

centrate for gas chromatographic analysis. The flow rates of nitrogen, air, and hydrogen in the chromatograph are adjusted to maximize the signal-to-noise ratio, typically about 30, 250, and 35 cm<sup>3</sup>/min, respectively. The sample peak area produced at the dinitramine retention time is compared with a log-log standard curve determined separately for this detector. Due to variation in detector sensitivity, a standard should be injected every few hours for calibration.

#### DISCUSSION

The method is quantitative to 0.01 ppm. Some sample types (e.g., low organic soils) present so little gas chromatographic background that levels of dinitramine much lower than 0.01 ppm are readily determined.

Tables I and II list the recoveries, ranging from 85 to 120%, which were obtained from spiked samples of untreated soil and plant tissue.

In field studies, analysis of soil samples from treated plots showed a steady dissipation of dinitramine content. This is

illustrated in Figures 1 and 2, showing reduction to 10% of the original value over a period of about 100 days. This dissipation is due to degradation rather than leaching or volatilization, and will be discussed in detail in a subsequent publication.

Plant tissue from treated field plots contained very little dinitramine. Values of 0.01–0.05 ppm have been obtained from some cotton and soybean roots, but plant tops contained detectable dinitramine only where plots were treated at exaggerated rates, and in no case was dinitramine found in cotton or soybean seeds.

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## Adsorption–Desorption of Parathion as Affected by Soil Organic Matter

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Influence of soil organic matter on the adsorption–desorption of parathion was studied by using tagged insecticide. It was found that the parathion adsorption by soils is dependent on the type of association between the organic and mineral colloids. In

aqueous solutions the parathion has a greater affinity for organic than for mineral adsorptive surfaces. Parathion bonding is stronger on organic than on mineral surfaces.

The adsorption–desorption of pesticides by the active soil surfaces is one of the main processes controlling soil–pesticide interactions. Although the organic colloid fraction has been shown to be the most active soil component in affecting pesticide fixation in soils (Wolcott, 1970), it was also noted that it cannot always be used as a single factor to predict the adsorptive capacity of soils (Meggitt, 1970). The character and the interaction between the organic and mineral colloids of the soil are finally defining the nature of the available adsorptive surfaces.

Soil adsorption of the organophosphorus insecticide parathion was found to be related to the organic matter content and to the soil mineralogy (Saltzman and Yaron, 1971). Swoboda and Thomas (1968), studying the adsorption mechanism of parathion by leaching experiments, found that parathion was retained in soils, mainly as a water-insoluble organic constituent of the soil, by partitioning between soil organic matter and the liquid phase. In a recent study, Leenheer and Ahlrichs (1971) stated that parathion affinity for organic surfaces depends on the magnitude of the hydrophobic nature of these surfaces, rather than on the type of organic matter. They assumed parathion adsorption on organic surfaces to be a physical adsorption with formation of weak bonds between the hydrophobic portion of the adsorbent and adsorbed molecule.

Little information on the influence of organic matter on the desorption of pesticides is found in the literature. In the

review of Wolcott (1970) concerning the retention of pesticides by organic materials in soils, it is mentioned that there is some evidence that similar treatments may result in complete release of pesticides from clays, but only in a partial desorption from high organic soils.

The aim of this work was to investigate the relative importance of mineral and organic surfaces in the parathion adsorption–desorption process in some semi-arid soils, characterized by low organic matter content and different mineralogy.

#### EXPERIMENTAL SECTION

**Materials.** Three mineral soils from various locations in Israel, having a relatively high organic matter content and different mineralogy, and a peat with 95% organic matter content, were selected for this experiment. The analytical characterization of the 20-cm upper layer is given in Table I.

The pesticide studied was the organophosphorus insecticide parathion (*O,O*-diethyl *O-p*-nitrophenyl phosphorothioate). Pure parathion (produced by Analabs, Inc.) and <sup>14</sup>C-labeled parathion (produced by Amersham Radiochemical Center) with a specific activity of 52 μCi/mg were used. The labeling was done in the alkyl chain.

**Apparatus.** For counting <sup>14</sup>C activity, a Packard 3003 Tri-carb liquid scintillation spectrometer was used. The scintillation liquid consisted of 50 g of naphthalene, 7 g of PPO (2,5-diphenyloxazole), and 0.05 g of POPOP [2,2-*p*-phenylenebis-(5-phenyloxazole)], brought to 1 l. with dioxane. The purity of the material was checked periodically by gas chromatog-

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Table I. Composition of the Soils Used in the Experiments

Type of soil (and origin)	Predominant clay	Clay, %	OM, %		pH	
			Natural soil	Oxidized soil	Natural soil	Oxidized soil
Dark rendzina (Bet Guvrin)	Montmorillonite	72	4.55	2.12	7.1	7.0
Mediterranean soil (Merón)	Mixed mineralogy	63	3.72	1.20	6.6	5.6
Terra rossa (Golan)	Kaolinite	64	4.88	1.95	7.1	5.1

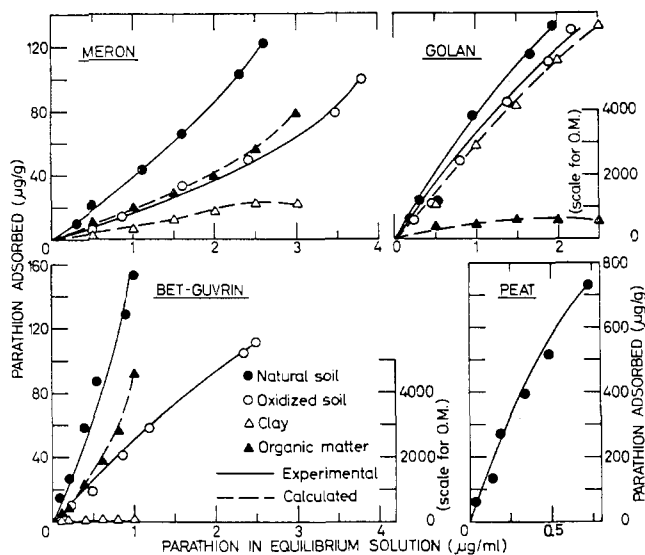


Figure 1. Parathion adsorption from aqueous solutions by soils, oxidized subsamples, organic, and mineral fractions

raphy; no decomposition products were detected during the experiments. An ultracentrifuge was used for sample separation at constant temperature.

**Procedure.** The destruction of organic matter in soils was obtained by hydrogen peroxide treatment according to the method recommended by Black (1965). For the Bet Guvrin soil, the treatment was interrupted at different phases in order to obtain different organic matter contents. Natural and treated soils were ground to pass a 60-mesh sieve, dried, and stored in a vacuum desiccator on  $P_2O_5$ . The organic matter content of the soils was determined by dry combustion, with the  $CO_2$  being adsorbed in potassium hydroxide.

The adsorption equilibria were studied by batch equilibrium experiments using the same technique as described in a previous paper (Yaron and Saltzman, 1972).

Parathion desorption was studied as follows. Soils were equilibrated in weighed centrifugation bottles with an aqueous solution containing 7.2 ppm of parathion, as previously described, and the amounts of parathion adsorbed were determined. After being analyzed, the supernatant was discarded, the bottles were reweighed, and distilled water was added up to the initial weight. The soils were equilibrated for 1 hr, since a previous experiment showed that a longer contact time does not improve parathion extraction. Parathion in the supernatant was determined, and this operation was repeated five times.

RESULTS AND DISCUSSION

The adsorptive affinity for parathion of the experimental soils was initially very different. The distribution coefficient,  $K_d$  ( $\mu\text{g adsorbed/g of adsorbent at an equilibrium concentra-$

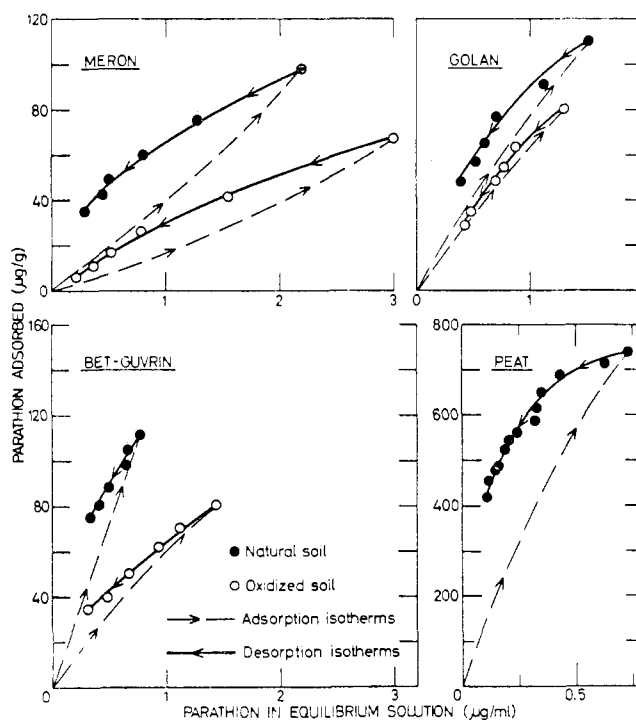


Figure 2. Parathion desorption by water from soils and oxidized subsamples

tion of 1  $\mu\text{g/ml}$ ) was 38.5 for Meron, 76.0 for Golan, 164.0 for Bet Guvrin, and 875.0 for the peat soil. The differences between the mineral soils cannot be explained by differences in the organic matter and clay content, which in Golan and Bet Guvrin soils, for instance, are rather similar. Therefore, it is reasonable to suppose that the specific interactions between organic and mineral colloids determine the nature of the adsorptive surfaces for each soil.

Following removal of organic matter by soil treatment with hydrogen peroxide, the adsorptive affinity of the mineral soils decreased (Figure 1). This decrease may be due mainly to the decrease in the organic matter content, and not to other soil modifications which may occur during organic matter oxidation. (The changes in soil reaction were of 2 pH units in Golan, of 1 pH unit in Meron, and of 0.1 pH unit in Bet Guvrin soil, in a pH range between 7.1 and 5.1. In a preliminary experiment, parathion adsorption by soils was not affected by changes in soil reaction in that pH range.)

The decrease in parathion adsorptive capacity of soils following oxidation shows that parathion has a relatively greater affinity for organic adsorptive surfaces than for mineral ones. Although the amounts of organic matter destroyed were similar for all soils, the decrease in parathion adsorption was different: 72% in Bet Guvrin; 60% in Meron; and 22% in Golan soil.

If one assumes that only the changes in organic matter con-

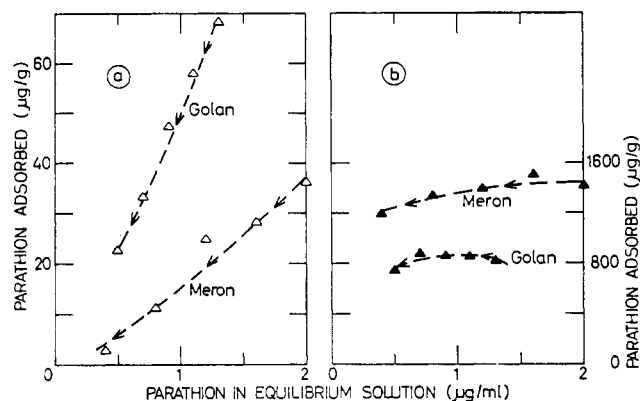


Figure 3. Calculated parathion desorption from the mineral (a) and organic (b) fractions of Golan and Meron soils

tent are responsible for the changes in parathion adsorption, then it is possible to estimate adsorption curves of the organic matter for each soil. The adsorptive capacity for organic matter and clay was estimated as follows. The differences in adsorption between natural and treated soil at several concentrations of the equilibrium solution were calculated. The adsorption per unit weight organic matter was calculated as the ratio between each of these values and the amount of organic matter lost by soil oxidation. Adsorption on the mineral soil fraction was obtained by subtracting the calculated adsorption on organic material from the adsorption on the natural soil.

From the calculated adsorption curves (Figure 1) a quantitative evaluation of the adsorptive capacity of organic and mineral surfaces is also possible. The distribution coefficients for the Meron and Golan mineral fractions are 8 and 60, respectively. The adsorptive capacity of the organic matter expressed as distribution coefficients is 450 for Golan, 950 for Meron, and 4500 for Bet Guvrin soil. The peat soil has a distribution coefficient of 875. The values found by Leenheer and Ahlrichs (1971) for parathion adsorption on organic materials separated from soils are in the same range.

The parathion desorption by water was also dependent on the nature of the soil adsorptive surfaces. After five consecutive desorptions, all the natural soils still contained more parathion than the treated soils. The parathion content of the natural soils was greater (with 8% in Golan, 24% in Meron, and 31% in Bet Guvrin soil) than in the oxidized subsamples. After the same number of desorption, the peat soil retained 2-3 times more parathion than the natural soils. The

stronger retention of parathion by natural soils and peat shows that parathion-organic complexes are stronger than parathion-mineral ones.

The desorption isotherms of the natural soils (Figure 2) do not overlap on the adsorption isotherms, showing that it is a "hysteresis" in the parathion adsorption-desorption process. Smaller differences between adsorption and desorption isotherms were found for soils treated with hydrogen peroxide.

With the same assumptions as for parathion adsorption, desorption of parathion from organic and mineral surfaces may be computed in a similar way. From the desorption curves obtained (Figure 3), a net difference between parathion release by organic and mineral colloids may be noted. The slope of the desorption curves of the mineral fraction is rather steep (especially in Golan soil), showing that adsorption is easily and totally reversible. For the organic matter, in the range of concentrations studied, only very small amounts of parathion seem to be released.

In conclusion, it may be emphasized that in aqueous solutions the parathion has a greater affinity for organic than for mineral adsorptive surfaces. The parathion adsorption by soils is dependent on the type of association between organic and mineral colloids, which determines the nature and the magnitude of the adsorptive surfaces. Consequently, oxidation of soil organic matter may have a greater or lesser effect on adsorption. Parathion bonding on organic surfaces is stronger than on mineral surfaces.

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