soil, clay, and caustic soda effects on solubility, sorption, and mobility of hexachlorocyclopentadiene

S.F. Joseph Chou
Robert A. Griffin

Prepared in cooperation with Municipal Environmental Research Laboratory U.S. Environmental Protection Agency

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Chou, S. F. Joseph


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Cincinnati, OH 45268

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DISCLAIMER

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The Environmental Protection Agency was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Numerous examples of noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem. This report summarizes the results of research funded in part by the Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, Cincinnati, Ohio and conducted by the Illinois State Geological Survey.

The Municipal Environmental Research Laboratory is concerned with research to develop new and improved technology and systems to prevent, treat, and manage wastewater and other pollutant discharges from municipal and community sources, to preserve and treat drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research. We view it as a vital communications link between the researcher and the user community.

This publication describes the attenuation mechanisms and capacity of selected clay minerals and soils for hexachlorocyclopentadiene (C-56), the effect of caustic-soda brine on the attenuation and solubility of C-56, the aqueous chemistry of C-56, and a chemical model to predict C-56 migration through soil materials.

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ABSTRACT

The aqueous chemistry, sorption, and mobility of hexachlorocyclopentadiene (C-56) in soil materials were studied in the laboratory. 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 concentration of the salt 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 effect of individual salts upon C-56 solubility was approximately additive.

The half-life of C-56 in water was approximately 3 months at both 22°C and 35°C, indicating little temperature dependence. When C-56 was exposed to sunlight and long-wave UV-light, the half-life of C-56 was less than 4 minutes in aqueous solution and less than 1.6 minutes in hexane or methanol solution. 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, tetrachlorobutene, and pentachloropentadienoic acid were the major products identified in mineralized water. Pentachlorocyclopentenone, unstable under high temperature conditions in hexane solution and in water, was dimerized and then converted to hexachloroindone.

Freundlich adsorption isotherm plots of C-56 sorption on soils, clay minerals, activated carbon, and Ambersorb XE-348 generally yielded linear regression lines with very high coefficients of correlation between the amount of C-56 adsorbed by a unit of adsorbent and the equilibrium concentration of C-56. 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. The increase in sorption was inversely related to the Setschenow parameter, indicating that the change in sorption was directly related to the effect of the salts on the solubility of C-56. The sorption capacity of C-56 was highly correlated with the total organic carbon (TOC) content of soil materials ($r^2 = 0.97$), which was the dominant soil characterization parameter; sorption appears to be predictable from the TOC content of soils.

The mobility of C-56 in six soils was measured with several leaching solvents using soil thin-layer chromatography (TLC) and column leaching studies. 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. A further conclusion was that several degradation products of C-56 migrated through soils faster than C-56 itself and that the degradation products of C-56 warrant further study.
INTRODUCTION

Recent environmental legislation (the Resource Conservation and Recovery Act [RCRA] and others) has created a demand for information regarding the land disposal of toxic organic waste substances such as hexachlorocyclopentadiene (called HCCPD, Hex, PCL, or C-56). Small amounts of C-56 are occasionally present as impurities in pesticides and some has undoubtedly entered the environment in this way. The most likely route of entry into the environment arises from disposal of residues from the manufacture of products using C-56. Currently, major environmental concern is the disposal of the large quantities of industrial wastes containing C-56. Although C-56 has been used in the chemical industries for decades, little is known about its environmental impact on aquatic or soil systems.

The purpose of this research was to determine the attenuation mechanisms and capacity of selected clay minerals and soils for C-56, to determine the effects of caustic-soda 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.

Chemistry of C-56

Hexachlorocyclopentadiene is a dense, oily, pale to greenish-yellow liquid. Its molecular formula is C₅Cl₆; its structure formula is:

\[
\text{Hexachlorocyclopentadiene (C-56)}
\]

C-56 has a molecular weight of 272.77; a vapor pressure of 1 mm Hg at 78-79°C, 0.1 mm Hg at 25°C (Atallah et al., 1980), and a density of 1.7119 (20°/4°C) (Ungnade and McBee, 1958). The solubility of C-56 in water has been variably reported as about 0.8 ppm (Lu et al., 1975), 1.8 ppm (Zepp et al., 1979), and 2 ppm (Atallah et al., 1980).

C-56 is extremely volatile and photoreactive in sunlight with near-surface half-lives in aquatic systems of less than 10 minutes (Zepp et al., 1979). C-56 shows an unexpected tendency to undergo the Diels-Alder reaction with many dienophiles at temperatures between 20° and 200°C. It condenses even with simple olefins, which normally do not react with dienes, and with polynuclear aromatic hydrocarbons, such as naphthalene and anthracene (Ungnade and McBee, 1958). Thus, the apparent disappearance of C-56 from the environment in routine multi-residue analyses should not be construed to mean that it is always degraded to smaller molecules, even though stable bioaccumulated metabolites of C-56 have been found (Lu et al., 1975).
Manufacture and industrial uses

In the United States only two chemical companies have produced C-56: Hooker Chemical Company at Montague, MI, and Niagara Falls, NY; and Velsicol Chemical Corporation at Memphis, TN (SRI, 1978). Hooker sold hexachlorocyclopentadiene as C-56®; Velsicol's trade name is PCL; it is occasionally referred to in the literature as "hex" or as "hex waste".

The total production of C-56 in the United States was approximately 50 million pounds in 1962 (Whetstone, 1964); Lu et al. (1975) estimated that the same amount was produced in 1972, and a report prepared for Hooker cited an annual production figure of about 50.5 million pounds (Equitable Environmental Health Inc., 1976). On the basis of these reports, the total production of C-56 in the 13-year period from 1962 to 1975 is estimated to be about 650 million pounds.

The major uses of C-56 have been in the preparation of the chlorinated cyclodiene insecticides aldrin, dieldrin, endrin, chlordane, heptachlor, endosulfan, Kepone®, and mirex; the fire-retardant monomers chlorendic acid (CA) and chlorendic anhydride (CAN), used primarily in polyester resins and to a lesser extent in alkyd resin coatings; and the fire-retardant plastic additives known as Dechloranes® (Kirk-Othmer, 1964; U.S. EPA, 1977; Sanders, 1978).

Although there are recently enacted governmental bans on the use of certain chlorinated pesticides, there is no documentation that the total production of C-56 has significantly subsided. The reason may be that C-56 continues to be used as a raw material in the production of fire retardants and of pesticides for export (Bell, Ewing, and Lutz, 1978; National Academy of Sciences, 1978).

Environmental effects

The toxicological hazards, persistence, and widespread environmental contamination of some of the C-56-derived insecticides are well known (IARC, 1974); however, very little is known about the health and environmental effects of C-56, and the available information on CA, CAN, and the dechlorane materials is very meager.

C-56 produces systemic toxicity of unknown mechanism in mammals via ingestion, inhalation, and dermal exposure. Degenerative changes in the brain, heart, adrenals, liver, kidneys, and lungs were observed in severely poisoned animals (U.S. EPA 1977).

In a model ecosystem study, Lu et al. (1975) reported that C-56 has considerable environmental stability and moderate ecological magnification potential in aquatic organisms. Spehar et al. (1977) reported in a laboratory study that the bioconcentration factor was 11 for whole-body fathead minnows after 30 days exposure. C-56 showed adverse effects to the fathead minnows at concentrations as low as 3.7 ppb. Significant decreases in survival occurred at 7.3 ppb. C-56 was also toxic to mammals (Treon, Cleveland, and Cappel, 1955). An incident at a sewage treatment plant in Louisville, Kentucky—in which scores of workers experienced a variety of toxic symptoms following the improper disposal of C-56.
manufacturing wastes—created a great demand for information on the effects of C-56 exposure on humans (Carter, 1977).

C-56 has been identified and quantified in waste water, receiving streams, rivers, fish, soil, sediment, and air surrounding pesticide plants (Spehar et al., 1977; Swanson, 1976; Carter, 1977). C-56 also has proven to be a potent irritant. Industrial and laboratory workers have experienced irritation of the eye, irritation of the upper airway passages and headaches upon exposure to C-56 vapors and burns upon contact of skin with the liquid (Ingle, 1953; Carter, 1977; personal experiences of the authors).

Disposal and soil attenuation

A literature search of Chemical Abstracts and Pollution Abstracts from 1970 to present yielded not one publication dealing specifically with the disposal, attenuation, or mobility of C-56 or "hex" waste in soil or soil materials.

In unpublished literature, Weber (1979) reported that C-56 was strongly adsorbed by soil colloids and Rieck (1977a, 1977b) demonstrated poor extractability of C-56 from soil treated with C-56, which provides indirect evidence of strong adsorption.

A major source of C-56 wastes is the manufacture of insecticides such as chlordane and heptachlor. The largest chlordane manufacturing plant in the U.S. is located in east-central Illinois. The liquid waste stream from the plant (considered typical waste for the industry) consisted of about 400,000 gallons per day that varied in chemical composition daily. Approximate organic composition consisted of a saturated suspension of hexachlorocyclopentadiene and small amounts of chlordane, hexachlorobenzene, heptachlor, and heptachlor epoxide. The mineral content averaged 12 percent sodium chloride, 4 percent sodium hypochlorite, and 3 percent sodium hydroxide (caustic-soda). The waste water pH was typically 11.9 to 12.0 (Gibb et al., 1978; Illinois EPA records; and personal communications). This mixture is referred to as "hex waste". The "hex waste" is not only generated during chlordane manufacture, but also during production of resins, adhesives, pesticides, fire retardants, and other related products. The study of C-56, therefore, has broad applicability to many industries.

There is a dearth of information regarding the attenuation and mobility of C-56 or "hex" wastes in soil or soil materials and of the effects of caustic-soda brines on the solubility and mobility of this compound. There are virtually no data with which to assess the migration of "hex" wastes through soil or soil materials such as clay liners of waste impoundments or landfills.

There are also complicating factors due to the effects of caustic brines on attenuation and solubility of C-56. For example, a short-term study commissioned by the plant showed that activated carbon was not feasible for removal of C-56 from the waste water because of interference from the sodium hypochlorite. Hypochlorite concentrations had to be less than 100 ppm to obtain adequate adsorption of C-56 by the carbon; plant waste waters usually contain 30,000 to 40,000 ppm of hypochlorite.
Caustic brines may also change the solubility of the C-56. The phenomenon of salting-out of a nonelectrolyte from an aqueous solution by addition of salt is well known. An empirical equation that yields a good first approximation of salting-out data that would be suitable for use in predicting environmental contamination is that of Setchenow (1892):

\[ \log \frac{S}{S_0} = Km \]

in which \( S_0 \) is the solubility in pure water, \( S \) is the solubility in a salt solution of molality \( m \), and \( K \) is a constant sometimes called the "salting coefficient". Determination of the salting coefficient experimentally for the "hex" waste would then allow prediction of the solubility of C-56 from a knowledge of brine concentration. Since sorption of C-56 by soil or clay is a function of concentration, knowledge of how the solubility changes with brine concentration is essential if accurate predictions of migration and mobility are to be made.

CONCLUSIONS

Studies of the aqueous chemistry, sorption, and mobility of C-56 have led to the following conclusions:

- C-56 reached saturation concentration in water in less than 15 hours.
- The solubility of C-56 in tap water, Sugar Creek water, soil extracts, and landfill leachates ranged from 1.03 to 1.25 ppm. The relatively small increases in the solubility of C-56 were related to the increasing total organic carbon (TOC) content of the respective waters.
- Increasing concentrations of sodium hydroxide and sodium chloride decreased the solubility of C-56 in water, while increasing concentrations of sodium hypochlorite slightly increased the solubility of C-56 in water. A caustic brine composed of a mixture of the above salts was intermediate in decreasing solubility. Sodium perchlorate was inert, and increasing its concentration did not significantly affect the solubility of C-56. The effect of the various soluble salts upon C-56 solubility was approximately additive and a function of the anion associated with the salt.
- The rate of hydrolysis of C-56 in water was not significantly affected by pH; however, additions of iron did increase the rate of the hydrolysis reaction. The half-life of C-56 in water in a sealed glass container protected from light was approximately 3 months at both 22°C and 35°C, thus indicating that the hydrolysis rate was not temperature dependent over this temperature range.
- The rate of photolysis of C-56 in aqueous solution and organic solvents followed a first-order reaction. The half-life of C-56 in water or organic solvents exposed to long-wave UV light or sunlight was less than 3.5 minutes; C-56 photolyzed much faster under long-wave UV light than under short-wave UV light.
- At least 12 products of photolysis and hydrolysis were identified. Hexachlorocyclopentenone and pentachlorocyclopentenone were the major
products found in distilled water. Cis- and trans-pentachloro-
butadiene, tetrachlorobutenylene, and pentachloropentadienoic acid were
the major products identified in mineralized water.

Pentachlorocyclopentenone was not stable under high-temperature
conditions—it was dimerized and then converted to hexachloroindone.

The sorption of C-56 by soils, clays, activated carbon, and Ambersorb
XE-348 from aqueous solutions could be described by the Freundlich
adsorption equation. All correlation coefficients ($r^2$) were high
except for low temperature ashed Catlin and Ava soil.

The presence of salts in solution dramatically affected the sorption
of C-56. Brine, NaCl, and NaOH caused an increase in sorption and
NaOCl caused a decrease in sorption. The increase in sorption was
inversely related to the Setschenow parameter, indicating that the
change in sorption was directly related to the effect of the salts on
the solubility of C-56.

A high direct linear correlation was found between the total organic
carbon (TOC) content (0.19 to 32.17%) of the soils studied and the
amounts of C-56 sorbed ($r^2 = 0.97$).

C-56 remained immobile in soils when leached with water, landfill
leachates, and caustic brine solution, but was highly mobile when
leached with organic solvents such as methanol, dioxane, acetone,
and/or acetone/water mixture (1:1 v/v). Mobility of C-56 in soil was
proportional to the soil organic carbon content and the solubility of
the compound in the leaching solvent. Some degradation products of
C-56 were more mobile than C-56 itself during soil column leaching
studies.

**RECOMMENDATIONS**

The results of this study showed that C-56 was very photoreactive and
subject to hydrolysis and sorption reactions. However, the disappearance
of C-56 from the environment should not be construed to mean that it is
always degraded to smaller molecules or sorbed to soil particles. C-56
has also been shown to have the potential 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 transformations 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.

METHODS AND 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 US-EPA, Research Triangle Park, NC. Both materials were essentially identical and the purity was approximately 98 percent.

Waters, soil extracts, and landfill leachates of varying content of dissolved organic carbon (TOC) were collected and analyzed. The samples used in studies of C-56 solubility and their respective TOC values are given in table 1. The water samples contained a range in TOC values varying from 0.32 to 271 ppm; this allowed us to determine if differences in solubility occurred as a result of dissolved organic matter in water.

The sorbents used in the sorption and mobility studies are given in table 2, along with some results from characterization measurements performed on the sorbents.

The organic matter content of some sorbents was varied by using the low-temperature ashing (LTA) techniques for bituminous coals described by

<p>| TABLE 1. Total organic carbon (TOC) analysis of waters used in C-56 solubility study |
|--------------------------------------|------|</p>
<table>
<thead>
<tr>
<th>Waters</th>
<th>TOC (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>0.50</td>
</tr>
<tr>
<td>Distilled water</td>
<td>0.32</td>
</tr>
<tr>
<td>Tap water</td>
<td>1.31</td>
</tr>
<tr>
<td>Sugar Creek water</td>
<td>7.62</td>
</tr>
<tr>
<td>Bloomfield soil extract (soil:tap water = 1:3)</td>
<td>16.00</td>
</tr>
<tr>
<td>Catlin soil extract (soil:tap water = 1:3)</td>
<td>49.80</td>
</tr>
<tr>
<td>Blackwell sanitary landfill leachate</td>
<td>235</td>
</tr>
<tr>
<td>DuPage sanitary landfill leachate</td>
<td>271</td>
</tr>
<tr>
<td>Material</td>
<td>Source</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Panther Creek montmorillonite</td>
<td>American Colloid Co.</td>
</tr>
<tr>
<td>Ca-bentonite</td>
<td>International Mineral and Chemical Corp.</td>
</tr>
<tr>
<td>Illite</td>
<td>Minerva Mine, Elizabethtown, Ill.</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Pike County, Ill.</td>
</tr>
<tr>
<td>Ottawa silica sand</td>
<td>Ottawa Silica Co., Ottawa, Ill.</td>
</tr>
<tr>
<td>Ava silty clay loam</td>
<td>Effingham County, Ill.</td>
</tr>
<tr>
<td>LTA* Ava (19 days)</td>
<td></td>
</tr>
<tr>
<td>Bloomfield loamy sand</td>
<td>Mason County, Ill.</td>
</tr>
<tr>
<td>Flanagan silty clay loam</td>
<td>Champaign County, Ill.</td>
</tr>
<tr>
<td>Catlin silt loam</td>
<td>Champaign County, Ill.</td>
</tr>
<tr>
<td>LTA Catlin (22 days)</td>
<td></td>
</tr>
<tr>
<td>#5 soil silty clay loam</td>
<td>Henry County, Ill.</td>
</tr>
<tr>
<td>Bryce silty loam</td>
<td>Iroquois County, Ill.</td>
</tr>
<tr>
<td>Houghton muck B</td>
<td>McHenry County, Ill.</td>
</tr>
<tr>
<td>LTA muck B (1 day)</td>
<td></td>
</tr>
<tr>
<td>LTA muck B (6 days)</td>
<td></td>
</tr>
<tr>
<td>LTA muck B (38 days)</td>
<td></td>
</tr>
<tr>
<td>Catlin muck B + muck A (1:1)</td>
<td></td>
</tr>
</tbody>
</table>

*LTA = low temperature ashed soil to reduce TOC content
Gluskoter (1965) and Kuhn, Fiene, and Harvey (1978). An aliquot of Catlin soil and Ava soil and three aliquots of muck soil were ashed, each for different periods of time. The changes in organic matter content and surface area due to ashing are shown in table 2.

Surface areas were measured by three methods, each selected to provide different information about the surface characteristics of the sorbents. The BET gas adsorption method was used as described by Thomas and Frost (1971). Both N\textsubscript{2} and CO\textsubscript{2} were used as adsorbates. The third method was ethylene glycol adsorption as described by Bower and Gschwend (1952). The carbonaceous sorbents, Ambersorb XE-348 (Rohm and Haas) and activated bone carbon (Fisher Scientific) were selected for study because of their potentially high sorption capacity for organics from aqueous solution.

**Solubility studies**

Aliquots of 350 mL of water, aqueous soil extract, or landfill leachate were placed into 500-mL amber-glass bottles. C-56 (0.5 mL) was added to each bottle, and the bottle was capped with a teflon-lined screw cap. Preliminary studies indicated that a shaking time of 12 hours in a Lab-Line Model No. 358/water bath of moderate speed was sufficient for the sample to reach equilibrium conditions. Therefore, all solubility studies were shaken overnight (15 hours) to ensure equilibrium. The water and C-56 mixtures were shaken in a constant temperature water bath (22\textdegree\pm1\textdegree C) at moderate speed for 15 hours and then left quiescent for 3 hours.

Aliquots of 25 mL of the aqueous solutions were placed into 50-mL stainless steel centrifuge tubes and centrifuged in a constant temperature centrifuge (Beckman Model J-21B) at 22\textdegree\pm1\textdegree C at 22,700 x gravity for 30 minutes; then 10-mL aliquots of the supernatant were carefully withdrawn and placed into 22-mL screw-capped vials. All samples were extracted three times with 5 mL portions of water-saturated hexane. Each extraction was obtained by shaking the vial on a vortex mixer at fast speed for 1 minute; the hexane extract was then transferred to a graduated test tube with a Pasteur pipette.

Results of preliminary studies showed that the extraction technique used in this study offered improved efficiency over conventional separatory funnel extraction techniques. The extraction efficiency was 95 percent or better in samples spiked with C-56 at three different concentrations. Approximately 2 grams of anhydrous sodium sulfate was added into each tube to remove trace amounts of water. The extracts were then analyzed on a Hewlett-Packard (HP 5840A) gas chromatograph or a Perkin-Elmer Sigma I gas chromatograph (GC). Tribromobenzene was used as the internal standard. Both gas chromatographs were equipped with Na\textsuperscript{63} electron capture detectors. A glass capillary column was used to facilitate the separation of the degradation products of C-56 from "pure" C-56 in distilled water and deionized water extracts. The conditions for the gas chromatographic analysis for C-56 are shown in table 3.

To determine the effect of caustic brines and soluble salts on the aqueous solubility of C-56, varying amounts of soluble salts were added to water and the change of solubility measured. The concentrations and salts used are listed in table 4.
TABLE 3. Conditions for gas chromatographic analysis

<table>
<thead>
<tr>
<th>Conditions</th>
<th>HP 5840A and P-E Sigma I GC</th>
<th>Sigma I GC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column</td>
<td>6 ft x 2 mm I.D. glass column, 5% OV-17 on 100/120 mesh chromosorb WHP</td>
<td>28 m x 0.25 mm I.D. grade (SE-30), split ratio: 100 : 1</td>
</tr>
<tr>
<td>Injector temperature</td>
<td>250°C</td>
<td>250°C</td>
</tr>
<tr>
<td>Column temperature</td>
<td>150°C</td>
<td>145°C</td>
</tr>
<tr>
<td>Detector temperature</td>
<td>300°C</td>
<td>280°C</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>methane/argon, flow 32 mL/min.</td>
<td>methane/argon, velocity: 28 cm/sec.</td>
</tr>
</tbody>
</table>

Photolysis and hydrolysis studies

In the photolysis study, 35 mL portions of C-56-saturated water solutions were placed into 50-mL stainless steel centrifuge tubes and centrifuged in a constant temperature centrifuge (22° ± 1°C) at 22,700 x gravity for 30 minutes; 20-mL aliquots of the supernatant were then carefully withdrawn from each centrifuge tube and placed into a 250-mL low-actinic Erlenmeyer flask. Aliquots of 10 mL of the supernatant of the C-56-saturated distilled water were placed into 22-mL screw-cap closed vials and exposed to either outdoor sunlight, long-wave, or short-wave UV-light (Chromato-Vue Cabinet, Model CC-20, Ultra-Violet Products Inc., San Gabriel, CA) for 0, 1, 3, 5, and 7 minutes. The sunlight intensity was measured by using a YSI-Kettering Model 65A Radiometer (Yellow Springs Instrument Co., Inc.,

TABLE 4. Salts and concentrations used in C-56 solubility studies in tap water

<table>
<thead>
<tr>
<th>Salts</th>
<th>Concentrations (mole/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0* 0.513 1.026 1.465 2.051</td>
</tr>
<tr>
<td>NaOCl</td>
<td>0 0.135 0.270 0.405 0.541</td>
</tr>
<tr>
<td>NaOH</td>
<td>0 0.188 0.375 0.563 0.750</td>
</tr>
<tr>
<td>NaClO₄</td>
<td>0 0.250 0.500 0.750 1.000</td>
</tr>
<tr>
<td>NaCl + NaOCl</td>
<td>0 0.648 1.296 1.870 2.592</td>
</tr>
<tr>
<td>NaCl + NaOH</td>
<td>0 0.701 1.401 2.028 2.801</td>
</tr>
<tr>
<td>NaOCl + NaOH</td>
<td>0 0.323 0.645 0.968 1.291</td>
</tr>
<tr>
<td>NaCl + NaOCl + NaOH</td>
<td>0 0.836 1.671 2.433 3.342</td>
</tr>
</tbody>
</table>

*0 means no salt added
Yellow Springs, OH). The average sunlight intensity was 740 joules/m² (or watts-sec/m²) outside the vial. To free C-56 from the ketone reaction products reported by Chou, Fisher, and Griffin (1981), 0.5 mL of 1 N NaOH solution was added into each vial before extraction for analysis. Analyses were conducted by gas chromatography (GC) using the methods previously described.

To identify the photodegradation products in water, higher doses of C-56 (204.5 and 17,000 μg of C-56) were injected into 125-mL serum bottles containing 100 mL of distilled water. The serum bottles were sealed with teflon-faced septa and then shaken for 1 hour. The C-56 suspended samples were exposed to sunlight for 0, 12, and 60 minutes. In a separate study, 204.5 μg portions of C-56 were injected into 22-mL screw-cap closed vials containing 10 mL of 0.5 N NaOH solution and exposed to sunlight for 0 and 10 minutes. All samples were extracted with two parts of 12.5 and 5 mL water-saturated hexane, respectively. For further identification, some extracts were condensed to 1 mL under a N₂ stream. The GC analytical conditions were as noted in table 3, except that the column temperature was programmed from 120° to 250°C at 6°C/min. The initial column temperature was held for 3 minutes. To identify the hydrolysis acids, some of the photolyzed water samples were made alkaline with 10 N NaOH solution and then acidified with concentrated HCl before being extracted with hexane.

In a separate study, 5 mL of C-56 (2 ppm) in hexane and methanol was individually placed in 15-mL vials capped with teflon-lined caps; the vials were then exposed to either sunlight or long-wave UV-light for 0, 1, 3, 5, and 7 minutes. In another study, 5 mL of 0.71 ppm C-56 in hexane was pipetted into 15-mL screw-capped vials. One set of vials was covered with aluminum foil and the other set was uncovered. All samples were set on a bench top and exposed to the ceiling fluorescent lights (48" tubes) in the laboratory during working hours (8:00 a.m. to 5:00 p.m.). Two replicate samples were analyzed at 0, 2, and 8 days. To identify photodegradation products in hexane and methanol, 30 ppm and 4500 ppm of C-56 solutions were exposed under sunlight or long-wave UV-light for 10, 22, and 60 minutes.

The photolyzed organic solutions were directly analyzed by gas chromatography. The photolysis rate and the half-life were calculated using the log form of the empirical first-order reaction equation:

\[ \log C = \frac{-Kt}{2.303} + \log C_0, \text{ where } t_{\frac{1}{2}} = \frac{0.693}{K} \]

\( C_0 \) = concentration of component at time zero
\( C \) = concentration of component at time t
\( K \) = first-order reaction rate constant

Several different approaches were used in conducting the hydrolysis studies. First, 0.5 mL of C-56 was individually pipetted into 500-mL amber glass bottles containing 350 mL of pH adjusted tap water. The pH values were 2.51, 5.80, 8.45 (tap), and 11.73. Mixtures of C-56 and water were shaken at constant-temperature (22° ± 1°C) for 18 hours and then left
quiescent for at least 3 hours. Aliquots of 50 mL of the C-56-water solutions were filtered through 0.22 μm Millipore® cellulose acetate membranes that had been soaked in C-56-saturated water prior to filtration. The membranes were then washed with deionized water and 200 mL of the C-56-saturated tap water were flushed through the membrane prior to filtration of the 50 mL aliquot.

In the second study, 50-mL aliquots of the filtered aqueous C-56 were placed in 125-mL amber serum bottles and sealed with teflon-faced septa and aluminum crimp cap seals. All samples were kept in darkness and two replicate samples were analyzed at 0, 1, 2, 4, 7, and 11 days. The extraction was accomplished by placing 10-mL aliquots of the filtrates into 15-mL-vials and then extracting as previously described. In another phase of this study, the 125-mL amber serum bottles were filled with C-56 saturated tap water and distilled water, respectively. The serum bottles were then sealed and kept in a constant-temperature water bath (22° ± 1°C) under darkness. Two replicate samples of each water were analyzed at 0, 4, 10, 16, and 24 days.

To free C-56 from the ketone reaction products, 0.5 mL of 1 N NaOH solution was again added into each vial before extraction for analysis.

In a third study, 100 mL of distilled water was placed into 125-mL amber glass serum bottles and 6 μL (122.7 μg) of 20,450 ppm C-56 dissolved in acetonitrile was individually injected into each bottle. The serum bottles were sealed and kept in a constant-temperature water bath (35°C) under darkness. Two replicate samples were analyzed at 0, 1, 4, 8, 16, and 32 days. Aliquots of 20 mL of water-saturated hexane were withdrawn by hypodermic syringe and directly injected into the serum bottle through the teflon-faced septum. All samples were set on a rotary shaker and shaken for 30 minutes at 300 rpm. The extracts were withdrawn with syringe and diluted for further analysis. The hydrolysis rates were calculated as previously described.

In a fourth study, 4250 μg of C-56 was individually injected into 125-mL amber glass serum bottles containing 100 mL phosphate buffer solutions of different pH (pH values were 2.6, 5.0, 7.0, 9.24, and 12.1). All samples were vigorously shaken for 1 hour and then set in a constant-temperature water bath (22° ± 1°C) for 5 days. After 5 days the water samples were extracted and diluted for analysis. The percentage of C-56 and all impurities were calculated on the basis of total peak areas from the gas chromatograms. The same amounts of C-56 added to distilled water and hexane were used as controls.

In a fifth study, the iron catalyzed hydrolysis of C-56 was measured. Freshly cut iron wire (approximately 2 mm of SWG 30 wire) or iron powder (<100 mesh) (1 g) was placed into 125-mL amber glass serum bottles. Aliquots of 100 mL of 0.5 N HCl were added into the serum bottle containing the iron wire, and 100 mL of distilled water was added individually to a second group of serum bottles; 4250 μg of C-56 was injected into both groups of serum bottles and then sealed. All samples were shaken for 1 hour and then set at room temperature under darkness for 0 and 2 weeks. Two replicate samples of each treatment were analyzed at the two indicated periods.
The major photolysis and hydrolysis products were identified by mass spectrometry by using a Hewlett-Packard 5985 GC mass-spectrometer and data system operated by the Institute for Environmental Studies Research Laboratory, University of Illinois. A Varian CH-7 mass-spectrometer coupled to a Varian 1900 GC and support computer operated by the Illinois Natural History Survey was used to analyze some of the samples. A 30-meter fused silica flexible capillary column (SP-2100) was used on the HP 5985 GC/MS and the column temperature was programmed from 4°C to 240°C at 3°C increments per minute. A 6-ft glass column containing 5 percent OV-17 Chromosorb WHP (100/120 mesh) was used with the Varian 1900 GC and the column temperature was programmed from 120°C to 250°C at 3°C increment per minute.

Sorption studies

The batch equilibrium method was adopted for the sorption studies. Various soil types and clays (table 2) were selected as sorbents. The carbon-aceous sorbents, Ambersorb XE-348 and activated carbon, were also selected because of their potentially high sorption capacity for organics from aqueous solution.

In the sorption studies, known volumes and concentrations of C-56 solution were shaken with varying weights of sorbents at a constant temperature of 22°C ± 1°C in 125-mL amber glass serum bottles. Amber glass was used to prevent photolysis of the C-56, and each bottle was sealed with a teflon-faced septum and an aluminum crimp-cap to prevent volatilization. The initial concentration of C-56 was kept at approximately 70 to 80 percent of its maximum solubility in the aqueous solution to be tested to prevent a possible precipitation or capillary condensation of C-56 that may confound the interpretation of the adsorption results.

A preliminary kinetic study was conducted. Two doses of the Catlin soil were used; 1.0 g and 3.5 g on a dry basis were placed into 125-mL amber glass serum bottles. Aliquots of 50 mL of the filtered C-56 solution were pipetted into the bottles. The serum bottles were sealed and shaken at constant temperature. Two replicate bottles of each dose of soil were removed from the shaker at 0.5, 1, 2, 4, 6, 8, 10, and 18 hours and placed directly into a Model JS-7.5 rotor and centrifuged at a constant temperature of 22°C ± 1°C. In a preliminary study, the centrifugation time and the final temperature of the aqueous solutions in the bottles were examined. The results showed that 15 minutes of centrifugation at 4000 rpm was sufficient to separate the clays and aqueous phases; the aqueous temperatures in the bottles remained at approximately 22°C ± 1°C. Therefore, all the samples were centrifuged at 4000 rpm for 15 minutes; the seals were then broken and 10-mL aliquots of the clear supernatants were pipetted into 22-mL screw-capped vials. All aqueous samples were extracted and analyzed as previously described. In the kinetic study, the rate of sorption of C-56 by soil materials was relatively rapid; a shaking time of 2 hours was sufficient for reaching constant concentrations of C-56 in solution. Therefore, samples were shaken 4 hours in all later studies to ensure equilibrium.
Blanks were carried through all experiments to determine the degree of sorption of C-56 onto the surface of the bottles. Approximately 17 to 24 percent of the C-56 was sorbed onto the surface of the serum bottles.

The amount of sorption in each case was determined from the difference between the initial concentration and the equilibrium concentration multiplied by the volume of solution. A blank was subtracted, and the amount sorbed by each test material was computed on a unit basis by dividing by the dry weight of the sorbent.

Catlin and Flanagan soils were selected for study of the effects of caustic brines of various dilutions on the sorption of C-56. Solutions of C-56-saturated NaCl, NaOCl, NaOH, and the three salt mixtures were filtered through 0.22 μm Millipore® membranes. Part of the C-56 was volatilized during filtration; the concentration of C-56 in those filtrates was never higher than its maximum solubility; therefore, all filtrates were directly used. The same procedures previously described were followed in these sorption studies.

Mobility studies: determination by soil TLC and soil column leaching

The method used to prepare soil TLC plates has been reported previously by Griffin and his co-workers (1977). The C-56 was spotted 2 cm from the base of the plate and eluted a distance of 10.5 cm with tap water, landfill leachate, caustic brines, acetone/water mixtures, methanol, acetone, or dioxane. The plates were immersed in 0.5 cm of the solvent (eluent solution) in a closed glass chamber and were removed when the wetting front reached the 10.5-cm line. The soil plates were removed and the soil was immediately scraped off in 1-cm increments, starting 1.5 cm above the base of the plate. The soil was placed in glass tubes and extracted with hexane or other suitable organic solvents. The concentration of C-56 in the extracts was measured by GC analysis.

In a soil column leaching study, 700 grams of Bloomfield loamy sand was placed into a chromatographic column (5 cm I.D. x 50 cm long), and 5 mL of C-56 was pipetted on the soil surface in the column. After being spiked with C-56, the soil column was covered with 100 grams of Bloomfield loamy sand to reduce volatilization and was then continuously leached with 3 L of tap water (192 inches of water at 24 inches/day, representing approximately 5 to 6 times the annual rainfall in Illinois). After each 1 L of water had percolated through the soil column, 250 mL of leachate was extracted with three 30 mL portions of hexane. The hexane extract was then analyzed in the same manner as described in previous sections.
RESULTS AND DISCUSSION

SOLUBILITY OF C-56 IN WATERS, SOIL EXTRACTS, AND LEACHATES

Solubility in waters and leachates

The data from the solubility-kinetic study are shown in figure 1. The solubility of C-56 reached equilibrium after 12 hours of shaking under the test conditions.

![Figure 1. Solubility of C-56 in tap water as a function of time at 22°C](image)

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 5. An increase in TOC content in the tested waters and leachates was correlated to the slight increase observed in the solubility of C-56. The slight decrease in solubility of C-56 in tap water and Sugar Creek water (as compared to distilled and deionized water) may be due to the presence of soluble salts. The solubility of C-56 in water has previously been reported as about 0.8 ppm (Lu et al., 1975), 1.8 ppm (Zepp et al., 1979), and 2 ppm (Atallah et al., 1980).

In preliminary studies, the concentration of C-56 in pure water could not be accurately quantified because of a degradation product that had a GC retention time almost identical with that of the C-56. However, after a series of studies, the problem was overcome. To free C-56 from the degradation product, 0.5 mL of 1 N NaOH was added in the supernatant before extraction for analysis. Resolution of GC peaks for the degradation product and for C-56 are illustrated with representative capillary column GC chromatograms of tap water and deionized water-soluble C-56 in figure 2. There is a possibility that previous researchers, using packed column GC techniques, may have measured the degradation product or a combination of the degradation product and C-56 rather than "pure" C-56. This may have led to the conclusion that greater concentrations of C-56 were present in water samples than was actually the case.
Figure 2. GC chromatograms (A) deionized water soluble C-56 (B) tap water soluble C-56 (28 m x 22 mm glass capillary column)
TABLE 5. Solubility of C-56 at 22°C after 15 hours equilibrium in waters and landfill leachates using centrifugation technique

<table>
<thead>
<tr>
<th>Waters and leachates</th>
<th>Concentration (mg/L)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>1.11</td>
</tr>
<tr>
<td>Deionized water</td>
<td>1.14</td>
</tr>
<tr>
<td>Tap water</td>
<td>1.08</td>
</tr>
<tr>
<td>Sugar Creek water</td>
<td>1.03</td>
</tr>
<tr>
<td>Bloomfield soil extract (soil:tap water</td>
<td>1.06</td>
</tr>
<tr>
<td>1:3)</td>
<td></td>
</tr>
<tr>
<td>Catlin soil extract (soil:tap water</td>
<td>1.20</td>
</tr>
<tr>
<td>1:3)</td>
<td></td>
</tr>
<tr>
<td>Blackwell leachate</td>
<td>1.19</td>
</tr>
<tr>
<td>DuPage leachate</td>
<td>1.25</td>
</tr>
</tbody>
</table>

*Each value is a mean of 2 replicates except tap water which is 20 replicates.

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 (1892):

\[ \log \frac{S_0}{S} = K_m \]  

The results are given in table 6; listed are the observed solubility ratios, \( S_0/S \)--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). Table 6 also includes the Setschenow parameter, \( K \). The best values of \( K \) were determined by linear regression analysis of \( \log S_0/S \) as a function of \( m \); the coefficient of correlation \( (r^2) \) between \( \log S_0/S \) and salt concentration is also given in Table 6. Representative data for C-56, plotted according to the Setschenow equation, are shown in figure 3. Of the three salts studied, sodium hydroxide and sodium chloride decreased the solubility of C-56 in tap water (\( K = \) positive) and sodium hypochlorite slightly increased its solubility (\( K = \) negative). The three salt mixtures (brine) were intermediate in their depression of solubility of C-56. 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 approximately additive. A similar additive effect of sea water upon hydrocarbon solubility has also been reported (Gordon and Thorne, 1967a, 1967b). The Setschenow K value for combined salt solutions can be calculated by knowing the values...
TABLE 6. Effect of dissolved salts on the water solubility of C-56 at 22°C and Setschenow parameter for C-56

<table>
<thead>
<tr>
<th>Salts</th>
<th>Setschenow parameter</th>
<th>m (mole/L)</th>
<th>So/S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>r²</td>
<td></td>
</tr>
<tr>
<td>NaClO₄</td>
<td>+0.020</td>
<td>0.706</td>
<td>0.250</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.750</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.000</td>
</tr>
<tr>
<td>NaCl</td>
<td>+0.161</td>
<td>0.970</td>
<td>0.513</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.026</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.465</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.051</td>
</tr>
<tr>
<td>NaOCl</td>
<td>-0.058</td>
<td>0.889</td>
<td>0.135</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.270</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.405</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.541</td>
</tr>
<tr>
<td>NaOH</td>
<td>+0.266</td>
<td>0.996</td>
<td>0.188</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.375</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.563</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.750</td>
</tr>
<tr>
<td>NaCl + NaOCl</td>
<td>0.200</td>
<td>0.877</td>
<td>0.648</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.296</td>
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<td>1.870</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>2.592</td>
</tr>
<tr>
<td>NaCl + NaOH</td>
<td>+0.248</td>
<td>0.995</td>
<td>0.701</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>1.401</td>
</tr>
<tr>
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<td></td>
<td>2.028</td>
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<td></td>
<td></td>
<td></td>
<td>2.801</td>
</tr>
<tr>
<td>NaOCl + NaOH</td>
<td>+0.340</td>
<td>0.993</td>
<td>0.323</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>0.645</td>
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<td>0.968</td>
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<td></td>
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<td></td>
<td>1.291</td>
</tr>
<tr>
<td>NaCl + NaOCl + NaOH</td>
<td>0.147</td>
<td>0.993</td>
<td>0.836</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.671</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.433</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.342</td>
</tr>
</tbody>
</table>
of K for the individual component salts and using the following equation presented by Gordon and Thorne (1967a, 1967b):

\[
\log S_1 = \log S_1^0 - \sum_{i=1}^{n} N_i K_i C_s
\]  

(2)

where \(S_1\) is the solubility of C-56 in the salt solution, \(S_1^0\) is the solubility of C-56 in pure water, \(N_i\) is the mole fraction of the \(i\)th salt component in the combined salt, \(K_i\) is the Setschenow parameter of the \(i\)th salt component in the combined salt solution, \(C_s\) is the sum of the individual salt molarities, and \(n\) is the number of salts in the solution. Agreement between the observed \(K\) value (0.147, L/mole) and the calculated \(K\) value (0.149, L/mole) using equation (2) for the caustic brine solution data reported in table 6 was quite good. From equation (2) we can also roughly predict C-56 solubility in salt solutions of varying concentration. Values of \(S_1\) calculated from equation (2) and the observed \(S_1\) values for the brine are shown in table 7. The agreement between observed \(S_1\) values and calculated \(S_1\) values was quite satisfactory for many environmental applications.

### Table 7. Solubility of C-56 in caustic brine solution (NaCl + NaOCl + NaOH) at 22°C

<table>
<thead>
<tr>
<th>(C_s) (mole/L)</th>
<th>(S_1) observ. (mole/L x 10^6)</th>
<th>(S_1) calcd. (mole/L x 10^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td>0.836</td>
<td>3.30</td>
<td>3.00</td>
</tr>
<tr>
<td>1.671</td>
<td>2.56</td>
<td>2.25</td>
</tr>
<tr>
<td>2.433</td>
<td>1.84</td>
<td>1.74</td>
</tr>
<tr>
<td>3.342</td>
<td>1.44</td>
<td>1.27</td>
</tr>
</tbody>
</table>

*Solubility of C-56 in tap water was 4.00 mole/L x 10^6 (1.08 ppm)*
AQUEOUS CHEMISTRY OF C-56

Photolysis and hydrolysis

In studies of photolysis, C-56 was found to be very 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 (t₁/₂), and correlation coefficient (r²) between concentrations and times for the photolysis of C-56 in solutions exposed to sunlight and long-wave UV light are given in table 8. C-56 photolyzed much faster in hexane than in tap water or methanol. The half-life due to photolysis of C-56 in water was less than 3.5 minutes. A similar result has also been reported elsewhere (Zepp et al., 1979). In a separate study, it was also observed that C-56 was very photosensitive to the laboratory ceiling fluorescent light; the results are summarized in table 9. The results clearly indicate that more than 65 percent of the C-56 had disappeared in the hexane solution after exposure for 8 days. It was also found that C-56 was much more photoreactive under long-wave UV light than under short-wave UV light (fig. 4). The photolysis rate of C-56 in water was at least 15 times higher when exposed to long-wave UV light than when exposed to short-wave UV light.

TABLE 8. First-order rate constant (K), half-life (t₁/₂), and correlation coefficient (r²) for the photodegradation of C-56 in distilled water, methanol, and hexane exposed to sunlight, long-wave UV light (L-UV), and short-wave UV light (S-UV)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>K (min⁻¹)</th>
<th>t₁/₂ (min)</th>
<th></th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sun</td>
<td>L-UV</td>
<td>S-UV</td>
<td>Sun</td>
</tr>
<tr>
<td>C-56 in water</td>
<td>0.24</td>
<td>0.30</td>
<td>0.019</td>
<td>3.47</td>
</tr>
<tr>
<td>C-56 in methanol</td>
<td>0.30</td>
<td>0.32</td>
<td>0.006</td>
<td>2.32</td>
</tr>
<tr>
<td>C-56 in hexane</td>
<td>0.45</td>
<td>0.45</td>
<td>0.013</td>
<td>1.55</td>
</tr>
</tbody>
</table>
Figure 5. Packed column GC chromatograms of variation in C-56 and degradation products in tap water at various pHs adjusted with either HCl or NaOH (A) 2.51 (B) 5.80 (C) 8.45 (original pH) (D) 11.73. IS = internal standard; lettered peaks are degradation products.
In a preliminary study reported by Chou, Fisher, and Griffin (1981), C-56 was not stable in distilled water, deionized water, or low pH water (figs. 2 and 5); however, after a more extensive series of studies, it was found that C-56 was actually fairly stable in those waters when they were kept in darkness. There were trace amounts of photolysis products (pentachlorocyclopentenone and hexachlorocyclopentenone isomers) found to be present in the reagent grade C-56 solution. The trace amount of photolysis products could be separated by using silica gel column chromatography (fig. 6); the photolysis products were much more soluble than C-56 in water and thus were easily separated. When additional C-56 was added to water the photolysis products dissolved rapidly and remained stable in pure (distilled or deionized) water and in low-pH water, but were converted by hydrolysis reactions into other components in mineralized water or water adjusted to high pH with NaOH.

The dissipation rate of C-56 in aqueous solution followed a first-order reaction. In our preliminary study (Chou, Fisher, and Griffin, 1981), the half-life of C-56 in tap water was reported as 16.1 days at 22°C. This result was consistent with that reported by Zepp et al. (1979) in which the hydrolysis rate constant at 25°C was $5.6 \times 10^{-7} \text{ sec}^{-1}$, corresponding

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**Figure 6.** GC chromatograms of C-56 and ketones separated using silica gel chromatography (A) C-56 fraction (B) ketone fraction
TABLE 9. Photolysis of C-56 in hexane solution under laboratory lighting conditions

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Concentration of C-56 (ppb)</th>
<th>covered with Al foil</th>
<th>uncovered</th>
<th>% disappeared</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>712</td>
<td>722</td>
<td>705</td>
<td>700</td>
</tr>
<tr>
<td>2</td>
<td>719</td>
<td>571</td>
<td>704</td>
<td>719</td>
</tr>
<tr>
<td>8</td>
<td>692</td>
<td>274</td>
<td>716</td>
<td>207</td>
</tr>
</tbody>
</table>

Wolfe et al. (1982) also reported the hydrolysis rate over most environmental pH values (pH 3 to 10) was 1.5 x 10^{-6} sec^{-1} at 30°C, corresponding to a half-life of 5.3 days.

In a second study volatilization losses during sampling for analysis were controlled; we found that the dissipation rate of C-56 in aqueous solution was much slower. The half-life of C-56 in both distilled water and tap water was approximately 90 days at 22°C. The difference was attributed to volatilization losses that occurred when the bottle was opened during sampling for analysis. Further study at 35°C confirmed that C-56 concentrations did not dramatically change with time when the experiments were conducted in a dark room and the organic extractant was injected directly into the serum bottles through the teflon-faced septum (the bottles were not opened). The half-life of C-56 in distilled water was 88.5 days at 35°C—not significantly different from the hydrolysis rate at 22°C.

TABLE 10. Percentage distribution of C-56 and impurities in hexane and water extracts under different pHs*

<table>
<thead>
<tr>
<th>Retention time of peaks</th>
<th>Hexane soluble C-56</th>
<th>Dist. water</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.08</td>
<td>1.39</td>
<td>1.24</td>
<td>2.60</td>
</tr>
<tr>
<td>6.98 (C-56)</td>
<td>92.04</td>
<td>89.13</td>
<td>88.90</td>
</tr>
<tr>
<td>7.62</td>
<td>4.82</td>
<td>7.87</td>
<td>6.82</td>
</tr>
<tr>
<td>12.43</td>
<td>0.45</td>
<td>0.55</td>
<td>0.73</td>
</tr>
<tr>
<td>14.28</td>
<td>0.84</td>
<td>1.21</td>
<td>0.01</td>
</tr>
<tr>
<td>16.70</td>
<td>0.46</td>
<td>0.66</td>
<td>0.74</td>
</tr>
</tbody>
</table>

*2.5 µL of C-56 was injected into 100 mL distilled water and phosphate buffers.
In separate hydrolysis studies in which the same precautions were taken to control volatilization losses during sampling, it was also found that concentrations of C-56 were nearly unchanged under different pH values. The percentages of C-56 and other components present in the extracts are summarized in table 10. It is evident that no major pH effect impacted the hydrolysis reaction. A similar result was also reported by Wolfe et al., 1982. The results indicate that photolysis and, to a lesser extent, hydrolysis are the predominant degradation processes.

Identification of degradation products

The mass-spectra of the major degradation products in the aqueous solutions and organic solvents were obtained using a Hewlett-Packard 5985 GC/MS operated by the Institute for Environmental Studies Research Laboratory, University of Illinois. The major photodegradation products found in water were five- and six-chlorine ketones. A representative GC chromatogram of a C-56 water mixture exposed to sunlight is shown in figure 7. Peak (a) shown in figure 7B is a five-chlorine ketone. The GC

![GC chromatograms of C-56 in distilled water after exposing to sunlight (A) 0 min (B) 12 min](image)

Figure 7. GC chromatograms of C-56 in distilled water after exposing to sunlight (A) 0 min (B) 12 min
retention time exactly matched a standard: 2,3,4,4,5-pentachloro-2-cyclopentenone (I). Peaks (b) and (c) were considered to be six-chlorine ketones. The key fragmentation patterns (fig. 8) show m/e, 286 (parent peak); m/e, 258 (-CO); m/e, 251 (-Cl); m/e, 223 (-CO, -Cl); m/e, 216 (-2Cl); and m/e, 188 (-CO, -2Cl). These fragmentation patterns were consistent with formation of hexachloro-2-cyclopentenone (II) and hexachloro-3-cyclopentenone (III), and GC and mass-spectral data are consistent with the formation of compound II and III in water. Compound II (m.p. 28°C) has been converted to compound III (m.p. 92°C) by heating (Newcomer and McBee, 1949). Schmitzer et al., (1979) also reported that compounds II and III were formed from C-56 on silica surfaces under UV light.

Peak (e) (fig. 7B) has a molecular weight of 252, but its chemical structure is unknown. Some of the compounds of higher molecular weight (peaks f, g, and h) can also be observed in figure 7B. These compounds are presumed to be dimers of compound I or Diels-Alder adducts of C-56 and its degradation products. Pentachlorocyclopentenone (I) has been found to undergo Diels-Alder adduction at 20°C under acetonitrile basic conditions with olefins such as norbornadiene and cyclopentadiene (Dietsche, 1966). Compound I was not stable in aqueous solution; it dimerized and then converted to hexachloroindone (IV). Past studies have indicated that hydrolysis of C-56 yielded the highly reactive compound tetrachlorocyclopentadienone (Newcomer and McBee, 1949; Dietsche, 1966). This compound has never been isolated because it rapidly dimerizes or reacts to form high molecular weight products. Compound IV has also been identified in the present study by GC/MS (peak g in fig. 7B). The key fragmentation patterns (fig. 9) show m/e, 334 (parent peak); m/e, 299 (-Cl); m/e, 271 (-CO, -Cl); m/e, 236 (-CO, -2Cl); and m/e, 166 (-CO, -4Cl). The key fragmentation patterns were identical to a standard hexachloroindone (IV) synthesized from compound I by using the methods of Newcomer and McBee (1949).
Figure 8. Mass spectrum of compounds II and III

Figure 9. Mass spectrum of compound IV
In acidified photolyzed aqueous extracts, one GC peak (fig. 10, peak d) also matched a standard, pentachloropentadienoic acid (V). This was confirmed by GC/MS (fig. 11) where the major key ions showed m/e, 268 (parent peak); m/e, 251 (-OH); m/e, 233 (-Cl); m/e, 223 (-COOH); and m/e, 188 (-COOH, -Cl). A reasonable explanation of the formation of compound V is the dissociation of the carbonyl-carbon bond of compound II or III by hydroxyl radical formed under photolysis conditions.

During the same study, addition of strong base into the photolyzed aqueous solution and subsequent acidification of the sample caused the acid (compound V) to be substantially increased, thus giving further credence to the proposed reaction sequence. The GC chromatogram of the basified and acidified aqueous extract (figure 10B) shows that peaks (a), (b), and (c) disappeared and that three new peaks were observed. GC/MS analysis results indicated that peak (f) was unresolved and contained two isomers of C₆HCl₅ (VI and VII) and that peak (g) was C₄Cl₆ (VIII). The mass-spectral data for compounds VI and VII (fig. 12) show m/e, 224 (parent peak); m/e, 189 (-Cl); and m/e, 153 (-2Cl, -H), for compound VIII (fig. 13) show m/e, 188 (parent peak); m/e, 153 (-Cl); and m/e, 118 (-2Cl). The structure was postulated to be:
Figure 10. GC chromatograms of C-56 extracted from distilled water after exposure to sunlight (A) acidified aqueous extract (B) basefiend, then acidified aqueous extract

Figure 11. Mass spectrum of compound V
Figure 12. Mass spectrum of compounds VI and VII

Figure 13. Mass spectrum of compound VIII
These results indicated that (1) ketones (compounds I, II, and III) can be disassociated under basic conditions and that (2) compounds VI and VII could be derived from decarboxylation of compound V and then, after dehydrochlorination, could form compound VIII. A similar result, cleavage of the dibromotetrachlorocyclopentenone to bromotetra-chloropentadienoic acid with alkali has been reported by Newcomer and McBee (1949).

Products from photolyzed C-56 in hexane and methanol were also examined. The GC chromatograms of photolyzed C-56 in hexane and methanol are shown in figures 14 and 15, respectively. The data clearly indicate that compound I was the major photolysis product of C-56 in both hexane and methanol solutions exposed under sunlight or long-wave UV light. However, the major photolysis product was not stable in hexane or methanol solution; it gradually dimerized and finally converted into hexachloroindone (figs. 14B-C). A similar result was also observed in methanol solution, but the final conversion product was not identified (fig. 16). We postulated that the unidentified component could be C₉HCl₅O or C₉Cl₈O as described by Butz, Yu, and Atallah (1982).

The secondary photolysis products in hexane were C₁₁H₁₂Cl₁₅ (IX), and hexachloroindone (IV); the secondary products in methanol were 1,2,3,4,-tetrachloro-5,5-dimethoxyl-cyclopentadiene (X), 1-methylol-pentachlorocyclodiene (XI), and unknown components. Trace amounts of pentachlorocyclopentadiene (XII) were also identified in the photolysis studies of C-56 in hexane and methanol solutions. The mass-spectra of compounds X, XI, and XII are shown in figures 17, 18, and 19, respectively.

Study results on the photolysis of C-56 indicated that two types of reactions were involved: one was dechlorination and the other was UV light-initiated oxygen oxidation. The C-Cl bond dissociation of C-56 formed product IX in hexane solution and gave products X and XI in methanol solution.

Replacement of C-Cl bonds by C-H is well known in environmental photo-chemistry (Mosier, Guenzi, and Miller 1969). The replacement product, pentachlorocyclopentadiene has been identified by GC/MS in samples exposed to light in this study; this product is thought to be an intermediary compound that could be oxidized to form compound I. Compound I was not only found during C-56 photolysis in water and methanol, but was also found in hexane. Thus we speculate that air, rather than the solvent, was the source of oxygen involved in the photo-oxidation. This interpretation is supported by Molotsky and Ballweber (1957), who showed that bubbling O₂ through a C-56 solution produced compounds II and III.
Figure 14. GC chromatograms of C-56 in hexane solution (30 ppm) exposed to sunlight (A) 0 min (B) 10 min (C) sample B set at room temperature overnight.
Figure 15. GC chromatograms of C-56 in methanol solution exposed to long-wave UV light (A) 30 ppm C-56 standard (B) 12 min (C) 22 min
Figure 16. GC chromatograms of C-56 in methanol exposed to long-wave UV light (A) 30 ppm C-56 exposed to UV light (B) sample A set at room temperature overnight
Figure 17. Mass spectrum of compound X

Figure 18. Mass spectrum of compound XI
From the mass-spectral data presented here, the laboratory data, and the limited information in the scientific literature, we postulated the degradation pathway of C-56 shown in figure 20. Experimental verification for the proposed sequence comes from several sources. Russian researchers (Simonov et al., 1975) noted CO₂ evolution in their studies as predicted in the step from pentachloropentadienoic acid to the pentachlorobutadiene isomers. These compounds and the formation of tetrachlorobutenyne were consistent with the mass-spectral data. These compounds were found only in the mineralized water samples; only ketones were found in distilled water. In addition, the postulated degradation pathway predicts that two isomers will form and that one isomer (compound VII) will be preferred because of steric considerations. This could possibly account for the uneven doublet peaks that occur in GC traces of samples from mineralized water samples.

To test this proposed degradation pathway, 204 µg of C-56 in 10mL of 0.5 N NaOH solution were exposed to sunlight for 10 minutes; a control was kept under darkness. The usual transformation products formed (fig. 21). The GC trace after acid addition showed that petachlorocyclopentenone (peak d), hexachlorocyclopentenone (peak f), pentachloropentadienoic acid (peak h), pentachlorobutadiene isomers (peaks b and c), and tetrachlorobutenyne (peak a) were present. Peak (g) was not identified, but was presumed to be tetrachloropentadienoic acid.
In studies of catalytic properties of iron on C-56 hydrolysis, two unknown hydrolysis products were observed in both 0.5 N HCl solution with freshly cut iron wire and in distilled water with iron powder. A representative GC chromatogram of C-56 extracted from a mixture of iron powder and distilled water is shown in figure 22. Peaks (a) and (b) were significantly increased with the addition of iron. GC/MS analysis results indicated that peak (a) contained four chlorines. The mass-spectral data show m/e, 202 (parent peak) and m/e, 167 (-Cl) (fig. 23). The structure was postulated to be tetrachloropentadiene (C₅H₂Cl₄). Two of the early eluted peaks (c and d) have a molecular weight of 168 and appear to be trichloropentadiene isomers (C₅H₃Cl₃, fig. 24). Newcomer and McBee (1949) reported that dechlorination of C-56 occurred when C-56 solution was refluxed with Zn dust. Peaks (a) and (b) were also observed in methanol soluble C-56 solutions. Compounds that produced peak (a) and small amounts of the early eluted peaks were also found in a soil-column leaching study to be reported in a later section. From this study it was clear that iron in soils could potentially catalyze the formation of secondary products of C-56 that might generate problems in natural environments because of their higher aqueous solubility. It is possible that similar hydrolysis products might be present in landfills containing C-56 wastes. In order to determine the chemical transformations of C-56 in soil, further study is necessary.
Figure 21. GC chromatograms of C-56 in 0.5 N NaOH solution exposed to sunlight, then acidified with HCl (A) 0 min (B) 10 min
Figure 22. GC chromatograms of C-56 in distilled water extract (A) non-iron powder (B) addition of 1 g of iron powder.
Figure 23. Mass spectrum of $C_5H_2Cl_4$

Figure 24. Mass spectrum of $C_5H_3Cl_3$
Figure 25. Sorption of C-56 by 1.00 g and 3.50 g Catlin soil from tap water as a function of time at 22° ± 1°C

SORPTION OF C-56 BY SOIL MATERIALS, ACTIVATED CARBON, AND AMBERSORB® CARBONACEOUS SORBENT

Sorption of C-56 by soil materials

The effect of reaction-time on sorption of C-56 by Catlin soil is shown in figure 25. It is clear that 2 hours of shaking is sufficient to reach equilibrium conditions. The results for C-56 sorption by various soil materials, activated carbon, and Ambersorb XE-348 are shown in figures 26, 27, and 28. All data were fitted by linear regression to the log form of the empirical Freundlich adsorption equation:

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

in which $x$ = µg of compound sorbed; $m$ = weight of sorbent (g); $C$ = equilibrium concentration of the solution (µg/mL); $K_f$ 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. These Freundlich parameters and the correlation coefficient ($r^2$) between the amount of C-56 adsorbed by a unit of adsorbent and the equilibrium concentration of C-56 are shown in table 11. The molar $K$ ($K_p$) (table 11) was calculated from mass $K$, ($K_f$) by using the equation described by Osgerby (1970).
TABLE 11. Freundlich $K_F$, $N$, correlation coefficient ($r^2$), and molar $K_F$ for sorption of C-56 by various sorbents from tap water aqueous solution at 22°C

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

*Average amount of C-56 sorbed by unit of sorbent ($\mu g/g$) (omitted from regression in figure 29).*
Figure 26. Freundlich adsorption isotherms of C-56 in seven soil materials from tap water 22° ± 1°C

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

in which Mol wt is molecular weight of the compound, $K_f \text{ (mass)}$ 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:

$$\text{muck} > \text{Bryce} > \text{muck} + \text{Catlin (1:1)} > \#5 \text{ soil} > \text{Catlin} > \text{Flanagan} > \text{Bloomfield} > \text{Ava}.$$  

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:

$$\text{Ca-bentonite} > \text{illite} > \text{montmorillonite} > \text{kaolinite}.$$  

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 in removing C-56 from water than were most earth materials.
Figure 27. Freundlich adsorption isotherms of C-56 on four clays from tap water at 22° ± 1°C

Figure 28. Freundlich adsorption isotherms of C-56 on activated carbon and Ambersorb XE-348 from tap water at 22° ± 1°C
Effect of earth material TOC on sorption

The relationship between total organic carbon (TOC) content of the 17 sorbents and sorption of C-56 by the earth materials was investigated. The molar $K$ ($K_F$), plotted as a function of TOC (percentages), is shown in figure 29. A high correlation ($r^2$) between $K_F$ and TOC (%) was found with a linear regression relation of:

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

$$(r^2 = 0.972)$$

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

Similar results were also found for PCB, PBB, and HCB on similar sorbents (Lee et al., 1979; Griffin and Chou, 1980). The slope of the line from figure 29 yields a new sorption constant ($K_{OC}$) normalized for the organic carbon content of the soils. The $K_{OC}$ determined for C-56 is approximately 4,265. The results clearly showed that the sorption capacity of the low-temperature ashed muck decreased with decreasing TOC content (for increased ashing time, see table 11). Very low measurable sorption of C-56 was found on low-temperature ashed Catlin and Ava soils. 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, low temperature ashing may have altered the physical and chemical nature of the native soil organic matter. This is evidenced by the relatively low adsorption by the ashed Catlin and Ava soils and the very sharp drop in surface area (table 1) and sorption of C-56 by the 38 day-ashed muck sample. Extended ashing time appears to have converted the native humus organic carbon to a more inert form relative to C-56 sorption.

A limited number of soil materials was used to develop the equation and the relationship between sorption and types of organic matter is unknown. Serious discrepancies between predicted and actual sorption for a given soil may occur, even though the overall relationship is highly significant. Therefore, caution should be used in interpreting these results.

![Figure 29. $K_F$ vs TOC for C-56 sorption by fifteen soil materials](image)
Effect of soluble salts on sorption

The results for C-56 sorption by Catlin and Flanagan soil from tap water, salt solutions, and caustic brine are shown in figures 30 and 31. All data were fitted by linear regression to the log form of the empirical Freundlich adsorption equation. The Freundlich parameters, correlation coefficient ($r^2$), and molar $K (K_p)$ values are shown in table 12. All the regression lines generated had coefficients of at least 0.98, which again indicated a good fit of the data by the Freundlich equation.

![Figure 30. Freundlich adsorption isotherms of C-56 on Flanagan soil from tap water, soil solutions, and caustic brine at 22°C](image)

![Figure 31. Freundlich adsorption isotherms of C-56 from tap water, salt solutions, and caustic brine at 22°C](image)
The results shown in figures 30 and 31 clearly indicate that all the salts and brine dramatically affected sorption. The change in sorption followed the inverse trend of the Setschenow parameters reported in table 6. The salts causing the greatest depression in solubility caused the largest increase in sorption and vice versa. The effect of soluble salts on the solubility of C-56 appears to be directly related to its sorption by soil materials.

**MOBILITY OF C-56 IN SOIL MATERIALS: DETERMINATION BY SOIL TLC AND SOIL COLUMN LEACHING**

**Mobility of C-56 in soils**

The mobility of C-56 in soils, expressed as $R_f$ values, is summarized in table 13. The results indicated that under the conditions tested, 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 leached with acetone/water mixtures as the percentage of acetone increased in water; the results are shown in figure 32. 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 recovery of C-56 from soil TLC plates in these studies was extremely low (ranging from 1.25 to 4.5%), which presented some difficulties. However, the relative mobility of C-56 was easily measurable, particularly when increased amounts of C-56 were applied on each spot and the analysis was done rapidly. In later studies, we found that the recovery of C-56 from soil TLC plates was higher (ranging from 20 to 78%) when the analysis was done immediately after the soil plates were leached. The low recovery of C-56 was probably due to losses from volatilization. It is obvious from our recent experience with polybrominated biphenyl (PBB) and hexachlorobenzene (HCB) that C-56 is much more volatile than PBB or HCB.
Figure 32. Mobility of C-56 in two soils leached with DuPage leachate and acetone/water mixtures (I) Ava soil (II) Catlin soil (A) DuPage (B) acetone/water (50:50, v/v) (C) acetone/water (80:20, v/v) (D) acetone
TABLE 13. Mobility of hexachlorocyclopentadiene in several soil materials leached with various solvents as measured by soil TLC

<table>
<thead>
<tr>
<th>Soil Materials</th>
<th>Caustic 12-4-3</th>
<th>Brine (1%)**</th>
<th>Tap water</th>
<th>Landfill leachate</th>
<th>Acetone/water (1:1)</th>
<th>Methanol</th>
<th>Acetone</th>
<th>Dioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muck soil</td>
<td>ND***</td>
<td>ND</td>
<td>0.002</td>
<td>0.005</td>
<td>0.093</td>
<td>0.053</td>
<td>0.137</td>
<td>0.640</td>
</tr>
<tr>
<td>Catlin silt loam</td>
<td>0.000</td>
<td>0.000</td>
<td>0.002</td>
<td>0.002</td>
<td>0.793</td>
<td>0.879</td>
<td>0.972</td>
<td>0.989</td>
</tr>
<tr>
<td>Flanagan silt clay loam</td>
<td>ND</td>
<td>ND</td>
<td>0.001</td>
<td>0.002</td>
<td>0.841</td>
<td>0.893</td>
<td>0.994</td>
<td>0.993</td>
</tr>
<tr>
<td>Ava silt clay loam</td>
<td>0.000</td>
<td>0.000</td>
<td>0.002</td>
<td>0.003</td>
<td>0.871</td>
<td>0.891</td>
<td>0.990</td>
<td>0.956</td>
</tr>
<tr>
<td>Bloomfield limestone</td>
<td>0.000</td>
<td>0.000</td>
<td>0.002</td>
<td>0.004</td>
<td>0.869</td>
<td>0.972</td>
<td>0.981</td>
<td>0.992</td>
</tr>
<tr>
<td>Ottawa sand</td>
<td>ND</td>
<td>ND</td>
<td>ND**</td>
<td>0.003</td>
<td>0.903</td>
<td>ND</td>
<td>ND</td>
<td>0.978</td>
</tr>
</tbody>
</table>

*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.

The above findings have significance in C-56 waste disposal. 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. The results of this study also suggest that migration of C-56 through soil in aqueous solutions may not be as important as vapor transport mechanisms.

Soil column leaching study

In a soil column leaching study, a sample of Bloomfield loamy sand that had been heavily spiked with C-56 to simulate a spill was leached with 192 inches of tap water. We found 0.0005 percent of the 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 much higher solubility in water than C-56 and are much more mobile in soil. This result was observed in the soil column leaching studies (note representative GC chromatograms of the leachate extracts in figs. 33 and 34). The figures clearly show that hydrolysis products were found in the first liter of leachate and that several extra peaks appeared and were substantially increased when additional water was percolated through the soil column. From this study, it is concluded that the secondary products of C-56, rather than C-56 itself, might migrate and generate environmental problems.
**Figure 33.** GC chromatograms of standard C-56 and soil column leachate (A) C-56 standard (B) soil column leached with 64 inches of tap water (IS = internal standard)

**Figure 34.** GC chromatograms of soil column leachate leached with (C) 128 inches of tap water (D) 192 inches of tap water (IS = internal standard)
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