Environmental Impact of Ongoing Sources of Recontamination on Remediated Aquatic Ecosystems

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February 14, 2019
2019 Sediment Conference
New Orleans, Louisiana

SRNL-L3200-2019-00010
Problem Statement

- Water is a precious resource supporting life, but only 0.5% of the water is in lakes and rivers and available for human use.
- Rapid industrialization and urbanization leads to the contamination of sediments with heavy metals and organic contaminants and creates a pervasive problem worldwide.
- Ten percent (1.2 billion yd³) of the sediment in U.S. waters is contaminated (PAHs, PCBs, metals, metalloids, and others).
- Contaminants pose a high risk to the environment and human health because they can harm aquatic organisms and enter aquatic food chains that lead to humans.
Contaminated Sediment – food chain transfer of contaminants and reduction in biodiversity

Clean Sediment - supports high biodiversity and healthy fish and benthic communities

Active Capping

Passive Capping

In-situ Remediation

Dredging

Monitored Natural Recovery

Reduction in Environmental Bioavailability and Accessibility

Reduction in Environmental Accessibility
Distribution of Completed and On-going Projects in the U.S. with Greater than 2000 Cubic Meters of Contaminated Sediments
Recontamination – a Challenge to Remedial Methods for Sediment

Remediated sediments may be exposed to contamination from uncontrolled point or nonpoint sources resulting in recontamination that reverses recovery.

The effects of recontamination on sediment remediation have not been evaluated

Contamination of dredged area by uncontrolled point source

Contamination of sediment cap by uncontrolled nonpoint sources

Benefits of dredging to remove legacy contaminants are negated by recontamination!

Benefits of sediment capping to isolate legacy contaminants are negated by recontamination!
Logical Progression in Remediation of Contaminated Sediments in Case of Controlled Sources

- Dredging and Source Control
- MNR 
- In Situ Treatment or EMNR
- Passive Capping or Active Capping

After dredging and source control additional engineering can be added if more than MNR is required

(Bridges et al., 2012. Integrated Environmental Assessment and Management 8: 331-338)

MNR - Monitored Natural Recovery
EMNR – Enhanced Monitored Natural Recovery
Logical Progression in Remediation of Contaminated Sediments in Case of Ongoing Sources

Dredging of Hot Spots

EMNR

In Situ Treatment or Active Capping

EMNR – Enhanced Monitored Natural Recovery
Passive versus Active Capping

Technologies that Remediate Existing Contaminants in Sediments and Control/Remediate Ongoing Sources are Needed

Passive Cap
Layer of inert material (e.g., sand) that isolates contaminated sediment from the surrounding environment

Active Cap
Reactive material that neutralizes or stabilizes contaminants in situ

ZOI – zone of influence
Technical Approach

Hypotheses:
1) A Zone of Influence (ZOI) will form in contaminated sediment that is deposited over active caps resulting in chemical changes to the contaminants that will reduce their environmental impact.

2) The amendments in active caps will sequester contaminants associated with the continued influx of contaminants.

Active caps remediate existing contaminants in sediments and control/remediate ongoing sources.
Remediation via Apatite

**Apatite**
- Stable end-products
- Can be placed by existing technology
- Does not affect sediment physical properties
- Can be mixed with other additives
- Low cost, readily available, non-toxic

**Facilitating Bioremediation via Metal Immobilization**

**Available metal species of concern in sediment**

- Ca$_{10}$(PO$_4$)$_6$OH

**Hydroxyapatite [Ca$_{10}$(PO$_4$)$_6$OH] sediment amendment**

- Adsorption and/or precipitation as metal phosphates

- High availability
- High toxicity
- Low bioactivity

- Reduced availability
- Reduced toxicity
- Increased bioactivity
Sequestering Agents

Zeolites “boiling stones”
- Naturally occurring aluminosilicate minerals
- Have three-dimensional framework with large vacant cages for cations and large molecules
- Clinoptilolite and phillipsite - common zeolites for metal removal
- Clinoptilolite is not toxic to aquatic organisms

Zeolite Structures

Survival of Hyalella azteca (%) for different treatments:
- CZ 0: 97.5%
- CZ 5: 93.3%
- CZ 10: 92.5%
- CZ 25: 92.5%
- CZ 50: 92.5%
- CZ 75: 97.5%
- CZ 100: 95.0%

Cage structure of zeolite.
Sequestering Agents

Organoclays

- Consist of modified bentonite with organic surface modifiers that increase the surface area of the mineral and create binding sites for $^{129}$I, $^{99}$Tc and other contaminants (organic and inorganic)
- Significant swelling and permeability reduction

Sequestering Agents

**Activated carbon (AC)** is particles of carbon that have been treated to increase their surface area and increase their ability to adsorb a wide range of contaminants - activated carbon is particularly good at adsorbing organic compounds.

**AC is a highly porous material**
- It has an extremely high surface area for contaminant adsorption
- The equivalent surface area of 1 pound of AC ranges from 60 to 150 acres
Comparison of metal removal by amendments in fresh and salt water
Average surface water concentrations of dissolved Zn in mesocosms with passive caps (sand), active caps (apatite, activated carbon and mixture of active amendments), and without caps or sediment (control) over a period of 2520 hours.

Spike solution (C), uncapped sediment (SED), sediment with passive sand caps (S-1: 2.5 cm, S-2: 5 cm), and sediment with several types of active caps (A-1: 2.5 cm apatite, A-2: 5.0 cm apatite, AC: activated carbon, MRM: 2.5 cm organoclay, and MC: 2.5 cm mixture of active amendments)
Average surface water concentration of metals in mesocosms at 2520 hours

Spike solution (C), uncapped sediment (SED), sediment with passive sand caps (S-1: 2.5 cm, S-2: 5 cm), and sediment with several types of active caps (SC: 2.5 cm silty clay, A-1: 2.5 cm apatite, A-2: 5.0 cm apatite, AC: activated carbon, MRM: 2.5 cm organoclay, and MC: 2.5 cm mixture of active amendments) (Knox et al., 2016)
**Effect of Passive and Active Caps on Contaminant Toxicity from Ongoing Sources of Contamination**

*Lumbriculus variegatus* were observed for toxicity. Sand caps and spike solution alone (0.5 mg/L of As, Cd, Cr, Cu, Ni, Se, Pb, and Zn) resulted in 100% mortality after 24 hours. However, active caps and clay cap showed minimal toxicity after one, six, and ten days in the presence of spike solution.

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**10 Day Evaluation**

- Spike
- Sed.
- Sand 1
- Sand 2
- Clay
- Apatite 1
- AC
- MRM
- MAAC

Sed. – uncapped sediment, AC – activated carbon, MRM – organoclay, MAAC – Multiple Amendment Active Cap
Effect of Cap Treatments on Metal Uptake by *Lumbriculus* from Ongoing Sources

Active caps remediate existing contaminants in sediments and control/remediate ongoing sources.

Analysis of variance of differences in *Lumbriculus variegatus* metal concentrations (whole body, 10 day exposure) among sediment treatments (BG = background, AC: activated carbon, SC: silty clay cap, A-1: apatite cap (2.5 cm), MRM: organoclay MRM cap, MC: mixture of active amendments, SED: untreated sediment). Geometric means connected by the same line are not significantly different at \( p < 0.05 \).

Knox et al., 2016
The bioavailable pool of metals in the water and sediment/cap was measured by two types of diffusive gradients in thin films (DGT)

DGT measurements were compared with metal uptake by caged California black worms (*Lumbriculus variegatus*)

Placement and retrieval of California black worms

Knox et al., 2016
Evaluation of Metal Bioavailable Pool in Contaminated sediment Treated with Passive and Active Caps

Metal concentrations in both *Lumbriculus* and sediment/cap were lowest in apatite, mixed amendment, and activated carbon treatments.

- Correlations between *Lumbriculus* and sediment concentrations measured by DGT sediment probes were strong, confirming the effectiveness of active caps.

Pearson correlations between metal concentrations in *Lumbriculus* (ten day test) and metal concentrations in the top 2.5 cm of sediment or cap measured by diffusive gradient in thin films (DGT) sediment probes were strong (as high as 0.98) and significant (p<0.05) for almost all tested metals.
Active Capping Advantages

- Can achieve greater risk reduction more quickly
- Creates less short-term risk
- Can be implemented more quickly and economically
- Does not require staging, handling, and treatment of removed sediment
- Can facilitate habitat restoration by using an eco-friendly surface layer
- **Active caps remediate existing contaminants in sediments and control/remediate ongoing sources**
Final Key Points

- All remediation technologies have their advantages and disadvantages
- Selection of remedial action should consider the risk from ongoing sources of contaminants and site characteristics
- Combinations of approaches and technologies that complement and reinforce each other are good options for remediating and managing contaminated sediments
The book is composed of three parts. “Understanding, processes, and needs,” provides fundamental knowledge concerning trace element geochemistry in waterlogged soils and sediments. The second part of the book, “Bioavailability (chapters 11 to 16),” provides detailed information on the bioavailability of trace elements in the aquatic and semi-aquatic ecosystems. The third part of the book, “Remediation” (chapters 17 and 18), discusses the remediation of metal contaminated sediments.