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Coloration Changes of Geologic Media After Addition of Gasoline, Diesel Fuel, and Ethylbenzene

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ABSTRACT: The coloration changes of three soils (Amarillo sandy loam, Anthony sandy loam, and Oakville sandy loam) and two clays (kaolinite and montmorillonite) were monitored following the addition of four solvents (distilled water, unleaded gasoline, diesel fuel, and ethylbenzene) over a time period of 1 year. Soil and clay coloration was measured using Munsell color charts. In general, the Amarillo soil experienced the most extensive changes to a darker, grayer color. Initial color changes occurred in as little as 1 week, with subsequent changes occurring throughout the next 41 weeks. This study indicates that solvents can alter geologic media color and that the inferred chemical reduction processes can be an ongoing process.

KEY WORDS: petroleum oxidation, soil gleying, free-radical oxidation, soil reduction.

I. INTRODUCTION

Petroleum and petroleum products can contain significant concentrations of numerous aromatic hydrocarbons. These include benzene, toluene, ethylbenzene, xylene, and many other dimethyl-, trimethyl-, tetramethyl-, and ethyl-substituted benzenes and polynuclear aromatic hydrocarbons (Dragun, 1988). These chemicals can undergo oxidation in soils and clays during which the organic chemical is oxidized via the removal of one electron from the molecule. Other authors have also demonstrated abiotic chemical reactions of pesticides in soils (Wolfe *et al*., 1990), including the oxidation of arsenious acid, amitrole, and organomercuric pesticides.

Free radicals are probably an important component of these reactions (Dragun, 1988; Dragun and Helling, 1982). Iron, manganese, aluminum, trace metals within soil minerals, and adsorbed oxygen (O_2) have been identified as the catalysts promoting free-radical oxidation in soil and clay. As the organic chemical is oxidized, iron and other metal oxides in the soil or clay are reduced (Wolfe *et al.*, 1990) as one electron is transferred from the organic chemical molecule to the soil. During this reaction, soils and clays can experience a color change commonly known as "gleying", the darkening of a soil's or clay's color due to the presence of a reducing soil environment (Richardson and Daniels, 1993).

Previous research has concluded that these reactions occur rapidly in soils (Dragun, 1988; Dragun and Helling, 1982; Pillai *et al.*, 1982) and that soil color may change as soil components are reduced by aromatic hydrocarbons. However, the rates of color changes of soils and clays, caused by petroleum and petroleum products, has not been reported. The objective of this portion of an ongoing study was to measure the rates of color change in three soils and two clays following the addition of gasoline, diesel fuel, and ethylbenzene.

II. MATERIALS

A. Soils and Clays

The characteristics of the three soils and two clays used in this study are listed in Table 1. Amarillo sandy loam (Lubbock County, TX) is a fine-loamy, mixed, thermic Aridic Paleustalf. The Amarillo series consists of deep, well-drained, moderately permeable soils that formed in calcareous loamy materials. These soils are on nearly level to gently sloping uplands with slope ranges of 0 to 5%. The Anthony sandy loam (Tucson, AZ) series consists of well-drained soils that are 60 in. or more in depth. These soils formed in stratified alluvium weathered from granite, rhyolite, tuffs, and limestone on alluvial fans and flood plains. Slopes range from 0 to 5%. The Oakville sandy loam (Macomb County, MI) series consists of well-drained, level to undulating, sandy soils. These soils reside on lake plains, outwash plains, and moraines. Slopes are 0 to 6%. Prior to the start of this experiment, the Oakville soil was sifted to remove gravel and rock.

Kaolinite was obtained from Aldrich Chemical Company, Milwaukee, WI. Montmorillonite (bentonite) was obtained from Fisher Scientific Company, Chicago, IL.

TABLE 1
Soil and Clay Characteristics

Soil	Texture (%) Sand	Silt	Clay	Organic matter (%)	CEC (meq/100 g)	pH
Oakville soil	69	24	7	0.3	37.7	8.4
Anthony soil	70	19	11	0.5	36.4	8.0
Amarillo soil	74	11	16	0.4	9.3	8.0
Kaolinite clay	0	2	98	0.5	5.6	4.0
Montmorillonite clay	26	1	74	0.3	23.2	8.7

B. **Solvents**

Distilled water, unleaded regular gasoline (octane 87), ethylbenzene from Aldrich Chemical Co., diesel fuel (Macomb County, MI).

C. **Apparati**

Pyrex test tubes 20 × 125 mm with Teflon-lined, plastic screw caps, Nalgene test tube storage racks, 1.8-ft^3 Avanti refrigeration units.

III. **METHODS**

During this experiment, three soils (Amarillo sandy loam soil, Anthony sandy loam soil, and Oakville sandy loam soil) and two clays (kaolinite and montmorillonite) were mixed with four solvents (distilled water, unleaded regular gasoline, ethylbenzene, and diesel fuel) and subsequently equilibrated at three temperatures (40, 55, and 70°F) for 1 year.

At the initiation of this experiment, distilled water was added to the air-dried soils and clays in order to attain moisture contents that could reasonably be found in the natural environment. Sufficient water was added so that the moisture content (w/w) was 10% for soils and 20% for clays.

Each experimental unit was comprised of one test tube containing one soil or clay and one solvent. Duplicate experimental units were assembled for each mixture. Ten grams of moisture-adjusted soil were placed in an experimental unit and 6.7 ml of one solvent were added. Because of the surface properties of the clays, only 2 g of each moisture adjusted clay was placed in test tubes. Fifteen milliliters of one solvent was added to each test tube containing clay. The increased solvent volume used with the clays was necessary in order to wet the clay and obtain a layer of solvent above the clay.

Silicone gel was placed on the threads of the test tubes, and the test tubes were sealed with the screw caps. The soil-solvent and clay-solvent mixtures were then agitated with a vortex mixer for approximately 30 s. After the soil or clay settled, all units contained a solvent layer, several millimeters thick. The experimental units were then placed in one of three refrigeration units, set at either 40, 55, or 70°F.

Color change in this experiment was followed by recording the change in the colors of the soil or clay within each test tube over time. The collection of charts used to quantify color was a modified version of the collection appearing in the *Munsell Book of Color;* these charts are published by Munsell Color, Baltimore, MD (Munsell, 1988). In these charts, three variables typically describe all colors: hue, value, and chroma. During this experiment, a change in color was considered to be significant when, according to the color notations identified in the Munsell

Index, either (1) a numerical change of at least one unit of chroma or value occurred or (2) a numerical or an alphabetical abbreviation change in hue occurred. Soil color was monitored and recorded immediately following solvent addition and once a week for the initial 10 weeks of this experiment; afterwards, color changes were monitored and recorded on a monthly basis. This paper presents data on the color changes that occurred in the three soils and two clays for the first year of this ongoing experiment.

IV. RESULTS AND DISCUSSION

Table 2 presents data on the color changes over time for the three soils and two clays. At the end of the first year of experimentation, approximately 53% of all the soil units and 75% of the clay units had changed color. In general, these changes were in the direction of a darker (increased value number) and/or grayer (increased chroma number) color.

In general, minimal color changes occurred with Oakville soil equilibrated with the four solvents over 1 year. Anthony soil equilibrated with unleaded gasoline, diesel fuel, and ethylbenzene experienced no color changes over 1 year; however, Anthony soil equilibrated with water experienced a unit change in chroma and value during the first year.

Of the three soils, Amarillo soil equilibrated with all four solvents experienced the most significant color changes. Amarillo soil equilibrated with water showed a major change in hue, from 7.5YR to 10YR. Amarillo soil equilibrated with ethylbenzene also showed a major change in hue, from 5YR to 7.5YR. Amarillo soil equilibrated with unleaded gasoline experienced changes in chroma and value, typically from 7.5YR 4/2 to 7.5YR 3/4. Also, Amarillo soil equilibrated with diesel fuel showed changes in chroma, from 7.5YR 3/4 to 7.5YR 3/3.

As presented in Table 2, kaolinite equilibrated with water showed no color change over 1 year. However, kaolinite equilibrated with unleaded gasoline and ethylbenzene experienced a unit change in value, from 2.5Y 8/2 to 2.5Y 7/2. Also, kaolinite equilibrated with diesel fuel showed changes in hue, value, and chroma, from 2.5Y 8/2 to 10YR 7/1.

Montmorillonite equilibrated with all solvents except ethylbenzene experienced color changes. Montmorillonite equilibrated with water showed a unit change in chroma, from 5Y 5/2 to 5Y 5/3, while montmorillonite equilibrated with diesel fuel showed a unit change in value, from 5Y 4/2 to 5Y 3/2. Also, montmorillonite equilibrated with unleaded gasoline showed a slightly perceptible change of chroma and value of less than one unit.

A further assessment of the data indicates that the range of the number of weeks for the first color change to occur (i.e., the second color listed in Table 2) was 1 to 29 weeks. In addition, the range of the number of weeks for the second color change to occur (i.e., the third color listed in Table 2) was 9 to 42 weeks. Forty-one percent of the first color changes occurred by 1 week after the initiation of this

TABLE 2

Rate of Color Changes for Three Soils and Two Clays Equilibrated with Four Solvents

Liquid	Temp (˚F)	Initial color[a] (hue, value/chroma)	Second color (hue, value/chroma)	Equilibration time (weeks)	Third color (hue, value/chroma)	Equilibration time (weeks
			Oakville Soil			
Water	40	2.5Y, 4/4[b]	NC			
	55	2.5Y, 4/4	NC			
	70	2.5Y, 4/4	NC			
Gasoline[c]	40	2.5Y, 4/4	NC			
	55	2.5Y, 4/4	NC			
	70	2.5Y, 4/4	5Y, 4/3	18	NC	
Diesel fuel	40	2.5Y, 4/4	5Y, 4/3	28	NC	
	55	2.5Y, 4/4	NC			
	70	2.5Y, 4/4	NC			
Ethylbenzene	40	2.5Y, 4/4	NC			
	55	2.5Y, 4/4	NC			
	70	2.5Y, 4/4	NC			
			Anthony Soil			
Water	40	10YR, 4/2	10YR, 4/3	4	10YR, 3/3	11
	55	10YR, 4/2	10YR, 4/3	4	10YR, 3/3	11
	70	10YR, 4/2	10YR, 3/3	24	NC	
Gasoline[c]	40	10YR, 3/3	NC			
	55	10YR, 3/3	NC			
	70	10YR, 3/3	NC			
Diesel fuel	40	10YR, 3/3	NC			
	55	10YR, 3/3	NC			
	70	10YR, 3/3	NC			

TABLE 2 (continued)

Rate of Color Changes for Three Soils and Two Clays Equilibrated with Four Solvents

Liquid	. Temp (˚F)	Initial color[a] (hue, value/chroma)	Second color (hue, value/chroma)	Equilibration time (weeks)	Third color (hue, value/chroma)	Equilibration time (weeks
Ethylbenzene	40	10YR, 3/3	NC			
	55	10YR, 3/3	NC			
	70	10YR, 3/3	NC			
			Amarillo Soil			
Water	40	7.5YR, 3/4	7.5YR, 4/4	1	10YR, 4/3	24
	55	7.5YR, 3/4	7.5YR, 4/5	3	10YR, 4/3	22
	70	7.5YR, 3/4	7.5YR, 4/4	5	10 YR, 4/3	25
Gasoline[c]	40	7.5YR, 4/2	7.5YR, 3/4	1	7.5YR, 3/3	42
	55	7.5YR, 4/2	7.5YR, 3/4	1	7.5YR, 3/3	41
	70	7.5YR, 4/2	7.5YR, 3/4	1	7.5YR, 3/3	41
Diesel fuel	40	7.5YR, 3/4	7.5YR, 3/3	29	NC	
	55	7.5YR, 3/4	7.5YR, 3/3	29	NC	
	70	7.5YR, 4/3	7.5YR, 3/3	25	NC	
Ethylbenzene	40	5YR, 3/3	7.5YR, 3/4	1	NC	
	55	5YR, 3/3	7.5YR, 3/4	1	NC	
	70	5YR, 3/3	7.5YR, 3/4	1	NC	
			Kaolinite Clay			
Water	40	5Y, 8/1	NC			
	55	5Y, 8/1	NC			
	70	5Y, 8/1	NC			

Gasoline[c]	40	2.5Y, 8/2	2.5Y, 7/2	4	NC	
	55	2.5Y, 8/2	2.5Y, 7/2	1	NC	
	70	2.5Y, 8/2	2.5Y, 7/2	1	NC	
Diesel fuel	40	2.5Y, 8/2	10YR, 8/1	1	10YR, 7/1	11
	55	2.5Y, 8/2	10YR, 8/1	1	10YR, 7/1	11
	70	2.5Y, 8/2	10YR, 8/1	1	10YR, 7/1	9
Ethylbenzene	40	2.5Y, 8/2	2.5Y, 7/2	1	NC	
	55	2.5Y, 8/2	2.5Y, 7/2	4	NC	
	70	2.5Y, 8/2	2.5Y, 7/2	5	NC	
			Montmorillonite Clay			
Water	40	5Y, 5/2	5Y, 5/3	11	NC	
	55	5Y, 5/2	5Y, 5/3	11	NC	
	70	5Y, 5/2	5Y, 5/3	11	NC	
Gasoline[c]	40	5Y, 4/3	Slight[d]	1	NC	
	55	5Y, 4/3	Slight[d]	1	NC	
	70	5Y, 4/3	Slight[d]	1	NC	
Diesel fuel	40	5Y, 4/2	5Y, 3/2	17	NC	
	55	5Y, 4/2	5Y, 3/2	17	NC	
	70	5Y, 4/2	5Y, 3/2	17	NC	
Ethylbenzene	40	5Y, 3/2	NC			
	55	5Y, 3/2	NC			
	70	5Y, 3/2	NC			

Note: NC, No change.

[a] Initial color recorded immediately following solvent addition to experimental unit.

[b] Duplicate experimental units were averaged to obtain hue, value/chroma numbers.

[c] Unleaded regular gasoline, octane 87.

[d] Although value/chroma did not change by one or more units, a slight perceptible change of value/chroma occurred after 1 week.

experiment. Sixty-three percent of the first color changes occurred by 5 weeks after the initiation of this experiment.

These soils and clays were equilibrated with solvents at three temperatures: 40, 55, and 70°F. This temperature range spans the range of subsoil and groundwater temperatures typically encountered in the U.S. and southern Canada. In general, as temperature rises, chemical reaction rates should increase. However, a review of the temperature and color change data presented in Table 2 revealed no significant effect of temperature on rate of color change.

This paper presents data and information obtained during the first year of this ongoing study. Although the mechanism(s) responsible for the color changes in the soil and clay mixtures has not been identified, previous reports suggest that oxidation of the organic chemicals by soil/clay components may be occurring. Further investigation of the soils, clays, and experimental units will be conducted in the future.

In summary, the data and information presented above provides some useful information to scientists and engineers who investigate sites at which a release of a petroleum product has occurred. First, some petroleum products such as gasoline, diesel fuel, and ethylbenzene can change the color of soils and clays; therefore, soil and clay color can potentially be useful for identifying areas affected by the release of some petroleum products. Second, initial color changes in soils or clays mixed with petroleum products tend to occur rapidly (within 1 week); however, changes in some soils and clays can take a half year or longer to occur. Third, color change in soils and clays can be an ongoing process with some petroleum products, such as in Amarillo sandy loam soil.

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