Bioavailability: what does it mean to be nanosized

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Pollutants:

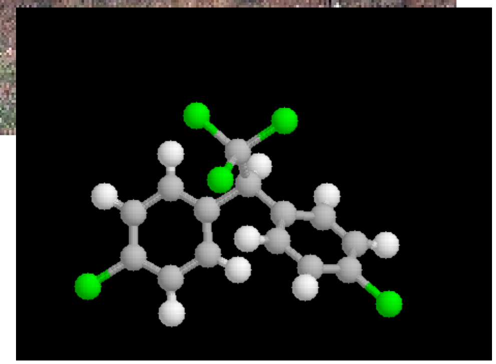
Organics-

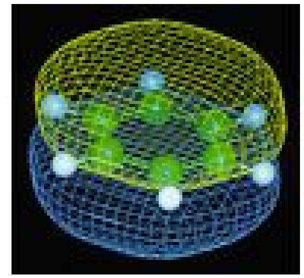
- **phenolics**
- **polycyclic aromatic hydrocarbons**
- **chlorinated aromatics**
- **chlorinated solvents**
- **fuels and explosives**
- **pesticides**

Inorganic-

- **heavy metals and metalloids**

Radioactive materials





Diverse compounds from diverse sources:
mines, industry, nature

SOIL- AIR- WATER

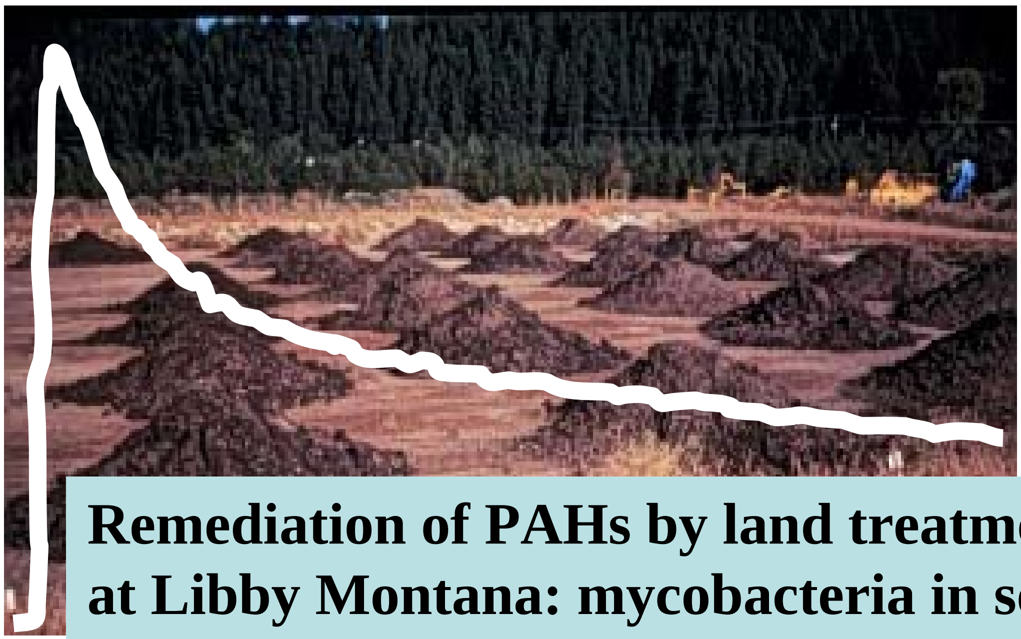
Remediation

Physical methods

Cover up
Drag and haul
Dilution
Bioventing/sparging
etc

Transformation

Toxic → Less toxic



Remediation of PAHs by land treatment at Libby Montana: mycobacteria in soil mineralize the PAHs

Transformation

Biological

Chemical

BOTH PROCESSES MAY INVOLVE NANOPARTICLES

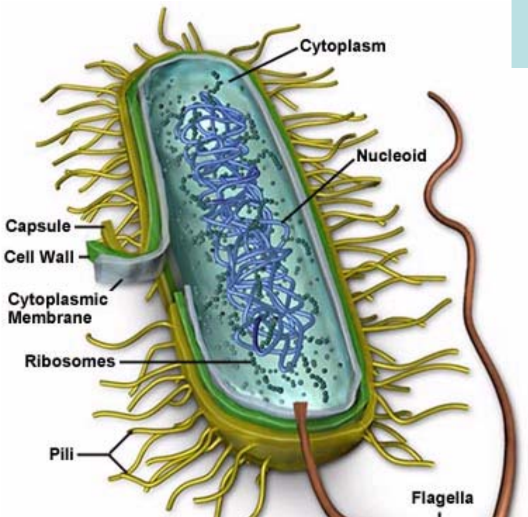
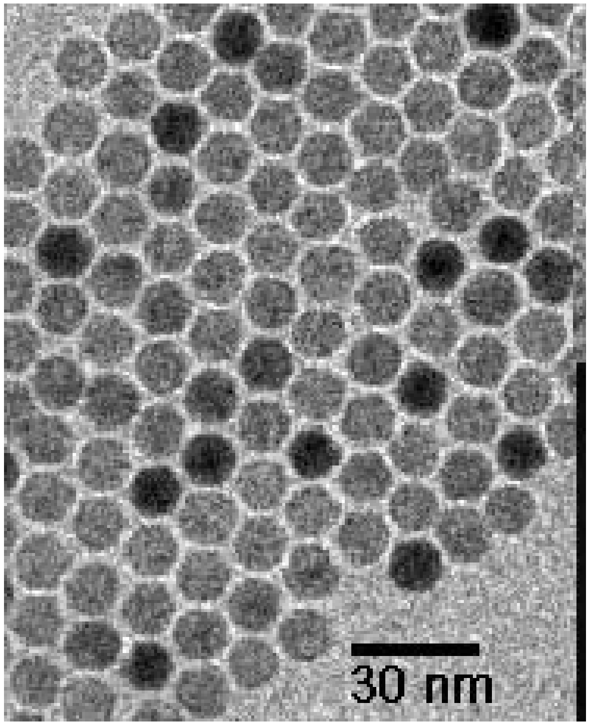


Figure 1

Nanoparticles in use include:

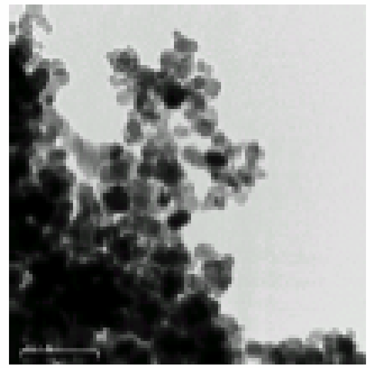
Fe and modified Fe (Fe/Pd etc).
Metal oxide
Metal sulphides

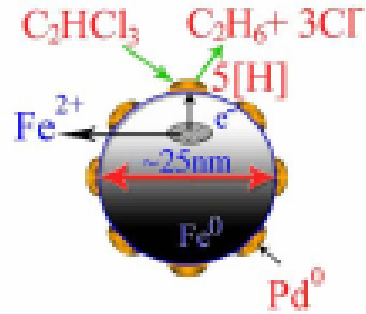


Iron oxide nanoparticles
Columbia University.

CHEMICAL TREATMENTS:

Remediation of Groundwater





Fe/Pd nanoparticle

Reduces and dechlorinates trichloroethane

Dr. W. Zhang, Lehigh University:

Chemistry of action of iron nanoparticles

$$2\,Fe^{O} + 4H^{+} + O_2 \longrightarrow 2Fe^{2+} + 2H_2O$$

$$Fe^{O} + 2\,H_2O \longrightarrow Fe^{2+} + H_2 + OH^{-}$$

Electron transfers from metallic Fe : iron corrosion

$$4Fe^{O} + 4H^{+} + C_2Cl_4 \longrightarrow 4Fe^{2+} + C_2H_4 + 4Cl^{-}$$

Tetrachloroethane Ethane

Reductive dechlorination of the toxic solvent

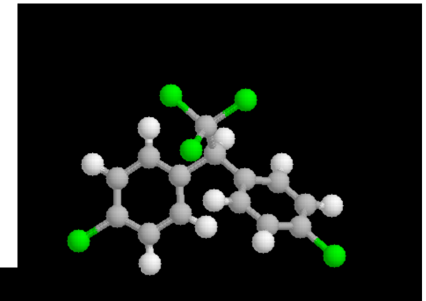
Zhang : 2003

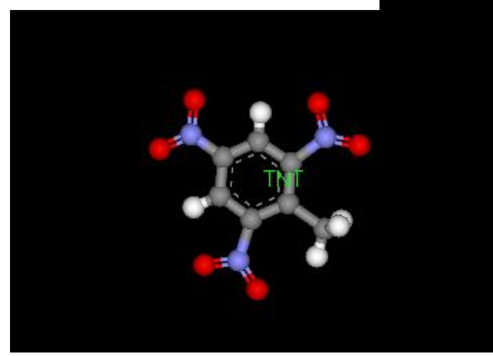
Zhang: 2003 J Nanoparticle Research 5:323-332

Compounds remediated by iron nanoparticles include:

<u>Chlorinated organics</u>

<u>Pesticides</u>: Lindane , DDT





<u>Dye materials</u>

<u>Metals and metalloids</u>
Hg
Ni
Cd

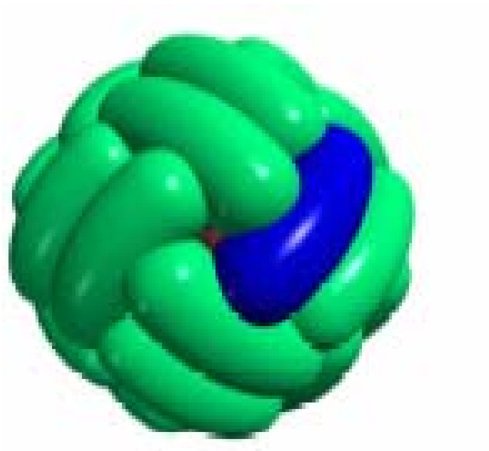
<u>Explosives</u>: Perchlorate, TNT

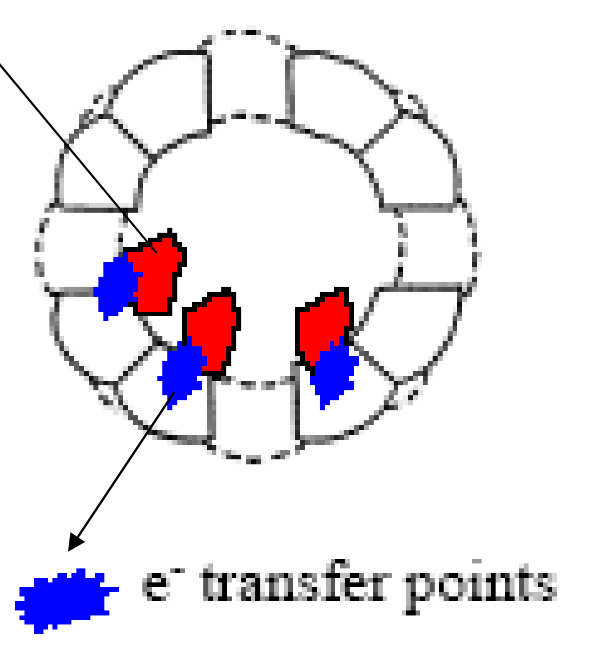
<u>Fertilizer</u>: NO_3

Ferritin or bacterioferritin :

protein shell

iron hydrates in inner core





Reduction of chlorinated compounds and Cr(VI) demonstrated

Daniel Strongin Temple University

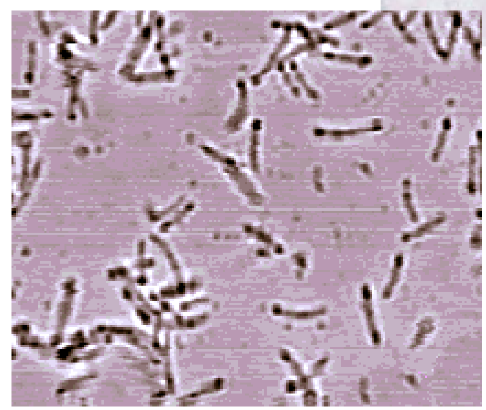
Modified from B. Karn

Electron transfer also can account for reductive dehalogenation by microbial metabolism

e.g. the anaerobic sulphate-reducing microbes
Dehalobacter, Desulfomonile, Desulfitobacterium, Dehalospirillum

$C_7H_4O_2Cl^- + H_2 \rightarrow C_7H_5O_2^- + H^+ + Cl^-$
Chlorobenzoate   Benzoate

All use H_2 as a electron donor, others can use some carbon sources (formate , pyruvate, lactate etc)

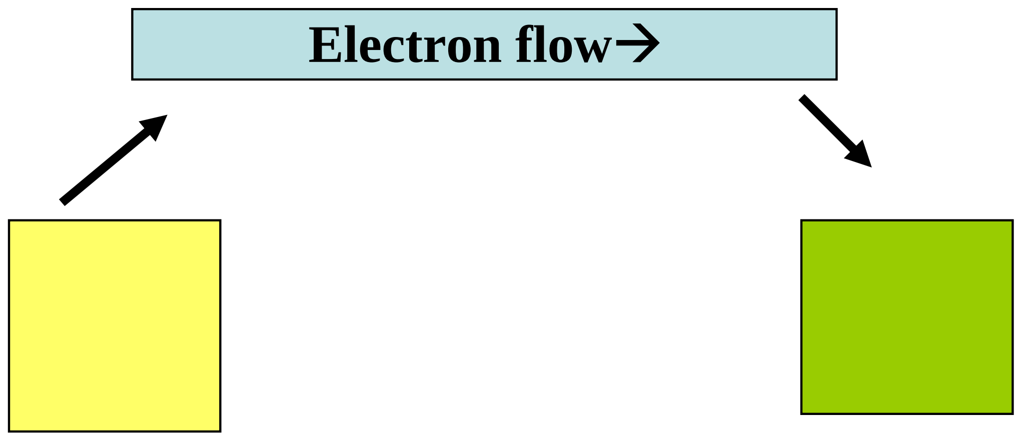


From JGI.

MICROBES have developed diversity in methods to transfer electrons

Electron transport chain →

- Fe-S centers
- Mo proteins
- Cytochromes
- Quinone pools



Electron donor:

NADH
But H_2
Fe^{2+}
etc

Electron acceptor:

Oxygen → water
Or $Fe^{3+} \rightarrow Fe^{2+}$
$SO_4^{2-} \rightarrow H_2S$ or S
XCl→ XH +Cl^-
U(VI)→ U(IV)

Microbial nanoparticle products include:

Ag from silver ions---fungi (*Phoma sp.*), Chen et al 2003

Au from Au(III) --- bacteria and archaea, Kashefi et al 2001

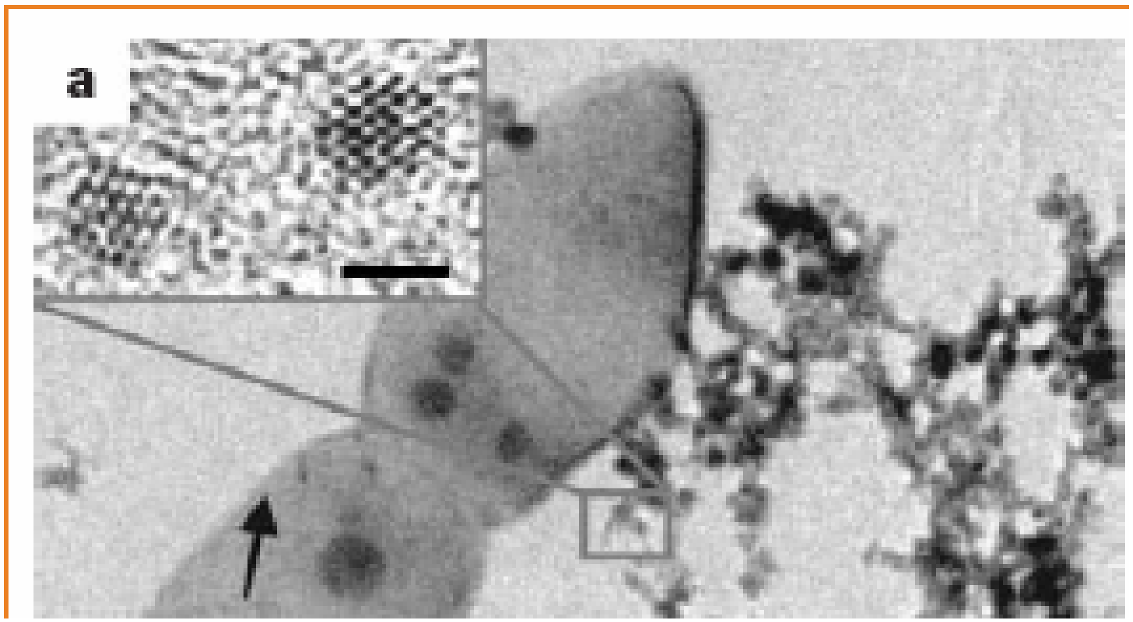
Zirconia ZrO_2 from ZrF_6 ---- *Fusarium oxysporum*, Bansal et al 2004

Reduced iron oxide minerals from Fe(III) oxyhydrates–
***Shewanella putrefasciens*,**
Glasauer et al 2002

Mn granules from MnO_2 --- *Shewanella*, Glasauer et al 2004

Magnetite Fe_3O_4 from Fe^{3+} ---*Magnetospirillum*, Komeili et al 2004/
***Pyrobaculum*, Kashefi and Lovely 2000**

MICROBIAL TRANSFORMATION:
The product of electron transfer may be a nanoparticle



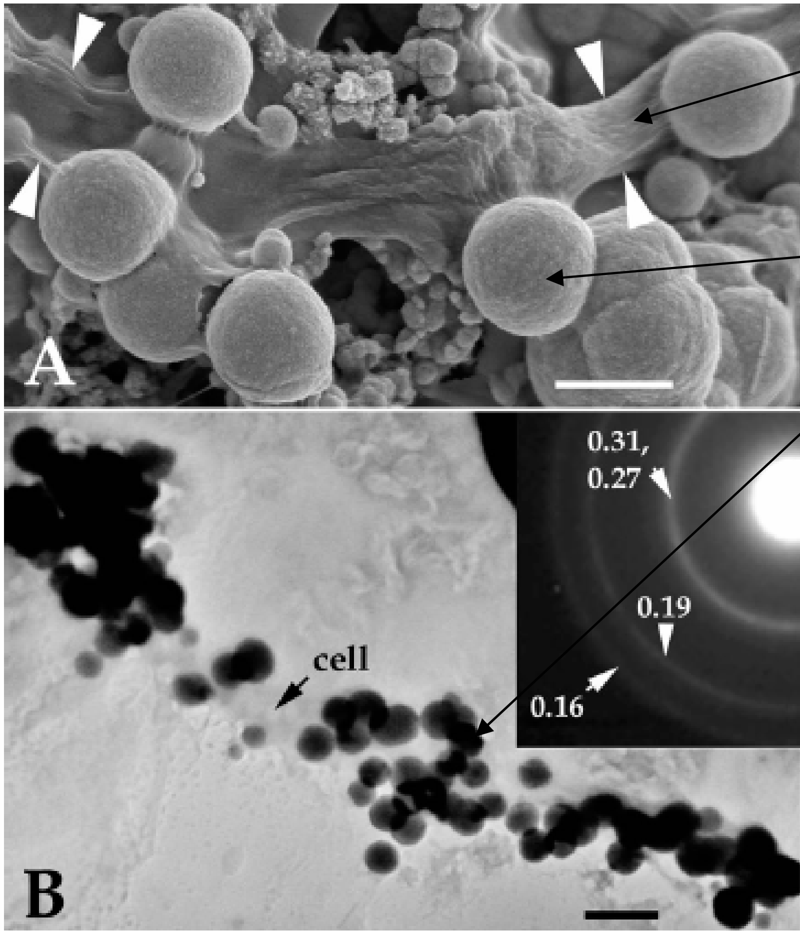
(Banfield group,2002)

***Desulfosporosinus* species bacterium (Gram +ve, sulphate reducing)**
remediation of U(VI) by conversion to U(IV)
seen as the nanoparticles of UO_2 around cell surface

U(VI) $\xrightarrow{\text{Electrons!}}$ U(IV)

SEM

TEM



Filamentous cells

Aggregates

random packed NANOCRYSTALS of ZnS

***Desulphobacteria*:**

Limit Zn contamination of water run off from mine because of ZnS deposition

Concept: to mimic mine conditions to precipitate toxic metals as sulfides

Banfield group, Science 2000

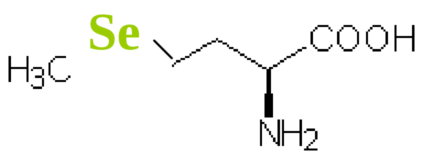
Selenium:

Problem from mine ores e.g. Cu_2Se
And from geological deposits as SeO_4^{2-} and SeO_3^{2-}

Cretaceous shales rich in Se ores

Significant environmental problem in Utah

Selenomethionine



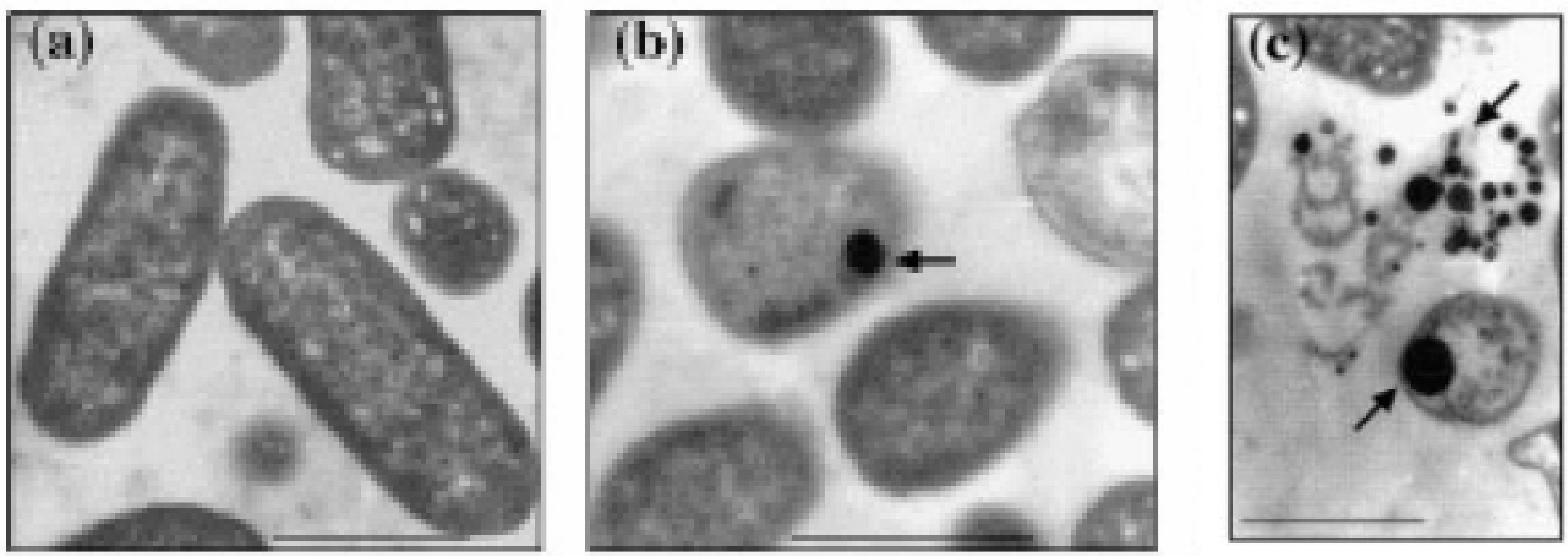
Selenium in sediments

Water : run off: rain and irrigation
well water, storage lagoons

Food chain – microbes, algae, plants, insects, animals
(alternative amino acids)

Toxic affects on fish and birds

Bebien et al Microbiology, 2002



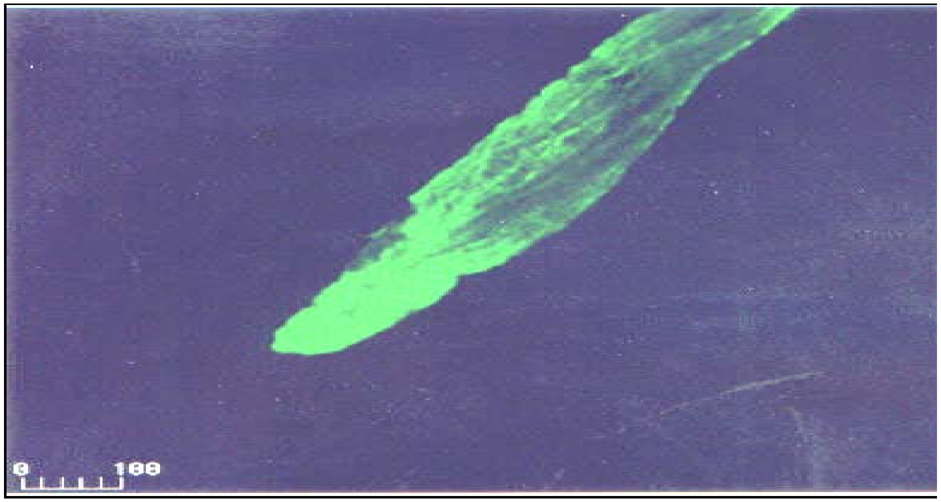
***E. coli* grown without (A) and with SeO_4^{2-} (B) or SeO_3^{2-} (C)**

Bacterial cells reduce the oxyanions to nanoparticles of elemental Se^O

*Pc*O6 growing from a barley root

Pseudomonas chlororaphis is an aggressive root colonist

THESE ROOT COLONIZERS CAN BE USED IN PHYTOREMEDIATION



GFP-labelled cells showing intense colonization at root tip

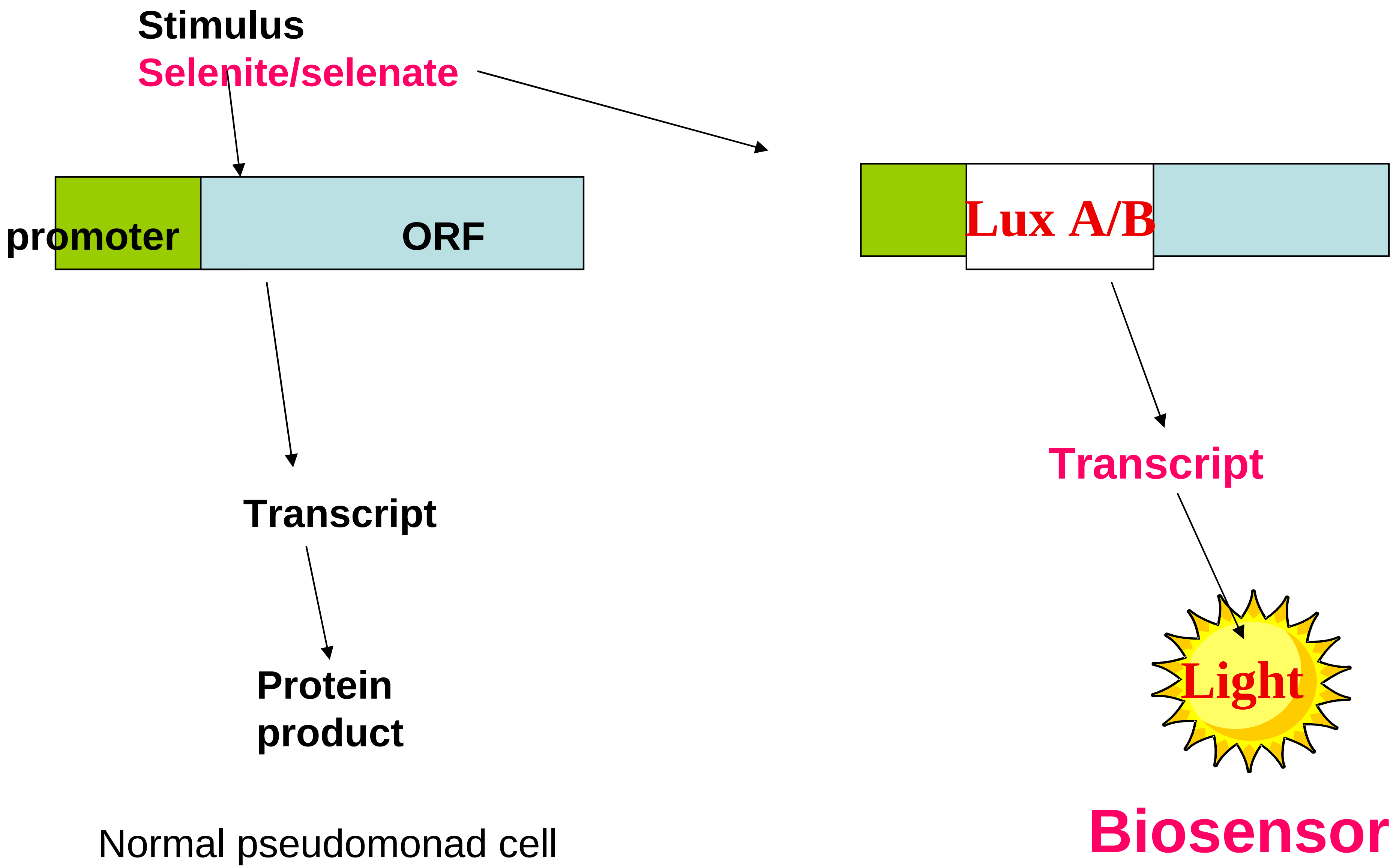
DO THE ROOT-COLONIZING PSEUDOMONADS METABOLIZE THE SELENIUM OXYANIONS?

Studies:

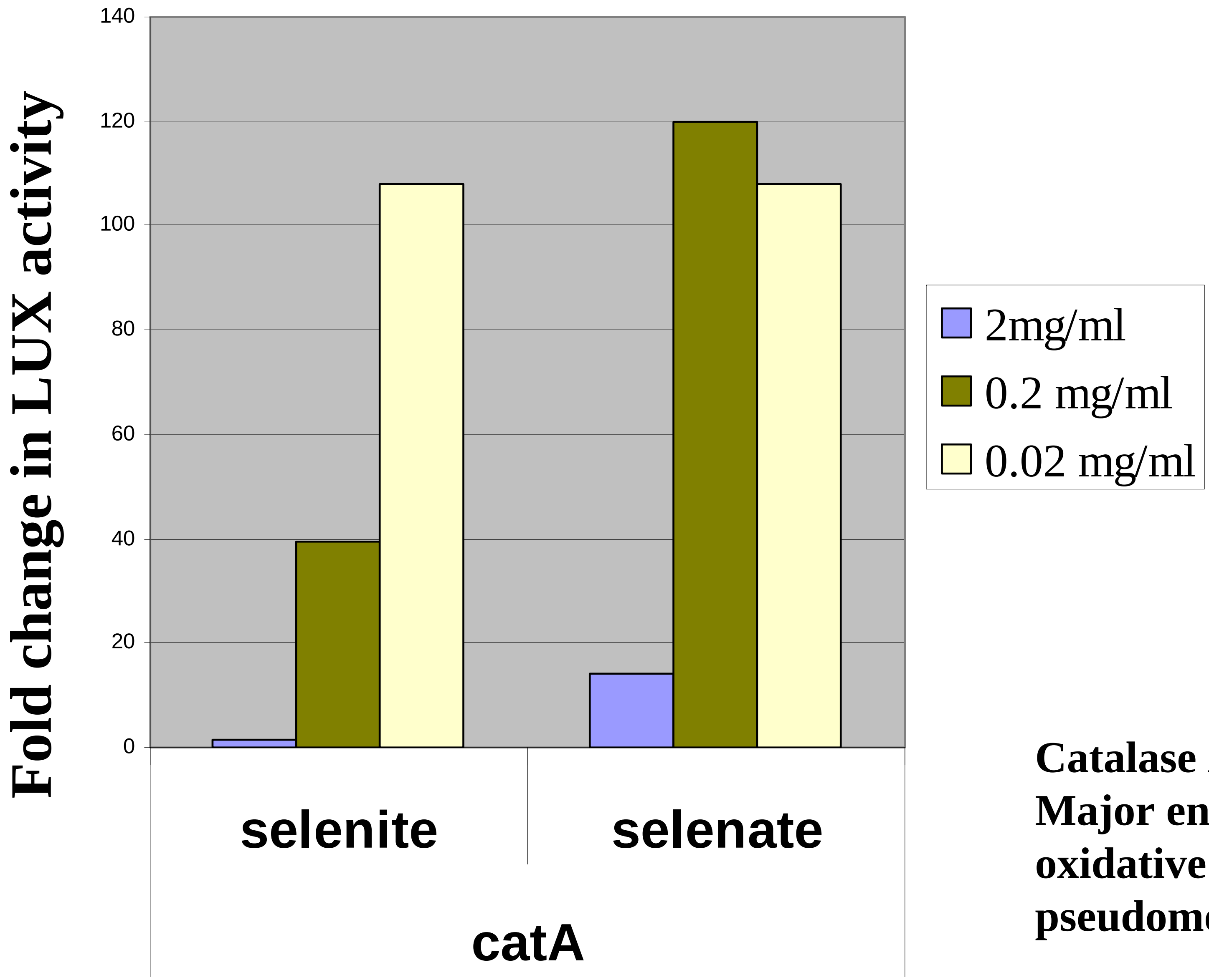
1) Examined change in expression from promoters of genes in the pseudomonad using a Lux ::promoter fusion constructs

2) Examined for the production of elemental Se from the oxyanions

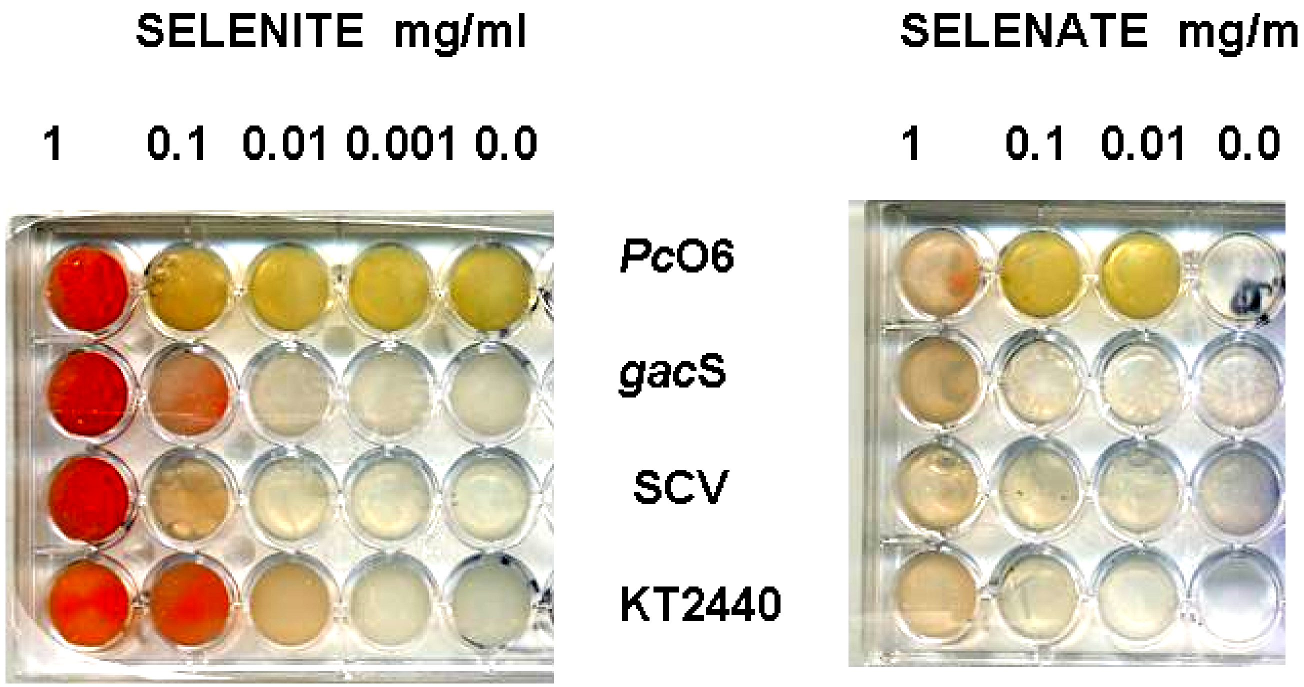
Generation of Luciferase Biosensor



Lux activity from pseudomonad biosensor changes after treatment with selenite or selenate



Catalase A
Major enzyme to combat oxidative stress in the pseudomonad



Oxyanions (selenite preferred) are reduced to red-colored insoluble nanoparticles of elemental selenium
AND release of gaseous hydrogen/methyl selenides occurs

POTENTIAL REMEDIATION SCHEME

Selenite/selenate contaminated water

↓

Biofilter system

↓

Insolubilization of Se as elemental particles and release as volatile methyl selenides because of microbial metabolism

Phytoremediation /stabilization with Se-active root colonizers and plant metabolism

Phytoremediation at Gunnerson,Colo

Bioavailability of toxic metals:

Biosensors for Cu and Cd ions : Development and Environmental Testing

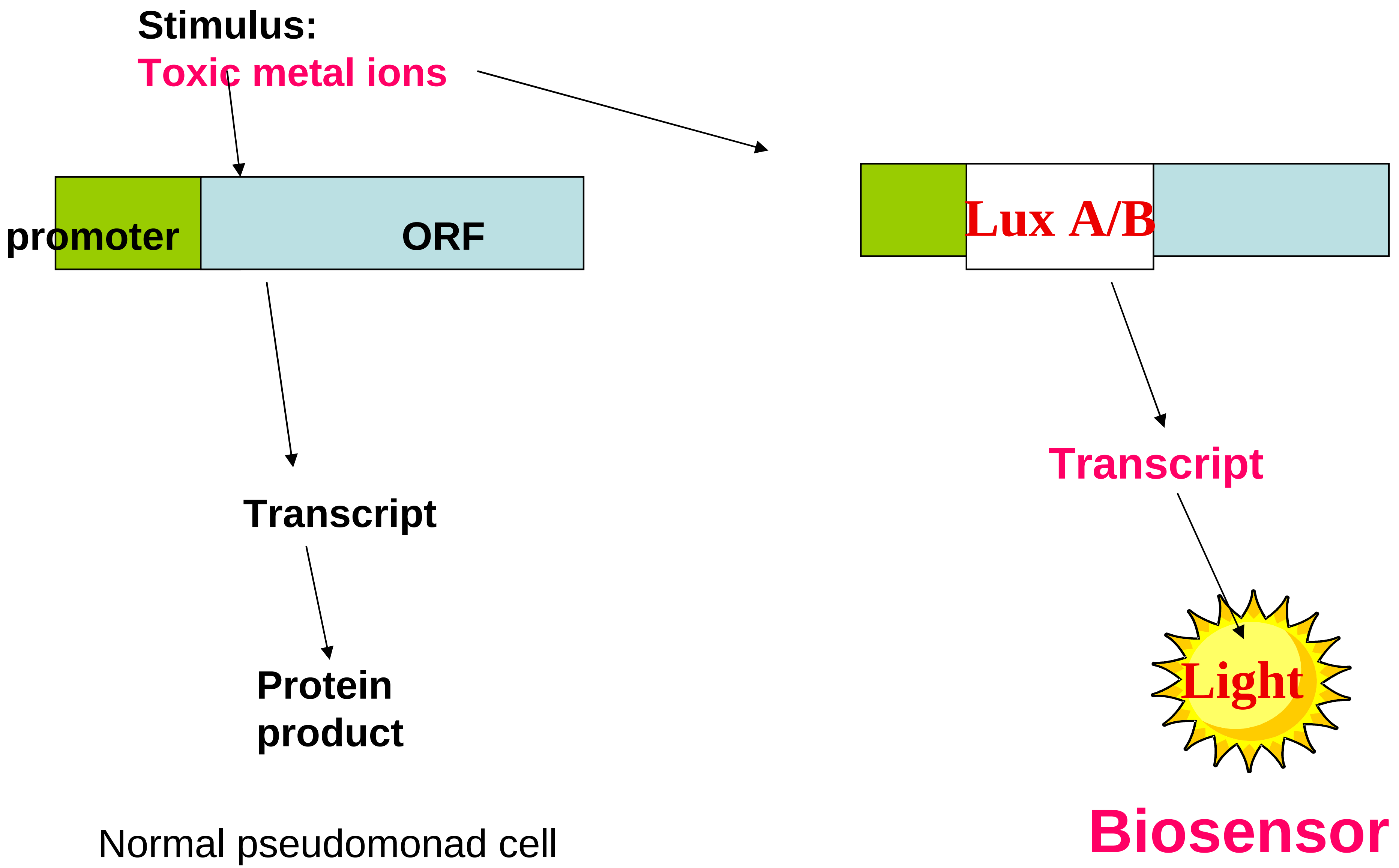
EPA STAR program

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # RD-83090701-0

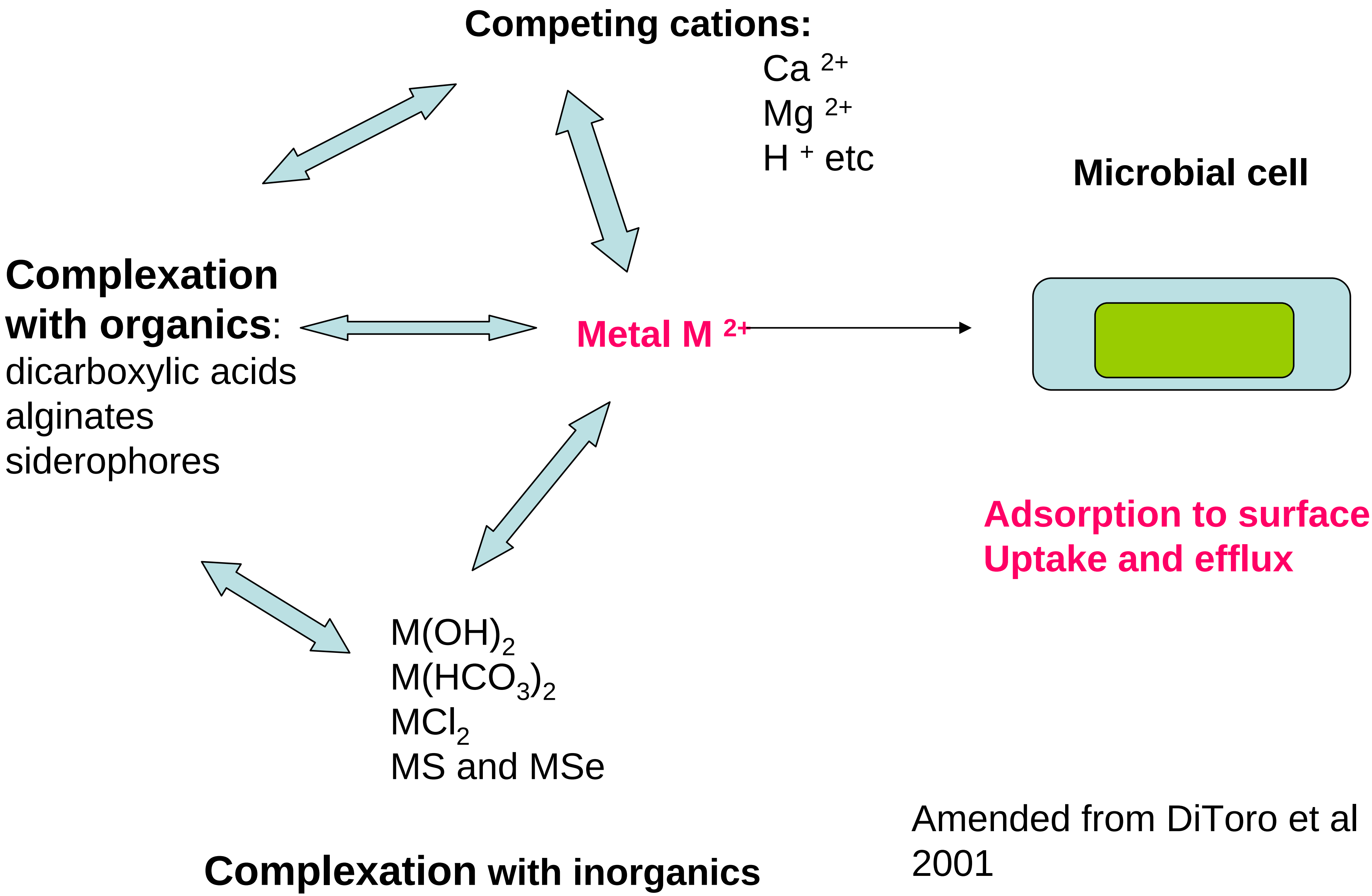
Investigators:
Anne J. Anderson, Charles D. Miller and Joan E. McLean

**Based on the difference between chemical assessments of total toxic metal
and its apparancy to a living cell.**

Generation of Luciferase Biosensor in Pseudomonads



Model for factors involved in bioavailability of metal ions



Amended from DiToro et al 2001

Are materials used as nanoparticles bioactive with the pseudomonads?

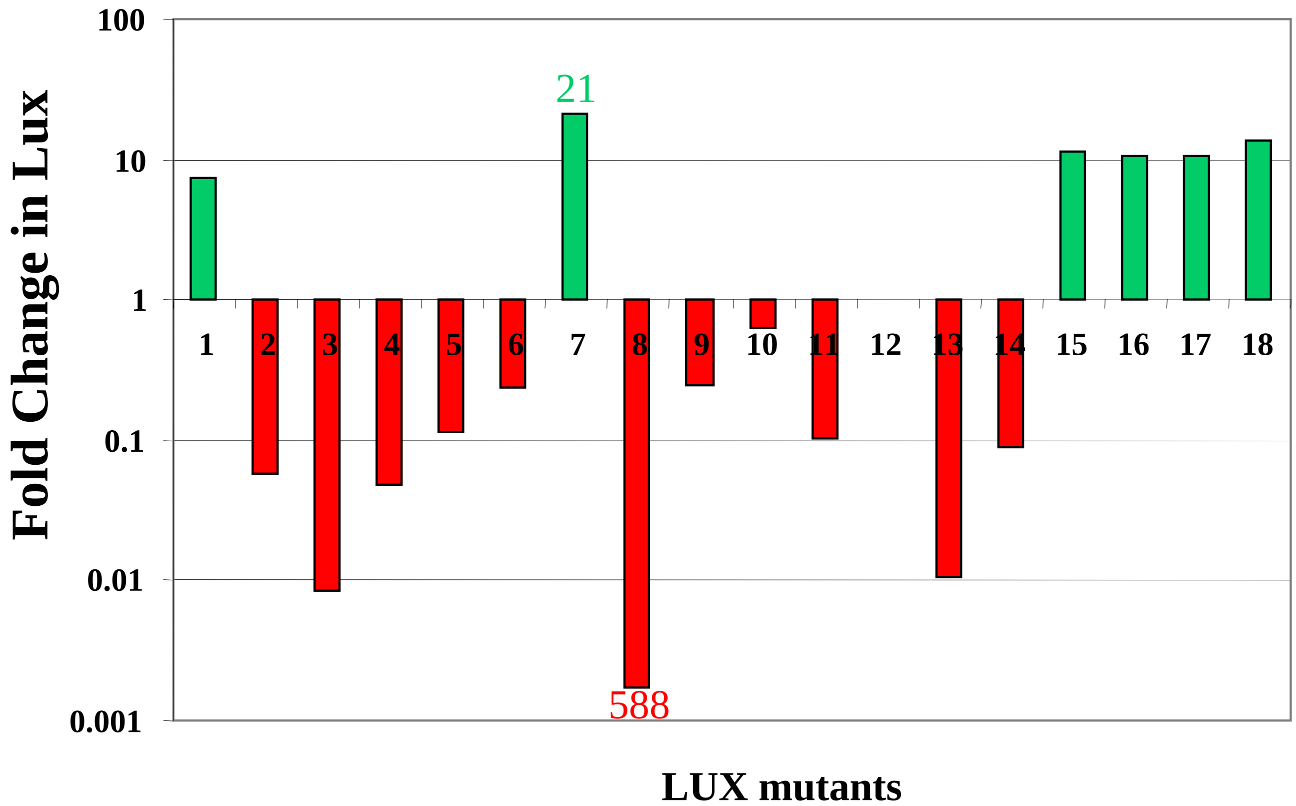
Studies with:

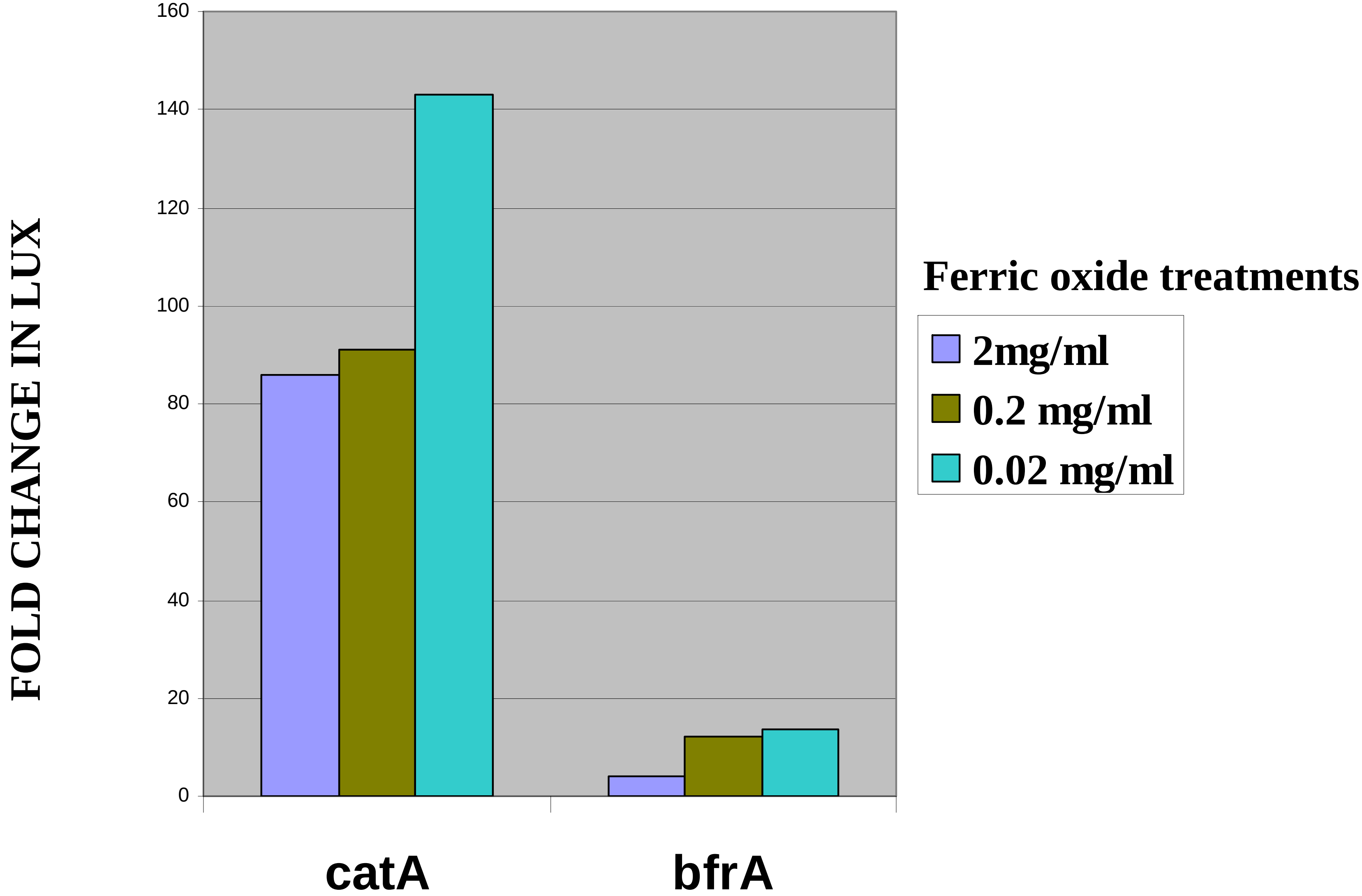
Ferric oxide

and CdSe and CdS

COMPLEXATION CHEMISTRY PREDICTS LITTLE EFFECT

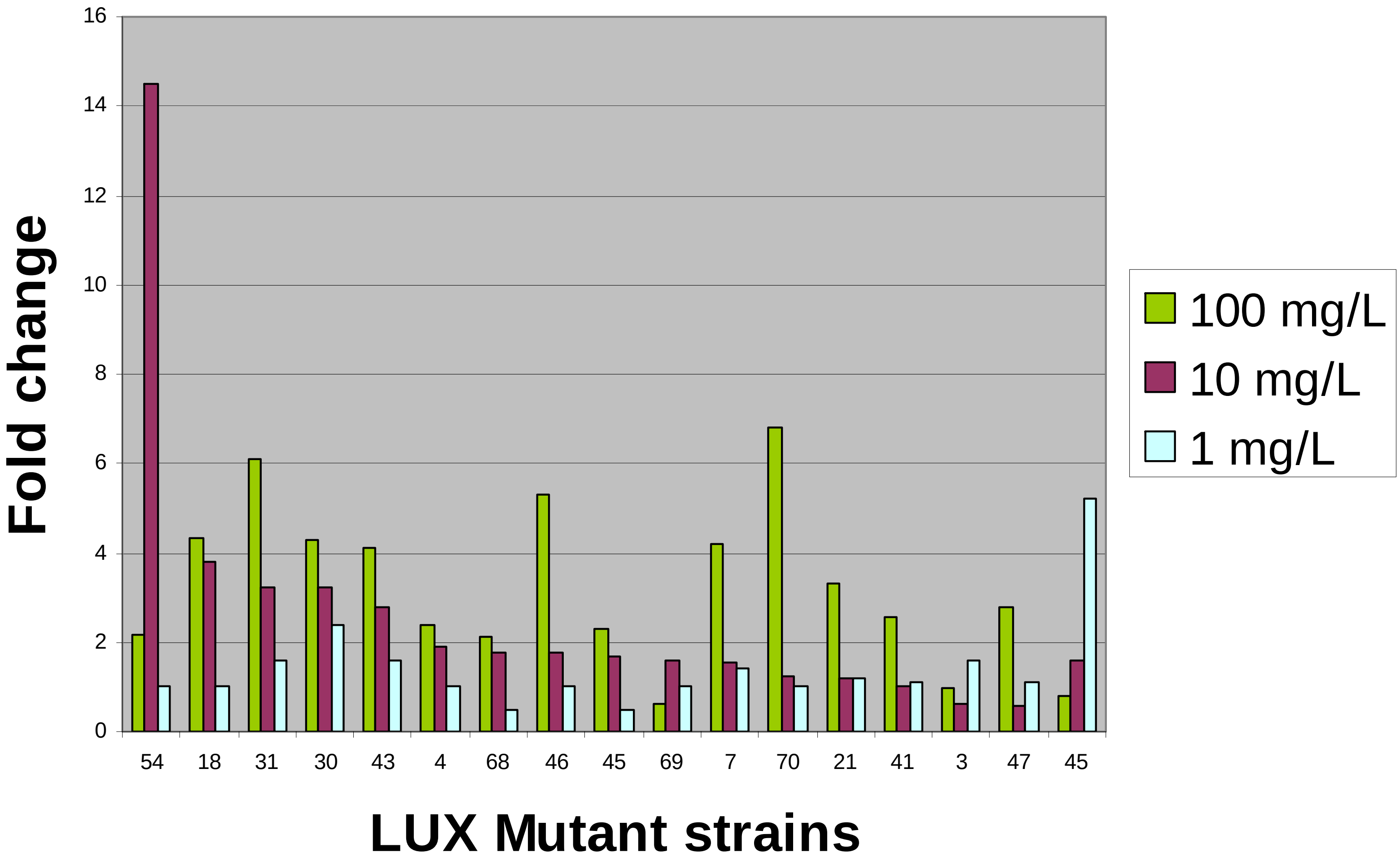
An array of KT2440 mutants change LUX expression when exposed to Fe^{3+} (1000 ppm)

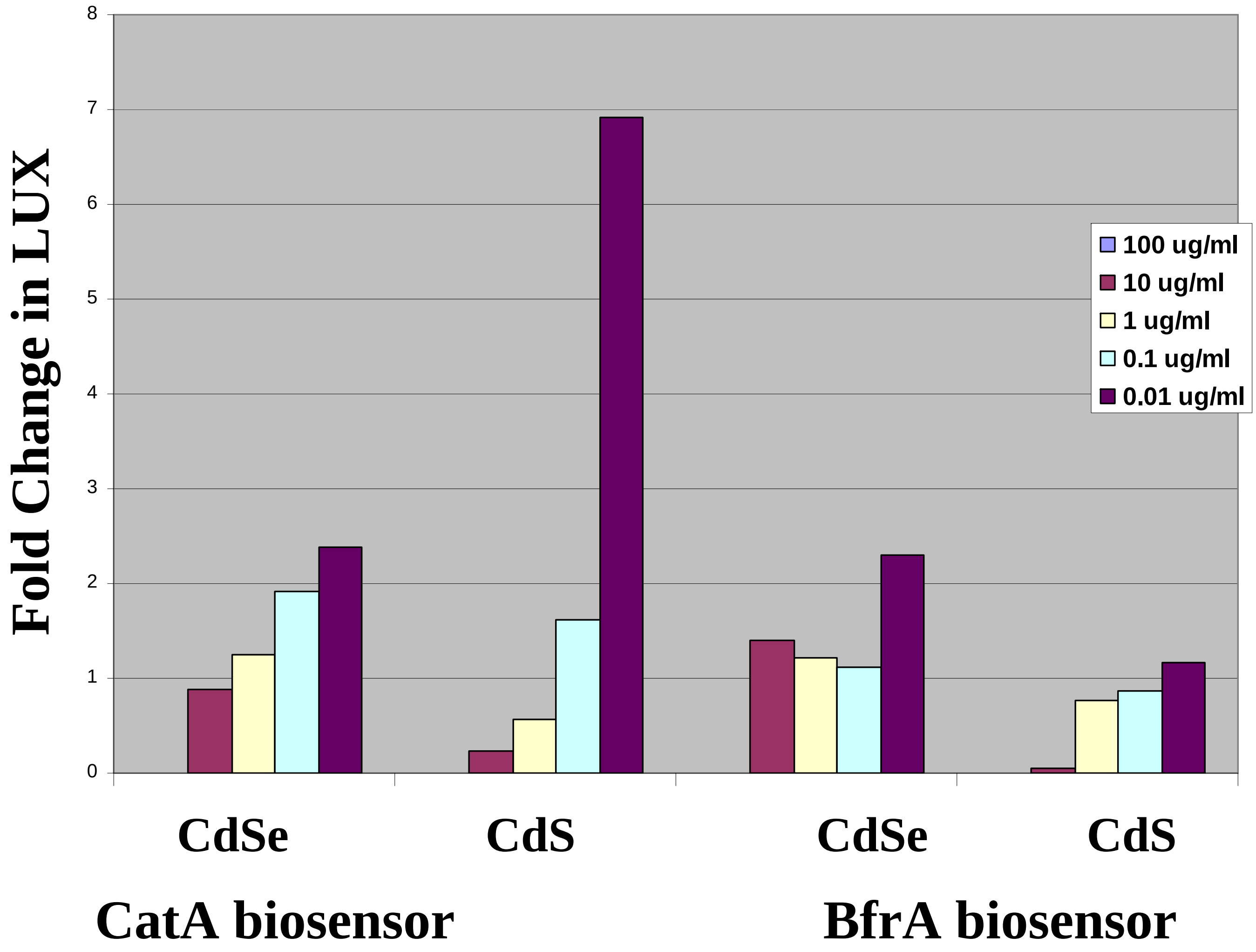




Pseudomonad cells respond to ferric oxide:
Is this an oxidative response?

Specific KT2440 mutants respond to Cd^{2+}:





Findings: TOXIC response at high doses
oxidative stress at lower doses?

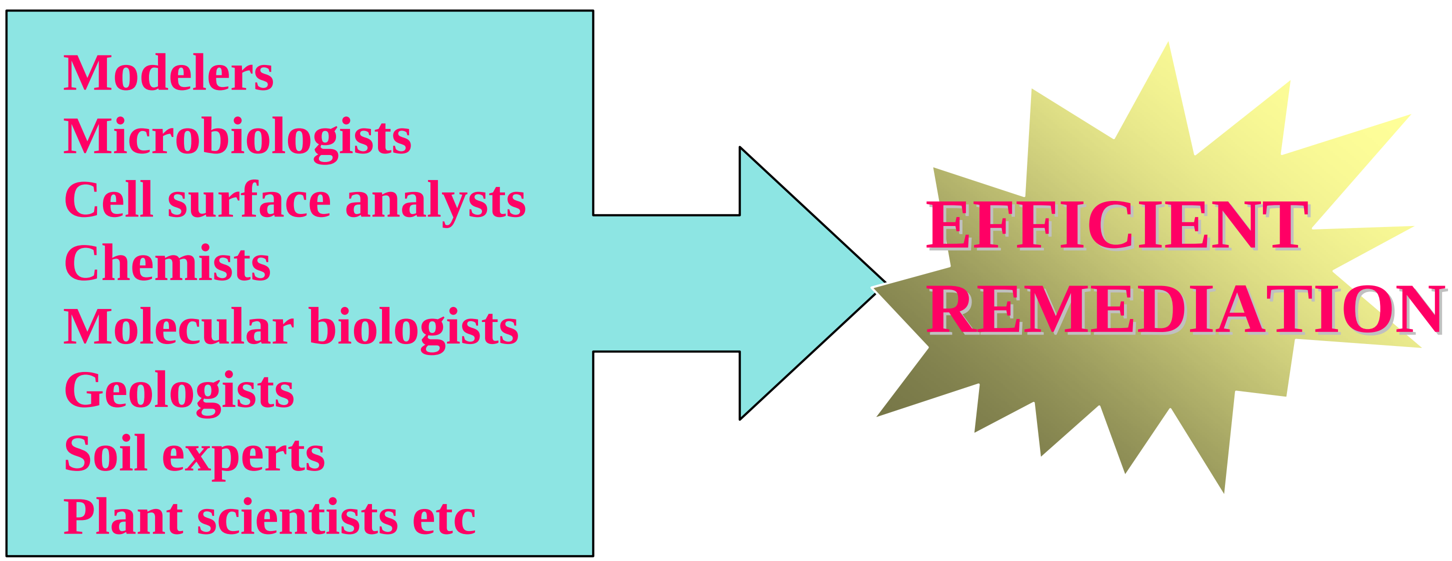
COULD THIS BE DUE TO CELL DAMAGE? (Klabunde et al Kansas State University)

Summary:

Bioactivity, reactivity and nanoparticle chemistry is intimately connected with remediation using man-made particles or microbes

Microbial depositions of nanoparticles during detoxification may bridge to other commercial uses

Future studies involving team work with scientists of different skills may enhance remediation efforts:



Support and Interaction:

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Utah Agricultural Experiment Station

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Mycobacteria and Root Colonization: role in phytoremediation of polycyclic aromatic hydrocarbons:

DOE/JGI Genomes for Life Sequencing project;

NSF phytoremediation program