

ABSTRACT

CHEMODYNAMICS OF SELECTED PESTICIDES UNDER TROPICAL CONDITIONS.

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Laboratory experiments were carried out to assess the degradation and soil sorption characteristics of six pesticides either currently in use in the Caribbean or with the potential for future use. The conditions of the experiments were designed to simulate as closely as possible those of tropical ecosystems. The pesticides investigated were the herbicides dacthal, metolachlor and bromacil, the insecticides dimethoate and disulfoton and the fungicide imazalil. Studies included measurements of the:

- i. Rates of hydrolysis in aqueous buffers of varying pH and temperature, and constant ionic strength.
- ii. Effect of copper ions on hydrolysis rates.
- iii. Rates of photolysis in hexane and aqueous buffer solutions of varying pH and constant ionic strength, by irradiation emitted from a 125W mercury lamp (medium pressure).
- iv. Rates of photolysis of imazalil in toluene and on two yam varieties, exposed to natural sunlight.

- v. Rates of volatilization from treated glass surfaces using the solvent trap or flux chamber technique.
- vi. Sorption coefficients redistribution patterns in different Jamaican soils at equilibrium moisture and field capacity conditions.

GC-ECD was used to follow the photochemical degradation and volatilization rates in situ for the experiments carried out in organic solvents. In all other matrices, the degradation was followed after initial liquid/liquid extraction. On the basis of dissipation data, half-lives ($t_{1/2}$) were calculated using regression analysis and the rate constant (k_{obs}) calculated from the first order rate equation $C_t = C_0 e^{-kt}$ where C_t is the concentration of the pesticide at time t , C_0 represents the initial concentration and k is the rate constant.

Hydrolytic degradation rates of dimethoate disulfoton and dacthal at 35°C increased with increasing pH, with relative rates in the sequence dimethoate > disulfoton > dacthal and $t_{1/2}$ values at pH 9.85 of 0.03, 7.2, and 36 days respectively for a first order model. Bromacil, metolachlor and imazalil were very resistant to hydrolysis with less than 10 % degrading after a period in excess of 60 days. The observed rate constants were calculated from their dissipation with time, using the equation $k_{obs} = \ln(C_1/C_2)/\Delta t$ where Δt is the time interval ($t_1 - t_2$) and C_1 and C_2 are the concentrations of the pesticides at times t_1 and t_2 respectively. Calculated $t_{1/2}$ values at pH 9.85 were imazalil 1949, bromacil 5377 and metolachlor 378 days respectively. Combining the data from the hydrolysis

from at least three different temperatures and pH, thermodynamic parameters were calculated. Activation enthalpies for base and spontaneous hydrolyses were of the order dimethoate $44 < \text{dacthal } 96 < \text{disulfoton } 171 \text{ kJ mol}^{-1}$ for base catalysed hydrolysis, and disulfoton $15 < \text{dacthal } 74 < \text{dimethoate } 91 \text{ kJ mol}^{-1}$ for spontaneous hydrolysis. Entropy of activation values were of the order dimethoate $113 < \text{disulfoton } 254 < \text{dacthal } -1 \text{ JK}^{-1}\text{mol}^{-1}$ for base catalysed hydrolysis, and disulfoton $-72 > \text{dimethoate } -73 > \text{dacthal } -124 \text{ JK}^{-1}\text{mol}^{-1}$ for spontaneous hydrolysis. Bromacil metolachlor and imazalil were resistant to hydrolysis over the experimental range of temperature and pH. No catalytic or inhibitory effect was observed for the copper catalysed hydrolysis of dimethoate, disulfoton, dacthal and metolachlor; however, the increase in rates for both imazalil and bromacil suggests some catalytic activity.

Photolytic degradation followed a first order kinetic model, with correlation coefficients generally greater than 0.950. Photolysis from direct sunlight exposure was significantly slower than photolysis with the mercury lamp. Photolytic $t_{1/2}$ values for direct exposure to mercury lamp were of the order of seconds compared to days with direct sunlight exposure. Photolysis rates were faster in hexane than in aqueous buffers. $t_{1/2}$ values in hexane ranged from a low of 40s for metolachlor, to 77s for disulfoton whereas the corresponding values in aqueous buffer were in the range, 45s for disulfoton, to 2189s for dimethoate at pH 7. $t_{1/2}$ from direct sunlight exposure ranged from 0.2 days (metolachlor), to 55.4 days for bromacil. Photolytic degradation rates for imazalil on two yam

varieties (*Dioscorea cayenensis* and *Dioscorea rotundata*) exposed to natural sunlight were very similar.

Volatilization rates for the pesticides on glass surfaces (temp 35°C, airflow rate of approximately 120 cm³ min⁻¹) were very low. Kinetic data provided first order plots of ln pesticide volatilised vs. time with t_{1/2} values in the range 482 ± 100 days for metolachlor to 26660 ± 4101 days for dacthal. Kinetic data also provided first order plots of ln F vs. t (F is the volatilization flux expressed as μg cm⁻² day⁻¹ and t the time in days), and fitted other models including ln F^{1/2} vs. t and log F vs. log t. models. The observed order of relative volatility based on the average rates over the duration of the experiment, was metolachlor > bromacil > imazalil > dimethoate > dacthal > disulfoton.

Mobility of the pesticides in soil was assessed in the laboratory using both continuous flow (column leaching) and batch equilibrium techniques to predict pesticide leaching potential and redistribution patterns in the field. Three different soil types – sandy loam, clay loam and sand were investigated at extreme conditions of moisture (equilibrium moisture and field capacity). Relative leaching potentials were determined using various models and the observed order showed some degree of variation with the model used, with dimethoate and metolachlor showing the highest propensity for ground water contamination. Generally, differences in the redistribution patterns at field capacity and equilibrium moisture were minimal.

Adsorption isotherms determined from batch equilibrium studies fitted the empirical Freundlich equation with correlation coefficients (r^2) generally greater than 0.9000. The Freundlich constant (K_f) indicated a soil sorption order;

clay loam > sandy loam > sand

Sorption intensities ($1/n$) were very close to unity for the pesticides on the clay loam soil.