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
    \[ [C]_i = \sum_{i=1}^{n} [C]_i e^{-k_i t} \]
  - 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

- Aquifer
- Lake
- Upper Soil Horizon
- Lower Soil Horizon
- Litter Layer
- Sediment & Gravel in Lake Bed
- Algae
- Aquifer
Practical Management Question:
Which is the more important source?

☐ allochthonous

or

☐ autochthonous

An Aquatic Humic “Structure”

From Thurman, 1985
Aliphatics: Haloform Reaction

- RLS is deprotonation ($k_1$) under many conditions
- Many LFERs exist for estimating $K_a$s
  - E.g., Perrin et al., 1982
- Then relate $k_1$ to $K_a$
An Aquatic Humic “Structure”

From Thurman, 1985

HPL=Hydrophilic
HPO=Hydrophobic
A=Acids
B=Bases
N=Neutrals
W=Weak
u=ultra

NOM Fractions:
Mass Balance

Forge Pond
Granby, MA
Northeast MA
Tap Water
Absorbance of Acid Fractions

Same DOC

Formation Potentials of NOM Fractions

FP
- High dose
- Forces reaction to endpoint
Aged leaves from 3 locations in Wachusett watershed

Leaching Experiments

White Pine
White Oak
Red Maple

Level 2 ecoregions
Leaching of leaves

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

\[ SUVA = \left( \frac{\text{UV}_{254}}{\text{DOC}} \right) \times 100 \]

Leaching: Sp-THAAFP

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

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

![Chemical structures of lignin monomers](image)

**Lignin**

From: Perdue & Ritchie, 2004
Other plant products

- Steroids
- Terpenoids
- Mevalonic acid
- Unsaponifiable Liquids
- Saponifiable Liquids
- Pyruvate
- Acetate
- Water Soluble Acids
- Shikimic Acid
- Flavonoids
- Porphyrins
- Amino Acids
- Nucleic Acids
- Misc. N & S compounds
- Proteins
- Nitrogenous precursors

Aromatic Amines

- Proposed degradation pathway for 3-amino benzoic acid.

From: Robinson, 1991
**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.


Fate & Transport:

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

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

- "Full-scale monitoring"
- "Lab-scale simulation"
- 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

Ratio climbs over very short distances and then declines

Effect of Bank Filtration on Precursors
The Future: Higher MW DBPs

- NOM research
  - ESI with Ultra High-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

- Benefits
  - Unambiguous molecular formulae

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**Raw Water - Winnipeg**

**ESI-TOF MS**

**ESI-FTICR MS**

Same: comparison side-by-side
Ultra-high resolution MS

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

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)).

Zone of low solubility
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
Fig. 1. pH dependent second-order rate constants ($k$) for the reaction of the oxidants, chlorine (HOCl), chlorine dioxide (ClO$_2$), ferrate$^{VI}$ ($\text{HFeO}_4^-$), hydroxyl radicals (HO$^-$), and ozone (O$_3$).


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.

Fig. 3. Logarithm of the residual concentrations (log(c/c0)) 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 (NH4+) and (b) nitrite (NO2−) 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.

Ferrate reaction with surface waters

- **25 µM ferrate dose, pH 6.2**

- **Low Dose, High pH**
  - **25 µM, pH 7.5**
High Dose, Low pH

- 50 µM, pH 6.2

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
Model for pollutant oxidation

- Simple 2\textsuperscript{nd} order kinetics
  - Pollutant (P) reacts with an oxidant (O)
    \[
    \frac{dP}{dt} = -k[P][O] \quad \frac{dP}{[P]} = -k[O]dt
    \]
- Integrate but keep [O] time variable
  \[
  ln[P]_P^t = -k \int_0^t [O]dt
  \]
- And you end up with an expression in terms of CT
  \[
  P_t = P_0e^{-k \int_0^t [O]dt} \quad P_t = P_0e^{-k(CT)}
  \]

Kinetic Analysis, high dose

- 50 µM dose, Houston Water

![Graph showing fraction remaining against pH for different compounds and phthalates.](image)
Kinetic Analysis, low dose

- **25 µM dose, Houston Water**

![Graph showing fraction remaining vs. pH for different compounds]

- Ethynlestradiol
- Sulfamethoxazole
- Bromide
- Sulfide
- Nitrite
- Phenol
- Analine

- Alkyl alcohols
- Alkyl amines
- Sulfides

The "problems" with ozone

Many important secondary oxidants, especially OH radical

Ozone decomposition in real waters does not match predictions

- Hoigné, Stanhill, and Basler mechanism: Ozone decomposition occurs in a chain process that can be represented by the following fundamental reactions (Hoigné 1955, Stanhill et al. 1984), including initiation step 1, propagation steps 2 to 6, and break in chain reactions steps 7 and 8.

1. \( \text{O}_3 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{O}_2^- \) \( k_1 = 7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \)
   - HO_2^-: hydroperoxide radical

2. \( \text{HO}_2^- \rightarrow \text{O}_2^- + \text{H}^+ \) \( k_2 = 5.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \)
   - \( k_2 \) (first-order rate constant) = \( 10^{-4.9} \)
   - \( \text{O}_2^- \): superoxide radical ion

3. \( \text{O}_3 + \text{O}_2^- \rightarrow 2\text{O}_2 + \text{O}_2 \) \( k_3 = 1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \)
   - \( \text{O}_2^- \): ozone radical ion

4. \( \text{O}_3 + \text{H}^+ \rightarrow \text{HO}_2^- + \text{O}_2 \) \( k_4 = 5.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \)
   - \( k_4 \) = \( 2.3 \times 10^5 \text{ s}^{-1} \)

5. \( \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \) \( k_5 = 1.1 \times 10^6 \text{ s}^{-1} \)

6. \( \text{HO}_2^- \rightarrow \text{OH} + \text{O}_2 \) \( k_6 = 2.0 \times 10^4 \text{ s}^{-1} \)

7. \( \text{HO}_2^- + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \) \( k_7 = 2.8 \times 10^5 \text{ s}^{-1} \)

8. \( \text{HO}_2^- + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \) \( k_9 = 2.8 \times 10^5 \text{ s}^{-1} \)

The overall pattern of the ozone decomposition mechanism is shown in Figure 6. The first fundamental element in the reaction diagram, and in the rate constant
Mechanistic model is “off”

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


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"

\[
\begin{align*}
\frac{d[O_3]}{dt} &= -\omega [O_3] \\
C_{O_3} &= C_{O_3,initial} e^{-\omega t}
\end{align*}
\]

- Specific ozone loss rate (\(\omega\)) in s^{-1}
  - Yurteri & Gurol (1988)
  \[\log \omega = -3.56 + 0.66pH + 0.61\log TOC - 0.42\log Alk\]
  - Orta de Velasquez et al. (1994)
  \[\log \omega = -3.93 + 0.24pH + 0.75\log Abs_{254} + 1.08\log TOC - 0.19\log Alk\]

Ozone loss: focus on decomposition

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

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

- Specific ozone loss rate (\(\omega\)) in s^{-1}
  - Yurteri & Gurol (1988)
  \[\log \omega = -3.56 + 0.66pH + 0.61\log TOC - 0.42\log Alk\]
  - Orta de Velasquez et al. (1994)
  \[\log \omega = -3.93 + 0.24pH + 0.75\log Abs_{254} + 1.08\log TOC - 0.19\log Alk\]
Ozonation of trace organics: Direct Rcn

- Shut down OH radical formation to isolate molecular ozone (O₃) rate.
- Oxidation of nitroimidazoles during ozonation.
  - $[\text{Nitroimidazole}]_0 = 10 \text{ mg/L}$, $T = 298 \text{ K}$.
  - $pH = 2$; $[\text{t-BuOH}] = 0.1 \text{ M}$
  - $\text{MNZ}$, $\text{DMZ}$, $\text{TNZ}$, $\text{RNZ}$.


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
    - $5 \times 10^{-9} \text{ M}^{-1}\text{s}^{-1}$ with OH radical, but $\leq 0.15 \text{ M}^{-1}\text{s}^{-1}$ with O₃

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 \( P_t \):

\[ k_p = k_{PCBA} \left\{ \ln \left( \frac{P_t}{P_0} \right) / \ln \left( \frac{pCBA_t}{pCBA_0} \right) \right\} \]

Determining OH• rate constants

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

\[ k_p = k_{PCBA} \left\{ \ln \left( \frac{P_t}{P_0} \right) / \ln \left( \frac{pCBA_t}{pCBA_0} \right) \right\} \]

\[ k_{rel} = \left( \frac{k_M}{k_{PCBA}} \right) = \left( \frac{\ln \left( \frac{M}{M_0} \right)}{\ln \left( \frac{pCBA_t}{pCBA_0} \right)} \right) \]

Can we simplify a bit?

- **Oxidation competition values**
  - Based on relatively linear pseudo-1st order loss rate for micropollutants (i.e., \( \ln(P/P_0) \) 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 \( \sim 0.5M/M \))


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 (\( S_1 \)) 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

Now:

\[ \frac{d(M)}{dt} = \eta \frac{d(\Delta O_3)}{dt} \frac{k_M[M]}{\sum k_i S_i} = \frac{d(\Delta O_3)}{dt} \frac{k_M[M]}{\sum k_i S_i} \]

Where the oxidation-competition value is defined as:

\[ \Omega_M = \frac{\sum k_i S_i}{\eta k_M} = \frac{\Delta O_3}{\ln\left(\frac{M_f}{M_0}\right)} \]

And rearranging:

\[ \ln\left(\frac{M_f}{M_0}\right) = \frac{\Delta O_3}{\Omega_M} \]

And as we've shown previously:

\[ \ln\left(\frac{P_f}{P_0}\right) = k_p \ln\left(\frac{pCA_t}{pCA_0}\right) \] or \[ \ln\left(\frac{P_f}{P_0}\right) = k_p \ln\left(\frac{M_f}{M_0}\right) \]

We can now use \( \Omega \) to estimate loss of “P” by simply measuring \( \Delta O_3 \)

\[ \ln\left(\frac{P_f}{P_0}\right) = k_p \frac{\Delta O_3}{k_M} \Omega_M \]

Field Values

Values of \( \Omega \) have been measured on many natural waters

Some complications

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

![Graph showing A and B over ozone added](image)

Recall from the discussion on simple consecutive reactions:

\[ A \xrightarrow{k_1} B \xrightarrow{k_2} C \]

- The ratio of the concentrations of intermediate to the reactant approaches a constant, when \( k_{ii} \gg k_{i} \)

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

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

\[ R_{CT} \equiv \frac{OH}{O_2} = \text{constant} \]
**R<sub>CT</sub> concept**

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

However, instead of measuring $\Delta O_3$, they chose to record the full ozone CT

![Reaction Scheme](image)

**R<sub>CT</sub> concept II**

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

- Which gives the final form used in experimental evaluation:
  \[
  R_{CT} = \frac{\ln \left( \frac{[pCBA]}{[pCBA_0]} \right)}{-k_{pCBA} \int_0^t [O_3]dt}
  \]
**RCT concept III**

- Simple model system

\[ R_{CT} = \frac{\ln \left( \frac{[PCBA]}{[PCBA_0]} \right)}{-k_{PCBA} \int_0^t [O_3] dt} \]


**RCT concept IV**

- Lake Zurich water
  - Apparent 2-stage kinetics
  - 1st stage may or may not be linear

\[ R_{CT} = \frac{\ln \left( \frac{[PCBA]}{[PCBA_0]} \right)}{-k_{PCBA} \int_0^t [O_3] dt} \]

Incorporating both pathways

The expanded 2nd order model is:

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

Rearranging and integrating we get:

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

or:

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

Porrentruy Water

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 \( \cdot OH \) as a function of the \( R_0 \) value. Calculations assume a rate constant \( k_{OH} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) for reaction of \( \cdot OH \) and P, and a range (1-1000 M/sec) of second-order rate constants for reaction of \( O_3 \) and P. Representative \( R_0 \) values and their ozoneation conditions for three waters tested are included.


Role of Temperature

Increase in \( R_{CT} \)

Figure 3: \( O_3 \)-exposure, \( \cdot OH \)-exposure, and \( R_0 \) values as a function of reaction temperature in Lake Zurich water.

Role of pH

- Increase in $R_{CT}$


Role of Bicarbonate

- Decrease in $R_{CT}$

Similar approach used for AOPs

- Advanced oxidation processes
  - UV with $\text{H}_2\text{O}_2$


To next lecture