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CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #21

Case Study: NOM-oxidant kinetics

Primary Literature as noted

Introduction

Kinetic Spectrum Analysis

- For mixtures of many closely related compounds
  - A new continuum of rate constants
    - E.g., NOM ⟶
      - Kinetic: Shuman model
      - Equilibria: Perdue model

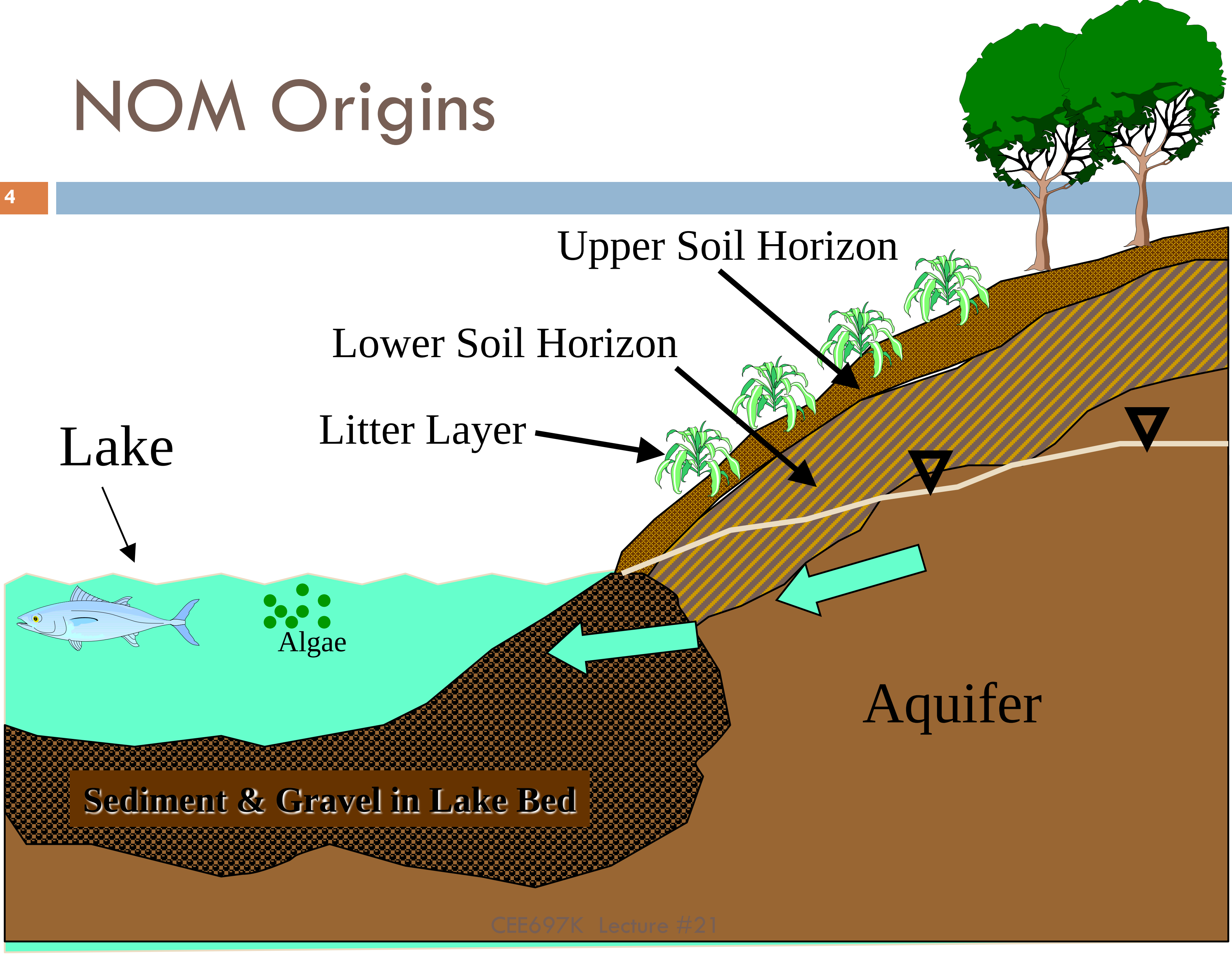
$$[C]_t = \sum_{i=1}^{n} [C_i]_0 e^{-k_i t}$$

  - Very general, but highly subject to errors

Factors affecting DBP levels

- Raw water NOM levels (e.g., TOC)
- Specific precursor content of the RW NOM
- NOM removal
- Disinfection regime
  - type & dose
  - location in plant
  - contact time & temp
  - pH
- Degradation in DS (affects some)

NOM Origins


Upper Soil Horizon
Lower Soil Horizon
Litter Layer
Lake
Algae
Aquifer
Sediment & Gravel in Lake Bed

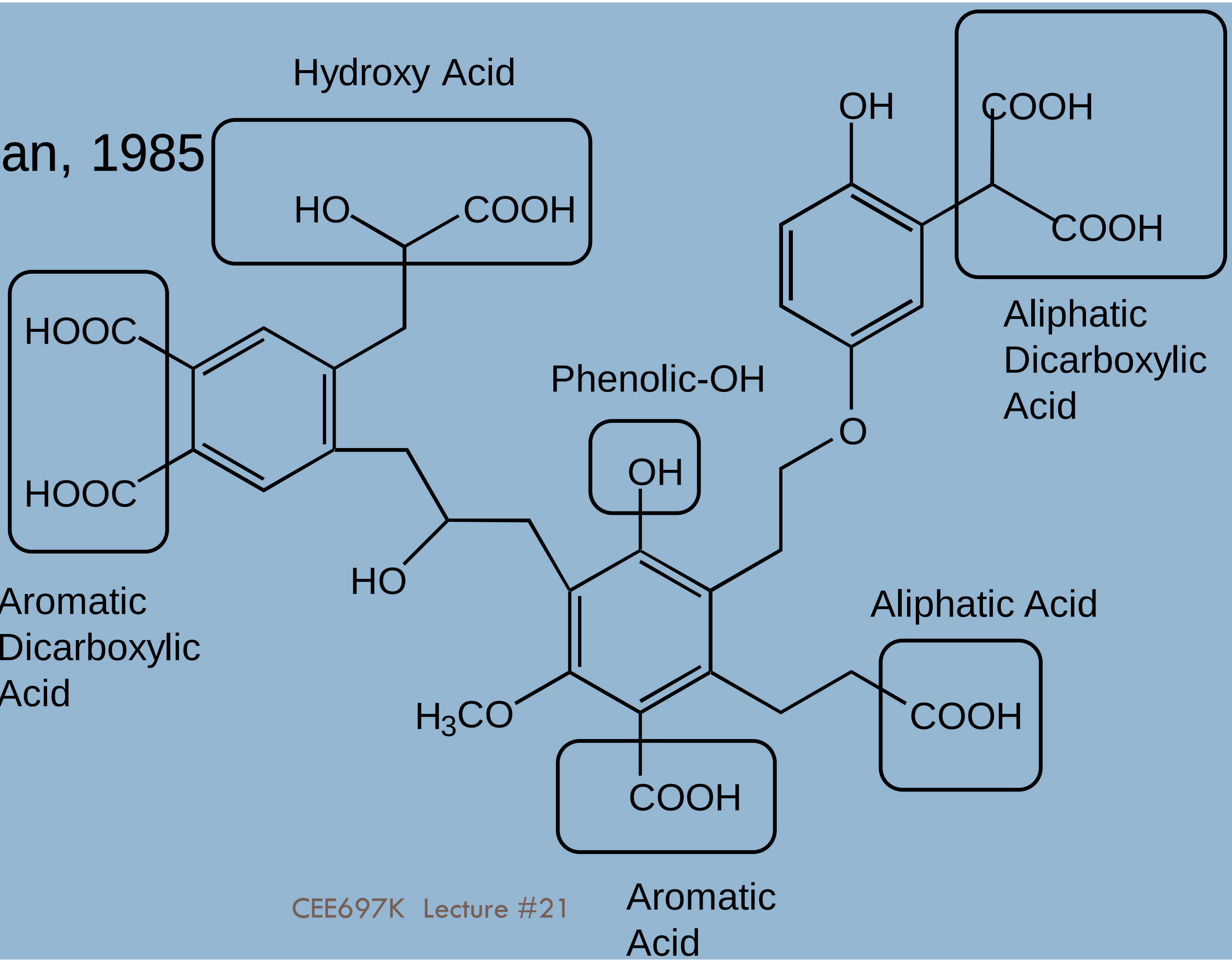
Practical Management Question: Which is the more important source?

or

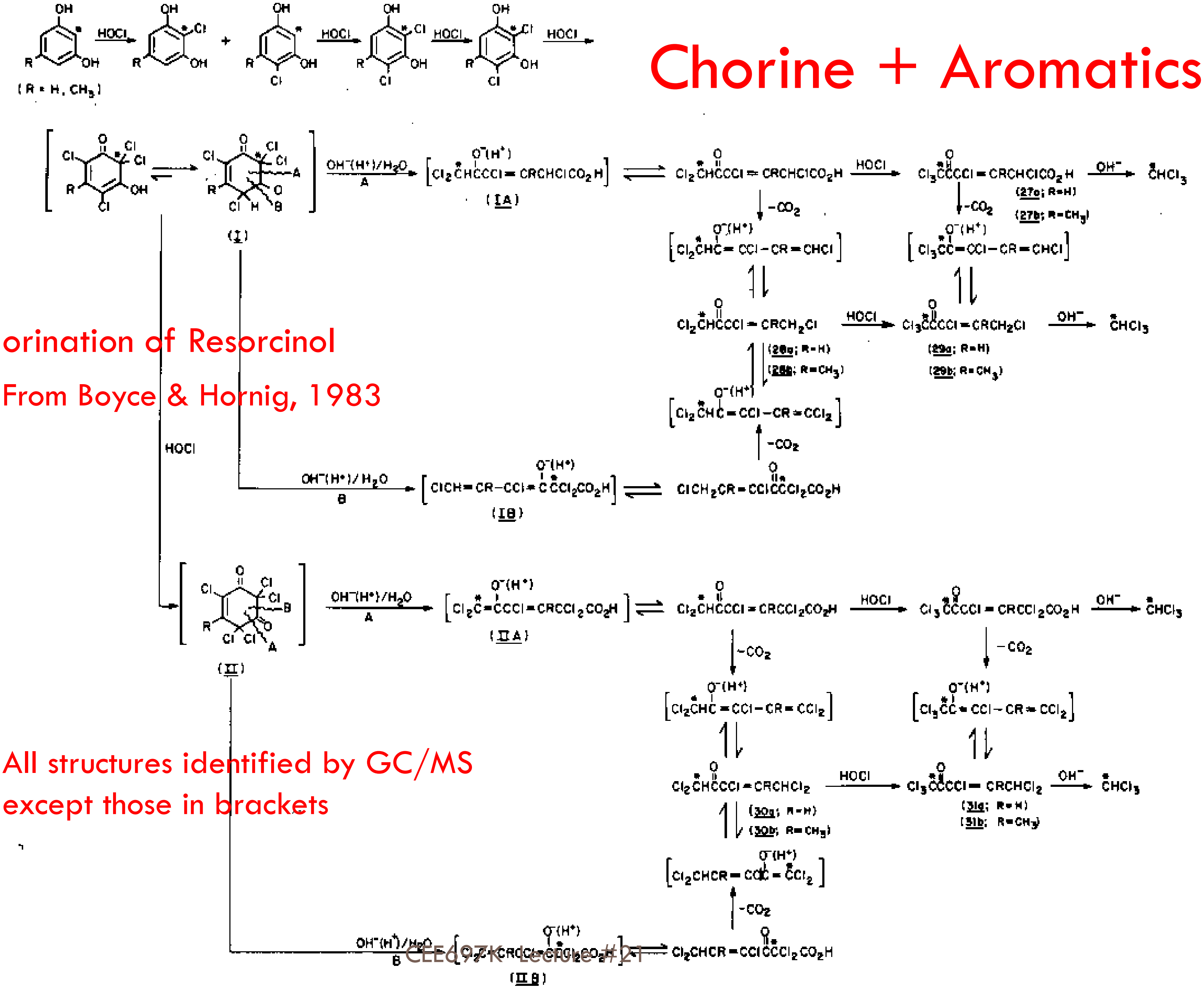
- allochthonous
- autochthonous

An Aquatic Humic "Structure"

From Thurman, 1985



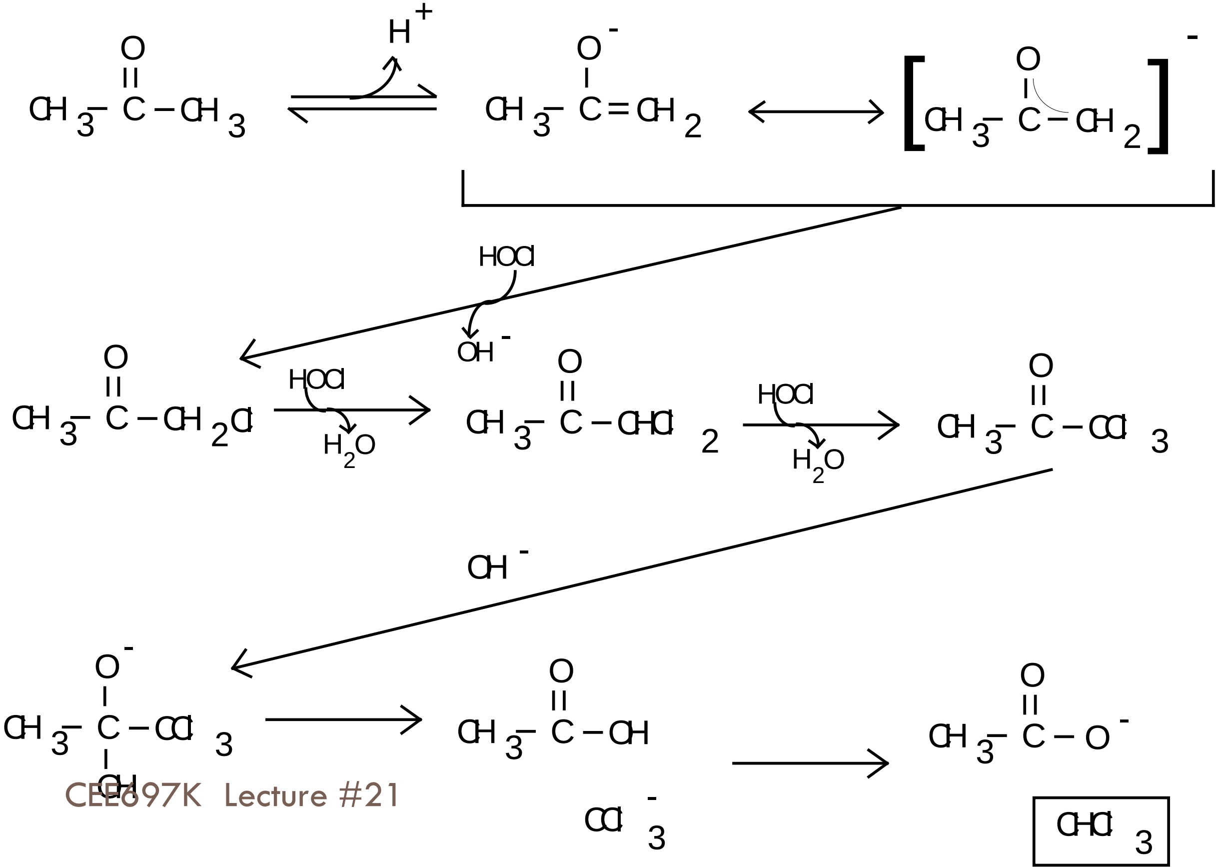
Chorine + Aromatics



- Chlorination of Resorcinol
  - From Boyce & Hornig, 1983
  - All structures identified by GC/MS except those in brackets

Aliphatics: Haloform Reaction

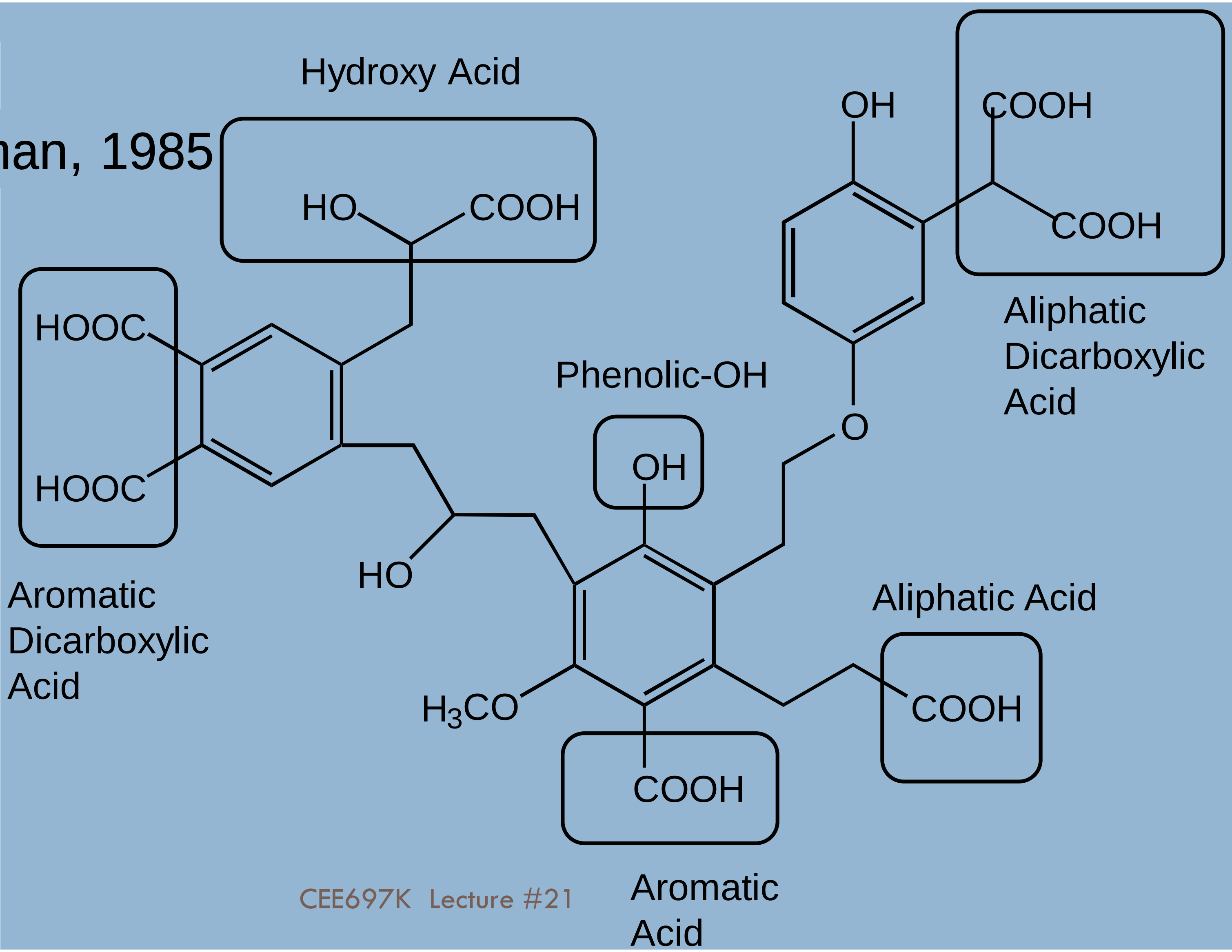
- RLS is deprotonation (k_1) under many conditions



- Many LFERs exist for estimating K_as
  - E.g., Perrin et al., 1982
- Then relate k_1 to K_a

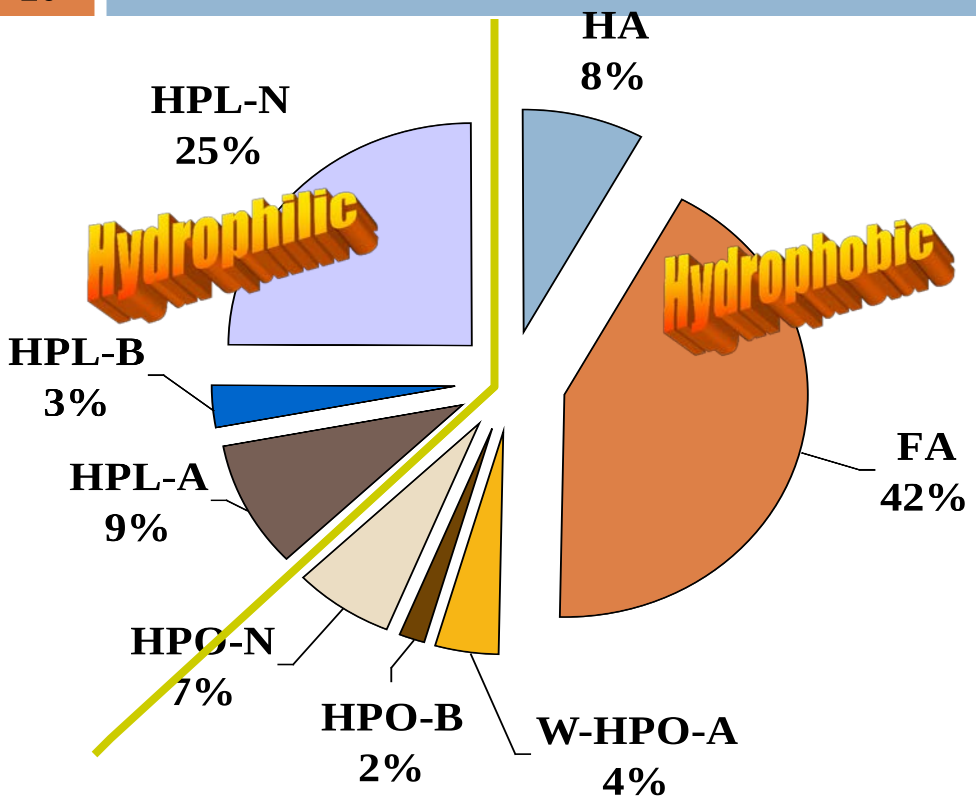
An Aquatic Humic “Structure”

From Thurman, 1985



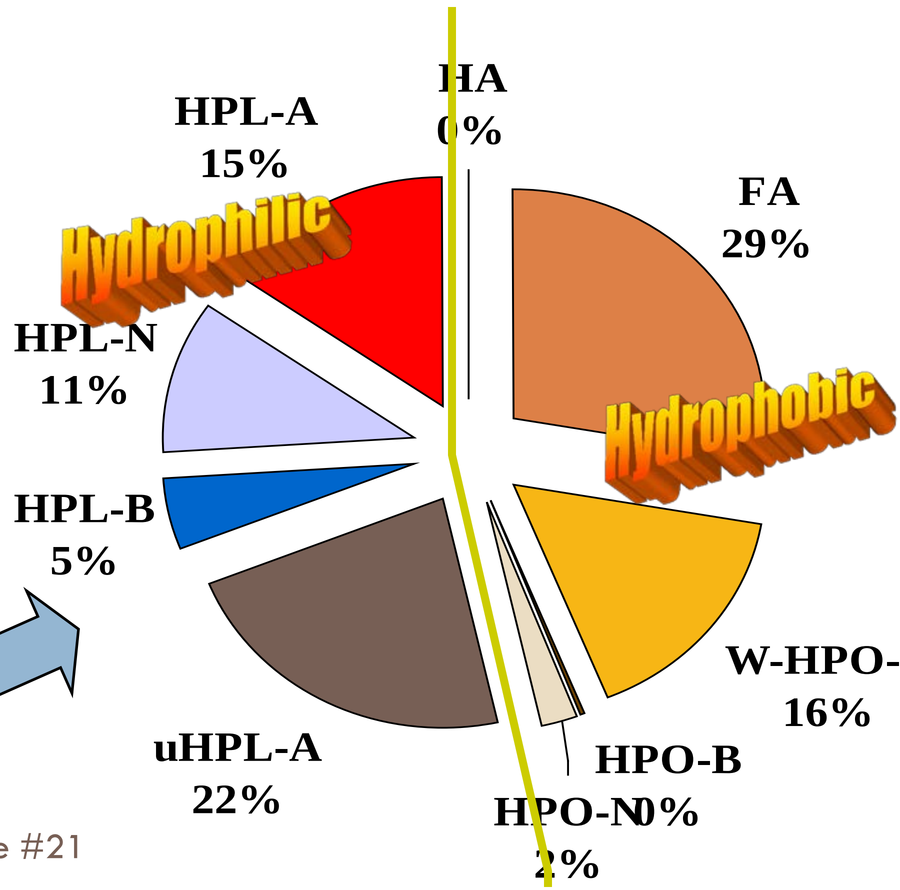
NOM Fractions: Mass Balance

HPL=Hydrophi**l**ic
HPO=Hydroph**o**bic
A=Acids
B=Bases
N=Neutrals
W=Weak
u=ultra

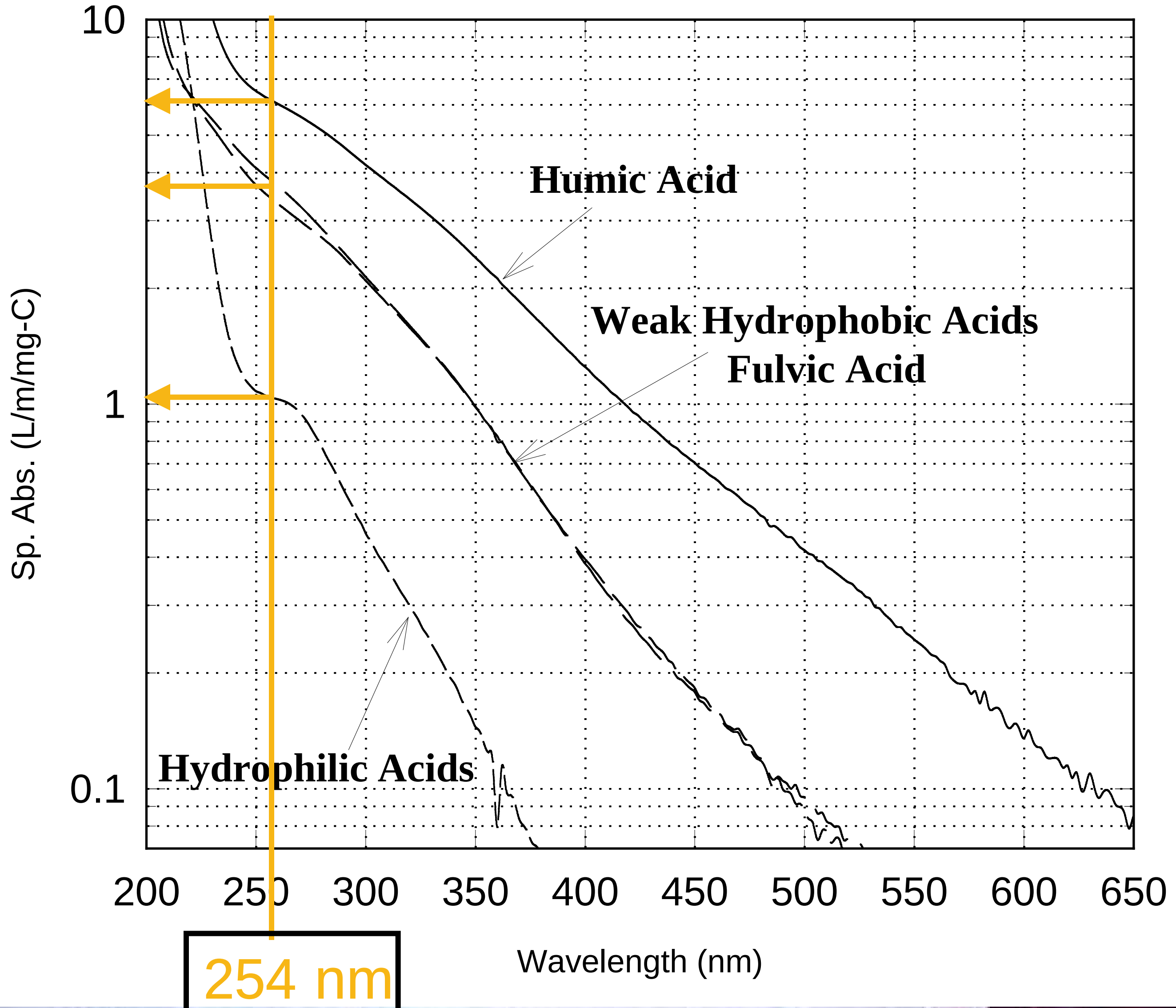


Forge Pond
Granby, MA

Northeast MA
Tap Water



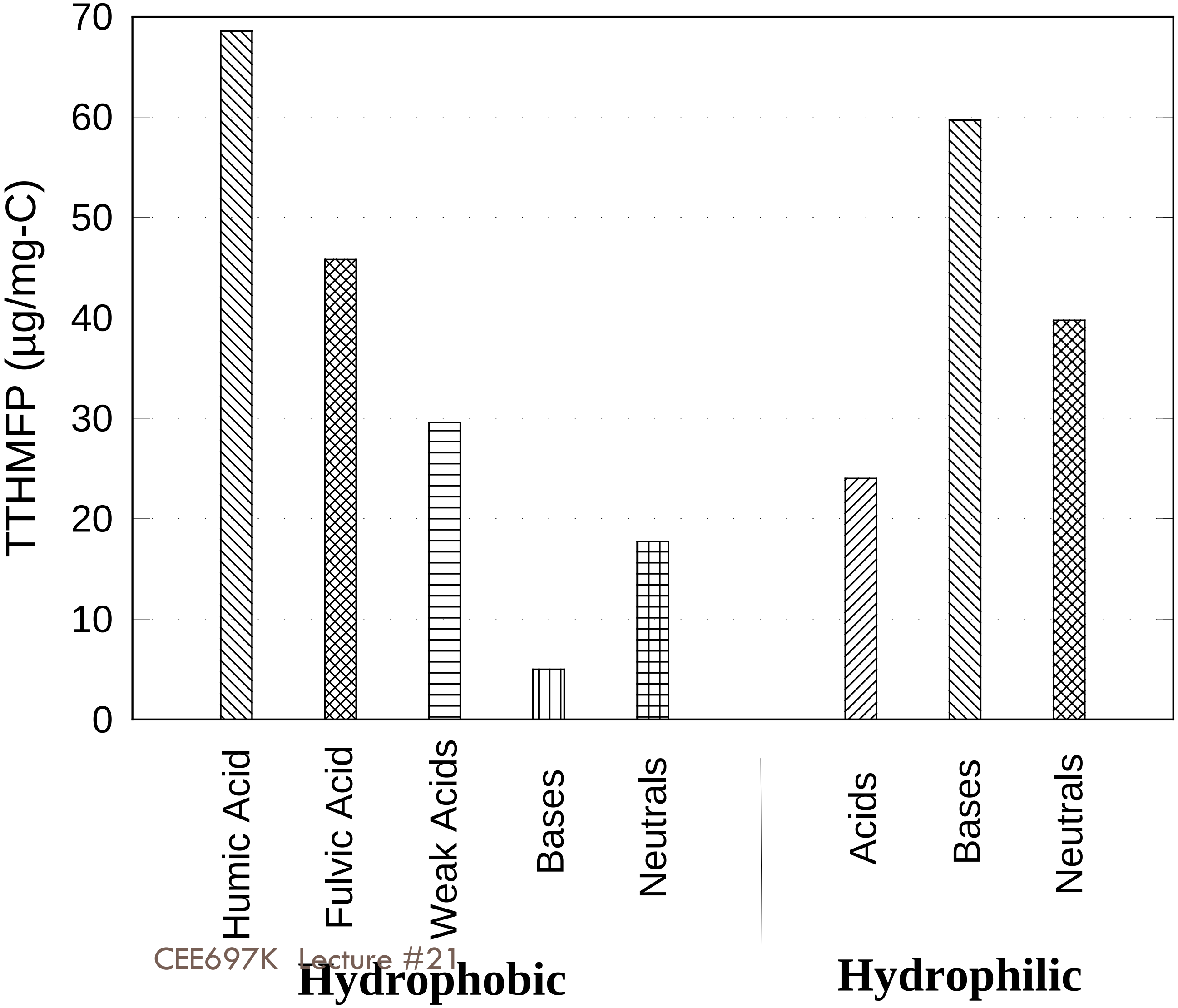
Absorbanc of Acid Fractions



Same DOC

Formation Potentials of NOM Fractions

- FP
  - High dose
  - Forces reaction to endpoint



Leaching Experiments

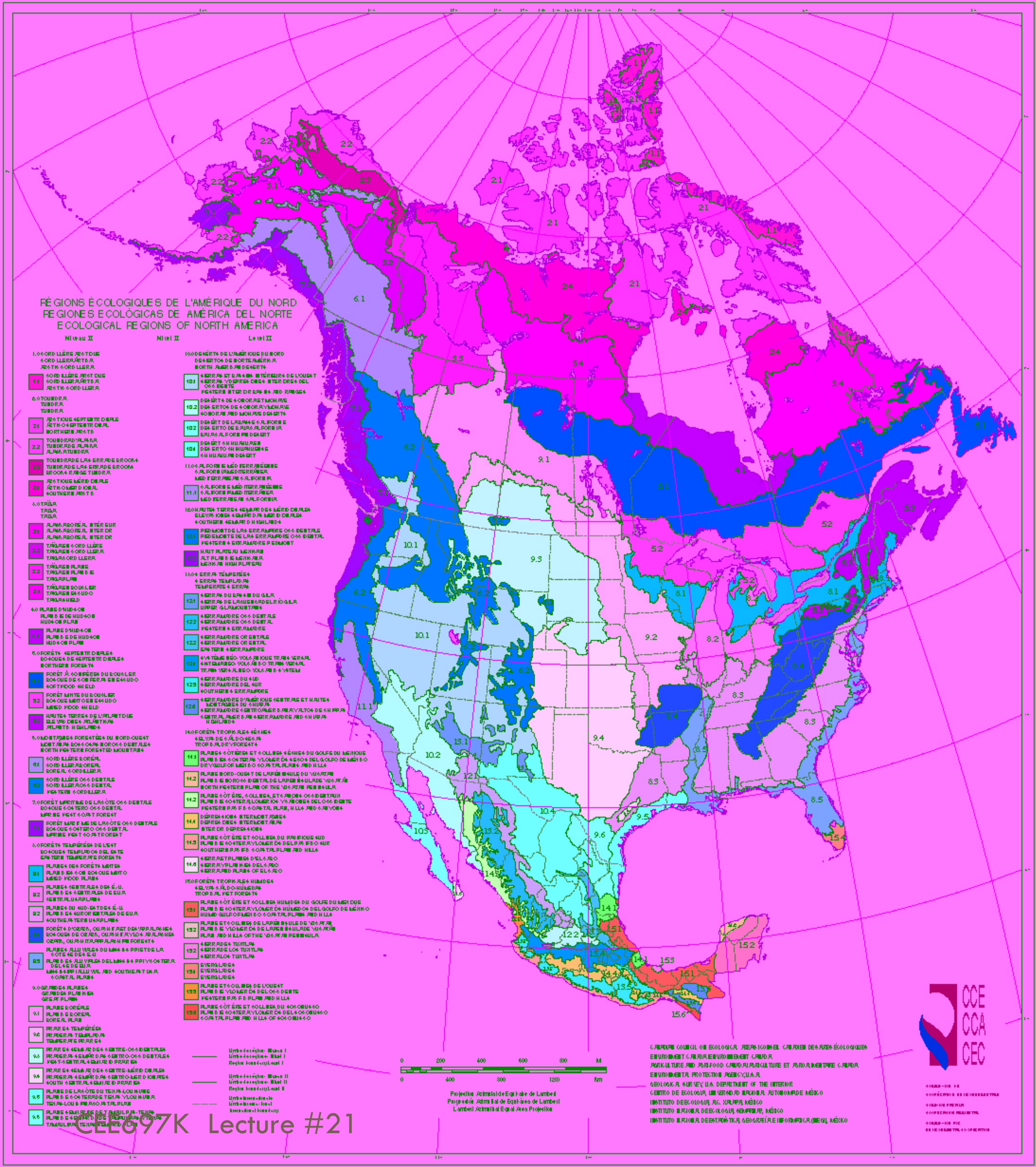
Aged leaves from 3 locations in Wachusett watershed

White Pine

White Oak

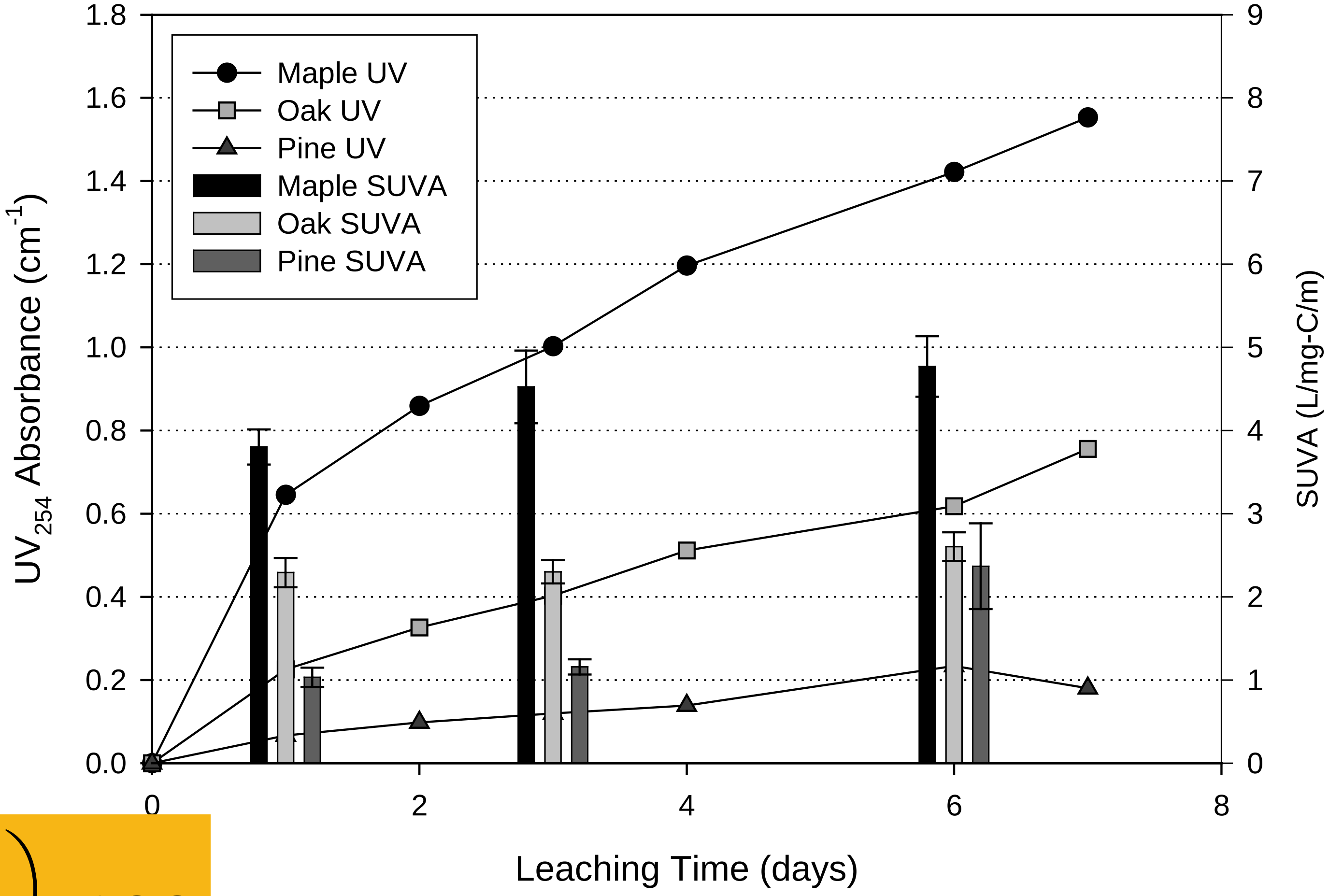
Red Maple

- Level 2 ecoregions



Leaching of leaves

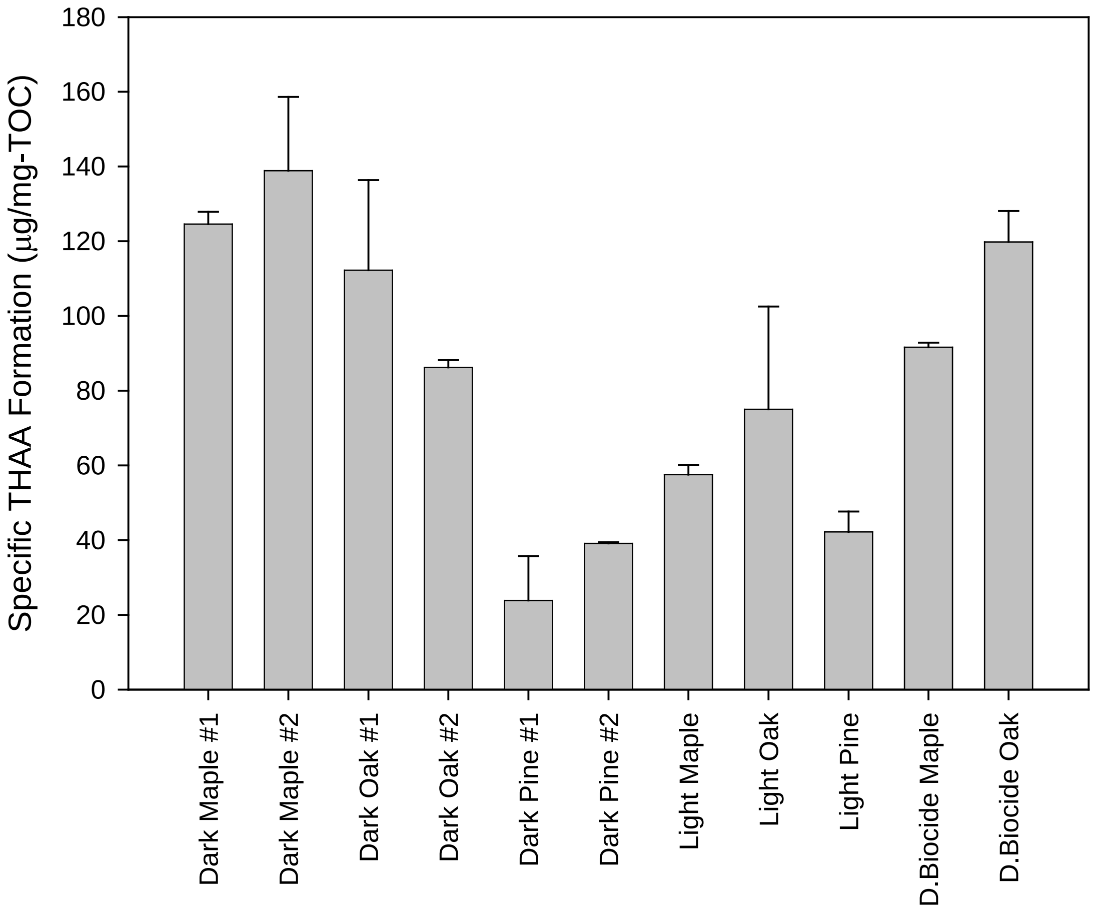
- Dark
- Non-sterile conditions
- Substantial slow leaching of organics



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

Leaching: Sp-THAAFP

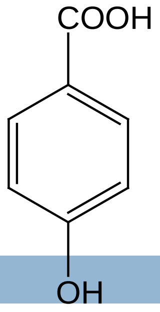
- Filtered leachate
- Chlorinated & analyzed for THAAs
  - Mostly trichloroacetic acid
- THAA yield divided by DOC
  - Specific THAA (precursors)



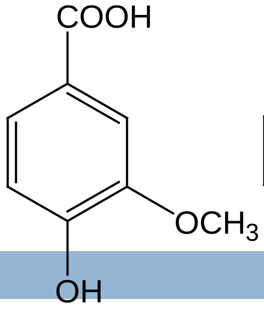
Specific THAA Formation for Leaching Study

Lignin Monomers

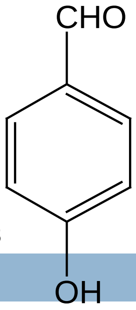
- Aromatic structures
  - from CuO degradation
- Syringyl
- Vanillyl
- Cinnamyl



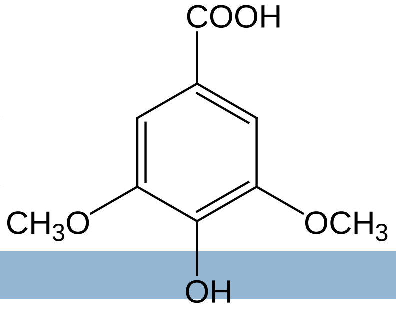
4-Hydroxy-benzoic acid



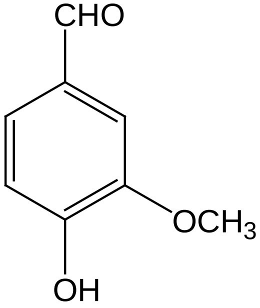
Vanillic acid



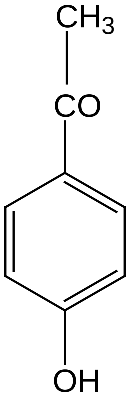
4-Hydroxy-benzaldehyde



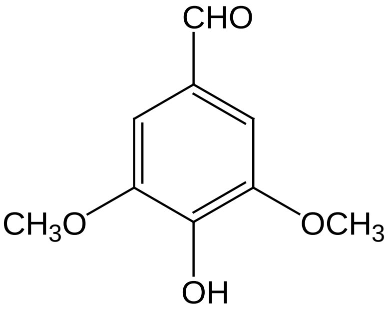
Syringic acid



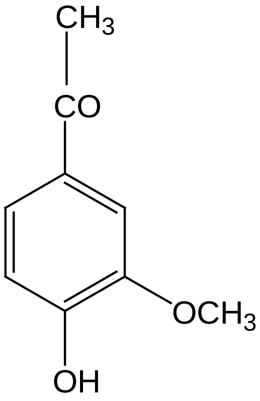
Vanillin



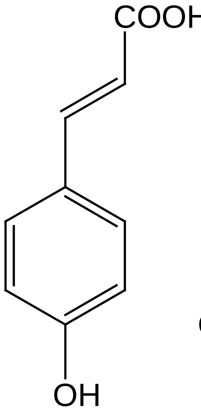
4-Hydroxy-acetophenone



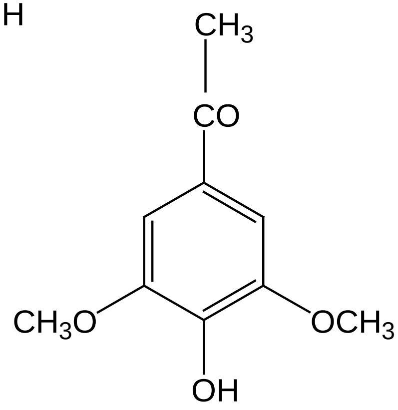
Syringaldehyde



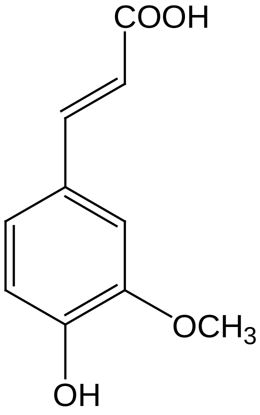
Acetovanilione



4-Hydroxy-cinnamic acid

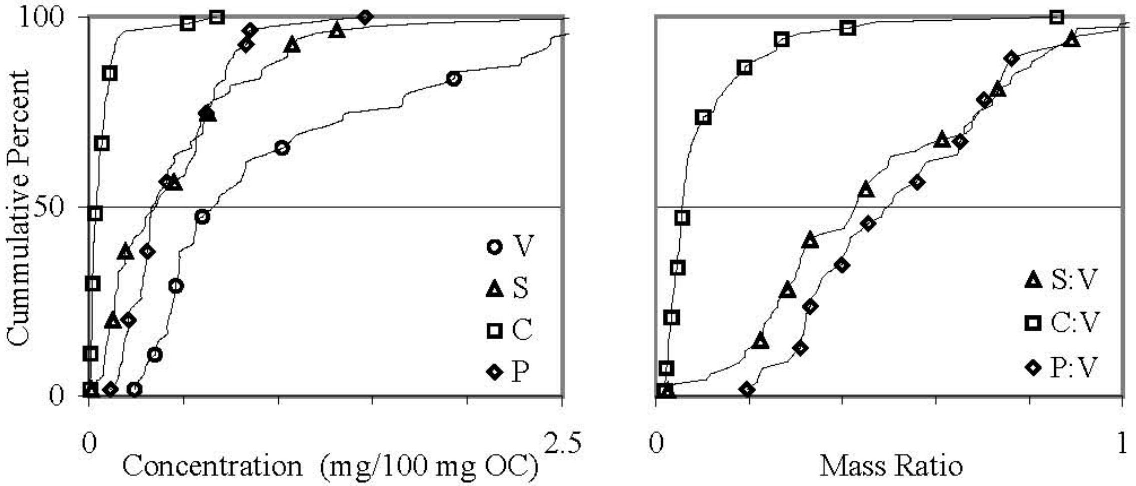


Acetosyringone



Ferulic acid

Lignin



Concentration (mg/100 mg OC)

Lignin Phenol Group	Obs.	Range	Median	Mean	Std. Dev.
Vanillyl[a] (V)	57	0.24 - 3.18	0.68	1.02	0.78
Syringyl[b] (S)	55	0.02 - 2.88	0.36	0.50	0.50
Cinnamyl[c] (C)	54	0.01 - 0.68	0.04	0.07	0.11
p-Hydroxy[d] (P)	57	0.12 - 1.46	0.36	0.45	0.27
Total Lignin Phenol[e]	55	0.59 - 6.66	1.41	2.06	1.47

Mass Ratio (Relative to Vanillyl Content)

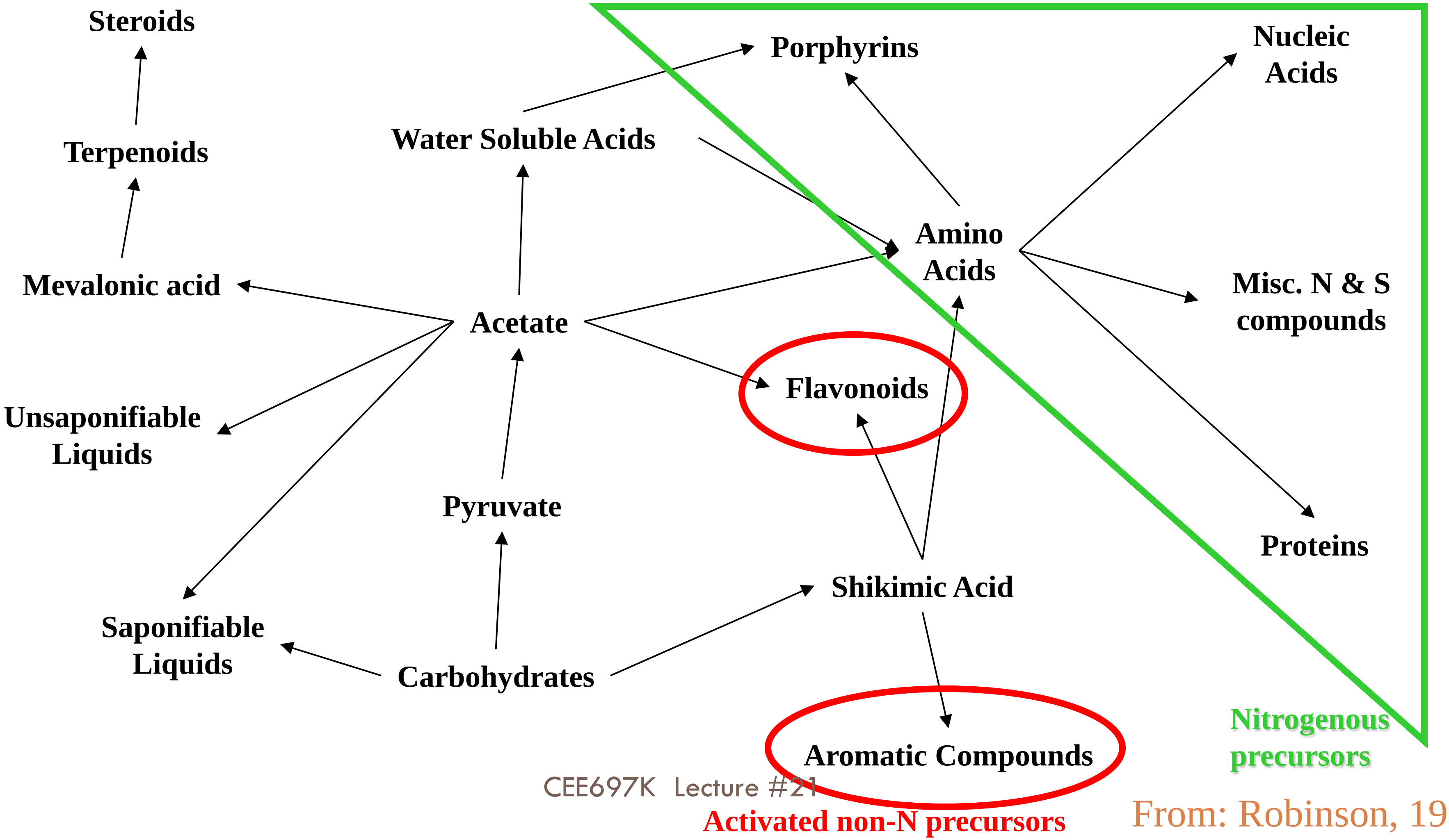
	Obs.	Range	Median	Mean	Std. Dev.
Syringyl (S:V)	68	0.03 - 1.75	0.43	0.50	0.32
Cinnamyl (C:V)	68	0.02 - 0.86	0.06	0.11	0.13
p-Hydroxy (P:V)	55	0.19 - 1.22	0.51	0.54	0.23

Concentration

	Obs.	Range	Median	Mean	Std. Dev.
Total Lignin[e] (μg L^{-1})	55	0.42 - 39.4	9.7	10.7	9.8
% DOC as Lignin	55	0.24 - 3.12	0.6	1.0	0.7

From:
Perdue & Ritchie, 2004

Other plant products



Steroids

Terpenoids

Mevalonic acid

Unsaponifiable Liquids

Saponifiable Liquids

Water Soluble Acids

Acetate

Pyruvate

Carbohydrates

Porphyrins

Nucleic Acids

Amino Acids

Misc. N & S compounds

Flavonoids

Proteins

Shikimic Acid

Aromatic Compounds

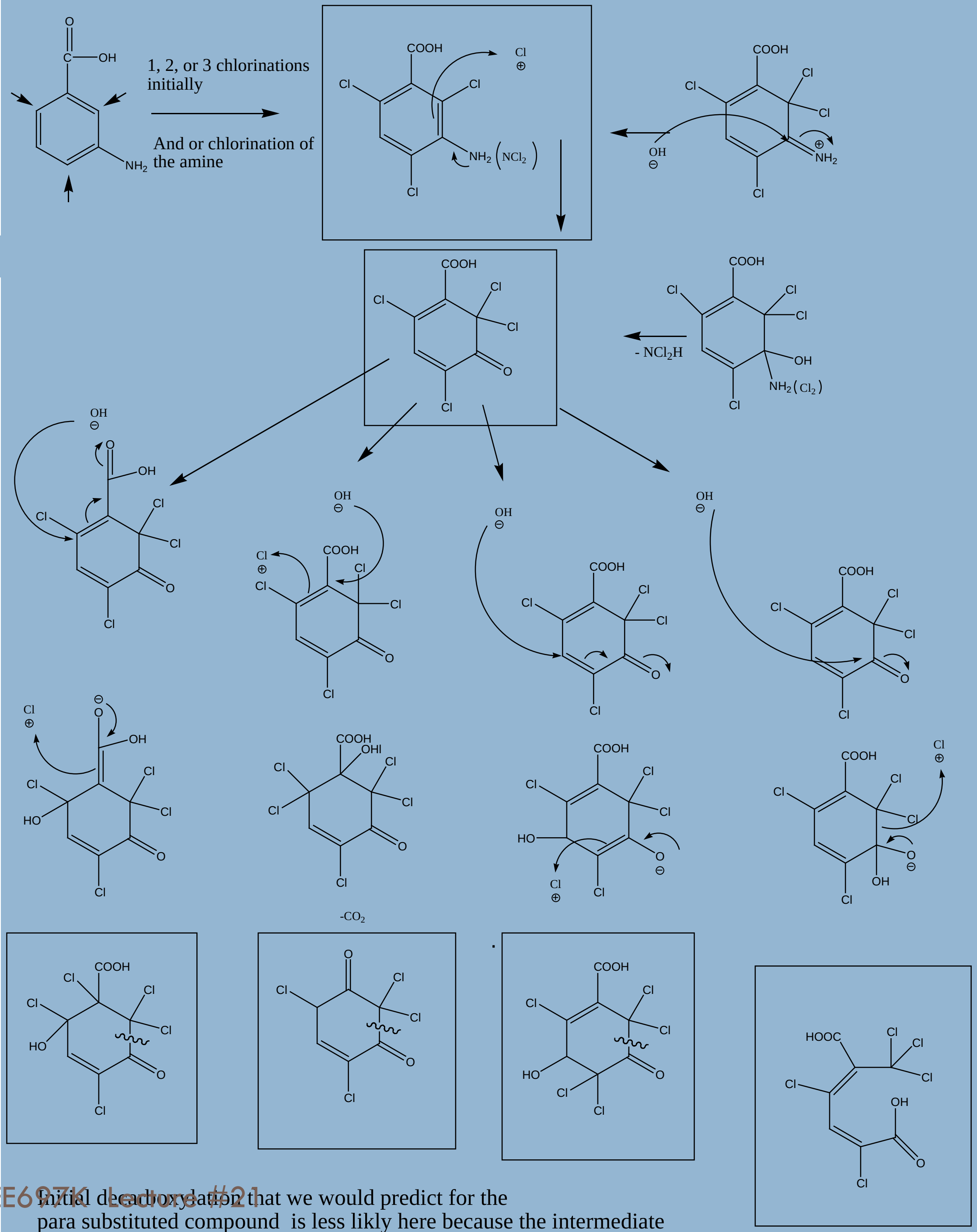
Nitrogenous precursors

Activated non-N precursors

From: Robinson, 1991

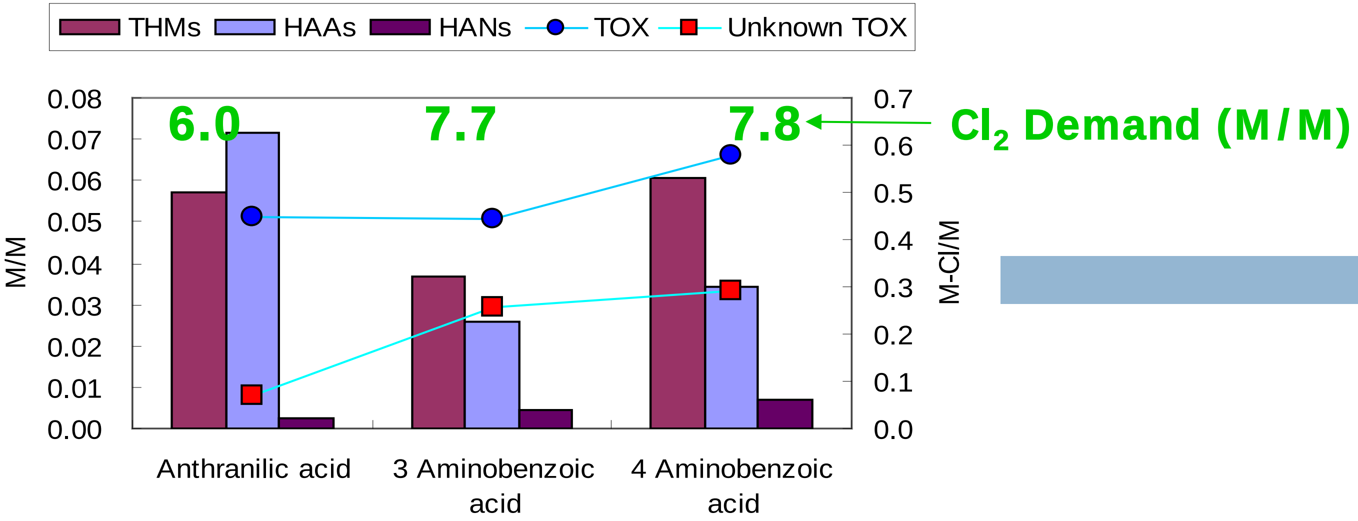
Aromatic Amines

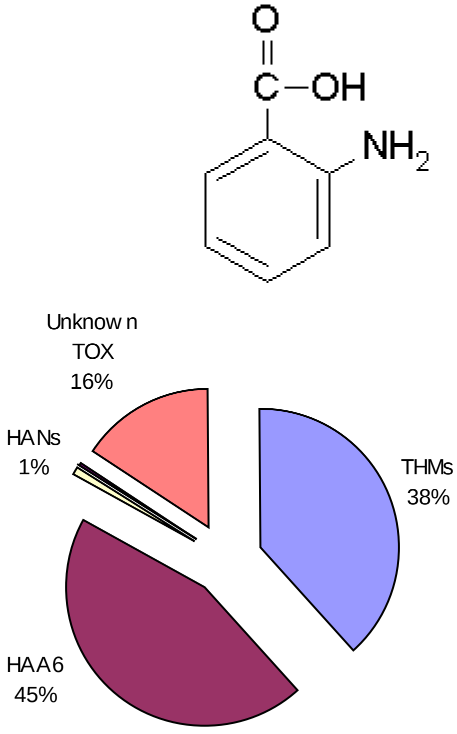
- Proposed degradation pathway for 3-amino benzoic acid.



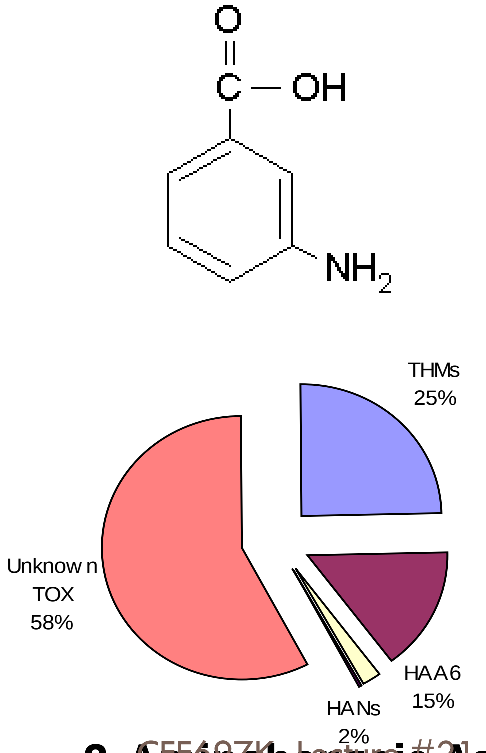
Initial dechlorination that we would predict for the para substituted compound is less likly here because the intermediate is not resonance stabilized

Aromatic Amines

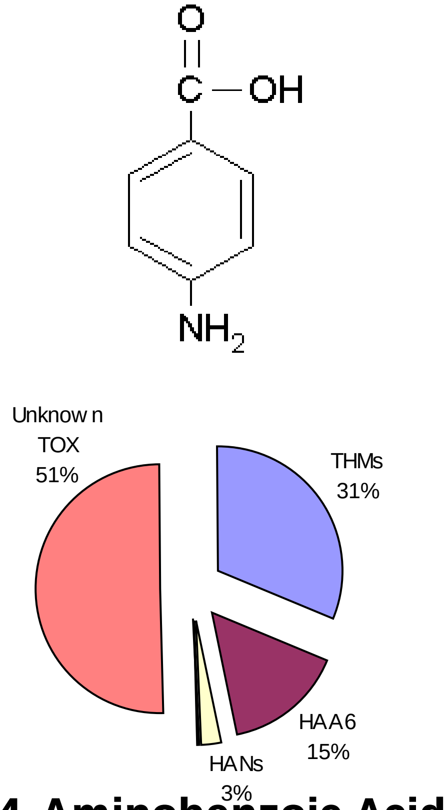




Anthranilic Acid



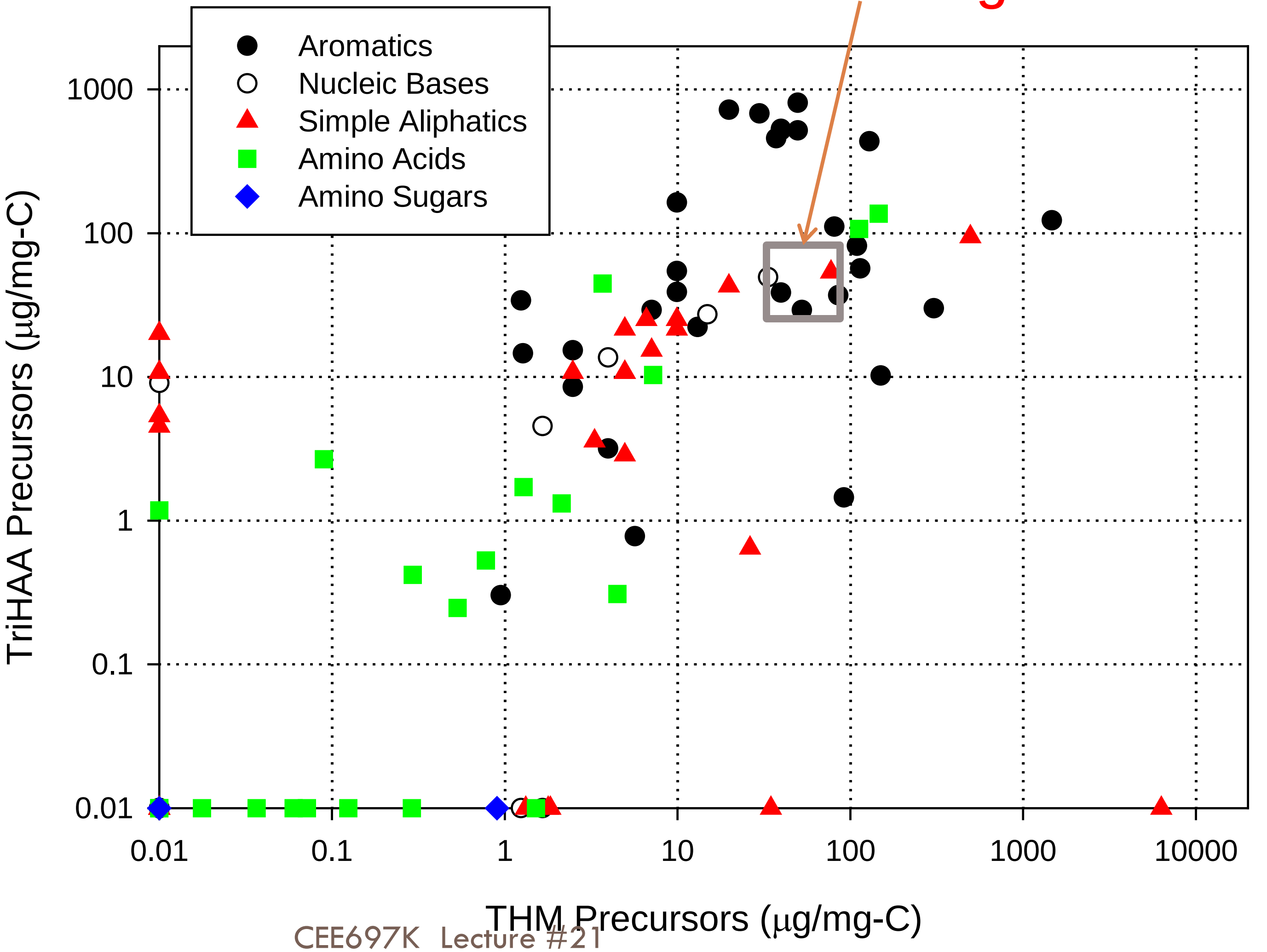
3-Aminobenzoic Acid



4-Aminobenzoic Acid

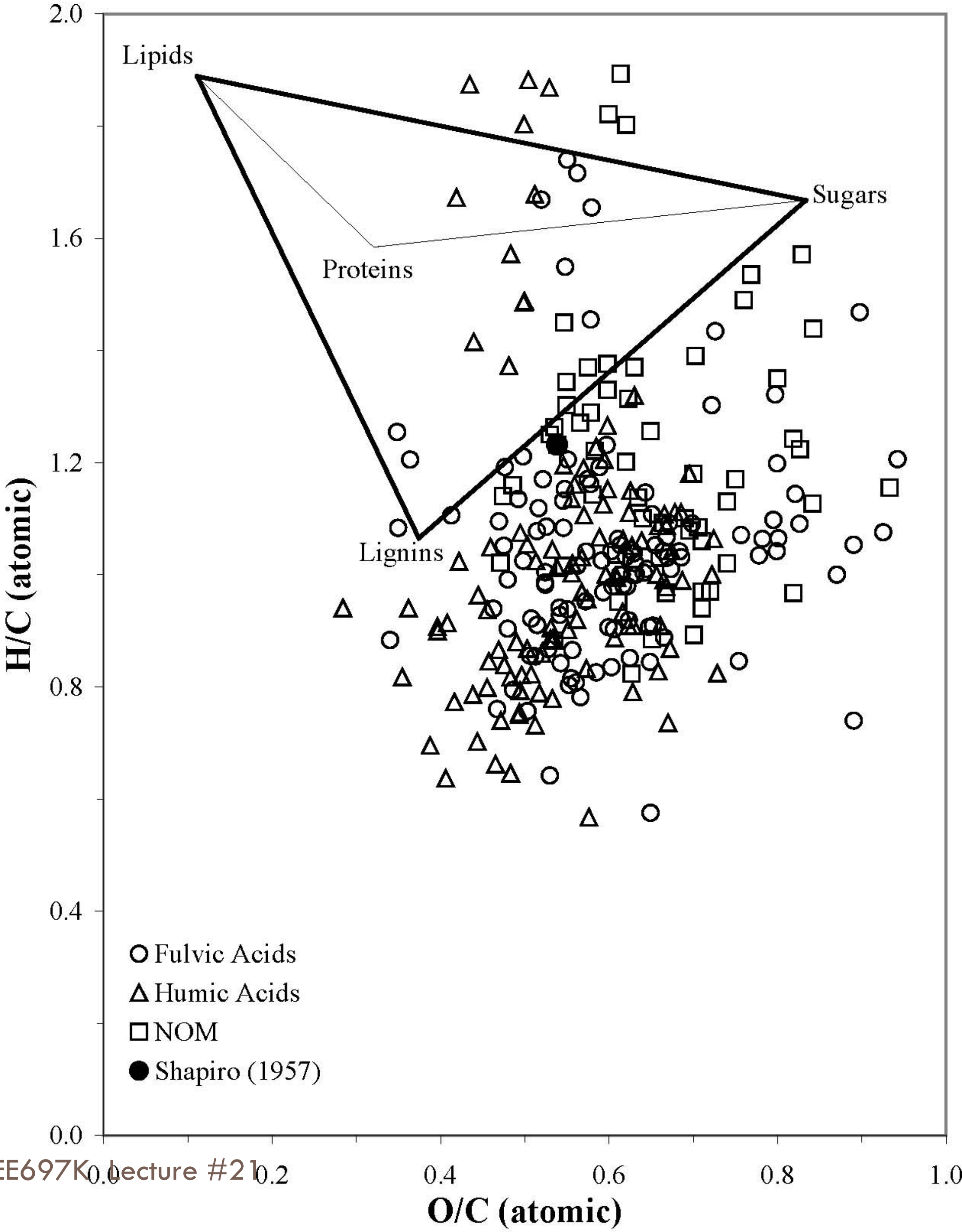
Compare with Model Compounds

- Wide range for models
- Narrow range for NOM



Elemental Ratios

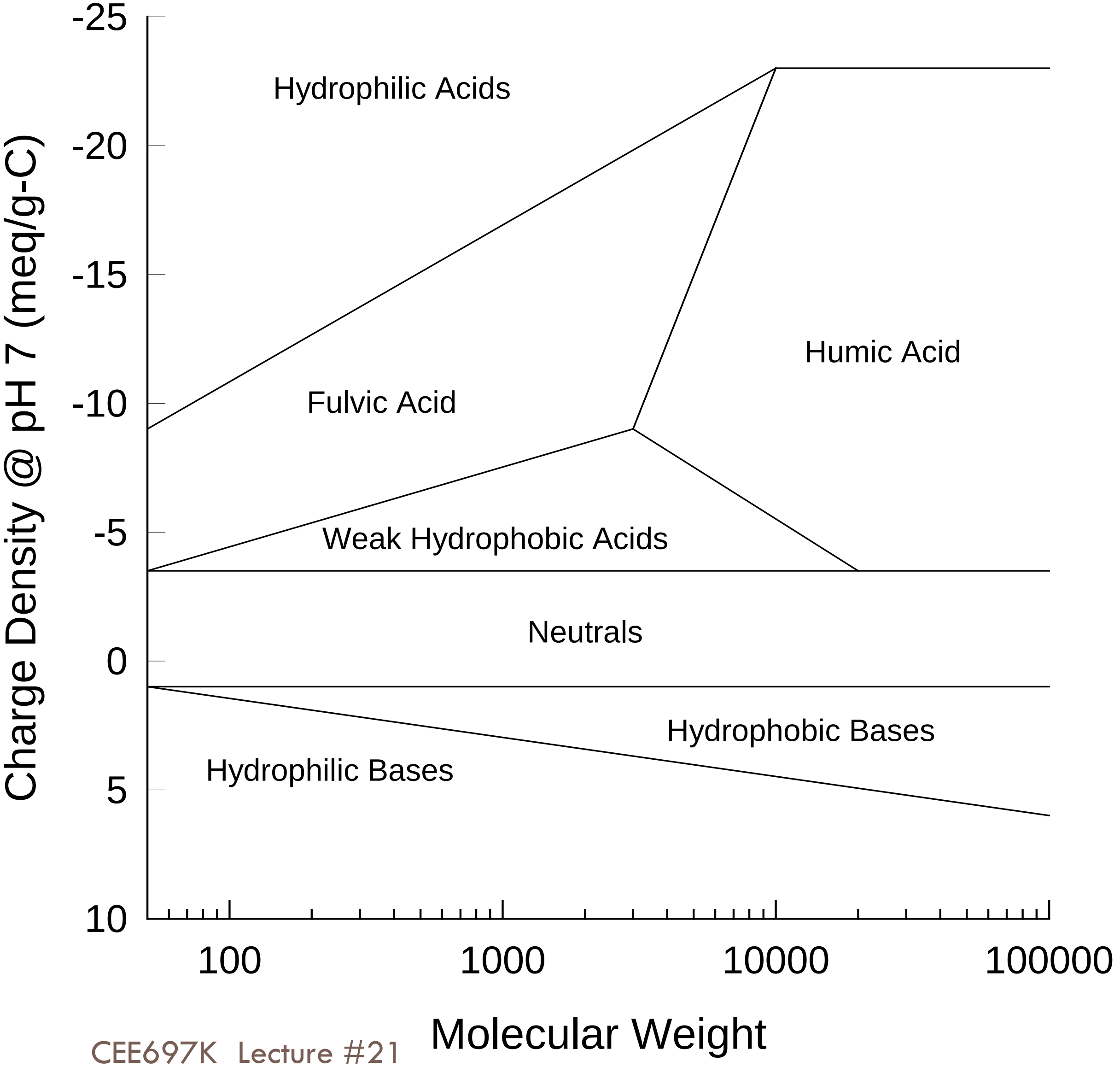
- Van Krevelen Plot

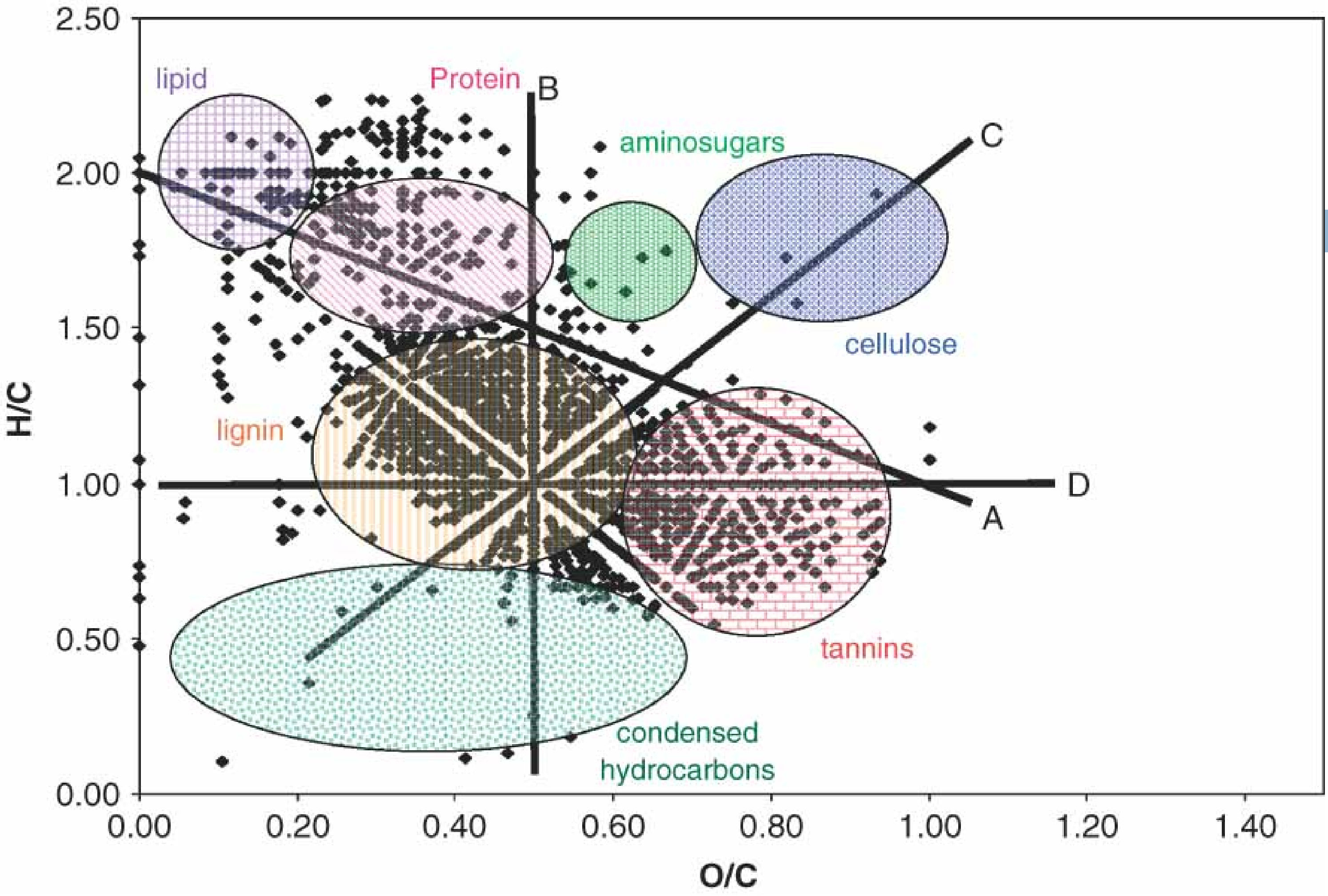


From:
Perdue & Ritchie, 2004

Size and Charge Relationships for NOM Fractions

from: Bezbarua and Reckhow, 1995

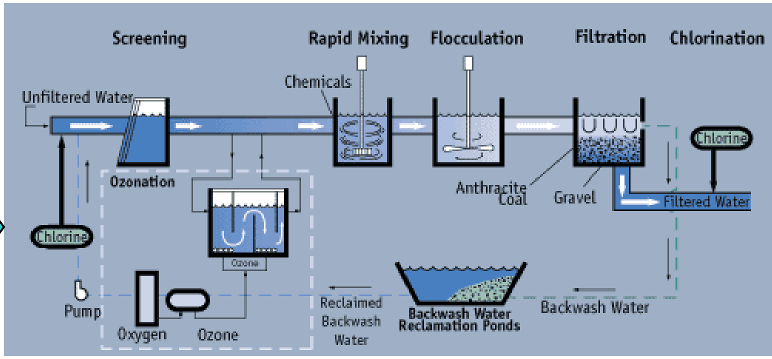




- Van Krevelen diagram for the Dismal Swamp DOM, compound classes are represented by the circles overlain on the plot. The distinctive lines in the plot denote the following chemical reactions: (A) methylation/demethylation, or alkyl chain elongation; (B) hydrogenation/dehydrogenation; (C) hydration/condensation; and (D) oxidation/reduction.

Sleighter & Hatcher, 2007 [J. Mass Spec. 42:559]

Fate & Transport:



- Watershed
- Natural system
  - Physical processes
  - Chemical processes
  - Biological processes

"Full-scale monitoring

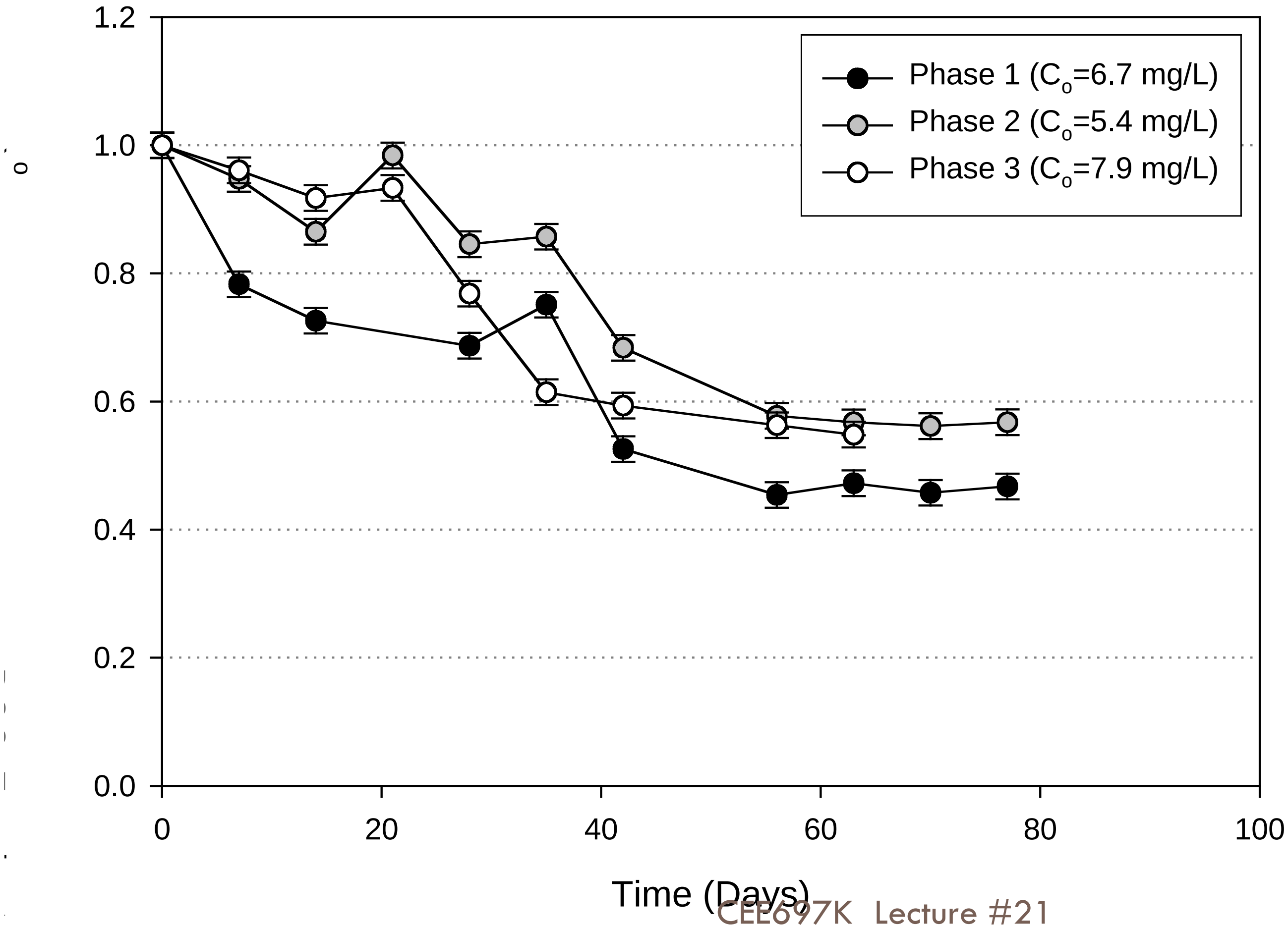
"Lab-scale simulation

- Water Treatment Plant
- Engineered System
  - Physical processes
  - Chemical processes
  - Biological processes

Fundamental Testing

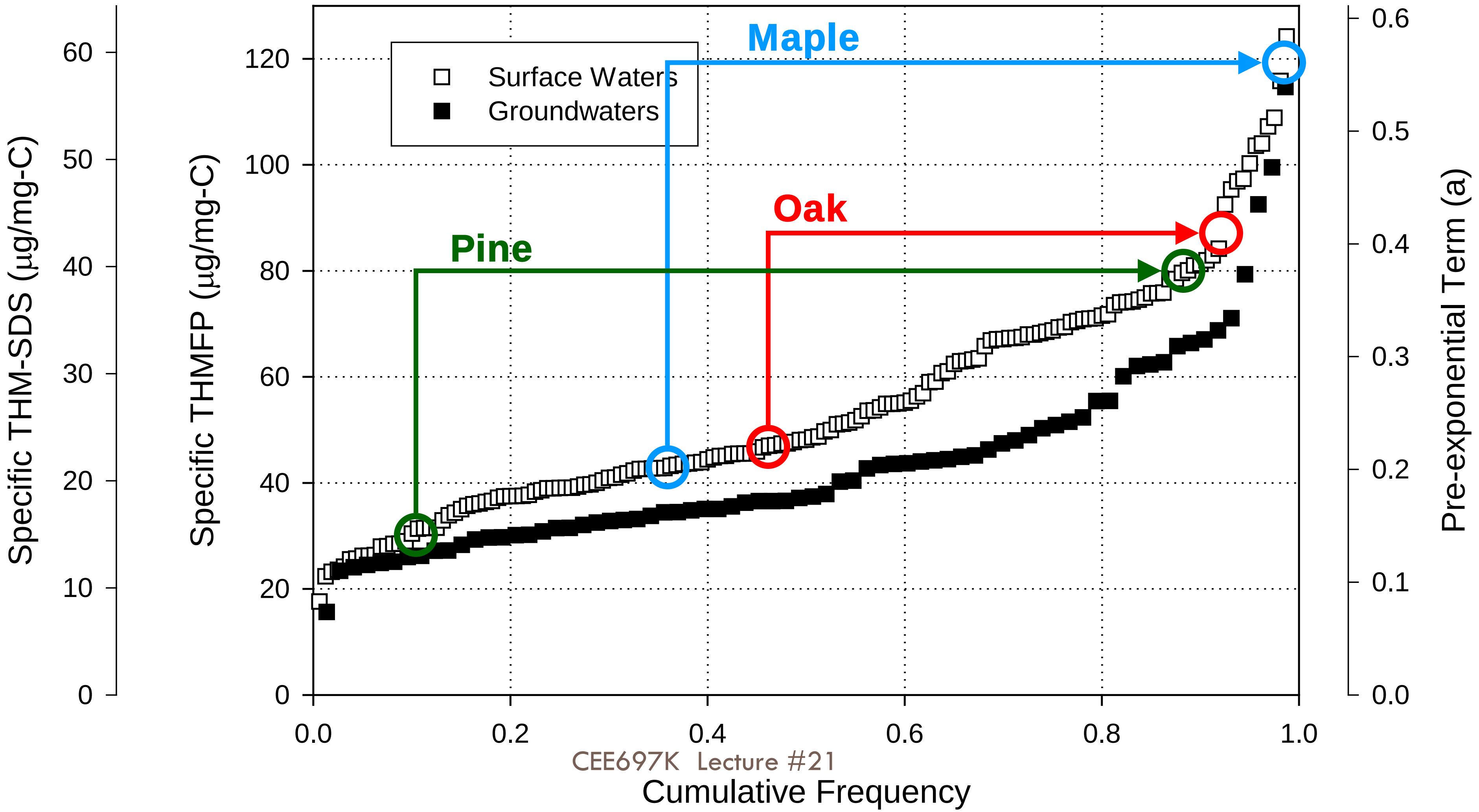
Biodegradation of leaf leachate

- ~ 50% biodegradable



- Bacteria grow preferentially on NOM <3000 amu

Leaching & Biodegradation



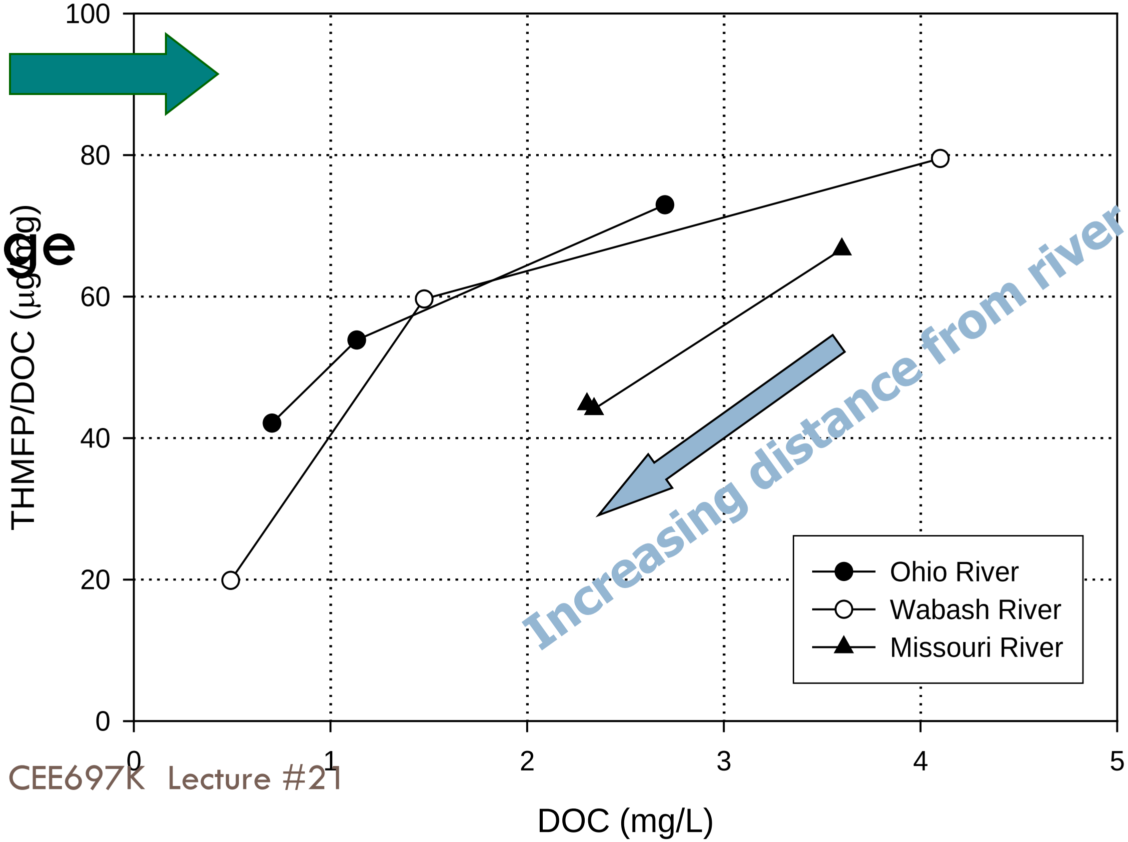
Transport & Soil Properties

- Case study: TOC & soil properties
  - 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
  - Presumed Attenuated of TOC by adsorption to clay soils
  - Impacts on specific NOM components & precursors ??

Subsurface processes

- River Bank Filtration
  - Weiss et al., 2001
    - AWWA ACE
- Groundwater recharge
  - Aiken & others

Effect of Bank Filtration on Precursors

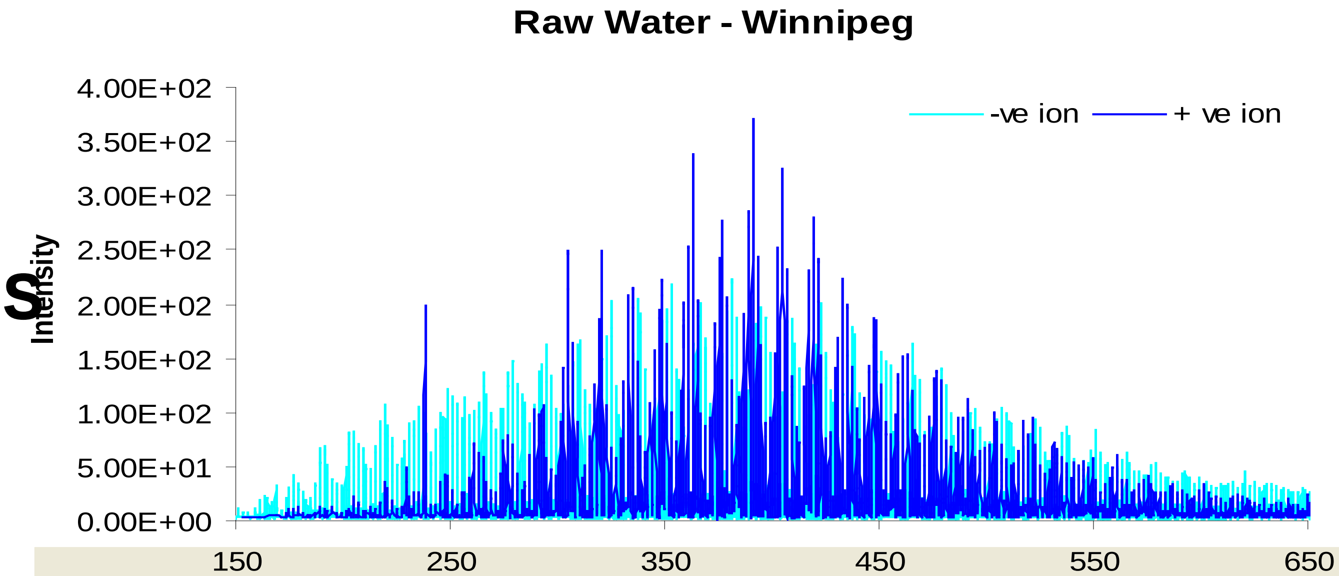


Ratio climbs over very short distances and then declines

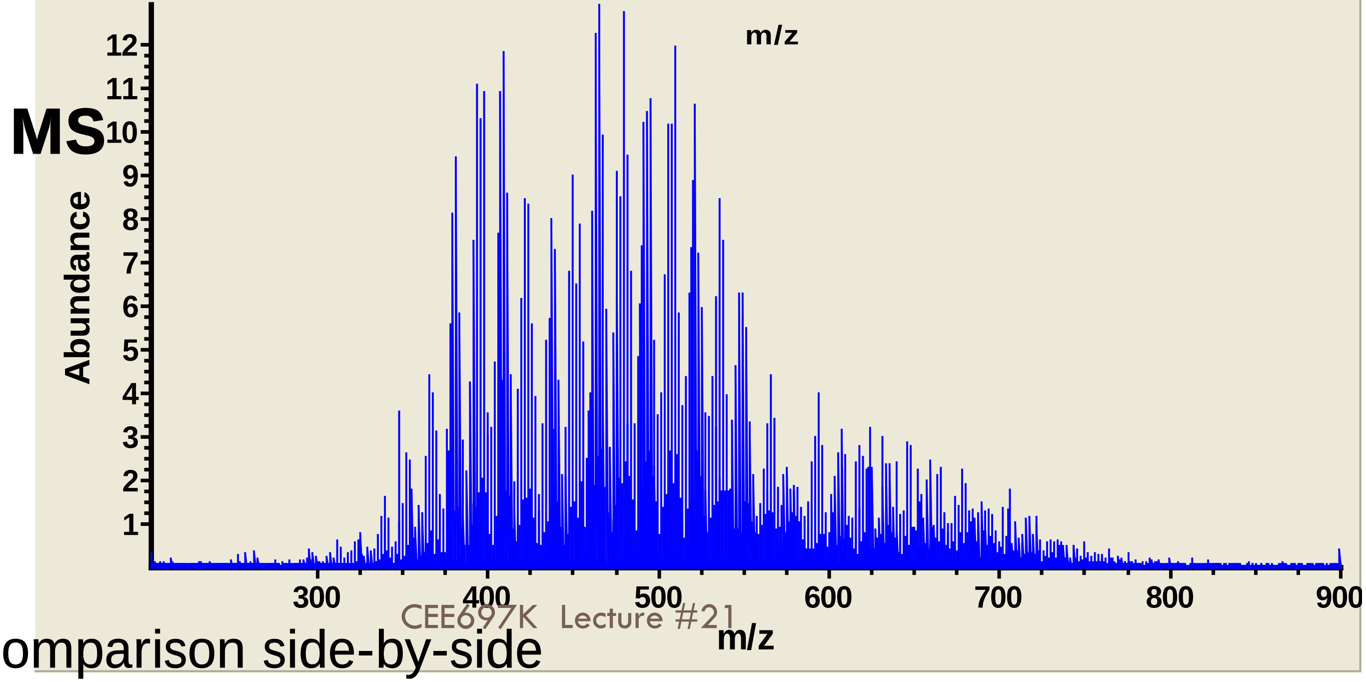
The Future: Higher MW DBPs

- NOM research
  - ESI with Ultra High-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
- Benefits
  - Unambiguous molecular formulae

ESI-TOF MS

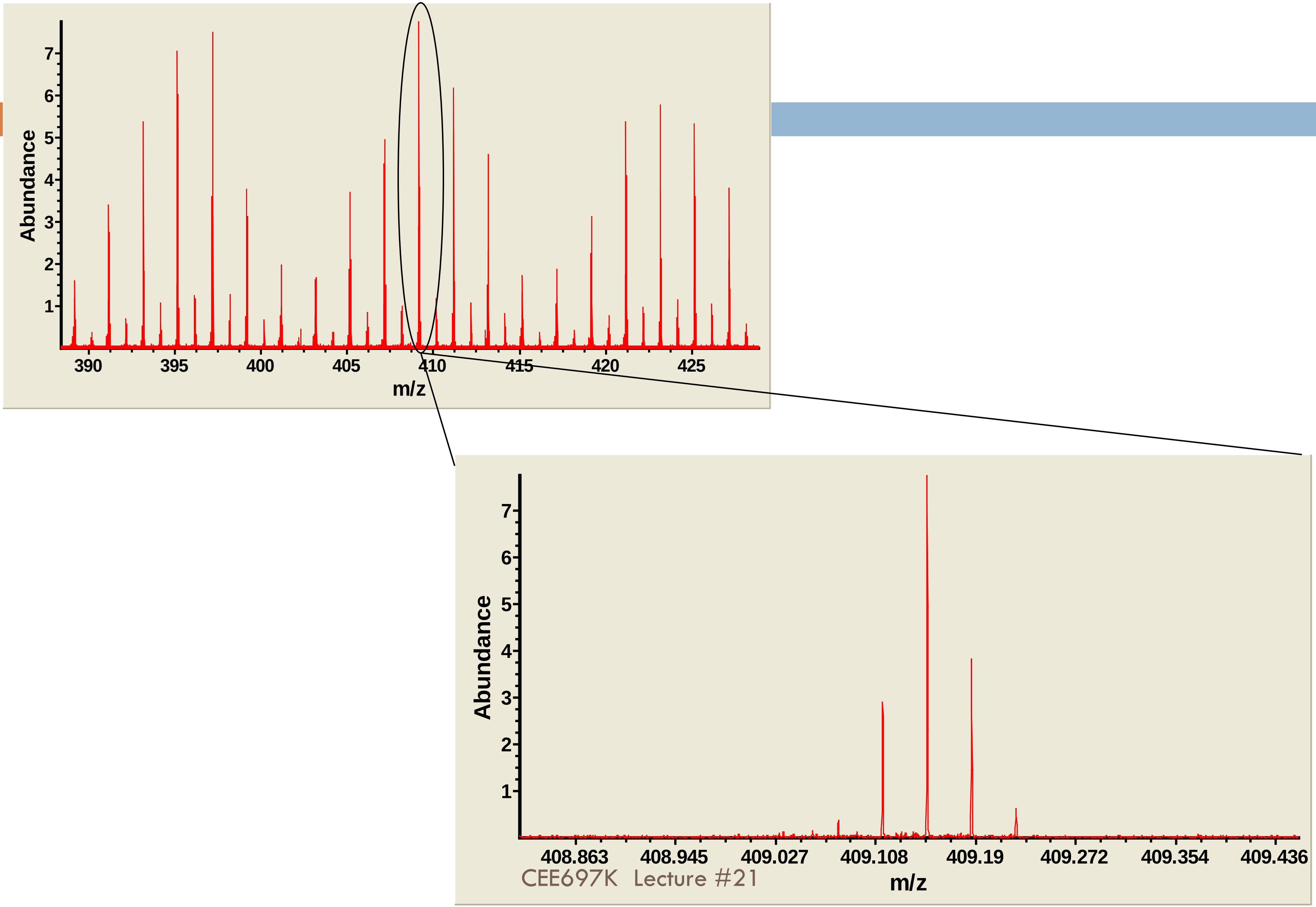


ESI-FTICR MS



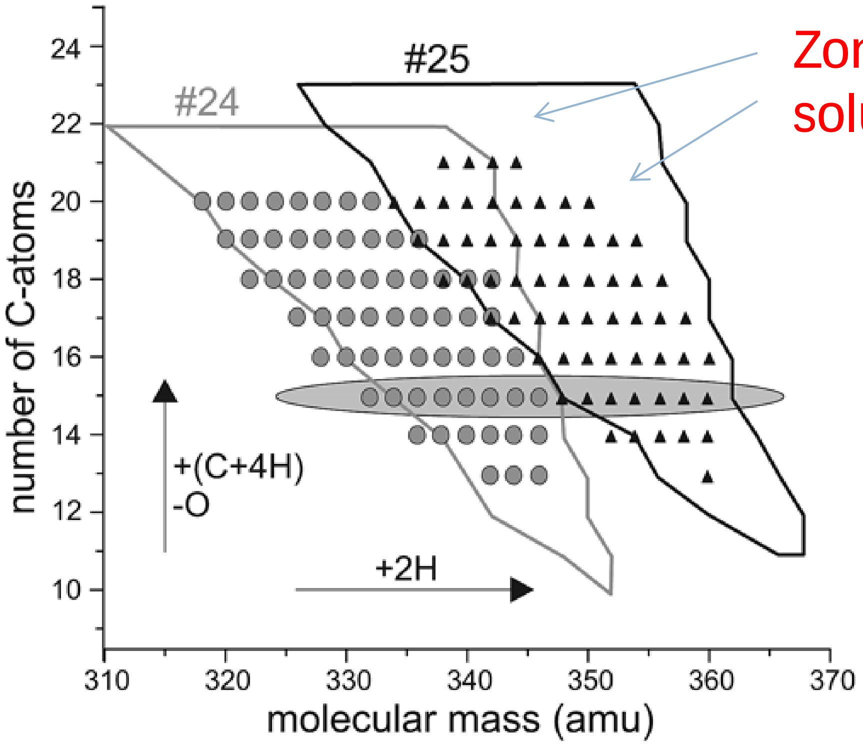
Same: comparison side-by-side

Chlorinated Water + Br Winnipeg



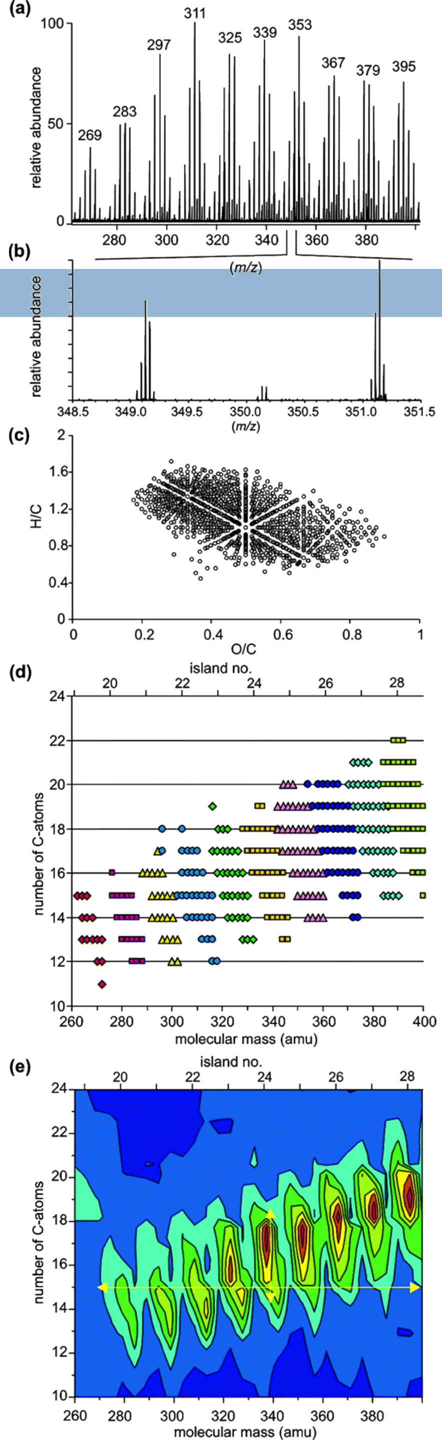
Ultra-high resolution MS

Reemtsma et al., 2006 [ES&T: 40:19:5839]



Zone of low solubility

Area of predicted fulvic acid molecules in a C- vs molecular mass diagram for the mass range *m*/*z* 310-370 (marked by the lines) and fulvic acid molecules detected by SEC-FTICR-MS in the river isolate (dots (island no. 24) and triangles (island no. 25)).



The dilemma of NOM

- How to model reaction kinetics in such a complex mixture?
  - Kinetic spectrum?
  - Fictive components?
  - Fully empirical?

Lee & Von Gunten, 2010

- Comparative study of 5 oxidants

  Lee, Y. and U. von Gunten (2010). "Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate(VI), and ozone) and non-selective oxidants (hydroxyl radical)." Water Research 44(2): 555-566.

- Looked at rates of removal for micropollutants for each
- Compared to bulk oxidant demand

Rate constants vs pH

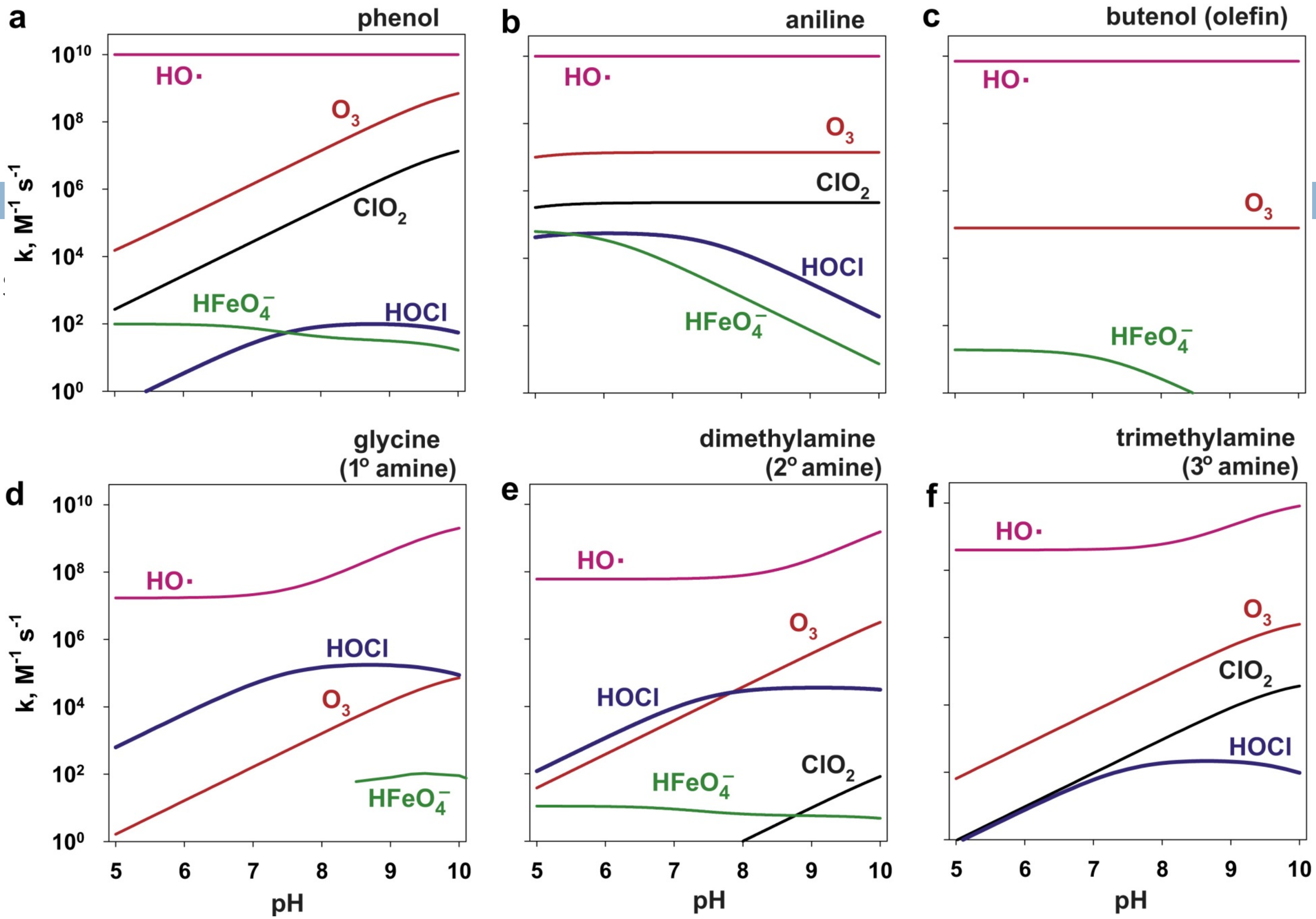


Fig. 1. pH dependent second-order rate constants (*k*) for the reaction of the oxidants, chlorine (HOCl), chlorine dioxide (ClO_2), ferrate^{VI} ($HFeO_4^-$), hydroxyl radicals (HO), and ozone (O_3)

Lee, Y. and U. von Gunten (2010). Water Research 44(2): 555-566.

Oxidant Residuals

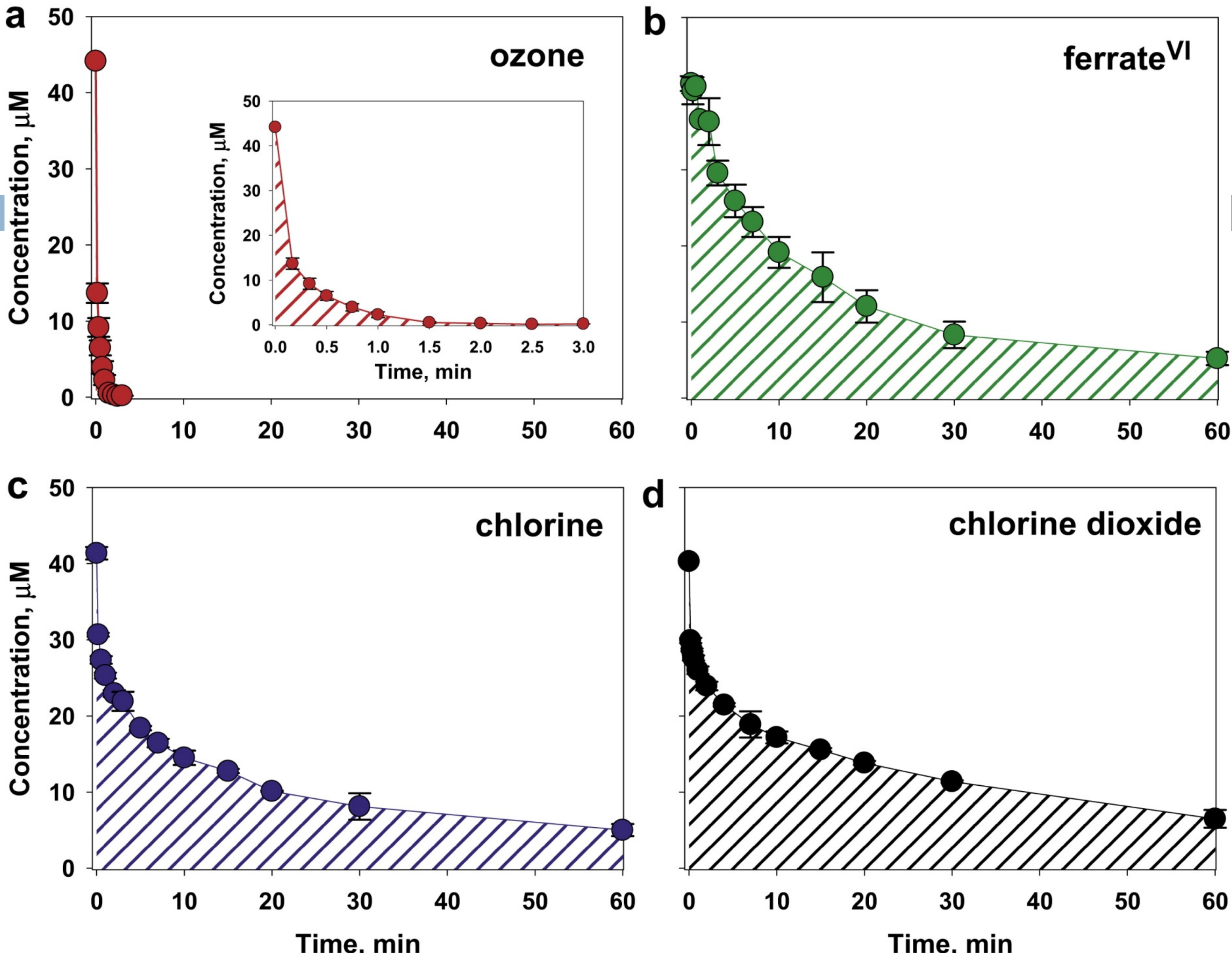


Fig. 2. Consumption kinetics of the selective oxidants, (a) ozone, (b) ferrate^{VI}, (c) chlorine, and (d) chlorine dioxide, in a **secondary wastewater effluent** (RDWW) at pH 8. Symbols represent measured data and lines connect each data point to show the trend.

Lee, Y. and U. von Gunten (2010). Water Research 44(2): 555-566.

Lee, Y. and U. von Gunten (2010). Water Research 44(2): 555-566.

Micropollutant Destruction

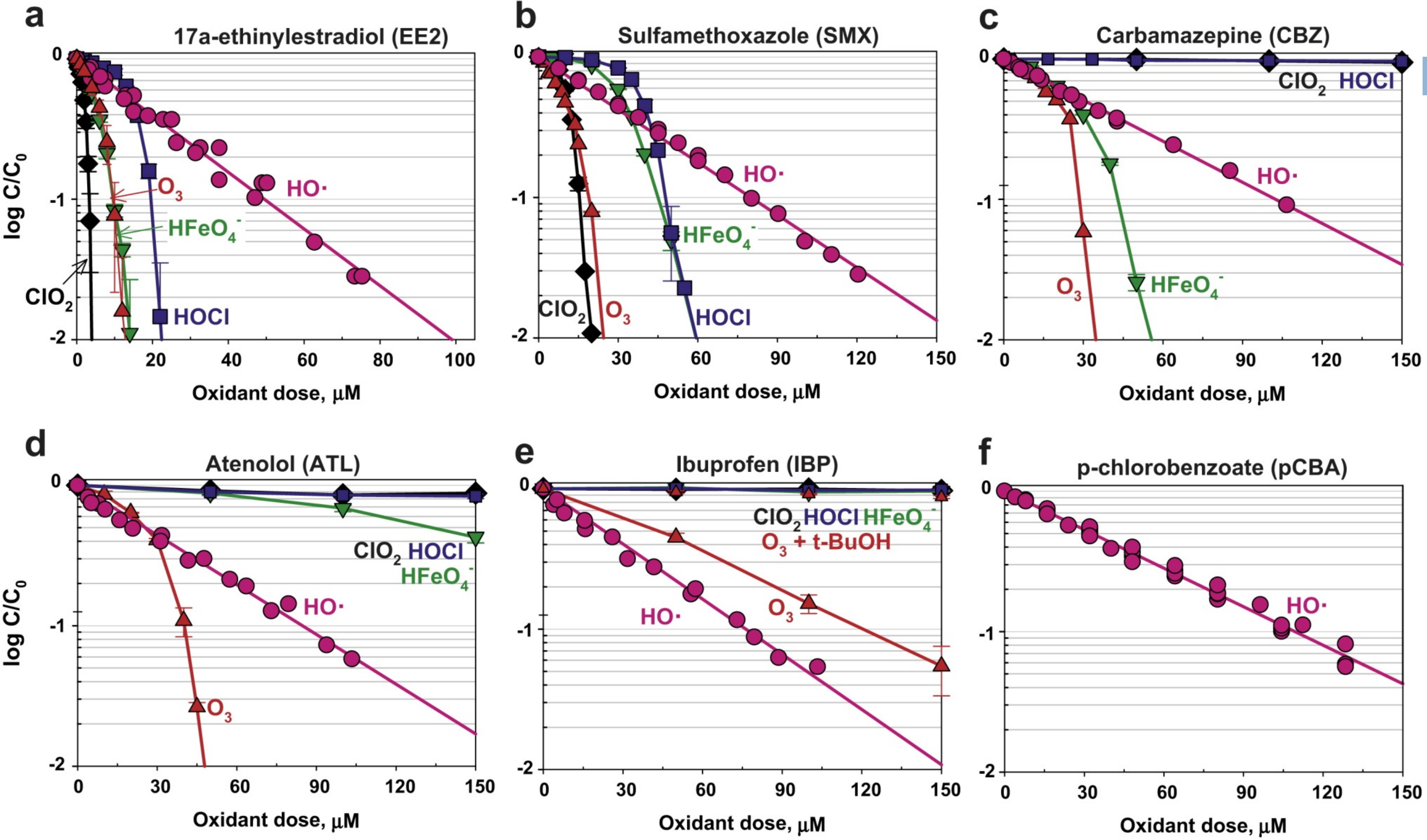


Fig. 3. Logarithm of the residual concentrations (log(c/c_0)) of selected micropollutants as a function of oxidant doses in a secondary wastewater effluent (RDWW) at pH 8: (a) EE2, (b) SMX, (c) CBZ, (d) ATL, and (e) IBP. Symbols represent measured data and lines connect each data point to show the trend. The lines for hydroxyl radicals represent the linear regression of data. For the selective oxidants, the reaction time of 1 h was given to simulate realistic treatment conditions.

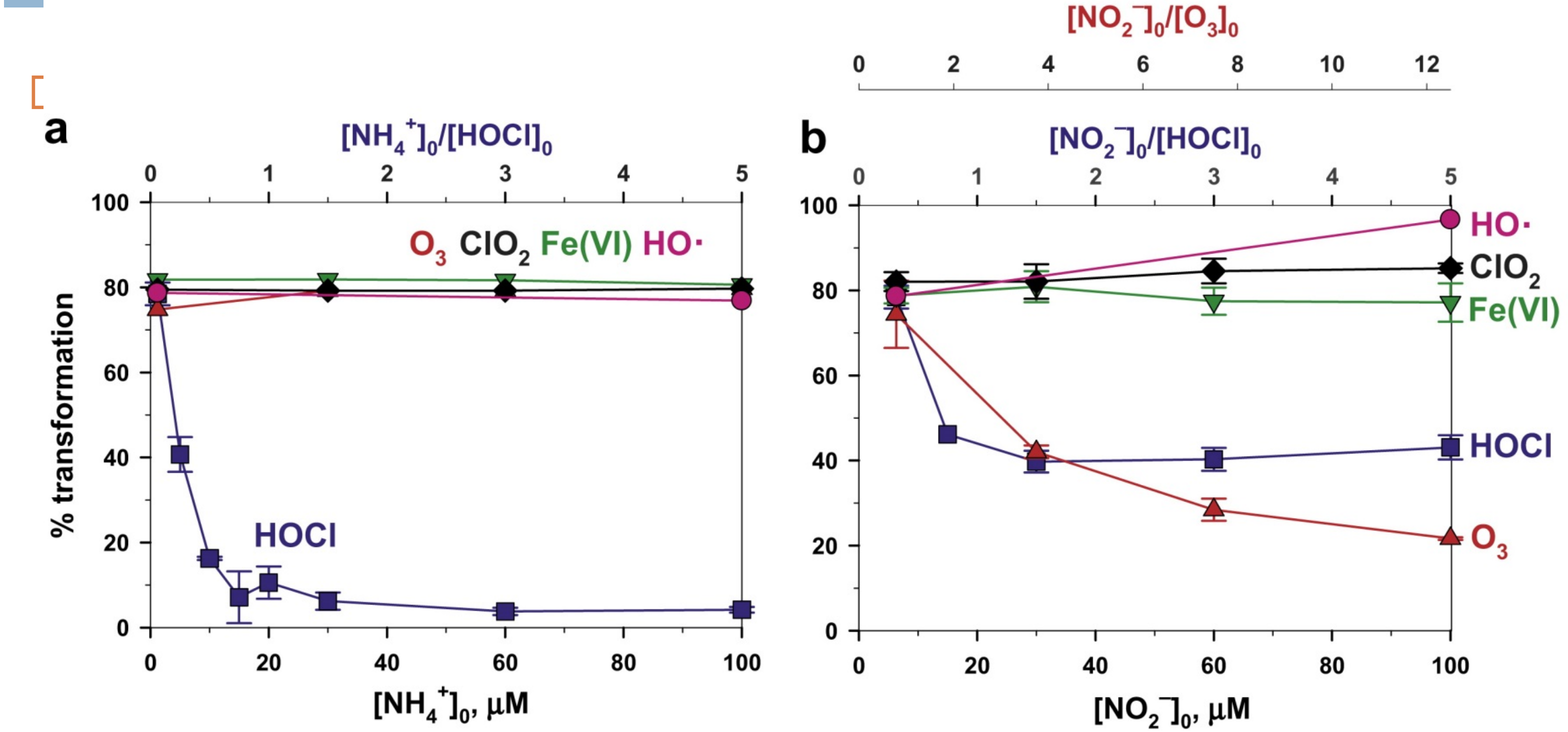
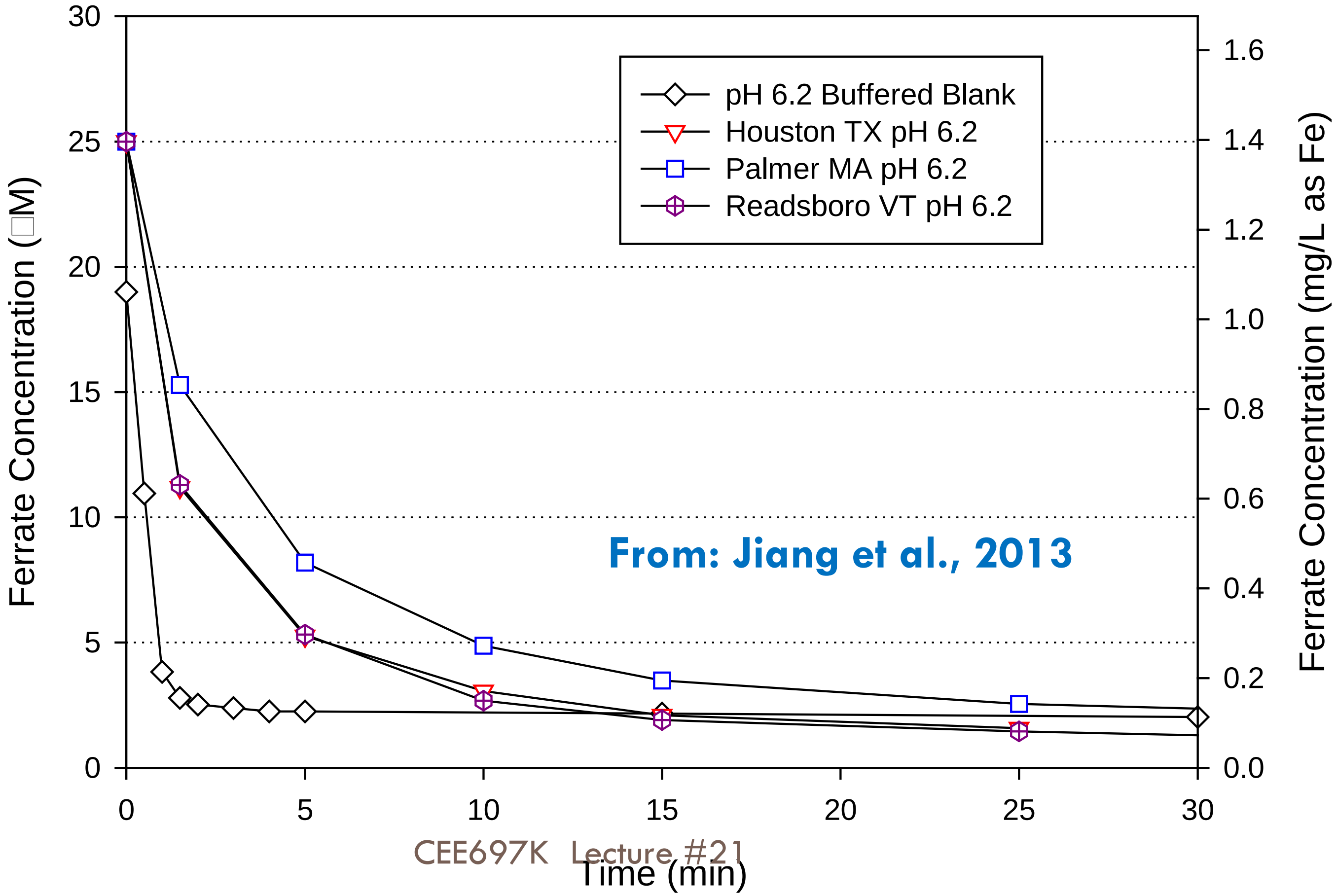


Fig. 4. Effect of (a) ammonia (NH_4^+) and (b) nitrite (NO_2^-) on the transformations of EE2 during treatment of a secondary wastewater effluent (RDWW) by different oxidants at pH 8. Preliminary experiments were conducted to determine the oxidant dose for each oxidant to achieve a 80% transformation of EE2 in RDWW without additionally spiked ammonia and nitrite. They were 20 μM for chlorine, 3 μM for chlorine dioxide, 8 μM for ozone, 8 μM for ferrate^{VI}, and 37 μM for hydroxyl radicals. Symbols represent measured data and lines connect each data point to show the trend.

Lee, Y. and U. von Gunten (2010). Water Research 44(2): 555-566.

Ferrate reaction with surface waters

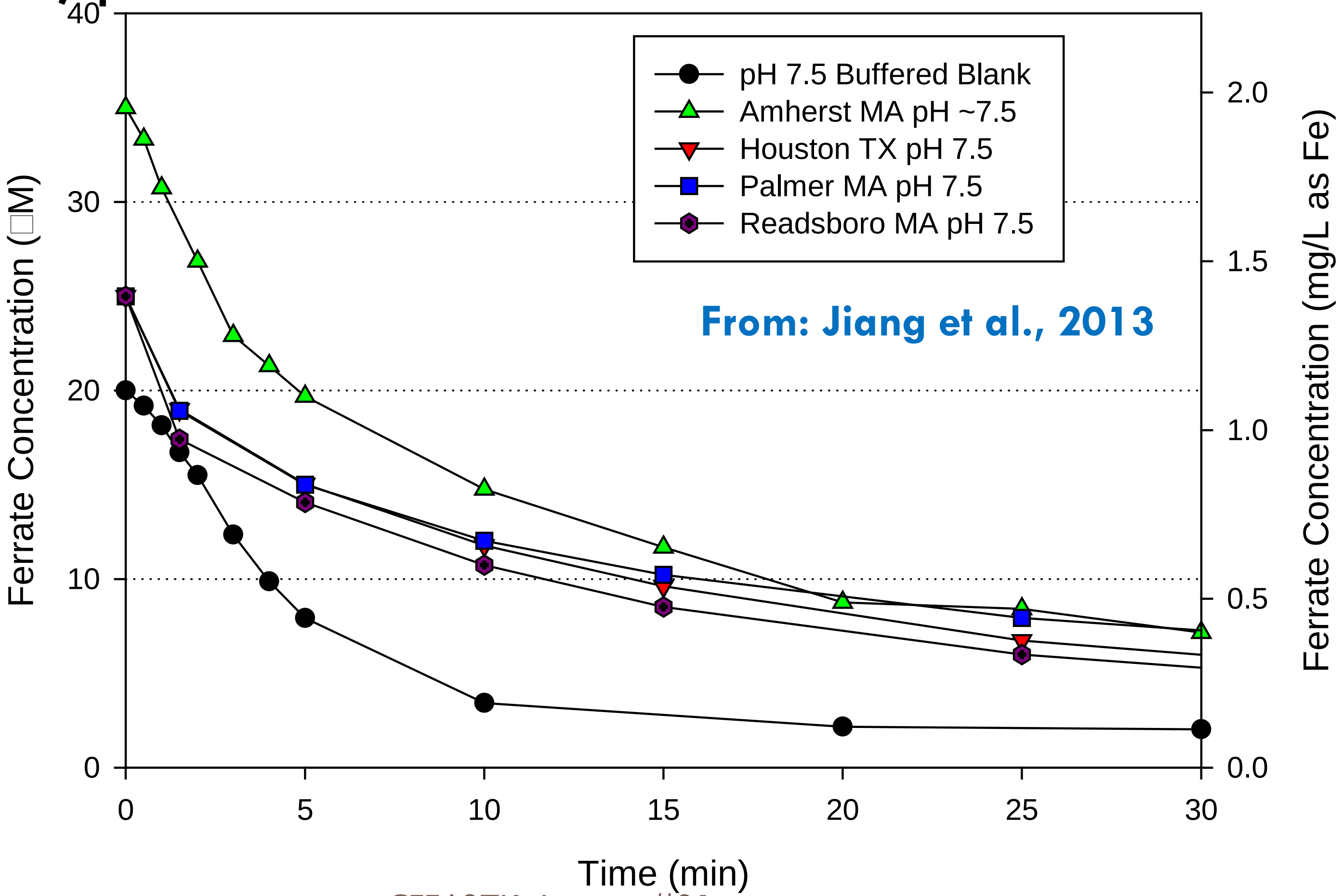
- 25 µM ferrate dose, pH 6.2



From: Jiang et al., 2013

Low Dose, High pH

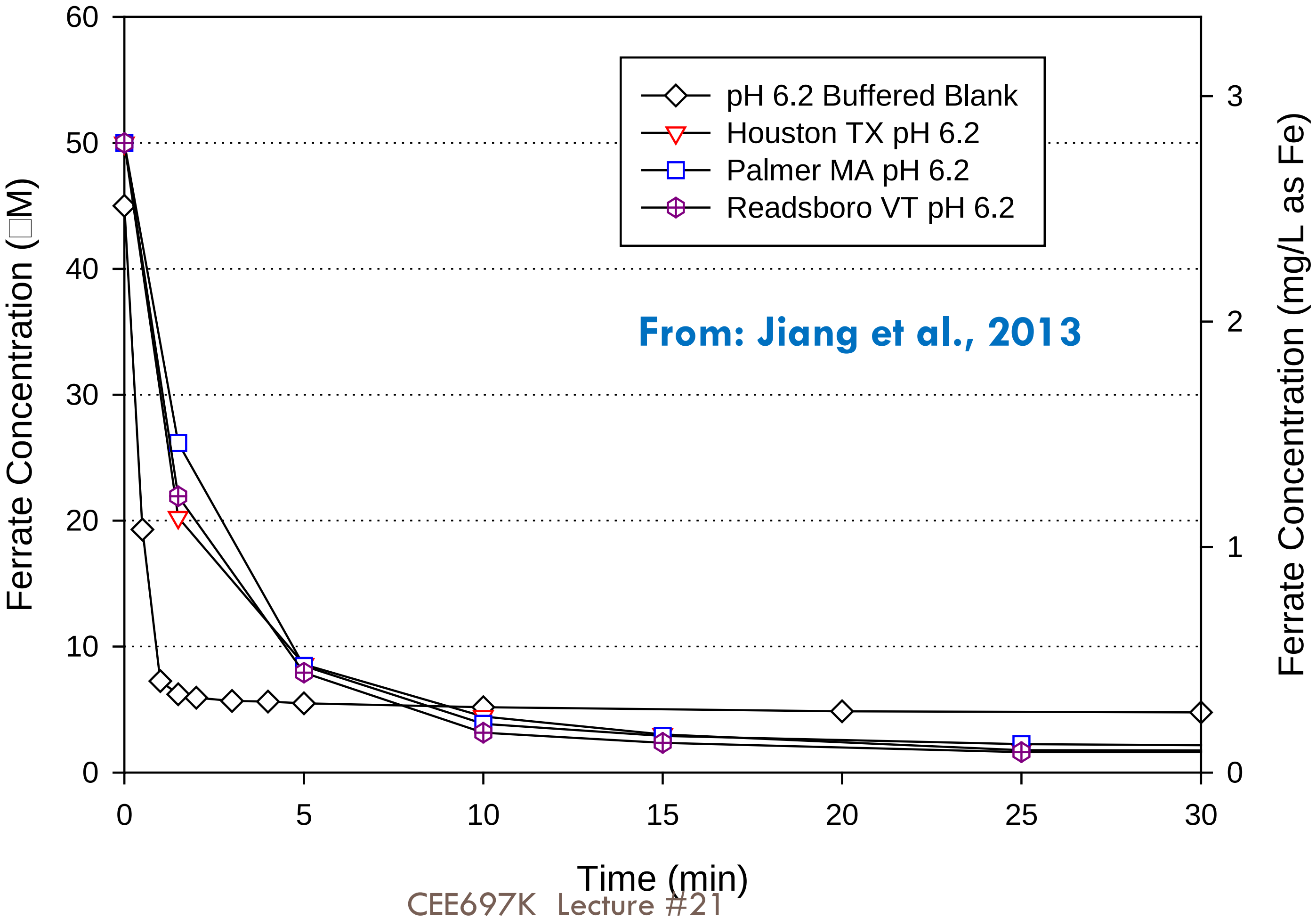
- 25 µM, pH 7.5



From: Jiang et al., 2013

High Dose, Low pH

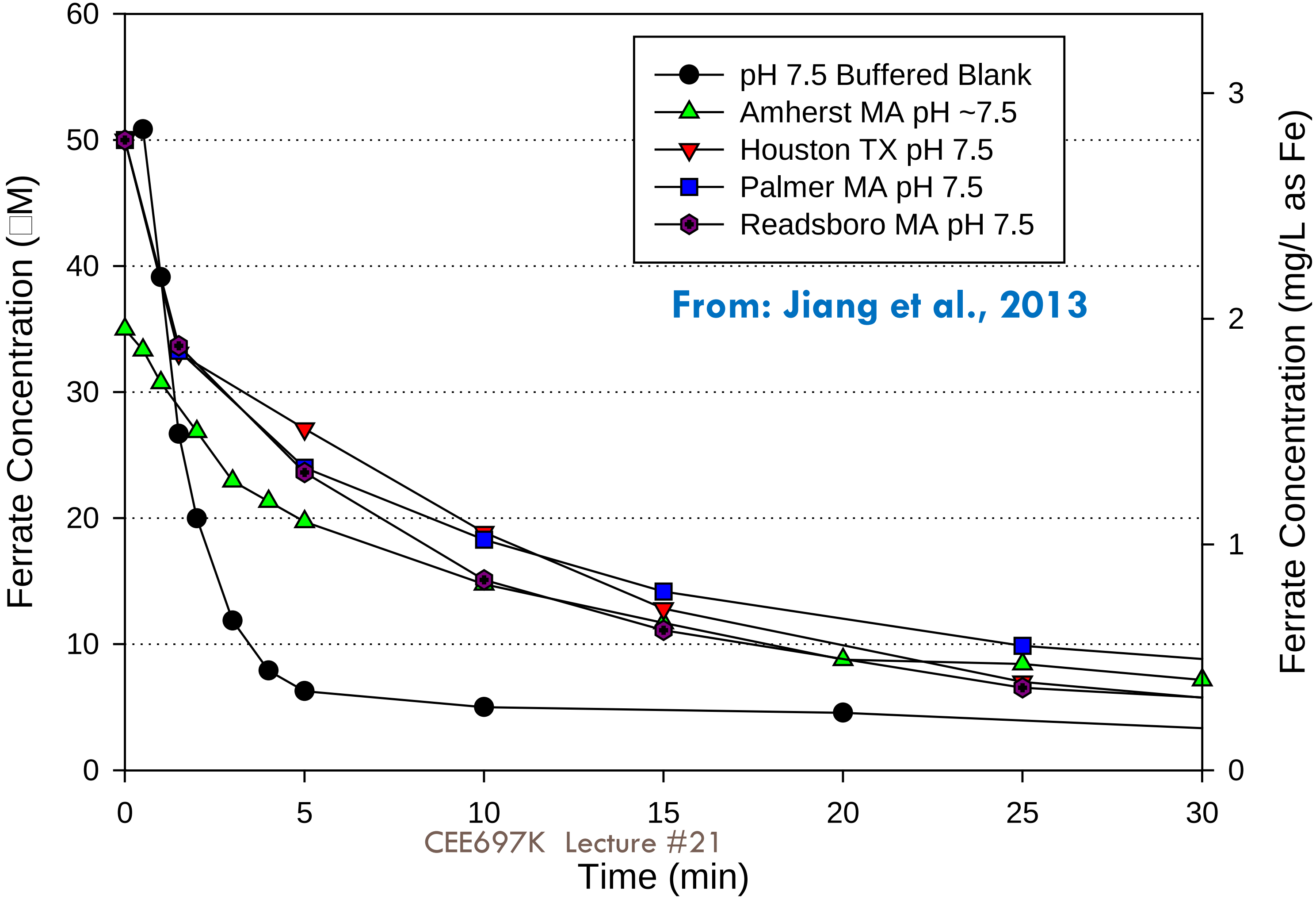
- 50 µM, pH 6.2



From: Jiang et al., 2013

High Dose, High pH

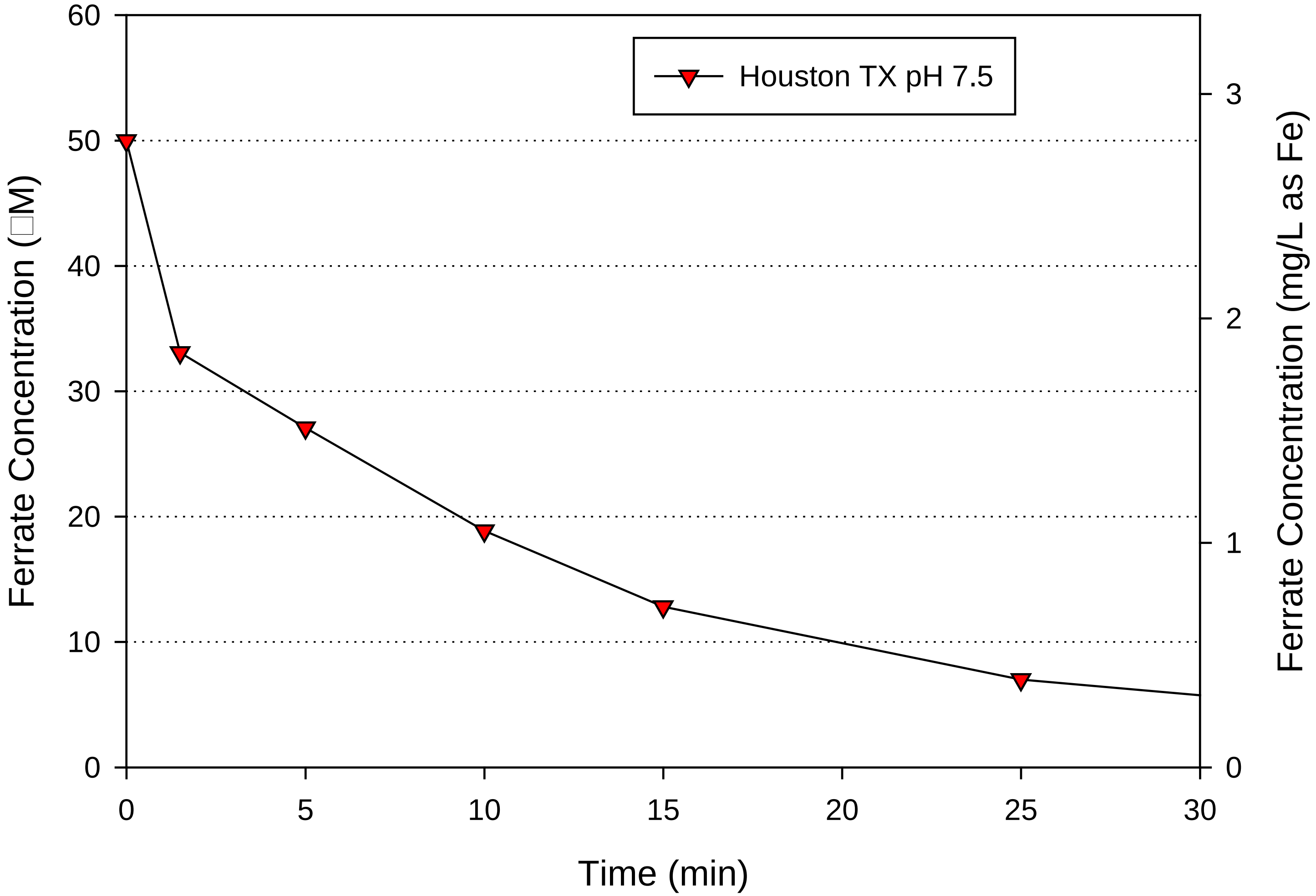
- 50 μM, pH 7.5



From: Jiang et al., 2013

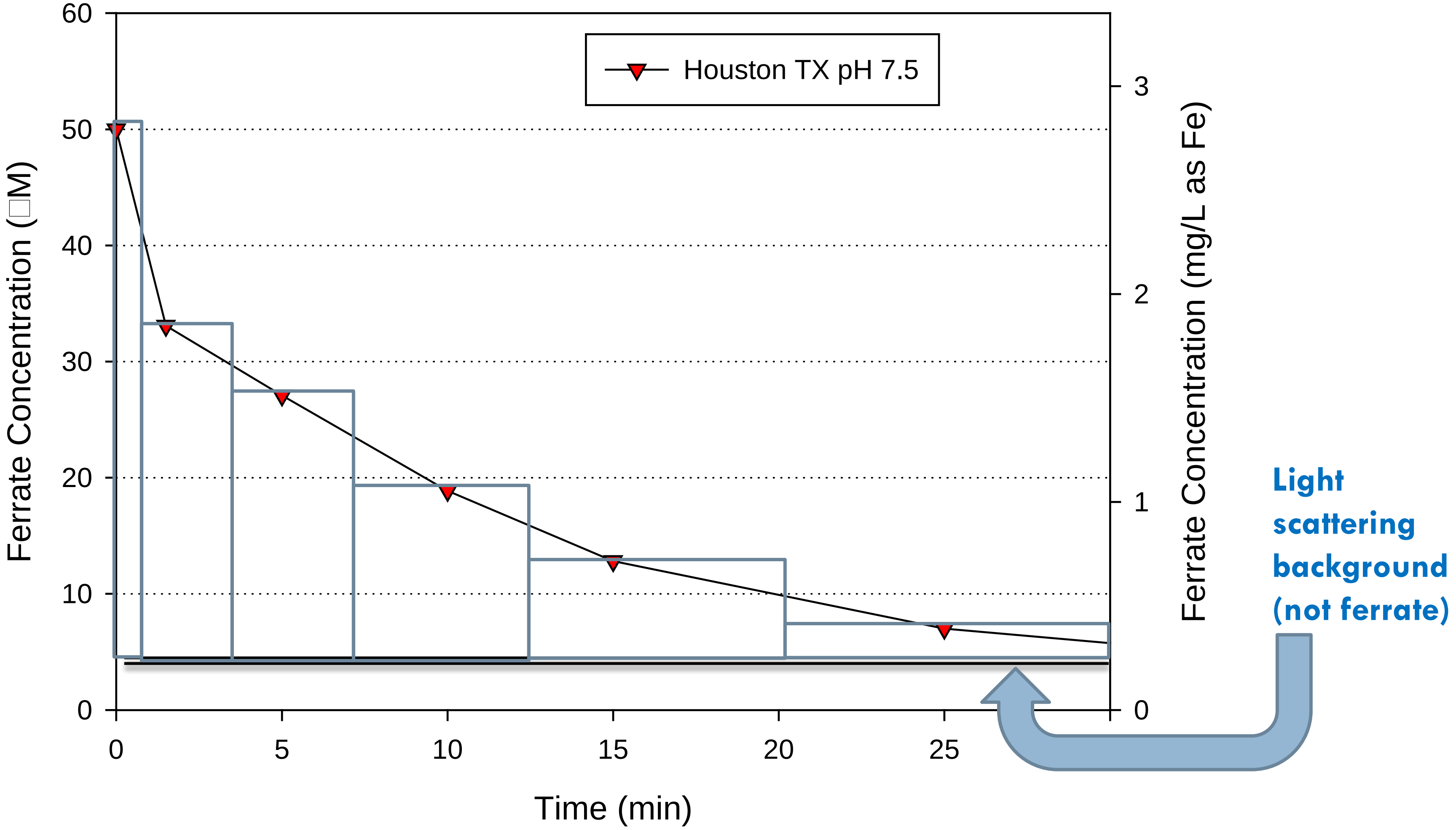
Houston Data Isolated

- More data improves accuracy



Integrate curve to get CT vs time

- Simple “rectangle” method



Light scattering background (not ferrate)

Model for pollutant oxidation

- Simple 2nd order kinetics
  - Pollutant (P) reacts with an oxidant (O)

$$\frac{dP}{dt} = -k[P][O] \qquad \frac{dP}{[P]} = -k[O]\mathrm{dt}$$

- Integrate but keep [O] time variable

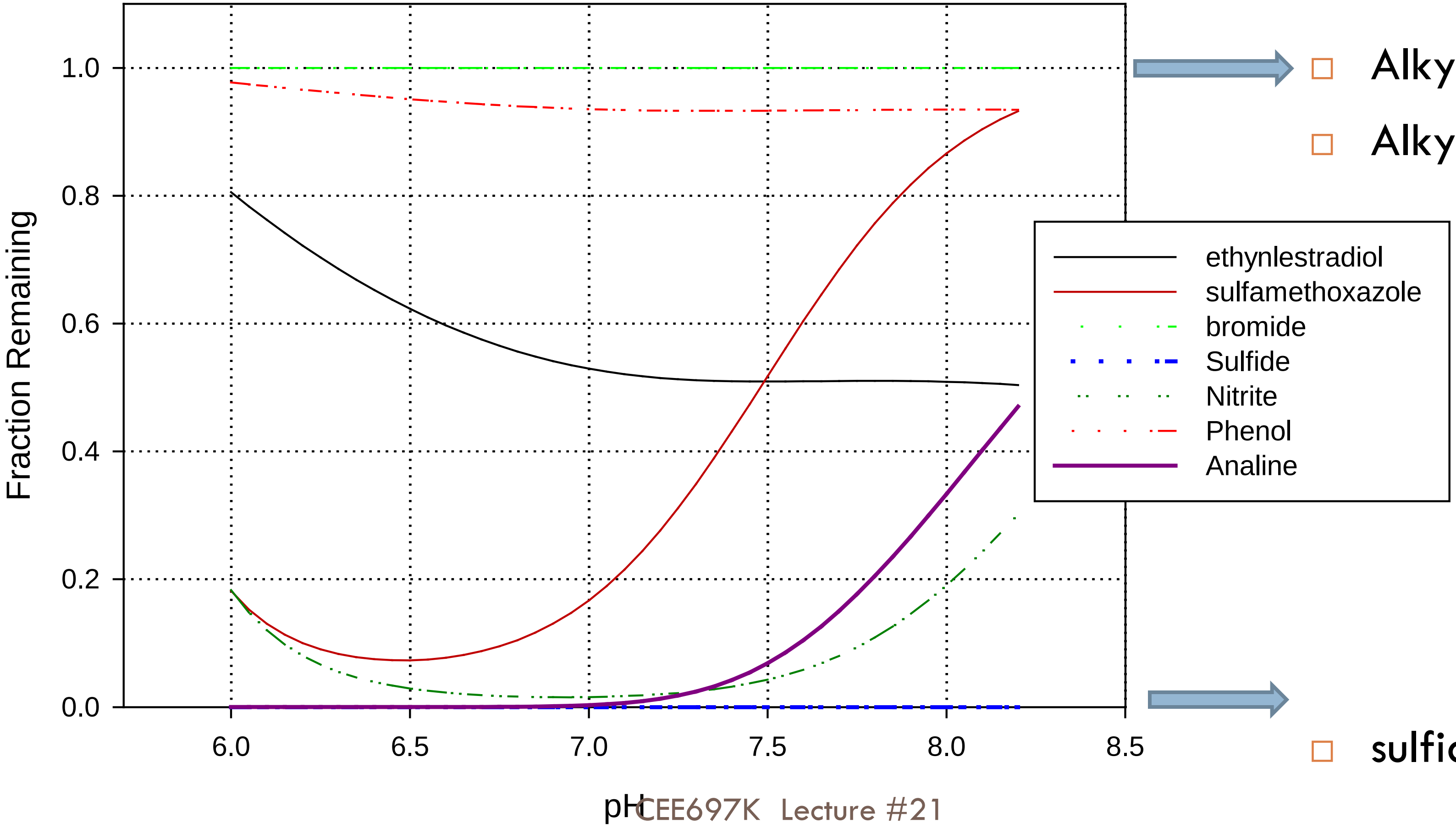
$$ln[P]\Big]_{P_o}^{P_t} = -k\int_0^t [O]dt \qquad ln[P_t] - ln[P_0] \;= -k\int_0^t [O]dt$$

- And you end up with an expression in terms of CT

$$P_t = P_0 e^{-k\underbrace{\int_0^t [O]dt}} \qquad P_t = P_0 e^{-k(CT)}$$

Kinetic Analysis, high dose

- 50 μM dose, Houston Water

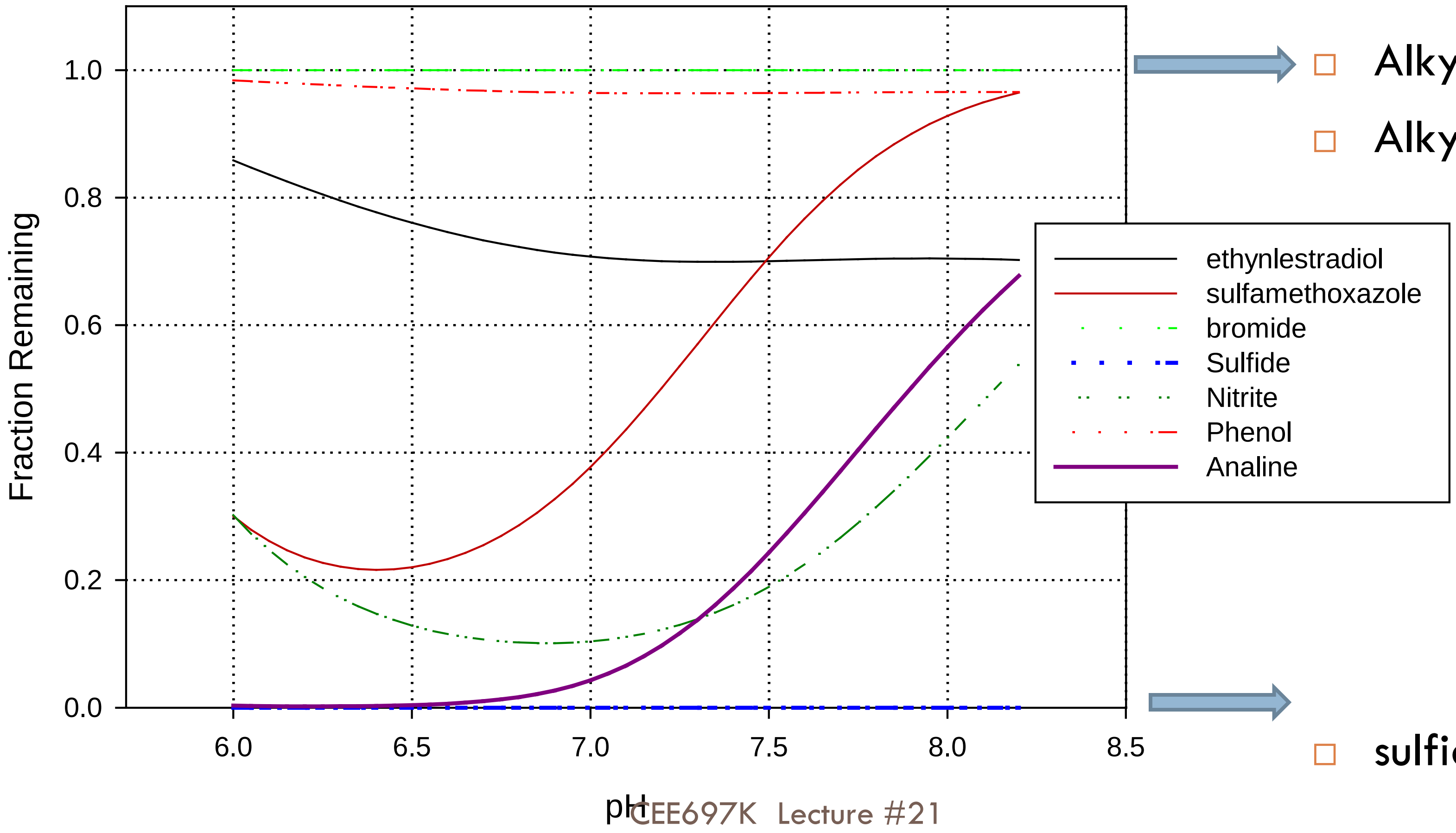


- Alkyl alcohols
- Alkyl amines

- sulfides

Kinetic Analysis, low dose

- 25 μM dose, Houston Water

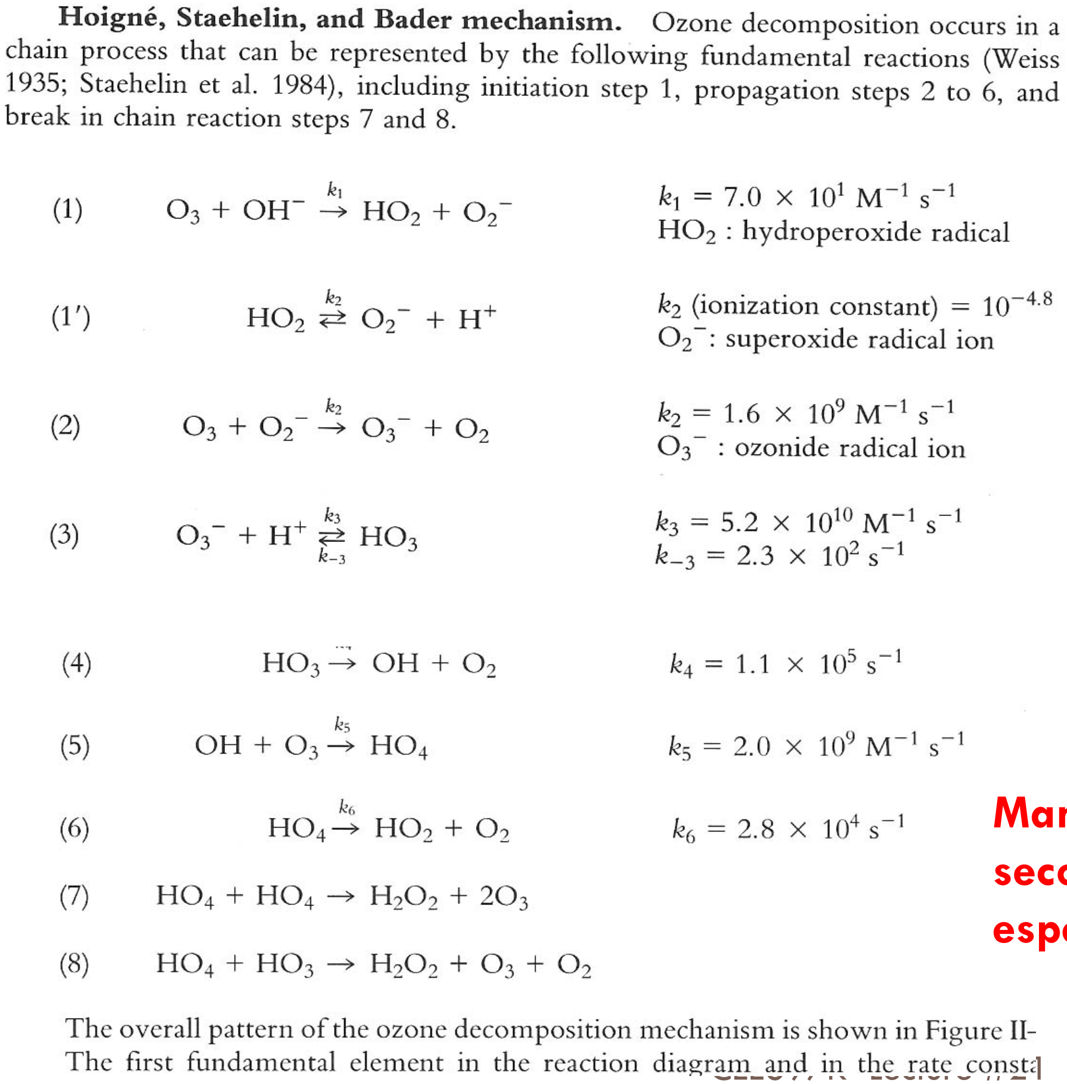


- Alkyl alcohols
- Alkyl amines

- sulfides

The “problems” with ozone

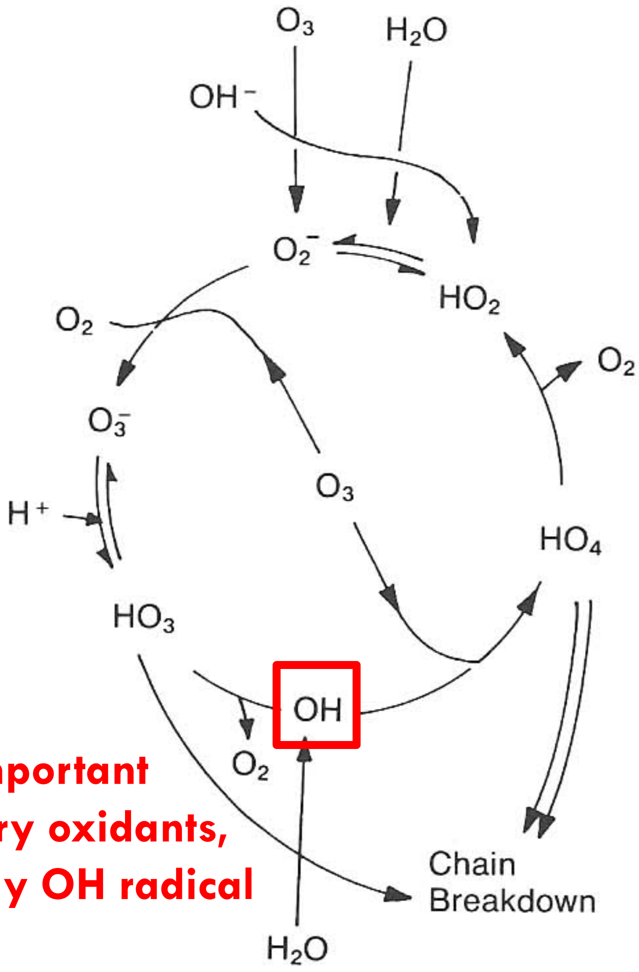
Ozone decomposition in real waters does not match predictions



Hoigné, Staehelin, and Bader mechanism. Ozone decomposition occurs in a chain process that can be represented by the following fundamental reactions (Weiss 1935; Staehelin et al. 1984), including initiation step 1, propagation steps 2 to 6, and break in chain reaction steps 7 and 8.

(1)	$O_3 + OH^- \xrightarrow{k_1} HO_2 + O_2^-$	$k_1 = 7.0 \times 10^1\ M^{-1}\ s^{-1}$ HO_2 : hydroperoxide radical
(1′)	$HO_2 \overset{k_2}{\rightleftarrows} O_2^- + H^+$	k_2 (ionization constant) $= 10^{-4.8}$ O_2^-: superoxide radical ion
(2)	$O_3 + O_2^- \xrightarrow{k_2} O_3^- + O_2$	$k_2 = 1.6 \times 10^9\ M^{-1}\ s^{-1}$ O_3^- : ozonide radical ion
(3)	$O_3^- + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} HO_3$	$k_3 = 5.2 \times 10^{10}\ M^{-1}\ s^{-1}$ $k_{-3} = 2.3 \times 10^2\ s^{-1}$
(4)	$HO_3 \rightarrow OH + O_2$	$k_4 = 1.1 \times 10^5\ s^{-1}$
(5)	$OH + O_3 \xrightarrow{k_5} HO_4$	$k_5 = 2.0 \times 10^9\ M^{-1}\ s^{-1}$
(6)	$HO_4 \xrightarrow{k_6} HO_2 + O_2$	$k_6 = 2.8 \times 10^4\ s^{-1}$
(7)	$HO_4 + HO_4 \rightarrow H_2O_2 + 2O_3$	
(8)	$HO_4 + HO_3 \rightarrow H_2O_2 + O_3 + O_2$	

The overall pattern of the ozone decomposition mechanism is shown in Figure II-
The first fundamental element in the reaction diagram and in the rate consta



Many important secondary oxidants, especially OH radical

Mechanistic model is “off”

- Initiation reaction rate constant must be “adjusted” to match actual data

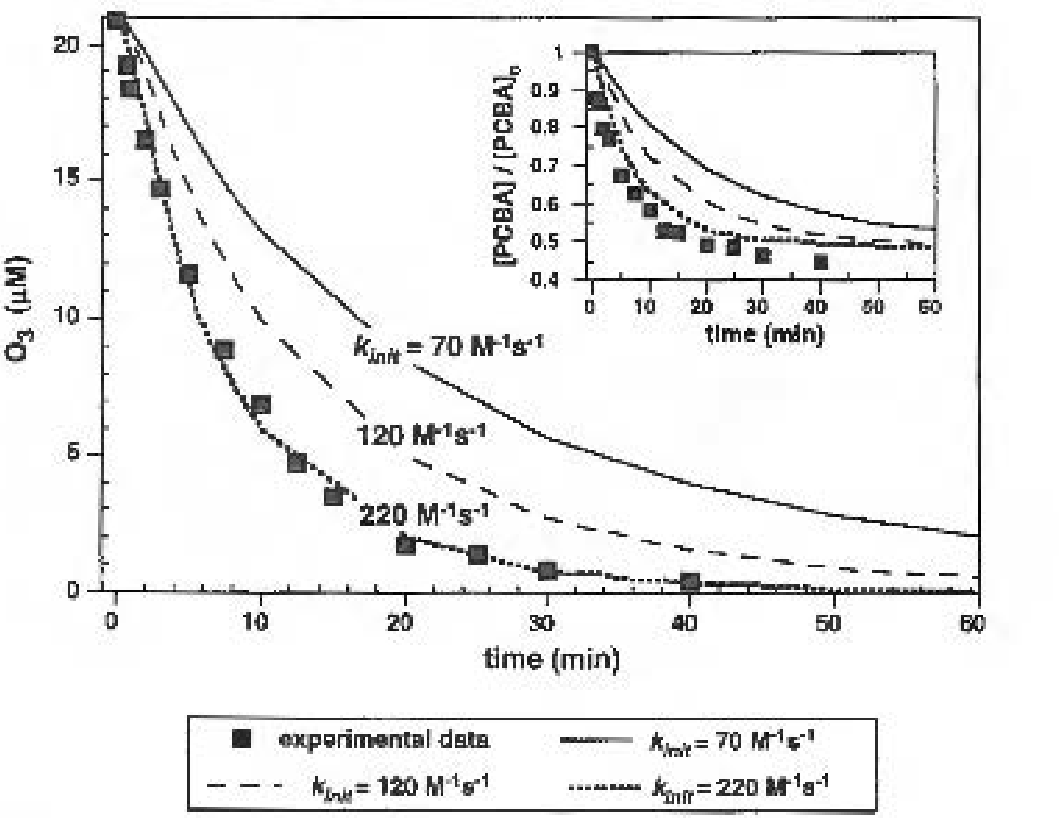
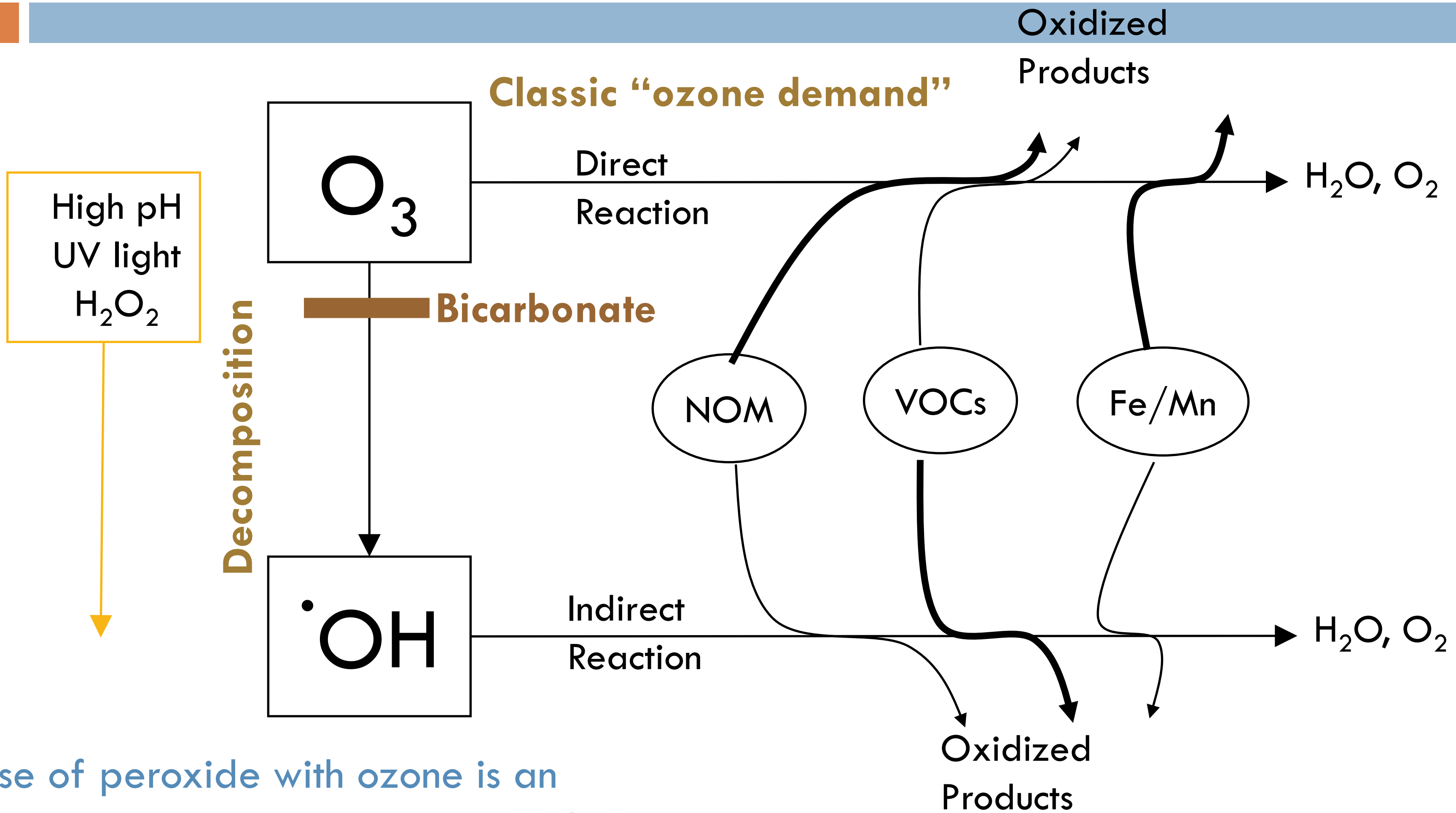


Figure 3a. Ozone decomposition as a function of time for $[O_3]_0 = 20.1$ µM, $[MeOH]_0 = 70$ µM, and $[acetate]_0 = 350$ µM in a 1 mM phosphate buffer at pH 8.0 and 23°C. Square symbols represent experimental data, and line-plots represent the ACUCHEM model results for the kinetic model described in the text. Inset: Data (symbols) and ACUCHEM simulations (line-plots) for pCBA loss.

Elovitz, M. S. and U. Von Gunten (1999). "Hydroxyl Radical Ozone Ratios During Ozonation Processes. I-the R-Ct Concept." Ozone-Science & Engineering 21(3): 239-260.

A simpler view: Direct & Indirect Pathways



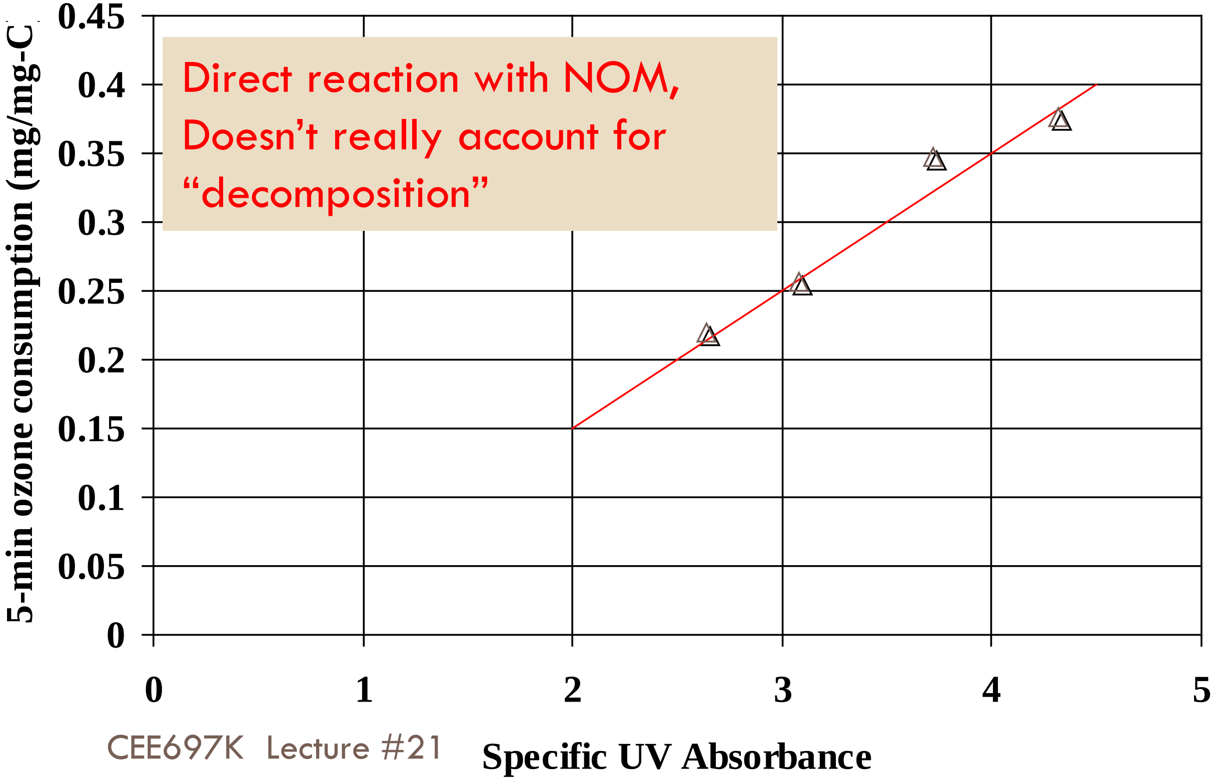
Use of peroxide with ozone is an "advanced oxidation process" (AOP)

Natural waters cause ozone decomposition to varying degrees without any added initiators

Ozone Loss: focus on NOM

- Organic Demand in colored waters
  - – Empirical stoichiometric approach

» Ozone loss in first 5 minutes
- fulvic acids
- data from Legube et al., 1989



Direct reaction with NOM, Doesn’t really account for “decomposition”

Ozone loss: focus on decomposition

- Incorporating Inorganic Reactions: Semi-empirical kinetic approach
  - First-order decay in solution

$$\frac{d[O_3]}{dt} = -\omega[O_3] \quad \Longrightarrow \quad C_{O_3} = C_{O_3,initial}\, e^{-\omega t}$$

  - Specific ozone loss rate (w) in s $^{-1}$
    - Yurteri & Gurol (1988)

$$Log\,\omega = -3.56 + 0.66\,pH + 0.61 \log TOC - 0.42 \log Alk$$

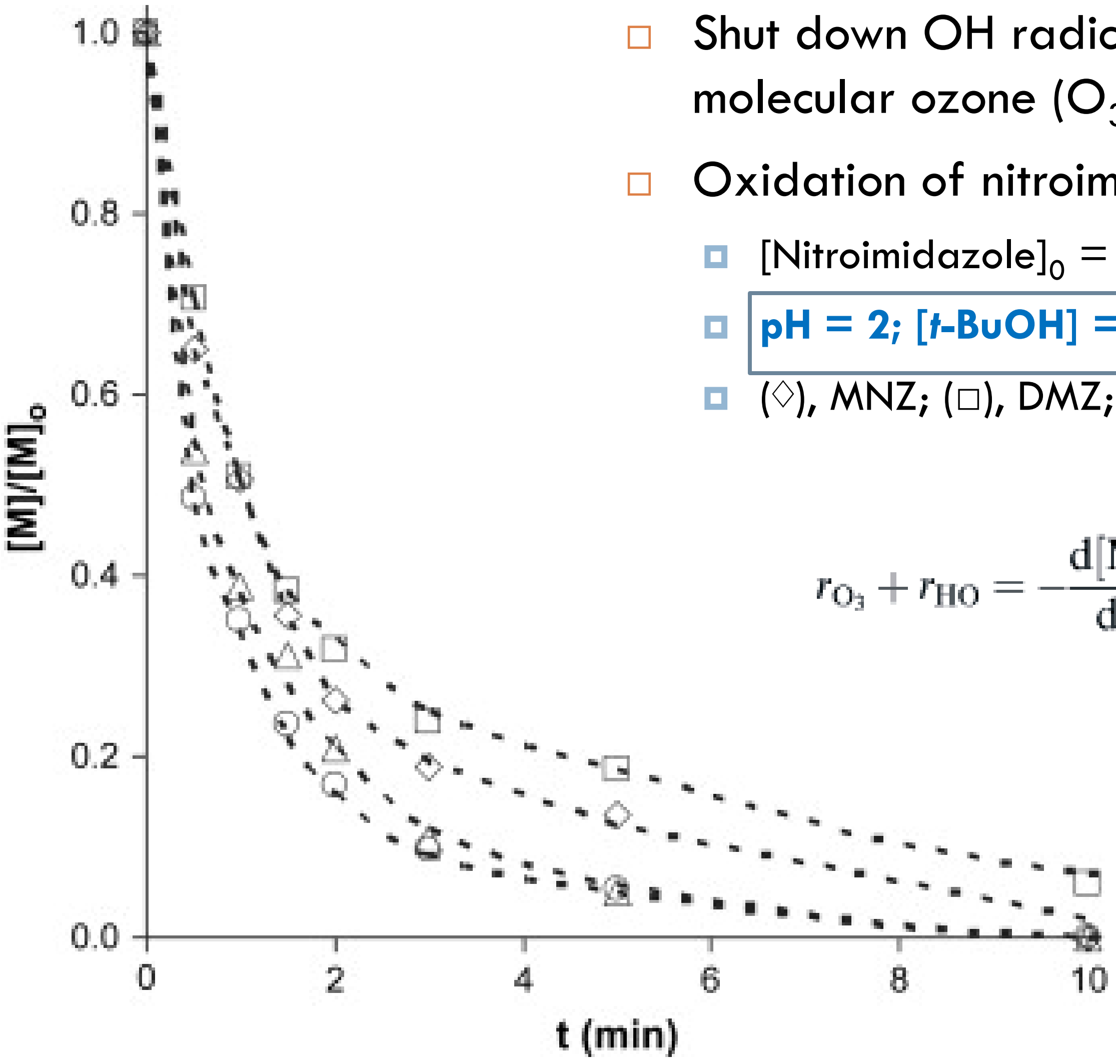
    - Orta de Velasquez et al. (1994)

$$Log\,\omega = -3.93 + 0.24\,pH + 0.75 \log Abs_{254} + 1.08 \log TOC - 0.19 \log Alk$$

Takes inorganic matrix into account, and allows for variable contact times, but treats all DOC as the same

Ozonation of trace organics: Direct Rcn

- Shut down OH radical formation to isolate molecular ozone (O_3) rate.
- Oxidation of nitroimidazoles during ozonation.
  - $[\text{Nitroimidazole}]_0$ = 10 mg/L., T = 298 K.
  - **pH = 2; [*t*-BuOH] = 0.1 M**
  - (◇), MNZ; (□), DMZ; (△), TNZ; (○), RNZ.

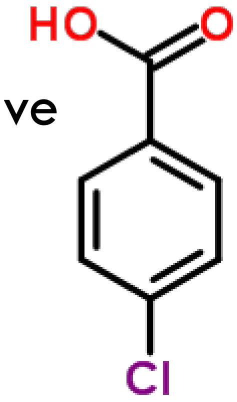


$$r_{O_3} + r_{HO} = -\frac{d[M]}{dt} = k_{O_3}[M][O_3] + k_{HO}[M][HO\bullet]$$

Sanchez-Polo, M., J. Rivera-Utrilla, et al. (2008). "Removal of pharmaceutical compounds, nitroimidazoles, from waters by using the ozone/carbon system." Water Research 42(15): 4163-4171.

Indirect Rcn: But we can't measure OH•

- If you can't measure them directly maybe you can do it indirectly
  - Use small amounts of a "probe compound"
    - Sacrificial reactant that is easy to measure and selective
  - Benzene (Hoigne & Bader, 1979) by GC
  - *p*-chlorobenzoic acid is now more common
    - Easy to measure by HPLC
    - $5\times10^{-9}\ M^{-1}s^{-1}$ with OH radical, but $\leq 0.15\ M^{-1}s^{-1}$ with O_3



Hoigne, J. and H. Bader (1979). "Ozonation of Water - Oxidation-Competition Values of Different Types of Waters Used in Switzerland." Ozone-Science & Engineering 1(4): 357-372.

Competitive kinetics with probe

- Pollutant (P) and probe compound (pCBA)

$$P_t = P_0 e^{-k_P(CT)}$$

$$ln\left(\frac{P_t}{P_0}\right) = -k_P(CT)$$

$$pCBA_t = pCBA_0 e^{-k_{pCBA}(CT)}$$

$$ln\left(\frac{pCBA_t}{pCBA_0}\right) = -k_{pCBA}(CT)$$

$$(CT) = -\frac{1}{k_{pCBA}} ln\left(\frac{pCBA_t}{pCBA_0}\right)$$

If you know k_p and want to estimate oxidation of P:

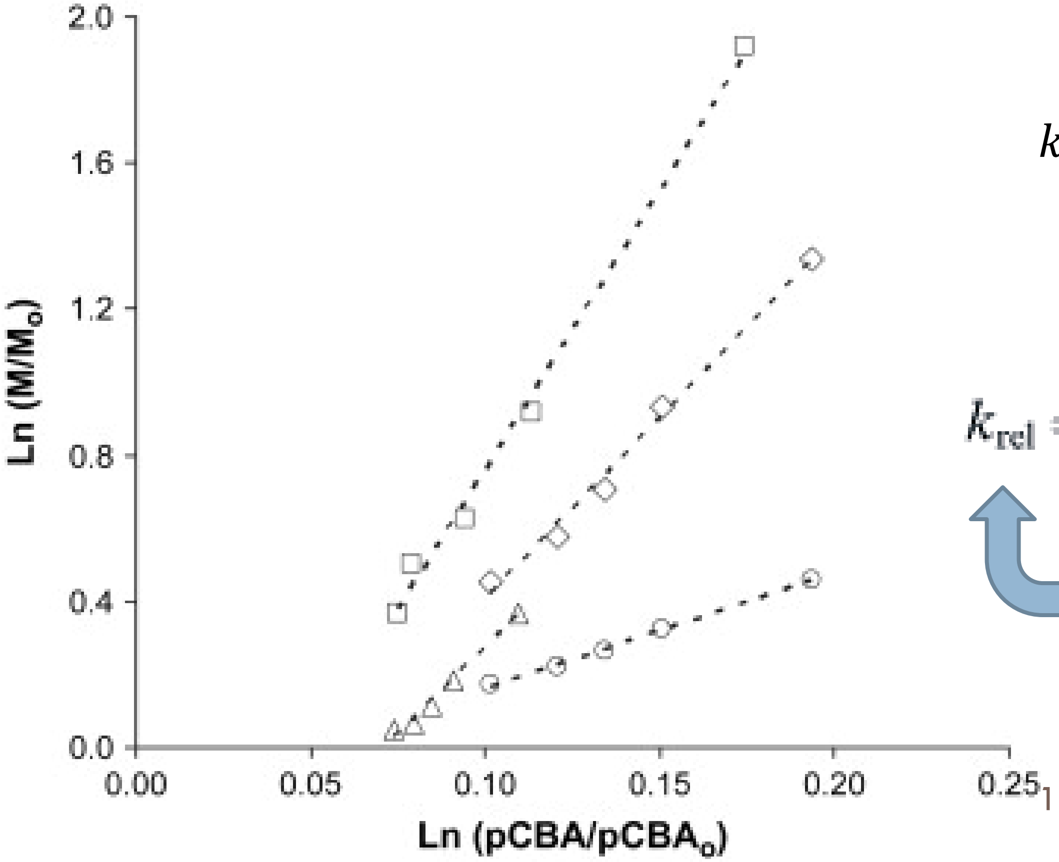
$$ln\left(\frac{P_t}{P_0}\right) = \frac{k_P}{k_{pCBA}} ln\left(\frac{pCBA_t}{pCBA_0}\right)$$

If you want to determine k_p from measurements of P:

$$k_P = k_{pCBA}\left\{ ln\left(\frac{P_t}{P_0}\right) \Big/ ln\left(\frac{pCBA_t}{pCBA_0}\right) \right\}$$

Determining OH• rate constants

- Fig. 3. Determination of OH radical reaction constant.
  - pH = 9; T = 298 K; [nitroimidazole]$_0$ = 7 × 10^{-5} M; [pCBA]$_0$ = 7.25 × 10^{-5} M. (◇), MNZ; (□), DMZ; (△), TNZ; (○), RNZ.



$$k_P = k_{pCBA}\left\{ ln\left(\frac{P_t}{P_0}\right) \Big/ ln\left(\frac{pCBA_t}{pCBA_0}\right)\right\}$$

$$k_{rel} = \left(\frac{k_M}{k_{pCBA}}\right) = \left(\frac{\ln\left(\frac{[M]_t}{[M]_0}\right)}{\ln\left(\frac{[pCBA]_t}{[pCBA]_0}\right)}\right)$$

Sanchez-Polo, M., J. Rivera-Utrilla, et al. (2008). "Removal of pharmaceutical compounds, nitroimidazoles, from waters by using the ozone/carbon system." Water Research 42(15): 4163-4171.

Can we simplify a bit?

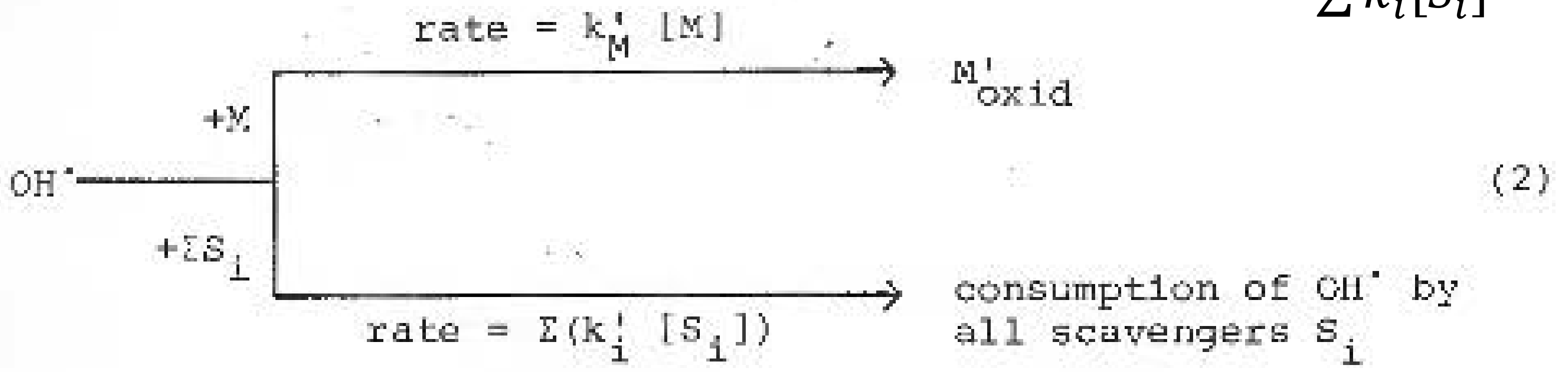
- Oxidation competition values
  - Based on relatively linear pseudo-1st order loss rate for micropollutants (i.e., $\ln(P/P_o)$ vs t gives a straight line)
    - Expected if aggregate OH• reacting substances do not undergo appreciable depletion during ozonation
  - Ozone decomposition produces a uniform yield of OH• over time and ozone dose (typically ~0.5M/M)

Hoigne, J. and H. Bader (1979). "Ozonation of Water - Oxidation-Competition Values of Different Types of Waters Used in Switzerland." Ozone-Science & Engineering 1(4): 357-372.

Oxidation-competition method

- First assume a near constant OH• yield from ozone decomposition so that monitoring loss of ozone provides an estimate of the OH reactions taking place
- Then all OH• produced either reacts with the target pollutant (M) or the background matrix (S_i) and the two are in direct competition
- And the fraction reacting with M is:

$$f = \frac{k_M[M]}{\sum k_i[S_i]}$$



From: Hoigne & Bader, 1979

Using M as a probe

Fraction of OH that reacts with M → $f = \frac{k_M[M]}{\sum k_i[S_i]}$

- Now:

$$-\frac{d(M)}{dt} = \boxed{\eta\frac{d(\Delta O_3)}{dt}}\boxed{\frac{k_M[M]}{\sum k_i[S_i]}} = \frac{d(\Delta O_3)}{dt\,\Omega_M}$$

Production rate of OH radicals

- Where the oxidation-competition value is defined as:

$$\Omega_M = \frac{\sum k_i[S_i]}{\eta k_M} = \boxed{\frac{\Delta O_3}{ln\left({}^{M_t}/_{M_0}\right)}}$$

And rearranging:

$$ln\left({}^{M_t}/_{M_0}\right) = \frac{\Delta O_3}{\Omega_M}$$

This is what we can actually measure

- And as we've shown previously

$$ln\left(\frac{P_t}{P_0}\right) = \frac{k_P}{k_{pCBA}}ln\left(\frac{pCBA_t}{pCBA_0}\right)$$

or

$$ln\left(\frac{P_t}{P_0}\right) = \frac{k_P}{k_M}ln\left(\frac{M_t}{M_0}\right)$$

- We can now use Ω to estimate loss of "P" by simply measuring ΔO_3

$$ln\left(\frac{P_t}{P_0}\right) = \frac{k_P}{k_M}\frac{\Delta O_3}{\Omega_M}$$

Field Values

- Values of Ω have been measured on many natural waters

Hoigne, J. and H. Bader (1979). "Ozonation of Water - Oxidation-Competition Values of Different Types of Waters Used in Switzerland." [Ozone-Science & Engineering 1(4): 357-372.]()

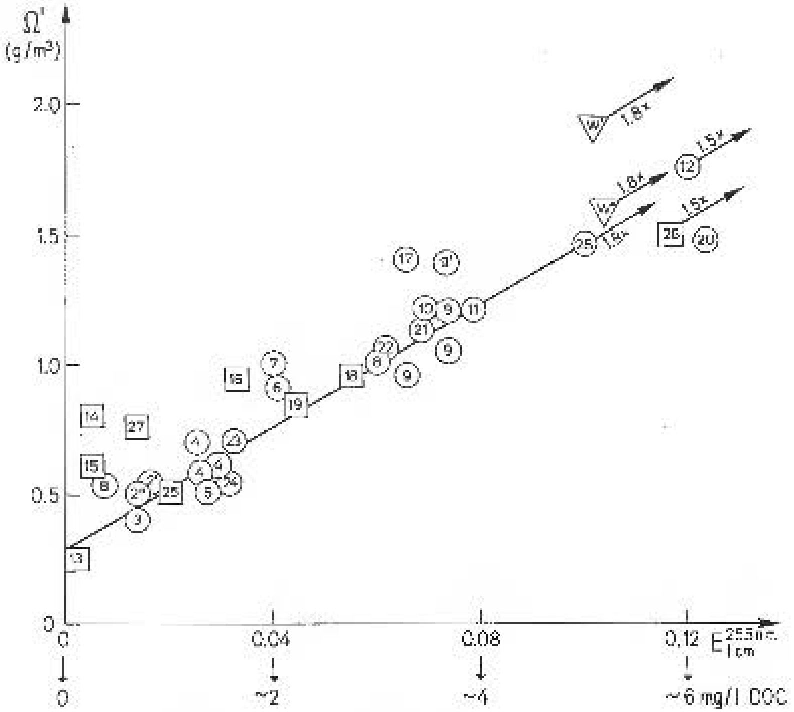


FIG. 8
Oxidation competition value of different types of rawwaters based on benzene as a reference micropollutant, vs. the uv absorbance of rawwater.

Water samples from:

1	Lake of Lucerne, Lucerne
2'	Lake of Geneva, St. Sulpice
2"	Lake of Geneva, Geneva
3	Lake of Lugano
4	Lake of Zürich, Lengg
5	Lake of Constance, St. Gallen
6	Lake of Biel, Biel
7	Rhine above Basel
8	Small mountain lake
9	Greifensee (all seasons)
10	Lac de Morat
11	Lac de Bret
12	Lützelsee
13	Mountain wellwater (Celerina, GR)
14	Well in Dübendorf forest
15	Groundwater Schaffhausen
16	Groundwater Dübendorf, EAWAG
17	Glatt, Glattfelden
18	Glatt, Glattfelden, infiltrated
19	Glatt, Glattfelden, infiltrated
20	Hüttnersee
21	Türlersee
22	Baldeggersee
23	Lac de Neuchâtel
24	Rhine, Rheinau
25	Rhine, Rheinau, infiltrated
26	Highly reduced groundwater
27	Groundwater Hallau
28	Chapel Hill, N.C., USA (University Lake)
W'	Diluted secondary effluent before nitrification
W"	Diluted secondary effluent after nitrification

Some complications

- Yet they noted an initial reaction that did not conform to their simple model

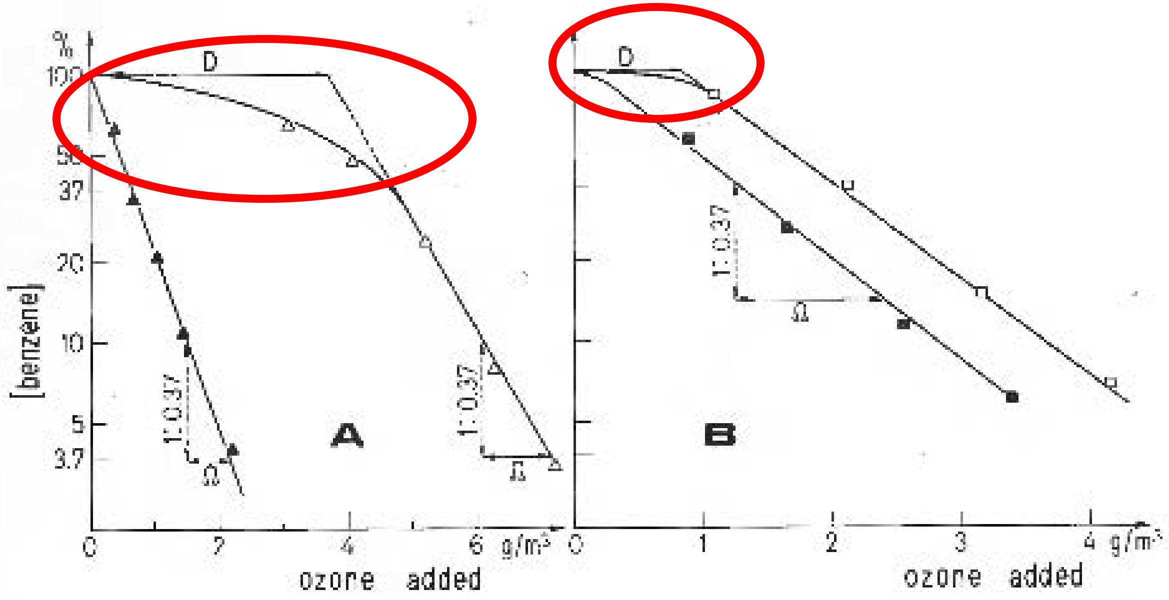


FIG. 4

A) Extremely reduced groundwater (DOC = 7 g/l; NH_3-N = 1.3 mg/l; dilution 0.5; pH = 8.0; phosphate buffer). △ before and ▲ after preozonation with 10 g/m³ ozone.

B) Water from Murtensee (DOC = 3.1 g/l; NH_3-N = 0.7 mg/l; dilution 0.75; pH - 8.2; phosphate buffer). □ before and ■ after preozonation with 2.5 g/m³ ozone.

R_{CT} concept

- Recall from the discussion on simple consecutive reactions:

$$A \xrightarrow{k_i} B \xrightarrow{k_{ii}} C$$

  - The ratio of the concentrations of intermediate to the reactant approaches a constant, when $k_{ii} >> k_i$

$$\frac{[B]}{[A]} \to \frac{k_i}{k_{ii} - k_i} \approx \frac{k_i}{k_{ii}}$$

  - Now consider A to be ozone and B to be OH radical, and we get:

$$R_{CT} \overset{\text{def}}{=} \frac{OH}{O_3} = constant$$

R_{CT} concept

- Elovitz & Von Gunten, 1999
  - Use the same competitive OH reaction approach with a probe compound as Hoigne & Bader

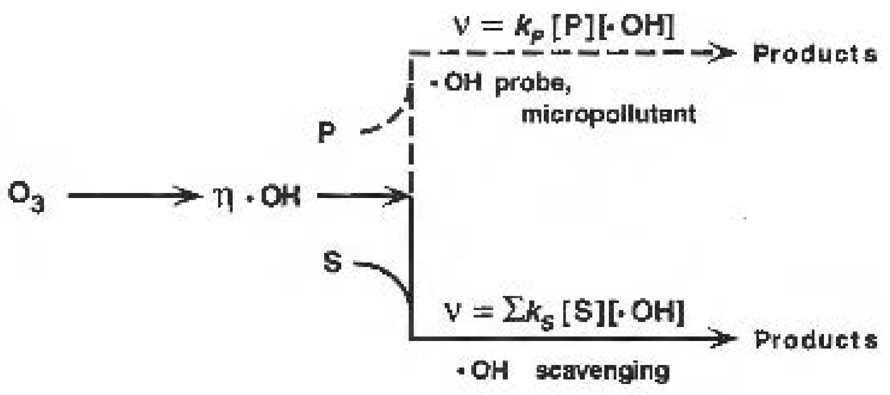


Figure 1. Reaction Scheme for the formation of •OH from O_3 decomposition and the subsequent quenching of •OH by scavengers (s, major pathway) and the probe compound or micropollutant (P, minor pathway). Adapted from reference (20)

However, instead of measuring ΔO_3, they chose to record the full ozone CT

Elovitz, M. S. and U. Von Gunten (1999). "Hydroxyl Radical Ozone Ratios During Ozonation Processes. I-the R-Ct Concept." Ozone-Science & Engineering 21(3): 239-260.

R_{CT} concept II

$$R_{CT} \overset{\text{def}}{=} \frac{OH}{O_3} = constant$$

- The simple 2nd order model is:

$$\frac{d[pCBA]}{dt} = -k_{pCBA}[pCBA][OH]$$

$$\frac{d[pCBA]}{dt} = -k_{pCBA}[pCBA]R_{CT}[O_3]$$

- Rearranging and integrating we get:

$$\frac{d[pCBA]}{[pCBA]} = -k_{pCBA}R_{CT}[O_3]dt$$

$$ln\left(\frac{[pCBA_t]}{[pCBA_0]}\right) = -k_{pCBA}R_{CT}\int_0^t [O_3]dt$$

- Which gives the final form used in experimental evaluation:

$$R_{CT} = {ln\left(\frac{[pCBA_t]}{[pCBA_0]}\right)}\Big/{-k_{pCBA}\int_0^t [O_3]dt}$$

R_{CT} concept III

- Simple model system

$$R_{CT} = \ln\left(\frac{[pCBA_t]}{[pCBA_0]}\right) \Big/ -k_{pCBA}\int_0^t [O_3]dt$$

Elovitz, M. S. and U. Von Gunten (1999). "Hydroxyl Radical Ozone Ratios During Ozonation Processes. I-the R-Ct Concept." Ozone-Science & Engineering 21(3): 239-260.

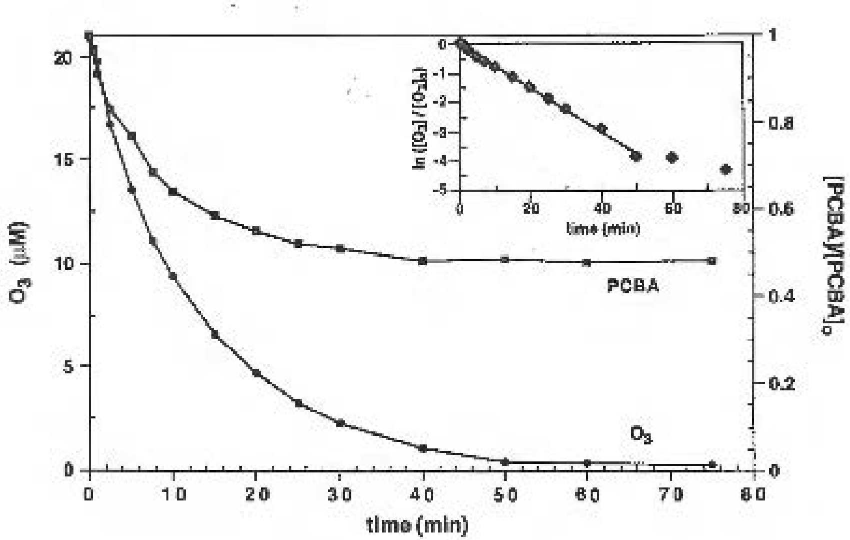


Figure 2a. Depletion of ozone and pCBA as a function of reaction time. $[O_3]_o = 20.1$ µM, $[MeOH]_o = 70$ µM, and $[acetate]_o = 350$ µM in a 1 mM phosphate buffer at pH 8.0 and 15°C. Inset: First-order kinetic plot for the decomposition of ozone.

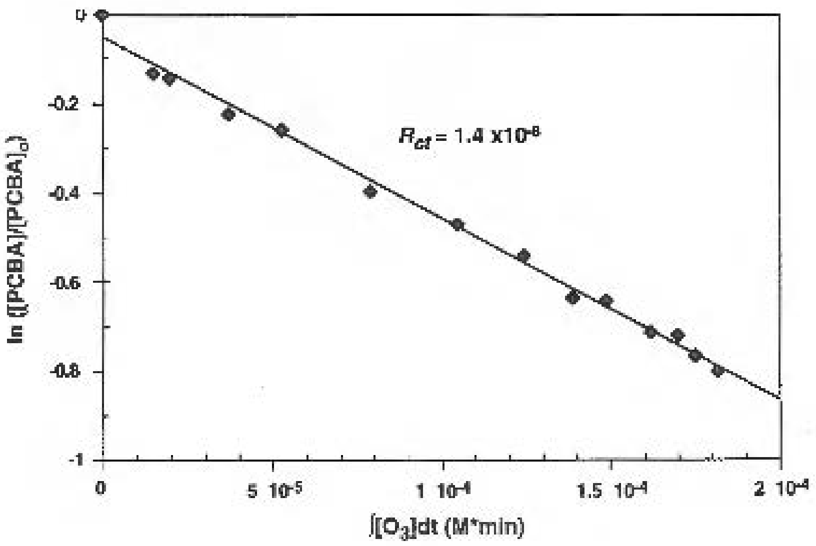


Figure 2b. •OH-exposure (•OH-ct) versus the corresponding O_3-exposure (O_3-ct) for ozonation of the model system of Figure 2a.

R_{CT} concept IV

- Lake Zurich water
  - Apparent 2-stage kinetics
  - 1st stage may or may nc be linear

$$R_{CT} = \frac{ln\left(\frac{[pCBA_t]}{[pCBA_0]}\right)}{-k_{pCBA}\int_0^t [O_3]dt}$$

Elovitz, M. S. and U. Von Gunten (1999). "Hydroxyl Radical Ozone Ratios During Ozonation Processes. I-the R-Ct Concept." Ozone-Science & Engineering 21(3): 239-260.

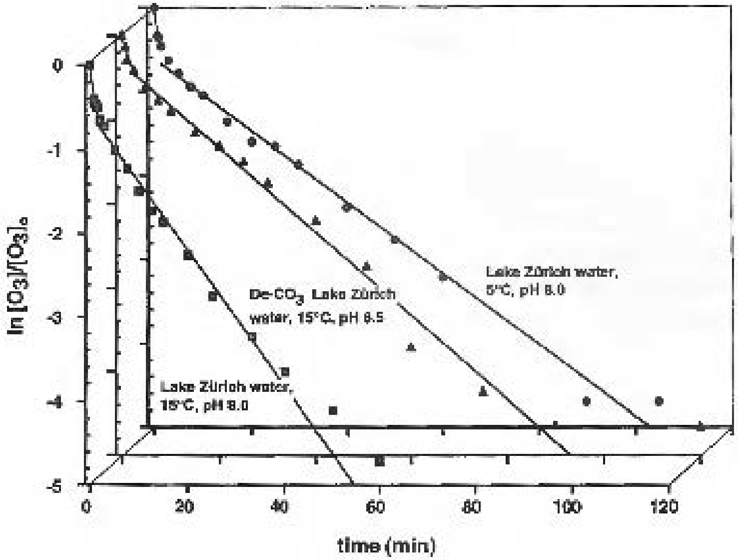


Figure 4a. First-order ozone decomposition kinetics for ozonation of Lake Zürich water (collected at a depth of 32m) at three different reaction conditions.

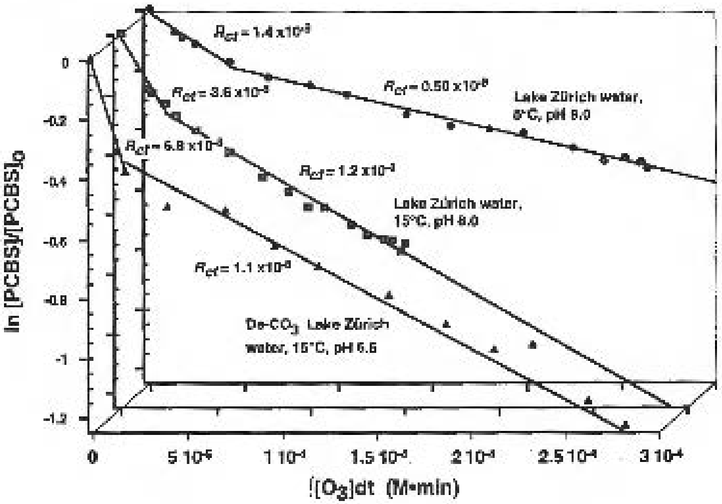


Figure 4b. R_{ct} plots for the ozonation experiments of Figure 4a showing the two linear R_{ct} regions.

Incorporating both pathways

$$R_{CT} \stackrel{\text{def}}{=} \frac{OH}{O_3} = constant$$

- The expanded 2nd order model is:

$$\frac{d[P]}{dt} = -k_{OH}[P][OH] + k_{O3}[P][O_3]$$

$$\frac{d[P]}{dt} = -k_{OH}[P]R_{CT}[O_3] + k_{O3}[P][O_3]$$

- Rearranging and integrating we get:

$$\frac{d[P]}{[P]} = -(k_{OH}R_{CT} + k_{O3})[O_3]dt$$

$$ln\left(\frac{[P_t]}{[P_0]}\right) = -(k_{OH}R_{CT} + k_{O3})\int_0^t [O_3]dt$$

- or:

$$[P_t] = [P_0]e^{-(k_{OH}R_{CT}+k_{O3})\int_0^t [O_3]dt}$$

both pathways II

- ☐ Porrentruy Water

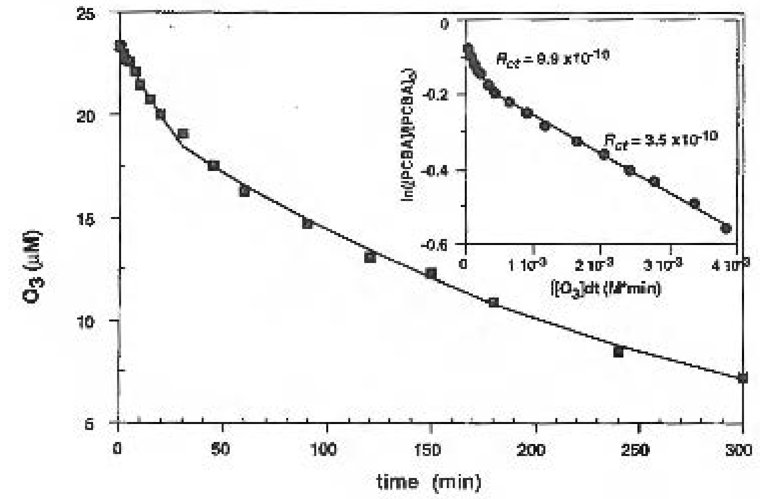


Figure 5a. Ozone decomposition as a function of reaction time for ozonation in Porrentruy water: $[O_3]_o$ = 23.4 µM; $[pCBA]_o$ = 0.25 µM; $[atrazine]_o$ = 0.25 µM; pH 7.2-7.25; and 10.8°C. Symbols show the experimental data, and the line-plot shows the kinetic model simulation based on fitting the ozone decomposition data with two first-order kinetic terms. Inset: R_{ct} plot using pCBA as the •OH-probe compound. Symbols show the experimental data, and the line-plot shows the linear fit for calculating the R_{ct} values for the initial and secondary reaction phases.

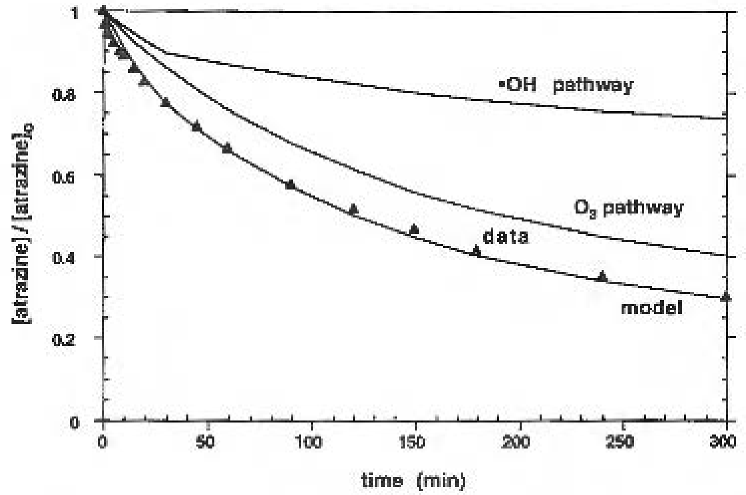


Figure 5b. Relative loss of atrazine during ozonation of Porrentruy water shown in Figure 5a. Symbols show the experimental data for atrazine disappearance, and the line-plots depict the kinetic simulation for total atrazine loss (model calculation based on Equation 10), as well as the loss of atrazine via the individual •OH and O_3 pathways.

Elovitz, M. S. and U. Von Gunten (1999). "Hydroxyl Radical Ozone Ratios During Ozonation Processes. I-the R-Ct Concept." Ozone-Science & Engineering 21(3): 239-260.

both pathways III

- Natural waters

$$f_{OH} = \frac{k_{OH}R_{CT}}{k_{OH}R_{CT} + k_{O3}}$$

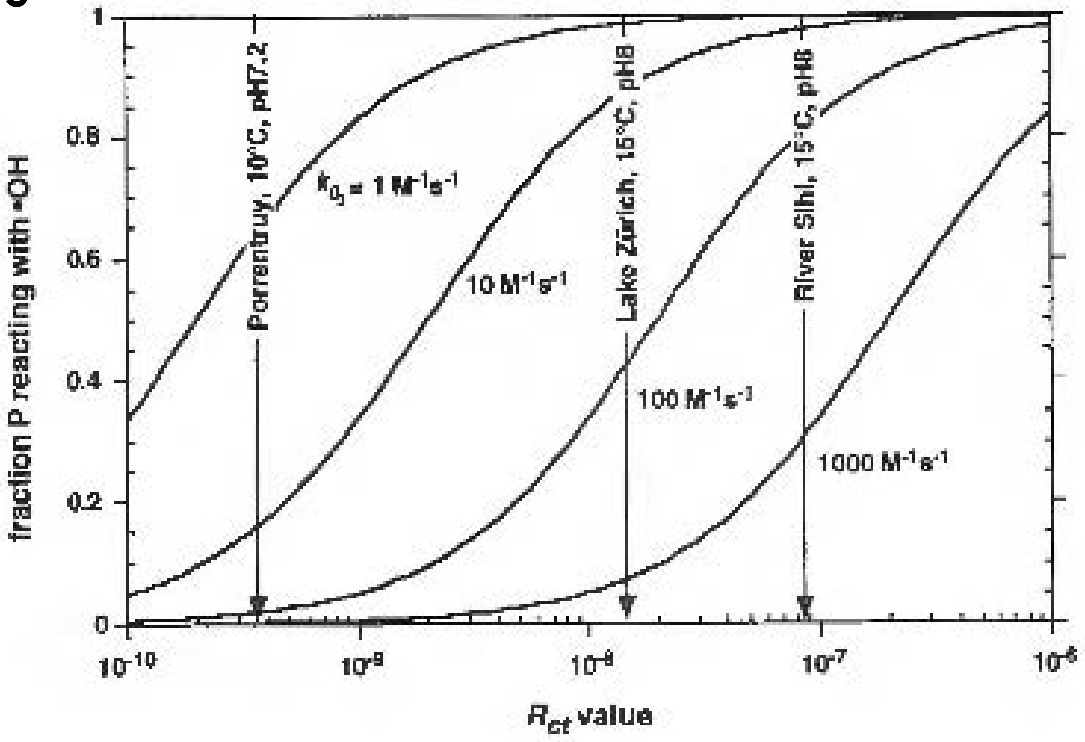


Figure 6. Fraction of micropollutant P reacting with •OH as a function of the R_{ct} value. Calculations assume a rate constant $k_{\bullet OH/P} = 5 \times 10^9$ $M^{-1}s^{-1}$ for reaction of •OH and P, and a range (1-1000 $M^{-1}s^{-1}$) of second-order rate constants for reaction of O_3 and P. Representative R_{ct} values and their ozonation conditions for three waters tested are included.

Elovitz, M. S. and U. Von Gunten (1999).

Role of Temperature

- Increase in R_{CT}

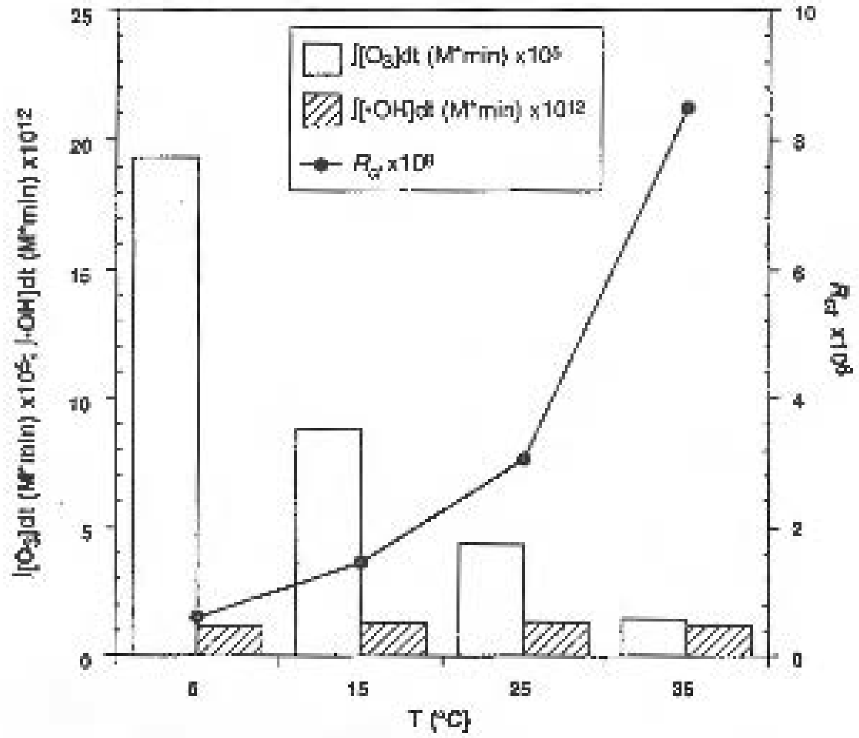


Figure 3: O_3-exposure, •OH-exposure, and R_{ct} values as a function of reaction temperature in Lake Zürich water.

Elovitz, M. S., U. Von Gunten, et al. (2000). "Hydroxyl Radical/Ozone Ratios During Ozonation Processes. II. The Effect of Temperature, pH, Alkalinity, and DOM Properties." Ozone-Science & Engineering 22(2): 123-150.

Role of pH

- Increase in R_{CT}

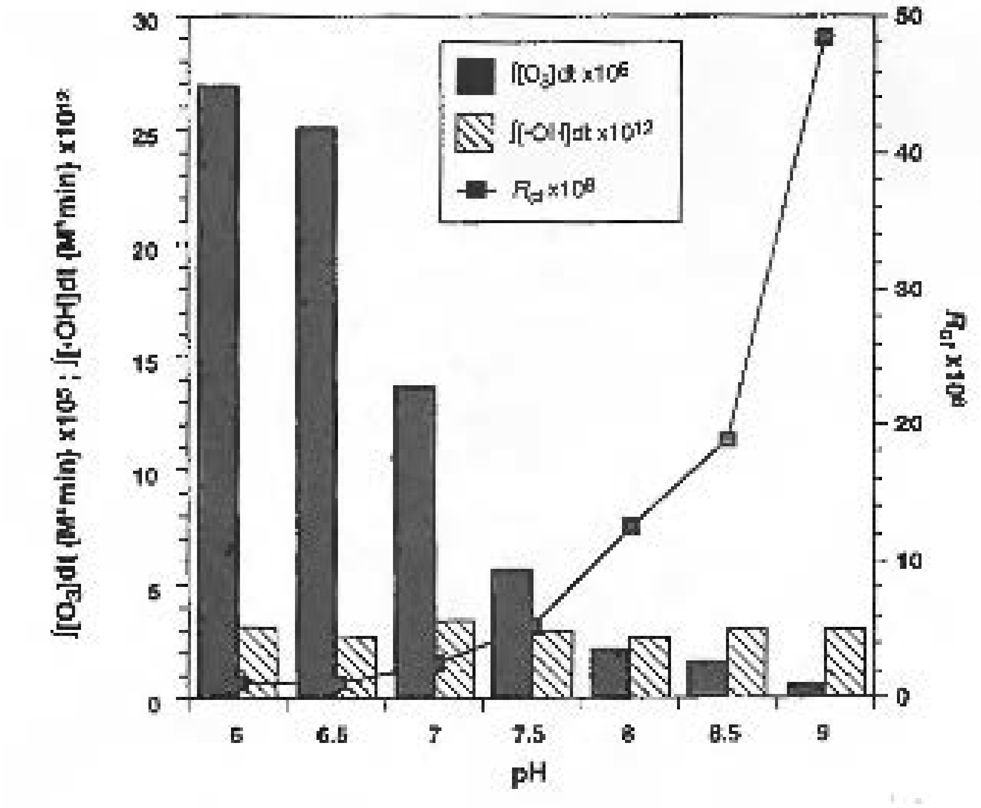
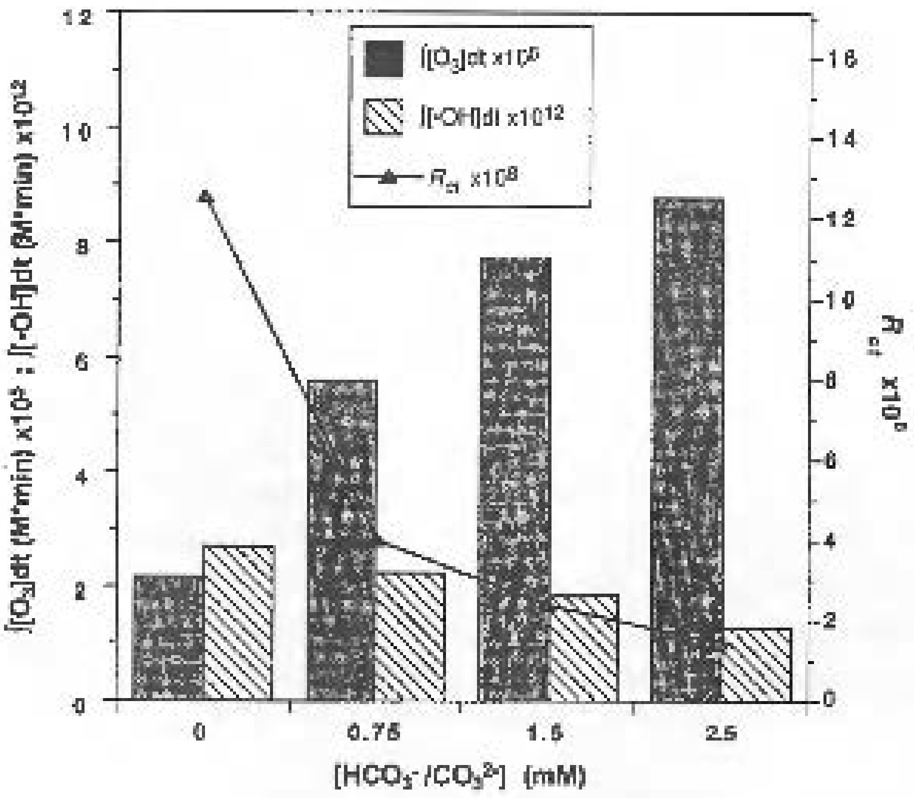


Figure 7: O_3-exposure, •OH-exposure, and R_{ct} values as a function of reaction pH in decarbonated Lake Zürich water.

Elovitz, M. S., U. Von Gunten, et al. (2000). "Hydroxyl Radical/Ozone Ratios During Ozonation Processes. II. The Effect of Temperature, pH, Alkalinity, and DOM Properties." Ozone-Science & Engineering 22(2): 123-150.

Role of Bicarbonate

- Decrease in R_{CT}



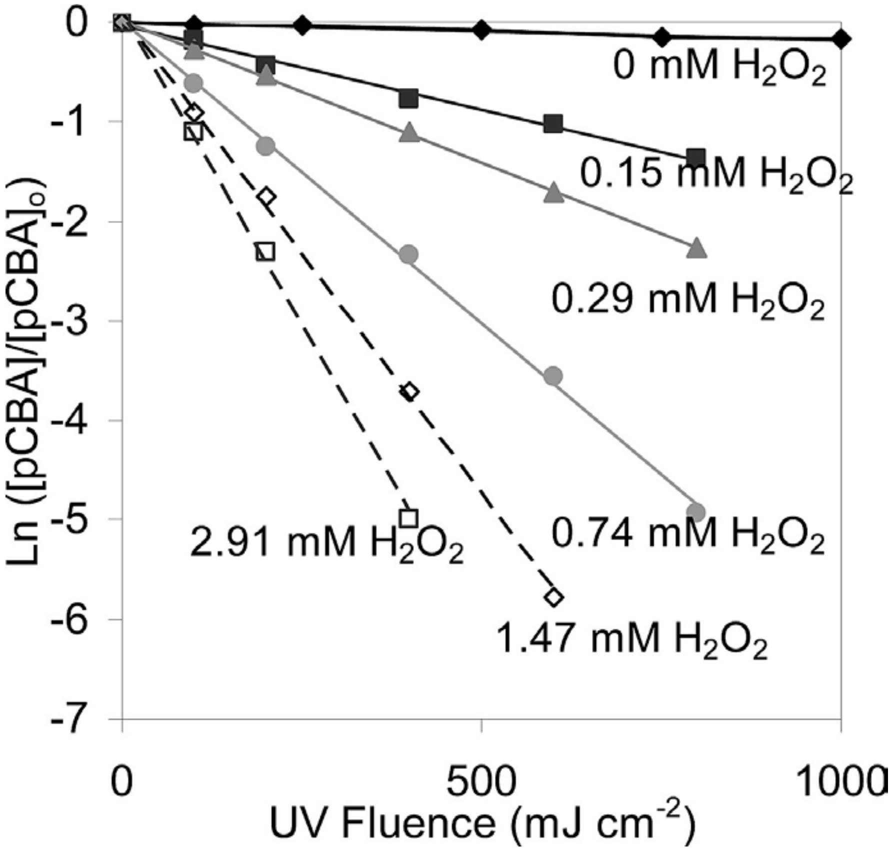
Elovitz, M. S., U. Von Gunten, et al. (2000). "Hydroxyl Radical/Ozone Ratios During Ozonation Processes. II. The Effect of Temperature, pH, Alkalinity, and DOM Properties." Ozone-Science & Engineering 22(2): 123-150.

Figure 8: O_3-exposure, •OH-exposure, and R_{ct} values as a function of carbonate alkalinity in Lake Zürich water.

Similar approach used for AOPs

- Advanced oxidation processes
  - UV with H_2O_2

Rosenfeldt, E. J. and K. G. Linden (2007). "The R-OH,R-UV concept to characterize and the model UV/H2O2 process in natural waters." Environmental Science & Technology 41(7): 2548-2553.



- To next lecture