $ED_{50}$ values of Prometryne exceeded the highest herbicide concentrations used in the case of about half the soils studied. This occurred at the end of the third crop (128 p.p.m. for the soil Caño Tiburones and

TABLE 2.—*Effect of time on herbicide activity of Atrazine, Ametryne, Prometryne and Diuron in 18 Puerto Rican soils as shown by* $ED_{50}$ *values for successive oat crops*

| Soil type | Crop number | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| | | | *Atrazine* $ED_{50}$ *p.p.m.w.* | | | |
| Alonso | 0.05 | 1.70 | 8.39 | 17.97 | over | over[1] |
| Bayamón | 0.25 | 4.43 | 15.38 | 11.78 | over | over |
| Caño Tiburones | 10.70 | 104.87 | over | over | over | over |
| Coloso | 0.42 | 4.52 | 18.63 | over | over | over |
| Coto | 0.04 | 0.27 | 0.71 | 1.63 | 1.96 | 3.03 |
| Fraternidad | 0.16 | 1.01 | 2.84 | 10.23 | 11.68 | 16.64 |
| Humata | 0.04 | 1.94 | 13.13 | 23.02 | over | over |
| Mabí | 0.57 | 1.85 | 7.97 | 21.56 | over | over |
| Moca | 0.46 | 4.15 | 7.03 | 17.86 | over | over |
| Múcara | 0.14 | 1.61 | 7.37 | 21.93 | over | over |
| Pandura | 0.06 | 1.37 | 5.14 | 12.15 | over | over |
| San Antón | 0.57 | 2.37 | 5.38 | 8.19 | 11.89 | 21.05 |
| Toa | 0.03 | 0.31 | 0.67 | 1.66 | 4.89 | 9.87 |
| LSD .05 | 0.51 | 9.82 | 3.62 | 7.66 | 3.24 | 6.13 |
| .01 | 0.69 | 13.31 | 4.93 | 10.45 | 4.91 | 9.29 |
| | | | *Ametryne* $ED_{50}$ *p.p.m.w.* | | | |
| Alonso | 0.66 | 5.44 | 3.57 | 5.35 | 6.22 | 11.40 |
| Bayamón | 0.68 | 1.71 | 2.81 | 2.80 | 3.18 | 4.78 |
| Caño Tiburones | 12.83 | 32.00 | 115.90 | 107.40 | over | over |
| Coloso | 1.89 | 5.77 | 16.90 | 17.98 | 17.22 | 21.24 |
| Coto | 0.10 | 1.34 | 4.06 | 7.23 | 19.23 | 20.16 |
| Fraternidad | 0.43 | 3.55 | 12.12 | 22.15 | 22.39 | 29.77 |
| Humata | 0.58 | 1.09 | 1.65 | 2.56 | 2.82 | 4.63 |
| Mabí | 1.56 | 6.37 | 8.51 | 9.47 | over | 19.52 |
| Moca | 1.53 | 3.51 | 7.64 | 6.59 | 7.73 | 20.18 |
| Múcara | 0.96 | 2.19 | 6.15 | 5.93 | 10.72 | 19.20 |
| Pandura | 0.18 | 1.91 | 2.89 | 4.02 | 5.56 | 9.47 |
| San Antón | 1.11 | 5.94 | 19.33 | 17.59 | 23.99 | over |
| Toa | 0.03 | 0.51 | 1.31 | 1.32 | 2.31 | 4.32 |
| LSD .05 | 0.77 | 8.80 | 4.78 | 5.54 | 3.12 | 4.24 |
| .01 | 1.03 | 11.93 | 6.48 | 7.50 | 4.26 | 5.78 |
| | | | *Prometryne* $ED_{50}$ *p.p.m.w.* | | | |
| Alonso | 1.50 | 4.97 | 21.23 | 22.55 | 26.04 | over[1] |
| Bayamón | 1.99 | 10.65 | 11.21 | 16.53 | 24.31 | over |
| Caño Tiburones | 48.67 | over | over | over | over | over |
| Coloso | 4.34 | over | over | over | over | over |

TABLE 2.—*Continued*

| Soil type | Crop number | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Coto | 0.29 | 2.70 | 15.58 | over | over | over |
| Fraternidad | 0.99 | 18.82 | over | over | over | over |
| Humata | 2.28 | 3.13 | 21.86 | 17.75 | 25.72 | over |
| Mabí | 31.33 | over | over | over | over | over |
| Moca | 2.88 | 9.89 | 28.50 | over | over | over |
| Múcara | 2.52 | 14.97 | over | over | over | over |
| Pandura | 0.28 | 4.73 | 4.70 | over | over | over |
| San Antón | 3.31 | 26.38 | over | over | over | over |
| Toa | 0.05 | 0.97 | 4.06 | 4.21 | 19.39 | over |
| LSD .05 | 4.19 | 4.45 | 12.33 | 15.06 | 14.31 | — |
| .01 | 6.68 | 6.10 | 18.54 | — | — | — |
| *Diuron $ED_{50}$ p.p.m.w.* | | | | | | |
| Alonso | 0.60 | 3.98 | 2.79 | 2.61 | 3.81 | 4.52 |
| Bayamón | 0.56 | 1.45 | 1.52 | 1.63 | 1.91 | 2.40 |
| Caño Tiburones | 18.40 | 53.80 | 51.22 | 62.55 | 97.14 | 103.97 |
| Coloso | 1.20 | 3.27 | 4.89 | 4.44 | 3.72 | 4.84 |
| Coto | 0.43 | 1.72 | 2.53 | 2.16 | 2.95 | 2.88 |
| Fraternidad | 0.81 | 1.96 | 2.62 | 3.33 | 2.93 | 3.14 |
| Humata | 0.07 | 0.71 | 0.93 | 1.26 | 1.01 | 1.51 |
| Mabí | 2.27 | 4.10 | 5.03 | 4.55 | 4.40 | 5.35 |
| Moca | 1.44 | 2.28 | 4.13 | 4.06 | 3.81 | 5.24 |
| Múcara | 0.40 | 1.25 | 1.21 | 1.32 | 1.39 | 1.31 |
| Pandura | 0.06 | 1.00 | 1.14 | 1.23 | 1.24 | 1.47 |
| San Antón | 1.76 | 3.92 | 5.26 | 6.60 | 5.62 | 9.88 |
| Toa | 0.03 | 0.22 | 0.49 | 0.58 | 0.62 | 0.77 |
| LSD .05 | 0.88 | 8.59 | 3.59 | 8.36 | 3.52 | 2.79 |
| .01 | 1.19 | 11.64 | 4.87 | 11.33 | 4.77 | 3.79 |

[1] "Over" indicates the $ED_{50}$ value exceeded the highest herbicide concentration used.

32 p.p.m. for all other soil types). Moreover, $ED_{50}$ values were no longer obtainable for Prometryne in the last oat cropping. This was an indication that this chemical was completely detoxified in the soil. The rapid inactivation of Prometryne in Caño Tiburones soil deserves special mention. This can be attributed to the high organic matter content of this soil and particularly to a high affinity of this herbicide for that soil fraction. Furthermore, Prometryne had practically disappeared from Coloso and Mabí soils right after the first crop of oats was harvested. Both soils were found to be relatively high in organic matter, cation exchange capacity, and silt and clay content.

Atrazine was found to be the second least persistent herbicide in most of the soils. The $ED_{50}$ values listed for Atrazine in table 2 demonstrate that this compound had lost its phytotoxic action in the Caño Tiburones soil by the end of the third crop of oats. It took about two more crops before Atrazine was completely inactivated in most soils. In fact, by that time, it was totally inactive in 9 of the 13 soils studied.

Ametryne exhibited considerably more persistence in the soil than either Prometryne or Atrazine. None of the $ED_{50}$ values for Ametryne exceeded the highest herbicide concentration to the fourth crop of oats. It was not until the sixth successive crop that the $ED_{50}$ value for Ametryne surpassed the highest herbicide concentration (in only 2 of the 13 soils tested). These two soils were Caño Tiburones and San Antón.

Diuron was found to be the most persistent herbicide in these experiments. This is indicated by the correspondingly low $ED_{50}$ values for Diuron as compared with the $ED_{50}$ values for the other three herbicides. None of the $ED_{50}$ values for Diuron exceeded the highest concentration used. The $ED_{50}$ value for Diuron even in Caño Tiburones soil did not exceed the highest concentration employed (128 p.p.m.), whereas the $ED_{50}$ value for other herbicides in this same soil were no longer obtainable long before reaching the end of the sixth crop.

Caño Tiburones soil appeared to possess the highest detoxifying capacity regardless of the concentration involved. This, of course, can be attributed to its high organic-matter content. It is well known that soils with such high organic-matter content often have a rich microbial flora. This may account for the rapid decomposition, detoxification, and inactivation of various herbicides in this soil. Atrazine, Ametryne, Prometryne, and Diuron, on the contrary, were highly persistent in Coto, Humata, Toa, and Pandura soils. Close examination of physical as well as chemical properties of these soils reveals that all four, in spite of their high clay and silt content, and notwithstanding their light texture, have this one thing in common; low organic-matter content. It appears that inactivation of the four herbicides in these soils is dependent largely on the amount of organic matter present: The higher the organic-matter content of a soil, the greater the degree of inactivation.

Our studies indicate that Diuron had greater persistence in sandy soils than in heavier soils. This finding agrees with results obtained by Loustalot *et al.* (*12*) with Monuron, a closely related, substituted urea herbicide. This marked persistence of Diuron in light textured soils also was observed by Cibes and González (*2*) while working with a Toa sandy loam in the greenhouse. Sheets (*13*) reached this same conclusion after studying relative toxicities of four urea herbicides. Sund (*16*) found in Hawaii that application of 2 rounds of Diuron (5 lbs. + 3 lbs./acre) gave the maximum net days of weed control. Other combinations, including Diuron, outperformed Monuron on all but one plantation.

The persistence of various triazine compounds in the soil was studied by Sheets and Shaw (*15*). They suggested that the methoxy and methyl mercapto derivatives were hydrolyzed more slowly than the chloro derivatives because of the presence of less reactive groups. This may account perhaps in part for the lower persistence of Atrazine (chloro derivative) when compared with that of Ametryne (methyl mercapto derivative). It should be pointed out, however, that Prometryne, another methyl mercapto derivative, was found to be the least persistent of all the herbicides included in these experiments. Because persistence or toxicity of herbicides in the soil is such a complex phenomenon, it is impossible to attribute it to any single factor *per se*. Biotic, climatic, and edaphic factors, as well as rate of application, are known to influence the action of herbicides in the soil. The behavior of Atrazine in the present investigation was found to differ somewhat from that reported for this compound in temperate regions. Injury to oats and other crops has been reported (*1*, *5*, *17*, *18*) in the United States in areas treated several months before with Atrazine. However, the recommended rate of 4 pounds per acre of Atrazine (approximately twice the rate used in the United States) has been found to lack the persistence desired for a prolonged period of weed control in the sugarcane fields of Puerto Rico. Harris and Sheets (*6*) also have reported the relatively rapid inactivation of Prometryne. Very little information is available on the persistence of Ametryne in the soil. The only reference found concerning detoxification of Ametryne was that of Sheets and Shaw (*15*), who demonstrated that Ametryne persisted considerably longer than Prometryne in a Bosket sandy loam.

## SUMMARY

The persistence of Atrazine, Ametryne, Prometryne, and Diuron in 13 Puerto Rican soils was studied under greenhouse conditions, using oats (*Avena sativa* L. var. Kanota) as the bioassay plant. Judging from the data obtained from six successive croppings of oats, Diuron was the most persistent herbicide in most soils while Prometryne was the least so. Ametryne and Atrazine were intermediate in persistence; however, the former was found to be more persistent than the latter in most of the soils studied.

Of all the soil components or properties studied, organic matter appeared to be the one most highly related to the persistence of the four herbicides. The degree of herbicide persistence was lower in soils having a high organic

matter content. This may be attributed to a greater microbial detoxification capacity associated with a higher organic-matter content of the corresponding soil.

## RESUMEN

Se estudió la persistencia del Atrazine, Ametryne, Prometryne y Diuron bajo condiciones de invernadero, en 13 suelos típicos de Puerto Rico, usándose la avena (*Avena sativa* L.) como planta indicadora. A juzgar por los datos recogidos a través de seis cosechas sucesivas de avena, el Diuron fue el yerbicida de mayor y el Prometryne el de menor persistencia. El Atrazine y el Ametryne fueron de persistencia intermedia, aunque el primero de estos dos yerbicidas demostró ser un tanto más persistente que el segundo en la mayoría de los suelos que se estudiaron.

De entre todos los componentes del suelo que se estudiaron, el que demostró guardar una relación más estrecha con la persistencia de los cuatro yerbicidas fué la materia órganica. El grado de persistencia resultó ser más bajo en aquellos suelos con un contenido más alto en materia orgánica. Esto puede atribuirse a que la actividad desintoxicadora microbiana fue mayor en los suelos con un alto contenido de materia orgánica.

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