Ozonation Process

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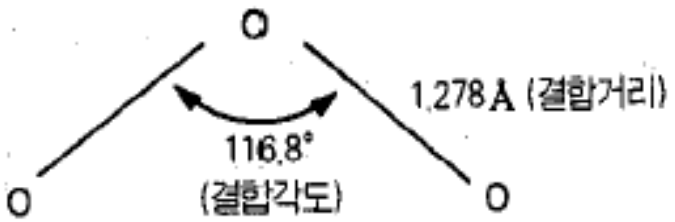
Properties of Ozone



- The name of ozone is derived from ‘ozein’, which is a Greek word meaning smell

  - Strong oxidant: ozone gives eye and skin irritations
  - Resonance structure: electrophilic & nucleophilic
  - MW: 48

- Unstable in water. Half-life at 20℃, neutral pH is around 20~30 min

  OH radical is produced during the decomposition of ozone in water.

  The ozone decomposition is accelerated under alkaline conditions

- UV absorbance : the absorption peak appears at 245 nm in gas phase, and at 260 nm in aqueous phase (ε = 3292 $M^{-1}cm^{-1}$)

- Henry’s constant:100 atm/M (20℃), 35 atm/M (0℃)

Oxidation Power of Ozone

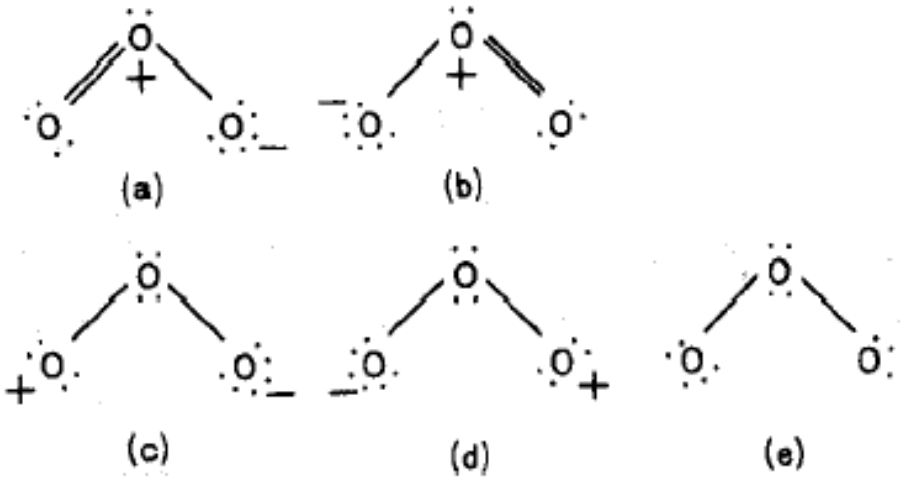
TABLE Standard Half-Cell Potentials for Chemical Oxidants Used in Water Treatment at 25°C

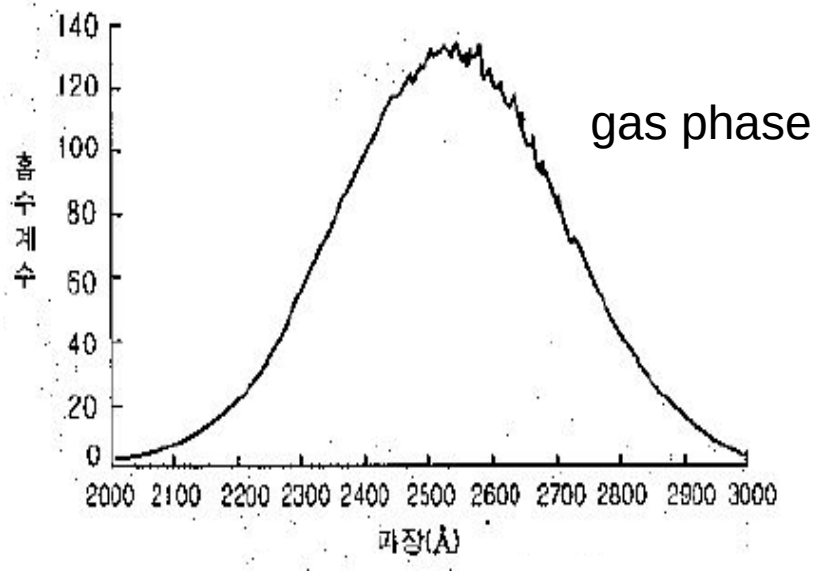
Oxidant	Reduction half-reaction	E^o_{red}, volts
Ozone	$\frac{1}{2}O_{3(aq)} + H^+ + e^- \rightarrow \frac{1}{2}O_{2(aq)} + \frac{1}{2}H_2O$	2.04
Hydrogen peroxide	$\frac{1}{2}H_2O_2 + H^+ + e^- \rightarrow H_2O$	1.78
Hydroxyl radical	$OH + H^+ + e^- \rightarrow H_2O$	2.59
Permanganate	$\frac{1}{3}MnO_4^- + \frac{4}{3}H^+ + e^- \rightarrow \frac{1}{3}MnO_{2(s)} + \frac{2}{3}H_2O$	1.68
Ferrate	$\frac{1}{3}FeO_4^{2-} + \frac{5}{3}H^+ + e^- \rightarrow \frac{1}{3}Fe(OH)_{3(s)} + \frac{1}{3}H_2O$	2.07
Chlorine dioxide	$ClO_2 + e^- \rightarrow ClO_2^-$	1.15
Hypochlorous acid	$\frac{1}{2}HOCl + \frac{1}{2}H^+ + e^- \rightarrow \frac{1}{2}Cl^- + \frac{1}{2}H_2O$	1.49
Hypochlorite ion	$\frac{1}{2}OCl^- + H^+ + e^- \rightarrow \frac{1}{2}Cl^- + \frac{1}{2}H_2O$	0.90
Hypobromous acid	$\frac{1}{2}HOBr + \frac{1}{2}H^+ + e^- \rightarrow \frac{1}{2}Br^- + \frac{1}{2}H_2O$	1.33
Hypoiodous acid	$\frac{1}{2}HOI + \frac{1}{2}H^+ + e^- \rightarrow \frac{1}{2}I^- + \frac{1}{2}H_2O$	0.98
Monochloramine	$\frac{1}{2}NH_2Cl + H^+ + e^- \rightarrow \frac{1}{2}Cl^- + \frac{1}{2}NH_4^+$	1.40
Dichloramine	$\frac{1}{4}NHCl_2 + \frac{3}{4}H^+ + e^- \rightarrow \frac{1}{2}Cl^- + \frac{1}{4}NH_4^+$	1.34
Oxygen	$\frac{1}{4}O_{2(aq)} + H^+ + e^- \rightarrow \frac{1}{2}H_2O$	1.27

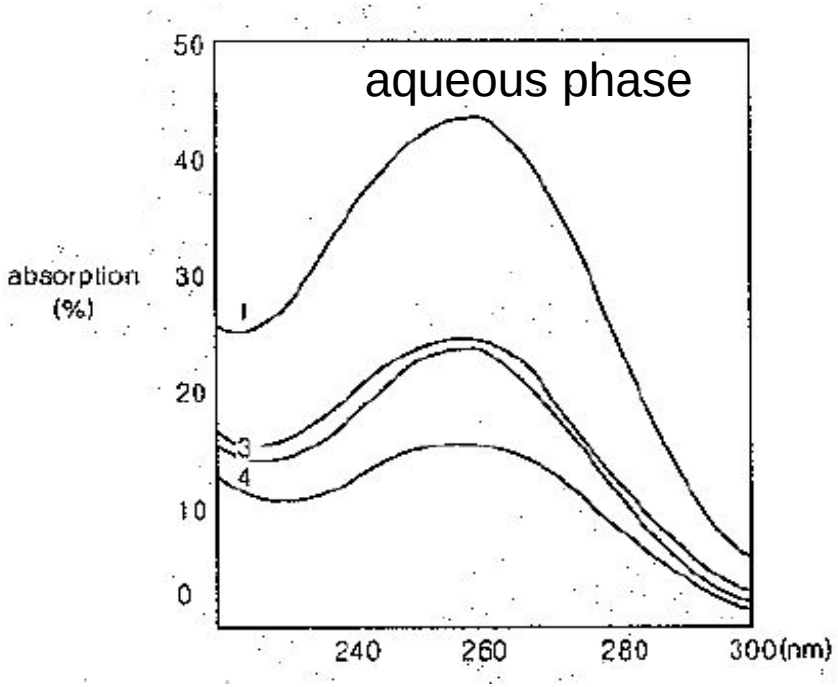
$O_3 + e^- \rightarrow O_3^{\bullet -}$ $E = 1.01$ V

Weak one-electron oxidant

Resonance Structure and UV Absorption



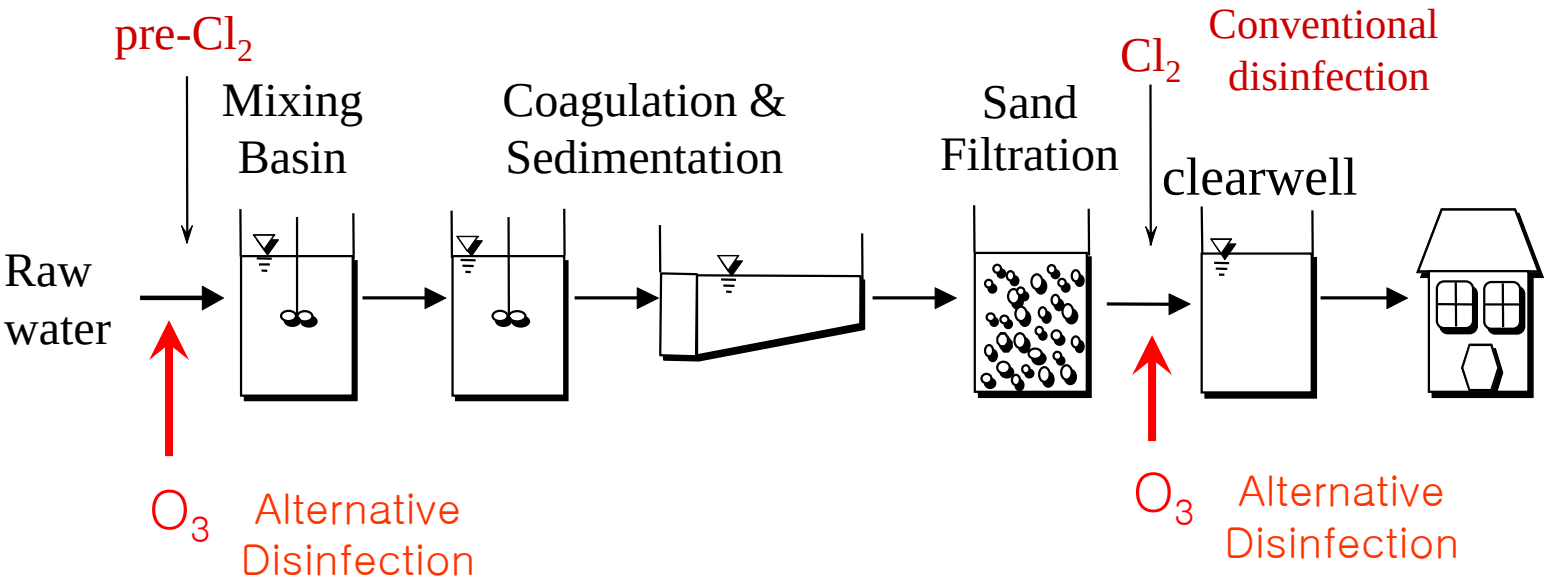




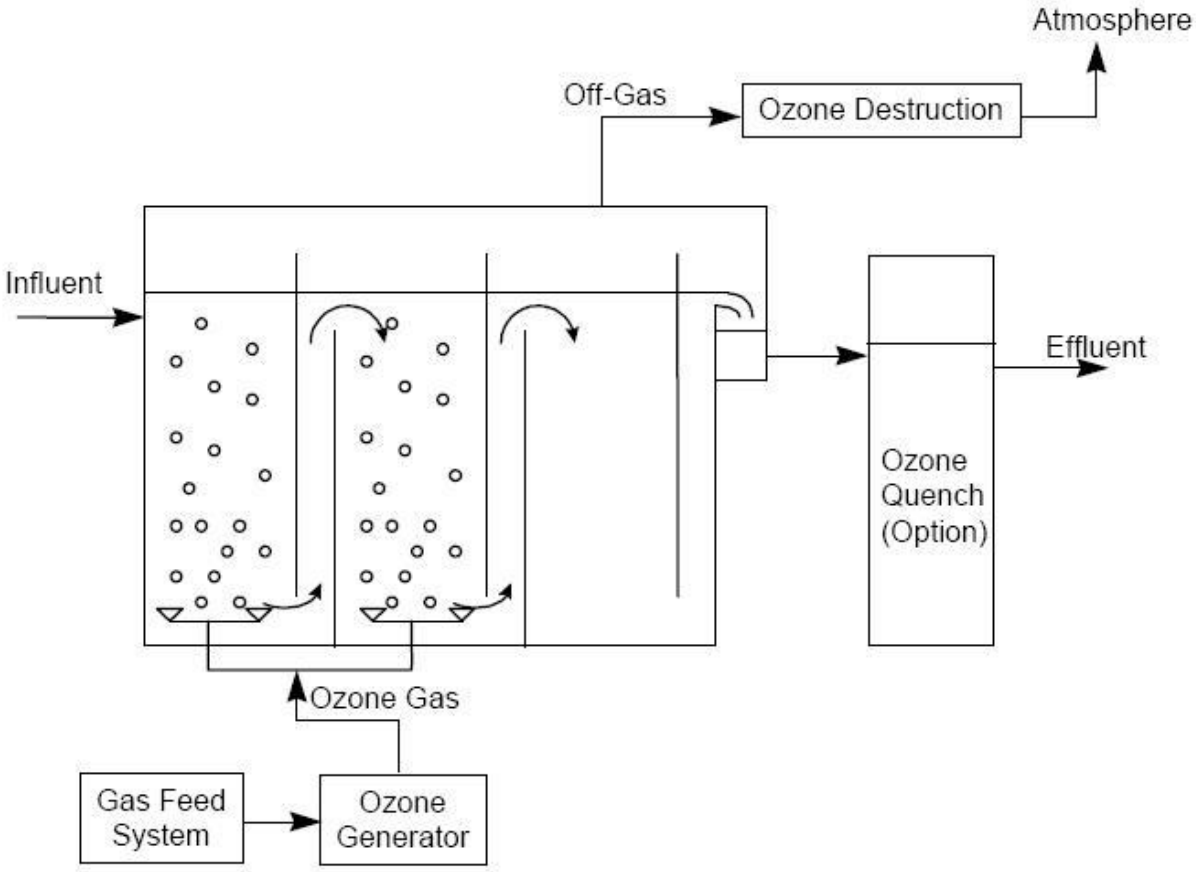
Ozonation for Water and Wastewater Treatment

- Drinking water treatment
- Waste water treatment
- Sewage water treatment
- Groundwater treatment

Ozonation for Water Treatment



Ozonation System for Water Treatment



Four basic components

The ozonation system for water treatment consists of four basic components;

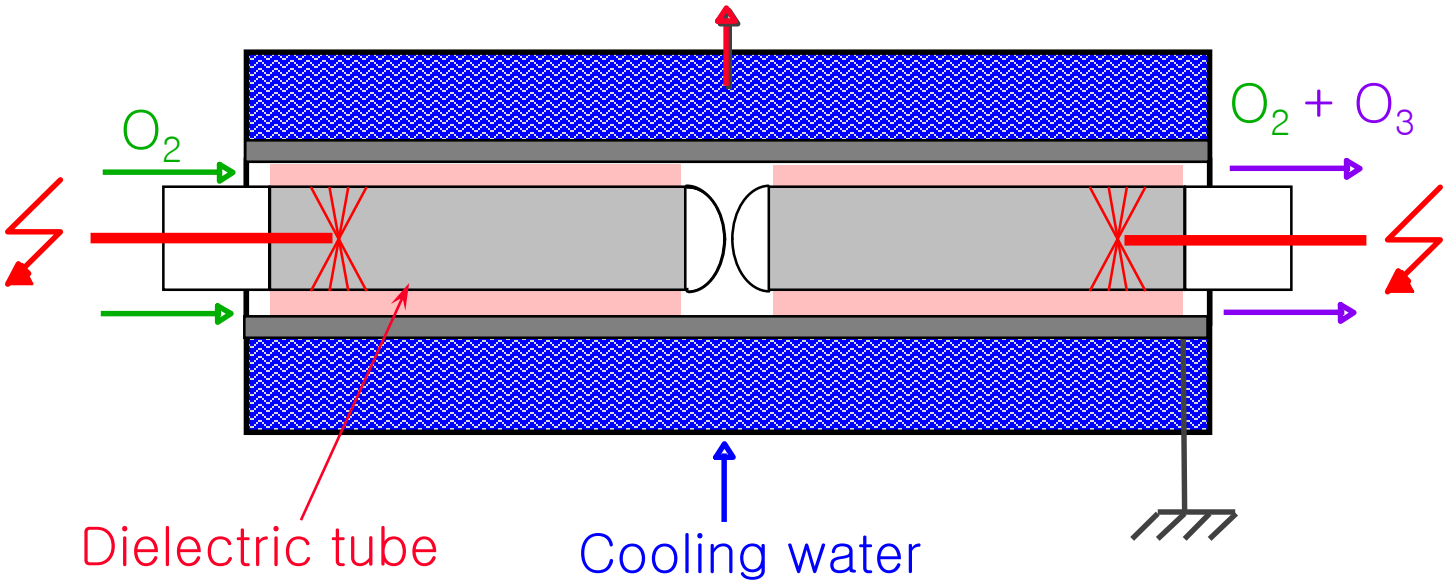
A. Gas feed system

B. Ozone generator

C. Ozone contactor

D. Off-gas destruction system

Ozone Generator



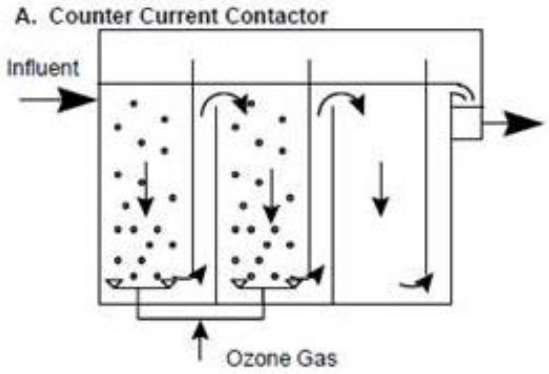
Ozone generation

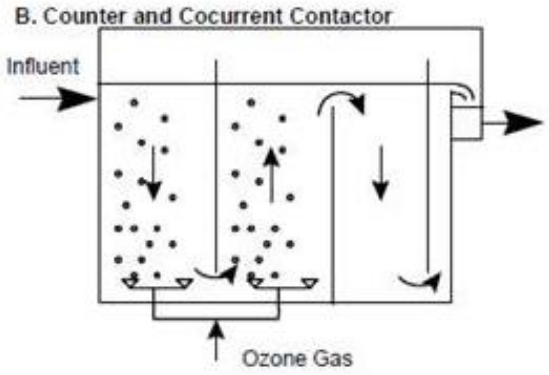
First, the ozone generation was discovered in the electrolysis of sulfuric acid. Ozone can be produced by several ways, but corona discharge is predominantly used in industry

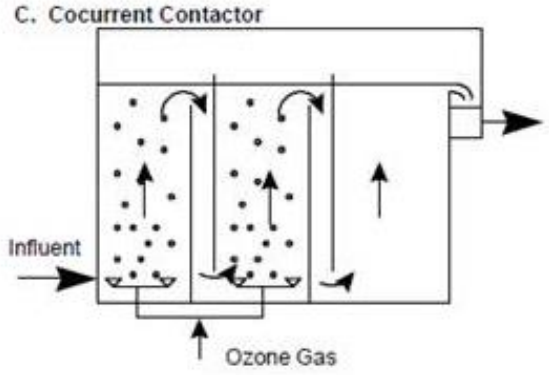
Corona discharge

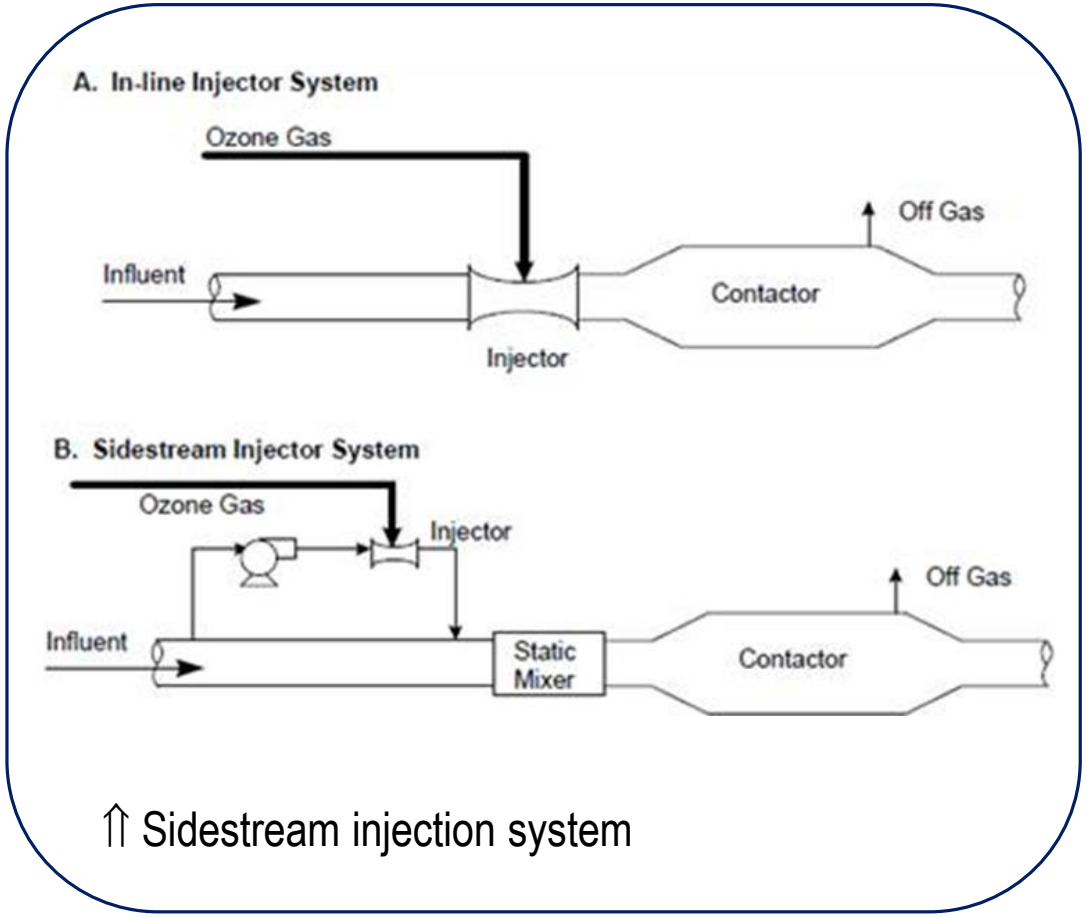
Oxygen-containing gas passes through two electrodes separated by dielectric discharge gap. These electrons provide energy to disassociate dioxygen molecules into atomic oxygen.

Ozone Contactor (Ozonation Reactor)









⇑ Sidestream injection system

⇐ Bubble diffuser contactor

Ozone Generator & Ozone Contactor

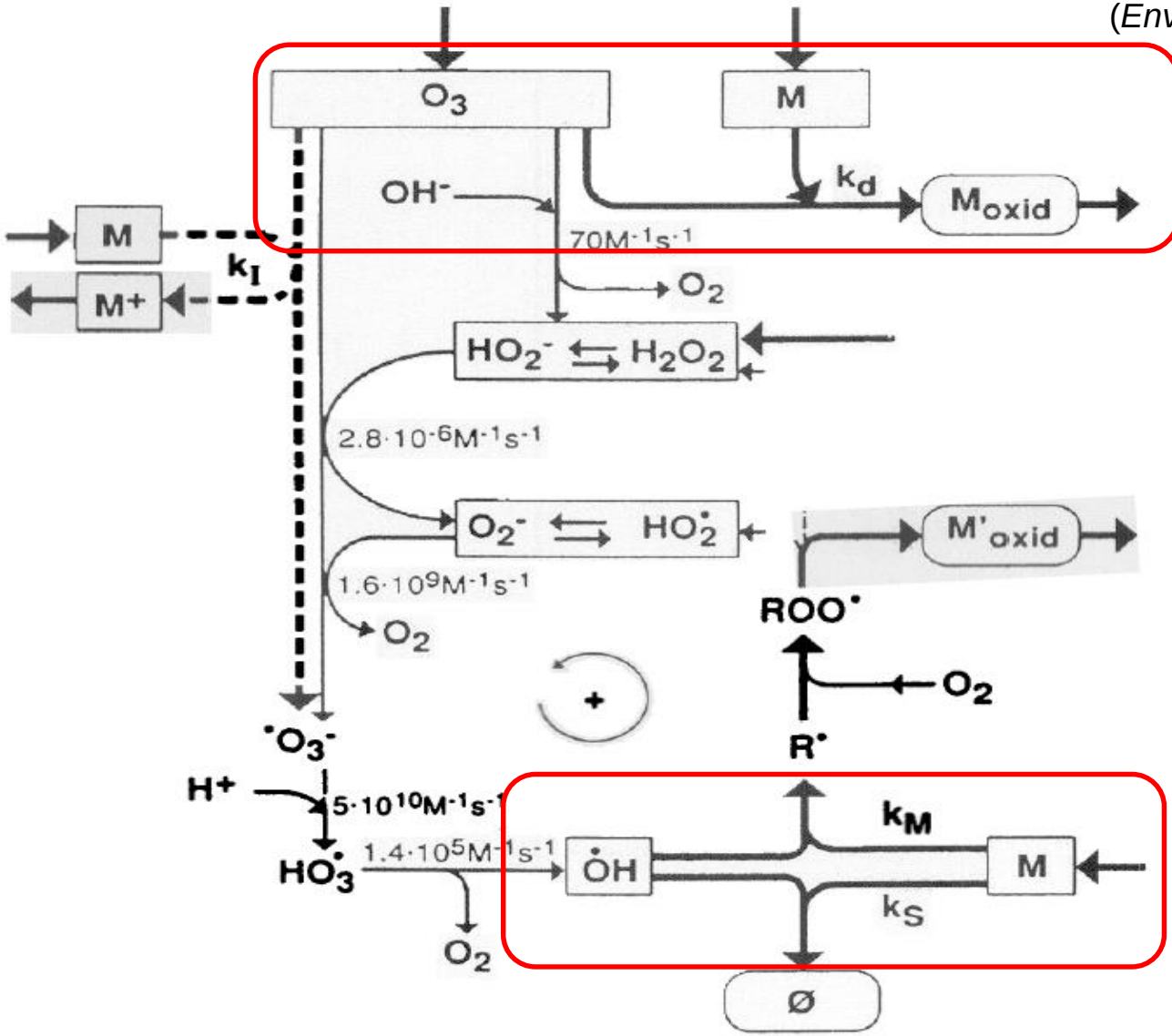
- Duksan DWTP, Busan, Korea

1. Ozone generator

2. Ozone contactor

Chemistry of Ozone Decomposition

Staehelln and Hoigne, 1985
(*Environ. Sci. Technol.*)



Chemistry of Ozone Decomposition

The pH of the water is important because OH^- initiates ozone decomposition

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad k = 70\ M^{-1}\ s^{-1}$$

$$O_3 + HO_2^- \rightarrow \cdot OH + O_2^{-}\cdot + O_2\ , \qquad k = 2.8 \times 10^6\ M^{-1}\ s^{-1}$$

$$O_3 + O_2^{-}\cdot \rightarrow O_3^{-}\cdot + O_2\ , \qquad k = 1.6 \times 10^9\ M^{-1}\ s^{-1}$$

The initiation of ozone decomposition can be accelerated by increasing pH or by adding hydrogen peroxide

$pK_a\ (H_2O_2) = 11.6$
$pK_a\ (HO_2\cdot) = 4.8$
$HO_2\cdot$: Hydorperoxide radical
$O_2\cdot$- : superoxide radical, O_3-$\cdot$: ozonide radical

Chemistry of Ozone Decomposition

pH < 8 $O_3^{-}\cdot + H^+ \Leftrightarrow HO_3\cdot$, $k_1 = 1.6 \times 10^9\ M^{-1}\ s^{-1}$, $k_2 = 3.3 \times 10^2\ s^{-1}$

$HO_3\cdot \rightarrow \cdot OH + O_2$, $k = 1.4 \times 10^5\ s^{-1}$

pH > 8 $O_3^{-}\cdot \Leftrightarrow O^{-}\cdot + O_2$, $k_1 = 2.1 \times 10^3\ M^{-1}\ s^{-1}$, $k_2 = 3.3 \times 10^9\ s^{-1}$

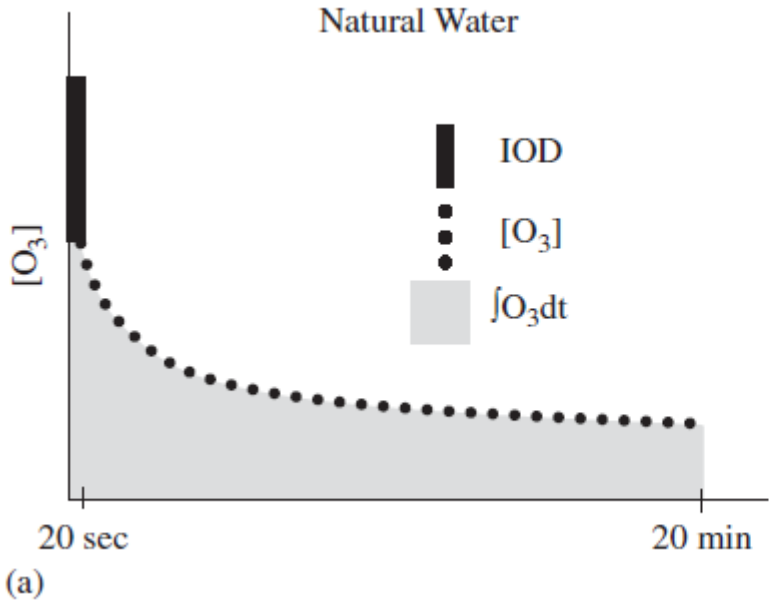
$O^{-}\cdot \rightarrow \cdot OH + OH^-$, $k = 10^8\ s^{-1}$

$\cdot OH + O_3 \rightarrow HO_2\cdot + O_2$ $k = 0.1 \sim 2 \times 10^9\ M^{-1}\ s^{-1}$

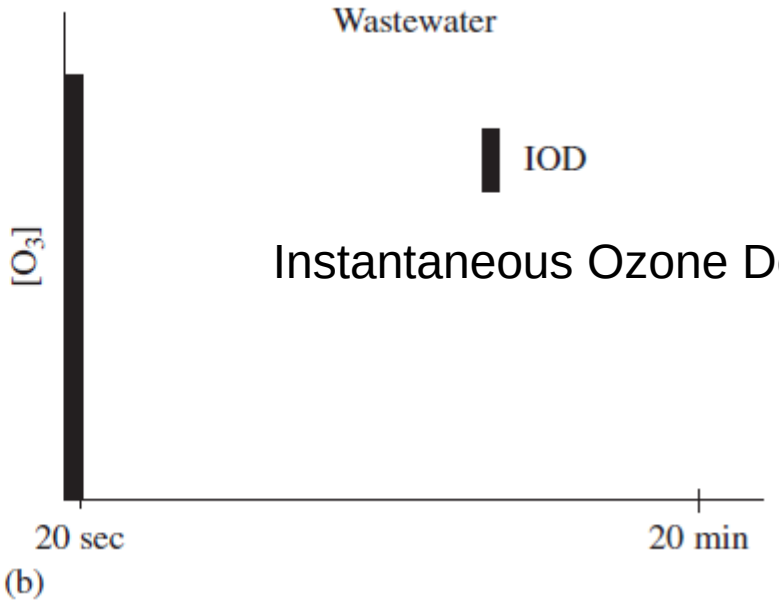
This reaction is fast and important particularly when the ·OH scavenger concentration is low in water.
It leads to the consumption of ozone and ·OH, lowering the oxidation capacity of the system.

Ozone Decay in Contaminated Waters

Oligotrophic surface water
Groundwater



Eutrophic surface water
Wastewater



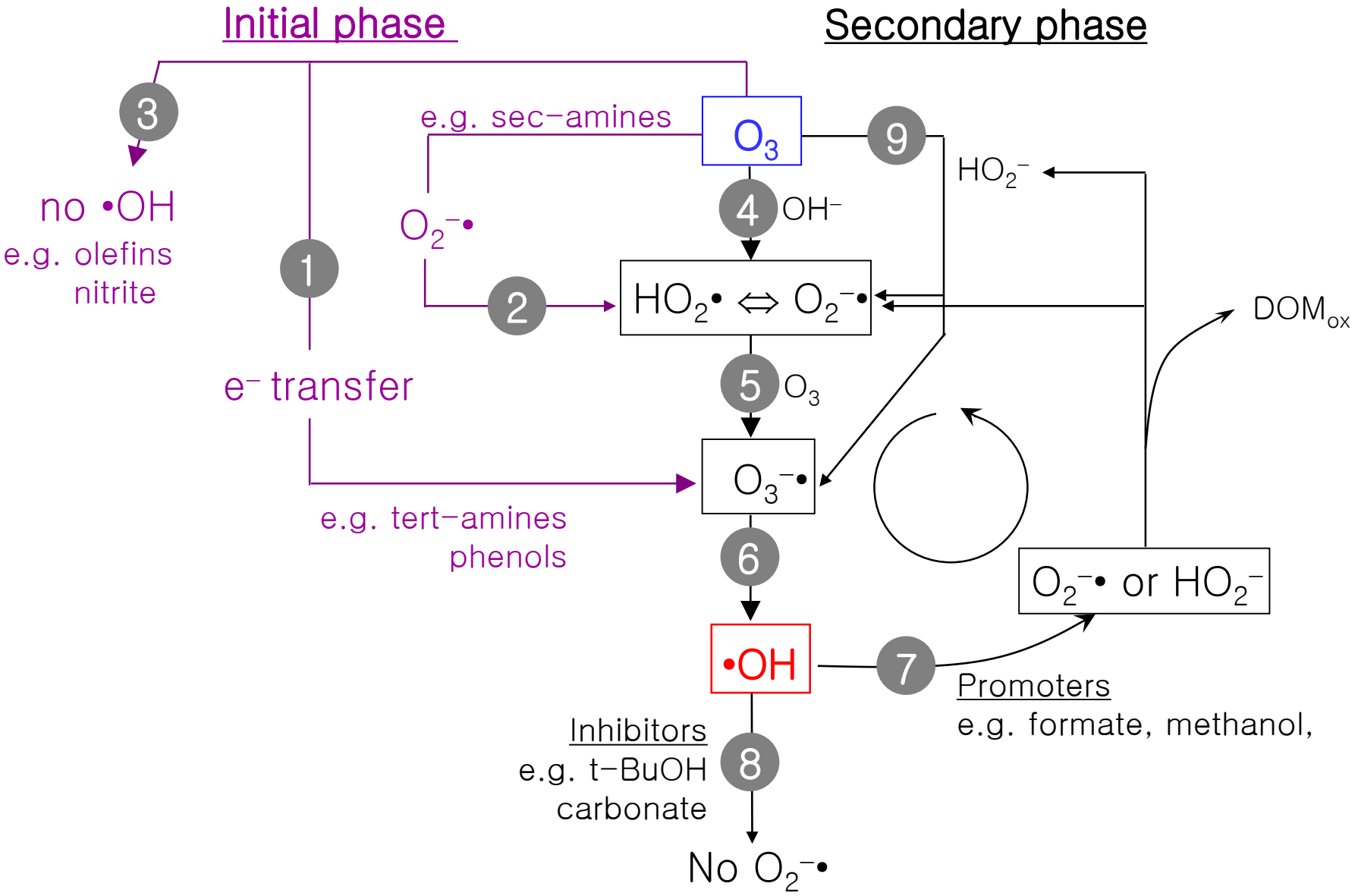
- Drinking water

  DOC $\leq$ 4 mg/L, $HCO_3^-/CO_3^{2-} \leq$ 6 mM, pH 6-8

- Wastewater

  6 $\leq$ DOC $\leq$ 15 mg/L, HCO_3^-/CO_3^{2-} 6 $\leq$ mM, pH 6-8

Promotors and Inhibitors for Ozone Decomposition



Reactions of Ozone with NOM and Carbonates

Molecular ozone reacts with NOM (natural organic matter) in different mechanisms.

(1) $O_3 + NOM_1 \rightarrow NOM_{1ox}$

(2) $O_3 + NOM_2 \rightarrow NOM_2^{+}\cdot + O_3^{-}\cdot$

(3) $\cdot OH + NOM_3 \rightarrow NOM_3^{\cdot} + H_2O$ or $NOM_3^{\cdot} + OH^-$

$NOM_3^{\cdot} + O_2 \rightarrow NOM\text{-}O_2^{\cdot} \rightarrow NOM_3^{+} + O_2^{\cdot -}$

(4) $\cdot OH + NOM_4 \rightarrow NOM_4^{\cdot} + H_2O$

$NOM_4^{\cdot} + O_2 \rightarrow NOM_4\text{-}O_2^{\cdot} \rightarrow$ no $O_2^{\cdot -}$ formation

Carbonates are important ·OH sinks in natural water (sources of $CO_3^{\cdot -}$).

$\cdot OH + CO_3^{2-} \rightarrow CO_3^{\cdot -} + OH^-$ $k=3.9 \times 10^8\ M^{-1}s^{-1}$

$\cdot OH + HCO_3^{-} \rightarrow CO_3^{\cdot -} + H_2O$ $k=8.5 \times 10^6\ M^{-1}s^{-1}$

Reactions of Ozone with NOM and Carbonates

$CO_3^{\cdot -}$ is also a reactive oxidant, and is easily scavenged by NOM

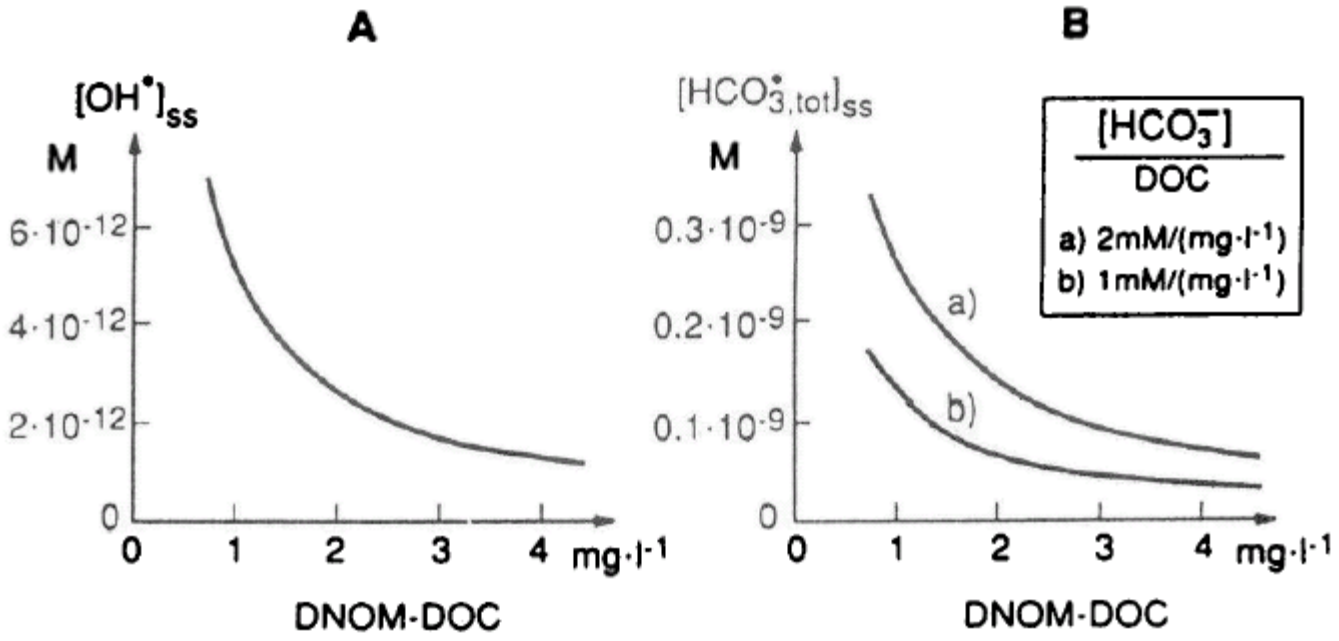
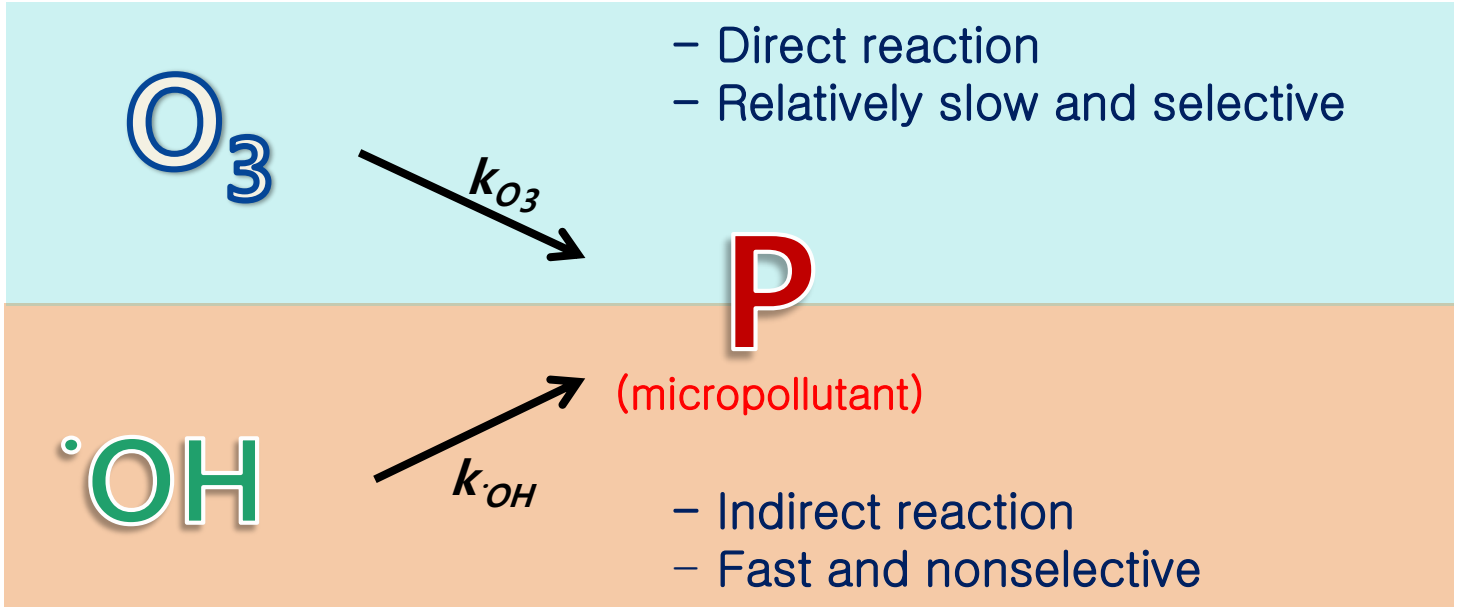


Fig. Steady-state concentrations of $OH^{\cdot}$ and $HCO_3^{\cdot}/CO_3^{\cdot -}$ that occur in a water as a function of DOC.

Assumptions: **A:** 2.4 mg/l O_3 are transformed within 100 s (i.e. 0.5 $\mu M \cdot s^{-1}$) to produce $OH^{\cdot}$ with a yieldfactor of 0.5; $OH^{\cdot}$-scavenging rate-coefficient from Fig. 14. **B:** As for A, and: half of the $OH^{\cdot}$ produced react with HCO_3^- to produce $HCO_3^{\cdot}/CO_3^{\cdot -}$; $HCO_3^{\cdot}/CO_3^{\cdot -}$-scavenging rate-coefficient are from Fig. 16

Oxidation of Contaminants by Ozonation



› Second-Order rate constant for the reaction of ozone and ·OH

Compound	k_{O3} ($M^{-1}s^{-1}$)	$k_{\cdot OH}$ ($M^{-1}s^{-1}$)
Atrazine	6	3×10^9
Geosmin	<10	8.2×10^9
Carbofuran	620	7×10^9
Dinoseb	1.5×10^5	4×10^9

Oxidation of Contaminants by Ozonation

Kinetics of pollutant oxidation by ozonation

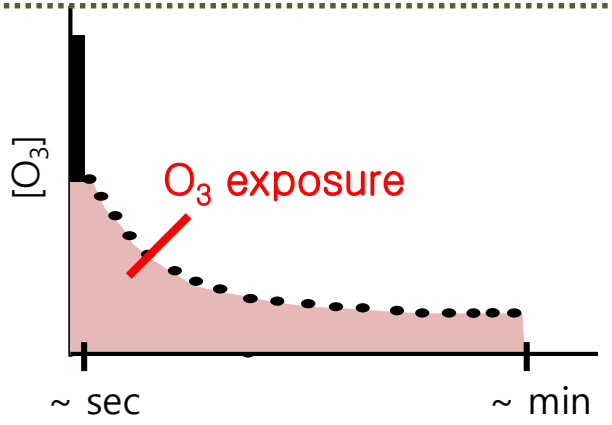
$$-d[P]/dt = k_{O3}[P][O_3] + k_{\bullet OH}[P][\bullet OH]$$

$$Ln([P]/[P]_0) = -(k_{O3} \int [O_3]dt + k_{\bullet OH} \int [\bullet OH]dt)$$

•OH exposure

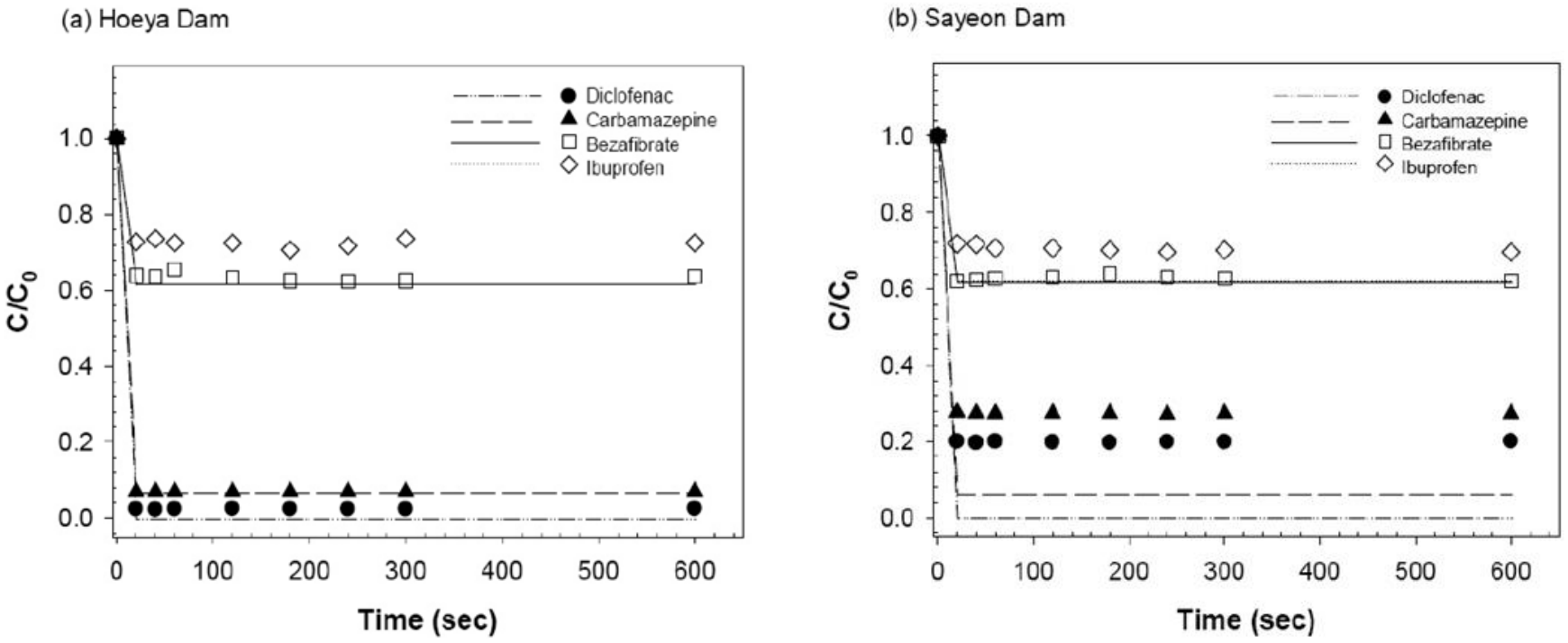
$$Ln([pCBA]/[pCBA]_0) = -k_{OH,,pCBA} \int [OH]_t dt$$

*pCBA: a •OH probe



Oxidation of Contaminants by Ozonation

Lee et al, 2013 (*JKSWW*)

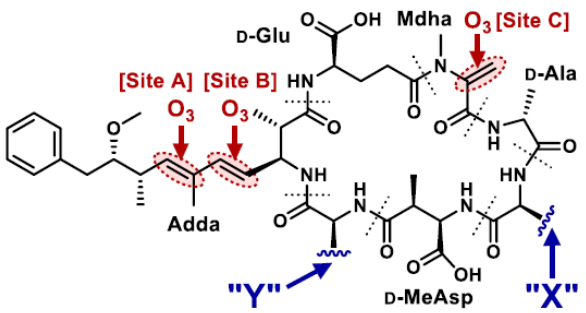


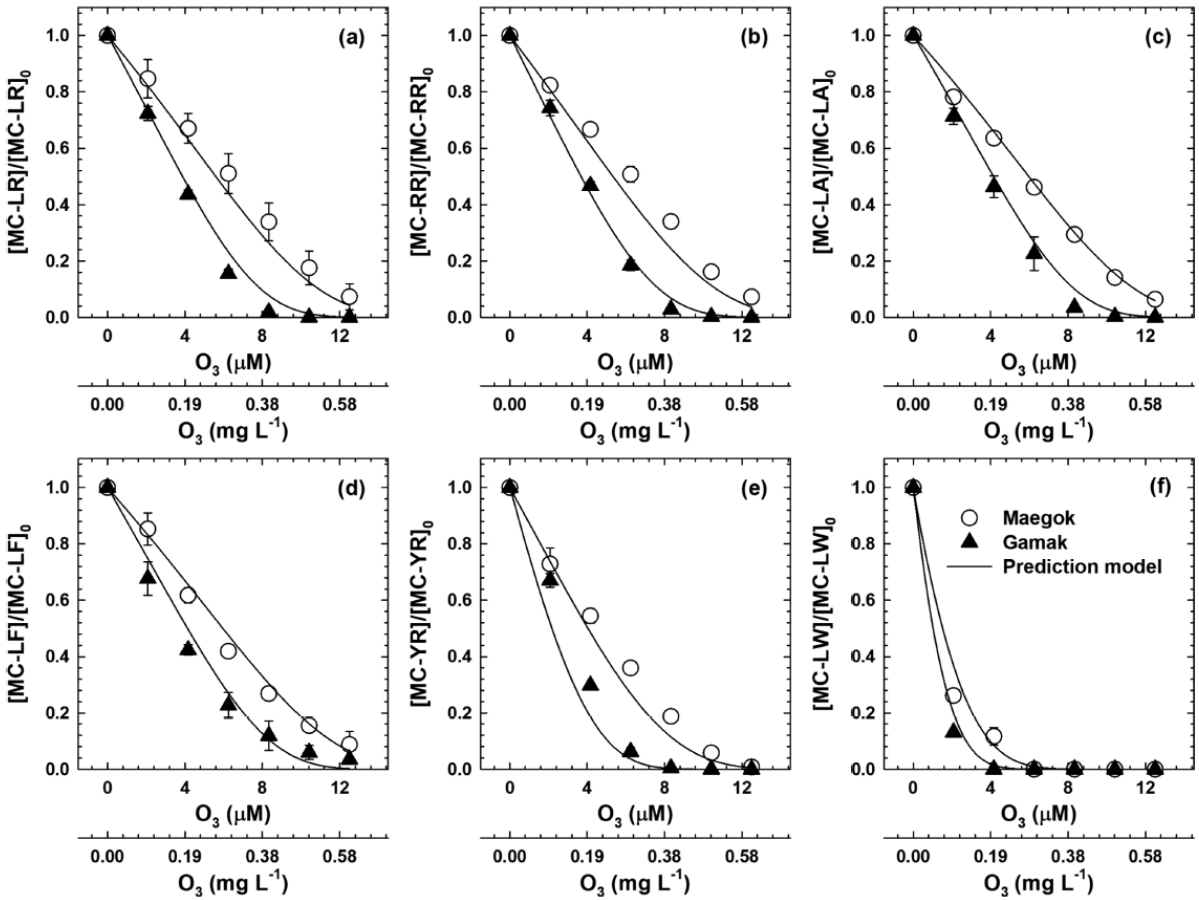
Symbols: experimental data, Lines: model predictions

Oxidation of Contaminants by Ozonation

Kim and Lee, 2019 (*Environ. Sci. Technol.*)

- Ozonation of microcystins





Symbols: experimental data, Lines: model predictions

The R_{ct} Concept

Elovitz and von Gunten (1999)

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

$$Ln([P]/[P]_0) = -(k_{O3} \int [O_3]dt + k_{\bullet OH} \int [\bullet OH]dt)$$

$$Ln([P]/[P]_0) = -(k_{O3} + R_{ct} k_{\bullet OH}) \int [O_3]dt$$

$$R_{ct} = \int [\cdot OH]_t / \int [O_3]_t$$

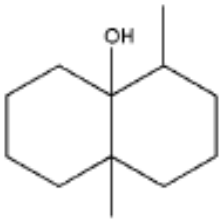
- R_{ct} : the ratio of •OH exposure to O_3 exposure (assumed to be almost constant over time)
- R_{ct} is dependent on water conditions and the O_3 dose and the input of H_2O_2.

The R_{ct} Concept

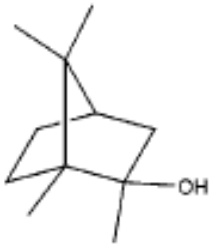
Table Comparison of R_{ct} values determined during ozonation of natural waters

No.		Conditions	R_{ct}	Reference
1	Surface waters of Ulsan, Korea	ozone, $[O_3]_0$ = 2 ppm	$(1.2 \sim 1.5) \times 10^{-7}$	This study
2	Han River of Seoul, Korea	ozone, $[O_3]_0$ = 1.56 ppm	4.6×10^{-8}	Cho et al., 2003
3	North Saskatchewan River water, Canada	ozone, $[O_3]_0$ = 5 ppm	1.8×10^{-8}	Chelme-Ayala et al., 2011
4	Lake Zurich water, Switzerland	ozone, $[O_3]_0$ = 2 ppm	1.9×10^{-8}	Lee et al., 2007
5	Lake Zurich water, Switzerland	O_3/H_2O_2, $[O_3]_0$ = 2 ppm	7.8×10^{-7}	Lee et al., 2007

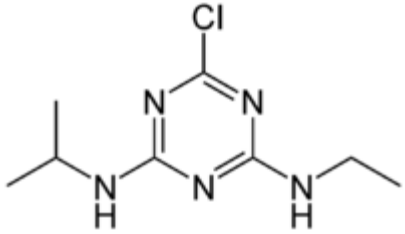
Ozone-Resistant Contaminants



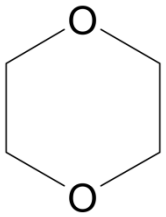
Geosmin



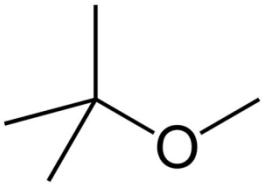
2-MIB



Atrazine



1,4-Dioxane



MTBE

Benzene

Fast conversion of O_3 into $^{\bullet}OH$ is needed.

Modified Ozonation Processes

O_3/H_2O_2 Process

$$H_2O_2 \Leftrightarrow HO_2^- + H^+ \quad pK_a = 11.8$$

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2$$

Source: Applied Process Technology, Inc.

UV/O_3 Process

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2$$

$$H_2O_2 \Leftrightarrow HO_2^- + H^+ \quad pK_a = 11.8$$

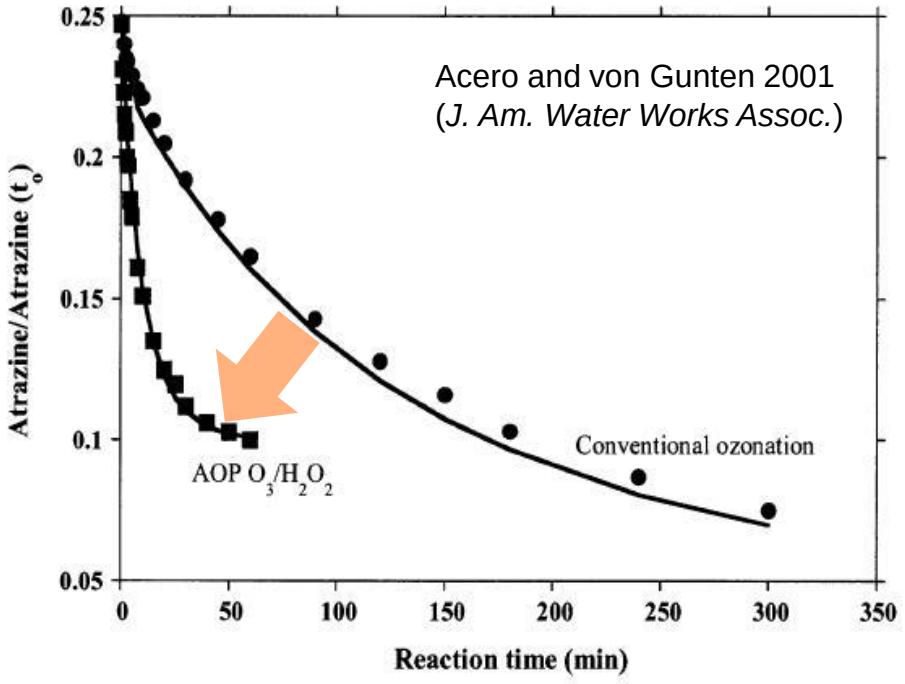
$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2$$

Source: Spartan Co.

Conventional Ozonation vs. O_3/H_2O_2 AOP

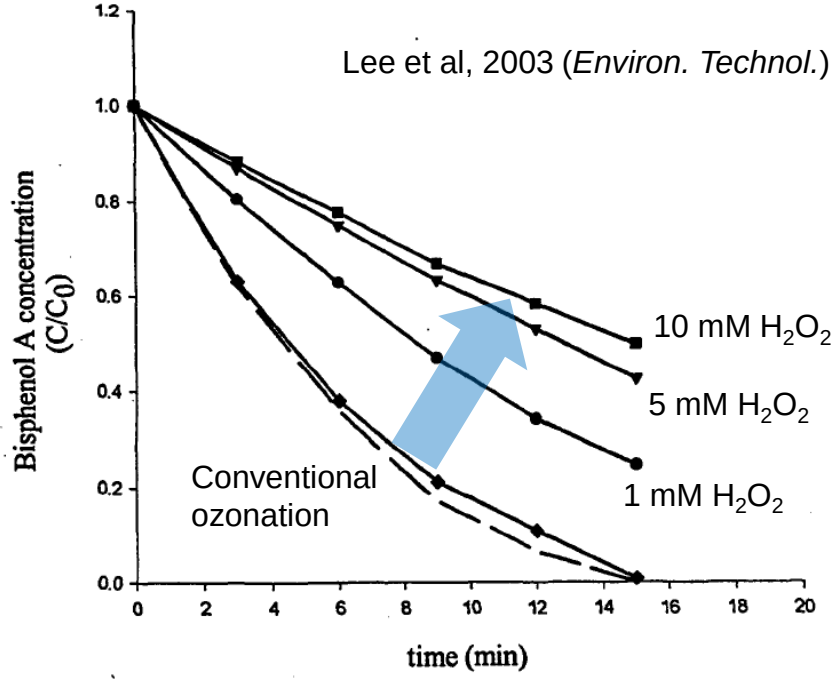
Atrazine

$k_{O3} = 6\ M^{-1}s^{-1}$



Bisphenol-A

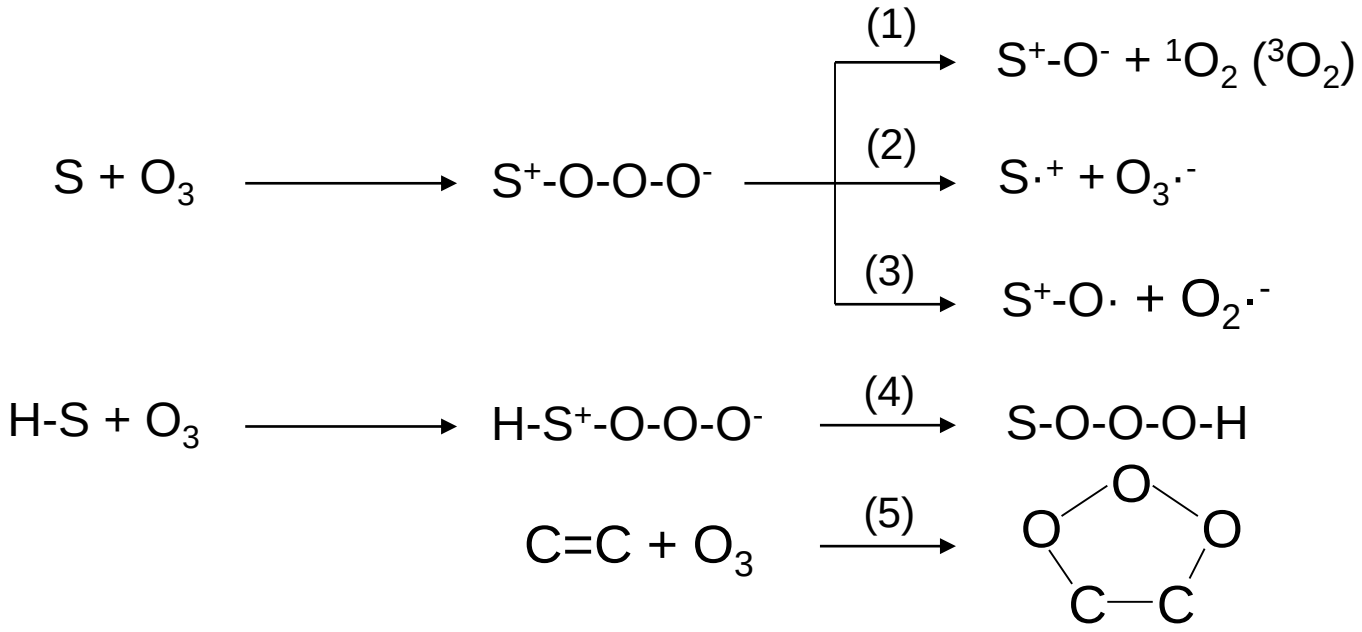
$k_{O3} = 2.7 \times 10^6\ M^{-1}s^{-1}$ at pH 7



Reactions of Ozone with Contaminants

- Mechanisms of ozone reactions

Primary reactions of ozone with a compound (S)



(1) Oxygen atom transfer to anionic, uncharged and cationic species

(2) Electron transfer (3) Formation of an oxyl radical

(4) Ozone insertion (5) Ring formation

Reactions of Ozone with Contaminants

- Electron transfer reactions

$$O_2^- + O_3 \longrightarrow O_2 + O_3^- \quad (1)$$

superoxide ion — *ozonide anion*

$$HO_2^- + O_3 \longrightarrow HO_2^{\bullet} + O_3^- \quad (2)$$

hydroperoxide anion — *hydroperoxyl* — *ozonide anion*

- Oxygen atom transfer reactions

$$OH^- + O_3 \longrightarrow HO_2^- + O_2 \quad (3)$$

hydroperoxide anion

$$Fe^{2+} + O_3 \longrightarrow FeO^{2+} + O_2 \quad (4)$$

$Fe^{(IV)}$

$$NO_2^- + O_3 \longrightarrow NO_3^- + O_2 \quad (5)$$

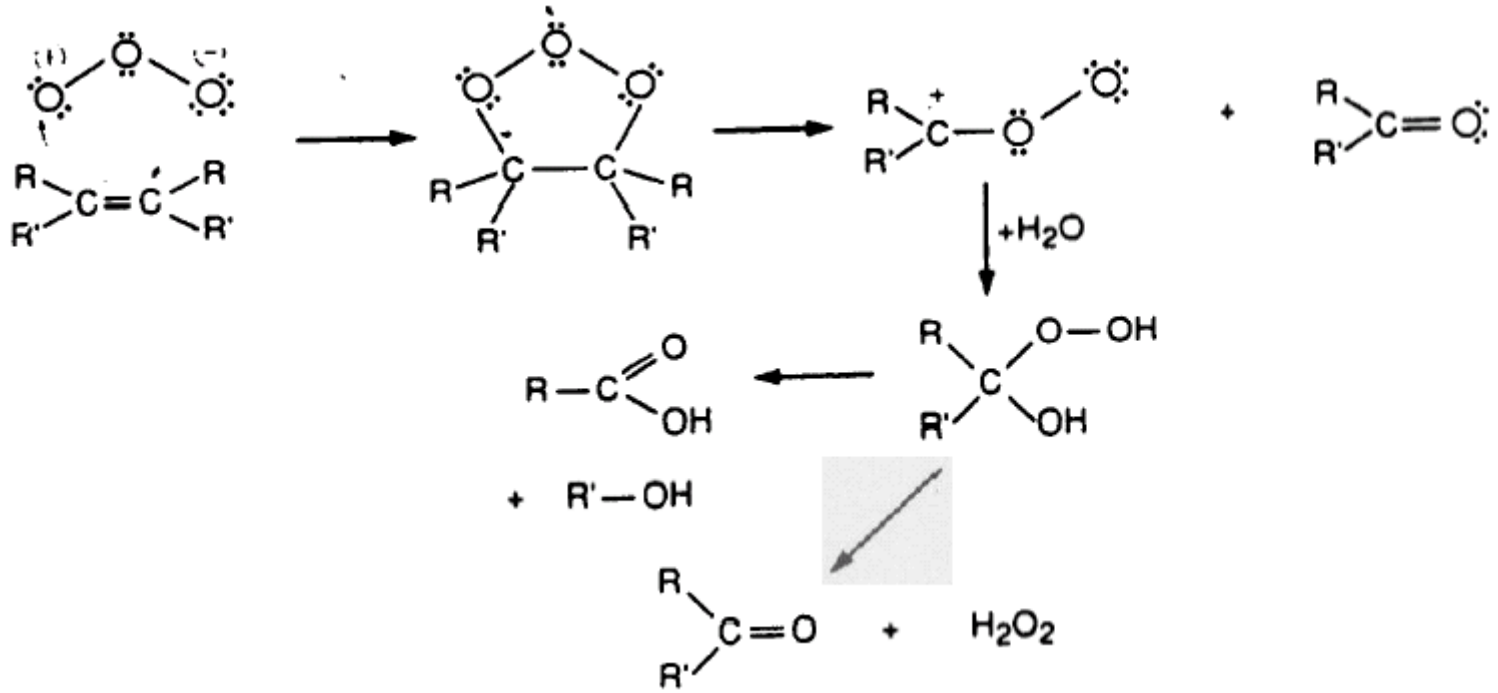
$$Br^- + O_3 \longrightarrow BrO^- + O_2 \quad (6a)$$

$$I^- + O_3 \longrightarrow IO^- + O_2 \quad (6b)$$

(at high $[I^-]$ follows: $IO^- + H^+ \rightarrow IOH + I^- \rightarrow I_2 + OH^-$)

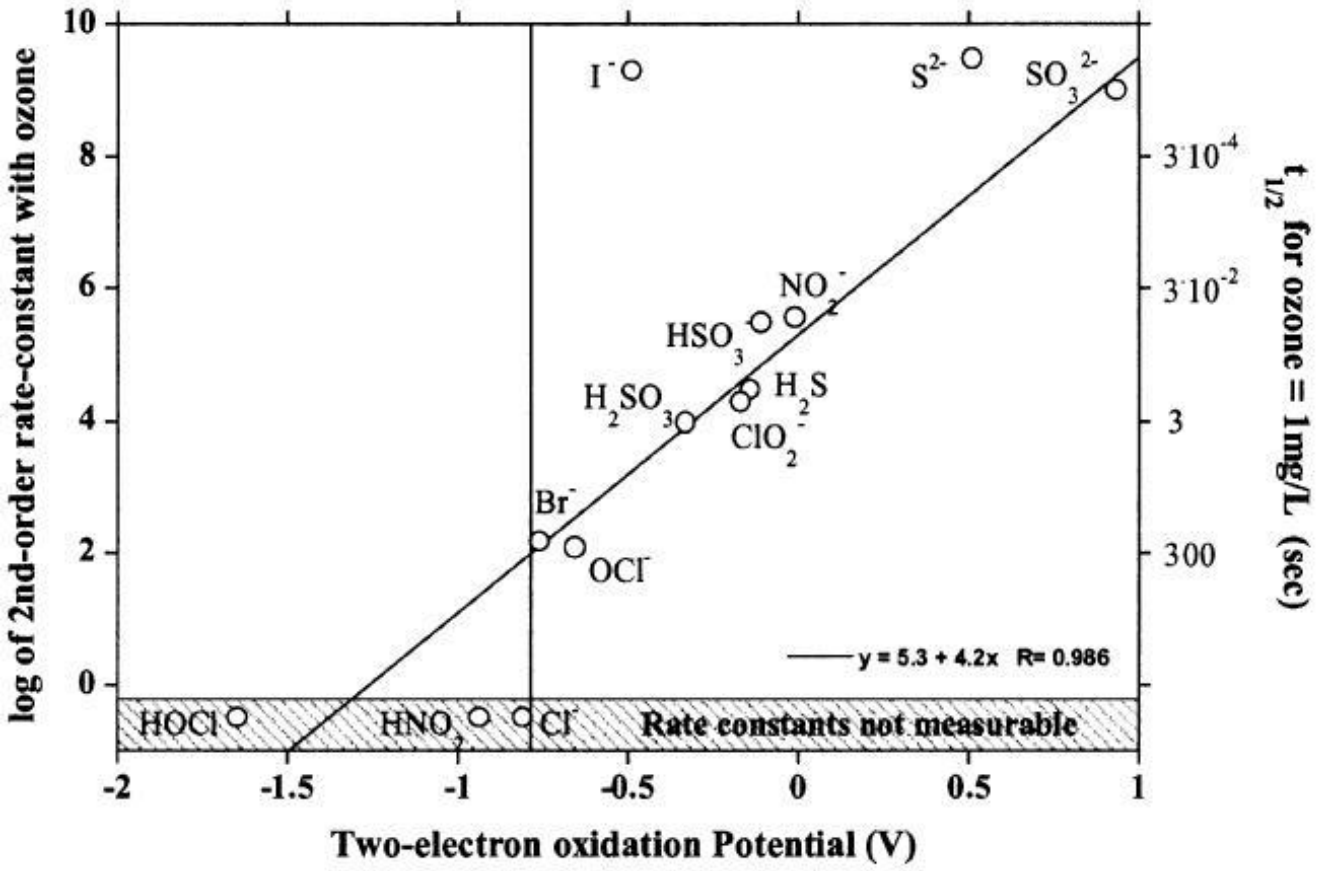
Reactions of Ozone with Contaminants

- Ozone addition reaction (Criegee mechanism)



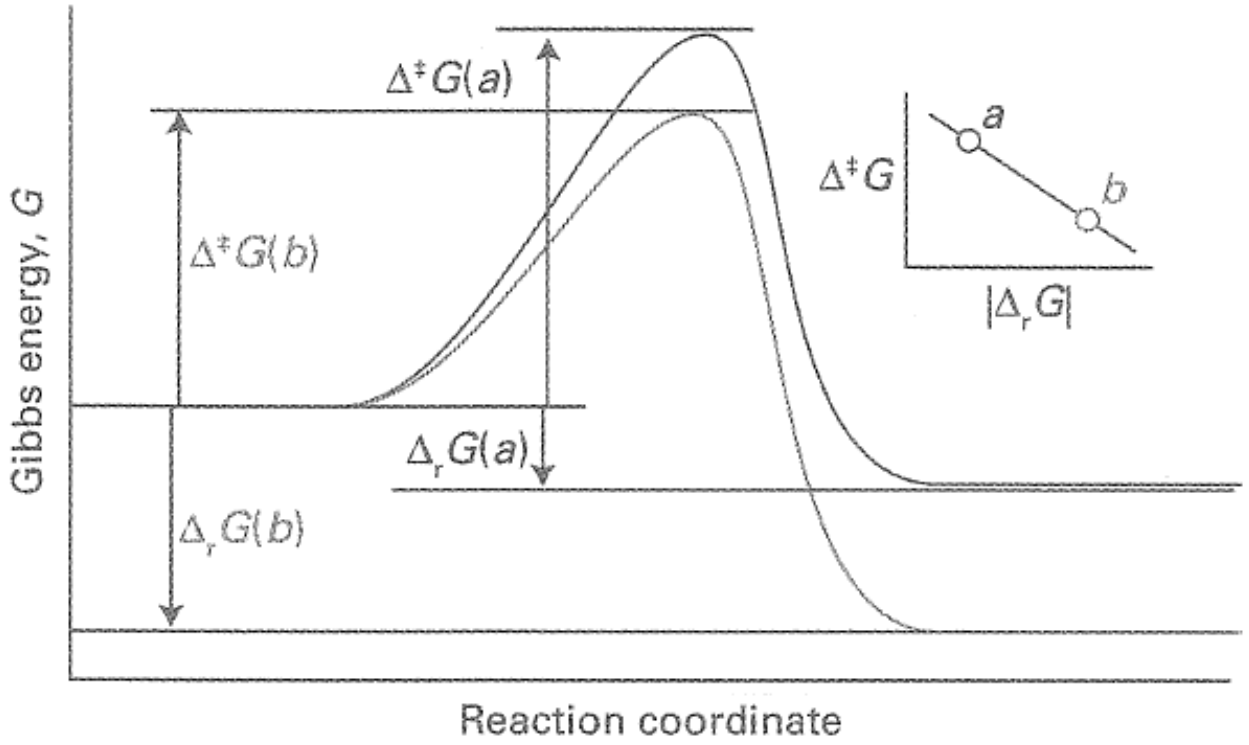
Reactions of Ozone with Contaminants

- Linear free energy relation between two electron redox potential and the rate constant by ozone



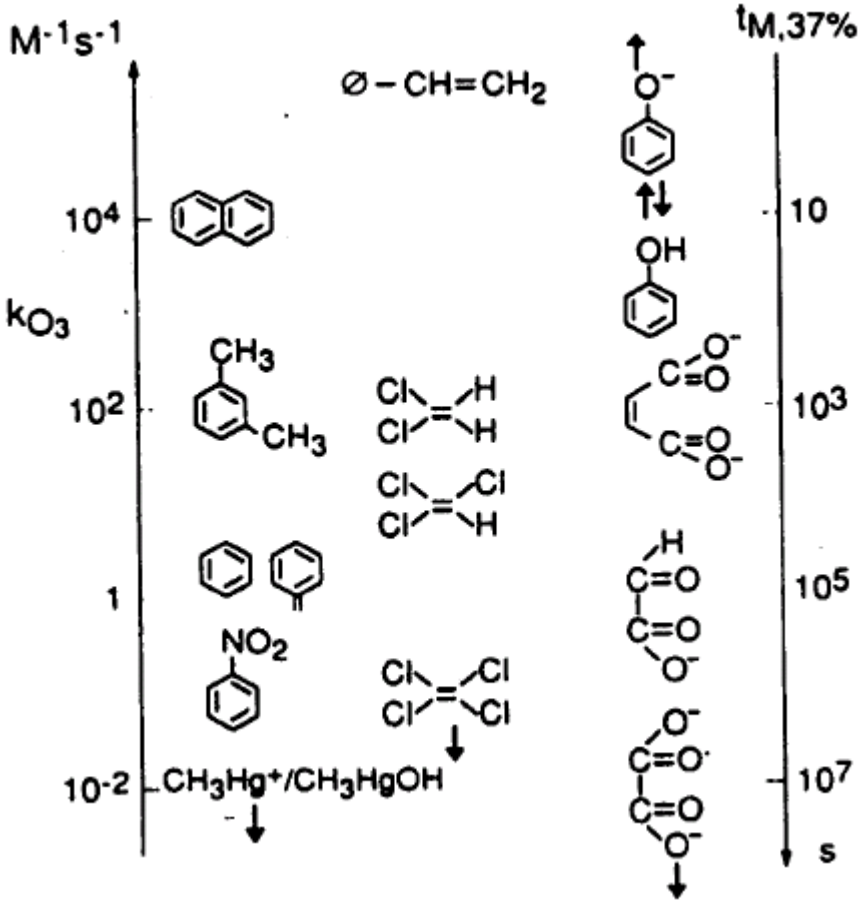
- **Thermodynamics vs. Kinetics**

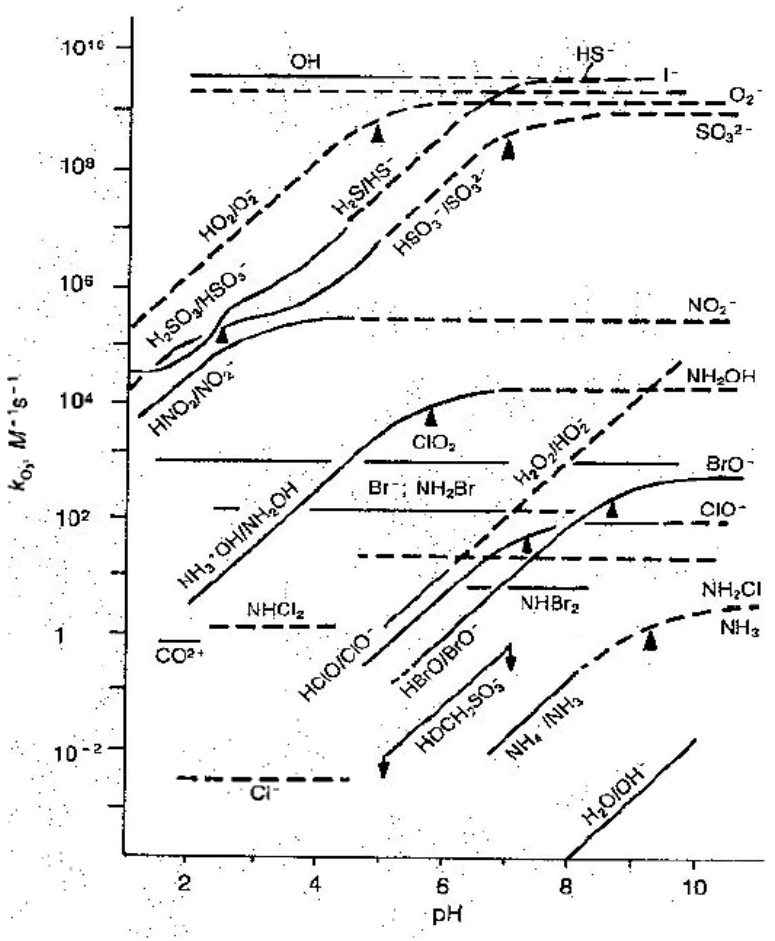
From Atkins' Physical Chemistry



Reactions of Ozone with Contaminants

- Second-order rate constants for reactions of ozone with various compounds





Reactions of Ozone with Contaminants

Compound	k_{O_3} ($M^{-1}\,s^{-1}$)	$t_{1/2}$	k_{OH} ($M^{-1}\,s^{-1}$)
Algal products			
Geosmin	$<10^{a}$	>1 h	8.2×10^{9}
2-Methylisoborneol (MIB)	$<10^{a}$	>1 h	$\approx 3 \times 10^{9}$
Mycrocystin-LR	3.4×10^{4}	1 s	

Compound	k_{O_3} ($M^{-1}\,s^{-1}$)	$t_{1/2}$	k_{OH} ($M^{-1}\,s^{-1}$)
Pesticides			
Atrazine	6	96 min	3×10^{9}
Alachlor	3.8	151 min	7×10^{9}
Carbofuran	620	56 s	7×10^{9}
Dinoseb	$1.5 \times 10^{5\,b}$	0.23 s	4×10^{9}
Endrin	<0.02	>20 d	1×10^{9}
Methoxychlor	270	2 min	2×10^{10}

Half life: 1 mg/L [O_3] at pH = 7

Reactions of Ozone with Contaminants

Compound	k_{O_3} ($M^{-1}s^{-1}$)	$t_{1/2}$	k_{OH} ($M^{-1}s^{-1}$)
Solvents			
Chloroethene	1.4×10^4	2.5 s	1.2×10^{10}
Cis-1,2-dichloroethene	540	64 s	3.8×10^9
Trichloroethene	17	34 min	2.9×10^9
Tetrachloroethene	<0.1	>4 d	2×10^9
Chlorobenzene	0.75	13 h	5.6×10^9
p-Dichlorobenzene	$\ll 3$	$\gg 3$ h	5.4×10^9

Compound	k_{O_3} ($M^{-1}s^{-1}$)	$t_{1/2}$	k_{OH} ($M^{-1}s^{-1}$)
Fuel (additives)			
Benzene	2	4.8 h	7.9×10^9
Toluene	14	41 min	5.1×10^9
o-Xylene	90	6.4 min	6.7×10^9
MTBE	0.14	2.8 d	1.9×10^9
t-BuOH	$\sim 3 \times 10^{-3}$	133 d	6×10^8
Ethanol	0.37	26 h	1.9×10^9

Half life: 1 mg/L [O_3] at pH = 7

Reactions of Ozone with Contaminants

Compound	k_{O_3} ($M^{-1}\,s^{-1}$)	$t_{1/2}$[c]	k_{OH} ($M^{-1}s^{-1}$)
Nitrite (NO_2^-)	3.7×10^5	0.1 s	6×10^9
Ammonia (NH_3/NH_4^+)	20/0	96 h	9.7×10^7 [d]
Cyanide (CN^-)	10^3–10^5 [a]	~1 s	8×10^9
Arsenite ($H_2AsO_3^-$)	>7[b]	82 min	8.5×10^9 [e]
Bromide (Br^-)	160	215 s	1.1×10^9
Sulfide			
H_2S	$\approx 3 \times 10^4$	~1 s	1.5×10^{10}
S^{2-}	3×10^9	20 µs	9×10^9
Manganese (Mn(II))	1.5×10^3	~23 s	2.6×10^7
Iron (Fe(II))	8.2×10^5	0.07 s	3.5×10^8

[a] Cyanide reacts with ozone via a radical chain reaction, rate constant given is a result of the overall process

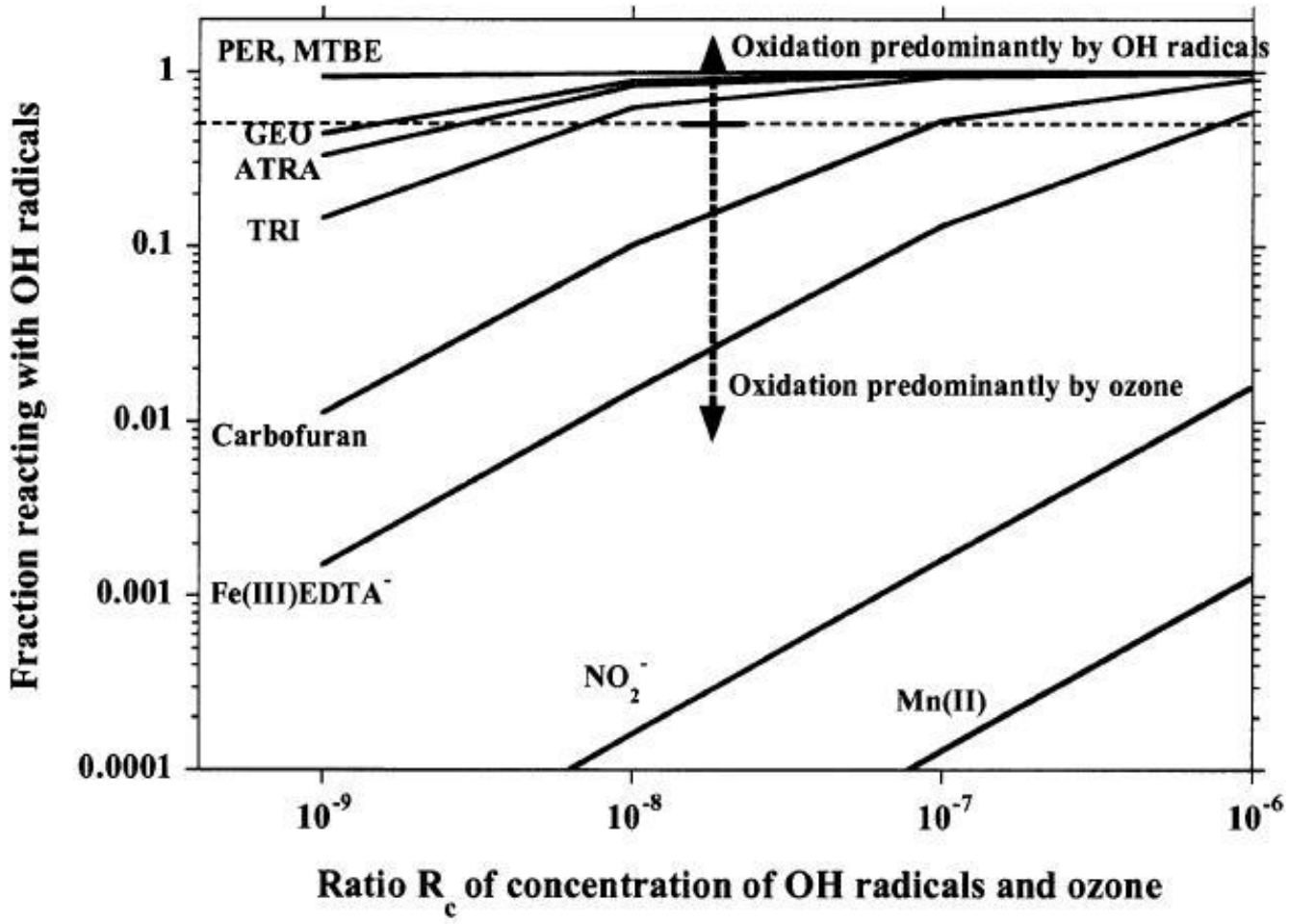
[b] estimated from ref. 2.

[c] Half-life time at pH 7 for $[O_3] = 1\,mgl^{-1}$ (ozone reaction only).

[d] Rate constant for NH_3.

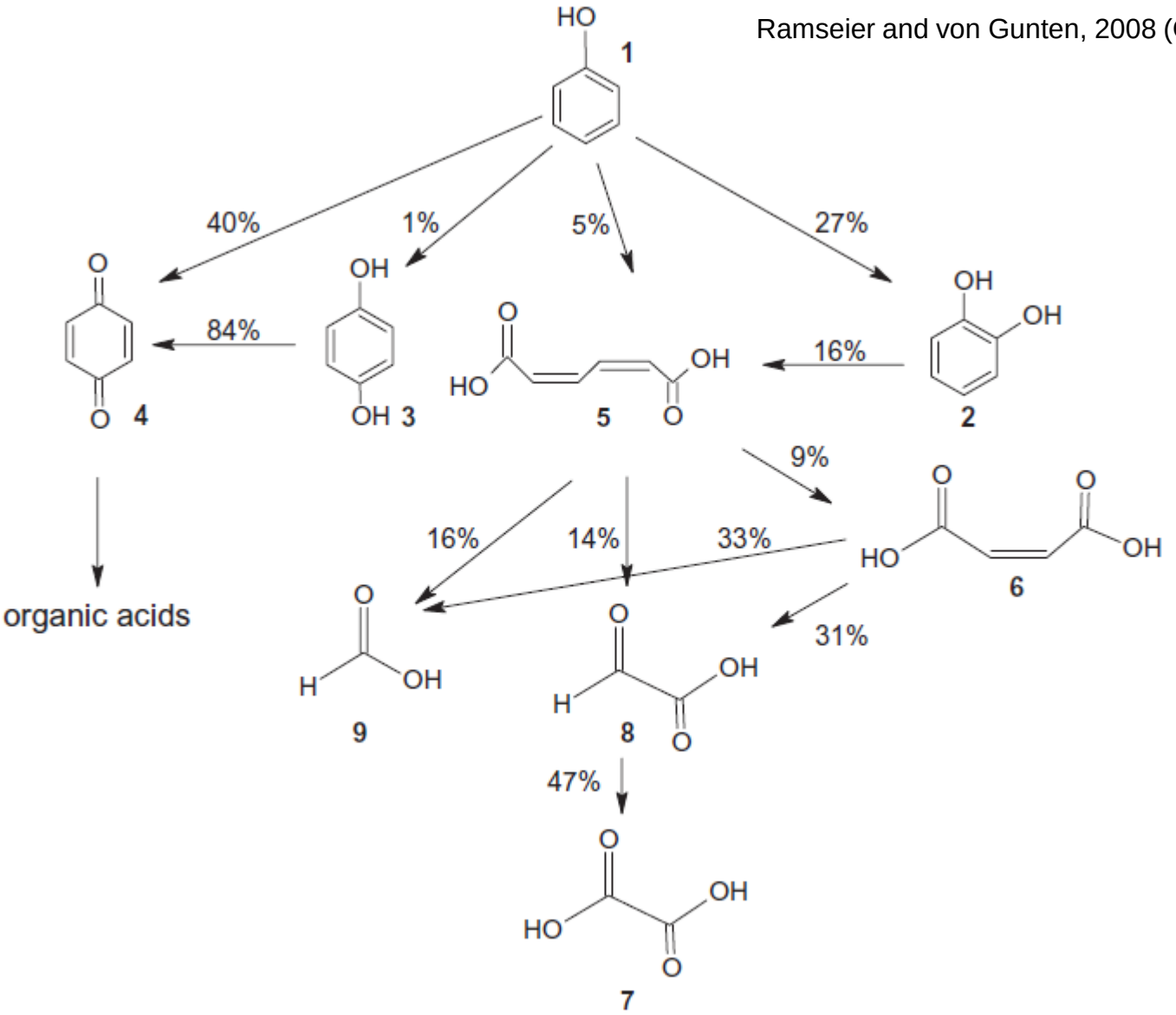
[e] Rate constant for H_3AsO_3.

Reactions of Ozone with Contaminants



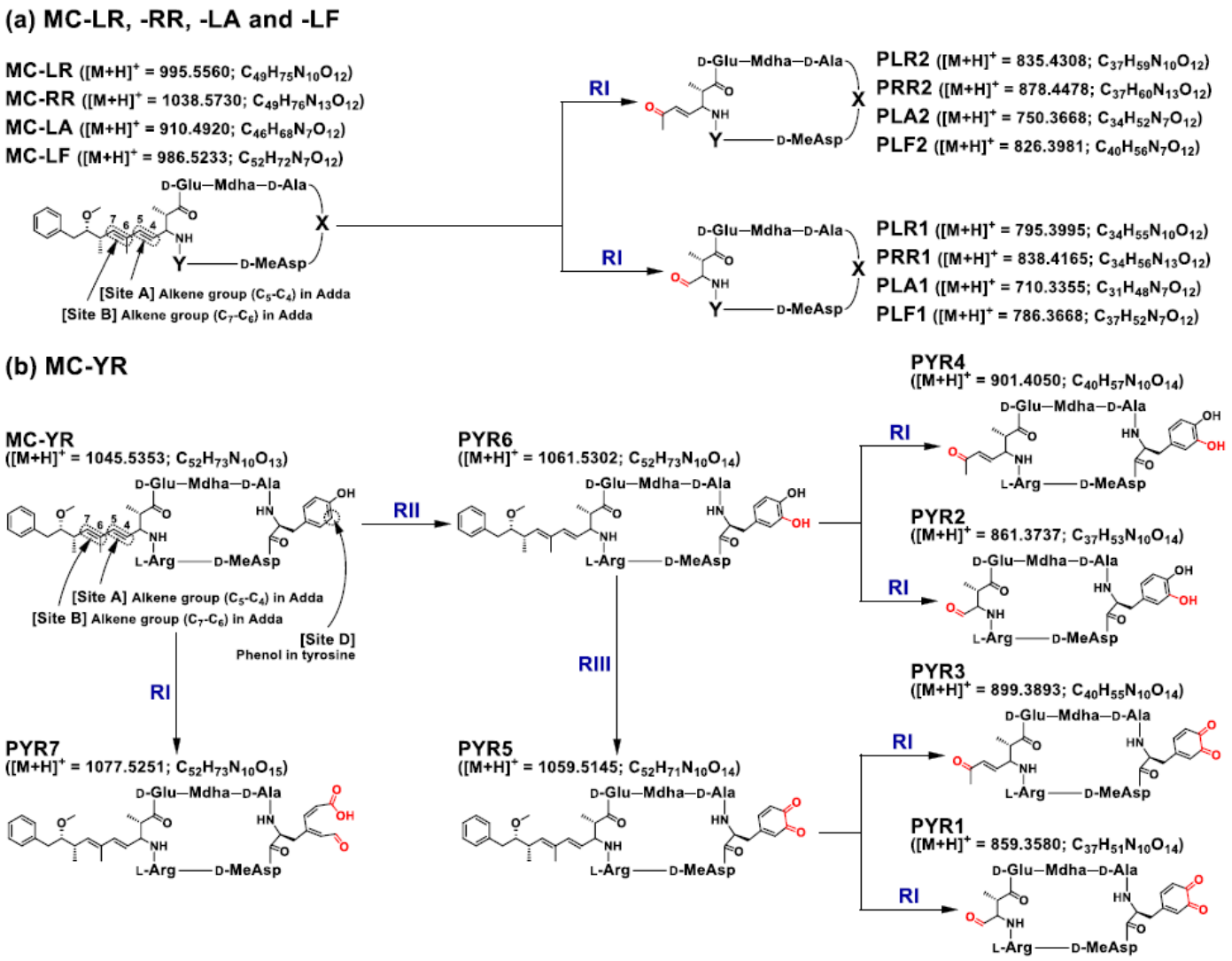
Reactions of Ozone with Contaminants (Product Study)

Ramseier and von Gunten, 2008 (Ozone Sci. Eng.)



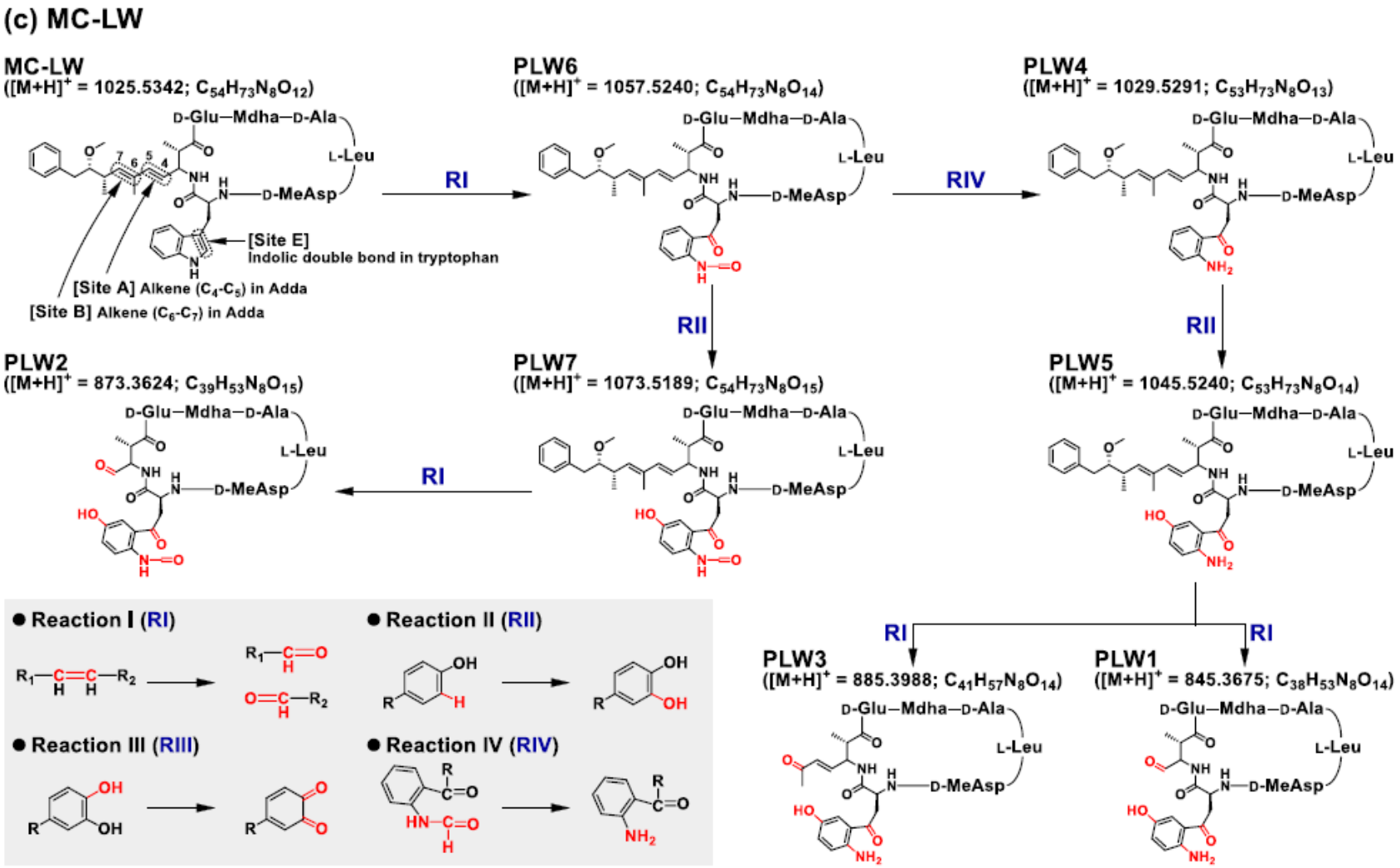
Reactions of Ozone with Contaminants (Product Study)

Kim and Lee, 2019 (*Environ. Sci. Technol.*)



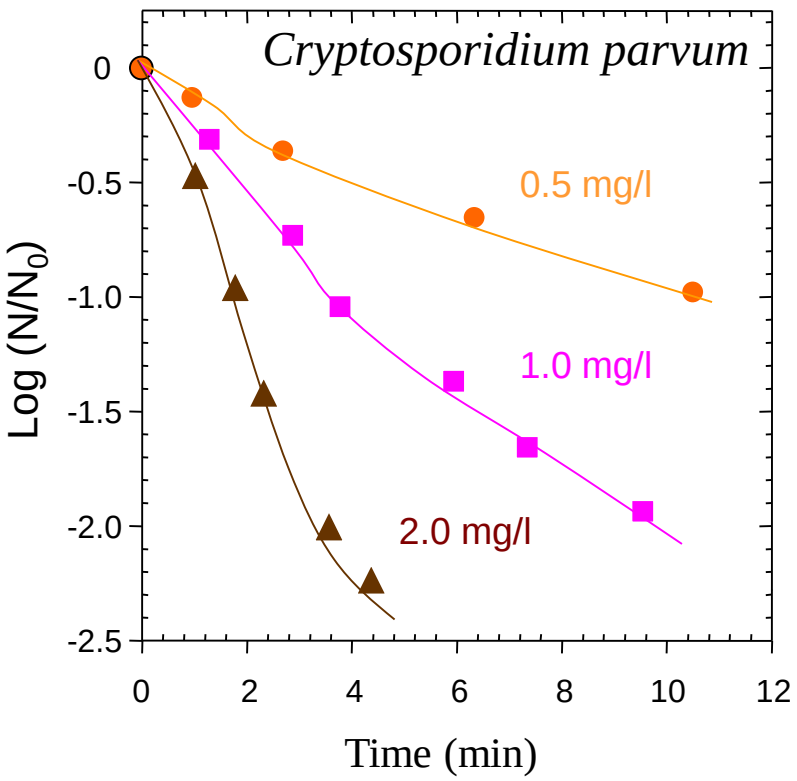
Reactions of Ozone with Contaminants (Product Study)

Kim and Lee, 2019 (*Environ. Sci. Technol.*)



Ozonation Disinfection

- Inactivation kinetics



Advantage

Ozone is a powerful oxidant able to achieve disinfection with less contact time and concentration than all weaker disinfectants, such as chlorine, chlorine dioxide, and monochloramine

Limitation

Ozone is only used as a primary disinfectant since it cannot maintain a residual in the distribution system. Thus, ozone disinfection should be coupled with secondary disinfection.

Disinfection Kinetics

- Disinfection model

Chick Model (1908)

$$Log\frac{N}{N_0} = -kT$$

Disinfectant : Phenol
Target : *Anthracnose* spore

Chick-Watson Model (1908)

$$Log\frac{N}{N_0} = -kCT$$

Disinfectant : Ozone
Target : *E. coli*

CT concept

Disinfection Kinetics

- Disinfection model

Hom Model (1972)

$$\frac{dN}{dt} = -kNC^n t^{m-1} \xrightarrow{\text{Integration}} \log\frac{N}{N_0} = -kC^n t^m$$

Disinfectant : Free chlorine
Target : *algal-bacteria*
Major parameter : t

Rational Model (1981)

$$\frac{dN}{dt} = -kN^x C^n \xrightarrow{\text{Integration}} \log\frac{N}{N_0} = -\frac{\log[\,1 + N_0^{x-1}(x-1)kC^nT\,]}{x-1}$$

Disinfectant : Ozone
Target : *Polivirus type 1*
Major parameter : N

Disinfection Kinetics

- Disinfection model

Modified Chick-Watson Model

$$Log\frac{N}{N_0} = -k\int_0^t Cdt \xrightarrow{\text{Integration}} \log\frac{N}{N_0} = -\frac{k}{k'n}C_0^n[1-\exp(-nk't)]$$

Delayed Chick-Watson Model

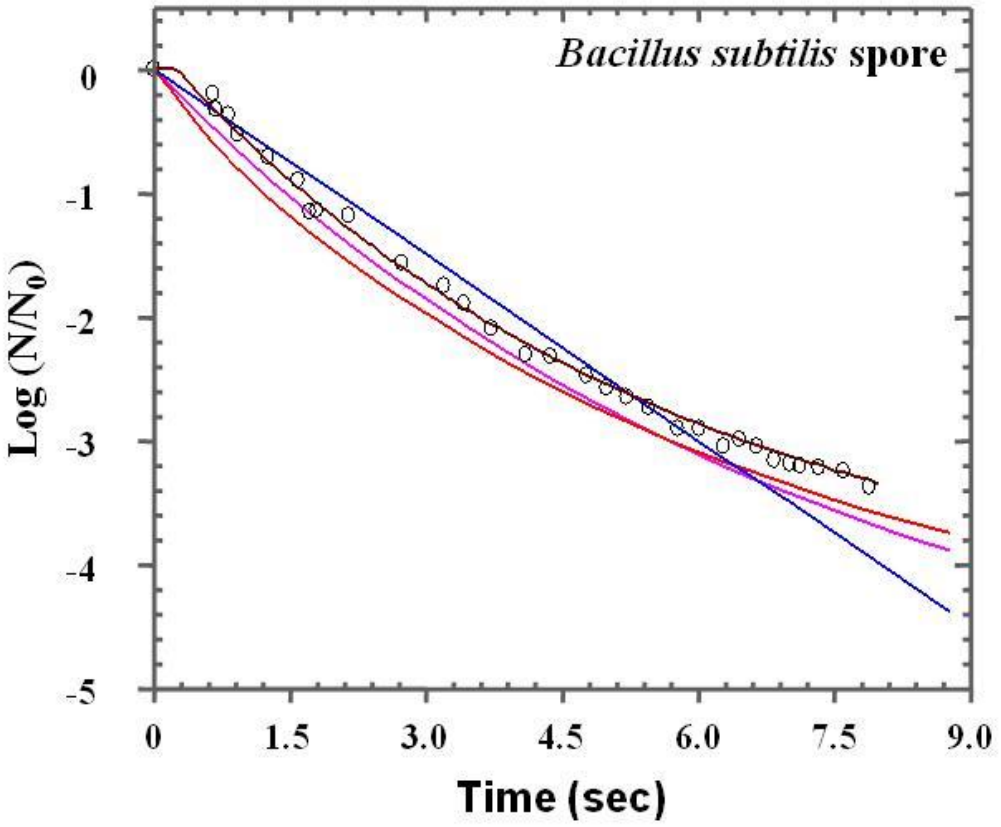
$$\log(\frac{N}{N_0}) = \begin{cases} 1 & if\ \ \overline{C}T \le \overline{C}_{lag}T = \frac{1}{k}\log(\frac{N}{N_0}) \\ -k(\overline{C}T - \overline{C}_{lag}T) & if\ \ \overline{C}T \ge \overline{C}_{lag}T = \frac{1}{k}\log(\frac{N}{N_0}) \end{cases}$$

$$where:\ \overline{C} = \int_0^t Cdt \ \Big/\ t$$

Disinfection Kinetics

- Disinfection model

Model fitting : Ozone disinfection



○ Observed results

Chick-Watson Model

Modified Chick-Watson Model

Modified Hom Model

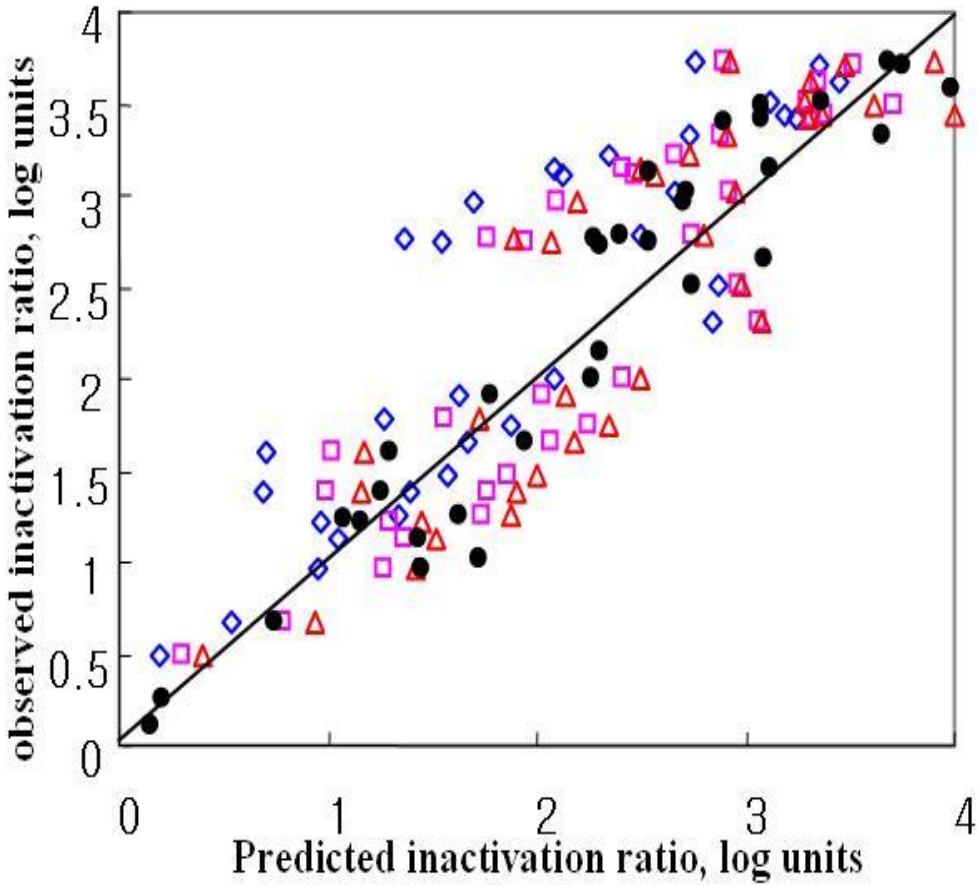
Delayed Chick-Watson Model

Initial ozone : 1.4 mg/l
pH 8.2, Temp. 20˚C

Disinfection Kinetics

- Disinfection model

Model fitting : Ozone disinfection



- Chick Watson Model
- Modified Chick Watson Model
- Modified Hom Model
- Delayed Chick Watson Model

Initial ozone : 1.4 mg/l
pH 8.2, Temp. 20˚C

Disinfection Kinetics

- Validation of disinfection model

$$ESS = \sum [\log(\frac{N}{N_0})_{observed} - \log(\frac{N}{N_0})_{fitted}]^2$$

Water Type	pH	ESS (Error sum of squares)			
		CWM	MCWM	MHM	DCWM
Buffer Condition	5.6	3.56	2.74	2.58	2.36
	7.1	4.49	3.90	2.24	2.11
	8.2	9.92	4.87	7.17	3.48
Humic Acid	7.1	0.45	0.97	0.09	0.09
	8.2	2.40	1.36	0.26	0.23
Han River	5.6	4.10	0.97	0.21	0.13
	7.1	2.45	1.12	0.32	0.31
	8.2	2.44	1.44	0.34	0.17

CWM: Chick-Watson Model
MCWM: Modified Chick-Watson Model
MHM: Modified Hom Model
DCWM: Delayed Chick-Watson Model

Comparison of CT values

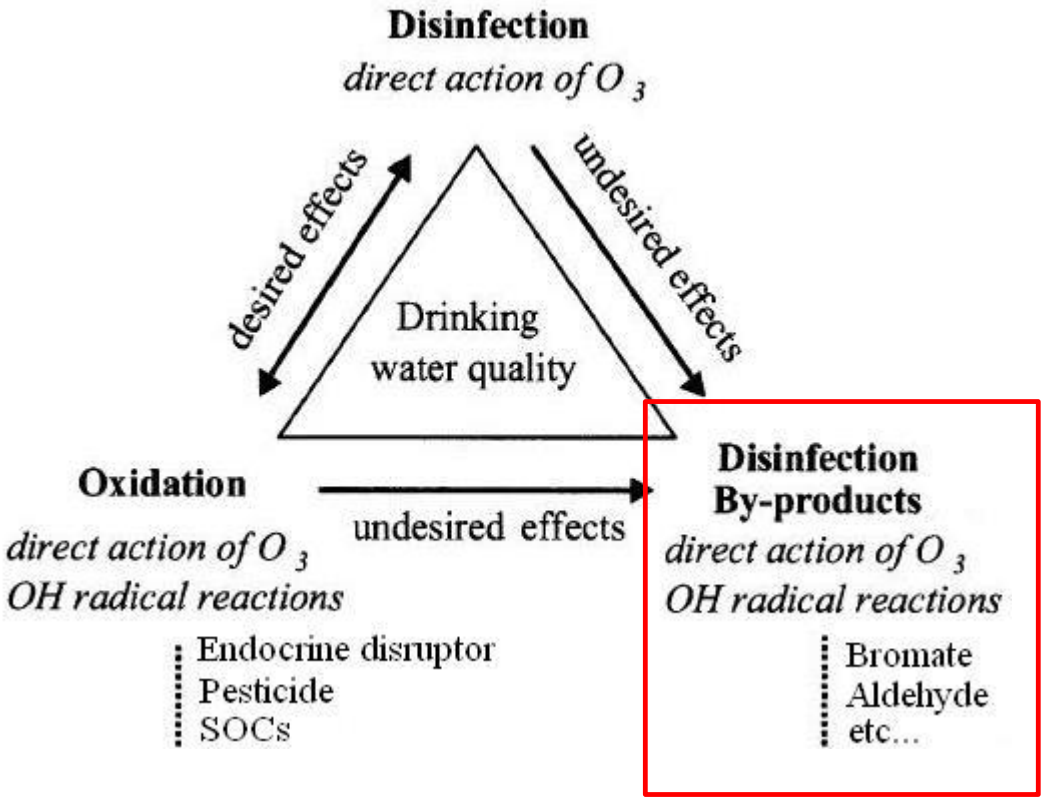
- CT values (for 2 log inactivation)

	Disinfectants			
	Ozone (pH 6~7)	Free chlorine (pH 6~7)	Chlorine dioxide (pH 6~7)	Chloramine (pH 8~9)
E. coli	0.02	0.03 ~ 0.05	0.4 ~ 0.8	95 ~ 180
Polio virus	0.1 ~ 0.2	1.1 ~ 2.5	0.2 ~ 6.7	768 ~ 3740
Rotavirus	0.006 ~ 0.06	0.01 ~ 0.05	0.2 ~ 2.1	3800 ~ 6500
Giardia lamblia	0.5 ~ 0.6	47 ~ 150	26	2200
Cryptosporidium parvum	5 ~ 10	7200	78	7200

CT values : disinfectant concentration (mg/l) × contact time (min)

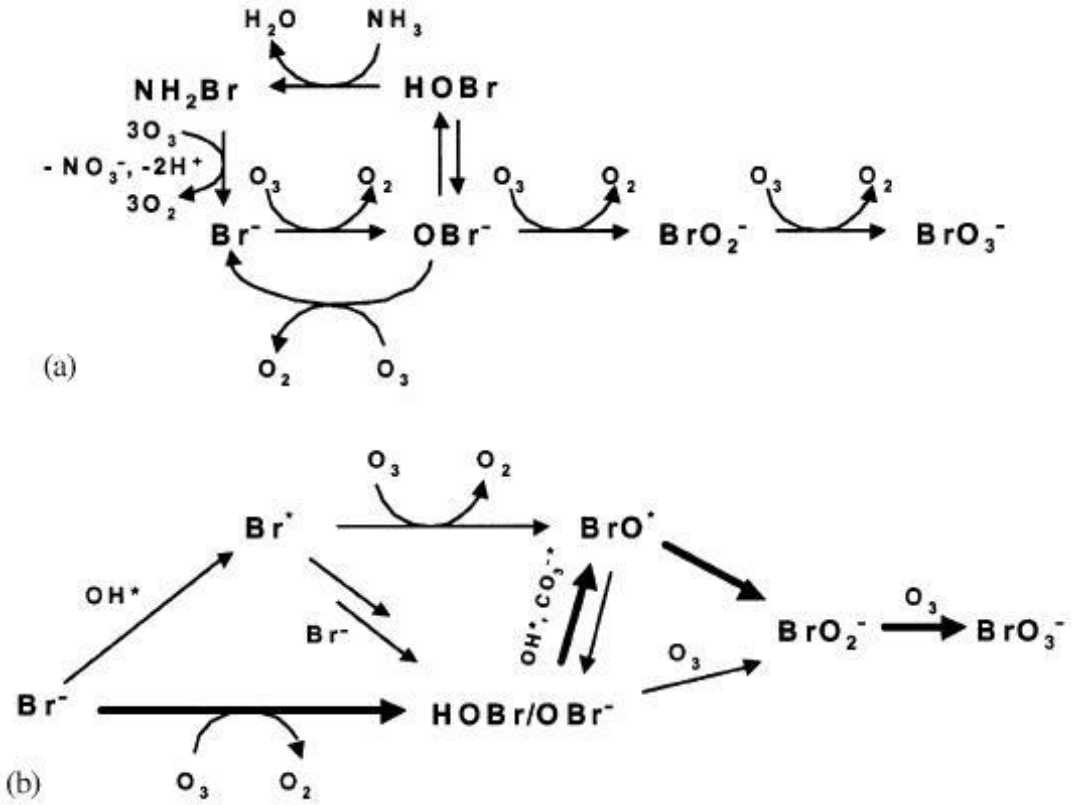
Ozonation Byproducts

- Desired and undesired effect of ozonation processes



Ozonation Byproducts

- Reaction scheme for bromate formation



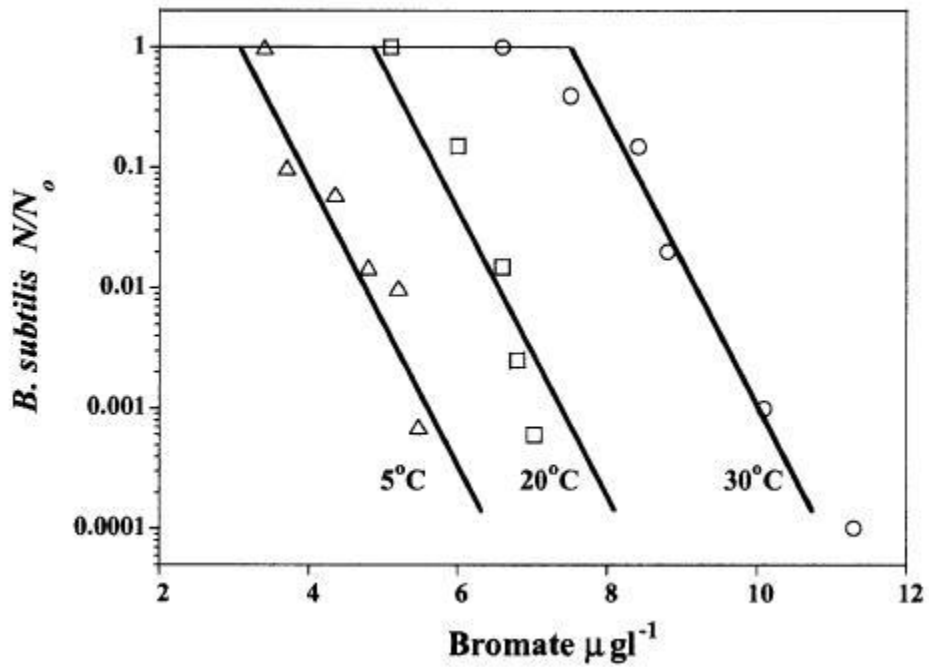
(a) Reaction with ozone

(b) Reaction with ozone and OH radicals

*The bold lines show the main pathways

Ozonation Byproducts

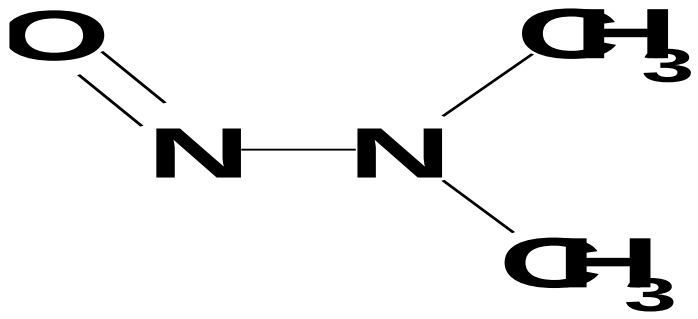
- Inactivation of *B. subtilis* spores and bromate formation



The occurrence of more resistant pathogens such as *C. parvum* oocysts leads to a demand for increased CT. Therefore, in waters with bromide levels above 50 ug/l, bromate formation may exceed the drinking water standard.

One of the decisive factors is the temperature of the treated water. Both the efficiency of inactivation of microorganisms and bromate formation increase with increasing temperature.

N-Nitrosamines (e.g. *N*-Nitrosodimethylamine, NDMA)



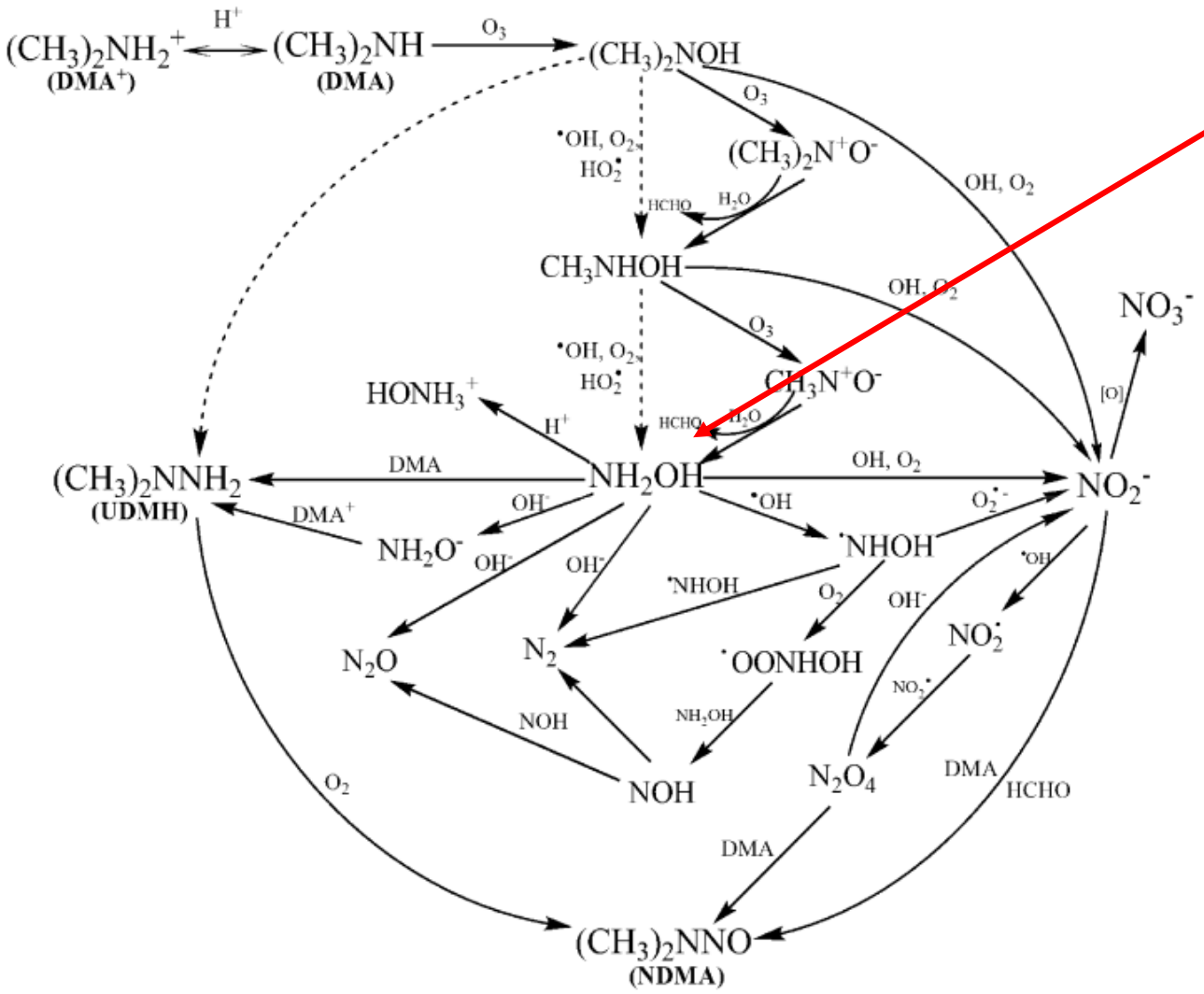
Genotoxic compound

1970~ discovered in beer and sausages,
1990~ detected in wastewater and drinking water

10^{-5} excess lifetime cancer risk concentration in drinking water (WHO):

NDMA	100 ng/L	(precautionary value 10 ng/L)
Bromate	3’000 ng/L	(drinking water standard 10’000 ng/L)
Bromoform	100’000 ng/L	

NDMA Formation by Ozonation of DMA



HOBr

↓ NH_2OH, fast

NH_2Br + DMA

↓ slow, low yield

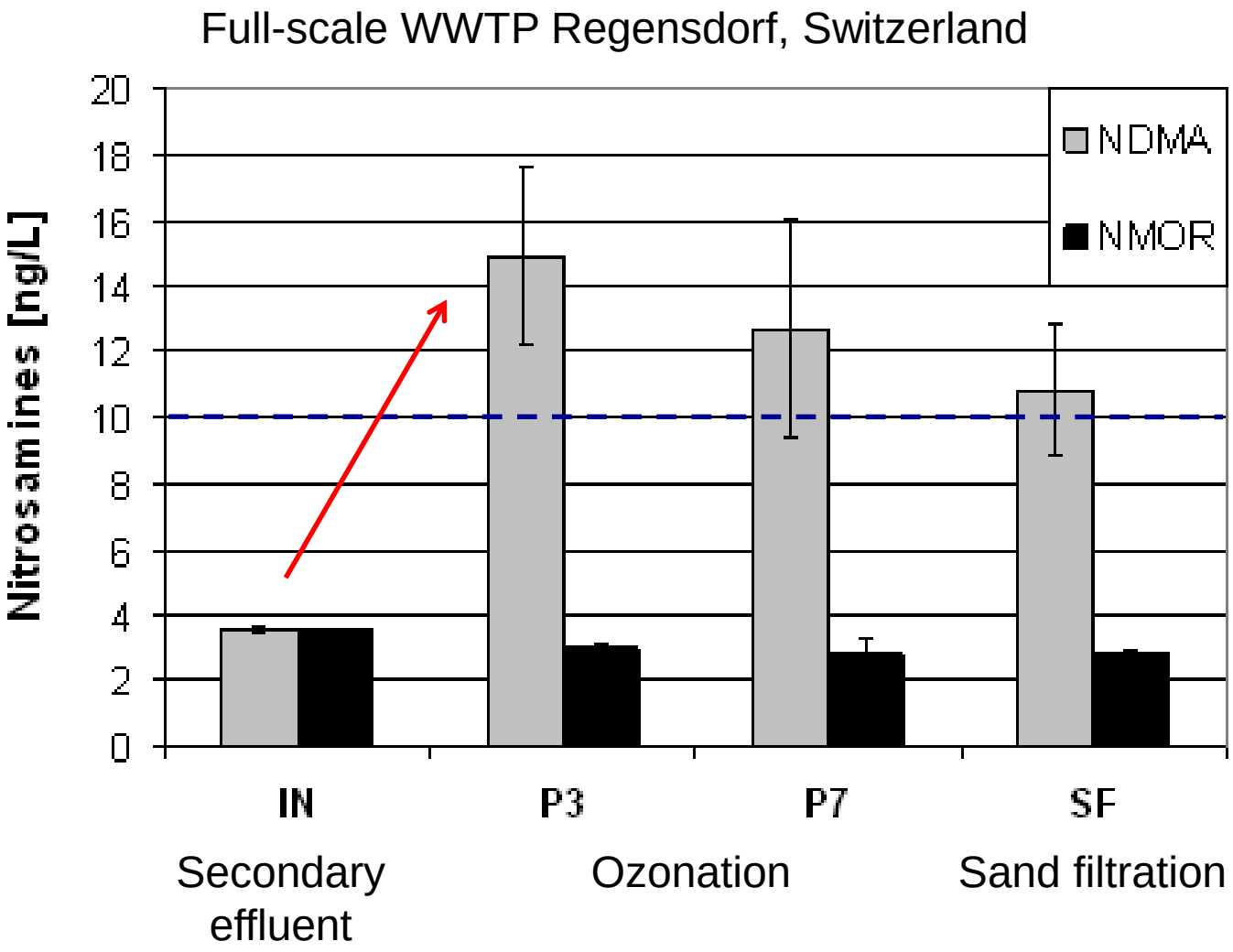
UDMH + O_3

↓ fast, high yield

NDMA

Yang et al. 2009

NDMA Formation by Ozonation of Wastewater

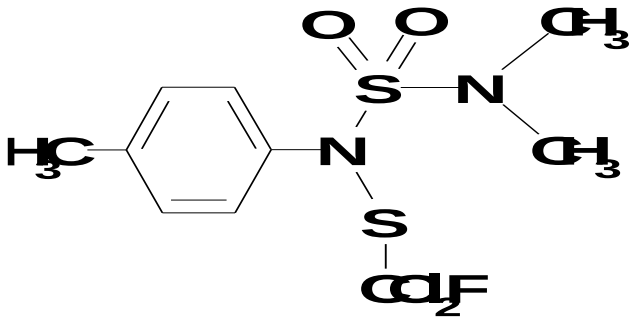


Recommendation drinking water

Formation from NOM or specific compounds?

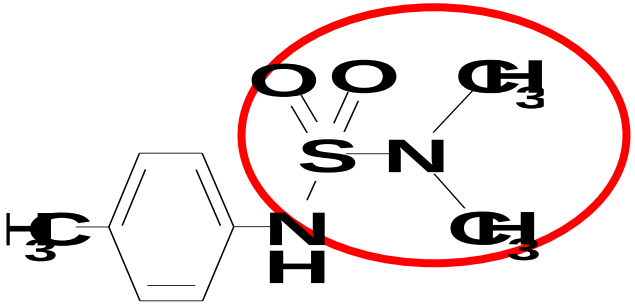
Hollender et. al. 2009

NDMA Formation by Ozonation of Micropollutants



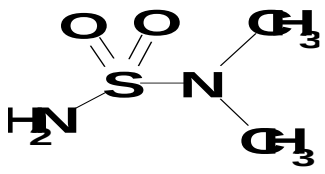
Fungicide Tolylfluanide
not in use in the USA

100 %



DMST

~ 20 %

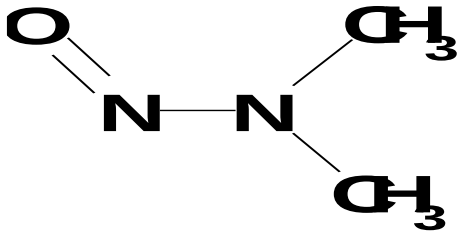


DMS

N,N-Dimethylsulfamide (DMS) is a newly discovered metabolite

+ O_3

50 %



NDMA

Ozonation of drinking water containing DMS in low mg/L levels

⇒ several 100 ng/L NDMA

Shutdown of ozonation

Ban of tolylfluanide

Schmidt and Brauch, 2008