An Investigation on Remediation of Transformer Oil Contaminated Soil by Chemical Oxidation Using Hydrogen Peroxide

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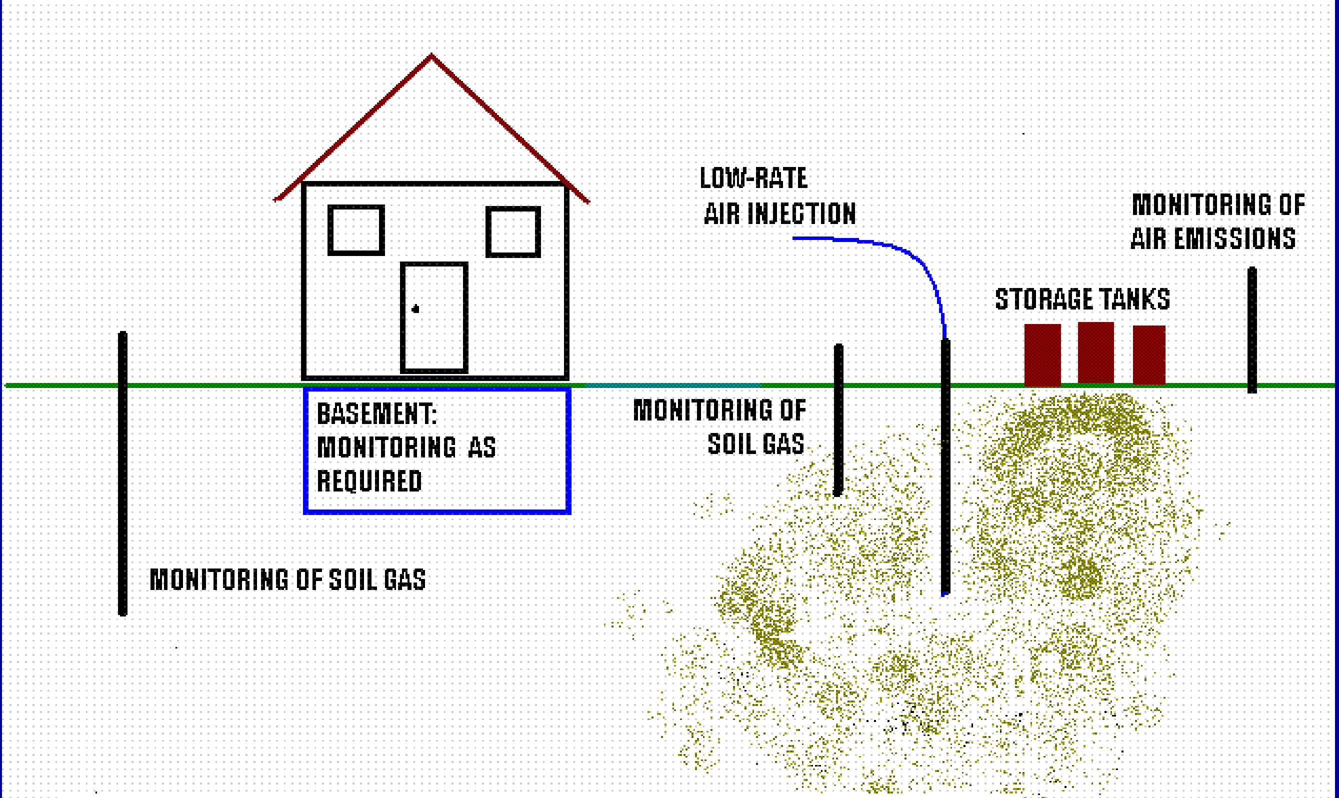
Biological remediation technologies



Bioventing by Kellyn Roth and Michael Shrader
http://ewr.cee.vt.edu/environmental/teach/gwprimer/biovent/biovent.html

Biological remediation technologies

- Process parameters:
  - Temperature, type of soils, moisture content
  - Soil pH, inorganic nutrients, and Redox potentials
  - Electron acceptors
- Advantages:
  - Low cost in investment and simplicity in operation
  - Widely accepted by most regulatory agencies
  - End products: CO_2, CH_4, H_2O, inorganic salts, and biomass
  - Lower MW HC easy to degrade: C_1-C_{15}, R-OH, Ar-OH, R-NH_2
- Limitations:
  - Relatively long time for treatment
  - Dependence on temperature and site conditions
  - Limited efficiencies for high molecular weight(>C_{20}) and multichlorinated HC, PAHs, PCBs, and pesticides

Physical remediation technologies

A soil washing plant

http://www.art-engineering.com/Projects%20Soil%20Treatment.htm

Physical remediation technologies

- Use contaminant's physical properties to remediate contaminated soils
- Physical properties include:
  - Density, solubility, liquid viscosity, etc.
  - Vapor pressure, Henry's law constant, $K_{ow,}$
- Physical removal of contaminants followed by treatments at a plant or off-site
- Process characteristics
  - Contaminants only go through physical changes
  - Less concerns of the generation of toxic intermediates or products
  - Need to treat the collected contaminants

Chemical oxidation technologies

A Soil Oxidation Plant

http://www.art-engineering.com/Projects%20Soil%20Treatment.htm

Chemical oxidation technologies

- Introduction of oxidants into soil to destroy organic contaminants
- Oxidants: Cl_2O, NaClO, $Ca(ClO)_2$, $KMnO_4$, O_3 and H_2O_2/Fenton Reagent
- Intermediates may impact the performance of the oxidant
- Oxidants are generally non-selective
  - Break C-H, C-C bonds of contaminant organic compounds
  - Oxidation of natural organic matters → substantial increase in total oxidant demand
- Selection of the appropriate oxidant is dependent upon the:
  - Nature and type of contaminant
  - Level of remediation required
  - Viability of oxidant delivery
  - Type of soil and hydrogeology of the site

Chemical Oxidation Technologies

Chemical oxidation potentials

Species	Oxidation power (V)
fluorine	3.03
hydroxyl radical	2.80
atomic oxygen	2.42
ozone	2.07
Hydrogen peroxide	1.78
MnO_4^-	1.60
chlorine	1.36

Hydrogen Peroxide/Fenton's Reagent

- Fenton/Fenton-like reaction yielding hydroxyl radicals (OH•) with oxidation power of 2.80V, second only to fluorine, which is the strongest known oxidant
- Reaction chemistry $H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^{-} + HO\bullet$
- Easily decompose to $H_2O_{(v)}$ & O_2
- Products: organic acids, salts, O_2, CO_2, (substantial gas and heat evolution)
- Low pH favorable (best pH of 2-4) up to near neutral pH
- OH• radicals are highly active and unstable
- Applicable in both vadose and saturated zones

Hydrogen Peroxide/Fenton's Reagent

- Other heavy metals involved: Cu^{+}, VO^{2+}, Ti^{3+}, Cr^{2+}, Co^{2+}, and Mn^{2+}
- Amendments: Fe^{2+} and acid (eg.$FeSO_4$)
- H_2O_2 stabilization may by needed (KH_2PO_4) for safe operation and influence radius extension
- Dosage: 5-50wt% H_2O_2, multiple dosing common
- Some contaminated site has been treated by it in Alberta
- Oxidizable contaminants include:
  - –Chlorinated solvents
  - –Non-chlorinated solvents
  - –PAH's
  - –Phenols, esters, and others
  - –Pesticides
  - –VOC's & SVOC's
  - –BTEX
  - –LNAPL & DNAPL

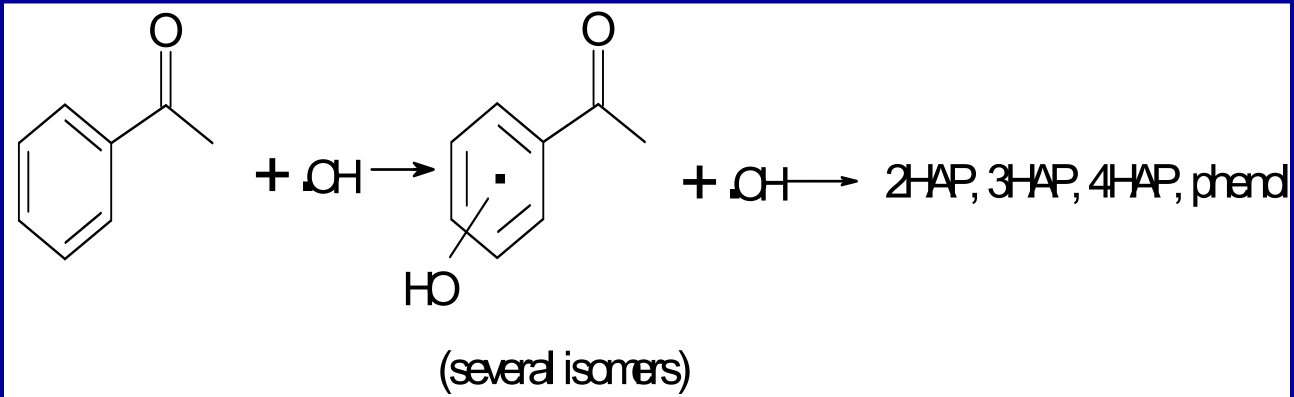
Hydrogen Peroxide/Fenton's Reagent

- H_2O_2/Fenton reagent reaction mechanism

David L. Sedlak and Anders W. Andren, Environmental Science and Technology (1991) 25, 777-782

Hydrogen Peroxide/Fenton's Reagent

H_2O_2/Fenton reagent reaction mechanism



Xu, Y. and Langford, C. H., *J. Phys. Chem. B* **1997,** 101 (16), 3115.

Hydrogen Peroxide/Fenton's Reagent

- Advantages:
  - Low chemical cost
  - Relatively rapid reaction process
  - Stimulation of aerobic biological activity
  - Applicable over a wide range of VOC & SVOC
  - Range of reliable field application information available
- Limitations:
  - Safety issues from its exothermal reaction (heat and gas)
  - Possible soil permeability impacted by Fe^{2+} colloid
  - Temperature increase (exothermic reaction)
  - Lowering of soil pH is not feasible (in situ)
  - Concern of Cr(III) oxidation to Cr(VI)
  - Adverse impact of Fenton's reagent on microbial populations

Costs Comparison of Biological, Physical, and Chemical Oxidation Treatment

Treatment methods	Biological	Physical (Soil Washing)	Chemical (H_2O_2 injection)
Contaminant	chlorinated pesticides	chlorinated pesticides	Pentachloro-phenol (PCP)
Non-capital cost (US$/908kg)	35~1,000	50~200	30

Richard J. Watts, matthew D. Udell, Robert M. Monsen (1993), Water Environ. Res., 65, 839

Objective

To understand hydrogen peroxide remediation efficiency on F3 fraction contaminated soil

Experimental background

- Canada Wide Standard for Petroleum Hydrocarbons:
  - F1: nC6 ~ nC10
  - F2: nC10 ~ nC16
  - F3: nC16 ~ nC34
  - F4: nC34 ~ nC50
- ~60% Canada contaminated sites contain PHC
- Although this remediation technology has been tested for various contaminants in soil, most of the contaminants are volatile or semi-volatile in the range of lighter than F3 section
- Transformer oil (TO) in F3 range has not been tested

Experimental background

- F3 fraction physical properties
  - Low H/C ratio compared with F1 and F2
  - Low vapor pressure (nC_{16}: 0.008~2 $\times 10^{-8}$ mmHg)
  - Low Henry's law constants
  - Low solubility in water (nC_{16}: 2 $\times 10^{-8}$ mg/L), hydrophobic
  - Low remediation efficiencies by bioremediation
  - High B. P. (b. p.: 287~301ºC) and $\log K_{ow}$
- F3 fraction related contaminants
  - Gas oil, residual fuel, asphalt, tar
  - Engine oil, lubricant oil, and transformer oil (may contain PCBs)
  - Weathered petroleum hydrocarbons

Experimental background

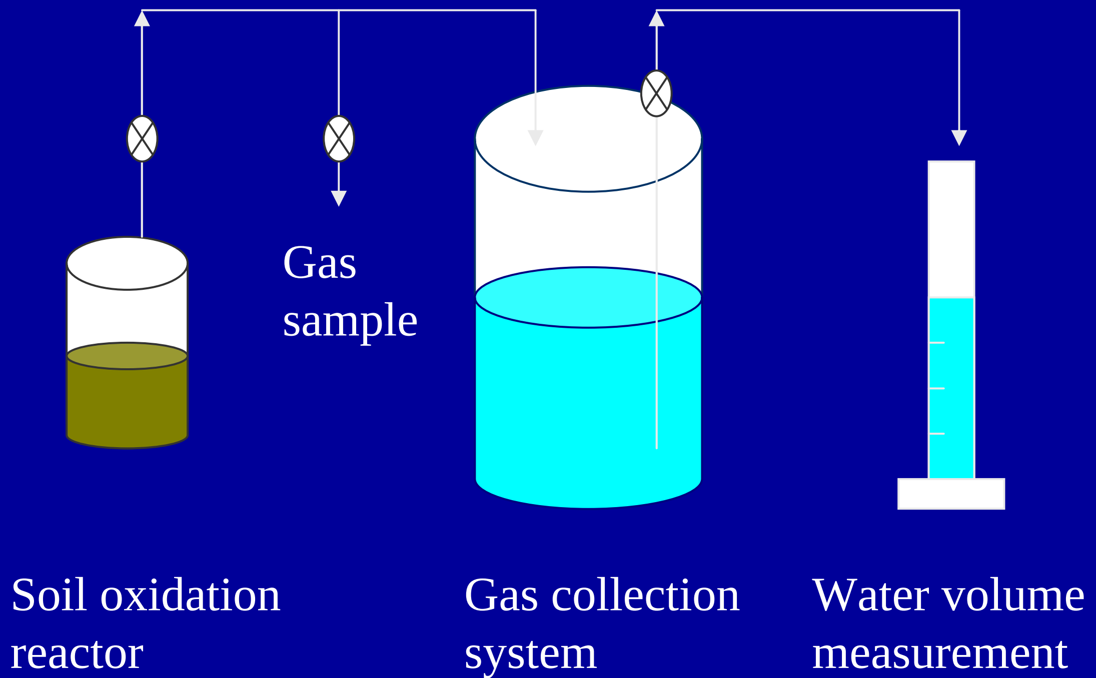
- Why TO - a target contaminant?
  - Main components fall with in the F3 fraction in Canada-Wide Standard for Petroleum Hydrocarbons
  - Related with PCBs contamination problem
  - Little understanding about how to treat TO contaminated soils

Experimental Conditions

- Soil Characteristics
  - Alberta New Children Hospital site clay soil, air dried
  - Soil particle size < 1.25 mesh,
  - Moisture content 0.56% (After air dried)
  - Organic Matter 2.10%
  - Iron content: 11,600 mg/kg
- TO: Voltesso N36 from Enmax (Calgary)
  - PCBs free (<2ppm)
  - Density d = 877 kg/m^3
  - Good oxidation stability and insulting property
  - ASTM analysis: 6% aromatic, 45%naphthenic, and 50% paraffinic hydrocarbons
  - Average carbon number C_{27}
- Spiked Soil
  - SOM content (0~5%)
  - TO content (0~5%)

Experimental

TO contaminated soil H_2O_2 oxidation test system diagram



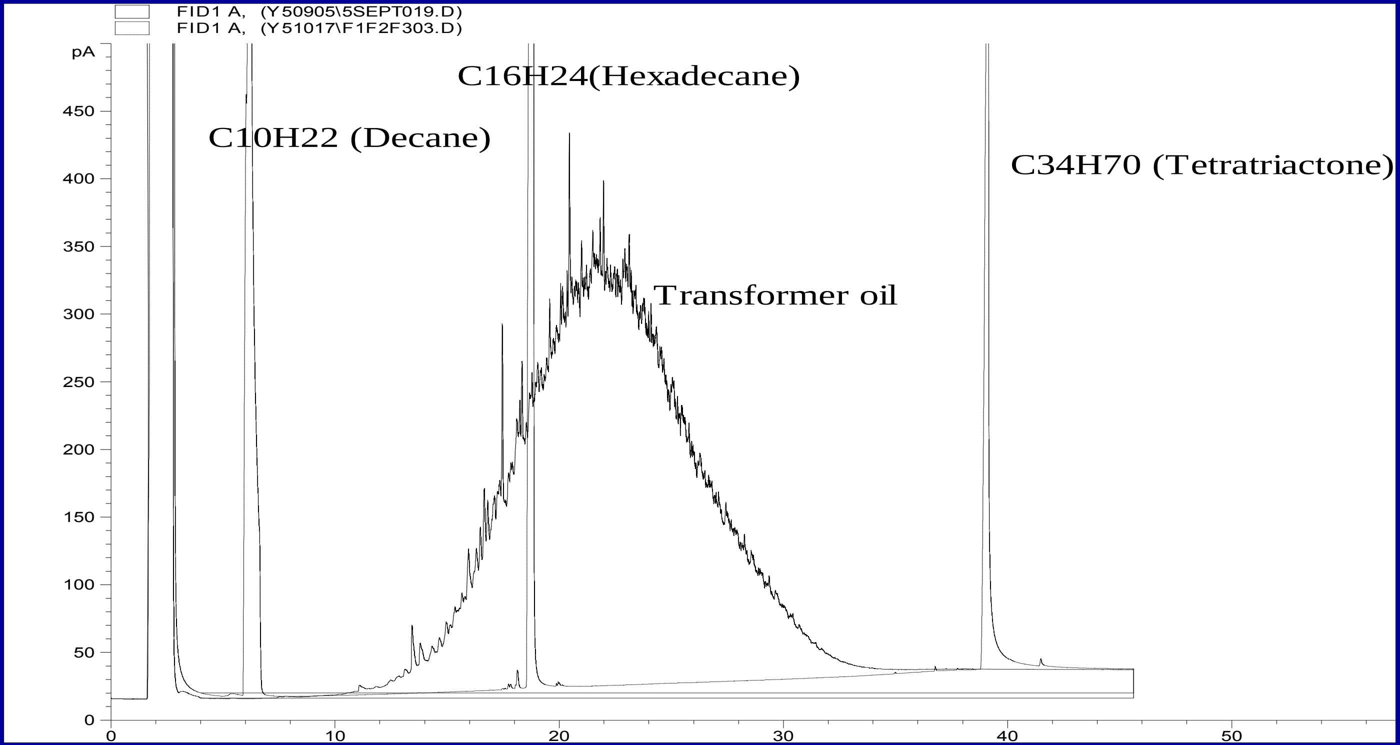
Results---Analytical

- Gas analysis
  - Agilent GC 6890N (FID) installed with ChemStation
  - Column:
    - 10 ft Haysep Q for CO_2
    - 12 ft Molesieve 13X for O_2, N_2
- Extracted TO analyses
  - HP 6890 auto-sampler GC, FID detector
  - Column HP-5(30m×0.25mm×0.25μm, ~325ºC)
  - ChemStation data analysis software

Results---Analytical

Extracted TO analyses---One hump method

80ºC(1minute) followed by 8ºC/minute up to 325ºC (10minutes)



Results---Analytical

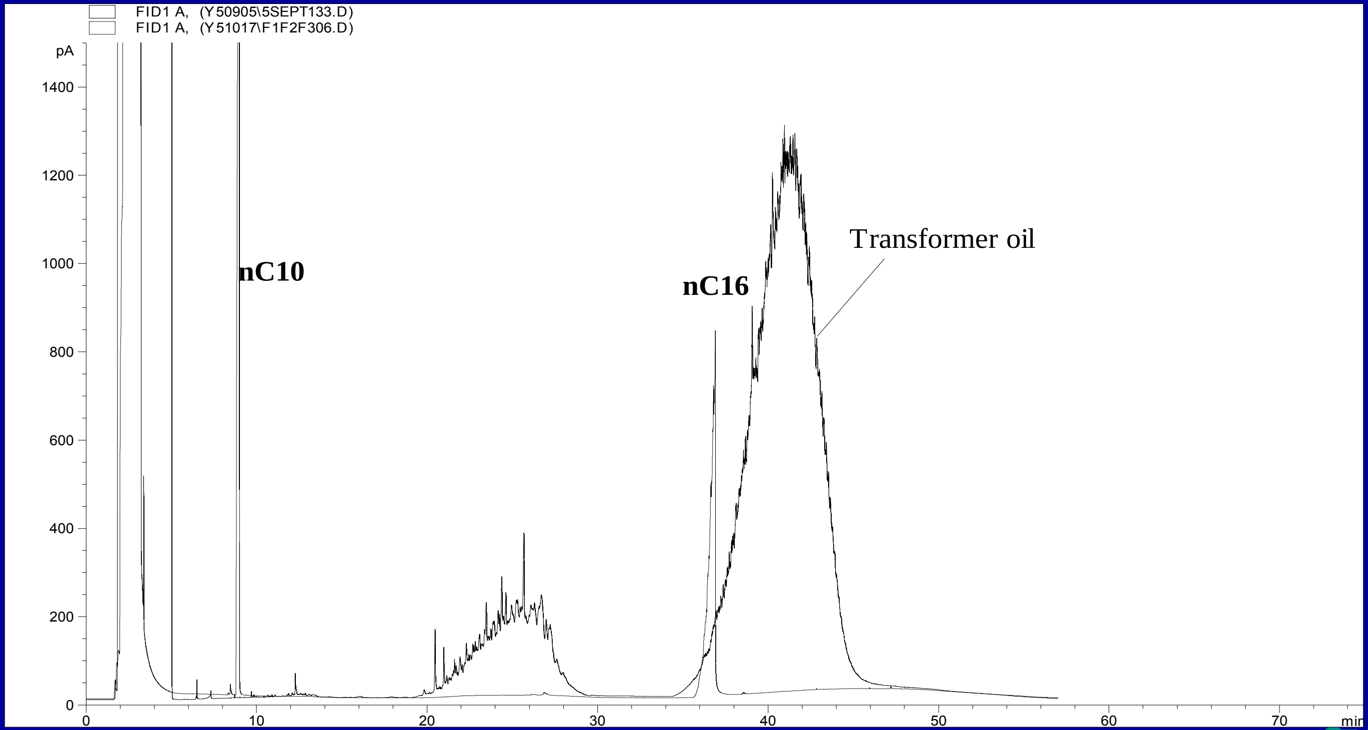
- Extracted TO analyses using a novel temperature profile which separates F3 fraction (three-humps method) from

  F2 fraction:

  Initial temperature (1minute)
  30ºC/minute up to 120ºC (8minute) followed by
  50ºC/minute down to certain ºC (1 minute) then
  30ºC/minute again up to 160ºC (5minute) then
  50ºC/minute down to certain ºC(1minute) and
  30ºC/minute up to 325ºC (for 7minutes)
- Three humps method advantages
  - TO content can be separated into three sections
  - F2 and F3 fraction can be tested individually in the H_2O_2 oxidation process

Results---Analytical

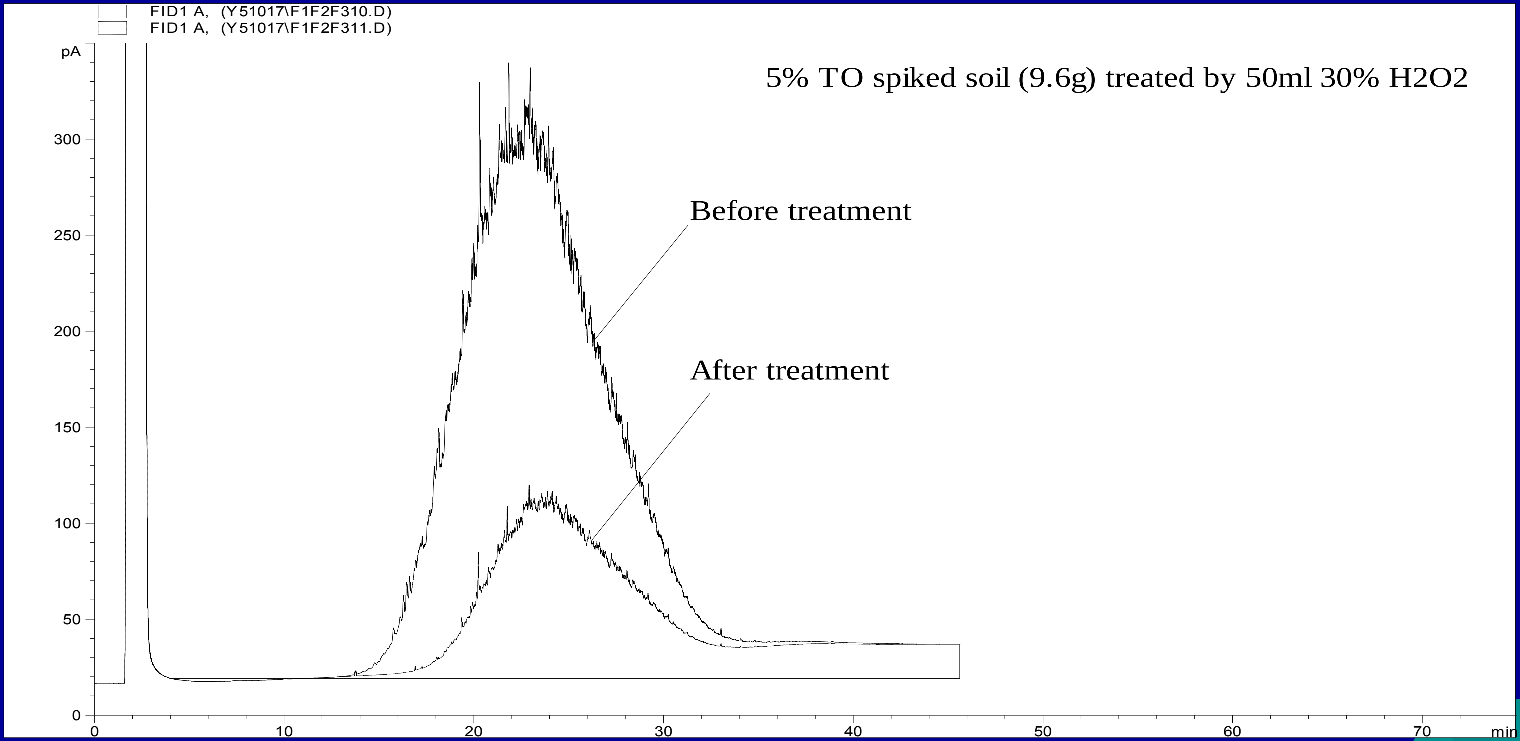
- Extracted TO analyses result (three-humps method)



Primary experimental results

--- ~10g 50,000ppm TO spiked soil + 50ml ~30% H_2O_2 results

--- Gas and heat was generated and the soil slurry was boiling for ~2 minutes during reaction



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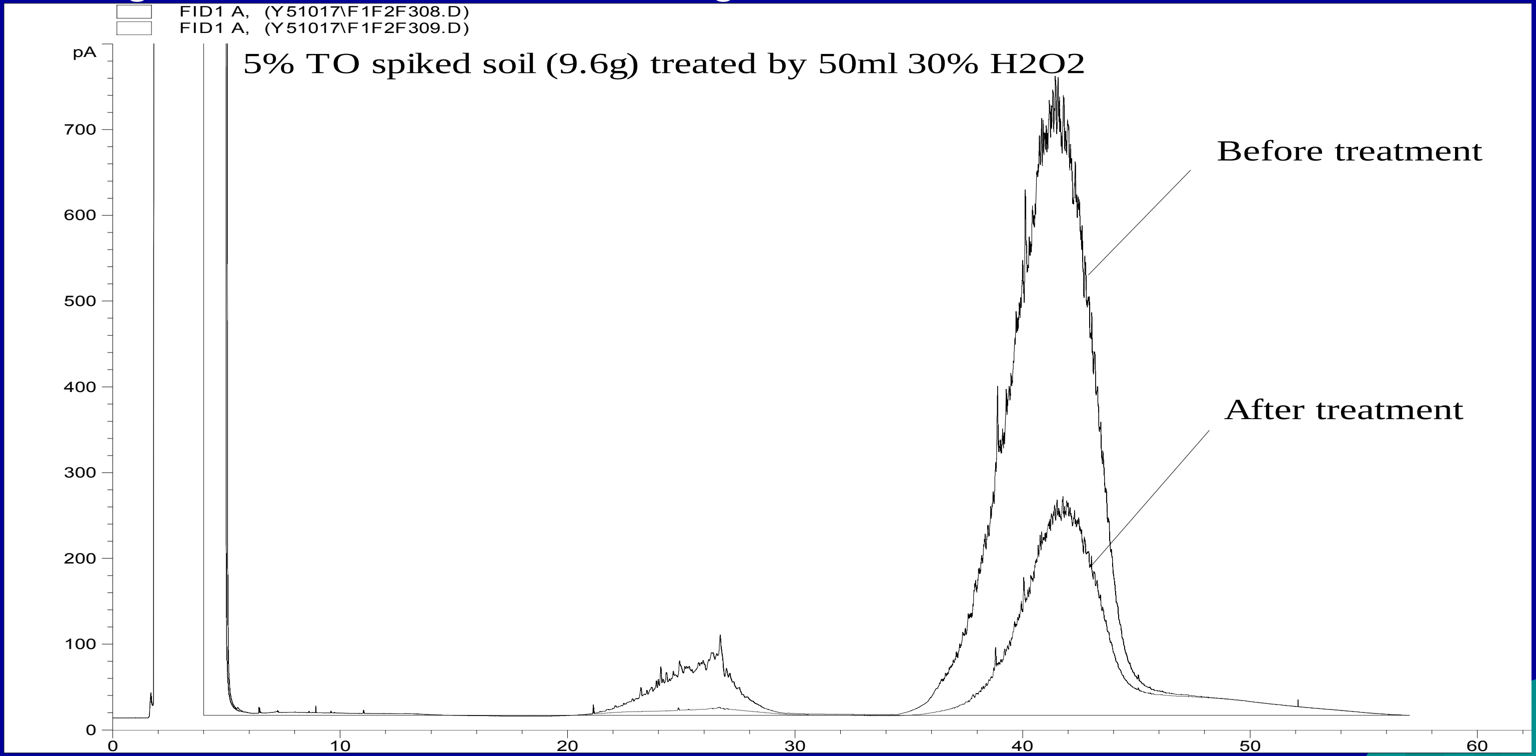
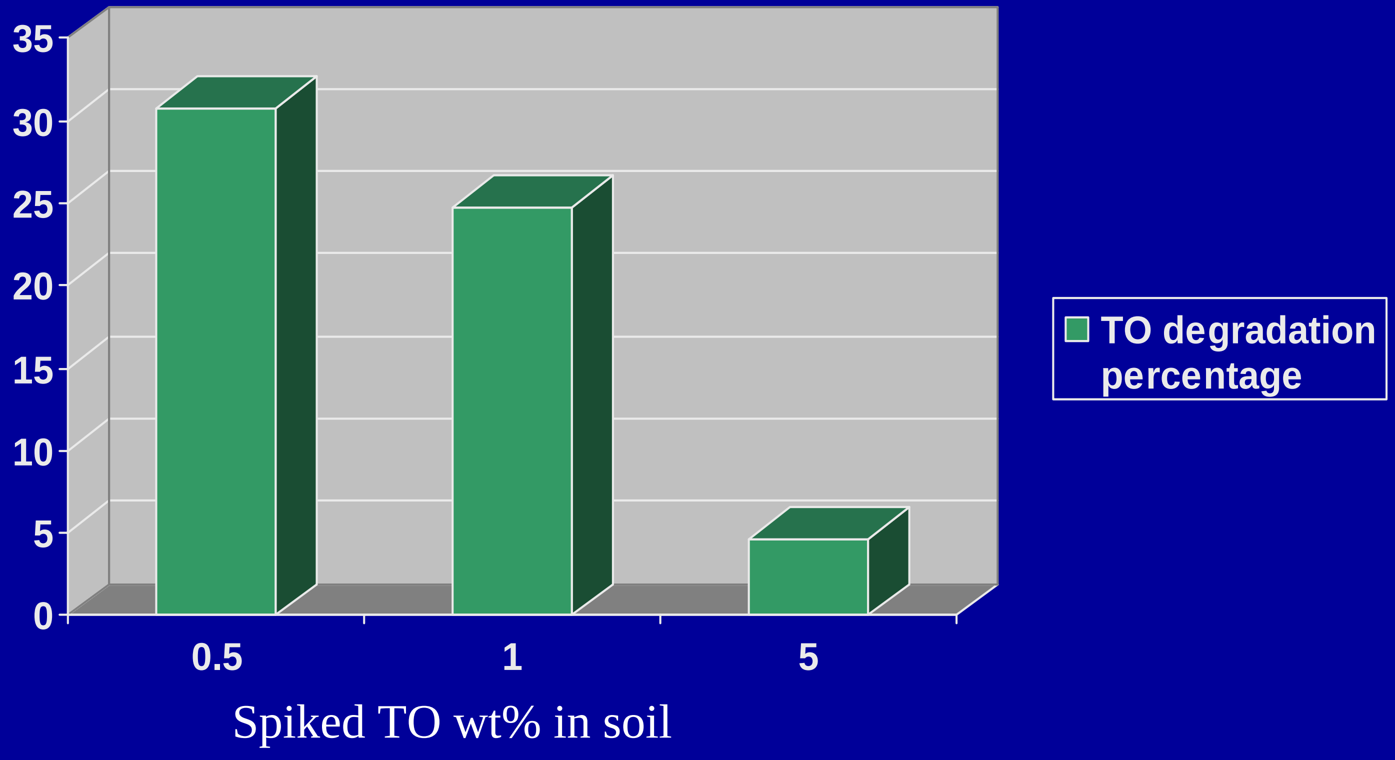


Primary experimental results

- TO degradation results(15% H_2O_2)
  - ~10g spiked soil (extractable SOM free, ~100ppm PCBs) + 40ml 15% H_2O_2



Spiked soils (TO%)	0.5	1.0	5.0
Absolute TO degradation (mg/kg soil)	880	1200	1270

Primary experimental results

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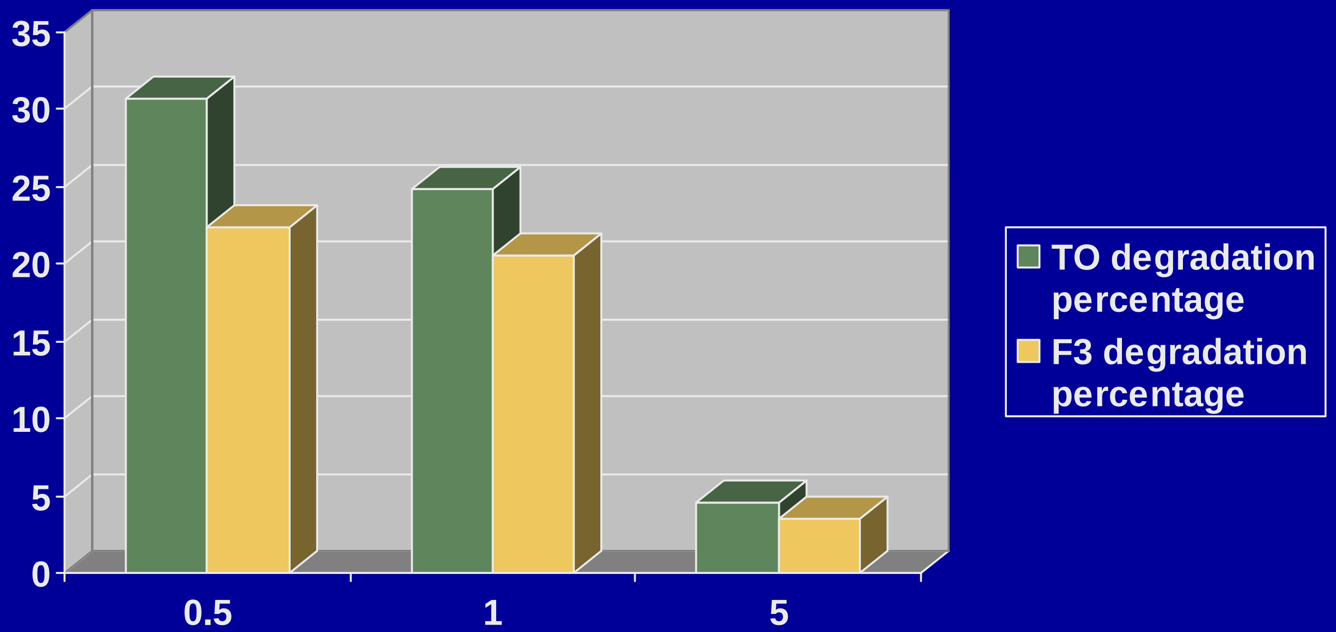

Spiked TO wt% in soil

Ongoing Work

- H_2O_2 concentration effects
- Co-contaminant (SOM) effects
- Fe content effects
- TO containing PCBs

Conclusions

- A soil oxidation system was set up to test evaluate H_2O_2 remediation technology in laboratory
- A three-hump GC method was developed to test TO degradation in term of F3 fraction
- Primary results indicated that TO can be oxidized by H_2O_2
- High H_2O_2 is preferred for TO oxidation
- About 20% TO was degraded by 40 ml 15% H_2O_2 for ~10g 10,000ppm spiked TO soil

Thank you!

Questions