PPCP and EDC removal using Advanced Oxidation Processes

CEE 697z
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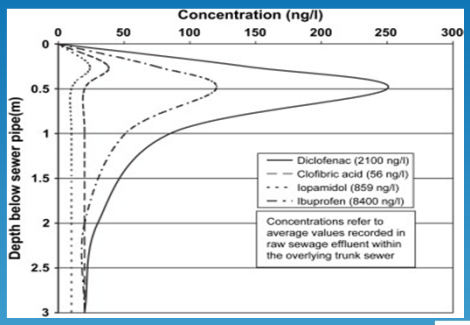
November 5, 2014

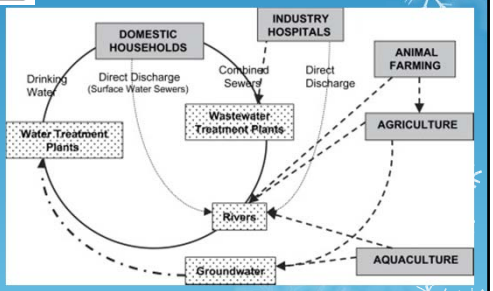
Sources of PPCPs and EDC

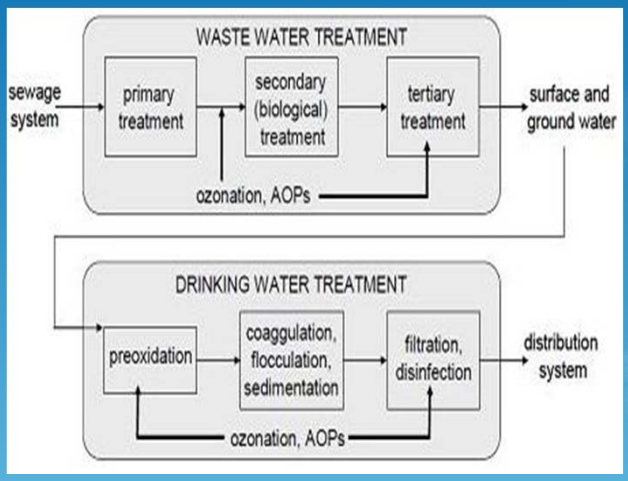
- Human activity (e.g., bathing, shaving, swimming)
- Illicit drugs
- Veterinary drug use, especially antibiotics and steroids
- Agribusiness
- Residues from pharmaceutical manufacturing (well defined and controlled)
- Residues from hospitals

PPCP depth–distribution curve (J.B Ellis, 2005)



Sources and pathways of PPCPs in the urban water cycle





Source: http://www.sswm.info

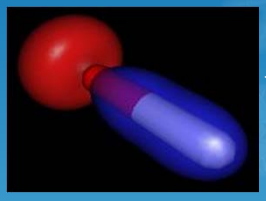
Conventional oxidation processes used in water treatment

- Chlorine
- Hypochlorous acid
- Ozone
- Hydrogen Peroxide
- Potassium Permanganate
- Chlorine dioxide

- Drawbacks-
  - Chlorine produces THMs and HAAs (DBPs)
  - The other oxidants are compound selective , not effective for micropollutant degredation

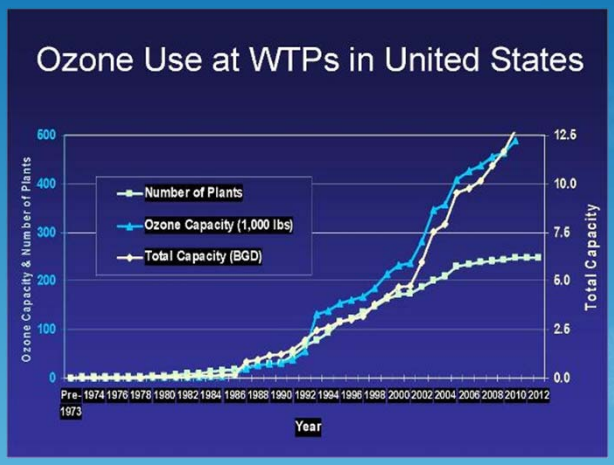
AOPs used in water treatment

- Ozone/UV
- UV/TiO2
- UV/H202
- Fenton process



AOPs rely on in-situ production of highly reactive hydroxyl radicals (·OH). These reactive species are the strongest oxidants that can be applied in water and can virtually oxidize any compound present in the water matrix, often at a diffusion controlled reaction speed. Consequently, ·OH reacts unselectively once formed and contaminants will be quickly and efficiently fragmented and converted into small inorganic molecules. Hydroxyl radicals are produced with the help of one or more primary oxidants

Time Line of Ozone Use In Drinking Water (Potable Water) Treatment



http://www.spartanwatertreatment.com

- Advantages of Advanced Oxidation Processes

  Rapid reaction rates

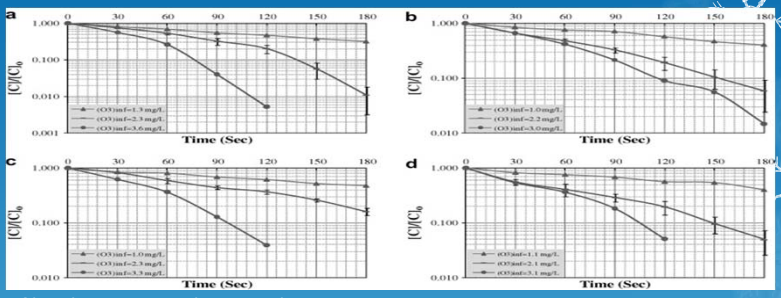
  - Small foot print
  - Potential to reduce toxicity of organic compounds
  - Mineralization of organics, i.e. conversion to salt and CO2
  - Does not concentrate waste for further treatment, such as membranes
  - Does not produce "spent carbon" such activated carbon absorption
  - Easily Automated and Controlled
  - Reduced Labor Input
  - Does not create sludge as with physical chemical process or biological processes (wasted biological sludge)
- Disadvantages of Advanced Oxidation Processes
  - Capital Intensive
  - Complex chemistry must be tailored to specific application
  - For some applications quenching of excess peroxide is required

Ozonization- Removal of Sulfonamides (synthetic antimicrobials)

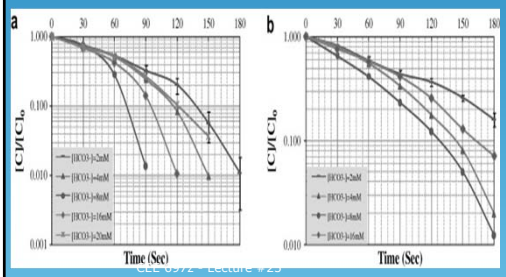
- SMZ is the most widely prescribed antibiotics in the US and hence, frequently detected in the environment
- Sulfonamides can be excreted by the body at high rates, as high as 30% for SDZ and 80% for SFZ of the administered dose
- all the sulfonamides were detected in the environment, including drinking water, surface water, and wastewater treatment plant effluent
- Degradation of sulfonamides under different experimental conditions was tested:
  - pH range: 2-10
  - Ozone gas concentration: 2-20 mM
  - Bicarbonate ion concentration: 1-3.2 mg/l

Garoma et.al, 2010

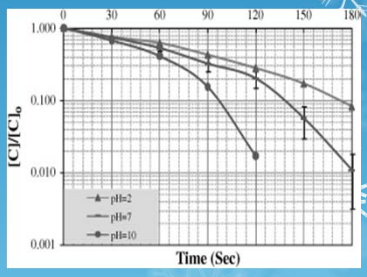
Effect of influent ozone gas concentration on the removal: (a) sulfamethoxazole, (b) sulfamethizole, (c) sulfathiazole, and (d) sulfadiazine



Effect of bicarbonate ion on the removal: (a) sulfamethoxazole and (b) sulfathiazole



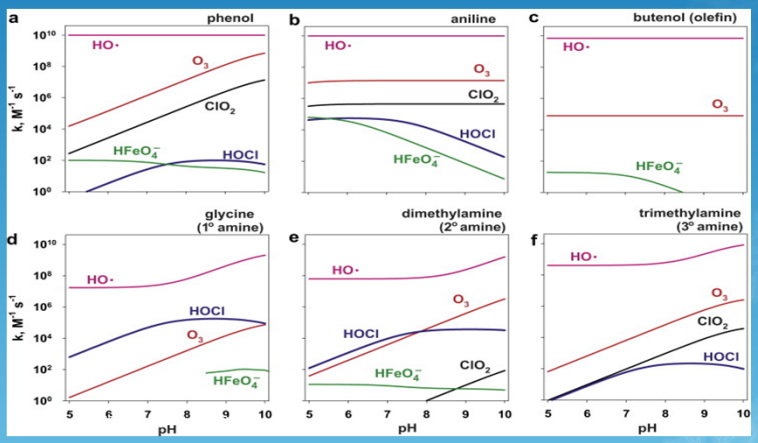
Effect of pH on the removal sulfamethoxazole.



Garoma et.al, 2010

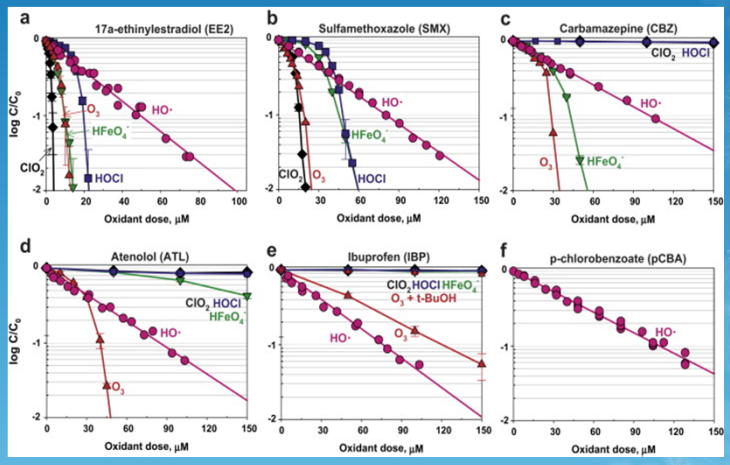
Oxidative transformations of micropollutants in water

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) with (a) phenol, (b) aniline, (c) butenol, (d) glycine, (e) dimethylamine, and (f) trimethylamine. k values for chlorine,for chlorine dioxide and ozone, for ferrate^{VI}, and for hydroxyl radicals



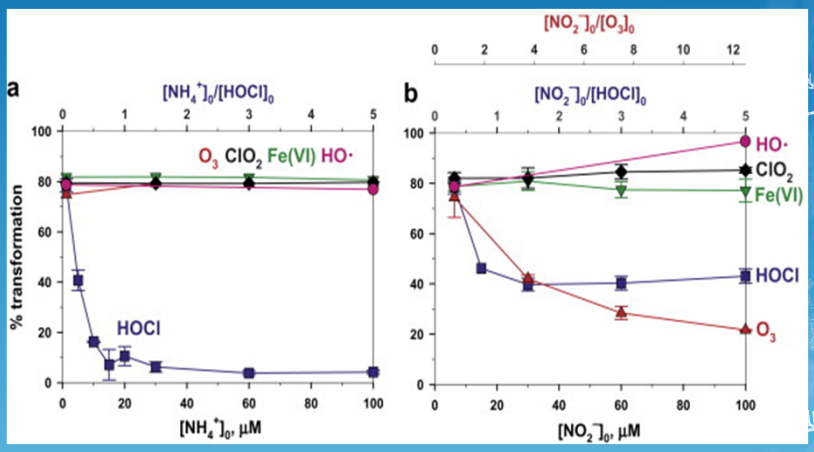
Lee, Von Gunten (2010)

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



Lee, Von Gunten (2010)

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



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Lee, Von Gunten (2010)

Effect of bromide

- Bromide is present in waters and wastewaters at concentrations of 10 to several hundred µg L^{-1}. Since the oxidation of bromide typically produces bromine, which is highly reactive to phenol- and amine-moieties, the presence of bromide during oxidative wastewater treatment can affect the transformation efficiency of micropollutants.
- Among the selective oxidants, only chlorine and ozone react with bromide generating bromine. Since bromine is about three orders of magnitude more reactive toward phenols than chlorine transformation of phenolic micropollutants can be significantly enhanced during chlorination of bromide-containing waters.
- A recent study showed that bromine produced from bromide was mainly responsible for 17α-ethinylestradiol transformation during chlorination of a wastewater. In the case of ozone, most phenolic- and amine-moieties are already oxidized by ozone before the significant formation of bromine from bromide. Hence, the presence of bromide affects little the transformation efficiency of micropollutants during ozonation.
- However, an enhanced transformation of 1° amine-containing micropollutants is expected due to the relatively low reactivity of ozone versus high reactivity of bromine to 1° amines
- Formation of potentially carcinogenic bromate during ozonation of bromide-containing waters is one of drawbacks of ozonation

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Lee, Von Gunten (2010)

Conclusions from the study

- The selective oxidants react only with some electron-rich organic moieties (ERMs), such as phenols, anilines, olefins, and amines, with the exception of the following reactions: chlorine and chlorine dioxide with olefins, chlorine dioxide with 1° and 2° amines, and ferrate^{VI} with 3° amines show a negligible reactivity. In contrast, hydroxyl radicals show a very high reactivity with almost all organic moieties, even including C-H bonds. Therefore, hydroxyl radicals can transform any type of micropollutant with a similar efficiency.
- Effluent organic matter (EfOM) as a major wastewater matrix component contains ERMs and thus consumes the oxidants. Therefore, competition for oxidants between target micropollutants and EfOM determines the transformation efficiency. The competition depends on the relative reaction rate of a given oxidant with ERMs present in a target micropollutant and the EfOM. Accordingly, a higher rate constant of an oxidant with a target micropollutant does not necessarily translate into more efficient transformation.
- For the selective oxidants, the competition disappears rapidly after the ERMs present in EfOM are consumed. In contrast, for hydroxyl radicals, the competition remains practically the same during the entire oxidation process. Therefore, the efficiency of hydroxyl radicals is much lower than that of the selective oxidants for transforming micropollutants containing ERMs. In addition, the difference in transformation efficiency becomes larger if higher extents of transformations of micropollutants should be achieved.
- Ammonia and nitrite can significantly decrease transformation efficiency of micropollutants (i.e. phenolic- and aniline containing) during chlorination. Nitrite can also decrease transformation efficiency during ozonation. Therefore, in poorly nitrified or -denitrified wastewaters, transformation of micropollutants can be low during a treatment with chlorine or ozone. In contrast, bromide can significantly increase transformation efficiency of phenolic-micropollutants by forming bromine during chlorination. In addition, an enhanced transformation of 1° amine-containing micropollutants is expected during ozonation of bromide-containing waters.

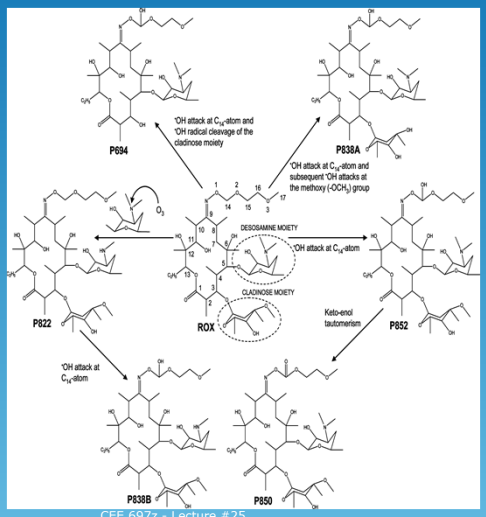
Lee, Von Gunten (2010)

Ozonation products of antibiotics- Roxithromycin and Trimethoprim

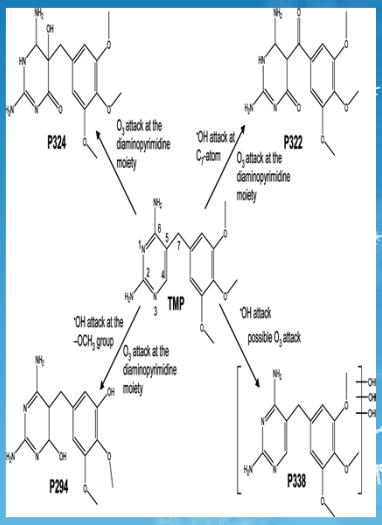
- Mechanisms of product formation of two frequently encountered antibiotics, trimethoprim (TMP) and a macrolide antibiotic roxithromycin (ROX) were investigated
- TMP was found to produce a toxic response in rainbow trout, while for both TMP and ROX ecotoxicological effects on the algal growth were reported
- The formation of persistent and structurally similar ozonation products of these antibiotics could reflect in their increased hazardousness. To elucidate the structures of ozonation products, analysis were performed by UPLC coupled to a (QqToF-MS)
- The lab-scale ozonation experiments were performed with distilled water (DW) and sewage effluent (SE), and evolution of products and removal efficiencies were compared
- *Daphnia magna* assay was used to estimate the toxicity of the parent compounds and their ozonation products.

J. Radjenovic et.al; 2009

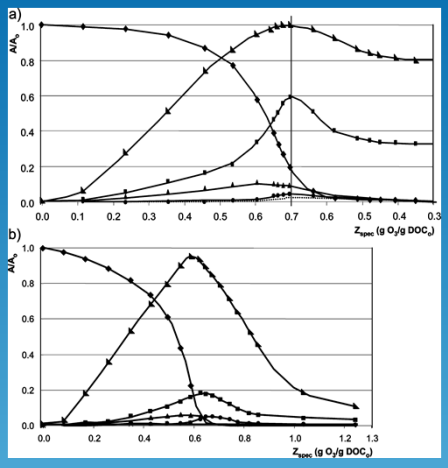
Degradation mechanism of ozonation of ROX in DW and SE matrix.



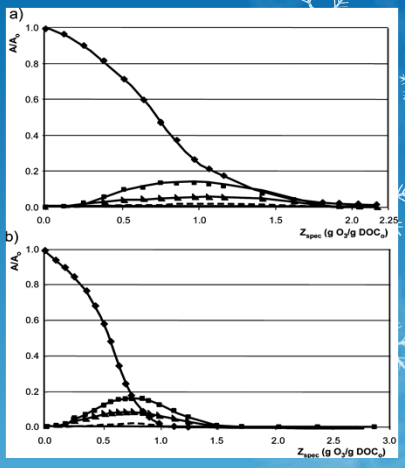
Degradation mechanism of ozonation of TMP in DW and SE matrix



J. Radjenovic et.al; 2009



Peak areas of ROX and its ozonation products normalized to the initial value of peak area of ROX (t = 0) presented vs Z_{spec} calculated for the DOC_o in the ozonation experiment with (a) distilled water (DW) and (b) sewage effluent (SE). ◆, ROX; ▼, P852; □, P694; ▼, P822; ●, P838A, ... P850.



Peak areas of TMP and its ozonation products normalized to the initial value of peak area of TMP(t=0) presented vs specific O_3consumption (Z_{spec}) calculated for the DOC_o in the ozonation experiment with (a) DW and (b) SE. ◆, TMP; ▼P324; □, P294, ... P338.

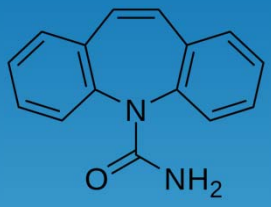
J. Radjenovic et.al; 2009

Results

- In the case of both TMP and ROX, the ozonation products formed were the same in DW and SE
- In the case of ROX unexpected persistence of P852 and P694 was observed during the ozonation in DW
- Contrary to DW matrix, SE enhanced the ozonation of ROX and its degradation products
- The degradation of TMP was slightly faster in the experiment with SE than with DW
- Ecotoxicity results showed no acute toxic effects for ROX and TMP in the tested concentration range
- Byproducts formed showed persistence of antimicrobial activity like the parent compounds
- Chronic toxicity of the compounds should be further investigated as the tertiary amine group seems to remain unchanged

J. Radjenovic et.al; 2009

Carbamazepine ozonation and assesment on algal toxicity

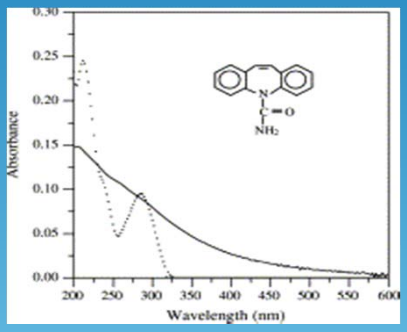


- The presence of carbamazepine (CBZ), an antiepilectic drug, has been reported in sewage treatment plant (STP) effluents as a result of its low biodegradability
- The persistence of CBZ in aquatic environment with respect to abiotic transformation processes along with its toxicity and capability of accumulating in single aquatic organisms (algae) are evaluated.

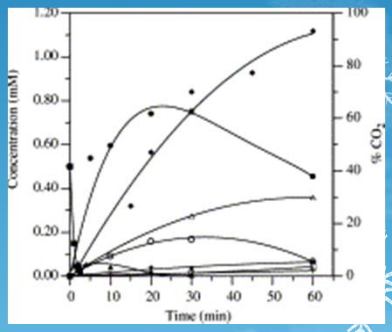
Roberto Andreozz et.al, 2001

Persistence in surface waters

- Absorbs UV radiation
- Undergoes photochemical transformations in surface waters

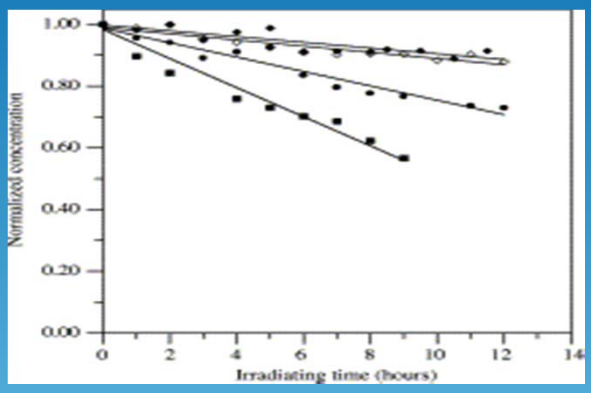


Ozonation of CBZ and reaction intermediates at pH=5.5. [CBZ]o=5.0×10−4 mol/dm³ ■ CBZ, • hydrogen peroxide, oxalic acid, ▽, glyoxylic acid, △, carbon dioxide, ✳, glyoxal, ★, oxamic acid, ▲, anthranilic acid and ◫, ketomalonic acid.



Roberto Andreozz et.al, 2001

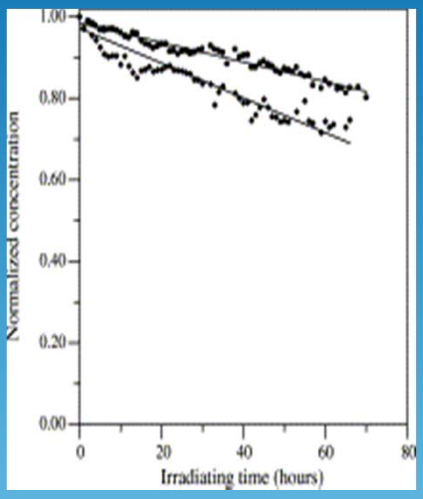
Nitrate-induced photodegradation of CBZ in bi-distilled water during exposure to sunlight at different concentrations of nitrate at pH=5.5 and *T*=25°C



Nitrite and nitrate are also indicated as capable of promoting the formation of OH radicals . The half life of CBZ decreased to 69.0, 24.5 and 11.2 h when the concentrations of nitrates were, respectively, of 5.0×10^{-4} g dm^{-3}, 1.0×10^{-2} g dm^{-3} and 1.5×10^{-2} g dm^{-3}

Roberto Andreozz et.al, 2001

Effect of Humic acid



The presence of dissolved humicacid(5.0×10^{-3}g/dm^3) on the other hand resulted into an increase of CBZ half-life. The addition of these compounds to CBZ aqueous solutions seems to hinder the spontaneous photochemical degradation of the pollutant.

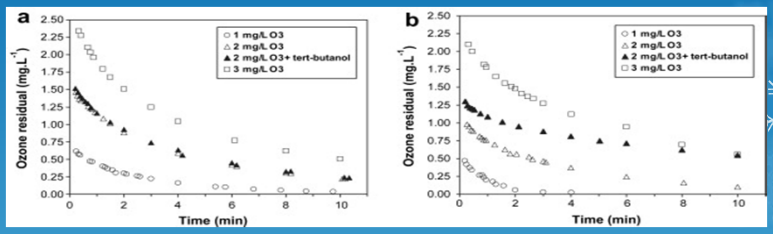
Roberto Andreozz et.al, 2001

Bench-scale experiments were performed using two natural waters that differed in alkalinity and dissolved organic carbon concentration (DOC). Filtered water samples (before the ozonation process) were collected from two municipal DWTPs in the province of Quebec, Canada.

Target compounds.				
Compound	Class/use	MDL (ng/L)	MW (g /mol)	pKa
Caffeine	Stimulant	9	194.2	10.4
Trimethoprim	Anti-infec	9	290.3	7.12
Carbamazepine	Anticonvu	2	236.3	0.37
Naproxen	Analgesic	12	230.3	4.15
Gemfibrozil	Anti-chole	24	250.3	4.42
Estrone	Estrogen	10	270.4	10.4
Estriol	Estrogen	50	272.4	10.4
Estradiol	Estrogen	3	288.4	10.4
17α-Ethinylestradiol	Synthetic	7	296.4	10.4
Progesterone	Progestro	3	314.5	NA
Medroxyprogesterone	Synthetic	2	344.5	NA
Norethindrone	Synthetic	7	298.4	NA
Levonorgestrel	Synthetic	5	312.4	NA
Cyanazine	Herbicide	4	240.7	1.1
Deethylatrazine (DEA)	Metabolit	5	187.6	1.4
Deisopropylatrazine (DIA)	Metabolit	17	173.6	1.5

Filtered water quality for DWTP A and DWTP B.			
Parameter	Unit	DWTP A	DWTP B
pH		8.24	6.62
Alkalinity	mg CaCO3/L	80	9
Dissolved organic carbon (DOC)	mg C/L	1.99	2.85
UV absorbance (254 nm)	/cm	0.027	0.047
Turbidity	NTU	0.112	0.058

Ozone decay for DWTP A (a) and DWTP B (b) natural filtered waters



Maximum concentration of target coompunds(ng/L) before and after ozonation

	DWTP A	DWTP B		
	Before O3	After O3	Before O3	After O3
Caffeine	214	60	267	54
Trimethoprim	19	<9	<9	<9
Carbamazepine	8	4	10	4
Naproxen	<12	<12	28	34
Gemfibrozil	<24	<24	<24	<24
Estradiol	3	<3	5	<3
Cyanazine	7	5	<4	<4
DIA	237	29	<17	<17
DEA	57	57	10	10

QUESTIONS????

References

- Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment; S.Vincent et.al 2009
- Removal of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole from aqueous solution by ozonation; Garoma et.al 2010
- Evidencing Generation of Persistent Ozonation Products of Antibiotics Roxithromycin and Trimethoprim; J. Radjenovic, et.al 2009
- Carbamazepine in water: persistence in the environment, ozonation treatment andpreliminary assessment on algal toxicity; Roberto Andreozzi 2001
- Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrateVI, and ozone) and non-selective oxidants (hydroxyl radical) Yunho Lee,von Gunten 2009
- http://www.spartanwatertreatment.com

End

- To next lecture