February 25, 2021

LECTURE 01

Introductory class

March 03, 2021

LECTURE 02

INTRODUCTION TO SOIL SCIENCES

Reference Book

“Elements of the Nature and Properties of Soil”, Nyle C. Brady and Ray R. Weil, 3rd Edition, Prentice Hall, 2010

What is “soil”?

(Ground, soil, earth, and dirt (terminologies) are distinguished on the basis of properties.)

- Soil is a material composed of minerals (including salts), gases, water, organic substances and microorganisms.
- Some people (usually not soil scientists) also refer to this material as dirt, especially when it is found where it is not welcomed (for example in your clothes or under your fingernails).
- Soils are crucial to life on Earth.
- To a great degree, the quality of the soil determines the nature of plant ecosystems and the capacity of land to support animal life and society.
- How many of us remember, as we eat a slice of pizza, that the pizza’s crust began in a field of wheat, and its cheese began with grass, clover and corn rooted in the soil of a dairy farm.
- We must greatly improve our understanding of the soil resources if we as a species are to survive.
- In parts of the world, the capacity of soil to produce food is being degraded (The causes of which are urbanization, sea water intrusion, overpopulation, industrialization, lack of nutrients, crop rotation and other natural phenomenon such as forest fire, soil erosion etc.).
- Revitalization and remediation of soil are used.
- Bringing the global environment back into balance is a defining challenge of our times.

FUNCTIONS OF SOIL

The many functions of soil can be grouped into six crucial ecological roles:

1. Medium for plant growth
2. System for water supply and purification
3. Recycling system for nutrients and organic wastes
4. Modifier of the atmosphere
5. Habitat for soil organisms
6. Engineering medium

Soil as a Media for Plant Growth

- Soil provides a medium for plant roots and supply nutrient elements that are essential to the entire plant.
- What a plant obtains from the soil in which its roots proliferate?
- Physical support
- Air
- Water
- Temperature moderation
- Protection from toxins (biological origin)
- Nutrient elements
- Of the 92 naturally occurring elements, 17 have been shown to be essential elements, meaning that plants cannot grow and complete their life cycles without them.
- The 17 essential elements are:

C. B. HOPKi**NS CaFe**

Closed **Mo**nday **M**or**n**ing and **Ni**ght

See You, Zoo**n,** the **Mg**

Soil as a Regulator of Water Supplies

- Most of the water in our rivers, lakes, estuaries, and aquifers has either travelled through the soil or flowed over its surface.
- Contaminated water is purified and cleansed by soil processes that remove many impurities and kill potential disease organisms.
- The nature and management of soils have a major influence on the purity as well as the amount of water finding its way to aquatic systems.

Soil as a Recycler of Raw Materials

- The soil system plays a pivotal role in the major geochemical cycles.

- Soils have the capacity to assimilate great quantities of organic waste turning it into beneficial humus, converting the mineral nutrients in the wastes to forms that can be utilized by plants and animals, and returning the carbon to the atmosphere as carbon dioxide where it again will become a part of living organisms through plant photosynthesis.

Soil as a Modifier of the Atmosphere

- The soil interacts in many ways with the earth's blanket of air.
- In places where the soil is dry, poorly structured, and un-vegetated soil particles can be picked up by winds and contribute great quantities of dust to the atmosphere reducing visibility, increasing human health hazards, from breathing dirty air and altering the temperature of the air and the planet.
- Soil also breathes in and out. They absorb oxygen and other gases such as methane, while they release gases such as CO_2 and nitrous oxide.
- These gas exchanges between the soil and the atmosphere have a significant influence on atmospheric composition and global warming.

Soil as a Habitat for Soil Organisms

- Soil is not a mere pile of broken rock and dead debris. A handful of soil maybe home to billions of organisms, belonging to thousands of species.
- In even this small quantity of soils, there exists predators, prey, producers, consumers and parasites.

Soil as Engineering Medium

- Soil is probably the earliest and certainly one of the most widely used building materials.
- Nearly half the people in the world live in houses constructed from soil.
- Unfortunately, some soils are not as stable as others.
- Reliable construction on soils and with soil materials requires knowledge of the diversity of soil properties.

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LECTURE 03

Soil: The Interface of Air, Minerals, Water and Life

- The four major components of soil are air, water, mineral matter and organic matter.
- The relative proportions of these four components greatly influence the behavior and productivity of soils.
- The relative proportions of water and air in a soil typically fluctuate greatly as water is added or lost.
- Soils with much more than 50 percent of their volumes in solids are likely to be too compacted for good plant growth.
- Volume composition of a loam surface soil when conditions are good for plant growth. The proportion of these two components (air and water) fluctuates as soil becomes drier or wetter.
- Soil solids: Minerals 45%, Organic 5%
- Pore Space: Air 20-30%, Water 20-30%

Mineral (Inorganic) Constituents of Soil

- The larger soil particles (stones, gravel and coarse sands) are generally rock fragments consisting of several different minerals. Smaller particles tend to be made of a single mineral.
- Excluding the large rock fragments such as stones and gravel, soil particles range in size over four orders of magnitude; from 20mm to smaller than 0.0002 mm in diameter.
- **Sand particles** are larger enough (2.0 to 0.05mm) to be seen by naked eye and feel gritty when rubbed between the fingers.
- **Silt Particles** are too small (0.05 to 0.002mm) to see without a microscope or feel individually. It feels smooth but not sticky when touched.
- **Clay particles** are the smallest mineral particles (< 0.002mm) and adhere together to form a sticky mass when wet and hard clods when dry.
- The proportion of particles in these different size ranges is described by **soil texture**. Terms such as sandy loam, silt clay and clay loam are used to identify the soil texture.
- Sand silt and clay particles can be thought of as the building blocks from which soil is constructed. The way these building blocks are put together is called **soil structure**.

Soil Organic Matter

- Soil organic matter consist of a wide range of organic (carbonaceous) substances, including living organisms (the soil biomass) carbonaceous remains of organisms that once occupied the soil, and organic compounds produced by current and past metabolism in the soil.

- By weight, typical well drained mineral surface soils contain from 1 to 6 percent organic matter. The organic matter content of subsoil is even smaller.
- As we go deeper the organic matter content decreases in soil. It is higher at the top.
- However, the influence of organic matter on soil properties and consequently on plant growth is far greater than the low percentage would indicate.
- Organic matter binds mineral particles into a granular soil structure.
- Organic matter also increases the amount of water a soil can hold and proportion of water available for plant growth (more organic matter, more withholding capacity).
- Abundant organic matter, including plant root, helps create physical conditions favorable for the growth of higher plant as well as microbes left. In contrast, soil in low organic matter especially if they are high in silt and dry are often clod.

Soil Water

- The presence of water in soils is essential for the survival and growth of plants and other soil organisms.
- Water is held within soil pores with varying degrees of tenacity depending on the amount of water present and size of the pores.
- The attraction between water and the surfaces of soil particles greatly restricts the ability of water to flow.
- Not all soil water is available to plants.
- Because soil water is never pure water but contains hundreds of dissolved organic and inorganic substances, it may be more accurately called the **soil solution**.
- The soil solution tends to resist changes in its composition. This ability to resist change is termed as the **soil buffering capacity**.

Soil Air

- Approximately half of the volume of the soil consists of pore spaces of varying sizes, which are filled with water or air.
- Soil air generally has a higher moisture content than the atmosphere; the relative humidity of soil air is 100 percent unless the soil is very dry.
- The content of CO_2 is usually much higher as compared to oxygen. Essential elements in humid region are drained by water while retained in arid regions.
- P, S, N are not exchangeable. They need oxygen. Ca, Mg, K are in ionic form, so they are exchangeable.

Soil Quality, Degradation and Resilience

- Managed carefully, soils are a reusable resource, but in the scale of human lifetimes they cannot be considered a renewable resource.

- In all regions of the world, human activities are destroying some soils far faster than nature can rebuild them.
- As each year brings millions more people to feed, the amount of crop land per person continuously declines.
- In addition, many of the world's major cities were originally located where excellent soils supported thriving agricultural communities.
- Finding more land on which to grow food is not easy.

Soil Quality

- Soil quality is a measure of the ability of a soil to carry out particular ecological functions. Soil quality reflects a combination of chemical, physical and biological properties.
- Mismanagement of forests, farms and rangeland causes widespread degradation of soil quality by erosion that removes the topsoil.
- Another widespread cause of soil degradation is the accumulation of salts in improperly irrigated soil in arid region.
- Contamination of a soil with toxic substances from industrial processes or chemical spills can degrade its capacity to provide habitat for soil organisms, to grow plants that are safe to eat or to safely recharge ground and surface waters.

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- Sustainable soil management means using soil in ways that will provide current benefits without jeopardizing capacity of the soil resources to specify the needs of future generation.
- While sustainable soil use that protects soil quality must be first priority, it is often necessary to attempt to restore the quality of soils that has already been degraded.
- Some soils have sufficient resilience to recover from minor degradation if left to revegetate on their own.
- Organic and inorganic amendments may have to be applied, vegetation must be planted, physical alterations by tillage or grading may have to be made, or contaminants may have to be removed.
- If we take the time to learn the language of the land, the soil will speak to us.

IDENTIFYING AND DEALING WITH CONTAMINATED SOILS

- Regulators are charged with ensuring that the public interest is protected.
- A range of scientific and engineering disciplines are relevant, including toxicology, hydrogeology, and civil engineering as well as environmental and analytical chemistry.
- Applying these disciplines to contaminated land in an integrated manner requires effective team working and honesty about the limits of understanding and practices.

Site Assessment

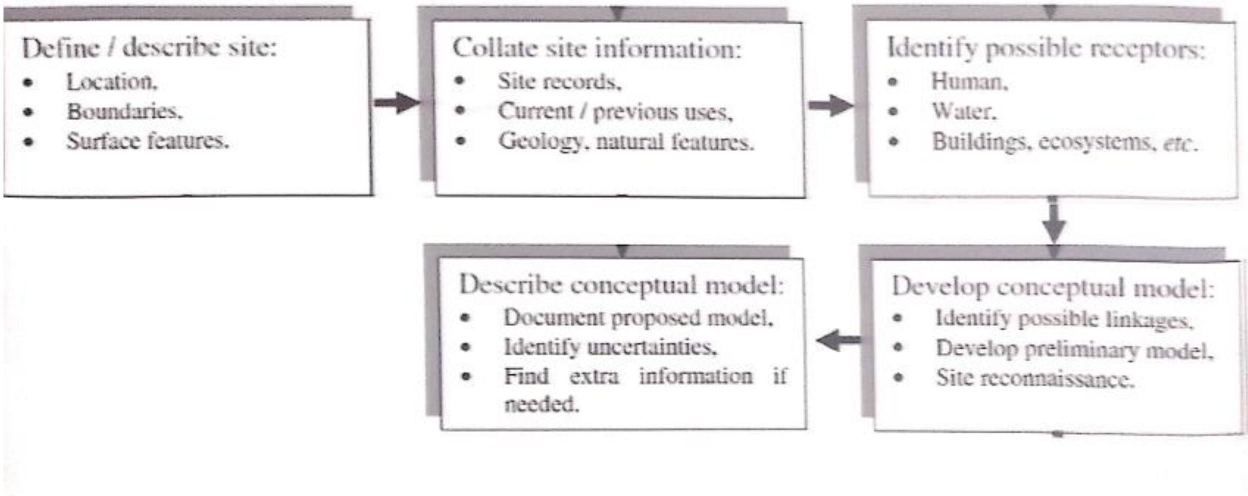
- The purpose of individual site assessment is to decide whether or not a site poses actual or potential risks to human health or the environment.
- A phased approach is recommended in accordance with recent guidance on environmental risk assessment and management.
- Three assessment phases are recognized widely:
- Phase 1a – Hazard Identification
- Phase 1b – Exposure Assessment
- Phase 2 Risk Assessment

Phase 1a-Hazard Identification

- The objective of this phase is to develop a conceptual model for the site, which describes the important source – pathway – receptor linkages for the site and makes a preliminary assessment of their importance.

Identifying and Dealing with Contaminated Soils

Phase 1a—Hazard Identification



- Using public, commercial, and private records, the important current and historic features of the site are identified.
- These include boundaries, buildings, waste disposal areas and made-ground, topography and natural features-such as surface waters, underlying geology and hydrogeology, and important habitats.
- The possible presence of sources of contamination is then assessed by reviewing the current and past use of the site.
- Whether the site is in use or not, historic sources of contamination have to be considered and often are the main concern.
- Information that has been assembled on potential sources is analyzed to identify the types and locations of possible contamination on the site.
- These are then mapped on to the physical description of the site and an initial identification is made of receptors that might be at risk.
- Consideration of the possible pathways between potential sources and receptors leads to a preliminary conceptual model for the site, in terms of candidate source-pathway-receptor linkages.
- The preliminary conceptual model is then tested and refined by observation, during a site reconnaissance.
- The objective of site reconnaissance is to explore the assumptions and conclusions of preliminary work that has been based on paper and other records.
- Some basic in-field chemical testing equipment is useful, such as commercial kits.
- Following the site reconnaissance and analysis of the information, conclusions are made on the relevant pollutant linkages.

- This requires systematic description of the receptors that are exposed, the sources of exposure and the pathway by which this occurs, together with an initial assessment of likely hazard.
- If actual harm to a receptor is identified, then recommendations are given for urgent remedial works, including more detailed investigation, if needed.

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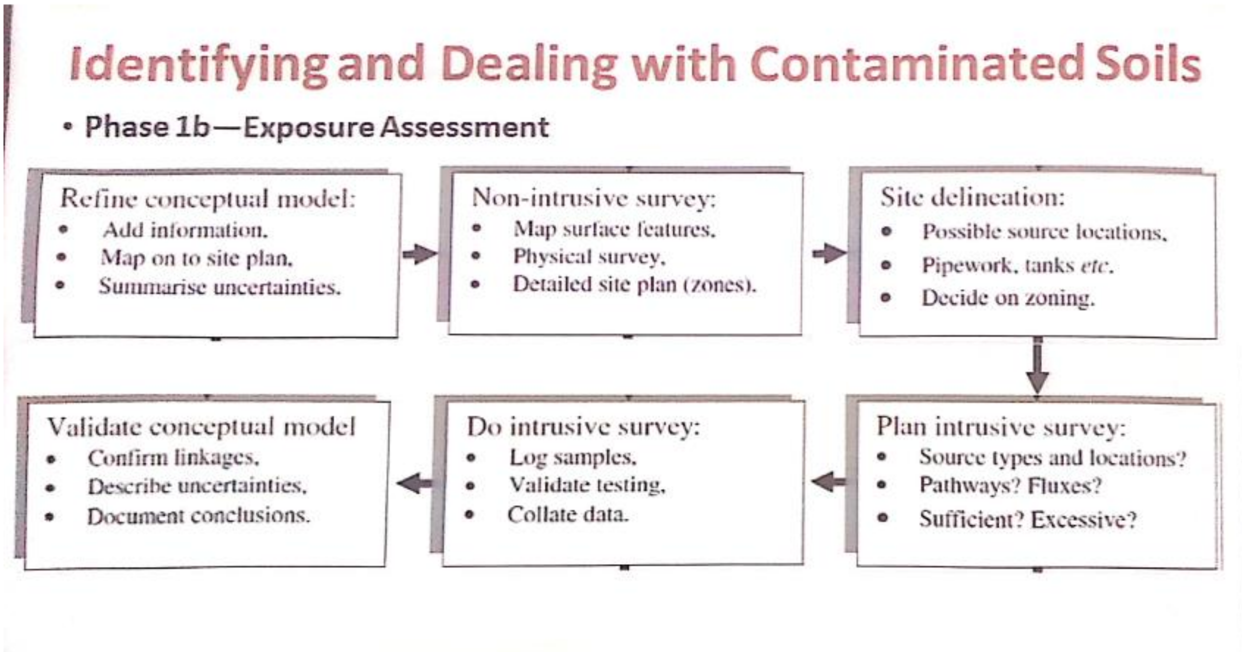
LECTURE 05

IDENTIFYING AND DEALING WITH CONTAMINATED SOILS

Phase 1b – Exposure Assessment

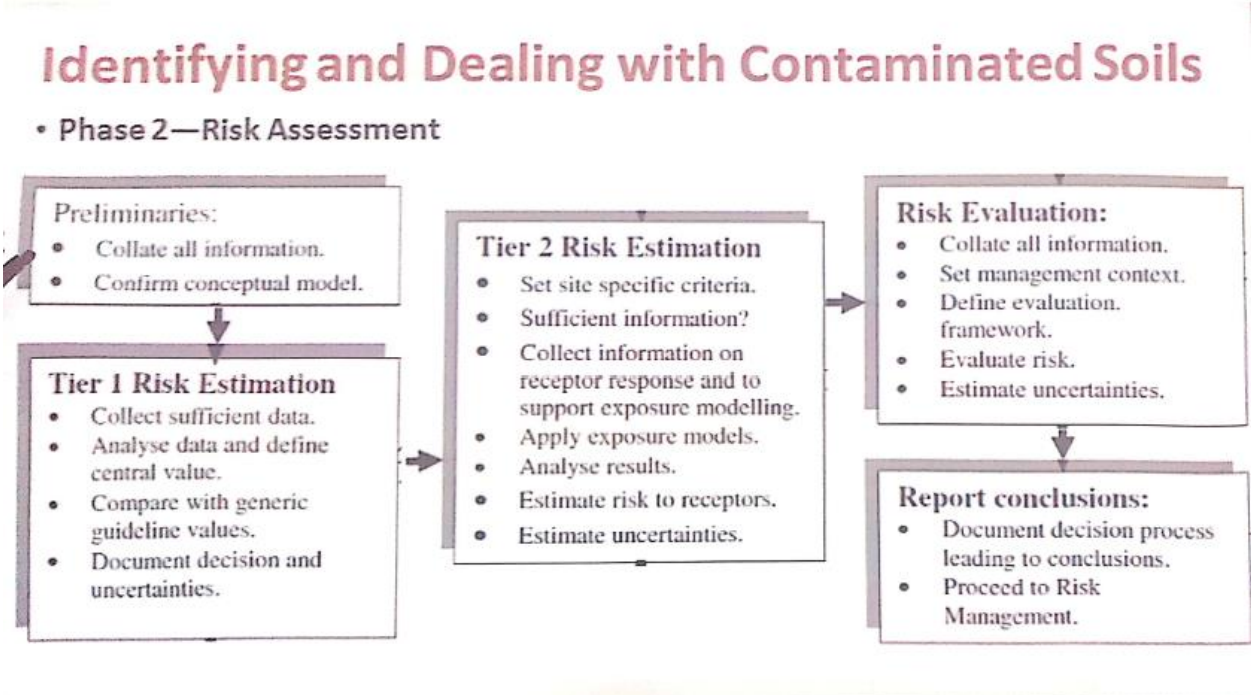
- The objective of this phase is to quantify the extent of sources and the possible transport of contaminants to receptors, and to classify confirmed pollutant linkages in terms of the risk presented to receptors.
- This phase often requires a site investigation, including the collection of samples from trial pits or boreholes.



- A first simplifying step is to break the site into a number of smaller zones that are expected to contain different types and levels of contaminants.
- Information on the location and extent of services, such as pipe work and surface drainage, is especially valuable as these identify areas where past spillage and leakage may have led to ground contamination.
- Estimates are made of the extent and strength of the contaminant source, its connectivity to the receptor and the level of hazard that is presented to the receptor.
- Finally, a preliminary assessment is made of the potential harm that hazards may pose to the receptors.

Phase 02 – Risk Assessment

- Where an actual or potential risk from contaminated land is identified, this has to be estimated and its impact evaluated as a basis for risk management.
- The first stage of Phase 2 assessment is risk estimation; this estimates the potential harm to all receptors within identified source-pathway-receptor linkages.
- The second stage is risk evaluation; this considers the acceptability of potential harm to receptors and identifies and assesses preliminary options to deal with unacceptable risks.



- Risk estimation process relies on 'generic' risk assessment criteria.
- These are 'guideline levels' of contamination that can be used to screen out those pollutant linkages that are unlikely to present a significant possibility of significant harm to particular types of receptor.
- They are derived by using validated models to estimate the quantity of contaminant transferred to a receptor within a generic land use scenario and then comparing the estimates obtained with toxicological and other information about receptor responses to contamination.
- The most likely outcome, when contamination has been found to exceed guideline values, is that site-specific risk estimation is needed.
- If no relevant guideline value is available for a receptor-contaminant combination, site-specific risk estimation is unavoidable.
- The precise nature of the contaminant on the site may be important to the risk estimation.
- In most cases, pathway characterization will require a good understanding, such as water movement on a site, if this is included within the conceptual model.

- Characterization of receptors and their response to contaminants is the third information collection stage within risk estimation.
- A pragmatic approach may be applicable where the main concern is protection of specified species, such as when the receptor is a nature conservation site.
- Site-specific factors such as irrigation of crops and supplementary feeding of livestock can influence receptor exposure.
- Risk estimation is often confined to assessing whether threshold values for unacceptable harm are likely to be exceeded.
- Understanding and reporting the risk factors attached to threshold values is therefore important.
- All facts and conclusions relevant to the site need to be considered in the risk evaluation.
- The general scheme for the technical evaluation is to take each receptor and to describe the level of risk that is presented to it by sources within the site.
- The results of evaluating risks within the evaluation framework are reviewed in the context of social and economic considerations.
- The acceptability of risk has to be determined by agreement around a combination of both technical risk estimation and the broader economic and social consequences of risk.
- Following risk evaluation, a consolidated risk assessment report is prepared, covering the description of the site and the pollutant linkages identified and the overall risk assessment, supported by validated data sets.

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LECTURE 06

IDENTIFYING AND DEALING WITH CONTAMINATED SOILS

Measurement of Site Contamination

Sampling

- Generally, contaminated sites are very heterogeneous, and this presents difficulties.
- Usually a pragmatic, stepwise methodology is most effective and efficient, based on a series of increasingly more intensive but spatially focused sampling exercises.
- On larger sites, a common approach is to sample the whole site on or within a grid with centers set between 20 and 50 meters apart.
- This can then be extended by additional sampling at locations where features are noted, such as the presence of waste materials or disturbed ground, or where contaminating activities are known to have taken place.
- Hand augers allow sampling to a restricted depth in looser ground.
- Motorized augers and drills are more versatile but require sufficient access and can be costly.
- Mechanical excavation of inspection pits has the advantage that the full profile can be examined and sampled with relative ease.
- Whatever method is used, it is essential to record and retain full sampling logs.
- As soon as samples are taken in the field, the concentrations, and forms of contamination within them may start to change.

Non-intrusive Measurement

- Field-based non-intrusive methods of contaminant investigation offer several potential advantages. They avoid errors that arise from contaminant changes during sample collection and transport.
- Often, they can be done quickly, so that a larger number of measurements can be made within available resources and time.
- To date, however, the application of field-based non-intrusive methods has been limited by the performance of available field instrumentation.

Laboratory Testing

- The methods used for laboratory testing of field samples should have validated performance and be conducted within a rigorous quality management system.
- In most cases, chemical analysis of environmental samples relies on an extraction step, followed by determination of the target chemical species in the extract obtained.
- As a result, the extent and variability of extraction must be known.

- A variety of instrumental analytical techniques are used to measure contaminants in extracts of both soil and water from contaminated land sites (e.g., ICP-OES, ICP-MS, AFS, GC-MS, LC-MS, etc.).

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LECTURE 07

IDENTIFYING AND DEALING WITH CONTAMINATED SOILS

Data Reporting

- Site investigation data should be reported according to accepted best practice.
- Full details are needed of sampling locations and depths, associated observations of site conditions and features, the sampling methods employed, and the procedures used for sample storage and transport.
- Details of sample preparation are important to record prior testing.
- Descriptions of laboratory testing methods, including validation data and quality control information, are essential.
- Estimates of uncertainty may have to rely on conservative judgment as well as on statistical methods.

SOIL CONTAMINANTS

Reference Books:

"Bioavailability of Contaminants in Soils and Sediments" by Richard G. Luthy. The National Academic Press, Washington, D.C., 2003.

"Elements of the Nature and Properties of Soil" by Nyle C. Brady and Ray R. Weil, 3rd Edition, Prentice Hall, 2010.

- Every year, millions of tons of industrial, domestic, and agricultural products find their way into the world's soils. Once there, they become part of biological cycles that affect all forms of life.
- Bioavailability of the contaminants determines their potential environmental risk.

Organic Contaminants

- Industrialized societies have synthesized thousands of organic (carbon containing) compounds for many uses (e.g., plastics and plasticizers, lubricants and refrigerants, fuels and solvents, pesticides and preservatives).
- Through accidental leakage and spills or through planned spraying or other treatments, synthetic organic chemicals can be found in virtually every corner of our environment – in the soil, in the groundwater, in the plants, and in our own bodies.
- Organic chemicals may enter the soil as contaminants in industrial and municipal organic wastes applied to or spilled on soils, as components of discarded machinery, in large or

small lubricant and fuel leaks, as military explosives, or as sprays applied to control pests in terrestrial ecosystems.

Classes of organic contaminants commonly found in soil

Compound Class	Examples of Compounds[a]	Sources
Polycyclic aromatic hydrocarbons (PAHs)	Naphthalene Phenanthrene Benzo[a]pyrene Pyrene	Combustion of coal, oil and wood Asphalt, creosote Automobile emissions, fuels, lubricating oils Coal tar[b]
Nitroaromatics	2,4,6-trinitrotoluene (TNT) Trifluralin Benefin Ethalfluralin Methyl parathion	Military installations Bombing ranges Bactericides Pesticides
Phenols, anilines	Pentachlorophenol Phenylamide herbicides: phenylureas, phenylcarba-mates, and acylanilides	Wood preservative Biocide Dyestuff wastewater Phenylamide herbicides
Halogenated aromatics	Polychlorinated biphenyls (PCBs) Dioxins[c]	Hydraulic oils, capacitor dielectric Pesticide application Incineration of medical/municipal sludge Forest fires and volcanic eruptions Cement kilns and boilers Petroleum, coal, and tire combustion Draft black liquor boilers Secondary lead smelting

Compound Class	Examples of Compounds[a]	Sources
Halogenated aliphatics	Chloroform Bromomethane Carbon tetrachloride Vinyl chloride 1,1-dichloroethylene Trichloroethylene (TCE) Tetrachloroethylene (PCE)	Degreasing solvents Former dry-cleaning facilities Plastics manufacturing
Pesticides[d]	Alachlor Aldicarb Atrazine BHC Carbofuran Chlordane 2,4-D Toxaphene DDT, DDD, DDE	Agriculture Residential and industrial pest control
Petroleum hydrocarbons	Benzene Xylenes Toluene Ethylbenzene Alkanes	Oil recovery and refining industry Automobiles and other forms of transportation Oil tankers, pipe lines, and other modes of transporting oil Industry

Inorganic Contaminants

- The toxicity of inorganic contaminants released into the environment every year is now estimated to exceed that from organic and radioactive sources combined.
- There are many sources of the inorganic chemical contaminants that can accumulate in soils. The burning of fossil fuels, smelting, and other processing techniques release into the atmosphere tons of these elements, which can be carried for miles and later deposited on the vegetation and soil.
- Irrespective of their sources, toxic elements can and do reach the soil, where they become part of the food chain: soil → plant → animal → human.
- Direct ingestion of soils and sludge is also an important pathway for human and animal exposure.

Classes of inorganic contaminants commonly found in soil

Chemical Classes	Example Contaminants[a]	Sources or Applications
Metals	Cr, Cu, Ni, Pb, Hg, Cd, Zn, As, Se	Mining, leaded gasoline, batteries, paints, fungicides, pesticides, irrigation drainage
Nonmetals	Ammonia Nitrate (Per)chlorate Phosphate	Fertilizers, paper manufacturing, disinfection, aerospace
Organometallics	Tributyltin Methylmercury	Paints, chemical manufacturing
Radionuclides	^{3}H, $^{238,239,240}Pu$, $^{235,238}U$, ^{99}Tc, ^{60}Co, ^{137}Cs, ^{90}Sr	Nuclear reactors, weaponry, medicine, food irradiation

Contaminant – Solid Interaction

- An important factor affecting bioavailability of contaminants is their interaction with solids in soils.
- Such interactions are termed as association (retention) and dissociation (release).
- The association reactions of organic and inorganic contaminants may differ appreciably.
- The terminology used to describe contaminant – solid interactions for both organic and inorganic contaminants is provided below:

Association, Retention, or Sorption: The binding of a species without implication to the mechanism (which may include adsorption, absorption, precipitation and surface precipitation).

Adsorption: The binding of an ion or small molecule to a surface at an isolated site – a two-dimensional surface complex. Binding can be electrostatic, chemical, or hydrophobic.

Absorption: The uptake of a species within another material (analogous to water uptake into a sponge).

Partitioning: The distribution of a population of molecules of a given compound between any two phases, determined by the compound's relative compatibility with each medium.

Precipitation: The formation of a three-dimensional structure without the association of a substrate (sorbent) material. This process occurs in solution directly and leads to discrete particles. Surface precipitation, a heterogeneous mechanism, refers to nucleation on previously existing particles.

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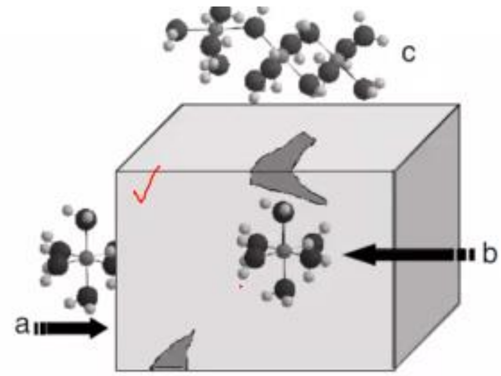
LECTURE 08

SOIL CONTAMINANTS

Retention of Inorganic Contaminants

- Inorganic contaminants retain on mineral and organic surfaces or they can form discrete precipitates.
- The predominant components of soil that retain inorganic compounds are clays and oxides of iron, aluminum, and manganese.

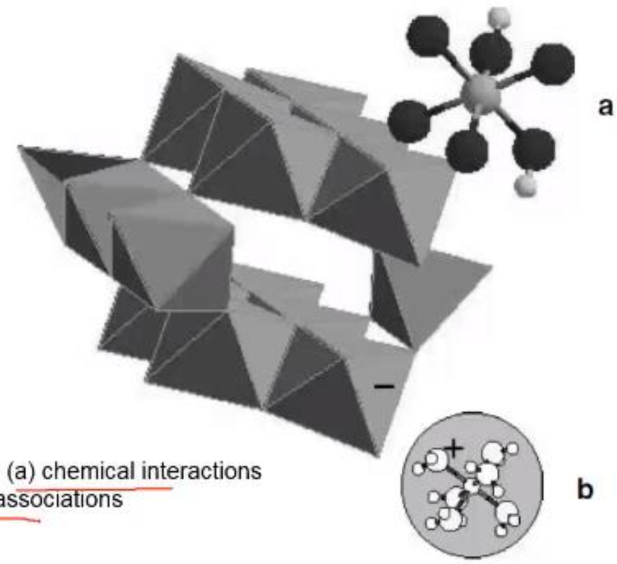
Ion retention mechanisms illustrating (a) adsorption, (b) absorption, and (c) precipitation reactions on a mineral surface



Inorganic Contaminant Reactivity[a] and Conditions Conducive for Precipitation

Class	Contaminant	Chemical Reactivity	Precipitation Conditions
Metal cations	Cr^{3+}, Al^{3+}	High	pH > 5
	Pb^{2+}, Cu^{2+}, Co^{2+}, UO_2^{2+}	High[b]	pH > 7
	Cd^{2+}, Zn^{2+}, Ni^{2+}	Moderate[c]	High carbonate or sulfide
	Sr^{2+}, Ca^{2+}	Low	High carbonate
	Cs^{+}	Low[d]	Limited
Oxyanions	AsO_4^{3-}, AsO_3^{3-}, PO_4^{3-} SeO_3^{2-}	High	High dissolved Al or Fe
	SO_4^{2-}, CrO_4^{2-}	Moderate	Limited
	NO_3^{-}, ClO_4^{-}	Low	None

[a]Contaminant reactivity is a necessary factor for chemical adsorption.
[b]Limited reactivity for U when carbonate complexes form.
[c]High for Cd and Zn in anaerobic environments.
[d]Binds strongly to vermiculite and illite clays.

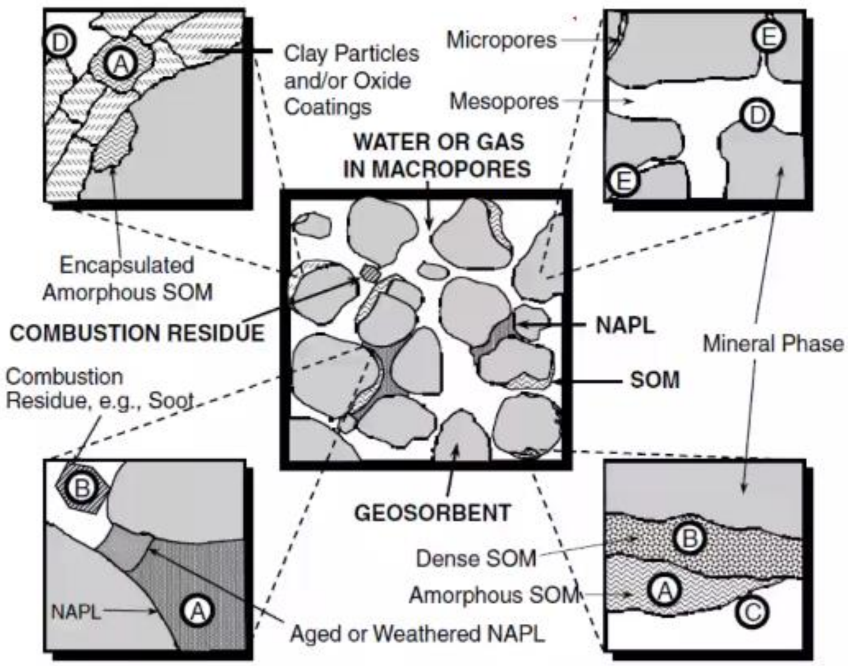


Adsorption reactions illustrating (a) chemical interactions and (b) electrostatic (physical) associations

- Ions retained strictly by electrostatic forces are generally easily displaced by ions of like charge and are thus termed exchangeable.
- Chemically retained ions form very strong associations with solids that are often considered to be irreversible. As a result, chemically bound ions will have a diminished potential for release and should therefore pose a lower risk than ions held strictly by electrostatic forces.
- Electrostatic binding increases as a result of greater charge on ionizable functional groups; chemical binding is facilitated by the formation of better leaving groups on the contaminant or surface.
- Precipitation reactions result from a solution being oversaturated with respected to a solid phase.
- Association of inorganic contaminants with solids in soil is typically dominated by adsorption processes. However, depending on the specific contaminant and site conditions, precipitation may play a large role in governing aqueous metal concentrations.

Retention of Organic Contaminants

- Nonpolar organic compounds are usually retained on organic components of soils such as condensed humic material or soot particles.
- Polar and ionizable organic compounds, in contrast, can associate with soils and sediments primarily through interaction with reactive sites on the mineral components.



Conceptual model of association and dissociation of *hydrophobic* organic compounds with soils. The geosorbent domains include different forms of soil organic matter (SOM), combustion residue particulate carbon such as soot, and anthropogenic materials including non-aqueous-phase liquids (NAPLs). Retention processes denoted within the diagram are (A) absorption or partitioning into amorphous or "soft" natural organic matter or NAPL; (B) absorption or partitioning into condensed or "hard" organic polymeric matter or combustion residue (e.g., soot); (C) adsorption onto water-wet organic surfaces; (D) adsorption to exposed water-wet mineral surfaces (e.g., quartz); and (E) adsorption into microvoids or microporous minerals (e.g., zeolites)

- Low polarity organic chemicals, which have had widespread use, generally associate with carbonaceous components of soils.
- Organic pollutants can undergo both solvent partitioning and adsorption mechanisms.
- Partitioning is an absorption process in that the sorbate exists and is essentially "dissolved" within the complex organic matrix.
- Low polarity organic compounds may also bind through adsorption mechanisms, which result in greater binding coefficients relative to partitioning.
- Thermally or diagenetically altered forms of carbonaceous materials such as coals, kerogen from shales, soot, and charcoal have particularly high binding coefficients.
- For organic compounds that have one or more ionic groups in their structure, electrostatic attraction – repulsion and bonding at specific surface sites can contribute to compound retention.
- Sorption can occur primarily through hydrophobic interactions with organic matter rather than site-specific reactions, depending on the nature of the chemical.
- In general, the more polar a compound, the less important is hydrophobic partitioning.
- Organic acids generally are retained most strongly to oxidic minerals at lower pH values and desorb as the pH increases. Thus, many organic acids will be more bioavailable at higher pH values where association with the aqueous phase is favored.
- A very specific adsorption interaction has been documented between nitro-aromatic compounds and clays.
- The aromatic nucleus of the nitro-aromatic compounds engages in electron donor/ acceptor interactions with the oxygen of the external siloxane surface of the clays.

- Such interactions are extremely fast and reversible, apparently independent of pH and ionic strength, and a strong function of the exchangeable cation.
- The retention of polar and ionizable compounds such as trinitrotoluene, chlorinated phenols, and other common compounds on soils is governed by a complex set of physical-chemical processes making it difficult to generalize about trends in behavior.

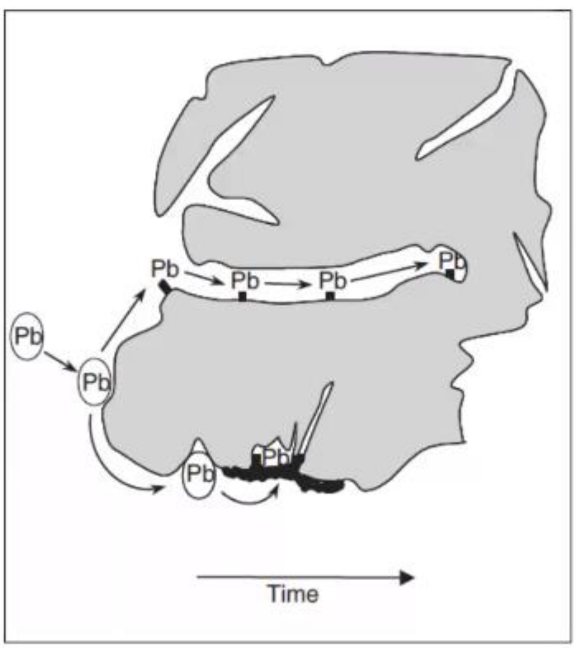
April 05, 2021

LECTURE 09

SOIL CONTAMINANTS

Aging Effects on Contaminants Retention in Soil

- With aging, a contaminant is generally subject to transformation that yields a more stable solid associated compound. This in turn leads to a decrease in the bioavailability of the contaminant with increased reaction time in soil.
- Contaminants that undergo a rapid uptake on organic or inorganic solids via electrostatic adsorption will gradually undergo a secondary transformation that may lead to the development of an inner-sphere complex. The latter species is more stable than the former and thus decreases the availability of the contaminant.
- Metal contaminants may actually become incorporated within the lattice structure of solids over time in such a way as to limit subsequent release.



An example of the effects of aging on Pb^{+2} retention. The initial step in adsorption is film diffusion and the formation of an electrostatic bond. With increased reaction time, a chemical bond may develop between the ion and surface functional group. Despite the strong retention, the ion may migrate along the surface (surface diffusion) into the interior of the particle (upper pathway). It is also possible that once within the micropore, addition material (mineral or organic) may coat the particle and occlude the micropore (bottom pathway). In either case, contaminants become less susceptible to release into the aqueous phase.

- Diffusional or reaction processes of the organic solute, and diagenetic processes that change the properties of the soil, are two general mechanisms involved in the retention of organic contaminants in soil with aging.
- Solute based aging processes include chemical oxidation reactions that lead to solute incorporation into natural organic matter; slow diffusion into very small pores; and absorption into organic matter.

- Diagenetic alterations of the sorbent are caused by various physical, chemical, and biological processes. For example, soil organic matter becomes more aromatic in character with time. This greater aromaticity of natural organic matter results in greater sorption capacity for hydrophobic organic contaminants.

Contaminant Release

Physical-Chemical Release Process

- Contaminants can be released (the opposite of retention) to water or gas in contact with soil by a variety of physical and chemical processes.
- These releases occur in response to changes in water saturation of the soil, to changes in water and gas chemistry, and to changes in soil surface properties.
- Rates of release can be relatively fast (minutes to hours) or extremely slow (many years) depending on the contaminant, solid phase, and fluid properties.
- Dissolution of solids in water can lead to the release of contaminants existing as part of, or entrapped in, a solid structure.
- For those contaminants bound to the surface of soil particles by adsorption or partitioning, desorption can occur in response to changes in water chemistry or surface properties.
- Volatile contaminants may be transferred to the gas phase.
- The rate of contaminant volatilization from soil or sediment to a gas phase depends not only on the specific contaminant but also on environmental factors such as temperature.

Biologically Mediated Release Processes

- Surfactants produced by some microbes (biosurfactants) have the potential to increase the amount of sparingly soluble organic compounds in the liquid phase via incorporation into surfactant micelles aggregates.
- Microbial surfactants have been characterized as polysaccharides, polysaccharide-protein complexes, or glycolipids.
- Plants can also influence contaminant release from solid surfaces.
- Some of the parameters that may be altered as a result of plant activity include pH, redox status, ionic strength of the soil solution, macronutrient concentration and nature, and concentration of organic ligands.
- Rhizosphere acidification or root proliferation and secretion of organic acids may increase the bioavailability of some metals.
- Bioturbation and resuspension can change the release of contaminants and consequently their bioavailability.
- Rates of desorption for both organic and inorganic contaminants from soils are highly variable and dependent on the mode of uptake, the time of reaction (aging), and on the current solution conditions.

April 06, 2021

Lecture 10

PATHWAYS OF SOIL CONTAMINANTS

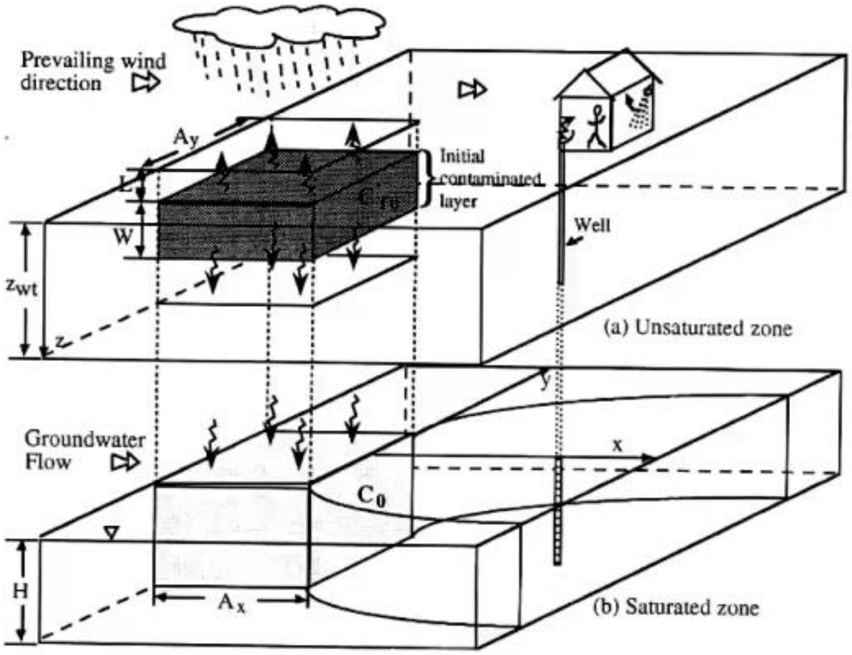
- Inorganic and organic contaminants associated with soils can be transported to biological receptors by a variety of pathways in environmental systems.
- The particular transport pathway depends on the initial location of the contaminant (such as occurrence in deep or shallow soil), the properties of the contaminant (such as volatility and aqueous solubility), and on the environmental properties (such as degree of water saturation in the soil).

Transport of Contaminants on Particles

- Contaminants on soil particles can be transported along with the particles themselves, via entertainment in moving water or air.
- This allows transport of contaminants that are strongly associated with the particles and have little potential for release in soluble form to water or in vapor form to air.
- There are three major transport pathways for soil particles and associated contaminants to reach receptors: entrainment in air, suspension in water, and colloidal movement in groundwater.
- Soil particles at the air-soil interface can be entrained in air flows moving over the ground surface, or they can be suspended in surface runoff following precipitation.
- These contaminant-bearing particles may be transported directly to receptors, e.g., through inhalation by animals or deposition on plants, or to other environmental media e.g., via atmospheric deposition or runoff to surface waters.
- Colloids have potential to move with groundwater through the near-surface unsaturated zone to the deeper, saturated zone and then to pumping wells, discharge areas, plant roots, and the other receptor locations.
- Significant contaminant transport by colloids in the subsurface appears to be possible only under special conditions, such as when contaminant adsorption is strong and not readily reversible, and when concentrations of mobilized colloids are high.

Transport of Released Contaminants

- Once contaminants are released to water, air, or soil gas, they are transported in those phases by the movement of the fluid, or advection.
- If the fluid into which the contaminant is released is not flowing or flowing only at very slow rates, such as groundwater in low permeability soil or pore water in fine-grained sediments, molecular diffusion will be the primary means of transport.



Schematic illustrating potential transport pathways for contamination in a soil layer at ground surface.

- Dispersion causes the contaminant mass to become distributed non-uniformly in a flowing fluid, even one that is moving in a uniform, steady state manner.

Transformation of Released Contaminants

- As contaminants are being transported to receptors upon release from soils, they can undergo transformation of chemical form by means of various chemical and biochemical processes.
- These include biotransformation, oxidation reduction reactions, reactions with water (hydrolysis and acid base reactions) and photochemical transformation.
- These transformations, relevant and important for both inorganic and organic contaminants can affect greatly the bioavailability and toxicity of the contaminant.
- Transformation processes fundamentally alter the chemical form of inorganic contaminant.
- Microorganisms can mediate the transformation of species of elements from one form to another.
- Varying chemical conditions can cause redox active elements such as arsenic and selenium to change oxidation states.
- Photochemical reactions can also affect inorganic contaminants. Light absorption by such compounds can result in their decomposition and subsequent redox transformation of the metal or the organic moiety.
- Organic compounds can also undergo a wide range of biochemical, thermochemical, and photochemical transformations, resulting in wholly different compounds.

Organic contaminants may undergo biodegradation by microorganisms, chemical reactions, or other processes, while inorganic contaminants can undergo transformations through precipitation, adsorption, or redox reactions

Animal Uptake

- Three types of uptake into animals that correspond to the three pathways of direct exposure evaluated in risk assessment are: direct ingestion, dermal contact, and inhalation.
- Because the gastrointestinal tract is the principal site of nutrient uptake, it is a prime location for uptake of chemical contaminants as well.
- For soil invertebrates, the relative importance of gut ingestion of contaminant vs. soil pore water as a source of exposure depends on the physical characteristics of the animal (soft or hard bodied) and the physiology of the gut.
- Soft bodied animals such as earthworms and some insect larvae are thought to be exposed mainly by the soil pore water.
- Those covered with a hard cuticle are thought to be exposed more through food and soil ingestion routes.
- In mammals. The stomach and even the oral cavity can be sites of absorption for a number of chemicals. However, most gastrointestinal absorption occurs in the intestine.
- The gastrointestinal absorption of most environmental contaminants probably occurs by passive diffusion.
- While it is often assumed that chemicals must exist in solution to be absorbed, there has been clear demonstration of the intestinal absorption of small particulates including colloids.
- In contrast to the gut and the lung, there is no mechanism for absorption of chemicals attached to soil particles through intact skin.
- Consequently, dermal absorption requires dissociation of the chemical from the soil or sediment matrix.
- The aqueous secretions of the sweat glands offer a pathway of entry for hydrophilic chemicals.
- Several factors can influence the absorption of chemicals through the skin. One is the age of the individual. Neonates do not possess a fully developed outer skin, and thus chemicals can be absorbed more readily through their skin.
- Similarly, disease and mechanical injury can increase the permeability of skin.
- Contact with chemicals with surfactant properties or solvents in particular are associated with increases in skin permeability.
- Chemicals can enter the respiratory tract as gases, vapors, or particulates.
- Chemicals in gas or vapor form could arise through volatilization from contaminated soils.
- Inhalation of particulates is important when contaminated soils give rise to respirable dust.
- Nasal mucous drains intro oral cavity where it swallowed, carrying with it particulates trapped in the nasal cavity.

- Potential sites of absorption of inhaled chemicals within the respiratory tract depend in part on the characteristics of the substance.