(강의노트)

지하수 및 토양 오염

Hazardous Wastes: Sources, Pathways, Receptors
(2nd Ed, Richard J. Watts)

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지구환경시스템공학부
3학년 2학기
담당교수: 남 경 필

Chapter 1. Introduction

1. Case Histories (p. 8)

1) Love Canal (NY): DDT, 2,4,5-T, chlorinated solvents
2) *Exxon Valdez* (Prince William Sound, AK)
   a) Oil spill in marine and coastal regions (March, 1989).
   b) Bioremediation used as a supplemental cleanup technology.
   c) <u>Biodegradation, 1992, 3:315-335.</u>
   d) Cleanup action finished. Ecological and toxicological studies left.
   e) Biodegradation indicator; n-C18/phytane ratio.
3) Stringfellow Acid Pits (CA): hazardous waste landfill
4) Hardeman County (TN): waste pesticides and solvents

2. The Magnitude of the Problem (p. 9)

1) ca. 60,000 Superfund sites in the US
2) over 1,200 sites listed on National Priorities List (NPL)
3) more than 600 chemicals found at Superfund sites
   : TCE, PCE; benzene, toluene; Pb, Cr, As, ...

3. Hazardous Waste Legislation (p. 13)

1) RCRA (Resource Conservation and Recovery Act, 1976)
   a) Hazardous waste must be "solid waste" first
   b) Solid wastes includes solid, liquid, semisolid, contained gaseous materials
   c) a cradle-to-grave system for the management of hazardous waste.
   d) requires a manifest system for the generation, transportation, treatment, storage, and disposal of hazardous wastes.
   e) requires permits for the treatment, storage, or disposal.
2) CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act, 1980) and SARA (Superfund Amendments Reauthorization Act, 1986)
   a) provides for remedial action at inactive or abandoned hazardous waste disposal sites.
   b) provides for removal (also cleanup) of spills of hazardous wastes.
   c) provides for reporting releases to the environment of wastes
   d) provides for natural resource damage assessments.

<u>◎ National Contingency Plan (NCP, p. 25)</u>

: the blueprint for the cleanup of contaminated sites (including guidelines for site ranking, site assessment, feasibility studies, and cleanup actions)

① site ranking based on a Preliminary Assessment (PA) and a Site Inspection (SI)
   --> Hazardous Ranking System (HRS) score

② Remedial Investigation/Feasibility Study (RI/FS)

- RI focuses on documenting sources, degree of contamination, environmental pathways, and potential adverse effects on human and the environment, and finally provides a risk assessment at the site of interest.
- FS focuses on assessing remedial designs and provides engineering criteria for feasibility, costs, operational control, etc.

③ Record of Decision (ROD)
- US EPA selects the appropriate remedial design.

◎ How clean is clean? (p. 26)

① Potential human health effects need to be evaluated by quantitative risk assessment on a site-by-site basis.
② reasonable and cost-effective cleanup level?
③ Applicable or relevant and Appropriate Requirements (ARARs)
e.g.) usually use Maximum Contaminant Levels (MCLs) as a cleanup level for contaminated groundwater (from Safe Drinking Water Act)
④ remediation vs. restoration

3) The Clean Water Act (1972)
4) The Toxic Substances Control Act (ToSCA, 1976)
5) The Safe Drinking Water Act (SDWA, 1974)
: MCLs of 39 chemicals --> related to cleanup standards
6) The Clean Air Act (1970)
7) The Federal Pollution Prevention Act (PPA, 1990)
a) to promote the minimization and source reduction of hazardous wastes
b) Pollution prevention (P2) and waste minimization are more important than recycling, treatment, and proper disposal (e.g., landfilling) receive lower priorities in the management of hazardous wastes.

4. The Nature of Hazardous Waste Management, Assessment, and Control (p. 34)

1) Site assessment: RI/FS
2) Risk assessment: risk = hazard + exposure
3) Emergency response
4) Soil and groundwater remediation
5) Brownfield development
a) usually for industrial properties; neither pristine nor blackened
b) cleanup to acceptable levels (based on risk, not on concentration)
6) Treatment, storage, and disposal design and permitting
7) Waste minimization and pollution prevention (*before contamination*)
8) Hazardous waste treatment (*after contamination*)
: incineration (physical), land treatment (biological), advanced oxidation (chemical)
9) Hazardous waste management

5. Source-Pathway-Receptor Analysis (p. 38)

: helps to decide cleanup level, degree of remediation, technology to be used,...

1) Sources

a) kinds of contaminants and their concentrations

b) physical, chemical properties (e.g., polarity...)

c) forms of existence (e.g., solid, solubilized, NAPL, gas, etc)

2) Pathways

a) degradation; biotic (by microorganisms), abiotic (by chemical, light...)

b) migration; sorption, leaching, volatilization,...

c) usually use mathematical models for predicting exposure

d) based on environmental conditions (soil and hydrogeological properties,...)

3) Receptors

a) human beings (human risk assessment, usually for cancer)

b) ecosystem (ecological risk assessment)

c) based on toxicological information and statistical analysis

Chapter 2. Common Hazardous Wastes: Nomenclature, Industrial Uses, Disposal Histories

1. Introduction to Organic Chemistry (p. 48)

: organic compounds; mainly C, H but O, N, P, S, and halogens (Cl, Br,..) also

1) Carbon bonding

a) ionic bonding; donation of a valence electron from an electropositive atom to an electronegative atom (e.g., NaCl, $MgCl_2$,...)

b) covalent bonding;

- occurs when two atoms share valence electrons
- usually N, O, C, S, or Si is involved (e.g., H_2O, NH_3, H_2S,...)
- The bonds of organic compounds are covalent!

◎ Polarity, nucleophilic attack, and degradation (p. 51)

① polarity due to the differences in electronegativity between atoms

② unequal distribution of electron clouds --> partial charges --> polarity

e.g.) compare the electron clouds of H_2 and H_2O

③ chemical reaction:

- Low electron density (i.e., electron poor region of a chemical) allows attack by nuclephiles (such as H_2O, OH^-); e.g.) parathion

④ biological reaction:

- Biological degradation rates are lowered by electron-poor areas of organic compounds; e.g.) pentachlorophenol

2) Nomenclature of organic compounds (p. 51)

a) aliphatic hydrocarbons;

alkanes (radical forms; alkyl groups), alkenes (PCE, TCE..), alkynes

b) aromatic hydrocarbons;

- monoaroatics (phenolics, BTEX,...)
- polyaromatics (PAHs,...)

c) isomers; same chemical formulas but different structural configurations (i.e., from 4-carbon aliphatic compounds)

d) IUPAC (International Union of Pure and Applied Chemists) nomenclaure vs. conventional name

- e.g.) CH_2Cl_2; 1,2-dichloromethane, methylene chloride

◎ Aromatic compounds (p. 63)

① resonance structure (alternating single and double bonds between C atoms)

② π-bonds between aromatic compounds (stacking of aromatic rings possible!)

③ more stable than alkenes (e.g., benzene vs. cyclohexene)

④ substitution reaction for benzene and addtion reaction for cyclohexene

e) Nomenclature of benzene derivatives (p. 64)

f) Polycyclic Aromatic Hydrocarbons (PAHs, p. 68)

; incomplete combustion of organic compounds, heavier fractions of petroleum products, cigarette smoke, blackened barbecued food,...

2. Petroleum Products (p. 77)

1) UST (Underground Storage Tank) leakage
2) aliphatic and aromatic hydrocarbons
3) BTEX (Benzene, Toluene, Ethylbenzene, Xylenes)
4) TPHs (Total Petroleum Hydrocarbons)
5) Characteristics of petroleum products (Table 2.11, Table 2.12)
6) Gasoline additives;
   - Pb (leaded vs. unleaded)
   - oxygenates (e.g., methyl *tert*-butyl ether, MTBE)

3. Nonhalogenated Solvents (p. 81)

1) Hydrocarbons
2) Ketones
3) Alcohols and Esters

4. Halogenated Solvents (p. 85)

: an important class of environmental contaminants (volatile, mobile, dense, moderate soluble, less degradable)

- halogenation of hydrocarbons --> lower flammability, higher density and viscosity --> improved solvent properties (for degreasing and cleaning)
- methane derivatives; methylene chloride (dichloromethane), chloroform (trichloromethane), carbon tetrachloride (tetrachloromethane)
- derivatives of ethane, ethene (ethylene); 111-trichloroethane (TCA), trichloroethylene (trichloroethene, TCE), perchloroethylene (tetrachloroethene, PCE)

5. Pesticides (p. 90)

1) Insecticides

a) organochlorine insecticides;
   - highly lipophilic, recalcitrant, bioconcentrated, chronic toxicity
   - most banned nowadays but present in the environment as residues
   - e.g.) DDT, methoxychlor, lindane, aldrin, dieldrin,...

b) organophosphorus esters;
   - less persistent (days to weeks), less adverse effects, more degradation, but, higher acute toxicity than organochlorine insecticides
   - e.g.) parathion, malathion,...

c) carbamate esters;
  - widely used along with organophosphorus esters
  - moderately labile in the environment, low acute toxicity
  - e.g.) carbaryl, carbofuran, aldicarb,...

2) Herbicides (generally less persistent and chronically toxic than organochlorines)
  a) acid amides; alachlor, propanil,,...
  b) aliphatics; glyphosate, methyl bromide,...
  c) phenoxy herbicides; 2,4-D (2,4-dichlorophenoxy acetic acid), 2,4,5-T (2,4,5-trichlorophenoxy acetic acids)
  d) substrate ureas; diuron, linuron (persist in soils for up to a year)
  e) triazines; atrazine (strongly sorb but mobile also, found in aquifers)

3) Fungicides
  a) pentachlorophenol (PCP); wood preservative and insecticide also
  b) ethylene dibromide (1,2-dibromoethane, EDB); soil fumigants

6. Explosives (p. 104)

: aliphatic or aromatic structure with substituted nitro ($-NO_2$) groups
- aliphatic nitrate esters; nitroglycerin
- nitramines; RDX (cyclotrimethylenetrinitramine),
  HMX (cyclotetramethylenetetranitramine)
- nitroaromatics; TNT (2,4,6-trinitrotoluene), picric acid (2,4,6-trinitrophenol)

7. Industrial Intermediates (p. 109)

- phthalene esters; plasticizers or softners (e.g., phthalic acid)
- chlorobenzenes, chlorophenols;
  2,4-dichlorophenol in the manufacture of 2,4-D
  2,4,5-trichlorophenol in the manufacture of 2,4,5-T
- anilines; in the synthesis of inks, dyes, frugs, photographic developers
- hexachlorocyclopentadiene; in the synthesis of aldrin, dieldrin, chlordane,,,,

8. Polychlorinated Biphenyls (p. 114)

- heat-stable nonflammable oils once used extensively as transformer and hydraulic fluids (--> high persistence and toxicity)
- banned in 1979, but still present in the environment
- biphenyl molecule with chlorine substitution up to 10 positions
- congeners; 207 products possible
- e.g.) Aroclor 1221, Aroclor 1232,...

9. Polychlorinated dibenzodioxins and dibenzofurans (PCDDs, PCDFs; p. 116)

- not intentionally manufactured chemicals
- trace impurities formed during the manufacture, chlorination or combustion of

other organic compounds

- collectively called "(chlorinated) dioxins", derivatives of dibenzo-*p*-dioxin
- 75 possible congeners

◎ Generation of dioxins and their toxicities

① In the course of manufacturing 2,4,5-T (i.e., trichlorophenol + chloroacetic acid), two molecules of trichlorophenols may dimerize to form 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD).

② Chlorinated dioxins are produced during (incomplete) combustion at low-to-moderate temperatures, even from innocuous materials such as firewood (like PAHs).

③ 2,3,7,8-TCDD is the most toxic (--> Toxic Equivalent Factor, TEF 1.0). Other dioxins' toxicities are expressed based on a reference TEF of 1.0

10. Metals and Inorganic Nonmetals (p. 119)

- semantic definitions of heavy metals; i) elements with atomic numbers greater than iron ii) metals with densities greater than 5.0 g/cm^3
- what about Al (atomic number 13)?; regarded as a heavy metal
- another definition; metals cause adverse biological (=toxic) effects

1) Arsenic (As)
   a) present as anionic forms in solution
   b) arsenite AsO_3^- (As^{3+}); under reduced conditions, more toxic
   c) arsenate AsO_4^{3-} (As^{5+}); under aerobic conditions, less toxic
   d) extensively used in agriculture (weed control, insecticidal ingredients,...)
2) Cadmium (Cd)
   a) always found as Cd^{2+}
   b) highly toxic and accumulative
3) Chromium (Cr)
   a) highly toxic, stable, soluble; Cr^{6+}(chromate CrO_4^{2-}, dichromate $Cr_2O_7^{2-}$)
   b) insoluble form in water; Cr^{3+} (low toxicity)
4) Lead (Pb)
   a) low water solubility and strong tendency to sorb and exchange on solids
   b) less mobile in the environment
5) Nickel (Ni)
6) Mercury (Hg)
   a) three forms possible; elemental, inorganic, organic
   b) Hg^0 present as a liquid at room temperature
   c) Hg^0 for porosity measurement (e.g., Mercury porosimeter)
   d) bioconcentration (in fish); methyl mercury (CH_3Hg^+)
   e) volatilization and global recycling; dimethyl mercury (CH_3HgCH_3)
   f) $HgCl_2$; biocide (used to sterilize environmental samples)

7) Cyanides (-CN)
   a) inorganic nonmetal anions
   b) HCN; highly toxic, acute poison
8) Asbestos
   a) a group of six mineral fibers (hydrated magnesium silicates)
   b) nonflammable, strong, resistant to acids
   c) indoor air pollution
   d) toxic only through inhalation (not from dermal contact, ingestion,..)
      --> "route of exposure" is important!!!

11. Nuclear Wastes (p. 127)

Chapter 3. Common Hazardous Wastes: Properties and Classification

1. Common Concentration Units (p. 155)

1) SI vs Non-SI units (SI; International System of Units)
2) conversion of ppm to concentration

2. Water Solubility (p. 160)

1) definition; "maximum (saturation) concentration of a substance that will dissolve in water in a given temperature"
2) soluble vs. insoluble (filtration through 0.45-μm pore sized membrane)
3) polar (hydrophilic) vs. nonpolar (hydrophobic); Table 3.5
   - e.g.) water vs. hexane
4) controls the environmental fate of waste chemicals
   a) inversely proportional to sorptivity, bioaccumulation, volatilization from aqueous solutions
   b) influence biodegradation, photolysis, chemical oxidation,...
5) determined by intermolecular attractive forces between solute-solvent molecules
   a) van der Waals force
   b) hydrogen bonding (mainly with -OH, $-NH_2$ groups)
   c) dipole-dipole interaction (by electronegativity difference)
6) related to the size and structure of a chemical
   a) functional groups may or may not affect
   b) molecular volume (halogens increase m.v. -> decrease water solubility)
   c) Table 3.1
7) water solubilities of weak organic acids (bases)
   a) basic (ionized) form is more soluble than acidic (unionized) form
   b) [ionized forms] $\propto$ water solubility
   c) pH vs. pKa (pH where [unionized forms] = [ionized forms])
      - pH < pKa ; protonated (acidic, unionized form)
      - pH > pKa ; deprotonated (basic, ionized form)
   d) solubility change depending on pH
   e) *Handerson-Hasselbalch* equation (Fig. 3.1)
      - calculates the degree of acidic dissociation at a given pH
   f) fraction of unionized acid (α);
      - $\alpha = (1 + \frac{K_a}{[H^+]})^{-1}$ (Ka = $\frac{[base][H^+]}{[acid]}$; acid dissociation constant)
      - used to correct transport models;
        ionized forms are miscible in water -> no retardation (p. 281)
8) acidity of chlorophenols with higher chlorine substitution (Table 3.2)
   a) Cl- is a highly electronegative element
   b) more Cl- on the ring -> proton(s) more easily released -> higher acidity

3. Density and Specific Gravity (p. 167)

- density; ratio of mass to volume (g/mL, kg/m^3)
- specific gravity; a compound's density to that of water (1.0 g/mL at 4°C)
- (aliphatic) hydrocarbons are lighter than water
- substitution of a chlorine atom on a hydrocarbon increases its density (density; H < C < Cl)
- influence contaminants' fate and remediation technology selection (esp. in groundwater); Table 3.6
- metals are more dense than water

4. Light and Dense Nonaqueous Phase Liquids (p. 170)

; NAPL(s) as a continuous source in the subsurface system

1) LNAPL (Light Nonaqueous Phase Liquid)
   a) floats on groundwater surface
   b) easily detected
   c) apliphatic hydrocarbons, BTEX, nonhalogenated solvents,...
   d) Fig. 3.2 (a)
2) DNAPL (Dense Nonaqueous Phase Liquid)
   a) sinks into the bottom of subsurface system (fractures, pores,...)
   b) form pools, lenses
   c) halogenated solvents,...
   d) Fig. 3.2 (b), Example 3.4
3) dissolution
   a) transfer of a compound from its insoluble phase into the water
   b) generally rate-limiting step in degradation (remediation) of a contaminant
   c) rate of dissolution [(mg/L)/min]

$$\frac{dC}{dt} = K \cdot (C_s - C)$$

K (min^{-1}); mass transfer coefficient (from NAPL to water phase)
C_s (mg/L); contaminant water solubility
C (mg/L); contaminant concentration at a site

4) effective solubility
   a) solubility of the mixtures of NAPLs
   b) usually less than the water solubility of a single compound
   c) effective solubility of compound i (mg/L)

$$S_i^e = X_i S_i \gamma_i$$

X_i = mole fraction of compound i in the NAPL mixture
S_i = water solubility of compound i found in literatures
γ_i = correction factor that normalizes solubility based on field conditions and water chemistry

5. Flammability Limits (p. 177)

6. Flash point and Ignition Temperature (p. 182)

7. Chemical Incompatibility (p. 184)
   - Chemicals must be combined and stored in a rational manner so that mixing does not result in chemical reactions that cause immediate safety and health hazards (e.g., fire, explosion, heat, toxic gases).

8. Labels and Placards (p. 191)

9. Chemical Abstract Service Registry Numbers (p. 198)
   - CAS registry number
     (e.g.) benzene; CAS 71-43-2

10. Priority Pollutants (p. 202)
    - 129 priority pollutants (Table 3.18)

11. Supplemental Data on Contaminant Properties (p. 202)
    - MSDS (Material Safety Data Sheets)

Chapter 4. Source Analysis

1. Materials Balances and Waste Audits (p. 212)
   - hazardous waste audit; tracking of hazardous wastes within an industry, a waste transfer station, or after excavation from a contaminated site

2. Hazardous Waste Site Assessments (p. 216)
   - Hazardous wastes sites must be assessed to determine the extent of contamination before cleanup is initiated.

   a) Phase I assessment
      - to confirm the suspicions of the presence of hazardous wastes
      - involves documents and paper research including
        a chemical inventory evaluation,
        interviews with current and former personnel and neighbors,
        regulatory agency record searches and interviews, and
        title searches and reviews of historical ownership,...
      - on-site inspection also required (i.e., to find clues of contamination)
      - to provide a basis for further investigation, not to determine whether a site is contaminated or not

   b) Phase II assessment
      - to confirm or deny the presence of hazardous wastes at the site
      - includes a detailed evaluation of pathways and potential receptors
      - extensive sampling and analysis around source areas

   c) Phase III assessment
      - conducted if Phase II assessment shows that the site is contaminated
      - to detail the extent of contamination in terms of the area, volume, and concentrations
      - more extensive sampling and analysis around the source and adjacent areas (i.e., soil, subsurface, groundwater)
      - to provide criteria for an appropriate remedial design

3. Estimation of Source Concentrations for Hazardous Material Spills (p. 218)

4. Source Sampling (p. 219)
   - one of the most important procedure
   - generally use statistical methods to minimize sampling errors
   - sampling errors mainly from heterogeneous media
   - "sampling errors are usually greater than analytical errors"

5. Source Sampling Procedures and Strategies (p. 229)

6. Sampling away from the Source (p. 232)

- often a prerequisite before designing remediation systems and documenting their effectiveness during operation

7. Priority Pollutant and Sample Analyses (p. 241)

- among a list of 129 chemicals, 114 organics, 13 metals, 1 mineral, and 1 inorganic nonmetal
- organics; extraction through simple solvent shaking or Soxhlet apparatus (continuous solvent flushing with heat)
- analysis; GC/FID (EDC...), HPLC, AA (Atomic Absorption) spectrophotometer, ICP (Inductively Couple Plasma)
- US EPA Method 600 series (for aqueous samples), 8,000 series (for soils and sludges); Table 4.3