

# A Review of Studies on the Adsorption Characteristics of Volatile Chlorinated Hydrocarbons in Soil

Yan Li<sup>1,2,3,4,\*</sup>, Yang Wei<sup>1,2,3,4</sup>, Nan Lu<sup>1,2,3,4</sup>

<sup>1</sup> Shaanxi Land Engineering Construction Group Co., Ltd., Xi'an Jiaotong University, Technology Innovation Center for Land Engineering and Human Settlements, Xi'an-712000, China

<sup>2</sup> Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an-710075, China

<sup>3</sup> Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an-710021, China

<sup>4</sup> Technology Innovation Center for Land Engineering and Human Settlements, Shaanxi Land Engineering Construction Group Co., Ltd and Xi'an Jiaotong University, Xi'an-710075, China

---

## Abstract

Adsorption is one of the main mechanisms of soil pollution by volatile chlorinated hydrocarbons (VCHs). The adsorption behavior of VCHs in soil not only directly affects the concentration and distribution of VCHs in soil, but also affects the migration and transformation of VCHs in soil, and has a significant impact on the remediation capacity of contaminated sites. Based on the investigation of the adsorption-desorption behavior of VCHs in soil, the main factors affecting the adsorption of VCHs in soil were summarized, and the investigation and control of soil pollution in urban areas provided theoretical reference.

## Keywords

**Volatile Chlorinated Hydrocarbons; Adsorption Properties; Soil Pollution; Soil Organic Carbon.**

---

## 1. Introduction

The rapid urban development and the transformation and upgrading of the economic structure have resulted in a large number of abandoned industrial sites, which affect the development of water and soil resources and urban construction, and even pollute the living environment such as soil, air and groundwater. Volatile chlorinated hydrocarbons (VCHs) are widely used in pharmaceutical, chemical, electronic and other industries as important raw materials and organic solvents for industrial production [1]. VCHs are chemically stable, dense, and difficult to degrade. After entering the environment, they are volatile, concealed, and persistent, which can easily cause soil and groundwater pollution. At the same time, most of VCHs have strong biological toxicity and carcinogenicity. Long-term exposure of human body to VCHs environment through skin contact, breathing or accidental ingestion can easily cause health problems such as liver and blood poisoning or nervous center poisoning. It is recognized as a potentially dangerous toxic pollution. It is also the focus of site volatile organic compound pollution control and restoration [2]. Studies have shown that VCHs, especially carbon tetrachloride (CT), Chloroform (CF), tetrachloroethylene (PCE), trichloroethylene (TCE), Solvents such as 1,1,1-trichloroethane (MC) and other single-carbon/double-carbon chlorinated hydrocarbons are widely polluted in soil and groundwater [3]. Since most VCHs have strong carcinogenic effects and neurotoxicity, soil pollution has a great potential threat to human health. Therefore, it is of great significance to understand the pollution mechanism of VCHs.

## 2. Adsorption-desorption Characteristics of VCHs in Soil

The adsorption of VCHs in the soil is small, the density is high, the viscosity is low, and it is volatile. After entering the soil from the surface, VCHs will infiltrate downward under the action of gravity. It is highly mobile and often forms a pollution center several meters or even tens of meters below the surface. If it is not treated in time, VCHs will eventually move to the surface and cause air pollution, and even reach the groundwater layer to cause groundwater pollution.

After VCHs liquid enters the soil, it distributes among soil solids, water phase, and soil air, or exists in the form of high-density non-aqueous phase liquids (DNAPL), forming a dynamic equilibrium system. The distribution behavior of VCHs among the three phases of soil air, water phase and DNAPL is relatively simple. The distribution between DNAPL-water phase depends on the solubility of VCHs, the distribution between DNAPL-soil-air mainly depends on the vapor pressure, boiling point, etc. of VCHs, while the distribution of VCHs between water-soil-air obeys Henry's law [4]. In contrast, the adsorption behavior of soil solids to VCHs is more complex, involving three types of interphase partitions: water-soil solids, soil air-soil solids, and DNAPL-soil solids. The VCHs in the soil water and gas phase will be adsorbed on the soil solids, and the VCHs adsorbed by the soil solids will also be desorbed and diffused into the soil water and gas phases. When DNAPL exists, a large number of VCHs droplets will remain on the migration path under the action of soil capillary force, becoming a long-term continuous pollution center. The adsorption of VCHs in soil will greatly retard their migration in the soil environment, thereby protecting groundwater resources. At present, there are many studies on the adsorption of VCHs in water and gas phases by soil solids, but less studies on the interaction between DNAPL and soil particles [5].

### 2.1 Adsorption Mechanism of Saturated Soil

The adsorption of VCHs in soil mainly includes the "adsorption" of soil organic carbon (SOC) and the "adsorption" of soil minerals. The main carrier for the adsorption of VCHs in saturated soil is SOC, and only a very small amount is adsorbed on soil minerals. The adsorption kinetics study found that it takes days or even months for VCHs to reach adsorption equilibrium in soil, and the adsorption under different conditions often presents nonlinear adsorption competitive adsorption, adsorption/desorption hysteresis and other non-ideal adsorption phenomena. The adsorption mechanism of VCHs in saturated soil is very complex. At present, only limited adsorption experimental data can be used to speculate the adsorption behavior. There are still many aspects about the microscopic interaction between soil components and compound molecules to be further studied.

### 2.2 Adsorption Mechanism of Unsaturated Soil

In unsaturated soils, besides SOC, the surface of soil minerals also plays an important role in the adsorption of VCHs [6]. The adsorption capacity of VCHs in dry soil was much larger than that in saturated soil, and soil minerals played a dominant role in the adsorption of VCHs. This is because soil minerals have a large specific surface area, and the mineral surface can adsorb a large amount of gaseous VCHs when dry. However, with the increase of soil water content, the adsorption of VCHs decreases significantly, and water molecules greatly inhibit the adsorption of VCHs on the mineral surface. Unger [7] pointed out that a part of the hydrated soil surface is directly exposed to the gas phase when the soil is at a high relative saturation. Since the gas-solid adsorption coefficient is several orders of magnitude higher than the liquid-solid adsorption coefficient, the study of VCHs in the adsorption behavior of soil in the saturated zone must comprehensively consider the effects of SOC and soil minerals on adsorption.

The adsorption of gaseous VCHs at the gas-liquid interface and condensation within the mineral micropores may also be important adsorption mechanisms. The adsorption kinetics of VCHs in soil is mainly affected by SOC, minerals, soil pore structure and other factors. Compared with other adsorption processes, the adsorption time of VCHs at the gas-liquid interface is very short, which can be considered to occur instantaneously, which can be ignored in quantitative studies.

### 3. Factors Affecting the Adsorption-desorption of Vchs

#### 3.1 Soil Properties

In the natural environment, the soil is generally wet or saturated, and dry soil is only common in deserts, beaches or soil surface layers. Therefore, the adsorption behavior of VCHs in natural soils is usually mainly affected by organic carbon and soil minerals in the soil.

**Soil organic carbon.** It refers to various carbon-containing organic compounds attached to minerals or in the form of discrete organic colloids, including animal and plant residues, microorganisms and products of different decomposition stages of these biological residues, and humus synthesized from decomposition products. Both the content and type of SOC have significant effects on the adsorption of VCHs in soil. SOC acts by adsorbing VCHs in the water phase or directly adsorbing VCHs in the gas phase. Studies have shown that in moist or saturated soil, SOC content is an important factor in determining the amount of VCHs adsorption. Low carbon soils such as clay have lower adsorption capacity. In addition, the chemical properties of SOC, the difference in polarity of different type of SOC and the content of aromatic species have important effects on the adsorption capacity of VCHs.

Depending on the origin and geological history of SOC, there are often large differences in its chemical properties. In the process of deposition and lithification, biopolymers will be degraded and cross-linked to form organic matter. Under geological action, organic matter will form kerogen, coal, graphite, etc. [8]. Geological effects such as weathering and metamorphism will change the organizational structure of SOC and change the molecular functional groups, thereby affecting the adsorption behavior. The higher the weathering degree of SOC, the more oxygen-containing functional groups, the stronger the polarity of SOC, and the greater the difference in the adsorption capacity of VCHs molecules with different polarities. Soil organic matter is an amorphous macromolecular solid, which is easily affected by environmental conditions (such as temperature, pH, moisture, NAPL, etc.) and changes its structure. The change of structure will inevitably affect the adsorption behavior of SOC.

**Soil Moisture.** The effect of soil moisture on the adsorption behavior of VCHs mainly acts by inhibiting the surface adsorption of soil minerals. The surface of soil minerals contains a large number of hydrophilic groups (groups bound by surface tension and surface hydroxyl groups). Adsorption on mineral surfaces. In general, the effect of water on the adsorption of VCHs in soil can be divided into three categories: at very low water content, the gas-solid adsorption of VCHs on mineral surfaces plays a leading role, which is positively correlated with soil specific surface area; at moderate humidity, VCHs There is a distribution equilibrium between the gas-liquid-solid three phases, and the adsorption capacity decreases sharply with the increase of water content, and tends to be stable when the water content reaches a certain value; while in the water saturation condition, the mineral surface is mostly occupied by water, and the VCHs It is first dissolved in the water phase and then adsorbed on the surface of soil particles.

**soil minerals.** The adsorption sites of VCHs on soil minerals mainly include the outer surface of minerals, the surface of expanded clay boundary layer and the inner surface of mineral pores. In soils with extremely low organic carbon content ( $\leq 0.2\%$ ), the microporous structure of minerals plays an important role in the adsorption of VCHs. Hydrophobic micropores are a type of micropores characterized by the sparse distribution of hydrophilic groups, and have extremely weak interaction with water molecules. Water molecules are easily detached under vacuum or heating conditions, and VCHs molecules can be condensed in large quantities. Soil is a heterogeneous mixture composed of various mineral particles and complex organic polymers. The structure and chemical properties of soil components are the fundamental reasons for determining soil adsorption characteristics. At present, there is still a lack of direct quantitative research on the physicochemical properties of soil components.

### 3.2 Physical and Chemical Properties of VCHs

The adsorption behavior of organic pollutants is first determined by its own properties [9]. The properties of VCHs, such as molecular polarity, solubility, molecular volume, and hydrophobicity, can affect their adsorption behavior. Polarity and H-bond formation play an important role in the adsorption of polar molecules (methanol, water, etc.) to soil organic carbon, while non-polar or weakly polar molecules (CT, TCE, benzene, etc.) The polar intermolecular forces are relatively small, which leads to a huge difference in the adsorption capacity of similar organic carbons to VCHs of different polarities. In recent years, many researchers have used the Linear free energy relationships (LFERs) of organic matter to study the Koc (Organic Carbon Normalized Partition Coefficient) values of organic pollutants. By comparing the LFERs of VCHs in soil, the Log Koc value can be quantitatively analyzed to determine the effects of soil composition and VCHs properties on adsorption. At present, many research results have been achieved in the study of the adsorption coefficient of organic pollutants based on the multi-factor LFERs theory.

### 3.3 Environmental Factors

Environmental factors such as temperature also have a certain influence on the adsorption behavior of VCHs. For most organic compounds whose solubility increases with temperature, the adsorption coefficient  $K_d$  decreases with increasing temperature. In the natural environment, the temperature difference of the surface soil varies greatly, which has a great influence on the water solubility and vapor pressure of VCHs. The increase of temperature will increase the molecular kinetic energy, promote the diffusion behavior, and have a certain impact on the soil adsorption behavior. In addition, the degradation of indigenous microorganisms in the subterranean environment can affect the distribution of VCHs in various soil phases, and soil aggregates or particles may encapsulate a small amount of SOC during deposition or weathering, and these SOCs cannot adsorb VCHs. In soil polluted for a long time, pollutants may be coated with SOC or clay minerals and it is difficult to get rid of them, which is one of the manifestations of pollutant aging.

## 4. Conclusion

The soil types in my country vary greatly between regions. The adsorption characteristics of pollutants such as VCHs in typical soils in my country are not fully understood. The adsorption mechanism of SOC and soil minerals to VCHs is still in the stage of hypothesis. In the future, basic research on the adsorption behavior of pollutants such as VCHs in typical soils in my country should be strengthened. It is necessary to use nuclear magnetic resonance, scanning electron microscopy, atomic force microscopy and other scientific instruments to conduct in-depth research to determine the specific existence of VCHs in soil. To understand the adsorption mechanism of VCHs in soil, to clarify the root cause of non-ideal adsorption.

Soil/groundwater pollution is concealed and hysteretic, cumulative and regional, irreversible, difficult to control and has a long cycle. In recent years, some soil and groundwater pollution surveys have shown that the soil and groundwater VCHs pollution in some areas of my country has been very serious, threatening people's health and safety at all times. However, there is not much on-site remediation work. This is a relatively new field in my country. The relative lack of basic research is an important reason for constraining pollution remediation. Therefore, it is necessary to increase research on related aspects in the future to lay the foundation for effective pollution remediation.

## Acknowledgments

This research was funded by the Technology Innovation Center for Land Engineering and Human Settlements, Shaanxi Land Engineering Construction Group Co., Ltd and Xi'an Jiaotong University (2021WHZ0094), Shaanxi Province Enterprise Innovation Striving for the First Young Talents Support Program Project (2021-1-2, 2020-4-1), Shaanxi Provincial Land Engineering Construction Group Internal Research Project (DJNY2021-24, DJNY2021-20), and Institute of Land Engineering

and Technology, Shaanxi Provincial Land Engineering Construction Group Internal Pre-research Project (2020-NBYY-23).

## References

- [1] Kobayashi T. Study of vapor extraction method for purifying volatile chlorinated organic compounds contaminated soil[D]. Japan, Yokohama National University,2004.
- [2] Kapp R. Comprehensive Environmental Response, Compensation, and Liability Act, USA[J]. Encyclopedia of Toxicology, 2005, 96(510):654-655.
- [3] Zuhail O, Tansel B, Katsenovich Y, et al. Highly organic natural media as permeable reactive barriers: TCE partitioning and anaerobic degradation profile in eucalyptus mulch and compost[J]. Chemosphere, 2012, 89(6):665-671.
- [4] Derx J, Blaschke A P, Bloschl G. Three-dimensional flow patterns at the reverser timescale interactions between surface water and ground water in the centra,2010,33(11):1375-1387.
- [5] Niu Z R, Li F F, Zhang Y J, et al. Spatial distribution and causes of chlorinated hydrocarbons pollution in soil in a typical contaminated site[J]. Environmental Engineering, 2022,40(3):94-101,228.
- [6] Deng Z Q. Experimental study on the remediation of volatile chlorinated hydrocarbons polluted low permeability vadose zone soil by thermal oxidation soil vapor extraction[D]. Jilin University,2020.
- [7] Unger D R, Lam T T, Schaefer C E, et al. Predicting the effect of moisture on vapor-phase sorption of volatile organic compounds to soils[J]. Environ Sci Technol,1996,30(4):1081-1091.
- [8] Ma X C, Xu H X, Sun Y Y. Research progress on biotic natural attenuation for the remediation of chlorinated hydrocarbon-contaminated sites [J/OL]. China Environmental Science, <https://doi.org/10.19674/j.cnki.issn1000-6923.20220616.028>.
- [9] Zhang S J. Study on the chlorinated hydrocarbon migration mechanism and pollution control of groundwater system in the Eastern area of a city[D]. University of Jinan,2021.