Monitoring Aquatic Contaminants with Time-averaged Concentrations by Programmable In Situ Extraction

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Cost-Effective, Ultra Sensitive Groundwater Monitoring for Site Remediation and Management
Agenda

1. Background and Rationale
2. *In Situ* Sampler
3. Demonstration
4. Applicability
5. Questions and Comments
1. Background and Rationale
Sustainability and Economics

- Characterization drives up to 25% of remediation expenditures\(^1,2\)
- $2 billion/year (US)
- Federal mandates to reduce energy use, carbon emission

25% Characterization and Monitoring

Side Remediation Expenditures (approximately $8 billion/year)
Environmental Characterization

• Taking measure
  – Sampling method in the field
  – Analytical method in the lab

• Sources of error
  – Sampling: >90%³
  – Analytical: <10%

• Training, SOPs, QA/QC cannot address all sources
Liquid Sample Challenges

- Preservation
- Mass and volume
  - Transportation
  - Hazardous waste
- Field extraction
  - Improves stability of analytes
  - Reduces mass, handling
Dynamic Environments

• Discrete sampling may be too infrequent

• Time-integrated sampling
  – Passive samplers (weeks)
  – Active samplers (days)
  – Reproducibility
Approach

• Reduce and manage sampling error
  – Active sampler
  – Simultaneous, replicate samples

• Eliminate liquid samples
  – *In situ* extraction with off-the-shelf consumables
  – Reduce sample mass, improve stability

• Time-integrated sampling
  – Programmable sampling rate
  – Sampling periods from days to weeks
2. *In Situ* Sampler (IS2)
Reduce and Manage Error

- Precision, programmable positive-displacement pumps
- Six parallel sampling channels for simultaneous replicates
- Autoclavable glass (5 mL) or plastic (10 mL) syringes

Photographs: Isaac Roll
Solid phase extraction (SPE)
Parallel and/or series extraction
Commercial, off-the-shelf cartridges and sorbents
Lab methods become field methods
Time-Integrated Sampling

- Programmable sampling rate
- Timed aliquots or nearly-continuous sampling
- Sampling periods from days to weeks
In Situ Sampler (IS2)

140 cm demonstration sampler (including optional liquid capture)
3. Demonstration
Demonstration: Coronado Island

- Shallow, coastal freshwater aquifer
- Sands, sandy silts
- Chromium-VI
- Demonstration well
  - 10-cm diameter
  - Water at 4 ft
  - Screened 9 – 19 ft
  - 0.25 mg/L Cr(VI) (July 2013)

Satellite Image: Google Earth
Pre-Demonstration Sampling

- 24-hour sampling at two-hour intervals
- Cr(VI) concentration fluctuated by ±20% of mean
- Fluctuation followed tide
- No observed change in depth to water
Demonstration Objectives

• Reduce and manage sampling error
  – 1.25 mL samples at 2-hr intervals
  – 420 mL total
  – Triplicate samples

• Eliminate liquid samples
  – Parallel SPE and liquid sampling to demonstrate equivalence

• Time-integrated sampling
  – 28-day, 420-mL composite sample
Demonstration: Coronado Island
Demonstration: Coronado Island

Photographs: Erin Driver (L) and Isaac Roll (R)
Reduce and Manage Sampling Error

- Triplicate samples provide inter-sample error (8%)
- Active sampling improved sampling rate ($R_S$) precision (3.4%) versus passive samplers\textsuperscript{7,8,9,10}

**Range of RSD (%) Observed for Sampling Rates**

<table>
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<th>CSS</th>
<th>MESCO</th>
<th>POCIS</th>
<th>SPMD</th>
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<td>(n = 46)</td>
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CSS: Constantly Stirred Sorbent
MESCO: Membrane-Enclosed Sorptive Coating
POCIS: Polar Organic Chemical Integrative Sampler
SPMD: Semipermeable Membrane Device
IS2: In Situ Sampler
Eliminate Liquid Samples

- 420-mL liquid samples yielded 4-g SPE samples
- Equivalent to 336 discrete samples
- No liquid handling by technicians
- 99% reduction in material leaving site

For 250-mL samples:

- Carbon Impact of Transportation\(^5\) -98%
- Cost of Transportation\(^6\) -92%
- Hazardous Material Production -98%
Time-Integrated Sampling

- 28-day time-integrated average
- 75% ± 6% recovery
- 8-fold improvement in reporting limit
Comparison of Costs

• Capital
  – Research instrument costs were similar to available commercial instruments ($4000)

• Operating
  – Technician time in field observed similar to other instruments
  – Waste and transportation costs reduced
4. Applicability
Method Development

• Environmental characteristics amenable to passive sampling (see ASTM D7929-14)

• Contaminant compatibility and degradation modes
  – Many contaminants are stabilized by field extraction\(^4\)
5. Conclusions
Conclusions

• *In Situ* Sampler
  – High-precision active sampling
  – Simultaneous replicate samples
  – *In situ* solid phase extraction
  – Commercial off-the-shelf consumables
  – Long time-base, time-integrated sampling
  – Large sample volume

Photograph: Erin Driver
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References


References


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