Monitoring Chemicals in the Environment

Principles of Environmental Toxicology
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Learning Objectives

- Understand the importance of tools such as quality assurance project plans to effective monitoring of environmental chemicals.
- Describe the elements of a quality assurance project plan.
- Describe the elements in the development of data quality objectives.
- Define quality assurance and quality control.

Learning Objectives

- Explore the arguments of chemical *vs.* biological monitoring of chemical in the environment.
- Explore the indicator species concept.
- Understand the critical elements of a quality-based sampling program.
- Use the NPDES program as case study to understand a basis and approach to environmental monitoring.

Why Monitor?

- Public health and safety.
  - Food quality, water quality, air quality.
  - Minimize risk.
- Environmental quality.
  - Ecological sustainability.
  - Minimize risk.
- Feedback on anthropogenic change.
- Feedback on potential for exposure.
- Baseline development.
- Remediation/reclamation success.

Example Monitoring Programs

- Safe Drinking Water Act.
- Food Quality Protection Act.
- Clean Water Act.
- Reconnaissance monitoring by state and Federal agencies.
- Environmental research investigations.
- Forensic studies.

Monitoring Approach

- Regulatory driven.
- Hypothesis driven.
- Incident driven.
- All require development of defendable data.
- QA/QC = confidence in final result.

Project

- Single or multiple data collection activities that are related through the same planning sequence.

Quality Assurance Project Plan

- An orderly assemblage of detailed procedures designed to produce data of sufficient quality to meet the data quality objectives for a specific data collection activity.

QA Project Plan (QAPP)

- Planning tool for an environmental data operation.
- Documents how environmental data operations are planned, implemented, and assessed with respect to quality during the life cycle of a project, program or task.
- Defines how specific QA and QC activities will be applied.

QAPP Elements

- Project management.
  - History and objectives, roles/responsibilities, goal definition.
- Measurement/data acquisition.
  - Measurement system design and implementation, methods, QC.
- Assessment/oversight.
  - Ensure QAPP was implemented.
- Data validation and usability.
  - QA activities after data collection; data conformance to criteria.

Data Quality Objectives

- A strategic planning tool for an environmental study.
  - Based on the scientific method.
  - Identifies and defines the type, quality and quantity of data needed to satisfy particular use.

DQO Elements

- Concisely defining the problem.
- Identifying the decision to be made.
- Identifying the key elements to that decision.
- Defining the boundaries of the study.
- Developing the decision rule.
- Specifying tolerable limits on errors.
- Selecting an efficient data collection design.

Quality Assurance

- An integrated system of management activities involving implementation, assessment, reporting, and quality improvement to ensure that a process, item or service, is of the type and quality needed and expected by the client or user.

Quality Control

- The overall system of technical activities that measures the attributes and performance of a process, item or service, against defined standards to verify the that they meet the stated requirements established by the customer or user.
  - Operational techniques and activities that are used to fulfill requirements for quality.

Chemical or Biological Monitoring?

- The basis of much, largely biased, debate.
- Pollution is a biological phenomenon and cannot be described without reference to organisms (which are variable).
- Pollution is usually measured in chemical terms (BOD, concentrations, etc.) but must be related to any possible biological effect.

"Use Chemicals" Argument

- Pros
  - Precision of measurements.
- Cons
  - Link to biological phenomena often not available or clear.
  - What part of the system/organism is measured?
  - Localization difficult unless pollution is continuous or sampling very extensive.
  - Sampling suffers major problems of temporal and spatial variations.

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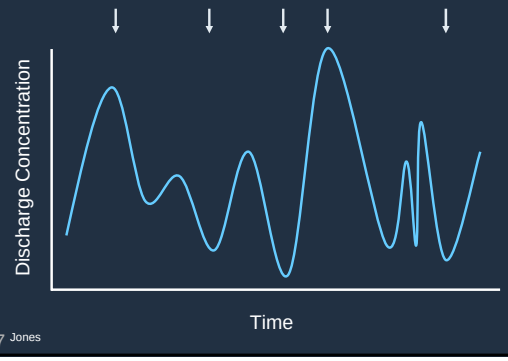
Temporal Sampling Problems



"Use Organisms" Argument

- Pros
  - Relevance is obvious but which organisms (in the light of previous discussion)?
  - Being present all time (SENTINEL spp) allows detection of sporadic events.
  - Biological systems (individuals, populations and communities) are "damped" and integrative over time.
  - Localization possible by following gradients.

"Use Organisms" Argument

- Cons
  - Spatial variability still significant.
  - Variability of organisms can be great, both within a species and between taxa.
  - Lack of specificity of biological responses.
    - Indicate stress only, not source of stress.
    - Sub-lethal effects may be difficult to identify.
    - Cause and effect can never be proven categorically - only correlation and probability.

Realistic Ideal is Combination

- Use biology to detect a problem through biological effect and then use chemistry to identify possible/probable causes
- Requires adequate baseline data (i.e.. pre-pollution levels)

The Indicator Concept

- Originated as *Indicator Species* concept.
  - A species or species assemblage that has particular requirements with regard to a known set of physical or chemical variables.
  - Changes in presence/absence, numbers, morphology, physiology or behavior of that species indicate that the given physical or chemical variables are outside its preferred limits.

Indicator Absence

- The absence of a species does not necessarily mean that critical environmental parameters are not present.
- Absence may be due to other factors.
  - Geographical barriers.
  - Competitive exclusion by ecological analogue.
  - Life-cycle events (predation, parasitism, etc).

Ideal Indicator Requirements

- Taxonomic soundness and easy recognition.
- Cosmopolitan distribution.
- Numerical abundance.
- Low genetic and ecological variability.
- Large body size.
- Limited mobility and long life-history.
- Autecology well-known.
- Laboratory tolerant.

Sentinel Study

- Sentinel species are used for studies of Bioaccumulation (body burdens)
  - e.g. the Mussel Watch program.
- The concept of Indicator Communities offers a more valid approach?
  - A good example is that of the "sewage community" found downstream of organic inputs to lotic systems.

Biological Variability

- Biological variability need not obscure trends …but care is needed in the use of statistical comparison techniques.
  - Sometimes the obvious can be statistically difficult to prove.

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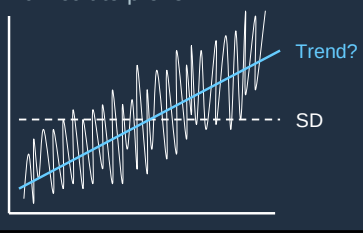

Sampling Program

- Are samples, and therefore the data developed from them, indicators of the target of monitoring?
- How is the sampling and analysis process controlled to determine (minimize) constant or proportional error (bias).
- Will all have confidence in the final result?
- What are the limits of performance?
  - e.g., Scientific capability, cost.

Sample Types

- Field duplicates.
- Blank samples.
- Laboratory control sample.
- Split samples.
- Matrix control samples.

Field Duplicates

- Independent samples which are collected as close as possible to the same point in space and time.
  - Two separate samples taken from the same source, stored in separate containers, and analyzed independently.
  - Useful in documenting the precision of sampling process.

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Blank Samples

- Trip blank: sample of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened.
  - Used to document contamination attributable to shipping and field handling procedures.
- Laboratory blank: sample of analyte free media prepared as a negative control for the laboratory analysis of a batch of samples.
  - Lab contamination control.

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Laboratory Control Sample

- A known matrix spiked with compound(s) representative of the target analytes. EPA
- Used to document laboratory performance.

Split Samples

- Aliquots of sample taken from the same container and analyzed independently.
- In cases where aliquots of samples are impossible to obtain, field duplicate samples should be taken for the matrix duplicate analysis.
- Usually taken after mixing or compositing and are used to document intra- or inter-laboratory precision.

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Matrix Control

- Matrix: component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.
- Matrix duplicate: intra-laboratory split sample which is used to document precision of a method in a given sample matrix.
- Matrix spike: aliquot of sample spiked with a known concentration of target analyte(s).
  - Occurs prior to sample preparation and analysis.
  - Used to document the bias of a method in a given sample matrix.

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Method Detection Limit (MDL)

- The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.

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Determined from analysis of a sample in a given matrix type containing the analyte.

Limits of Quantitation

- "Quantitative interpretation, decision-making and regulatory actions should be limited to data at or above the limit of quantitation" (ACS).
- "Analytical chemists must always emphasize to the public that the single most important characteristic of any result obtained from one or more analytical measurements is an adequate statement of its uncertainty level."
  - "Lawyers usually attempt to dispense with uncertainty and try to obtain unequivocal statements; therefore, an uncertainty interval must be clearly defined in cases involving litigation and/or enforcement proceedings. Otherwise, a value of 1.001 without a specified uncertainty, for example, may be viewed as legally exceeding a permissible level of 1."

 ACS

NPDES Program

- National Pollutant Discharge Elimination System.
- History.
  - 1965, legislation required states to have water quality standards by 1967.
    - Only 50% of states complied by 1971.
  - 1970, Refuse Act and Permit Program (RAPP).
    - 1971, struck down via NEPA (1969) EIS concern.
  - 1972, permit concept survives in federal Water Pollution Control Act amendments (conventionals)
  - 1977, Clean Water Act amendments (toxics).
  - 1987, Water Quality Act (effluent control).

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Important Principles

- The discharge of pollutants to navigable waters is not a right.
- A discharge permit is required to use public resources for waste disposal and limits the amount of pollutants that may be discharged.
- Wastewater must be treated with the best treatment technology economically achievable - regardless of the condition of the receiving water.
- Effluent limits must be based on treatment technology performance.
  - More stringent limits may be imposed if technology based limits do not prevent violations of water quality standards in the receiving water.

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NPDES Scope

- All facilities which discharge pollutants from any point source into the waters of the US are required to obtain a NPDES permit.

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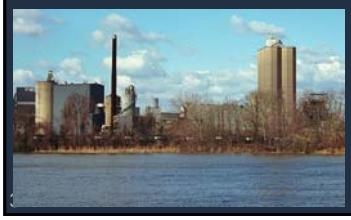

NPDES Program Areas

- Municipal.
  - Municipal effluent discharge.
  - Indirect industrial/commercial discharges.
  - Municipal sludge use and disposal.
  - Combined sewer overflow (CSO) discharge.
  - Storm water discharge.
- Industrial.
  - Process water discharges.
  - Non-process water discharges.
  - Storm water discharges.

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Pollutants

- Conventional.
  - BOD_5 (5-day biological oxygen demand), TSS (total suspended solids), fecal coliform, pH, oil and grease.
- Toxic.
  - 126 priority pollutants listed in 40 CFR §401.15
- Non-conventional.
  - NH_3, N, P, COD (chemical oxygen demand), WET (whole effluent toxicity).

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Point Source

- Agricultural, domestic and industrial.
  - Non-point agricultural operations exempt.
- Publicly owned treatment works (POTW).
  - Indirect
    - Industry, domestic → POTW → discharge.
  - Direct
    - Industry → discharge.

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Waters of the United States

- Navigable waters.
- Tributaries of navigable waters.
- Interstate waters.
- Interstate lakes, rivers and streams.
  - Used by interstate travelers for recreation and other purposes.
  - Used as a source of fish or shell fish sold in interstate commerce.
  - Utilized for industrial purposes by industries engages in interstate commerce.
- Interpreted: wetlands and ephemeral streams.

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NPDES Permit Components

- Cover page.
  - Name, location, authorization, specific discharge.
- Effluent limitations.
  - Based on applicable technology and water quality standards.
- Monitoring and reporting reqs.
  - Characterization, compliance.
- Special conditions.
  - e.g. BMPs, add'l surveys.
- Standard conditions.
  - Administrative requirements.

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NPDES Effluent Limitations

- Technology-based effluent limits.
  - ELGs, effluent limitation guidelines
    - Process/industry based.
    - BAT, best available control technology.
    - BPT, best practical control technology.
  - BPJ, best professional judgment (case by case).
- Water quality-based effluent limits, WQBEL.
  - Site specific evaluation of a discharge and its effect on receiving water; use water quality stds.
    - Use classifications.
    - Numeric/narrative water quality criteria.
    - Anti-degradation policy.

Water Quality Criteria

- Typically have 3 components.
  - Magnitude.
    - Concentration of pollutant.
  - Duration.
    - Averaging period of time for concentration.
  - Frequency.
    - How often criteria can be exceeded.
- Narrative
  - "Free from toxics at toxic levels"
- Numerical
  - 2 μg Cd/L or

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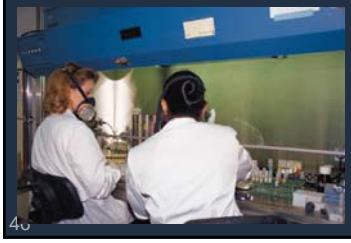
 $e^{(0.7852[\ln(\text{hardness})]-3.490)}$

Future Standards

- Biological criteria.
  - Reference biological integrity; communities.
- Sediment criteria.
  - Contaminants deposited over time.
    - Phenanthrene, fluoranthrene, dieldrin, acenaphthene, endrin.
- Wildlife criteria.
  - Protection of mammals/birds from adverse effects from consumption of contaminated water/food.

Water Quality Determinations

- Chemical Specific Approach.
- Whole Effluent Toxicity.
- Bioassessments.



Chemical Specific Approach

- Capabilities.
  - Human health protection.
  - Complete toxicology.
  - Straightforward treatability.
  - Fate understood.
  - Less expensive testing.
  - Prevents impacts.

Chemical Specific Approach

- Limitations.
  - Does not considers all toxics present.
  - Bioavailability not measured.
  - Interactions of mixtures (e.g. additivity) not measured.
  - Complete testing can be expensive.
  - Direct biological impairment not measured.

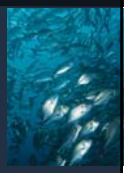
Whole Effluent Toxicity (WET)

- Acute (e.g. 48 hrs).
- Chronic (e.g. 7 days)
- Capabilities.
  - Aggregate toxicity.
  - Unknown toxicants addressed.
  - Bioavailability.
  - Accurate toxicology.
  - Prevents impacts.

WET

- Limitations.
  - No direct human health protection.
  - Incomplete toxicology (few species may be tested).
  - No direct treatment.
  - No persistency or sediment coverage.
  - Conditions in ambient may be different.
  - Incomplete knowledge of causative toxicant.

Bioassessments



- Capabilities.
  - Measures actual receiving water effects.
  - Historical trend analysis.
  - Assesses quality above standards.
  - Total effect of all sources, including unknown sources.

Bioassessments

- Limitations.
  - Critical flow effects not always assessed.
  - Difficult to interpret impacts.
  - Cause of impact not identified.
  - No differentiation of sources.
  - Impact has already occurred.
  - No direct human health
  - protection.

Whole Effluent Toxicity

- Toxic unit (TU), the inverse of the sample fraction, is the preferred toxicity representation.
  - Ex. If a chronic test result is a NOEC of 25% effluent, the result can be expressed as 100/25 or 4.0 chronic toxic units (4.0 TU_c).
  - Ex. If an acute test result is an LC_{50} of 60%, that result can also be expressed as 100/60 or 1.7 acute toxic units (TU_a).

Acute to Chronic Ratio (ACR)

- Compares TU_a to TU_c.
  - Conversion/comparison factor.
  - Determination of most important in discharge.
- ACR = LC_{50} / NOEC = $(100/TU_a)/(100/TU_c)$ = TU_c / TU_a
  - Ex. Given: LC_{50} = 28%, NOEC = 10%
    ACR = LC_{50} / NOEC = 28% / 10% = 2.8
  - Ex. TU_c = 10.0, TU_a = 3.6
    ACR = TU_c / TU_a = 10.0 / 3.6 = 2.8
- Recommended default ACR = 10.

Mass Balance Equation

$$Q_dC_d + Q_sC_s = Q_rC_r$$

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- Q_d = waste discharge flow in million gallons per day (mgd) or cubic feet per second (cfs).
- C_d = discharge pollutant concentration (mg/L).
- Q_s = bkgd stream flow (mgd, cfs).
- C_s = bkgd in-stream pollutant conc. (mg/L).
- Q_r = resultant in-stream flow after discharge.
- C_r = resultant in-stream pollutant conc. after mixing.

Example

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- Q_s = 1.2 cfs
- Q_d = 0.31 cfs
- C_s = 0.8 mg/L
- C_d = 2.0 mg/L
- Water quality criterion = 1.0 mg/L
- $C_r = (Q_dC_d + Q_sC_s) / Q_r$
- $C_r = \frac{(0.31 \text{ cfs})(2.0 \text{ mg/L}) + (1.2 \text{ cfs})(0.8 \text{ mg/L})}{(1.2 \text{ cfs}) + (0.31 \text{ cfs})}$

  $= 1.05$ mg/L
- Since the downstream concentration exceeds the water quality criterion, there is a reasonable potential for water quality standards to be exceeded.

Example 2

$$C_r = (Q_dC_d + Q_sC_s) / Q_r$$

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- C_s = 0 TU
- Q_s = 23.6 cfs (acute); 70.9 cfs (chronic).
- Q_d = 7.06 cfs
- $C_d = TU_a = 2.49$; $TU_c = 6.25$
- Acute criterion: 0.3 TU_a; Chronic criterion: = 1.0 TU_c
- $C_r = [(2.49)(7.06) + (0)(23.6)] / (7.06 + 23.6) = 0.57\ TU_a$
- $C_r = [(6.25)(7.06) + (0)(70.9)] / (7.06 + 70.9) = 0.57\ TU_c$
- Since downstream concentration, C_r exceeds the water quality criterion for acute toxicity, there is reasonable potential for water quality standards to be exceeded.