Cátedra FACSA de Innovación del Ciclo Integral del Agua

1ª JORNADA TÉCNICA sobre procesos de oxidación avanzada en el CICLO INTEGRAL DEL AGUA

Viernes 15 de enero de 2016

Salón de Actos, Edifici Centre de Postgrau i Consell Social.
Universitat Jaume I

Aplicación del ozono para el tratamiento de aguas residuales urbanas

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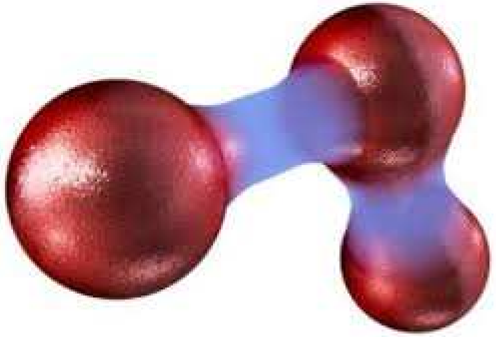
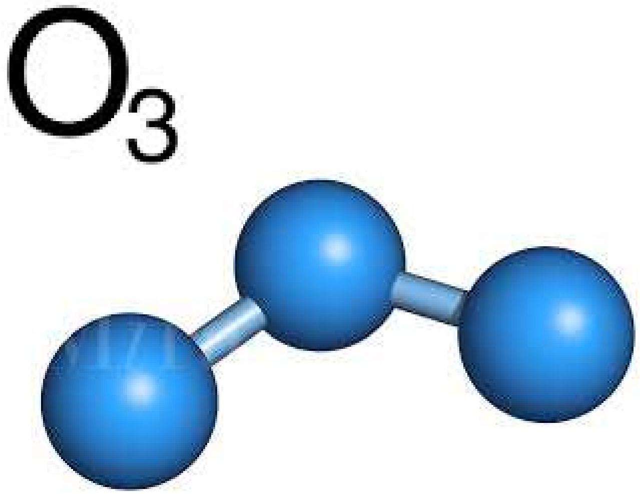
OVERVIEW OF THE PRESENTATION



- Ozone: Properties
- Ozone generation
- Ozone reactivity and AOP’s

- Water Reuse and Emerging Contaminants
- Ozone to improve WWTP outlet effluents
- Some results of ozone experimentation at lab scale
- Conclusions

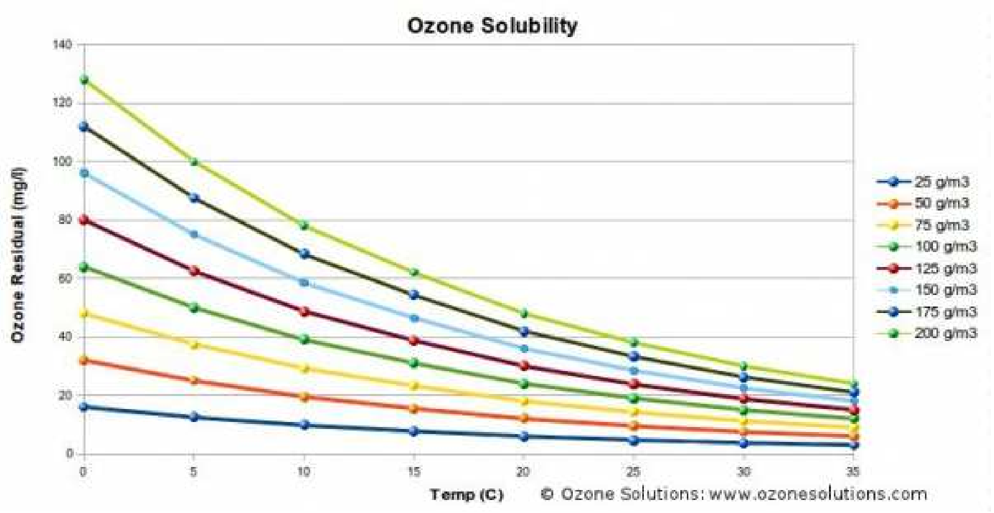
PROPERTIES OF OZONE



Bluish, irritating, heavier than air, reactive and unstable gas, it must be generated "in-situ".

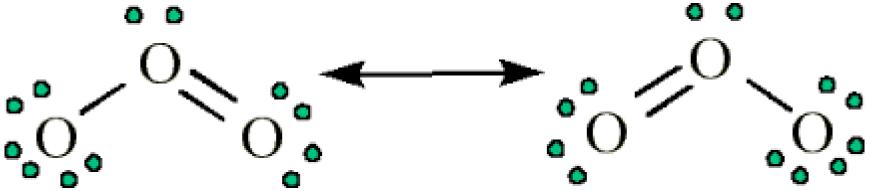
$$3\,O_2 \leftrightarrow 2\,O_3$$

It is 14 times more soluble in water than oxygen. The solubility decreases with temperature and increases with pressure.



PROPERTIES OF OZONE

Oxidant	E° (V)
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42*
Ozone	2.07
Hydrogen peroxide	1.77
Potassium permanganate	1.67
Hypobromous acid	1.59
Chlorine dioxide	1.50*
Hypochlorous acid	1.49
Chlorine	1.36
Oxygen	1.20*
Bromine	1.09

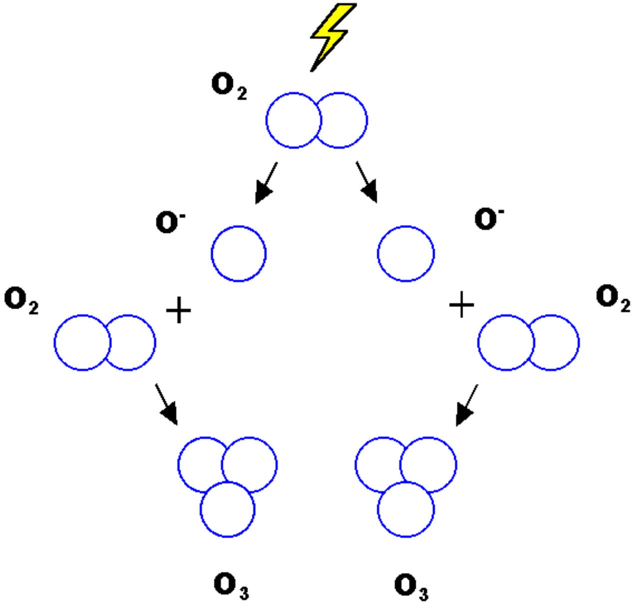


POWERFUL OXIDANT

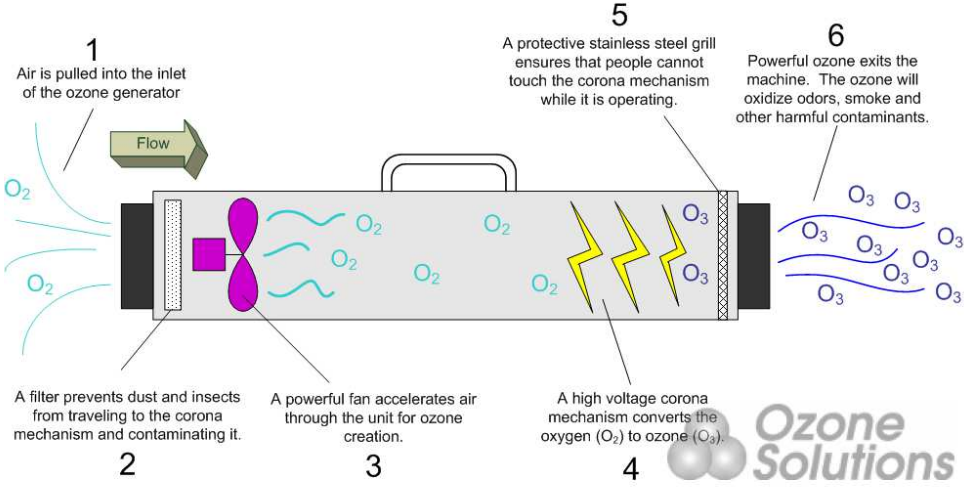
OZONE GENERATION

Electric discharge

The electrical discharge breaks the bond of oxygen and produces two oxygen atoms



What happens inside an Ozone Generator?



1 Air is pulled into the inlet of the ozone generator

2 A filter prevents dust and insects from traveling to the corona mechanism and contaminating it.

3 A powerful fan accelerates air through the unit for ozone creation.

4 A high voltage corona mechanism converts the oxygen (O_2) to ozone (O_3).

5 A protective stainless steel grill ensures that people cannot touch the corona mechanism while it is operating.

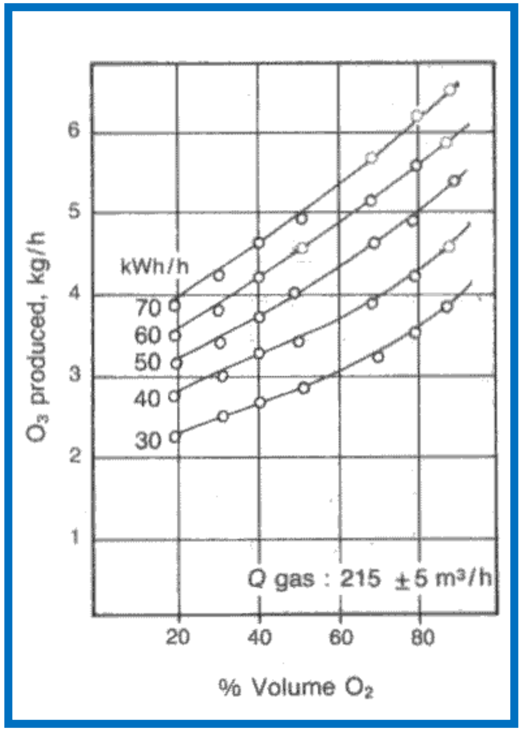
6 Powerful ozone exits the machine. The ozone will oxidize odors, smoke and other harmful contaminants.

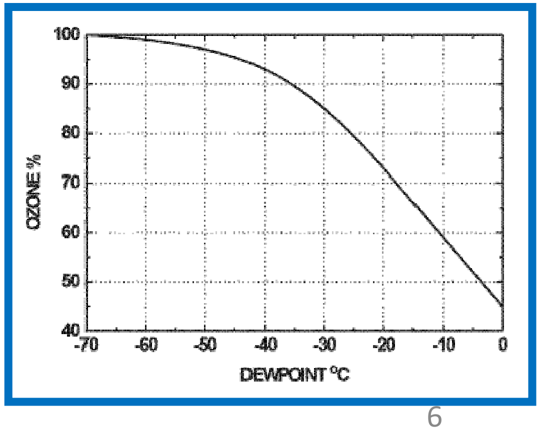
OZONE GENERATION

Electric discharge

- Can be generated from air or oxygen.
- 2-3 times higher production of ozone from oxygen to air.
- Important: Gas pre-treatment.
  - Gas compression.
  - Filtration of gas (remove any impurities).
  - Removal of humidity, to decrease NOx (corrosion!).

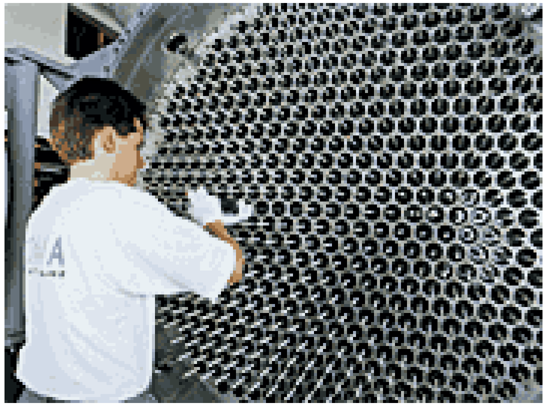
Problem: **costs**. Only **10% (BUT INCREASING!!!)** of the electrical energy applied to ozonizer is used in the production of ozone. The rest is lost as heat and light radiation. Dielectric tubes should be cooled with water





OZONE GENERATION

Electric discharge



Industrial scale

Lab scale

OZONE REACTIVITY: INORGANIC COMPOUNDS

Compound	Products	Rate of oxidation	Remarks
Fe^{2+}	$Fe(OH)_3$	Fast	Filtration of solids required; application in the beverage industry
Mn^{2+}	$MnO(OH)_2$ MnO_4^-	Fast Fast	Filtration of solids required; application in the beverage industry At higher residual ozone conc., reduction and filtration required
NO_2^-	NO_3^-	Fast	Nitrite is a toxic compound
NH_4^+ / NH_3	NO_3^-	Slow at pH<9 Moderate at pH>9	Not relevant
CN^-	CO_2, NO_3^-	Fast	Application in waste water
H_2S / S^{2-}	SO_4^{2-}	Fast	Not relevant
As-III	As-V	Fast	Preoxidation for subsequent As-removal
Cl^-	HOCl	Near zero	Not relevant
Br^-	HOBr / OBr^- , BrO_3^-	Moderate	Bromination of organic compounds possible; bromate as toxic by-product
I^-	HOI / OI^- , IO_3^-	Fast	Not relevant
HOCl / OCl^-	ClO_3^-	Slow	Loss of free chlorine
Chloroamines, Bromamines		Moderate	Loss of combined chlorine
ClO_2 ClO_2^-	ClO_3^- ClO_3^-	Fast Fast	Loss of free chlorine dioxide
H_2O_2	$OH^{\cdot}$	Moderate	Basis of O_3/H_2O_2 – process (AOP)

$$2\,Fe^{2+} + O_3 + H_2O \rightarrow 2\,Fe^{3+} + O_2 + 2\,OH^-$$

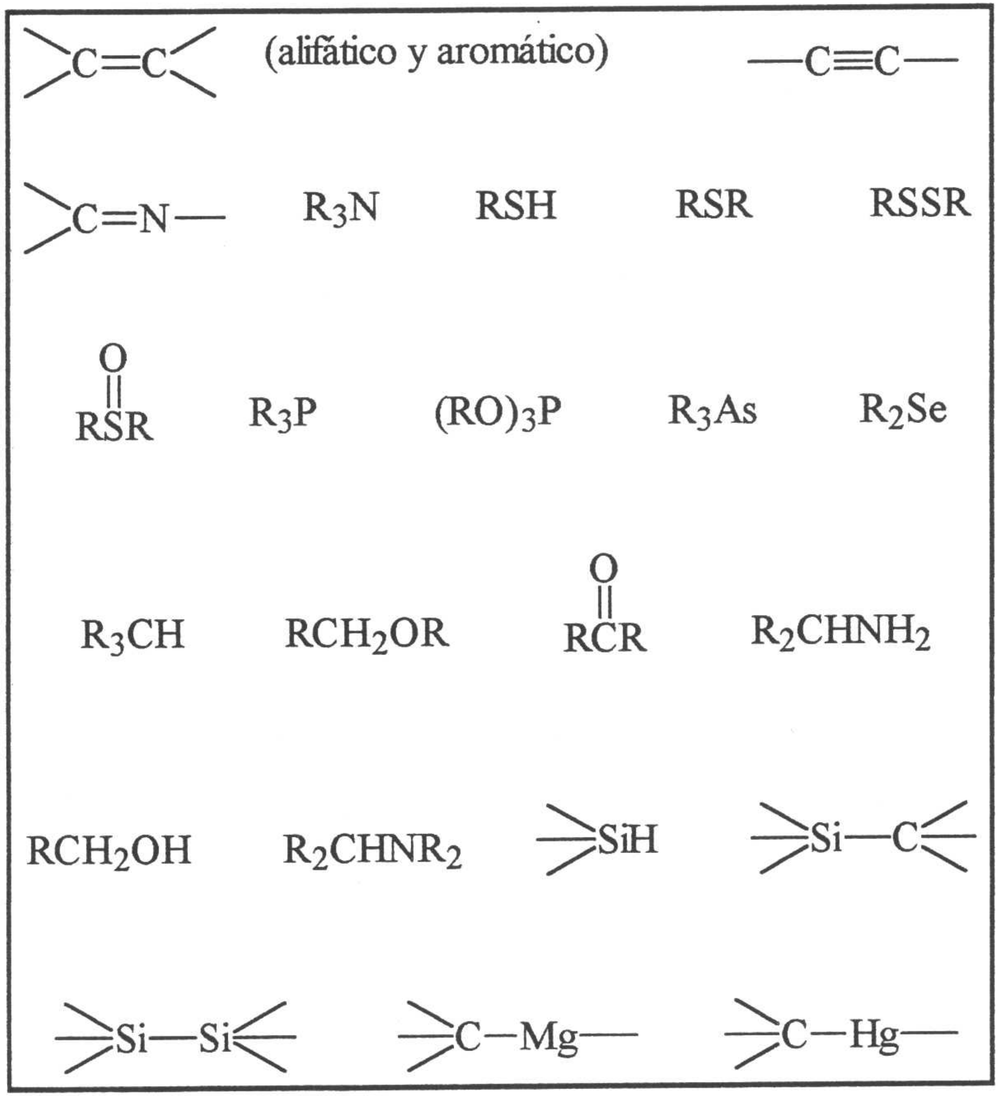
$$Fe^{3+} + 3\,H_2O \rightarrow Fe(OH)_3 + 3\,H^+$$

$$Mn^{2+} + O_3 + H_2O \rightarrow Mn^{4+} + O_2 + 2\,OH^-$$

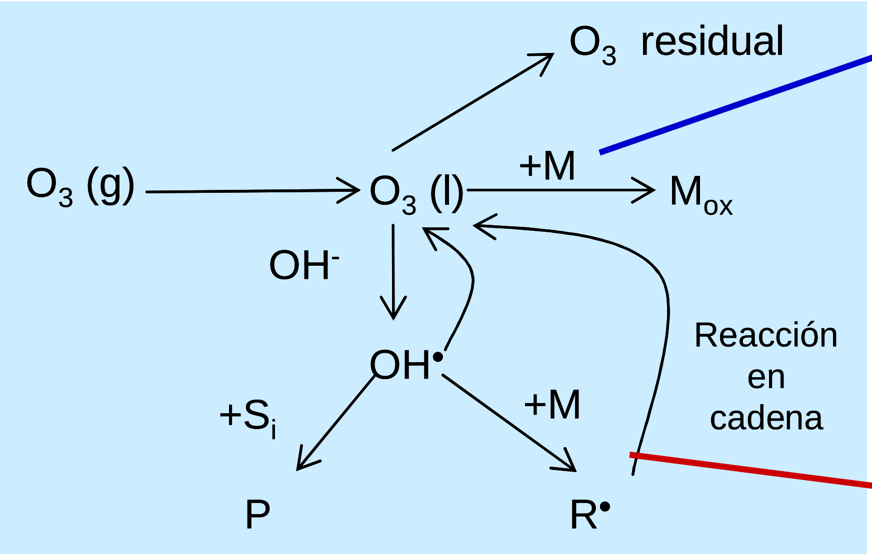
$$Mn^{4+} + 4\,OH^- \rightarrow Mn(OH)_4 \rightarrow MnO_2^- + 2\,H_2O$$

OZONE REACTIVITY: ORGANIC COMPOUNDS

Typical kinetic constant:
K_D= 1,0-10^3 $M^{-1}s^{-1}$



OZONE REACTIVITY: MECHANISM



Direct reaction: pH < 4

Direct or indirect reaction?

- Solution pH
- Type of compound

Indirect reaction (radical). pH > 10

R = Free radicals
M = Substrate
S_i = Scavengers
M_{ox} = Oxidized substrate
P = Products

+ OH^-

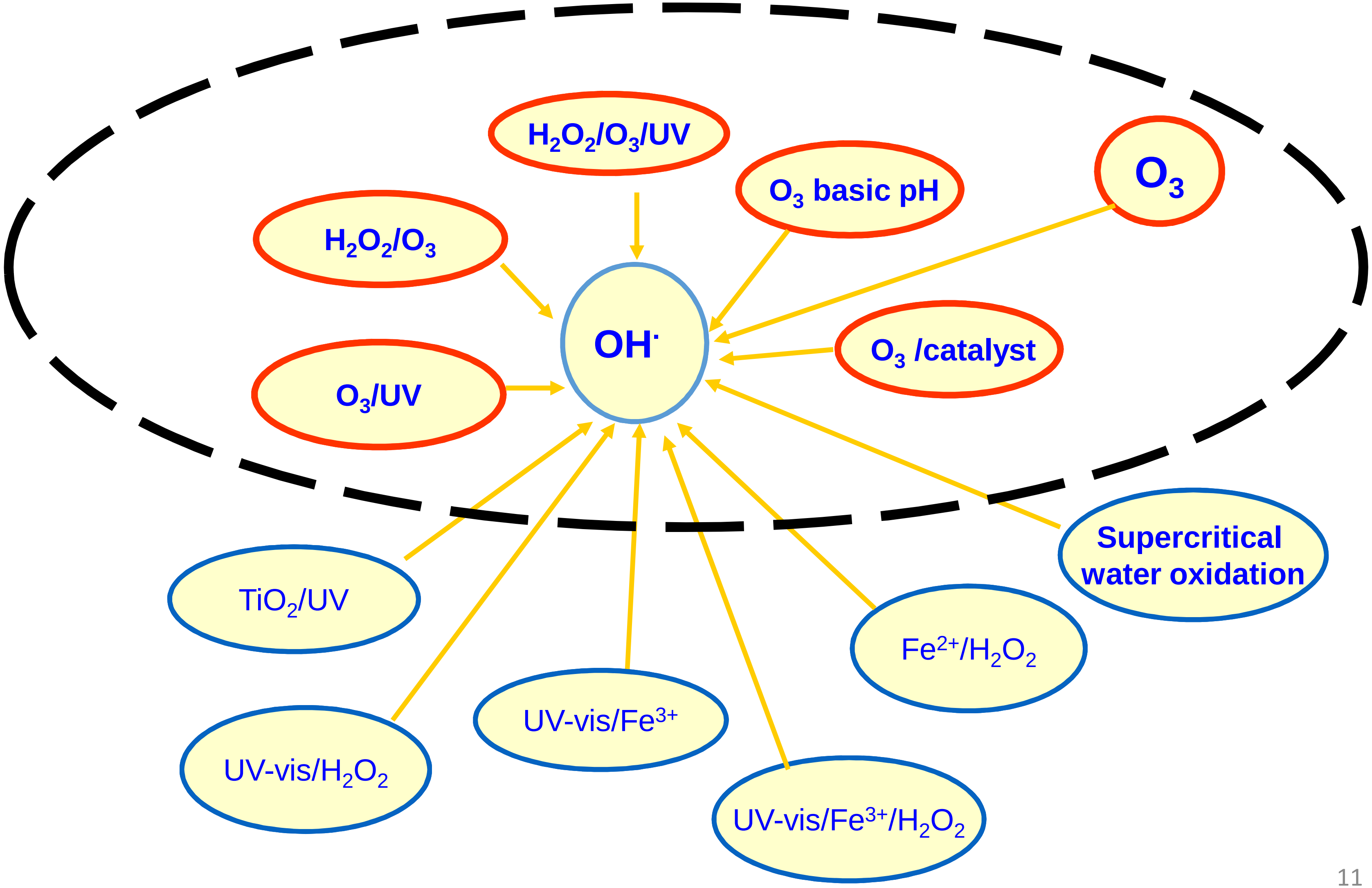
+ H_2O_2

+ UV

+ Transition Metals

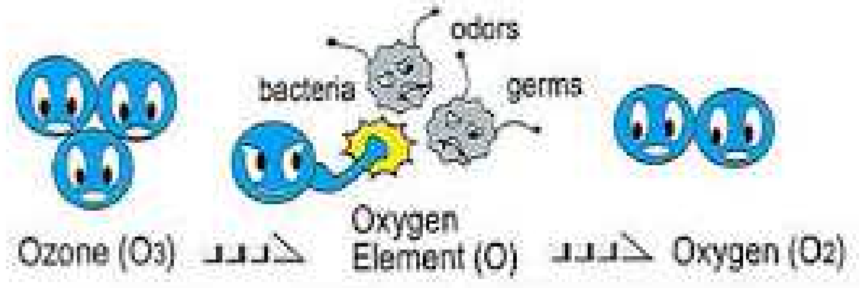
Reaction rate of OH· 10^6-10^9 times faster than O_3

AOP's BASED ON OZONE



ADVANTATGES OF OZONE

- Ozone is **more effective than chlorine**, chloramines, and chlorine dioxide for inactivation of viruses, *Cryptosporidium*, and *Giardia*.
- Ozone **oxidizes iron, manganese, and sulfides**.
- Ozone can sometimes **enhance the clarification process and turbidity removal**.
- Ozone **controls color, taste, and odors**.
- In the absence of bromide, **halogen-substitutes DBPs are not formed**.
- Upon decomposition, the **only residual is dissolved oxygen**.
- Biocidal activity is **not influenced by pH**.



DISADVANTATGES OF OZONE

- DBPs are formed, particularly by **bromate and bromine-substituted DBPs**, in the presence of bromide, aldehydes, ketones, etc.
- The initial **cost of ozonation equipment** is high.
- The generation of ozone requires **high energy** and should be generated **on-site.**
- Ozone requires **higher level of maintenance** and operator skill.
- Ozone is highly **corrosive and toxic.**
- Ozone provides **no residual**.

OZONE: APPLICATIONS

- Water purification (Disinfection, odor removal, etc..).
- Production of high purity water.
- **Wastewater treatment** (pollutants and odors removal, etc.)
- Reusable water for pools, aquaculture, aquariums, etc.
- Gas treatment (removal of odors in gas streams, etc..).

Blanqueo de pasta de papel con ozono.

IOA3 OZONE NEWS

INTERNATIONAL OZONE ASSOCIATION

Volume 22 / No. 3 May / June 1994

OZONE PULP BLEACHING HAS ARRIVED

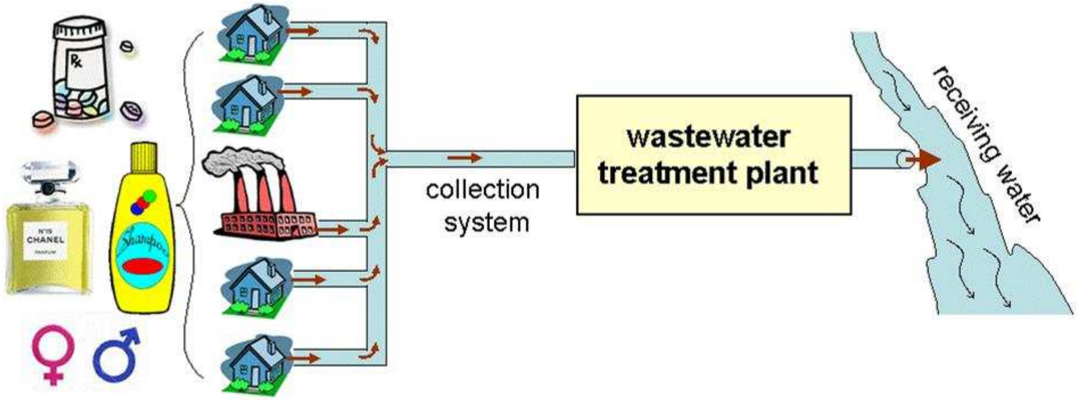
Capacity: 365 ADMT / 24 h

OZONE PULP BLEACHING STAGE AT LENZING, AG, AUSTRIA

World's First Zero Discharge Pulp Mill

NEW APPLICATION: WATER REUSE

RESORCES RECOVERY: WATER



New challenge:
EMERGING CONTAMINANTS REMOVAL

EMERGING CONTAMINANTS



Metallic or organic substances present **in very low concentrations** in the environment and that may have a toxic action at small concentration.

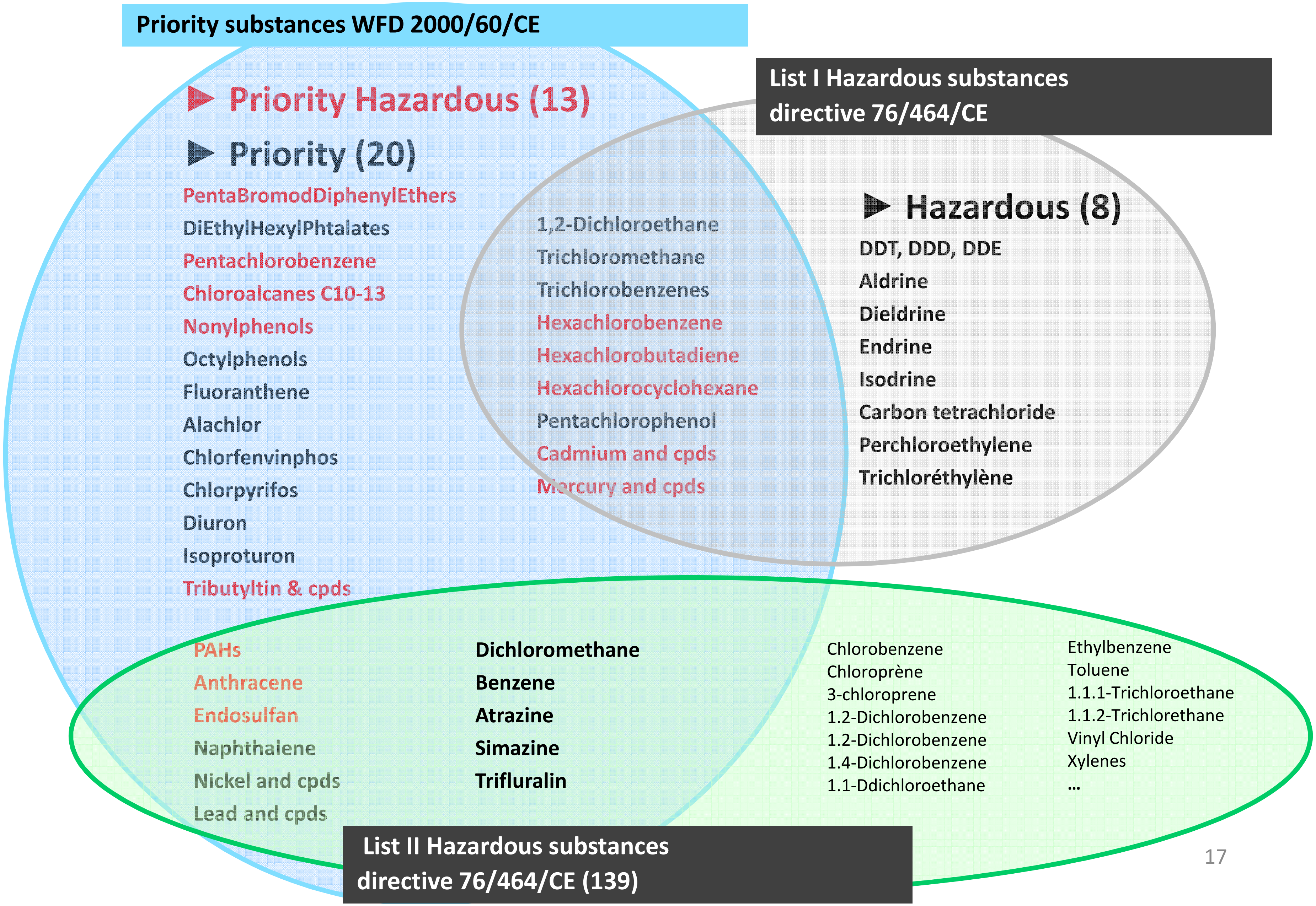
CHARACTERISTICS

- **Frequently used** products
- **Released** to the environment
- **Not** specifically **regulated**
- **Recalcitrant** properties
- Unknown **environmental impact**
- **Include** PPCP, pesticides, **antibiotics**...

✓ **Approximately 63 000 chemicals are in common use worldwide.**

✓ **200 to 1.000 new synthetic chemicals enter the market each year.**

EMERGING CONTAMINANTS



Priority substances WFD 2000/60/CE

- ▶ Priority Hazardous (13)
- ▶ Priority (20)

PentaBromodDiphenylEthers
DiEthylHexylPhtalates
Pentachlorobenzene
Chloroalcanes C10-13
Nonylphenols
Octylphenols
Fluoranthene
Alachlor
Chlorfenvinphos
Chlorpyrifos
Diuron
Isoproturon
Tributyltin & cpds

1,2-Dichloroethane
Trichloromethane
Trichlorobenzenes
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclohexane
Pentachlorophenol
Cadmium and cpds
Mercury and cpds

List I Hazardous substances directive 76/464/CE

- ▶ Hazardous (8)

DDT, DDD, DDE
Aldrine
Dieldrine
Endrine
Isodrine
Carbon tetrachloride
Perchloroethylene
Trichloréthylène

PAHs
Anthracene
Endosulfan
Naphthalene
Nickel and cpds
Lead and cpds

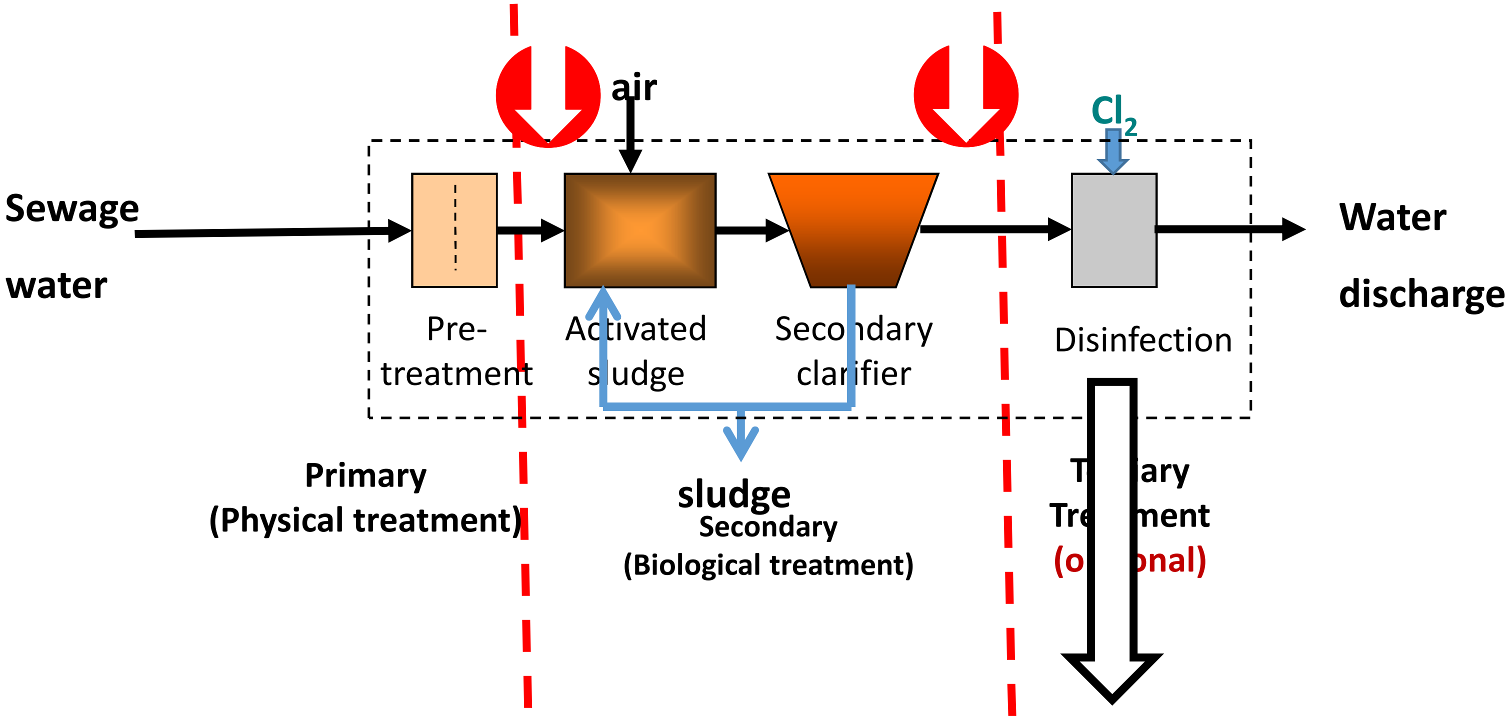
Dichloromethane
Benzene
Atrazine
Simazine
Trifluralin

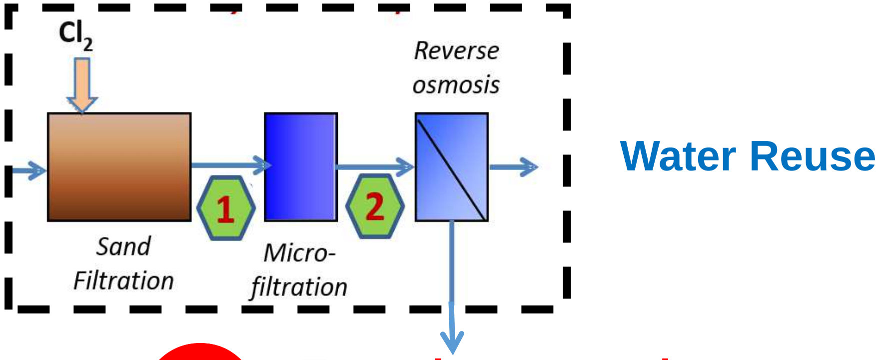
Chlorobenzene
Chloroprène
3-chloroprene
1.2-Dichlorobenzene
1.2-Dichlorobenzene
1.4-Dichlorobenzene
1.1-Ddichloroethane

Ethylbenzene
Toluene
1.1.1-Trichloroethane
1.1.2-Trichlorethane
Vinyl Chloride
Xylenes
…

List II Hazardous substances directive 76/464/CE (139)

CLASSICAL WASTEWATER TREATMENT PLANT (WWTP)



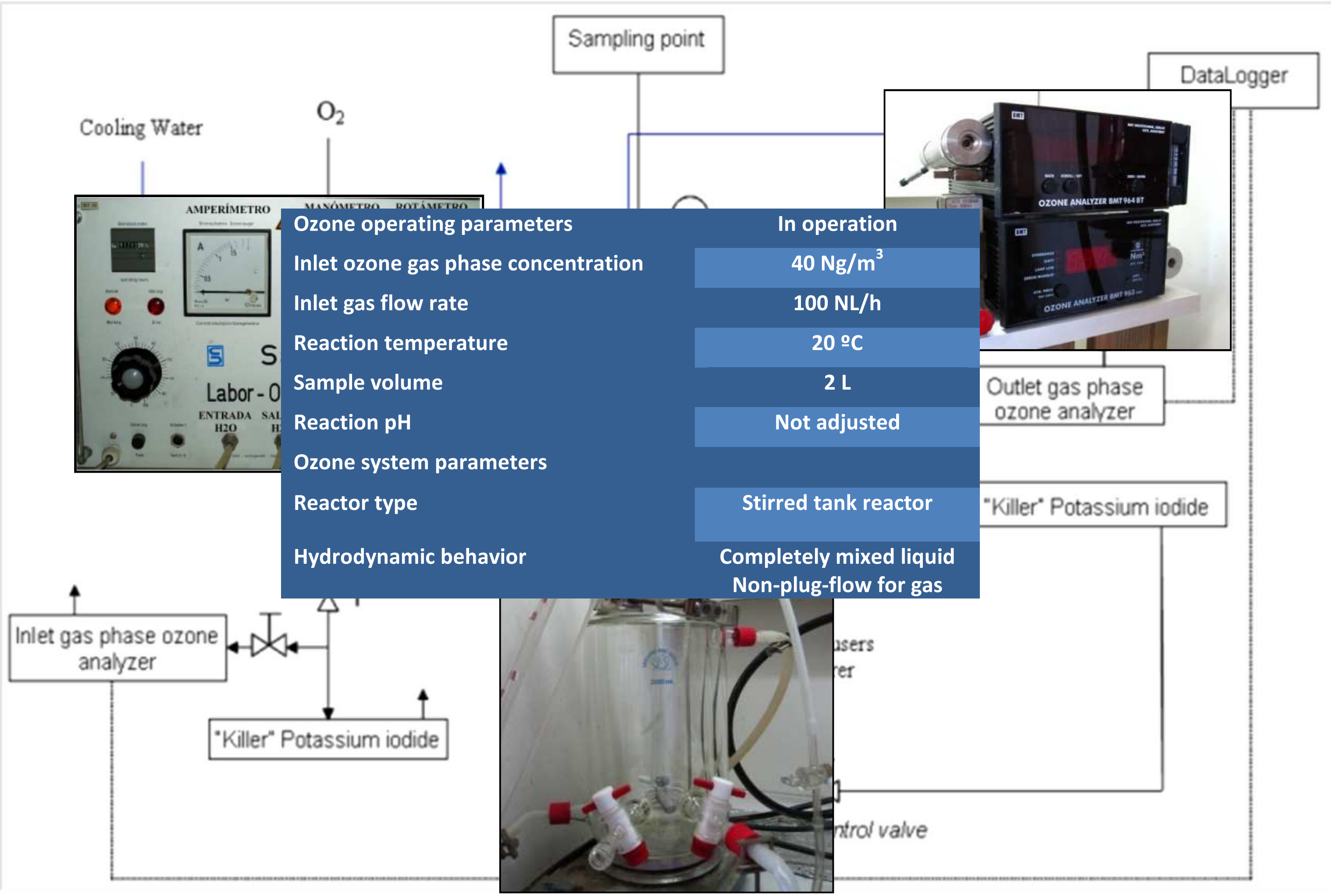


O_3 **?**

- ✓**Emerging contaminants**
- ✓**Toxicity**
- ✓**Effluent organic matter**

➡ **Emerging contaminants concentration**

OZONE LAB SCALE SEMI-BATCH REACTOR



Ozone operating parameters	In operation
Inlet ozone gas phase concentration	40 Ng/m^3
Inlet gas flow rate	100 NL/h
Reaction temperature	20 ºC
Sample volume	2 L
Reaction pH	Not adjusted
Ozone system parameters	
Reactor type	Stirred tank reactor
Hydrodynamic behavior	Completely mixed liquid Non-plug-flow for gas

STUDIED EFFLUENTS: RO BRINE

- RO brine → WWTP El Prat de Llobregat (Barcelona)
- RO brine → WWTP Calafell (Tarragona)

Average physicochemical parameters:

	RO brine Barcelona	**RO brine Tarragona**	
	Appendix III	*Appendix IV*	*Appendix V*
TOC (mg C L^{-1})	27.6	24.4	23.9
DOC (mg C L^{-1})	27.3	24.2	23.7
COD (mgO_2 L^{-1})	77.0	76.9	61.5
BOD_5 (mgO_2 L^{-1})	2.2	2.3	5.5
pH	8.3	7.4	6.9
UV_{254} (m^{-1})	59.5	46.4	40.5
Turbidity (NTU)	1.07	0.53	0.37
Alkalinity (mg $CaCO_3$ L^{-1})	914	583	308
Cl^- (mgCl^- L^{-1})	1540	1511	1627

- Low biodegradability (BOD_5/COD = 0.03 – 0.09)

  High recalcitrant organic matter content.

- High chloride concentration and significant alkalinity content

  Important from a mechanistic point of view since CO_3^{2-} (alkalinity) and Cl^- are HO· scavengers.

STUDIED EFFLUENTS: RO BRINE

Pharmaceutical concentrations (ng L^{-1}):

	RO brine Barcelona
Naproxen	1080
Indometacin	895
Diclofenac	605
Propyphenazone	258
Paroxetine	508
Codeine	673
Carbamazepine	1038
Sulfamethazine	635
Sulfamethoxazole	1638
Trimethoprim	235
Atenolol	1028

235 – 1638 ng L^{-1}

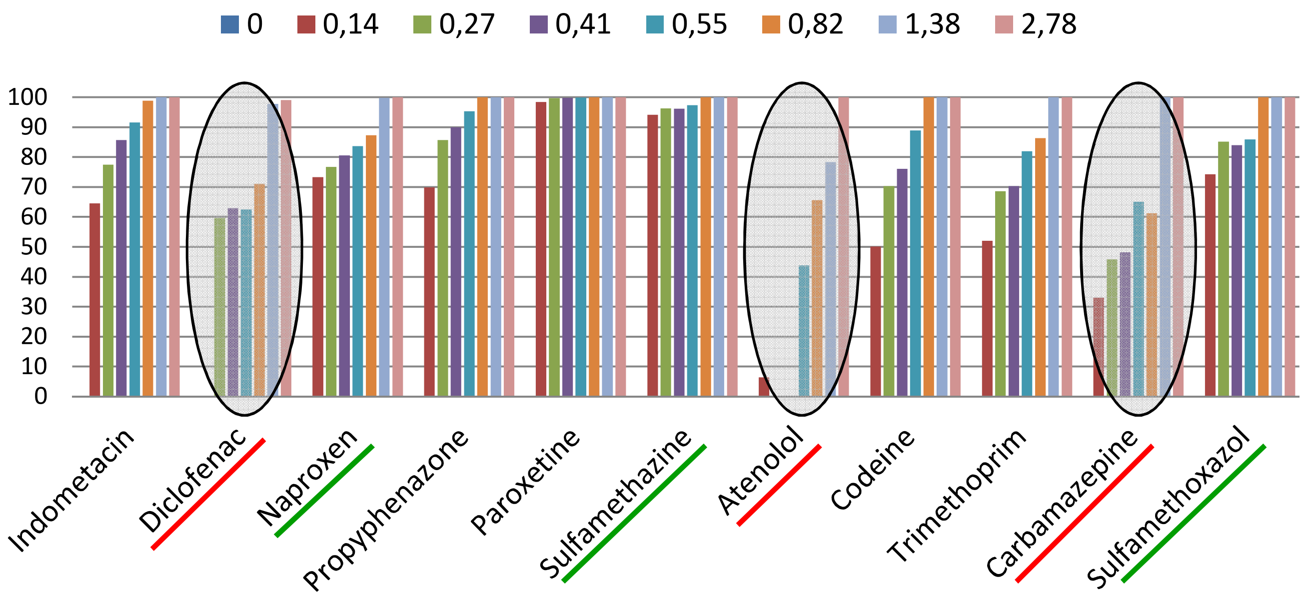
	RO brine Tarragona	
Naproxen	169	254
Ketoprofen	259	628
Diclofenac	935	283
Gemfibrozil	1275	3443
Diazepam	102	135
Lorazepam	45	195
Carbamazepine	17	98
Clarithromycin	77	46
Sulfamethoxazole	87	26
Trimethoprim	81	20
Atenolol	28	361

17 – 1275 ng L^{-1}

20 – 3443 ng L^{-1}

As expected: **remarkable concentrations** of micropollutants were found.

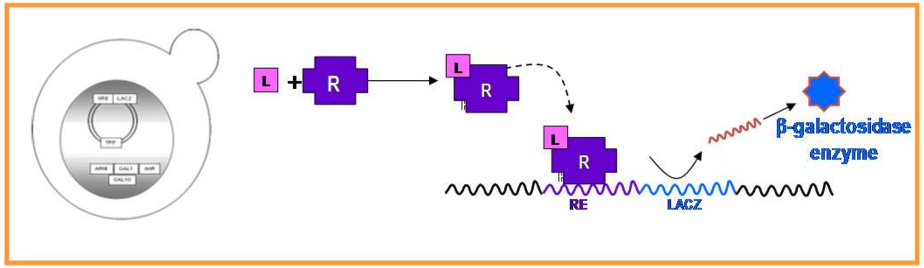
O_3: Pharmaceuticals removal in RO brines

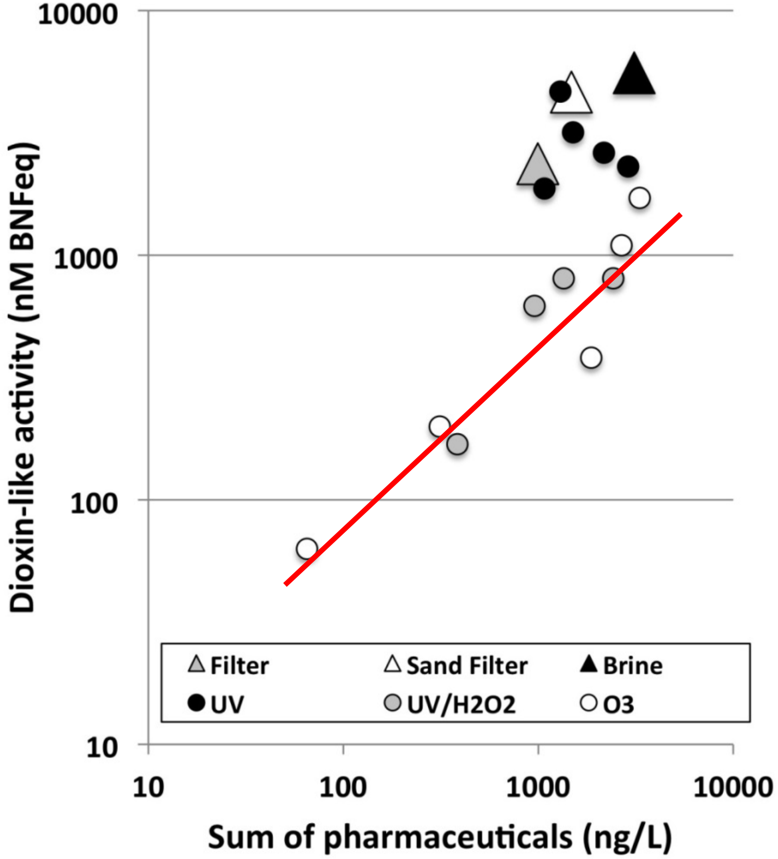

Removal for O_3 doses (mgO_3 mgC^{-1})

- Dominant mechanism: **direct ozone attack** (high alkalinity and Cl^-).
- **Sulfamethoxazole, Sulfamethazine** and **Naproxen**, among others, showed high k_{obs} values and **good percentage removals** even at low ozone doses because these pharmaceuticals have electron-rich functional groups.
- **Atenolol, Carbamazepine** and **Diclofenac** showed the **worst eliminations** and, Atenolol and Carbamazepine showed the lowest initial k_{obs} values.

O_3: removal of DIOXIN-LIKE ACTIVITY

Recombinant Yeast Assays (RYA)

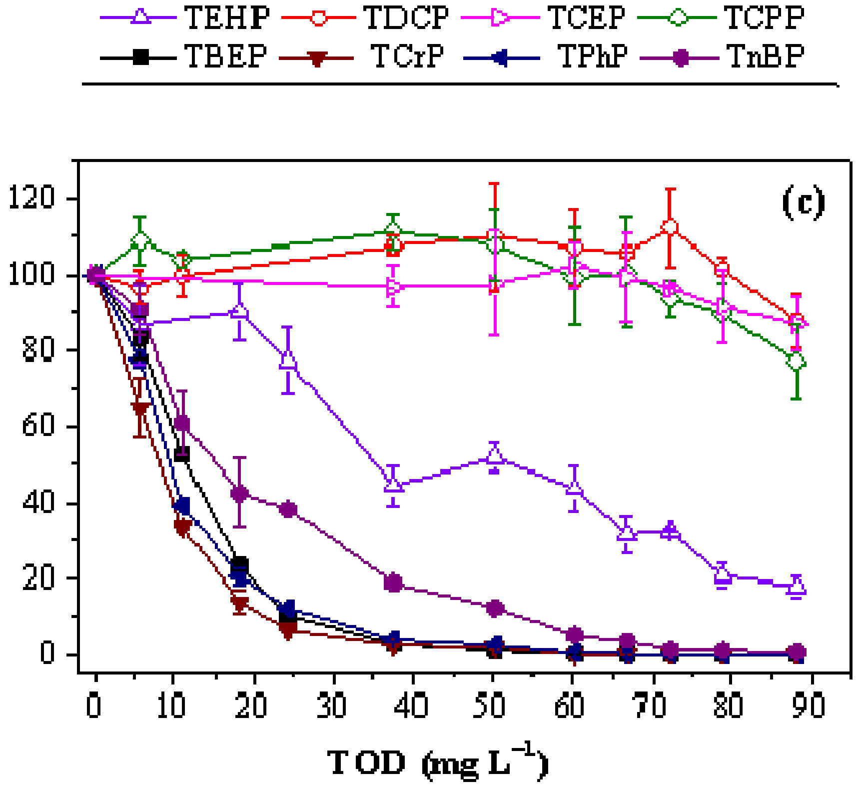




Direct correlation between **dioxin-like activity** and **pharmaceuticals** removal

69% **dioxin-like activity** removal after 20s of treatment

O_3: Flame Retardants removal in SE



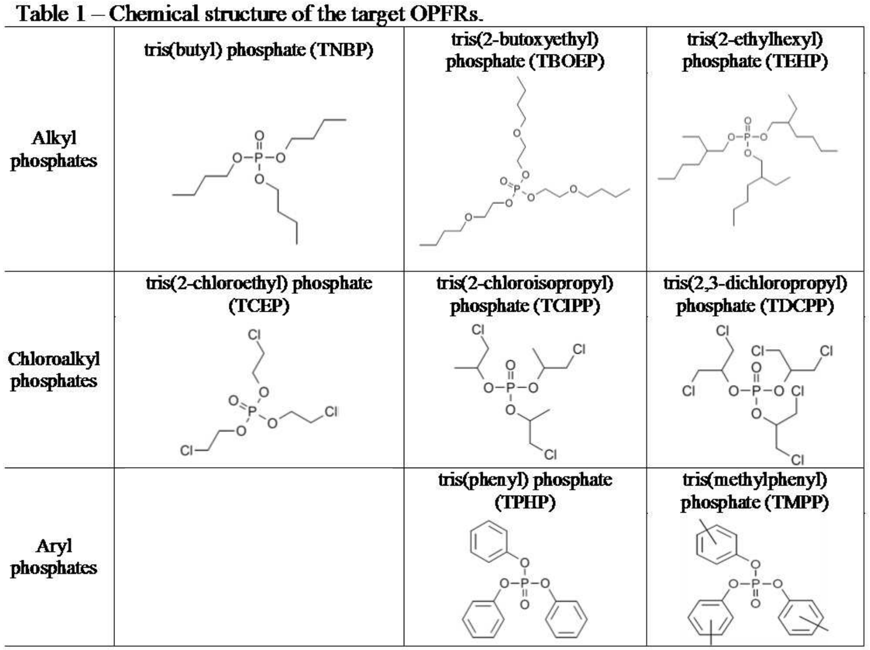
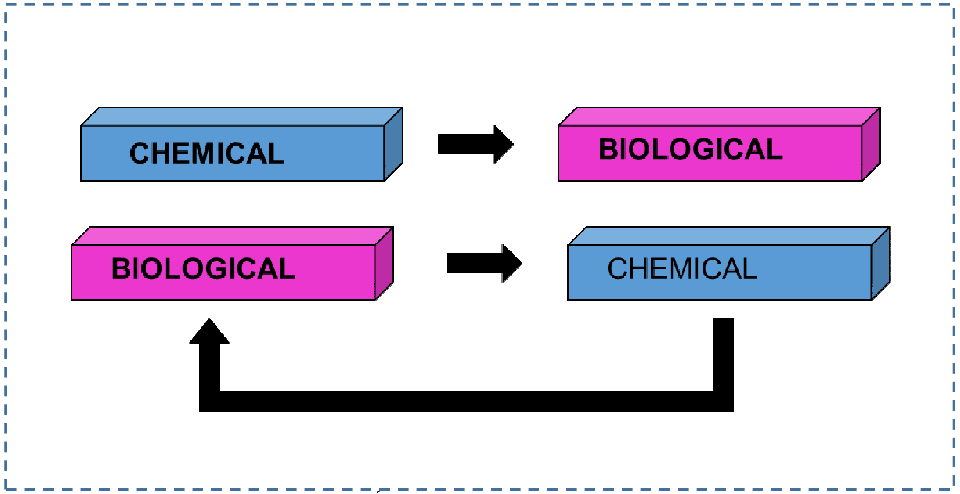


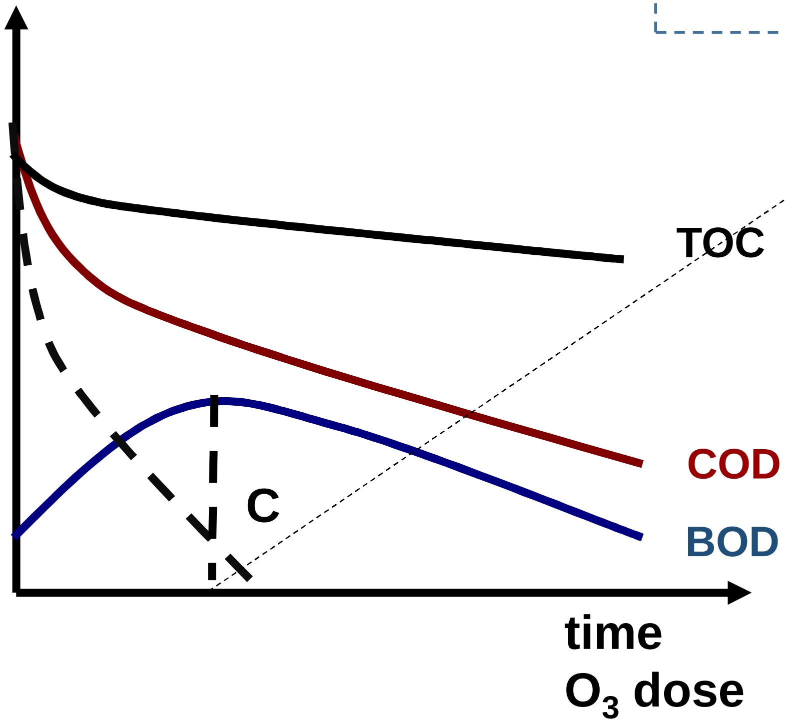
Table 1 – Chemical structure of the target OPFRs.

Alkyl phosphates	tris(butyl) phosphate (TNBP)	tris(2-butoxyethyl) phosphate (TBOEP)	tris(2-ethylhexyl) phosphate (TEHP)
Chloroalkyl phosphates	tris(2-chloroethyl) phosphate (TCEP)	tris(2-chloroisopropyl) phosphate (TCIPP)	tris(2,3-dichloropropyl) phosphate (TDCPP)
Aryl phosphates		tris(phenyl) phosphate (TPHP)	tris(methylphenyl) phosphate (TMPP)

O_3 and AOPs: WASTEWATER CHANGES

- **Contaminant removal**
- **COD removal**
- **TOC removal**
- **BOD changes**



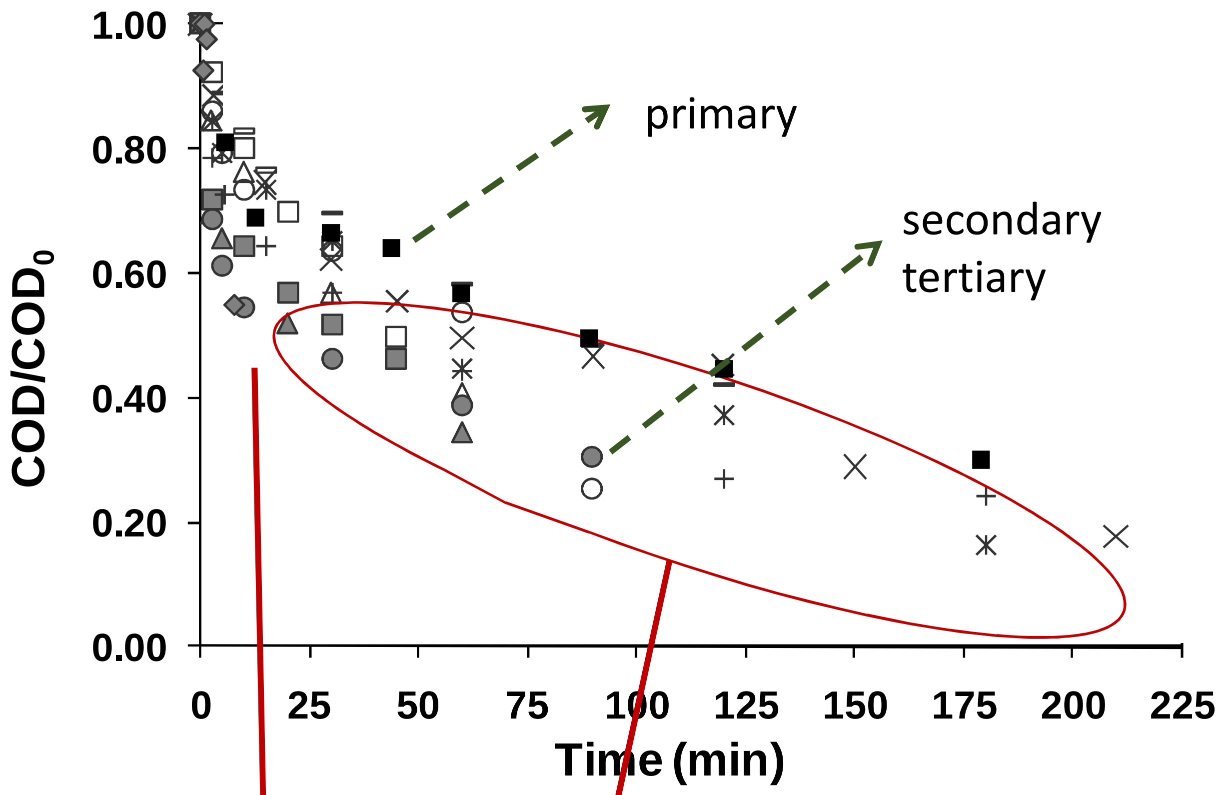


Stoichiometry
g (C, TOC, COD,UVA)
removed/g O_3

Kinetics (C, TOC,COD, UVA)
1st fast reaction
2nd slow reaction

Maximum of BOD

O_3: Effect on the EfOM of WWTP’s

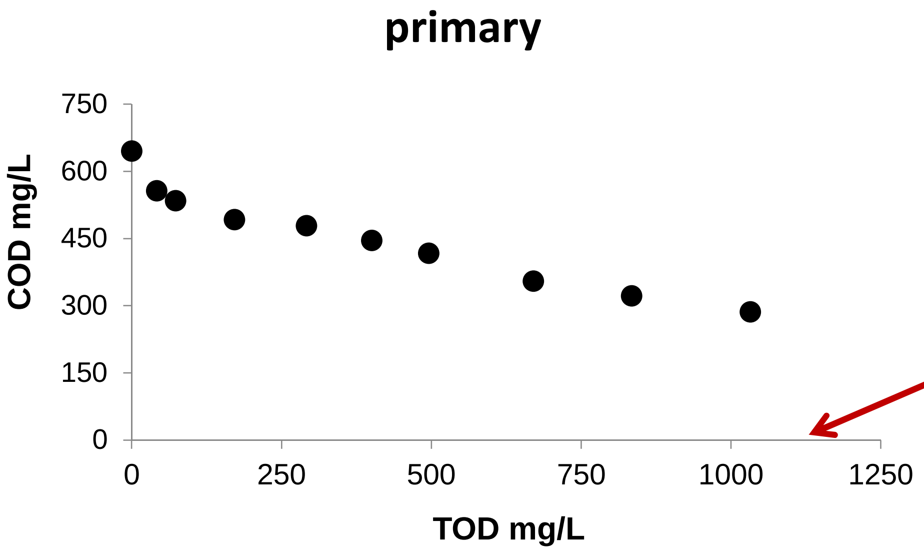


Filled symbols
correspond to
presence
of SS and turbidity

good COD removal and similar behavior in all cases

faster COD removal at initial time

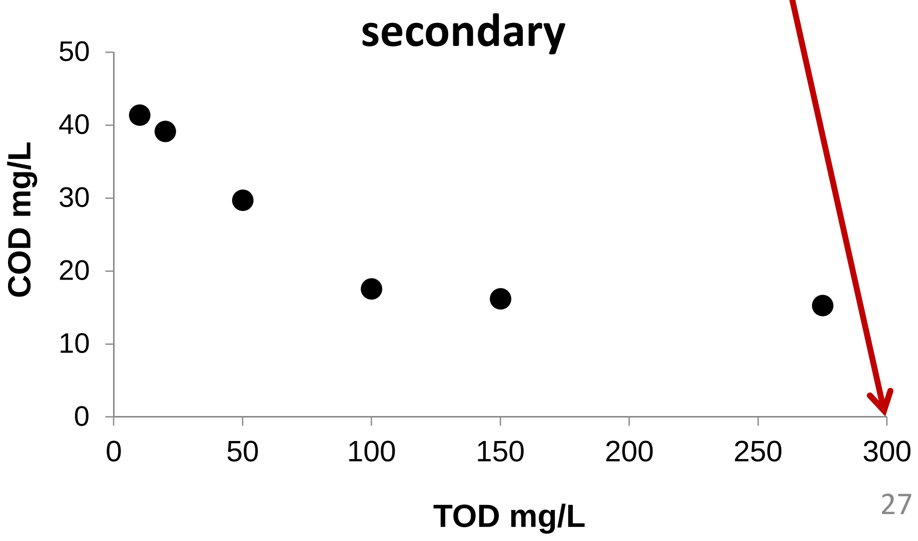
O_3: Effect on the EfOM of WWTP’s



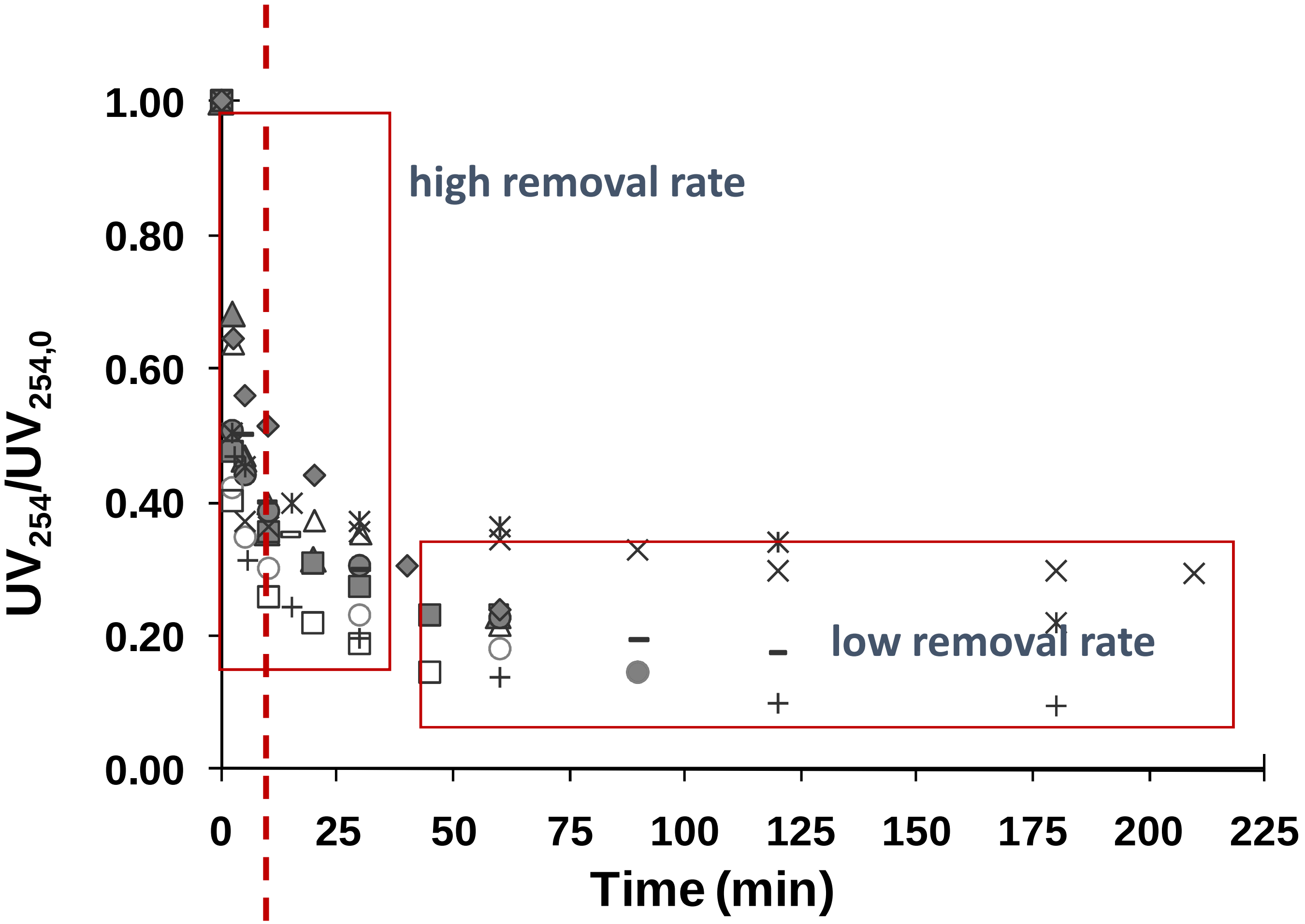
similar behavior
but HIGHER
values of TOD for
primary effluents

Transferred Ozone Dose (TOD)
accumulated ozone transferred to the water per unit of sample volume

$$\mathrm{TOD} = \int_0^t \frac{Q_{Gas}}{V_{Liq}} \times ([O3]_{gas\ in} - [O3]_{gas\ out}) \times dt_r$$



O_3: Effect on the EfOM of WWTP's



Aromatic compounds readily eliminated during the first minutes of the reaction, from 50 to 80 %.

O_3: Effect on the Molecular Size Distribution

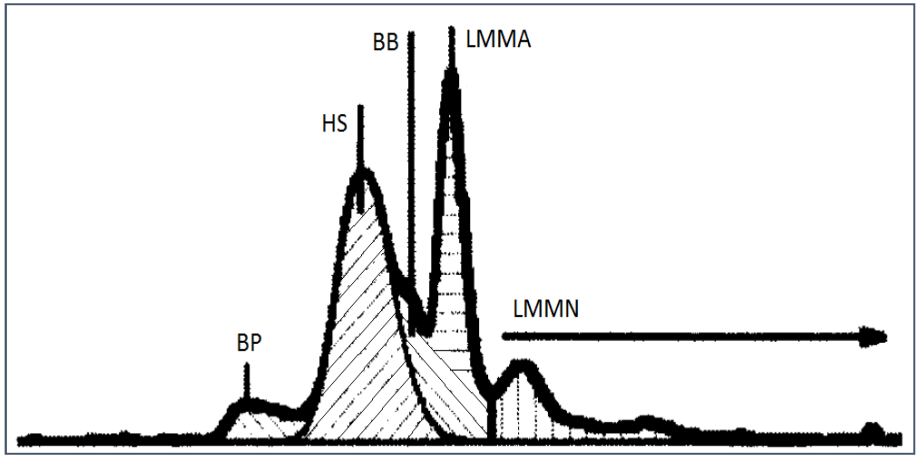
Liquid Chromatography - Organic Carbon Detector (LC-OCD)

- Organic Carbon Detector
- Size Exclusion Chromatography
- UV detection

acciona
Agua

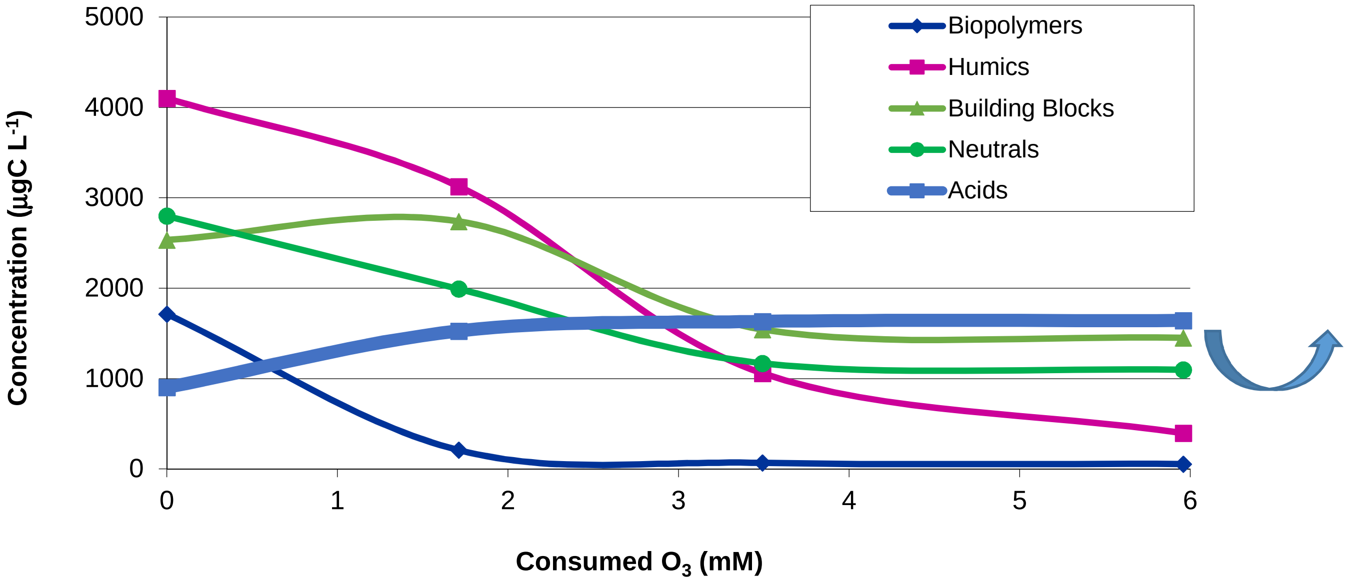
DOM fractions:

- Biopolymers (BP)
- Humic Substances (HS)
- Building Blocks (BB)
- LMM organic Acids (LMMA)
- LMM Neutrals (LMMN)



Typical Chromatogram of surface water

O_3: Effect on the Molecular Size Distribution

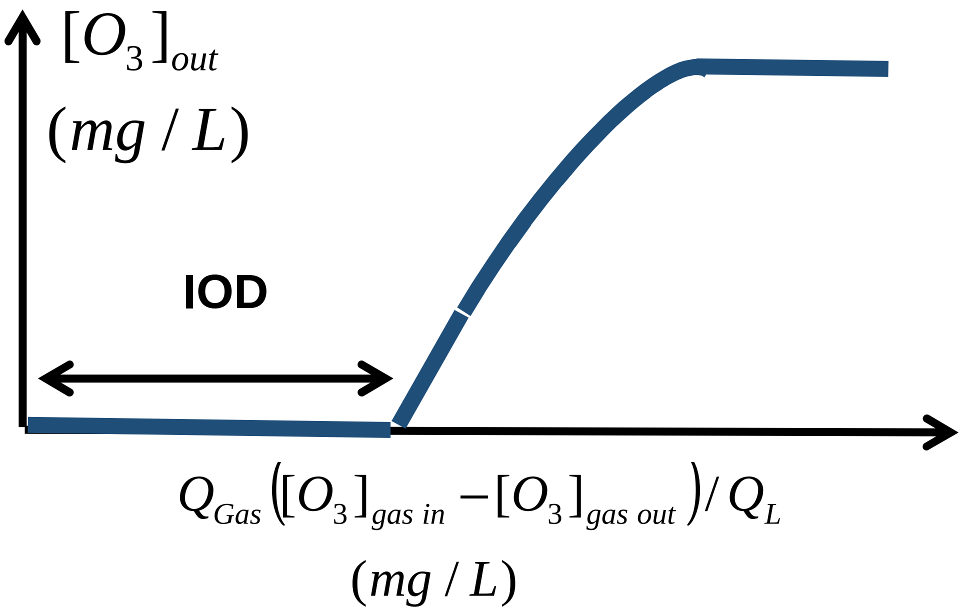


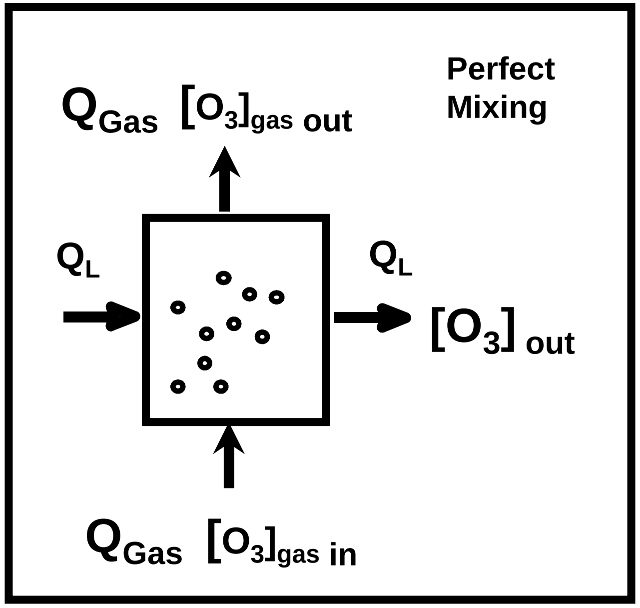
Increase of biodegradability of effluents treated by ozone

- Indirect **ozone** attack minimized due to scavenging effects (high alkalinity and high Cl^- concentration).
- Removal of BP but also **HS** and **LMMN** occurred from the first oxidation steps.
- **Low Molecular Mass Acids** accumulation from the beginning.

MODELLING O_3 MASS TRANSFER: IOD, K_La, k_d

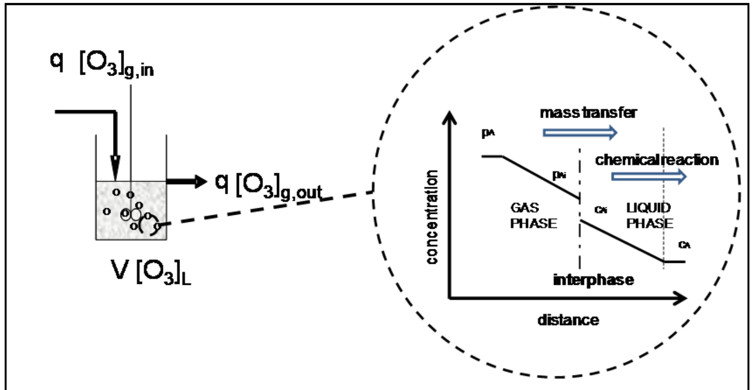
IMMEDIATE OZONE DEMAND (IOD) :
minimum amount of ozone dose (mg/L) to be transferred to have dissolved ozone in water (continuous flow)





IOD, $K_L a$, k_d estimation at lab scale

MODELLING



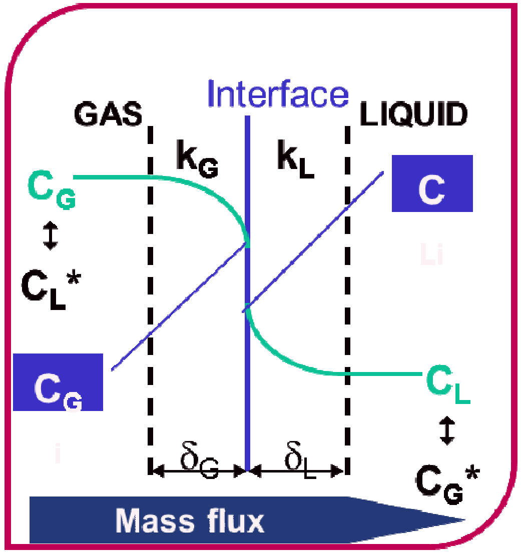
$$N_{O3}(\mathrm{mol}/(\mathrm{m}^2 .\mathrm{s})) = k_g(p_{o3} - p_{o3*}) = k_l([O3]^* - [O3])$$

$$N_{O3}(\mathrm{mol}/(\mathrm{m}^2 .\mathrm{s})) = k_G(p_{o3} - H[O3]) = k_L\left(\frac{p_{o3}}{H} - [O3]\right)$$

HENRY`S constant

$$p_{O3} = H[O3]$$

$$p_{O3} = Hx_{O3}$$



Ozone balance in liquid phase

TOD < IOD $[O3] = 0$

TOD > IOD $\frac{d[O3]}{dt} = K_L a \times ([O3]^* - [O3]) - k_d \times [O3]$

$P_{O3} = Hx_{O3^*}$ Henry's law

$$H = 3.810^7 [HO^-]^{0.035} \exp(-2428/T)$$

$$276.5K < T < 333K \quad 0.65 < pH < 10.2$$

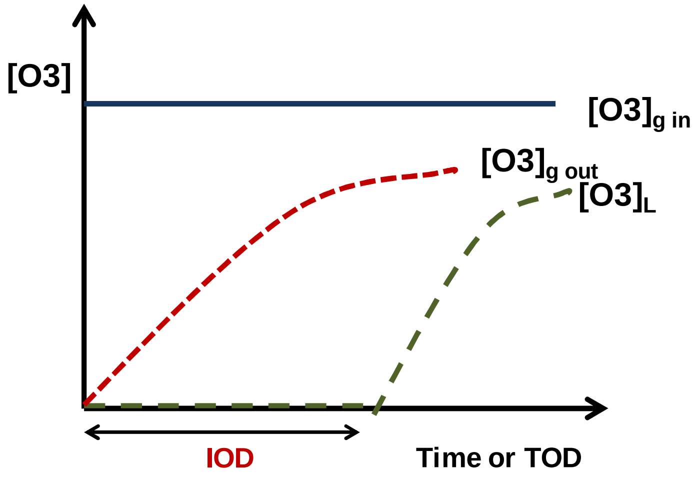
Roth and Sullivan equation

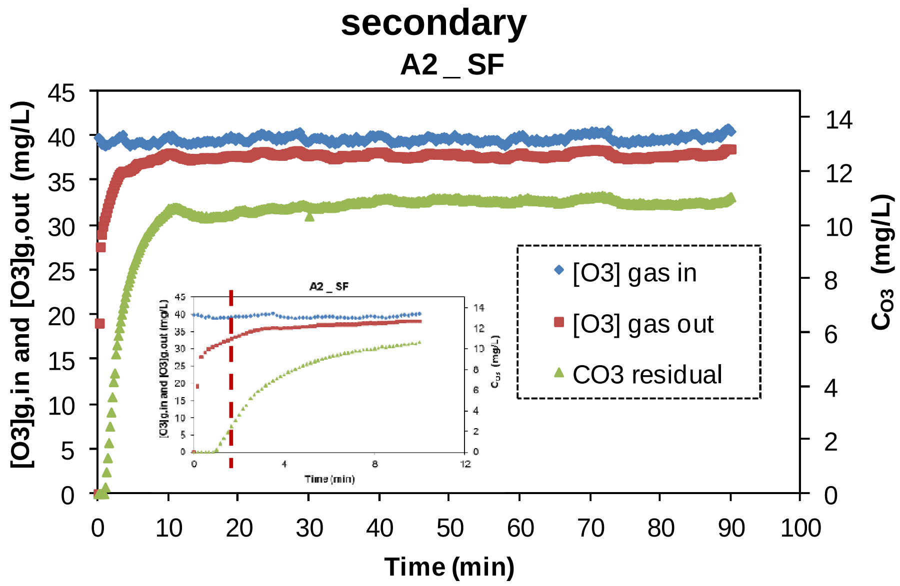
Ozone balance in gas phase

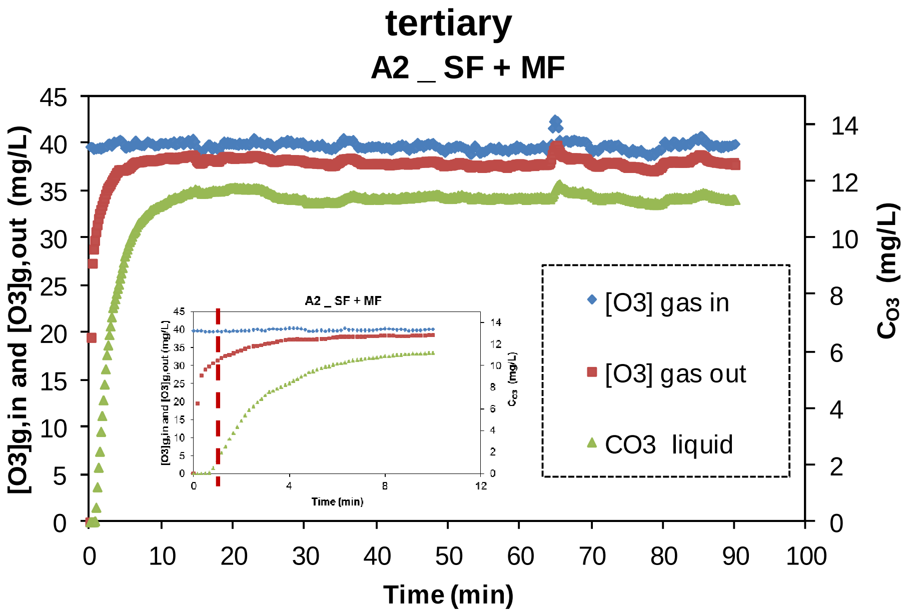
$$Q_{Gas}\left([O3]_{gas\ in} - [O3]_{gas\ out}\right) = K_L a([O3]^* - [O3]\ )V_{Liq} = k_d [O3]\ V_{Liq} + \frac{d[O3]}{dt} V_{Liq}$$

IOD, K_La, k_d estimation at lab scale

THEORETICAL
BEHAVIOUR
(K_La and k_d constant)





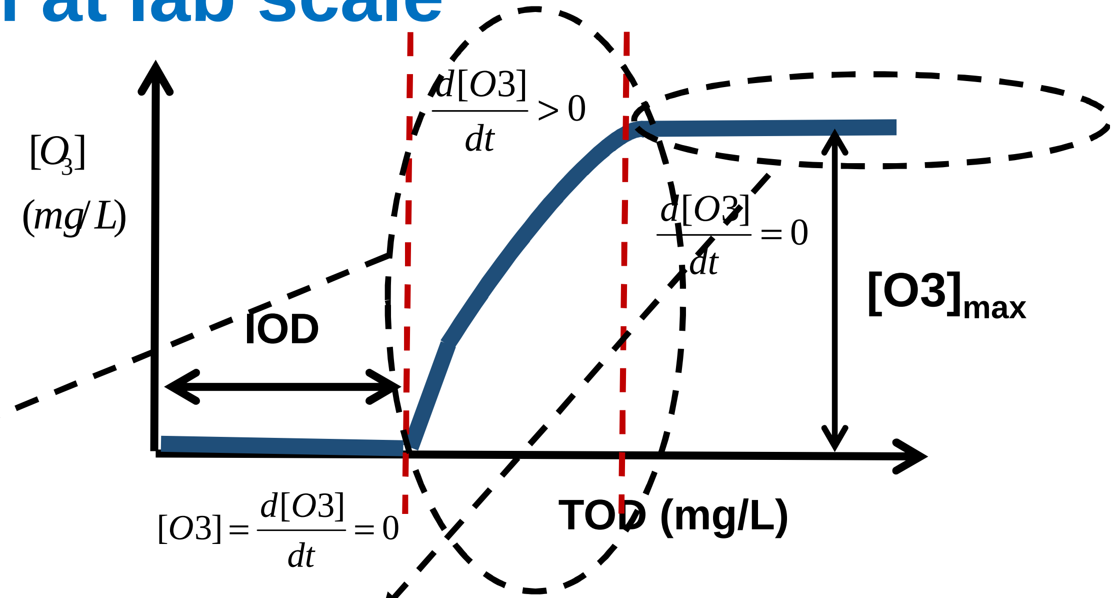


IOD = 5 - 8 mg/L, contact time = 1 min

From these data it is possible to estimate K_La and k_d

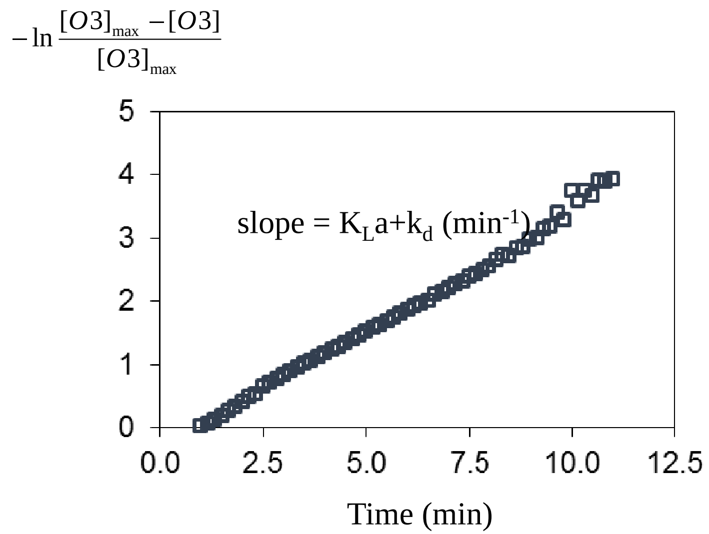
IOD, K_La, k_d estimation at lab scale

Behavior ozone in water



$$\frac{d[O3]}{dt} > 0$$

$$\ln\frac{[O3]_{max}-[O3]}{[O3]_{max}} = -(K_La+k_d)t$$



$$\frac{d[O3]}{dt} = 0$$

$$k_d = \frac{Q_{Gas}\left([O3]_{gas\ in}-[O3]_{gas\ out}\right)}{[O3]\ V_{Liq}}$$

$$\frac{[O3]^*}{[O3]_{max}} = \frac{K_La+k_d}{K_La}$$

$P_{O3} = Hx_{O3^*}$ Roth and Sullivan

$$H = 3.810^7[HO^-]^{0.035}\exp(-2428/T)$$

$$276.5K < T < 333K \quad 0.65 < pH < 10.2$$

IOD, K_La, k_d estimation at lab scale

K_La, k_d and IOD values primary, secondary and tertiary samples

Sample	K_La (min^{-1})	k_d (min^{-1})	IOD (mg/L)
P1	0.83	0.80	83
P2	0.76	0.19	64
P3	0.50	0.66	348
P4	0.79	0.30	249
S2	0.29	0.09	8.0
T1	1.90	0.08	5.0
T2	0.67	0.10	5.0

CONCLUSIONS

- **Ozonation of wastewater effluents** is able to reduce **COD, DOC, UVA, Turbidity** at the same time than **emerging contaminants concentration.**
- **At low ozonation doses** there is an increase of the biodegradability, **BOD/COD**, of the effluent.
- **During ozonation** there are important changes in the **Size Molecular Distribution of the Organic Matter.**
- Examination of the ozone mass balance provides three fundamental parameters: **the instantaneous ozone demand, ozone mass transfer coefficient and the ozone decay kinetic constant**.
- **Their knowledge is of primary importance for the design of ozone contactors and for the determination of the appropriate operating conditions.**

Universitat de Barcelona

ADVANCED OXIDATION PROCESS ENGINEERING
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Thank you

http://www.ub.edu/eq/cat/recerca_AOP.html