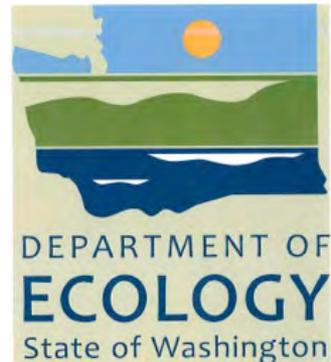


## **Green Chemistry Webinar Series for HS Teachers:**

**Connecting Chemistry Concepts to Cutting-Edge Science  
Innovations**

**Kate Anderson**  
**Director of Education**  
**Beyond Benign**  
**Wilmington, MA**

**Richard Cooper**  
**High School Teacher and Science**  
**Department Chair**  
**London, Ontario**



- Visit the WA State Department of Ecology Green Chemistry pages:

[http://www.ecy.wa.gov/programs/hwtr/P2/GreenChem/greenchem\\_ecy.html](http://www.ecy.wa.gov/programs/hwtr/P2/GreenChem/greenchem_ecy.html)

[http://www.ecy.wa.gov/programs/hwtr/P2/GreenChem/greenchem\\_resources.html](http://www.ecy.wa.gov/programs/hwtr/P2/GreenChem/greenchem_resources.html)

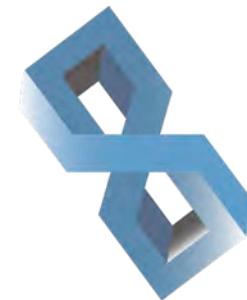
- Participate by asking questions during the webinar and providing feedback with the follow-up survey
- WA State teachers will receive 1 clock hour for attending & participating in this webinars.
- Please contact Saskia van Bergen :  
[Saskia.vanBergen@ecy.wa.gov](mailto:Saskia.vanBergen@ecy.wa.gov) by 10/31/13

## MISSION AND VISION

Beyond Benign is dedicated to providing future and current scientists, educators and citizens with the tools to teach and learn about green chemistry in order to create a sustainable future.

Beyond Benign's vision is to revolutionize the way chemistry is taught to better prepare students to engage with their world while connecting chemistry, human health and the environment.





# Program areas:

## K-12

- Curriculum Development and Teacher Training
  - Green Chemistry
  - Green Math & Engineering
  - Biotechnology
- On-line Courses
- Professional Development Workshops
- K-12 and Community Outreach
- College Student Fellows program

## College/University

- The Green Chemistry Commitment
- Curriculum Development and Training
  - Technical Training
  - Green Chemistry training for workers
  - Green Chemistry tools



# Green Chemistry HS Curriculum

3 types of lesson plans:

## Type 1: What is Green Chemistry?

- Introduces students to the concepts of green chemistry

## Type 2: Green Chemistry in Industry

- Learn about chemistry within context
- All lessons are linked to state and national learning standards

## Type 3: Green Chemistry Replacement Laboratory Exercises

- Drop-in replacements
- Eliminates or reduces the use of hazardous chemicals in the classroom
- Linked to state and national learning standards

Available for download free-of-charge at: [www.beyondbenign.org](http://www.beyondbenign.org)

Direct link: <http://www.beyondbenign.org/K12education/highschool.html>

# Next Generation of Science Standards

## *High School*

### **HS-ETS1-3 Engineering Design**

Students who demonstrate understanding can:

**HS-ETS1-3. Evaluate a **solution** to a complex real-world problem based on prioritized criteria and trade-offs that account for a range of constraints, including cost, safety, reliability, and aesthetics as well as possible social, cultural, and environmental impacts.**

### **HS-ESS3-2 Earth and Human Activity**

Students who demonstrate understanding can:

**HS-ESS3-2. Evaluate competing **design solutions** for developing, managing, and utilizing energy and mineral resources based on cost-benefit ratios.**



# Green Chemistry ties to WA Environmental & Sustainability Standards

Principles of Green Chemistry		Environmental & Sustainability Standards
1	Prevention	<b>Standard 1 &amp; Standard 2</b>
2	Atom Economy	
3	Less Hazardous Chemical Syntheses	<b>Standard 3</b>
4	Designing Safer Chemicals	<b>Standard 1 Standard 2</b>
5	Safer Solvents and Auxiliaries	
6	Design for Energy Efficiency	<b>Standard 1 &amp; Standard 2</b>
7	Use of Renewable Feedstocks	<b>Standard 3</b>
8	Reduce Derivatives	
9	Catalysis	
10	Design for Degradation	<b>Standard 1 &amp; Standard 3</b>
11	Real-time analysis for Pollution Prevention	
12	Inherently Safer Chemistry for Accident Prevention	

## Environmental & Sustainability Standards:

### **Standard 1: Ecological, Social, and Economic Systems**

Students develop knowledge of the interconnections and interdependency of ecological, social, and economic systems. They demonstrate understanding of how the health of these systems determines the sustainability of natural and human communities at local, regional, national, and global levels.

### **Standard 2: The Natural and Built Environment**

Students engage in inquiry and systems thinking and use information gained through learning experiences in, about, and for the environment to understand the structure, components, and processes of natural and human-built environments.

### **Standard 3: Sustainability and Civic Responsibility**

Students develop and apply the knowledge, perspective, vision, skills, and habits of mind necessary to make personal and collective decisions and take actions that promote sustainability.

# Presidential Green Chemistry Challenge



## The Presidential Green Chemistry Challenge

### Awards Opportunities

**T**he Pollution Prevention Act of 1990 established a national policy to prevent or reduce pollution at its source whenever feasible. The Pollution Prevention Act also provided an opportunity to expand beyond traditional EPA programs and devise creative strategies to protect human health and the environment. Green chemistry, or the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances, is a highly effective approach to pollution prevention. Green Chemistry applies innovative scientific solutions to real-world environmental situations, all through voluntary partnership programs. In order to successfully effect the technical and behavioral changes necessary to accomplish wide-spread pollution prevention through green chemistry, the benefits of the approach must be clearly demonstrated and communicated.

#### OBJECTIVE:

The Presidential Green Chemistry Challenge seeks to recognize outstanding accomplishments in green chemistry through an annual awards program in environmental and economic benefits that green chemistry technologies offer.

#### DESCRIPTION:

The Presidential Green Chemistry Challenge Awards Program is an opportunity for individuals, groups, and organizations to compete for annual awards in recognition of innovations in cleaner, cheaper, smarter chemistry. The Challenge Award Program provides national recognition for outstanding chemical technologies that incorporate the principles of green chemistry into chemical design, manufacture, and use and that have been or can be utilized by industry to achieve its pollution prevention goals.

#### BACKGROUND:

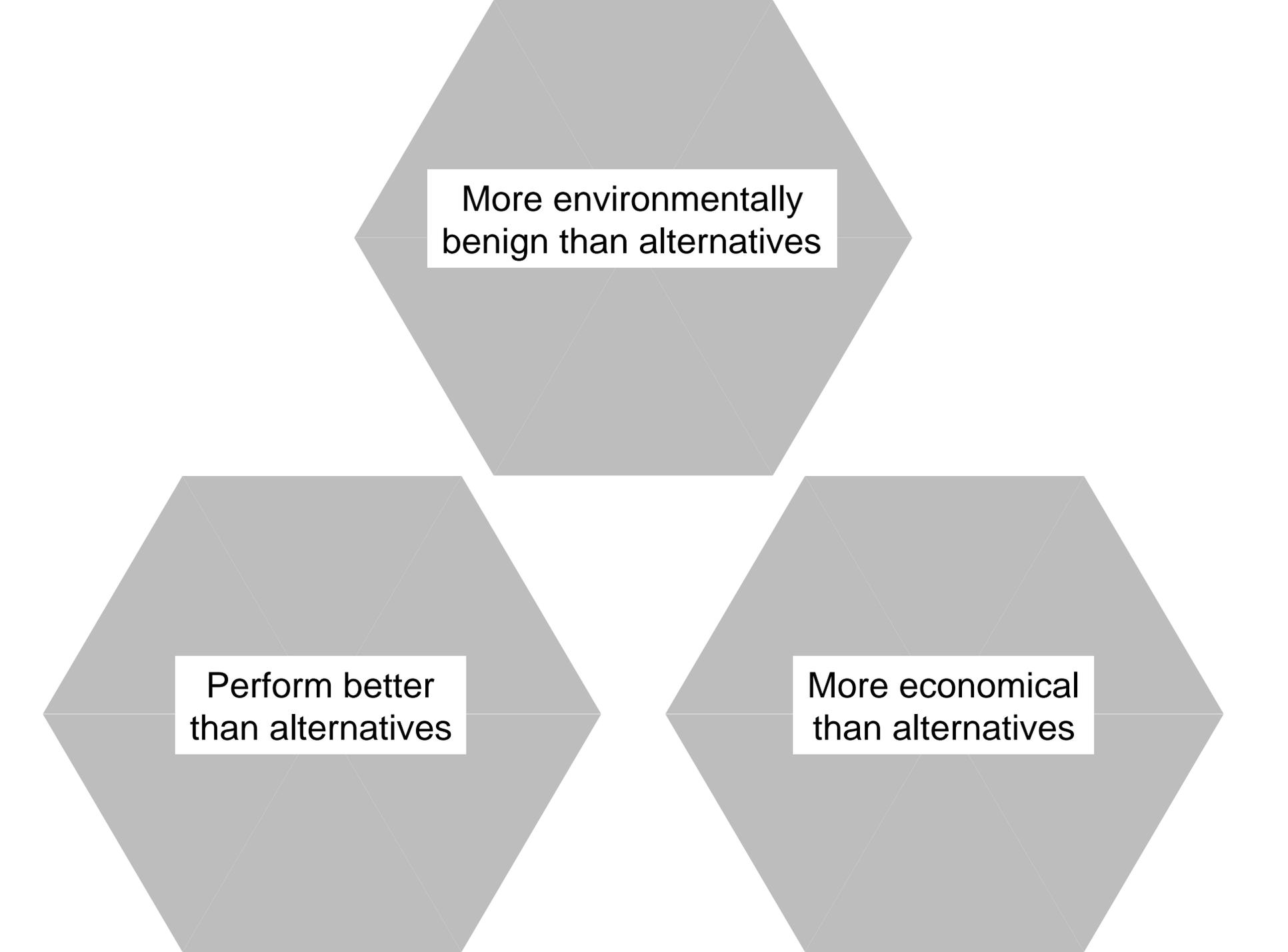
The Presidential Green Chemistry Challenge was implemented as a voluntary EPA Design for the Environment (DfE) partnership with the chemical community. DfE partnerships encourage economic development and benefit industry by identifying cost-effective ways to prevent pollution.

Nominations received for the awards are judged by an independent panel of technical experts convened by the American Chemical Society. Typically, five awards are given annually to industry and government sponsors, an academic investigator, and a small business for this program. Individual projects selected for support may be funded by EPA, NSF or jointly by both agencies. This is at the option of the agencies, not the grantees.



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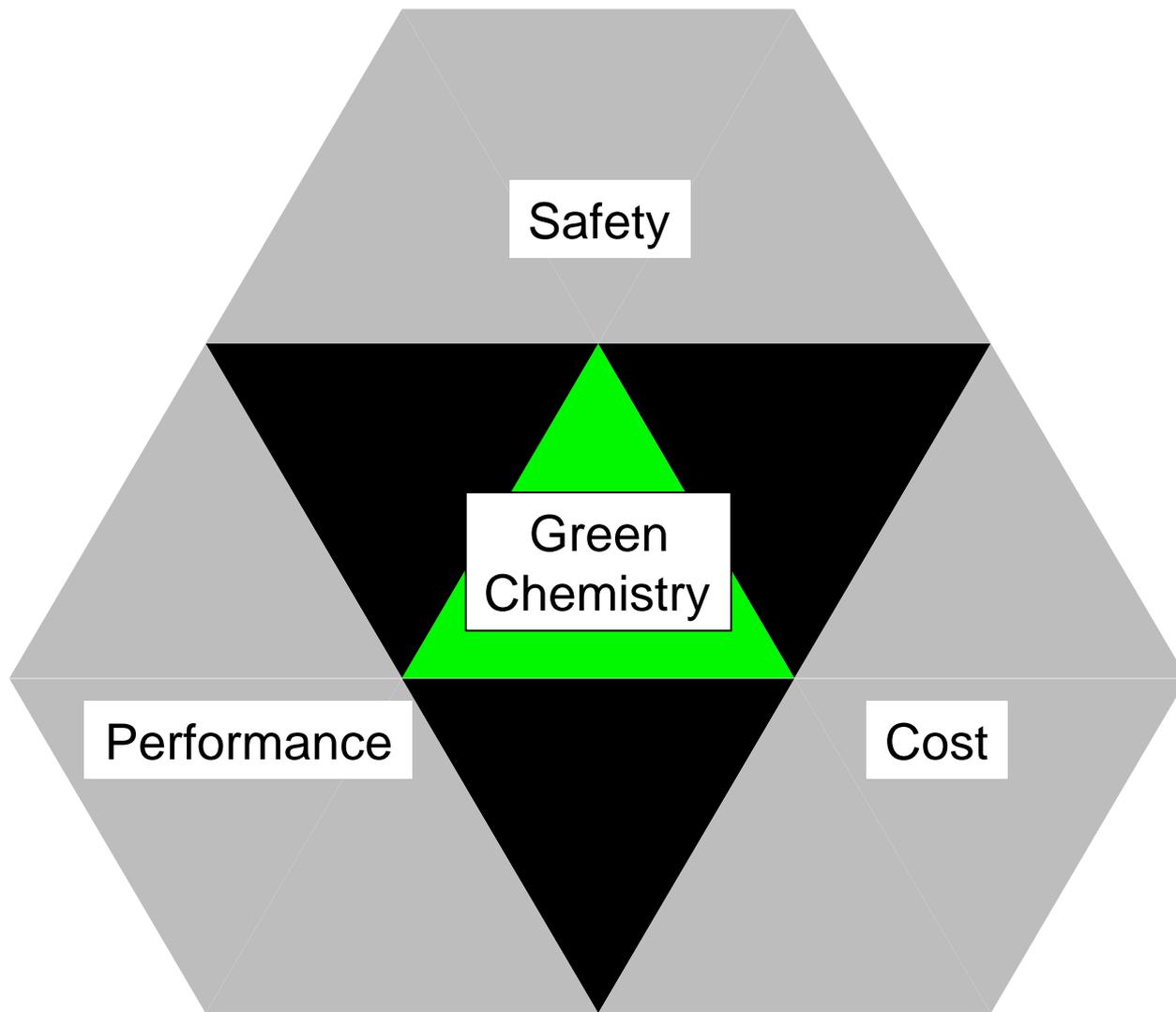




More environmentally  
benign than alternatives

Perform better  
than alternatives

More economical  
than alternatives



Safety

Green  
Chemistry

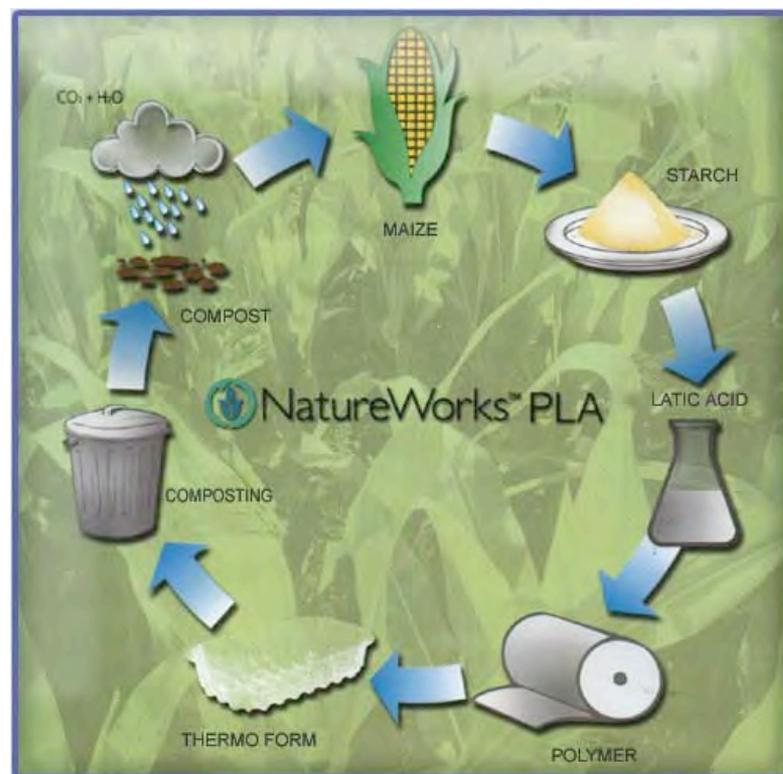
Performance

Cost

	1996	1997	1998	1999	2000
Academic	Mark Holzapple	Joseph DeSimone	Barry Trost Karen Draths John Frost	Terry Collins	Chi Hue Wong
Small Business	Donlar Corporation	Legacy Systems	PYROCOOL Technologies	Biofine	RevTech
Alternative Synthetic Pathway	Pharmacia	BHC Company	Flexsys America	Lilly Research Laboratories	Roche Colorado
Alternative Solvents and Reaction Conditions	Dow	Imation	Argonne National Labs	Nalco Chemical Company	Bayer Corporation
Designing Safer Chemicals	Rohm and Haas	Albright and Wilson Associates	Rohm and Haas	Dow AgroSciences	Dow AgroSciences

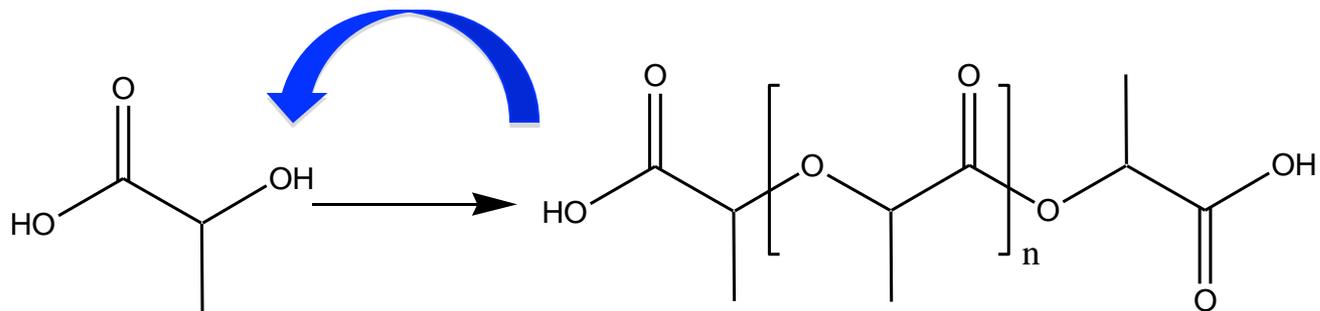
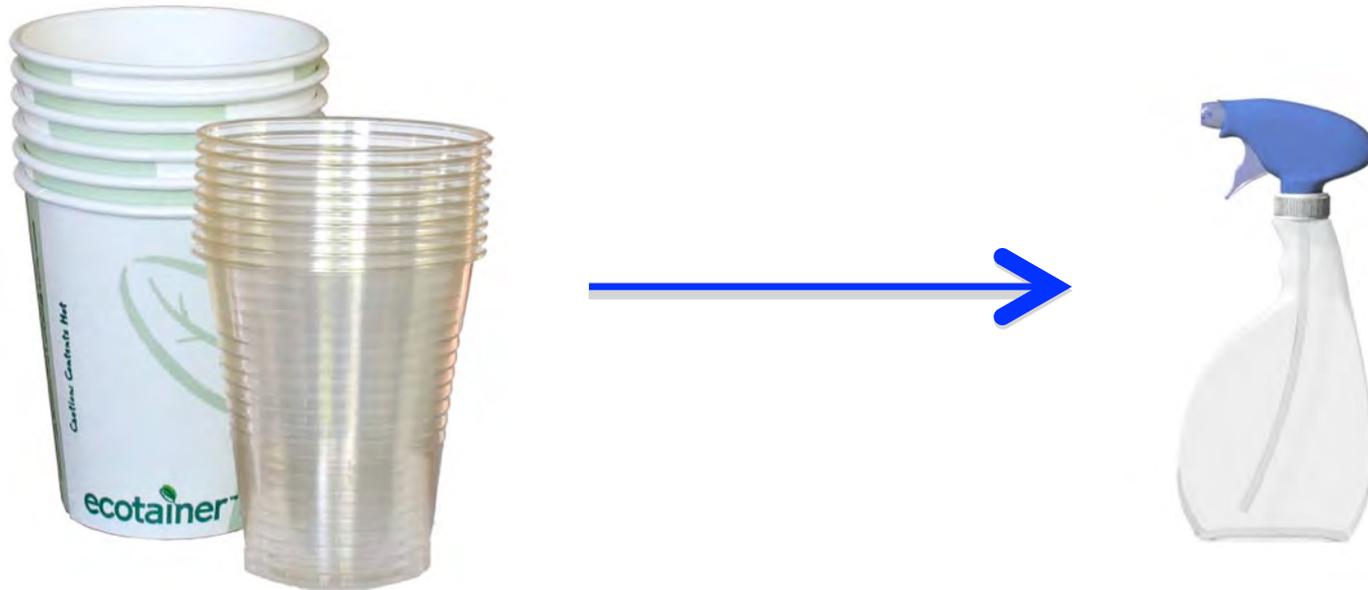
# 2002 Greener Reactions Conditions

- Cargill Dow LLC (now NatureWorks LLC)
- Polymers from Renewable Resources: Poly(lactic acid)
- Bio-polymer made from corn
- Designed to be bio-compostable



# Recycling Polylactic Acid

(Lab inspired by PGCC Award Winner & Professor Rich Gurney Simmons College)



# 2007 Greener Synthetic Pathways Award

- Team of Winners:
  - Professor Li (Oregon State University)
  - Columbia Forest Products
  - Hercules Inc. (now Ashland Inc.)
- Safer Adhesives for Wood Composites (PureBond)
  - Replacement for formaldehyde in manufacture of plywood
  - Made with soy
  - Inspired by mussels' adhesive protein



# Green Chemistry, Biomimicry and Intermolecular Forces

- Cross-curricula
- Case study on adhesives
- Lesson intermolecular forces
- Biomimicry inspired

# Richard Cooper

- Ontario Chemistry Teacher and Science Department Chair
- Attended the summer institute on Green Chemistry in Summer of 2006
- Worked with Beyond Benign since Summer of 2007 writing curriculum for Green Chemistry Instruction and Delivering Workshops at various locations on Implementation for the 12 Principles of Green Chemistry in Senior and Junior Science and Chemistry courses.

# Industry Examples Using the 12 Principles of Green Chemistry

1. **Petretec** ( A chemical process that permits the closed loop recycling of PETE waterbottles through the use of a revolutionary new process to “unzip” the polymer and reproduce the polymer. Developed by Dupont in 2003)
2. **Sea Nine-211** (An antifoulant used as an alternative to Tributyl Tin Oxides on the hulls of ships. Developed by Rohm and Haas in 1996)
2. **TAML Oxidative Activators** (A catalyst that activates Hydrogen Peroxide to be able to bleach paper rather than using chlorine containing compounds. Developed by Professor Terry Collins in 1999)

# Presidential Green Chemistry Challenge Winners

	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
<b>Academic</b>	Mark Holzapple	Joseph DeSimone	Barry Trost Karen Draths John Frost	Terry Collins	Chi Hue Wong	C.-J. Li	Eric Beckman	Richard Gross	Charles Eckert Charles Liotta	Robin Rogers	Galen Suppes
<b>Small Business</b>	Donlar Corporation	Legacy Systems	PYROCOLO Technologies	Biofine	RevTech	Eden Bioscience	SC Fluids	AgraQuest	Jeneil Biosurfactant Co.	Metabolix	Akron Cons. Nupro Tech.
<b>Alternative Synthetic Pathway</b>	Pharmacia	BHC Company	Flexsys America	Lilly Research Laboratories	Roche Colorado	Bayer Corporation	Pfizer	Sud-Chemie	Bristol-Myers Squibb Co	Archer Daniels Midland and Merck	Merck
<b>Alternative Solvents and Reaction Conditions</b>	Dow	Imation	Argonne National Labs	Nalco Chemical Company	Bayer Corporation	Novozymes	Cargill Dow	DuPont	Buckman Laboratories	BASF	Codexis
<b>Designing Safer Chemicals</b>	Rohm and Haas	Albright and Wilson Associates	Rohm and Haas	Dow AgroSciences	Dow AgroSciences	PPG	CSI	Shaw Industries	Engelhardt Co	Archer Daniels Midland	SC Johnson

# What has been developed for Teachers?

- Everything is available in an editable format. Use what works for your classroom and edit it as you need to modify it for your students
- Lessons link back to the 12 Principles of Green Chemistry
- Each Industrial Example includes:
  1. PowerPoint Lesson
  2. Teacher handouts
  3. Case Study
  4. Laboratory Examples



# **Green Chemistry and beverage bottles (Petretec)**



# The problem with PET bottles

- Made from a non-renewable resource
  - Do not biodegrade
- Do not recycle on a closed-loop system

# Lets start at the beginning

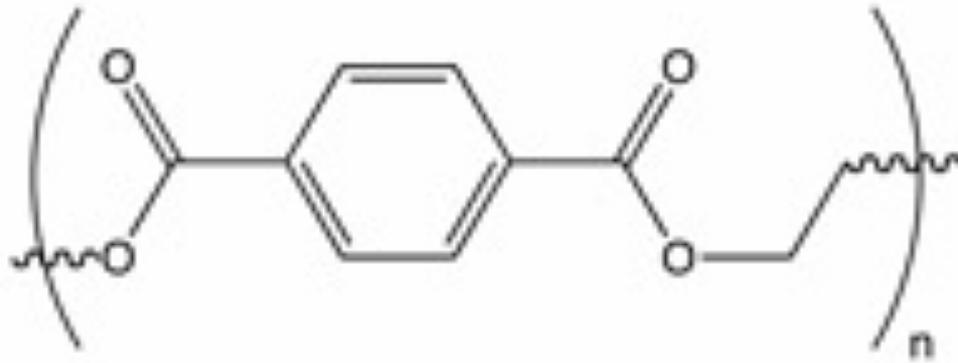
In the process of making the bottle, two dimers are zipped together to form a polymer, like the chain you made at the beginning of the lesson

DMT

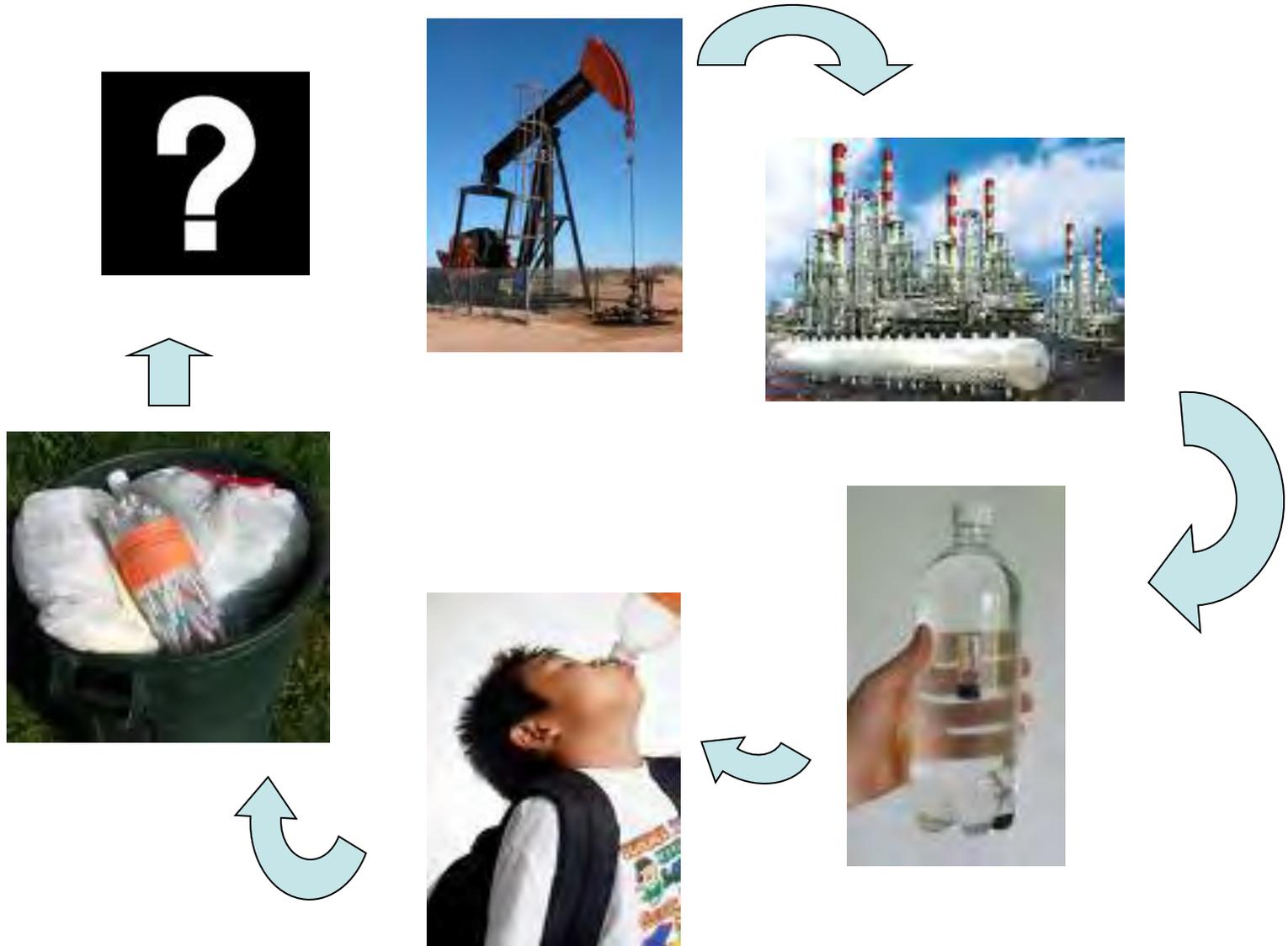


Ethylene Glycol

This zipping produces a polymer  
(or many monomers) to form the  
PET molecule



# Lifecycle of a PET beverage bottle

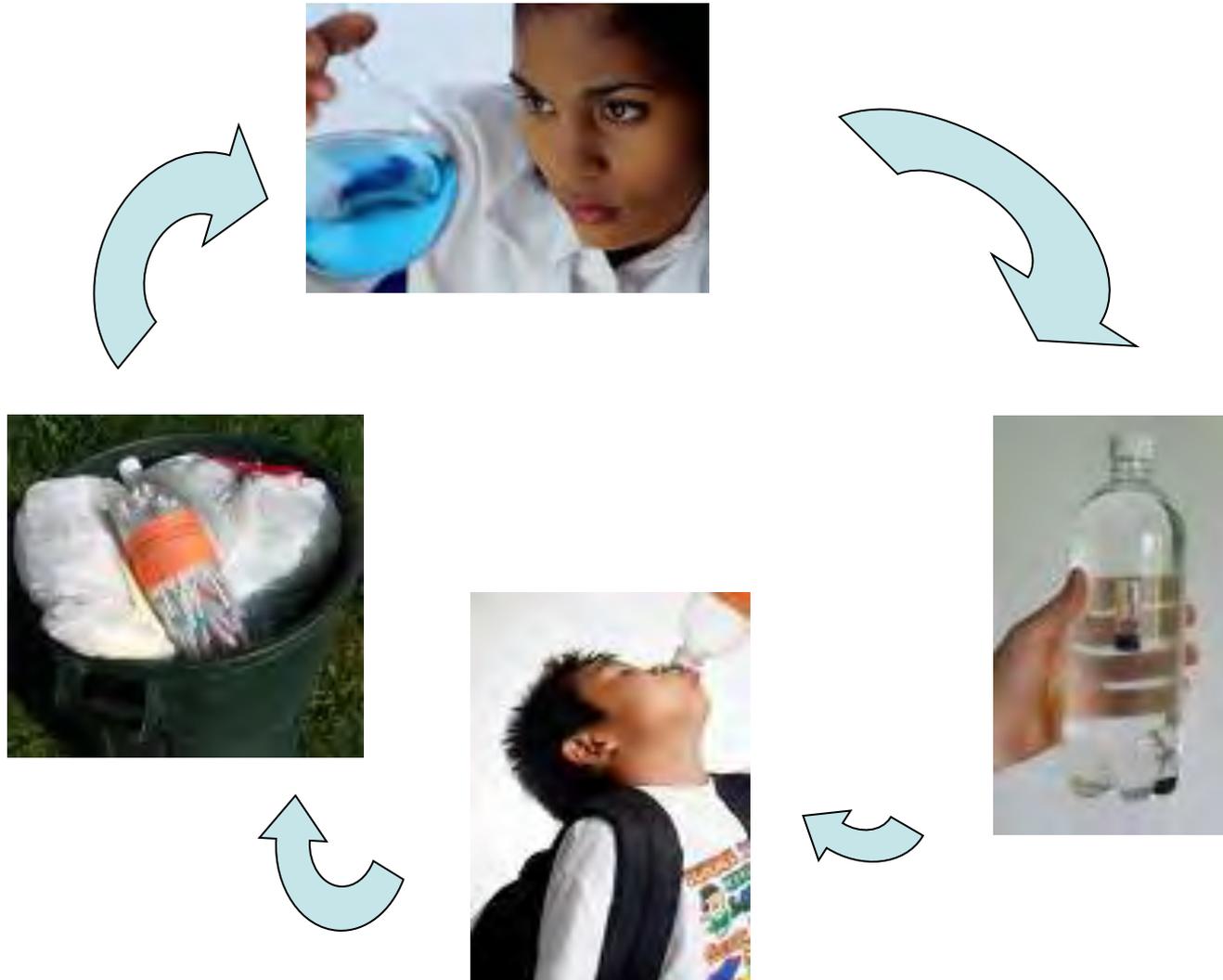


# Recycling can make this..

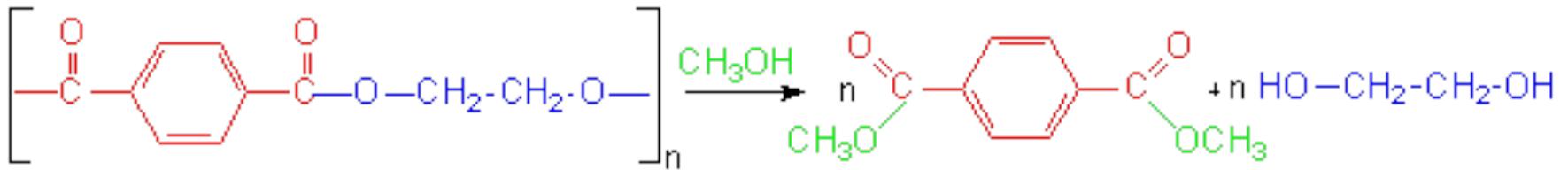


**But we still use PET bottles so  
we are still using petroleum**

# What if the Lifecycle of a PET beverage bottle looked like this...



# Petretec chemical reaction



<http://academic.scranton.edu/faculty/CANNM1/industrialchemistry/industrialchemistrymodule.html>

**The DuPont Company at their plant in North Carolina uses this process to recover 100 million lbs of PET annually**

In 1996 the DuPont Company  
won a presidential Green  
Chemistry Award for Petretec -  
or the unzipping of the  
polymers in PET



# Petretec Case Study

- **Students read article about Fuel, Oil and Synthetic Polymer Industry**
- **Study Questions:**
  1. What is the molecular composition range for each of the categories listed in the “Uses of Crude Oil”? What is meant by terms such as still gas, residual fuel oil, coke, etc.?
  2. What is octane number? What types of compounds have the highest octane numbers, what compound class has the lowest octane numbers? Why is this so?
  3. Draw a reasonable mechanism for the alkylation reaction that is part of the conversion processes involved in reforming of petroleum. What factors would determine whether the reaction involves free radicals or ionic intermediates?
  4. Outline a mechanism for the reactions between TA and ethylene glycol and DMT and ethylene glycol to produce PET.
  5. What would be the economic advantages of using TA (as PTA) in the production of PET, rather than DMT?
  6. Outline a synthesis of poly(butylenes)terephthalate from both TA and DMT. What are the major uses of PBT?
  7. Outline a reasonable mechanism for the transesterification reaction that is the heart of the Petretec process.
  8. What is an azeotrope? What is the boiling point range of an azeotrope ?

# Petretec Pre-Lab

## Three Pre-Lab Activities to make Polymers

### Lab #1

- For each lab station provide the following:
  - Guar gum 0.5% solution.
  - 4% borax solution
  - Glass stirring rod

### Lab #2

- For each lab station provide the following:
  - 100 ml skim milk
  - Approx 50 ml Vinegar
  - Glass Stirring rod
  - 500 ml glass beaker
  - 1 Hot plate
  - Metal pan
  - Water

### Lab #3

- For each lab station provide the following:
  - 4% PVA solution
  - Borax Solution
  - Glass beaker

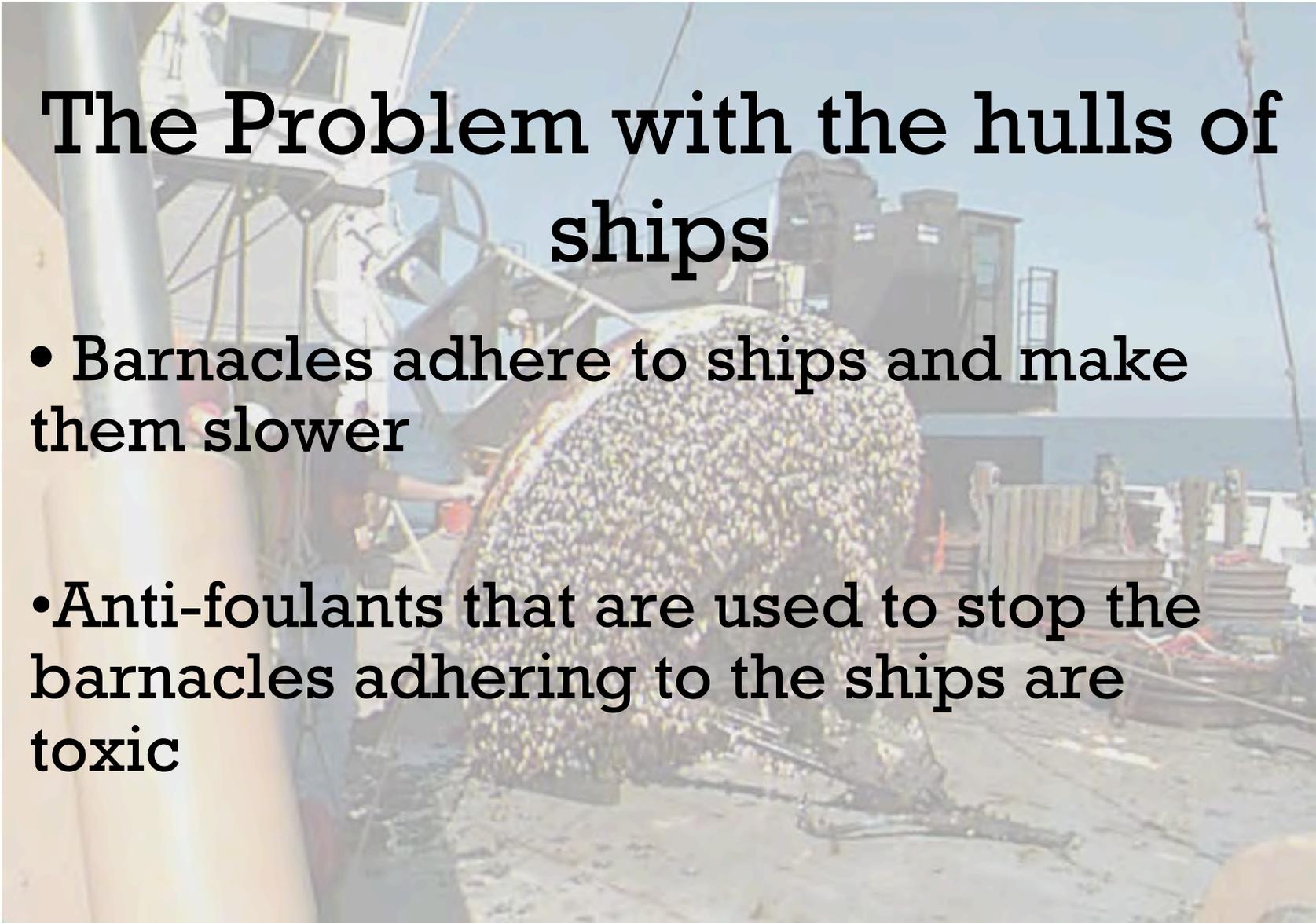
# Petretec Lab

- Students use molecular kits to build the comonomers of DMT and Ethylene Glycol
- Class polymerize their comonomers to produce a 10 foot long model of PETE.
- Teacher superglues at linkage to symbolize the difficulty in separating the comonomers back into their original form.



# Green Chemistry and Ships (Sea Nine 211)

# The Problem with the hulls of ships

A photograph of a ship's deck with a large, circular object, possibly a propeller or a large wheel, completely covered in a dense layer of barnacles. The background shows the ship's structure and the sea under a clear sky.

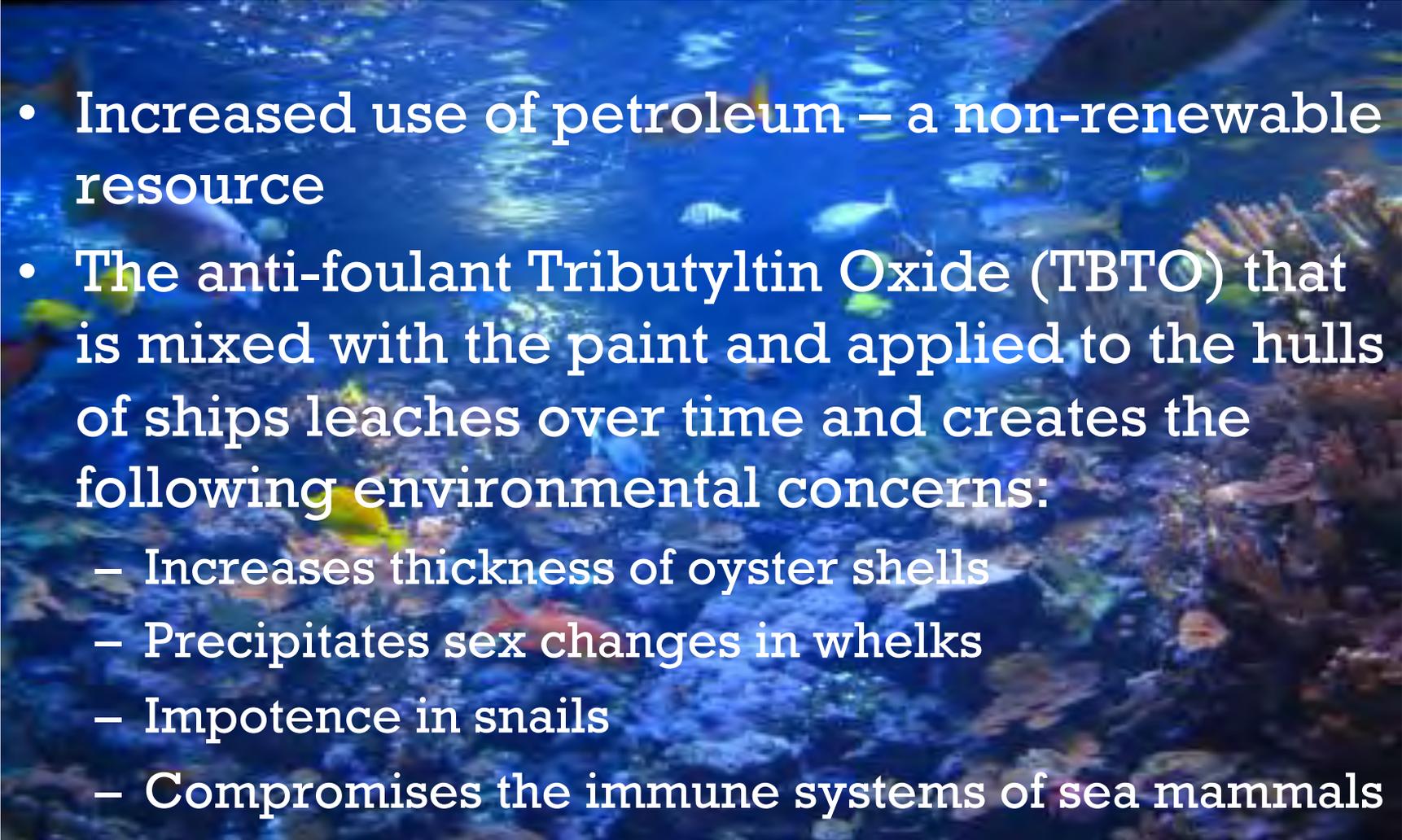
- Barnacles adhere to ships and make them slower
- Anti-foulants that are used to stop the barnacles adhering to the ships are toxic

# What is a Foullant?

- Algae
- Seaweed
- Barnacles
- Diatoms

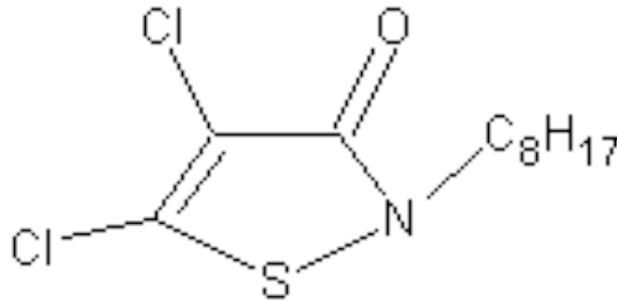


# The cost to the environment

- 
- Increased use of petroleum – a non-renewable resource
  - The anti-foulant Tributyltin Oxide (TBTO) that is mixed with the paint and applied to the hulls of ships leaches over time and creates the following environmental concerns:
    - Increases thickness of oyster shells
    - Precipitates sex changes in whelks
    - Impotence in snails
    - Compromises the immune systems of sea mammals

# Sea-Nine 211

Replaces the TBTO with 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI)



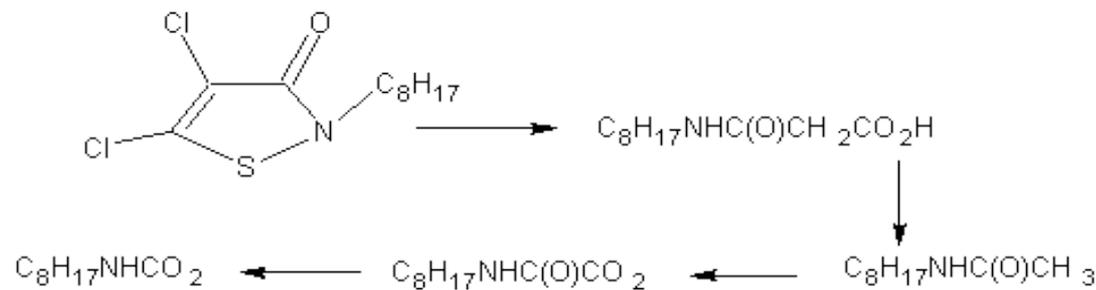
4,5-dichloro-2-n-octyl-4-isothiazolin-3-one

DCOI

# Rapid Biodegradation

Sea-Nine 211 only last less than one hour in the water

- The DCOI on the hull is toxic but what leaches off reacts with the sea water to degrade quickly



Decomposition of DCOI in Natural Seawater

# Sea Nine 211 Case Study

- **Students read article about Shipping Industry and Antifoulants**
- **Study Questions:**
  1. Describe what is meant by hard and soft foulants.
  2. What are the economic consequences of not using an antifoulant on the hull of a ship? What are the environmental consequences?
  3. What is the structure of TBTO?
  4. Compounds which have a tendency to bioconcentrate in organisms are relatively nonpolar and degrade rather slowly (persistent). Is TBTO nonpolar (explain your answer)?
  5. Why do nonpolar compounds have a greater tendency to bioconcentrate than polar compounds?
  6. Are there laboratory methods (that do not use living organisms) that can be used to quantitatively predict the tendency of a substance to bioconcentrate (explain your answer)?
  7. Why do compounds that are nonpolar but degrade rapidly in the environment, not bioconcentrate to any appreciable extent?
  8. What is the structure of DCOI?
  9. From the structure of DCOI would you expect it to be very polar (explain your answer)?
  10. Based on your prediction of the polarity of DCOI (in question 9) would you predict that DCOI would have an appreciable tendency to bioconcentrate (explain your answer)?
  11. Does DCOI bioconcentrate? Explain why it does or does not bioconcentrate.
  12. Would you expect the final product shown in the decomposition of DCOI to bioconcentrate (explain your answer)?
  13. What are PEC and PNEC? Explain how PEC/PNEC supplies a measure of risk.
  14. If both TBTO and DCOI are placed in seawater at the same concentration how long would it take for each of them to decline to 1/16 of their original concentration.
  15. According to the [Organotin Antifouling Paint Control Act of 1988](#) what release rate of organotin compounds is acceptable? Is the use of organotin antifoulants on all ships prohibited by this act?
  16. Describe the difference between the terms acute toxicity and chronic toxicity? Are TBTO and DCOI acutely toxic or chronically toxic (explain your answer)?
  17. The technologies nominated for the [Presidential Green Chemistry Challenge](#) Awards must fall under one (or more) of three different categories. What are these three categories? Which category does Sea-Nine best fit under?
  18. The "[Twelve Principles of Green Chemistry](#)" provide guidelines for developing green chemistry. Which of these twelve principles does Sea-Nine embody

# Sea Nine 211 Lab

- Two part Bioassay Lab
- Students perform six serial dilutions of 4 different road salts (24 solutions)
- Each solution is tested on Daphnia (fauna) and Lettuce seeds(flora) to establish the toxicological properties of each solution.
- The efficiency of each de-icer can then be compared from both an effect on the environment as well as its ability to melt ice.



# Green Chemistry and Paper (TAML Activator)

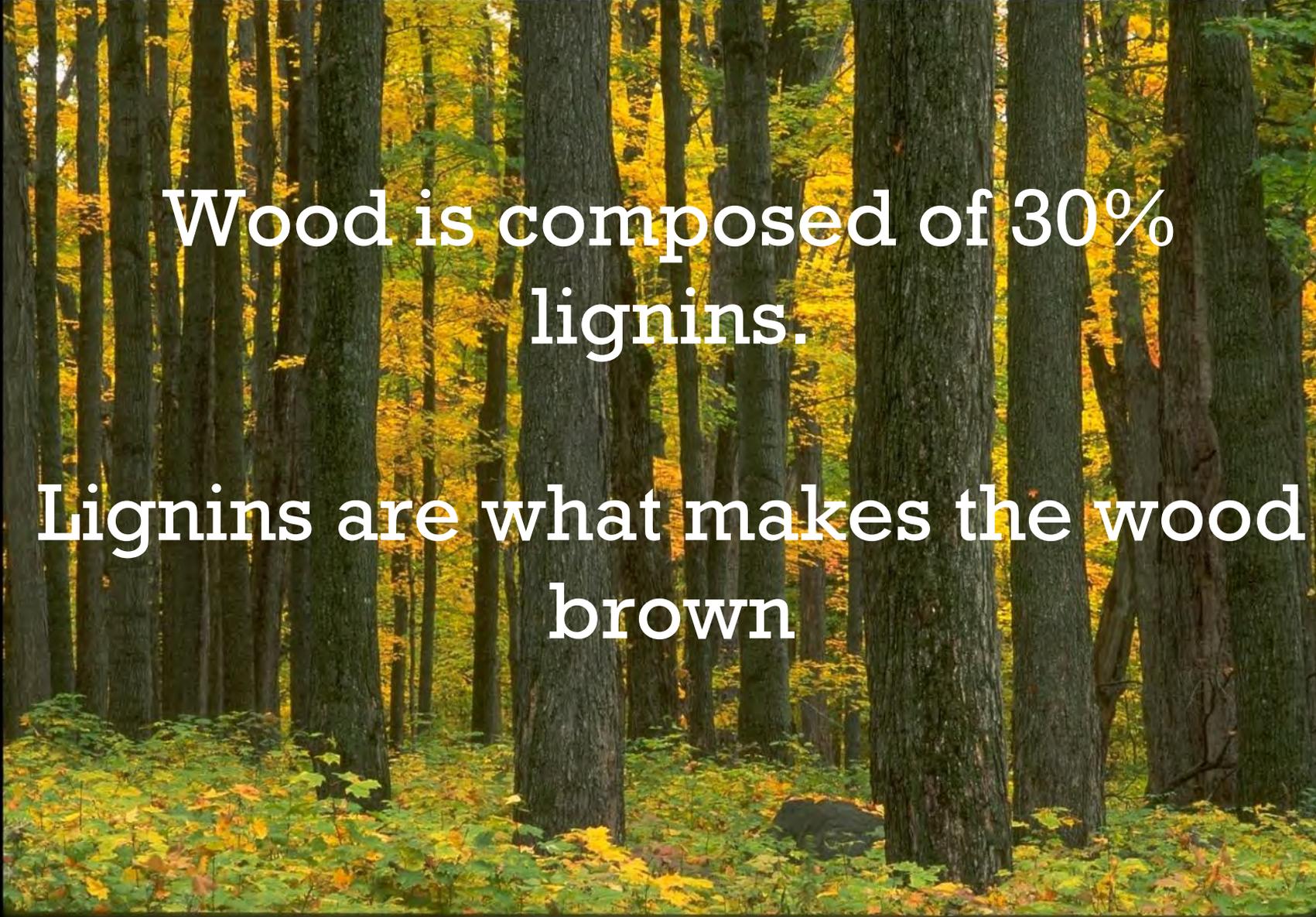
# The problem with office paper

- Produces toxic by-products
- Organochlorine by-products cause health problems in animals and humans
- Uses high temperature energy in the process

# Chlorine is used to make this paper

- Organochlorines are generally foreign to nature, they tend to be:
  - extremely toxic
  - long living in the environment
  - fat soluble





Wood is composed of 30%  
lignins.

Lignins are what makes the wood  
brown

# TAML Oxidant activators

In 1999 professor Terry Collins and Carnegie Mellon University won the Presidential Green Chemistry Award for TAML

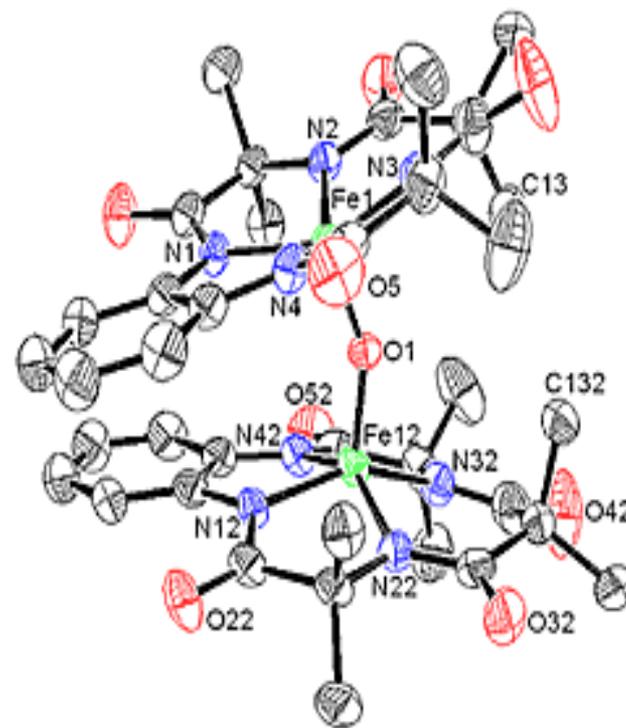


# TAML

## Tetra-amido macrocyclic Ligand

### How does it work?

- TAML activators act as a catalyst to make  $\text{H}_2\text{O}_2$  a more efficient bleaching agent
- The TAML activator has a ligand structure that surrounds the iron
- TAML activates the hydrogen peroxide releasing free radicals (unpaired electrons) that destroy pigment.



# TAML Activator Case Study

- **Students read article about the Paper Industry and Bleaching of paper**
- **Student Questions**
- 1. What are some advantages of using the TAML™/hydrogen peroxide bleaching system over chlorine systems?
- 2. What is the difference between PCF and TCF paper? (see the [Association of Vermont Recyclers](#))
- 3. What is a metallo-redoxactive oxidant?
- 4. What metals other than iron would you propose for you in this type of system? Why?
- 5. Why is a macrocyclic tetraamide ligand a good choice over other ligands for this reaction?
- 6. What would be the by-product of the hydrogen peroxide decomposition in the delignification process?
- 7. How do lignin's aromatic rings become chlorinated in the presence of chlorine gas? Show a mechanism.
- 8. What other macrocyclic ligands would you suggest studying for their potential to catalyze hydrogen peroxide delignification reactions?
- 9. When considering only the donor atoms of the tetraamide ligands, along with the iron center and coordinated water molecule as shown in Figure 5, what is the point group of the complex?
- 10. Where do you commonly encounter Kraft paper in your life. Cite some examples over the last week.

# TAML Lab Activity

- Lab demo of Chlorine Bleach and Hydrogen Peroxide on Saw Dust. (Extension to actually make paper with the pulp)
- Students recognize the  $\text{H}_2\text{O}_2$  is not effective, and required an activator
- Lab utilizes the effect of activators in society
  - Addition of a water softener to hard water to improve soaps ability to form suds
  - Hard water is synthesized by adding magnesium ions to tap water. Hard water will NOT form soap suds
  - Adding carbonate to the solution will precipitate the Magnesium and activate the soaps ability to form suds.

# QUESTIONS



# Thank you! Please Join Us Again!

\*\*\*\*You must register for all the webinars individually

**November 13, 2013, 3:00 pm - 4:00 pm PST**

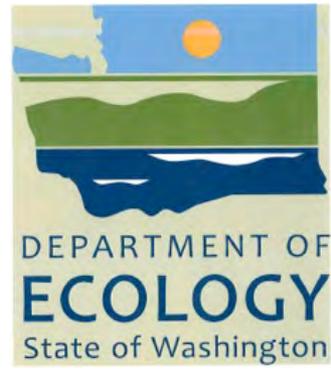
- **Safer Chemistry: Drop-In Replacement Labs**

<https://attendee.gotowebinar.com/register/4847586590197116416>

Reminder:

WA State teachers will receive 1 clock hour for attending & participating in this webinar

contact: Saskia van Bergen      [Saskia.vanBergen@ecy.wa.gov](mailto:Saskia.vanBergen@ecy.wa.gov) by **10/31/13**



[http://www.ecy.wa.gov/programs/hwtr/P2/GreenChem/greenchem\\_ecy.html](http://www.ecy.wa.gov/programs/hwtr/P2/GreenChem/greenchem_ecy.html)