

# ETHYLENE DIBROMIDE IN TWO SOIL PROFILES

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Ethylene Dibromide in Two Soil Profiles

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## ABSTRACT

Soil properties and Ethylene Dibromide (EDB) concentrations were measured at two locations with histories of EDB applications. The objective was to explain the presence of EDB residues in a well near one location and the lack of residues in a well near the other location. The soil profile was sampled at each location from the surface to ground water, and ground water samples were collected at the profile base. A combination of statistical analyses (stepwise linear regression and discriminant analyses) was applied to soil data to interpret differences within each location. EDB concentrations occurred at location 1 between 0 and 3.2 feet and ranged from 0.3 to 12.5 ppb, correlating with organic carbon. Location 1, composed of a silty clay with a mean soil moisture content of 23% contained a deeper band of EDB lying between 7.7 and 9.8 feet below the soil surface. Within the band, EDB concentrations ranged from 0.2 to 0.6 ppb. The presence of this deeper band was not correlated with any measured variables, including organic carbon, and may represent accumulating or leaching EDB. The fumigant was also found in the upper 18 inches of location 2 and was correlated with organic carbon. EDB was not found in deeper soil layers of location 2 which was characterized as a more coarsely textured soil than location 1 with a mean moisture content of 15.6%. A previous study by the California Department of Food and Agriculture (CDFA) reported that EDB detected in the surface soil of a profile was associated with organic carbon, clay and moisture, but EDB found between 8 and 40 feet was statistically uncorrelated with measured variables. The authors of that study suggested that the deeper portions represented accumulating or leaching EDB. Depth to ground water was 17 and 13 feet at locations 1 and 2 respectively, and EDB was not detected in water sampled at the profile bases.

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## Introduction

In 1954, Ethylene Dibromide (EDB) was introduced as a product for the preplant treatment of agricultural fields to control nematodes and is still used worldwide. EDB is a volatile, halogenated hydrocarbon that is usually marketed as a liquid. The liquid is injected 6 to 12 inches beneath the soil surface with a tractor driven chisel tool where the vapors permeate soil air spaces and kill the parasites. Amounts of applied active ingredient range from 50 to 400 lbs. per acre depending upon soil characteristics and severity of the nematode problem. Because of high product cost, fumigation is carried out on soil used to grow crops with relatively high monetary yields such as tobacco, vegetable, vineyard and orchard crops (1).

During 1983, EDB residues were identified in well samples collected in Florida, Georgia, California and South Carolina (2). In addition, a soil coring study in California revealed EDB residues from the soil surface to a depth of 40 feet (3). As a result of water monitoring and soil coring studies, the Environmental Protection Agency (EPA) issued a suspension order in October, 1983 to discontinue the use of EDB as a pesticide (2).

As a regulatory agency, the California Department of Food and Agriculture (CDFA) is concerned with creating a strategy to selectively control the application of ground applied pesticides to reduce the potential for groundwater contamination. This regulatory design should incorporate results of laboratory, well sampling, soil coring and computer modeling studies to help estimate the potential for a pesticide to reach groundwater. A CDFA study in progress (4), is statistically comparing well sample data of dibromochloropropane (DBCP) residues with soil types. Preliminary results indicate a very high correlation between wells containing DBCP levels and highly permeable soils. Although seeming to point out an obvious correlation, the data allow statistically based predictions for well contamination as a result of agricultural pesticides in areas as small as 1 square mile. This use of well sampling data, in addition to soil coring and variables measured in the laboratory such as sorption, solubility in water and volatility can support local pesticide use decisions perhaps to a resolution of 1 square mile.

Soil core data can provide real evidence of pesticides leaching to ground water. This paper describes a soil coring study designed to examine relationships between soil properties of two agricultural locations and the

presence or absence of EDB. Sampling locations were nearly a mile apart with similar soils, EDB application histories, and agricultural practices. One location was near a well where EDB residues had been found, and the other location was near a well where EDB residues were not found. Soil cores were taken at both locations from the soil surface to the point at which groundwater was first reached. Soil properties, such as texture, moisture, % organic carbon, pH and electrical conductivity were measured. In addition, clay types and relative amounts of clay types were measured. The study objective was to compare measured variables at both sites and suggest an explanation for the presence of EDB in well water at one location and absence of the chemical in well water at the other location. Appendix III provides a report for general review of pesticides in soil.

#### Materials and Methods

Sample Site Description Two soil coring sites were selected in the western portion of Stanislaus County on the west side of the San Joaquin Valley, California. Selection was based on well sampling survey results conducted during the summer of 1983 (5). Both soil coring locations consisted of agricultural fields as close as possible to one of the previously sampled wells. Location 1 was 203 feet from a domestic well 140 feet deep where EDB residues were detected. The well had a sanitary seal 20 feet deep and was perforated between 103 and 123 feet. Location 2 was 365 feet from a domestic well 120 feet deep where EDB residues were not detected. This well also had a sanitary seal 20 feet deep and was perforated from 102 to 112 feet.

For more than 10 years, EDB was applied at location 1 in 3 out of every 4 years at a rate of 1.5 to 2 gallons/acre. EDB at location 2, about 1 mile from location 1, was also applied at a rate of 1.5 to 2 gallons/acre for over 10 years in 3 out of every 4 years. A formulation of 86% active ingredient was used most recently at both locations and applied in the Spring of 1983 in preparation for lima bean crops. The fields were historically used for vegetable crop production with water supplied through furrow irrigation. About 4 acre feet were used in 1983 to irrigate lima bean crops at location 1 and 3.5 acre feet were used to irrigate the same crop at location 2. The average precipitation total in the area was 11.31 inches for 1980, 14.33 inches for 1981, 20.51 inches for 1982 and 20.08 inches in the months of 1983 prior to coring (6).

Soil type at location 1 was Meyer's clay, described as a very deep, well-drained clay soil that cracks when dry to a depth of about 3 feet producing an angular, blocky structure (7). Location 2 was characterized in the El Solyo Series which consists of moderately well drained, fine textured silty clay loams. Subsurface soils are described as compact and consisting of calcareous heavy silty clay loams (7).

Soil Coring. Soil coring was accomplished with a truck-mounted Mobile Drill, model B-53 drilling rig and 8 inch diameter hollow-stem augers. Segments of the soil profile were collected with a split barrel sampler, 20 inches long and containing three stainless steel cylinders stacked end to end. Each 6x2.5 inch cylinder was numbered and weighed before being placed into the split barrel. The interiors of the cylinders were rinsed with ethyl acetate, the solvent used for EDB extraction in the laboratory, and the split barrel was attached to a Moss Wireline sampler and lowered by a steel cable into the hollow auger. Drilling and soil sampling occurred simultaneously but the split barrel did not rotate during the sampling process and was pressed into the soil ahead of the auger. After drilling 20 inches of soil, the sampler was withdrawn. The cutting tip of the split barrel held a 2 inch segment of sampled soil which was discarded. Thus, 18 inches of soil was sampled for every 20 inches drilled. Soil samples remained encased in the cylinders when removed from the split barrel. After removal, the cylinder ends were sealed with aluminum foil and tightly fitting plastic caps. Soil filled cylinders were reweighed to obtain soil bulk weight and then frozen on dry ice (-70 C).

When water saturated soil was reached during the drilling process, soil sampling stopped. A 2 mil thick Teflon sheet, about 4x8 inches, was attached inside the split barrel with a basket-like steel insert. The sampler was lowered through the auger and allowed to sink into the water-saturated layer before being raised to the surface. The Teflon sheet allowed water to move into the sampler, but when raised, weight from the column of water in the barrel caused the Teflon to collapse and sealed the opening. The split barrel was removed and the water poured into 1 liter amber bottles. Two bottles were filled to capacity and sealed with foil-lined caps.

During soil coring, water samples were collected from the well associated with the soil core locations. Fresh recharge water was sampled after operating the well pump long enough to completely purge and replace water in

the casing, usually about 30 minutes. All water samples were collected while the pumps were operating. A Teflon tube was attached to a Schrader aeration valve, located between the pump and storage tank. With the core of this valve removed, water from the well was directed into 1 liter amber glass bottles that were filled to capacity and sealed with aluminum foil-lined caps. If the well was not equipped with a Schrader valve, a faucet between the pump and storage tank was used as a sampling port. A Teflon tube was inserted into the faucet opening and pushed into the pipe to reduce aeration before the sample bottles were filled. One well required water to be sampled from a faucet after it had passed through a storage tank. The tank was emptied and filled three times before the sample was collected. Bottles containing water samples were stored on wet ice immediately after filling.

Soil Core Splitting and Analysis. A mechanical sample splitter was constructed to remove frozen soil from the steel cylinders and divide it longitudinally into three portions. This device was an electronically controlled hydraulic pump that pushed the frozen soil past two steel blades and into three shoots which channeled the samples into collection containers: one for moisture determination, one for quantitative chemical analysis and one for physical analyses. Soil samples were kept frozen for about 2 weeks before being split and two weeks more were required to split the samples.

The sample portion used for moisture determination was split into a pre-weighed half-pint jar which was immediately re-weighed after addition of the soil and then sealed. Moisture in the samples was driven off at 150 C, and the jars were reweighed to determine percent moisture. A pint jar was used to contain the portion of soil reserved for chemical analysis and was immediately sealed. The pint jars were stored on dry ice and shipped within 3 days to the CDFA Chemistry Laboratory in Sacramento, California for analysis. The third portion of the sample was used to determine texture, % organic matter, pH, electrical conductivity and % moisture. This portion was collected in a plastic bag and stored in a refrigerated chamber at 38 F.

Textural analysis was conducted using the Bouyoucos hydrometer method (8) in temperature controlled water baths but with 2 modifications. First, soil samples were agitated for 20 seconds with plastic plungers instead of mixing the soil by inverting the container, and second, the clay suspension was not washed and sieved to determine fractional sizes. Organic matter percentages

were determined with a dichromate reduction method (9). Electrical conductivity (ec) and pH were measured from the saturation extract of a 100 gm. sample. A Beckman Solubridge model SD26 was used for the ec measurements and pH was determined with a Corning model 125 and separate pH and reference electrodes. In addition, the weight of the saturated soil paste was used to estimate water holding capacity for each sample. X-ray diffraction analysis was performed on the clay fraction, obtained from textural analysis, to determine clay types in each sample. A quantitative analysis was performed on each X-rayed sample to determine proportions of clay types. Both analyses were performed by the Department of Geology and Physical Science at CSU Chico. The methods are presented in Appendix II. EDB in both soil and water samples was extracted with ethyl acetate and injected into a Perkin-Elmer gas chromatograph using Ni <sup>63</sup> electron capture detector (10).

### Results

Chemical analysis of the soil profile segments at location 1 revealed EDB residues between 0 and 3.2 feet and between 7.7 and 9.8 feet below the surface (Table I).

The chemical was not detected in the profile basal water or in concurrent samples collected from the domestic well 203 feet away. Chemical analysis of the soil profile at location 2 (Table I) detected EDB between 0 and 1.5 feet below the soil surface while water sampled at the profile base contained no residues. However, EDB was detected in water sampled on the day of coring from the domestic well 365 feet away. Table II summarizes water sample data.

Soil property variables were entered into statistical analyses as individual data points and were not in other ways summarized. For purposes of discussion, however, the mean percentage values for moisture were 23% and 15.6% for locations 1 and 2 respectively. The results of measured soil property variables for both core locations appear in Figures 1, 2 and 3. Portions of the profiles were not sampled and appear as breaks in the figure columns. Occasionally the split barrel sampler would not contain a full allotment of soil although the auger drilled a complete 20 inches. Most often the soil was probably compressed, but a portion of the sandy and water-saturated sample collected near the profile base of location 2 dropped out as the sampler was raised. Another profile section at location

Table I. EDB Concentrations (ppb) in Soil Segments

Location	Concentration*	Depth (inches)	Feet
1	4.3	1-6	
	6.1	6-12	
	12.5	12-18	0 - 3.2
	0.8	26-32	
	0.3	32-38	
	0.6	92-98	
	0.3	100-106	7.7 - 9.8
	0.3	106-112	
	0.2	112-118	
2	5.4	1-6	
	1.3	6-12	0 - 1.5
	0.3	12-18	

\* Minimum detectable level = 0.1ppb

2 between 7 and 8 feet was drilled out and not sampled because the split barrel could not penetrate. X-ray analysis revealed montmorillonite, illite and kaolinite in samples from both locations. Relative proportions are presented in Table III.

Table II. EDB Concentrations (ppb) in Water Samples

Location	Wells sampled June, July, Aug., 1983	Water at base of core, Oct. 15, 1983	Well sampled Oct. 15, 1983
1	N.D. <sup>a</sup>	N.D.	N.D.
2	0.2 <sup>b</sup>	N.D.	0.2 <sup>c</sup>

a. None detected

b. Mean of 3 replicated samples

c. Mean of 2 replicated samples

# LOCATION 1

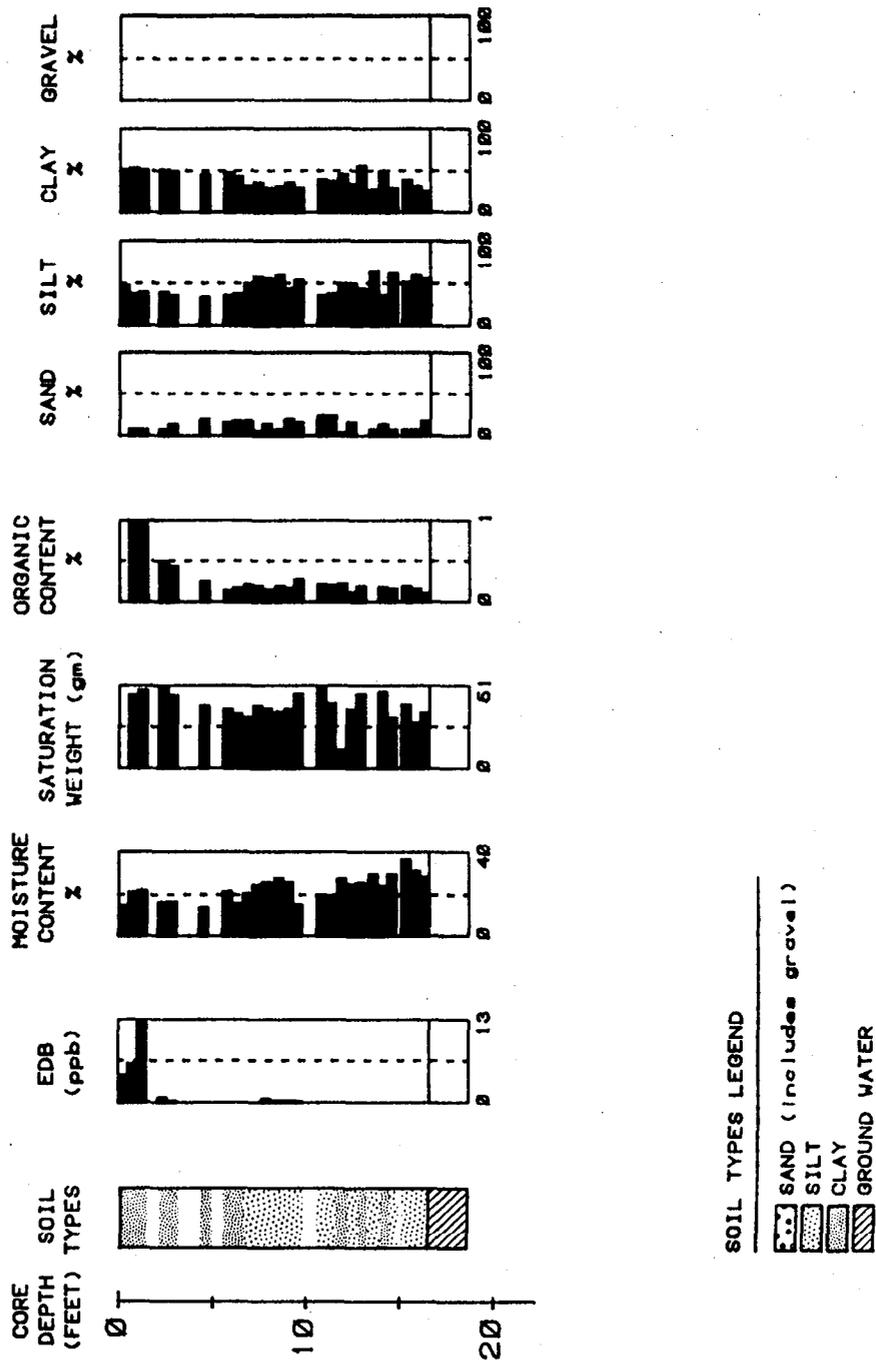
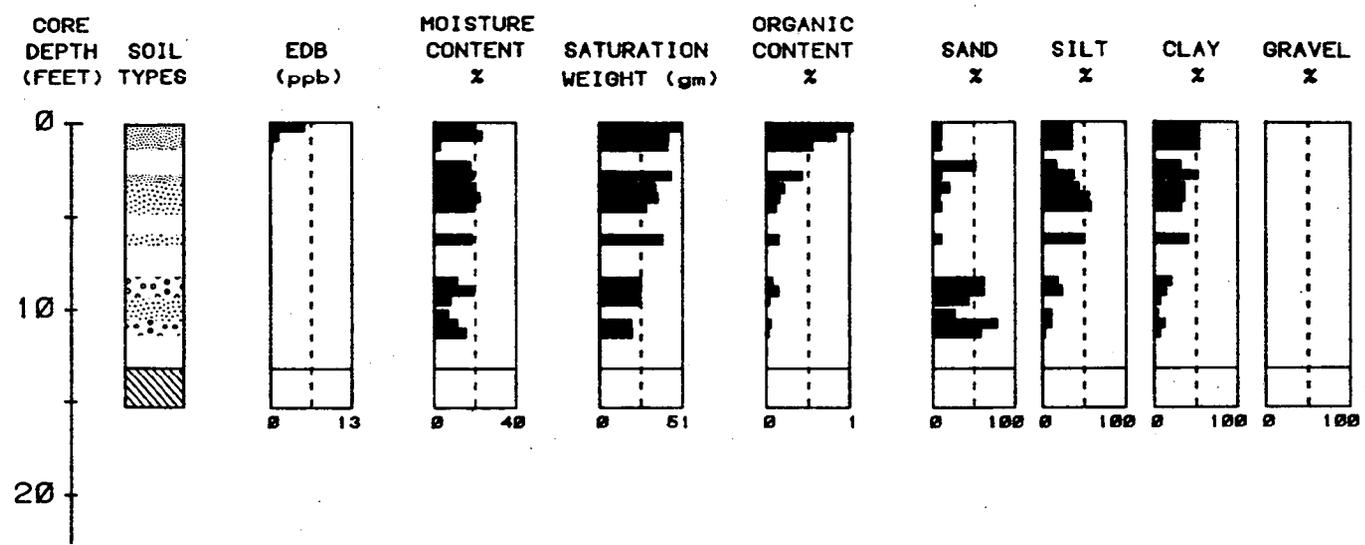


Figure 1. Histograms of measured variables at location 1

## LOCATION 2

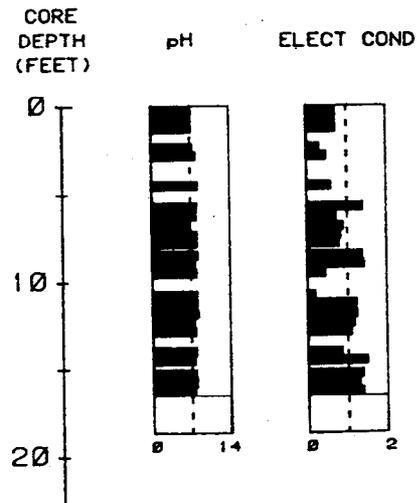


**SOIL TYPES LEGEND**

- SAND (includes gravel)
- SILT
- CLAY
- GROUND WATER

Figure 2. Histograms of measured variables at location 2

LOCATION 1



LOCATION 2

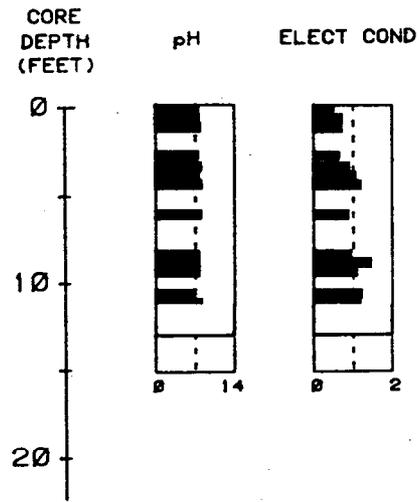


Figure 3. Electrical conductivity and pH measured at locations 1 and 2

Table III. Clay Types and Relative Proportions

Location	Montmorillonite	Kaolinite	Illite
1	59.4	26.6	14.0
2	57.0	27.0	16.0

Statistical Analysis. Stepwise multiple linear regression analysis was used to determine the measured soil properties most correlated with EDB residues and to formulate a predictive equation to estimate chemical concentration. The regression analysis was performed on results from location 1 (Table IV) only because the number of segments containing residues at location 2 were not sufficient to produce an analysis.

Table IV. Regression Analysis for Location 1

F Ratio	Variables	R <sup>2</sup>
76.23	Organic Matter	0.7840

$$y = -1.883 + 9.597 (\text{organic matter})$$

The regression of location 1 revealed organic matter ( $p > .001$ ) as the single and only important variable in predicting EDB residues and explained 78% of the variability in the data. The standard error of 1.372 produced confidence limits of +2.74 ppb EDB. An additional regression analysis was performed on data from location 1 (Table V) to determine if residues found in the upper portion of the profile were correlated with the same variables as residues in the lower profile portion.

Table V. Regression Analysis for Location 1, Divided

	F Ratio	Variables	R <sup>2</sup>
Upper Core	14.5	Organic Matter	0.8286
Lower Core	Nonsignificant		

The division was made just above the four lower segments containing residues. The analysis excluded any samples that did not have a measurement for each variable. Thus, the low F ratio for the upper portion was probably due to the small sample size, but organic matter still accounted for a significant ( $p > .05$ ) portion of the variability. The lower portion, however, produced no significant F ratio, indicating the presence of EDB residues was apparently unassociated with organic matter and all other measured variables.

Discriminant analysis created a model to predict the presence or absence of residues in soil segments of location 1 and was used to verify the outcome of the divided regression analysis. The analysis used a stepwise linear regression to determine which variables were important in predicting residues. As expected, organic matter was produced as the predictive or discriminating variable. The analysis assigned probability scores to each sample based on the relationship between the discriminating variable and the presence or absence of EDB in each sample. The probabilities were then used to classify each sample as theoretically containing or not containing residues. The results of this hypothetical classification were compared with experimental results to determine the accuracy of the model (Table VI). EDB in the four profile segments near the soil surface at location 1 was strongly predicted by the model. However, the four profile segments between 7.6 and 9.8 feet that contained EDB were strongly predicted to contain no residues. EDB residues in the lower profile segments were not associated with any of the measured variables.

Table VI. Discriminant Analysis of Location 1

<u>Classification Matrix</u>			
	Correct	No. of Cases Classified	
		No Residues	Residues
No Residues	100.0	15	0
Residues	50.0	4	4
<b>Total</b>	<b>82.6</b>	<b>19</b>	<b>4</b>

Discussion

The correlation between EDB residues and soil organic matter as a result of sorption is a well documented association (11,12). This relationship would also be expected because the fumigant was applied near the soil surface where the greatest amounts of organic matter occur. However, the deeper group of segments at location 1 containing EDB residues were unassociated with any variables in the regression. The discriminant analysis also incorrectly predicted the lower portion as being free of residues. An explanation for this condition may be derived from the consistently high moisture content throughout the soil profile. Moisture content at location 1 was sufficiently high (mean of 23%) to consider most of the profile wet. It has been shown that high moisture levels reduce the potential for chemical adsorption to soils and the high cation exchange capacity (CEC) surfaces of clay (13,14) and that EDB will desorb from clay surfaces if sufficient water is present (15). Therefore, EDB in the lower segments may have leached with the water flux initiated by irrigation and rainfall, or accumulated as a result of leaching. A soil core study by Zalkin et al. (3) found organic matter, moisture and clay to be significant predictive variables of EDB residues above 8 feet in a sandy soil. In this study, core segments between 8 and 40 feet that contained EDB levels were generally unassociated with measured soil properties in a

regression analysis and the authors suggested the residues were accumulating or leaching. Again, the lack of significant residue predictors in the lower half of the hole with relatively low organic matter would suggest that the EDB was migrating. This is speculation, but it appears to fit the analysis.

Clay type at locations 1 and 2 was not significant in predicting the presence or absence of EDB. Adsorption of a nonionic compound like EDB to wet clays would not be expected (11).

The movement of volatile pesticides in very moist soil has been studied by McKenry and Thomason who found that 1,3-Dichloropropene moved no more than 45.7cm into a silty clay loam with 23% moisture (16) in 20 days. The fine texture and generally high moisture levels throughout the profile at location 1 would probably make the transport of EDB from the surface to lower profile levels a lengthy process. Therefore it may be of significance that the well associated with location 1 did not have a history of detected EDB residues despite a 10 year history of EDB use on a nearby field.

In contrast to location 1, the profile at location 2 was more shallow, less moist, contained more sand and below a depth of 2 feet would be considered a loam. The sandy layers at the profile base would tend to accelerate movement of the pesticide associated with the bulk flow of water and perhaps would account for the lack of residues in the deeper layers of the profile and for contaminated well water nearby. Based on texture and moisture analyses, one would expect a longer time required for downward movement of EDB at location 1 compared with location 2.

In summation, EDB may tend to leach more slowly through the "wet" and fine textured soil of location 1 than through the relatively coarser and somewhat drier soil of location 2. This is a possible explanation for the presence of EDB in well water at location 2 and the lack of it in well water at location 1.

Comparisons between soil core analyses and the presence or absence of pesticides in nearby wells are speculative because of well and profile depth differences and because of a lack of information about strata within the specific ground water region of the field and well sampled. However, correlations between residues in well water and soil types can be shown. Work in progress by Teso and Younglove (4), shows that a discriminant analysis performed on well sample results for DBCP in association with soil type classifications correctly predicts contamination or no contamination 75% of the time. A total of 532 wells were sampled in agricultural areas where DBCP

had been used. The results were compared with soil type data on township, range, section surveyed coordinates. This suggests that well data may be related spatially to soil core data with some degree of certainty. The relationship can be used to help focus soil core research on specific areas where ground water residues are found due to agricultural usage. Ultimately, this data in addition to laboratory results and predictions made from models will be used to support the development of measures to refine regulation of pesticide use.

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**APPENDIX I**

Core #	Segment #	Depth (in.)	pH	% Moisture	% Organic	% Sand	% Gravel	% Silt	% Clay	Electrical Cond.	Saturation wt.	EDB (ppb)
1-001	000-006	---	15.18	---	000.0	---	049.0	052.0	---	---	---	04.3
1-012	005-012	07.18	21.38	1.09	008.0	---	038.0	054.0	00.75	45.58	06.1	---
1-003	012-018	07.24	22.18	1.04	008.0	---	040.0	052.0	00.72	42.86	12.5	---
1-004	020-026	---	---	---	---	---	---	---	---	---	---	00.0
1-005	026-032	07.42	16.60	0.50	008.0	---	040.0	052.0	00.82	50.89	00.8	---
1-006	032-038	07.94	16.89	0.44	014.0	---	036.0	050.0	00.45	45.81	00.3	---
1-007	040-046	---	---	---	---	---	---	---	---	---	---	---
1-008	046-052	---	---	---	---	---	034.0	046.0	00.60	59.03	00.0	---
1-009	052-058	08.37	14.31	0.26	020.0	---	034.0	046.0	00.60	59.03	00.0	---
1-010	060-066	---	---	---	---	---	---	---	---	---	---	---
1-011	066-072	08.14	21.89	0.14	016.0	---	036.0	048.0	01.40	36.93	00.0	---
1-012	072-078	08.06	16.08	0.18	016.0	---	038.0	044.0	00.73	34.20	00.0	---
1-013	080-086	07.02	20.80	0.22	018.0	---	050.0	032.0	00.91	31.89	00.0	---
1-014	086-092	08.20	24.79	0.20	006.0	---	059.0	036.0	00.84	35.93	00.0	---
1-015	092-098	08.20	26.17	0.15	014.0	---	056.0	030.0	00.80	37.28	00.6	---
1-016	100-106	08.31	28.10	0.20	008.0	---	060.0	052.0	01.39	35.41	00.33	---
1-017	106-112	07.84	26.19	0.18	020.0	---	044.0	036.0	01.42	37.15	00.33	---
1-018	112-118	09.08	15.56	0.28	016.0	---	054.0	050.0	00.45	46.48	00.25	---
1-019	120-126	---	---	---	---	---	---	---	---	---	---	---
1-020	126-132	08.16	20.19	0.22	024.0	---	036.0	040.0	00.15	50.01	00.0	---
1-021	132-138	08.18	20.08	0.21	024.0	---	038.0	038.0	01.23	40.34	00.0	---
1-022	140-146	08.34	27.82	0.23	004.0	---	050.0	046.0	01.25	11.50	00.0	---
1-023	146-152	07.69	25.25	0.21	016.0	---	050.0	034.0	01.13	36.62	00.0	---
1-024	152-158	07.89	25.95	0.20	000.0	---	044.0	056.0	01.10	46.25	00.0	---
1-025	160-166	---	29.94	---	008.0	---	064.0	028.0	---	---	---	00.0
1-026	166-172	07.97	24.38	0.19	014.0	---	036.0	050.0	00.85	47.42	00.0	---
1-027	172-178	07.64	29.84	0.17	008.0	---	052.0	030.0	01.50	31.67	00.0	---
1-028	180-186	07.90	36.72	0.20	008.0	---	052.0	040.0	01.38	39.74	00.0	---
1-029	186-192	08.01	31.34	0.17	008.0	---	050.0	032.0	01.30	28.11	00.0	---
1-030	192-198	07.72	28.57	0.11	018.0	---	056.0	026.0	01.33	35.01	00.0	---
2-001	000-006	07.67	20.07	1.04	010.0	---	036.0	054.0	00.31	50.12	05.4	---
2-002	006-012	07.76	23.08	0.83	010.0	---	036.0	054.0	00.72	42.23	01.3	---
2-003	012-018	07.97	02.79	0.55	010.0	---	036.0	054.0	00.71	41.85	00.3	---
2-004	020-026	---	---	---	---	---	---	---	---	---	---	---
2-005	026-032	---	17.80	---	052.0	---	017.0	031.0	---	---	---	00.0
2-006	032-038	07.57	18.98	0.42	010.0	---	038.0	052.0	00.64	43.36	00.0	---
2-007	040-046	08.12	20.29	0.21	020.0	---	044.0	036.0	00.90	34.28	00.0	---
2-008	046-052	07.75	22.10	0.15	008.0	---	056.0	036.0	01.07	35.60	00.0	---
2-009	052-058	08.21	19.45	0.11	010.0	---	058.0	032.0	01.20	28.50	00.0	---
2-010	060-066	---	---	---	---	---	---	---	---	---	---	---
2-011	066-072	---	---	---	---	---	---	---	---	---	---	---
2-012	072-078	6.07	18.21	0.14	010.0	---	050.0	040.0	00.85	39.21	00.0	---
2-013	082-088	---	---	---	---	---	---	---	---	---	---	---
2-014	086-092	---	---	---	---	---	---	---	---	---	---	---
2-015	092-098	---	---	---	---	---	---	---	---	---	---	---
2-016	100-106	07.76	11.18	0.07	062.0	---	018.0	020.0	00.95	26.24	00.0	---
2-017	106-112	07.84	19.25	0.14	062.0	---	024.0	014.0	01.46	24.95	00.0	---
2-018	112-118	07.76	07.87	0.03	043.0	50.0000	0.007.0	01.10	25.23	00.0	---	---
2-019	120-126	---	06.65	---	026.0	60.0010	0.004.0	---	---	---	---	00.0
2-020	126-132	06.90	11.18	0.05	078.0	---	010.0	012.0	01.22	19.22	00.0	---
2-021	132-138	08.14	15.26	0.02	058.0	32.0003	0.007.0	01.18	19.74	00.0	---	---
2-022	140-146	---	---	---	---	---	---	---	---	---	---	---
2-023	146-152	---	---	---	---	---	---	---	---	---	---	---
2-024	152-158	---	---	---	---	---	---	---	---	---	---	---

APPENDIX II

Report on X-Ray Analysis  
of Clay Minerals

Submitted to Department of  
Food and Agriculture,  
State of California

by Terence T. Kato  
Richard Flory  
Howard Stensrud

Department of Geology  
California State University,  
Chico, CA 95929

## Analytical Method

X-Ray analyses of clay samples are performed at California State University, Chico, California using a General Electric x-ray diffractometer.

Separated clay samples (less than 2 micron particle size) are mounted on pyrex glass thin section slides. Three runs are performed for each sample: 1) an untreated slide, 2) a slide exposed to ethylene glycol vapor for one day in a dessicator, 3) a slide heated to 550°C for one hour.

Standard settings for typical runs are as follows:

### X-ray tube

voltage = 50 MV

current = 18 mamps

### Detector tube

voltage - 2.5 MV

### Goniometer

scan rate - 2° of 2θ per minute

### Strip chart recorder

speed = 4cm/min.

### Proportional counter

range = 250 multiplier = 4

time constant = 2.5 sec.

The vertical scale on strip chart should be multiplied by 10,000 to determine counts per second. Thus, 7 on the chart corresponds to 70,000 c.p.s.

## Analytical results

The major components of the clay samples analyzed appear to be montmorillonite, illite, and kaolinite. The montmorillonite-illite is interpreted to be randomly interstratified. The relative proportion of montmorillonite to illite is quite variable. Vermiculite is also inferred to exist in some of the samples, perhaps interstratified in the mixed-layer structure. These determinations were made by the following methods.

### Kaolinite

A prominent peak at  $7.2 \text{ \AA}$  d-spacing ( $2\theta = 12.3^\circ$ ) (Figs. 1 and 2) on untreated and glycolated samples which disappears on heating (Fig. 3) is interpreted as kaolinite. This is present in all samples tested.

### Illite - montmorillonite mixed layer

The illite constituent of the mixed-layer clay is present as the high angle (low d-spacing) side of a "hump" ranging from  $5.8^\circ$  ( $d = 15 \text{ \AA}$ ) to  $8.8^\circ$  ( $d = 10 \text{ \AA}$ ) (Fig. 1). Pure illite has a d spacing of  $10 \text{ \AA}$ .

The montmorillonite end member forms the opposite side of the "hump." It is less defined than the illite peak ranging from  $13 \text{ \AA}$  to  $15 \text{ \AA}$ . When exposed to ethylene glycol vapor the basal spacing (001) of montmorillonite expands to  $17 \text{ \AA}$  ( $2\theta = 5.2$ ).

Vermiculite can be distinguished from montmorillonite by being unresponsive to glycol treatment.

## Quantitative Estimates

The X-ray diffraction method is at best semi-quantitative. Differences in absorption, stacking, ordering, sample size, and solid solution between clay minerals all can affect peak height intensities. Assuming non-systematic variation in many of these parameters, however, can allow us to infer relative changes in the amounts of various constituents. For example, an increase of the  $10\text{\AA}$  illite (001) peak relative to the  $7\text{\AA}$  kaolinite (001) peak probably represents an increase in the illite constituent relative to kaolinite.

Montmorillonite exhibits the largest variation in d spacing ( $12 - 15\text{\AA}$ ) which decreases peak intensity for a given amount of clay. Upon treatment with glycol, the large size of the  $17\text{\AA}$  peak ( $2\theta = 5.1^\circ$ ) suggests a sizeable proportion of montmorillonite. Based on these criteria, the montmorillonite component is estimated as greater than 50% for all samples.

The relative peak intensities of illite and kaolinite is thought to reflect more their relative amounts.

Crude proportions could be estimated using these ratios but better estimates might be made by experimenting with mixtures of standard clay minerals with the unknown clays.

LOCATION 1

Samp. No.	K	I	M	I/K	M/K	M/I
1-01	3.5	2.1	4.7	.60	1.34	2.24
1-02	5.6	4.5	4.0	.80	.71	.89
1-03	5.5	3.8	4.2	.69	.76	1.11
1-05	3.6	2.4	2.6	.67	.72	1.08
1-06	3.5	3.0	3.7	.86	1.06	1.23
1-09	2.7	2.8	3.1	1.04	1.15	1.11
1-11	5.0	5.0	6.2	1.00	1.24	1.24
1-12	6.0	5.8	8.0	.97	1.33	1.38
1-13	5.3	6.2	8.2	1.17	1.55	1.32
1-14	3.8	4.2	6.1	1.11	1.61	1.45
1-15	4.5	4.4	5.3	.98	1.18	1.20
1-16	5.0	3.8	3.8	.76	.76	1.00
1-17	5.4	4.8	5.8	.89	1.07	.80
1-18	5.1	5.4	6.2	1.06	1.22	1.15
1-21	4.2	4.2	6.0	1.00	1.43	1.43
1-22	3.9	2.2	4.1	.56	1.05	1.86
1-23	6.3	5.0	6.2	.79	.98	1.24
1-24	4.1	2.8	3.2	.68	.78	1.14
1-26	6.1	5.3	5.0	.87	.82	.94
1-27	5.5	4.9	7.6	.89	1.38	1.55
1-28	5.1	5.3	6.8	1.04	1.33	1.28
1-29	4.5	4.1	5.6	.91	1.24	1.37
1-30	3.8	3.6	4.8	.95	1.26	1.33

Peak Height Intensities

K = Kaolinite

I = Illite

M = Montmorillonite

**Semi-quantitative Estimate of  
Relative Clay Mineral Content in  
a Mixture Using X-Ray Diffractometry**

Partial summary of results presented  
to Environmental Hazards Assessment,  
Department of Food and Agriculture,  
State of California

By

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Department of Geology  
California State University  
Chico, California

95929-205

### Purpose

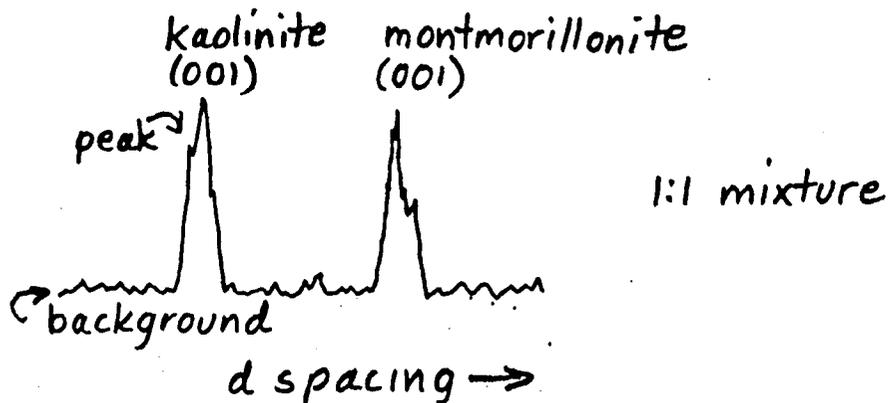
To determine relative amounts of the various constituents of a clay mixture where the major constituents were determined by qualitative X-ray diffractometry.

### Procedure

The method employed requires running X-ray diffraction scans of glycolated samples of the clay, determining the relative areas underlying 001 peaks for the various clay minerals, and multiplying these quantities by an absorption factor to determine relative weight percentage.

### Theory

The X-ray diffractometer measures X-rays diffracted by the crystal lattice of minerals which are in proper orientation and with appropriate lattice spacing. The mineral is ground into a powder so that sufficient orientations are present to diffract X-rays. The intensity of diffracted X-rays for a specific mineral should be proportional to the amount of the mineral. If two minerals such as kaolinite and montmorillonite coexist in a mixture, the peak intensities should be proportional to their relative amounts. For example,

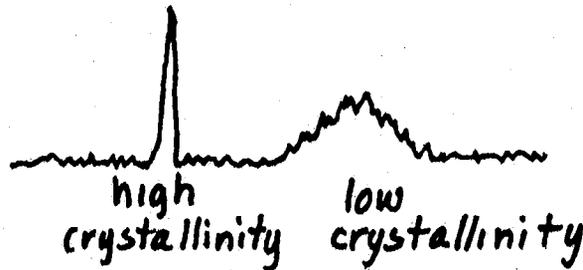


Unfortunately, other complications make the situation far more complex.

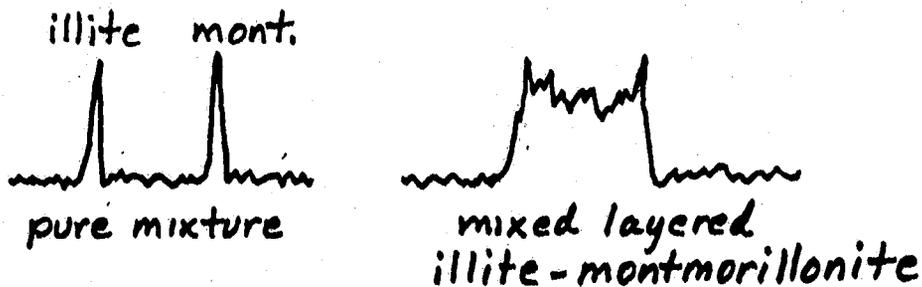
These include:

1) Differing degrees of crystallinity:

Due to differences in the internal bonding characteristics of minerals, some show much greater variability of d spacing than others. Minerals with little variation in their lattice have little d spacing variation and exhibit sharp peaks on a diffractometer trace.



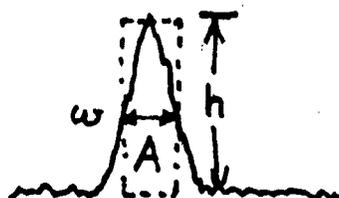
2) Random interlayered clays can be thought of as a composite mineral ranging between two end members. The effect on a diffractometer trace is as follows.



This is poorly understood, but like any form of electromagnetic radiation, X-rays are absorbed differently by different substances. The greater the absorption, the less X-rays emitted. It was observed during this study that different clay minerals in the unknowns had about the same absorption properties.

Each of these factors was studied in trying to estimate a reasonable relative percentage for the clays.

First, it was decided from mixtures of known clay standards that the area beneath peaks was a better quantity to use than peak height because of differing peak shapes. Theoretically, this is reasonable since a substance with low crystallinity would spread over a broader d spacing range than one with high crystallinity. The area is estimated from half peak heights, as follows:



$$A = w \times h$$

Second, in order to separate the illite from montmorillonite constituent in the mixed clays, the samples were treated with ethylene glycol. Since glycolation expanded the montmorillonite but not the illite, the two peaks are resolved. (See also Figure 0)



untreated



treated w/ ethylene glycol

Third, absorption differences were estimated by two methods.

(a) known quantities of pure kaolinite, etc. were added to dried samples of the unknown clay. the mixture was reground together and analyzed. By varying the proportion of standard to unknown the effect on specific peaks could be measured. (Figures 1 and 2)

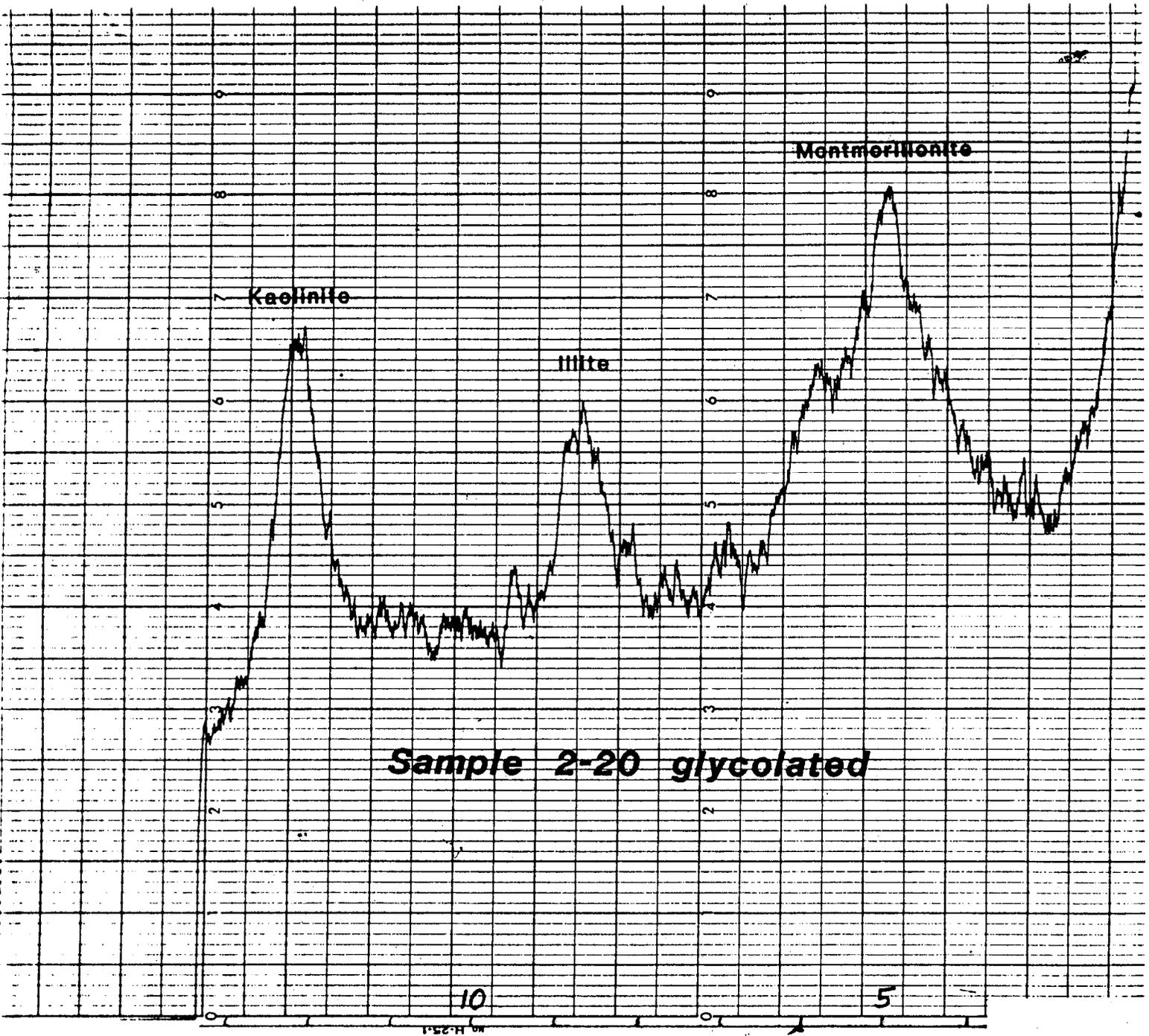


Figure 0 Unknown clay sample (2-20) treated with ethylene glycol

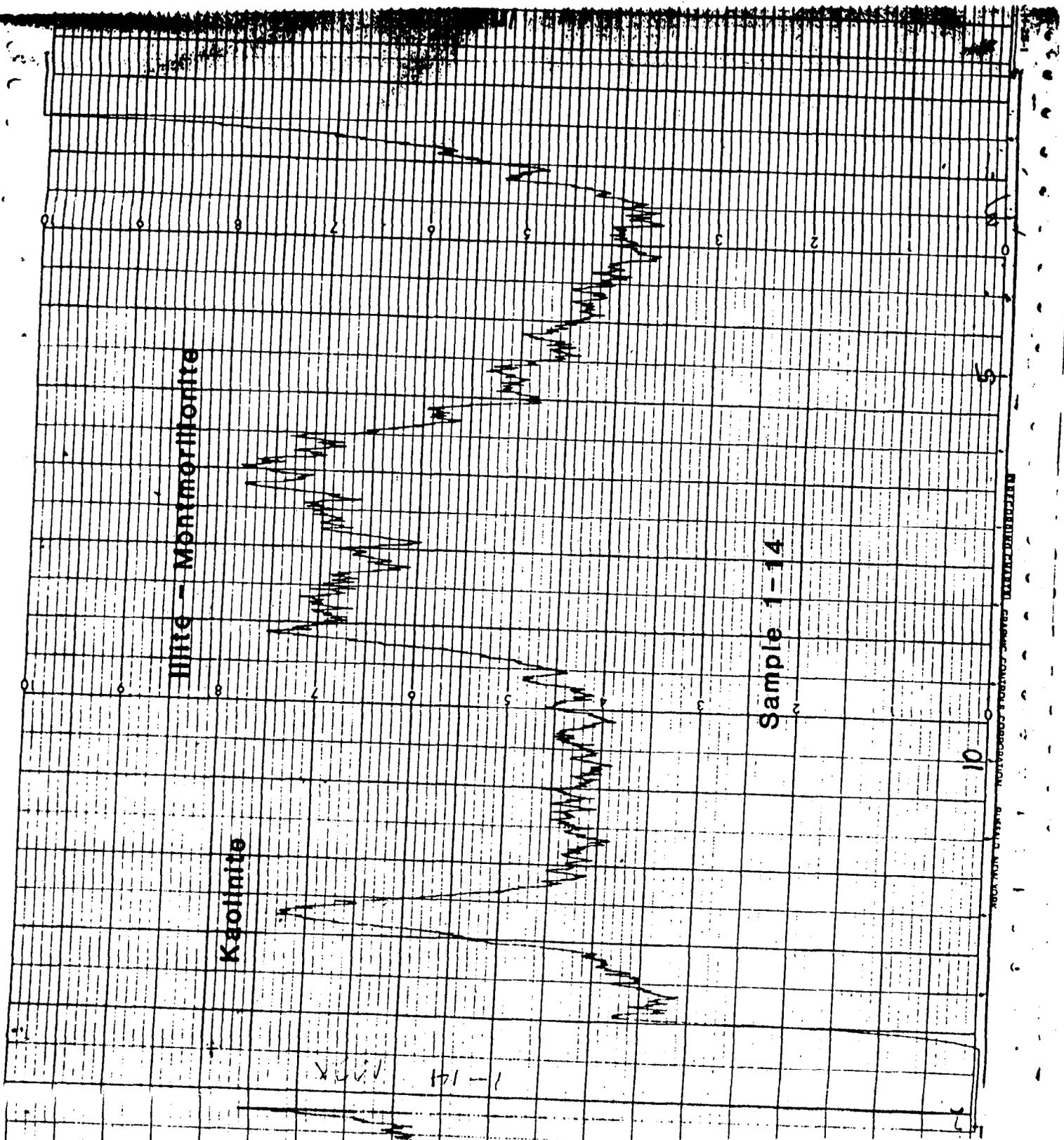


Figure 1 Diffractometer scan of untreated unknown (1-14).

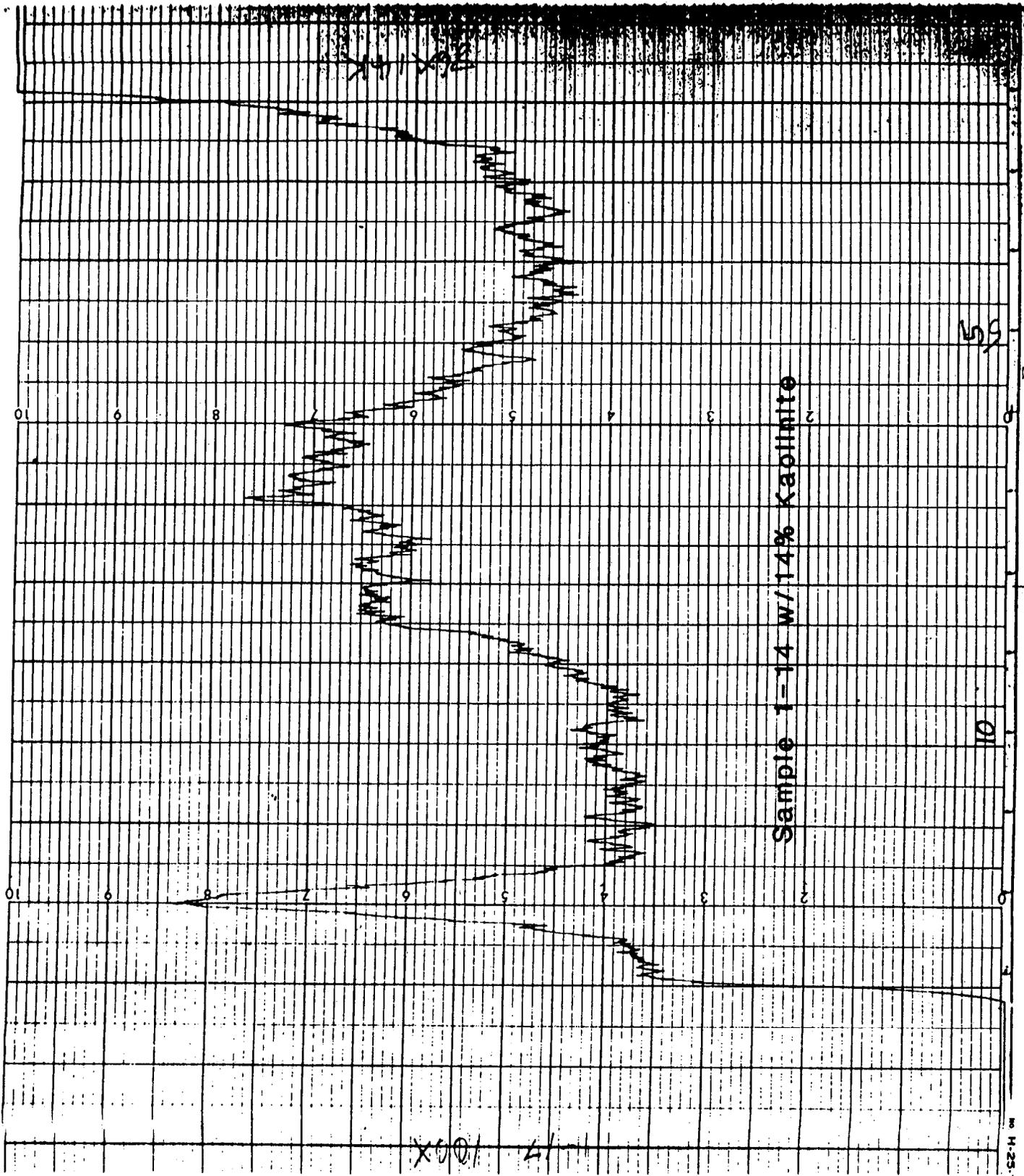


Figure 2 Diffraction scan of untreated unknown with 14% kaolinite admixture. Note relative increase of kaolinite peak relative to Illite-Montmorillonite mixed layer peak.

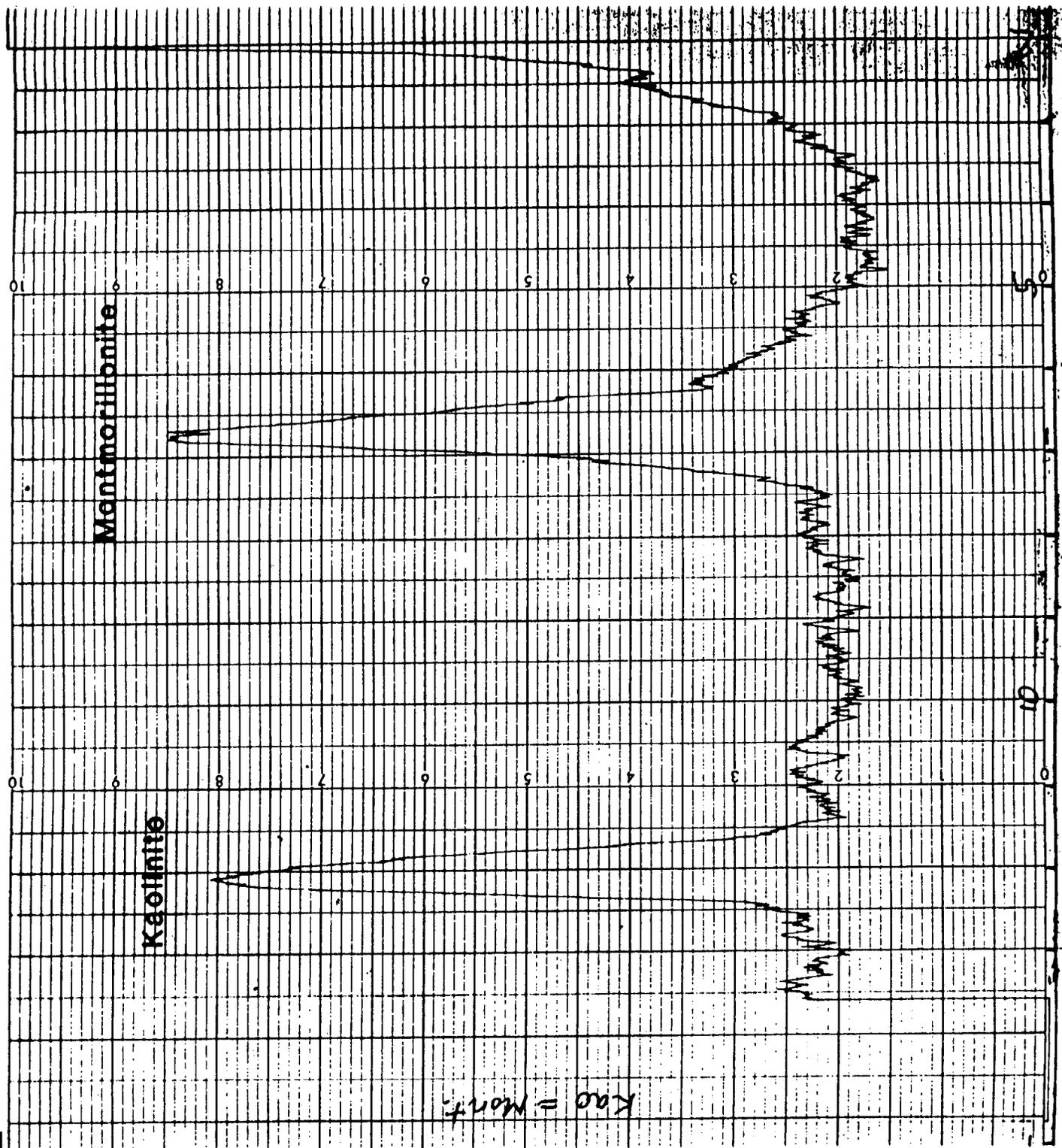
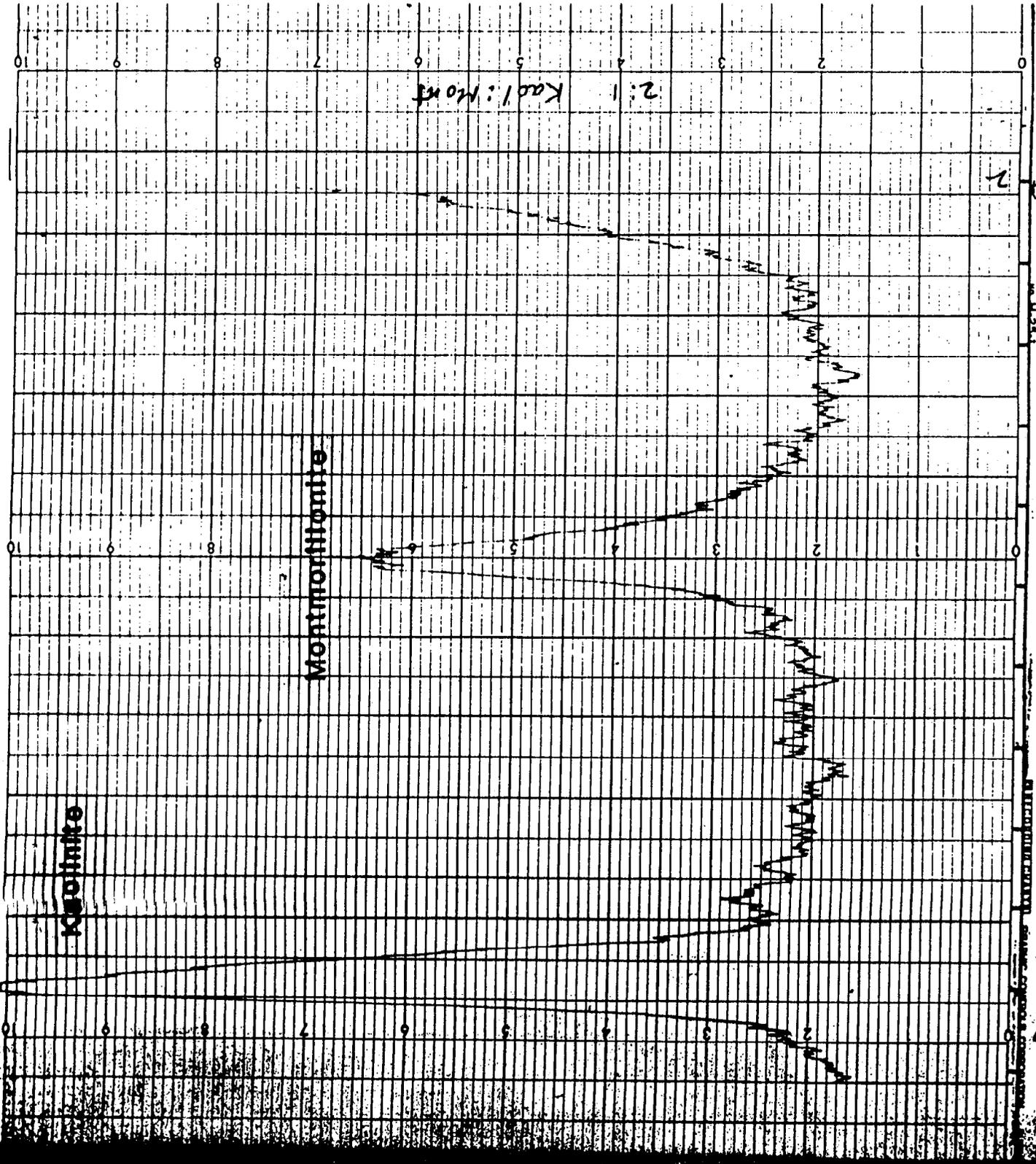


Figure 3 Diffractometer scan of mixture containing 50% kaolinite and 50% montmorillonite standard clays.

Figure 4 Diffractometer scan of mixture containing 67% kaolinite and 33% montmorillonite standard clays.



(b) Standard mixtures were made and compared (Figures 3 and 4). This has the advantage of having strict knowledge of which clays were present in specific amounts. It had the disadvantage that structural differences may exist between the standard and the mineral in the unknown.

These studies indicated that absorption differences between the clay minerals is probably not significant relative to other considerations.

The highest degree of uncertainty is in the illite which shows some inconsistency between samples.

### Results

The results of the analysis are shown in Table I. the quantities listed are peak height (H), 1/2 height width (W), peak area (A), and % weight. Because independent means of clay percentage determination are not available, it is difficult to provide a quantitative estimation of error. A precision of  $\pm 5\%$  for the illite and montmorillonite and  $\pm 3\%$  for the kaolinite is reasonable for the actual area measurement made on the peaks. The greatest deviation from the "true value" is probably due to differences in crystallinity between the various clay constituents.

Other clays present in very minor quantities may alter the percentages to a minor degree.

In the samples presented, trace quantities (probably less than 5%) of vermiculite was detected in some samples. Vermiculite forms a major peak at  $14\text{\AA}$  which is irresolvable from montmorillonite in the untreated sample. Upon glycolation the montmorillonite basal spacing expands to  $17\text{\AA}$  whereas the vermiculite is unaffected. Small traces of vermiculite were thus inferred

but this might also be caused by incomplete swelling of montmorillonite. Because of this ambiguity, and the difficulty of resolving the small 14A peak from the much larger 17A peak in glycolated samples, all was recorded as montmorillonite to compute final percentages.

## LOCATION 1

Samp	Kaolinite			Illite			Mont.			At	%K	%I	%M
	H	W	A	H	W	A	H	W	A				
1-01	30	3.5	105	14	5	70	13	16	208	311	27	18	54
1-02	27	4	108	10	4	40	17	15	255	359	27	10	63
1-03	48	3.6	172	16	5	80	20	17	340	524	29	14	57
1-05	29	3.6	104	5	5	25	12	11	132	261	40	10	50
1-06	28	4.2	117	11	5	55	29	9	261	433	27	13	60
1-09	32	3	96	12	3	36	15	8	120	214	38	14	48
1-11	27	3.4	92	10	5	50	26	10	260	365	23	12	65
1-12	28	3.5	98	14	3	42	31	9	279	380	23	10	67
1-13	29	4.5	130	14	4	64	34	6.5	221	363	31	15	53
1-14	34	3.8	129	9	7	63	25	4.5	112	252	42	21	37
1-15	26	3.8	99	12	5	60	35	12	420	579	17	10	73
1-16	29	4	116	10	4	40	24	8.5	204	313	32	11	57
1-17	33	4	132	11	5	55	23	6.5	150	283	39	16	45
1-18	30	3.5	105	12	5	60	20	12	240	363	26	15	59
1-21	23	4.6	106	13	4.8	62	28	7.6	212	380	28	20	69
1-22	40	3.5	106	18	3	54	32	9	288	448	24	12	64
1-23	17	3	51	19	4	76	20	10	200	327	16	23	61
1-26	38	4	152	18	6	108	45	9	405	625	18	17	65
1-27	38	3	114	18	2.5	45	45	7.5	337	450	23	9	68
1-28	40	2.8	112	18	6	108	45	9	405	625	18	17	65
1-29	33	3.2	105	13	3.5	46	42	6	252	361	26	11	63
1-30	23	3.2	73	7	3	21	30	5	150	215	30	9	61

Note: Units used are 10 units = 1 inch

## LOCATION 2.

Samp	Kaolinite			Illite			Mont.			At	%K	%I	%M
	H	W	A	H	W	A	H	W	A				
2-01	32	2.6	83	15	4	60	9	13	117	260	32	23	45
2-02	20	5	100	11	4	44	10	4	40	184	54	24	22
2-03	22	4	88	12	4	88	25	9	225	361	24	13	62
2-06	20	4	80	7	4	28	11	11	121	229	35	12	53
2-07	22	3.6	79	8	5	40	28	11	308	427	19	9	72
2-08	34	3	102	13	3.5	46	33	9	297	445	23	10	67
2-09	27	4.4	119	15	5	75	19	10	190	384	31	20	49
2-12	21	4.1	86	12	5	60	16	14	224	370	23	16	61
2-16	30	4	120	15	3.7	56	30	7	210	386	31	15	54
2-17	20	3.6	72	6	6	36	33	9.5	313	421	17	9	74
2-18	6	3.5	21	6	4	24	14	8	112	157	13	15	71
2-20	29	4.4	128	20	5	100	33	10	330	558	23	18	59
2-21	32	3.6	115	24	4	96	25	9	225	436	26	22	52

APPENDIX III

**Pesticides in Soils**

**Report prepared for:  
Environmental Hazards Assessment,  
Department of Food and Agriculture,  
State of California**

**by**

**R. A. Flory  
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## PESTICIDES IN SOIL

### Introduction

Kunze (1966) has identified five factors that are primarily responsible for determining the fate of pesticides in soil:

1. the type of soil, including its makeup and structure
2. the type of pesticide
3. the climatic conditions, including rainfall, pressure temperature and sunlight
4. the biological population of the soil
5. the method of application of the pesticide

This paper will primarily emphasize the first two factors: the type of soil and the type of pesticide, although some attention will be paid to the other three factors as they relate to the relationship between pesticides and soil.

### Soil Constituents

Soil is composed of many constituents, but only a few of them are important in terms of pesticide reactions; these include clay minerals, organic matter, and oxides and hydroxides of aluminum and silicon.

Clay minerals are phyllosilicates composed of two dimensional arrays of silicon-oxygen tetrahedra and two dimensional arrays of aluminum (or magnesium)-oxygen-hydroxyl octahedra. In the silicon-oxygen sheets, the oxygen atoms are in fourfold co-ordination around the silicon atom, with

three of the four oxygen atoms of each tetrahedron being shared with three adjacent tetrahedra. In the aluminum-oxygen-hydroxyl sheets the aluminum (or magnesium) atoms are coordinated by six oxygen or hydroxyl atoms in an octahedral pattern (van Olphen, 1977). In many cases iron, manganese, magnesium and other elements substitute for aluminum and silicon within both the tetrahedral and octahedral sheets (Haque, 1974).

Clay minerals may be subdivided into two main structural groups on the basis of the ratio of octahedral and tetrahedral sheets within the unit layer. 1:1 structure clays such as kaolinite, dickite and halloysite consists of one octahedral sheet and one tetrahedral sheet, and with the exception of halloysite, do not expand when wetted. Clays with a 1:1 structure are generally neutrally charged or have a very low negative charge. 2:1 structure clays are formed of a single octahedral sheet sandwiched between two tetrahedral sheets, and include the micas, montmorillonites, vermiculites, chlorites and talc. The 2:1 structure clays often carry a net negative charge on the unit layer; this negative charge is balanced within the clay structure by positive ions or atoms which fill the spacing between adjacent 2:1 unit layers. Most of the 2:1 clays expand upon wetting (White, 1976).

Another important constituent of soil is organic matter which is formed by the degradation of plant and animal tissues in soil. Soluble organic material is referred to as humic acid and consists primarily of free radicals of polymeric organic acids and minor amounts of proteins, enzymes, sugars, lignin, amino acid, resin and wax, which are generally soluble in alkalis and acids. Insoluble organic material is called humin.

The reaction of pesticides with soil is sometimes the result of

amorphous mineral colloids such as oxides of aluminum and silicon with some substitution by iron (Haque, 1974).

### Pesticide Reactions in Soil

Haque (1974) has identified three factors controlling the behavior of pesticides in soil:

1. adsorption of pesticides in soil
2. desorption and diffusion of pesticides in soil
3. degradation of pesticides in soil

Adsorption is, by far, the most important factor in the retention and movement of pesticides in soil. Pesticides adsorbed on clay and humus surfaces will be unavailable or at least, less available for leaching and movement. When, and if, adsorbed pesticides are eventually released into the soil, the type and rate of desorption will to a great extent determine the pattern of dispersal and rate of dispersal of the pesticide within the soil layers (Hamaker, 1974).

### Adsorption of Pesticides in Soil

The mechanisms by which pesticides are adsorbed by soil are extremely complex and are not presently well understood. Three mechanisms of adsorption, though, are generally recognized (Kunze, 1966; White, 1976; Lippman and Schlesinger, 1979; Bailey and White, 1970):

1. Chemical adsorption: involves coulombic forces which are the result of ion-exchange or charge transfer. This is the strongest type of adsorption and usually results in the adsorption of polar or polarizable organic ions, especially cations (Lippman and Schlesinger, 1979).

Most clays commonly found in soils (i.e., kaolinite, halloysite,

interstratified

FROM TWO MAJOR FACTORS: (1) the total surface area available for adsorption and (2) the total charge of the surface area (i.e. cation exchange capacity or CEC)(Greenland, 1965; Weber, 1970; Bailey and White, 1970).

The amount of a particular pesticide which is adsorbed by a particular clay mineral is directly proportional to the surface area of the clay mineral. As mentioned earlier, 1:1 structure clay minerals, with the exception of halloysite, are non-expandable; therefore, the active surface area for adsorption of the pesticide is limited to the external surfaces of the clay layer. Most 2:1 structure clay minerals (especially montmorillonite and vermiculite) are expandable and have a great surface area when so expanded. In addition, these expandable clays not only adsorb pesticides on their external surfaces, but also on interior surfaces between the expanded tetrahedral sheets. As a result of this greater surface area, the 2:1 structure expandable clay minerals have a ten to one hundred times greater adsorption capacity than the 1:1 non-expanding clays. The 2:1 structure non-expanding clay minerals such as chlorite and illite are intermediate between 1:1 structure and the 2:1 structure expanding clay minerals (Weber, 1970; Bailey and White, 1970; White, 1976)(see table 1).

The amount of pesticide that can be adsorbed and the mechanism of adsorption is also determined by the total charge of the surface area of the clay mineral, i.e. the greater the total charge the greater the amount adsorbed. Clays with a 1:1 structure have a small net charge and therefore have a limited ability to adsorb pesticides. 2:1 structure have a high cation exchange ratio (i.e. a large net negative charge) and therefore, a greater capacity to adsorb pesticides (White, 1976; Bailey and White, 1970) (see table 1). Interlayer cations in 2:1 structure expandable clays, especially vermiculite and montmorillonite, also play a role in pesticide adsorption. These interlayer cations (i.e.  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$ ) neutralize the negative charges on the surface of the clay minerals and interact very

<u>Soil Constituent</u>	<u>Cation Exchange capacity (meq./100g.)</u>	<u>Surface area (sq.m./g.)</u>
organic material	200-400	500-800
vermiculite	100-150	600-800
montmorillonite	80-150	600-800
dioctahedral vermiculite	10-150	50-80
illite	10-40	65-100
chlorite	10-40	25-40
kaolinite	3-15	7-30
oxides and hydroxides	2-6	100-800

Table 1: Physical properties of soil constituents (after Bailey and White, 1964).

strongly with water molecules and polarizes them, resulting in a greater dissociation of water adjacent to the clay surfaces. This ability of clays to donate protons characterizes them as Bronsted acids and plays an important role in the adsorption of basic pesticides (White, 1976).

In addition to clay, organic material also plays an important role as an adsorbent of pesticides in soil. Studies by Stevenson (1976) indicate that most pesticides (prometon and prometryn being two major exceptions) have a greater affinity for organic material than for clay minerals. On the other hand, Hayes and others (1975) have found that while the bipyridylium cations of paraquat do have an affinity for organic substances, this is only true in soils which lack clay minerals. When clay is added to the organic rich soil, the bipyridylium cations are transferred from the surfaces of the organic material to the clay surfaces. There is also evidence that indicates that organic material and clay can function as a single unit to adsorb pesticides. In soils with an organic content up to six percent, the organic material is bound to the clay surfaces as a clay-metal-organic complex and the clay and organic material act as a single adsorbing surface.

In soils with the same organic and clay content, the contribution of the organic material as an adsorbent will depend on the type of clay present. The contribution of the organic material will be greatest when the clay is kaolinite and least when the main clay component is montmorillonite (Stevenson, 1976; Hayes and others, 1975).

#### Physical and Chemical Characteristics of the Adsorbate

Numerous physical and chemical properties determine the role of the adsorbate in the adsorption of pesticides by soil constituents; six of these

properties will be discussed here: (1) the chemical character of the adsorbate, (2) the dissociation constant, (3) the water solubility, (4) the charge distribution of the organic cation, (5) the molecular size of the cation and (6) the polarity of the cation.

The chemical characteristics of pesticides vary widely depending on the particular pesticide that is being employed. No attempt will be made here to try to give a comprehensive chemical description of pesticides, but some generalizations can be made concerning the relationship of particular pesticides and their affinities to particular adsorbents.

Large quantities of insecticides become available to the soil for possible adsorbance. Edwards (1964) has estimated that 50 percent of all sprayed insecticides are incorporated into the soil because of missing the desired target or due to washing of insecticides from foliage. The most common insecticides consist of chlorinated hydrocarbons which have non-polar molecules and are therefore not adsorbed by clay minerals. Rather, they are accumulated in organic material which is a solvent for these hydrocarbons (Edwards, 1964; Kunze, 1966). Arsenical insecticides generally react with iron in the soil to form iron arsenate compounds, while fumigants, such as ethylene dibromide, are adsorbed on the external surfaces of montmorillonite, kaolinite and illite (Kunze, 1966).

Herbicides are adsorbed by both clay and organic material. Among the various clay minerals, montmorillonite has the greatest adsorption capacity for herbicides, followed in decreasing order of adsorption capacity by illite and kaolinite (Bailey and White, 1970). The most widely studied herbicides have been diquat and paraquat. Coats and others (1966) have found that the adsorption of the bipyridylium cations by clay minerals is the major cause of

the biological inactivation of diquat and paraquat in soils. Coulombic forces appear to be the major mechanism for the adsorption of these two herbicides in 1:1 structure non-expanding clays. The mechanism for adsorption in expanding clays is much more complex and not well understood (Hayes and others, 1975). Large quantities of paraquat and diquat can be adsorbed by clays. Montmorillonite, illite and kaolinite are readily able to adsorb these herbicides to an extent that approaches their cation exchange capacities. (Hayes & other, 1972a). The adsorption of paraquat and diquat by kaolinite, illite, montmorillonite, and  $\text{Na}^+$  and  $\text{Li}^+$  vermiculites occurs very rapidly, being completed in less than thirty minutes.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$  vermiculite has a slower adsorption ability, but is still able to complete adsorption in less than two hours (Hayes and others, 1972b). Herbicides containing phenoxy acetic acid are also readily adsorbed by both clay and organic material, but is generally adsorbed in lesser amounts than either paraquat or diquat (Weber, 1972).

The dissociation constant (pKa) of the organic compounds in the pesticide indicates the degree of acidity or basicity of that compound and plays a major role in determining the extent to which the pesticide will be adsorbed. Basic compounds are more strongly adsorbed by bentonite and illite, than are either acidic or neutral compounds. Vermiculite, kaolinite and illite are not capable of adsorbing acidic or neutral compounds, while montmorillonite readily adsorbs both of these compounds (Bailey & White, 1970).

Bailey and others (1968) have found a direct relationship between water solubility and the adsorbability of S-triazines on montmorillonite. Further studies by Bailey and White (1970) indicate that for any chemical family of

pesticides the magnitude of adsorption on clay minerals is related to and governed by the degree of water solubility of the adsorbate.

The adsorption of organic compounds in pesticides is also influenced by the distribution of the electrostatic charge of the organic cation. Paraquat is preferentially adsorbed over diquat by montmorillonite, kaolinite and the external surfaces of vermiculite, while diquat was preferred on the internal surfaces of vermiculite and the external surfaces of non-expanding micas. Bailey and White (1970) have attributed this to differences in the separation of the electrical charge on the organic cations of diquat and paraquat.

The molecular size of the organic cation also plays a role in the adsorption process. Generally, larger ions tend to decrease the magnitude of adsorption on clays, because the large ions have a tendency to cover more than one electrostatic exchange site on the clay surfaces, thus reducing the possible number of exchanges that can occur. In some cases the large size of the cation may completely prohibit adsorption; for example, molecules larger than 5A cannot be adsorbed on the internal surfaces of vermiculite (Bailey and White, 1970).

The polarity of the organic cation is very important in determining whether or not adsorption can occur between the clay sheets in certain clay minerals. The presence of polar groups in organic molecules is necessary to enable clay sheets to be separated one from the other (Bailey and White, 1970).

#### pH of the Soil Solution

The adsorption of the organic molecules of pesticides on clay surfaces is greatly affected by the solvent involved. The most common solvent in

soils is water, and the pH of the clay - water system has a decided effect on adsorption. Talbert and Fletchall (1965) found that an increase in pH caused a decreased adsorption of simazine and atrazine in soils, and Bailey and White (1970) indicate a similar relationship between pH and the adsorption of herbicides on clay surfaces. This relationship was further refined by Weber (1970) who indicated that adsorption increases with a decrease in pH above pH4, and that adsorption decreases with increasing acidity below a pH of 4.

#### Desorption and Diffusion of Pesticides in Soil

The desorption of pesticides (i.e. the release of organic compounds of pesticides from surfaces of the adsorbents) and the diffusion of these pesticides (i.e. their dispersion through the soil) is to a great extent a function of adsorption. The greater the magnitude of adsorption the lesser the magnitude of desorption and diffusion (Saxena, 1974; Hamaker, 1974; Haque and others, 1974). The ability of particular pesticides to desorb and diffuse can be measured by their adsorption coefficient (see table 2). The lower the adsorption coefficient the greater the tendency for the pesticide compound to desorb and diffuse (Hamaker, 1974). The bipyridylum cations in paraquat and diquat are readily, and strongly, adsorbed by montmorillonite and once adsorbed penetrate so deeply into the interlamellar spacings of the montmorillonite that they are extremely hard to desorb (Weed and Weber, 1968; Hayes and others, 1975). In fact, Tomlinson and others (1968) found that very little paraquat is desorbed from montmorillonite even by the addition of very large amounts of solvent. These same two herbicides are somewhat easier to adsorb from the surfaces of illite and kaolinite, but even in these cases a large excess of ammonium ions is required (Hayes and others, 1975).

<u>Pesticide</u>	<u>Adsorption</u> <u>Coefficient</u>
Chloramben	13
2,4-D	32
Propham	51
Bromacil	71
Monuron	83
Simazine	135
Propazine	152
Dichlobenil	164
Atrazine	172
Chlorpropham	254
Prometone	300
Ametryne	380
Diuron	485
Prometryne	513
Chloroxuron	4,986
Paraquat	20,000
DDT	243,000

Table 2: Adsorption coefficients for a selected group of pesticides (after Hamaker and Thompson, 1972).

For those pesticides which are more readily desorbed, the adsorption coefficient tends to determine the underlying pattern of diffusion. Desorption tends to proceed at a slower rate than adsorption, thus the pattern of diffusion tends to be irregular. The main body of diffused pesticide tends to have a considerable tail trailing behind it; this has sometimes been referred to as the "frictional effect" and is the result of the slow release of the pesticide during desorption (Hamaker, 1974).

The texture of the soil also appears to affect the diffusion of pesticides. Bailey and White (1970) suggest that the leaching of pesticides occurs to a greater extent in light-textured soils than in heavier-textured soils. Hamaker (1974) indicates that pesticide leaching is inhibited by an increase in the organic carbon content of soil.

Most pesticides are diffused by water movement within the soil. Initially water tends to disperse the pesticide downwards, but then drying of the soil and the accompanying capillary action moves the chemical upwards again. Under natural conditions little, if any, of even the most easily dispersed pesticides is leached by water to sufficient depths to enter the ground water (Hamaker, 1974). Hartley (1961) indicates that several years is necessary for even one percent of the concentration of surface applied herbicides to migrate by diffusion to a depth of two feet in moist soils.

Some pesticides, especially those with high vapor pressures, such as soil fumigants, are dispersed through the air spaces in soil. The porosity of the soil appears to be the most important factor in this type of diffusion, but high clay content also plays a role, because it tends to decrease pore openings in the soil and decreases the amount of diffusion (Bailey and White, 1970).

### Degradation of Pesticides in Soil

The degradation of pesticides in soil results from basically two processes: chemical degradation and microbiological degradation. Chemical degradation is very widespread and uses water as the main reaction medium. Hydrolysis is generally the most common form of chemical degradation, but oxidation and isomerization may also play important roles. Clays, metallic cations (especially iron and copper), iron and aluminum oxides, and organic materials often act as catalysts for these chemical reactions (Goring, 1967; Goring and others, 1974; Lippman and Schlesinger, 1979). Microbiological degradation results from micro-organisms in the soil which are capable of producing enzymes which degrade pesticides. The end products of the chemical and microbiological degradation of pesticides in soil include: carbon dioxide, water, mineral salts and organic material (Goring and others, 1974).

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