Nanotechnology and in Situ Remediation: Benefits and Potential Risks

Barbara Karn (US EPA), Todd Kuiken (PEN), Martha Otto (US EPA)

Woodrow Wilson Center
Project on Emerging Nanotechnologies

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Outline

- Remediation regulations
- Size and scope of the problem
- Current remediation techniques
- Nano-remediation
- Potential benefits and risks
- Recommendations

Hazardous Waste Site Remediation

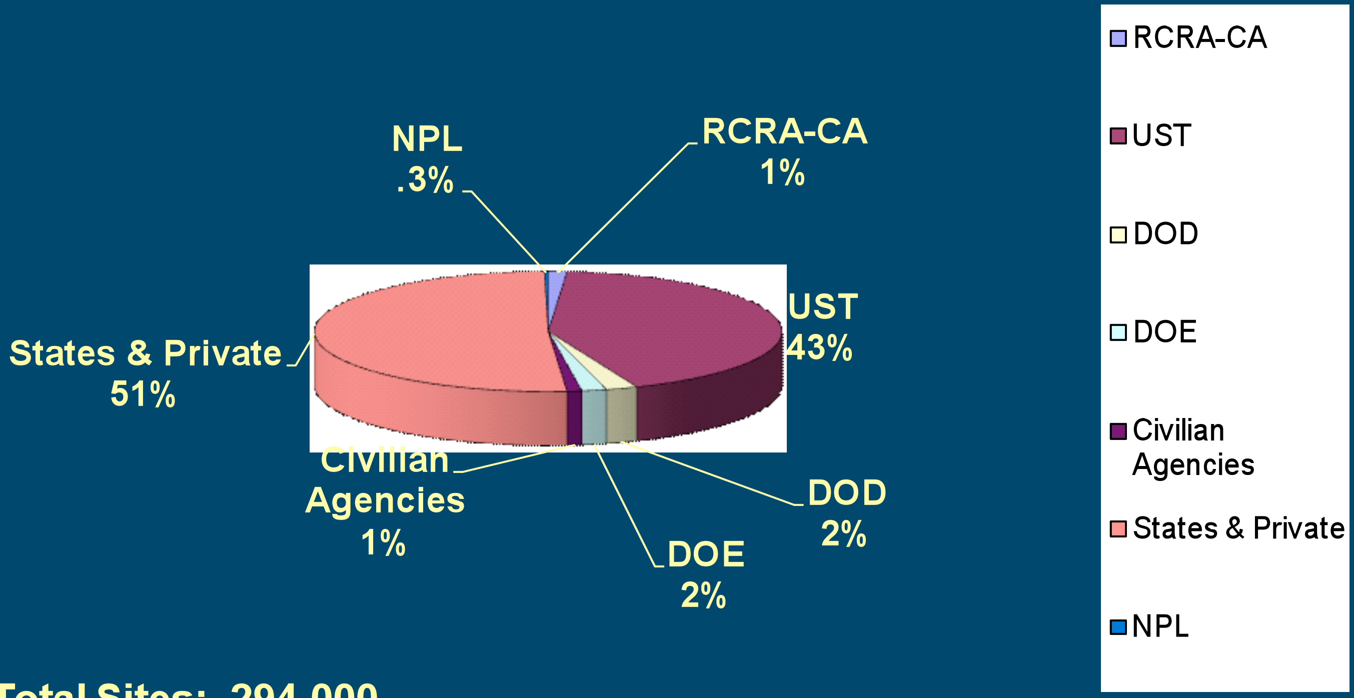
Resource Conservation and Recovery Act (RCRA) (1976)

- Subtitle C Corrective Action
- Subtitle I Underground Storage Tanks (1986)

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (1980)

- Superfund and the National Priorities List
- Brownfields Amendments: Small Business Liability Relief and Brownfields Revitalization Act (2002)

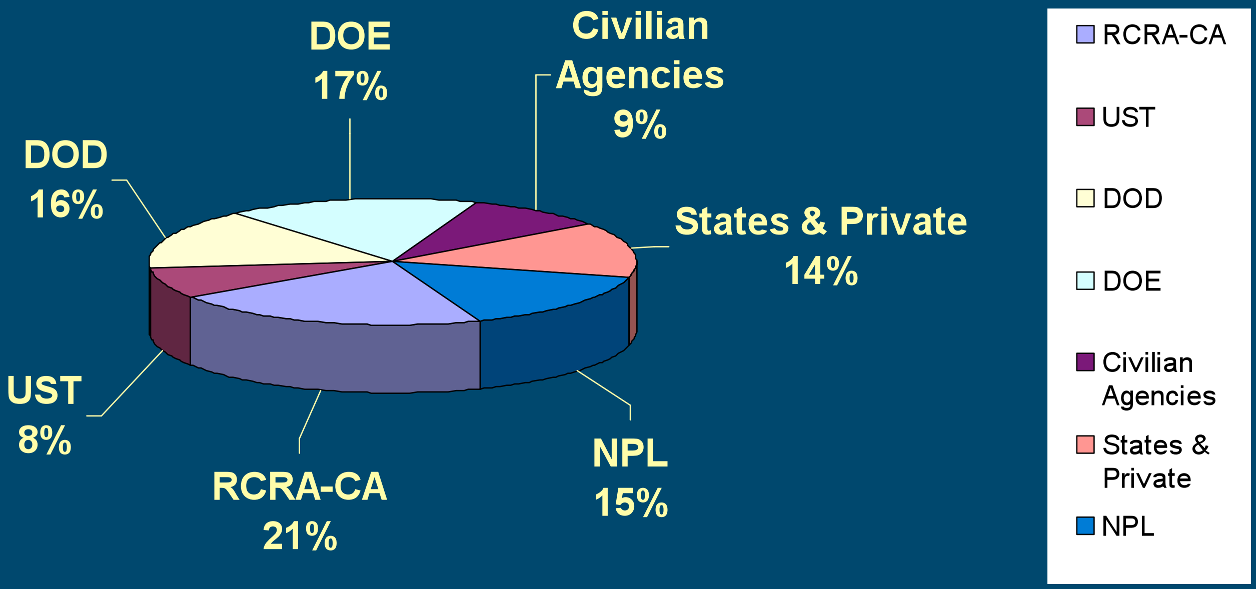
Breakdown of Hazardous Waste Sites



Total Sites: 294,000

(EPA, 2004)

Estimated Costs of Cleanup



Total = $210 Billion

(EPA, 2004)

Present Cleanup Market

Contaminated groundwater is a major problem

- More than half of the US population relies on groundwater for drinking
- Contaminated groundwater is difficult and costly to remediate
- Over 80% of NPL sites have contaminated groundwater

It’s a long term problem

The solution is costly

Ex situ Remediation

Pump and Treat is used
most commonly for
groundwater contamination

http://www.epa.gov/reg3hscd/
super/sites/VAD980705404/index.htm

Record of Decision (ROD) data:
Pre-1992: 80% of RODs selected Pump and Treat alone
2001 – 2005: Pump and Treat dropped to 20%

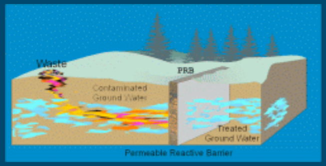
Percentage of RODs selecting *in situ* groundwater treatment
- Pre-1986: 0%
- By 2005: 31%

***In situ* treatment saves time, money, eliminates waste disposal problems**

In Situ Remediation

Permeable Reactive Barriers

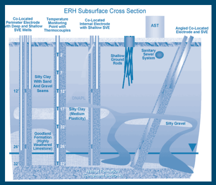
- Built in the path of a migrating plume
- Contaminant must be in flow pattern



http://www.epa.gov/ada/research/pics/prb.gif

Thermal (*in situ*)

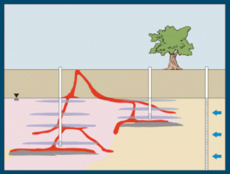
- Heat applied to polluted soil and/or groundwater
- Can be costly



http://www.cluin.org/products/
newsltrs/tnandt/images/200412_fig2.gif

Chemical Oxidation (*in situ*)

- Chemically removes contaminants from soil
- Sulfate/metals concentrations may increase in groundwater



www.epa.gov/ada/topics/pics/oxidation1.gif

Bioremediation

- Relatively cost effective
- Range of contaminants on which it is effective is limited

http://www.epa.gov/oust/mtbe/envirogn.jpg

Nano Remediation

In situ

Small size

Greater Surface Area

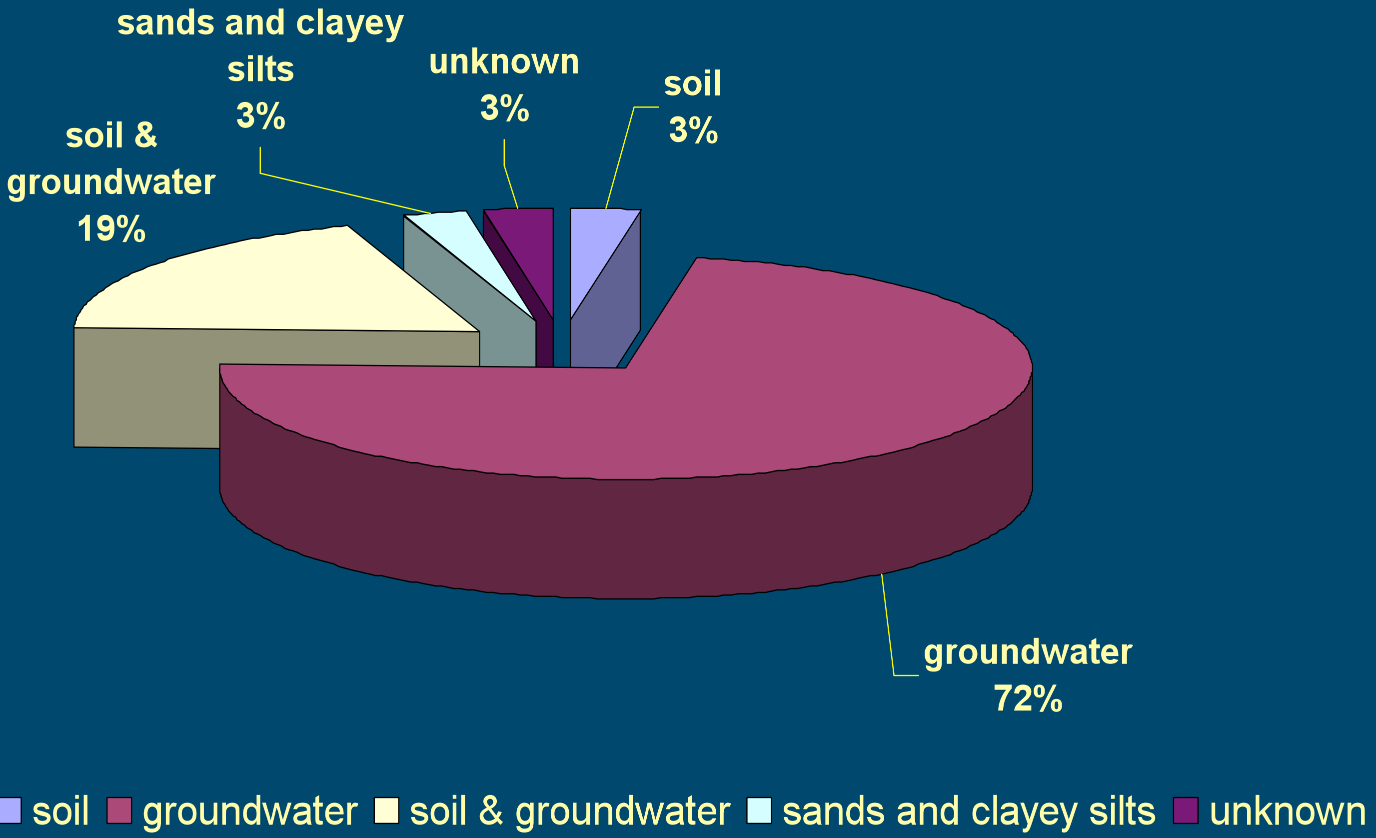
Higher Reactivity

Lower Cost (potentially)

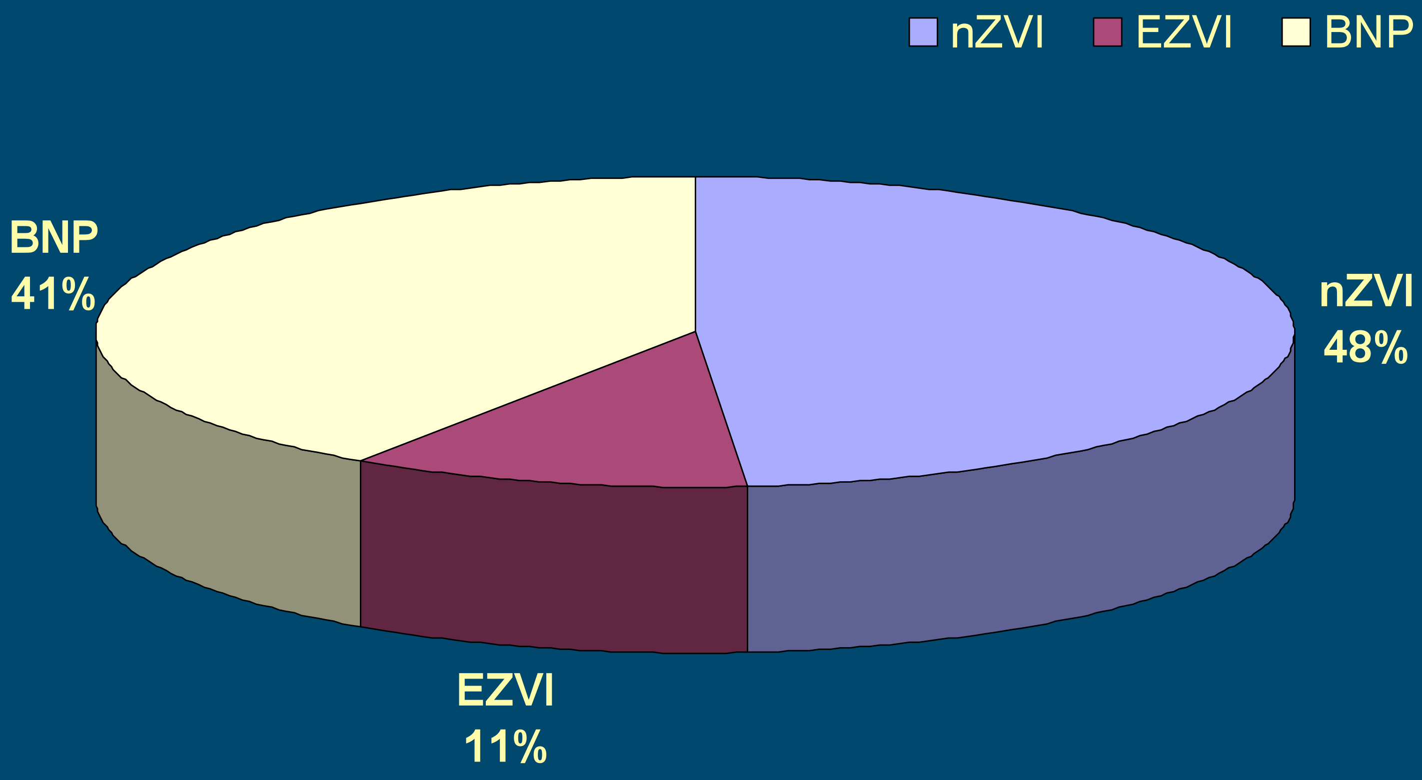
Variety of Materials:

Zeolites
Metal Oxides
Carbon-based nanomaterials
Enzymes
Bi-metallic nanoparticles (BNP)

Media Treated (37 sites)



Type of Nanoparticles Used (37 Sites)



Chemistry of nZVI

- Can be used in both aerobic and anaerobic conditions
- Reacts with halogenated hydrocarbons

$$\text{TCE} + \text{Fe}^0 \longrightarrow \text{HC products} + \text{Cl}^- + \text{Fe}^{2+}/\text{Fe}^{3+}$$

Potential Pollutants treated with nZVI

Chlorinated methanes Carbon tetrachloride (CCl_4) Chloroform ($CHCl_3$) Dichloromethane (CH_2Cl_2) Chloromethane (CH_3Cl)**Trihalomethanes** Bromoform ($CHBr_3$) Dibromochloromethane ($CHBr_2Cl$) Dichlorobromomethane ($CHBrCl_2$)

Chlorinated benzenes Hexachlorobenzene (C_6Cl_6) Pentachlorobenzene (C_6HCl_5) Tetrachlorobenzenes ($C_6H_2Cl_4$) Trichlorobenzenes ($C_6H_3Cl_3$) Dichlorobenzenes ($C_6H_4Cl_2$) Chlorobenzene (C_6H_5Cl)

Chlorinated ethenes Tetrachloroethene (C_2Cl_4) Trichloroethene (C_2HCl_3) *cis*-Dichloroethene ($C_2H_2Cl_2$) *trans*-Dichloroethene ($C_2H_2Cl_2$) 1,1-Dichloroethene ($C_2H_2Cl_2$) Vinyl chloride (C2H3Cl)**Pesticides** DDT ($C_{14}H_9Cl_5$) Lindane ($C_6H_6Cl_6$)

Other polychlorinated hydrocarbons **PCBs** **Dioxins** Pentachlorophenol (C_6HCl_5O)

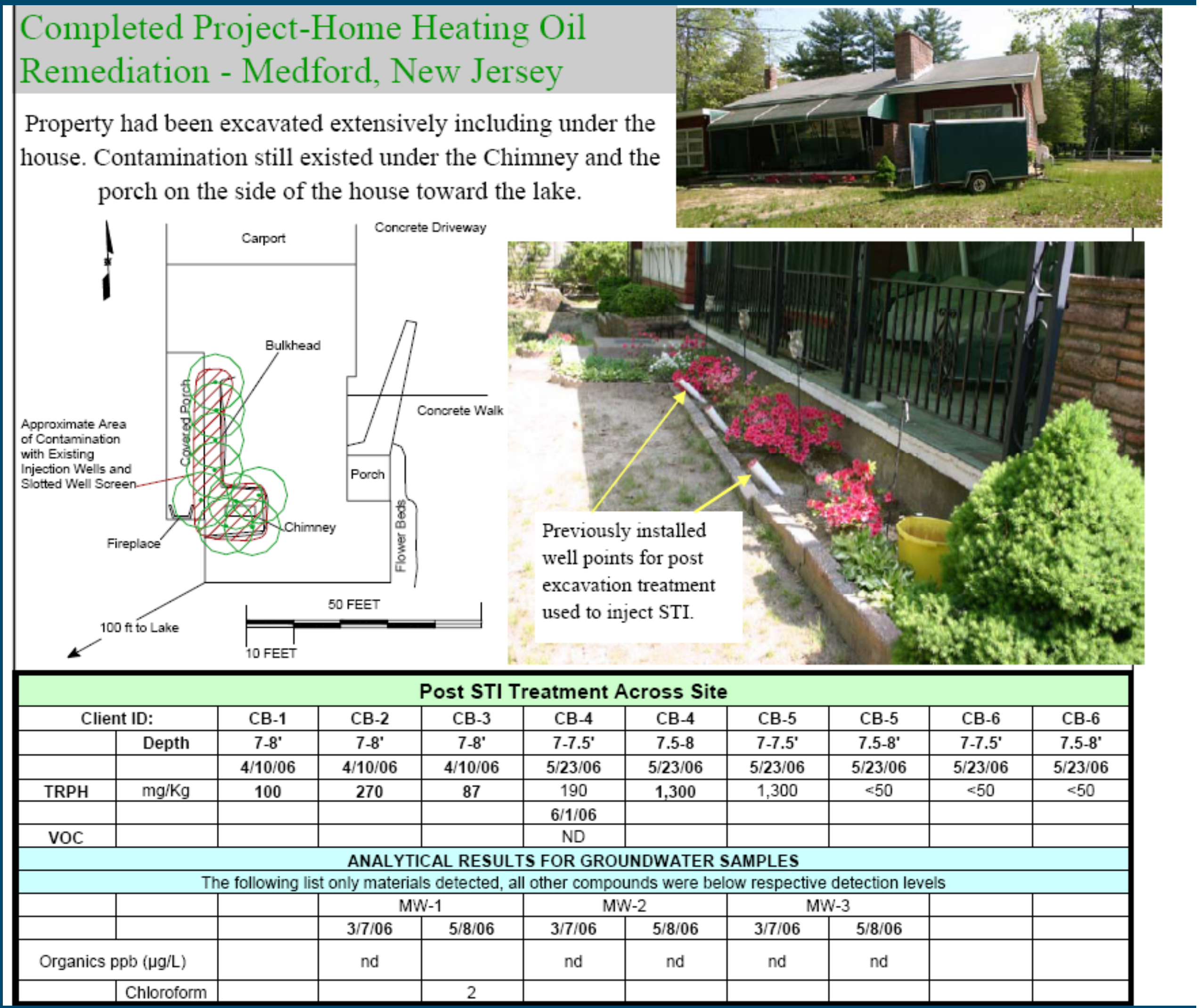
Organic dyes Orange II ($C_{16}H_{11}N_2NaO_4S$) Chrysoidine ($C_{12}H_{13}ClN_4$) Tropaeolin ($C_{12}H_9N_2NaO_5S$) Acid Orange Acid Red

Other organic contaminants N-nitrosodimethylamine (NDMA) ($C_4H_{10}N_{2O}$) TNT ($C_7H_5N_3O_6$)

Heavy Metal ions Mercury (Hg^{2+}) Nickel (Ni^{2+}) Silver (Ag+) Cadmium (Cd^{2+}) **Inorganic anions** Dichromate ($Cr_2O_7^{2-}$) Arsenic (AsO_4^{3-}) Perchlorate (ClO_4^-) Nitrate (NO_3^-)

Nano-Peroxide Results

Boomsnub Site, USEPA
http://yosemite.epa.gov/R10/CLEANUP.NSF/sites/boomrv



Completed Project-Home Heating Oil Remediation - Medford, New Jersey

Property had been excavated extensively including under the house. Contamination still existed under the Chimney and the porch on the side of the house toward the lake.

Previously installed well points for post excavation treatment used to inject STI.

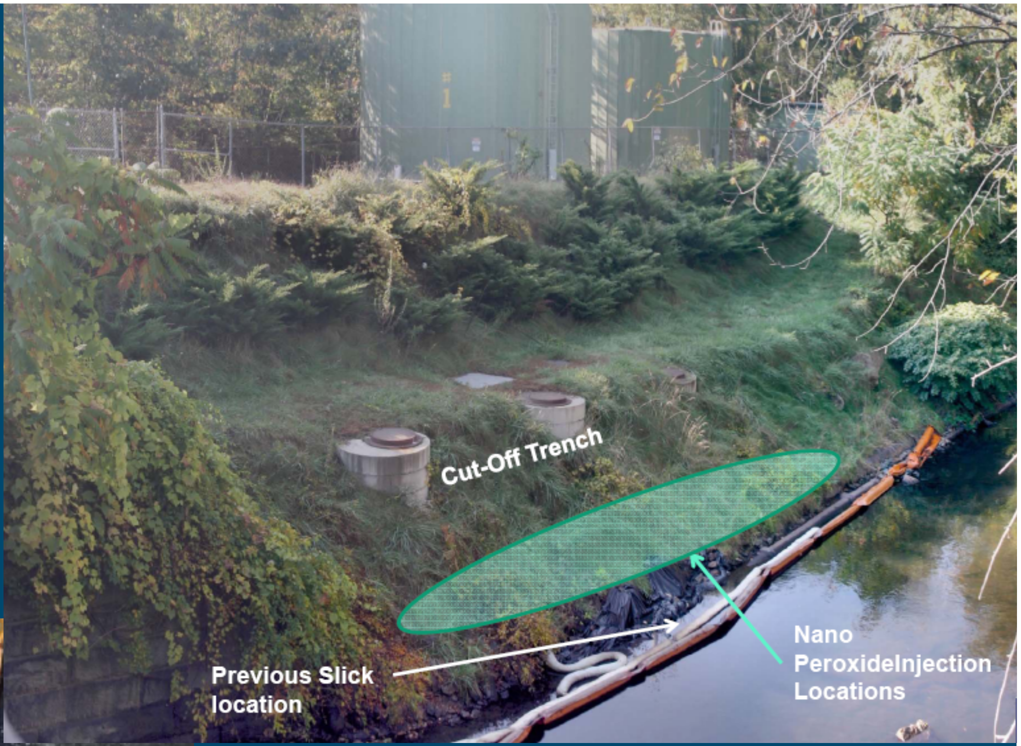
Post STI Treatment Across Site										
Client ID:		CB-1	CB-2	CB-3	CB-4	CB-4	CB-5	CB-5	CB-6	CB-6
	Depth	7-8'	7-8'	7-8'	7-7.5'	7.5-8	7-7.5'	7.5-8'	7-7.5'	7.5-8'
		4/10/06	4/10/06	4/10/06	5/23/06	5/23/06	5/23/06	5/23/06	5/23/06	5/23/06
TRPH	mg/Kg	100	270	87	190	1,300	1,300	<50	<50	<50
					6/1/06					
VOC					ND					
ANALYTICAL RESULTS FOR GROUNDWATER SAMPLES										
The following list only materials detected, all other compounds were below respective detection levels										
			MW-1		MW-2		MW-3			
			3/7/06	5/8/06	3/7/06	5/8/06	3/7/06	5/8/06		
Organics ppb (µg/L)			nd		nd	nd	nd	nd		
	Chloroform			2						

(Continental Remediation, LLC)

Storage tank located adjacent to river

Soil/groundwater contaminated with No. 6 oil

Excavation not practical due to utilities around and under the site

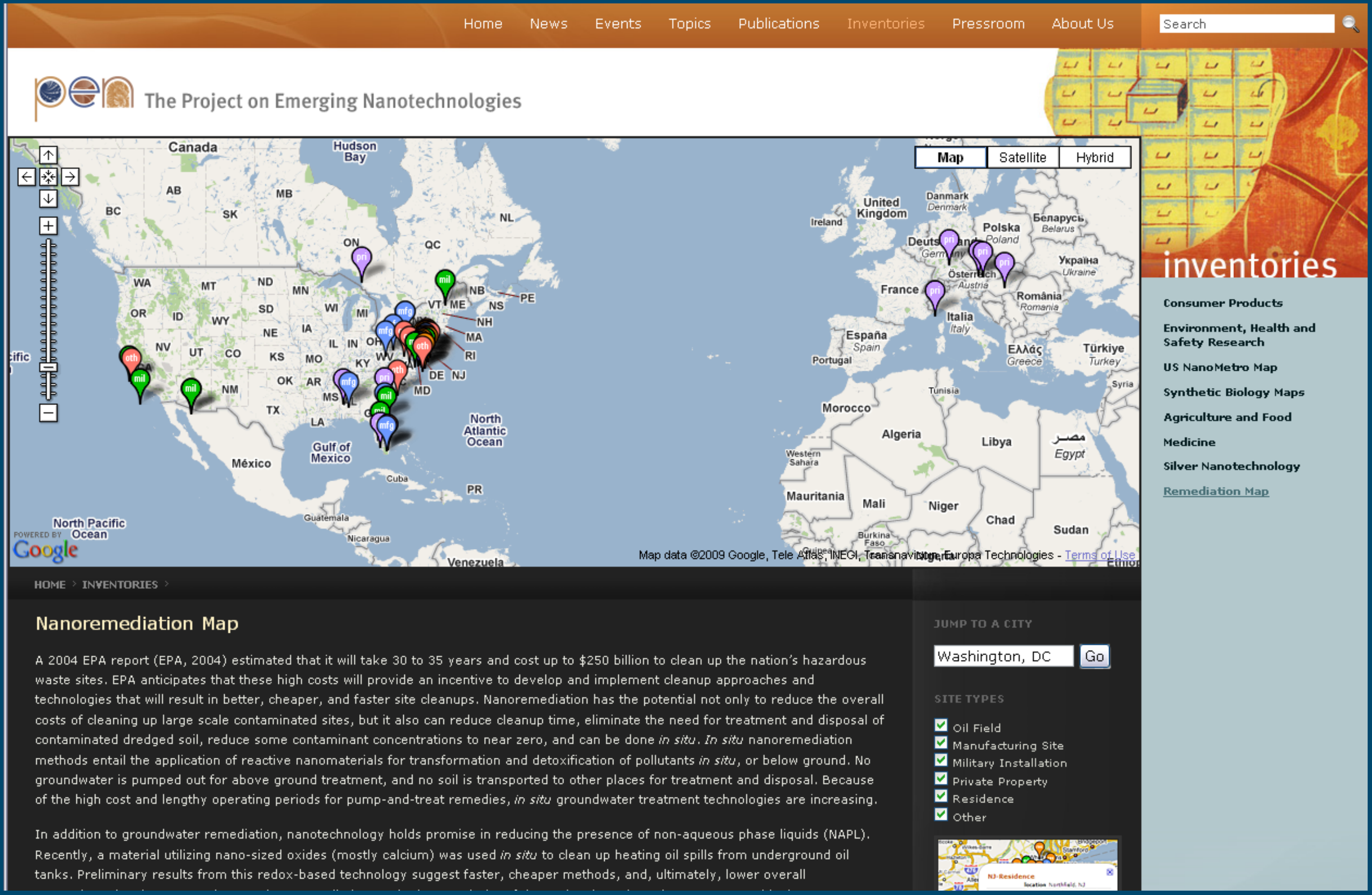


Discharge to river stopped

Free product was reduced from 13” to 1” in monitoring wells after 30 days

(Continental Remediation, LLC (2007))

Interactive Nanoremediation Map



Nanoremediation Map

A 2004 EPA report (EPA, 2004) estimated that it will take 30 to 35 years and cost up to $250 billion to clean up the nation's hazardous waste sites. EPA anticipates that these high costs will provide an incentive to develop and implement cleanup approaches and technologies that will result in better, cheaper, and faster site cleanups. Nanoremediation has the potential not only to reduce the overall costs of cleaning up large scale contaminated sites, but it also can reduce cleanup time, eliminate the need for treatment and disposal of contaminated dredged soil, reduce some contaminant concentrations to near zero, and can be done *in situ*. *In situ* nanoremediation methods entail the application of reactive nanomaterials for transformation and detoxification of pollutants *in situ*, or below ground. No groundwater is pumped out for above ground treatment, and no soil is transported to other places for treatment and disposal. Because of the high cost and lengthy operating periods for pump-and-treat remedies, *in situ* groundwater treatment technologies are increasing.

In addition to groundwater remediation, nanotechnology holds promise in reducing the presence of non-aqueous phase liquids (NAPL). Recently, a material utilizing nano-sized oxides (mostly calcium) was used *in situ* to clean up heating oil spills from underground oil tanks. Preliminary results from this redox-based technology suggest faster, cheaper methods, and, ultimately, lower overall

- ☑ Oil Field
- ☑ Manufacturing Site
- ☑ Military Installation
- ☑ Private Property
- ☑ Residence
- ☑ Other

http://www.nanotechproject.org/inventories/remediation_map

Benefits of *in situ* nZVI

- **Cost Reduction**

Cost Example:

New Jersey Manufacturing Site

Pump & treat	$4.16M
PRB	$2.2M
nZVI	$0.45M

(PARS, 2008)

Estimate of the potential cost savings:

$87-98B using nanoremediation over 30 years

- **Reduction** in time to clean up the site:

Pump & Treat	about 18 years
nZVI	99% reduction in days

(Zhang, 2003)

- Less worker exposure to contaminated site

- Fewer environmental disturbances

Potential Implications

Fate and Transport

Possibility of nanoclusters carrying sorbed contaminants

(Gilbert, 2007)

Possible effect on microbes in parallel bioremediation

(Hochella, 2005)

Toxicity

Excess free chelating Fe linked to DNA damage lipid peroxidation & oxidative protein damage

(Valko, 2005)

Inhalation exposures to FeO nanoparticles lead to reactive oxidative stress

(Keenan,2008)

Mammalian nerve cells experience oxidative stress

(Phenrat, 2009)

Societal Issues

2003 ETC Grey Goo

Based on Drexler—which he later clarified

2004 Royal Society

Free nanoparticles in the environment be prohibited until research shows benefits outweigh risks

2005 European Commission

Environmental remediation is a benefit of nanotechnology
Need research on possible risks

2006 Quebec Commission

Biggest source of environmental exposure; need research

2007 EPA Nanotechnology White Paper

Positive aspects of nanoparticles in remediation; need research on negatives

2007 Dupont/Environmental Defense Nano Framework

Would not use technology until rx end products assessed

Consensus is caution; more research needed.

Technology generally viewed as more beneficial than harmful.

Recommendations

➢ Develop analytical tools to measure and monitor nanoparticles in the environment

➢Increase research to evaluate the effects of nanoparticles on the full ecosystem

➢Improve engineering applications using nanotechnology for in situ remediation

➢Develop “smarter” nanomaterials for remediation, e.g., improved dispersion & mobility, multi-functionality, wider spectrum, self-termination, etc.

Thanks!

Martha Otto, US EPA

Todd Kuiken, Woodrow Wilson International Center for Scholars, Project on Emerging Nanotechnologies

Barbara Karn, US EPA

Karn, B., Kuiken T., Otto, M. 2009. Nanotechnology and *In Situ* Remediation: A Review of the Benefits and Potential Risks. Environmental Health Perspectives 117 (12): 1823-1831.