Green Chemistry: systematically dealing with toxics

Terry Collins

Delta Chelsea Toronto, May 18, 2006, Toronto, Canada

Western Civilization is not sustainable as it is currently constituted

— flawed technologies are an important component of the sustainability dilemma

The Fundamental Green Chemistry Concept

$$\text{Risk} = f_1(\text{exposure}) \times f_2(\text{hazard})$$

Paul Anastas and John Warner

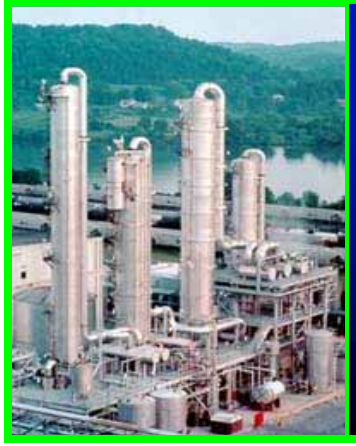
Safe Energy

New chemistry for solar-to-electrical or solar-to-chemical energy conversions

Renewable Feedstocks

Economical feedstocks for chemical and polymer industries from plants

The Chemical Goals for Sustainability



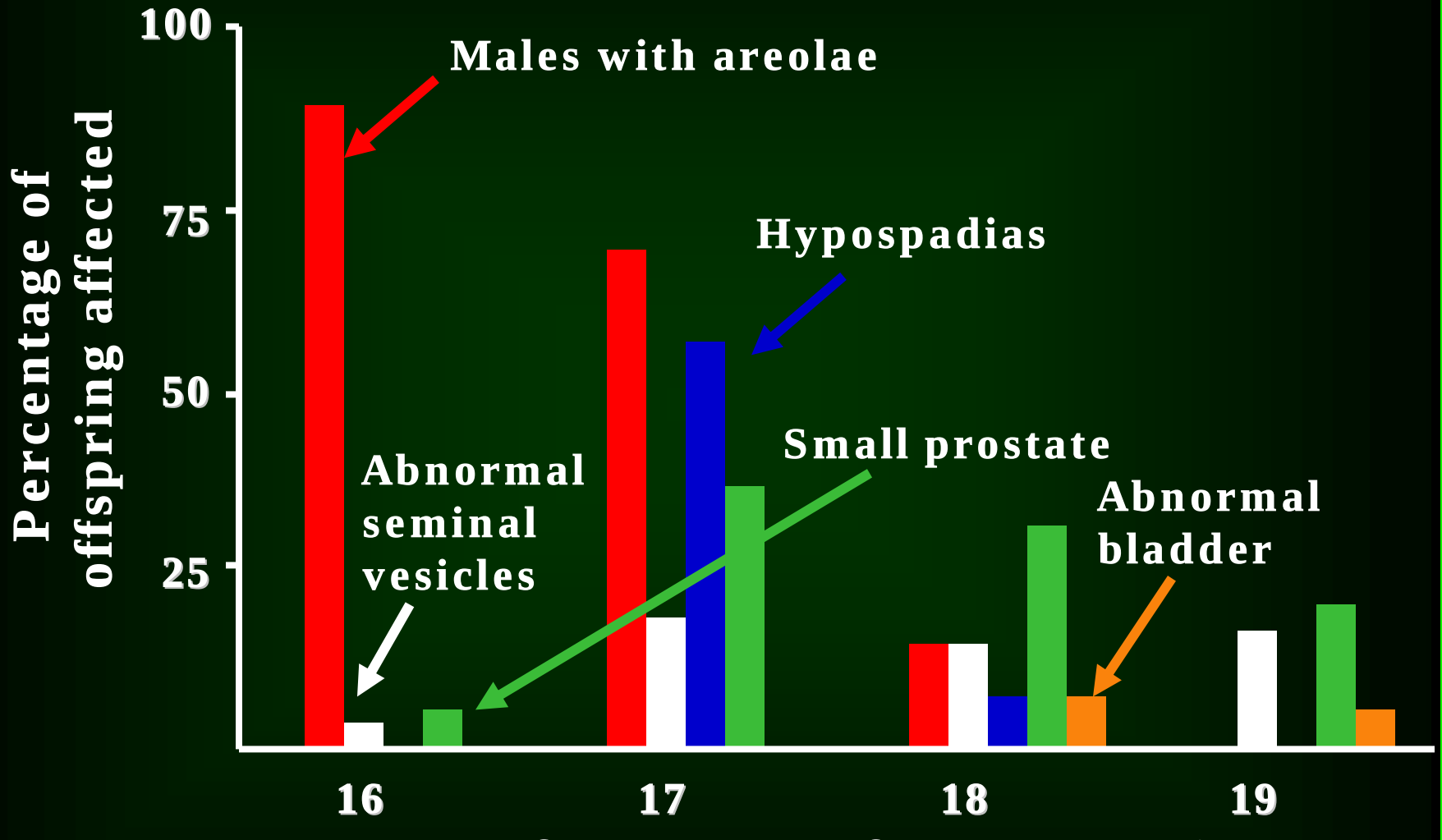
Pollution Reduction

Move the elemental composition of technology closer to biochemistry to eliminate persistent environmentally mobile pollutants

The stakes of failing to address toxicity and ecotoxicity are incredibly high.

- Decrease in anogenital distance among male infants with prenatal phthalate exposure, Shanna Swan et al., *Environmental Health Perspectives* on-line May 27, **2005**
- Exposure to methoxychlor and vinclozolin produces male reproductive problems down 4 generations, Michael Skinner et al., *Science* **2005**, *308*, 1391-1392**2005**.
- Perinatal exposure to low levels of the environmental anti-androgen vinclozolin alters sex-differentiated social play and sexual behaviors in the rat, Vincent Markowski, et al., *Environmental Health Perspectives*, **2005**, *113*, 700-707
- Use of di(2-diethylhexyl)phthalate-containing medical products and urinary levels of mono(2-diethylhexylphthalate) in neonatal intensive care units, Howard Hu et al., *Environmental Health Perspectives*, on-line, June 10, **2005**.

Exposure to anti-androgen, Flutamide



Courtesy of
J. Peterson Myers

Paul Foster and Martha Harris, *Toxicol Sci*, **2005**, 1591

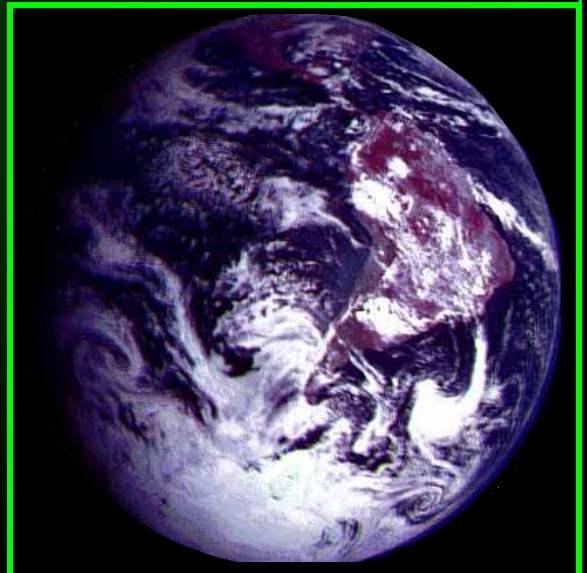
How might chemists learn how to avoid known hazards in the design of products and processes: ***how should we teach green chemistry?***

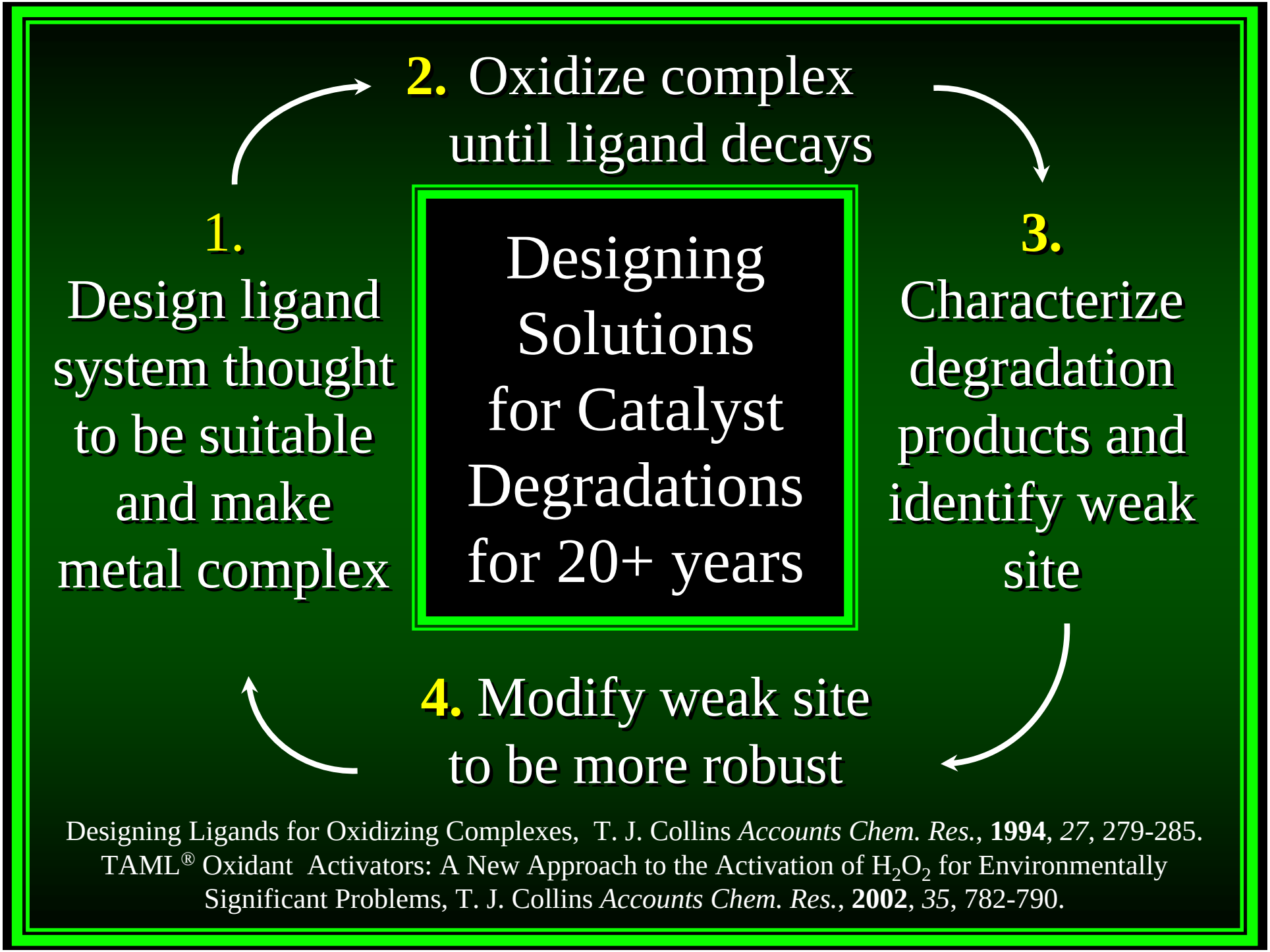
- Historical analyses building from the anecdotal, to the epidemiology, to the molecular level understanding — ***grounding and importance***.
- Toxicity education and testing as an integral component of chemical research ***—need universally accepted assays for endocrine disruptors and to teach endocrine disruption to chemists!— guidance***.
- More interdisciplinary research involving chemists and toxicologists — ***synergy***.
- An outright rejection of “spin” — ***obligation***.

Greening Oxidation Chemistry

Replace chlorine technologies with alternatives based on Nature's oxidants oxygen or hydrogen peroxide

Develop oxidation catalysts for oxygen or hydrogen peroxide comprised of the common elements of biochemistry—C, H, O, N, Fe

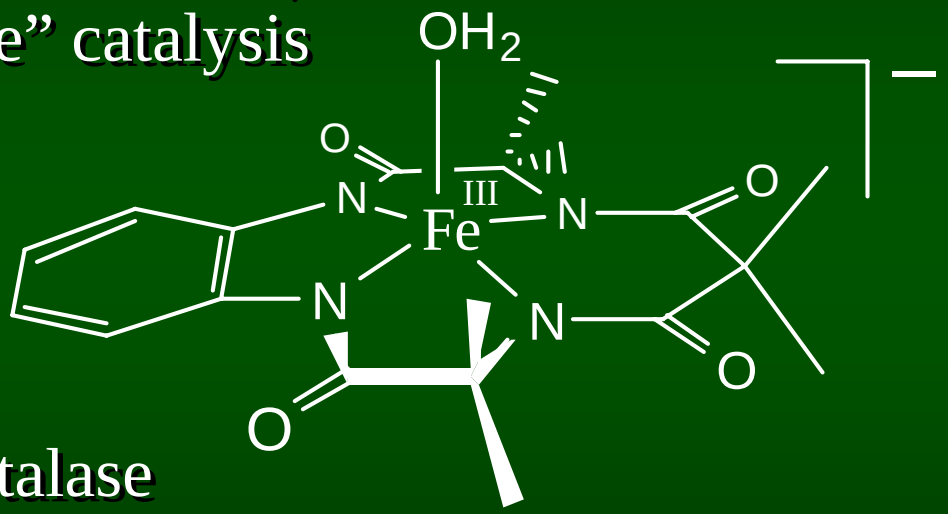




Designing Ligands for Oxidizing Complexes, T. J. Collins *Accounts Chem. Res.*, **1994**, *27*, 279-285.
TAML® Oxidant Activators: A New Approach to the Activation of H_2O_2 for Environmentally Significant Problems, T. J. Collins *Accounts Chem. Res.*, **2002**, *35*, 782-790.

TAML® Catalyst Features

- biochemically common elements — prototype v. low toxicity
- effective at 0.1 to 4 ppm = nM to low μM
- beginning of “dial-a-lifetime” catalysis
- economical to synthesize
- water-soluble
- usable from pH 1 to 14.5
- efficient users of peroxide
  —fast peroxidase/slow catalase



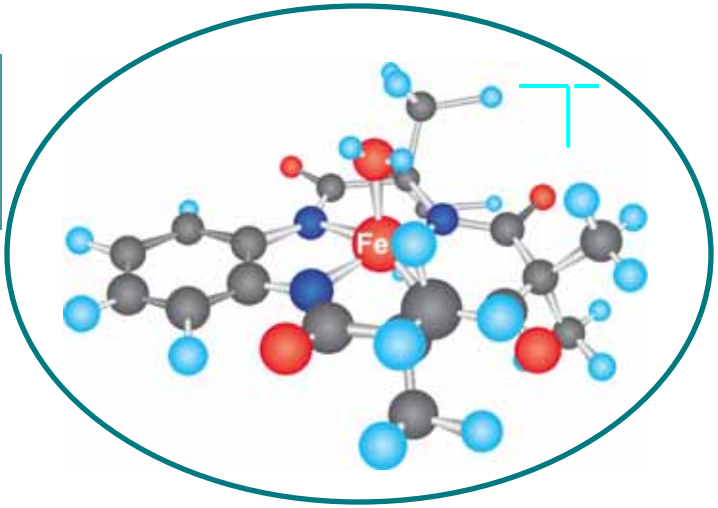
- 10 US patents, 86 counting foreign nationalizations
- two licenses in place
- ~ 100 companies have CDA with Carnegie Mellon University
- next step is multi-ton production

Peroxidase Mimics
first effective peroxide-using enzyme mimics

Mechanism
detailed understanding of catalytic mechanism

High Oxidation state Chemistry
synthesis and characterization of rare or unprecedented species

Water Cleaning
chlorinated pollutants, phenols destruction



Oxygen Chemistry
direct reaction of oxygen with ferric ion

Biological Warfare
Rapid destruction of anthrax-like spores

Textiles
dye bleaching, effluent decolorization

Pesticides Decon
major class (thiophosphates) rapidly-completely destroyed

Pulp and Paper
pulp bleaching, effluent smell, organochlorine and color removal

Military Chemical
rapid destruction of toxic residuals & CWAs

Laundry
dye transfer inhibition, stain removal

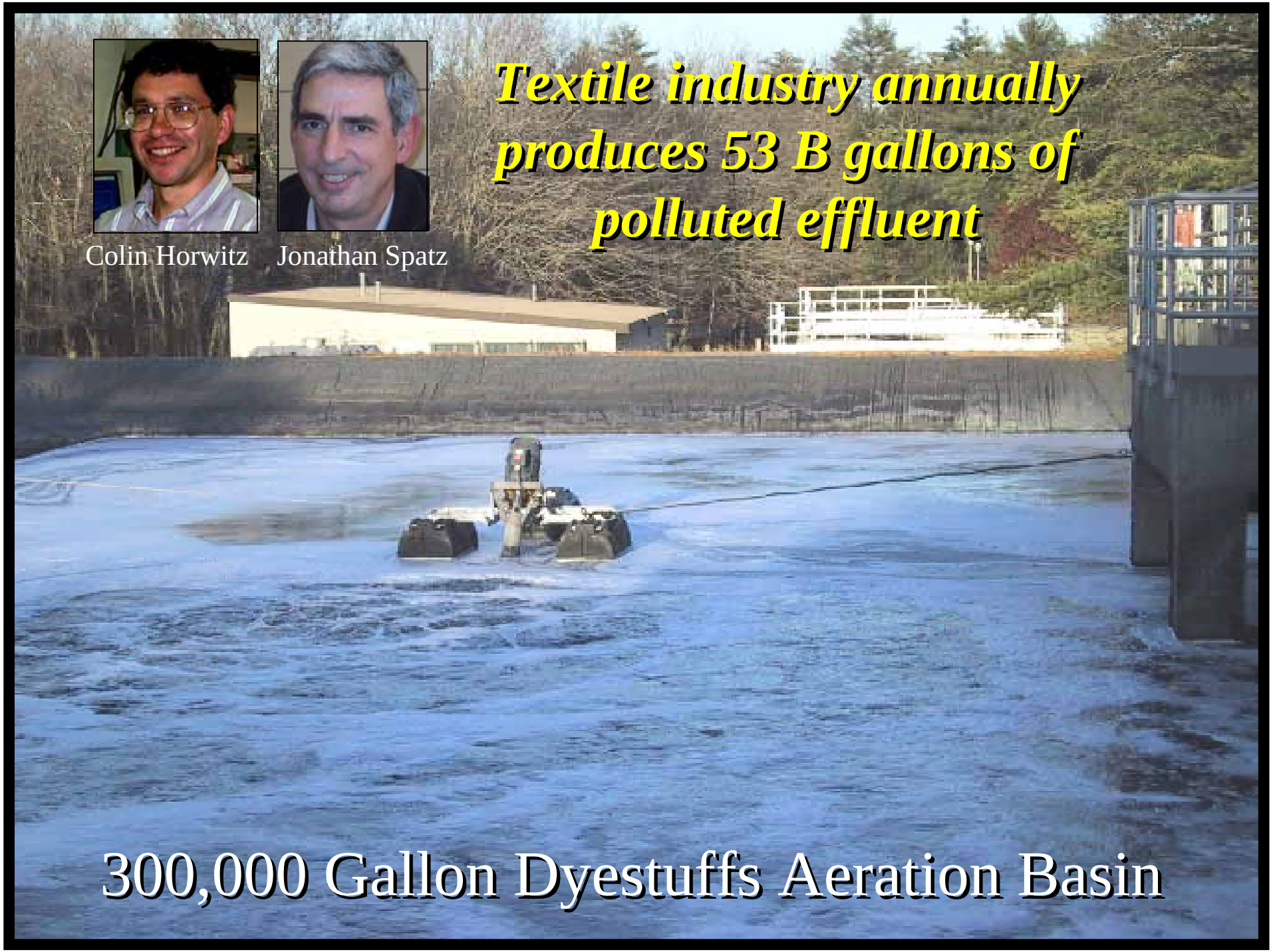
Pharmaceuticals Decon
trace pharmaceuticals removed from water supply

Petroleum Refining
removal of sulfur contaminants in diesel & gasoline

Drinking Water Disinfection
safer drinking water free of chlorinated disinfection byproducts

Agricultural
animal husbandry, renewable feedstocks

Others
metal refining, carpet recycling, hospital disinfection

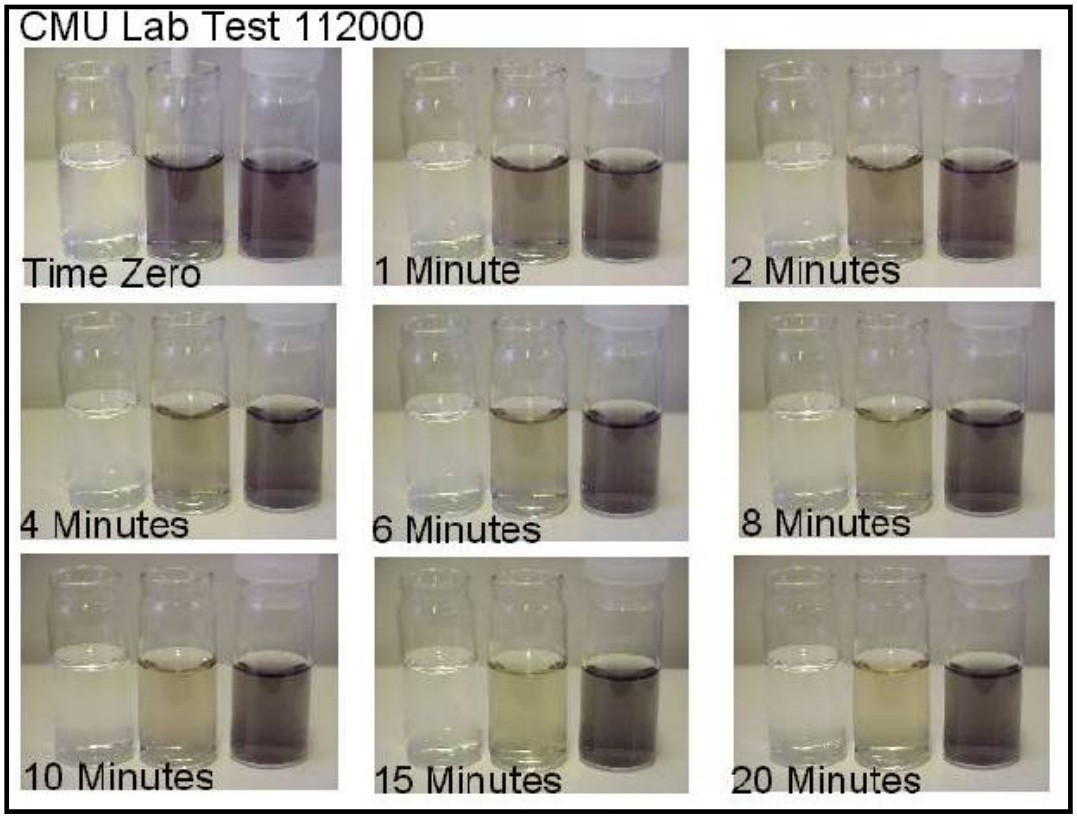

Colin Horwitz
Jonathan Spatz
Textile industry annually produces 53 B gallons of polluted effluent
300,000 Gallon Dyestuffs Aeration Basin

TAML®-Activated Bleaching of Composite Textile Industry Effluent

8 hr Composite Effluent

- Clay dispersion
- Ammonium sulfate
- Isopropanol
- Alkyl ether salts
- Anionic leveling agents
- Quaternary compound
- Acetic acid
- Anionic reserving agent
- Intralan black MRL
- Nylanthrene black
- Intralan black RB
- Acid green 25
- Acid orange 116

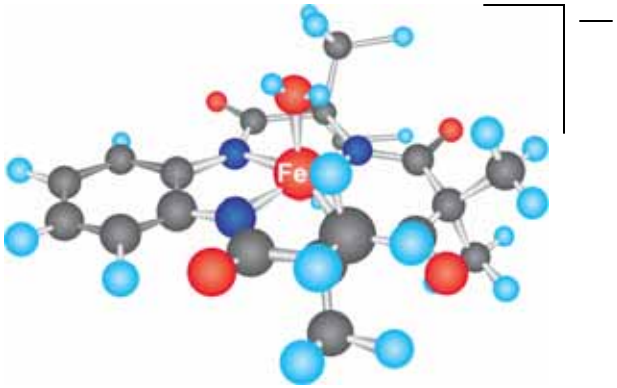
Conditions: 2.3 μM FeB*, 5 mM H_2O_2, pH ~ 12, T = 25ºC



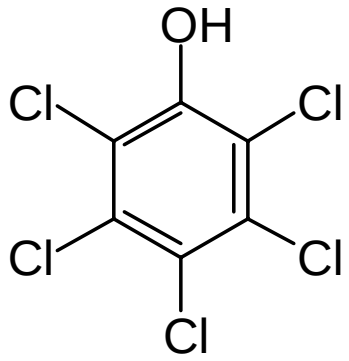
Degradation of Pentachlorophenol (PCP)

Sayam Sen Gupta

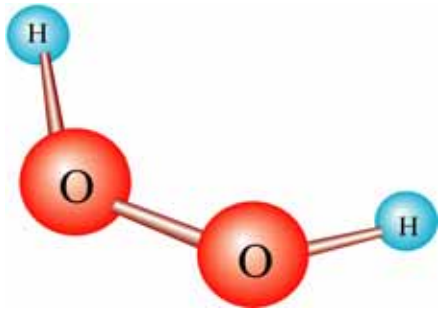
Reaction Conditions



1 equivalent
(7 μM)



715 equivalents
(5 mM)



100,000 equivalents
(0.5 M)

- pH 10, carbonate buffer—used to dissolve PCP
- 25 °C, 9 minutes reaction time—quench with HCl
- 9 equivalents of H_2O_2 stoichiometric for complete mineralization

Chris Noser

Mathew Stadler

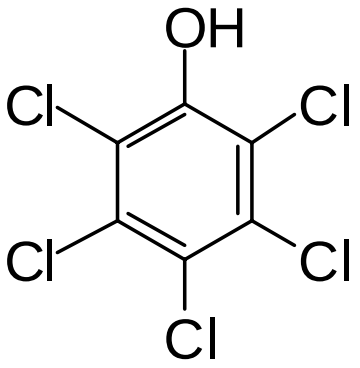
PCP Degradation Profile

S. Sen Gupta et al. *Science*, **2002**, *296*, 326-328

Sayam Sen Gupta

No dioxins within limits of experimental detection

TAML activators, low toxicity

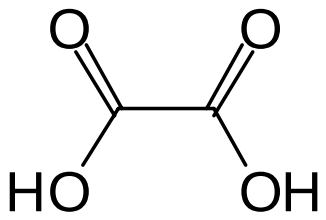


Cl^-

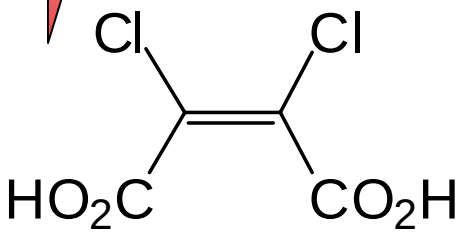
87±4% Cl

CO_2 + CO

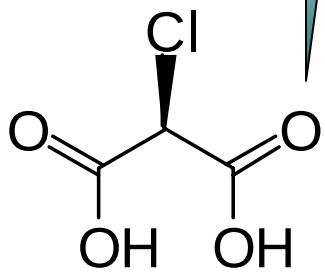
45±3% C



23±1% C



17±1% C



6% C

FOUND

- 91±5% C
- 99±4% Cl

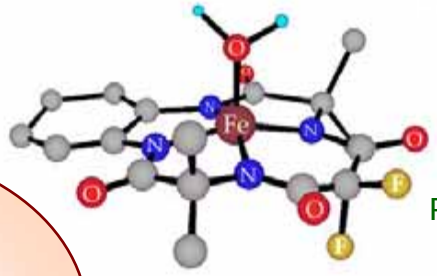
Single treatment

pH 7 treatment removes RX

Arani Chanda

Summary of Results

Sushil Khetan



Fenitrothion

Minor Pathway

Fenitrooxon

Peroxide assisted Hydrolysis

Fe-TAML®

H_2O_2

Major pathway

Oxidative hydrolysis

p-nitrocresol

Oxidation

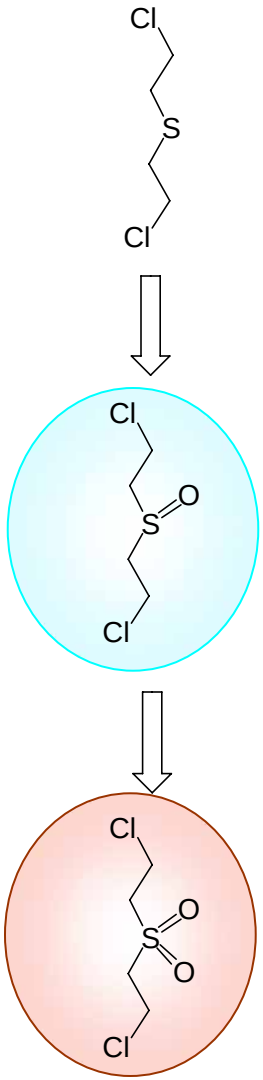
Formic Acid | Oxalic Acid | Maleic acid | Methyl maleic acid | Mineralization

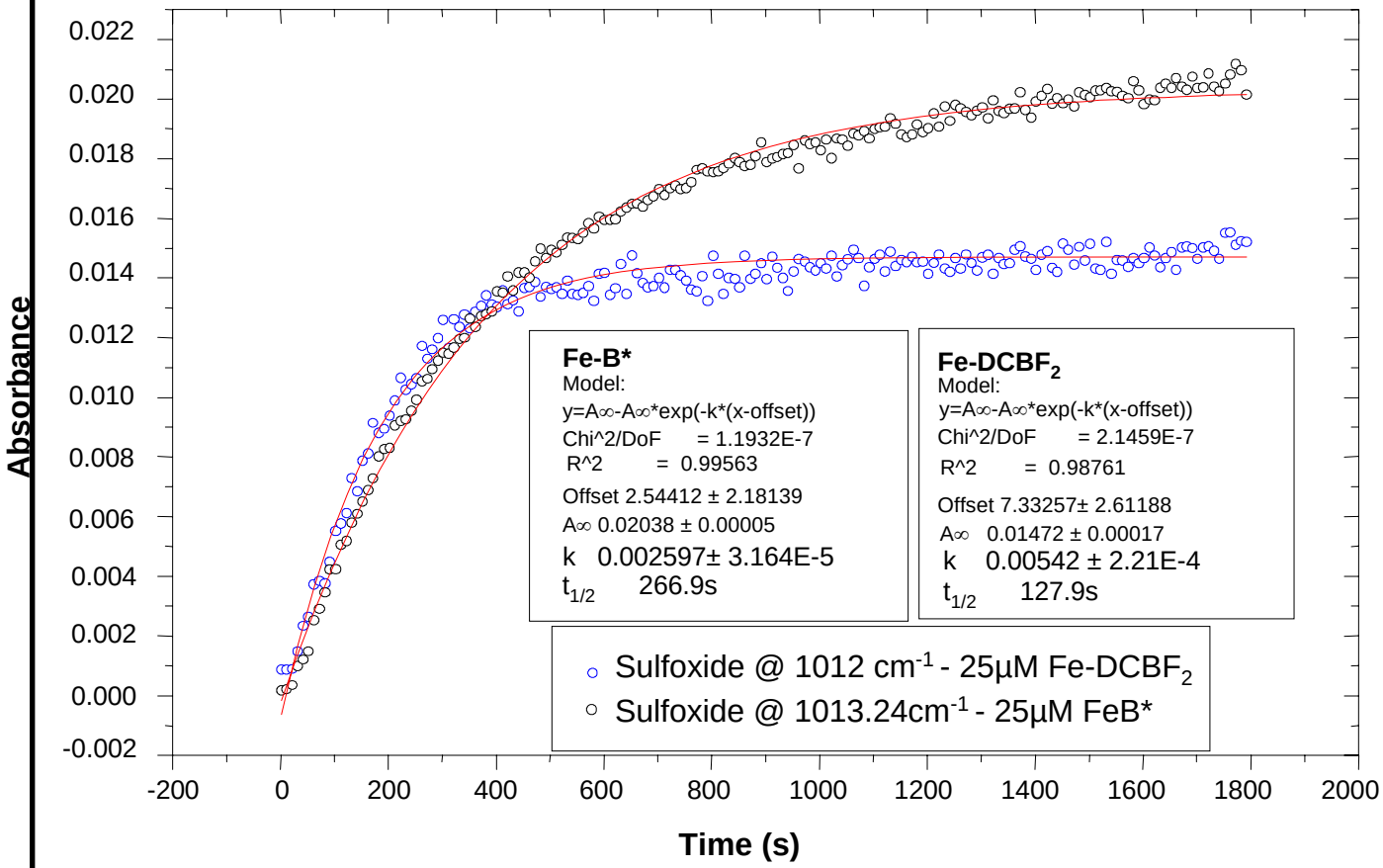
$CO_2 + H_2O + SO_4^{2-} + NO_3^- + NO_2^{--}$

HD Decon

TAML activated H_2O_2 Oxidation of Sulfur Mustard

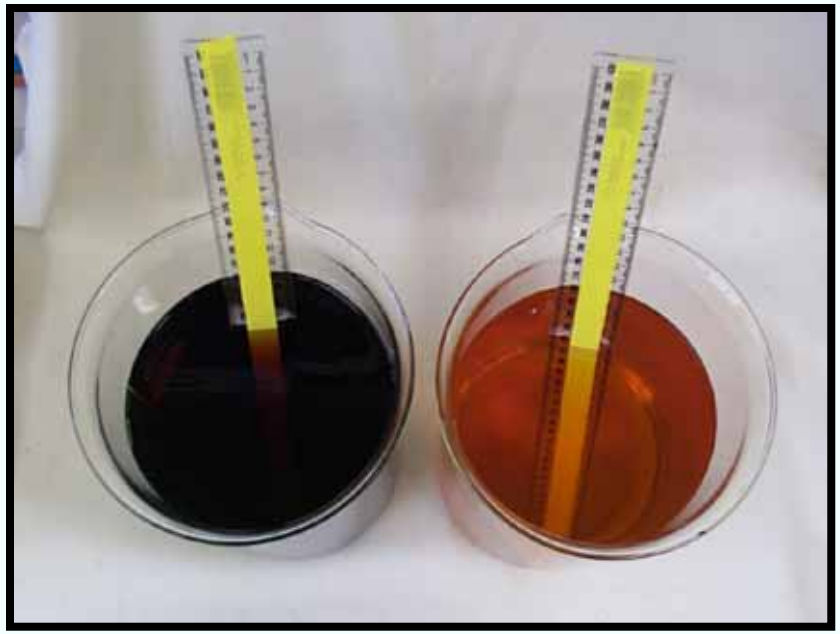
(In 30% ^{t}BuOH and 70% aqueous peroxide (5%)





A pseudo-first order fitting curve reveals that oxidation catalyzed by $FeDCBF_2$ proceeds with a measured “half-life” of 128 seconds, or just over 2 minutes. This is now approaching the speed necessary for a viable battlefield decon system. - Dr. S.J. Mitchell, DSTL, England

TAML®-Activated Peroxide Reduces "Color" Significantly

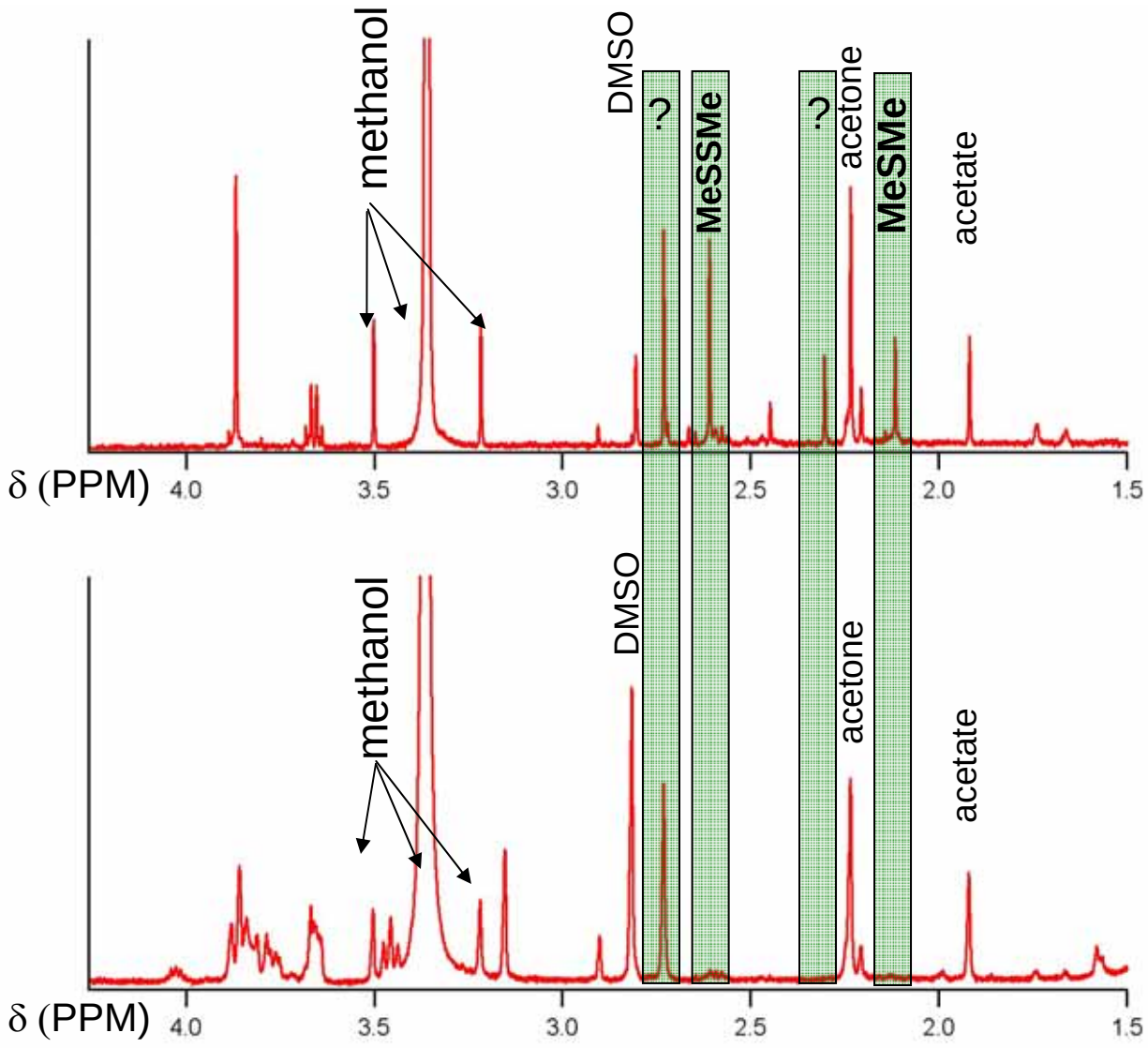


Removal of Foul Condensate Sulfur Odor Compounds

Evan Beach

NSF Predoctoral Fellow

^{1}H NMR Spectrum of Foul Condensate



$1x10^{-4}$ M NaFeB*
1 M H_2O_2
70°C
10 min.

Biological Warfare Agents

"Green" Oxidation Catalysis for Rapid Deactivation of Bacterial Spores, D. Banerjee, A. L. Markley, T. Yano, A. Ghosh, P. B. Berget, E. G. Minkley, Jr. , S. K. Khetan, and T. J. Collins*, *Angew. Chem. Int. Ed.* **2006**, *45*, 0000

Deboshri Banerjee

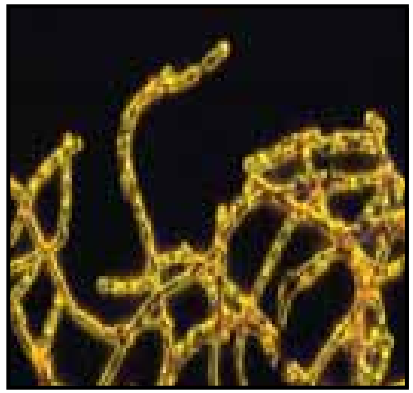
Teresa Heinz Scholar for the Environment (2005)

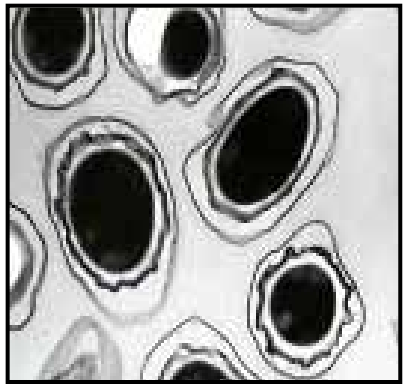
A microorganism or its by-product (toxin), which causes disease in man or plants or deterioration in materials; weapons of warfare and/or terrorism

Major Threats

- **Bacterial Diseases**
  - **Anthrax**
  - Tularemia
  - Plague
- **Viral Diseases**
  - Smallpox
  - Viral hemorrhagic fevers
- **Toxins**
  - Botulinum Toxins
  - Ricin

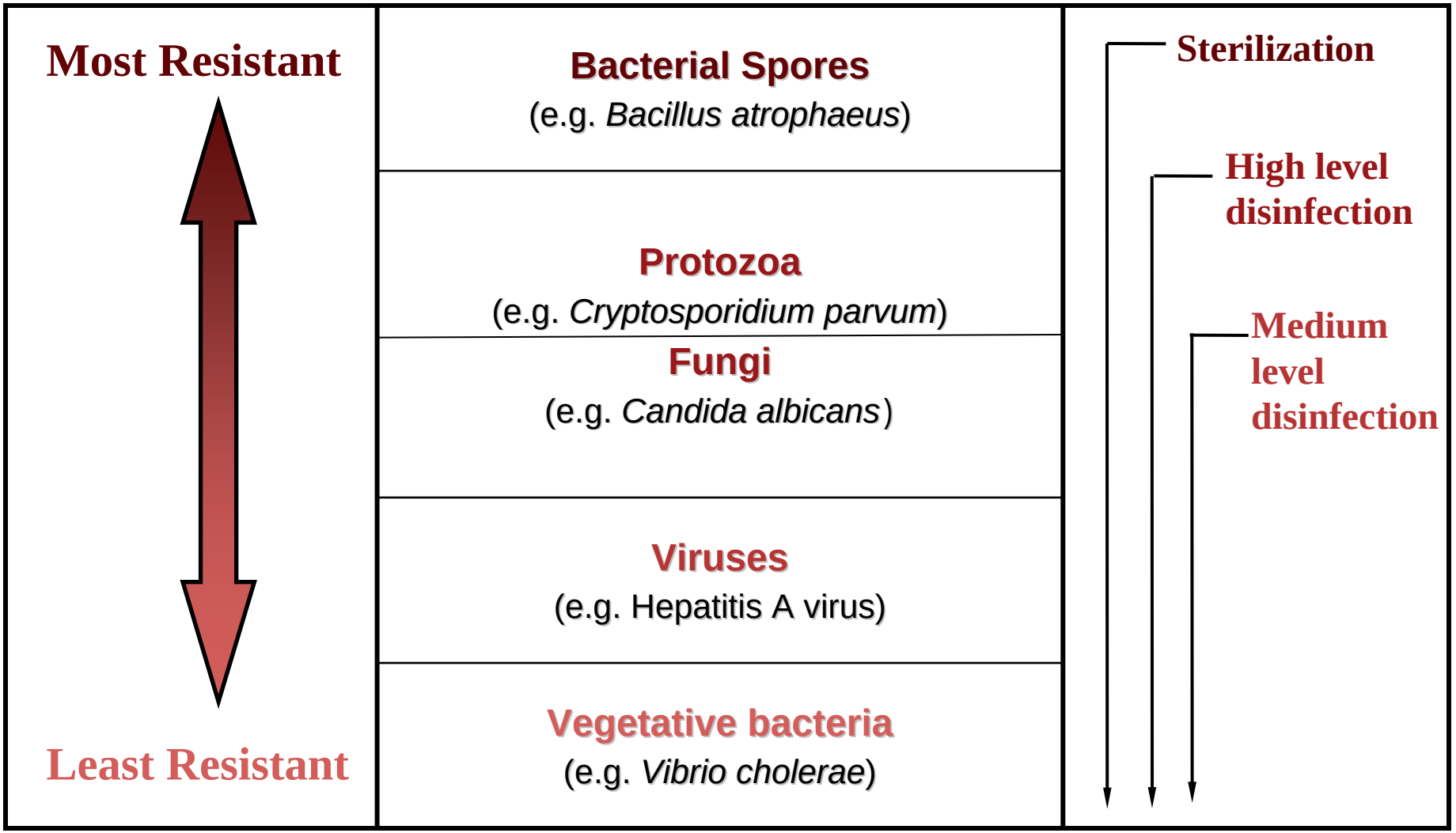
Bacillus anthracis Spores





- Dormant survival form of the vegetative bacterium
- Resistant to stress conditions, e.g. heat, ultra-violet radiations and chemical treatments
- Germinates on encountering favorable conditions

Microorganism Resistance to Biocides



Deboshri Banerjee

Breakthrough in Enhanced Spore Mortality

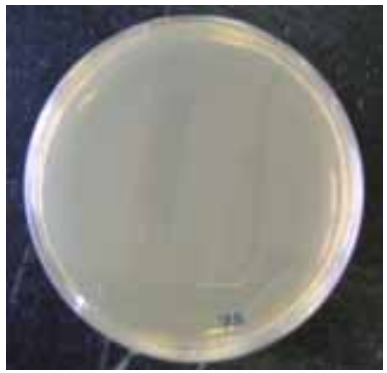
Carnegie Mellon Environmentally Safe Technologies
Institute for Green Oxidation Chemistry

Sushil Khetan

10× dilution

~75% mortality

with *tert*-butyl hydroperoxide



10× dilution

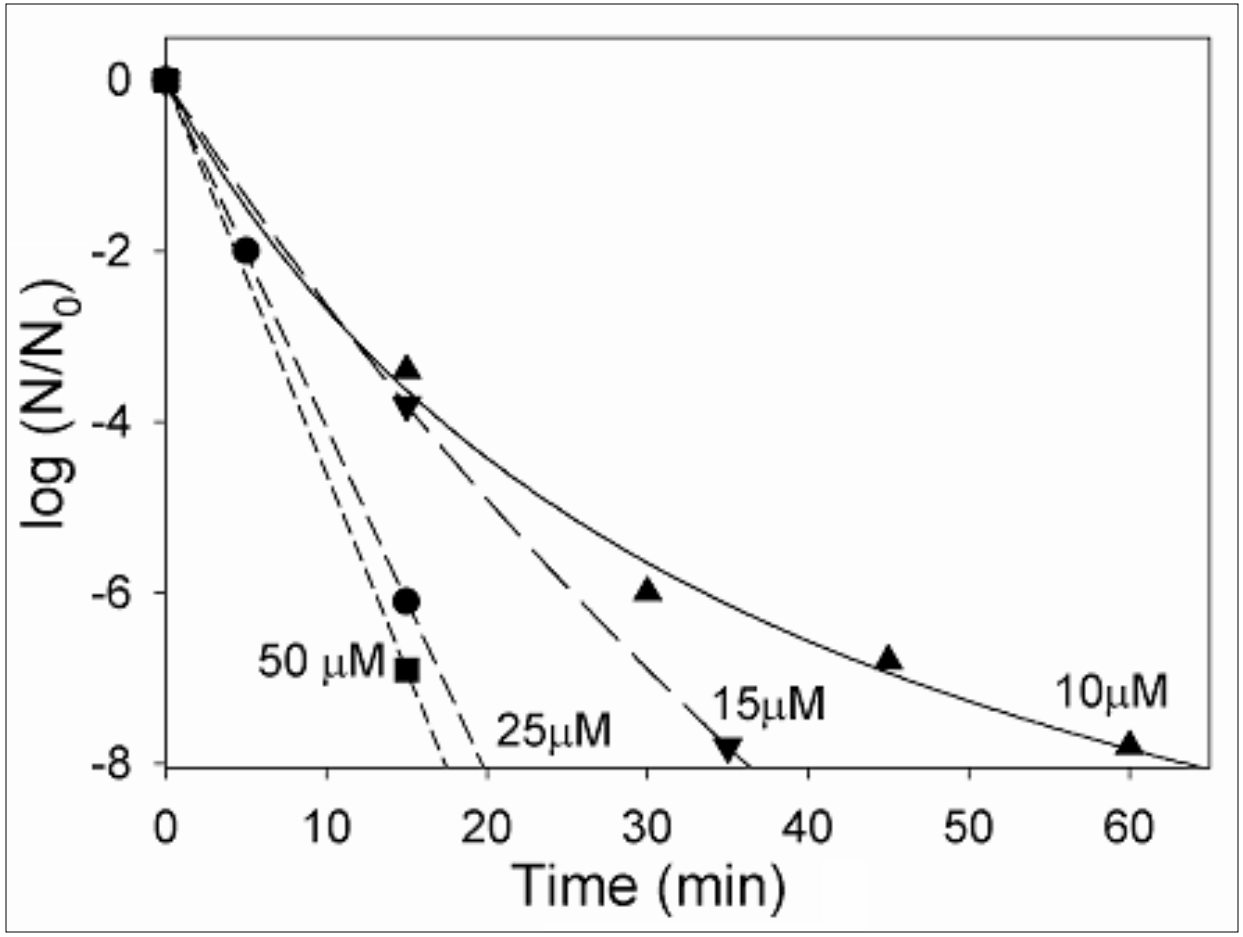
99.99999% mortality

with Fe-TAML® activator, *tert*-butyl hydroperoxide

- Treatment time: 0.75 hour
- **99.99999% (7-log) kill of spores**
- Fe-TAML®: 5 μM; ^{t}BuOOH: 0.5 M
- Spore population: 1×10^{8} cfu/ml

[TAML] Relationship to Rate of Spore Mortality

Carnegie Mellon
Environmentally Safe Technologies
Institute for Green Oxidation Chemistry



Fe-TAML (50μM)/ t-Butylhydroperoxide (0.5M) treatment resulted in spore mortality (7-log) in 15 minutes - the performance being sought by the DoD

Urgency Addiction: Chemistry

Just as it is the bane of professional life, urgency addiction could suffocate the healthy scientific pursuit of sustainability

	Urgent	Not urgent
Important	Necessity Short-term thinking	Originality Long-term thinking *Sustainability*
Not important	Deception Short-term thinking *Industrial labs*	Waste Nonthinking

INSTITUTE COLLEAGUES

Research/Business

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Dr. Sushil Khetan
Dr. Alexander Ryabov
Jonathan Spatz

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Dr. Sujit Mondal
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Governments of:

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- Japan
- Germany

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