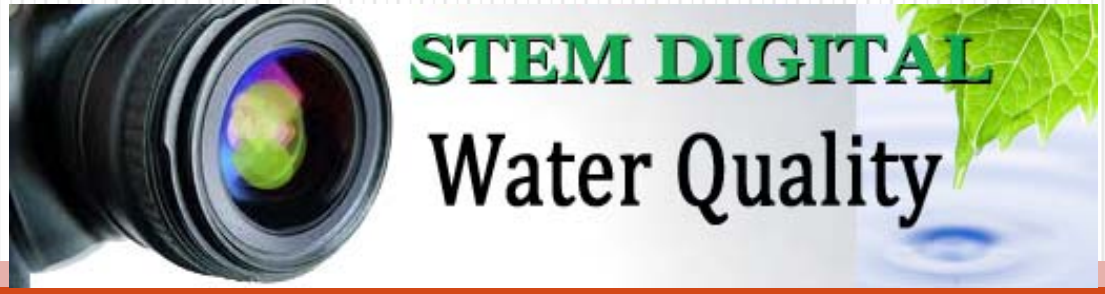


Natural Organic Matter in Water

Formation in Watersheds and Removal in Water Treatment

David A. Reckhow
University of Massachusetts

Outline

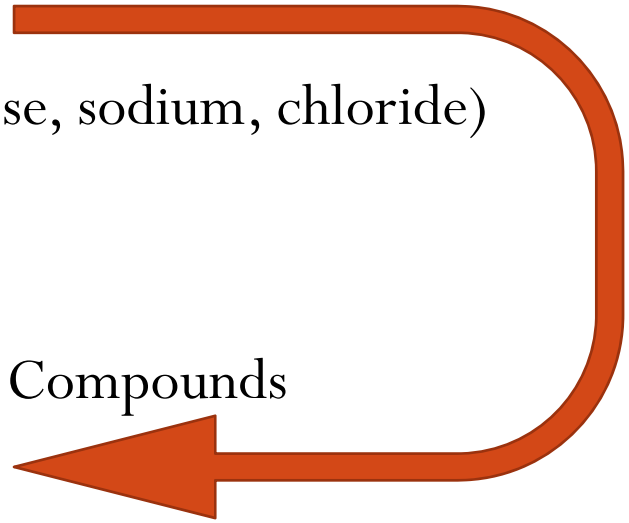
- Intro & Definitions
- NOM Generation
  - The Hydrologic Cycle
  - Land vs Water sources
  - Compounds in NOM
- Water Treatment
  - Historical
  - Types of Treatment
  - Components or Processes
- Some current issues & popular books

It's one of my favorite recipes. I call it NOM

NOM = Natural Organic Matter

What's in the Water?

- Natural Substances
  - **Natural Organic Matter (NOM)**
  - Inorganic Substances (Iron, Manganese, sodium, chloride)
- Anthropogenic Substances
  - Pesticides
  - Organic Solvents & Other Industrial Compounds
  - **Carcinogens**
  - Pharmaceuticals
  - Endocrine Disrupting Compounds
  - Flame Retardants
- Pathogens and other microorganisms



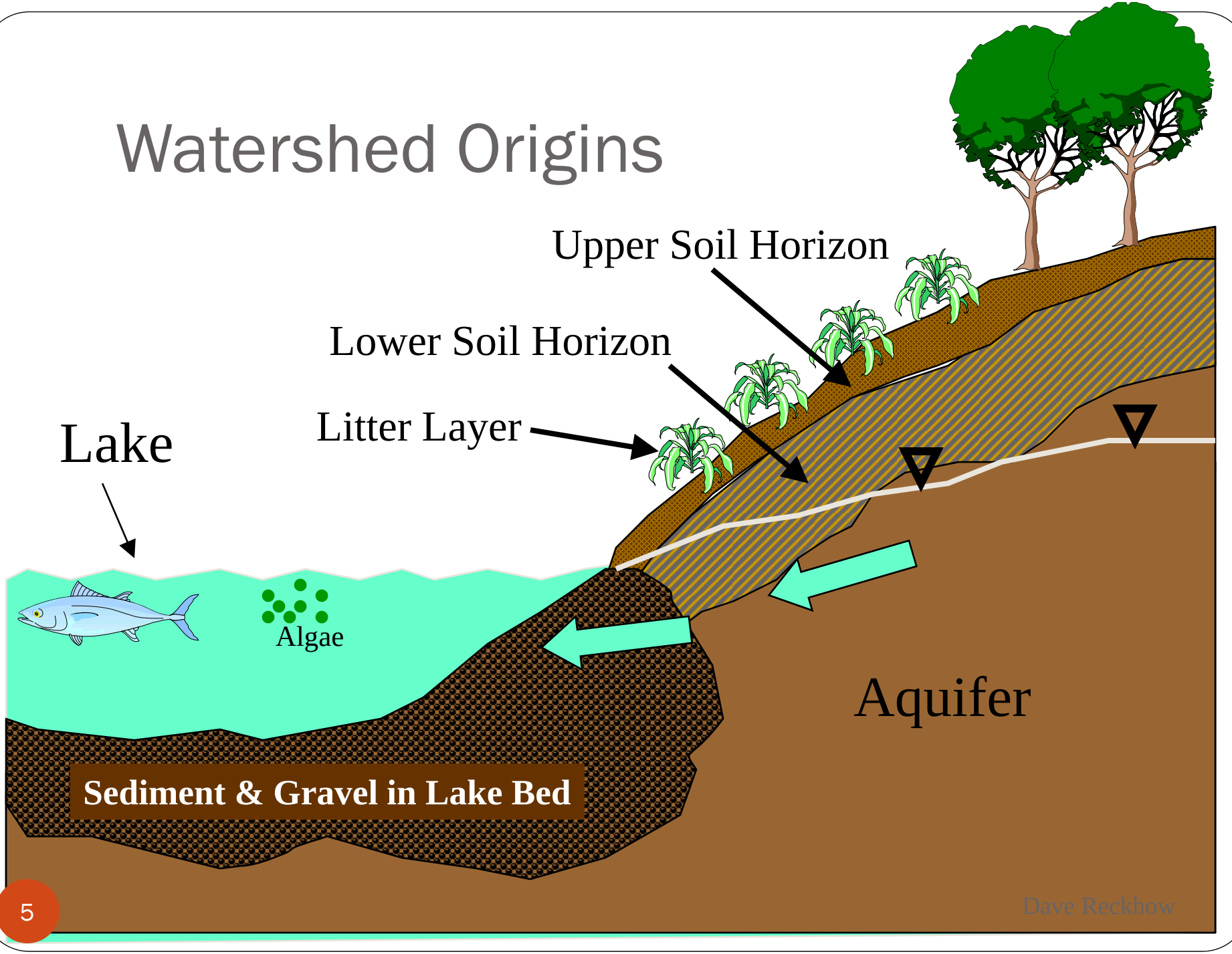
NOM in Natural Waters: Some definitions

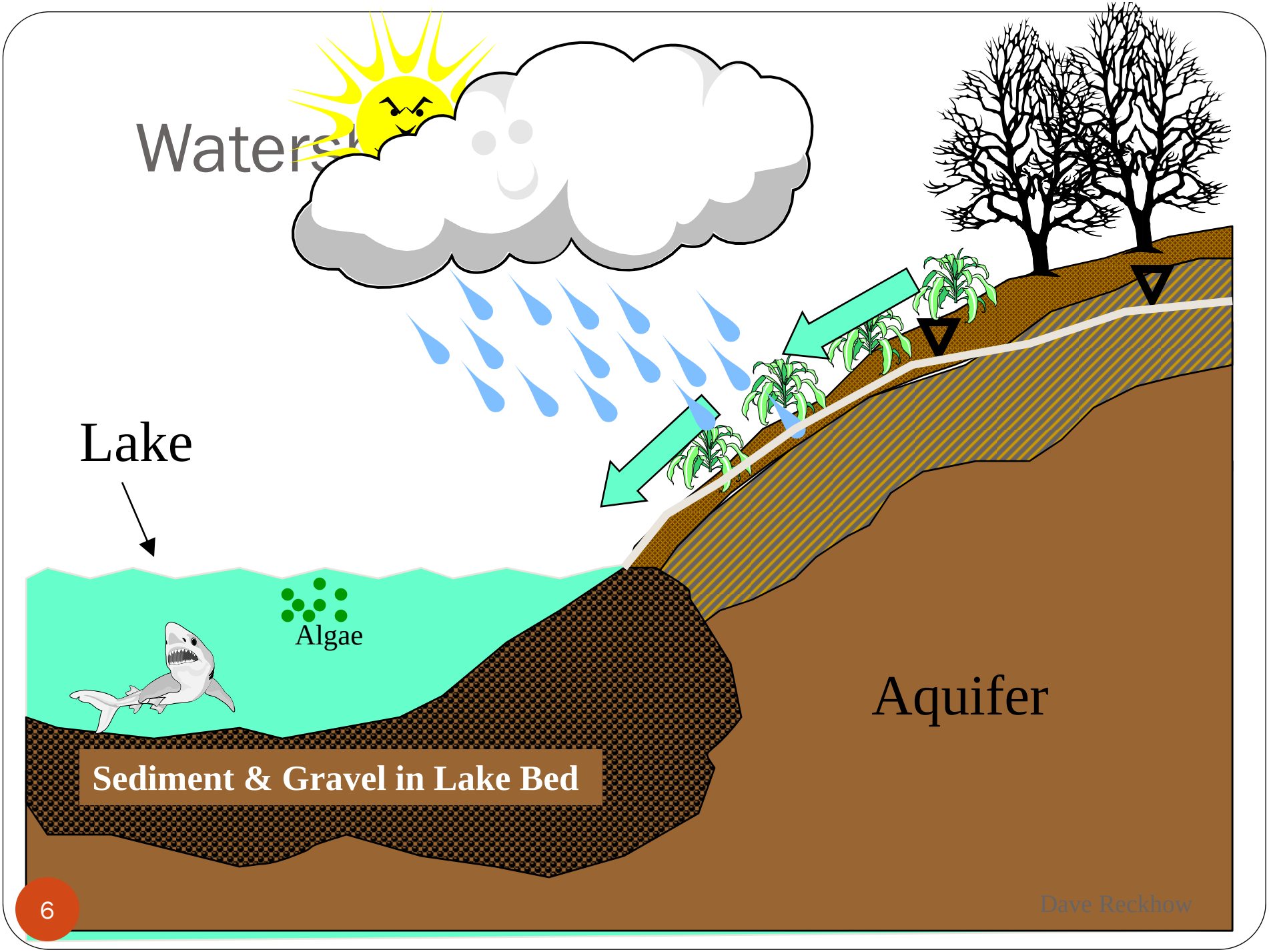
Groupings Based on Origin

- **autochthonous** compounds are created within the water body
- **allochthonous** compounds can originate from either the soil or from upstream water bodies

- **aquagenic**, substances originating from any water body
- **pedogenic** for substances originating from soil

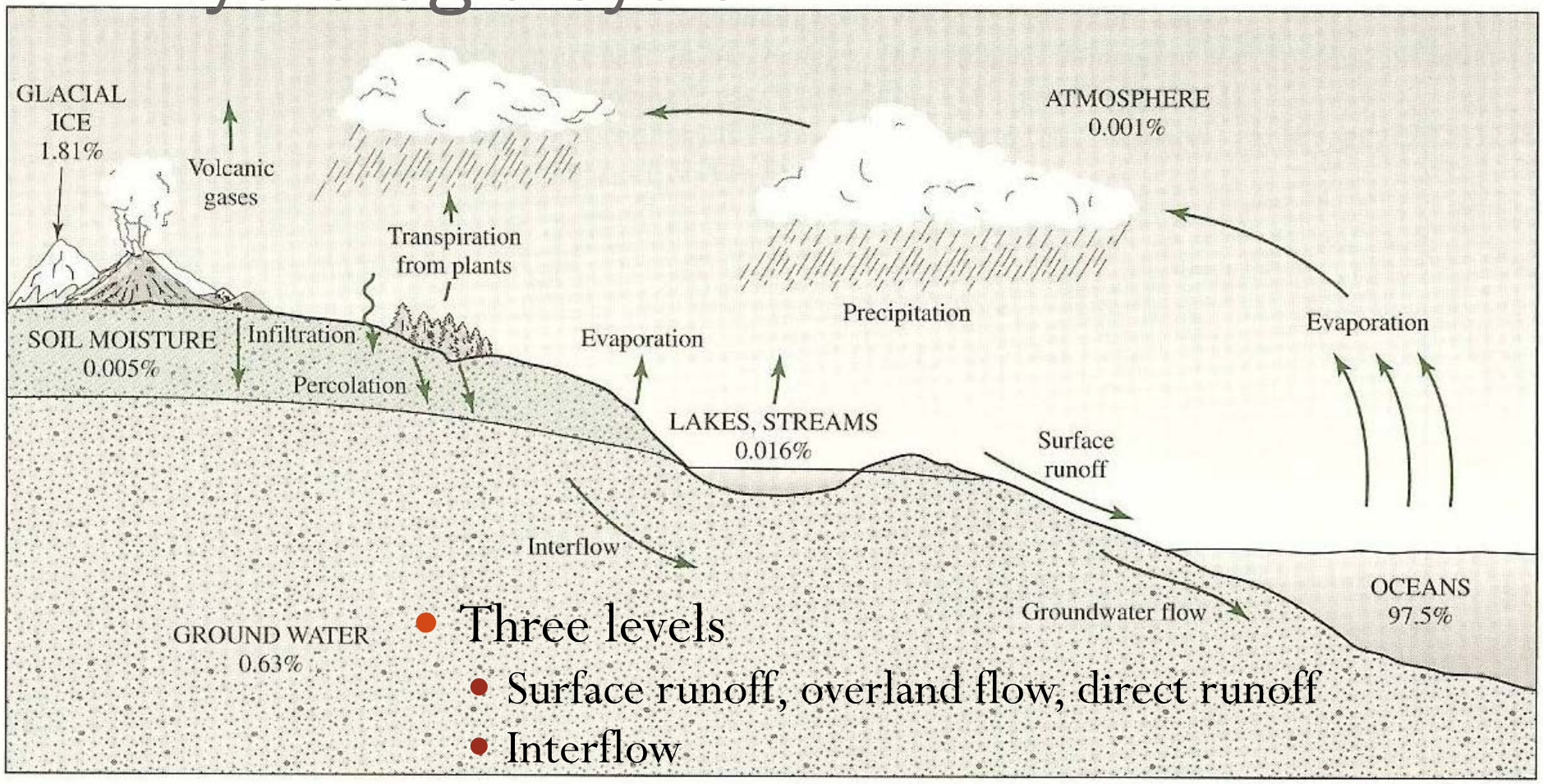
Watershed Origins




Watersh
Lake
Algae
Aquifer
Sediment & Gravel in Lake Bed
Dave Reckhow

D&M, Fig 6-1

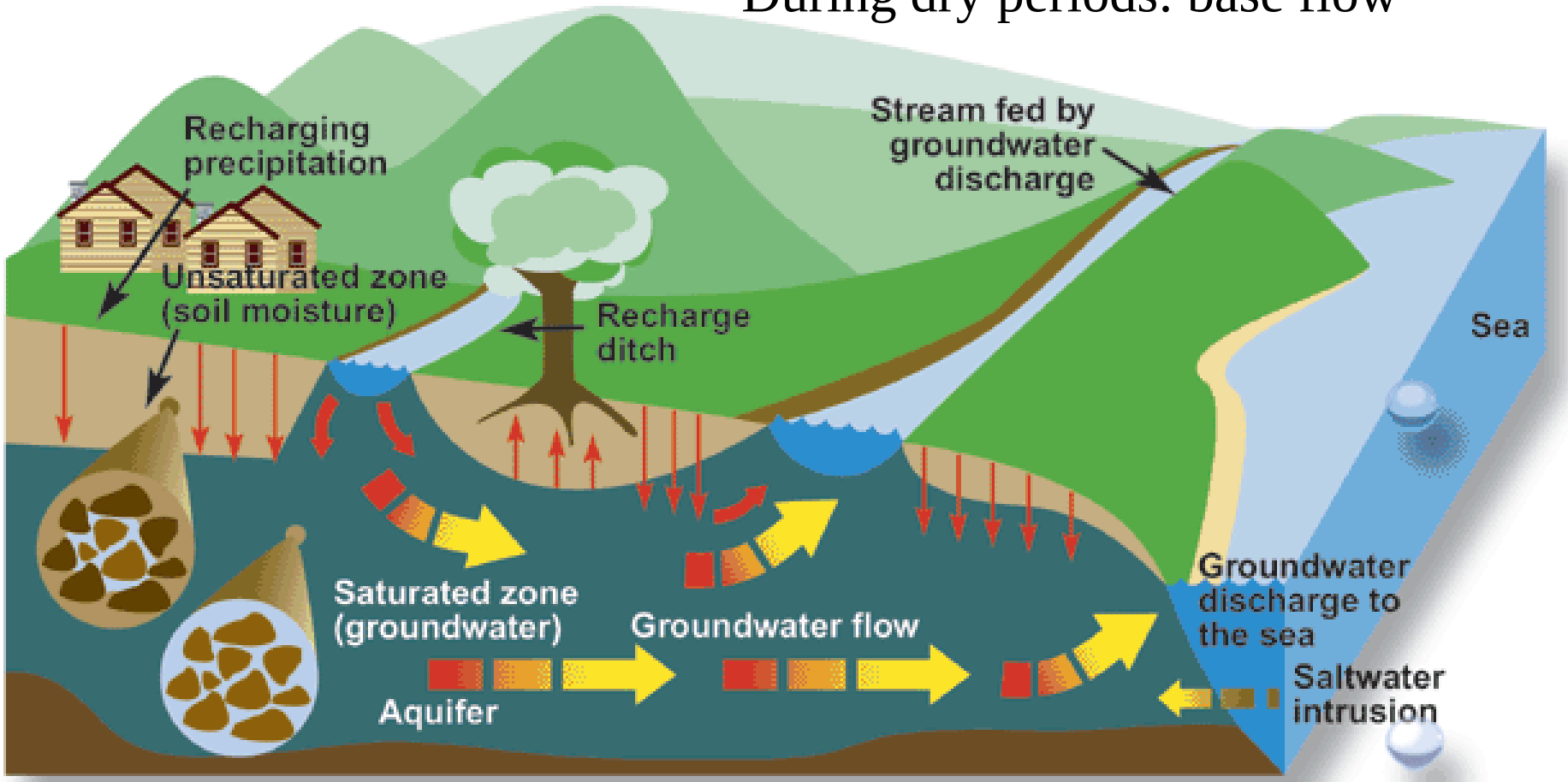
Hydrologic Cycle



- Three levels
  - Surface runoff, overland flow, direct runoff
  - Interflow
  - Infiltration, percolation, groundwater flow

Groundwater flow

During dry periods: base flow



http://www.ec.gc.ca/water/images/nature/grdwtr/a5f2e.htm

NOM: Which is the bigger source?

or

- Allochthonous
  - land plants
- Autochthonous
  - Aquatic plants

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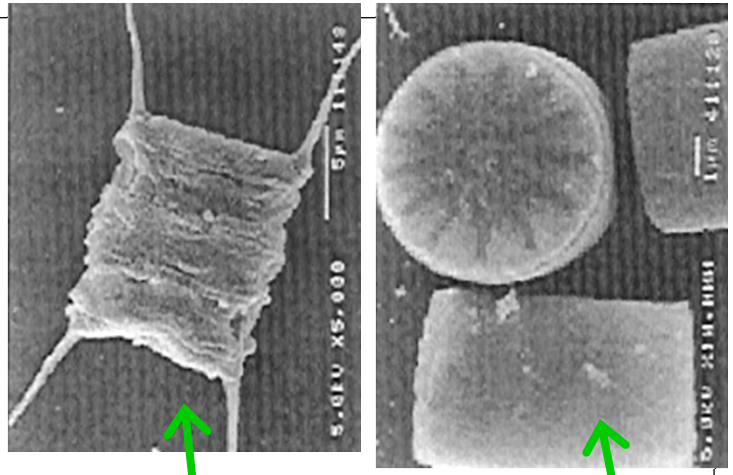
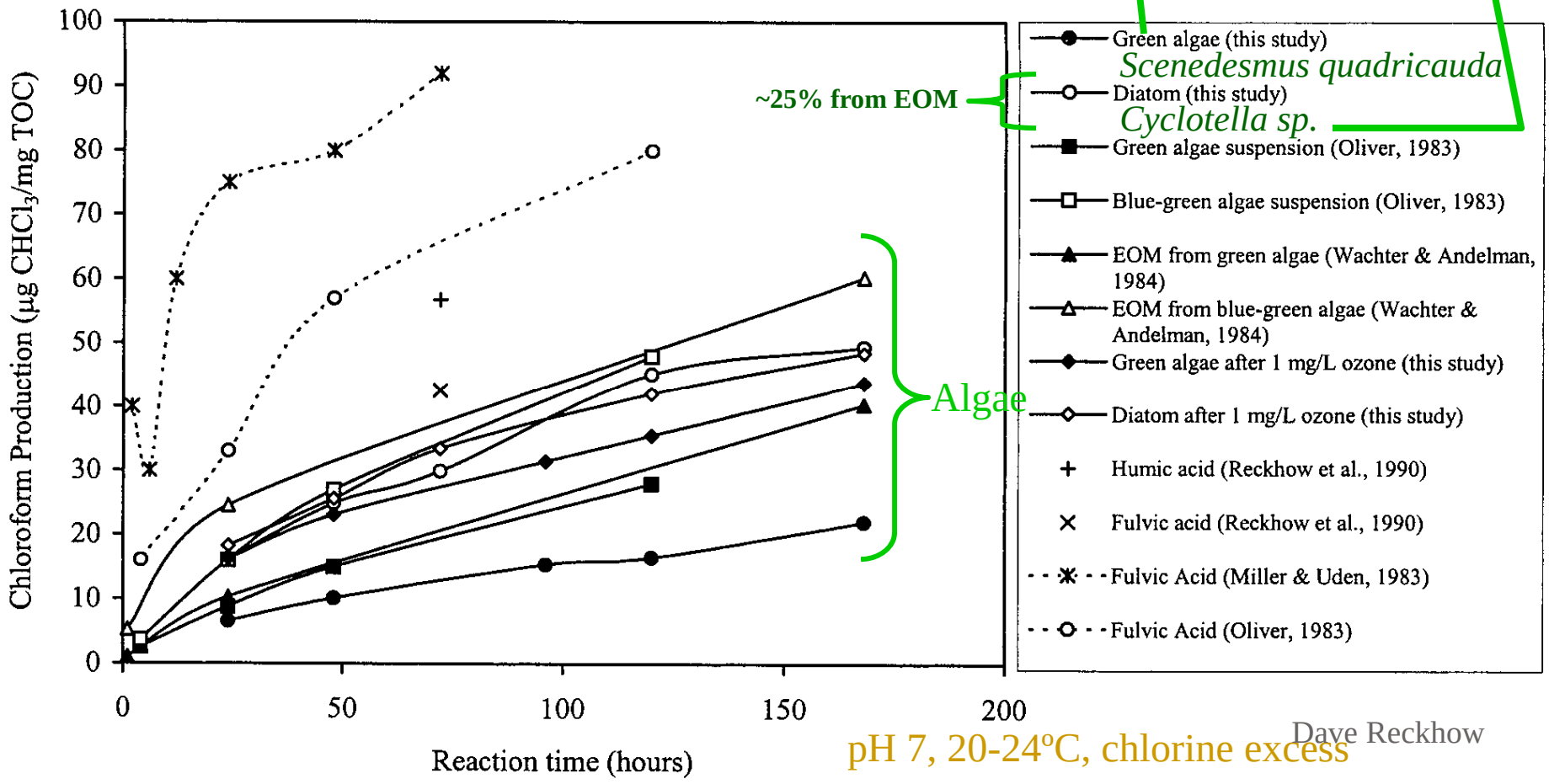
Aquatic sources: Algae

- From: Plummer & Edzwald, 2001
  - [ES&T:35:3661]





pH 7, 20-24ºC, chlorine excess

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Terrestrial Sources: Leaching Experiments

Darleen Bryan's study

White Pine

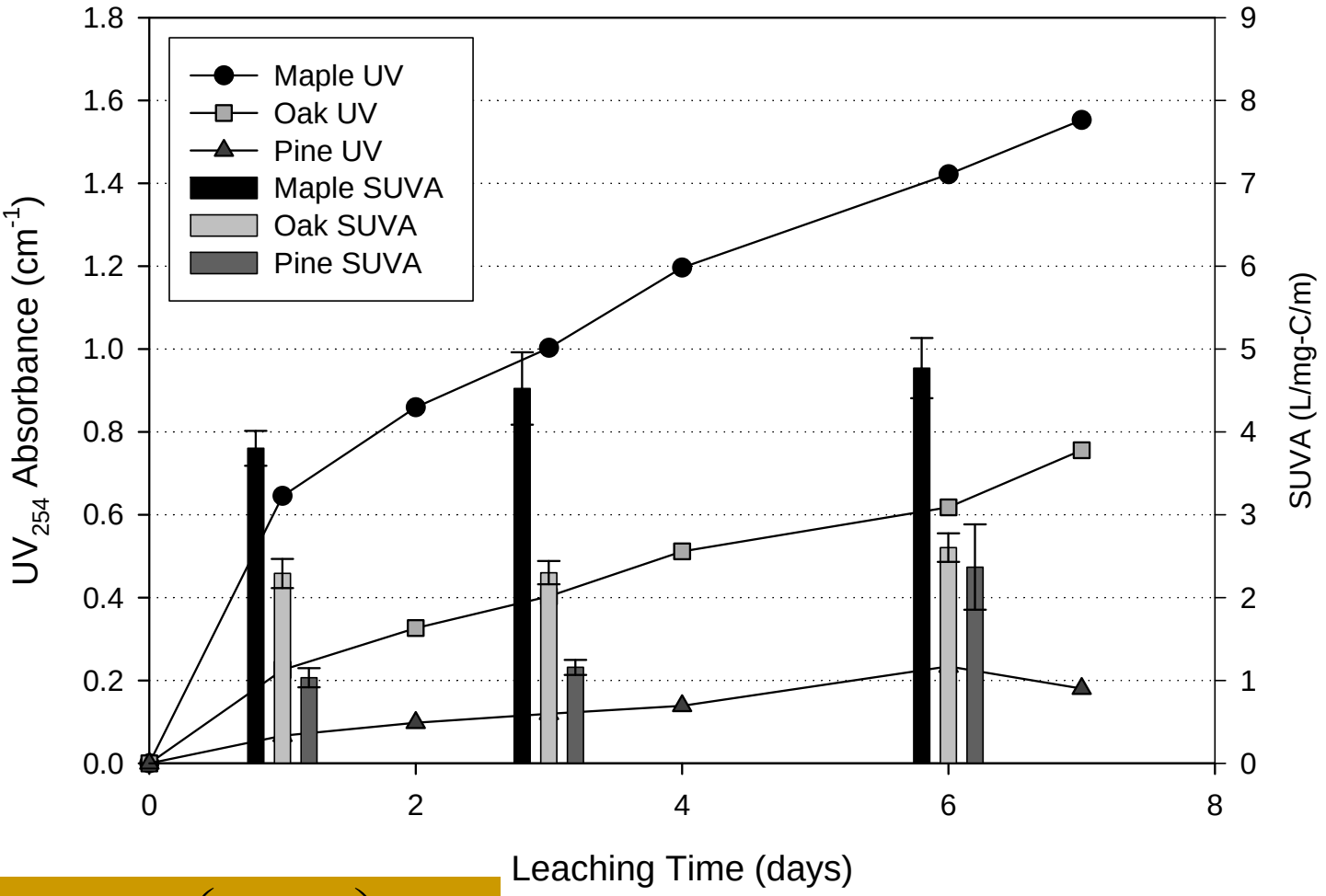
White Oak

Red Maple

Dave Reckhow

Leaching of leaves

- More organic matter released as the leaves remain submerged
- Ultraviolet (UV_{254}) absorbance measures a certain fraction
- The ratio of UV_{254} to dissolved organic carbon (DOC) concentration is called SUVA and reflects organic matter reactivity



$$SUVA \equiv \left(\frac{UV_{254}}{DOC} \right) x100$$

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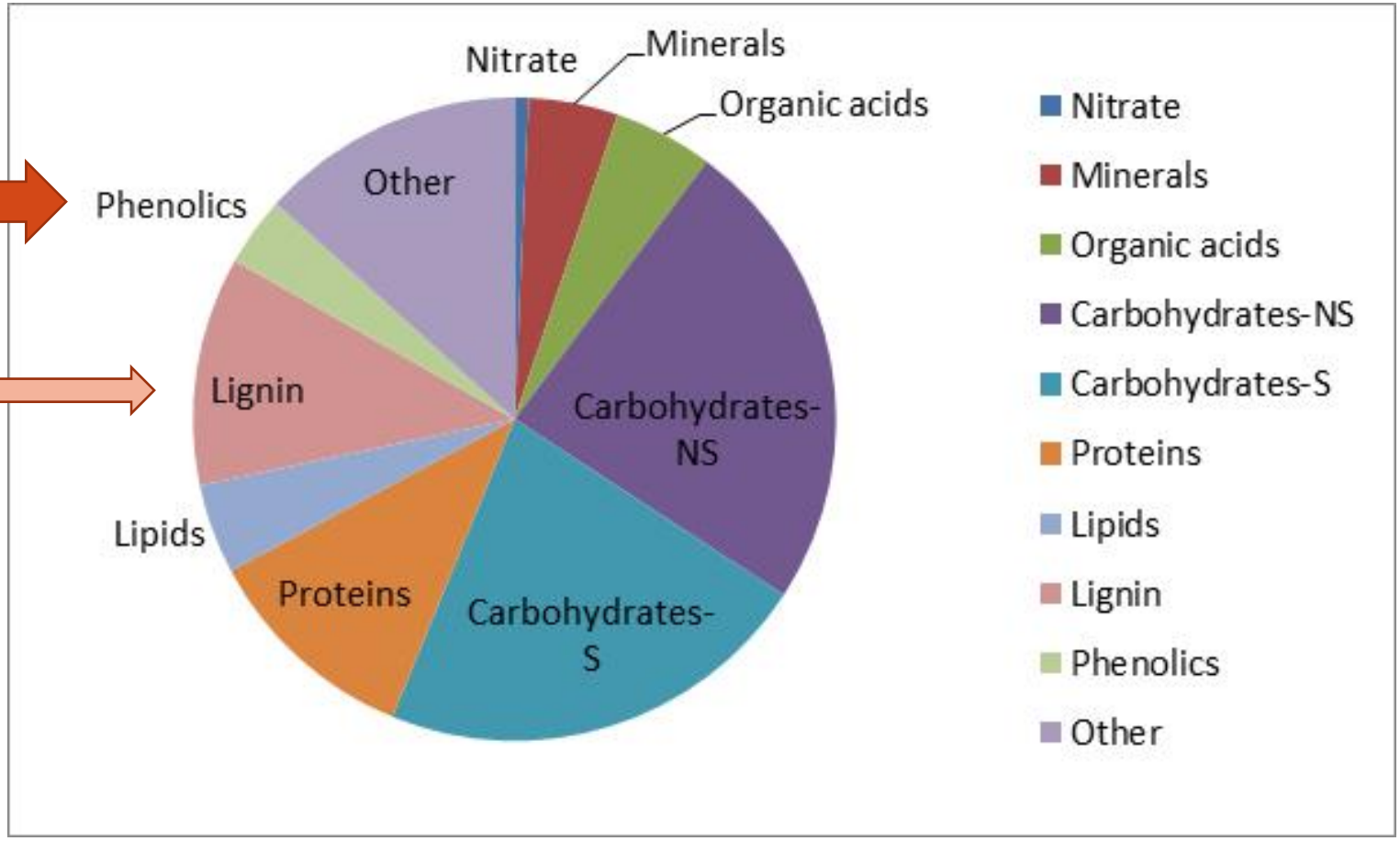
Composition of an "average" leaf

- 250 g/m^2/yr EABP

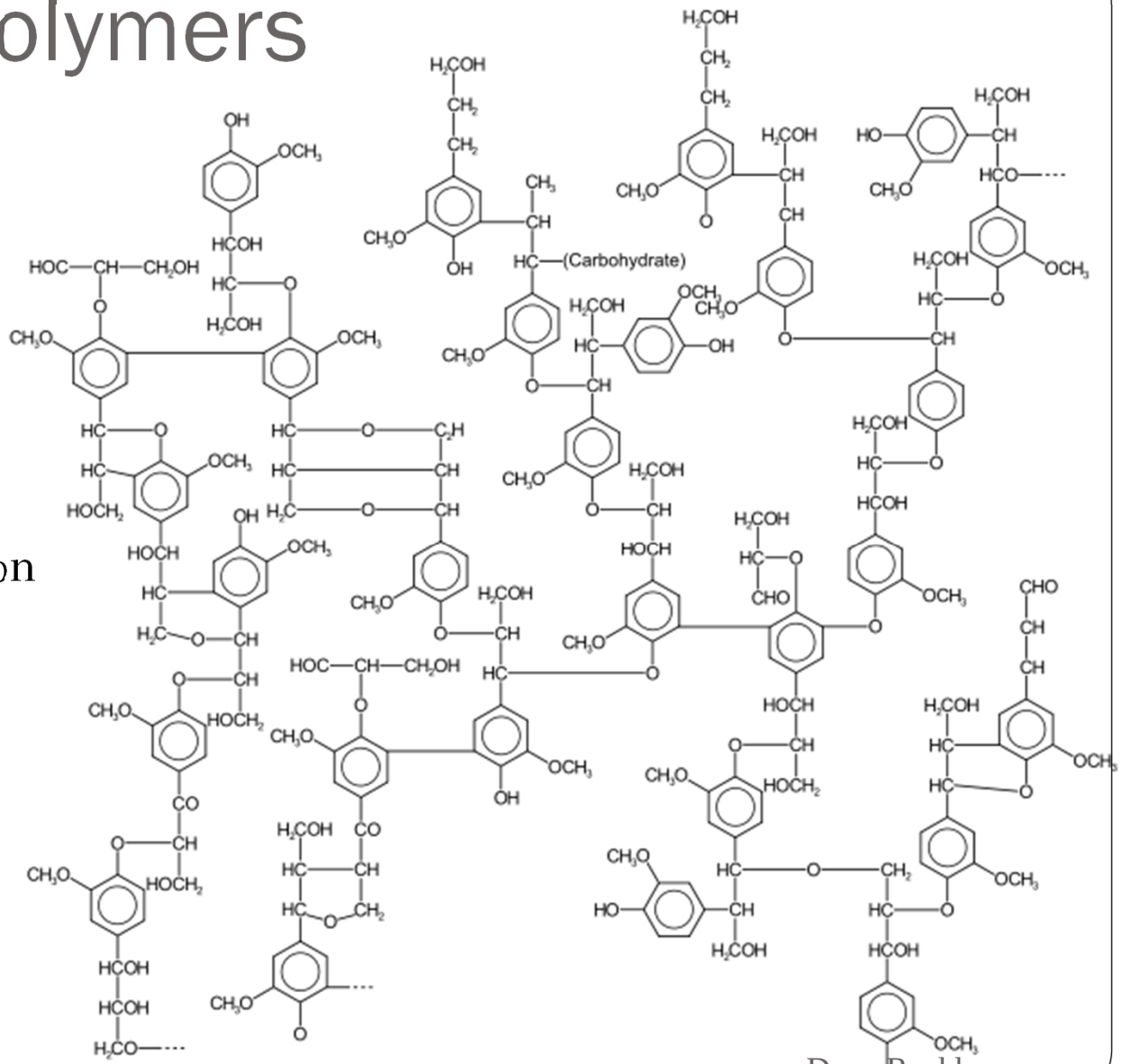
Highly-colored

Some color



Plant biopolymers

- Cellulose
- Lignin
  - Phenyl-propane units
  - Cross-linked
  - Radical polymerization
  - Ill defined structure
- Hemicellulose
- Terpeniods
- Proteins



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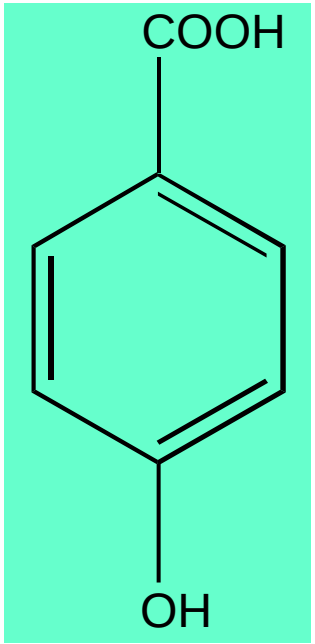
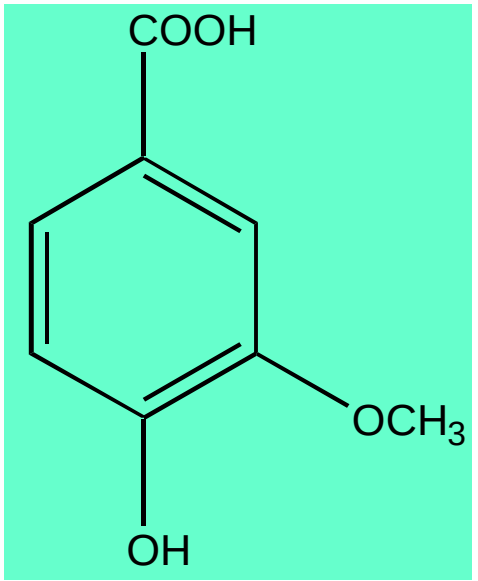
Tannins, Aromatic Acids and Phenols, cont.

- Lignin monomers

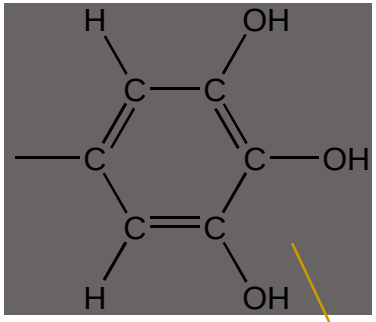


p-Hydroxybenzoic Acid



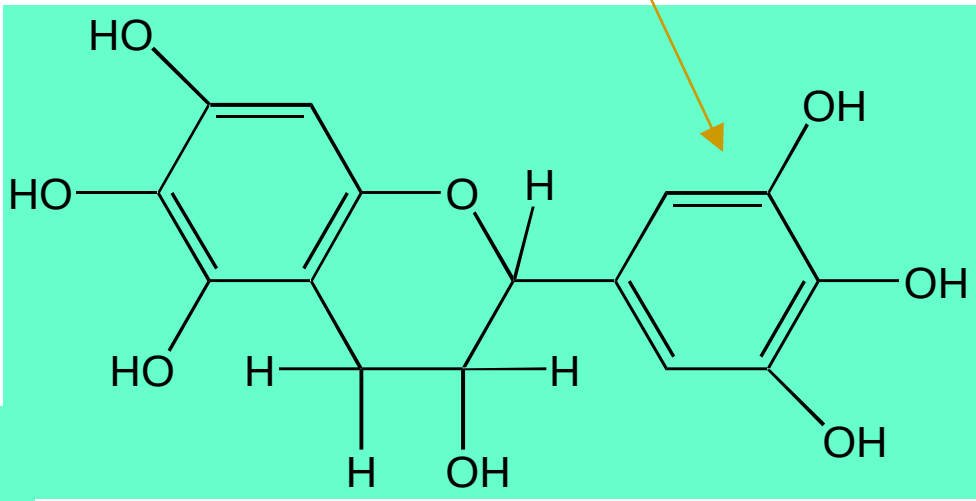
Vanillic Acid

Tannins, Aromatic Acids and Phenols



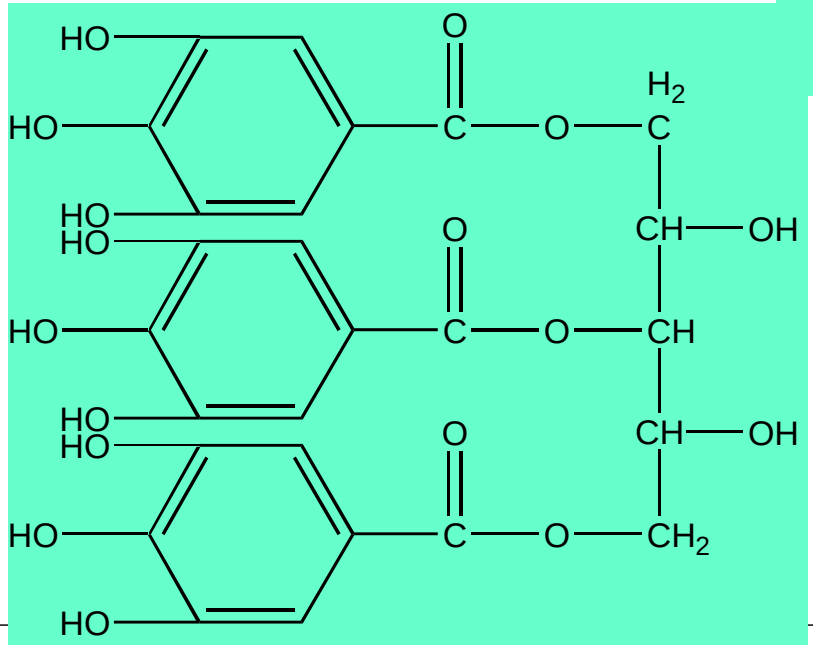
Chemical Symbols

- About 0.5% of Total
- Plant Products
- Likely THM Precursors
- Source of Color & DBPs



Condensed Tannin

Gallic Acid monomers

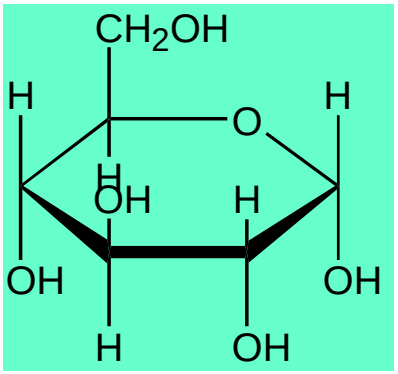


Hydrolyzable Tannin

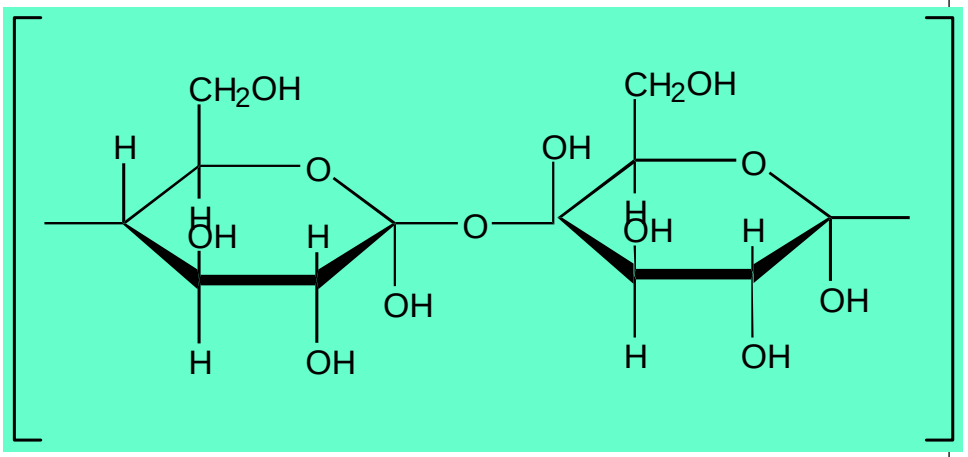
Dave Reckhow

Carbohydrates

- empirical formula: $C_x(H_2O)_y$

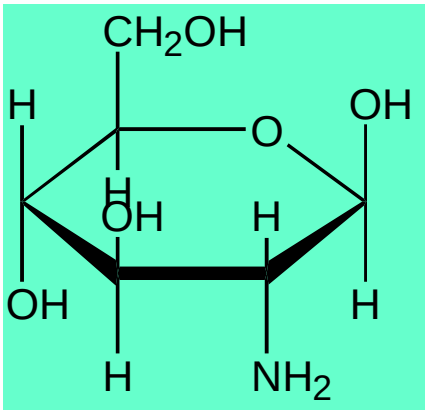


Glucose (monosaccharide)



Cellulose (polysaccharide)

Glucosamine (amino sugar)



Fatty Acids

At neutral pH's most lose H^+

CH_3-COO$^-$

- maybe 4% of DOC
- other mixed acids may account for 2%

H-COOH
Formic Acid

CH_3-COOH
Acetic Acid

CH_3-CH_2-COOH
Propionic Acid

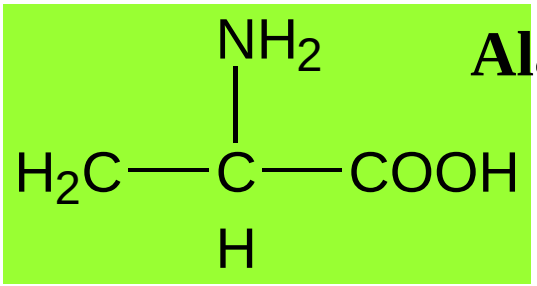
CH_3-CH_2-CH_2-COOH
Butyric Acid

H_3-CH_2-CH_2-CH_2-COOH
Valeric Acid

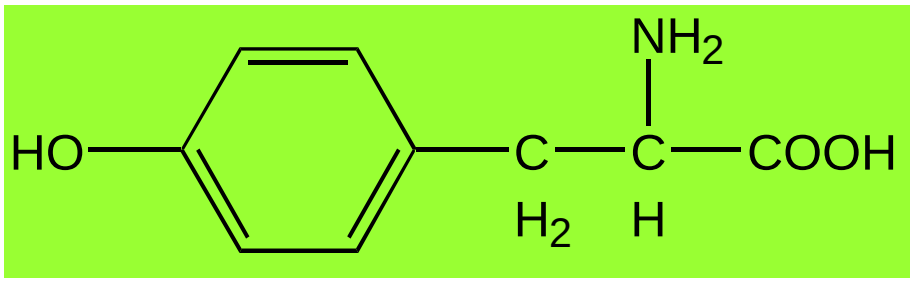
Common Volatile Fatty Acids in Natural Waters

Amino Acids and Proteins

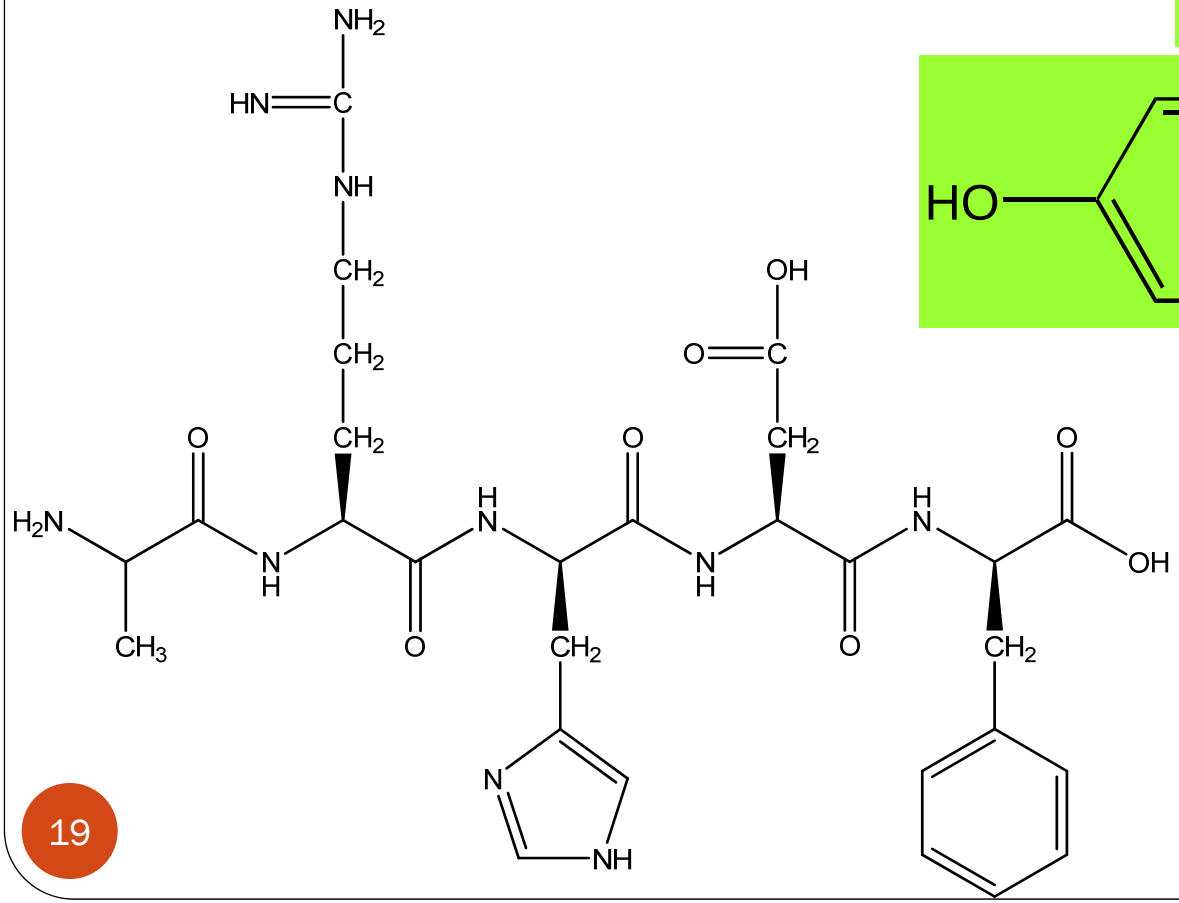
- Simple Amino Acids
  - Amine and acid groups



Alanine



Tyrosine



- Polypeptides & Proteins
  - Comprised of many AAs

NOM Quantification: TOC & DOC

Filter

Principle: oxidize all organic matter to Carbon dioxide and water. Then measure the amount of carbon dioxide produced

$$C_aH_bN_cO_d + (a + \frac{b}{4} - \frac{d}{2})O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O + \frac{c}{2}N_2$$

Oxidation

- High Temperature Pyrolysis
- UV Irradiation
- Heated Persulfate
- UV/Persulfate

Concentrations: Pedogenic

- Land Sources
  - From Woody & non-woody plants
  - Depends on vegetation, soil, hydrology
  - Most biodegradable fractions are quickly lost
- Attenuated by adsorption to clay soils
  - Parallel watersheds in Australia (Cotsaris et al., 1994)
    - Clearwater Creek, high clay content: 2.5 mg/L TOC
    - Redwater Creek, sandy soil: 31.7 mg/L TOC

Increasing?; link to global warming?

Concentrations: Aquagenic

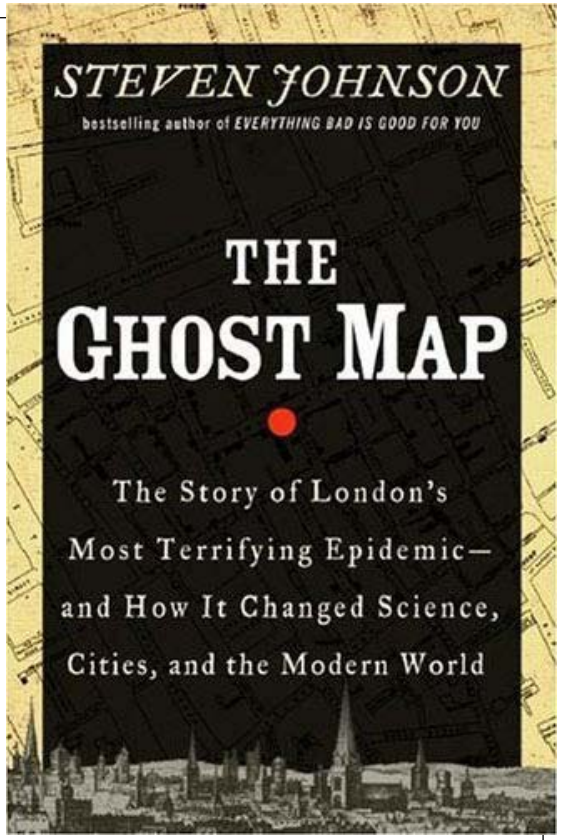
- Algal & aquatic plant Sources
  - Depend on nutrient levels / trophic state
- Concentrations in Lakes (mg/L) (Thurman, 1985)

Trophic State	Mean DOC	Range
Oligotrophic	2	1-3
Mesotrophic	3	2-4
Eutrophic	10	3-34
Dystrophic	30	20-50

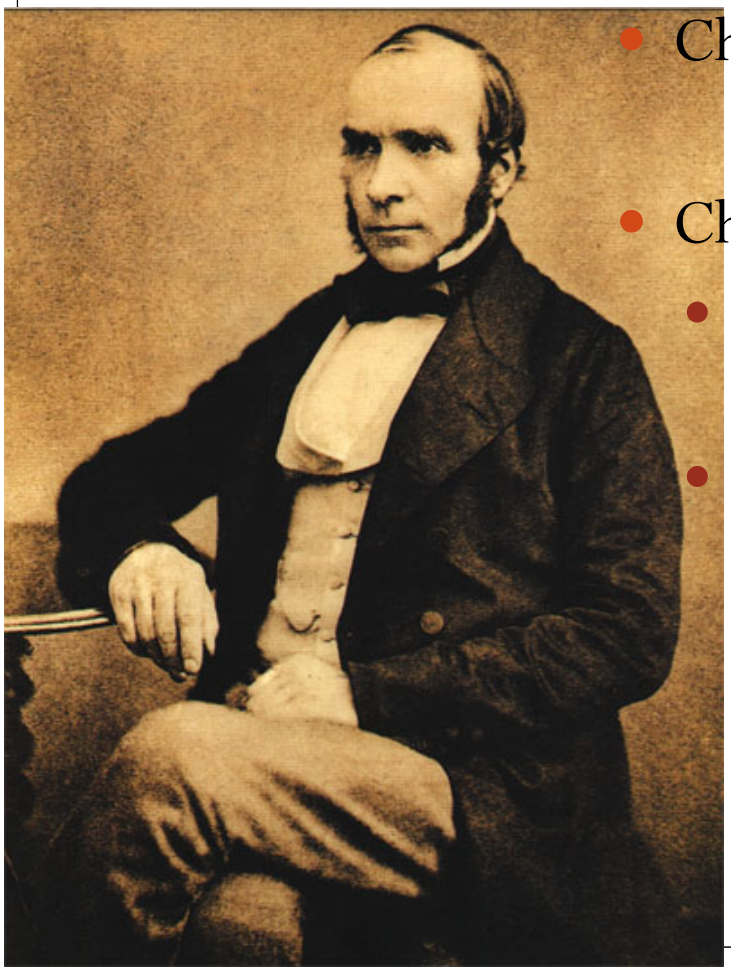
- Groundwater average: 0.7 mg/L
  - No algae, much soil attenuation

John #I: Dr. John Snow

2006



1813-1858



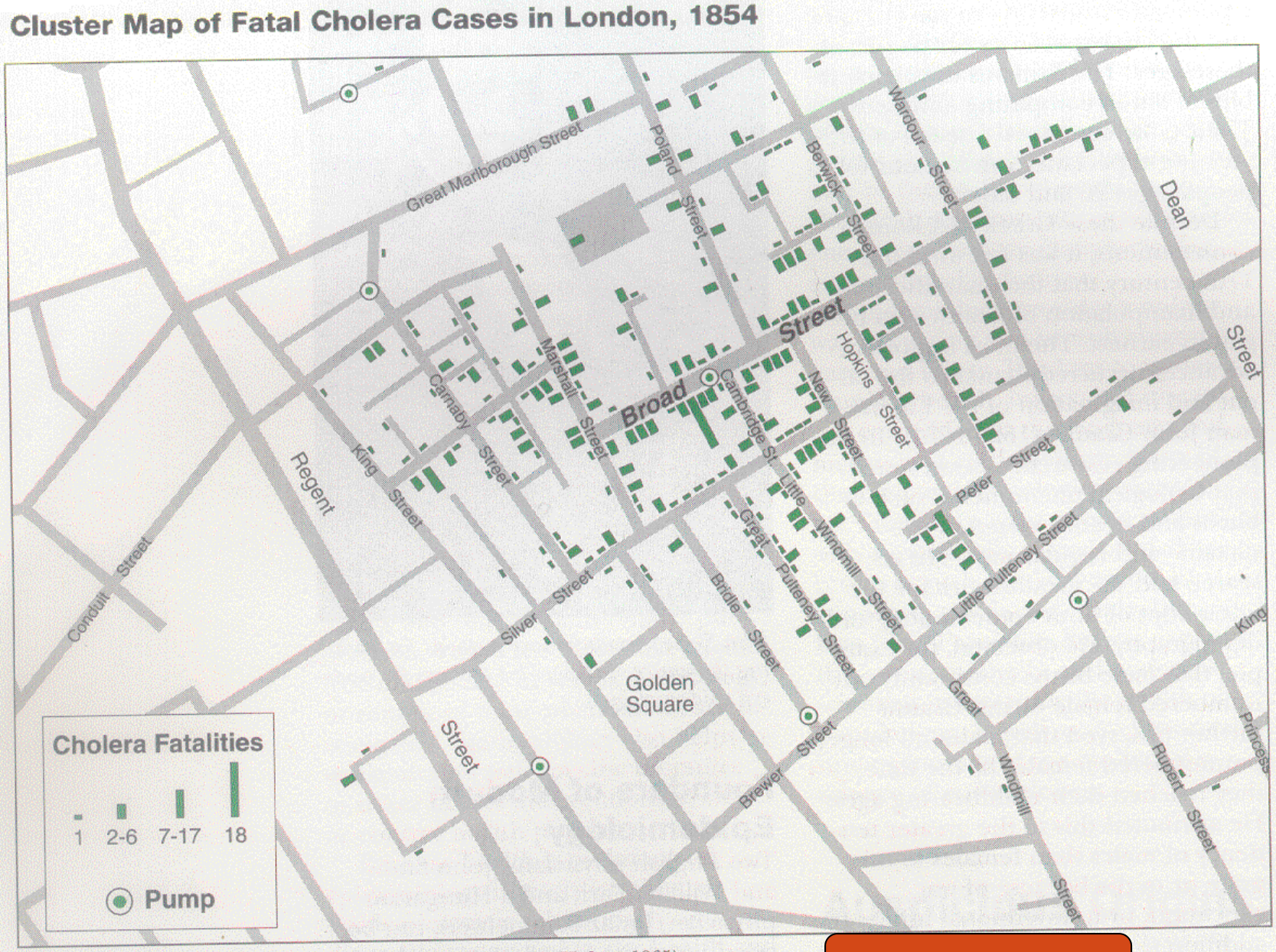
- Characterizing "the acute problem"
- Cholera
  - First emerged in early 1800s
  - 1852-1860: The third cholera pandemic
    - Snow showed the role of water in disease transmission
      - London's Broad Street pump (Broadwick St)
    - Miasma theory was discredited, but it took decades to fully put it to rest

Cholera in London & Dr. John Snow

- During an outbreak of cholera in London in 1854, John Snow plotted on a map the location of all the cases he learned of. Water in that part of London was pumped from wells located in the various neighborhoods. Snow's map revealed a close association between the density of cholera cases and a single well located on Broad Street.
- Removing the pump handle of the Broad Street well put an end to the epidemic. This despite the fact that the infectious agent that causes cholera was not clearly recognized until 1905.
- John Snow's map showing cholera deaths in London in 1854 (courtesy of The Geographical Journal). The Broad Street well is marked with an X (within the red circle).

http://www.ph.ucla.edu/epi/snow.html

Soho, Westminster



Source: Adapted from John Snow, *Snow on Cholera* (New York: Hafner, 1965).

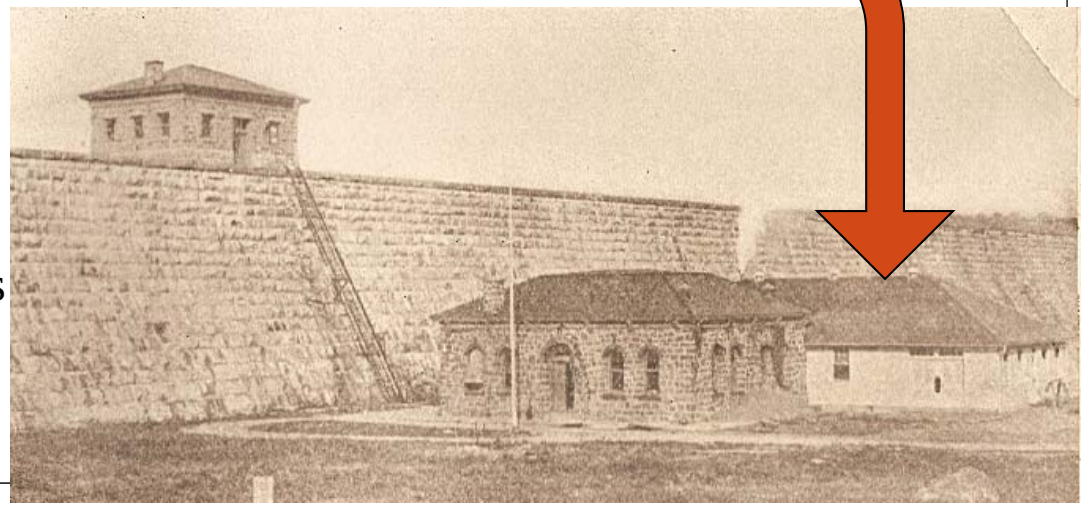
Picadilly Circus

Photo courtesy of the Leal family and Mike McGuire

1858-1914

John #2: Dr. John L. Leal

- Solutions to "the acute problem"
  - Jersey City's Boonton Reservoir
  - Leal experimented with chlorine, its effectiveness and production
    - George Johnson & George Fuller worked with Leal and designed the system (1908)

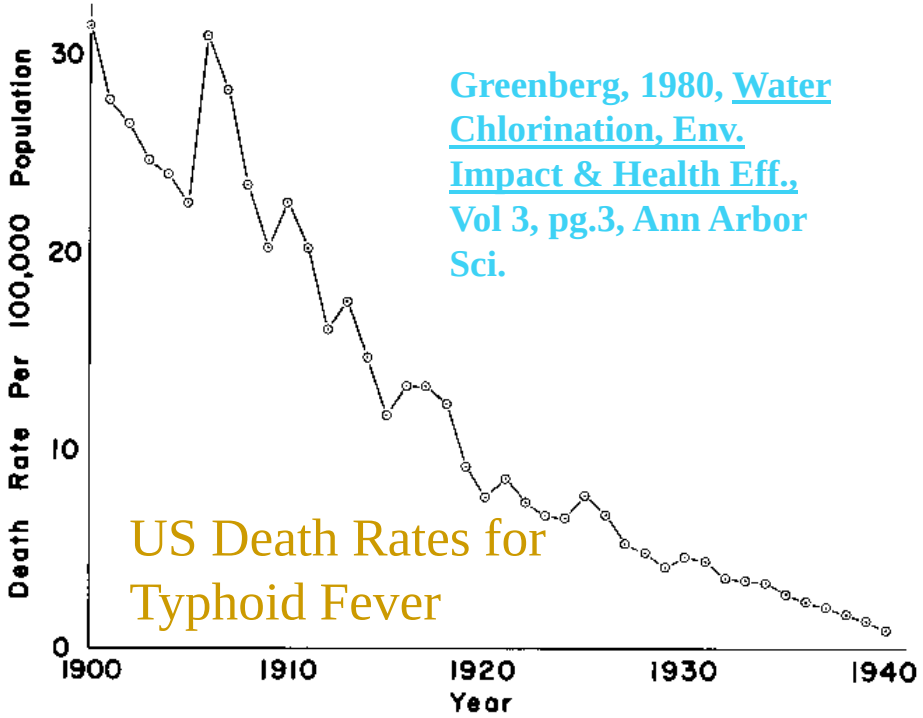


"Full-scale and continuous implementation of disinfection for the first time in Jersey City, NJ ignited a disinfection revolution in the United States that reverberated around the world"

M.J. McGuire, JAWWA 98(3)123

Chlorination

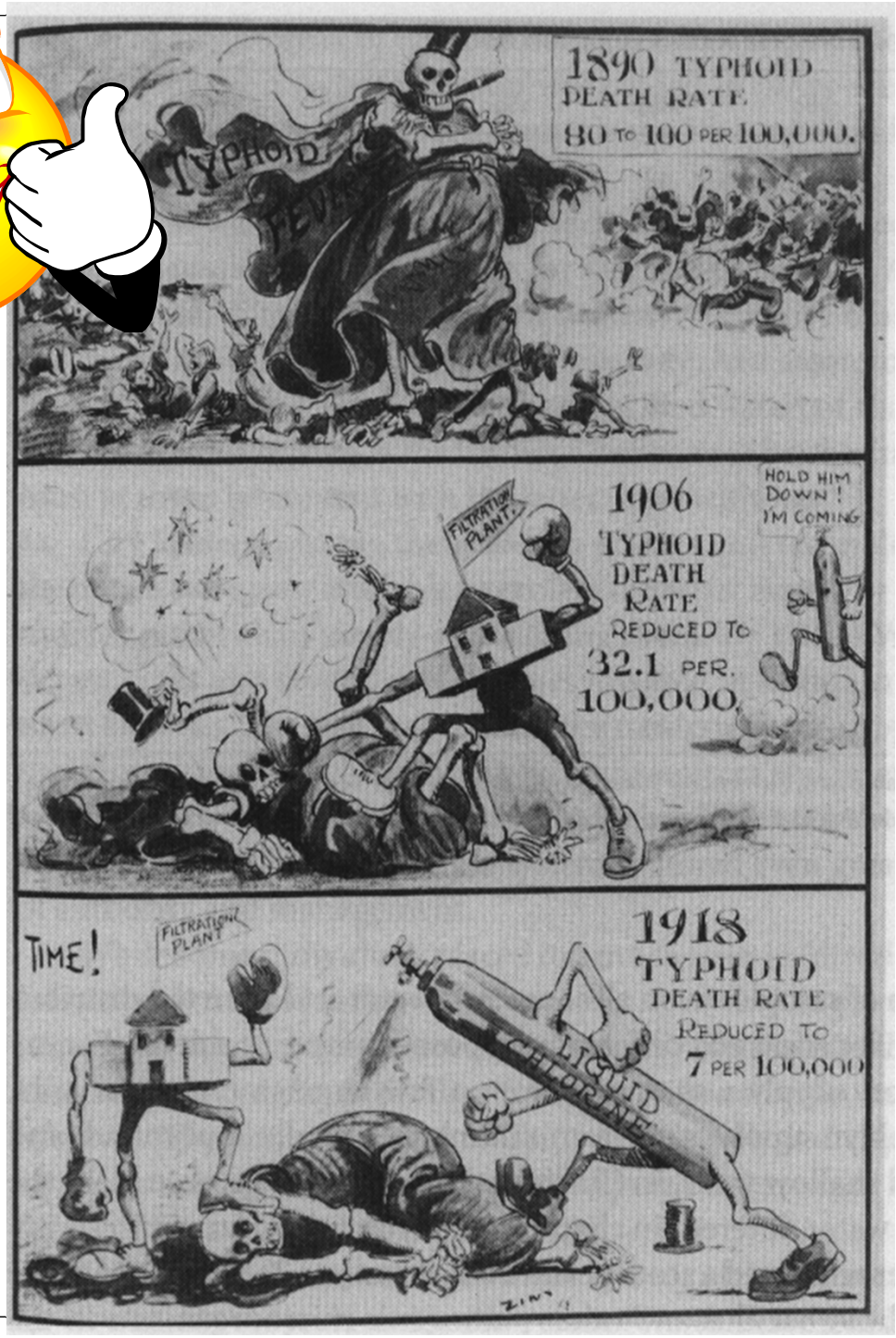
- 1-2 punch of filtration & chlorination



US Death Rates for Typhoid Fever

Greenberg, 1980, Water Chlorination, Env. Impact & Health Eff., Vol 3, pg.3, Ann Arbor Sci.

Melosi, 2000, The Sanitary City, John Hopkins Press



Today's Conventional Treatment

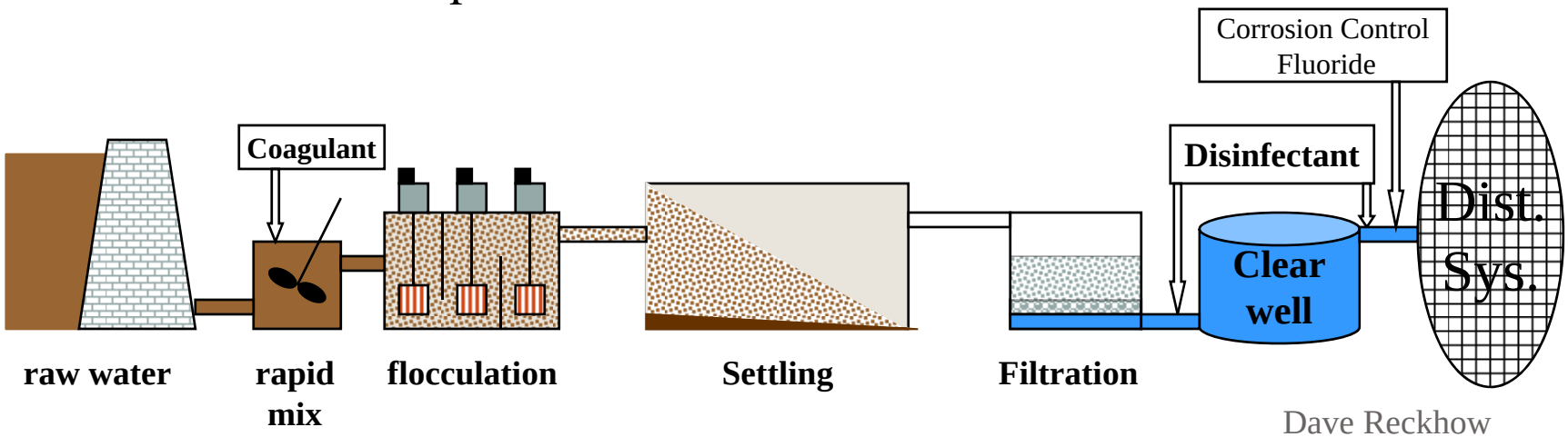
- Coagulation & solids separation
  - Use of alum or another chemical coagulant
  - rapid mix, flocculation, settling, filtration

Removes some of the NOM & suspended particles

- Disinfection
  - including clearwell for contact time

Kills or inactivates pathogenic organisms

- Most common sequence for surface water



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Coagulation chemistry

Ferric Sulfate

$$Fe_2(SO_4)_3 + 6\,OH^- \rightarrow 2Fe(OH)_3\Downarrow + 3\,SO_4^{2-}$$

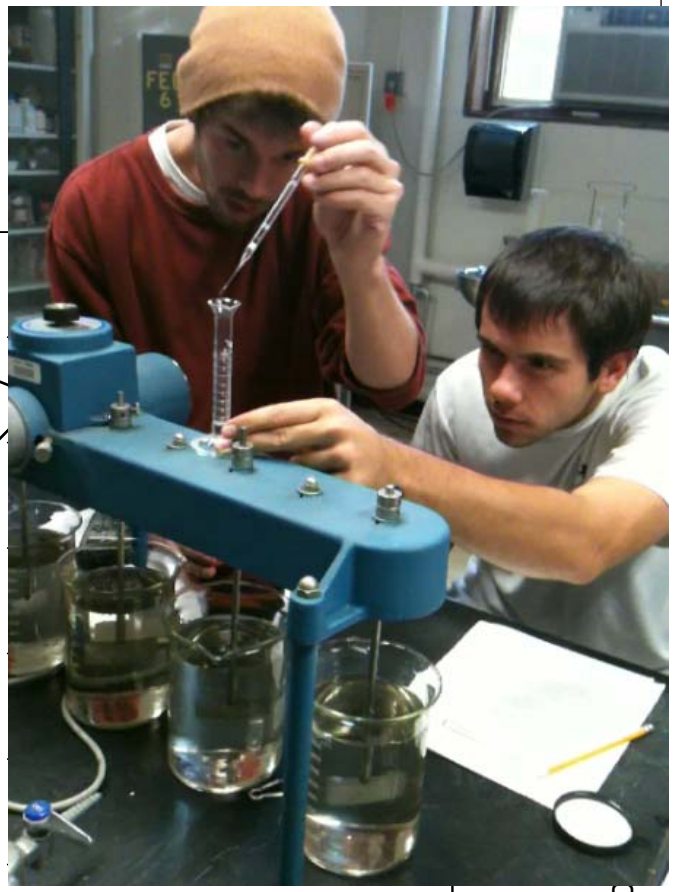
Alum

$$Al_2(SO_4)_3 \bullet 18H_2O \rightarrow 2\,Al(OH)_3\Downarrow + 3SO_4^{-2} + 6H^+ + 12\,H_2O$$

Mechanisms

- Precipitation of metal hydroxide, then:
  - Adsorption of contaminants
  - Enmeshment of particles

NOM removal by alum coagulation



- Impacts of pH and dose

Control (no alum)

24 mg/L dose

48 mg/L dose

96 mg/L dose

Manganese

Mn precipitation

Rennes IV Raw Water
(France) 11/19/84
Reckhow & Bourbigot (unpublished data)

DOC (mg/L)

pH

0 1 2 3 4 5 6 7 8 9

4 5 6 7 8 9 10 11 12

0 50 100

Flocculation

- An Empty full-scale rectangular flocculation tank in Southern CA

Can be done in the lab by slowly mixing your sample with a stirrer or on a shaking table

Settling

- Circular and rectangular designs

Can be done in the lab by letting your sample sit in a jar quiescently

Filtration

- Sand media
  - Empty filter, not in service (Cincinnati)

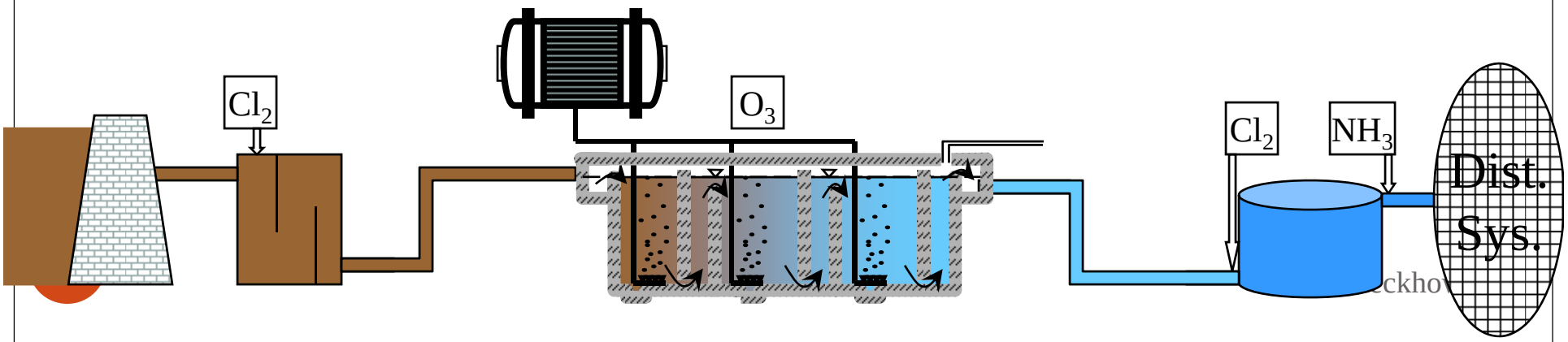
Dave Reckhow

Chlorination

- Chlorine tanks
  - Left side is currently feeding
  - Right side is on reserve

Other Types: Ozone Plants

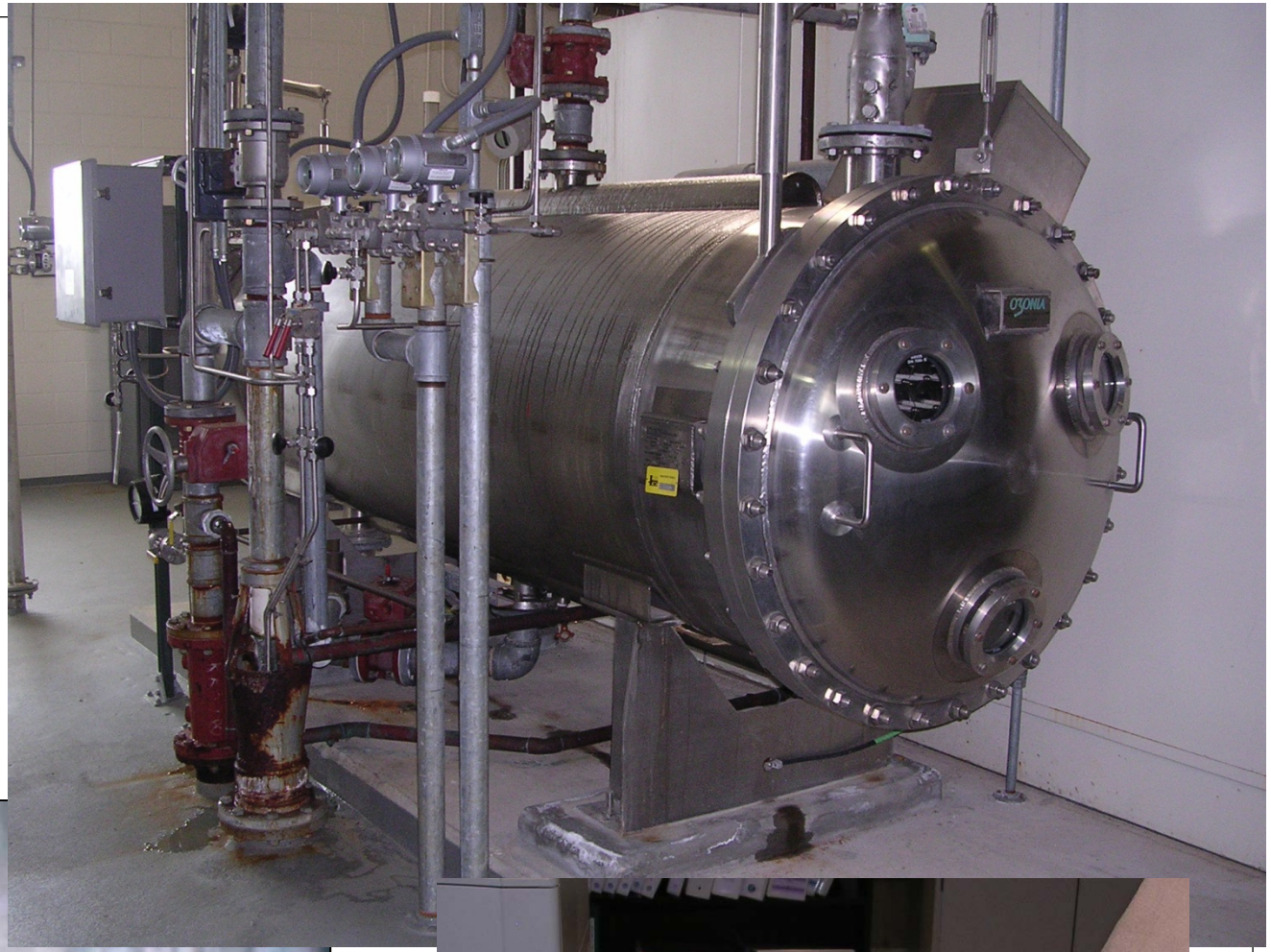
- Many types
  - Simplest type: ozone, non-filtration shown below
    - examples: MWRA (Boston), Portland ME
  - More complex: including coagulation & Filtration
    - examples: Andover MA, Amherst MA
  - Always includes final disinfection with chlorine or chloramines

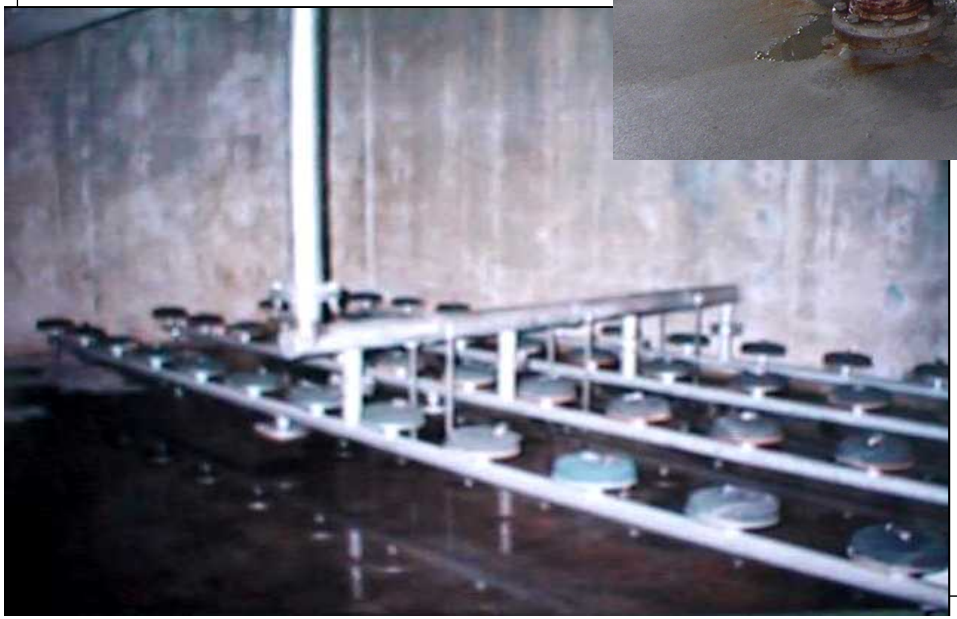


Ozone

- Generator
- Diffusers

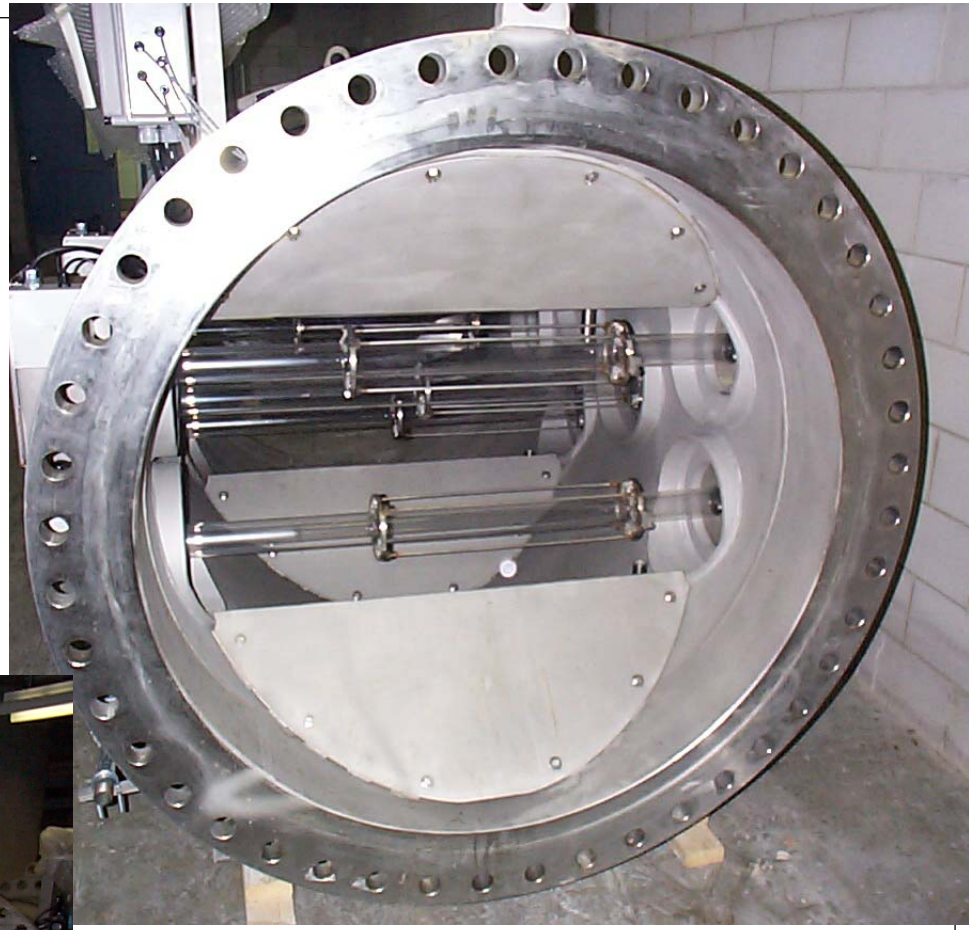
Can be done in the lab with a $70 fish tank sized ozone generator

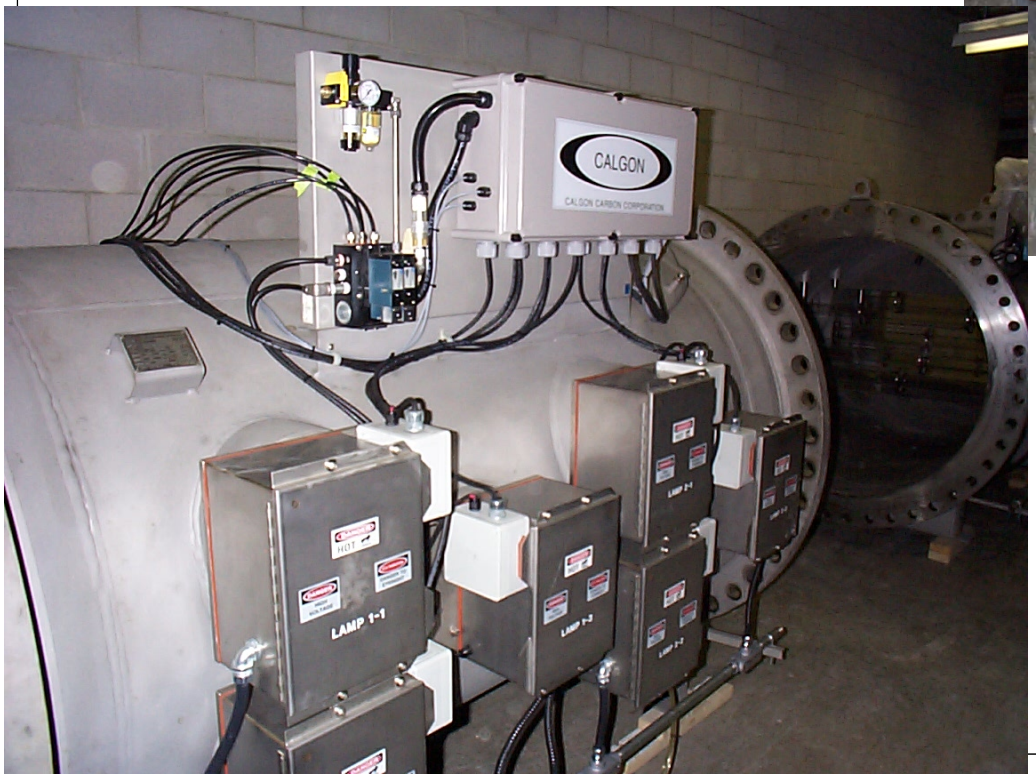




Ultraviolet Light

- Waterloo, Ont





Membrane Treatment

- National City, CA

1921-2010

John #III: John Rook

- Chlorine: "the chronic problem"
  - Brought headspace analysis from the beer industry to drinking water
  - Found trihalomethanes (THMs) in finished water
    - Carcinogens !?!
  - Published in Dutch journal H2O, Aug 19, 1972 issue
  - Deduced that they were formed as byproducts of chlorination
  - Proposed chemical pathways

Rook, 1974, Water Treat. & Exam., 23:234

Reactions with Disinfectants: Chlorine

The Precursors!

HOCl

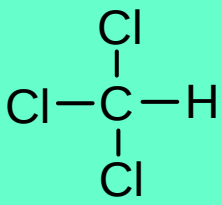
+ natural organics

(NOM)

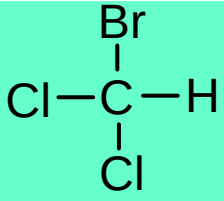
Oxidized NOM
and inorganic chloride
- Aldehydes

Chlorinated Organics
- TOX
- THMs
- HAAs

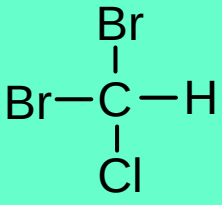
The THMs



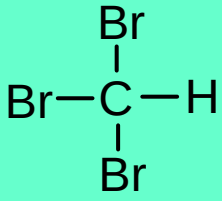
Chloroform



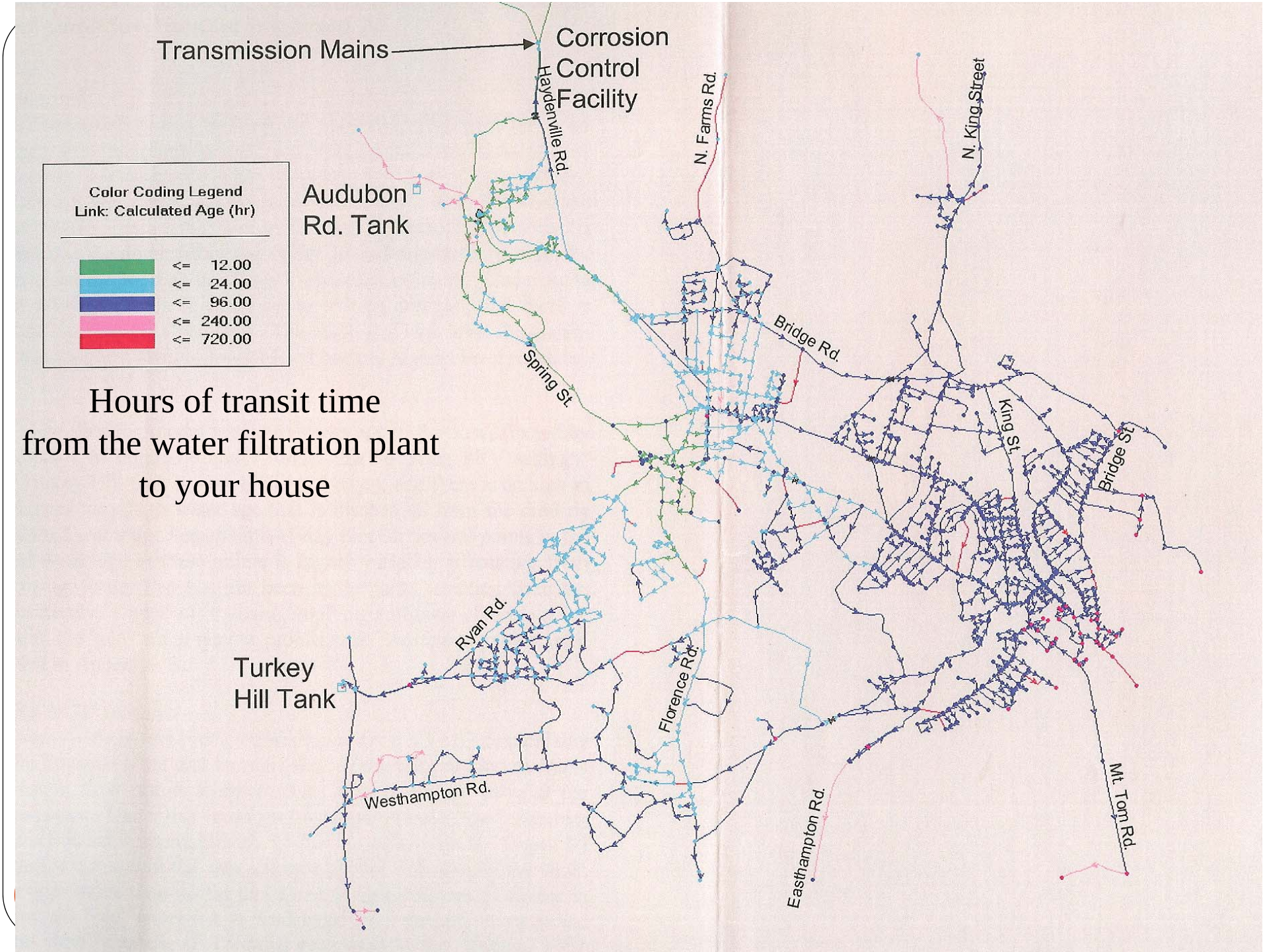
Bromodichloromethane

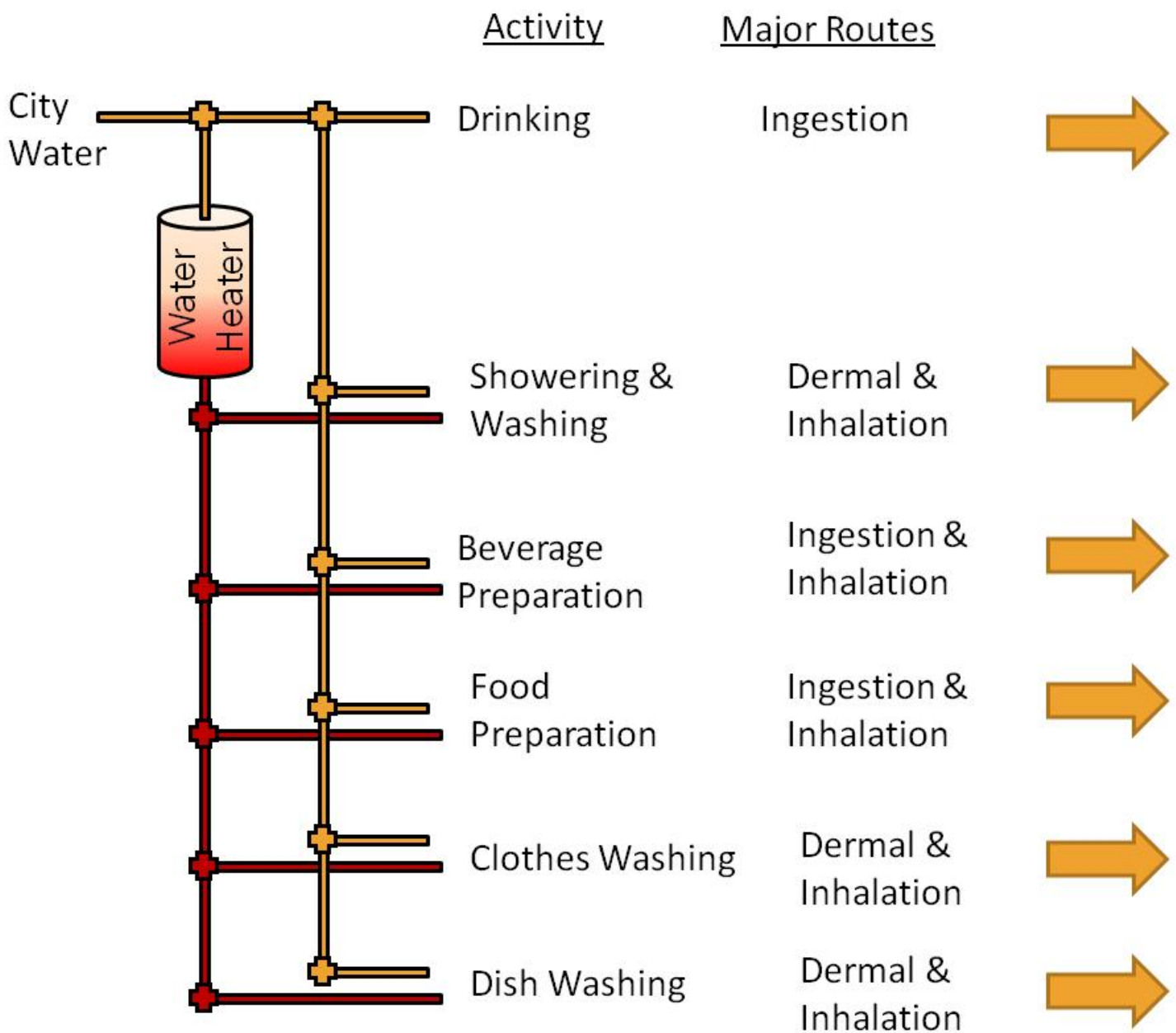


Chlorodibromomethane

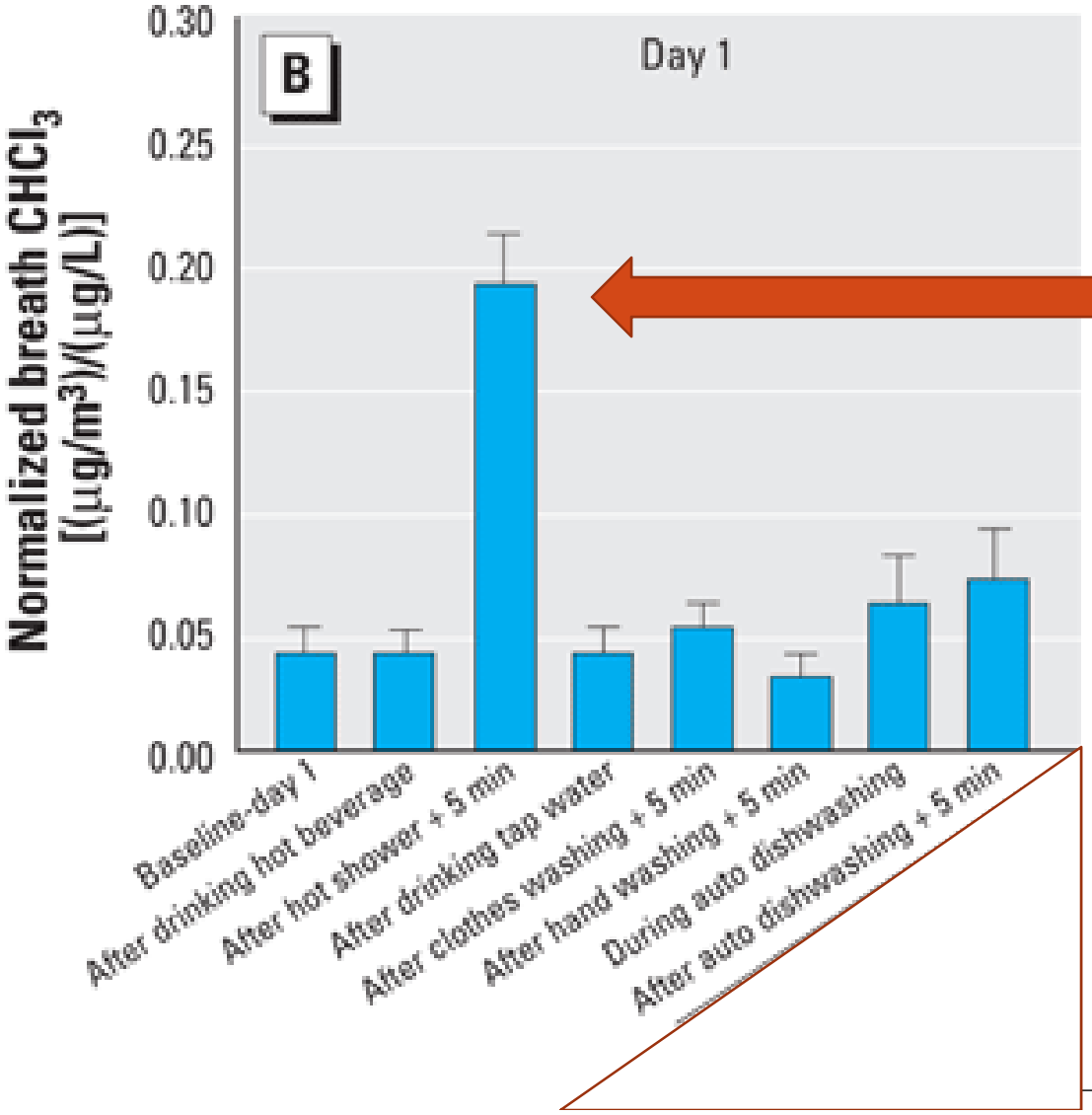


Bromoform


Transmission Mains
Corrosion Control Facility
Haydenville Rd.
N. Farms Rd.
N. King Street
Audubon Rd. Tank
Color Coding Legend
Link: Calculated Age (hr)
<= 12.00
<= 24.00
<= 96.00
<= 240.00
<= 720.00
Bridge Rd.
Spring St.
King St.
Bridge St.
Hours of transit time from the water filtration plant to your house
Ryan Rd.
Turkey Hill Tank
Florence Rd.
Westhampton Rd.
Easthampton Rd.
Mt. Tom Rd.


Activity
Major Routes
City Water
Water Heater
Drinking
Ingestion
Showering & Washing
Dermal & Inhalation
Beverage Preparation
Ingestion & Inhalation
Food Preparation
Ingestion & Inhalation
Clothes Washing
Dermal & Inhalation
Dish Washing
Dermal & Inhalation
Human Exposure

Multiple Routes of Exposure

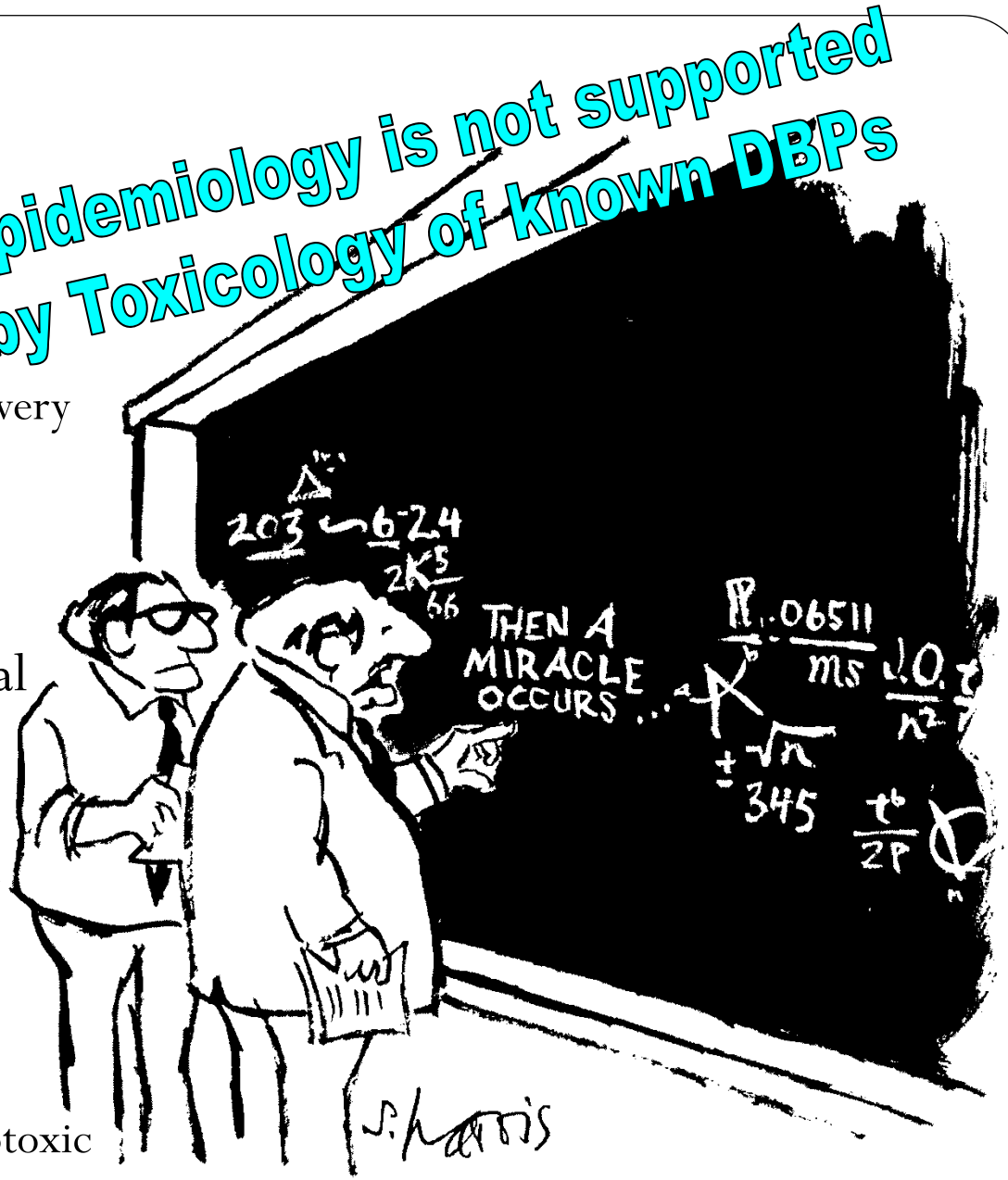


- Inhalation in the shower produces highest blood level and response is fast

Gordon et al., 2006 [Env. Health Persp.114:514-521]

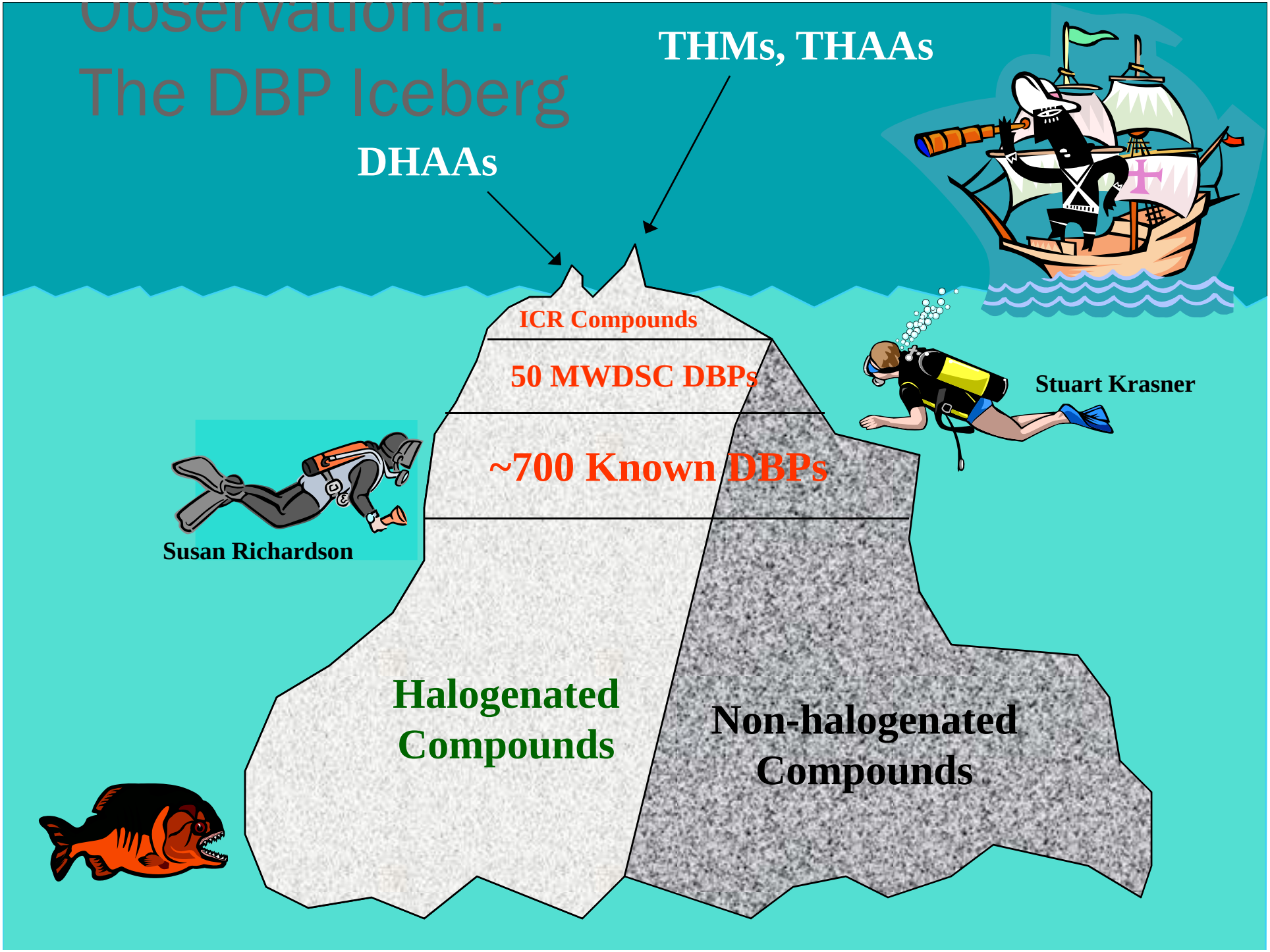
Epidemiology

- Bladder Cancer
  - DBPs linked to 9,300 US cases every year
- Other Cancers
  - Rectal, colon
- Reproductive & developmental effects
  - Neural tube defects
  - Miscarriages & Low birth weight
  - Cleft palate
- Other
  - Kidney & spleen disorders
  - Immune system problems, neurotoxic effects



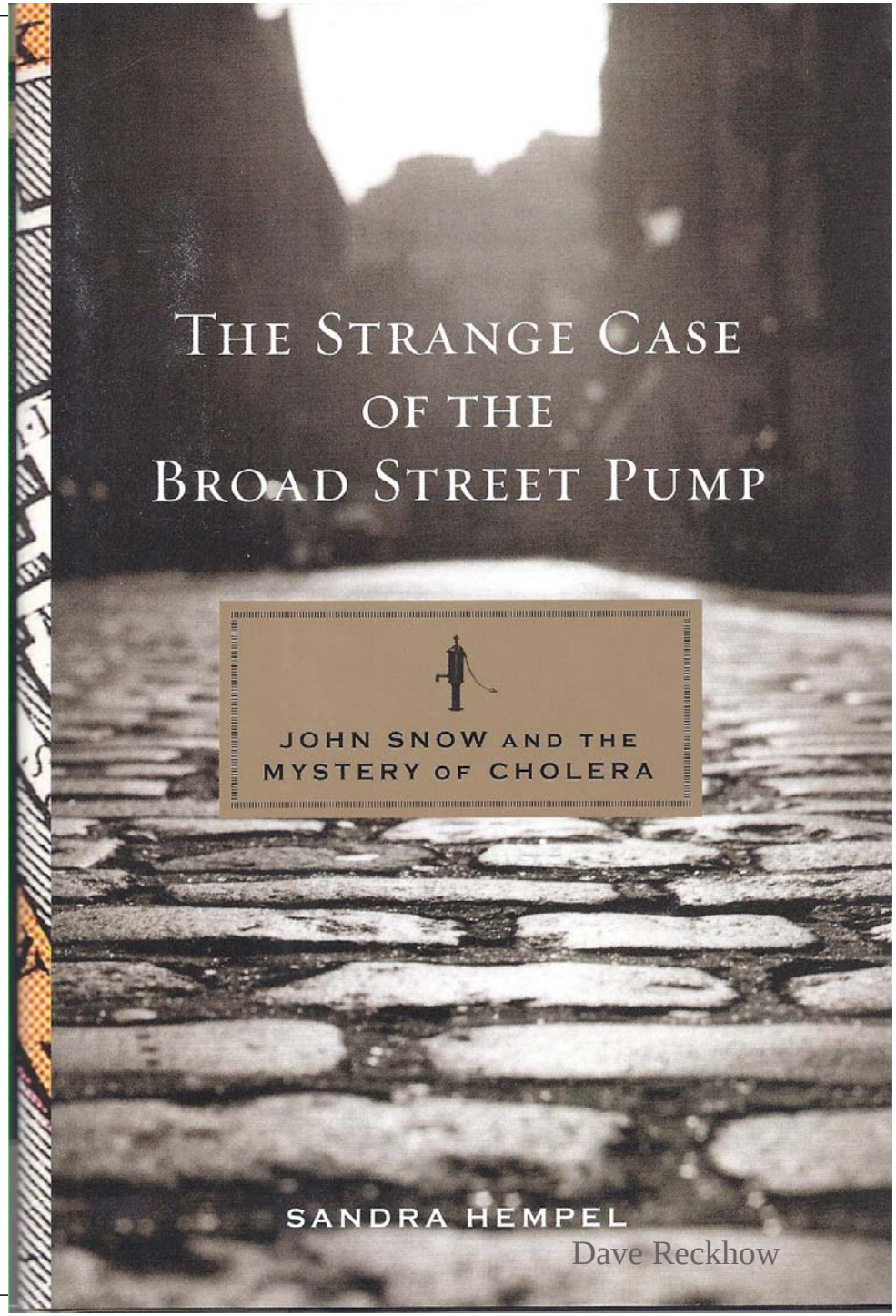
"I think you should be more explicit here in step two"

Observational: The DBP Iceberg



Another

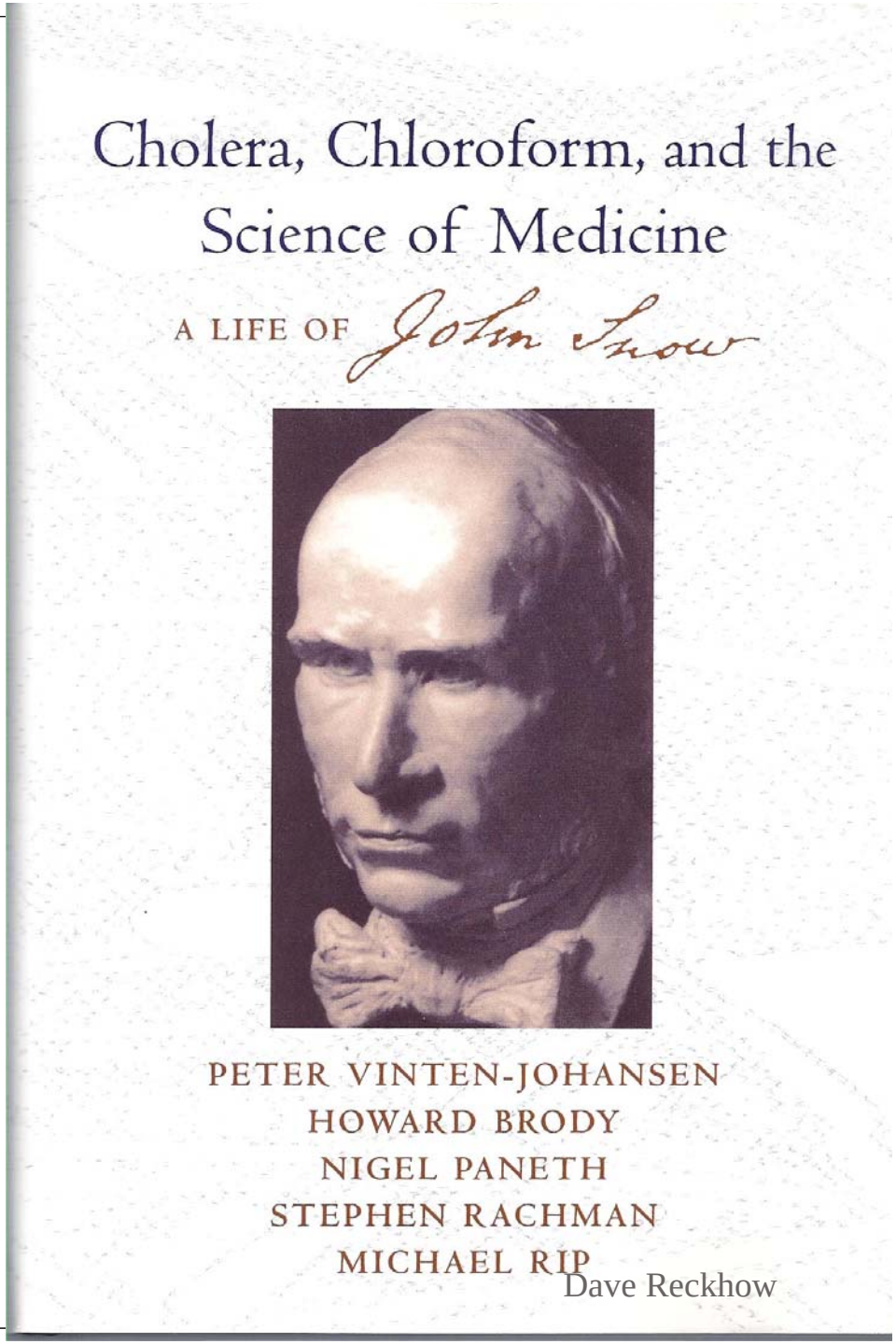
- Sandra Hempel
  - Journalist
- 2007 publication date
- Similar in many ways to Johnson's book



Dave Reckhow

Biography

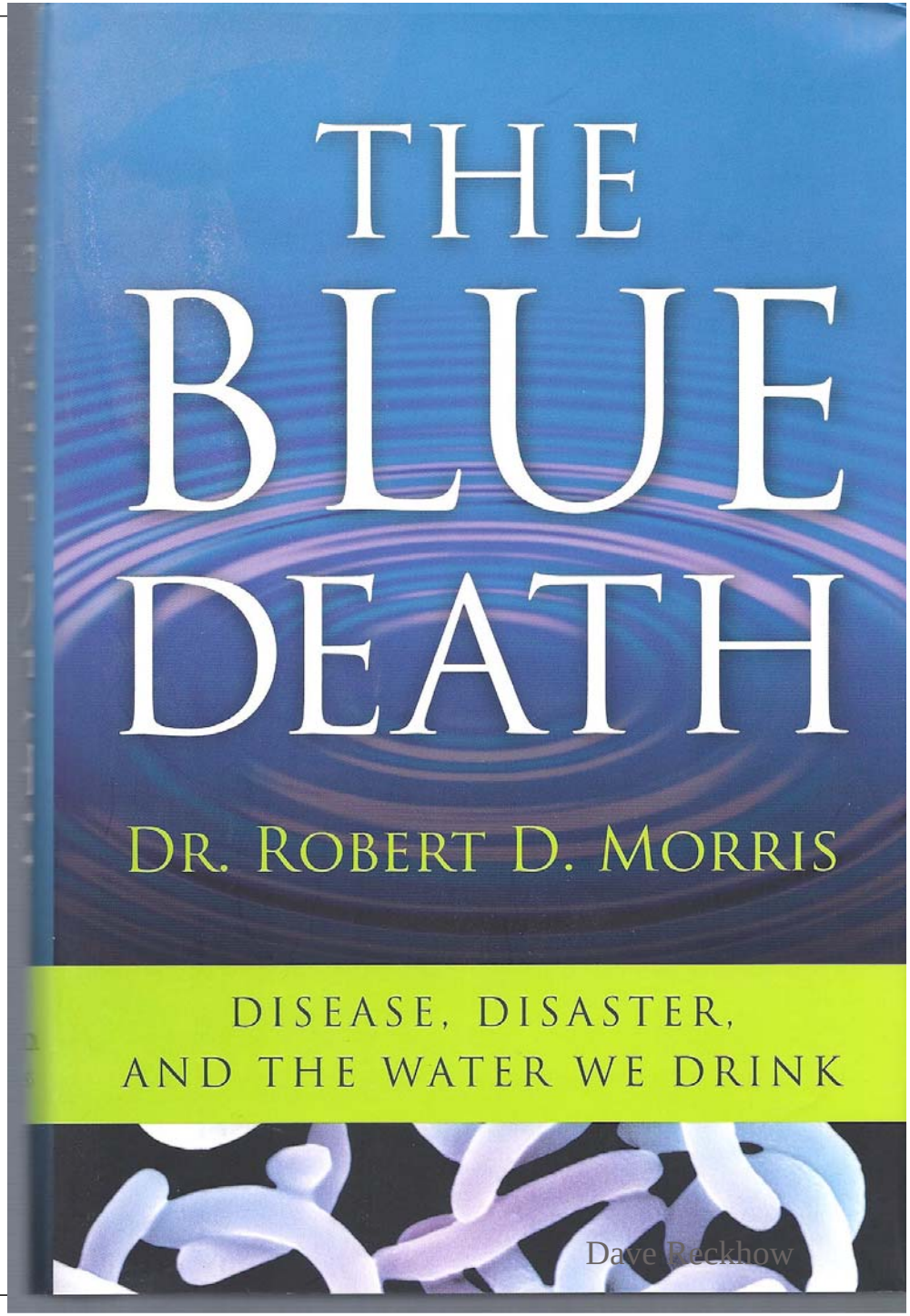
- A serious biography
  - 2003 publication
- Primarily written by MDs



Dave Reckhow

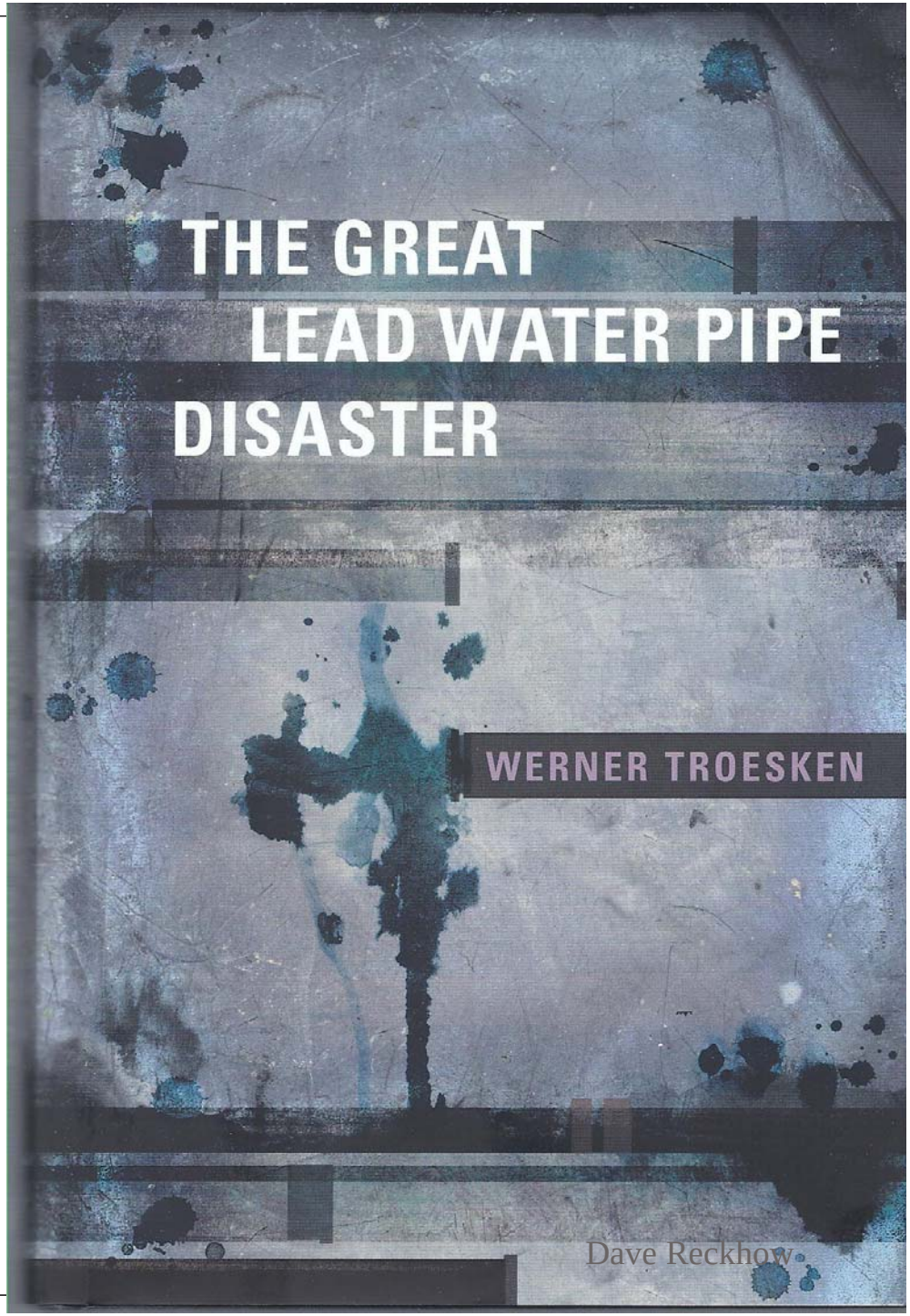
Cholera & beyond

- Robert Morris
  - Environmental epidemiologist
  - 2007 publication date
- More comprehensive
  - Cholera to DBPs to Crypto



Lead Hazards

- 2006 publication date
- Werner Troesken
  - Professor of History
- Presents many historical lessons on society's failure to balance public health with profit



Dave Reckhow

The End