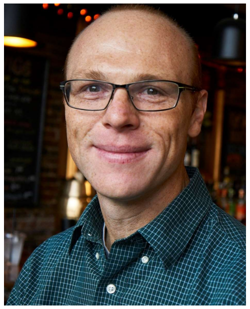
Introduction to Harmful Algal Blooms & An In-Situ Treatment Strategy

Paul M. Dombrowski, P.E.

ISOTEC Remediation Technologies, Inc.



Dick Raymond

Terra Systems, LLC.

ISOTEC – Soil & Groundwater Remediation

- **Experience with a broad range of remediation technologies**

Chemical Oxidation	Bioremediation
Injectable Activated Carbon	Chemical Reductants
In-Situ Stabilization	Surfactants
Permeable Reactive Barriers	Combined Remedies

- **Technical Experts & Experienced Field Staff**
  - **Most staff 5 to 10+ years of experience with ISOTEC**
- **Safety**
  - **28+ years without major safety incident**
  - **Zero OSHA reportable incidents**
- **Nationwide Service**
  - **25+ states & Ontario (2018-2023)**

ISOTEC REMEDIATION TECHNOLOGIES

Terra Systems

Terra Systems

- Founded in 1992
- 1st field demonstration of anaerobic bioremediation of PCE (DuPont, Victoria, TX)
- 1st EVO patent in the US (2002)
- Worldwide footprint

Core Competencies – "Brick and Mortar"

1. Research and Development
2. QA and QC on Manufacturing Floor
3. Treatability Study Laboratory
4. Pre and Post Sales Support
5. Sustainability
6. Manufacturing and Customization
    a. Droplet size
    b. Nutrient formulation
    c. Emulsifier packages (nonionic, anionic)
    d. ZVI particle size (4, <44, <125 µm)
    e. ZVI % (5-40%)

2016 AEHS LIFETIME ACHIEVEMENT AWARD

FOR HIS PIONEERING IN-SITU BIOREMEDIATION RESEARCH

DICK RAYMOND, SR.

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Harmful Algal Blooms (HABs)

theguardian.org

Animals farmed

Lethal algae blooms – an

CBS NEWS NEWS SHOWS LIVE LOCAL Login

U.S. ›

Toxic algae is r animals – and i

BY LI COHEN
JULY 18, 2023 / 9:21 AM / CBS NEWS

University of New Hampshire SEPTEMBER 25,

NEWSROOM

Researchers Identify Unu
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SCIENTIFIC AMERICAN

E&E NEWS

CLIMATE CHANGE

Algal Blooms Have Boomed Worldwide

Climate change is likely at least partially to blame for an uptick in the size and frequency of algal blooms in parts of the world's oceans

By Chelsea Harvey, E&E News on March 2, 2023

NOAA FISHERIES

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NEWS

Toxic Algal Bloom Spreads Along California Coast, Poisoning Sea Lions

August 29, 2022

Stranding teams ask public to report sea lions in distress and stay clear.

Feature Story | West Coast

More Information

- California Department of Fish and Wildlife Health Advisories for Seafood
- NOAA Harmful Algal Blooms
- SCCOOS Harmful Algal Blooms

Recent News

FEATURE STORY

Tide to Table Profile: Holdfast Aquaculture
West Coast

FEATURE STORY

NOAA Fisheries Releases Updated National Saltwater Recreational Fisheries Policy
Alaska, New England/Mid-Atlantic,

Harmful Algal Blooms (HABs)


Photo Source: NOAA


Photo Source: Boston Globe


Photo Source: NOAA


Red Tide (Alexandrium Tamarense)

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What is a harmful algal bloom?

"Harmful algal blooms, or HABs, occur when colonies of **algae** **grow out of control** and produce **toxic or harmful effects on people, fish, shellfish, marine mammals and birds**. The human illnesses caused by HABs, though rare, can be debilitating or even fatal."
https://www.noaa.gov/what-is-harmful-algal-bloom

- **Algae**
  - aquatic, photosynthetic, organisms
  - group of organisms with wide range of characteristics
  - seawater and freshwater
- **Out of Control Growth**
  - Many factors contribute to create a bloom
- **Toxic and Harmful Effects**
  - Humans and environmental receptors

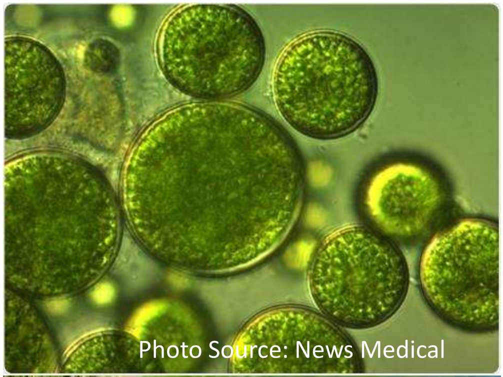
Photo Source: News Medical


Photo Source: capecod.net

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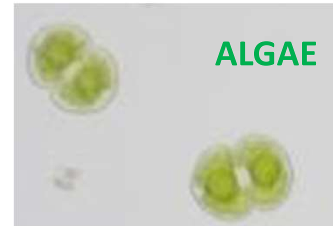
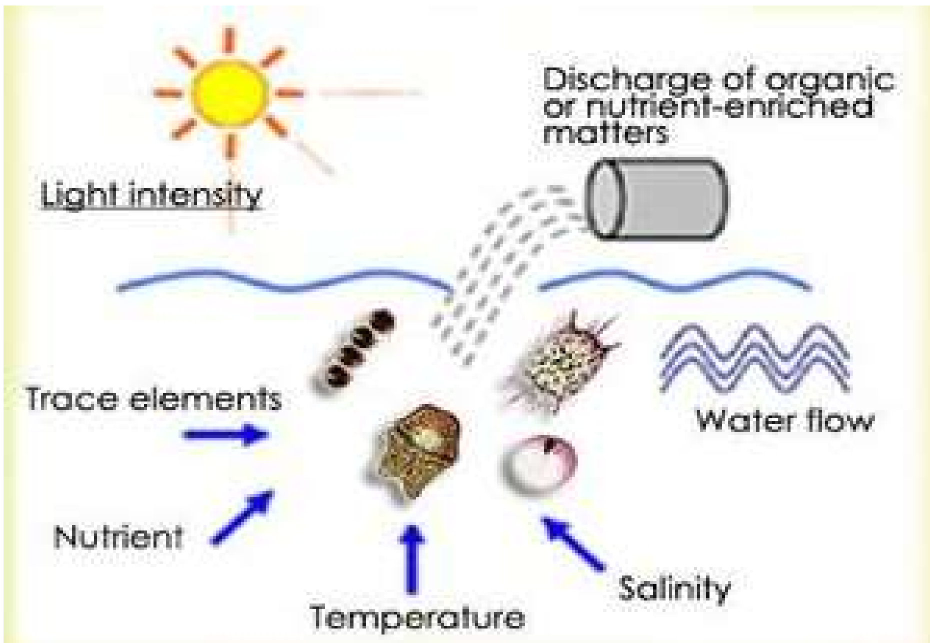
What causes algal blooms?



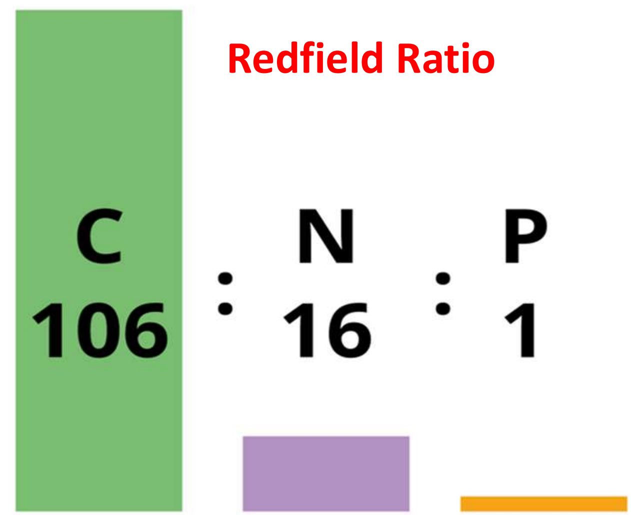
$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 112H_2O + 18H^+ + \text{energy} + \text{trace element} \rightarrow (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2$$

Wang, et al., 2017



Agriculture, Fisheries and Conservation Department
The Government of the Hong Kong Special Administrative Region

Redfield Ratio



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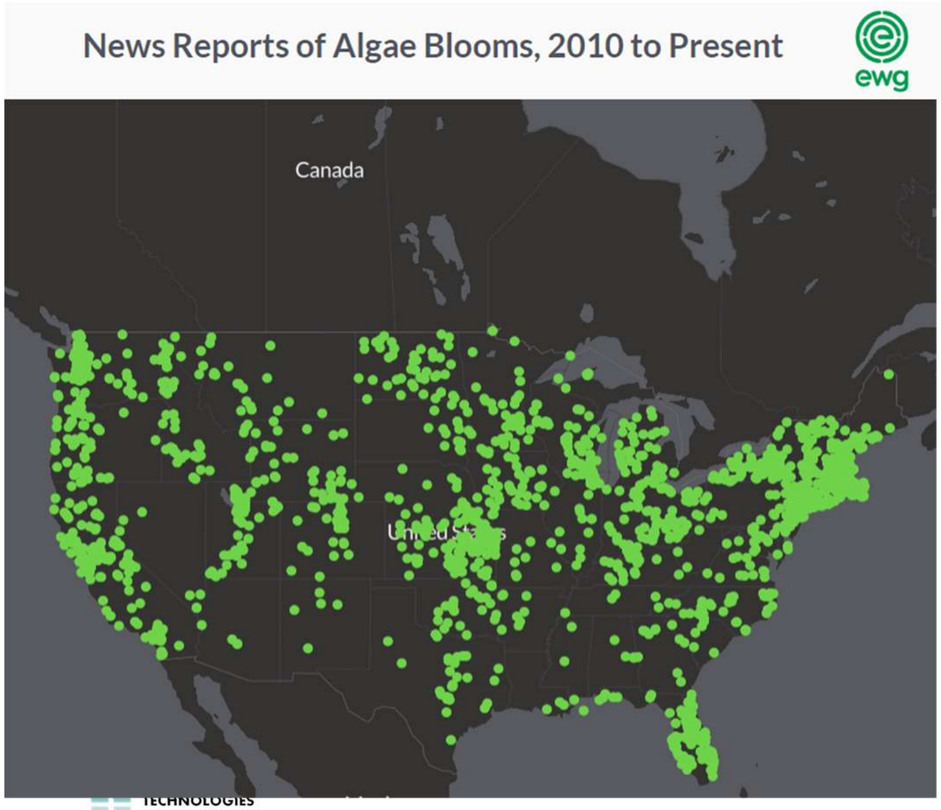
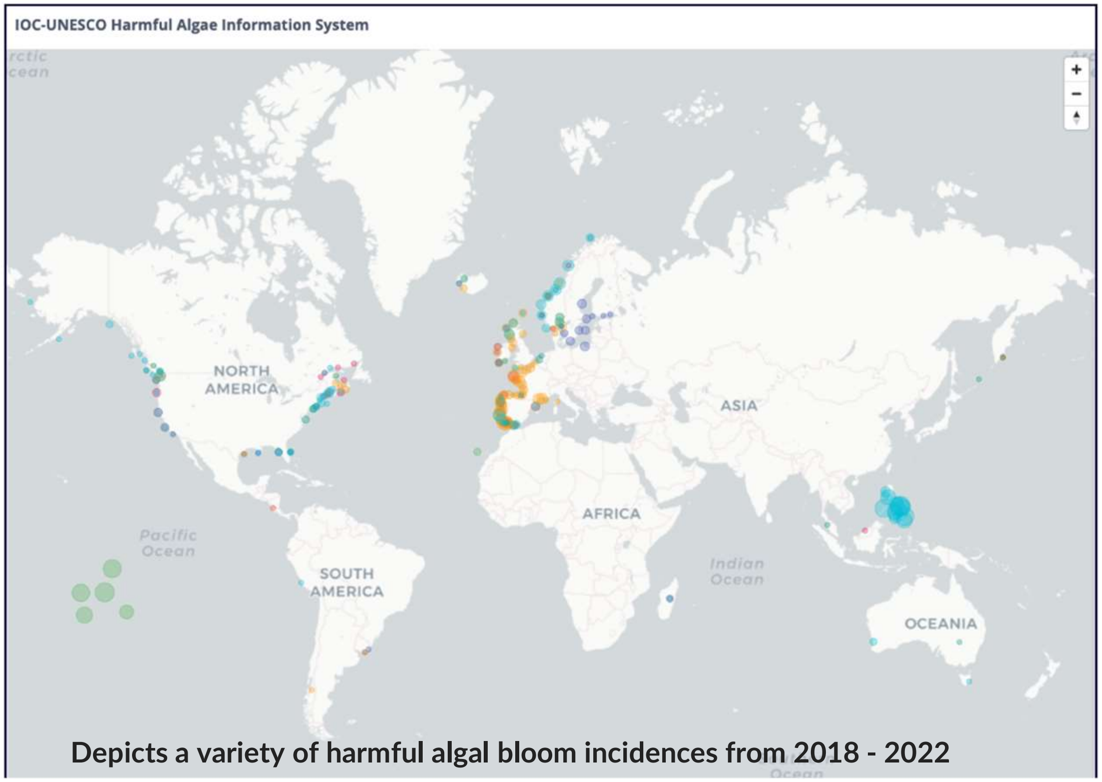
Where do HABs happen?





Depicts a variety of harmful algal bloom incidences from 2018 - 2022

Eutrophication

- Excessive plant and algal growth due to the increase of limiting growth factors
  - Primarily nitrogen or phosphorus
- Accelerated rate and extent due to human activities
  - Point-source discharges & non-point loadings of limiting nutrients
- Environmental Impacts
  - Dense blooms of noxious, foul-smelling phytoplankton
  - Limit light penetration
    - Reduce growth of submerged vegetation
  - Elevated pH
  - Anoxic dead zones
    - Decomposition of dead algal mass

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Eutrophication – Financial Impacts

- Waterfront real-estate / property taxes
- Commercial and recreational fishing
- Drinking water
- Tourism
- Recovery costs of threatened & endangered species

- >65% of U.S. estuaries are moderately to highly eutrophic due to high N loads [1]

- ~$2.2 billion annual loss due to eutrophication in U.S. freshwaters[2]

1. National Centers for Coastal Ocean Science
2. Dodd, et al. , 2009

Bell's Neck West Reservoir in Cape Cod. Photo by Heinz Profit

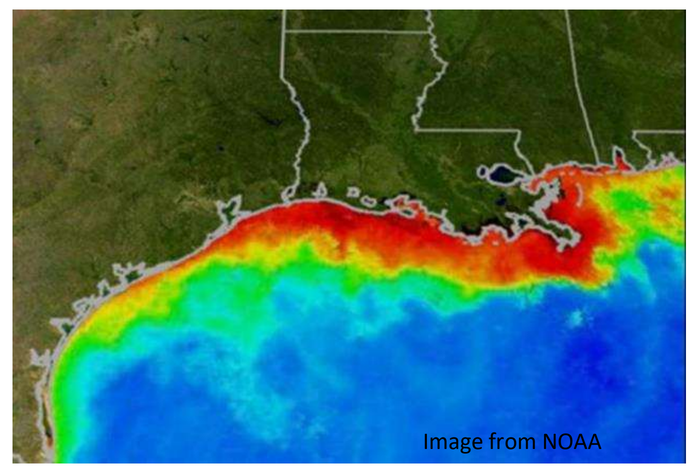

Image from NOAA

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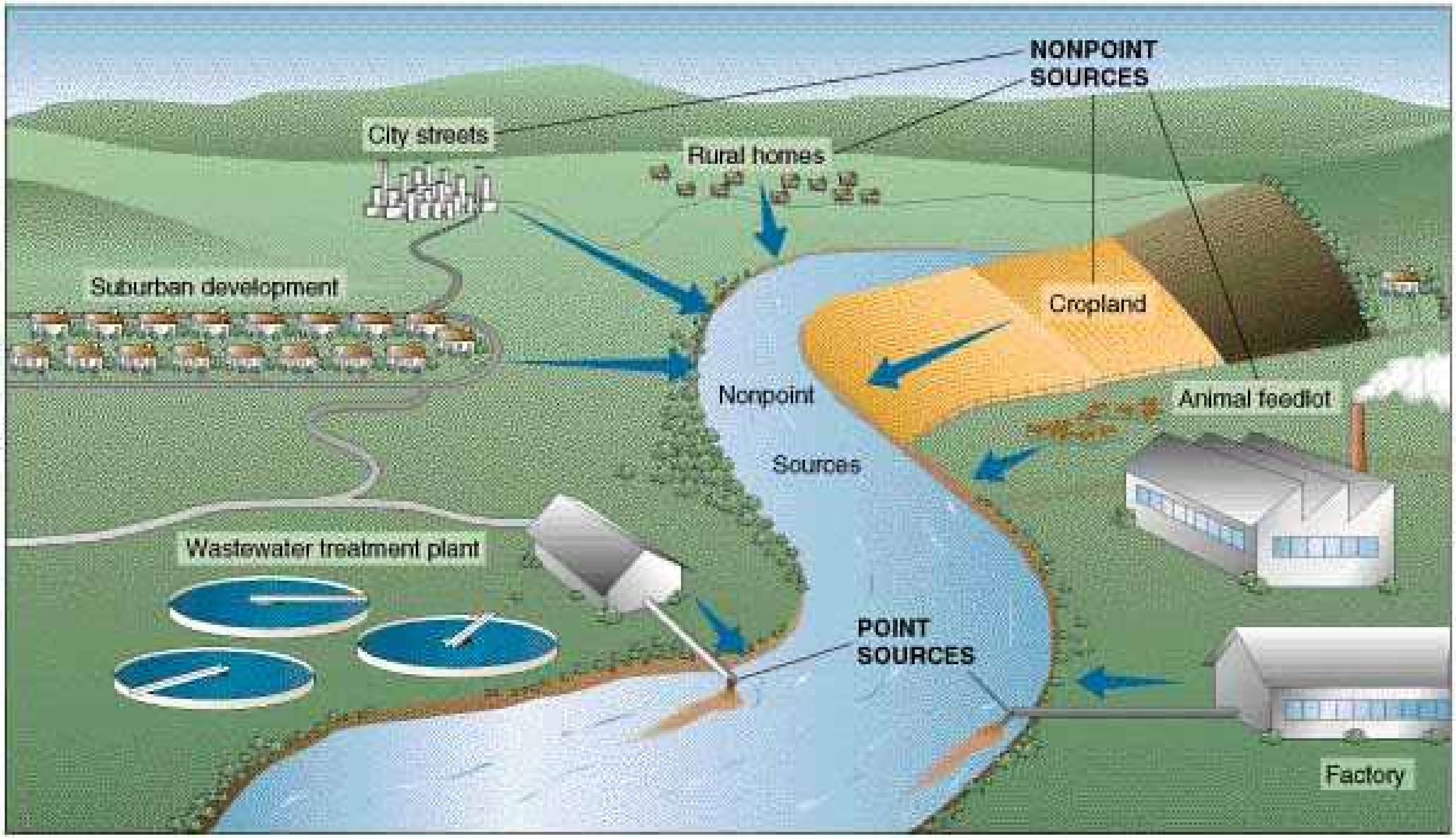
How do excessive nutrients enter waterways?

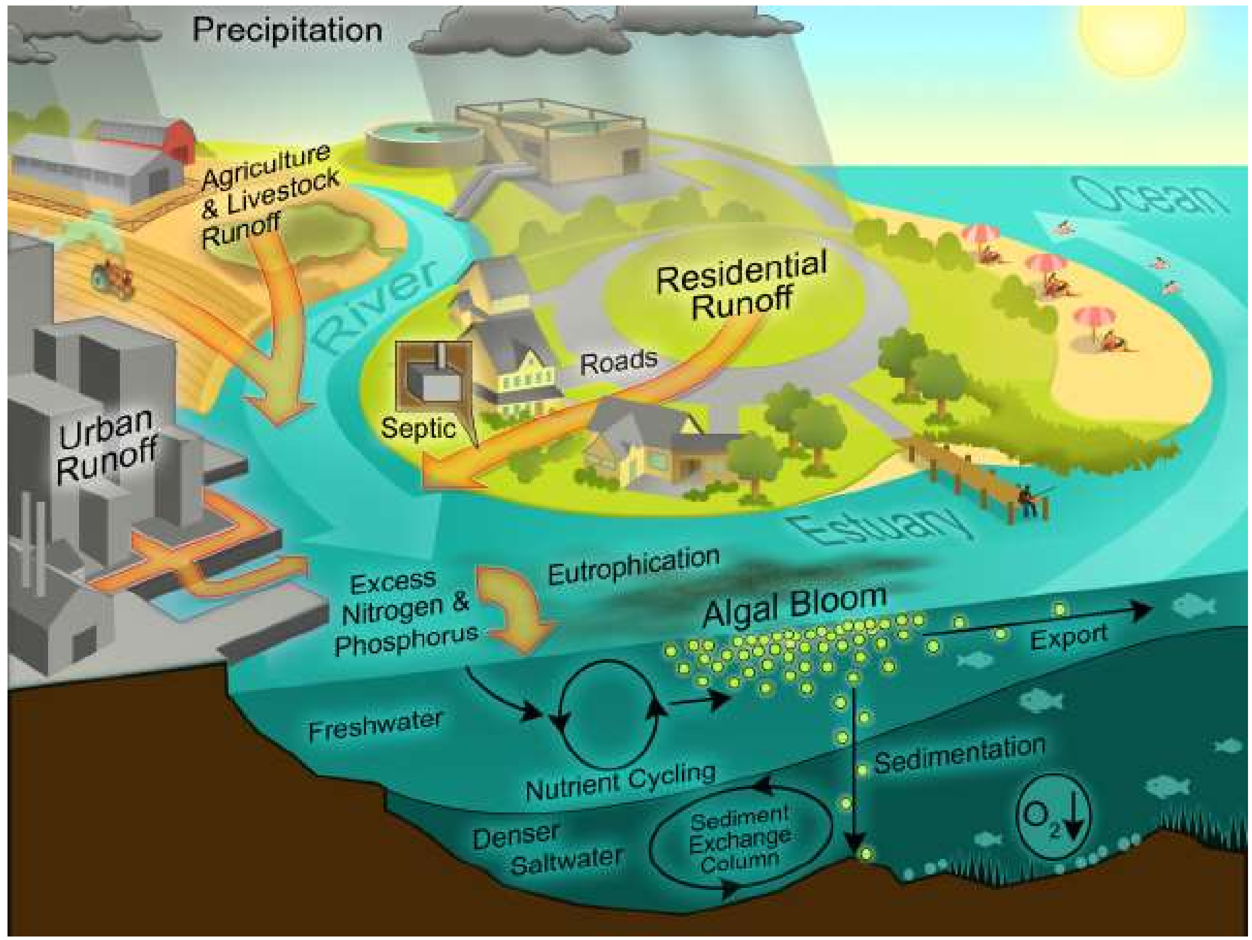
- Point Sources: direct discharge to surface water
- Non-Point Sources: surface run-off & groundwater transport



Clark Fork Watershed Education Program, 2021

Where does eutrophication happen most often?

- Agricultural Areas
  - Fertilizer
- N &P chemical manufacturing
- Areas with high septic use
- Urban & suburban area
  - Surface run-off
- River discharge / estuary



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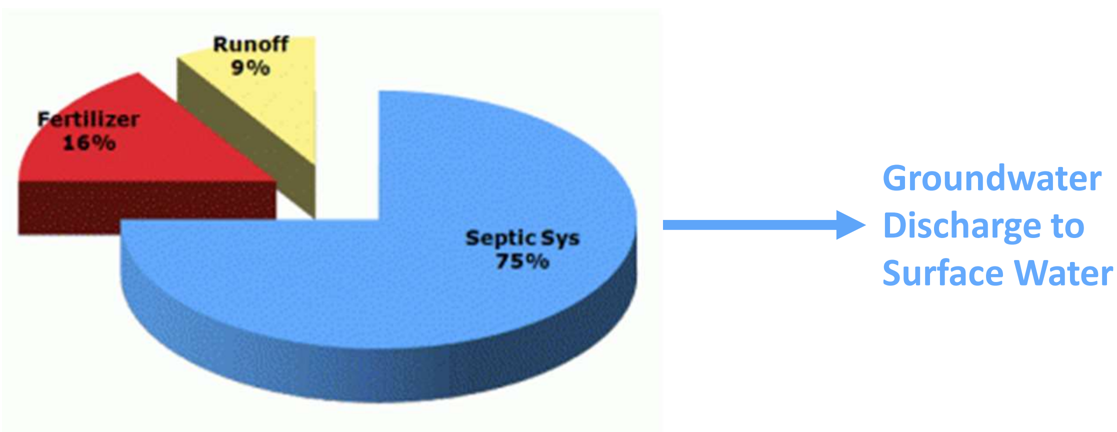
What is being done to limit HABs?

- USEPA announced a framework for implementing the Clean Water Act in 2013
  - states implement a water-quality based approach to determines pollutant reduction requirements
  - develop total maximum daily load (TMDLs) to achieve water quality goals
    - **load based versus a target concentration standard to achieve water quality goals**



Sources of Nitrogen – Pleasant Bay Watershed (Pleasant Bay Alliance)

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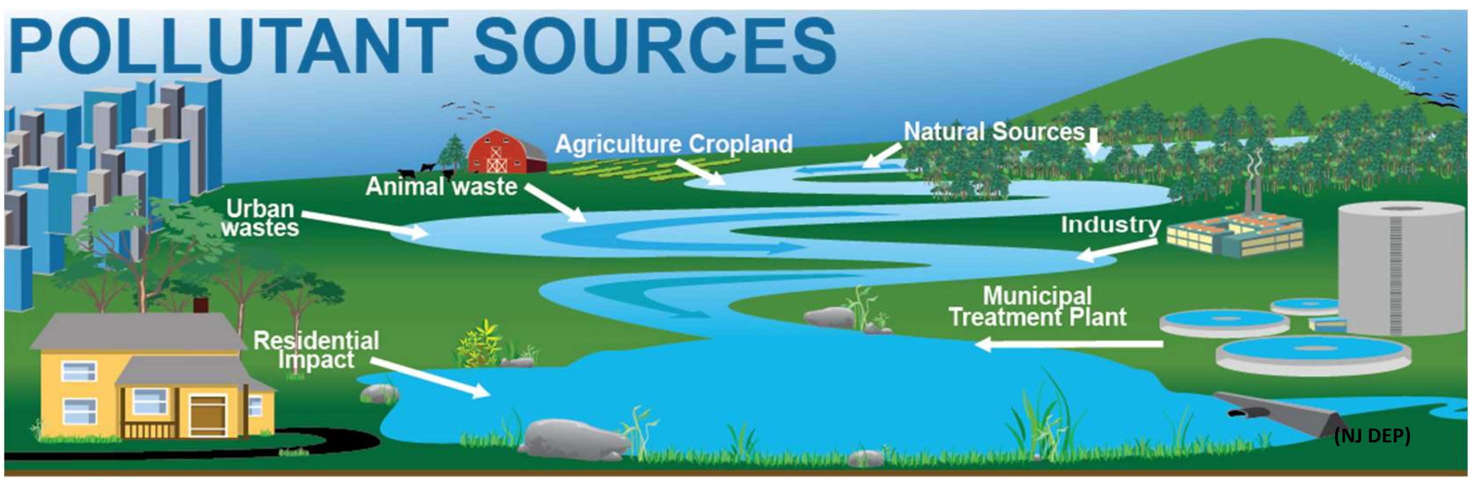
What is a TMDL?

- TMDL = total maximum daily load
  - represent a mass load-based standard to achieve water quality restoration goals
- Mass load reduction is the treatment objective
  - Do not need to meet a target concentration
  - Actions can be selected to treat the portion of the WLA or LA with highest nitrogen flux



Waste Load Allocations (WLA)
- point sources

Load Allocations (LA)
- non-point sources
- background

Cape Cod's Nitrogen Problem

- 85% reliance on septic systems
  - Title 5 septic systems (permitted by local boards of health)
  - Designed to remove pathogens but <u>not nutrients</u>

- Bacterial reactions in the septic tank and in the aquifer transform organic nitrogen to ammonia and then to nitrate

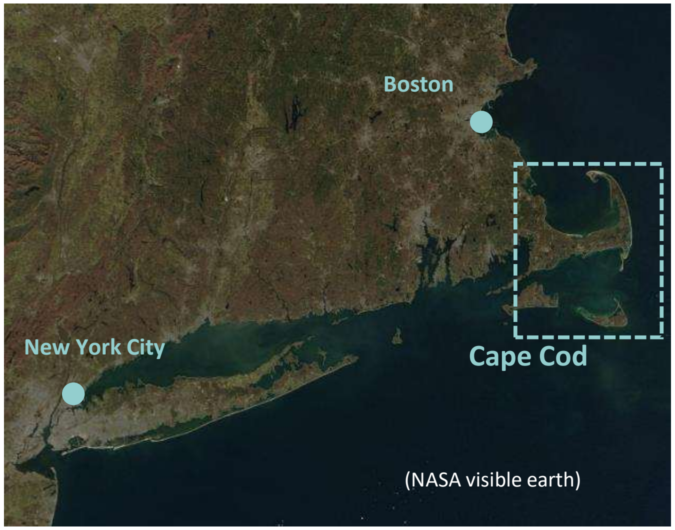
↓

Large dilute nitrate plumes in flow into coastal waters resulting in eutrophication

↓

Poor water quality, loss of habitat, aesthetic and economic impacts


(Boston Globe, 2011)



(NASA visible earth)

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Cape Cod's Nitrogen Path

- Regional Cape Cod 208 Water Quality Plan: watershed-based approach to restore coastal embayments and achieve water quality

- Combine traditional wastewater (sewer) and non-traditional treatments
  - Sewer infrastructure in high density areas
  - In-situ groundwater treatment with permeable reactive barriers (PRBs)
  - Innovative/Alternative (I/A) septic systems
  - Shellfish/aquaculture

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Goal: minimize the proposed area of towns and properties to be sewered ($)

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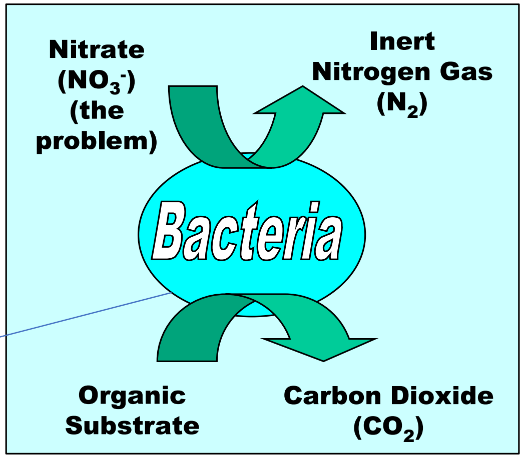
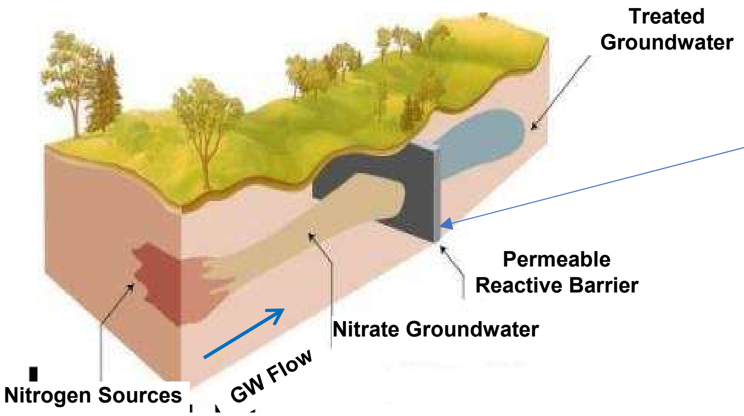
Denitrification PRBs

- Denitrification – well understood process for wastewater treatment
  - Bacteria convert nitrate to inert nitrogen gas (N_2)

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_{2\,(g)}$$

  - Denitrifying bacteria are anaerobic
  - Ubiquitous in soil



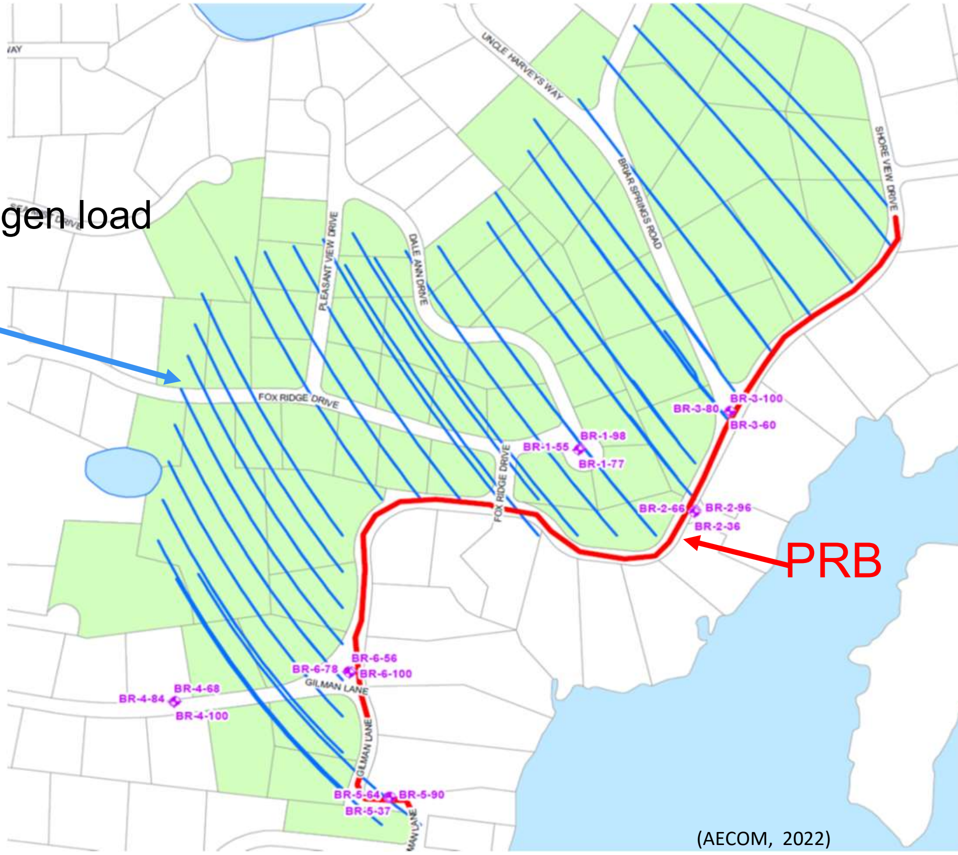


(ITRC, 2011)

- PRBs – accepted groundwater treatment approach
  - Permeable - groundwater flows through (passive)
  - Reactive - promote biological denitrification
  - Barrier - prevents nitrate migration to coastal waters

PRBs for TMDLs

PRB Capture Zone = Source of intercepted nitrogen load



(AECOM, 2022)

- A PRB does not need to meet a target concentration
- PRB(s) can be located to only treat the areas with highest nitrogen flux

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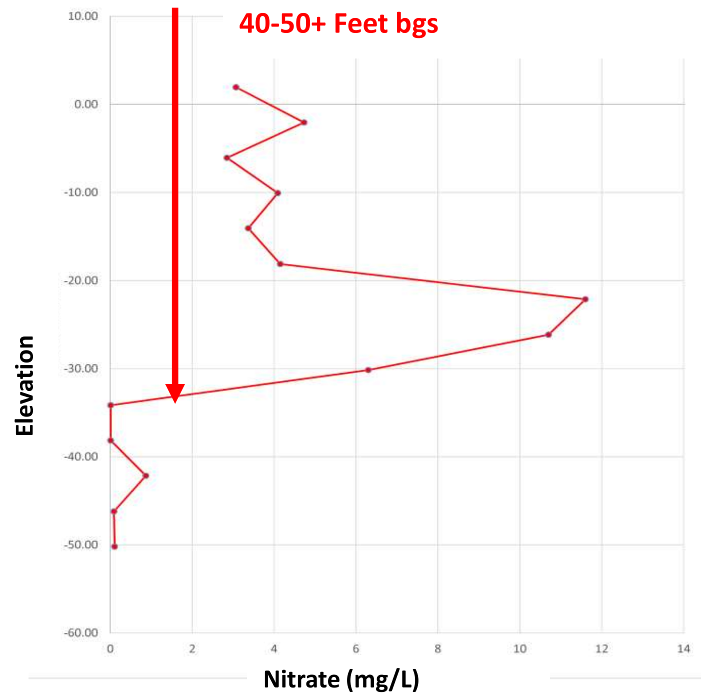
Cape Cod PRB Challenges

- Regulatory acceptance and public concerns
  - Injecting oil?
  - "Hazardous waste site"
  - Migration of oil / impacts to surface water
  - Permitting
- Implementation challenges
  - Treatment intervals of 70+ feet bgs
  - Fast groundwater seepage velocity
  - High fluxes of oxygen and nitrate
  - Highly developed region / access
  - 1,000s of feet of PRB
  - Persistence / rejuvenation frequency
- Adequate assessment of hydrogeology & nitrate distribution



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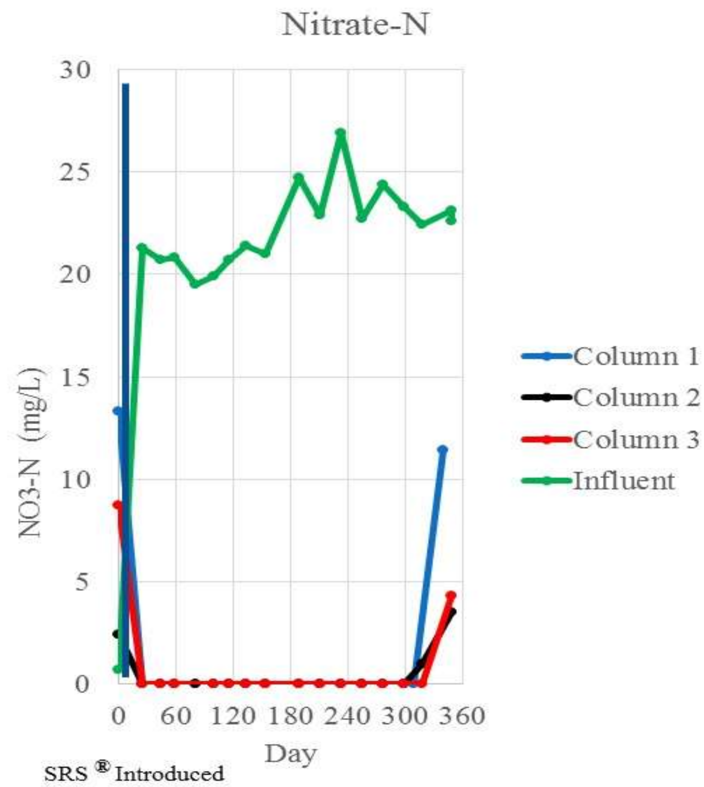
PRB Bench Scale Testing

- Evaluate EVO to support denitrification
  - **Effectiveness**
  - **Persistence**
  - **Migration (Community Concern)**

- EVO (2 Dosages) & EVO+ZVI
  - Off the shelf SRS-SD®
  - Complete removal of nitrate for >310 days
  - Nitrate breakthrough when TOC <4.0 mg/L

- **How to make EVO last longer?**
- **Can EVO be made stickier?**



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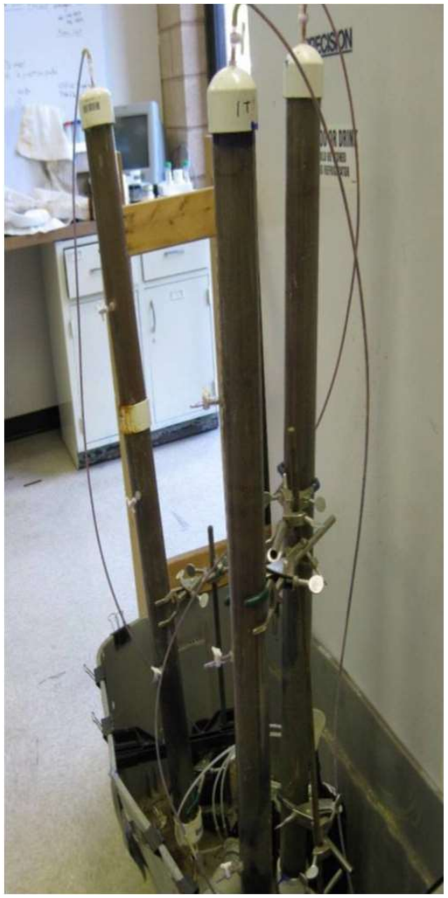
PRB Bench Scale Testing

- Adjust properties of EVO for high flow aquifers
  - Larger oil droplet (5 micron mean droplet)
  - Anionic surfactant
  - With or without sodium lactate
  - SRS®-NR
- Higher column flow rate (1.9 ft/d)
  - Emulsion did not appear in effluent
  - Emulsion was observed in effluent in previous column
  - Sustained nitrate removal at 2.9 mg/L TOC in effluent
- SRS®-NR better retained on soil matrix



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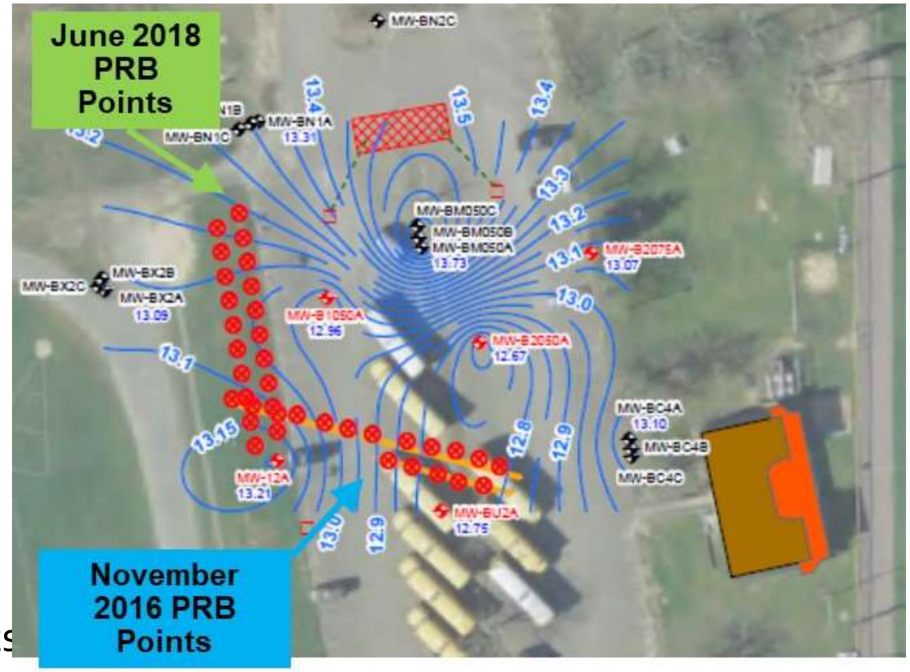
Field Demonstration

- 4 denitrification PRB demonstration tests implemented on Cape Cod and Martha's Vineyard to date (2016 – 2020)
  - 3 – 7 years of groundwater monitoring

Demonstration 1

- 110-Foot PRB (November 2016)
    - 17 injection Points
    - 10' spacing - 1 & 2 rows of points
    - 36 – 70' bgs
    - 10,800 gallons injected with 2,600 gallons EVO
- Objective: >3 years persistence
- Extended PRB to the north to intercept groundwater from the west (June 2018)
    - 110-feet added
    - 20 Injection points – 10' spacing – 2 rows of points
    - 14,800 gallons injected with 3,700 gallons EVO
    - Lactate added as quick release substrate



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Demonstration 1

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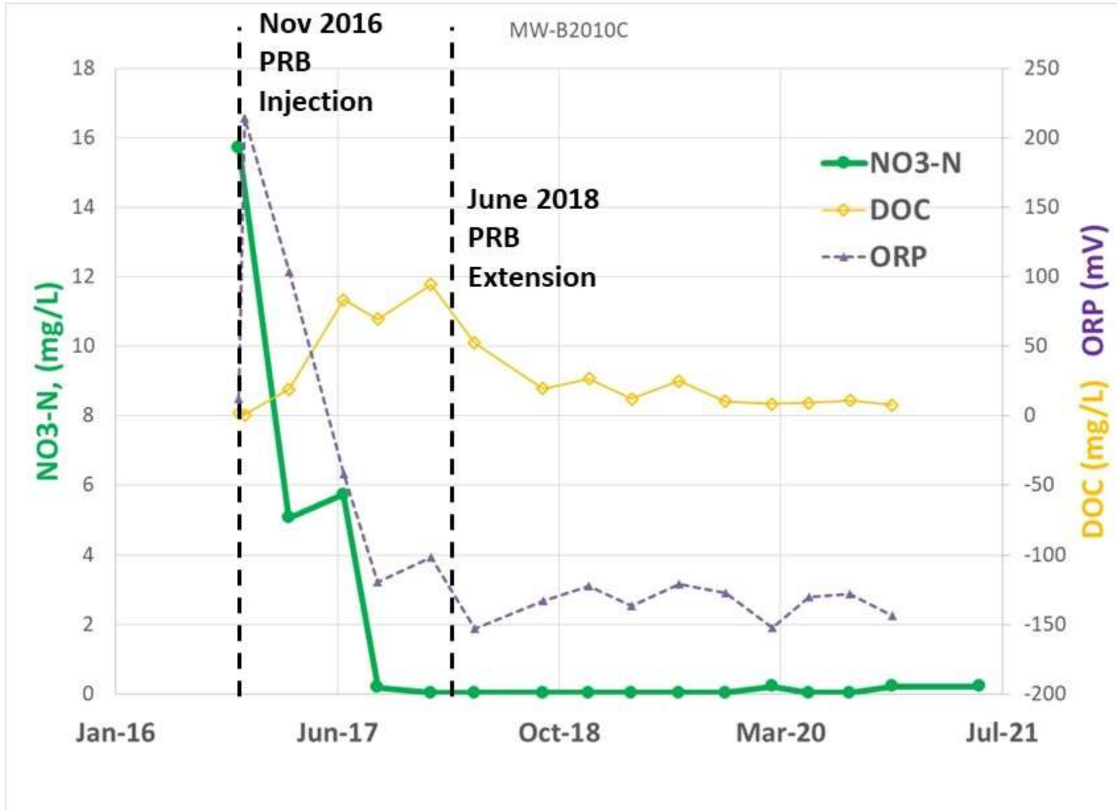
Demonstration 1 - Results

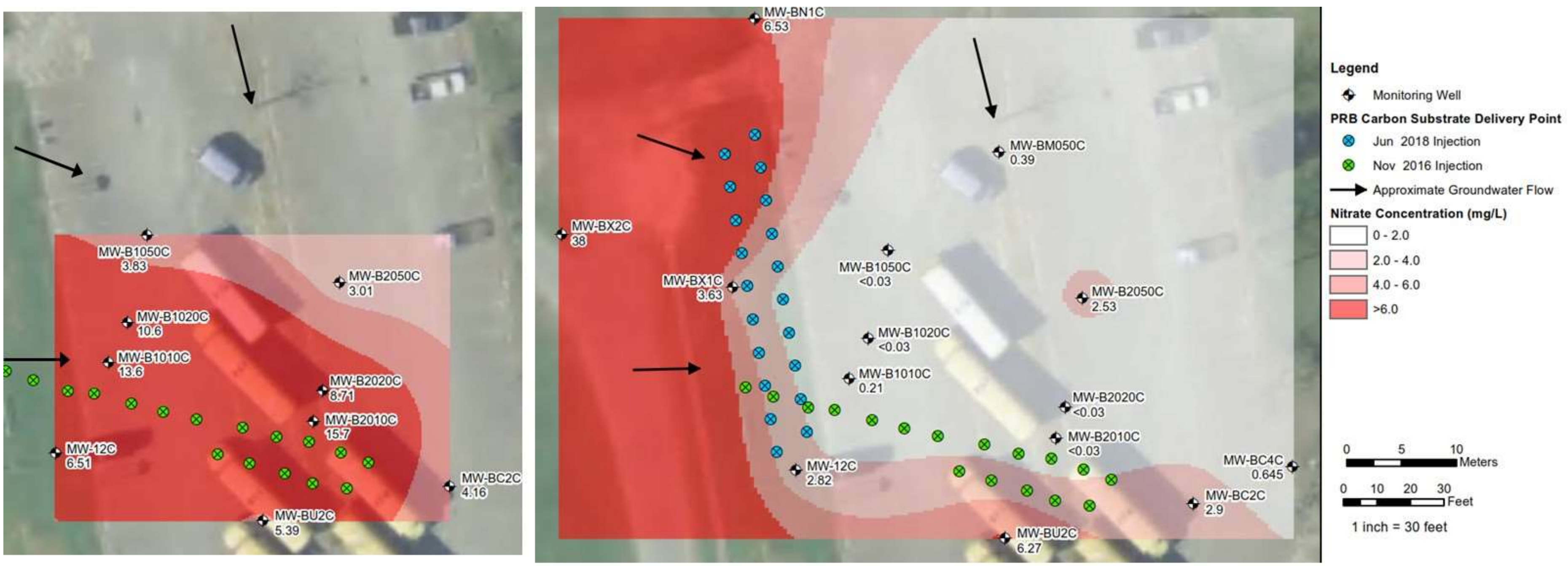
- Negligible impact of EVO observed 6 to 10 feet downgradient during injection

- Demonstrated persistence
  - >6 years after first injection

- Estimate nitrogen flux reduction 0.6 kg N/ft-yr
  - Nitrate: 10-25 mg/L
  - Groundwater flow ~0.25 ft/d
  - Based upon estimated flux ~0.7 pounds of nitrate-N removed per pound of SRS®-NR



Demonstration 1 - Results



NOVEMBER 2016
(Pre-Injection)

JULY 2019

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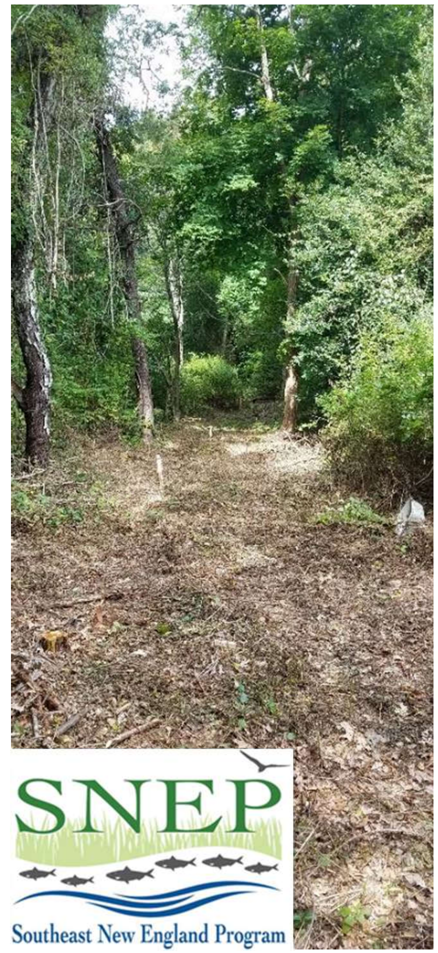
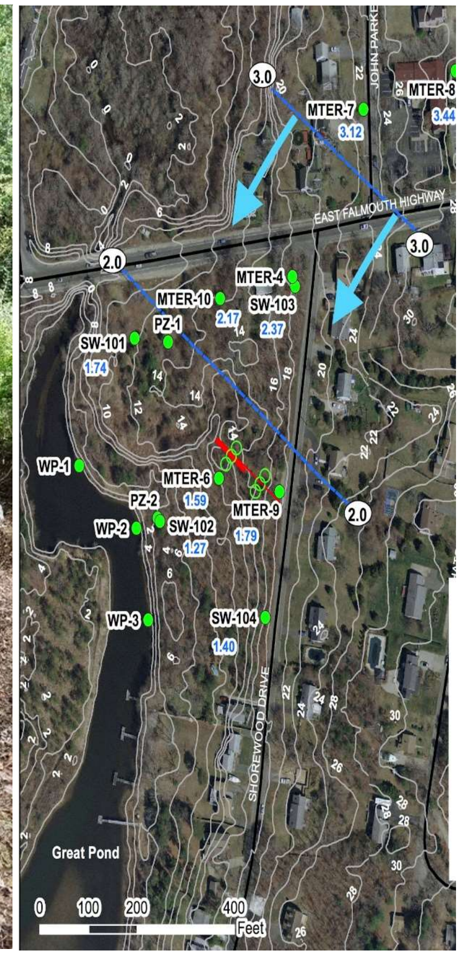
Demonstration Test 2

- Funded through 2019 SNEP Grant
- Town owned property
  - Previous investigation
  - Potential for PRB expansion
- Higher GW flow site
  - Reported 2-3 feet/day
- Low pH (4.3 – 6.0)
- Apply 2 dosages
  - Objective to see failure in 2-year monitoring period
- Multi-level monitoring
- Secondary groundwater parameters

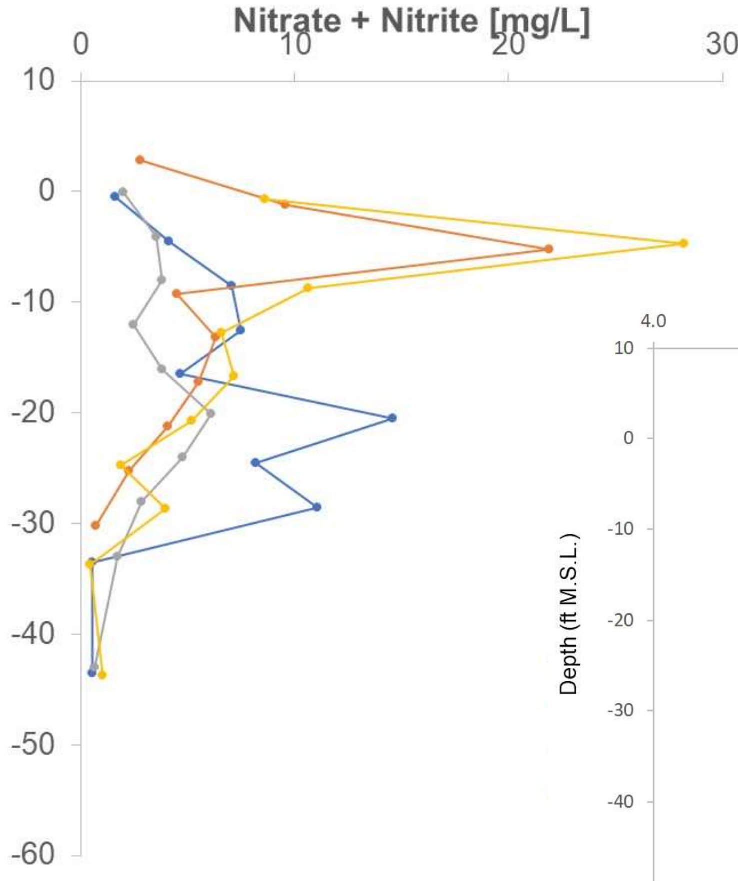


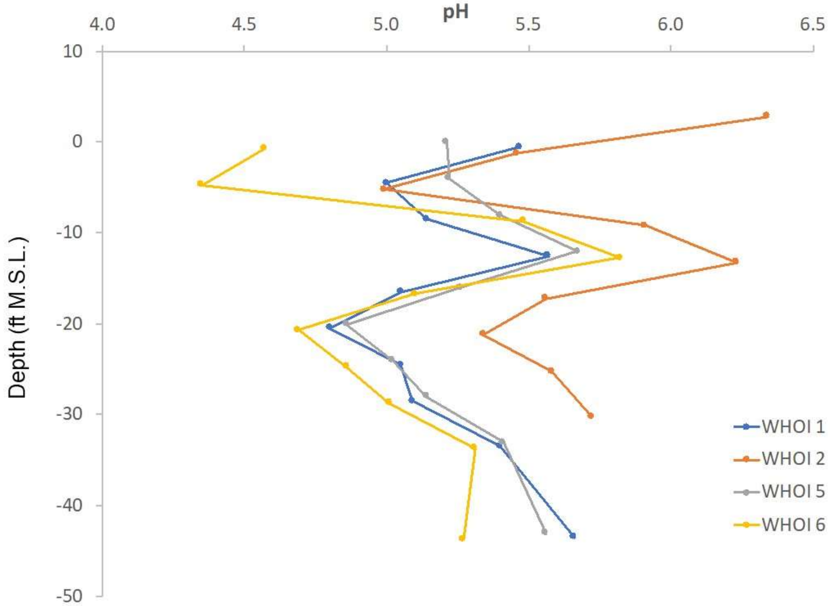
SNEP
Southeast New England Program



ISOTEC
REMEDIATION TECHNOLOGIES

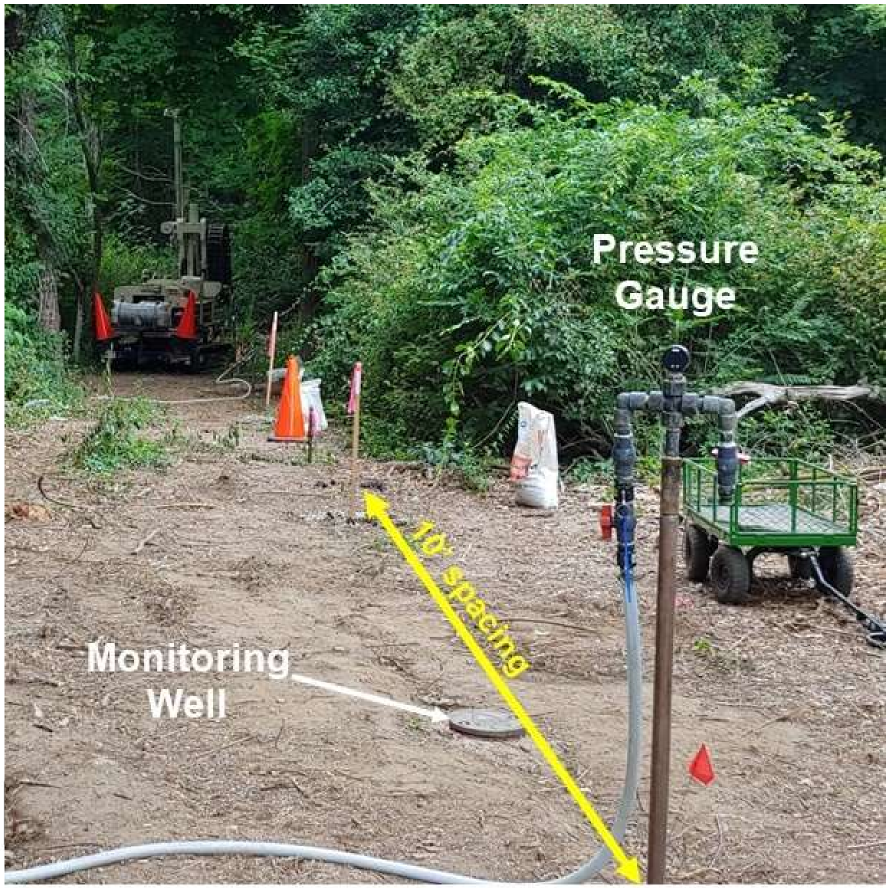
Demonstration Test 2





- Multi-level wells installed upgradient and downgradient with 2 transects along PRB

Demonstration Test 2

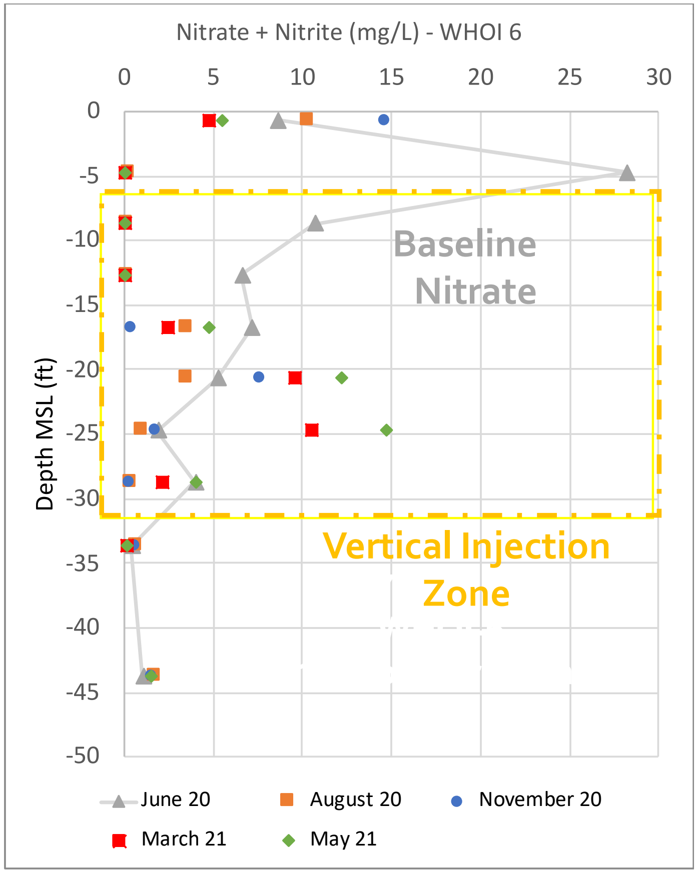


Permeable Reactive Barrier Design Parameters	July 2020 Injection	
PRB Width (ft)	60	60
Vertical Interval (ft)	24	24
PRB Design Life (months)	24	12
Total Injection Volume (gallons)	6,300	6,300
% of Total Pore Volume to Inject	16.2%	16.2%
EVO Dilution (of 60% soybean oil)	3:1	6:1
EVO (60% stock) (gallons)	2,100	1,100
Total CaCO3 Buffer (lbs.)	725	725
Total Injection Points	12	12
Average Flow Rate (gal/min)	3.7	

Demonstration Test 2

- Effective denitrification where EVO distributed
  - Nitrate reduction
  - DO, ORP, pH
- Dense/finer/siltier interval at lower depths
  - Higher injection pressure
  - Lower injection flow rate
  - Smaller distribution (15' downgradient)
  - Lower N flux

2-Year Dose
WHOI-6 915' downgradient)



Injection Pressure (psi)

	IP-7	IP-8	IP-9	IP-10	IP-11	IP-12
Upper	5	4	5	5	3	3
Middle	16	5	10	7	2-5	3
Lower	40-64	40-80	20-72	45-70	10	16-22

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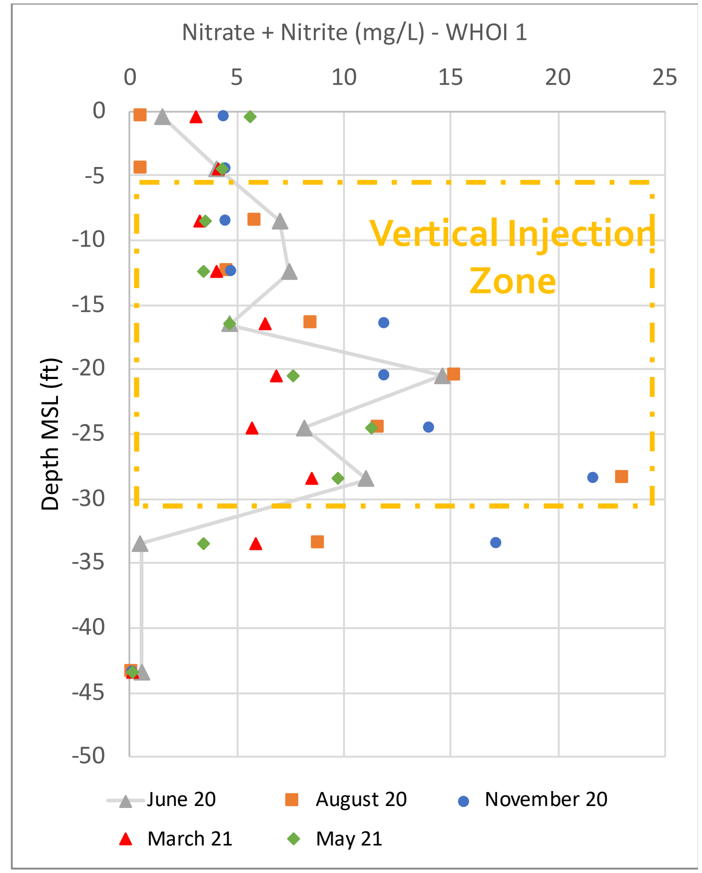
Demonstration Test 2

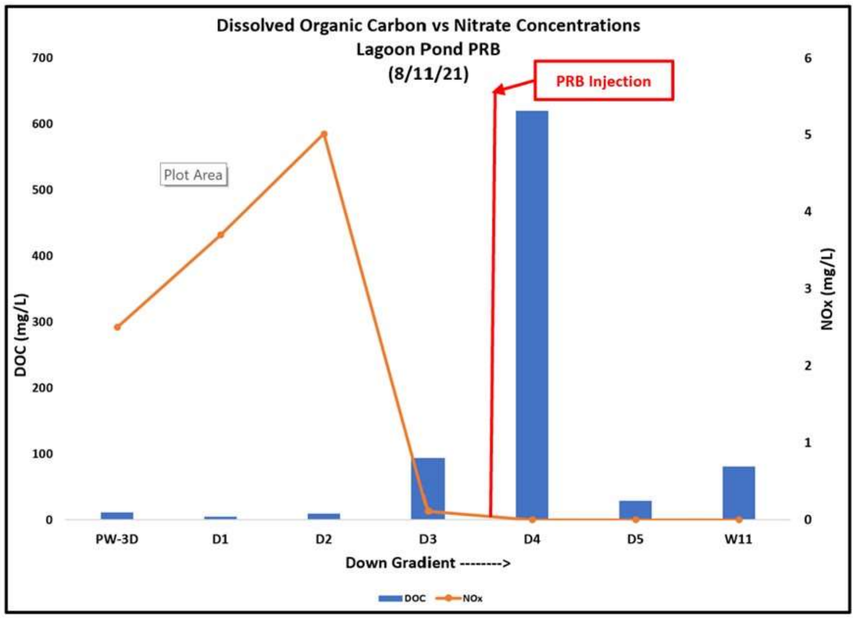
- 1-year dose PRB – limited nitrate removal
  - EVO dose important, especially for high flux
- Seasonal variability in nitrate
- Slug testing calculated lower Hydraulic Conductivity than soils suggested
  - Impact on flux
- Buffer increased pH in wells 60 to 120 feet downgradient
- Mobilization of redox sensitive metals limited to 10s of feet

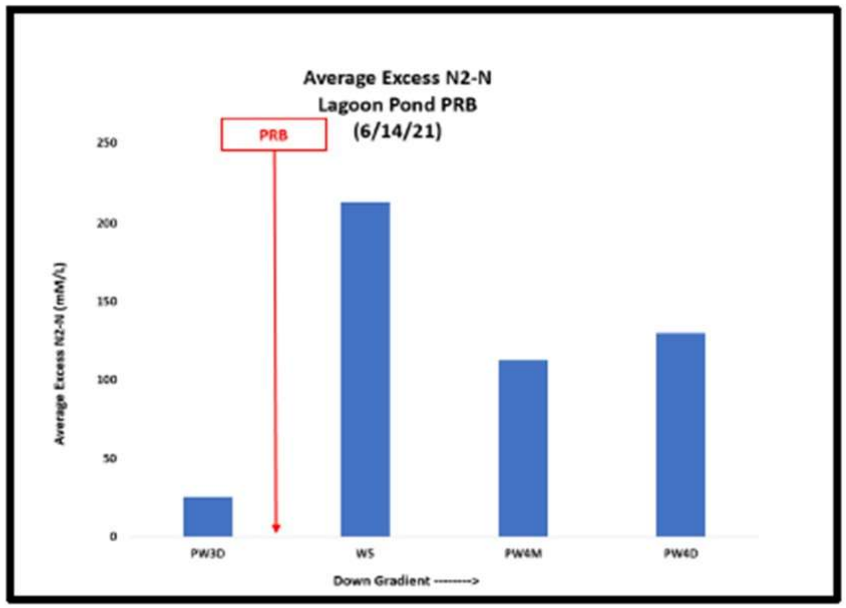
Upgradient Well - WHOI-1



Other Observations

- Denitrification PRBs effective for range of nitrate concentrations
  - 4 demonstrations nitrate ranged from 1 to 40+ mg/L
- Demonstration Test 4
  - Complete denitrification achieved





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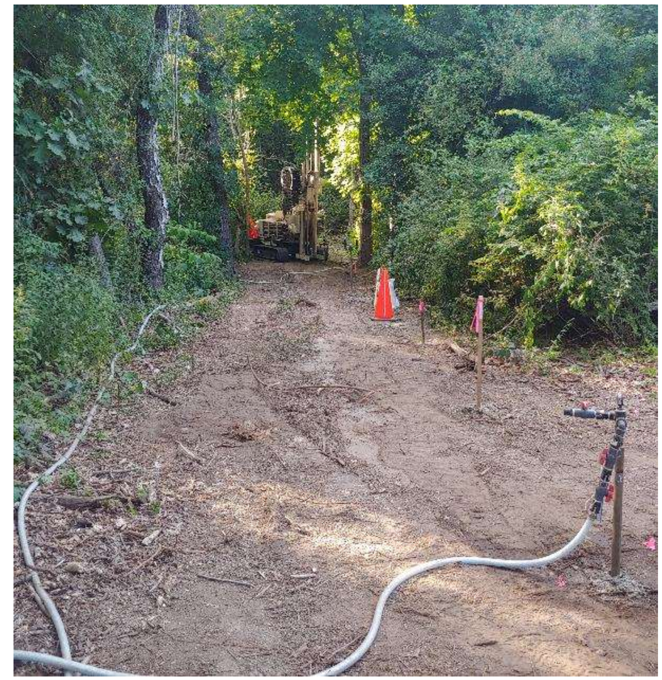
Denitrification PRBs Summary

- PRBs demonstrate denitrification in-situ using EVO
  - Demonstration Test 1 observes effective denitrification for 5+ years
- EVO dosage is a critical design parameter
- 1 vs. 2 injection rows
- Limited migration of secondary water quality concerns
  - Metals
  - Emulsion
- Groundwater Flow Direction and Velocity Critical to Design & Interpretation



ISOTEC REMEDIATION TECHNOLOGIES

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Denitrification PRB Design Manual

PERMEABLE REACTIVE BARRIERS FOR REMOVAL OF NITRATE FROM GROUNDWATER THROUGH INJECTION OF EMULSIFIED VEGETABLE OIL
Engineering Design Manual

JUNE 2023

PREPARED FOR:

SOUTHEAST NEW ENGLAND PROGRAM

PREPARED BY:

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TERRA SYSTEMS, INC.
130 HICKMAN ROAD, STE 1
CLAYMONT, DE 19703
www.terrasystems.net

- Engineering Design Manual developed based on 4 Cape Cod demonstration tests and EVO injection experience
  - prepared with support of a Southeast New England Program (SNEP) Watershed Grant.
- Available at https://www.terrasystems.net/technical-resources/

Next Steps

- Communities assessing locations and access
  - 500' to 2000'+ PRBs with 30,000+ linear feet anticipated in a single town
  - Communities installing monitoring wells to assess groundwater flow, direction, and vertical nitrogen distribution
  - Assessment of groundwater flow paths
  - Field data collected to be used for life cycle cost analysis
- PRBs can be a means to temporarily meet TMDLs
  - Timeline to fund, design, and build sewers and wastewater treatment
- Microbial assessments

ISOTEC REMEDIATION TECHNOLOGIES

Terra Systems

Thank You

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