

ABSTRACT

DYNAMICS OF THE DEGRADATION OF SELECTED S-TRIAZINE HERBICIDES IN TROPICAL ECOSYSTEMS

Kerrie-Ann Marie Bartley-Hynes

The degradation and soil sorption characteristics for four herbicides of the triazine family were assessed by performing laboratory based experiments that simulated conditions existing in Jamaica and by extension the wider Caribbean. The herbicides investigated were atrazine, propazine, prometon and prometryn. The potential for atrazine runoff from sugarcane fields to contaminate the nearby Rio Minho river in Clarendon Jamaica was also assessed.

Degradation of the above mentioned pesticides were carried out in acidic, neutral and basic aqueous media at a constant ionic strength and at varied temperatures (35.5°C, 45.5°C and 55.5°C). Rate constants (k) were calculated from the first order rate equation, $C_t = C_0 e^{-kt}$ where C_t is the herbicide concentration at time t and C_0 is the initial herbicide concentration. The rates of degradation varied with the change in pH values. The pseudo first order rate constant, k_{obs} increased with increase in acidity (pH 2.2-5.4); remained constant close to neutral pH and then increased again with increase in pH (8.0-11.54). Hydrolysis of atrazine and propazine was generally faster than that for prometon and prometryn with k_{obs} for propazine > atrazine > prometryn > prometon at all

studied temperatures with $t_{1/2}$ values at pH 2.2 being 1.08, 1.43, 3.28 and 25.7 days respectively at 35.5°C. Hydrolysis was also faster in the acidic region as opposed to the basic region. Under neutral conditions degradation rates of the pesticides were extremely slow (half-life estimated to be > 6 months). The half-lives for atrazine, propazine, prometon and prometryn were 462, 330, 433 and 307 days respectively at 35.5°C and pH 7.0. The k_{obs} values at the three different temperatures were used to calculate second order rate constants using our derived rate equation:

$$k_{obs} = \frac{k_1[H^+] + k_2K_1 + k_3K_1(k_w/[H^+])}{(K_1 + [H^+])}, \text{ where } k_1, k_2 \text{ and } k_3 \text{ are the second order}$$

rate constants with respect to the acid, base and spontaneous hydrolyses and K_1 the acid dissociation constant for the pesticides. The second order rate constants obtained were then used to determine the activation parameters, ΔH^\ddagger and ΔS^\ddagger . Activation enthalpies (ΔH^\ddagger) derived were of the order: prometryn (9 kJmol⁻¹) < propazine (43 kJmol⁻¹) < atrazine (64 kJmol⁻¹) < prometon (92 kJmol⁻¹) for the acid catalysed hydrolysis, prometryn (32 kJmol⁻¹) < propazine (60 kJmol⁻¹) < prometon (73 kJmol⁻¹) < atrazine (123 kJmol⁻¹) for base catalysed hydrolysis and prometryn (61 kJmol⁻¹) < prometon (92 kJmol⁻¹) < propazine (108 kJmol⁻¹) < atrazine (123 kJmol⁻¹) for spontaneous hydrolysis.

Entropies of activation (ΔS^\ddagger) values were of the order propazine (-217 JK⁻¹mol⁻¹) < prometryn (-207 JK⁻¹mol⁻¹) < atrazine (-185 JK⁻¹mol⁻¹) < prometon (-176 JK⁻¹mol⁻¹) for acid catalysed hydrolysis; prometryn (-223 JK⁻¹mol⁻¹) < prometon (-186 JK⁻¹mol⁻¹) < propazine (-188 JK⁻¹mol⁻¹) < atrazine (-163 JK⁻¹mol⁻¹) for base

hydrolysis and prometryn ($-195 \text{ JK}^{-1}\text{mol}^{-1}$) < prometon ($-184 \text{ JK}^{-1}\text{mol}^{-1}$) < propazine ($-176 \text{ JK}^{-1}\text{mol}^{-1}$) < atrazine ($-171 \text{ JK}^{-1}\text{mol}^{-1}$) for spontaneous hydrolysis. The mechanism of hydrolysis in the studied aqueous media seemed to be similar for all the herbicides as an isokinetic relationship was established between the pesticides at acidic, basic and neutral regions. Small concentrations of copper ($\sim 5 \times 10^{-6} \text{ M}$) in solution was found to enhance hydrolysis of the s-triazines studied with $t_{1/2}$ ranging from 32 days ($5 \mu\text{g mL}^{-1} \text{ Cu}^{2+}$) to 18.9 days ($100 \mu\text{g mL}^{-1} \text{ Cu}^{2+}$) for atrazine and 47 days ($5 \mu\text{g mL}^{-1} \text{ Cu}^{2+}$) to 11.5 days ($100 \mu\text{g mL}^{-1} \text{ Cu}^{2+}$) for propazine. Prometon degraded slowly even with 5 ppm Cu^{2+} ($t_{1/2} = 161$ days) compared to atrazine and propazine but at $100 \mu\text{g mL}^{-1} \text{ Cu}^{2+}$ $t_{1/2}$ was 25.5 days. Prometryn also followed the same trend with $t_{1/2} = 100$ days in the presence of 5 ppm Cu^{2+} and 27 days for $100 \mu\text{g mL}^{-1} \text{ Cu}^{2+}$.

Photolysis also followed first order kinetics. Under natural sunlight conditions photolysis was generally slow. The half-lives for the photodegradation of the herbicide dissolved in toluene ranged from 9.7, 7, 21 and 13 days for atrazine, propazine, prometon and prometryn respectively for experiments conducted in December. During the summer months (July-August) however, degradation was faster with $t_{1/2}$ ranging from 1, 3, 6.7 and 4 days for atrazine, propazine, prometon and prometryn respectively. The effect of sunlight on the degradation of the herbicides from soil surface seemed to be significant when compared to photolysis in the toluene medium exposed to sunlight. Half-lives for the degradation from soil surface ranged from 92 hrs for atrazine, 93 hrs for propazine, 159 hrs for prometon and 248 hrs for prometryn. Under high intensity

UV radiation (from a 125 W Hg lamp) degradation was much faster than in sunlight and was fastest in aqueous buffer solutions compared to hexane solutions exposed to UV radiation. The photodegradation rates of the herbicides decreased in the following order for the hexane solutions with $t_{1/2}$ being: prometon (3466 s) < propazine (1575 s) < atrazine (332 s) < prometryn (196 s). In aqueous buffer, photolysis was much faster as half-life was 62, 71, 950 and 127 s for atrazine, propazine, prometon and prometryn respectively at pH 4.5.

Volatilisation was extremely slow for all studied s-triazines with 0.023%, 0.065%, 0.021% and 0.011% being volatilised after 206 days for atrazine, propazine, prometon and prometryn respectively.

The extent of mobility of the herbicides in soil using controlled continuous flow (leaching) and batch equilibrium experiments to predict pesticide leaching potential in the field was assessed in laboratory experiments. Varying soil types, sandy loam, clay loam and sand were investigated and moisture content at equilibrium and field capacity assessed. The observed potentials for leaching from continuous flow experiment showed propazine having the least propensity for contaminating ground water. The order of leaching for these compounds was propazine < prometon < atrazine < prometryn for the different soil types. Leaching seemed to be dependent on soil type with greater adsorption occurring generally on the clay loam soil. Moisture content seemed to be a significant factor in the retention of these herbicides on soil. Leaching potentials were assessed using GUS (groundwater ubiquity score) and leaching potential index. Based on the GUS and LI model for leaching potential assessment prometon posed the

greatest threat to groundwater. Batch equilibrium studies showed adsorption isotherms to be linear ($r^2 > 0.9$) and $1/n$ values close to unity. The order of K_f (Freundlich constant) was generally the same for all soil types:

HPRD prometon > propazine > atrazine > prometryn

MHILL prometon > propazine > atrazine > prometryn

GTWN propazine > prometon > atrazine > prometryn

BLOD prometon > propazine > atrazine > prometryn

The presence of the microorganism *Phanerochaete chrysosporium* had a significant effect on the degradation of atrazine with 75 % of the herbicide being degraded after 23 days.

In field studies we were able to detect atrazine concentrations ranging from 0.54 - 46 μgL^{-1} in runoff water and 3.5 - 1339 μgKg^{-1} in sediments at the 0 - 10 cm depth collected from plots through which runoff water flowed.