



Dioxin Photoproducts of Triclosan and Its Chlorinated Derivatives in Sediment Cores

Chuck Sueper
Pace Analytical Services, Inc.

Background – Anti-bacterial Soap



Background – Anti-bacterial Soap



The New York Times

January 8, 1981

Liquid Soap Grows Steadily

Those bits of soap that slip through fingers, dissolve into jelly or slide down the drain may be a problem of the past. At least that's the claim of the makers of "liquid soap," the hottest entry in the soap market.

Liquid soap, packaged in plastic pump-type dispensers, was first developed by Minnetonka Inc., a relatively obscure company based in Chaska, Minn. Minnetonka, founded with \$3,000 in 1964, last year sold about 75 percent of all liquid soap in the country with its Softsoap brand.

Background – Anti-bacterial Soap



The Associated Press
June 22, 1984

Soap Companies Lathered Up Over Liquid Soap Ad

MINNETONKA, Minn. - The makers of Dial soap are in a lather over a magazine ad for a liquid cleanser that showed disease-causing microorganisms superimposed over a picture of a soap bar.

The ad by Minnetonka Inc. for its Softsoap and Derma Scrub liquid soaps is deceptive and sensational, says John Heinze, chief of microbial testing for Armour-Dial Inc., based in Scottsdale, Ariz.

Liquid soaps make up 10 percent of the \$1 billion hand soap market

Background – Anti-bacterial Soap



Advertising Age
October 26, 1987

Liquid Dial fights germs Jennifer Pendleton

Dial Corp. is re-entering the \$120 million liquid-soap business with a liquid version of its venerable Dial deodorant soap and an unusual marketing strategy. Unlike its competitors in this growing segment of the \$1.2 billion hand-and-body soap market, [Liquid Dial contains an anti-bacterial ingredient called Triclosan](#) that the company says can help stop the spread of cold and flu-causing germs.

TV commercials breaking this week in the distribution areas show a mother, father and child in a bathroom talking about Liquid Dial's anti-bacterial properties as the reason they switched from their regular soap. The spots also will point out that Liquid Dial is the only product in the category to contain such an ingredient.

Background – Anti-bacterial Soap



Advertising Age
July 24, 1989

Dial, Softsoap face germ war

By Laurie Freeman

Dial Corp.'s Dial anti-bacterial liquid soap is cleaning up in the revitalized segment, and liquid pioneer Softsoap is ready for a fight. Dial's pump-dispensed liquid has been available nationally less than a year but has already helped boost year-to-date sales in the liquid soap segment to \$200 million, up 73.9% from last fall. The segment now represents 13.3% of the \$1.5 billion toilet soap category.

[Softsoap](#), a Colgate-Palmolive Co. division, will aim to solidify its position this fall with the [introduction of its own pump-dispensed, anti-bacterial extension](#).

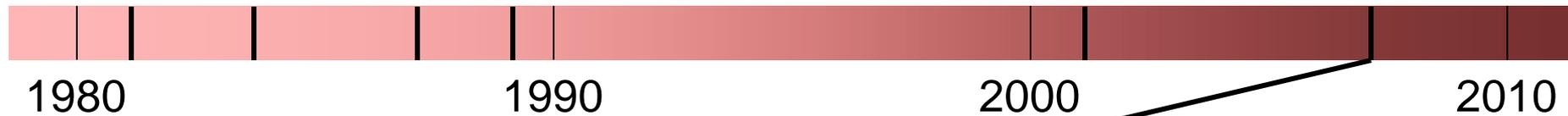
Anti-bacterial liquid soaps now represent 23% of liquid-soap sales and account for more than half the segment's growth.

Background – Anti-bacterial Soap



Triclosan used in 76% of commercial liquid handsoaps
Environ. Health Persp. **2001**, 109, A18.

Background – Anti-bacterial Soap



Business Wire
September 20, 2007

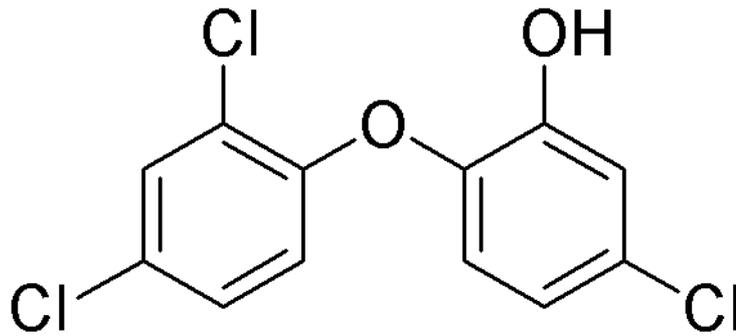
No Crest For the Anti-Bacterial Wave

CHICAGO - Heightened levels of "germaphobia" have given rise to a huge influx of new [anti-bacterial] products...[which] increased from fewer than 200 worldwide in 2003 to some 1,610 in 2006 - an impressive 713% growth.

"Interest in anti-bacterial products first came to light in the early 1990s. But more recently the market has picked up again on the back of the SARS epidemic of 2002-2003, outbreaks of avian flu, and other high profile stories such as superbugs in hospitals across Europe and the UK in particular," comments Lynn Dornblaser.

Some 71% of American adults..."prefer anti-bacterial and germ-killing cleaning products". It is the youngest adults, aged 18-24, who are the most likely to agree with this statement (80%), which bodes well for the future of these products as these young adults are likely to take their cleaning preferences with them as they age.

Triclosan



triclosan

- Broad-spectrum antimicrobial
- Trade name **Irgasan DP300** (Ciba-Geigy)
- Found in many personal care products
 - Handsoap
 - Toothpaste
 - Footwear
 - Acne creams
 - Plastics



New triclosan containing product?

French's Introduces Antibacterial Mustard

April 13, 2005 | [Issue 41•15](#)

ROCHESTER, NY—In response to increasing American demand for tangier, more hygienic meals, condiment giant French's has introduced a new antibacterial mustard.

"Each year, 15 million cases of bacterial food poisoning originate in U.S. home ...



Source: The Onion, April 13, 2005

Triclosan in the Aquatic Environment

2002, Tixier, Singer, Canonica, Mueller

- **Triclosan fate and transport** from a wastewater treatment plant to a lake
- **Microbial degradation** and **sedimentation** important in the plant
- **Photolysis** and/or **microbial degradation** important in the lake

2002, Kolpin, et al.

- **139 streams analyzed** for a suite of contaminants
- Triclosan was one of the most **commonly found** (58%)
- Median concentration **0.14 ppb**, maximum concentration **2.3 ppb**

Pharmaceuticals in US Surface Waters



139 Streams/Rivers studied; analyzed for 95 compounds

- Pharmaceuticals detected at 80 % of sites
- Concentrations detected in US waters
 - Streams: 0.13 -1.9 mg/L
 - Fish hatcheries: 0.10 - >15 mg/L

Kolpin, D. W.; *et al.* *Environ. Sci. Technol.* **2002**, 36, 1202-1211.; Thurman, E. M.; *et al.*; *USGS Fact Sheet 120-02*, **November 2002**.

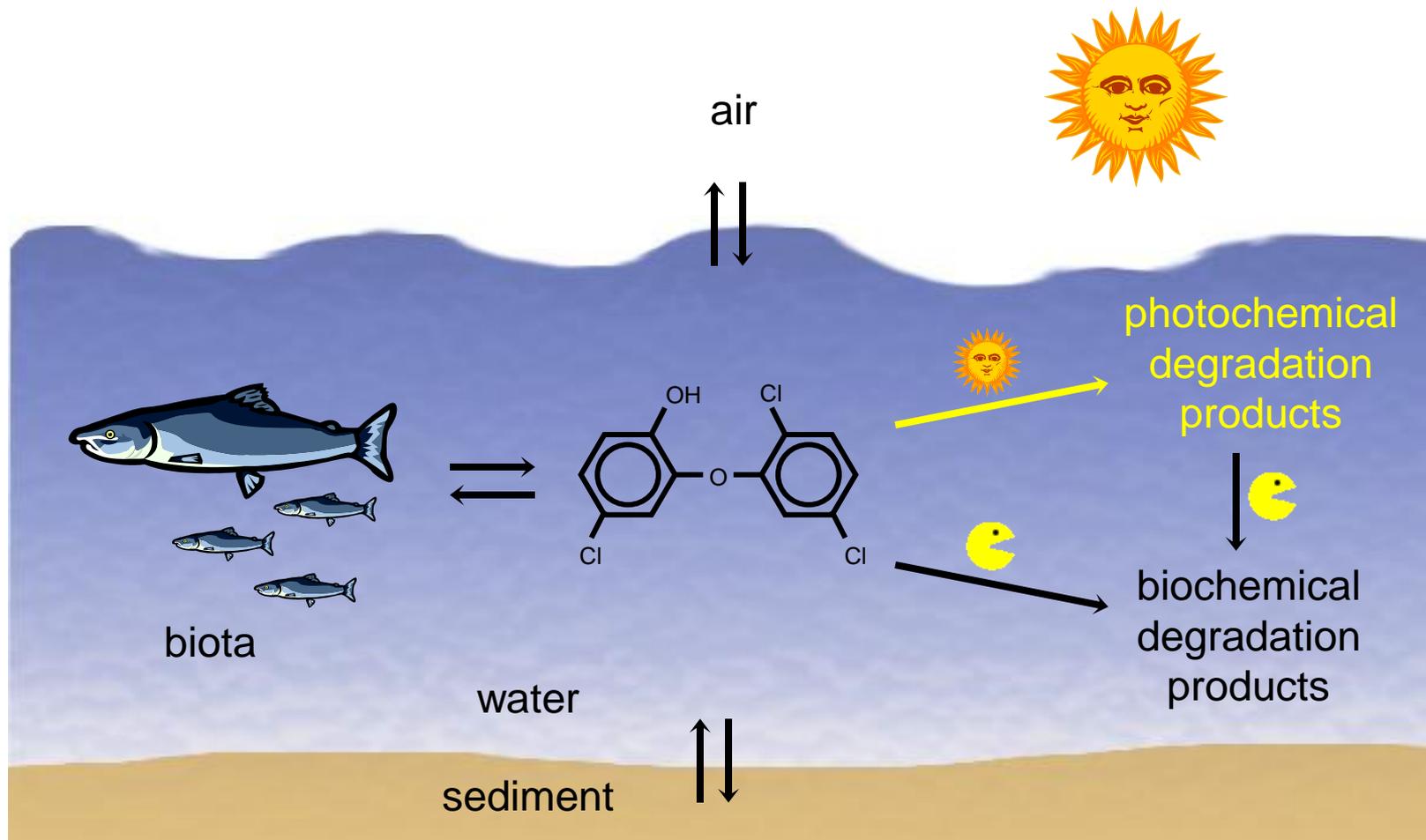
Triclosan in the Aquatic Environment (2)

2002, Adolfsson-Erici, Pettersson, Parkkonen, Sturve
(*Chemosphere*, 2002, 46, 1485).

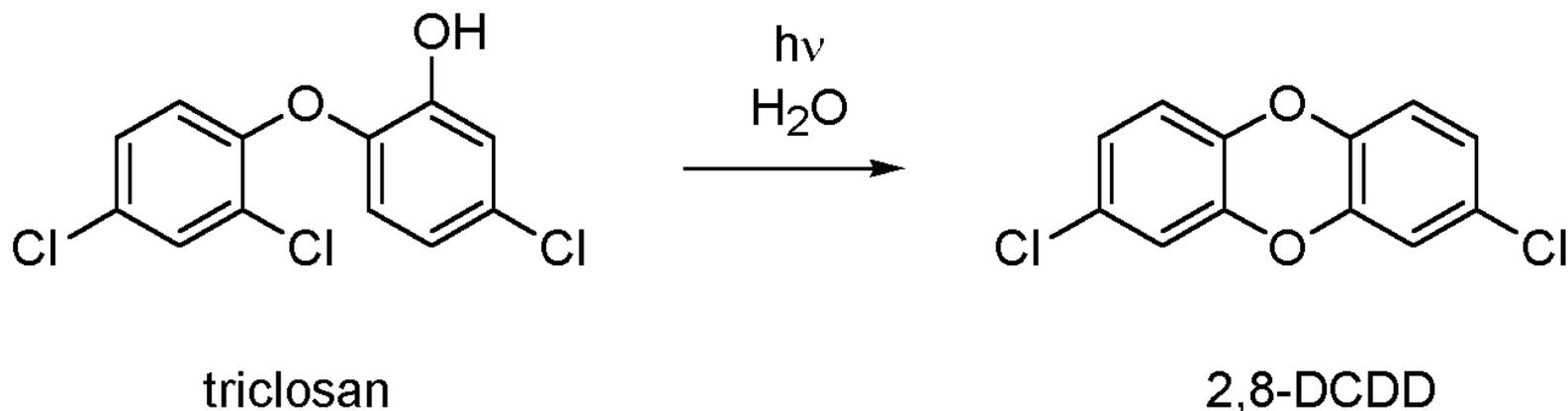
- Triclosan found in **wild living fish** from receiving waters of municipal wastewater plants in Sweden
- Triclosan detected in 3 of 5 **human breast milk** samples



Aquatic Environmental Fate



Photochemical Formation of 2,8-Dichlorodibenzo-*p*-dioxin from Triclosan



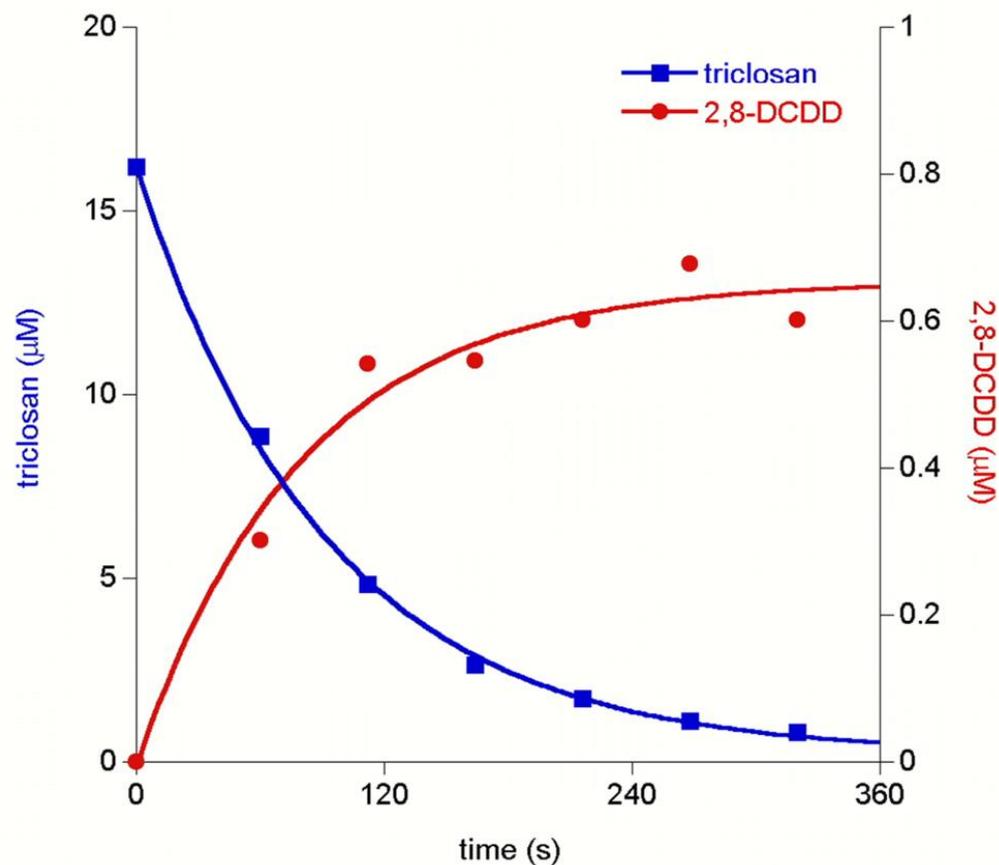
Conversion Efficiency

Yield 3-4 % at pH 8

pH dependence

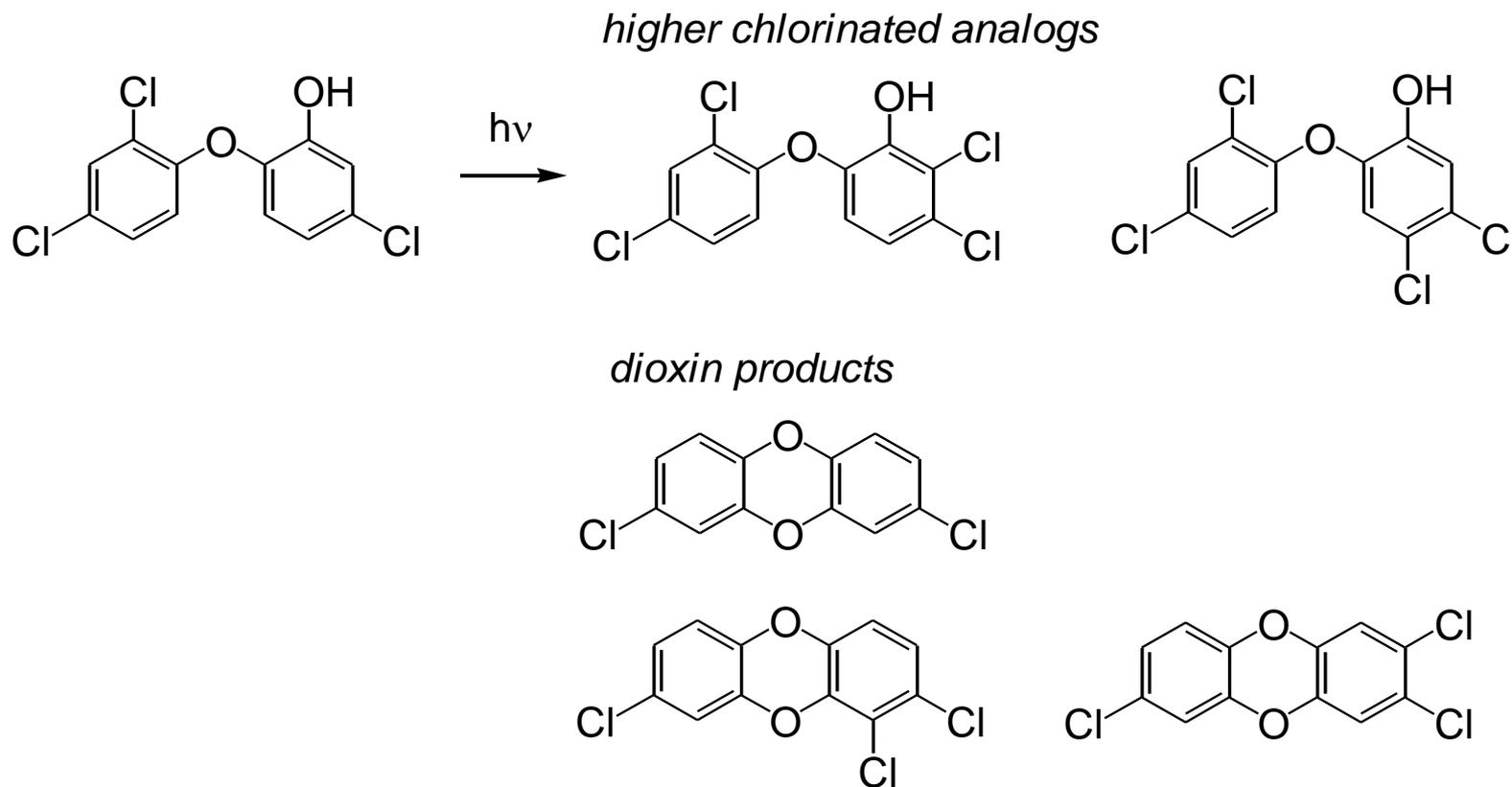
- Faster rates at high pH
- No 2,8-DCDD formed below pH 8

2,8-DCDD is photolabile



Spiked Mississippi River water yields 2,8-DCDD upon photolysis

Previous Report of Dioxin Formation



Kanetoshi, Ogawa, Katsura, Kaneshima, Miura
J. Chromatography A **1988**, 145-155.

Media reports

QuickTime™ and a
decompressor
are needed to see this picture.

April 15, 2003

Fears over antibacterial ingredient

Researchers at the University of Minnesota found that when triclosan in water was exposed to sunlight, it was chemically converted into a dioxin.

This reaction produces only a very mildly toxic chemical - perhaps 150,000 times less toxic than the types of dioxin considered the most dangerous.

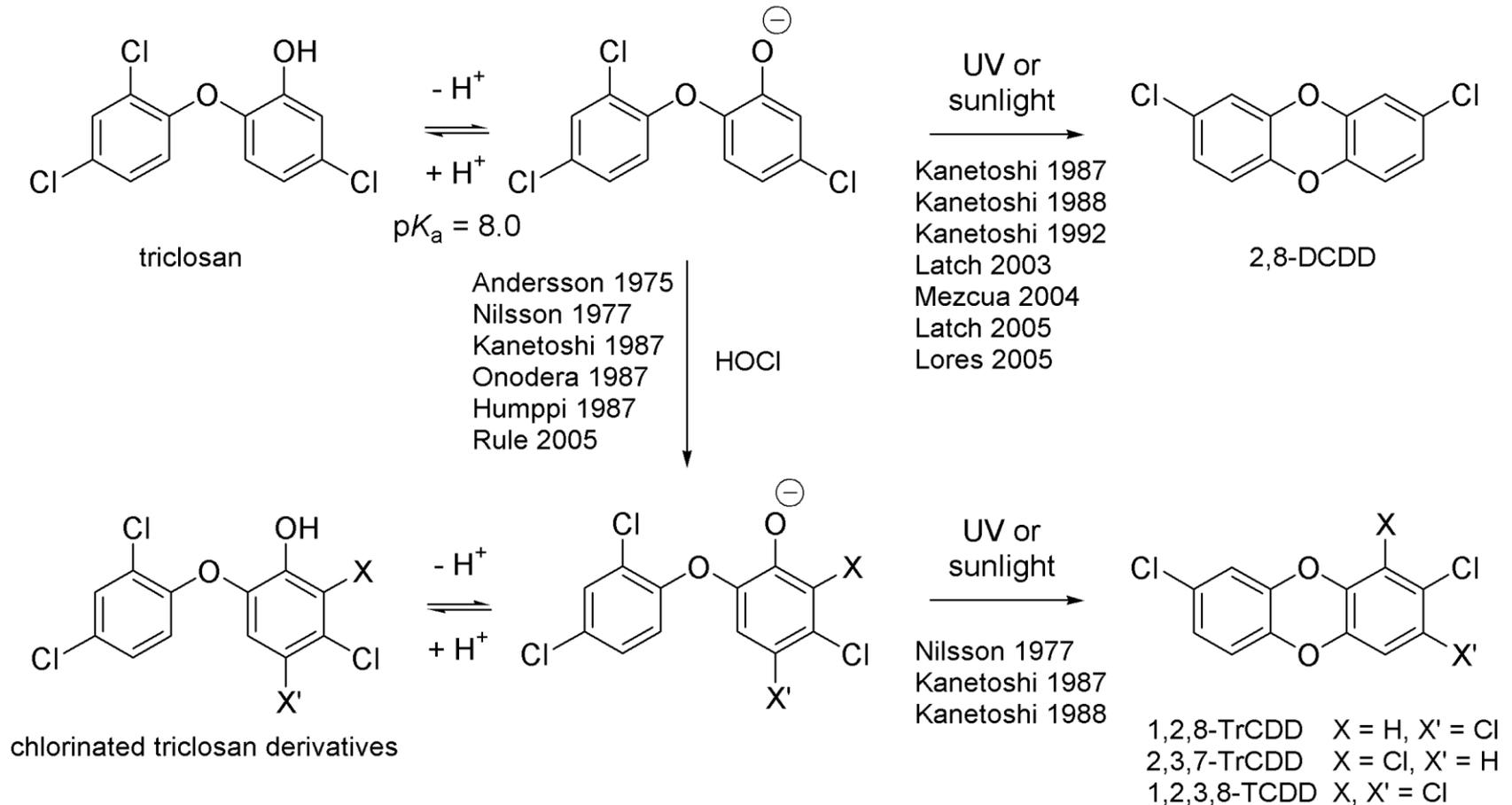
Bigger problem

However, the scientists believe that triclosan-tainted water treated with chlorine at water treatment plants could then be broken down into something far more potent.

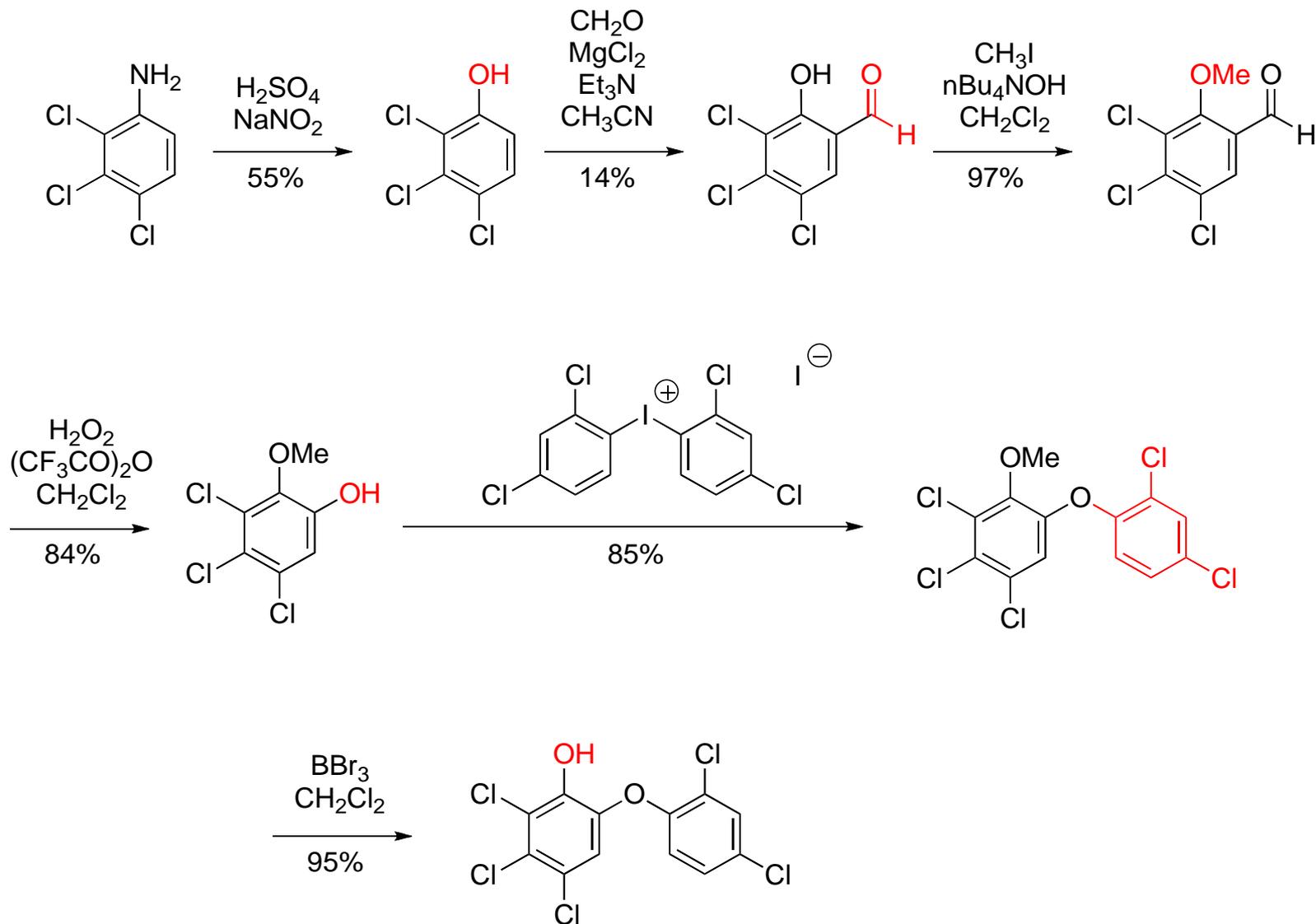
Dr Kristopher McNeill, one of the researchers, said: "Repeated exposure to chlorine could chlorinate triclosan.

"After chlorinated triclosan is discharged, sunlight could convert it into more toxic dioxins. Such a process might be a source of highly toxic dioxin in the environment."

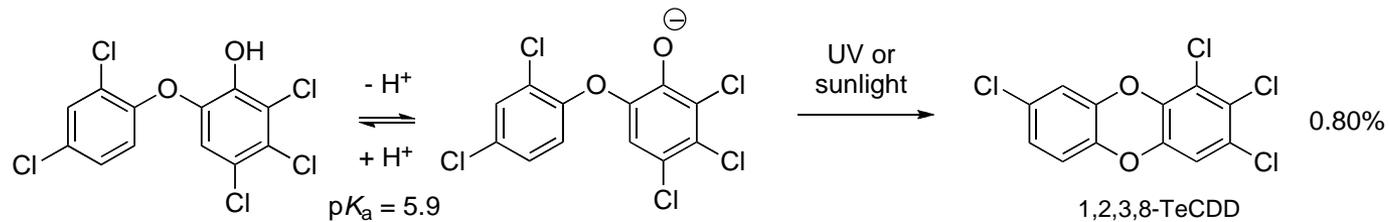
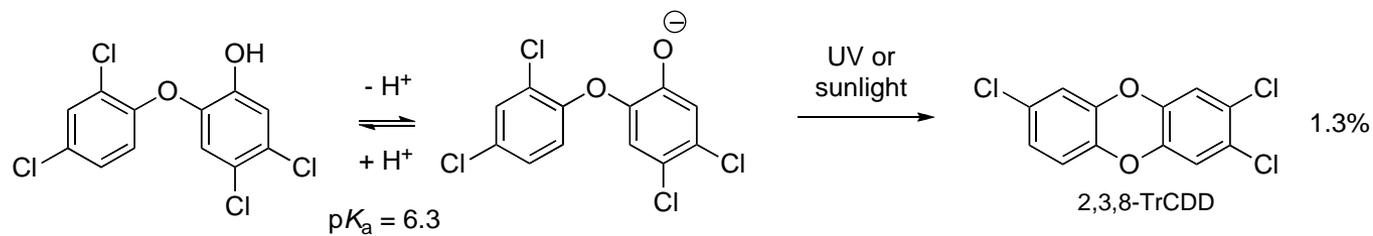
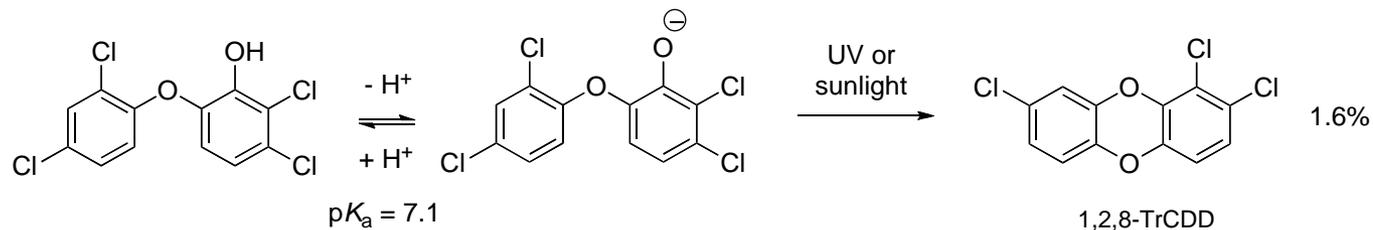
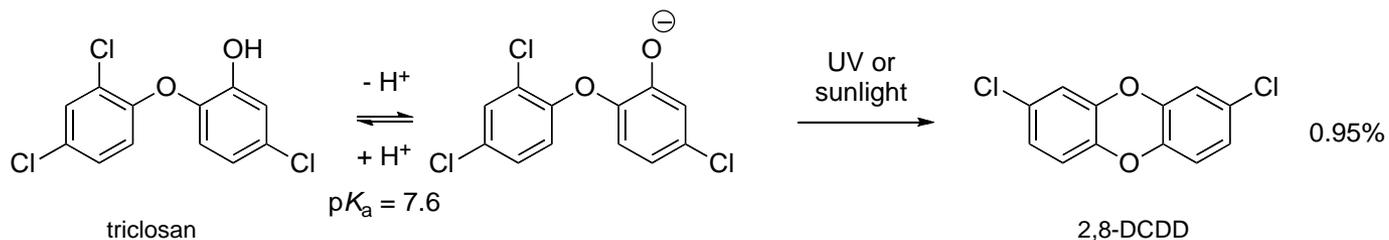
Precedents suggesting higher dioxin formation



Synthesis of chlorinated triclosan derivatives



Mississippi River photolysis results



Estimation of national load of TCS and CTD

- Assumptions
 - Wastewater influent triclosan conc. = 3 mg/day per capita
 - US population = 300 million
 - Wastewater treatment removal efficiency
 - 75% activated sludge (96% removal)
 - 25% other processes (85% removal)
 - Total CTD conc. = 1/25 of triclosan conc.
 - Same removal efficiency for CTDs as triclosan
- Results
 - 22 metric tons triclosan/yr discharged
 - 0.88 metric tons CTDs/yr discharged

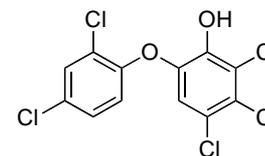
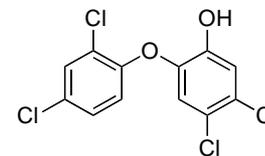
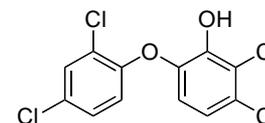
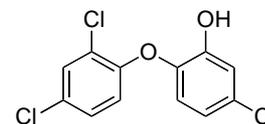
Estimation of national TCS-derived dioxin load

- Assumption
 - 10% of triclosan and CTDs lost from water column due to photolysis
 - Dioxin yield = 1%
- Results
 - 22 kg/yr 2,8-DCDD
 - 0.8 kg/yr tri- and tetra-dioxins
- Toxicity Equivalent Units (TEQs)
 - Relative to 2,3,7,8-TeCDD
 - Di: 0.001
 - Tri and tetra: 0.01
 - 30 g/yr TEQ for TCS-derived dioxins
 - CTD-derived dioxins represent 40% increase in TEQ over TCS-derived dioxin
 - Estimated dioxin load is 1% of air emissions

Wastewater Treatment Plant

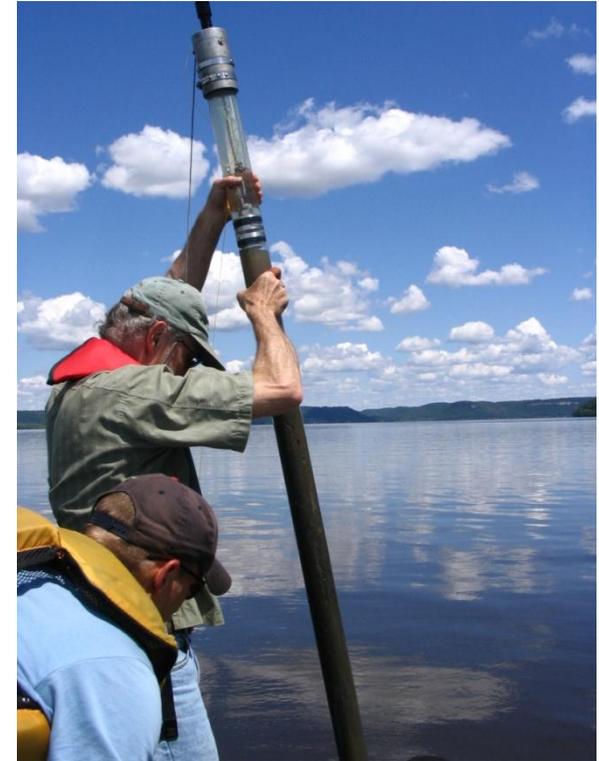
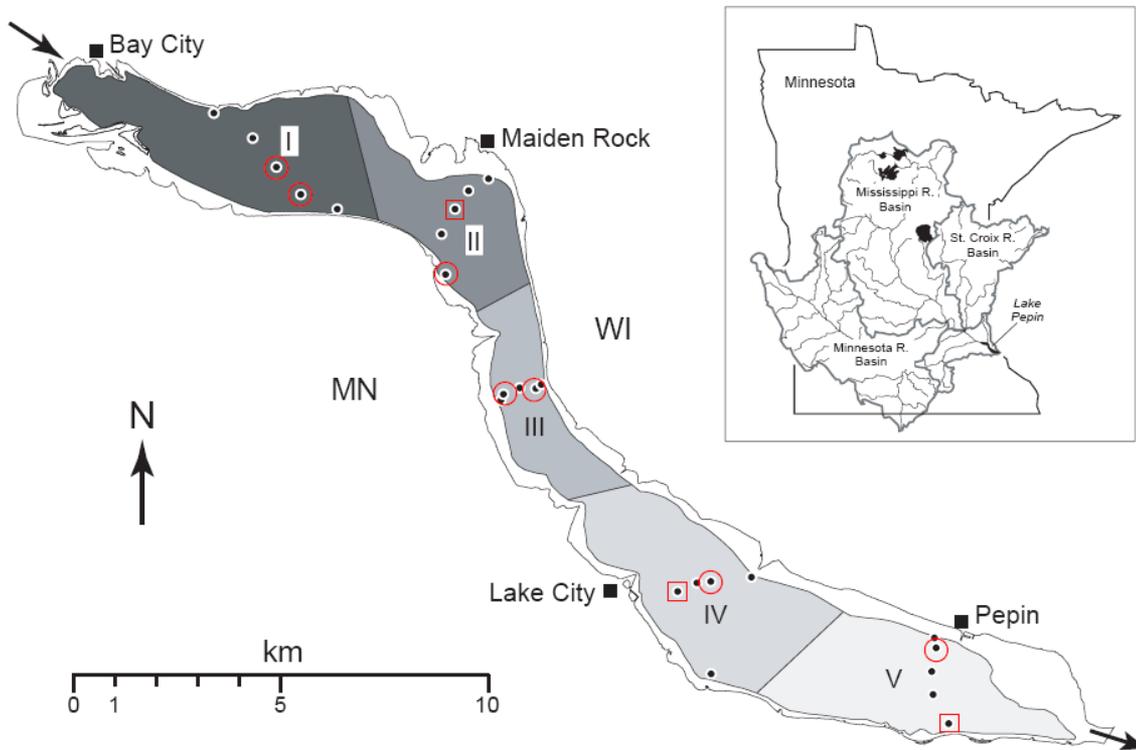


Wastewater Effluent Analysis (pre- and post-chlorination)



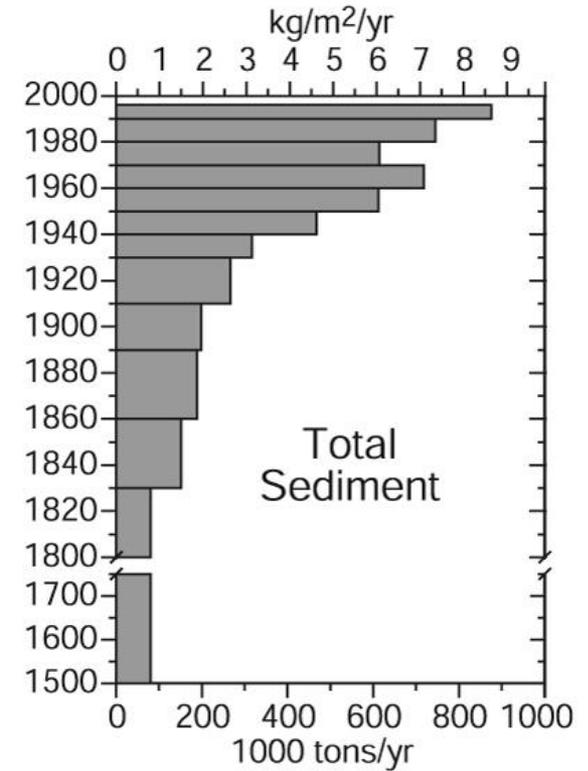
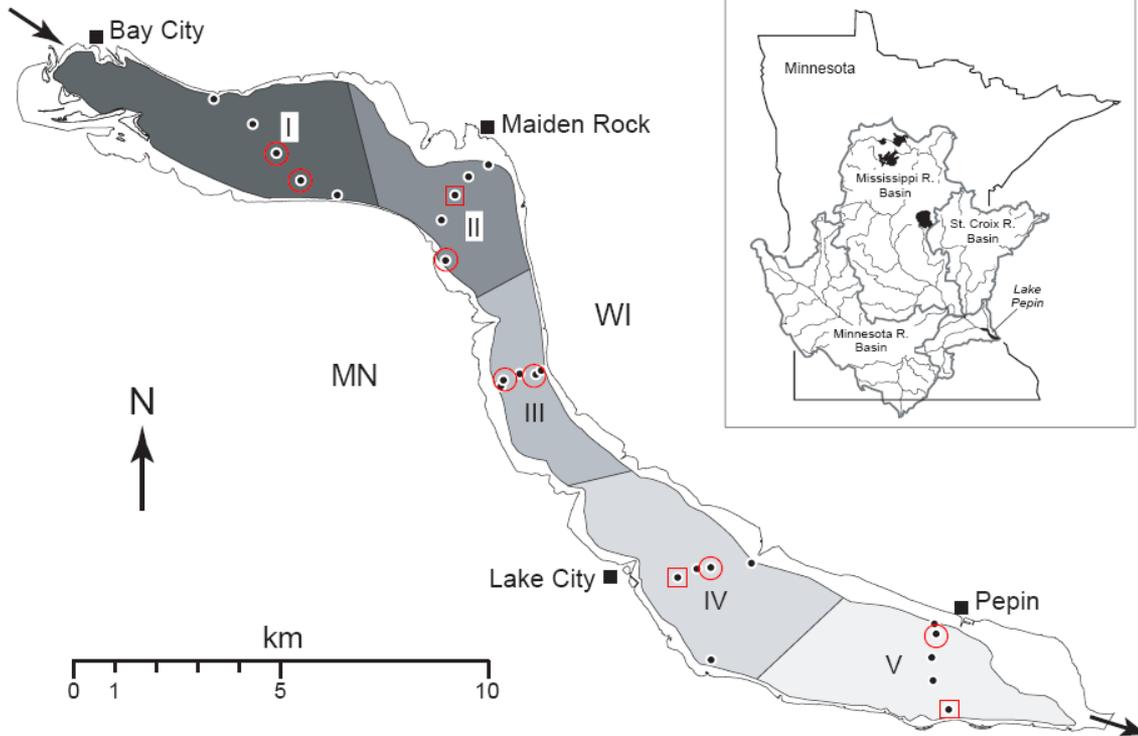
Lake Pepin - Minnesota

- Analysis of Lake Pepin sediment cores

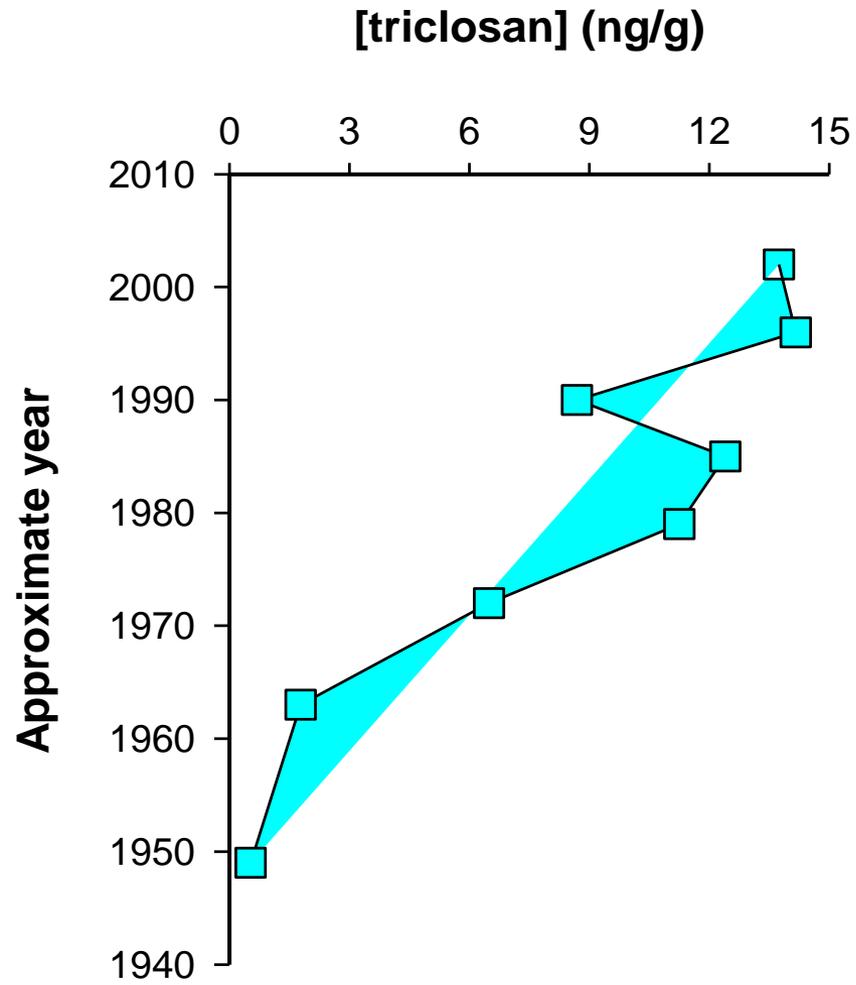


Lake Pepin - Minnesota

- Analysis of Lake Pepin sediment cores

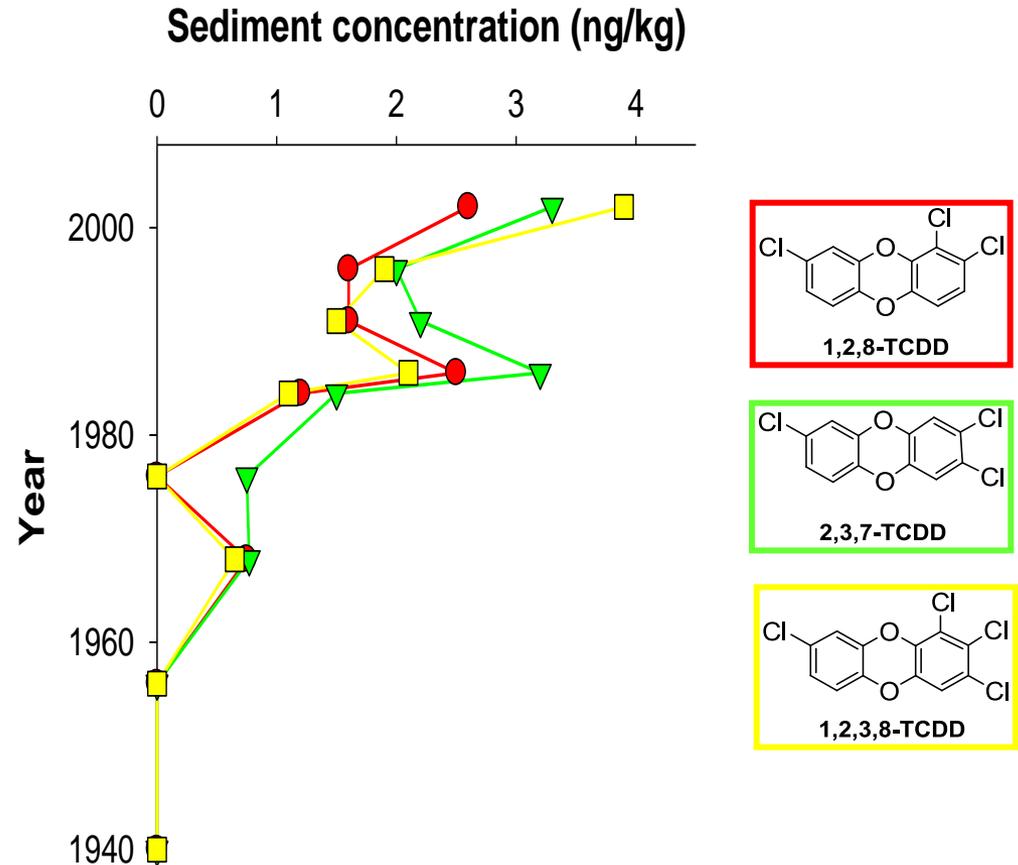
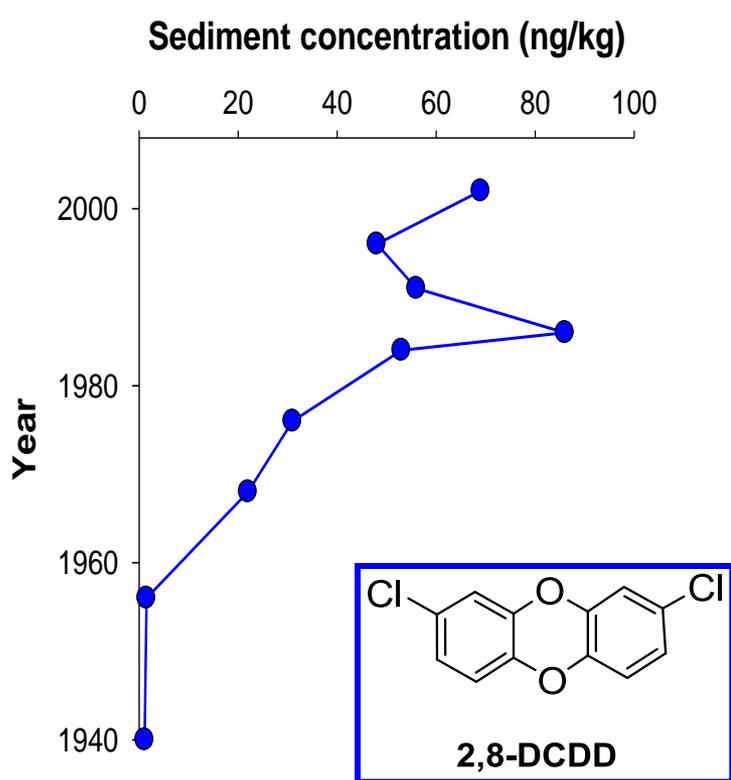


Triclosan Timeline

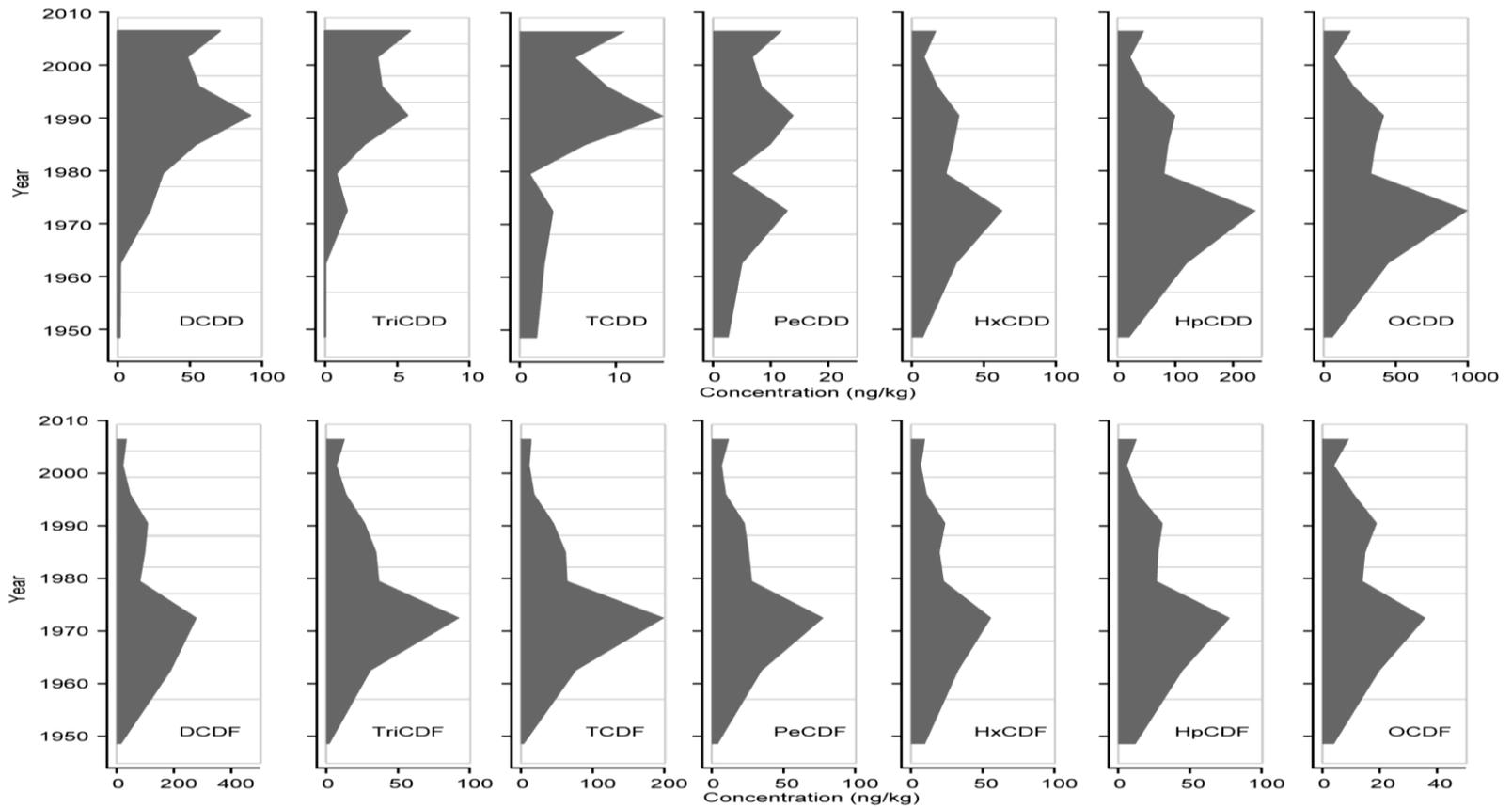


Triclosan as Dioxin Source

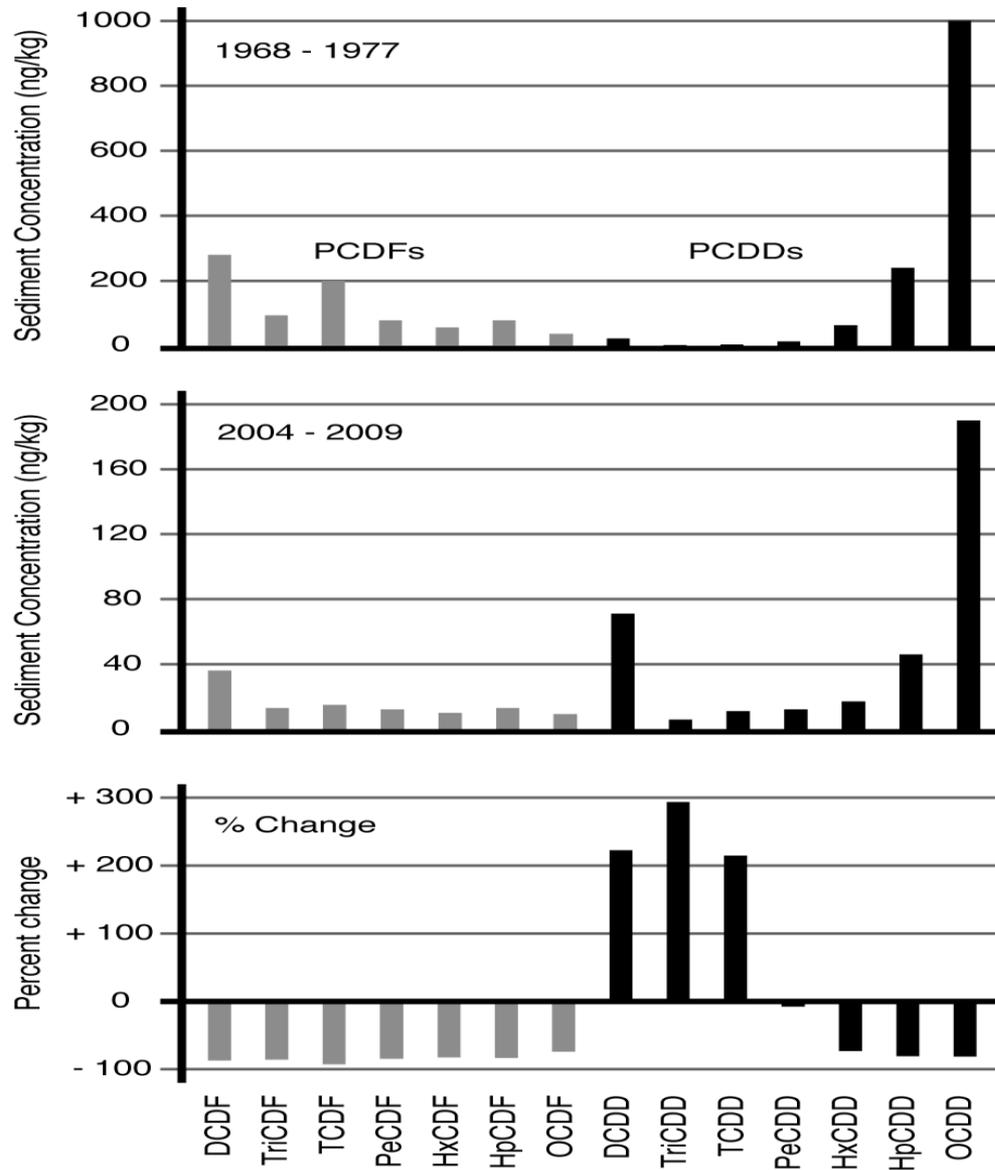
di- and trichlorinated dioxins consistent with triclosan as the source



Congener Profiles



Congener Profile Changes



Other Potential Sources - Impurities

- Not likely due to more efficient removal of more hydrophobic PCDDs
- Tri- and tetra- congeners in sediment don't match those in Triclosan

Other Potential Sources - Reduction

- Not likely since older cores would have more time for anaerobic reduction to occur and had lowest levels of di-, tri- and tetra- congeners
- Not likely because more recent cores have lower levels of possible precursors and less time for reduction – but higher levels of di-, tri- and tetra- congeners

Conclusions

- Trends suggest a distinct source of selected di-, tri- and tetra-chlorinated dibenzo-p-dioxin congeners
- This profile for this source varies from the typical deposition profile associated with other congeners.
- This source appears to be the photochemical transformation of Triclosan

Ongoing studies

- Funding was approved for five additional sites
- Sites to include locations with urban sources as well as more remote locations

Thank You

- University of Minnesota team – especially Jeff Buth, Bill Arnold and Kris McNeill
- Pace Analytical HRMS team
- Thank you for your attention