

Oxidation and Disinfection Processes in Water Treatment

1. Oxidation

Urs von Gunten

Learning Objectives

- Chemistry and application of chemical oxidants (chlorine, chlorine dioxide, ozone)
- Kinetics of oxidation and disinfection processes
- pH-dependence of reaction rates
- Calculation of extent of disinfection and transformation of micropollutants for given oxidation conditions

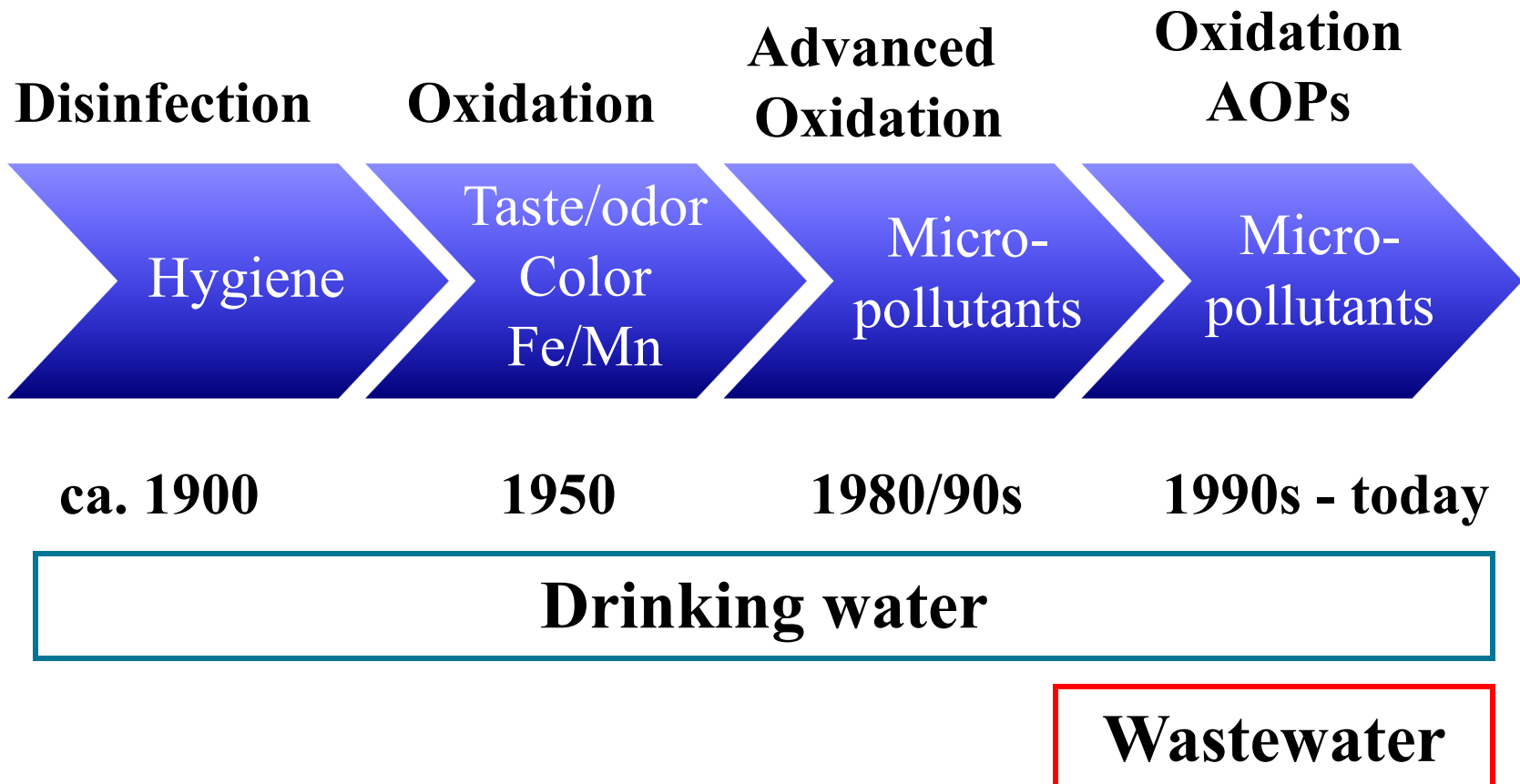
Oxidation Processes in Water Treatment

- Advantage: Self-renewing processes
- Drinking water
 - Disinfection
 - Oxidation
- Municipal wastewater and water reuse
 - Disinfection
 - Polishing treatment
- Industrial wastewater
- High purity industrial process waters
- Pulp and paper
- ...

Role of oxidants in water treatment

- Disinfection of intake pipes
- Primary disinfection in water works
- Disinfection of wastewater treatment plant effluents
- Disinfection of distribution system to maintain a residual to the tap
- Disinfection of reservoirs
- Oxidation processes in water works
- Oxidation of secondary effluents (micropollutant control)

Application of oxidation processes in water treatment



Oxidation Processes in Water Treatment: Are We on Track?

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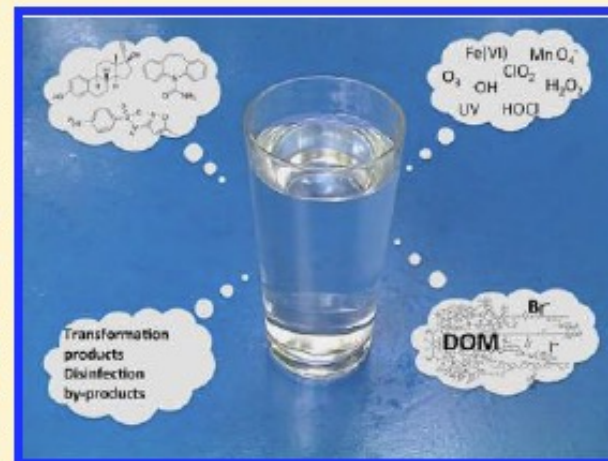
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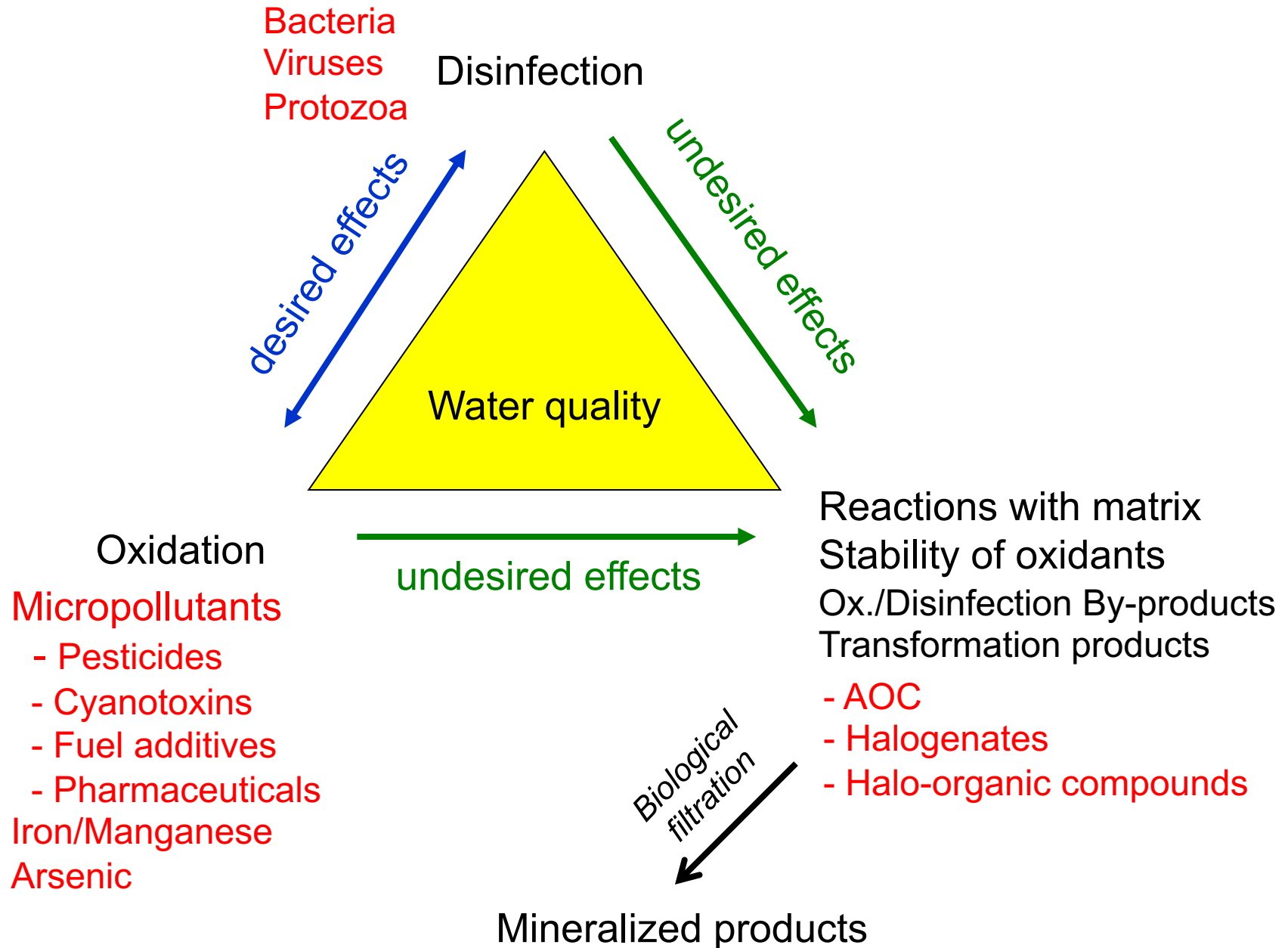
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Supporting Information

ABSTRACT: Chemical oxidants have been applied in water treatment for more than a century, first as disinfectants and later to abate inorganic and organic contaminants. The challenge of oxidative abatement of organic micropollutants is the formation of transformation products with unknown (eco)toxicological consequences. Four aspects need to be considered for oxidative micropollutant abatement: (i) Reaction kinetics, controlling the efficiency of the process, (ii) mechanisms of transformation product formation, (iii) extent of formation of disinfection byproducts from the matrix, (iv) oxidation induced biological effects, resulting from transformation products and/or disinfection byproducts. It is impossible to test all the thousands of organic micropollutants in the urban water cycle experimentally to assess potential adverse outcomes of an oxidation. Rather, we need multidisciplinary and automated knowledge-based systems, which couple predictions of kinetics, transformation and disinfection byproducts and their toxicological consequences to assess the overall benefits of oxidation processes. A wide range of oxidation processes has been developed in the last decades with a recent focus on novel electricity-driven oxidation processes. To evaluate these processes, they have to be compared to established benchmark ozone- and UV-based oxidation processes by considering the energy demands, economics, the feasibility, and the integration into future water treatment systems.



Oxidation processes for drinking water and wastewater treatment



Oxidants and disinfectants in water treatment

- Oxygen: Oxidation of iron, biological oxidation processes
- Chlorine: disinfection, oxidation of inorganic micropollutants (NH_3 , Fe(II) , Mn(II) , HS^- , Br^- , etc.)
- Monochloramine: Disinfection
- Chlorine dioxide: disinfection, (organic micropollutants)
- Permanganate: oxidation of Fe(II) , Mn(II) , taste and odor control

Oxidants and disinfectants in water treatment

- Ozone: decoloration, disinfection, oxidation of inorganic/organic micropollutants, transformation into OH radicals → Advanced Oxidation Processes (AOPs)
- Ultraviolet light: disinfection, advanced oxidation (UV/H₂O₂)
- OH radicals: AOPs; O₃/H₂O₂, UV/H₂O₂, UV/O₃, Fe(II)/H₂O₂, oxidation of micropollutants

History of chlorination

- 1774 production of chlorine gas - Scheele
- 1785 Eau de Javelle KOH
- 1789 Eau de Labarraque NaOH
- 1890 commercial electrochem. production of Cl_2
- 1846 Hospital application - Vienna
- 1881 bacterial toxicity (Koch)
- 1902 Water treatment with OCl^- (Belgium)
- 1903 Water treatment with Cl_2 (Belgium)
- 1974 Discovery of THMs

Forms of chlorine addition



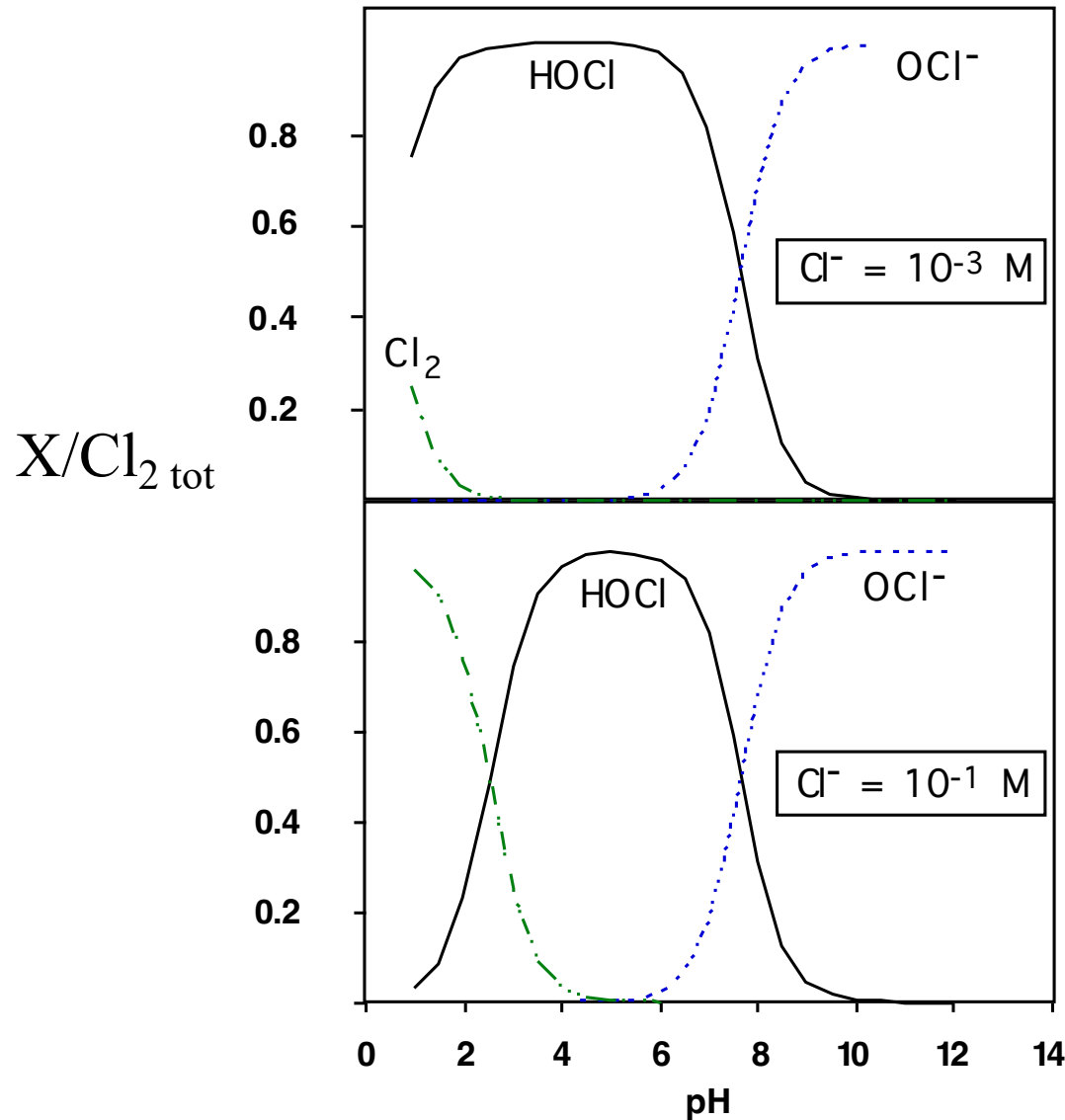
Chlorine gas containers

Forms of chlorine addition to the water

- Gas: $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad K = 5.1 \times 10^{-4}$
- Liquid: $\text{NaOCl} \xrightarrow{\text{H}_2\text{O}} \text{OCl}^- + \text{Na}^+$
- Solid: $\text{CaCl}(\text{ClO}) \xrightarrow{\text{H}_2\text{O}} \text{OCl}^- + \text{Cl}^- + \text{Ca}^{2+}$
- $\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+ \quad \text{p}K_a = 7.5$

Equilibrium constants for 25 °C

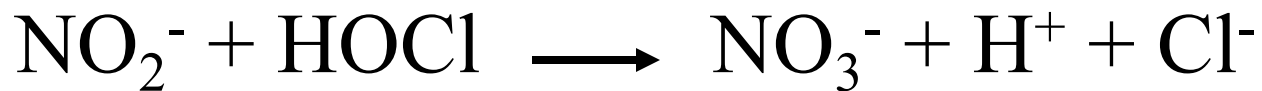
Speciation of aqueous chlorine



$\text{pK}(\text{HOCl}) \sim 7.5$

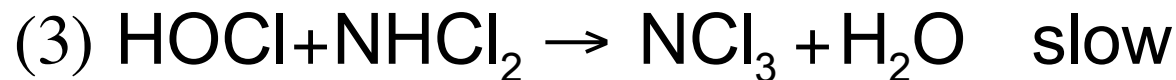
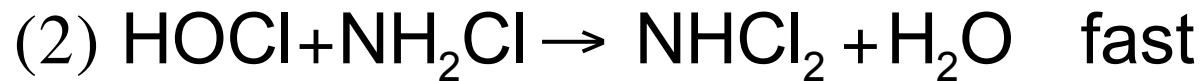
Reactions of chlorine in water

- Oxidation of iron and manganese (heterogeneous)
- Oxidation of arsenite (As(III)) to arsenate (As(V))
- Oxidation of Nitrite



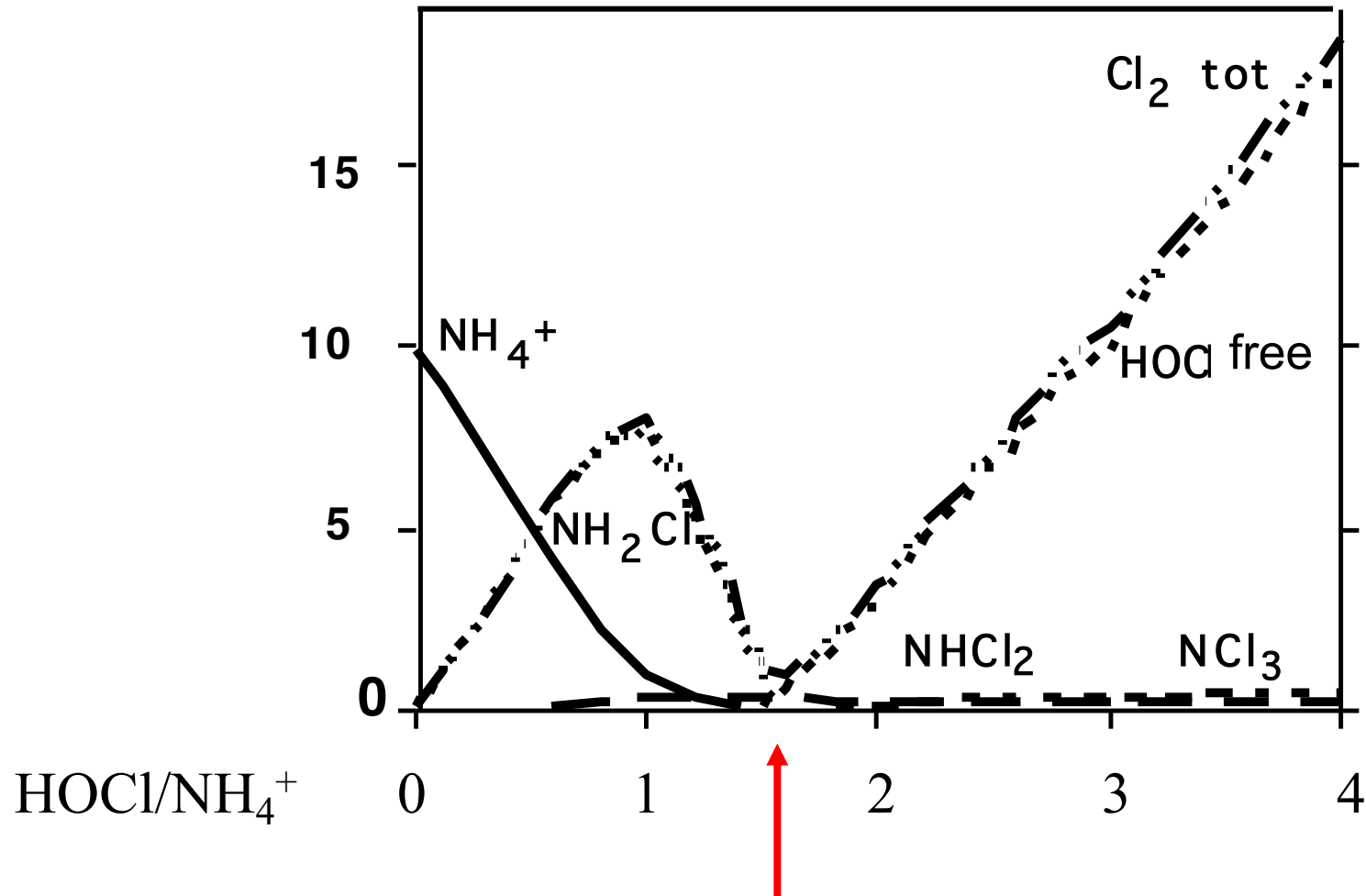
- Oxidation of Sulfide: Sulfate
- Oxidation of Sulfite: Dechlorination
- Ammonia: Chloramines, Breakpoint
- Oxidation of bromide: Disinfection by-products
- Reaction with NOM: Disinfection by-products

Chlorine ammonia reactions: breakpoint chlorination



Breakpoint: At a molar ratio of $\text{HOCl}:\text{NH}_3 = 3:2$
no more disinfectant, ammonia elimination

Breakpoint chlorination



Breakpoint, no more disinfectant residual

Chlorination processes:

Water quality is decisive for success

- pH (speciation of HOCl for disinfection)
- Ammonia concentration (chloramines, breakpoint)
- Bromide concentration (bromo-organic compounds)
- Temperature of the water (disinfection, disinfection by-products)
- Content of NOM (measured as DOC)



Pre-treatment may be necessary

Ozone

Discoverer of ozone:

Christian Friedrich Schönbein
1799-1868

Professor at University of Basel

Ozone: 1839

Greek: ὀζειν (ózein): to smell

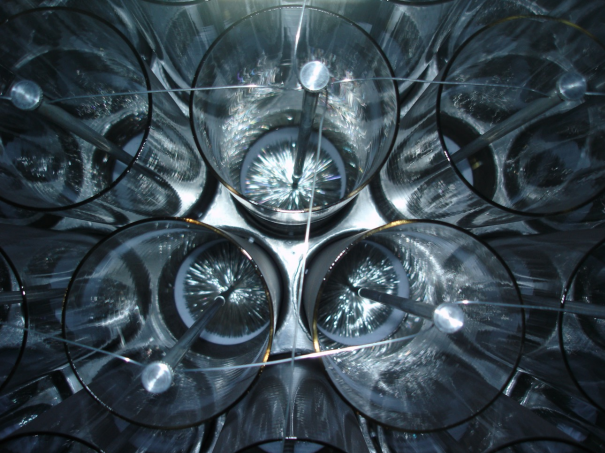
Indigo method to measure O_3

Fuel cell: 1839

Gun cotton: 1846

Fenton reaction: 1857





Ozone

- Electrophilic agent

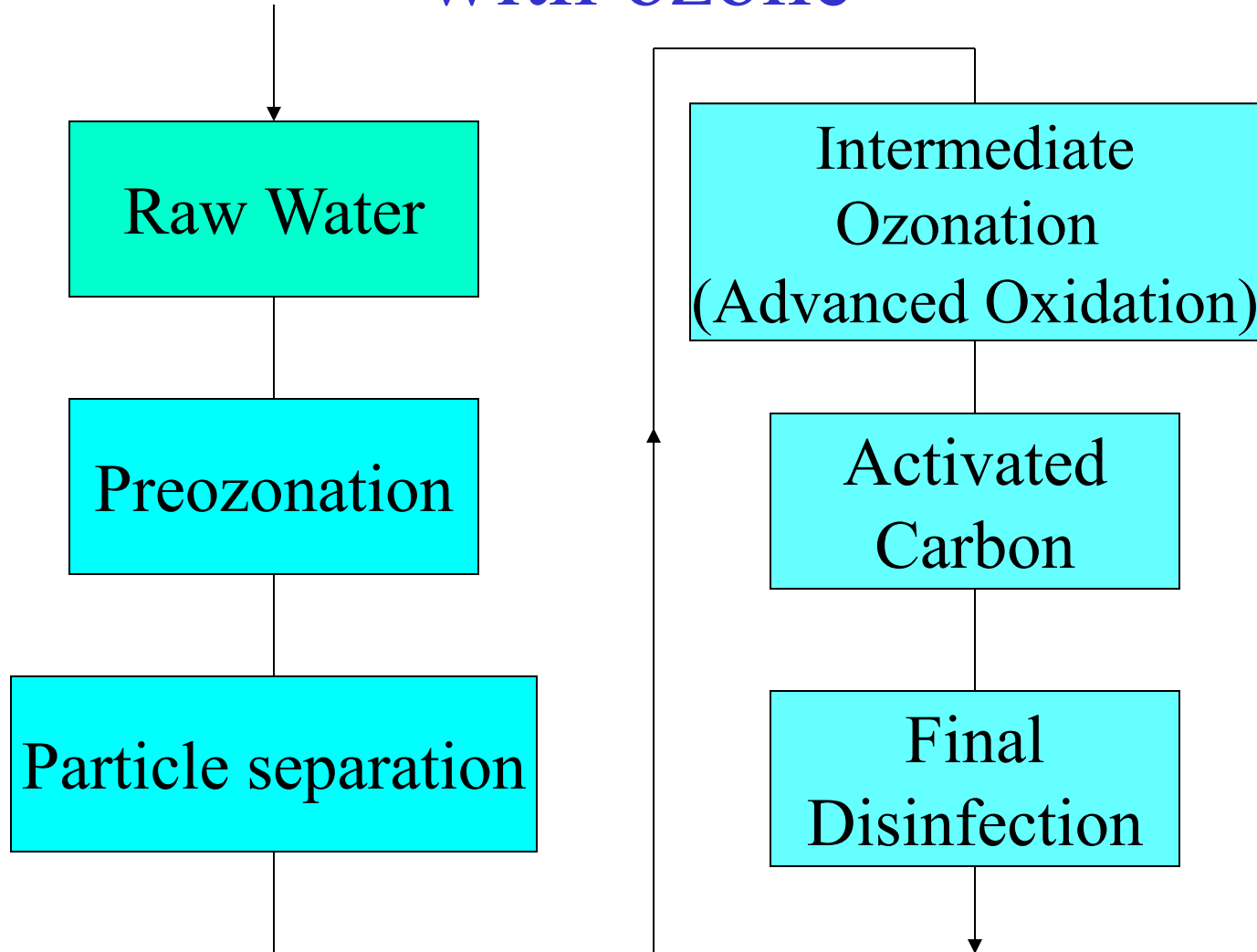


- Onsite production (unstable for storage)
- Production from oxygen via corona discharge (5 – 15% in gas)
- Addition as gas (bubble diffusers, static mixers)

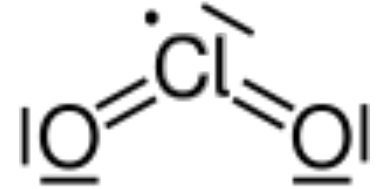
Ozone - Characteristics

- Excellent disinfectant, no acid-base speciation
- Unstable in water (hours-sec), only primary disinfection
- Selective but widely applicable oxidant
 - phenols, amines, olefines
 - Fe(II), Mn(II), HS⁻, NO₂⁻, Br⁻
 - removal of taste and odor, color
 - No reaction with ammonia
- Disinfection by-products: Bromate, aldehydes, ketones, organic acids (assimilable organic carbon, AOC)
- Formation of secondary oxidants: OH radicals (→ advanced oxidation processes AOPs)

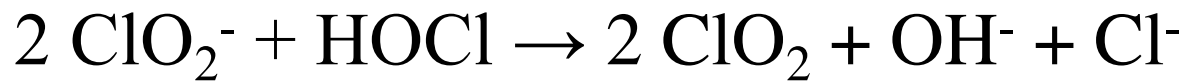
Typical drinking water treatment with ozone



Chlorine dioxide



- Stable radical ($\angle \text{OClO} = 110^\circ$)
- On site production (not stable for storage)
- Chlorite/Chlorine process



- Chlorite/acid process



- Addition as a concentrated solution

Chlorine dioxide - Characteristics

- Good disinfectant
- Unstable in waters containing high DOC or non pre-treated water $\Rightarrow$ final disinfection
- Speciation independent of pH
- Fast reaction with phenols/tertiary amines
- Main disinfection by-products: chlorite/chlorate (blood poison), but also aldehydes, ketones
- Limited THM formation (chlorine formation from reaction with dissolved organic matter)
- No reaction with bromide and ammonia

Oxidation

Oxidation kinetics: rate law

Typically second-order kinetics for the oxidation of Micropollutant P:

$$-\frac{d[P]}{dt} = k \cdot [ox] \cdot [P]$$

$$\ln \frac{[P]}{[P]_0} = -k \cdot [ox] \cdot t$$

Oxidant	Number of available second-order rate constants k
Ozone	~ 500
OH radical	~ 2000
Chlorine	~ 300
Chlorine dioxide	~ 100
Ferrate(VI)	~ 50

pH, T

Half-life time of P for an oxidant concentration [ox]

$$t_{\frac{1}{2}} = -\frac{\ln \frac{1}{2}}{k \cdot [ox]} = \frac{0.69}{k[ox]}$$

pH-dependence of apparent second-order rate constants: one acid-base equilibrium

Oxidant does not undergo acid-base equilibrium (O_3 , ClO_2)

Substrate PH is an acid that is in equilibrium with P^- , the rate law can be formulated as:

$$\begin{aligned}-\frac{d[P]_{tot}}{dt} &= \left(\alpha \times k(O_3 + PH) + (1 - \alpha) \times k(O_3 + P^-) \right) \times [P]_{tot} \times [O_3] \\ &= k_{app}(pH) \times [P]_{tot} \times [O_3]\end{aligned}$$

PH: α : degree of dissociation

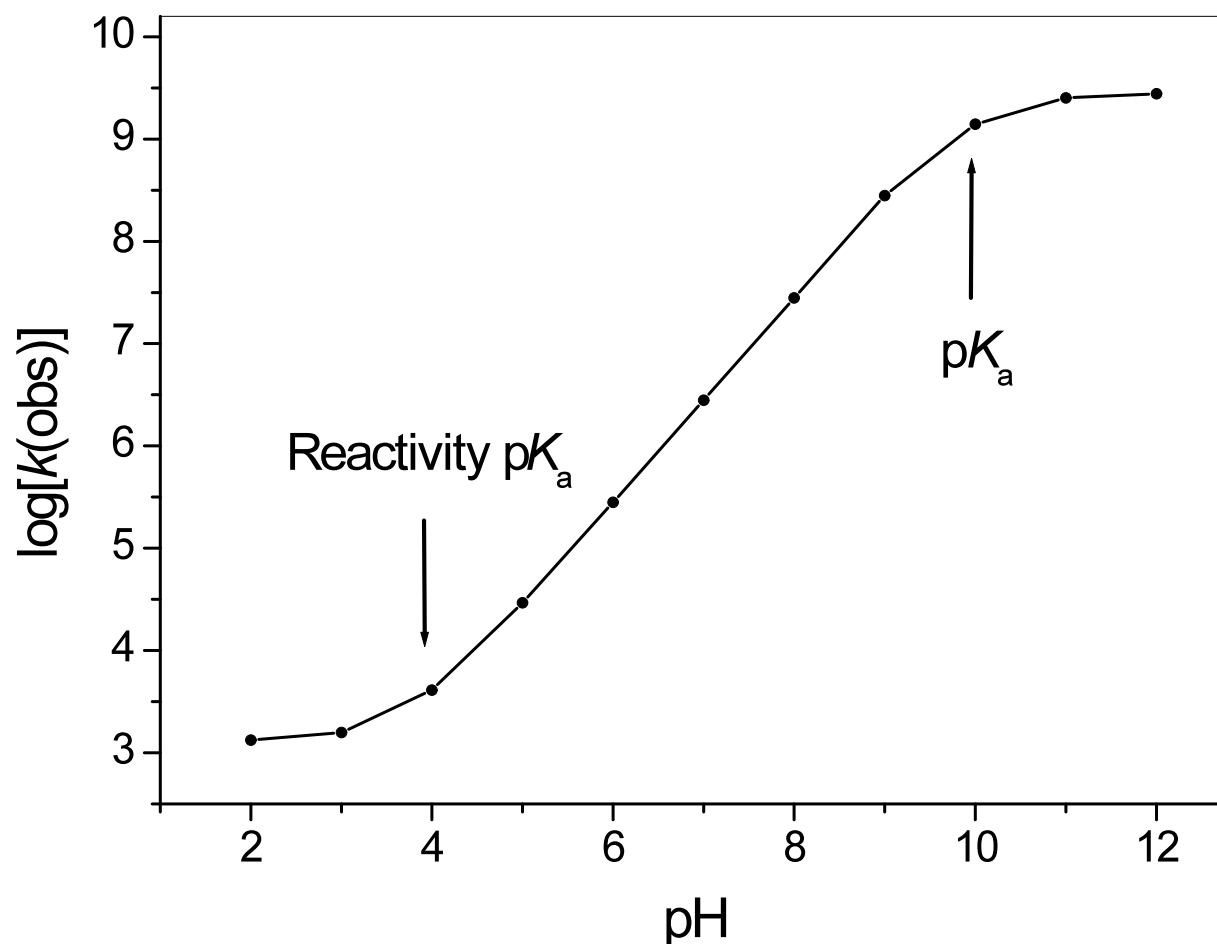
$$\alpha = \frac{1}{1 + K/[H^+]}$$

Oxidation of phenol with ozone

pK (phenol): 10

k (O_3 + phenol (PH)) = $1.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$

k (O_3 + phenolate (P^-)) = $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$



Reactivity pK_a :

At this pH, both phenol and phenolate contribute equally to the apparent second-order rate constant.

Above this pH value mainly phenolate is oxidized despite a real acid-base pK_a of 10!

pH-dependence of apparent rate constant: two acid-base equilibria

Oxidant undergoes acid-base equilibrium (e.g., HOCl)

Substrate PH is an acid that is in equilibrium with P⁻, often only HOCl reacts

The rate law can be formulated as (**only HOCl reaction**):

$$\begin{aligned}-\frac{d[P]_{tot}}{dt} &= \left(\alpha \times \beta \times k(\text{HOCl} + \text{PH}) + (1 - \alpha) \times \beta \times k(\text{HOCl} + \text{P}^-) \right) \times [P]_{tot} \times [\text{HOCl}]_{tot} \\ &= k_{app}(pH) \times [P]_{tot} \times [\text{HOCl}]_{tot}\end{aligned}$$

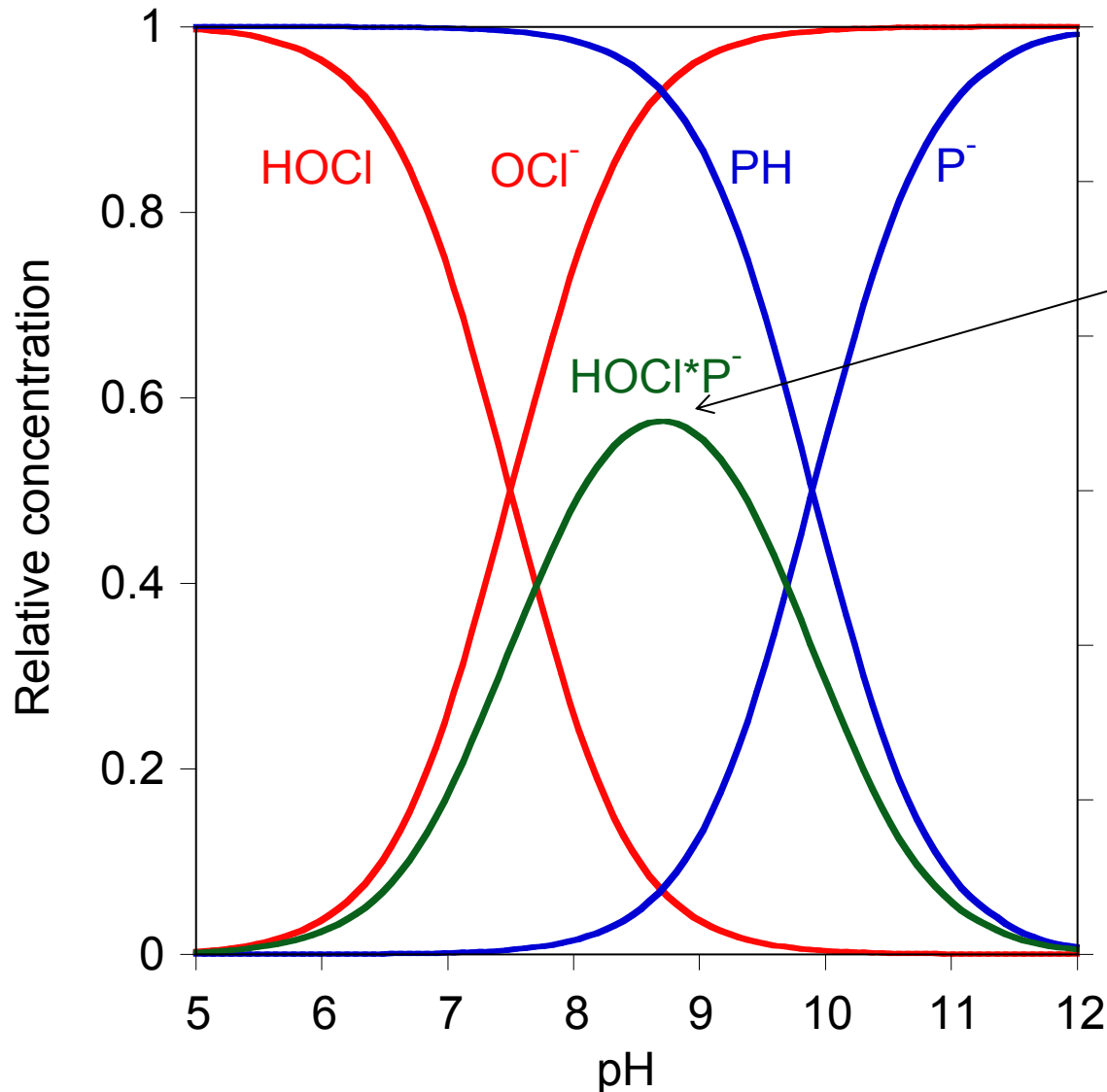
α : degree of dissociation of PH (pK_1)

β : degree of dissociation of HOCl (fraction of HOCl) (pK_2)

$$\alpha = \frac{1}{1 + K_1/[H^+]}; \quad \beta = \frac{1}{1 + K_2/[H^+]}$$

Examples: reaction of HOCl, HOBr with NH₃/NH₄⁺, phenol, etc.

pH dependent speciation of phenol and chlorine

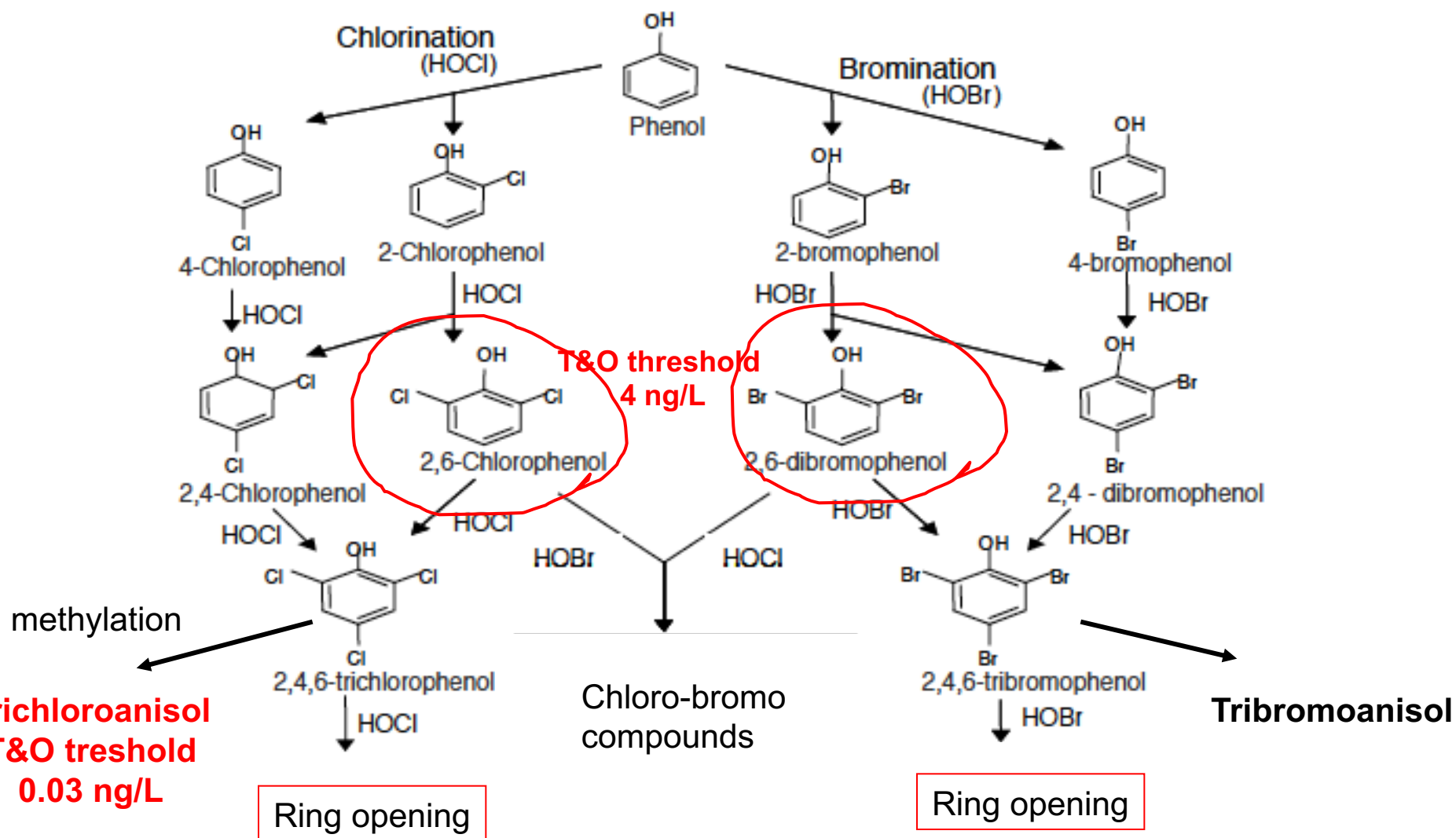
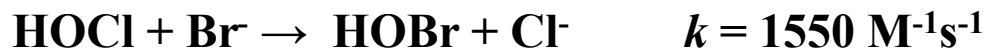


Second-order
rate constant:
Maximum: HOCl x P⁻
 $0.5(pK_1 + pK_2) =$
 $0.5(9.9 + 7.5) =$
8.7

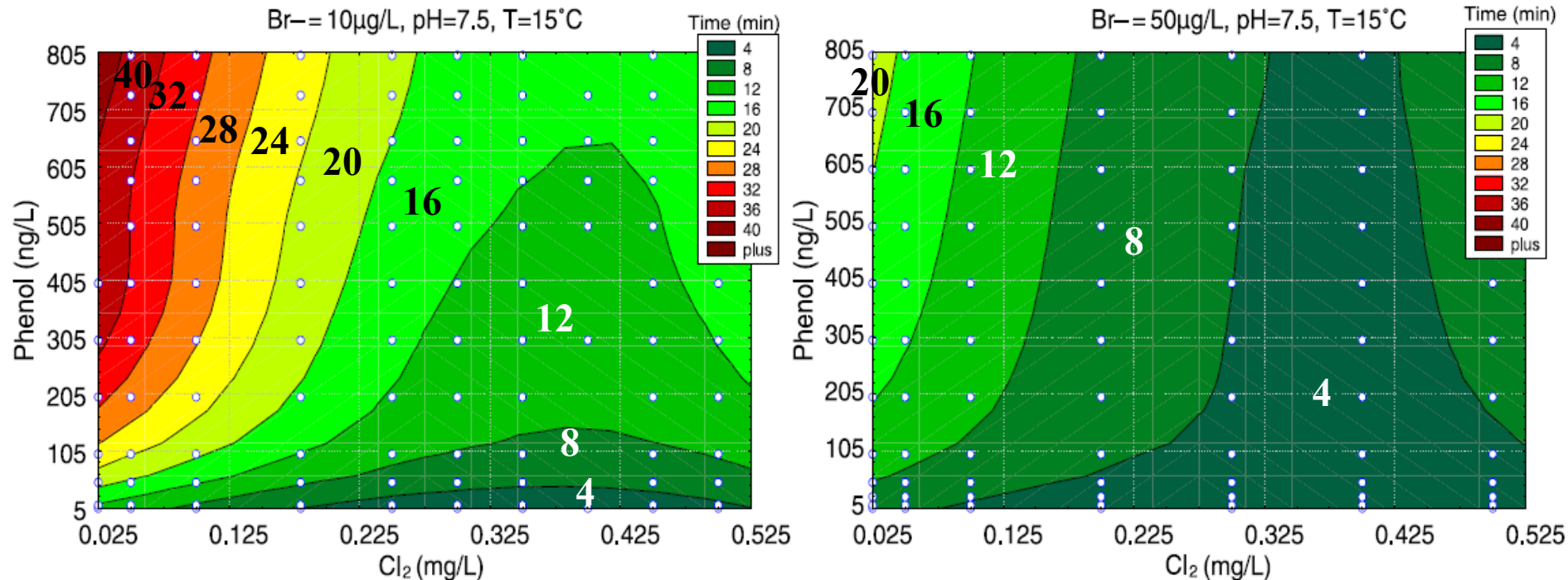
2. Chloro- and bromophenol formation during post-chlorination

- Medicinal taste in drinking water of the cafeteria of CIRSEE (Suez Environment); detected by CEO!
 - Analysis reveals chloro-/bromophenols (2,6-dibromophenol/2,6-dichlorophenol with T&O thresholds of $\approx 4\text{ng/L}$)
- ⇒ Kinetics and mechanisms of chloro-/bromophenol formation
- ⇒ Mitigation strategies

Formation of chloro-/bromophenols during chlorination of bromide-containing water



Model calculations: duration (min) of T&O episodes for two bromide concentrations (10 and 50 $\mu\text{g/L}$)



Mitigation strategies:

Optimized chlorine dose, longer contact times

Phenol destruction by oxidative pre-treatment (ozone, chlorine dioxide)

⇒ Application of same procedure to other phenolic compounds (e.g. EDCs)

⇒ Drinking water and wastewater

Kinetics of micropollutant oxidation during ozonation

- Oxidation in ozonation systems: direct oxidation by ozone and indirect oxidation by OH radicals, which are formed from ozone decomposition
- OH radical concentration extremely low: cannot be measured directly
- Indirect measurement of OH radicals
- OH radical concentration is proportional to ozone concentration

Kinetics of micropollutant oxidation during ozonation

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

$$R_{ct} = \frac{[OH]}{[O_3]}$$

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

$$\ln\left(\frac{[P]}{[P]_o}\right) = -(k_{O_3} + R_{ct}k_{OH})[O_3]t, [O_3] = \text{const.}$$

$$\ln\left(\frac{[P]}{[P]_o}\right) = -(k_{O_3} + R_{ct}k_{OH})\int [O_3]dt, [O_3] = \text{variable}$$

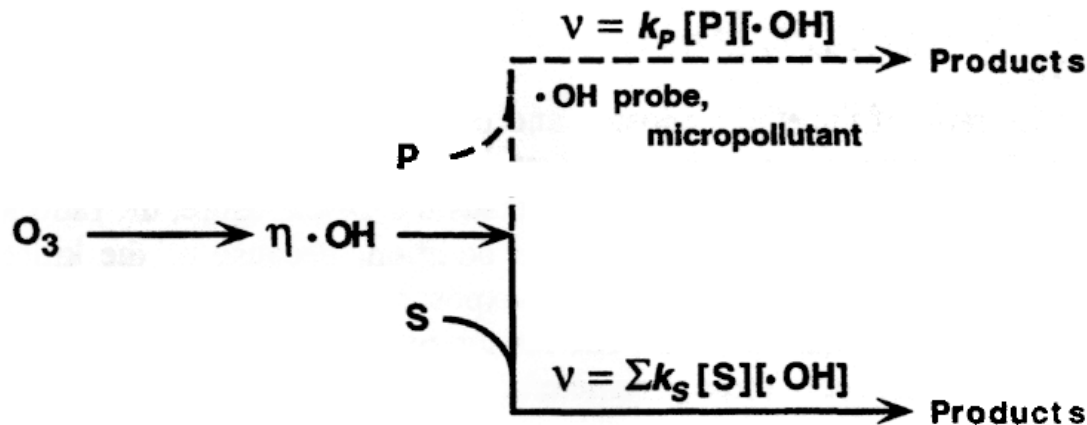
$$\int [O_3]dt : \text{Ozone exposure}$$

Measurement of OH radicals during ozonation

OH radicals cannot be measured directly (lifetime μs)

Use of a probe compound which does not react with ozone

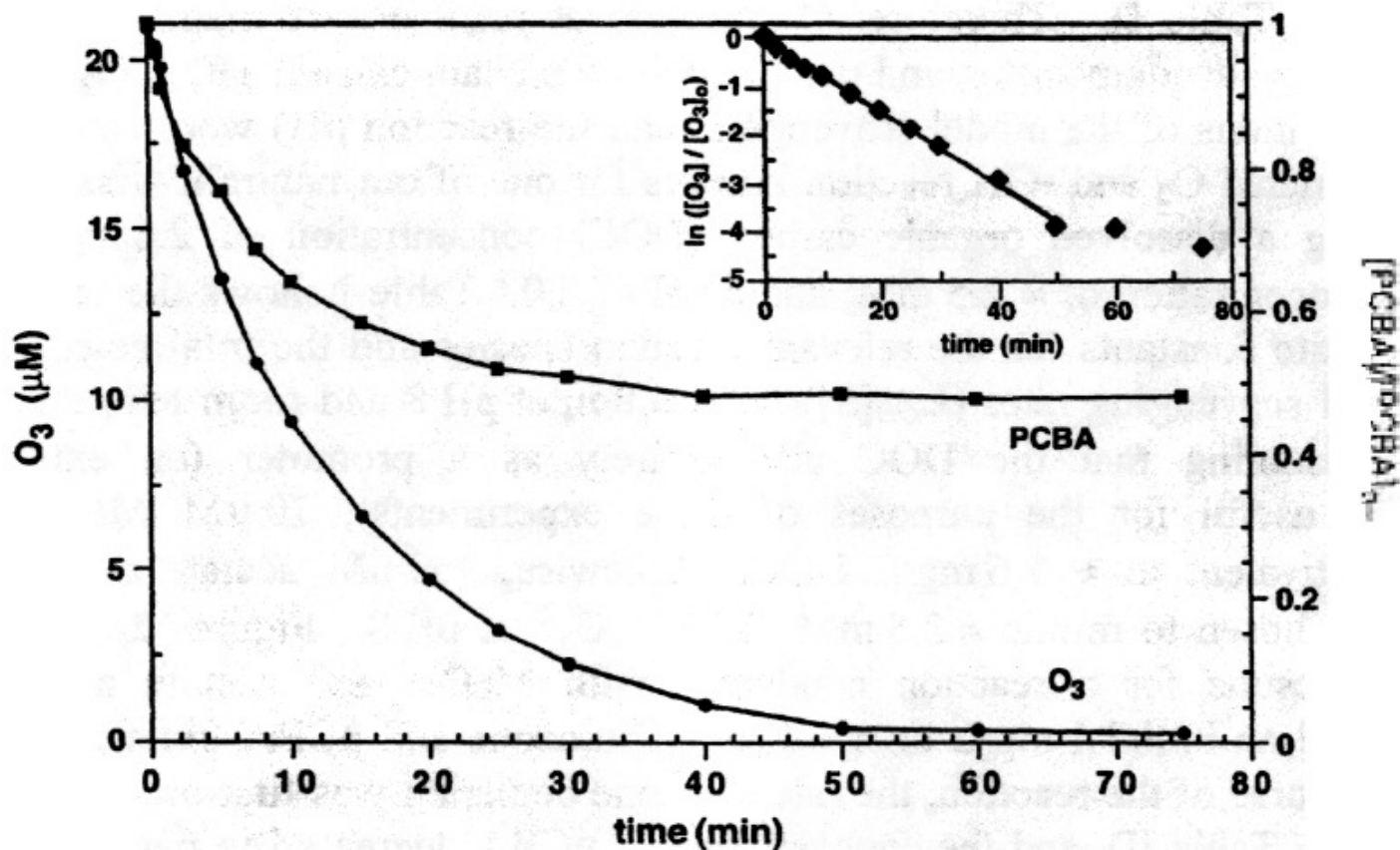
Probe compound does not influence ozone chemistry



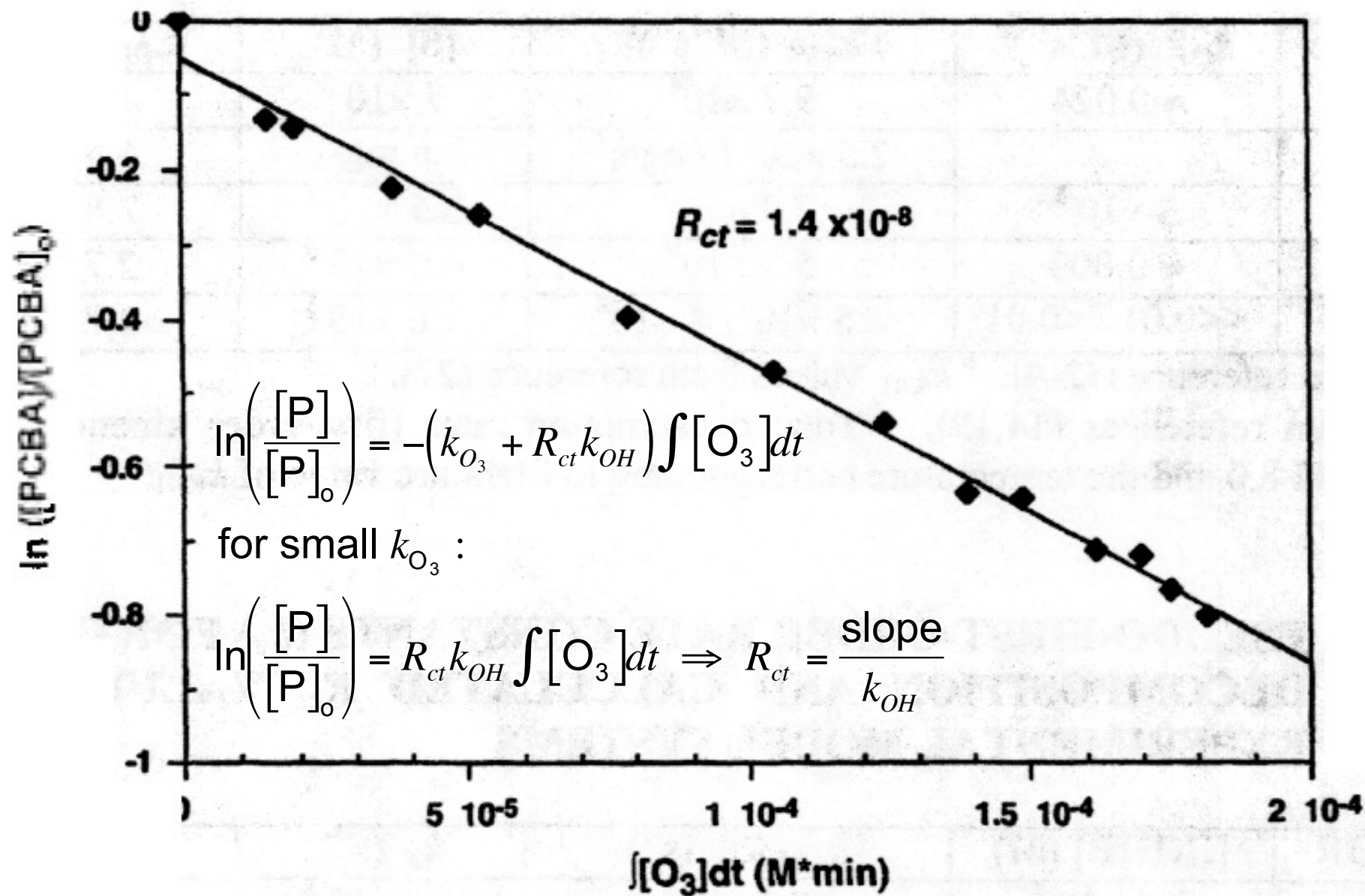
Probe compound: parachlorobenzoic acid *p*CBA

$$k_{\text{O}_3} < 0.15 \text{ M}^{-1}\text{s}^{-1}, k_{\text{OH}} = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$$

Decrease of ozone and para-chlorobenzoic acid pCBA during ozonation of a synthetic water (mimicking lake water) (MeOH 70 μM , acetate 350 μM , pH 8)



Determination of R_{ct}



Conclusions

- The most common chemical oxidants in water treatment are chlorine, chlorine dioxide and ozone
- Chlorine, chlorine dioxide mostly for disinfection
- Ozone for disinfection and oxidation
- Oxidation kinetics can be applied to estimate extent of micropollutant transformation (pH-, T-dependence): typically second-order processes
- Special case for ozone, because hydroxyl radicals are formed and act as oxidants simultaneously