Enhanced degradation of atrazine in soils with a history of repeated use

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Summary Residual herbicides are the principal means for achieving good weed control in maize crops in New Zealand. The most frequently used herbicides belong to the triazine and chloroacetamide groups. In recent years many maize farmers have noticed a shorter period of effective weed control from these compounds. As New Zealand was the first country to note enhanced degradation of EPTC + antidote some 30 years ago, we investigated if a similar phenomenon exists for atrazine, the most commonly used compound in maize. Its degradation rates were measured in seven soils, six with a long history of atrazine use and one that had never been used for cropping. One half of each soil was sterilised by autoclaving and samples fortified with atrazine were incubated at 10, 20 or 30°C for 1–35 days and analysed afterwards through HPLC. In general, microbial degradation appeared to be the major pathway and the rate of breakdown was highest in the two soils that had a very long history of atrazine use. The degradation in sterilised soils followed 1st order kinetics, however, the decay rate in unsterilised soils was up to five times faster and could not be explained by simple exponential decay.

Keywords Enhanced degradation, atrazine, maize, arable cropping.

INTRODUCTION

Residual herbicides are the principal means for achieving good weed control by arable farmers, in particular maize growers in New Zealand. The most frequently used herbicides in maize are the triazines (atrazine and terbuthylazine) for control of broadleaf weeds and some grasses, and the chloroacetamides (acetochlor, metolachlor and alachlor) for control of grass weeds and some broadleaf weeds. More than 95% of all maize fields in 2008/09 season were treated with one or both of these herbicide groups (A. Pearson, FAR, pers. comm.). In recent years many maize growers have observed a shortened period of effective weed control from these herbicides where they have been used annually. The general symptom is the escape of certain weeds 3–6 weeks after the residual herbicide has been applied. In these situations growers are forced to use a post-emergence herbicide to control the surviving weeds to get them through the critical weed-free period of the crop.

The increasing use of post-emergence herbicides in maize crops in New Zealand indicates the widespread failure of the pre-emergence herbicide to adequately control weeds during the early stages of crop growth. There are several possible reasons for this reduced activity but the three most plausible are: (1) with maize often planted a month earlier than it was 30 years ago, the critical weed-free period is longer due to crop's slower initial growth and the pre-emergence herbicide fails to persist for the extended time, (2) the weed spectrum is changing towards more difficult to control weeds, especially grass weeds, and (3) pre-emergence herbicides do not persist for long periods in soils with a long history of maize production.

Based on our past knowledge and experience, it was postulated that the most likely cause of this reduced residual activity in fields with a long history of herbicide use is enhanced microbial degradation of the herbicide in soil. This has previously occurred in New Zealand in the 1980s with EPTC + antidote (Rahman and James 1983), and accelerated degradation of atrazine has been reported in France and Canada (Krutz *et al.* 2007).

The aim of this study was to positively identify whether enhanced microbial degradation is causing the reduced efficacy of the herbicide atrazine in some maize fields. If confirmed, this would then necessitate the industry to develop alternative strategies to overcome the problem.

MATERIALS AND METHODS

This study was carried out in the laboratory with seven soils, six of which had a long history of atrazine use while the seventh had never been exposed to the herbicide (HSL1, control soil). The soils are listed in Table 1. HSL1 is a Horotiu silt loam soil from Waikato with no previous exposure to any herbicides, while HSL2 is a similar soil that has been treated with atrazine annually for about 20 years (both soils about 6.5% organic carbon (OC)). SL is sandy loam from Manawatu (2.7% OC), OtSL is Otorohanga silt loam from south Waikato (4.5% OC), KSL is Kaiti silt loam from Poverty Bay (2.5% OC), OhSL is Ohinepanea silt loam from Bay of Plenty (3.0% OC) and WSL is Waihou silt loam from Waikato (5.6% OC); all these

soils have been exposed to annual applications of atrazine for many years.

Degradation rates were determined with an atrazine concentration in soil equivalent to a field application of twice the recommended rate incorporated to a depth of 100 mm. This high rate was used as the worst case scenario that could arise when spray overlap occurs during applications in the field. The studies were carried out at 10°C, 20°C and 30°C in the dark at 80% water holding capacity (WHC) with both sterilised and unsterilised soils. Soils were sterilised by autoclaving three times with soil mixing between each one.

The soil moisture contents were determined gravimetrically by drying duplicate samples (10 g) at 105°C for 24 h. The soil was then weighed into 250 mL Erlenmeyer flasks (50 g dry wt equivalent) and brought to 2 g below the 80% WHC weight by adding deionised water. The flasks were fortified by adding the required amount of atrazine in 2 mL of water and shaken by hand to mix the herbicide and soil. Four additional aliquots of 2 mL were placed directly into small glass vials, sealed and frozen, to be used as controls. The atrazine solution was made up from the formulated product Gesaprim (500 g kg^{-1} atrazine) to better match the field situation. The flasks were loosely sealed with aluminium foil and placed in the respective temperature regimes. They were weighed at weekly intervals and water was added as required to maintain the moisture content to 80% WHC. Four flasks were frozen immediately after shaking (Day 0) and two were removed from each temperature regime and frozen after 1, 3, 7, 10, 14, 21, 28 and 35 days had elapsed. All flasks remained frozen at −20°C until required for analysis.

The extraction method was a slight modification of James *et al.* (1994). After the flasks containing atrazine were defrosted, deionised water was added to bring the weight of water in the flask (including soil water) to 30 g and 70 mL of methanol was added. The flasks were sealed and shaken on an orbital shaker at 50°C for 3 h and then allowed to settle overnight at ambient temperature (20°C). After settling, a 10 mL aliquot of supernatant liquid was drawn off. The aliquot was placed in a Schott bottle and 90 mL deionised water added. This was aspirated under vacuum through Extract-Clean™ solid phase extraction columns containing 0.5 g of C18 silica based sorbent material. The sorbed material was eluted twice with 2 mL of methanol and the combined eluent evaporated to dryness under a gentle stream of nitrogen at 30°C. The residue was re-dissolved in 0.5 mL of methanol and 0.5 mL of water added. The resolubilised extract was filtered through an Anatop 10™, 0.2 µm PTFE syringe filter in preparation for quantification by high performance liquid chromatography (HPLC).

All analyses were run on a Shimadzu™ HPLC system. The analyses were run isocratically using a C-18, reverse-phase, 5 µm, 100 Å, 150 × 4.6 mm, ODS3 column (Prodigy®, Phenomenex®), a mobile phase flow rate of 1 mL min^{-1} and a column temperature of 35°C. Sample injection volume was 20 µL. Quantification was by integration of peak areas. Calibration curves were made using a dilution series (0.05 to 50 ppm) of atrazine prepared in methanol/water (50/50, v/v). Confirmation was by visual inspection of the peak and base line and by using external standards (1.0 and 10.0 mg L^{-1}) that were run after every 6–8 samples.

RESULTS

The degradation of atrazine in the control soil at three temperatures is illustrated in Figure 1. Degradation was slowest at 10°C and fastest at 30°C with 20°C being intermediate. Also, degradation was faster at all three temperatures in the unsterilised soil, illustrating that microbial degradation contributed to the overall degradation but was the smaller component. In all cases, however, the degradation appeared to follow first order kinetics with the decay curves becoming straight lines when plotted semi-logarithmically.

Degradation of atrazine in the six soils with a long history of atrazine use was much faster than in the control soil (Figure 2). This was most likely to be due to microbial decomposition of atrazine since autoclaved soils with a history of atrazine application showed the

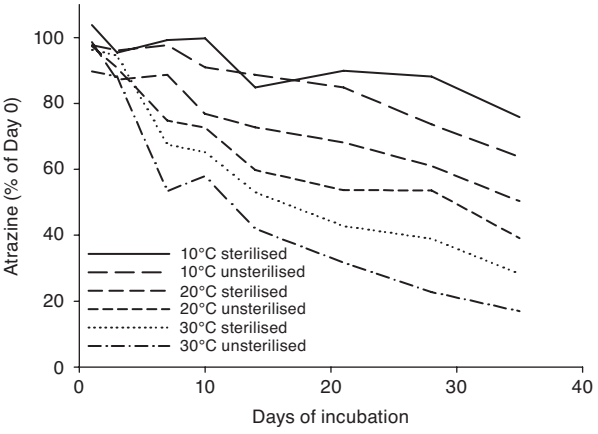

Figure 1. Degradation of atrazine at 10, 20 and 30°C in both sterilised and unsterilised soil with no previous history of atrazine use (HSL1).

same rate of degradation as the control soil (Figure 3). Also, degradation in these soils did not follow simple first order kinetics.

One of the best measures to compare degradation rates in different soils is the time taken for the applied herbicides to dissipate to 50% of that applied concentration (DT_{50}). These data are presented in Table 1 and show that in the control soil the DT_{50} values for sterilised soils were only up to 1.5 times longer than those for the unsterilised soils, whereas in the other six soils the DT_{50} values between sterilised and unsterilised differed by factors from 2.5–7 times faster.

Thus it was clearly demonstrated that atrazine was more rapidly degraded (enhanced degradation) in soils with a long history of herbicide use and that half of the applied atrazine dissipated in as little as 5 days at 20°C.

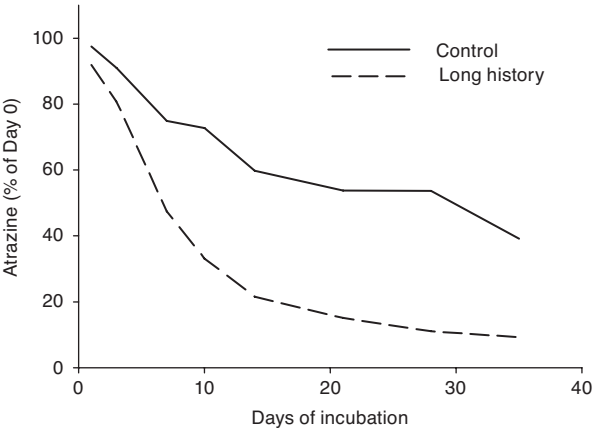

Figure 2. Degradation of atrazine at 20°C in long term herbicide use soils (average of all six soils) and the control soil (HSL1) with no previous history of atrazine use. All soils were **unsterilised**.

DISCUSSION

The degradation rates of herbicides in soils are usually dictated by the chemical's stability to microbial and chemical degradation. Herbicides belonging to the triazine sub-group (e.g. atrazine) are more soluble at low pH levels and become prone to greater chemical degradation through hydrolysis. This would normally be the case with most New Zealand soils where pH levels are below pH 7. Also research in New Zealand and overseas has established that in soils with high organic carbon content (generally >6%), the primary factor controlling degradation of most herbicides is microbial activity. All the soils in this study have low organic carbon contents leaving pH as the principal determinant of degradation rate.

However, after several years of atrazine applications the degradation profile appears

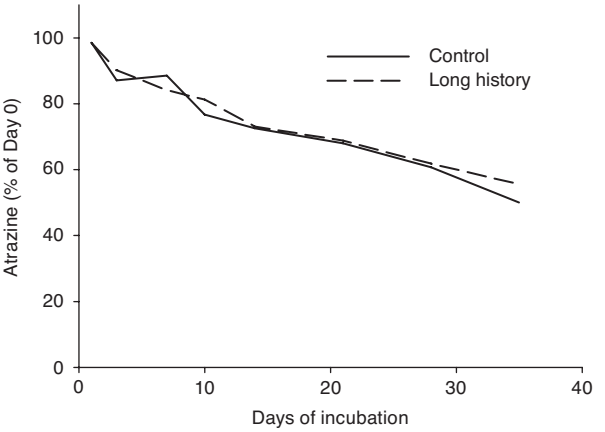

Figure 3. Degradation of atrazine at 20°C in long term herbicide use soils (average of all six soils) and the control soil (HSL1) with no previous history of atrazine use. All soils were **sterilised.**

Table 1. DT_{50} values (d) for atrazine in each of the seven test soils at three temperatures for both unsterilised and sterilised soil samples.

	10°C		20°C		30°C	
Soil	Unsterilised	Sterilised	Unsterilised	Sterilised	Unsterilised	Sterilised
HSL1	50[1]	80	30	35	11	15
HSL2	18	50	5	37	3	22
SL	27	65	10	41	7	25
OtSL	16	80	6	50	4	23
KSL	18	55	7	37	4	19
OhLS	55	55	13	31	10	17
WSL	18	50	5	37	3	23

[1] DT_{50} values longer than 35 days are based on extrapolated data and are estimates only.

to have changed considerably and the best explanation could be that of enhanced microbial degradation (Krutz *et al.* 2007). These researchers have also noted a trend that soils with a long history of using particular herbicides also have the ability to break down related herbicides more rapidly (Krutz *et al.* 2008). This is supported by previous experience in New Zealand with maize growers in the 1980s where repeated applications of the herbicide EPTC over a 5-year period led to its enhanced degradation and failure to control weeds effectively (Lee e*t al.* 1984).

Typically in New Zealand maize is repeatedly cropped in the same fields without other rotational crops. This means that the same (or related) herbicides are also used repeatedly without a break, year after year. This repeated use of herbicides has led to problems on another front, where certain weeds have become resistant to and are not controlled by some herbicides any longer (Rahman *et al.* 2001). Further, Rahman *et al.* (1983) have also shown that in the case of atrazine-resistant fathen (*Chenopodium album*), this biotype was also cross resistant to all the other triazine herbicides. It appears from the work of Krutz *et al.* (2008) that the phenomenon of enhanced degradation is also likely to apply to other products within the same chemical family. For New Zealand, this may mean that the other pre-emergence herbicides commonly used to control broadleaf weeds in maize, terbuthylazine and metribuzin, are also likely to suffer the same fate in the soil.

Another concern is the apparent widespread nature of the enhanced degradation identified in this study. The soils tested here from Waikato, Bay of Plenty, Poverty Bay and Manawatu represent all the major maize growing areas of New Zealand. Soil samples were collected from targeted fields, i.e. those fields where maize had been cropped continuously for a long period and also where there were reports of less than optimal weed control. As all the targeted fields tested positive to enhanced degradation and it is not difficult to conclude that there may be many other fields that are similarly affected. Unfortunately there appears to be no easy remedy for these fields as past experience with EPTC + antidote showed that even after 'resting' a field for several years, EPTC + antidote could only be used for a year or two before its activity declined.

In addition to EPTC + antidote, enhanced degradation in a Horotiu silt loam soil of the sulfonylurea herbicide nicosulfuron has also been reported from laboratory studies (James 2008). This suggests that other herbicide groups might also be at risk. In New Zealand the chloroacetamides dominate the maize market and if this group were to suffer the same fate as atrazine it would prove catastrophic for the maize industry. With this in mind we are now investigating potential soils for enhanced degradation of the chloroacetamide herbicides as well as looking for post-emergence options where pre-emergence herbicides are suffering from loss of efficacy due to enhanced degradation.

ACKNOWLEDGMENTS

Financial support for this study was provided by MAF Sustainable Farming Fund and Foundation for Arable Research.

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