Lecture 3: Environmental Sampling and Chemical Analysis
Part One:

Fundamentals of Environmental Sampling
1. Objectives

The purpose of environmental sampling is:

- To determine the background, natural concentrations of chemical constituents in the environment
- To determine the concentrations of harmful pollutants in the environment
2. Environmental Sample Design

- Planning and sampling protocols
  - Data quality objectives
  - Sampling plan

- Environmental sampling strategies
  - Where and when
  - How many samples
(1) Planning and sampling protocols

- Project Manager
- Sampling
  - Field personnel
  - Field Engineer
  - Geologist
  - Soil specialist
- Lab Analysis
  - Chemist
- Data Analysis - Statistician
- QA/QC specialist
- Data User
  - Client
  - Decision maker

Data quality objectives

- State the Problem
- Identify the Decision
- Identify Inputs to the Decision
- Define the Study Boundaries
- Develop a Decision Rule
- Specify Limits on Decision Errors
- Optimize the Design for Obtaining Data

US EPA 1994 “Guidance for Data Qualitative Objectives” QA/G-4
Sampling plan

1. Objectives
   - Baseline monitoring
   - Trend detection
   - Search for hot spot
   - Margin of error allowable

2. Variability
   - Spatial variation
   - Temporal variation

3. Cost factors
   - Sampling cost
   - Analytical cost
   - Fixed vs. minimum cost

4. Nontechnical factors
   - Sampling convenience
   - Accessibility
   - Availability of resource
   - Regulations

Figure 3.3 Criteria for selecting a sampling plan

*Samples must be “representative”.*

(2) Environmental sampling strategies

Where and When?

- Judgmental
- Simple random
- Stratified random
- Systematic
- Other
  - Composite
  - Transect
**Judgmental**

- Selection of sampling locations based on professional judgment using prior information on the sampling site, visual inspection and/or personal knowledge and experience

- Schedule and budget ➔ tight, early stage when objective is just screen the area

- Primary representative sampling approach for groundwater assessment

- No randomization and does not support any statistical interpretation of sampling results
Simple random

- Arbitrary collection of samples by a process that gives each sample unit in the population the same probability of being chosen
- Assumes variability of sampled medium is insignificant – homogenous population
- Applies for sites with little background information
- Not applicable for heterogeneous population
- Ignoring prior information leads to more samples
- Statistical analysis of data → simple and straightforward
Stratified random

- Sampling population is divided into several non overlapping strata
- Each strata is more homogenous than whole population
- Strata could be temporal or spatial
- Sample size can be adjusted
Systematic sampling

- Systematic random \(\rightarrow\) subdivides the area into grids and collects samples using simple random sampling
- Systematic Grid \(\rightarrow\) easy to implement
- Uniform distribution over the space or time domain
- Critical part \(\rightarrow\) choose right grid spacing
Other

- **Composite sampling**
  - Sampling cost much less than analytical cost
  - Average concentration rather than variability
    e.g., Trace metal analysis

- **Transect sampling**
  - Variation of systematic grid sampling ➔ one or more transect lines across a surface
  - Regular intervals along the transect lines
  - Parallel or non parallel to one another
    e.g., characterizing waste piles and water flow
Where and when: sampling contaminants

- In space domain → contaminant variations can be in 3 dimensions and hence sampling points can be designed by the coordinates in 1-D, 2-D or 3-D

- In time domain → there is only one dimension and hence sampling points can be designed in a time period such as days, weeks, months or years

- Space and time are of interest – both spatial and temporal patterns of a contamination

- Obtain representative samples
  - Solids - contaminants accumulates at certain depth
  - Air - wind velocity and direction
  - Water – seasonal variations
  - Biological – different species, size, sex
Environmental sampling strategies

How many samples?

- Largest sample number possible
- Avoid taking too few samples
- No Universal formula
- Simple random sampling
  \[ n = 4 \times \text{variability}^2 / \text{acceptable error}^2 \]
3. Sampling Techniques

- General guidelines common to all environmental sampling
  - Sequence of sampling matrices
  - Sample amount
  - Sample preservation and storage
  - Selection of sample containers
  - Selection of sampling equipments
(1) Sequence of sampling matrices
- Least to most contaminated sampling locations
- Sediment and water at same site ➔ collect water first
- Sampling at different depths ➔ collect surface water samples first

(2) Sample amount
- Sufficient to perform all required laboratory analyses and with an additional amount remaining for QA/QC analysis
- Representativeness factor
- Water/waste water samples
  - 100 ml for trace metals
  - 1 L for total organics
  - 20~40 L for an effluent acute toxicity test
- Soil/sediment/solid waste samples
  - 200 g per sample
- Air samples
  - Trial and error method
  - 10 m³ may be required per sample
(3) Sample preservation and storage

- Purpose to minimize any physical, chemical and biological changes from time of sample collection to the time of analysis

**Figure 4.1** Methods of sample preservation to minimize potential changes of analytes during sample transportation and storage

- Cold storage $\rightarrow$ reduce metal solubility
- Chemical addition or pH change $\rightarrow$ reduce metal adsorption to glass container walls

<table>
<thead>
<tr>
<th>Analytical object</th>
<th>Change during storage</th>
<th>Preservation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals</td>
<td>Adsorption to glass wall precipitation</td>
<td>Use plastic bottles and add HNO$_3$ to pH &lt; 2</td>
</tr>
<tr>
<td>Oil</td>
<td>Adsorption to plastics</td>
<td>Use glass bottles</td>
</tr>
<tr>
<td>Organics</td>
<td>Biodegradation</td>
<td>Low pH and temp; add HgCl$_2$ to kill bacteria</td>
</tr>
</tbody>
</table>

- No sample can be stored for an extended period of time

- Maximum Holding Times (MHTs) – Length of time a sample can be stored after collection and prior to analysis without significantly affecting the analytical results

<table>
<thead>
<tr>
<th></th>
<th>ASAP</th>
<th>6 - 48 h</th>
<th>7 - 28 days</th>
<th>6 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Color</td>
<td>Oil and grease (28 days)</td>
<td>Metals</td>
<td></td>
</tr>
<tr>
<td>Salinity</td>
<td>Chlorophyll (48 h)</td>
<td>Solids (7 d)</td>
<td>Hardness</td>
<td></td>
</tr>
<tr>
<td>DO</td>
<td>Turbidity (24 h)</td>
<td>Pesticide (7 d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>Odor (6 h)</td>
<td>Total P (28 days)</td>
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</table>

(4) Selection of sample containers

- Glass vs. plastic
- Headspace vs. no headspace
- Special containers
- Biological samples ➔ aluminum foil and closed glass containers with inert seals or cap liners
- Aluminum foils should not be used if mercury is the target
(5) Selection of sampling equipments

- Made of plastic, glass, Teflon, stainless steel and other materials for
- Surface water and waster water sampling
- Groundwater sampling
- Soil sampling
- Sediment sampling
- Hazardous waste sampling
- Biological sampling
- Air and stack emission sampling
4. Environmental Sampling

(1) Soil sampling

- Soft surface soil samples - scoop or trowel
- 1~10 ft - tube sampler
- 3 inches ~ 10 ft - auger sampler
- Will disrupt and mix soil horizons
- Hard soils - split spoon sampler

Figure 4.5 Common sampling tools used for soil: (a) Scoop or trowel, (b) Tube sampler, (c) Bucket auger, (d) Hand auger, and (e) Standard split spoon sampler (U.S. Army Corps of Engineers, 2001)
(2) Surface water and waste water sampling

- Pond sampler - near shore sampling
- Weighted bottle sampler - collect samples in a water body at a predetermined depth
- Kemmerer bottle – Teflon, acrylic or stainless steel tube attached to a rope and best used when access is from a boat or structure such as bridge or pier
Figure 4.3  Common sampling tools used for surface water and wastewater: (a) Pond sampler, (b) Weighted bottle sampler, and (c) Kemmerer bottle sampler (U.S. Army Corps of Engineers, 2001)
(3) Ground water sampling

- Collected from a well by a bailer
- Bailer – an open pipe with an open top and a check valve at the bottom.
- Peristaltic pump – rotor with ball bearing rollers
- Well – with a small diameter and has a depth limitation of 25 ft
Figure 4.4  Common sampling tools used for groundwater: (a) Bailer, (b) Peristaltic pump, and (c) Bladder pump (U.S. Army Corps of Engineers, 2001)
(4) Sediment sampling

- Scoops and trowels – for sample sediments around shoreline and slow moving waters
- Ekman dredge – small and light weight (10 lbs) and collects soft sediments
- Petersen or Ponar dredges
Figure 4.6  Common sampling tools used for sediment: (a) Ekman dredge, (b) Petersen dredge, (c) Ponar dredge, and (d) Sediment core sampler (U.S. Army Corps of Engineers, 2001)
(5) Hazardous waste sampling

- Ponar or Ekman sampler – sludge sampling
- Composite liquid waste sampler – stratified liquid in drums and other similar containers
- Thief – drum sampling device particularly useful for grain like materials
- Trier – sampling sticky solids and loosened soils
Figure 4.7  Common sampling tools used for wastes: (a) Composite liquid waste samplers (coliwasa), (b) Thief (grainer sampler), and (c) Trier (U.S. EPA, 1986)
(6) Biological sampling

- Unique and diverse equipments
- Mammals – trapping
- Fish – trawl nets gill nets
- Vegetation – harvested during growing season
- Benthic macro invertebrate samples – Petersen and Ekman dredges can be used
(7) Air and stack emission sampling

- Direct reading instruments and type of monitoring instruments
- Expensive and complex techniques
- Professional stack – testing firms
- High volume, total suspended particle (TSP) sampling system
- PM-10 sampling system
Figure 4.8  Common sampling equipments used for air. (a) Total suspended particulate matter (TSP) sampling system (Girard, JE, principles of Environmental Chemistry, 2005, Jones and Bartlett publishers, sudbury, MA. WWW.jbpub.com. Reprinted with permission.), and (b) PM-10 sampling system (Norwegian Institute for Air Research, 2001)
5. Quality Assurance/Quality Control

- Standard Methods
  - EPA Methods for Air, Water, Wastewater and Hazardous waste
  - SSSA for soil

Project point of view ➔

- Objectives for accuracy, precision
- Sampling & custody
- Analytical procedures
- Calibration (when, how)
- Data analysis & management
- Corrective action plan
Part Two:
Environmental Chemical Analysis
1. Water Analysis

- Turbidity
- Color
- pH
- Acidity/Alkalinity
- Hardness
- Residual Chlorine and Chlorine Demand
- Dissolved Oxygen
- Biochemical Oxygen Demand
- Chemical Oxygen Demand
- Solids
(1) Turbidity

- Result of interference of passage of light through the water containing suspended materials
- Turbidity determination
  - Nephelometer ==> scattering of light from particles
  - Turbidimeter ==> interference to light passage in a straight line
- NTU is commonly used
- Samples with turbidities > 40 NTU must be diluted
Schematic diagram of a turbidimeter and a nephelometer
(Zhang, 2005. “Chemistry for Environmental Engineering” )
(2) Color

- Apparent color ➔ caused by suspended matter ➔ determined on the sample “as is”
- True color ➔ caused by colloidal vegetable or organic extracts ➔ remove suspended matter by centrifugation then determine color of clarified liquid

1 standard unit of color

= 1 mg/L of Pt (as K2PtCl6)

- Nessler tubes ➔ 0 ~ 70 color units

Color-comparison tubes ➔ (Nessler tubes)

(Zhang, 2005. “Chemistry for Environmental Engineering”)
(3) pH and acidity/alkalinity

- pH ➔ condition of a solution related to \([H^+]\]
  
  \[\text{pH} = - \log[H^+] \Rightarrow \text{determined by a pH meter}\]

- Acidity/Alkalinity ➔ the ability of natural water to neutralize base/acid ➔ determined from a titration

- Acidity = (Volume need to reach end point) \(\times\)
  (concentration of the strong base)

- Mineral acidity = \([H^+] + [H_2CO_3] - [OH^-] \Rightarrow\)
  titration to pH = 3.7 (methyl orange end point)

- Total acidity = \([H^+] + 2[H_2CO_3] + [HCO_3^-] - [OH^-] \Rightarrow\)
  titration to pH = 8.3 (phenolphthalein end point)
- Alkalinity = (Volume need to reach end point) × (concentration of the strong acid) ➞ tiritated with 0.02 N \( \text{H}_2\text{SO}_4 \)

- Phenolphthalein alkalinity (mg/L) = \([\text{OH}^-] + [\text{CO}_3{}^{2-}] - [\text{H}^+]\) ➞ titration to pH = 8.3

- Total Alkalinity = Bromcresol-Green alkalinity (mg/L) = \([\text{HCO}_3^-] + [\text{OH}^-] + 2[\text{CO}_3{}^{2-}] - [\text{H}^+]\) ➞ titration to pH = 4.5

End points for Acidity/Alkalinity titration

(Zhang, 2005. “Chemistry for Environmental Engineering”)
(4) Hardness

- Hardness \( \rightarrow \) caused mainly by divalent metallic cations (e.g. \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), \( \text{Sr}^{2+} \), \( \text{Fe}^{2+} \), \( \text{Mn}^{2+} \)) \( \rightarrow \) determined by EDTA titrimetric method

- EDTA = ethylenediaminetetraacetic acid (\( \text{H}_4\text{Y} \))
  \[ \text{M}^{2+} + \text{EDTA} \rightarrow [\text{M-EDTA}]_{\text{complex}} \]

- Total hardness = Ca hardness + Mg hardness (in most cases)

(Zhang, 2005. “Chemistry for Environmental Engineering” )
(5) Residual chlorine

- Chlorine (Cl₂) → used for disinfection of water supplies and wastewater effluent to prevent water-borne diseases
- Free chlorine residuals → Cl₂ + HOCl + OCl⁻
- Combined chlorine residuals → NH₂Cl + NHCl₂ + NCl₃
- Total chlorine residuals = free chlorine residuals + combined chlorine residuals
- Measurement of total chlorine residuals
  \[ \text{Cl}_2 + 2 \text{I}^- \rightarrow \text{I}_2 + 2 \text{Cl}^- \]
  \[ \text{I}_2 + \text{starch} \rightarrow \text{blue color} \]
  \[ \text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow 2\text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \]
(6) Dissolved oxygen

- The concentration of DO in water is small and therefore precarious from ecological point of view.
- The dissolution process

\[ \text{O}_2\text{(gas)} \Leftrightarrow \text{O}_2\text{(dissolved)} \]

- The equilibrium constant is the Henry’s Law constant \( K_H \)

\[ K_H = \frac{\text{O}_2\text{(dissolved)}}{\text{Partial Pressure}_{\text{O}_2}} \]

- DO analysis \( \Rightarrow \) the Winkler Method
DO: Thermal pollution

- River and lake water that has been artificially warmed can be considered to have undergone Thermal Pollution. Why?
- Gas solubility decreases with increasing temperature.
- Warm water contains less oxygen than cold water. To sustain life, most fish species require at least 5 ppm of DO.
- Consequently, their survival in warm water can be problematic.
(7) Biochemical oxygen demand (BOD)

- BOD: amount of O2 required by bacteria to stabilize decomposable organic matter under aerobic conditions
- High BOD value = high organic-matter concentration = poor water quality
- Decomposition of organic matter is a slow process
  - 20 days $\Rightarrow$ decompose 95 to 99% of organic matter
  - 5 days $\Rightarrow$ decompose 60 to 70% of organic matter
- Measurement of BOD $\rightarrow$ BOD$_5$

- BOD$_5$ = DO$_5$ - DO$_0$
  
  where $\text{DO}_0$ = DO before incubation (day 0)
  
  $\text{DO}_5$ = DO after 5 days of incubation at 20ºC (day 5)

- BOD$_5$ for domestic sewage = several hundreds mg/L

- BOD$_5$ for industrial sewage = several thousands mg/L

$\rightarrow$ when the sewage is discharged to water $\rightarrow$ quick depletion of oxygen
- **initial stage**  
  (Zhang, 2005. “Chemistry for Environmental Engineering”)  
  ==> DO curve drops (i.e. rate of O₂ consumption by bacteria > rate of reaeration with atmosphere)

- **at the point where [DO] = minimum**  
  ==> rate of consumption = rate of reaeration

- **beyond minimum point**  
  ==> rate of consumption < rate of reaeration (DO level eventually returns to normal)

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This sequence is called "**natural self-purification of water**"
(8) Chemical oxygen demand (COD)

- COD $\Rightarrow$ a measure of total organic strength of wastes
- The basis for the COD test $\Rightarrow$ nearly all organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions.
- COD determination $\Rightarrow$ potassium permanganate ($\text{KMnO}_4$) was used for years $\Rightarrow$ potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) becomes the most effective oxidant now (it is relatively cheap, easy to purify, and is able to nearly completely oxidize almost all organic compounds)

\[
\text{C}_n\text{H}_a\text{O}_b\text{N}_c + d \text{Cr}_2\text{O}_7^{2-} + (8d+c) \text{H}^+ \rightarrow \\
n \text{CO}_2 + [(a + 8d - 3c)/2] \text{H}_2\text{O} + c \text{NH}_4^+ + 2d \text{Cr}^{3+}
\]

where \(d = 2n/3 + a/6 - c/2\)
(9) Residue (Solids)

- Usual definition of solids = residue upon evaporation and drying at 103 ~ 105 °C
2. Soil Analysis

- Physical properties
  - Particle size
  - Density
  - Porosity
  - Texture

- Soil contaminants
  - Heavy metals (e.g. Pb, Cd, Cr)
  - Organic pollutants (e.g. Pesticides, Petroleum hydrocarbons)

- Chemical analysis
  - Soil pH
  - Soil organic matter
  - Cation exchange capacity
(1) Soil particle size

<table>
<thead>
<tr>
<th>Clay</th>
<th>Silt</th>
<th>Fine</th>
<th>Coarse</th>
<th>Gravel</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 µm</td>
<td>20 µm</td>
<td>200 µm</td>
<td>2.0 mm</td>
<td></td>
</tr>
</tbody>
</table>

Soil ↔ Non-soil
(2) Soil density

- Soil particle density
  
  $< 1 \text{ g/mL for organic matter, } > 5 \text{ g/mL for some metals oxides; average } 2.5 \sim 2.8 \text{ g/mL}$

- Soil bulk density

  - Include the pore spaces between particles
  
  - Smaller than particle density; average $1.2 \sim 1.8 \text{ g/mL}$
(3) Porosity and texture

- **Porosity**
  
Pore space (%) = 100 - \((\text{bulk density/particle density})\) * 100

- **Texture**
  - Clay
  - Sand
  - Silt

(Zhang, 2005. “Chemistry for Environmental Engineering”)
(4) Soil pH

- How acidic or alkaline the soil is
- 0 to 14
- pH = -log [H⁺]
- At pH 6 there are 10x more H⁺ than at pH 7
- At pH 5 there are 100x more H⁺ than at pH 7
(5) Soil organic matter

- Soil organic matter includes
  - Humic substances (humic acid, fulvic acid, and humin)
  - Fats, resin, and waxes
  - Polysaccharides
  - Amino acids

- Main constituents
  - C (52 - 58 %), O (34 – 39 %), H (3.3 – 4.8 %) and N (3.7 – 4.1 %) with other prominent elements being P and S

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Organic Matter Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agriculture soils</td>
<td>1 – 5 %</td>
</tr>
<tr>
<td>Forest soils</td>
<td>&gt; 10 %</td>
</tr>
<tr>
<td>Peat Soils</td>
<td>&gt; 20 %</td>
</tr>
</tbody>
</table>
(6) Cation exchange capacity

- Capacity of a soil exchange of positively charged ions between the soil and the soil solution
- Clay particles and organic matter have negatively charged sites that can hold positively charged ions on their surfaces
- Expressed in meq/100g of soil
- 1 m eq of CEC has $6.02 \times 10^{20}$ adsorption sites
- CEC of most soils increases with an increase in soil pH
- Highly dependent upon soil texture and organic matter content

<table>
<thead>
<tr>
<th>Soil Texture</th>
<th>CEC (meq/100g soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sands</td>
<td>3 - 20</td>
</tr>
<tr>
<td>Loams</td>
<td>10-15</td>
</tr>
<tr>
<td>Silt loams</td>
<td>15 - 25</td>
</tr>
<tr>
<td>Clay and clay loams</td>
<td>20 - 50</td>
</tr>
<tr>
<td>Organic soils</td>
<td>50 - 100</td>
</tr>
</tbody>
</table>
(7) Soil contaminants

- Inorganic contaminants (e.g. heavy metals) ➔ AAS or AES analysis
- Organic contaminants (e.g. Petroleum hydrocarbons and pesticides) ➔ GC analysis
Part Three:
Information Sources on Environmental Sampling and Analysis
Water/Soil /Sediments Sampling and Analysis

- US EPA Office of Water Analytical Methods online
- US EPA's SW-846 Online Test Methods for Evaluating Solid Waste Physical/Chemical Methods - all approved methods and draft update IV are available
- US EPA Technical Support Centre for Monitoring and Site Characterisation and National Laboratory Accreditation Programme
- FAQ's on Oil & Grease analysis from US EPA
- Canadian sampling strategy for Sediments, Fresh Water and Effluent, Lake Sediments, Stormwater
- USFDA Pesticides, Metals, Chemical Contaminants & Natural Toxins
- Guidelines for Soil Sampling
- FAQ's about Soil and Plant Analysis
- DOE Methods for Evaluating Environmental and Waste Management Samples
- Environmental analysis techniques from the Association of Official Analytical Chemists
- Free software for Environmental Sampling from American Chemical Society
- US source on Bethnic Macroinvertebrate Identification
- US EPA on Biological Indicators and Bethnic Macroinvertebrate identification
- Canadian information on Biological Sampling, Invertebrate Sampling, Fish and Fish Tissue, Algae, Microbiology, Aquatic Pathogens, Aquatic Plants and Weeds
- Canadian Water Sampling Manuals
- US Source on Environmental SOPs
- How to carry out ecological sampling
Air Sampling and Analysis

- US based OSHA Manual on Personal Air Sampling, Sampling for Surface Contaminants, Sample Shipping and Handling, indoor air quality investigations
- NIOSH Manual of Analytical Methods
- Air sampling information on the SKC Website with Sampling Guides
- US EPA Ambient Air Monitoring Information, air toxics methods, inorganics methods, open path analysers, air pollution training institute, index to EPA test methods
- Fast Analysis of Hazardous Organics in Fire and Chemical Accidents by Mobile GC/MS
- WORKPLACE ATMOSPHERES - GENERAL REQUIREMENTS FOR THE PERFORMANCE OF PROCEDURES FOR THE MEASUREMENT OF CHEMICAL AGENTS INTERNET AND OTHER SOURCES OF METHODS FOR THE ASSESSMENT OF WORKPLACE AIR QUALITY
Laboratory Quality Control

- OECD Series on Principles of Good Laboratory Practice and Compliance Monitoring
- UK based Aqua check International Proficiency Testing for Chemical Analytical Laboratories
Environmental Quality Standards

- **US EPA** Water Quality Criteria
- **US EPA Air** information including *Ambient Air Quality Standards*
- **Netherlands** - Contaminated Land at the Ministry of Housing, Spatial Planning & Environment, *Contaminated Land Guidance* and *Contaminated Land Tables of Values*
- **US EPA** soil screening guidelines
- US survey of *Soil and Groundwater Clean-up Standards*