INFLUENCE OF CLAY MINERALS ON DESORPTION
OF SIMAZINE FROM SOILS

R. I. Farcasanu, T. Yamaguchi, and T. Fukushima
Hiroshima University, Faculty of Engineering

Introduction

The persistence of simazine and other s-triazine herbicides in the environment is considered second only to organochlorine pesticides, such as DDT. Evidence of s-triazines persistency is found in wide occurrence in both surface and groundwater. Because of its persistency in the environment and potential health effects, a maximum contaminant level for simazine at 0.004 mg/L has been established for drinking water. The organic matter content is known to be the main factor controlling the sorption but if the time of pesticide residence in the soil increases, the clay minerals may become more important in the adsorption/desorption processes. In the present work, the long-term desorption kinetics of simazine in various soil/water systems was investigated.

Mathematics

Based on mass balance equation the amount of simazine adsorbed/desorbed and degraded was computed. A linear transformation of the first-order reaction was used to described the measured data.

$$Log(C/C_0) = k(t-t_0) \qquad [1]$$

where C is the amount of simazine (mg) at time t (days) and C_0 is the amount of simazine at time t_0.

Materials and Method

Duplicate samples of 5 g soil (Decomposed Granite; 0.212-0.425 mm, 0.075-0.150 mm grain size fractions and Hiroshima type loam; <1.0 mm), were equilibrated for 36 hours with 5 or 10 mL simazine solutions of various concentration (1, 2, and 2.5 mg/L). The loam soil texture is 68.5% sand, 23.6% silt, and 4.9% clay (represented by kaolinite). Therefore, for checking the influence of clay minerals in the desorption process, we carried out similar additional experiments with the sterilized 0.212-0.425 mm fraction of DG where 4% of pure kaolinite were added. After equilibration two patterns were followed. In pattern I the soil/solution mixture kept together were incubated at 25°C, and in pattern II the supernatant was extracted after equilibration and the liquid phase and the solid phase (moist soil) were separated incubated in similar conditions at 25°C. For each sample, at various times, the supernatant was centrifuged, filtered, and the simazine concentration in liquid phase measured by HPLC. In the desorption experiments, the supernatant was replaced with fresh 0.005 M CaSO₄ solution (simazine free) and the samples were equilibrated again for 36 hours, centrifuged, filtered, and subjected to

HPLC. The simazine that remained in the soil after the desorption process was extracted with methanol using a soxhlet extraction method. Autoclavation and Co^{60} irradiation were used for soil sterilization.

Results and Discussion

Similar with the results reported by other researchers there were very slight differences between the amounts of simazine measured under sterile and non-sterile conditions. Therefore, we assume that the decrease in the amounts of simazine in the systems were due to chemical degradation. Almost no variation in time of simazine concentration was observed in the cases of both grain size fractions of DG for all initial concentrations. Also, the amount desorbed from the DG fractions did not change in time (Fig. 1).
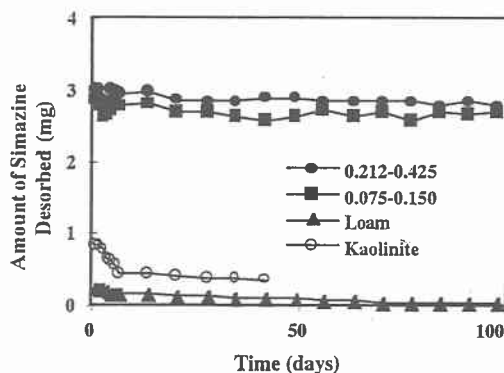

Fig. 1 Pattern I soil/solution mixture incubated together at 25°C for various time. Desorption of simazine (2 mg L⁻¹ initial concentration) from soil and soil size fractions (0.212-0.425 mm and 0.075-0.150 mm are the decomposed granite fractions, Loam is loam soil <1.0 mm and Kaolinite is the DG 0.212-0.425 mm fraction where 4% of kaolinite were added).

A fast decrease of the amounts of simazine desorbed from the loam soil was observed in the first week followed by a continuos slower decrease (Fig. 1). Higher amounts of simazine were desorbed from the loam soil in Pattern I for the 2/1 solution/soil ratio and lower amounts of simazine were desorbed from the loam soil in Pattern II for the 1/1 solution/soil ration. Generally, both for Pattern I and II and for all solution/soil ratio (2/1, 1/1, and 0.4/1) a similar trend was observed. The desorption behavior of simazine from the

DG 0.212-0.425 mm fraction with 4% of kaolinite was similar with desorption of simazine from the loam soil, a faster desorption during the first week was followed by a slower desorption after this period of time. However, a plot of the amounts desorbed from the soils given as percentage of the amount of simazine in soil at the desorption time shows a very different behavior in the desorption of simazine from the DG 0.212-0.425 mm fraction with 4% kaolinite compared to the desorption from the loam soil. Similarly, after the initial decrease in the first week the amount desorbed from the DG 0.212-0.425 mm with 4% kaolinite markedly increased (Fig. 2).
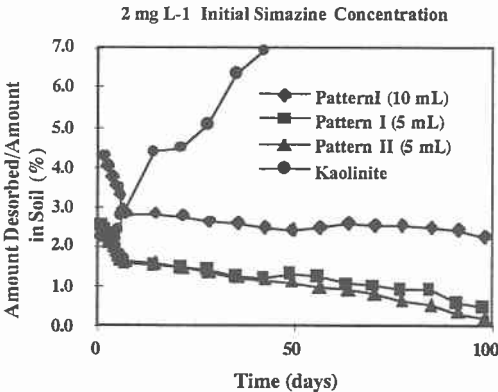
2 mg L-1 Initial Simazine Concentration

Fig. 2 Comparison between the amounts of simazine desorbed from the Loam soil or DG 0.212-0.425 mm fraction with 4 % Kaolinite (note: the amount desorbed from the DG fraction is given as promile). Pattern I - liquid phase and solid phase were incubated together and Pattern II - liquid phase and solid phase were incubated separately.

The different behavior in the desorption of simazine from the natural loam soil and DG with 4% kaolinite illustrates the influence of clay minerals and organic matter in sorption processes. There are 1.4% of organic matter in the loam soil but no organic matter in the DG 0.212-0.425 mm soil size fraction and therefore the amounts initially adsorbed were also different. The simazine adsorbed on the clay minerals (kaolinite) is easily desorbed and might easily be subject of degradation process while simazine adsorbed on the loam soil' organic matter is hardly released. In agreement with the findings of other researchers, the clay minerals seem to catalyze the degradation process as it was observed when we compared the variation in time of simazine concentration in DG soil size fractions with and without kaolinite. The degradation process seems to take place mainly in the stagnant or pelicular water, covering the soil particles. The measured simazine concentrations in solution little decreased when Pattern II was followed and markedly decreased in Pattern I (Fig. 3). The first-order reaction (Eq. [1]) well described the measured data between 10 days (= t_0 in

Eq. [1]) and 100 days. The desorption rates decreased with the increasing liquid/soil ratio (Fig. 4).
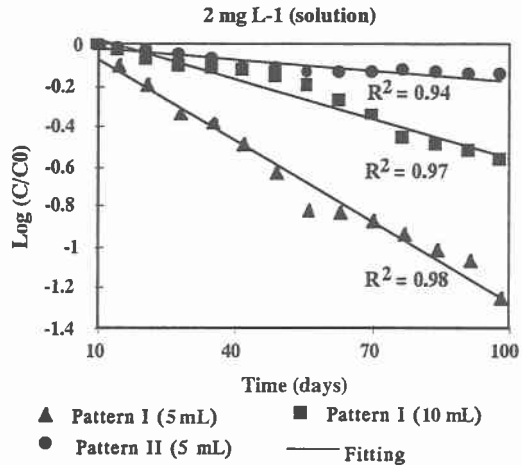
2 mg L-1 (solution)

Fig. 3 Degradation of simazine in solution (C is simazine concentration in liquid phase at time t and C_0 is concentration of simazine in liquid phase after the equilibration time ($t_0 = 36$ hours)). Pattern I - liquid phase and solid phase were incubated together and Pattern II - liquid phase and solid phase were incubated separately.
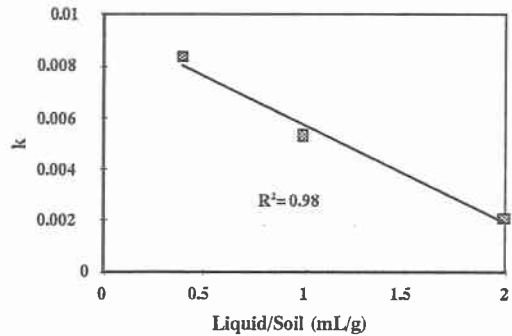

Fig. 4 Correlation between the desorption rates and the liquid (amount of solution)/solid (amount of soil) ratio for loam soil.

Conclusions

For the organic matter rich soils a continuous decrease of the amounts desorbed, especially for lower solution/soil ratio, was observed. The amounts desorbed from the clay minerals-containing soils were easily degraded and the clay minerals seem to catalyze the degradation process. Only desorption from the sand-size soils, without organic matter content and clay minerals, remained constant in time and no degradation occurred, thus, constituting a serious threat for surface and groundwater pollution.