

# Environmental Engineering

The background is a light blue gradient. In the top left, there is a large, faint gear-like pattern. In the bottom right, there is a prominent, 3D-style staircase or terraced pattern made of blue steps, receding into the distance.

LIU Yang

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## Introductiony

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# Chapter 12 Hazardous waste management

## Learning Objectives

- know what constitutes a hazardous compound or hazardous waste;
- recognize the important regulations governing hazardous waste management in the United States and understand the context of their promulgation;
- understand the terms “life cycle assessment” and “pollution prevention”;
- know the important physical and chemical characteristics of a contaminant that determine its fate, the treatment options available, and the likely risk and pathways for exposure;
- know Henry’s Law, the systems in which it is relevant, and what it means in terms of hazardous waste management; know the octanol-water partition coefficient and how it can be used to evaluate potentially hazardous compounds; know Darcy’s Law and how it can be used along with the retardation factor to determine the movement of contaminants in the subsurface; know what a NAPL is;
- know how redox affects remediation and treatment;
- recognize different remediation options and what considerations are relevant for deciding on an appropriate treatment option;
- understand the advantages and disadvantages of in situ and ex situ treatment.



# Chapter 12 Hazardous waste management

## 12.1 Introduction

### 12.1.1 A brief history of the hazardous waste problem

- In 1940s and early 1950s, when chemical production rapidly expanded. This has led to a long history of hazardous waste problems.
- In 1962 Rachel Carson published Silent Spring, In 1972, DDT was banned in the United States under The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).
- In the 1970s, attention focused on the Stringfellow California hazardous waste disposal site, This site contained over 200 hazardous chemicals, primarily wastes from metal finishing金属表面处理, electroplating电镀 and pesticide disposal, which were disposed of during the site's 16-year operation.
- The Hudson River survey, conducted in 1974 by the Environmental Protection Agency (EPA), showed high levels of polychlorinated biphenyls (PCBs 多氯联苯) in fish from the river. The cleanup began in 2009 at an estimated cost of over \$750 million.
- Love Canal&The “Valley of the Drums”,
- In 1984, in Bhopal India, 45 tons of methyl isocyanate (MIC异氰酸甲酯 ) was released from a Union Carbide plant, resulting in nearly 300 deaths and over 350,000 injured, with an estimated 100,000 to 200,000 people with permanent disabilities.

# Chapter 12 Hazardous waste management

## 12.1 Introduction

### 12.1.2 Important regulations

- The two most important US laws are the Resource Conservation and Recovery Act (RCRA, passed in 1976) and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund, passed in 1980).

#### 12.1.2.1 Resource Conservation and Recovery Act

- RCRA implemented a hazardous material tracking system referred to as “cradle to grave”, that uses the tracking program for radioactive wastes as its model. In addition, a definition of what constitutes a hazardous material was provided.
- The definition included two features: either the waste material is on a specific list or it has the “characteristics” of a hazardous waste.
- Characteristic hazardous wastes are materials that fit RCRA-defined criteria of toxicity, flammability, corrosiveness, or reactivity. Of these, the toxicity test procedure, called the toxicity characteristic leaching procedure (TCLP) is most used.
- RCRA was modified in 1984 by the Hazardous and Solid Waste Amendments, and these regulations generally placed additional restrictions on the methods of disposal, increased fines and prison terms and put into place the so-called “hammer provisions” that forced the EPA to meet specific deadlines for promulgating industry-specific hazardous waste regulations.

# Chapter 12 Hazardous waste management

## 12.1 Introduction

### 12.1.2 Important regulations

#### 12.1.2.2 Comprehensive Environmental Response, Compensation and Liability Act

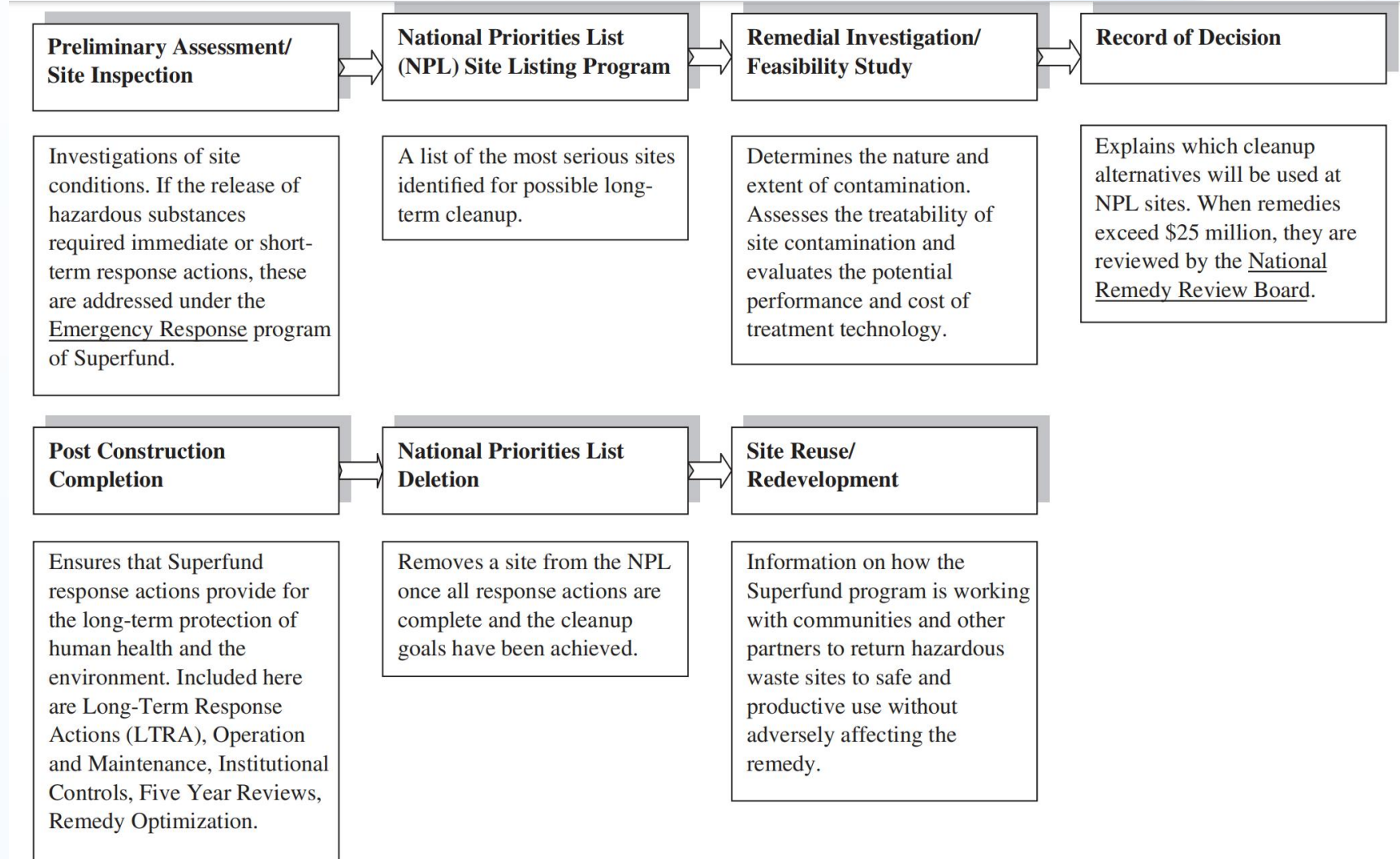
- CERCLA was initially established as a five-year program to force responsible parties to clean up their sites. CERCLA, also known as “Superfund”, was designed to deal with old and abandoned hazardous waste sites, while RCRA addressed newly created hazardous materials. An allotment of \$1.6 billion, the superfund, was provided to clean up sites where no responsible party could be found or the responsible party(s) were financially unable to pay for the cost of the cleanup.
- CERCLA established a procedure for forcing cleanup action by placing sites on the National Priorities List (NPL), based on the Hazardous waste site Ranking System (HRS), which ranks the site based on risks to human health and the environment.
- In 1986, the Superfund Amendments and Reauthorization Act (SARA) was enacted to extend superfund for five more years and add \$8.5 billion to the fund.
- In addition to the extension of CERCLA, the Leaky Underground Storage Tank (LUST) trust fund, the Emergency Planning and Community Right-to-Know Act (EPCRA) and the Toxics Release Inventory (TRI) were established.

# Chapter 12 Hazardous waste management

## 12.1 Introduction

### 12.1.2 Important regulations

#### 12.1.2.2 Comprehensive Environmental Response, Compensation and Liability Act





# Chapter 12 Hazardous waste management

## 12.1 Introduction

### 12.1.2 Important regulations

#### 12.1.2.3 Europe and European Regulations

- The EC has adopted a broad precautionary stance regarding the production and use of chemicals that could be considered hazardous.

([http://ec.europa.eu/environment/index\\_en.htm](http://ec.europa.eu/environment/index_en.htm)).

- This “precautionary principle,” “预防原则 ” as it is known, is exemplified by the law REACH, which was promulgated in 2007. According to the EC, the goal of REACH is, “to ensure a high level of protection of human health and the environment,” primarily by:

1 replacing chemicals that are considered particularly hazardous; and

2 placing the burden on industries to prove that chemicals are safe for use  
(<http://ec.europa.eu/environment/chemicals/index.htm>).



# Chapter 12 Hazardous waste management

## 12.1 Introduction

### 12.1.3 The future of hazardous waste management

- In 1984, HSWA stated that it was to be “a national policy of the US that, where feasible, the generation of hazardous waste is to be reduced or eliminated as expeditiously as possible,”
- The idea of pollution prevention began in the 1970s, so it is not new. Nevertheless, not all companies have embraced pollution prevention and the economic and liability benefits that it brings. Pollution prevention can be as simple as covering tanks to prevent chemical volatilization and adding automatic flow controllers to prevent tank overflows, or as complex as reformulating products, including changing input chemicals or manufacturing processes.
- In the end, however, the focus of pollution prevention remains on reducing environmental impact during the manufacture phase of product development and not on the product's use or final disposal phase.
- The integration of an entire product lifecycle – mining and processing raw materials, manufacture, use, and disposal – into a complete picture of an “environmental footprint” is the domain of lifecycle assessment (LCA). This concept goes beyond simple recycling and pollution prevention, incorporating the environment into the entire design of a product. This is a move away from looking at single risks (e.g., liver disease in humans) and looking at global sustainability.

# Chapter 12 Hazardous waste management

## 12.1 Introduction

### 12.1.3 The future of hazardous waste management

- For LCA, all environmental implications are investigated and, if possible, quantified: energy and material use, manufacture and packaging, transportation, consumer use, reuse, recycling, and disposal. In addition, traditional design considerations (cost, quality, manufacturing process, and efficiency) need to be considered as well .
- Although LCA is embraced by more companies every year, two major problems remain:
  - 1 a lack of quantitative detail regarding the impact of various materials, processes, and chemicals on the environment; and
  - 2 the difficulty in assessing and addressing trade-offs with respect to environmental impacts.
- How do you weigh the health impacts of lead in solder 焊料 with the scarcity 稀缺性 and environmental impacts of using a replacement such as indium 铟? How do you weigh local groundwater impacts of increased natural gas extraction to global impacts of climate change?

# Chapter 12 Hazardous waste management

## 12.2 Common hazardous compounds and wastes

- Over 700 compounds are categorized by RCRA as hazardous. ([www.atsdr.cdc.gov/SPL/index.html](http://www.atsdr.cdc.gov/SPL/index.html)).

2011 Rank	Substance	Common current and historical uses and sources
1	Arsenic	Wood preservative, pesticide
2	Lead	Lead based paint, solder, batteries, ammunition
3	Mercury	Production of chlorine gas and caustic soda, coal combustion
4	Vinyl chloride	Manufacturing processes
5	Polychlorinated biphenyls	Insulator, coolant and lubricant in transformers and capacitors, carbonless copy paper
6	Benzene	Gasoline, plastics, resins, synthetic fibers, rubber, dyes and lubricants
7	Cadmium	Batteries, metal plating, pigments
8	Benzo(a)pyrene	Formed during combustion of organic matter, creosote
9	Polycyclic aromatic hydrocarbons	Coal combustion, petroleum refining, incomplete combustion of organic matter, creosote, coal tar and asphalt
10	Benzo(b)fluoranthene	Leaches from coal tar and asphalt, combustion of organic matter
11	Chloroform	Chemical manufacturing
12	Aroclor 1260	Lubricant, hydraulic fluid, insulator, plasticizer
13	DDT	Pesticide
14	Aroclor 1254	Lubricant, hydraulic fluid, insulator, plasticizer
15	Dibenzo(a,h)anthracene	Found in vehicle exhaust, cigarette smoke, soot, coal tar
16	trichloroethylene	Degreaser, paint remover
17	Hexavalent chromium	Chrome plating, dyes, pigments, leather tanning, wood preserving
18	Dieldren	Insecticide
19	White phosphorus	Ammunition, fertilizers, food additives
20	Hexachlorobutadiene	Produced as a by-product in the production of carbon tetrachloride and tetrachloroethylene

# Chapter 12 Hazardous waste management

## 12.2 Common hazardous compounds and wastes

### 12.2.1 Petroleum products

- Petroleum products consist of a mixture of **aliphatic and aromatic** organic chemicals. The number of these individual chemicals and the specific concentrations present in a mixture depend on the composition of the original crude oil and the processing method used to generate specific petroleum products.
- Aliphatic hydrocarbons :alkanes \alkenes \alkynes
- Aromatic compounds: benzene, toluene, the xylenes and ethyl benzene, are collectively called **BTEX**.
- **Benzene** is of most concern as **potent carcinogen**.All of the BTEX compounds are regulated, however, because of health concerns.
- **Polycyclic aromatic hydrocarbons (PAHs)** contain two or more fused benzene rings, with these fused rings sharing two carbons.These compounds are associated with the heavier fractions of petroleum products and with industrial processes and the incomplete combustion of fossil fuels.



# Chapter 12 Hazardous waste management

## 12.2 Common hazardous compounds and wastes

### 12.2.2 Chlorinated compounds 氯化物

- **Chlorinated aliphatics** 氯化脂肪族 are widely used for degreasing, as dry cleaning solvents, and as manufacturing chemicals. These compounds have contaminated many groundwater resources as a result of improper disposal practices. Some of these compounds are suspected, or known, **carcinogens, and many cause kidney or liver damage**. Other chlorinated compounds, often aromatic in nature, are considered **persistent and bioaccumulative toxins (PBTs)** and build up in the fatty tissues of biota.
- tetrachloroethylene (also known as PCE or PERC 四氯乙烯), which is still widely used as a dry cleaning solvent,
- trichloroethylene (TCE 三氯乙烯), which is a widely used and excellent solvent and degreaser,
- and vinyl chloride (VC 氯乙烯), which is used in the manufacture of polyvinylchloride (PVC) products.
- TCE and VC, along with dichloroethylene (DCE 二氯乙烯), are also found as microbiological degradation intermediates and/or products of PCE,

# Chapter 12 Hazardous waste management

## 12.2 Common hazardous compounds and wastes

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# Chapter 12 Hazardous waste management

## 12.2 Common hazardous compounds and wastes

### 12.2.2 Chlorinated compounds 氯化物

- PBTs that are included among the top 20 compounds in the CERCLA Priority List, the pesticide DDT and its degradate DDE, and the insecticide dieldrin, all of which are now banned in the US.
- Not only do these chemicals accumulate in biological tissue over time, but they tend to magnify as one moves up the food chain as well, as organisms at higher trophic levels (large carnivorous fish, for example) eat a lot of organisms at lower trophic levels (small vegetarian or omnivorous fish). Some of these PBTs have been linked to reproductive and developmental problems, particularly in organisms at high trophic levels. More recent research has suggested that exposure to PBTs can cause even broader health effects, such as PCB exposure being linked to diabetes糖尿病, and dieldrin狄氏剂 exposure linked to Parkinson's disease.

# Chapter 12 Hazardous waste management

## 12.2 Common hazardous compounds and wastes

### 12.2.3 Other organic compounds of concern

- **Pesticides, herbicides, and fungicides** have been used over the past 50 years in agriculture and in urban environments. Even though most of these were applied according to procedures that were considered appropriate at the time, we now know that some of these have resulted in serious environmental contamination.
- A huge variety of **industrial chemicals from munitions** 弹药 manufacturing, including munitions themselves, can be found at contaminated sites. These have been particularly problematic at former military production facilities.
- Finally, **some compounds used in plastics and as surfactants** in household and industrial products are also considered hazardous, depending on their concentration. A summary of the structure, chemical properties, and potential hazards of these chemicals can be found in Watts (1998).



# Chapter 12 Hazardous waste management

## 12.2 Common hazardous compounds and wastes

### 12.2.4 Inorganic compounds of concern

- Inorganic hazardous chemicals are also commonly found at contaminated sites and as industrial waste products. Some of the more important of these are **lead**铅, **cadmium**镉, **chromium**铬, **cyanides**氰化物, **arsenic**砷, and **asbestos**石棉:
- Lead, a chemical known to interfere with precognitive development in infants and young children, is primarily used in lead batteries and for a variety of other industrial uses.
- Cadmium is a cumulative contaminant that is thought to lead to cancer and hypertension高血压. It is widely used in batteries, plastics, paint, and as a plating metal电镀金属.
- Chromium is also used in plating and as a paint pigment. Chromium can be found in a range of oxidation states ranging from -2 to +6, and is most toxic in the +6 oxidation state.
- Cyanide is typically found in the ionic form  $\text{CN}^-$ , or as  $\text{HCN}$ . Cyanide is an excellent chelator螯合剂. Cyanide is an acute poison.
- Arsenic can be found as a natural contaminant in groundwater. Copper chrome arsenate (CCA砷酸铜铬) has been used as a wood preservative木材防腐设施,
- Asbestos石棉 is a mixture of inorganic fibers that contain silica oxides, magnesium, and iron含有氧化硅、镁和铁的无机纤维混合物. This material has been widely used in insulation绝缘材料 and in asbestos-cement pipe. Inhalation of asbestos fibers can cause serious illnesses, including cancer,

## Chapter 12 Hazardous waste management

### 12.3 Physical and chemical characteristics

The physical and chemical characteristics of a contaminant will determine its fate, the treatment options available, and the likely risk and pathways for exposure. Important characteristics include:

- solubility
- volatility
- density
- octanol-water partition coefficient (KOW)
- oxidation state

# Chapter 12 Hazardous waste management

## 12.3 Physical and chemical characteristics

### 12.3.1 Solubility 溶解性

- The solubility of a compound in water will determine its potential for movement in the environment and the concentration that it can reach when added to water. For compounds that are sparingly soluble, the risk that they will move through the environment is reduced, but their biodegradability may also be reduced because microorganisms typically degrade compounds that are in the aqueous, or dissolved, phase. In addition, sparingly soluble compounds are more likely to be found in another phase when in contact with water.
- With respect to hazardous organic chemicals, the solubility of aromatic compounds decreases as the number of rings increases. For chlorinated aliphatics, the solubility generally decreases as the number of chlorine atoms increases. Among the least soluble hazardous organic chemicals are the dioxins and furans 二恶英和呋喃.
- Solubility is also very important for inorganic hazardous chemicals. The solubility of metals such as lead and cadmium depend very strongly on pH, with solubility increasing at the extremes of the pH scale and minimum solubilities reached at pH values around 8–10. For chromium, the solubility depends on both the oxidation state of chromium and pH. Trivalent chromium is much less soluble than hexavalent chromium. Cyanide can exist as HCN or as  $\text{CN}^-$ . Both forms are soluble, but HCN is also volatile. Arsenic can range from slightly soluble to very soluble, depending on the form and oxidation state.

# Chapter 12 Hazardous waste management

## 12.3 Physical and chemical characteristics

### 12.3.2 Volatility 挥发性

- The volatility of a compound in water is described by its Henry's Law constant and, like solubility, is a function of its chemical structure. Henry's Law describes the partitioning of a compound between the soluble and gaseous phase according to the following:

$$P = HX \quad (12.1)$$

where:

$P$  = partial pressure, atm

$X$  = concentration of the compound in water, moles/m<sup>3</sup>

$H$  = Henry's Law Constant, atm·m<sup>3</sup>/mole.

- Henry's Law constant is highly dependent on temperature and atmospheric pressure. Compounds with Henry's Law constant values greater than  $10^{-3}$  can be considered to be volatile, while those with a Henry's Law constant less than  $10^{-7}$  may be considered non-volatile. Over the range of  $10^{-5}$  to  $10^{-2}$ , volatilization can be considered to affect the concentration of these species in water significantly over time.



# Chapter 12 Hazardous waste management

## 12.3 Physical and chemical characteristics

### 12.3.2 Volatility 挥发性

- For the aromatics, the BETX compounds have Henry's Law constants between  $10^{-2}$  and  $10^{-3}$ , meaning that they will volatilize readily. While this means that these compounds may expose a population via the gas phase, this also means that BETX-contaminated groundwater can be remediated by volatilizing it out of the water under highly controlled conditions.
- Many chlorinated aliphatics are also volatile and can be removed from groundwater by taking advantage of this chemical property. PAHs and larger ring compounds tend to be less volatile, but there are a number of exceptions to this.
- The metals lead, cadmium, and chromium are not volatile. Cyanide in the form of HCN is volatile; therefore, pH will control cyanide volatility. Arsenic is volatile in its methylated 甲基化

# Chapter 12 Hazardous waste management

## 12.3 Physical and chemical characteristics

### 12.3.3 Octanol-water partition coefficient 辛醇-水分配系数

- The octanol-water partition coefficient,  $K_{OW}$ , is a general measure of the hydrophobicity 疏水性 of a chemical, and specifically describes the tendency for a chemical to move into a separate organic phase rather than remain in water.
- Because the affinity of commonly-encountered chemicals for octanol over water can vary by over seven orders of magnitude, we frequently use the log10 value of  $K_{OW}$ , or  $\log K_{OW}$ . Therefore, **a compound with a high  $K_{OW}$  will be sparingly soluble and is more likely to have limited volatility.**
- For soil partitioning ( $K_d$ , or the soil distribution coefficient), the amount of a contaminant that binds to soil is typically related to its  $K_{OW}$  value and to the fraction of organic carbon on the soil.

# Chapter 12 Hazardous waste management

## 12.3 Physical and chemical characteristics

### 12.3.3 Octanol-water partition coefficient 辛醇-水分配系数

- The sorption of nonpolar hydrophobic compounds to a particular soil matrix can be described by a relationship called an isotherm 非极性疏水化合物对特定土壤基质的吸附作用可以用一种称为等温线的关系来描述

$$K_d = s/C_L \quad (12.2)$$

where:

$K_d$  = soil distribution coefficient, L/g

$K_d$  = mass of contaminant sorbed (mg/g soil)/mass of contaminant dissolved (mg/L water)

$s$  = mass of solute (contaminant) sorbed per mass of dry soil, unitless, and

$C_L$  = liquid phase equilibrium concentration of the contaminant, mg/L or g/m<sup>3</sup>.

The soil distribution coefficient ( $K_d$ ) is related to the soil adsorption coefficient ( $K_{oc}$ ) by the following equation:

$$K_d = K_{OC} \cdot f_{OC} \quad (12.3)$$

where:

$K_{OC}$  = soil adsorption coefficient, L/g

$K_{OC}$  = mass of contaminant sorbed (mg/g soil organic carbon)/mass of contaminant dissolved (mg/L water)

$f_{OC}$  = the fraction of organic carbon in the soil.

The relationship between  $K_{OC}$  and  $K_{OW}$  has been described by the general equation:

$$\log K_{OC} = A \log K_{OW} + B \quad (12.4)$$

Where  $A$  and  $B$  are unitless and vary, depending on the soil type and the nature or family of contaminants.

One such relationship, provided by Kenaga and Goring (1980) is:

$$K_{OC} = 0.544 \log K_{OW} + 1.377 \quad (12.5)$$

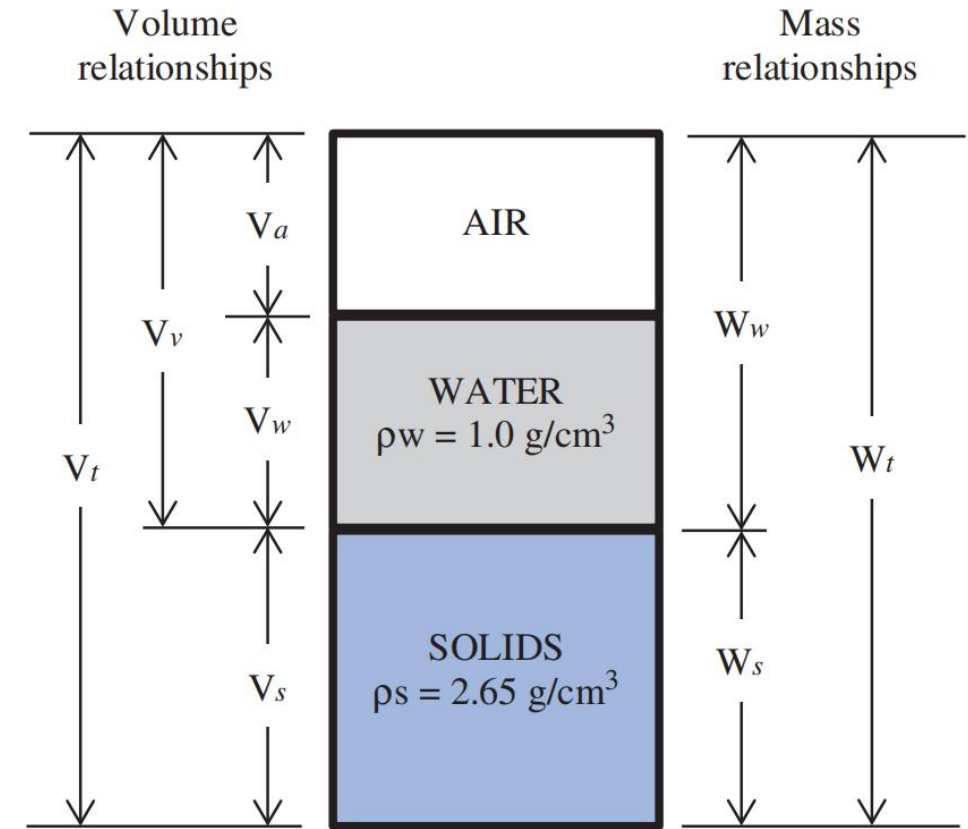
and is appropriate for use with PAHs, PCBs, organochlorine insecticides, benzene, and a range of pesticides, chlorinated compounds, and other organic contaminants.

# Chapter 12 Hazardous waste management

## 12.3 Physical and chemical characteristics

### 12.3.4 Soil and groundwater interactions

- The improper disposal of hazardous wastes often impacts groundwater systems. The soil-water matrix 土壤-水基质 governs the movement of contaminants through the soil, either in the vapor phase 蒸气相, the dissolved phase 溶解相, or as a separate phase. The soil system represented in Figure 12.4 can be used to describe the soil matrix.
- Important relationships and properties for soil and soil constituents are shown in Table 12.5, along with a mathematical description. The total weight of soil includes the weight of solids plus the weight of water. The weight of air is neglected. The total volume includes the volume of air, water and solids, and the sum of the air and water volumes is considered to be the void 空隙 volume.



**Figure 12.4** Phase diagram for partially saturated soil. Source:



# Chapter 12 Hazardous waste management

## 12.3 Physical and chemical characteristics

### 12.3.4 Soil and groundwater interactions

**Table 12.5** Volume-mass relationships of soil constituents.

Property	Symbol	Definition	Mathematical expression
Porosity	$\eta$	$\eta = \frac{\text{volume of voids}}{\text{total volume}}$	$\eta = V_v/V_t$
Volumetric water content	$\Theta$	$\Theta = \frac{\text{volume of water}}{\text{total volume}}$	$\Theta = V_w/V_t$
Bulk density	$\rho_w$	$\rho_w = \frac{\text{total weight}}{\text{total volume}}$	$\rho_w = W_t/V_t$
Dry bulk density	$\rho_b$	$\rho_b = \frac{\text{mass of solids}}{\text{total volume}}$	$\rho_b = M_s/V_t$

Source: Mines and Lackey (2009) pg. 319 Reprinted by permission of Pearson Education, Inc., Upper Saddle River, NJ.

## Chapter 12 Hazardous waste management

### 12.3 Physical and chemical characteristics

#### 12.3.4.1 Darcy's Law

Darcy's Law is a generalized relationship that is used to describe the flux通量 (discharge per unit area) of fluid in porous media多孔介质.

$$q = K_C(dh/dL) \quad (12.6)$$

where:

$q$  = Darcy's flux along the flow path (often called the superficial velocity, discharge velocity of Darcy's velocity), m/s

$K_C$  = hydraulic conductivity, m/s

$dh/dL$  = hydraulic gradient, dimensionless.

## Chapter 12 Hazardous waste management

### 12.3 Physical and chemical characteristics

#### 12.3.4.1 Darcy's Law

- The actual velocity of fluid in the pores is larger than the Darcy's flux because the flow through the subsurface is limited by the available pore space in the matrix. The pore velocity,  $v$ , (also referred to as the average linear velocity and the seepage velocity, m/s) is related to the porosity ( $\eta$ ) and the Darcy's flux by:

$$v = q/\eta \quad (12.7)$$

- Sorption of contaminants carried in groundwater results in the contaminant(s) traveling at a lower speed than the fluid flow. This characterization is referred to as retardation 阻滯, and it is fundamental to understanding contaminant transport. The retardation factor 阻滯因子,  $R$  (unitless), is related to the seepage velocity and the velocity of the contaminant ( $v_p$ , m/s):

$$R = v/v_p \quad (12.8)$$

- A conservative, non-interactive material that travels with the speed of the seepage velocity has an  $R$  value of 1. A contaminant with an  $R$  value of 2 will travel at half the groundwater seepage 流动 velocity.

$$R = 1 + \frac{\rho_b}{\eta}(K_d) \quad (12.9)$$

# Chapter 12 Hazardous waste management

## 12.3 Physical and chemical characteristics

### 12.3.5 Density

- The density of a hazardous chemical becomes particularly important for hydrophobic compounds that tend to form their own phase in water once they have exceeded solubility.
- Many hazardous organic chemicals, individually and as mixtures, will form a separate liquid phase when in contact with water, as a result of their sparingly soluble nature 稀溶性 and high KOW. This separate phase is often called “free product”.
- These separate phases are commonly encountered in hazardous waste treatment and remediation and are called on-aqueous phase liquids (NAPLs 非水相液体). Those NAPLs that are light and float on top of the water phase are called light non-aqueous phase liquids (LNAPLs 轻质非水相液体), while those that are dense and settle to the bottom of an aquifer or water-filled area are called dense non-aqueous phase liquids (DNAPLs 密度非水相液体). Gasoline and the individual BTEX compounds are LNAPLs. Chlorinated aliphatics and most of the PAHs are DNAPLs.



# Chapter 12 Hazardous waste management

## 12.3 Physical and chemical characteristics

### 12.3.6 Oxidation state

- A common definition of oxidation is when a molecule loses electrons, and a common definition of reduction is when electrons have been added to a molecule. For hazardous chemicals, and organic chemicals, in particular, the best way to deal with a hazardous chemical may be simply to change the chemistry of that compound, or react it, to make it non-toxic or less toxic. One commonly used option to accomplish this is to oxidize or reduce that hazardous chemical, chemically or microbiologically.
- Common molecular clues that suggest that the oxidation of a chemical is appropriate:
  - The presence of **electron donating groups on a carbon** (OH, NH<sub>2</sub>, CH<sub>3</sub>).
  - The chemical is lightly (1–2) chlorinated.
  - Unsubstituted benzene rings are present.
- Common molecular clues that suggest that the reduction of a chemical is appropriate:
  - The presence of **electron-withdrawing groups on a carbon** (Cl, NO<sub>2</sub>).
  - The chemical is heavily (3+) chlorinated.

# Chapter 12 Hazardous waste management

## 12.4 Remediation

### 12.4.1 Considerations for determining treatment options

- Many options exist for treatment of contaminated material and contaminated sites. The treatment will depend on the nature of the material, the physical and chemical characteristics, as discussed in the previous section of this chapter, and its physical location. Some additional considerations in selecting a treatment approach and treatment technologies are listed below.
  - Is the contamination in the groundwater, the soil, or above ground?
  - Is it a liquid, a solid, or a sludge?
  - Is it organic, inorganic, or a mixture?
  - It is difficult or risky to handle?
  - Is the risk to people and the environment immediate?

# Chapter 12 Hazardous waste management

## 12.4 Remediation

### 12.4.1 Considerations for determining treatment options

**Table 12.6** Proposed treatment approach for remediation of various contaminants.

<b>Treatment Process</b>	<b>BTEX, light hydro-carbons</b>	<b>PAHs</b>	<b>Halogenated solvents</b>	<b>Halogenated PBTs</b>	<b>Aqueous metals</b>	<b>Metal solids and sludges</b>	<b>Cyanide</b>	<b>Chromium</b>	<b>Aqueous pesticides/herbicides/fungicides</b>
Carbon adsorption				×					×
Air or steam stripping	×		×						
Vacuum extraction	×								
Ion exchange					×		×	×	
Chemical precipitation					×			×	
Oxidation/reduction				×			×	×	
Incineration		×		×					
<i>In situ</i> bio-degradation	×		×						
Pump and treat bio-degradation	×		×						
Solids slurry reactor biotreatment		×		×					
Bioventing	×								
Solidification		×		×		×			
Landfilling		×		×		×			

# Chapter 12 Hazardous waste management

## 12.4 Remediation

### 12.4.1 Considerations for determining treatment options

**Example 12.3** Determining best treatment option for various contaminants. How would you choose to treat a waste stream containing PAHs,  $\text{Ni}^{+2}$ , and  $\text{Cd}^{+2}$ ?

#### Solution

- a) First, we must recognize that there are a number of appropriate options for treatment.
- b) Next, look at each waste component and determine if it is best volatilized, adsorbed, absorbed, oxidized, or reduced.

$\text{Ni}^{+2}$  and  $\text{Cd}^{+2}$  are metals and cannot be changed into a non-toxic form. The most appropriate way to treat these two compounds is to remove them from solution, making them as insoluble as possible. This is best accomplished by altering the pH of solution to 8–10.

PAHs (shown in Table 12.3) tend to be reduced compounds, making them easier to oxidize. We can therefore chemically or biologically oxidize the PAHs. We can also see in Table 12.3 that PAHs generally have high KOW values and varying, but generally low, Henry's Law constants. This suggests that adsorption onto a hydrophobic solid, such as activated carbon, is also an option for treatment. Further processing of the carbon will be required after adsorption, such as incineration.



# Chapter 12 Hazardous waste management

## 12.4 Remediation

### 12.4.2 Overriding principles

- Treatment of contaminated sites can be performed in place (in situ) or the material can be removed and treatment can be performed on site or at another location (ex situ). Both approaches are common.
- Treating **in situ** requires that the reactants used **are able to reach the contamination effectively**, and it also requires a very clear understanding of the **geology and hydrogeology of the site**. Removal of contaminants requires care to **avoid spreading the contamination**; nevertheless, it also facilitates the use of a variety of treatment options, with a great deal of control.
- For **ex situ** treatment, it is common to **excavate contaminated soil and treat the entire mass of soil above ground**. This “**pump and treat**” approach may be successful for contaminants that have a low affinity for soil surfaces (low  $K_{OW}$ ). For contaminants that adhere to soils, however (high  $K_{OW}$ ).
- To determine how best to treat a chemical or mixture of chemicals, one must first **evaluate the chemical properties**. Is the material **volatile**? Is it **soluble**? Is it **oxidized or reduced**? Another critical criteria is whether it is **biodegradable or chemically degradable**.

# Chapter 12 Hazardous waste management

## 12.4 Remediation

### 12.4.3 Degradability and biodegradation

- The goal with degrading an organic compound is to form a non-toxic or less toxic product, such as  $\text{CO}_2$  or  $\text{C}_2\text{H}_4$ . To chemically degrade a compound, a reactant is often added. In the case of oxidation or reduction, these reactants are often strong chemicals that are hazardous in themselves and must, therefore, be handled with care. Excess quantities of the reactants are often added to ensure that the target hazardous chemical(s) are degraded efficiently. The kinetics of reaction (Chapter 5) are often critical in such cases.

#### 12.4.3.1 Introduction to Biodegradation

- Biodegradation or microbiological treatment is a frequently used remediation technology because it is usually inexpensive and, if designed properly, it destroys the compounds of interest and changes them into innocuous (or non-harmful) products. To degrade a compound microbiologically, microorganisms (often bacteria, but sometimes fungi) serve as catalysts to enhance the rate.
- Reactants are still typically added, to ensure the efficient degradation of the target chemical(s).
- To design a system to take advantage of microbial processes, one needs to understand the basics of microbial metabolism.

# Chapter 12 Hazardous waste management

## 12.4 Remediation

### 12.4.3 Degradability and biodegradation

#### 12.4.3.2 Metabolism and Metabolic Needs

- Because microorganisms are alive, they have the same basic metabolic needs that other living organisms have. These are:

- 1 a carbon source for cell synthesis;
- 2 an energy source or electron donor for cell maintenance and growth
- 3 an electron acceptor
- 4 nutrients.

Because microorganisms are alive, they also need water, the correct temperature range (typically 20–50° C for engineered systems), the correct pH range (typically 6.5–7.5 for engineered systems), the absence of toxic compounds, adequate contact, and sufficient time for the reaction to occur.

- Hazardous chemicals serve as the electron donor/carbon source or the electron acceptor for microorganisms. To serve as an electron donor, sufficiently reduced so that electrons can be taken from it to “feed” the microorganism. To serve as the electron acceptor, sufficiently oxidized such that it can accept electrons. Some organisms are able to hyper-accumulate certain hazardous compounds, such as metals.

# Chapter 12 Hazardous waste management

## 12.4 Remediation

### 12.4.4 Physical and chemical treatment

#### 12.4.4.1 In Situ Processes

- **NAPLs are often targeted for removal first**, so that the continuous release of hazardous chemicals from this separate phase is stopped.
- **LNAPLs** are typically easier to locate, and they can be removed from soil and groundwater by a variety of techniques, including **pumping the concentrated “free product”** from the surface of the groundwater table.
- **DNAPLs can be particularly difficult to locate in the subsurface**, because they can sink and flow into cracks and fissures at the bottom of aquitards. **If located, DNAPL free product is also removed for reprocessing and reuse.**



# Chapter 12 Hazardous waste management

## 12.4 Remediation

### 12.4.4 Physical and chemical treatment

#### 12.4.4.1 In Situ Processes

- Pump and treat processes are widely used, especially for gasoline spills containing relatively low  $K_{OW}$  chemicals.
- Chemically enhanced pump and treat can be used for hazardous chemicals that have a higher  $K_{OW}$  value. This is accomplished by the use of surfactants or cosolvents to promote the release of sorbed contaminants. These chemicals can be added to water, upgradient of the contamination, and this will increase the contaminant yield as the surfactant and cosolvents help to increase the solubility of hazardous chemicals.
- Because light petroleum products, such as gasoline, diesel oil, and fuel oils, are volatile, they can be volatilized by either drawing a vacuum directly over the contaminant plume (vacuum extraction真空萃取) or by adding air directly into the plume to promote movement of the contamination to the water-air interface (air sparging空气喷射). These two techniques can be combined, or combined with biological processes (bioventing生物通气)

# Chapter 12 Hazardous waste management

## 12.4 Remediation

### 12.4.4 Physical and chemical treatment

#### 12.4.4.2 Ex Situ Processes

- For contaminated groundwater that is pumped to the surface for treatment, the treatment will depend on the nature of the contamination. Fuels and BTEX can be treated by **air stripping** 空气剥离法 (if they have a high Henry's Law Constant), adsorption onto activated carbon (if they have a high  $K_{OW}$  value), or biological treatment. In this way, the contaminants move from the aqueous phase to the gaseous phase, where they can then be treated (often by incineration or carbon adsorption) prior to venting into the atmosphere.
- **Activated carbon** is a hydrophobic solid with an extremely high surface area. It is often used to remove dilute hydrophobic hazardous chemicals from an aqueous or gas stream. This occurs because chemicals with a higher  $K_{OW}$  value prefer to stick to a hydrophobic surface, rather than reside in the water or gaseous phase.

# Chapter 12 Hazardous waste management

## 12.4 Remediation

### 12.4.4 Physical and chemical treatment

#### 12.4.4.2 Ex Situ Processes

- Cyanides may be oxidized using chlorine gas, hypochlorite (most common), ozone, or hydrogen peroxide. Cyanide can also be oxidized using oxygen, but this requires activated carbon and a copper catalyst .
- Chromium (VI) can be reduced to chromium (III) by the addition of a strong chemical reductant – sulfur dioxide or ferrous sulfate 硫酸亚铁 are common. The chromium (III) is then precipitated by increasing the pH. Chromium (present as negatively charged chromate ions 以带负电荷的铬酸盐离子形式存在) can also be removed by ion exchange.
- Halogenated PBTs and solvents can be dehalogenated 脱卤 and detoxified by chemical or biological reduction, through the addition of a strong chemical, or in a manner similar to in situ bioremediation.

# Chapter 12 Hazardous waste management

## 12.4 Remediation

### 12.4.4.2 Ex Situ Processes

- Ion exchange can be used to remove dilute ions from solution, such as cyanide, radionuclides, or heavy metals. In ion exchange, the solid packing material 填料, such as an engineered polymer bead 聚合物微球, contains fixed ionic groups. **Electroneutrality must be maintained.** Ion exchange resins 树脂 can be very general or very selective. Clays and some soils can also function as ion exchangers.
- For groundwater that contains heavy metals, chemical precipitation 化学沉淀法 is frequently used. **Because heavy metals are more soluble at the extremes of the pH scale, this usually requires pH adjustment.** A flocculating 絮凝 chemical may also be added, much like in drinking water treatment, to improve precipitation.
- Precipitation results in the production of a metal-laden sludge that requires further treatment or disposal. These metals can be re-smelted from the sludge and reused. The addition of specialty chemicals or pozzolanic 泡沫塑料 materials for fixation or solidification 固定或固化 can greatly reduce the potential for leaching of the metals once the sludge is placed in the landfill or disposal site.
- For solid organic wastes, such as PAH sludges and sediment contaminated with halogenated PBTs, incineration can be used to destroy the hazardous chemicals. It is difficult to get permits for hazardous waste incinerators, and they can be very expensive and energy-intensive to operate, as air pollution control is a major consideration.



# Chapter 12 Hazardous waste management

## 12.4.5 Bioremediation

- Bioremediation can take place in situ or ex situ and is often used for the oxidation or reduction of hazardous waste. Typically, oxidation and reduction reactions take place under very specific conditions.
- It is helpful to remember that organisms thrive where they have a competitive advantage over other organisms. Part of good engineering is providing this competitive advantage for microorganisms capable of degrading hazardous chemicals, through the targeted addition of a carbon source, electron donor, electron acceptor, and/or nutrients.
- In situ treatment often consists of the addition of nutrients and sometimes an electron acceptor, electron donor, or microorganisms to a site through the use of wells. This is called biostimulation生物刺激. If the target chemical is reduced, such as BTEX, nutrients and an electron acceptor such as oxygen are often added so that the BTEX compounds can serve as the electron donor (or “food”). If the target chemical is oxidized, such as PERC, an electron donor (such as molasses or vegetable oil) is often added to “feed” organisms, such that they use the PERC as an electron acceptor. Microorganisms from off-site can also be added to degrade hazardous chemicals. This is called bioaugmentation生物增殖. Ex situ treatment is similar.

## ● Chapter 12 Hazardous waste management

### Summary

- Hazardous wastes are defined as wastes that are likely to cause a threat to the human or environmental health as a result of their **toxicity or flammable, explosive, or corrosive nature**.
- RCRA defines a hazardous waste as, “**a solid waste, or combination of solid wastes, which because of their quantity, concentration, or physical, chemical, or infectious characteristics, may:**
  - **cause, or significantly contribute to an increase in mortality or an increase in serious irreversible, or incapacitating reversible illness, or**
  - **pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.”**
- CERCLA broadens this definition to include, “**any chemical regulated under the Clean Water Act, the Clean Air Act, the Toxic Substances Control Act, or the Resource Conservation and Recovery Act; also, any other chemical or agent that will or may reasonably be anticipated to cause harmful effects to human or ecological health.”**
- **RCRA and CERCLA** are the two of the most important laws regarding the management of hazardous waste. **RCRA** is generally considered to describe the management of hazardous compounds as they are generated. **CERCLA** describes the management of old or abandoned hazardous waste sites.

## ● Chapter 12 Hazardous waste management

### Exercises

1. Characteristic hazardous wastes are materials that fit RCRA-defined criteria of \_\_\_\_\_ , \_\_\_\_\_ , \_\_\_\_\_ , or \_\_\_\_\_ .
2. \_\_\_\_\_ and \_\_\_\_\_ are the two of the most important laws regarding the management of hazardous waste.
3. Because microorganisms are alive, they have the same basic metabolic needs that other living organisms, such as humans, have. These are: 1). \_\_\_\_\_ ; 2). \_\_\_\_\_ ; 3). \_\_\_\_\_ ; 4). \_\_\_\_\_ .
4. Petroleum products can be volatilized by either drawing a vacuum directly over the vacuum extraction or \_\_\_\_\_ , \_\_\_\_\_ or \_\_\_\_\_ .
5. Treatment of contaminated sites can be performed \_\_\_\_\_ or the material can be removed and treatment can be performed on site or at another location \_\_\_\_\_ .

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Thanks!