Effects of temperature and moisture on the persistence of terbuthylazine in two Malaysian agricultural soils

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Summary

The persistence of terbuthylazine in Sungai Buloh and Serdang series soils incubated at different temperature and moisture content was investigated under laboratory conditions using cucumber (*Cucumis sativus* L.) as the bioassay species. A faster degradation of terbuthylazine was observed in the non-autoclaved soil as compared to the autoclaved soil samples. At higher temperatures the degradation rate in the non-autoclaved soil samples improved with increasing soil moisture content. In non-autoclaved Sungai Buloh and Serdang series soils, the half-life was reduced from 20.3 to 10.7 days and from 38.5 to 16.1 days respectively, when the temperature was increased from 20 to 35°C at 70% field capacity. In the autoclaved soil, the herbicide residue appeared to have been broken down by non-biological processes. The rate of dissipation was slightly increased after the second application of the herbicide to the non-autoclaved Sungai Buloh and Serdang series soils incubated at 35°C with soil moisture of 30 and 50% field capacity. However the half-life is shorter in non-autoclave soil of the Sungai Buloh and Serdang series soils after the second treatment followed by incubation at 35°C and 70% moisture. The half-life was slightly longer after the second treatment in autoclaved soils of both Sungai Buloh and Serdang series. A shorter half-life of terbuthylazine in non-autoclaved soils as compared to autoclaved soils indicates the importance of microorganisms, besides other non-biological process, that contribute to the dissipation of terbuthylazine.

Introduction

Terbuthylazine is a member of the triazine group and is used to control annual grasses and broadleaf weeds in rubber, oil palm and cocoa plantations as well as in orchards and non-cropped land. This herbicide is a relatively new triazine developed for pre-emergence use on a wide spectrum of weeds, causing rapid inhibition of growth of young plants.

The persistence of the triazine group in the soil depends on the rate of application and environmental factors such as soil moisture, temperature, pH and constituents (Anon 1989). Weber and Weed (1974) reported that the degradation of triazine increased at higher levels of soil temperature and soil moisture. Adsorption and bioactivity of many herbicides are correlated with organic matter, clay content and other soil parameters. Organic matter has been reported to be the primary adsorbing surface in the soil (Weber and Weed 1974, Nishimoto and Rahman 1985). The influence of the organic content of the soil is illustrated by the fact that the half-life of simazine and atrazine ranged from 22 to 44 days, depending on the organic content of the soil (Walker and Thompson 1977, Durand and Barcelo 1992). A longer half-life was observed in soils with high organic matter content. Degradation of atrazine has been reported to be faster in moist than in dry soils (Walker and Zimdahl 1981). The active ingredients of triazines are stable chemical compounds which, however, degrade rapidly in the soil due to microbial activity (Anon 1989). The maximum movement of terbuthylazine down the soil profile under natural rainfall conditions was 20 cm after 21 days (Bowman 1989). While much is known about the activity and mode of action of other compounds in the triazine group, little quantitative information is available concerning the mode of dissipation of terbuthylazine in soils especially under tropical conditions.

In this study, bioassays have been used to measure the plant-available residue fraction in soil. This method had been used to study the persistence of atrazine, one of triazine group in soils (Marriage 1975, Reinhardt and Nel 1993). The presence of large amounts of the residue in soils could cause detrimental effect on the crop and other cash crops grown between the rows of young plants. If the compounds persist in the soil they could cause contamination in soil and water. The present experiments were designed to determine the persistence of terbuthylazine effected by single and double applications at various moisture and temperature levels in two different soil types viz. Sungai Buloh and Serdang series.

Materials and methods

Two different soil types were used: Sungai Buloh series (89% sand, 4.4% silt, 7.6% clay and 2.0% organic C at $pH_{(water)}$ 4.8) and Serdang series (50.6% sand, 14.6% silt, 34.8% clay and 0.78% organic C at $pH_{(water)}$ 5.1). The Sungai Buloh series soil was collected from the Rubber Research Institute, Sungai Buloh, whilst the Serdang series soil was obtained from the University Putra Malaysia Research Station, Serdang, Selangor. The soil samples were collected from the top 10 cm of the soil surface. These soils had not been treated with any herbicides for more than two years, therefore the soil samples were considered free from any pesticide contamination. The herbicide used in the study was Gardoprim® which contains terbuthylazine (2-chloro-4-ethylamino-6-terbuthylamino-1,3,5-triazine) at 500 g L^{-1}. The experiments were conducted in one of the university's greenhouses under natural light and normal temperature that fluctuated between 25 and 32°C.

Dose response trials

Dose response tests were conducted twice using the two soil types viz. Sungai Buloh and Serdang series. Cucumber (*Cucumis sativus* L.) was bioassayed to define linearly the concentration range of the herbicide in the soils used for the greenhouse studies. The required volume of the herbicide was thoroughly mixed with the air-dried soil to obtain a final concentration of 40 ppm active ingredient (w/w). Other required concentrations were prepared by diluting the treated soil with untreated soil to obtain a series of concentrations as follows: 0 (untreated soil), 0.01, 0.05, 0.1, 0.3, 0.5, 1.0, 4.0, 7.0, 10.0 and 20.0 ppm active ingredient (w/w). The soil from each series was transferred separately into pots, each containing 200 g of soil. Six cucumber seeds were planted in each pot at 1 cm depth. The pots were placed in a growth incubator at 35°C, and moisture content of 50% field capacity. After emergence, the plants were thinned to four per pot. Ten days after emergence, the plants were cut at soil level and the fresh weight recorded. First-order linear regression curves were obtained by plotting the average plant fresh weight of four replicates as a percentage of the untreated control, against the log of the herbicide concentration. Based on the response curve, the percentage fresh weight of the seedlings grown in soil samples containing unknown concentrations of the herbicide were converted to herbicide concentrations remaining in the soil.

Effect of temperature and moisture on the half-life

Six 8.5 kg batches of autoclaved air-dried soil (autoclaved at a pressure of 103 kPa and 120°C for 15 min) and non-autoclaved soil were treated with the herbicide to give a final concentration of 20 ppm active ingredient (w/w). The soil was thoroughly mixed and moistened to either 30, 50 or 70% field capacity. The bags of soil at each moisture level were kept in a growth incubator at either 20 or 35°C and weighed weekly; the soil was stirred after adding water in order to maintain the required moisture level. Each treatment had a similar untreated control. Three soil samples (200 g each) were removed from each bag, placed in a black plastic bag for each moisture-temperature combination on day 0, 3, 6, 10, 15, 25, 30 and 37 and kept at -4°C.

After 37 days of incubation, each sample was thawed, air-dried overnight and then placed in a styrofoam pot (22 cm diameter); ten cucumber seeds were planted in each pot at a depth of 1 cm. After emergence, the plants were thinned to four per pot. Ten days after emergence, the plants were cut at soil level and the fresh weight recorded and expressed as a percentage of the fresh weight of the respective control plants grown in untreated soil. The concentration of the herbicide in the soil was determined by comparing the dry weight of the plants with those obtained in a dose-response curve trial that was run concurrently. Half-lives were calculated assuming first-order kinetic behaviour (Ismail and Teoh 1994). The experimental design was randomized complete block with four replications.

Effect of two applications on the half-life
The experiment was performed using the remaining non-autoclaved soil samples (at 30, 50 and 70% of field capacity) and autoclaved (70% of field capacity only) soils of Sungai Buloh and Serdang series that had been incubated for 30 days at 35°C in the previous experiment. The soil samples were retreated with terbuthylazine to give a final concentration of 20 ppm (w/w) on air-dried basis. The herbicide was thoroughly mixed into the soil, which was then placed in polythene bags and incubated at 35°C, and 70% field capacity for autoclaved soil. Meanwhile, the polythene bags containing the non-autoclaved soil samples, were kept at 35°C, with soil moisture of either 30, 50 or 70% field capacity. Each treatment had a similar untreated control. The experimental design was a randomized complete block with four replications. Four soil samples (200 gm each) were removed from each bag on 0, 3, 6, 10, 15, 25, 30 and 37 days, and kept at -4°C. After day 37, the soil samples were analysed as described before for determination of the half-life.

Results

Preliminary experiments have shown cucumber to be the most sensitive of the species tested, therefore it was used as the bioassay species for the determination of residues. A graph of fresh weight (expressed as a percentage of the control value) against the log of herbicide concentration gave a first-order linear relationship with correlation coefficients of -0.92 and -0.96 for the Sungai Buloh and Serdang series soil respectively.

In the non-autoclaved Sungai Buloh series soil the half-life of terbuthylazine was much shorter at the incubation temperature of 35°C than at 20°C, irrespective of moisture levels (Table 1). The half-life in the non-autoclaved soil ranged from 10.2 to 13.7 days at 35°C, depending on soil moisture and temperature. A similar pattern of degradation was observed in the autoclaved soil, however, the half-life was slightly longer than that in non-autoclaved soil at both 20 and 35°C. In autoclaved soil, the half-life was shortest (16.5 days) at 70% field capacity as compared to those at other moisture levels at 35°C.

The half-life of terbuthylazine in the Serdang series soil was shorter in non-autoclaved than in the autoclaved soil (Table 2). The half-life was shorter at 35°C than at 20°C and shorter at the higher moisture content than at the lower.

Table 3 shows the effect of repeated applications of terbuthylazine on the half-life in non-autoclaved and autoclaved soil of the Sungai Buloh series. The half-life was longer after two applications than after one application for each combination of temperature and moisture levels except at 35°C and 70% field capacity. The same pattern of degradation occurred in the Serdang soil as in Sungai Buloh soil series (Table 4). In autoclaved soils, the half-life was longer after two applications than after one application in both soil types.

Discussion

The degradation of terbuthylazine was slightly more rapid in non-sterilized than in sterilized soil samples. This shows an involvement of microbial activity in non-sterilized soil, indicated by the slower disappearance of the residue in sterilized soil,

Table 1. Half-life (days) of terbuthylazine in non-autoclaved and autoclaved Sungai Buloh series soil at different temperature and moisture levels.

Temperature (°C)	Moisture content (% field capacity)	Half-life (days)	Correlation coefficient (r)
Non-autoclaved			
20	30	23.7	-0.96
20	50	23.1	-0.94
20	70	20.3	-0.91
35	30	13.7	-0.93
35	50	10.2	-0.96
35	70	10.7	-0.95
Autoclaved soil			
20	30	32.5	-0.94
20	50	28.6	-0.97
20	70	29.2	-0.93
35	30	18.6	-0.95
35	50	17.3	-0.95
35	70	16.5	-0.95

All correlation coefficients are significant at the 5% level.

Table 2. Half-life (days) of terbuthylazine in non-autoclaved and autoclaved Serdang series soil at different temperature and moisture levels.

Temperature (°C)	Moisture content (% field capacity)	Half-life (days)	Correlation coefficient (r)
Non-autoclaved			
20	30	38.4	-0.96
20	50	35.7	-0.97
20	70	38.5	-0.96
35	30	18.5	-0.92
35	50	17.1	-0.98
35	70	16.1	-0.97
Autoclaved soil			
20	30	39.4	-0.95
20	50	37.4	-0.96
20	70	47.2	-0.95
35	30	19.2	-0.97
35	50	17.7	-0.94
35	70	20.1	-0.93

All correlation coefficients are significant at the 5% level.

Table 3. Half-life (days) of terbuthylazine in Sungai Buloh series soil after the second treatment.

Temperature (°C)	Moisture content (% field capacity)	Half-life (days)	Correlation coefficient (r)
Non-autoclaved			
35	30	22.2	-0.91
35	50	19.8	-0.91
35	70	8.1	-0.94
Autoclaved			
35	70	21.5	-0.95

All correlation coefficients are significant at the 5% level.

Table 4. Half-life (days) of terbuthylazine in Serdang series soil after the second treatment.

Temperature (°C)	Moisture content (% field capacity)	Half-life (days)	Correlation coefficient (r)
Non-autoclaved			
35	30	31.4	-0.95
35	50	26.7	-0.98
35	70	14.1	-0.94
Autoclaved			
35	70	27.9	-0.91

All correlation coefficients are significant at the 5% level.

in line with other previous reports using different groups of herbicides, as specific literature on terbuthylazine is very limited (Walker and Welch 1989). Voets *et al*. (1974) have shown that the degradation rate of triazine in the soil was positively correlated to bacterial and fungal populations.

The results of this experiment indicate that degradation could still occur in the sterilized soil. The decrease in half-life in sterilized soil at higher temperatures and higher field capacities in both soils, suggests that the degradation of terbuthylazine also involves non-biological processes. Soil pH is an important factor influencing degradation of most triazine herbicides (Best and Weber 1974, Hance 1979). The chemical hydrolysis of triazine herbicides is particularly important at low soil pH (Hance 1979) with faster degradation at lower pH values. The soil pH used in these experiments was quite low (pH 5.1 for Serdang soil; 4.8 for Sungai Buloh soil), so it is possible that, in addition to microbial activity, low soil pH contributed to the dissipation of the herbicide. Persistence of atrazine increased with increasing soil pH (Hiltbold and Buchanan 1977).

Temperature and soil moisture content affect the degradation rate of terbuthylazine in non-autoclaved and autoclaved soils. In the non-autoclaved soil of the Sungai Buloh series, the half-life of terbuthylazine decreased with increasing soil moisture levels. Similarly, in non-autoclaved Serdang series soil, the half-life of terbuthylazine was lower at higher soil moisture content. An increase in herbicide degradation at higher soil moisture content is expected since higher moisture levels hinder herbicide adsorption onto soil particles, making the herbicide molecules more readily available for degradation by soil microbes. These results are similar to previous reports showing that moisture and temperature have an influence on the degradation rate of atrazine, one of the triazine group herbicides (Walker and Zimdahl 1981, Singh *et al.* 1990).

In general, the breakdown of the herbicide was slower at 20°C than at 35°C. The direct relationship between soil temperature and herbicide degradation is well established (Ismail and Teoh 1994). Generally, the increased rate of degradation at higher temperatures probably reflects the effects of microbial activity, especially in non-sterilized soils. Therefore, in warm and moist soils such as those found in tropical regions, a faster rate of degradation of the herbicide is expected, when compared with soils in temperate or arid regions.

Repeated application of the herbicide increased the half-life in the non-autoclaved Sungai Buloh and Serdang series soils, except at 35°C, and at soil moisture content of 70% field capacity. The soil microbes might show some adaptation to the herbicide with repeated application at 35ºC and 70% field capacity. Studies of the microbiological characteristics that control enhanced biodegradation are needed to increase our understanding of the complex relationships involved. The second application of the herbicide to the autoclaved Serdang and Sungai Buloh series soils prolonged the half-life of the terbuthylazine.

In conclusion, the results of this study demonstrate that half-life of terbuthylazine in tropical conditions was found to be shorter than that in temperate regions, where it was reported the half-life of terbuthylazine was 5.5 weeks (Bowman 1989). Meanwhile, under arid conditions, the residue of terbuthylazine was still found in the soil 12 months after application (Chivinge and Mpofu 1990). The half-life of atrazine was recorded between 24 to 178 days, depending upon soil type, pH and atrazine rate (Hiltbold and Buchanan 1977). However, direct comparison between the data obtained with other studies are not feasible because of different soil types and climatic conditions. Literature on dissipation of terbuthylazine in tropical soils is scarce (Ismail and Teoh 1994). In the tropics, the application of terbuthylazine at recommended rates is not likely to be detrimental to the subsequent crops or crops planted inter-rows. However, the degree to which the effects obtained in the above greenhouse studies can be extrapolated to field conditions requires further attention, because other factors (soil texture, soil composition, rainfall etc.) could influence the effect of this agrochemical.

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