Atrazine Dissipation in Triazine-Adapted and Non-Adapted Soil from Colorado and Mississippi: Implications of Enhanced Degradation on Atrazine Fate and Transport Parameters

L.J. Krutz[1], D.L. Shaner[2], C. Accinelli[3], R.M. Zablotowicz[1], and W.B. Henry[4]

[1] USDA-ARS-SWSRU, Stoneville, MS 38776; [2]USDA-ARS-WMRU, Fort Collins, CO 80526; [3]Dept. of Agro-Environmental Science and Technology, University of Bologna, Bologna, Italy 40127; [4]USDA-ARS-CPHRU, Mississippi State, MS 39762

Introduction

Enhanced degradation is the phenomenon whereby a soil-applied pesticide is rapidly degraded by a population of microorganisms that has developed the ability to use the compound as a carbon, energy, and (or) nutrient source. Soil bacteria have recently developed novel metabolic abilities resulting in enhanced atrazine degradation (Figure 1).

Fate and transport models typically contain sub-models that describe pesticide persistence as a function of temperature and moisture. Analysis conducted on these models indicate that pesticide persistence in a sensitive input parameter. Consequently, if atrazine persistence is drastically altered in adapted soils, then models that continue to rely on historic atrazine dissipation pathways and persistence estimates may not accurately describe the compounds fate and transport in the environment.

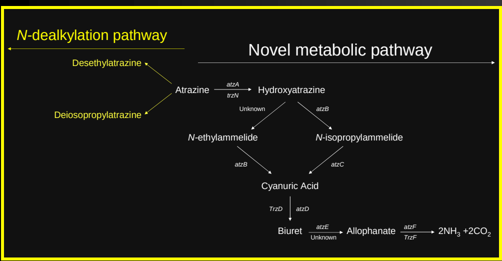

Figure 1. Initial steps in the historic *N*-dealkylation pathway and the complete metabolic pathway likely responsible for enhanced atrazine degradation. Abbreviations denote genes coding for the following enzymes: *atzA*, atrazine chlorohydrolase; *trzN*, triazine hydrolase; *atzB*, hydroxyatrazine ethylaminohydrolase; *atzC*, *N*-isopropylammelide isopropylaminohydrolase; *trzD*, cyanuric acid amidohydrolase; *atzD*, cyanuric acid hydrolase; *atzE*, biuret hydrolase; *atzF*, allophanate hydrolase, and *trzF*, allophanate hydrolase.

Objectives

The objectives of this study were:
1) Screen Colorado (CO) and Mississippi (MS) adapted and non-adapted soil for *atzA*, *atzB*, *atzC*, (i.e. *atzABC*) and *trzN* genes;
2) Determine atrazine persistence in CO and MS adapted and non-adapted soil as a function of temperature (10 and 20 °C) and moisture [40 and 70% field capacity (FC)];
3) Compare Q_{10} and β between adapted and non-adapted soils;
4) Contrast the formation and persistence of deiosopropylatrazine (DIA), desethylatrazine (DEA), and hydroxyatrazine (HA) between adapted and non-adapted soils;
5) Evaluate the mineralization potential of ring-labeled ^{14}C-atrazine in adapted and non-adapted soil as a function of temperature and moisture.

Materials and Methods

Classification of atrazine adapted and non-adapted soil was based on the method of Shaner et al. 2007. Evaluated soil properties are presented in Table 1. The biological and herbicide fate methods have previously been reported (Krutz et al. 2008; Zablotowicz et al. 2007).

Results

Table 1. Soil texture, organic matter (OM), and water holding capacity of adapted and non-adapted soils from Colorado and Mississippi.

State	Soil	Sand	Silt	Clay	OM	-33 kPa
		----------------g kg^{-1}----------------				g g^{-1}
Colorado	Adapted	555	255	200	6	18.5
	Non-adapted	830	130	50	6	8.0
Mississippi	Adapted	300	480	230	16	23.9
	Non-adapted	280	550	180	20	24.8

Table 2. Degradation rate constant (k) and half-life values for atrazine in Colorado (CO) and Mississippi (MS) adapted and non-adapted soil as a function of incubation temperature and moisture.

Soil	Temperature	Moisture	k	Half-life	r^2
	---C---	--% FC--	--d^{-1}--	--d--	
MS adapted					
	10	40	0.0753	9	0.97
	10	70	0.2236	3	0.99
	20	40	0.2410	3	0.99
	20	70	0.6686	1	0.99
CO adapted					
	10	40	0.0581	12	0.95
	10	70	0.0651	11	0.94
	20	40	0.1950	4	0.97
	20	70	0.1854	4	0.96
MS non-adapted					
	10	40	0.0065	107	0.93
	10	70	0.0056	124	0.90
	20	40	0.0329	21	0.95
	20	70	0.0220	32	0.99
CO non-adapted					
	10	40	0.0037	187	0.57
	10	70	0.0107	69	0.77
	20	40	0.0116	60	0.90
	20	70	0.0193	36	0.93

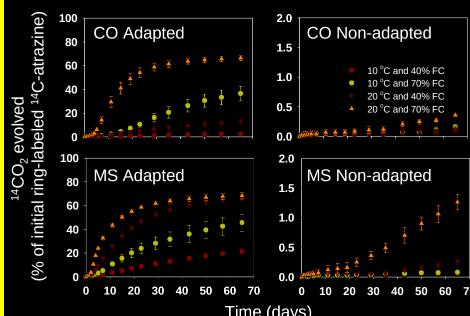

Figure 5. Cumulative $^{14}CO_2$ evolved reported as percent of total ring-labeled ^{14}C-atrazine applied to Colorado (CO) and Mississippi (MS) adapted and non-adapted soil as a function of incubation temperature (10 or 20 °C), soil moisture [40 or 70% field capacity (FC)], and time. $LSD_{0.05}$(Temperature*moisture*soil*time) = 2.7120.

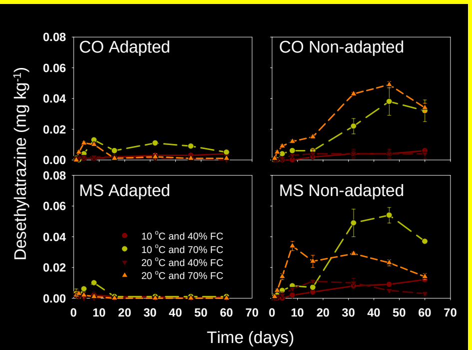

Figure 2. Desethylatrazine (DEA) concentrations in Colorado (CO) and Mississippi adapted and non-adapted soil as a function of incubation temperature (10 or 20 °C), soil moisture [40 or 70% field capacity (FC)], and time. $LSD_{0.05}$(Temperature*moisture*soil*time) = 0.003.

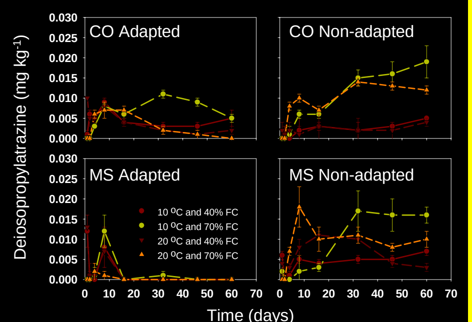

Figure 3. Deiosopropylatrazine (DIA) concentrations in Colorado (CO) and Mississippi (MS) adapted and non-adapted soil as a function of incubation temperature (10 or 20 °C), soil moisture [40 or 70% field capacity (FC)], and time. $LSD_{0.05}$(Temperature*moisture*soil*time) = 0.006.

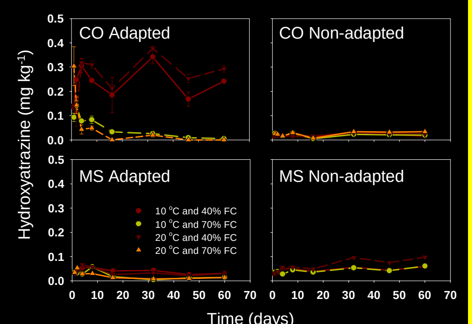

Figure 4. Hydroxyatrazine (HA) concentrations in Colorado (CO) and Mississippi (MS) adapted and non-adapted soil as a function of incubation temperature (10 or 20 °C), soil moisture [40 or 70% field capacity (FC)], and time. $LSD_{0.05}$(Temperature*moisture*soil*time) = 0.021.

Conclusions

GENE PROBING. The *atzABC* and (or) *trzN* were detected only in adapted soils. Thus, enhanced degradation likely arises from the procurement and (or) development of these genes by soil bacteria. Moreover, *atzABC* and (or) *trzN* are likely widespread throughout the Western and Southern United States.

PERSISTENCE ESTIMATES. Pooled over temperature and moisture, atrazine persistence in adapted soil (Table 2) was 13-fold lower than that of the non-adapted soil, 10-fold lower than Wauchope et. al. (1992) estimate (60 d), and 18-fold lower than USEPA (2003) estimate (103 d). Thus, separate estimates for atrazine persistence are likely needed for adapted and non-adapted soils.

Q_{10} EFFECTS. FOCUS has concluded that 1) Q_{10} does not vary significantly among pesticides; 2) the mean Q_{10} for 148 observations is 2.20; and 3) the ninety- and ninety-five percentile values for Q_{10} are 2.8 and 3.1, respectively (FOCUS 1997). Thus, the Q_{10} values for atrazine in non-adapted soil (1.9) is within the ninety percentile, but the Q_{10} estimate for adapted soil (2.9) is between the ninety and ninety-five percentile. Consequently, separate estimates are likely needed for adapted and non-adapted soils.

MOISTURE EFFECTS. A definitive trend with regards to the effect of moisture on atrazine dissipation was not obtained. Thus, we concur with FOCUS in that an average *beta* of +0.8 be used to adjust for moisture effects (FOCUS 1997).

***N*-DEALKYLATED METABOLITES**. *N*-dealkylated metabolites were generally lower in adapted than non-adapted soil (Figure 2,3). This likely arises from 1) *atzABC* and (or) *trzN* circumventing the n-dealkylation pathway; 2) DEA and DIA are substrates for *atzA* and *trzN* (Seffernick et al. 2000; Shapir et al. 2005). This observation is significant since USEPA includes the concentrations of all dealkylated metabolites of atrazine in the herbicide's risk assessment.

HYDROXYATRAZINE. Under the historic atrazine dissipation pathway, HA concentrations in aerobic soils rarely, if ever, exceeded 10% of the parent compounds initial concentration. Consequently, USEPA has not considered HA as a major degradate (USEPA 2003). However, HA is the obligatory metabolite for the enhanced degradation pathway (Figure 1). Thus, in light of HA concentrations in CO adapted soil exceeding 30% of the initial atrazine concentration at sub-optimal moisture levels (Figure 4), HA needs to be reclassified as a major degradate in soils positive for *atzA* and (or) *trzN*.

MINERALIZATION. Cumulative $^{14}CO_2$ evolution was greater in adapted than non-adapted soil, particularly under optimal temperature and moisture levels (Figure 5). Thus, total triazine residues are lower in adapted than non-adapted soil.

MODEL IMPLICATIONS. In adapted soils that are positive for *atzABC* and (or) *trzN*, models that assume historic atrazine degradation pathways and persistence estimates will likely over predict the compounds transport and risk to the environment.

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