# Persistence of Atrazine and Occurrence of Its Primary Metabolites in Three Soils

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Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine) degradation in various soils under laboratory conditions was studied. Atrazine was depleted mostly through microbial degradation in alkaline soil and was degraded in acidic soil mainly through chemical transformation or both chemical and microbial transformation. The microbial degradations of atrazine produced desethylatrazine and desisopropylatrazine as primary metabolites, while chemical degradation of atrazine yielded hydroxyatrazine. Atrazine decreased 3−4 times faster in soils at 25 °C than at 10 °C.

**Keywords:** *Atrazine; metabolite; degradation; soil; persistence*

Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine) has been used in plant production intensively for the last several decades. It is relatively persistent, and soil and water contamination by atrazine is more and more a public concern.

Atrazine is primarily degraded into desethylatrazine (2-chloro-4-amino-6-(isopropylamino)-*s*-triazine), desisopropylatrazine (2-chloro-4-(ethylamino)-6-amino-*s*-triazine), or hydroxyatrazine (2-hydroxy-4-(ethylamino)-6-(isopropylamino)-*s*-triazine) through different pathways. Mechanistically, soil humus and clay minerals can catalyze chemical hydrolysis of atrazine to yield hydroxyatrazine (Burkhard and Guth, 1981; Russel et al., 1968). Various microorganisms, however, metabolize atrazine to desethylatrazine and desisopropylatrazine (Giardiina et al., 1982). Behki and Khan (1986) reported that a strain of bacteria, *Pseudomonas putida*, hydrolytically dechlorinated atrazine to yield hydroxyatrazine. The authors have studied atrazine depletion and the occurrence of the primary metabolites in soils of Hesse, Germany (Qiao and Hummel, 1990, 1992). The direct and indirect effects of soil pH value on the persistence of atrazine in fields were evaluated. In this paper, determination of the persistence, abiotic, and microbial transformation of atrazine in soils under laboratory conditions and the relationships between the different pathways are presented.

## MATERIALS AND METHODS

**Selected Soils.** Three soils were selected from Hesse, Germany, for the experiment (Table 1).

**Soil Treatment**. The three soils were spiked with atrazine to a concentration of 5 mg/kg, Duplicate portions of the soils were put into covered aluminium cups of 250 mL volume and incubated for measuring degradation and metabolites under temperature conditions of 10 and 25 °C. They were kept at 60% and 100% of field water capacity through weekly refilling with distilled water. A unique autoclaved sample was prepared parallel to each treatment and was not kept sterile after being spiked with atrazine.

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**Table 1. Soil Parameters of Selected Soils**

| | soil code | | |
|---|---|---|---|
| | B1 | B2 | B3 |
| soil species | silty loam | silty loam | sand |
| pH($CaCl_2$) | 5.1 | 7.6 | 4.7 |
| org substance (%) | 2.2 | 1.8 | 3.8 |
| water capacity (%) | 37.1 | 37.8 | 30.6 |

**Table 2. DT50 of Atrazine in Selected Soils**

| | | DT50 (day) | |
|---|---|---|---|
| soil | temp (°C) | unautoclaved | autoclaved |
| B1 | 10 | 128.8 | 160.9 |
| | 25 | 39.4 | 55.7 |
| B2 | 10 | 77.7 | 695.1 |
| | 25 | 24.9 | 133.8 |
| B3 | 10 | 102.3 | 131.8 |
| | 25 | 23.8 | 37.4 |

**Soil Sampling.** At the time of 0, 10, 30, 60, and 110 days after atrazine spiking, soil samples were taken for residue analysis and water contents determination or stored at −20 °C for a short time before cleanup.

**Sample Analysis.** Atrazine and its metabolites [desethylatrazine (DEA), desisopropylatrazine (DIA), hydroxyatrazine (HOA)] were analyzed by the HPLC method as described earlier (Qiao et al., 1991, 1995). The cleanup procedure consisted of a methanol shaking extraction, centrifugation, and concentration and was followed by a gradient reversed-phase HPLC separation with subsequent UV detection at 220 nm.

## RESULTS AND DISCUSSION

The persistence of atrazine in various soils was characterized by the half-life of disappearence time (DT50) of atrazine. The DT50 was calculated according to the mathematical models recommended by Timme et al. (1986) and using the residue analysis data of atrazine in soils under given conditions. In Table 2, the DT50 value of each soil is shown.

The atrazine depletion in soils depended on soil temperature. With increasing soil temperature from 10 to 25 °C, the mean of DT50 of atrazine in three soils was reduced from 102.9 to 28.4 days. This shows that under higher temperature atrazine has degraded 3−4 times faster. But the rate of DT50 reduction in various soils was significantly different (see unautoclaved column in Table 2). In soil B2, the higher temperature caused a shortening of the DT50 value by 53 days, while

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**Table 3. Depletion of Atrazine and Appearence of Metabolites in Three Selected Soils (25 °C, 60% FC)[a]**

| | | soil residues (mg/kg) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | unautoclaved | | | | autoclaved | | | |
| soil | days after spiking | atrazine | DEA | DIA | HOA | atrazine | DEA | DIA | HOA |
| B1 | 0 | 4.671 | nd | nd | 0.015 | 5.389 | nd | nd | 0.036 |
| | 10 | 3.964 | 0.070 | 0.011 | 0.058 | 4.855 | 0.096 | 0.042 | 0.092 |
| | 30 | 2.875 | *0.128* | *0.020* | *0.161* | 3.650 | *0.164* | *0.056* | 0.192 |
| | 60 | 1.478 | 0.077 | 0.017 | 0.047 | 2.019 | 0.107 | 0.028 | 0.312 |
| | 110 | 0.989 | 0.056 | 0.015 | 0.017 | 1.454 | 0.097 | 0.023 | *0.437* |
| B2 | 0 | 5.478 | 0.011 | nd | nd | 5.716 | nd | nd | nd |
| | 10 | 3.808 | 0.227 | 0.048 | *0.015* | 5.380 | nd | nd | nd |
| | 30 | 2.907 | 0.571 | *0.095* | nd | 4.599 | 0.032 | nd | 0.019 |
| | 60 | 1.396 | 0.486 | 0.079 | nd | 3.584 | 0.041 | nd | nd |
| | 110 | 1.148 | *0.668* | 0.077 | nd | 3.389 | *0.074* | *0.022* | *0.117* |
| B3 | 0 | 5.359 | nd | nd | nd | 5.697 | nd | nd | nd |
| | 10 | 3.742 | 0.053 | *0.021* | 0.094 | 4.818 | 0.051 | 0.015 | 0.121 |
| | 30 | 2.533 | *0.079* | 0.018 | 0.315 | 3.431 | *0.057* | *0.022* | 0.206 |
| | 60 | 1.165 | 0.061 | 0.015 | 0.481 | 1.905 | 0.030 | 0.006 | 0.321 |
| | 110 | 0.501 | 0.032 | 0.016 | *0.554* | 1.232 | 0.025 | nd | *0.472* |

[a] nd, not detectable (≤0.005 mg/kg). Italic data, maxima in the series of measurements.

in soil B3 and B1, it was 77 and 90 days, respectively. Futhermore, atrazine was degraded in soil B2, especially at 10 °C, faster than in soils B1 and B3. These results indicated that less activation energy or a lower energy threshold may be needed for atrazine degradation in soil B2 than in soils B1 and B3.

A unique soil autoclaving caused a reversed persistence order of atrazine in the three tested soils. Here, the DT50 of atrazine in alkaline soil B2 grew from the shortest one (51 days, mean value of DT50s under 10 and 25 °C) in the unautoclaved variety to a longest one (414 days) in the autoclaved soil, while in the acidic soils B1 and B3 only a moderate increase in DT50 was observed after autoclaving (Table 2). The DT50 increased in B1 and B3 by only 23−24 days after autoclaving. This was probably due to differentiated degradation pathways in various soils, as quantitative different metabolite patterns were observed in the soils with or without autoclaving (Table 3).

There are two pathways for the atrazine transformation in the soil: chemical degradation and biotic degradation (Burkhard and Guth, 1981; Giardina et al., 1982). The experiments show that microbial degradation was the key degradation pathway of atrazine in alkaline soil B2, as there was only little HOA, and chemical transformation appeared to play an important role mainly in acidic soils B1 and B3, as the main transformation product was HOA. Through a unique autoclaving, the microbial activity of soil B2 was limited to a lower level, so that the DT50 increased to a large extent. As the chemical degradation of atrazine in soils B1 and B3 was less affected by the autoclaving, the DT50 increases were only in a smaller scale. Under higher temperature, the microbial biomass in autoclaved soil B2 could be recovered sooner, and some species of the microorganisms could enhance the degradation of atrazine, so that the DT50 of atrazine was much smaller at 25 °C than that at 10 °C (561.3 days difference) in soil B2, while in the case of B1 and B3, the DT50 was nearly the same scale as that of the unautoclaved variety (84.0 days difference by unautoclaved variety and 99.8 days difference by autoclaved variety, respectively).

These results supported the assumption discussed above, that less activation energy would be needed for atrazine degradation with mainly biological processes in soil B2. Once the condition of enough energy supply is fulfilled for a chemical process, the transformation of atrazine could become more effective to atrazine degradation, and the DT50 was decreased as given in soil B3 at 25 °C (Table 2).

Under the two pathways of atrazine transformation in soils, the chemical degradation transforms atrazine abiotically to the hydroxylated product HOA, and the microbial degradation metabolizes atrazine to N-desalkylated products DEA and DIA. The data from metabolite analysis provide some proof for the discussion above (Table 3).

In the unautoclaved alkaline soil B2, the main primary metabolites were DEA and DIA, these could be produced through microbial metabolism of atrazine. Soil autoclaving weakened the microbial pathway, so that the primary biotic transformation products stayed at a lower level (Table 3) and the DT50 increased to its biggest value (Table 2).

In the acidic soil B3, the quantitative transformation product was HOA, which could be produced by the hydroxylation of atrazine. The DT50 of atrazine in soil B3 would not be seriously affected by the unique autoclaving, and the difference of metabolites between autoclaved and unautoclaved treatments was minimal.

In the unautoclaved weakly acidic soil B1, the situation was similar as in soil B3. Both microbial and chemical transformation products were detected in a comparable scale. More HOA was detected after autoclaving.

All of these findings indicated that chemical transformation of atrazine occurred predominantly in acidic soils and that microbial metabolizing of atrazine played a more important role in alkaline soil. This could be an explanation to the strong differentiation of the DT50 of atrazine in B2 by even only a unique soil autoclaving.

The results that the occurrence of more HOA in acidic soil and more DEA and DIA in alkaline soil, such as soil pH value dependent depletion of atrazine, were in agreement with previous field investigations by the authors (Qiao and Hummel, 1992) and by Obrador et al. (1991).

In this work, the bound residues of atrazine and its metabolites could not be included. Degradation of the metabolites was not traced too. Microbial function on a species level was to be determined. All these aspects were less, and further work is demanded for a better understanding of the environmental behavior of atrazine.

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