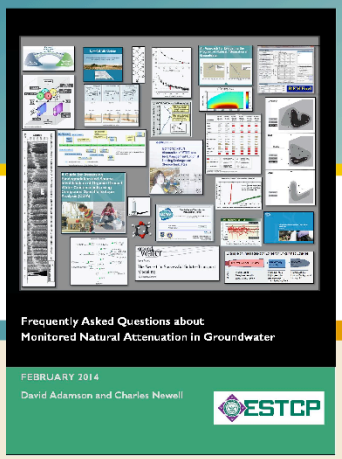
FREQUENTLY-ASKED QUESTIONS ABOUT MONITORED NATURAL ATTENUATION IN GROUNDWATER

GSI ENVIRONMENTAL

Charles Newell, Ph.D., P.E.,
David Adamson, Ph.D., P.E.



PROJECT TEAM

Presenters and Project PIs:

Charles Newell, GSI Environmental Inc.

David Adamson, GSI Environmental Inc.

Other Key Contributors:

Peer Review Panel

Poonam Kulkarni, GSI Environmental Inc.

Shahla Farhat, GSI Environmental Inc.

Travis McGuire, GSI Environmental Inc.

Michal Rysz, GSI Environmental Inc.

Mindy Vanderford, GSI Environmental Inc.

Project Sponsored by: ESTCP

PRESENTATION OUTLINE

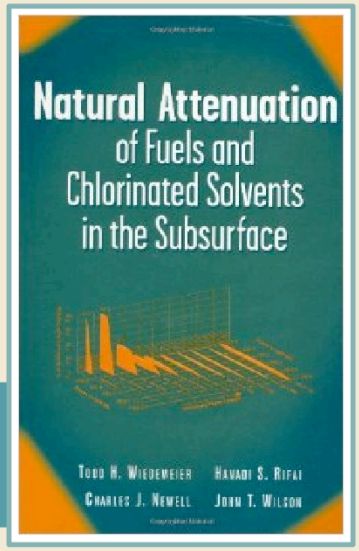
1. Motivation
2. What's an "FAQ" document?
3. MNA themes – Part I
4. Interview w/ John Wilson (followed by Initial Q&A)
5. MNA themes – Part II (including poll questions)
6. Tour through the interactive version
7. Final Q&A

3

MOTIVATION

- MNA in 2014: multiple sources of info, different vintages, different focus, need a library
- Example: 1999 MNA book
  - Great info, but we've learned a lot in the last 15 years!

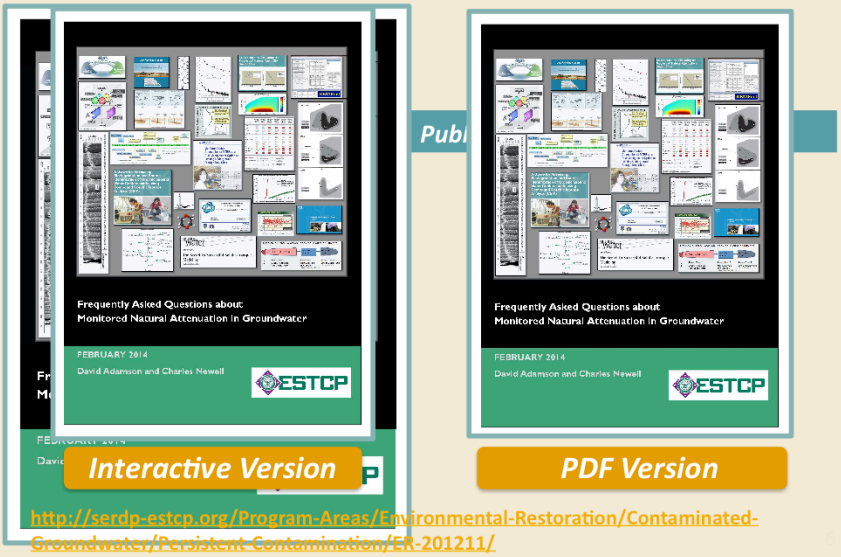
SOLUTION: Frequently-Asked Questions document about MNA to easily communicate MNA issues and alternatives



4

Answers to Frequently Asked Questions
About Managing Risk at LNAPL Sites

WHAT'S AN "FAQ" DOCUMENT?



http://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201211/

6

MNA THEMES

- *MNA AS AN EVOLVING TECHNOLOGY:*
- *THE BASIS FOR MNA:*
- *NEW CONTAMINANTS FOR THE MNA LINEUP:*
- *NEW TECHNIQUES, NEAT TOOLS:*
- *EMERGING ISSUES FOR EVALUTING MNA AS A REMEDY:*
- *IMPLEMENTATION AND SITE CLOSURE:*

7

MNA THEMES

MNA AS AN EVOLVING TECHNOLOGY:

1. Do we still need MNA?
2. What key protocols explain how to implement MNA?
3. What are the most important new MNA developments?

THE BASIS FOR MNA:

NEW CONTAMINANTS FOR THE MNA LINEUP:

NEW TECHNIQUES, NEAT TOOLS:

EMERGING ISSUES FOR EVALUTING MNA AS A REMEDY:

IMPLEMENTATION AND SITE CLOSURE:

8

FAQ 1: *Do we still need MNA?*

MNA from a Technical-Regulatory-Scientific Perspective:

3 Views on How MNA fits in (quotes from recent ITRC docs)

1. *Active remediation technologies rarely achieve complete remediation of all contaminant mass; thus, in effect, MNA is typically a component of every chlorinated-solvent site remedy.*

2. *(Natural Source Zone Depletion) is also of significance because engineered remedial actions typically do not always completely remediate soils and NSZD may be useful to address the residual hydrocarbon.*

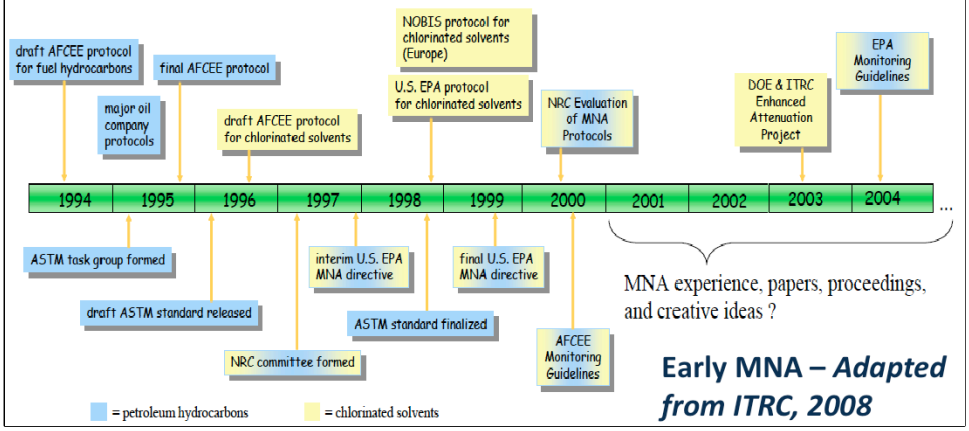
3. *Monitored natural attenuation (MNA) may also be a viable remedial alternative for situations in which the potential for adverse impacts to public health or sensitive environmental receptors is very low.*

9

FAQ 2: *How has MNA changed over time?*

New technologies, concepts, and increasing use **Through 2004**

Timeline –
Natural Attenuation of hydrocarbons and chlorinated solvents

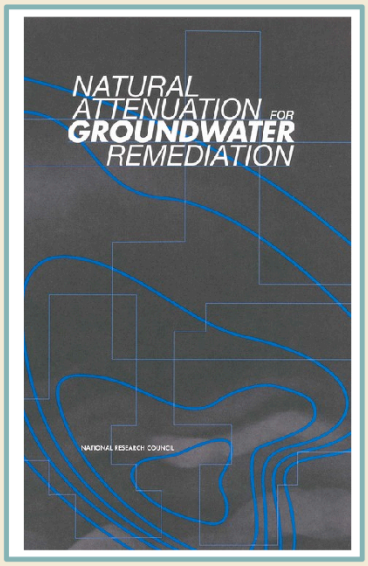


Early MNA – *Adapted from ITRC, 2008*

FAQ 2: *How has MNA changed over time?*

KEY POINTS:

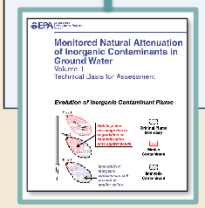
- Move away from scoring systems following National Research Council review of early protocols
- Better understanding of attenuation processes
- More contaminants, settings
- Incorporate new generation of tools

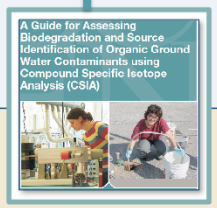


11

FAQ 3: *What are the most important new MNA developments?*

Year	*New Contaminant*	*New Measurement*	*New Process*	*New Tools*
2000-2005	MTBE-TBA	Two types of rates	Source attenuation of hydrocarbon sites	BIOChlor MAROS NAS SourceDK
2005-2010	Metals-Rads	Compound-Specific Isotopes Molecular Biological Tools	Biogeochemical/ abiotic trans. of chlor. solvents Matrix diffusion Oxidation of chlor. solvents at low DO	REMChlor Mass flux toolkit BIOBALANCE Scenarios for chlor. solvents MNA Sustainability



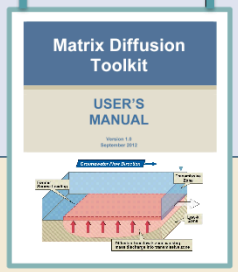


Probably the most important "recent" development?

12

FAQ 3: *What are the most important new MNA developments?*

Year	*New Contaminant*	*New Measurement*	*New Process*	*New Tools*
2010-present	"Emerging Contaminants"	CO_2 traps for NSZD	Natural source zone depletion (NSZD) Source attenuation of chlorinated solvent sites Attenuation in low-k zones	PREMChlor Matrix Diffusion Toolkit Scenarios for metals/rads Source History Tool



Coming Attractions: ESTCP ER-201129

Development and Validation of a Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches (MNA, Biostimulation and/or Bioaugmentation) at Chlorinated Solvent Sites

13

MNA THEMES

MNA AS AN EVOLVING TECHNOLOGY:

4. What is the philosophy behind MNA?

THE BASIS FOR MNA:

5. What evidence is needed for MNA?

NEW CONTAMINANTS FOR THE MNA LINEUP:

6. MNA lines of evidence—how have they changed?
7. MNA for the source zone—how does this work?

NEW TECHNIQUES, NEAT TOOLS:

EMERGING ISSUES FOR EVALUTING MNA AS A REMEDY:

IMPLEMENTATION AND SITE CLOSURE:

14

What is the philosophy behind MNA?

Nature can help!

It is harder and more expensive to clean these sites up than first thought.

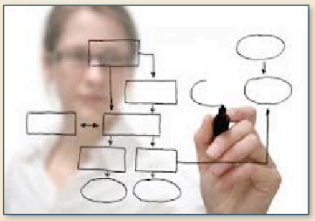
Nature is amazing and seems to be degrading or sequestering some of these chemicals.

Let's let nature do the job.

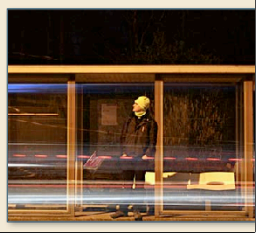
But you have to do three things:

Protect

Understand



Watch



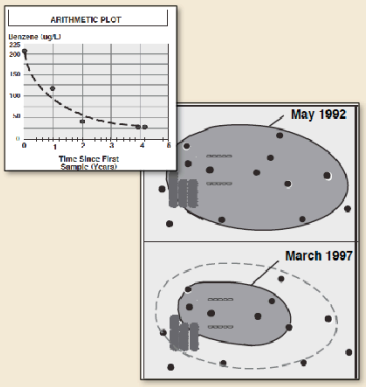
FAQ 5: *What evidence is needed for MNA?*

Typically Multiple Lines of Evidence

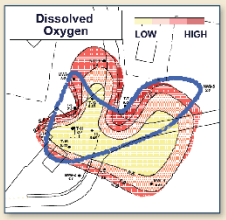
Historical (based on USEPA, 1999)	*WHY*	*WHAT*	*WHEN*
LOE 1: Historical contaminant mass reduction - monitoring data vs. time	"I shrink, therefore I am"	Direct method to demonstrate decreasing trend	Always
LOE 2: Hydrogeologic or geochemical data	Need to know more than just it is decreasing	Indirect method to demonstrate degradation process or rate	Most of the time
LOE 3: Field or microcosm studies	Need to know for than LOE 1 or 2	Direct method to demonstrate particular knowledge	Rarely; used to prove specific process

16

FAQ 5: *What evidence is needed for MNA? New Trends in LOEs*



***LOE 1:** Historical contaminant mass reduction*



***LOE 2:** Hydrogeologic or geochemical data*

***LOE 3:** Microcosm or Field data*

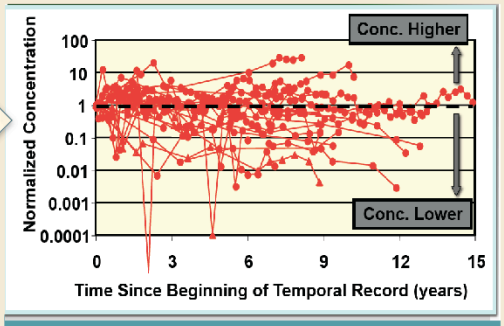
LOE: "Lines of Evidence"

17

FAQ 7: *MNA for the source zone too?*

An emerging consensus: YES

1. **Long-term monitoring data showing source attenuation**
2. **Source attenuation modeling tools (BIOChlor, REMChlor, NAS)**



Long-term temporal records from 22 monitoring wells at 13 Untreated TCE Sites (Newell et al., 2006)

2004 survey of 191 plumes - MNA was the sole remedy (no active source remediation) at 21% of sites with CVOC concentrations > 10 mg/L (McGuire et al., 2004)

18

FAQ 7: *MNA for the source zone too?*

An emerging consensus: YES

3. **Source attenuation protocols**
4. **Field studies demonstrating Source Zone Natural Attenuation (SZNA)**

ITRC, 2009

"[Natural source zone depletion (NSZD)] is of significance because engineered remedial actions typical do not always completely remediate soils and NSZD may be useful to address the residual hydrocarbon"

Methodology developed at Arizona St. Univ.

Site	Contaminant	Hydrogeology	Loss Rate from Dissolution (kg/year)	Loss Rate from Dissolved Transport Related Biodegradation (kg/year)	Loss Rate Estimate Due to Vadose Transport* (kg/year)
Guadalupe Diluent Tanks	Hydrocarbon	Sand dune	500 - 1600	600 - 1600	140,000 (O_2 Flux)
Guadalupe Compressor	Hydrocarbon	Sand dune	300 - 500	0	16,000 (O_2 Flux)
NAS Jacksonville	Chlorinated Solvent	Silty sand, clay	12 - 32	-	0.27 - 0.79 (Vapor Flux)
Parris Island	Chlorinated Solvent	Silty clay, sand stringers	1.8 - 5	-	0.22 - 0.68 (Vapor Flux)

Selected results from NSZA studies at several sites (Ekre et al., ESTCP ER-0705 Short Course, 2011)

19

MNA THEMES

MNA AS AN EVOLVING TECHNOLOGY:

THE BASIS FOR MNA:

8. Can I apply MNA to metals, inorganics, and radionuclides?
9. I can apply MNA to BTEX, but how about oxygenates?

NEW CONTAMINANTS FOR THE MNA LINEUP:

10. Which emerging contaminants are MNA candidates?

NEW TECHNIQUES, NEAT TOOLS:

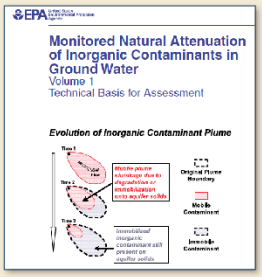
EMERGING ISSUES FOR EVALUTING MNA AS A REMEDY:

IMPLEMENTATION AND SITE CLOSURE:

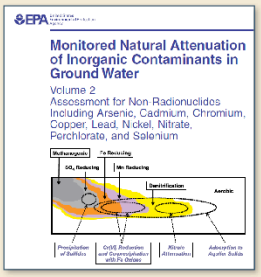
20

FAQ 8: *Can I apply MNA to metals, inorganics, and radionuclides?*

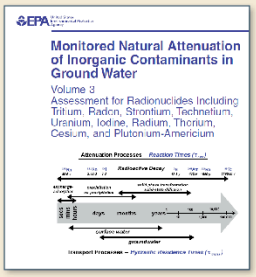
YES, says USEPA



2007



2008



2010

Tiered Lines-of-Evidence Approach *(similar to protocols for organics)*

1. **Plume is not expanding and sorption is occurring**
2. **ID the attenuation mechanism and estimate rate**
3. **Determine capacity and sustainability**
4. **Develop monitoring and contingency measures**

21

FAQ 8: *Can I apply MNA to metals, inorganics, and radionuclides?*

KEY POINTS:

- **Primary attenuation pathway for many inorganics is transformation to less mobile forms through co-precipitation or sorption**
- **Reactions are generally more complex and highly influenced by geochemical conditions**

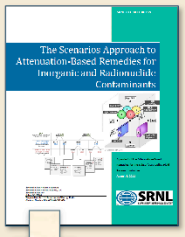
Contaminant	Biological Reaction		Abiotic Reaction	Sequestration
	Anaerobic	Aerobic		
Nitrate	Yes, degradation	No	Yes (reactive iron)	No
Perchlorate	Yes, degradation	No	Conflicting Data	No
Chromium (Cr), Selenium (Se), Copper (Cu), Cadmium (Ca), Lead (Pb), Nickel (Ni), Zinc (Zn), Beryllium (Be), Arsenic (As) (metalloid)	Valence change, generally favorable	Valence change, generally unfavorable	Valence change, generally favorable	Yes (sorption, co-precipitation)
Uranium, Technetium, Strontium, Cesium, Radium, Iodine	Valence change, generally favorable	Valence change, generally unfavorable	Valence change, generally favorable	Yes (sorption, co-precipitation)

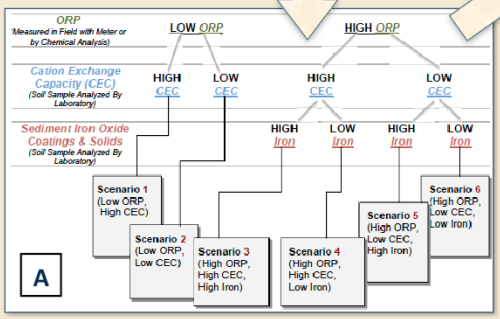
22

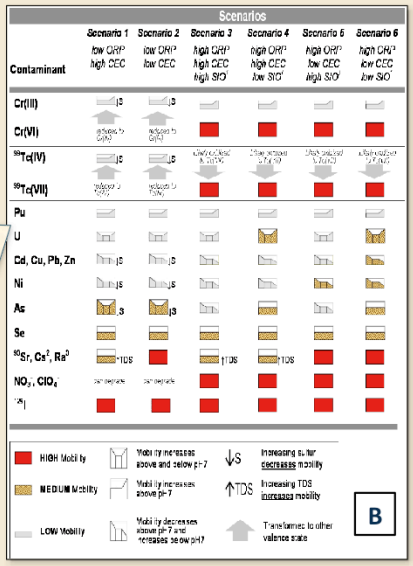
FAQ 8: *Can I apply MNA to metals, inorganics, and radionuclides?*

ADDITIONAL GUIDANCE:

"SCENARIOS" DOE, 2011



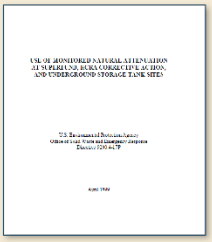




FAQ 9: *I can apply MNA to BTEX, but how about oxygenates?*

Originally No, But Now YES

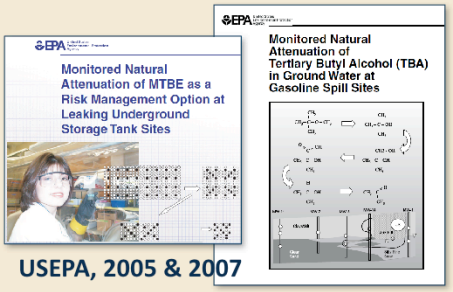
USEPA MNA Directive, 1999



- **Not promising in early protocols**

  MTBE had been found to "*…migrate large distances and threaten downgradient water supplies at the same sites where the BTEX component of a plume has either stabilized or diminished due to natural attenuation*" and included MTBE among compounds "*…that tend not to degrade readily in the subsurface*".

- **Lots of research and field work in the following 5-10 years, and we ended up with a completely different story!**

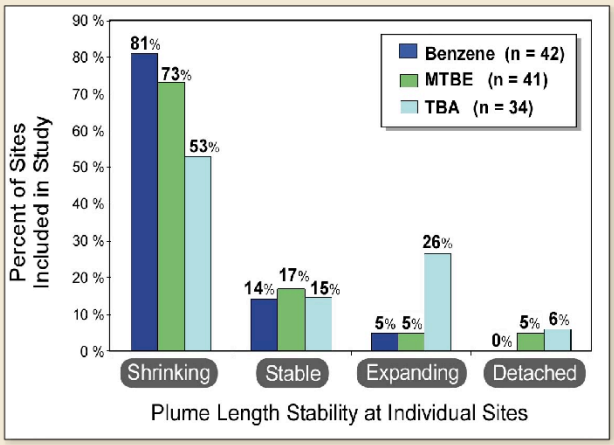


USEPA, 2005 & 2007

FAQ 9: *I can apply MNA to BTEX, but how about oxygenates?*

What do the data say?

Several plume studies have documented that majority of MTBE/TBA plumes are relatively short and/or attenuating



Kamath et al., 2012

- MTBE exhibits similar characteristics to BTEX in terms of median plume size (142 ft) and attenuation rate (-0.63 yr^{-1})
- TBA also similar to BTEX but fewer are stable/shrinking

25

FAQ 9: *I can apply MNA to BTEX but how about oxygenates?*

Contaminant Class	Biological Degradation	
	Anaerobic	Aerobic
MTBE	**YES** (may require acclimation period)	**YES**
TBA	**YES** if electron acceptors are readily available (may be limited in methanogenic conditions)	**YES** (generally faster than in anaerobic conditions)
Ethanol	**YES** (tends to be preferentially degraded over BTEX)	**YES** (tends to be preferentially degraded over BTEX)

26

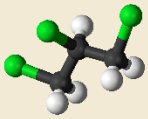
FAQ 10: *Which emerging contaminants are MNA candidates?*

Dioxane, TCP, NDMA, Phthalates, and Maybe Others?

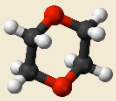
- **DoD general goal for emerging contaminants:**

  "Identify chemicals or materials that either lack human health standards or have an evolving science and regulatory status."

- **Other problems**
  - **Prevalence at individual sites is largely unknown**
  - **Absence of well-established treatment technologies**
  - **Absence of tools for establishing MNA (e.g., CSIA, MBTs)**



1,2,3-Trichloropropane



1,4-Dioxane

27

FAQ 10: *Which emerging contaminants are MNA candidates?*

Emerging Contaminant	Biological Degradation		Abiotic Degradation	Sequestration
	Anaerobic	Aerobic		
1,4-Dioxane	Limited	**YES** (mostly lab studies; can be cometabolic or used as a carbon source)	Not documented	**No** (poor sorption)
Perfluorinated Compounds	Very limited (incomplete pathway)	Very limited (incomplete pathway)	Limited (a reliable light +Fe(III) reaction has been established)	Moderate (primarily electrostatic sorption to ferric iron minerals; limited organic carbon sorption)
N-Nitrosodimethylamine (NDMA)	**YES**	**YES** (cometabolic)	**No** (several ex situ methods, including UV photolysis)	**No** (poor sorption)
1,2,3-Trichloropropane	**YES** (slow, often incomplete pathway)	**YES** (slow, incomplete pathway)	Very limited (reactive iron, base hydrolysis)	Limited (moderate sorption)

28

MNA THEMES

MNA AS AN EVOLVING TECHNOLOGY:

THE BASIS FOR MNA:

11. Can isotopes prove contaminants are being destroyed?
12. How can molecular biological tools help me with MNA?
13. How can you show attenuation that occurred before the start of your monitoring program?

NEW CONTAMINANTS FOR THE MNA LINEUP:

14. Can DO measurements be a problem for MNA studies?

NEW TECHNIQUES, NEAT TOOLS:

15. What are CO2 traps and how do they help me show attenuation?
16. How do I estimate rates and timeframes for MNA?
17. What is required for MNA monitoring?

EMERGING ISSUES FOR EVALUTING MNA AS A REMEDY:

18. What is the new thinking about monitoring frequency?
19. Statistics for 2 questions: how far and how long?
20. Which computer models work best for MNA?

IMPLEMENTATION AND SITE CLOSURE:

21. Are MNA reactions sustainable? Is MNA sustainable?

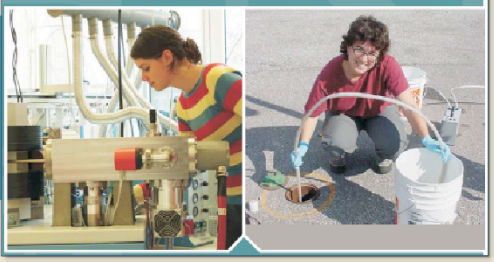
29

FAQ 11: *Can isotopes prove contaminants are being destroyed?*

Yes, and more

"Stable isotope analyses can provide unequivocal documentation that biodegradation or abiotic transformation processes actually destroyed the contaminant."
USEPA, 2008

A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA)

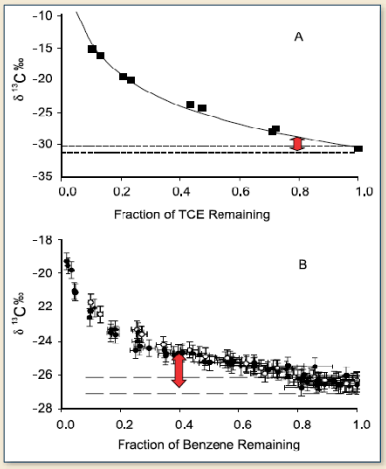


30

FAQ 11: *Can isotopes prove contaminants are being destroyed?*

KEY PRINCIPLE: **Isotopic Fractionation** = Lighter isotopes are used preferentially during degradation, such that the remaining non-degraded compound becomes enriched in the heavier isotope

carbon ($^{13}C/^{12}C$)
oxygen ($^{18}O/^{16}O$)
nitrogen ($^{15}N/^{14}N$)
chlorine ($^{37}Cl/^{35}Cl$)
hydrogen ($^{2}H/^{1}H$)



KEY BENEFITS (continued next page):

- **Demonstrating that parent compound is being degraded**
- **Estimating the extent of degradation**

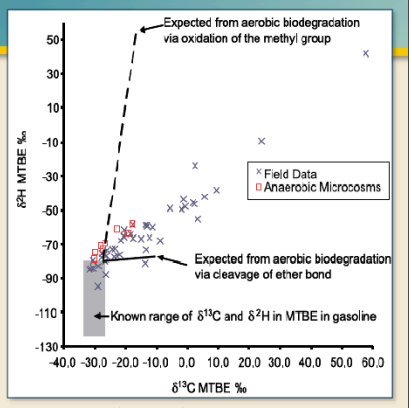
$\delta^{13}C$ data from several studies as compiled in Hunkeler et al., USEPA, 2008

31

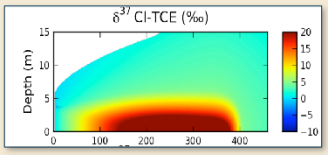
FAQ 11: *Can isotopes prove contaminants are being destroyed?*

KEY BENEFITS (continued):

- Differentiating between destructive and non-destructive pathways
- Differentiating between various destructive pathways
- Demonstrating that complete degradation has occurred
- Estimating rate of degradation
- Source identification and differentiation
- Can be incorporated into reactive transport modeling



2-D plot of $\delta^{13}C$ and $\delta^{2}H$ in MTBE in groundwater to associate natural biodegradation of MTBE in groundwater with an anaerobic process (from Hunkeler et al., USEPA, 2008)



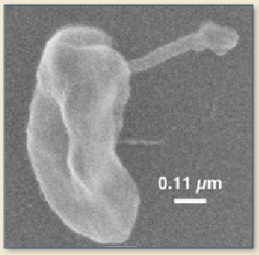
Example of CSIA-based reactive transport modeling from ESTCP ER-201029 (see Van Bruekelen et al., 2008 for method description)

32

FAQ 12: *How can molecular biological tools help me with MNA?*

MBTs provide strong, but not definitive evidence of MNA

1. **Show that key organisms are present (e.g., *Dehalococcoides*, *Dehalobacter*)**
2. **Show that key enzymes are present (e.g., *vcrA*, oxygenase-encoding genes)**
3. **Establish relative abundance of key microbial populations**



Our friend, Dehalococcoides (Apkarian and Taylor)

KEY ISSUE: **Most tests focus on presence, not activity!**

33

FAQ 12: *How can molecular biological tools help me with MNA?*

MOST POPULAR? **Evaluating chlorinated solvent degradation using PCR-based methods for tracking *Dehalococcoides (Dhc)***

Tools	MNA Application	MNA Limitations
• PCR / qPCR	• Identify if key organisms / enzymes • Determine if abundance of key biomarkers is increasing	• Many techniques cannot differentiate between live and inactive cells • Attempts to correlate in situ activity and gene expression still in infancy • Target mostly well-known pathways (others in development)

Others:

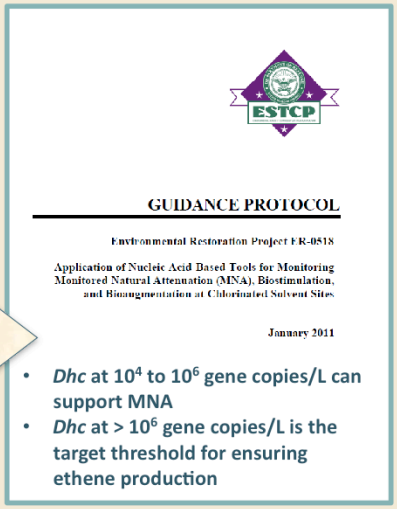
Stable Isotope Probing (SIP), microbial fingerprinting, microarrays, enzyme activity probes

34

FAQ 12: *How can molecular biological tools help me with MNA?*

HOW TO COLLECT AND USE THE DATA?

- **Groundwater or Soil using established procedures**
  - starting at about $200 per sample/ target)
- **Quantitative Rules for MNA.**
  - Specific recommendations for MNA
  - Lu et al., 2006: "generally useful" attenuation rates of *cis*-1,2-DCE and VC (> 0.3/yr) were associated with sites where *Dhc* was detected, while no attenuation was observed at sites where it was absent



- ***Dhc* at 10^4 to 10^6 gene copies/L can support MNA**
- ***Dhc* at > 10^6 gene copies/L is the target threshold for ensuring ethene production**

35

INTERVIEW: *John Wilson*

1. What are the most important new developments you've seen since the original protocols were developed in the 1990s?

2. How did you get involved in isotopes? What is the key message in the the document you wrote with Hunkeler and others in 2008?

INTERVIEW: *John Wilson (continued)*

3. You just completed a Short Course at Battelle on calculating and applying rates for MNA processes. What is the key message from your short course?

4. You got involved in MNA statistics with your 2011 document: "An Approach for Evaluating the Progress of MNA in Groundwater". Why did you write this one? Are you a pretty good statistician? Any thoughts on sampling frequency?

5. What is the big question to answer for MNA?

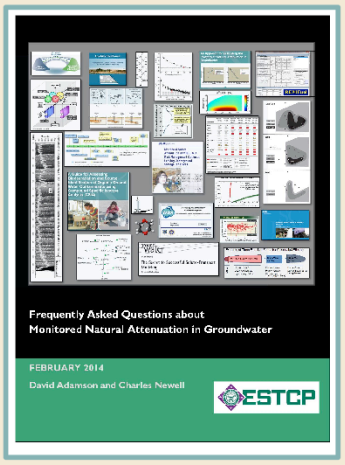
BREAK FOR INITIAL Q&A

Go to:

http://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201211/

Or Google:

"MNA" + "FAQ" + "ESTCP"



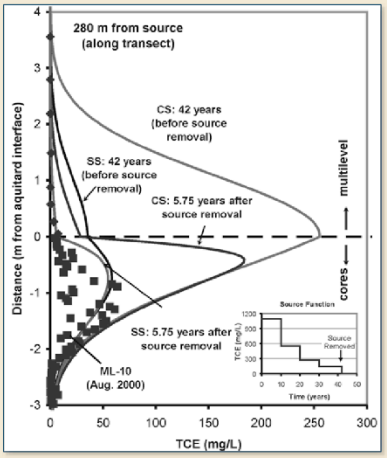
FAQ 13: *How can you show attenuation that occurred before the start of monitoring?*

By Using Clay Diffusion Profiles or Tree Rings

"Source History" using soil data from Low Permeability Zone (e.g., clay)

- Combo of high-res characterization and inverse modeling
- Core acts like "tree ring" to provide information on the source concentration over time in adjacent aquifer

New FREE software tool developed for applying this method: http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201032



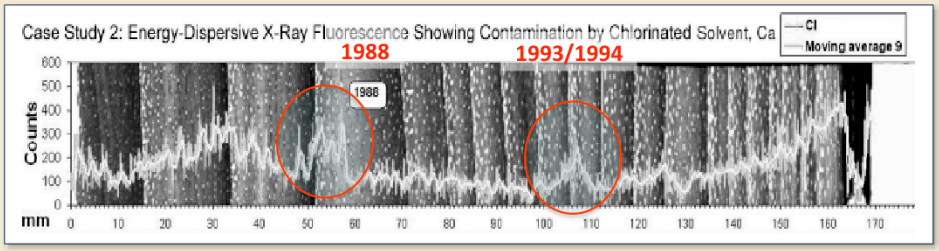
Example of "Source History" estimate from Chapman and Parker, 2005 – best fit with *Stepped Source* (SS) (see inset)

39

FAQ 13: *How can you show attenuation that occurred before the start of monitoring?*

ALTERNATIVE: Use actual tree rings as part of a "phytoforensic" approach

- **Assay cores for Cl for chlorinated solvents, S for petroleum hydrocarbons**
- **Applied at > 20 sites**



Cl^- patterns (shown on y-axis as x-ray fluorescence counts) over time in tree core (shown on x-axis in mm of core). Pattern identifies potential exposure events (releases) in 1988 and 1993/1994, along with continuing impact at date when core was collected (far right hand side)

(from Balouet et al., 2007)

40

FAQ 14: *Can DO measurements be a problem for MNA studies?*

YES, if not carefully done

Some early conclusions of ESTCP 2011-29 project:

- *Great care should be taken to minimize oxygen introduction by measuring at well head using a flow-through cell*
- *Erroneous DO measurements are often recorded and reported which can cause misinterpretation of subsurface conditions*
- *Measured and actual DO concentrations rarely coincide*

41

FAQ 15: *What are CO_2 traps and how do they help me show attenuation?*

A new tool for measuring natural source zone attenuation at LNAPL sites

- **What's the principle?**
  - LNAPL is subject to degradation following release, with essentially all being converted to CO_2
- **How do they work?**
  - Collect CO_2 that has migrated to surface using a passive adsorption device installed at grade
  - Correct for background/non-fossil fuel-related CO_2
  - **Convert CO_2 to LNAPL attenuation rate (gallons/acre/yr)**

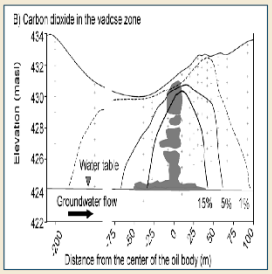
Example of Colorado State University CO_2 trap installation; other approaches have been developed by Ariz. St. Univ. and Univ. of Brit. Columbia

42

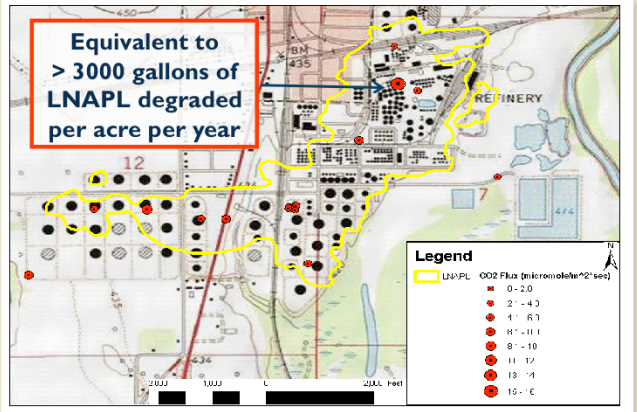
FAQ 15: *What are CO_2 traps and how do they help me show attenuation?*

What do the data say?

Traps have been deployed at multiple sites and have documented large CO_2 fluxes equivalent to 100s to 1000s of gallons of LNAPL per acre per year



Sihotra et al., 2011



Example of field site where CO_2 traps were used to delineate LNAPL natural loss rates.

43

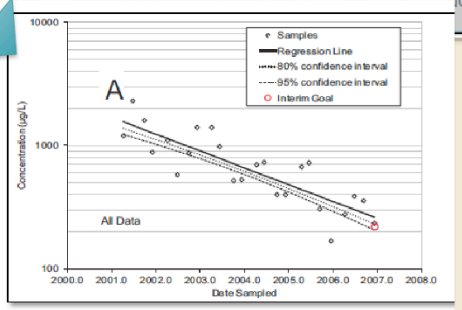
BREAK FOR POLL QUESTIONS

44

FAQ 16: *How do I estimate rates and timeframes for MNA?*

By extrapolating monitoring well data and the right rate…

Rate Constant	Method of Analysis	Significance	Use of Rate Constant		
			Plume Attenuation	Plume Trends?	Plume Duration?
Point Attenuation Rate (Fig. 1) (k_{point}, time per year)	C vs. T Plot	Reduction in contaminant concentration over time at a single point	NO*	NO*	YES
Bulk Attenuation Ra… (Fig. 2) (k; time per year)	…Plot	Reduction in dissolved …contaminant concentration with…	YES	NO*	NO



Example of extrapolation method to estimate MNA remediation timeframes with confidence limits.[12]

from Wilson, USEPA, 2011

45

FAQ 16: *How do I estimate rates and timeframes for MNA?*

By using mass balance methods in simple models…

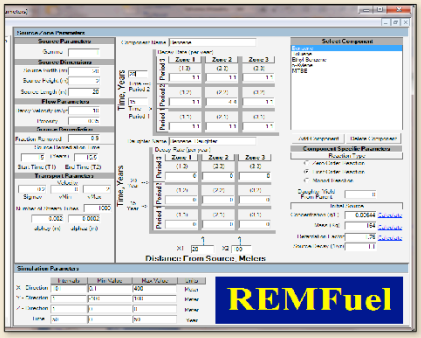
Simple mass balance model for first order decay in source concentration

$$k_{source}\ (\text{per year}) = \frac{\text{Mass discharge (kg/yr)}}{\text{Mass (kg)}}$$

REMChlor Model
(Falta et al., 2007)

and

NAS Software
(Widdowson et al, 2005;
Chapelle et al., 2007)

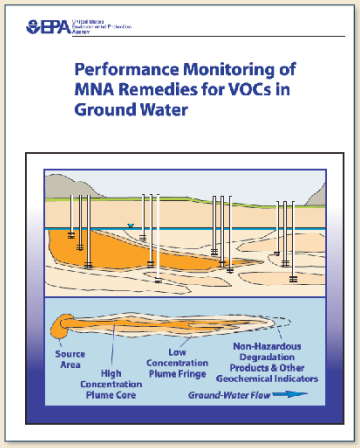


46

FAQ 17: *What is required for MNA monitoring?*

Follow and understand USEPA Guidance

From USEPA Performance Monitoring of MNA	Our Comments
Sample both contaminated and uncontaminated areas.	Source zones can change the geochemical conditions
Monitor areas supporting site hydrogeology.	Use piezometers to better understand groundwater flow
Match screen length to stratigraphic unit or contaminant loading interval.	it is critical to get flow-weighted concentrations from transmissive zones that would be utilized by a receptor. This may mean long well screens.
Be aware of changing groundwater flow directions.	See graphics in USEPA 2004 doc

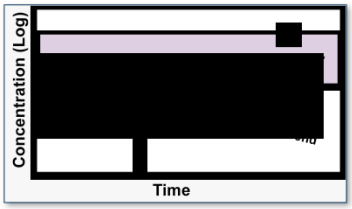


USEPA, 2004

47

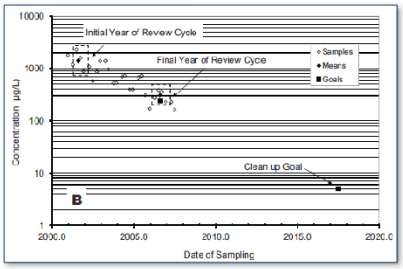
FAQ 18: *What is the new thinking about monitoring frequency?*

KEY POINT:
Groundwater monitoring data can be highly variable, so it may take many years to establish attenuation trends



SERDP ER-1705 Monitoring Variability Study: Short-term variability masks long-term trend

Wilson, USEPA Guidance, 2011: Focus on longer review cycles to answer these questions



48

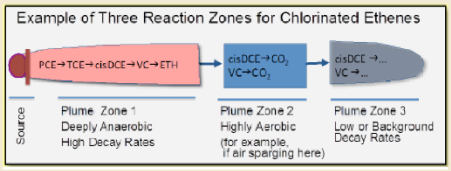
FAQ 19: *Statistics for two questions: How far and how long?*

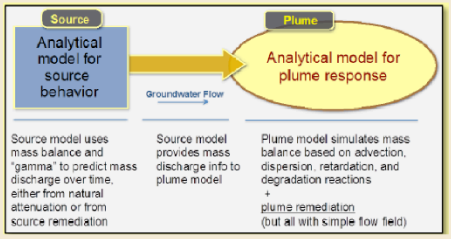
Mann-Kendall Statistic	Confidence Factor: CF > 95%	Confidence Factor: 90% < CF < 95%	Confidence Factor: CF < 90%
S < 0	Decreasing	Prob. Decreasing	If COV < 1, *Stable* If COV > 1, *No Trend*
S > 0	Increasing	Prob. Increasing	No Trend

49

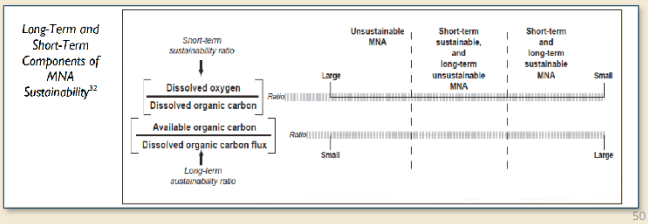
FAQ 20, 21: *Which computer models work best for MNA? Are MNA Reactions Sustainable?*

REMChlor and REMFuel
(Falta et al., 2007; USEPA, 2012)





NAS Software
(Widdowson et al, 2005; Chapelle et al., 2007)



50

MNA THEMES

MNA AS AN EVOLVING TECHNOLOGY:

THE BASIS FOR MNA:

22. What is matrix diffusion? How does it affect MNA?
23. Do contaminants in low-permeability units attenuate?
24. Why are interfaces important for MNA?

NEW CONTAMINANTS FOR THE MNA LINEUP:

25. How do reactive mineral species contribute to attenuation?

NEW TECHNIQUES, NEAT TOOLS:

26. What is a low-risk site? How is MNA involved?

EMERGING ISSUES FOR EVALUTING MNA AS A REMEDY:

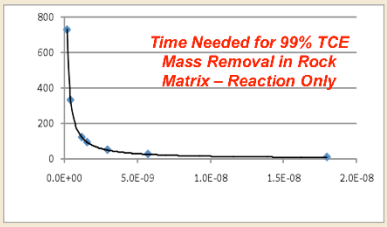
IMPLEMENTATION AND SITE CLOSURE:

51

FAQ 23: *Do contaminants in low-permeability units attenuate?*

Sometimes, we think

- **Some evidence based on lab/ field studies, but simply not investigated much yet**
- **Even slow attenuation could be significant**



Impact of Abiotic Degradation Rates in Rock Matrix on Mass Reduction Timeframes (data described in Schaefer et al., 2013)

Characteristics That Favor Attenuation	Characteristics That Hinder Attenuation
Long retention times (little advection/ flushing)	Smaller pore throat size restricts migration of microbes, influx of nutrients/carbon sources, and growth density
Reducing conditions are common; favorable for biological and biogeochemical reductive dechlorination	Salinity can be high and may limit microbial activity
Potentially large reservoir of organic carbon (silts/organo-clays)	Limited bioavailability of organic carbon
Potentially large reservoir of reactive mineral species	Reactivity of mineral species may be limited due to dependence on microbial activity (e.g., iron reduction)

53

FAQ 23: *Do contaminants in low-permeability units attenuate?*

Potential lines of evidence for low k zone attenuation to support MNA

- Molecular biological data confirming presence and/or activity of degraders within low k zone
- Daughter product distribution suggests greater extent of degradation in low k zone relative to adjacent transmissive zone
- Favorable geochemical conditions within low k zone
- CSIA data showing higher fractionation within low k zone
- Mineralogical analysis of low k zone soil samples that show minerals capable of abiotic degradation of contaminants

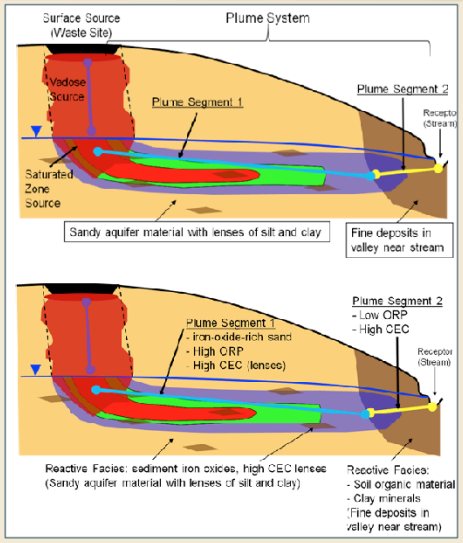
Example of high-resolution sub-sampling of soil cores for assessing attenuation in low-k zones

54

FAQ 24: *Why are interfaces important for MNA?*

Interfaces are where the action is at many sites!

- **Interfaces between groundwater and surface water – hyporheic zone**
- **Transitions between aerobic zones and more reducing conditions**
- **Biogeochemical gradients at the interface between different geologic conditions**
- **Interface between vadose zone and saturated zone**



55

FAQ 24: *Why are interfaces important for MNA?*

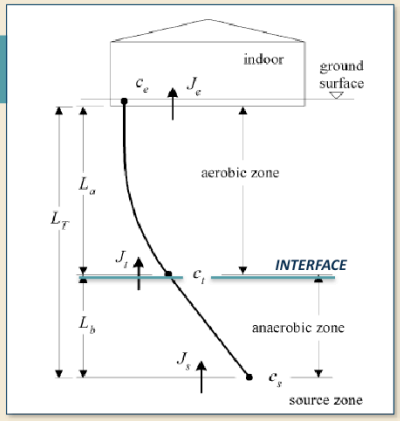
KEY POINT: Big changes that occur across short distances can drive attenuation

- **Hyporheic zone example (USGS study by Landmeyer et al., 2010)**

  "MTBE, TBA, and TAME concentrations in groundwater discharge in a 5-foot (1.5-m) thick section of the hyporheic zone were attenuated between 34% and 95%, in contrast to immeasurable attenuation in the shallow aquifer during contaminant transport between 0.1 and 1.5 miles (0.1 to 2.4 km)".

- **Vadose zone example (Kurt, Shin, & Spain, 2012)**

  Thin (2-3 mm) anaerobic/aerobic interface was found to have a "remarkable capacity" to degrade chlorobenzene (2000 to 4200 milligrams per meter squared per day) and nitrobenzene.



Conceptual model for vadose zone degradation (from Devaull, 2007)

56

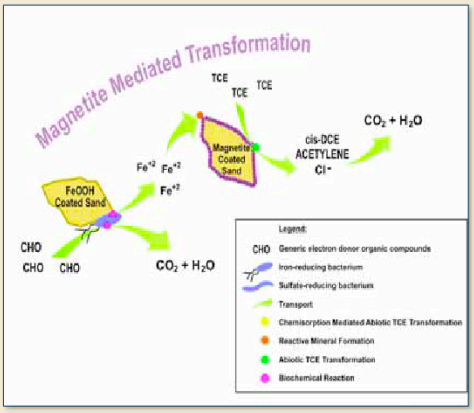
FAQ 25: *How do reactive mineral species contribute to attenuation?*

Naturally-occurring minerals can degrade contaminants

- **CVOC degradation that is abiotically-mediated by a number of reactive mineral species**

  Iron(II) Sulfide (FeS)
  Mackinawite –($Fe_{1+x}S$)
  Pyrite (FeS_2)
  Magnetite (Fe_3O_4)
  Goethite (α-FeO(OH))
  Hematite (Fe_2O_3)
  Lepidocrocite (γ-FeO(OH))
  Green Rust--(Fe^{2+} and Fe^{3+} cations, O^{2-} and OH^- anions, with loosely bound $[CO_3]^{2-}$ groups and H_2O molecules between the layers)

- **Basis for ZVI and other PRB designs, but significant evidence of natural attenuation in anaerobic environments**

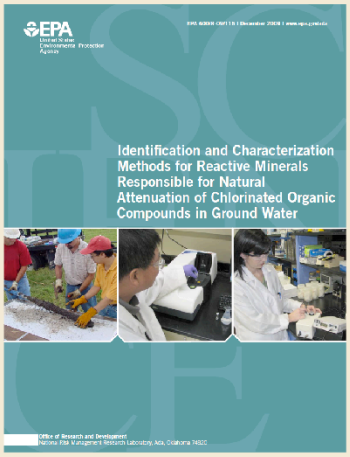


Example of abiotic TCE degradation by magnetite (from ESTCP/AFCEE/NAVFAC, 2007)

57

FAQ 25: *How do reactive mineral species contribute to attenuation?*

- While contaminants are degraded abiotically, formation of reactive minerals typically have a biological component
  - e.g., biological iron reduction and/or sulfate reduction to produce iron sulfide
- Methods for assessing abiotic degradation capacity are available and/or being developed
  - E.g., magnetite in sediments via magnetic susceptibility testing
- Current research suggests slow but sustainable attenuation rates



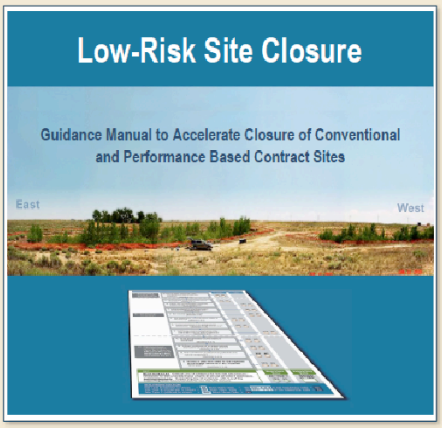
EPA, 2009 – detailed descriptions of important methods

58

FAQ 26: *What is a low-risk site? How is MNA involved?*

Low-Risk means MNA the rest of the way

- Recognition that at many sites complete closure is difficult and/or unattainable
- Concentrations may be very low and pose no significant risk
- Being adopted as part of state regulatory programs (e.g., California)

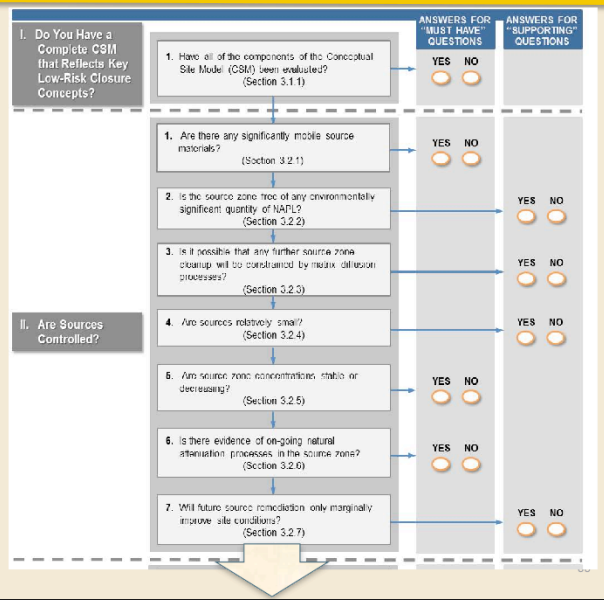


Low-Risk Site Closure Guide for Air Force (Farhat et al., 2012)

59

FAQ 26: *What is a low-risk site? How is MNA involved?*

Air Force LoRSC Manual Methodology to Determine Low Risk Sites – Parts I and II



MNA THEMES

MNA AS AN EVOLVING TECHNOLOGY:

THE BASIS FOR MNA:

27. Can MNA be a stand-alone remedy? When should you transition a site to MNA?

NEW CONTAMINANTS FOR THE MNA LINEUP:

28. How can stakeholders considering MNA make better decisions?

NEW TECHNIQUES, NEAT TOOLS:

EMERGING ISSUES FOR EVALUTING MNA AS A REMEDY:

IMPLEMENTATION AND SITE CLOSURE:

61

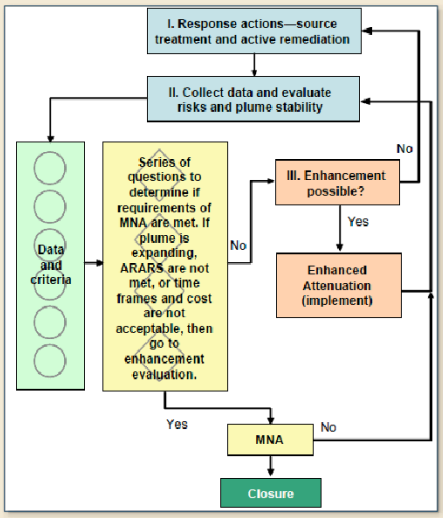
FAQ 27: *Can MNA be a stand-alone remedy? When should you transition to MNA?*

It depends

- **1999 EPA Directive:**

  MNA should not be considered a default or presumptive remedy, and that it should be applied *"very cautiously as the sole remedy"* and that *"source control will be fundamental components of any MNA remedy."*

- **Lots of data suggesting MNA being used extensively**
  - **Sole remedy**
  - **Some source treatment with MNA as sole grounwater remedy**
- **Many states have specific risk-based criteria for MNA as default remedy (e.g., Florida)**



62

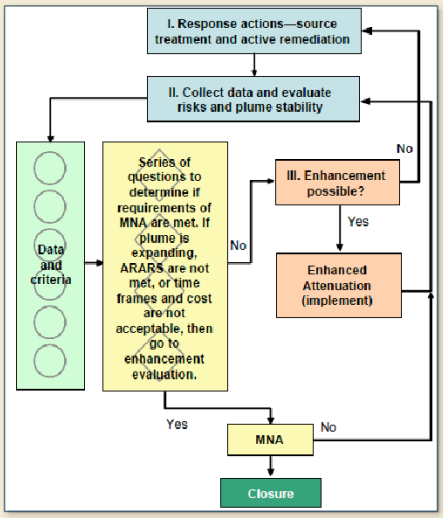
FAQ 27: *Can MNA be a stand-alone remedy? When should you transition to MNA?*

MNA Transition Flowchart, ITRC 2008

Are the risks acceptable?
Is the plume stable or shrinking?
Are conditions sustainable?
Is the remediation timeframe acceptable?
Are the cost-benefits acceptable?

NO?

Enhanced Attenuation (instead of MNA)



63

FAQ 27: *Can MNA be a stand-alone remedy? When should you transition to MNA?*

NRC "Complex Sites" Report, 2012

Transition Assessment Concept

At many complex sites, contaminant concentrations in the plume remain stalled at levels above cleanup goals despite continued operation of remedial systems. There is no clear path forward to a final end state embodied in the current cleanup programs, such that money continues to be spent, with no concomitant reduction in risks. ***If the effectiveness of site remediation reaches a point of diminishing returns prior to reaching cleanup goals and optimization has been exhausted, the transition to monitored natural attenuation or some other active or passive management should be considered using a formal evaluation.*** *This transition assessment would determine whether a new remedy is warranted at the site or whether long-term management is appropriate.*

64

FAQ 28: *How can stakeholders considering MNA make better decisions?*

Use SMART Objectives

"***Absolute*** *(objectives based on broad social values, such as protection of public health) or* ***functional*** *(steps or activities taken to achieve absolute objectives, such as supplying bottled water to affected residents). Functional objectives are established to demonstrate attainment of absolute objectives and have often been missing, difficult to measure, or unattainable"*

Functional Objectives must be:

- **Specific**
- **Measurable**
- **Attainable**
- **Relevant**
- **Time-Bound**

from ITRC Integrated DNAPL Site Strategy (IDSS), 2012

S **Specific**—The objectives should specify what is to be achieved through a remedial action. They should be concrete, detailed, and well defined.
- Diagnostic questions:
  - What exactly are we going to do?
  - Is the objective well understood?
  - Will this objective lead to a desired result?
- *S does not mean "shifting"!*

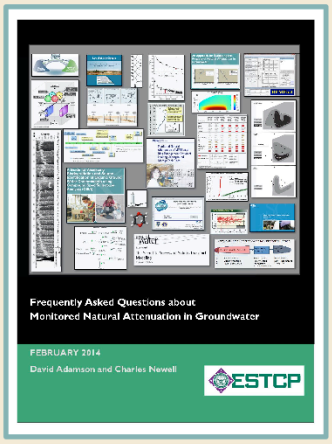
M **Measurable**—Managers should be able to measure whether or not the objectives are being met. Numbers, quantities, or comparisons should be specified, and the uncertainty in key measurements should be understood.
- Diagnostic questions:
  - How will we know that the change has occurred?
  - Can these measurements be obtained?
- *M does not mean "magical"!*

A **Attainable**—Objectives should be realistic, given the proposed time frame, political climate, and/or the amount of money available.
- Diagnostic questions:
  - Can we get this done in the proposed time frame?
  - Do we understand the limitations and constraints?
  - Can we do this with the resources we have?
  - Is this possible?
  - Has anyone else done this successfully?
- *A does not simply mean "ambitious"!*

R **Relevant**—The objective should have a value and represent a realistic expectation.
- Diagnostic questions:
  - Does the outcome of the objective directly support achievement of the absolute objective?
  - Do we have the resources available to achieve this objective?
- *R does not mean "remarkable"!*

T **Time-bound**—The time allotted for achieving the objective should be clearly defined and short enough to ensure accountability.
- Diagnostic questions:
  - When will this objective be completed?
  - Is someone still going to be accountable for meeting the time frame?
- *T does not mean "timeless"!*

INTERACTIVE "FAQ"



Interactive Version

Advantages:

- Easy to navigate
- Hosted on ESTCP and GSI websites
- Does not require download

LET'S TAKE A QUICK TOUR!

http://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201211/

INTERACTIVE "FAQ"

LET'S TAKE A QUICK TOUR!

5 minute run-through of interactive version

FINAL Q&A

Go to:

http://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201211/

Or Google:

"MNA" + "FAQ" + "ESTCP"