Cleaning Polluted Groundwater: The Nano Option

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Washington, DC
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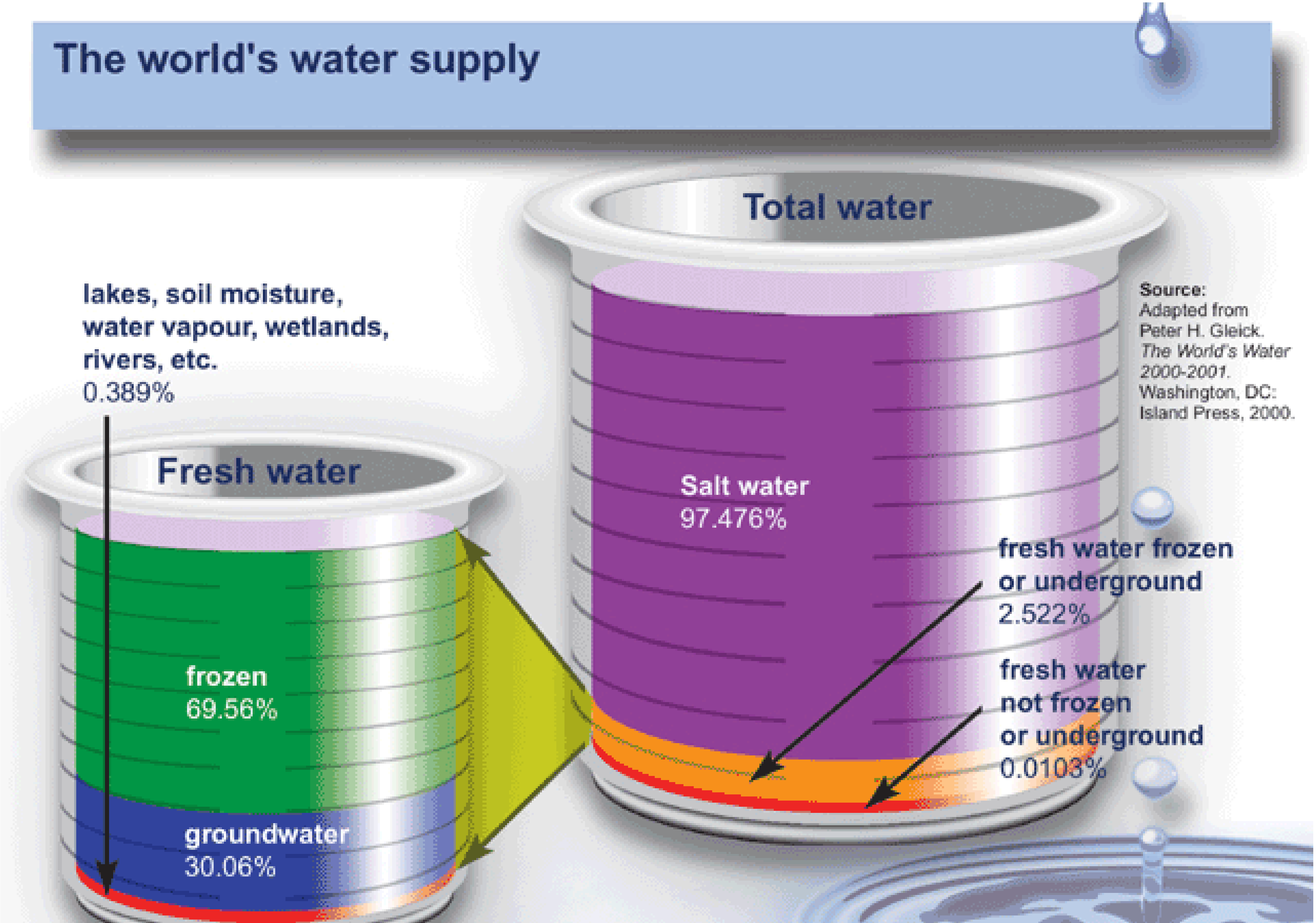
RICE UNIVERSITY

Environmental pollution

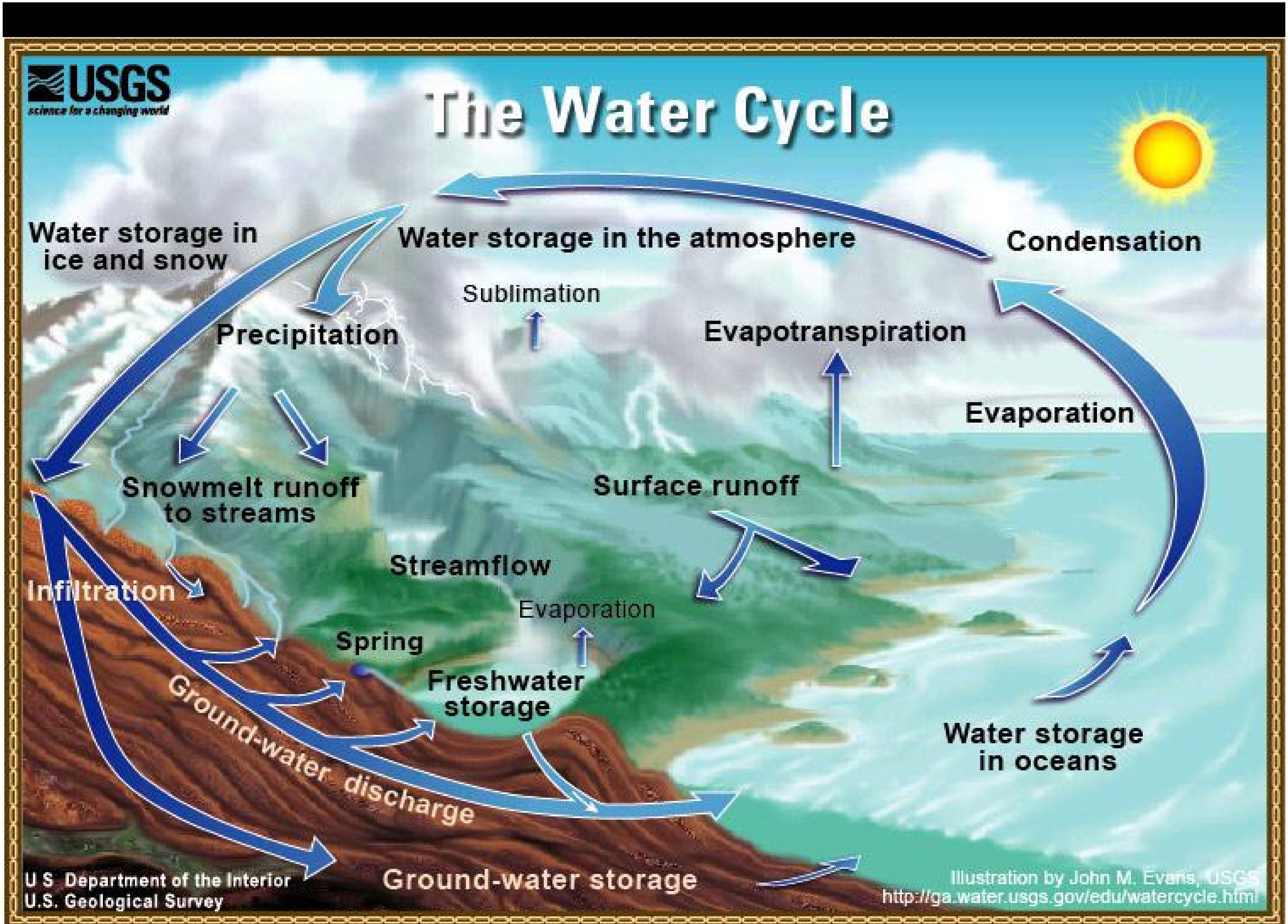
ATMOSPHERE

HYDROSPHERE

LITHOSPHERE



(http://www.ec.gc.ca/WATER/e_main.html)

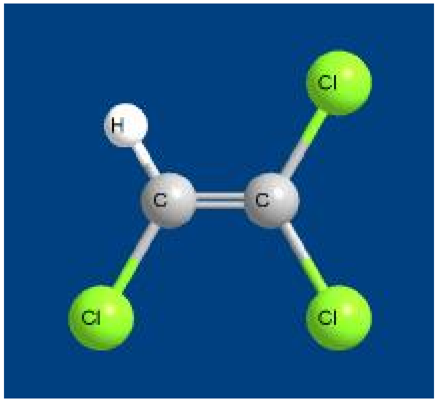

USGS
science for a changing world
The Water Cycle
Water storage in ice and snow
Water storage in the atmosphere
Condensation
Sublimation
Precipitation
Evapotranspiration
Evaporation
Snowmelt runoff to streams
Surface runoff
Streamflow
Infiltration
Evaporation
Spring
Freshwater storage
Ground-water discharge
Water storage in oceans
Ground-water storage
U S Department of the Interior
U.S. Geological Survey
Illustration by John M. Evans, USGS
http://ga.water.usgs.gov/edu/watercycle.html

Partial list of groundwater pollutants

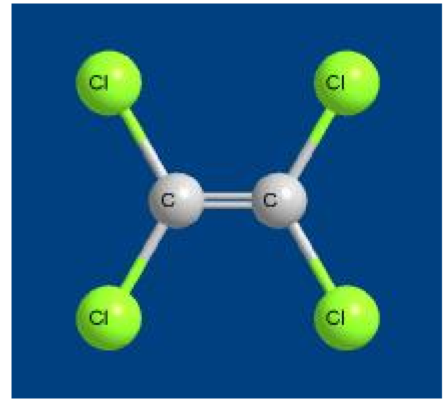
Chlorinated methanes	Trihalomethanes
Carbon tetrachloride (CCl_4)	Bromoform ($CHBr_3$)
Chloroform ($CHCl_3$)	Dibromochloromethane ($CHBr_2Cl$)
Dichloromethane (CH_2Cl_2)	Dichlorobromomethane ($CHBrCl_2$)
Chloromethane (CH_3Cl)	Chlorinated ethenes
Chlorinated benzenes	Tetrachloroethene (C_2Cl_4)
Hexachlorobenzene (C_6Cl_6)	Trichloroethene (C_2HCl_3)
Pentachlorobenzene (C_6HCl_5)	*cis*-Dichloroethene ($C_2H_2Cl_2$)
Tetrachlorobenzenes ($C_6H_2Cl_4$)	*trans*-Dichloroethene ($C_2H_2Cl_2$)
Trichlorobenzenes ($C_6H_3Cl_3$)	1,1-Dichloroethene ($C_2H_2Cl_2$)
Dichlorobenzenes ($C_6H_4Cl_2$)	Vinyl chloride (C_2H_3Cl)
Chlorobenzene (C_6H_5Cl)	Other polychlorinated hydrocarbons
Pesticides	PCBs
DDT ($C_{14}H_9Cl_5$)	Dioxins
Lindane ($C_6H_6Cl_6$)	Pentachlorophenol (C_6HCl_5O)
Organic dyes	Other organic contaminants
Orange II ($C_{16}H_{11}N_2NaO_4S$)	N-nitrosodimethylamine (NDMA) ($C_4H_{10}N_2O$)
Chrysoidine ($C_{12}H_{13}ClN_4$)	TNT ($C_7H_5N_3O_6$)
Tropaeolin O ($C_{12}H_9N_2NaO_5S$)	Inorganic anions
Acid Orange	Dichromate ($Cr_2O_7^{2-}$)
Acid Red	Arsenic (AsO_4^{3-})
Heavy metal ions	Perchlorate (ClO_4^-)
Mercury (Hg^{2+})	Nitrate (NO_3^-)
Nickel (Ni^{2+})	
Silver (Ag^+)	
Cadmium (Cd^{2+})	

W.-X. Zhang, *J. Nanopart. Res.* **2003**, 5, 323-332

Chlorinated solvent compounds



- TCE, trichloroethylene
- Industrial solvent
- ~5000 DOD, DOE, and Superfund sites contaminated with chlorinated solvents
- Up to ~$10MM/site for remediation (life-cycle cost)
- Total of $50 billion needed(!)

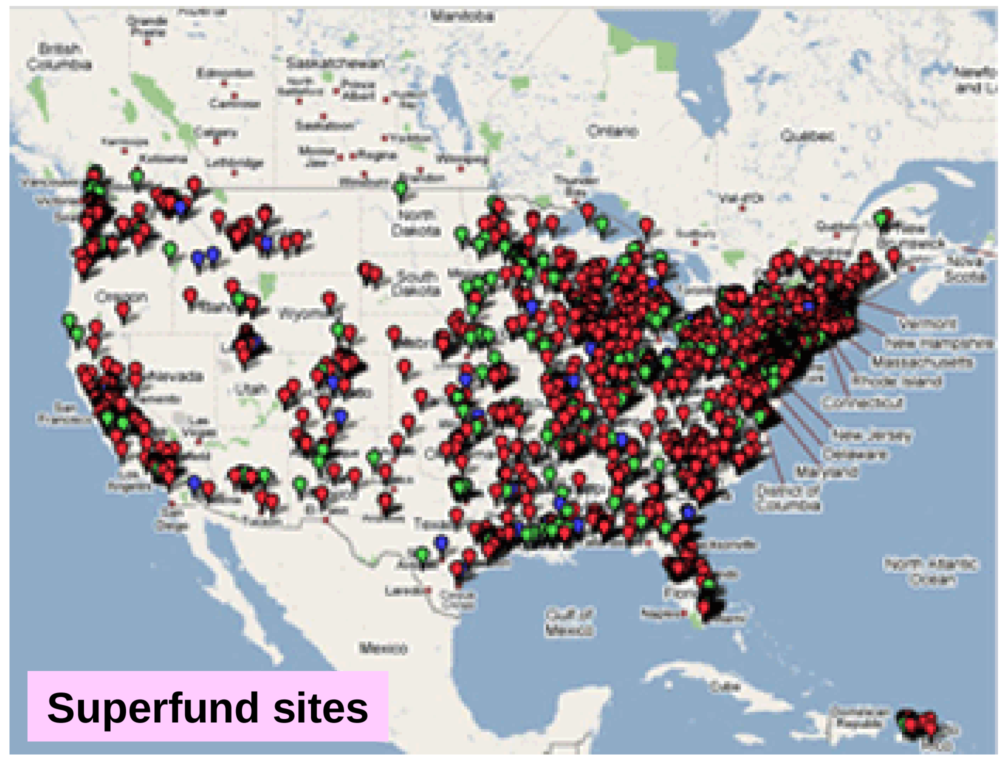


- PCE, perchloroethylene
- Drycleaning fluid
- ~27,000 contaminated dry cleaning sites
- $250K/site for remediation
- Total of $6.5+ billion needed for remediation

68th Street Dump, Baltimore, Maryland

Parawax Refinery, Oklahoma City, Oklahoma

Eastland Woolen Mill, Corinna, Maine



Superfund sites

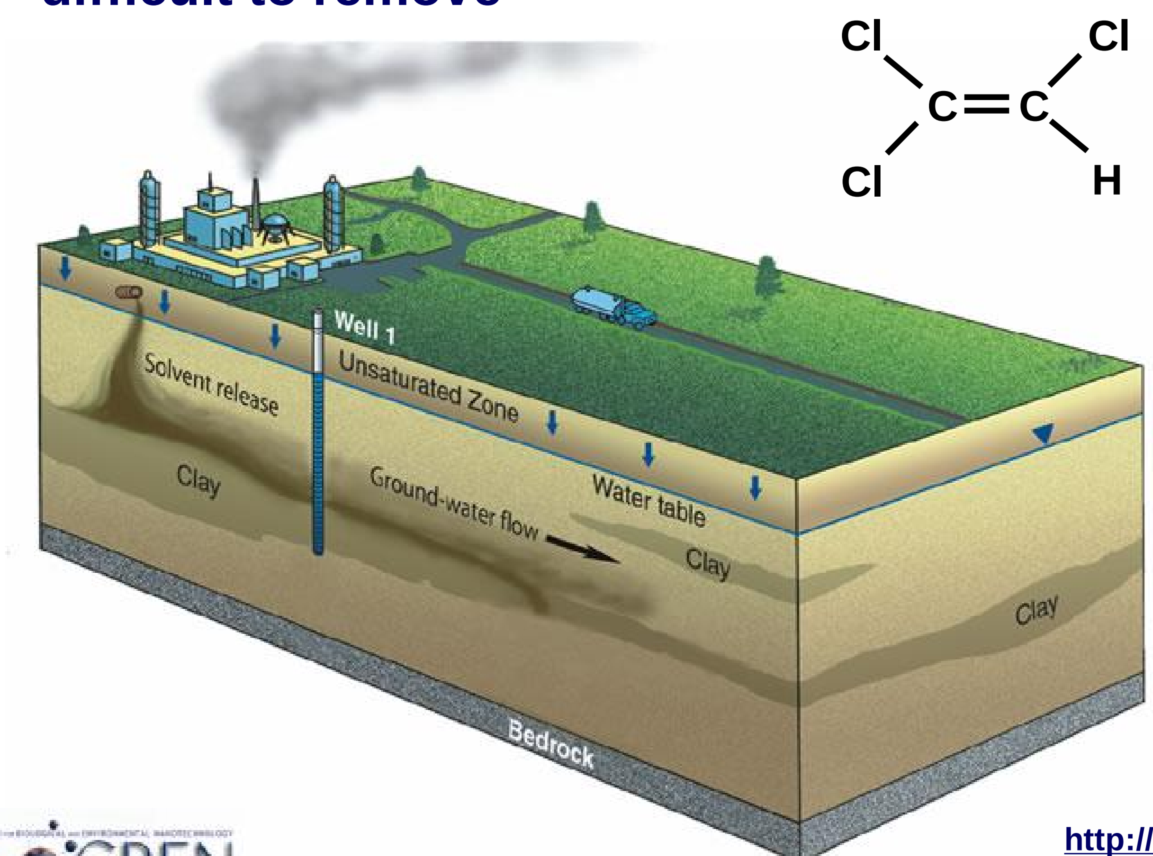
TCE in groundwater

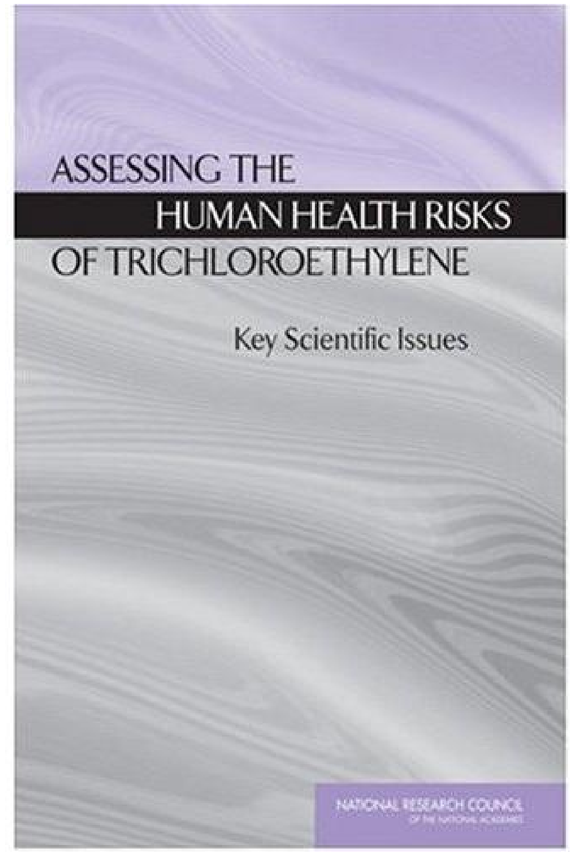
Widely used as a degreasing solvent

Found in 60% of Superfund sites

Highly persistent in groundwater, difficult to remove

Health effects: cancer, organ damage, developmental toxicity



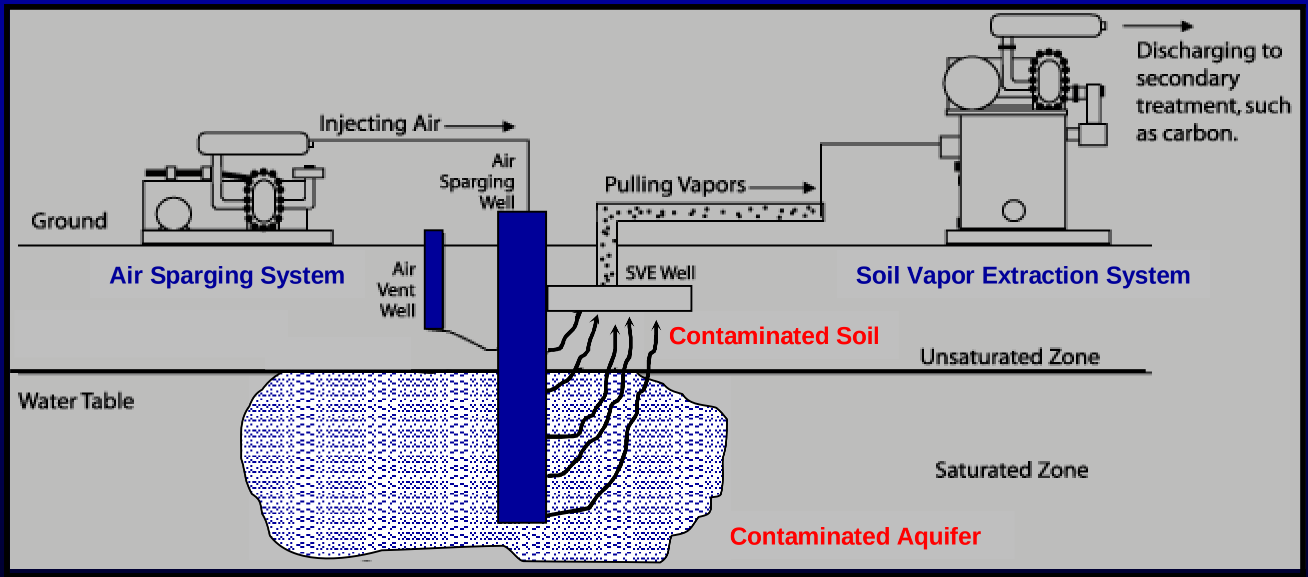


(NRC, July 2006)

http://water.usgs.gov/nawqa/vocs/national_assessment/report/chapter5.html

TCE remediation technologies

- Carbon adsorption
  - Contaminated groundwater is pumped out of the aquifer and into a series of carbon beds (*i.e. ex situ* treatment)
  - TCE is transported from liquid to solid phase
- Air stripping
  - Contaminated groundwater is contacted with an air stream
  - In aquifer remediation possible (*in situ* treatment)
  - TCE is transported from liquid to gas phase



➡ Major drawback is the required further treatment (i.e. incineration)

Hydrodechlorination (HDC) of TCE

- Catalysts: Pd black, Pd/alumina[1,2]
  - Remediated chlorinated ethenes, CCl_4, $CHCl_3$

$CHCl{=}CCl_2 + 4H_2$ à $CH_3CH_3 + 3\ HCl$

TCE *ethane*

- Large scale pilot operation at LLNL showing long term results[3]

- Catalyst cost is an issue

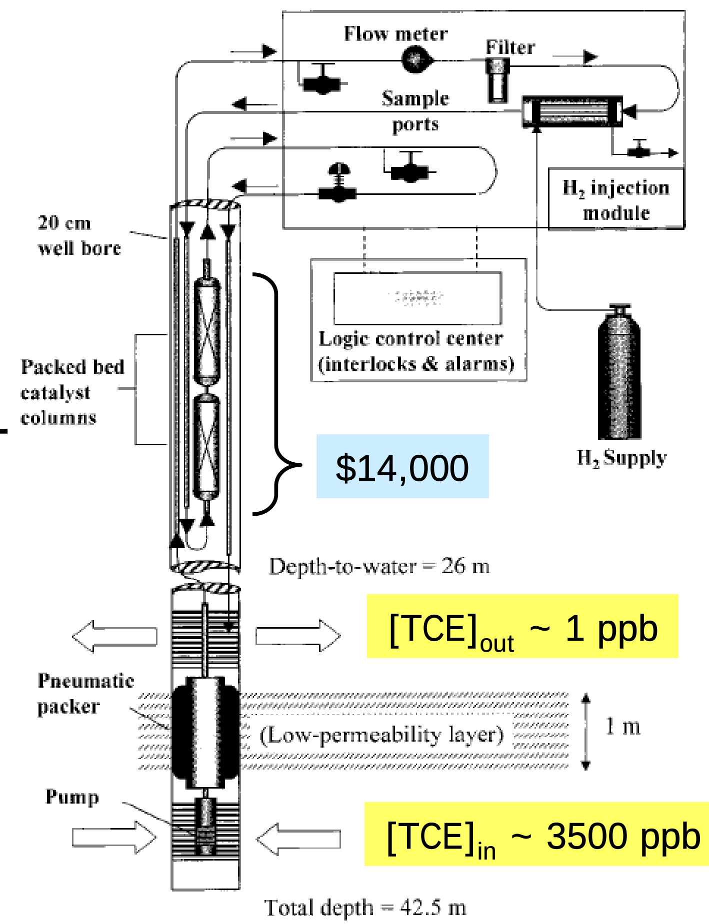


FIGURE 1. Reactive well configuration using catalytic reductive dehalogenation.

1. Lowry and Reinhard, *Environ. Sci. Technol.* (**1999**) 33, 1905
2. Lowry and Reinhard, *Environ. Sci. Technol.* (**2001**) 35, 696
3. McNab et al. *Environ. Sci. Technol.* (**2000**) 34, 149

Example of how catalysis happens

Dehydrogenation of ethylene using Ni nanoparticle catalysts

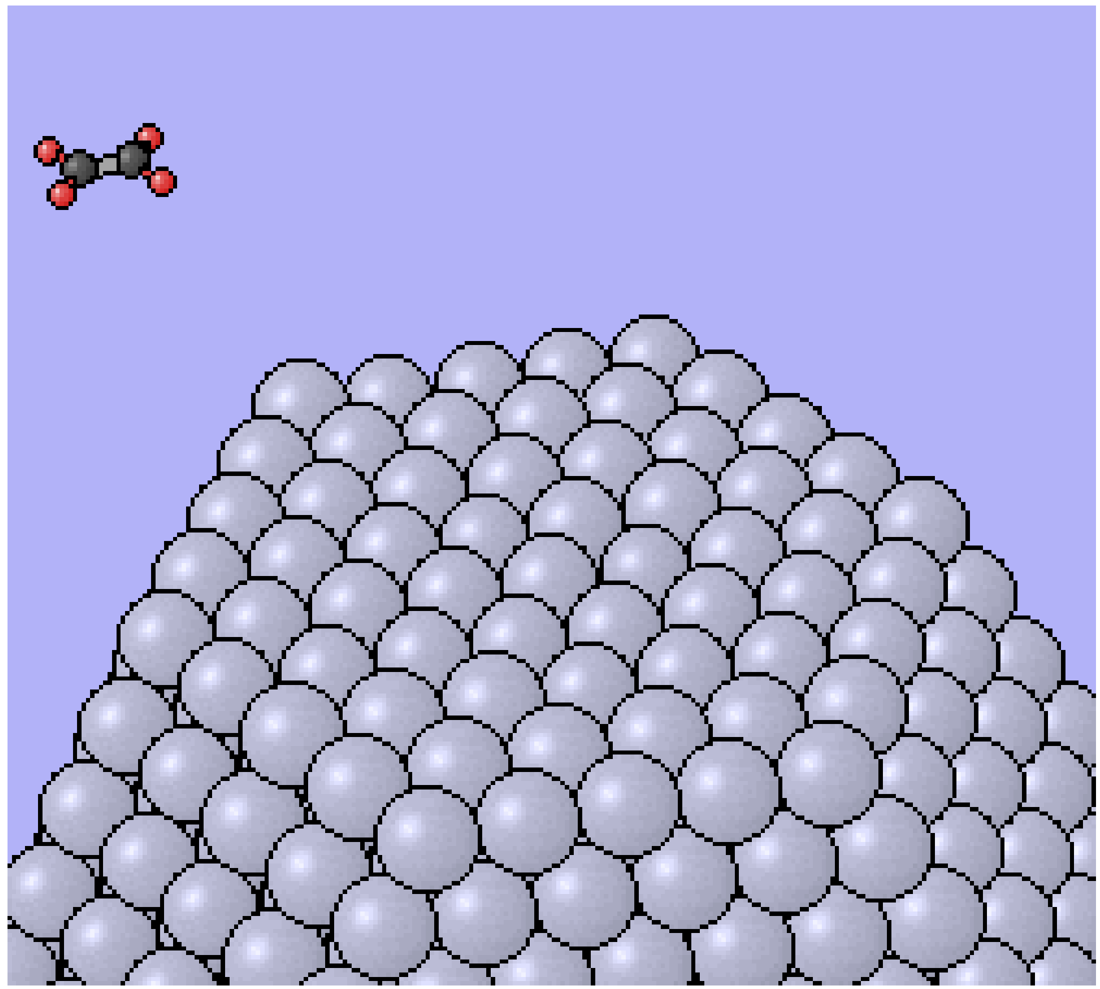
Ethylene: $H_2C{=}CH_2$

↓

Acetylene: HC≡CH

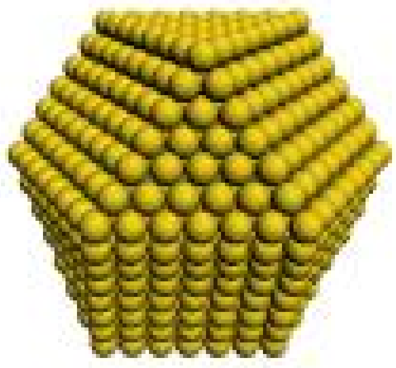
+

Hydrogen: H_2



http://leung.uwaterloo.ca/CHEM/750/

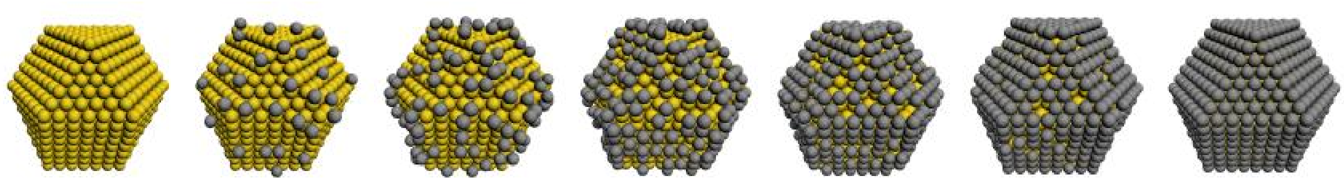
Gold NPs coated with palladium atoms



Comprised of a central atom surrounded by a closed shell of identically-sized atoms

Consider Pd layer as 8th shell

Shell #	# atoms in shell	# total atoms	NP Diameter (nm)
0	1	1	0.27
1	12	13	0.80
2	42	55	1.34
3	92	147	1.88
4	162	309	2.41
5	252	561	2.95
6	362	923	3.48
7	492	1415	4.02
8		**642 Pd atoms = 1 complete layer**	

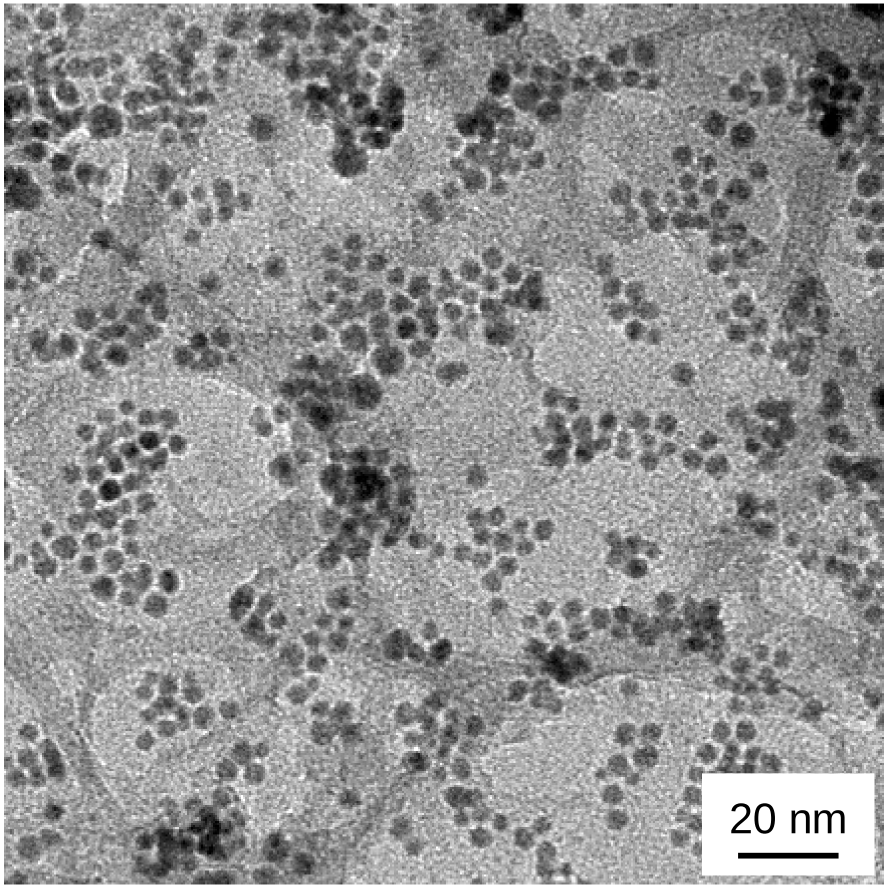


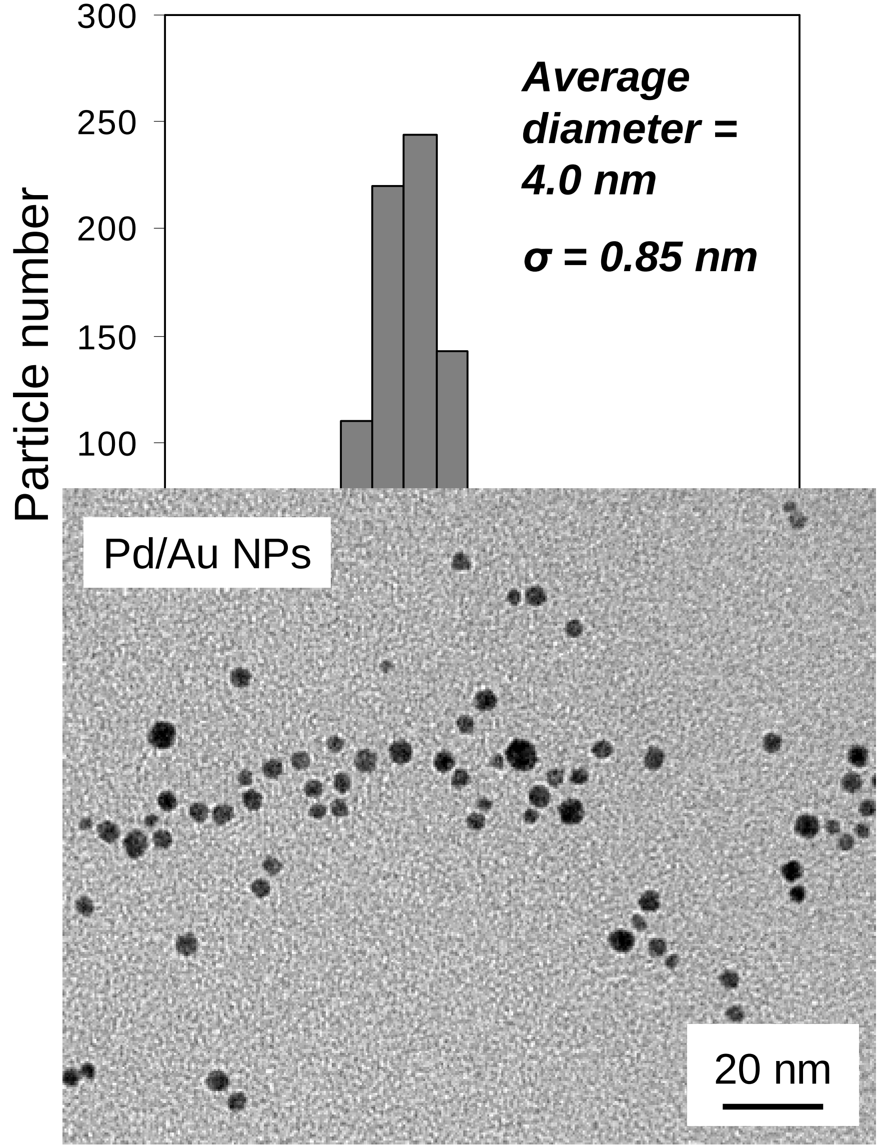
Pd content (wt%)

0% 2.4% 5.8% 10.9% 15.5% 18.1% 19.7%

TEM of resultant Au NPs

RICE





(850 particles analyzed)

Nutt *et al.*, *Appl. Catal. B Env.* **69**, 115-125 (2006)

E 2456-06
Terminology for Nanotechnology

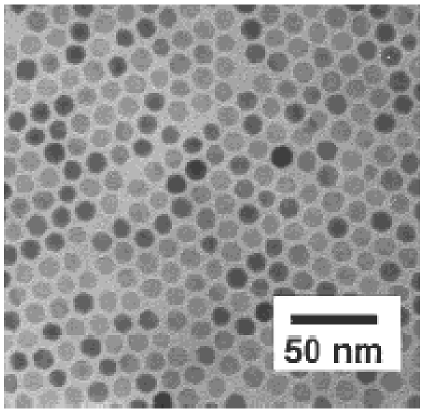
1.1 Nanotechnology is an emerging field; this standard defines the novel terminology developed for its broad multi- and interdisciplinary activities. As the needs of this area develop, this standard will evolve accordingly. Its content may be referenced and/or adopted, in whole or in part, as demanded by the needs of the individual user.

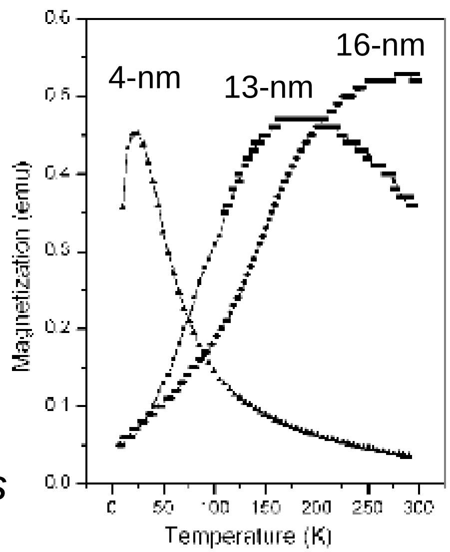
nanotechnology, *n*—A term referring to a wide range of technologies that measure, manipulate, or incorporate materials and/or features with at least one dimension between approximately 1 and 100 nanometers (nm). Such applications exploit the properties, distinct from bulk/macroscopic systems, of nanoscale components.

nanoparticle, *n*—*in nanotechnology*, a sub-classification of ultrafine particle with lengths in two or three dimensions greater than 0.001 micrometer (1 nanometer) and smaller than about 0.1 micrometer (100 nanometers) and which may or may not exhibit a size-related intensive property.

Size-dependent properties of NPs

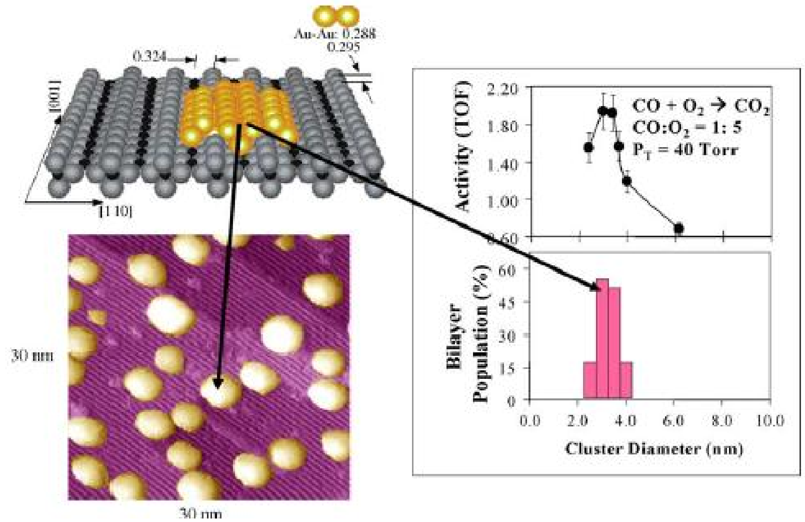
γ-Fe_2O_3 NPs (magnetism)





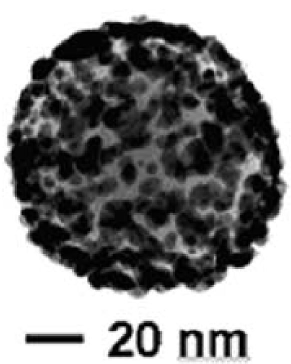
Hyeon and co-workers

TiO_2-supported Au NPs (catalysis)



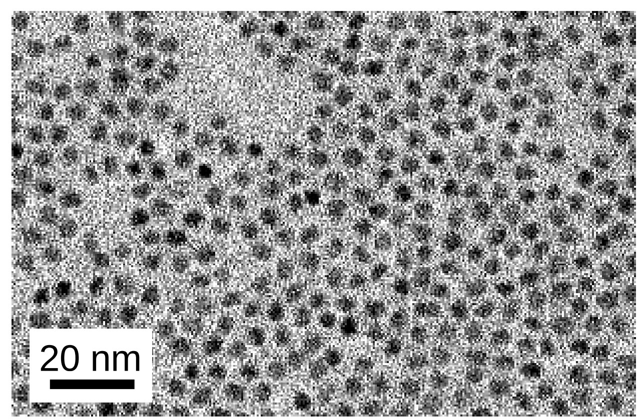
Goodman and co-workers

Gold-shell/SiO_2-core particles (absorbance)

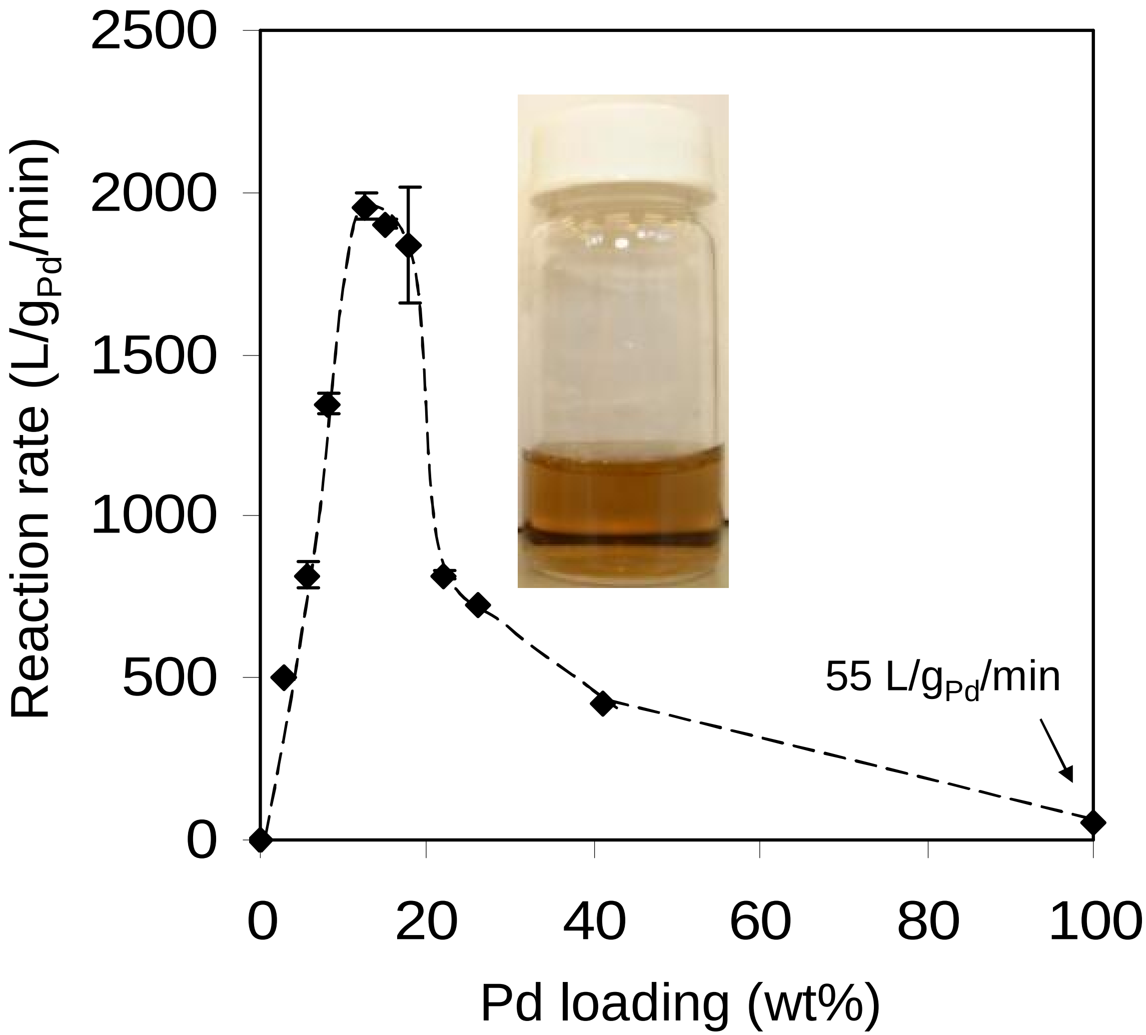


Halas, West, and co-workers

CdSe quantum dots (emission)



Reaction rate as function of wt% Pd



TCE in H_2O
T = 22-25 °C
H_2 gas in headspace

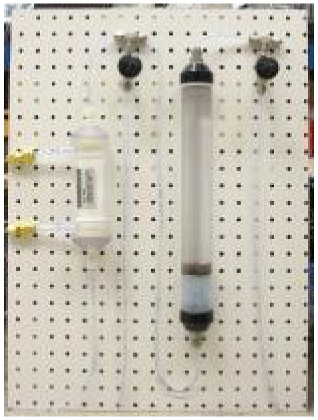
Pd content in reactor was constant (6.4×10^{-8} moles)

Batch reactor

Headspace

Aqueous reaction medium

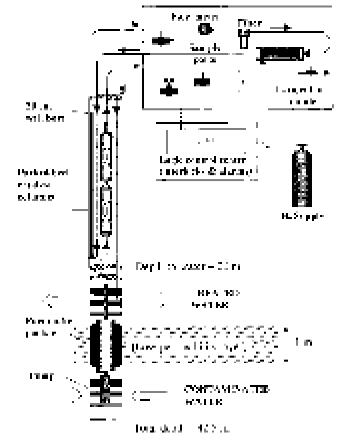
Our nano-catalyst is cheaper



Pd/Au-NP/IER

$k = 8.4 \times 10^{7}$ L/kg_{Pd}/day

Pd/Al_2O_3



$k = 5.3 \times 10^{4}$ L/kg_{Pd}/day

For example, to treat 1000 L (~1 ton) water (100 ppm to 5 ppb TCE) in 2 days (flowrate = 0.35 L/min),

Total Pd needed: 0.0589 g
Total Au needed: 0.343 g
Total IER needed: 9404 g

IER: $0.014 USD/g
Spot prices (Oct. 12, 2007):
Pd: $377 USD/oz
Au: $748 USD/oz

Overall price: $135

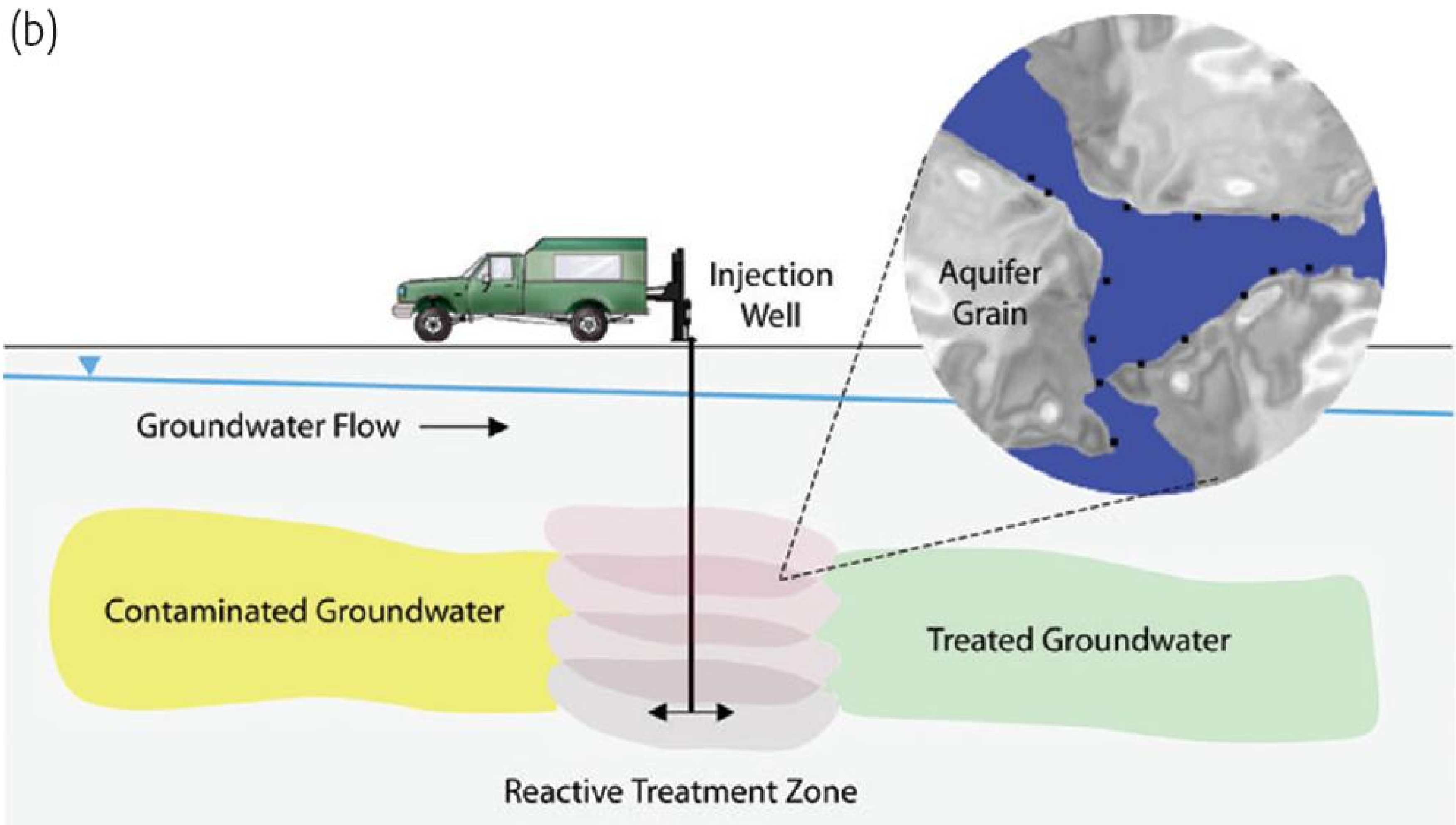
Total Pd needed: 94.17 g
That is, total Pd(1 wt%)/Al_2O_3 needed: 9417 g

Pd/Al_2O_3: $0.27 USD/g

Overall price: $2543

McNab et al., *Environ. Sci. Technol.*, **2000**, *34*, 149.

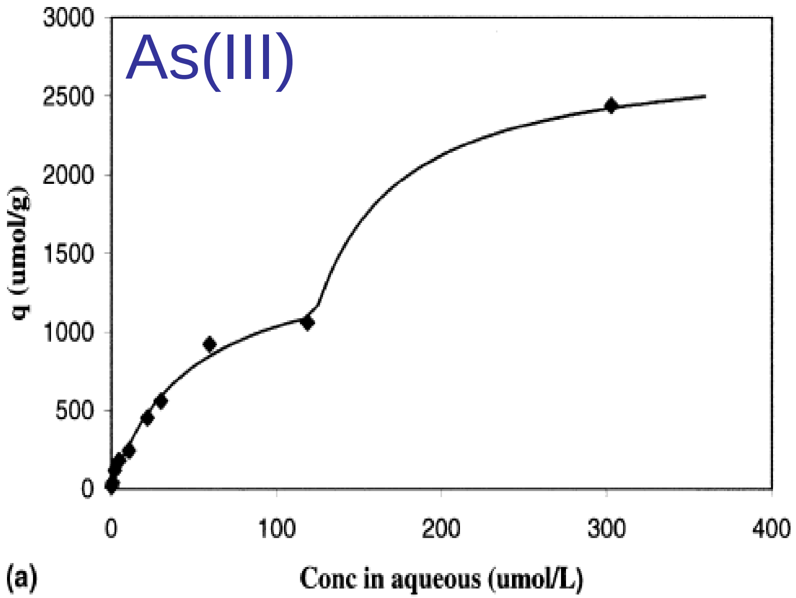
Zero-valent iron NPs for *in situ* treatment

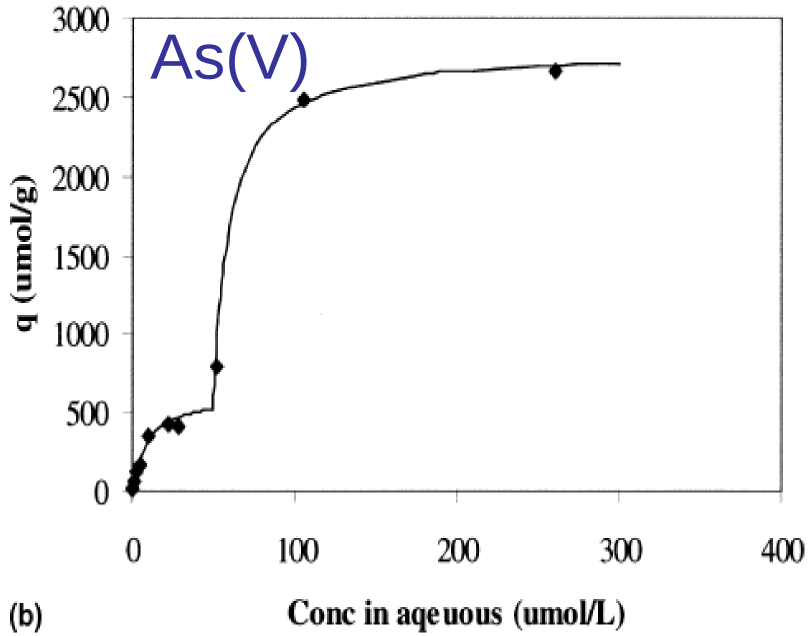


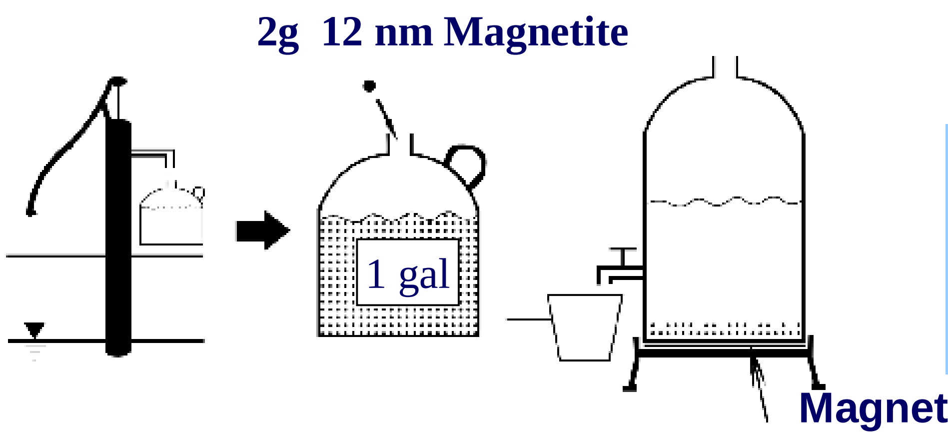
Tratnyek and Johnson, *Nano Today* 1, 44-48 (2006)

Arsenic Adsorption by Nano-Magnetite

Yavuz, Mayo, Yu, Prakash, Falkner, Yean, Cong, Shipley, Kan, Tomson, Natelson. & Colvin. Science 314, 964-967 (2006).

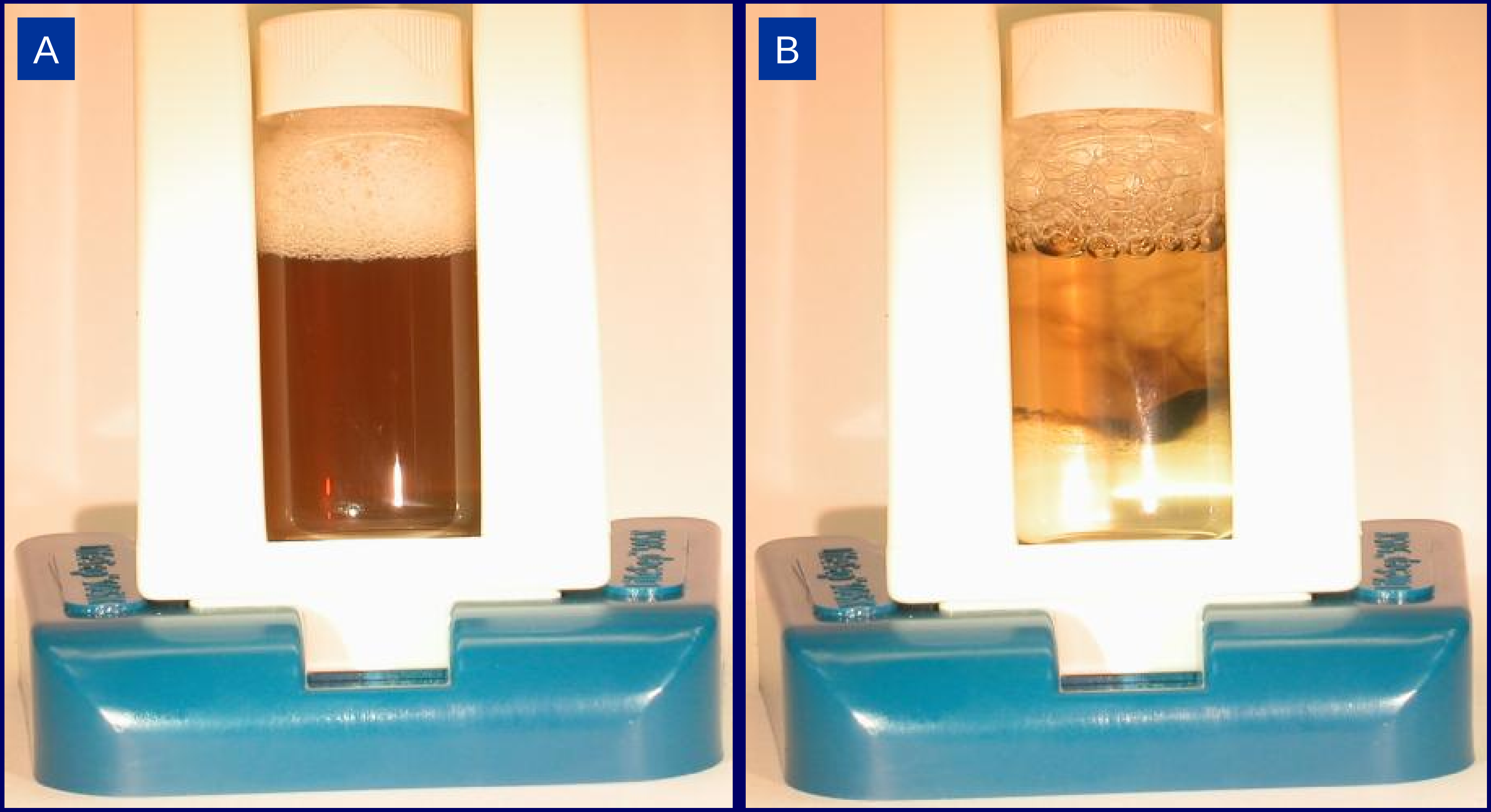






*For a family of four, using 900 L water/month, at 500 ppb As levels (pH = 7.9), annual cost would be on the order of **$4/year***

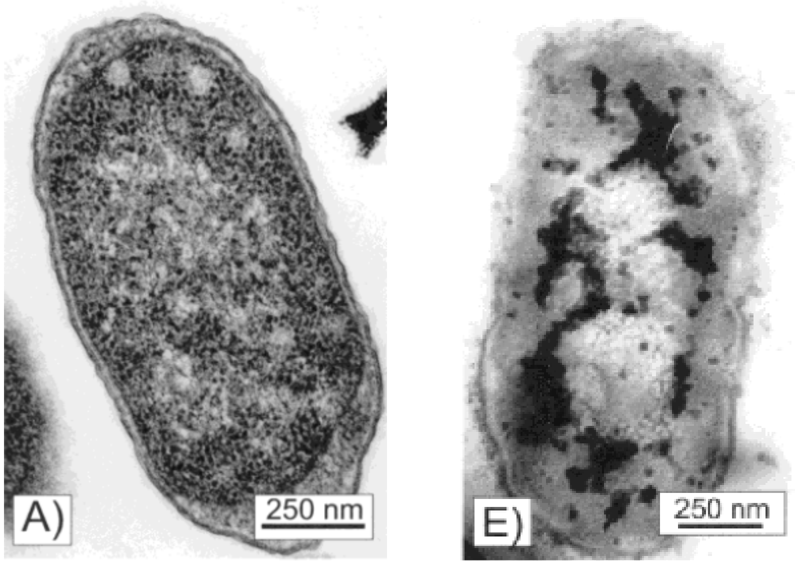
Nanocrystals Can Move in Low Fields



0.0 Tesla → 0.36 Tesla

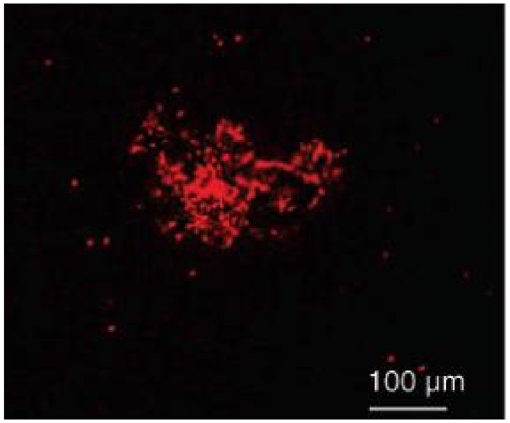
Antimicrobial Nanomaterials

- Ag
- TiO_2
- Metal oxide/X_2
- Fullerenes and fullerols
- Carbon nanotubes



E. Coli before and after MgO/Cl_2 treatment

Stoimenov et al., Langmuir, 2002



E. coli K12 inactivated by SWNT deposited on surface

Kang et al., Langmuir, 2007

Nanotechnology-enabled Water Treatment (NeWT) Workshop

Hilton Houston Plaza – Houston, Texas

February 25-27, 2007

Nanotechnologies for environmental cleanup

Risks

The above discussion of the morphology, reactivity, and mobility of nanoparticles in the context of environmental remediation demonstrates that our current understanding of the basic processes involved in this technology is still evolving and incomplete. In addition to making it difficult to move forward with the engineering of full-scale implementations, these uncertainties make it very difficult to assess the risks that this technology might have to human or ecological health[35].

Tratnyek and Johnson, *Nano Today* 1, 44-48 (2006)

Concluding remarks

- Clean, accessible, affordable water is becoming scarce
  - Due to climate change, population growth, emerging pollutants
- Nanotechnology is a valuable approach to treating contaminated water
  - Value depends on source of water, desired quality, type of water distribution, end-user
  - Some nanotech examples are already in use
  - Needs to be affordable
- Nano-enabled water treatment (“NEWT”) takes advantage of unique properties of nanomaterials
- Nano-catalysis is a promising route to treat water
  - Complete destruction of contaminant
  - Energy and materials efficient