

ATRAZINE DEGRADATION IN SOILS - THE EFFECT OF pH
AND SOME POSSIBLE CATALYSTS

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Atrazine disappearance from a series of sandy loam soils was, as described in the previous paper, pH-dependent in the range studied (pH 3.1-7.6); this was consistent with descriptions of the hydrolysis of atrazine (Armstrong *et al.*, 1967) and other triazines (Horrobin, 1963), as a reaction catalyzed by hydrogen ions. More important, observed rates of disappearance from these and two other contrasting soils were ten- to a thousand-fold faster than estimated rates of degradation in buffered solution extrapolated to comparable temperature and pH. Studies outlined in the previous paper suggested that microbiological processes could not account for this discrepancy; apparently a non-biological reaction occurs, catalyzed by something in the soil.

The effects of pH and some possible catalysts were investigated by adding well-defined surfaces to buffered solutions of atrazine. Atrazine disappearance was measured by gas-liquid chromatography and - in solution and clay suspension - by the release of chloride ion. Good agreement between the methods indicated that the degradation pathway was to hydroxyatrazine.

CLAY SURFACES

Armstrong *et al.* (1967) speculated on the effect of a concentration of hydrogen ions around soil particles which would result in more rapid hydrolysis than predicted from the pH of the system.

Experimental observations, far from suggesting that clay surfaces accelerate hydrolysis, indicated a protective effect. Conditions were varied by using different clay minerals or different quantities of montmorillonite. In some experiments the surface characteristics of montmorillonite were modified by adding or removing iron oxide or by treatment with cetyl pyridinium bromide. The effect of clay minerals in slowing hydrolysis was proportional to atrazine adsorption. When atrazine was totally adsorbed, rate of hydrolysis estimated by linear regression was very small.

From the configuration of the atrazine molecule it seems reasonable to assume planar sorption on layer-lattice clays, but the formation of a non-planar intermediate complex as a step in

the hydrolysis mechanism would require desorption. Calculations show that when energy of desorption (Frissel, 1961; Walker 1968) is added energy of hydrolysis determined in solution, the reaction is slowed by a factor of 150-250, which is comparable with the effect of adsorption on clays on rates of hydrolysis.

As pH fell below about 5, atrazine adsorption on to kaolinite, illite, and two samples of montmorillonite increased rapidly. pH will therefore affect hydrolysis in opposing ways. The balance between increasing rate of hydrolysis at lower pHs in free solution and increasing protection through adsorption will depend on the pH of the system and the nature and extent of the clay. Exploratory experiments suggest that sesquioxide surfaces do not act as catalysts to hydrolysis.

ORGANIC SURFACES

Atrazine disappearance was accelerated up to four-fold when humic acids (0.5% w/v) were added to buffered solutions.

Armstrong and Chesters (1968) reported that atrazine hydrolysis was accelerated by carboxyl resins. Carboxyl groups in humic acids may catalyze hydrolysis. However, this would be inconsistent with the theory (Walker 1968) that atrazine adsorption on organic soils is an accumulation of molecules at hydrophobic surfaces rather than adsorption at particular groups.

The application of these studies to soil systems is complicated.

- (1) The surfaces will not act independently. In many soils organic matter or sesquioxides may be sufficient to mask the clay and dominate atrazine adsorption.
- (2) There are problems of knowing atrazine distribution between organic surfaces, clay surfaces, and soil solution. pH effects will also be important and difficult to disentangle from factors of surface chemistry.

Further work is required before it will be possible to predict the influence of climate and soil type on the persistence of triazine residues in soils.