



Project Summary

Soil, Clay, and Caustic Soda Effects on Solubility, Sorption, and Mobility of Hexachlorocyclopentadiene

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This study on the aqueous chemistry, sorption, and mobility of hexachlorocyclopentadiene (C-56) in soil materials was initiated to provide information on its behavior in the environment, particularly on its movement through soil at land disposal facilities for hazardous wastes. Studies showed that the solubility of C-56 in water, soil extracts, and sanitary landfill leachates ranged from 1.03 to 1.25 ppm. Sodium hydroxide (caustic soda) and sodium chloride decreased the solubility of C-56 in water as the salt concentration increased; sodium hypochlorite slightly increased the solubility of C-56; and sodium perchlorate had no significant effects due to increasing salt concentration on the solubility of C-56. A caustic brine composed of a mixture of the salts was intermediate in decreasing solubility.

The half-life of C-56 in water was about three months at both 22°C and 35°C, indicating little temperature dependence. C-56 is very photosensitive, and its half-life was less than four minutes in aqueous solution and less than 1.6 minutes in hexane or methanol solution. Studies also indicated that pH did not significantly affect the C-56 hydrolysis rate in aqueous solution; however, iron caused an increase in the hydrolysis rate. At least 12 products of photolysis and hydrolysis were identified. Pentachlorocyclopentenone, hexachlorocyclopentenone, pentachloropentadienoic acid, cis- and trans-pentachlorobutadiene, and tetrachlorobutenyne were the major products identified.

The presence of salts in solution dramatically affected the sorption of C-56; brine, NaCl, and NaOH caused an increase in sorption while NaOCl caused a decrease in sorption. There was also a high direct correlation between the total organic carbon (TOC) content of soils and the amount sorbed.

C-56 remained immobile in the soils when leached with water, landfill leachate, or caustic brine but was highly mobile when leached with organic solvents. In a soil column leaching study, some hydrolysis products of C-56 were much more mobile than C-56, indicating they might migrate and generate environmental problems.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Environmental concerns have created a demand for information on land disposal of toxic organic substances such as hexachlorocyclopentadiene (C-56 or "hex" waste). C-56 is a highly toxic compound that produces systemics of unknown mechanism in mammals and has been reported to have caused significant decreases in survival of fathead minnows at concentrations as low as 7.3 ppb.

C-56 has no end uses of its own but is commercially important as a chemical

intermediate for producing chemical feed stocks, pesticides, adhesives, resins, and other related products. The present environmental concern is the disposal of large quantities of industrial wastes containing C-56. A major source of C-56 wastes comes from manufacturing chlorinated insecticides.

The phenomenon of salting-out a nonelectrolyte from an aqueous solution by adding salt is well known. Thus, the high salt content of the caustic soda brine waste water would be expected to cause changes in the aqueous solubility of C-56. Because sorption of C-56 by soil materials is a function of concentration, knowledge of how the solubility changes with brine concentration is important to accurately predict attenuation and mobility.

C-56 is extremely volatile and photoreactive in sunlight. Near-surface half-lives of C-56 in aquatic systems are less than 10 minutes. C-56 shows an unexpected tendency to undergo the Diels-Alder reaction with many dienophiles at temperatures between 20°C and 200°C. It condenses even with simple olefins which normally do not react with dienes and with polynuclear aromatic hydrocarbons. Thus, the apparent disappearance of C-56 from the environment should not be construed to mean that it is always degraded to smaller molecules; it may condense into larger molecular weight compounds. Although C-56 has been used in the chemical industry for decades, there is a dearth of information on the environmental impacts of the compound on aquatic or soil systems.

The principal objectives of this research were to determine the attenuation mechanisms and capacity of selected clay minerals and soils for C-56, to determine the effects of caustic brine on the attenuation and solubility of C-56, to study the aqueous chemistry of C-56, and to develop a chemical model to predict C-56 migration through soil materials.

Experimental Materials

A reagent grade C-56 was obtained from Pfaltz and Bauer, Inc., Stamford, CT, and was used without further purification. An analytical standard of C-56 (lot #0213) was also obtained from EPA in Research Triangle Park, NC. Both materials were identical and the purity was about 98 percent. Water, soil extracts, and landfill leachates of varying content of dissolved organic carbon (TOC) were collected and analyzed. The samples

used in the C-56 solubility studies and their respective TOC values are given in Table 1. TOC values in water samples ranged from 0.32 to 271 ppm; this allowed us to determine if solubility differences occurred as a result of dissolved organic matter in water.

The sorbents used in the sorption and mobility studies were four clay minerals, seven soils, a clean sand, and some low temperature ashed soils and muck. The carbonaceous sorbents Amborsorb XE-348 and activated bone carbon were also selected for study because of their potentially high sorption capacity for C-56 from aqueous solution.

Results

Solubility of C-56 in Waters and Leachates

The solubility of C-56 in distilled water, deionized water, tap water, Sugar Creek water, soil extracts, and landfill leachates varied from 1.03 ppm in Sugar Creek water to 1.25 ppm in DuPage landfill leachate. The results are given in Table 1.

Effect of Dissolved Salts on the Solubility

The effect of several soluble salts on the solubility of C-56 was treated by fitting the solubility data to the Setschenow equation:

$$\log \frac{S_0}{S} = Km$$

where S_0 is the solubility (ppm) of C-56 in tap water and S its solubility (ppm) in a salt solution of concentration m (mole/L). Representative data for C-56 plotted according to the Setschenow equation are shown in Figure 1. Of the three salts studied, sodium hydroxide and sodium

chloride decreased the solubility of C-56 in tap water and sodium hypochlorite slightly increased its solubility. The three salt mixtures (brine) were intermediate in depressing C-56 solubility. Sodium perchlorate did not significantly affect the solubility of C-56. The results indicated that there was an anion effect and that the effect of the individual salts upon C-56 solubility was additive.

Photolysis and Hydrolysis

C-56 was found to be photoreactive. The rate of photolysis in aqueous solution and organic solvents followed a first-order reaction. Values of the first order rate constant (K), the half-life ($t_{1/2}$), and correlation coefficient (r^2) between concentrations and times for the photolysis of C-56 in solution exposed to sunlight, long-wave UV, and short-wave UV light are given in Table 2. Representative first-order degradation plots of C-56 photolysis in tap water exposed to long and short-wave UV light are given in Figure 2. C-56 photolyzed much faster in hexane than in tap water or methanol.

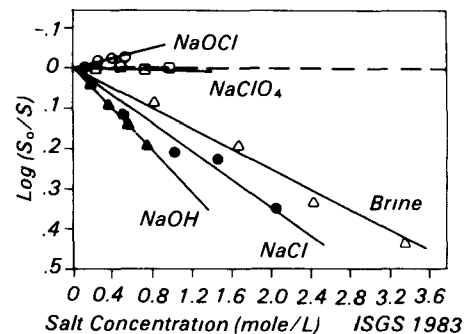


Figure 1. Effect of dissolved salts on the water solubility of C-56 at 22°C ± 1°C—plot according to the Setschenow equation.

Table 1. Solubility of C-56 at 22°C ± 1°C After 15 Hours Equilibrium in Waters and Landfill Leachates Using Centrifugation Technique

Waters and Leachates	TOC of Waters and Leachates (ppm)	Concentration (mg/L)
Distilled water	0.32	1.11
Deionized water	0.50	1.14
Tap water	1.31	1.08
Sugar Creek water	7.62	1.03
Bloomfield soil extract (soil:tap water = 1:3)	16.00	1.06
Catlin soil extract (soil:tap water = 1:3)	49.80	1.20
Blackwell sanitary landfill leachate	235.00	1.19
DuPage Sanitary landfill leachate	271.00	1.25

Table 2. First-Order Rate Constant (K), Half-Life ($t_{1/2}$), and Regression Coefficient (r^2) for the Photodegradation of C-56 in Distilled Water, Methanol, and Hexane Under Sunlight, Long-Wave UV Light (L-UV), and Short-Wave UV Light (S-UV)

Treatment	K (min ⁻¹)			$t_{1/2}$ (min)			r^2		
	Sun	L-UV	S-UV	Sun	L-UV	S-UV	Sun	L-UV	S-UV
C-56 in water	0.24	0.30	0.019	3.47	2.28	36.47	1.00	1.00	1.00
C-56 in methanol	0.30	0.32	0.006	2.32	2.17	115.50	1.00	0.99	1.00
C-56 in hexane	0.45	0.45	0.013	1.55	1.55	53.31	1.00	1.00	0.99

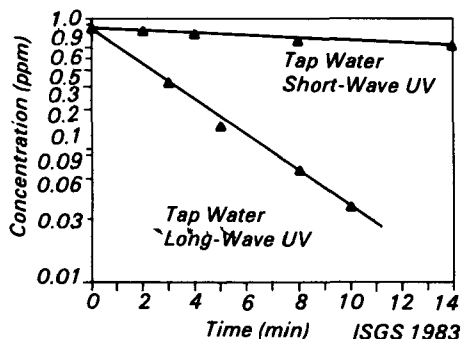


Figure 2. First-order degradation plot of tap water soluble C-56 exposed under long- and short-wave UV light.

The half-life due to photolysis of C-56 in water exposed to long-wave UV or sunlight was less than 3.5 minutes (Figure 2). The half-life of C-56 in water in the dark was about three months at both 22°C and 35°C, indicating little temperature dependence. Although pH did not significantly affect the C-56 hydrolysis rate in aqueous solution, the presence of iron caused an increase in the hydrolysis rate. At least 12 products of photolysis and hydrolysis were identified. Pentachlorocyclopentenone and hexachlorocyclopentenone were the major products found in distilled water. Cis- and trans-pentachlorobutadiene, tetrachlorobutenyne, and pentachloropentadienoic acid were the major products identified in mineralized water. Pentachlorocyclopentenone which is unstable under high temperature conditions in hexane solution and in water was dimerized and then converted to hexachloroindone. A postulated degradation pathway of C-56 is shown in Figure 3.

Sorption by Soil Materials, Activated Carbon, and Amborsorb^R Carbonaceous Sorbent

All data were fitted by linear regres-

sion to the log form of the empirical Freundlich adsorption equation:

$$\log \frac{x}{m} = \log K_f + N \log C$$

where $x = \mu\text{g}$ of compound sorbed; $m = \text{weight of sorbent (g)}$; $C = \text{equilibrium concentration of the solution } (\mu\text{g/mL})$; and K_f and N are constants. Values of K_f and N were obtained

from the regression equations as the intercepts at a concentration of 1 ppm and the slope, respectively. The Freundlich parameters and the correlation coefficient (r^2) between the amount of C-56 sorbed by a unit of sorbent and the equilibrium concentration of C-56 are shown in Table 3. The molar K (K_f) was calculated from mass K (K_f) by using the equation described by Osgerby:

$$K_f(\text{molar}) = \frac{K_f(\text{mass}) \times \text{Mol wt}^N}{\text{Mol wt}}$$

where Mol. wt. is molecular weight of the compound, K (mass) is the Freundlich K_f , and N is the slope of the isotherm plotted according to the Freundlich equation.

The sorption of C-56 on these seven soils followed the series: muck > Bryce > muck + Catlin (1:1) > #5 soil > Catlin > Flanagan > Bloomfield > Ava.

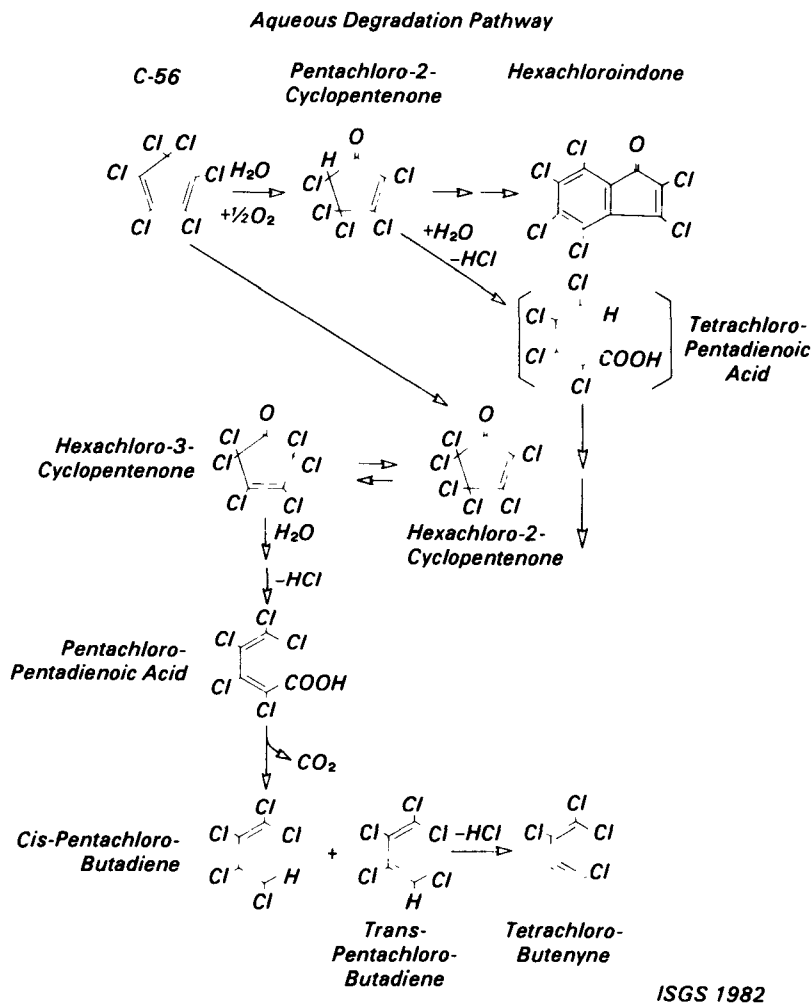


Figure 3. Proposed pathway for the degradation of C-56 in aqueous solution.

Table 3. Freundlich K_f , N , Correlation Coefficient (r^2), and Molar K_F for Sorption C-56 by Various Sorbents from Tap Water Aqueous Solution at 22°C

Sorbents	Freundlich parameters			
	K_f ($\mu\text{g}^{(1-n)}\text{mL}^n\text{g}^{-1}$)	N	r^2	K_F ($\text{nmole}^{(1-n)}\text{mL}^n\text{g}^{-1}$)
Carbon Sorbents				
Activated carbon	16,854	0.60	0.9982	28,371
Ambersorb	2,706	0.63	0.9736	4,381
Soil Materials				
Houghton Muck B	1,045	0.80	0.9822	1,356
Muck B ashed 1 day	910	0.76	0.9759	1,235.8
Muck B ashed 6 days	637	0.71	0.9641	924.5
Muck B ashed 38 days	64	0.68	0.9506	97
Bryce silty loam	385	0.86	0.9946	462
Muck A + Catlin silt loam (1:1)	284	0.76	0.9971	388
#5 soil	97	0.66	0.9725	151
Catlin silt loam	54	0.93	0.9982	59
Catlin ashed 22 days	4.74*		0.0140	4.7*
Flanagan silt clay loam	30	0.95	0.9943	32
Bloomfield loamy sand	14	0.55	0.9085	25
Ava silt clay loam	9	0.94	0.9148	10
Ava ashed 19 days	1.18*		0.0392	1.2*
Ca-bentonite	32	0.63	0.9838	52
Illite	24	0.55	0.9991	43.1
Montmorillonite	18	0.60	0.9928	30.3
Kaolinite	4.4	0.58	0.9924	7.6

*Average amount of C-56 sorbed by unit of sorbent ($\mu\text{g/g}$) (omitted from regression in Figure 4).

This suggests a relationship between the organic matter content of these soils and their sorption capacity for C-56. The sorption of C-56 on four clays followed the series: Ca-bentonite > illite > montmorillonite > kaolinite. C-56 was strongly sorbed by activated carbon and Ambersorb XE-348. The sorption constants (K_f) for activated carbon and Ambersorb XE-348 were 16,854 and 2,706, respectively. The results indicated that activated carbon and Ambersorb XE-348 were much more effective than most earth materials in removing C-56 from water.

Effect of Earth Material TOC on Sorption

The relationship between the total organic carbon (TOC) content of 15 earth materials used as sorbents and sorption of C-56 (Table 3) was investigated. The molar K (K_F) plotted as a function of TOC (percentages) is shown in Figure 4. A high correlation (r^2) between K_F and TOC (%) was found with a linear regression relation of:

$$K_F = 42.65 \text{ TOC (\%)}$$

$$(r^2 = 0.972)$$

$$K_{oc} = 4,265$$

The slope of the line from Figure 4 yields a new sorption constant (K_{oc}) normalized for the organic carbon content of the soils. The K_{oc} determined for C-56 was approximately 4,265. The results indicated that the sorption properties of soil materials for C-56 can be predicted relatively accurately when the TOC content of the involved earth materials is known. However, only a few soil materials was used to develop the equation and the relationship between sorption and types of organic matter is unknown. Even though the overall relationship is highly significant, serious discrepancies

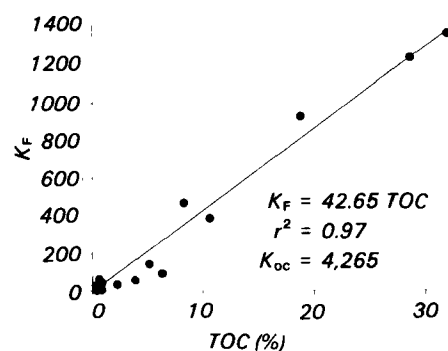


Figure 4. K_F vs. TOC for C-56 sorption by 15 soil materials.

between predicted and actual sorption for a given soil may occur. Therefore, caution should be used in interpreting and using these results.

Effect of Soluble Salts on Sorption

The results showed that all the salts and brine dramatically affected sorption. The change in sorption followed the inverse trend of the Setschenow parameters (K). Salts causing the greatest depression in solubility also caused the largest increase in sorption and vice versa. The effect of soluble salts on C-56 solubility appears to be related to its sorption by soil materials.

Mobility of C-56 in Soils: Determination by Soil TLC

The mobility of C-56 in soils, expressed as R_f values, is summarized in Table 4. According to the results, C-56 stayed immobile in all soils when leached with tap water, caustic brines or landfill leachate. However, C-56 was highly mobile when leached with organic fluids such as acetone/water mixtures, acetone, methanol, or dioxane. The mobility of C-56 increased when

Table 4. Mobility of Hexachlorocyclopentadiene in Several Soil Materials Leached With Various Solvents as Measured by Soil TLC

Soil Materials	<i>R_i Value*</i>							
	Caustic 12-4-3	Brine (%)** 3-1-0	Tap water	Landfill leachate	Acetone/water (1:1)	Methanol	Acetone	Dioxane
Muck soil	ND***	ND	0.00	0.00	0.09	0.05	0.14	0.64
Catlin silt loam	0.00	0.00	0.00	0.00	0.79	0.88	0.97	0.99
Flanagan silt clay loam	ND	ND	0.00	0.00	0.84	0.89	0.99	0.99
Ava silt clay loam	0.00	0.00	0.00	0.00	0.87	0.89	0.99	0.96
Bloomfield limestone	0.00	0.00	0.00	0.00	0.87	0.97	0.98	0.99
Ottawa sand	ND	ND	ND**	0.00	0.90	ND	ND	0.98

*Computed from statistical peak analysis of data by using values of 1st moment for grouped data.

**NaCl - NaOCl - NaOH (in tap water).

***ND = Not determined.

leached with acetone/water mixtures as the percentages of acetone increased in water. Mobility of C-56 in soil was proportional to the solubility of C-56 in the solvent and to the soil organic content. C-56 was significantly more mobile in sandy soil than in muck soil.

The above findings are significant in C-56 waste disposal. To decrease the risk of C-56 migration from a landfill, C-56 wastes should not come in contact with leaching organic solvents or highly organic leachates. This study also suggests that migration of C-56 through soil as vapor transport may be an important mechanism.

Soil Column Leaching Study

In this study, a sample of Bloomfield loamy sand heavily spiked with C-56 to simulate a spill was leached with 192 inches of tap water. We found that 0.0005 percent of the applied compound was leached from the soil column. This loss suggests that C-56 will not be readily leached from even highly contaminated soils by percolating water. However, some hydrolysis products apparently have higher solubility in water than C-56 and were much more mobile in soil. From this study, it was concluded that the secondary products of C-56, rather than C-56 itself, might migrate and cause environmental problems.

Recommendations

The results of this study showed that C-56 was photoreactive and subject to hydrolysis and sorption reactions. However, the disappearance of C-56 from the environment does not mean that it is always degraded to smaller molecules or sorbed to soil particles.

C-56 has also been shown to condense into compounds of larger molecular weight. To determine the full environmental impacts of C-56 on aquatic systems, further study of the toxicity and mobility of C-56 breakdown and/or condensation products is essential.

Almost no attenuation of C-56 by soils occurred when soil contaminated with C-56 was leached with organic solvents. To decrease the risk of potential migration of C-56 from a landfill, C-56 wastes and organic solvents should not be disposed of in the same landfill location and C-56 waste should not come in contact with leaching organic solvents or highly organic leachates. Additional research is also needed to determine the chemical transformation of C-56 in soils, in real environmental settings, especially in landfills where buried C-56 wastes may come in contact with organic solvents, acids, or iron drums.

The results and conclusions derived from this study deal specifically with attenuation and mobility of C-56 in the liquid phase. Vapor phase transport through soil pores was ignored; for compounds such as C-56 which have an appreciable vapor pressure—this means of migration may be a significant mechanism for redistribution. More information is needed to assess the magnitude of this means of migration for all organic wastes including C-56.

The full report was submitted in partial fulfillment of Grant No. R806335 by the Illinois State Geological Survey. The report, entitled "Soil, Clay, and Caustic Soda Effects on Solubility, Sorption, and Mobility of Hexachlorocyclopentadiene," was published as Environmental Geology Note 104 by the Illinois State Geological Survey.

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Mike H. Roulier is the EPA Project Officer (see below).

The complete report, entitled "Soil, Clay and Caustic Soda Effects on Solubility, Sorption, and Mobility of Hexachlorocyclopentadiene," (Order No. PB 84-116 060; Cost: \$11.95, subject to change) will be available only from:

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