

University of Massachusetts, Amherst April 24-25, 2012

"Food Safety and Chemophobia"

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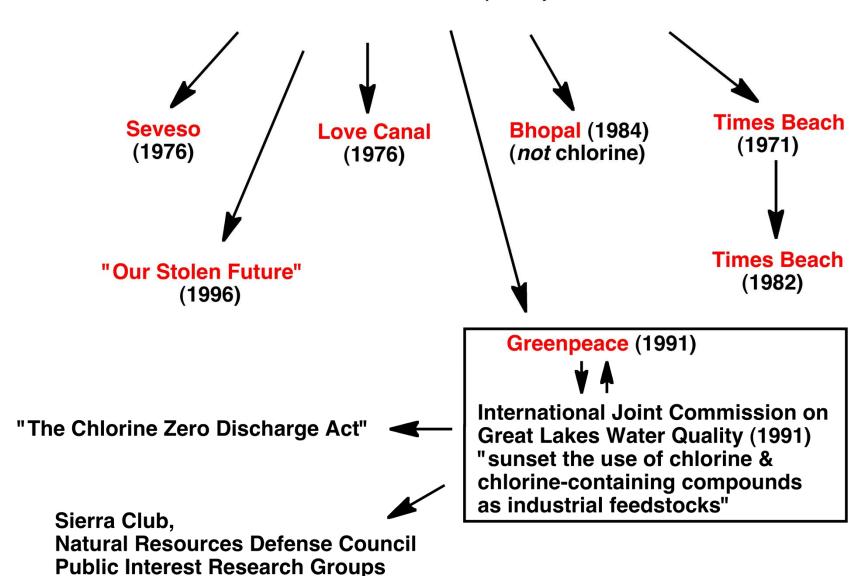
### Education....

What we need in order to discuss

these issues intelligently

### The Birth of "Chlorophobia" and "Chemophobia"

*"SILENT SPRING"* (1962)



### What You Won't See on the Front Page –

- The Love Canal Final Report: "Victims" were found to possess somewhat better health and showed lower incidences of all forms of cancer than the general population of the rest of the state of New York.
- A second, larger study to examine a possible connection between breast cancer risk and exposure to DDT and PCBs has found no strong evidence to support such a link (*J. Nat. Cancer Inst.* 1994, *86*, 589).
- The EPA official who ordered the evacuation of Times Beach, Missouri, later admitted that this was a mistake and was unnecessary.

### How and Why I Got Involved

- "Some types of synthetic compounds, including halogenated hydrocarbons such as PCB, are not found in nature." (1)
- "Organochlorines are so rare in natural systems that living organisms cannot cope with them when they enter the ecosystem." (2)
- "Organochlorines are not known to occur naturally in the tissues of humans, vertebrates." (3)
- "Practically none exist under natural conditions [organochlorines]." (4)
- "Unlike metals, most of these compounds [halogenated hydrocarbons] are man- made and do not occur naturally." (5)
  - 1. Science 1990, 250, 745
  - 2. Greenpeace documentation
  - 3. International Joint Commission, 1989
  - 4. Thornton, "Pandora's Poison," 2000
  - 5. Clark, "Marine Pollution, 5th ed." Oxford, 2001

### **Cholera Epidemic in Peru (and more recently in Haiti)**

One million cases

19,000 deaths since 1991

20 countries affected (South and Central America, and Mexico)

Originated from a ship's bilge water from the Far East

Peruvian officials curtailed water chlorination apparently out of fear from the EPA that chlorine or chlorine water purification byproducts cause cancer (and a misinterpretation of EPA studies)

\$770 million in costs to Peru

Data and analyses linking chlorination of drinking water and increased cancer risk have since been discredited by EPA's own Science Advisory Board

U.S. cases due to the Peru outbreak were 53 (1991-94); whereas only 5 were reported in U.S. from 1965-91

Despite the fact that **EVERYTHING** we see, smell, and touch is a chemical, there is a pervasive fear and loathing of the word "Chemical" by the public at large, and to some extent by regulators and the government

### "Chemical" is a Dirty Word so euphemisms abound!

We speak of:

Wine "aroma"
Flower "bouquet"
Perfume "fragrance"
Restaurant "odor"
Bakery "smell"
Garbage "stench"
Skunk "scent"
Air "fresheners"

All of which are organic chemicals!

## People also need to understand that

Molecules are really small

and that

**Concentration is important** 

#### **How Much is a Part-Per-Billion?**

```
1 ppb = 1 step to the moon
```

1 ppb = 1 minute in 2,000 years

1 ppb = 1 person in the entire population of China

1 ppb = 1 medium-size crouton in a 500-ton salad

1 ppb = 1 nine-iron golf shot towards the sun

#### **How Much is a Part-Per-Trillion?**

```
1 ppt = 4#coconut \q#d#\rz #ri#frfrqxw\#\wr\#\wk\h\#\vxq
```

1 ppt = 1 second in 33,000 years

1 ppt = 1 penny in ten billion dollars

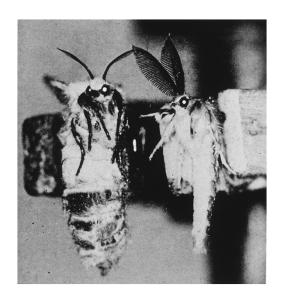
1 ppt = 1 drop of vermouth in 16 million gallons of gin (a VERY dry martini!)

The point being that very few chemicals are toxic at these levels, if at all

Just because we can smell a chemical doesn't mean it is necessarily toxic

For example, we can smell HCN and H<sub>2</sub>S well below the toxic (lethal) levels

### The Nose Knows



- The male Gypsy moth can detect as few as 10,000 molecules of sex pheromone secreted by the female!
- In a single drop of water there are 1,000,000,000,000,000,000,000 molecules of water (H<sub>2</sub>O), which is equal to the number of grains of sand on earth!!!

Molecules are really, really small

### Dioxin in a Glass of Milk (100 mL)

<u>Concentration</u> <u>mg Dioxin</u>

1 part per million (ppm) = 0.1

1 part per billion (ppb) = 0.0001

1 part per trillion (ppt) = 0.0000001

or 180 billion molecules of dioxin!

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1 part per quadrillion = 0.000000001

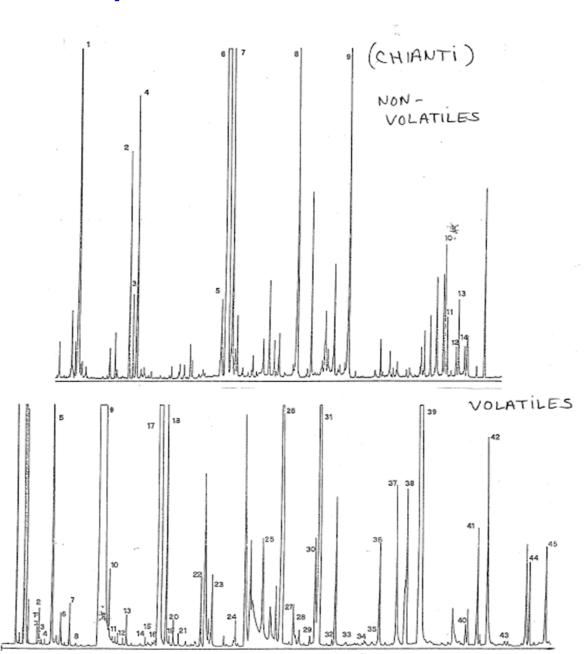
1 part per quintillion = 0.000000000001

or 180,000 UNDETECTABLE molecules of dioxin!

### Natural Chemicals in Wine

Concentration Compounds		Number of
parts per hundred (1–90%)	(1 in 100)	5 (water, EtOH, tartaric acid)
parts per million (micrograms/g	•	60
parts per billion (nanograms/gi	,	320
parts per trillion (picograms/gra	•	2,500
parts per quadrillion (1 in 10 <sup>15</sup> ) (femotograms/gram) unidentified)		20,000!! (observed, but most

### Compounds in a Chianti Wine



Wine:

**Aroma:** 

### Pyrazines in Sauvignon Blanc

Odor detection (2 ppt!) is 100 times lower than HPLC detection limit

Pyrazines are higher in grapes grown under cool conditions

Pyrazines decrease during ripening (up to 96% from veraison to harvest)

"A" at ≥ 8 ng/L (ppt) added to pyrazine-free white wine significantly contributes to vegetative aroma

Pyrazines are be present in California Cabernet Sauvignon from Monterey and also in bell peppers and other vegetables

### **Methyl Chloride (Chloromethane)**

- Found in marine algae, giant kelp, wood-rotting fungus, ice plant, cultivated mushrooms, white cedar, pencil cedar, evergreen cypress, fungi, phytoplankton, forest and brush fires, volcanoes, tobacco smoke, and potatoes
- 3 5,000,000 tons/year is produced from the biomass
- 26,000 tons/year from man-made emissions
- 1 gram cellulose (wood) → 2.2 mg CH<sub>3</sub>Cl when burned
- it is estimated that we inhale 10<sup>12</sup> 10<sup>13</sup> molecules of CH<sub>3</sub>CI with each breath! (molecules are really small...)

### Any chemical – natural or synthetic – can be toxic,

"The Dose Makes the Poison"

### **Water Toxicity**

- Chico State University, CA, 2005
- Chi Tau "Hell Week"
- Water hazing: pledges forced to drink up to 5 gallons of water
- The "winning" pledge drank 6 gallons of water in less than 4 hours and died; two others in comas
- Sodium ion concentration plummets
- Cells swell and burst
- Brain enlarges and is "water logged"
- In 2008, a California radio contest to see how much water a person could drink without urinating resulted in the death of a young woman who drank 2 gallons of water in a short period

NaCl: Essential for life in small daily amounts, yet can be lethal in children (2 tablespoons); LD<sub>50</sub> 3,000 mg/kg

NaF: 1-2 mg/day useful for good dental health, but high acute toxicity: LD<sub>50</sub> 35 mg/kg!

### Caffeine can be lethal

- Five-year-old girl ingested 53 "Tri-Aqua" tablets and died six hours later
- Tri-Aqua is a caffeine-containing over-the-counter diuretic
- The victim ingested 3 grams of caffeine, which is equivalent to 30 cups of coffee
- Other fatal caffeine episodes:

35-year-old women accidentally given 3.2 grams intravenously

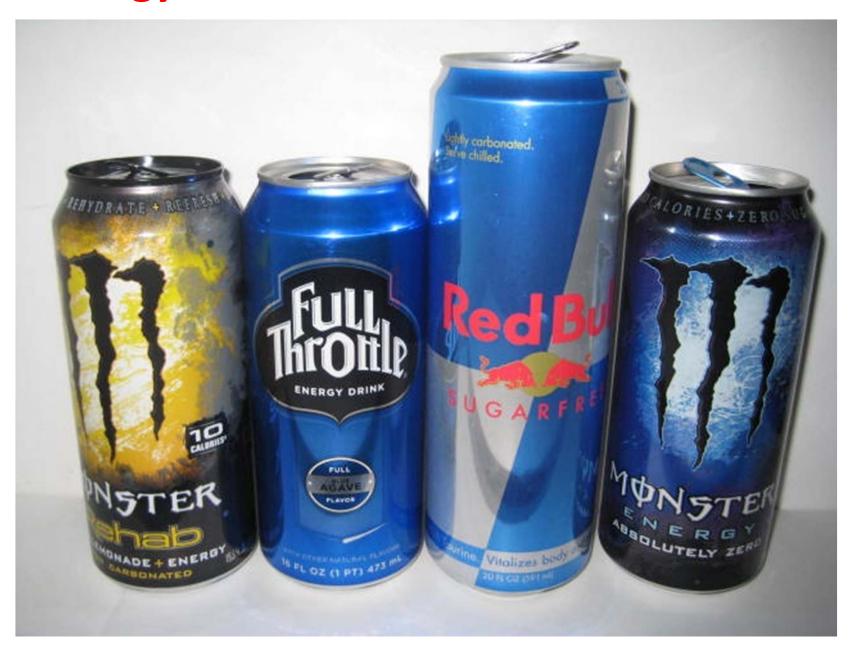
15-month-old child mistakenly given 90% mL of 20% caffeine solution, instead of a 2% solution!

45-year-old woman given 50 grams of caffeine instead of 50 grams of glucose!

27-year-old woman committed suicide by taking 10 grams of caffeine

Dimaio *et al.*, *Forensic Sci. 3*, 275 (1974)

### "Energy Drinks" are Loaded with Caffeine



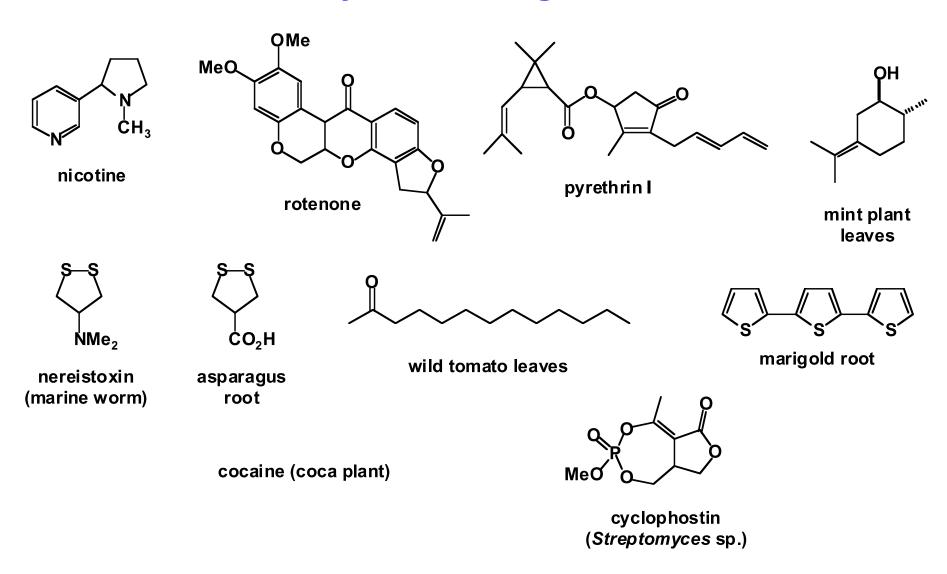
### Caffeine can be beneficial

- Coffee (caffeine) protects against alcoholic cirrhosis, the liver-scarring disease
- 5 million Americans have cirrhosis
- A cup of coffee per day and the risk of cirrhosis drops 22%

# Nature's own arsenal of pesticides

ALL plants, trees, fruits, and vegetables produce their own pesticides

### **Naturally Occurring Pesticides**



### **Natural Pesticides**

Humans ingest 10,000 times more natural than synthetic pesticides, up to 1.5 grams per day

Of 64 natural plant pesticides tested in the typical high doses, 35 were found to be carcinogenic

Of 26 such compounds found in roasted coffee, 19 were found to be carcinogens

The following foods contain natural pesticides that cause cancer in rats or mice and are present at levels ranging from a few ppb to 4 million ppb: apples, bananas, basil, broccoli, cabbage, carrots, cauliflower, celery, cinnamon, cloves, cocoa, comfrey tea, honeydew melon, kale, mushrooms, mustard, nutmeg, parsley, peaches, black pepper, pineapples, radishes, raspberries, tarragon, and turnips

B.N. Ames and L.S. Gold, *Science* 1989, *244*, 755

### **Examples of Natural Pesticides**

- Apple juice contains 137 natural volatile chemicals, of which only five have been tested for carcinogenicity; of these, three have been found to be carcinogenic (benzyl alcohol, ethanol, acetaldehyde).
- Black pepper extracts cause tumors in mice at a level of 4 mg per day for 3 months (160 mg/kg [ppm]); average human intake is 140 mg/day.
- False morel mushroom contains 11 hydrazines, 3 of which are known carcinogens. One of these is present at a concentration of 50 mg/100 g of mushroom (500 ppm) and causes tumors in mice at the level of 0.02 mg per mouse per day.

### **Methyl Bromide from Terrestrial Plants**

Methyl bromide is produced from natural soil bromide by these plants:

broccoli rapeseed pak-choi cabbage radish alyssum

mustard turnip wild mustard

Chinese cabbage

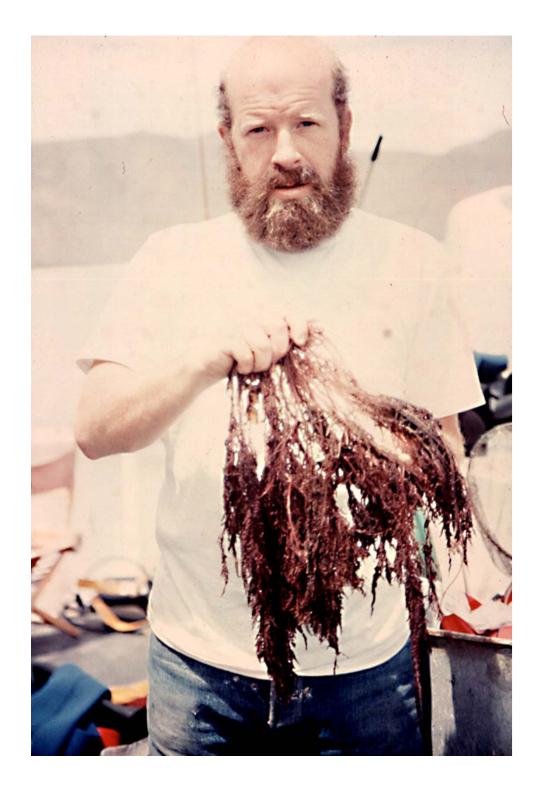
Rates of production are 18 – 36 ng/g/day from 0.06 – 0.31 mg/kg soil bromide

Estimated global annual production of methyl bromide from these two plants is:

rapeseed: 6,600 tons cabbage: 400 tons

"Given the ubiquitous distribution of bromide in soil, methyl bromide production by terrestrial higher plants is likely a large source for atmospheric methyl bromide"

J. Gan et al. Geophys. Res. Lett. 1998, 25, 3595.



## Asparagopsis taxiformis, favorite seaweed of native Hawaiians

(contains 100 different organohalogen compounds, several of which are highly reactive S<sub>N</sub>2 substrates; see next page in the Syllabus)

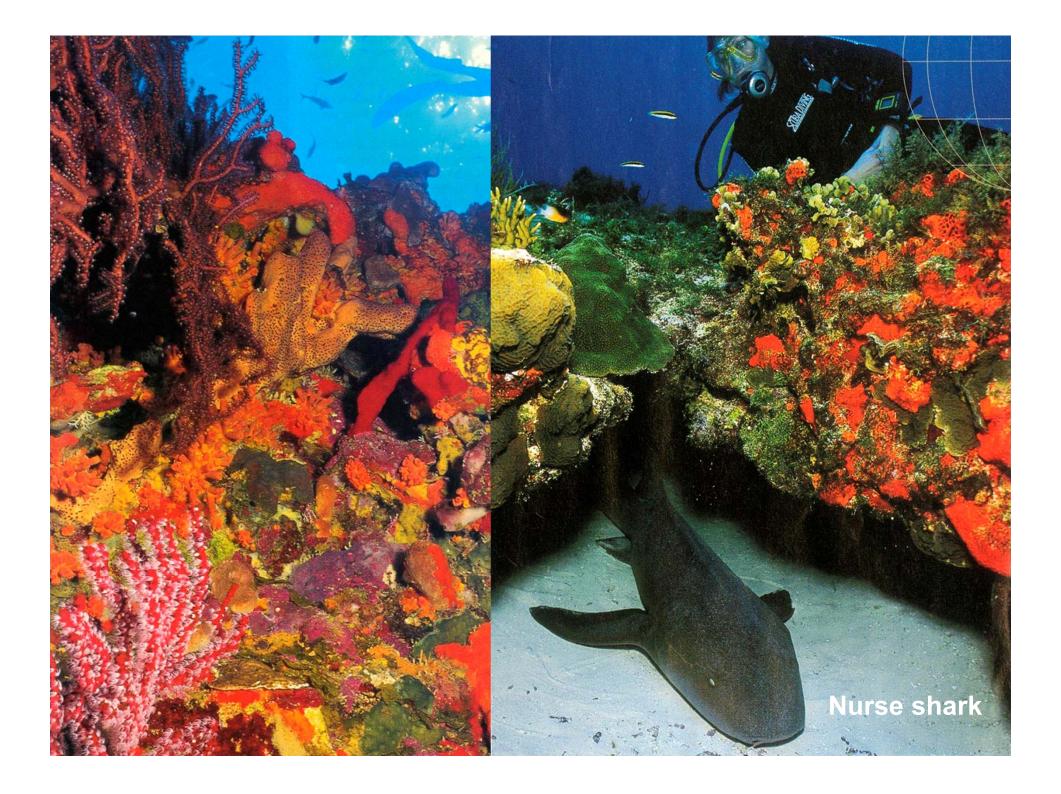
### Organohalogens from Hawaiian Red Alga (Asparagopsis taxiformis)

$$Br + H \qquad Br + H \qquad CI_3C + CCI_3 \qquad HO$$

$$Br + Br \qquad Br + Br \qquad Br + CI \qquad CI_3C + CCI_3 \qquad HO$$

$$Br + CI \qquad CI \qquad CI + CI \qquad CI + Br \qquad Br + CI \qquad CI + Br \qquad$$

• more than 100 different halogenated compounds have been identified (alkanes, alkenes, alcohols, ketones, aldehydes, carboxylic acids and amides, and epoxides)

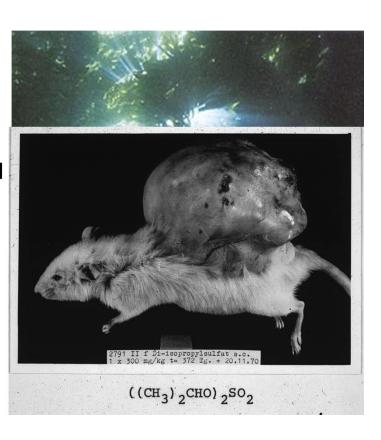


### **Natural Marine Haloalkanes**

• The following compounds have been isolated from marine algae and/or have been found in the oceans

CH <sub>3</sub> CI CH <sub>3</sub> Br CH <sub>3</sub> I	CH <sub>2</sub> Br <sub>2</sub> CH <sub>2</sub> I <sub>2</sub>	CHCI <sub>3</sub> CHBr <sub>3</sub> CHI <sub>3</sub>
CH <sub>3</sub> CH <sub>2</sub> Br	CH <sub>2</sub> ClBr	CHBr <sub>2</sub> CI
CH <sub>3</sub> CH <sub>2</sub> I	CH <sub>2</sub> CII	CHBrICI
BrCH <sub>2</sub> CH <sub>2</sub> I	CH <sub>2</sub> BrI	CHBrl <sub>2</sub>
	_	CHBr <sub>2</sub> I
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br		CHBrCl <sub>2</sub>
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> I		
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> I		(CH <sub>3</sub> )CHI
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br		CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C		3 2 ( 3)

"The Smell of the Ocean?!"



CCI<sub>4</sub> CBr<sub>4</sub>

