Using embedded and rapid physiochemical and microbiological sensors to study and monitor environmental systems

Christine Lee
Advisor: Jenny Jay
CENS Technical Seminar
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Discussion of two studies

- Arsenic contamination in Bangladesh village groundwater (CENS - Tiffany Lin and Chuching Lin, MIT)

- Rapid microbe sensing for coastal water quality
Bangladesh - Roadmap

• Background and motivation
  – Public health crisis
  – Site description

• Research approach and discussion
  – Hypotheses and deployment of sensors
  – Data

• Future and current work
  – Mesocosms
  – Next deployment
Bangladesh

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Brief history and numbers

- Contaminated surface water (microbial)

- UNICEF & World Bank drilled wells to access “clean” groundwater

- Groundwater contaminated (naturally) – first detected in 1993
  - 3000 cases per year (death)
  - 2,000,000 w/ arsenicosis
  - 100,000 w/ skin cancer
How extensive is the problem?
Arsenic chemistry and cycling

Oxidation of these minerals re-sorbs As to Iron hydroxides

As (III)-Sulfide minerals

Rapid oxidation in surface water
(Dittmar et al, 2007 ES&T, Roberts et al, 2007 ES&T)

Transported to Depth

Iron hydroxides Fe(III)

Aqueous As$^{3-}$

Microbial respiration liberates arsenic (III) from iron hydroxides
Monsoon season flooding creates conditions for this cycle

As (V)

As (III)

Diagram based on that in (Polizotto et al, 2006 Chemical Geology)

(Harvey et al, 2006 Chemical Geology)
Bangladesh

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Village of Srinigar

- Mushiganj District, 25km south of major city Dhaka in Bangladesh
- Rice cultivation/farming
- Weekly irrigation (paddies are flooded)
- 500ppb arsenic concentration in irrigation water
Bangladesh

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Hypotheses

• Working hypothesis:
  Arsenic is mobilized in near surface where sediments are weathered by seasonal changes in the redox state that drive a cycle of pyrite oxidation and iron oxide reduction and the dissolved As is transported into the aquifers by recharge.

• Specifically:
  What is the role of rice cultivation and irrigation? Does flooding/drying cycle of irrigation expedite arsenic mobilization?
2006 CENS deployment goal: temporally dense investigation of oxidation-reduction processes leading to arsenic mobilization at our field site in Mushiganj district in Bangladesh.
Daily trends were observable in several redox active geochemical parameters.

Other accomplishments:
* Post deployment improvements to sensor board
* Post deployment software development
2007 CENS deployment

Investigate:

* magnitude and extent of daily redox cycling
  (longer term deployment)

* composition of unsaturated layer
In situ calibration and ground truthing with alternative methods increased reliability of data.
Bangladesh

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DATA: Diurnal Cycles in Data Collected During Field Campaign, Mar 2007

The graph shows the concentration of Ammonium (blue line) and Nitrate (pink line) over a period from March 29th to April 6th, 2007. The concentrations are plotted on a logarithmic scale for better visualization of the data.

Date (2007)
Dissolved Oxygen 1’ – 1st Week April 2007

DO Concentration [%]
Photosynthesis by Plants & Algae: lowers nitrate during the day, outputs carbonate and ammonium

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2
\]

\[
\text{O}_2/\text{NO}_3^- + \text{“CH}_2\text{O-orgN”} \rightarrow \text{NH}_4^+ + \text{N}_2/\text{CO}_3^{2-}
\]

Mineralization/Denitrification
Bangladesh - Roadmap

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Microcosms: controlling redox chemistry

Purge with Air

Purge with CO$_2$/N$_2$

Diagram based on that in (Pulzotto et al., 2006 Chemical Geology)

Microbial respiration liberates arsenic (III) from iron hydroxides
Monsoon season flooding creates conditions for this cycle

Oxidation of these minerals resorbs As to iron hydroxides
Rapid oxidation in surface water (Ditombe et al., 2008 ES&T, Roberts et al., 2007 ES&T)

As (II)-Sulfide minerals
Transported to Depth
Aqueous As$^3$

Time (hr)

Ctrl, No C Expt, No C Expt, No C Expt, No C Ctrl, C Ctrl, C Expt, C Expt, C Expt, C
Coastal water quality – microbial sensing

• Background and motivation
  – What is our current system for monitoring water quality and protecting public health, and weaknesses in this system?

• Observing these weaknesses
  – Beach Studies

• Research approach & discussion
  – Rapid detection, epidemiological study & source tracking, NIMS
Motivation

• “Time-to-results”
  – Does a 24-hr delay in results/postings protect swimmers from being exposed to poor water quality?

• Adequacy of indicators
  – Do indicator concentrations correlate with pathogen concentrations?

• Public health
  – Do health standard exceedances correlate with hazardous conditions?
Reports of illness

> 400 51-100 < 50 0

--- decreasing distance to storm drain

Haile et al 1999
## Background Information

### Current pathogen indicators

<table>
<thead>
<tr>
<th>Type</th>
<th>Health standard (AB411 in CA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fecal Coliforms (<em>E. coli</em>)</td>
<td>400 cells per 100mL (4 cells/mL)</td>
</tr>
<tr>
<td>Enterococci (E. faecalis, E. faecium)</td>
<td>104 cells per 100mL (~1 cell/mL)</td>
</tr>
<tr>
<td>Total Coliforms</td>
<td>10,000 cells per 100mL (~100 cells/mL)</td>
</tr>
</tbody>
</table>

### Why have indicators instead of actual pathogens?

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indicator abundance</td>
<td>Difficult to correlate</td>
</tr>
<tr>
<td>Ease of measurability</td>
<td>Too conservative</td>
</tr>
<tr>
<td>Simplifies/downsizes</td>
<td>Regrowth in/sediments as a source?</td>
</tr>
</tbody>
</table>
How do we currently measure water quality?

- Culture (~ 24 hrs incubation)
- Special media for selective indicator growth (like E.coli)
- IDEXX
- Membrane Filtration
Preliminary Research

• Pathogen indicators (PI) throughout/following storm event
  – Water and sediment concentrations

• Three sites in Santa Monica Bay (North to South)
  – Surfrider Beach (Malibu)
  – Santa Monica Beach (north of pier)
  – Mother’s Beach (Marina del Rey)
Mother’s Beach
Results: pathogen indicators in water and sediment throughout and following a storm event
Enterococci concentrations in water throughout the storm

Inches of Rain

Date

Surfrider Beach
Santa Monica
Mother's Beach

Inches Recorded

MPN Enterococci/100mL

2/9 2/10 2/11 2/12 2/13 2/14 2/15 2/16 2/17

Inches Recorded

MPN Enterococci/100mL

2/9 2/10 2/11 2/12 2/13 2/14 2/15 2/16 2/17

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Inches Recorded

MPN Enterococci/100mL
Beach Survey - Enterococci concentrations in water and sediment

Portion of water samples in exceedance
No health standard set for sediment!!

Water

Sediment

Cabrillo (enclosed)
Mother's (enclosed)
Dockweiler
Latigo Cyn
Manhattan
Redondo
Santa Monica North
Santa Monica South
Surfrider
Topanga
Venice
Will Rogers
Two sets of questions

Does beach sediment promote pathogen growth along with indicator growth?

- YES
  - Sediment standard?
  - Indicators good?

- NO
  - Other weaknesses?
  - Variability of PI concentrations?
  - More than one measurement/day?
Research approach to address the issues

Does beach sediment promote pathogen growth along with indicator growth?

- **YES**
  - Sediment standard?

- **NO**
  - Indicators good?
     - Rapid detection & NIMS
     - Epidemiology study
     - Source Tracking

  - Other weaknesses?
  - Variability of PI concentrations?
  - More than one measurement/day?
Develop and optimize method.

Method characteristics:
- Rapid
- Deployable
- Modifiable/customizable

Test method in the field (beach site)

Deployment with NIMS sensors (environmental monitoring sensor networks)
• Quantitative Polymerase Chain Reaction (Q-PCR)
  – Rachel Noble
  – Trish Holden
  – Jenny Jay

• Transcription-mediated Amplification (TMA)
  – Gen-Probe, Inc.

• Immunomagnetic Separation and ATP quantification (IMS/ATP)
  – JiYoung Lee and Rolf Deininger*
  – USGS
  – Jenny Jay
Immunomagnetic Separation/ATP quantification

Explain the process:
1. Isolate target using antibody-magnetic bead complex
2. Extract target ATP and add enzymes
3. Enzymes degrade ATP, light is a byproduct
4. Measure light emission, sends data to computer

Diagram:
- Magnets
- Light sensor
- Enzymes degrade ATP, light is a byproduct
Preliminary IMS/ATP work: testing photomultiplier tube, attachment efficiency of antibody-bead complex
Antibody-magnetic bead complex efficiency

- Binds target cells, use a magnetic field to separate out of solution
- Testing efficiency of attachment mechanism
- Antibodies are commercially available

<table>
<thead>
<tr>
<th>Hydrophobic Sorption</th>
<th>Covalent Attachment</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="Diagram1" alt="Diagram" /></td>
<td>![Diagram2]</td>
</tr>
<tr>
<td>Uncated Microspheres</td>
<td>CML</td>
</tr>
<tr>
<td>Purified Ligand</td>
<td>LDAC</td>
</tr>
<tr>
<td>Gentile Mixing</td>
<td>CmH</td>
</tr>
<tr>
<td>(in 3-10x excess of</td>
<td>o-aminoacryl</td>
</tr>
<tr>
<td>calculated monolayer)</td>
<td>intermediate</td>
</tr>
<tr>
<td>Excess reagent addition ensures forced, upright adsorption</td>
<td>Ligand with available amin</td>
</tr>
</tbody>
</table>

- Easier
- Cheaper
- More permanent/robust
- Requires more steps & unstable reactants
<table>
<thead>
<tr>
<th></th>
<th><strong>Luminometer</strong> (previous instrument)</th>
<th><strong>Photomultiplier</strong> (current instrument)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ease of use</td>
<td>Easy to use, but only one option/setting</td>
<td>Multiple settings, can log and be monitored continuously</td>
</tr>
<tr>
<td>Field</td>
<td>Much smaller (well-packaged)</td>
<td>More pieces, but doable</td>
</tr>
<tr>
<td>Price (&quot;start-up&quot;)</td>
<td>Around $2000 for instruments</td>
<td>(does not include computer price, can use a dmm instead)</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>Very sensitive, @ fixed 10 sec integration</td>
<td>Adjustable int. period depending on range/need</td>
</tr>
<tr>
<td>Expandable</td>
<td>Not at all</td>
<td>Bluetooth transmission, field-deployable</td>
</tr>
</tbody>
</table>
Calibrating R928P photomultiplier

ATP Standard Calibration Curve

\[ y = 0.7387x + 14.388 \]

\[ R^2 = 0.9676 \]
Calibrating R928P photomultiplier

lab culture E.coli calibration

$y = 0.5751x + 1.8035$

$R^2 = 0.8714$
Optimization (the beginnings)

- Time Dependence and Integration period

![Graph showing time dependence and integration period with data points and error bars for averages and blank averages. The graph includes labels for 'avgs', 'average = 29829', 'blank avg', 'average = 2256', 'avg counts/5sec', 'average = 166942', 'blank avg', 'average = 11833'.]
Summer study (2008): SCCWRP (SoCal Coastal Water Research Project) epidemiological study
Evaluate alternative indicator methods in epidemiology study

- **Methods:**
  - QPCR, Luminex, TMA, IMS

- **Indicators/targets include (selected):**
  - Adenovirus, norovirus
  - Phages, rapid phage
  - Enterococci, E.coli
Future goals: NIMS deployment

Figure 4. NIMS systems may be deployed in natural environments in terrestrial, marine, and atmospheric monitoring applications. This includes monitoring of atmospheric gases and their thermodynamic properties, investigation of water systems with chemical and biological probes, and monitoring of forest soil systems.
Consider: San Joaquin and Merced River confluence

www.research.cens.ucla.edu
Tom Harmon at UC Merced
Networked InfoMechanical Systems (NIMS) in brief

Dataset snapshot (profiles at San Joaquin River)

Conductivity

Flow distribution

Nitrate

Singh et al 2007
Research Overview (Concluding Remarks)

- **Optimization and testing**
  - Antibody-bead complex
  - Light sensor

- **Lab and field calibration**
  - Mother’s Beach

- **Further development**
  - Bluetooth
  - Increasing field-portability (power)
  - Streamlining process (multiple sample detection)

- **Field study on aquatic systems with NIMS**
  - Medea Creek, Redondo Beach
Acknowledgments 😊

- My advisor: Prof. Jenny Jay
- Committee: JAJ, KDS, MKS
- Funded by National Science Foundation (Grant No. ANI-00331481), PI Prof. Bill Kaiser
- Beach study - UC Toxic Substances Research and Teaching Program
- Based on work done by Lee (different one) and Deininger (*Luminescence* 2004)
- Southern California Coastal Water Research Project
- Heal the Bay
Lab (Thanks everyone!!!)
Thank you for listening. Questions?