2nd Summer School on Environmental applications of AOPs, Porto (Portugal), July 10-14, 2017

Ionizing radiation as an efficient AO(R)P method for remediation of waters and wastewaters

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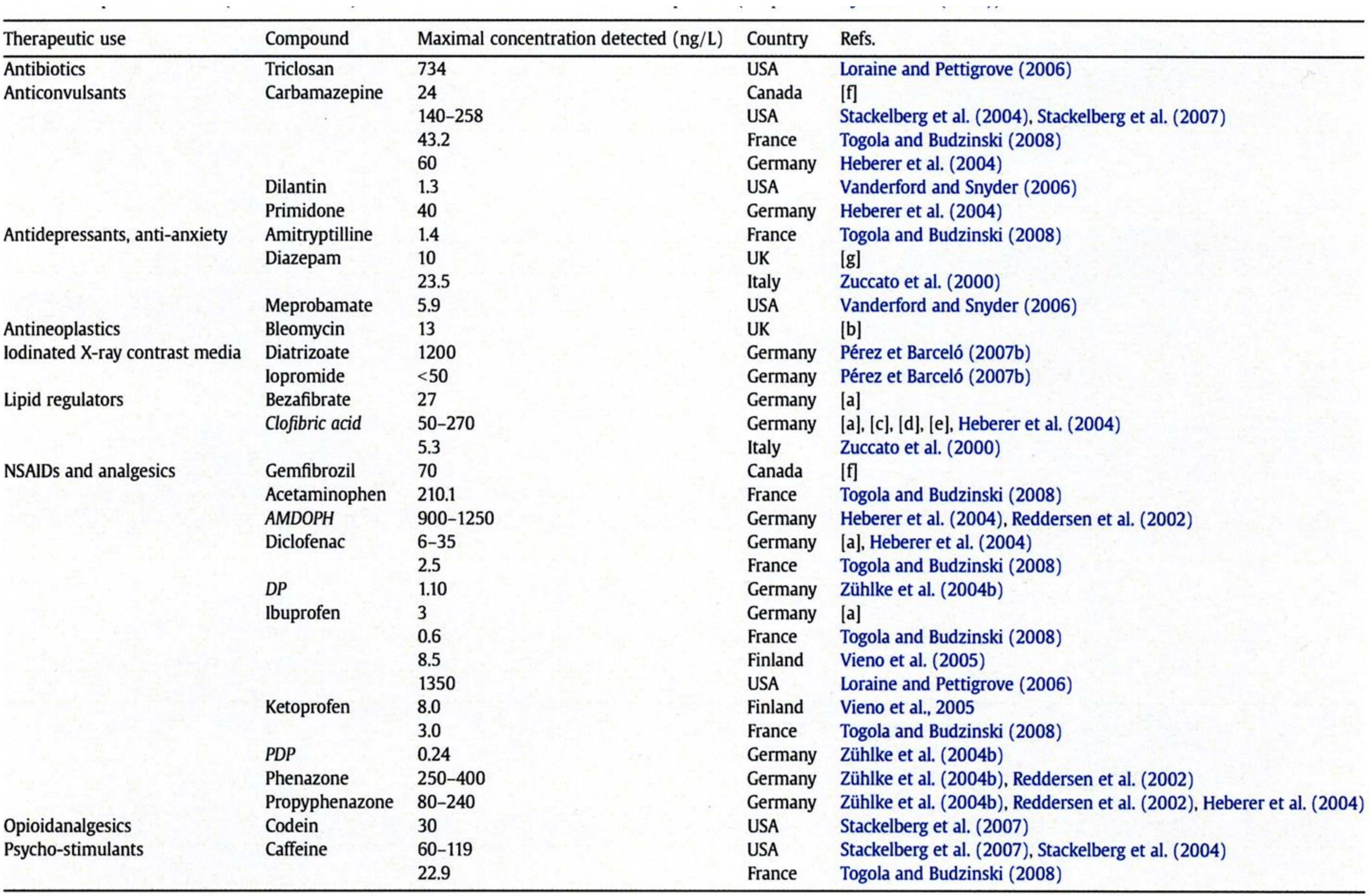
PROBLEM

PRESENCE OF DIFFERENT CLASSES OF HARD-TO-REMOVE CONTAMINANTS IN WATERS AND WASTEWATERS

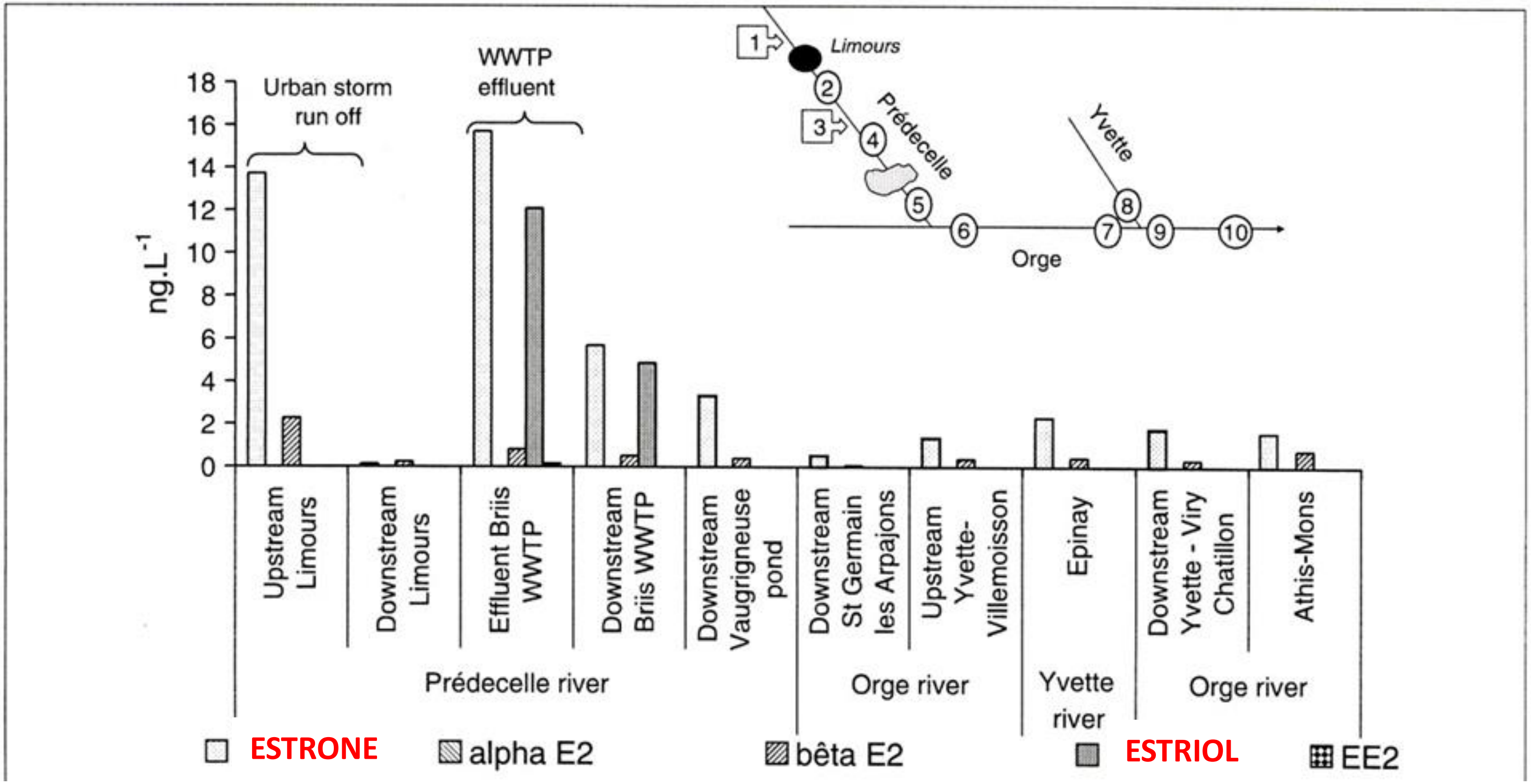
Presence of pharmaceutical compounds (and their metabolites) in worldwide TAP WATER



Therapeutic use	Compound	Maximal concentration detected (ng/L)	Country	Refs.
Antibiotics	Triclosan	734	USA	Loraine and Pettigrove (2006)
Anticonvulsants	Carbamazepine	24	Canada	[f]
		140–258	USA	Stackelberg et al. (2004), Stackelberg et al. (2007)
		43.2	France	Togola and Budzinski (2008)
		60	Germany	Heberer et al. (2004)
	Dilantin	1.3	USA	Vanderford and Snyder (2006)
	Primidone	40	Germany	Heberer et al. (2004)
Antidepressants, anti-anxiety	Amitryptilline	1.4	France	Togola and Budzinski (2008)
	Diazepam	10	UK	[g]
		23.5	Italy	Zuccato et al. (2000)
	Meprobamate	5.9	USA	Vanderford and Snyder (2006)
Antineoplastics	Bleomycin	13	UK	[b]
Iodinated X-ray contrast media	Diatrizoate	1200	Germany	Pérez et Barceló (2007b)
	Iopromide	<50	Germany	Pérez et Barceló (2007b)
Lipid regulators	Bezafibrate	27	Germany	[a]
	Clofibric acid	50–270	Germany	[a], [c], [d], [e], Heberer et al. (2004)
		5.3	Italy	Zuccato et al. (2000)
NSAIDs and analgesics	Gemfibrozil	70	Canada	[f]
	Acetaminophen	210.1	France	Togola and Budzinski (2008)
	AMDOPH	900–1250	Germany	Heberer et al. (2004), Reddersen et al. (2002)
	Diclofenac	6–35	Germany	[a], Heberer et al. (2004)
		2.5	France	Togola and Budzinski (2008)
	DP	1.10	Germany	Zühlke et al. (2004b)
	Ibuprofen	3	Germany	[a]
		0.6	France	Togola and Budzinski (2008)
		8.5	Finland	Vieno et al. (2005)
		1350	USA	Loraine and Pettigrove (2006)
	Ketoprofen	8.0	Finland	Vieno et al., 2005
		3.0	France	Togola and Budzinski (2008)
	PDP	0.24	Germany	Zühlke et al. (2004b)
	Phenazone	250–400	Germany	Zühlke et al. (2004b), Reddersen et al. (2002)
	Propyphenazone	80–240	Germany	Zühlke et al. (2004b), Reddersen et al. (2002), Heberer et al. (2004)
Opioidanalgesics	Codein	30	USA	Stackelberg et al. (2007)
Psycho-stimulants	Caffeine	60–119	USA	Stackelberg et al. (2007), Stackelberg et al. (2004)
		22.9	France	Togola and Budzinski (2008)

Mompelat et al., Environ. Internat., 35 (2009) 803

Presence of estrogenic hormones in SURFACE WATER



PRESENCE OF 5 DISSOLVED ESTROGENIC HORMONES IN SURFACE WATERS, STORM RUNOFF AND WWTP EFFLUENT AT DIFFERENT SITES IN THE ORGE BASIN (FRANCE)

Miege et al., Trends Anal. Chem., 28 (2009) 186

How efficient is the removal of organic/emerging pollutants in conventional treatment plants (incl. AOPs)?

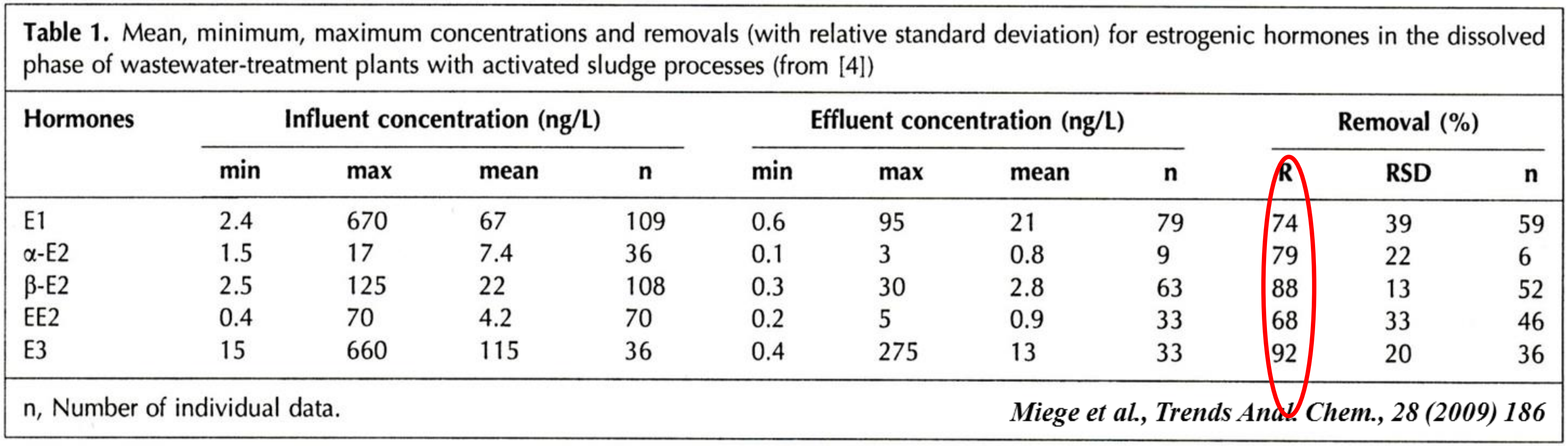
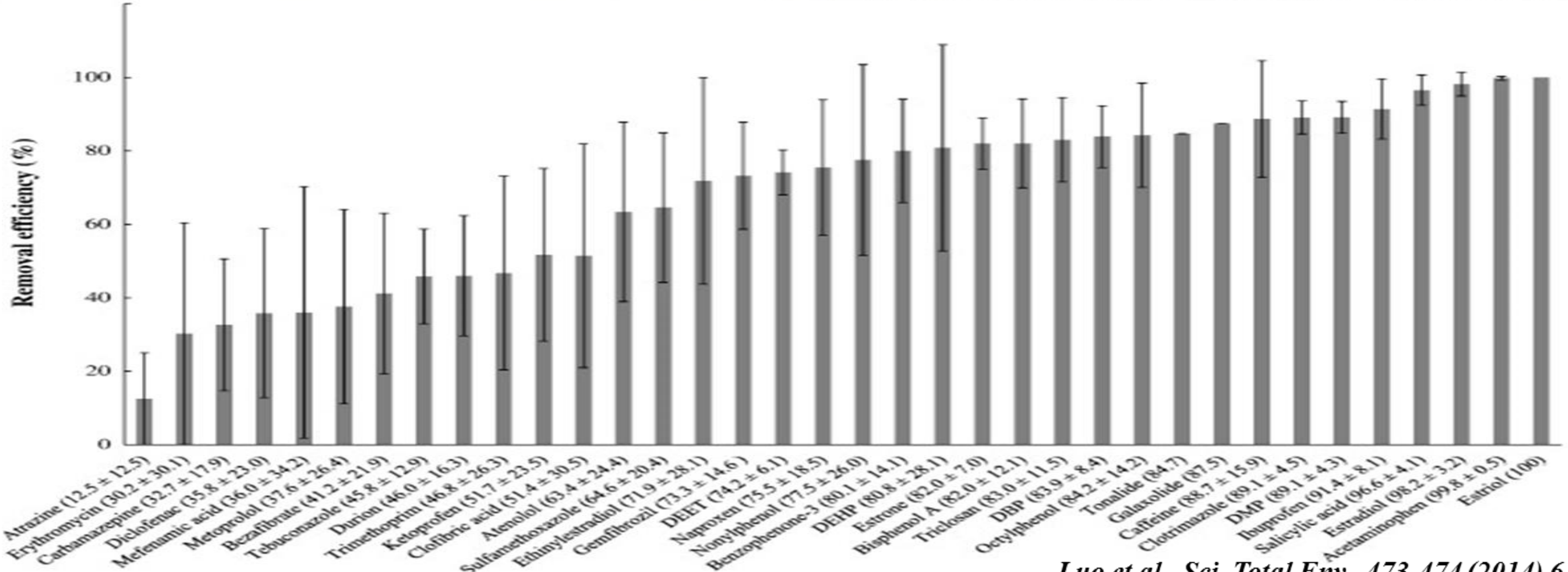


Table 1. Mean, minimum, maximum concentrations and removals (with relative standard deviation) for estrogenic hormones in the dissolved phase of wastewater-treatment plants with activated sludge processes (from [4])

Hormones	Influent concentration (ng/L)				Effluent concentration (ng/L)				Removal (%)		
	min	max	mean	n	min	max	mean	n	R	RSD	n
E1	2.4	670	67	109	0.6	95	21	79	74	39	59
α-E2	1.5	17	7.4	36	0.1	3	0.8	9	79	22	6
β-E2	2.5	125	22	108	0.3	30	2.8	63	88	13	52
EE2	0.4	70	4.2	70	0.2	5	0.9	33	68	33	46
E3	15	660	115	36	0.4	275	13	33	92	20	36

n, Number of individual data.

Miege et al., Trends Anal. Chem., 28 (2009) 186



Luo et al., Sci. Total Env., 473-474 (2014) 610

How efficient is the removal of organic/emerging pollutants in conventional treatment plants (incl. AOPs)?

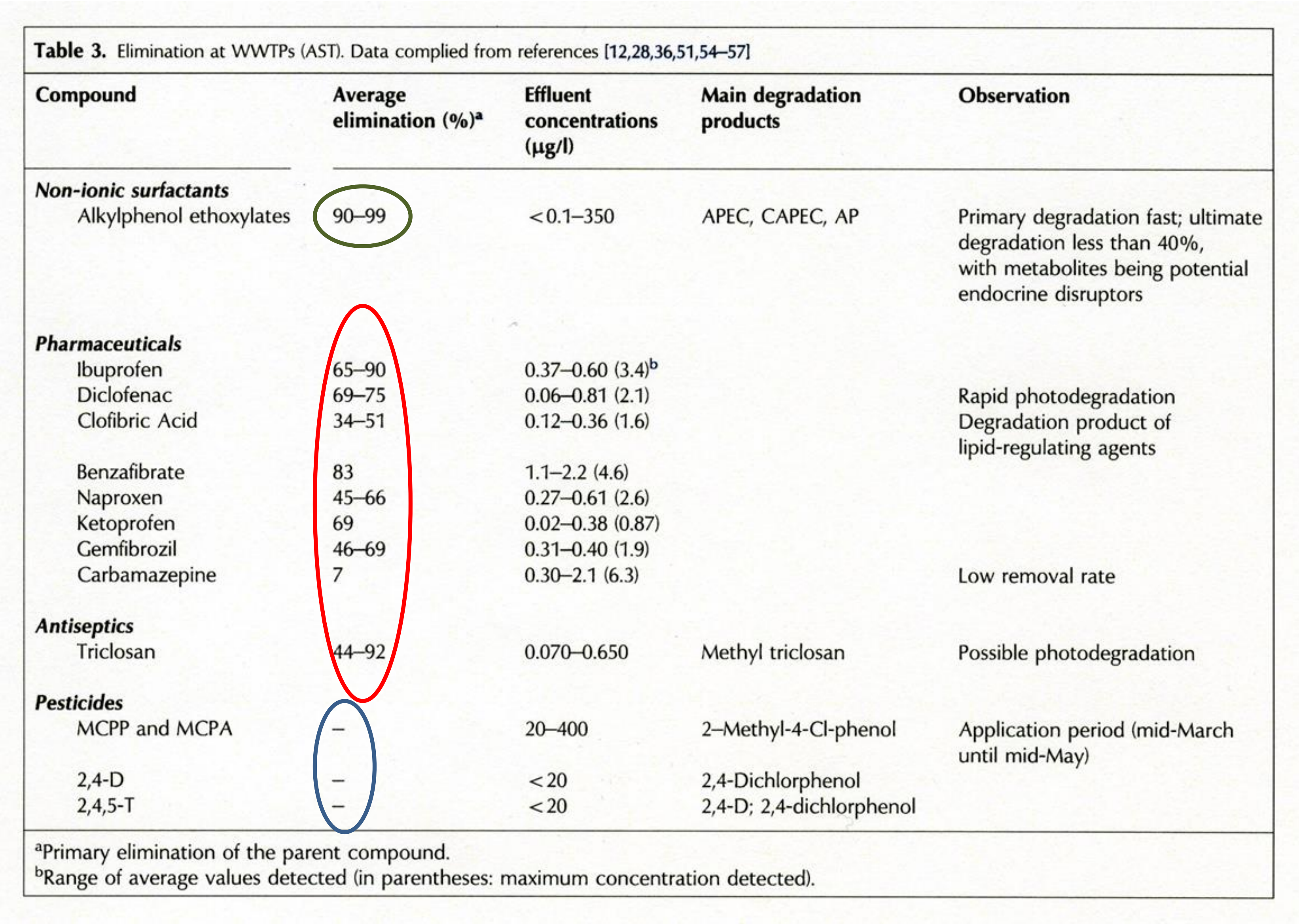


Table 3. Elimination at WWTPs (AST). Data complied from references [12,28,36,51,54–57]

Compound	Average elimination (%)[a]	Effluent concentrations (µg/l)	Main degradation products	Observation
Non-ionic surfactants				
Alkylphenol ethoxylates	90–99	< 0.1–350	APEC, CAPEC, AP	Primary degradation fast; ultimate degradation less than 40%, with metabolites being potential endocrine disruptors
Pharmaceuticals				
Ibuprofen	65–90	0.37–0.60 (3.4)[b]		
Diclofenac	69–75	0.06–0.81 (2.1)		Rapid photodegradation
Clofibric Acid	34–51	0.12–0.36 (1.6)		Degradation product of lipid-regulating agents
Benzafibrate	83	1.1–2.2 (4.6)		
Naproxen	45–66	0.27–0.61 (2.6)		
Ketoprofen	69	0.02–0.38 (0.87)		
Gemfibrozil	46–69	0.31–0.40 (1.9)		
Carbamazepine	7	0.30–2.1 (6.3)		Low removal rate
Antiseptics				
Triclosan	44–92	0.070–0.650	Methyl triclosan	Possible photodegradation
Pesticides				
MCPP and MCPA	–	20–400	2–Methyl-4-Cl-phenol	Application period (mid-March until mid-May)
2,4-D	–	< 20	2,4-Dichlorphenol	
2,4,5-T	–	< 20	2,4-D; 2,4-dichlorphenol	

[a] Primary elimination of the parent compound.

[b] Range of average values detected (in parentheses: maximum concentration detected).

Petrovic, Barcelo et al., Trends Anal. Chem., 10 (2003) 685

Removal Yield of Selected Organic Pollutants from Wastewaters of common treatments

UV Irradiation

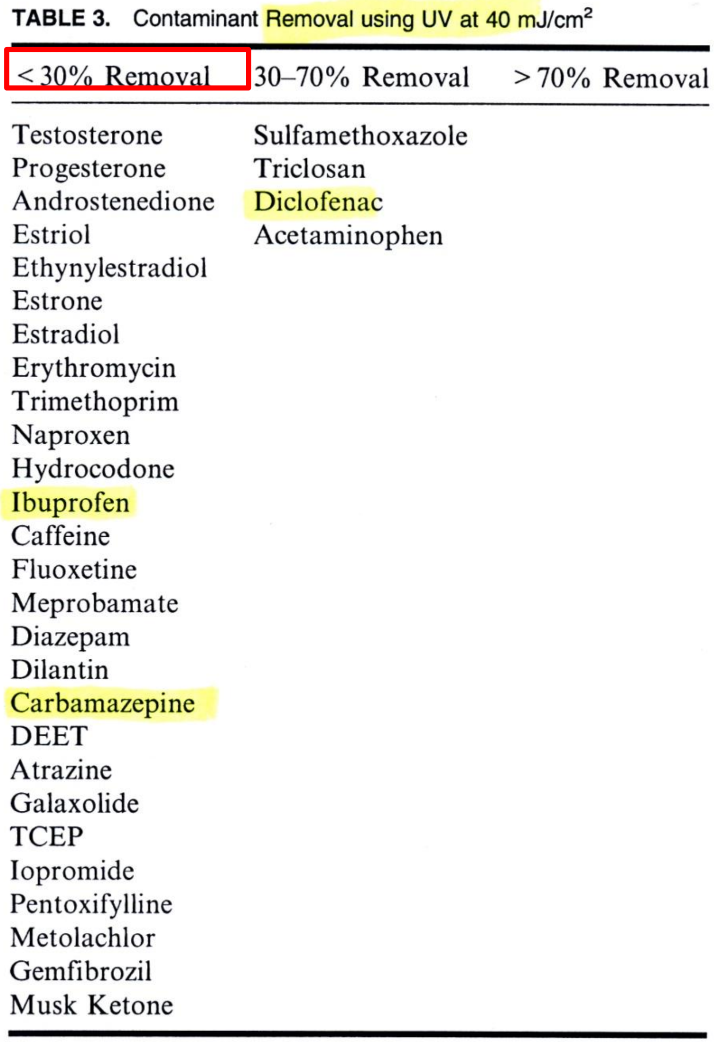


TABLE 3. Contaminant Removal using UV at 40 mJ/cm²

< 30% Removal	30–70% Removal	> 70% Removal
Testosterone	Sulfamethoxazole	
Progesterone	Triclosan	
Androstenedione	Diclofenac	
Estriol	Acetaminophen	
Ethynylestradiol		
Estrone		
Estradiol		
Erythromycin		
Trimethoprim		
Naproxen		
Hydrocodone		
Ibuprofen		
Caffeine		
Fluoxetine		
Meprobamate		
Diazepam		
Dilantin		
Carbamazepine		
DEET		
Atrazine		
Galaxolide		
TCEP		
Iopromide		
Pentoxifylline		
Metolachlor		
Gemfibrozil		
Musk Ketone		

Chlorination

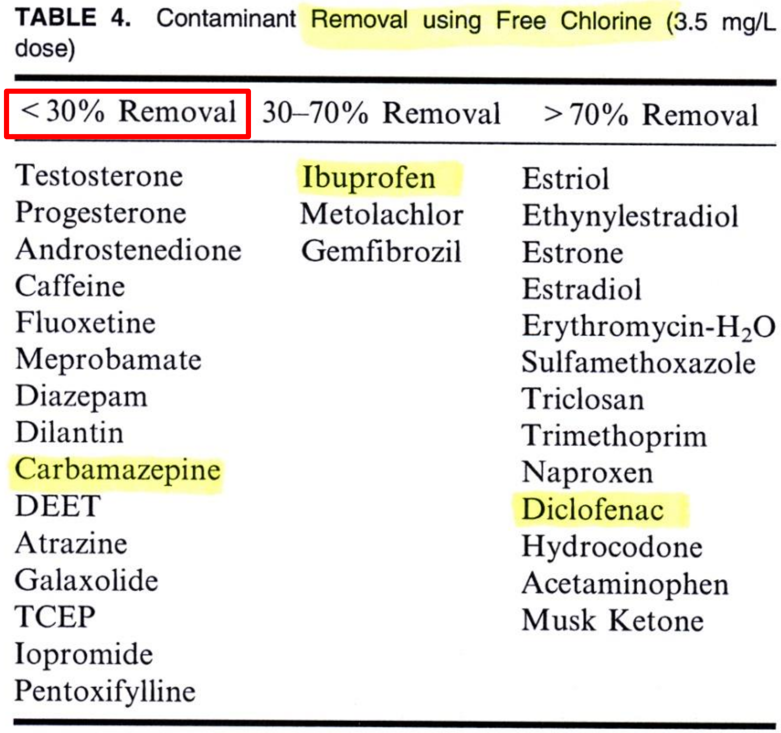
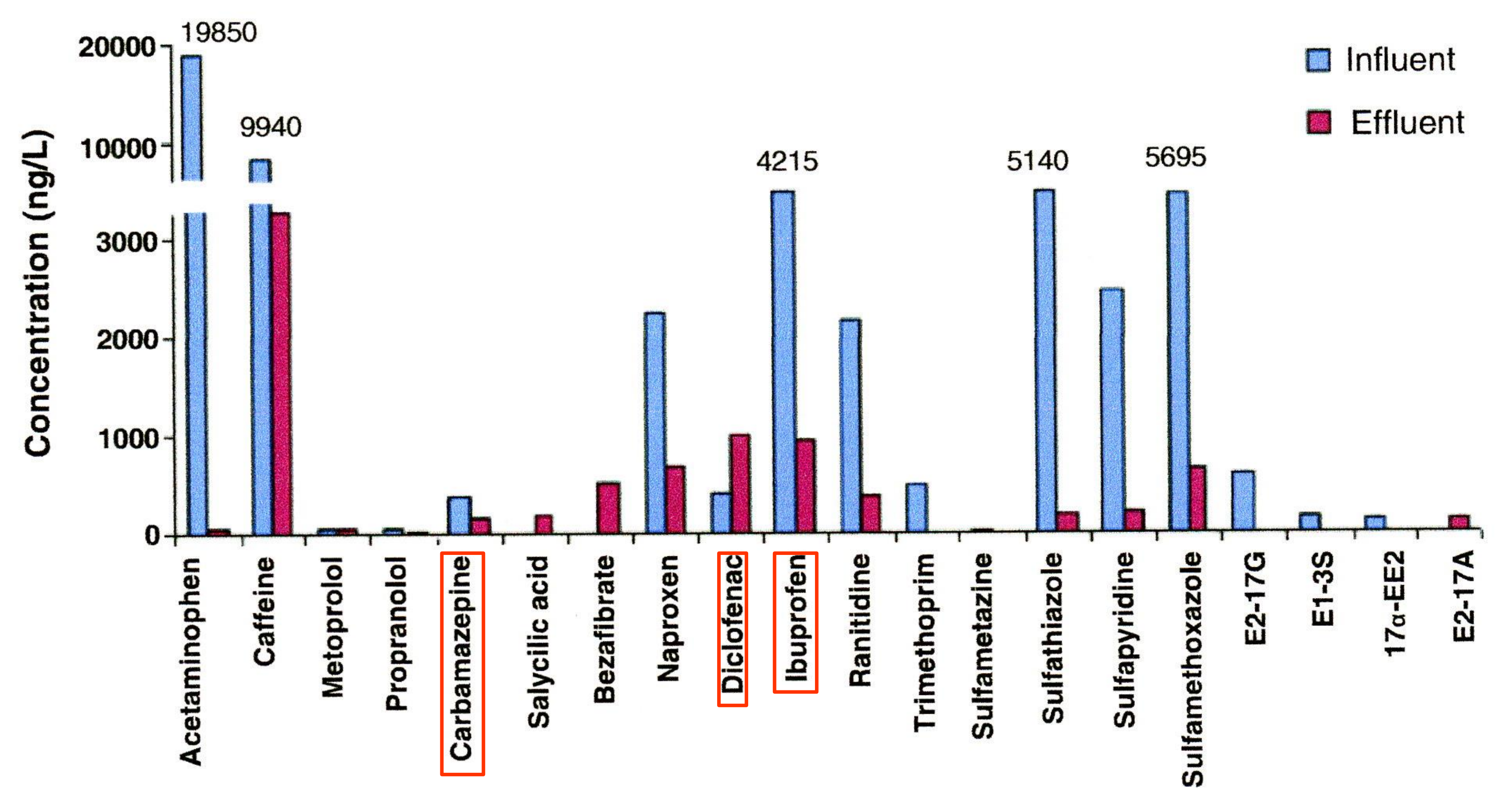


TABLE 4. Contaminant Removal using Free Chlorine (3.5 mg/L dose)

< 30% Removal	30–70% Removal	> 70% Removal
Testosterone	Ibuprofen	Estriol
Progesterone	Metolachlor	Ethynylestradiol
Androstenedione	Gemfibrozil	Estrone
Caffeine		Estradiol
Fluoxetine		Erythromycin-H_2O
Meprobamate		Sulfamethoxazole
Diazepam		Triclosan
Dilantin		Trimethoprim
Carbamazepine		Naproxen
DEET		Diclofenac
Atrazine		Hydrocodone
Galaxolide		Acetaminophen
TCEP		Musk Ketone
Iopromide		
Pentoxifylline		

Snyder, Ozone Sci. Eng., 30 (2008) 65

How efficient is the removal of organic/emerging pollutants in conventional treatment plants (incl. AOPs)?



▭ **Resistant in conventional STP, and examined in our work in radiation processing**

Pedrouzo et al., Water Air Soil Pollut., 217 (2011) 267

How efficient is the removal of organic/emerging pollutants in conventional treatment plants (incl. AOPs)?

''mixed'' results in reporting, BUT

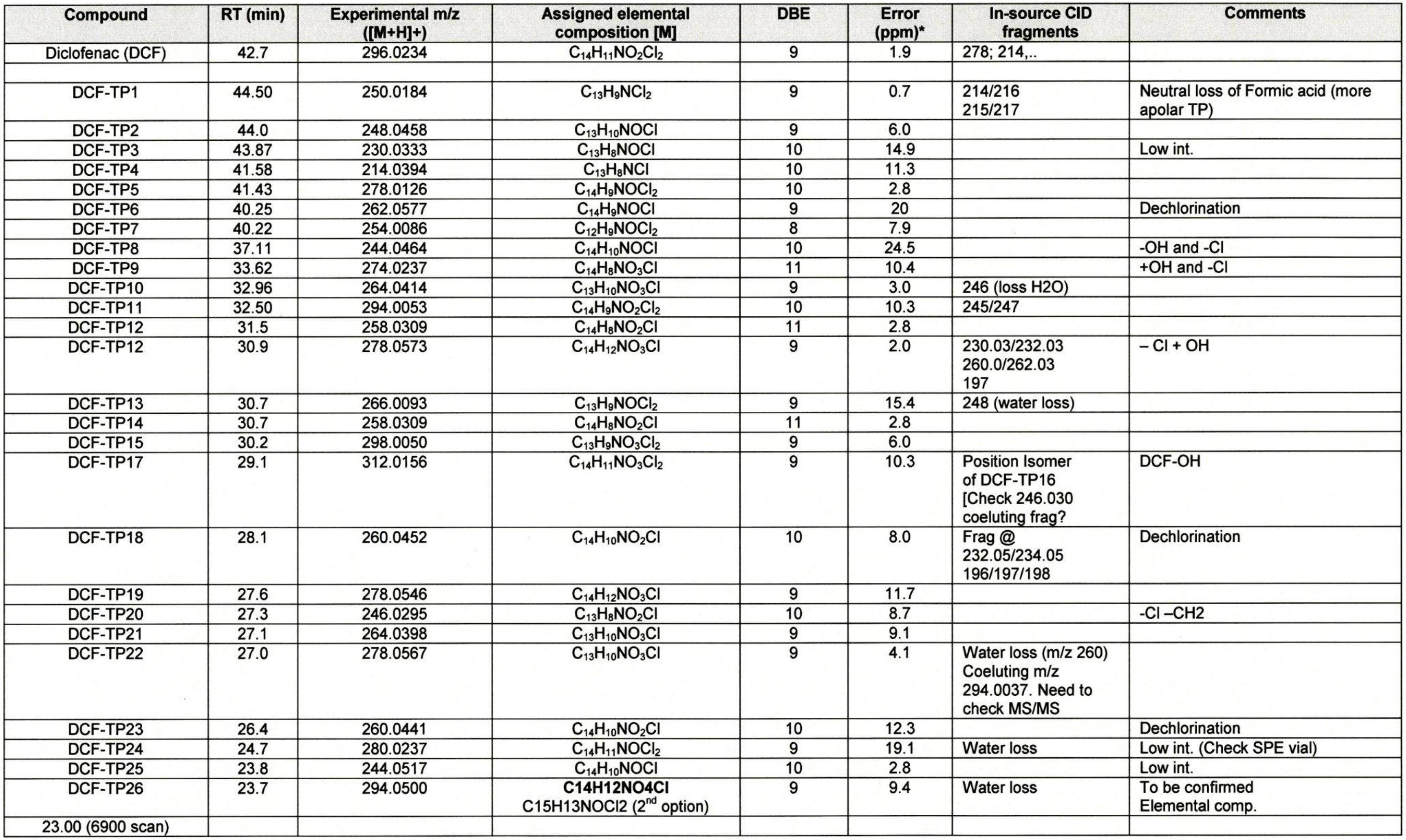
how reliable is that?

Removal ≠ Degradation ≠ Mineralization

***Removal from solution*: what about the other phase(s)?**
***Degradation in each phase*: what about by-procucts?**
***Mineralization*: it is the only 100% safe option. (must be verified by TOC mass balance).**

HOW MANY PRESENTATIONS HERE HAVE ADDRESSED THE ISSUE?
(Need of a common Benchmarking system?)

Tentative list of detected products of radiolytic decomposition of diclofenac by LC-TOFMS



Compound	RT (min)	Experimental m/z ([M+H]+)	Assigned elemental composition [M]	DBE	Error (ppm)*	In-source CID fragments	Comments
Diclofenac (DCF)	42.7	296.0234	$C_{14}H_{11}NO_2Cl_2$	9	1.9	278; 214,..	
DCF-TP1	44.50	250.0184	$C_{13}H_9NCl_2$	9	0.7	214/216 215/217	Neutral loss of Formic acid (more apolar TP)
DCF-TP2	44.0	248.0458	$C_{13}H_{10}NOCl$	9	6.0		
DCF-TP3	43.87	230.0333	$C_{13}H_8NOCl$	10	14.9		Low int.
DCF-TP4	41.58	214.0394	$C_{13}H_8NCl$	10	11.3		
DCF-TP5	41.43	278.0126	$C_{14}H_9NOCl_2$	10	2.8		
DCF-TP6	40.25	262.0577	$C_{14}H_9NOCl$	9	20		Dechlorination
DCF-TP7	40.22	254.0086	$C_{12}H_9NOCl_2$	8	7.9		
DCF-TP8	37.11	244.0464	$C_{14}H_{10}NOCl$	10	24.5		-OH and -Cl
DCF-TP9	33.62	274.0237	$C_{14}H_8NO_3Cl$	11	10.4		+OH and -Cl
DCF-TP10	32.96	264.0414	$C_{13}H_{10}NO_3Cl$	9	3.0	246 (loss H2O)	
DCF-TP11	32.50	294.0053	$C_{14}H_9NO_2Cl_2$	10	10.3	245/247	
DCF-TP12	31.5	258.0309	$C_{14}H_8NO_2Cl$	11	2.8		
DCF-TP12	30.9	278.0573	$C_{14}H_{12}NO_3Cl$	9	2.0	230.03/232.03 260.0/262.03 197	– Cl + OH
DCF-TP13	30.7	266.0093	$C_{13}H_9NOCl_2$	9	15.4	248 (water loss)	
DCF-TP14	30.7	258.0309	$C_{14}H_8NO_2Cl$	11	2.8		
DCF-TP15	30.2	298.0050	$C_{13}H_9NO_3Cl_2$	9	6.0		
DCF-TP17	29.1	312.0156	$C_{14}H_{11}NO_3Cl_2$	9	10.3	Position Isomer of DCF-TP16 [Check 246.030 coeluting frag?	DCF-OH
DCF-TP18	28.1	260.0452	$C_{14}H_{10}NO_2Cl$	10	8.0	Frag @ 232.05/234.05 196/197/198	Dechlorination
DCF-TP19	27.6	278.0546	$C_{14}H_{12}NO_3Cl$	9	11.7		
DCF-TP20	27.3	246.0295	$C_{13}H_8NO_2Cl$	10	8.7		-Cl –CH2
DCF-TP21	27.1	264.0398	$C_{13}H_{10}NO_3Cl$	9	9.1		
DCF-TP22	27.0	278.0567	$C_{13}H_{10}NO_3Cl$	9	4.1	Water loss (m/z 260) Coeluting m/z 294.0037. Need to check MS/MS	
DCF-TP23	26.4	260.0441	$C_{14}H_{10}NO_2Cl$	10	12.3		Dechlorination
DCF-TP24	24.7	280.0237	$C_{14}H_{11}NOCl_2$	9	19.1	Water loss	Low int. (Check SPE vial)
DCF-TP25	23.8	244.0517	$C_{14}H_{10}NOCl$	10	2.8		Low int.
DCF-TP26	23.7	294.0500	**C14H12NO4Cl** C15H13NOCl2 (2nd option)	9	9.4	Water loss	To be confirmed Elemental comp.
23.00 (6900 scan)							

HPLC Method: A: Water 0.1 % Formic acid; B: Acetonitrile, 0.1 % formic acid. Flow-rate: 0.5 ml/min. Gradient: 0-3min: 30 % B, then from 3-10 min, 30-40 % → then 10-40 min, from 40 % to 65 %, then 40-45 min, from 65% to 100%, 45-46, 100% , then 46-47, from 100% to 30% (equilibration) and from 47-55 min, 30 % (initial mobile phase composition for equilibration).

IT-TOF Conditions: full-scan acquisition with polarity switching; mass range: m/z 150-1000; ion trap accumulation time: 50 ms

DCF solution irradiated with 3.6 kGy dose

Advanced Oxidation Processes (AOPs)

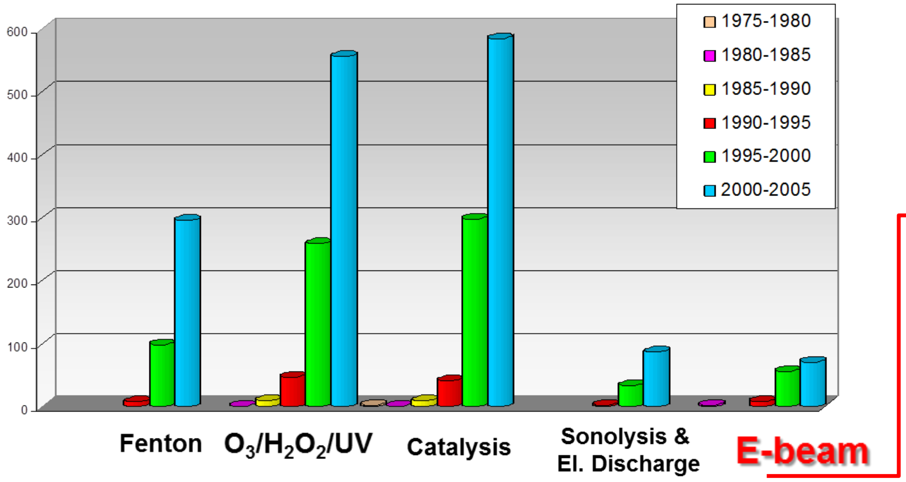
defined as near ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals (especially hydroxyl radicals) in sufficient quantity to effect water purification

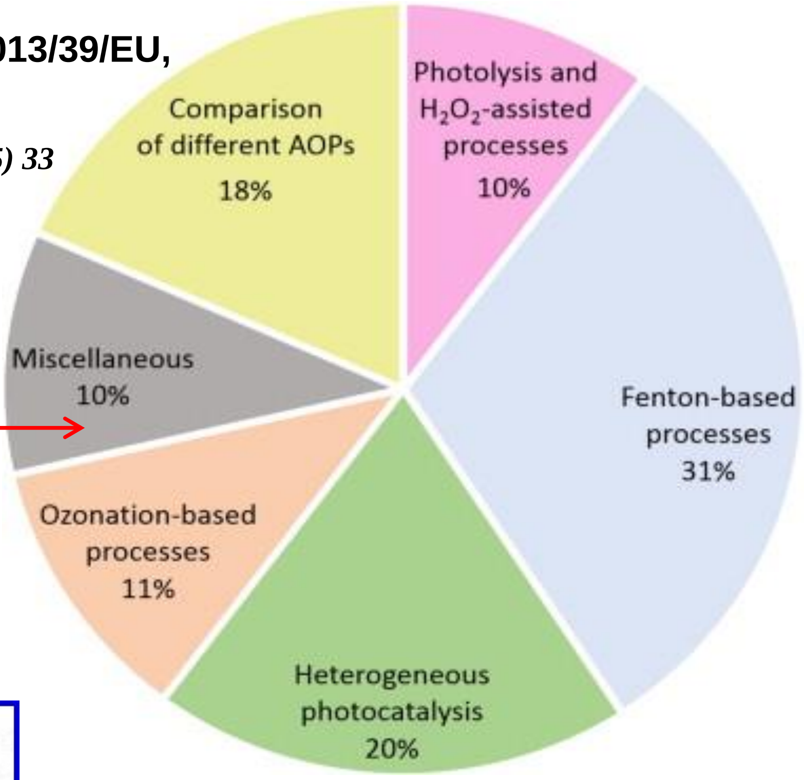
Glaze et al., Ozon Sci. Eng., 9 (1987) 335

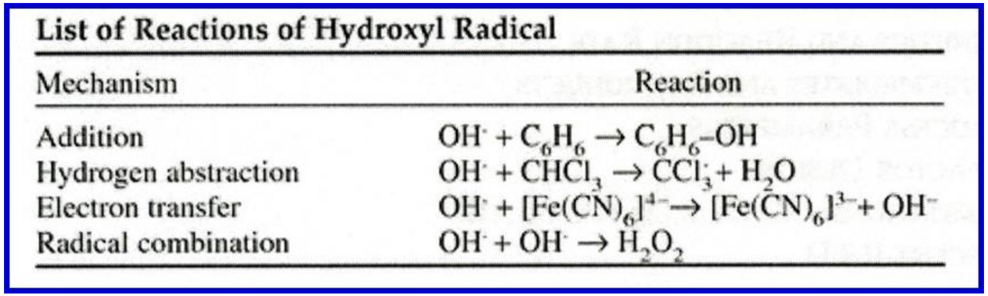
Relative Frequency of Reports of Different Types of AOPs (2004-2015)

Search on Scopus database using as keywords
1. name of each org. compound listed in Directive 2013/39/EU,
2.”advanced oxidation process”

Ribeiro et al., Environ. Int. 75 (2015) 33





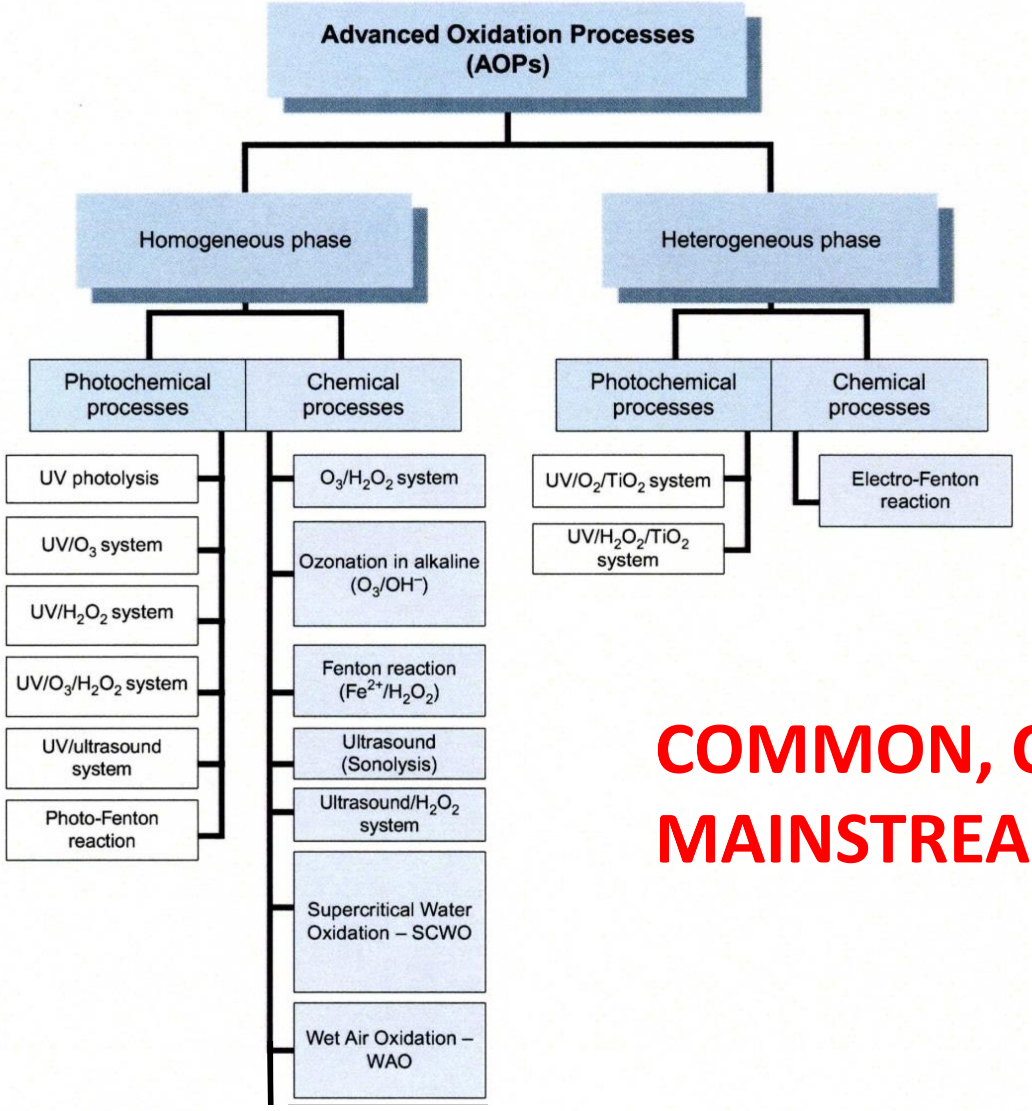


List of Reactions of Hydroxyl Radical

Mechanism	Reaction
Addition	$OH^{\cdot} + C_6H_6 \rightarrow C_6H_6\text{–}OH$
Hydrogen abstraction	$OH^{\cdot} + CHCl_3 \rightarrow CCl_3^{\cdot} + H_2O$
Electron transfer	$OH^{\cdot} + [Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + OH^-$
Radical combination	$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2$

Advanced Oxidation Processes Classification

(i.e. chemical degradation via oxidative radical, *e.g.* $^{\bullet}$OH generation)



COMMON, CURRENT AOPs MAINSTREAM CLASSIFICATION

Bin, Sobera-Madej, Ozone Sc. Eng., 34 (2012) 136

Advanced Oxidation Processes Classification

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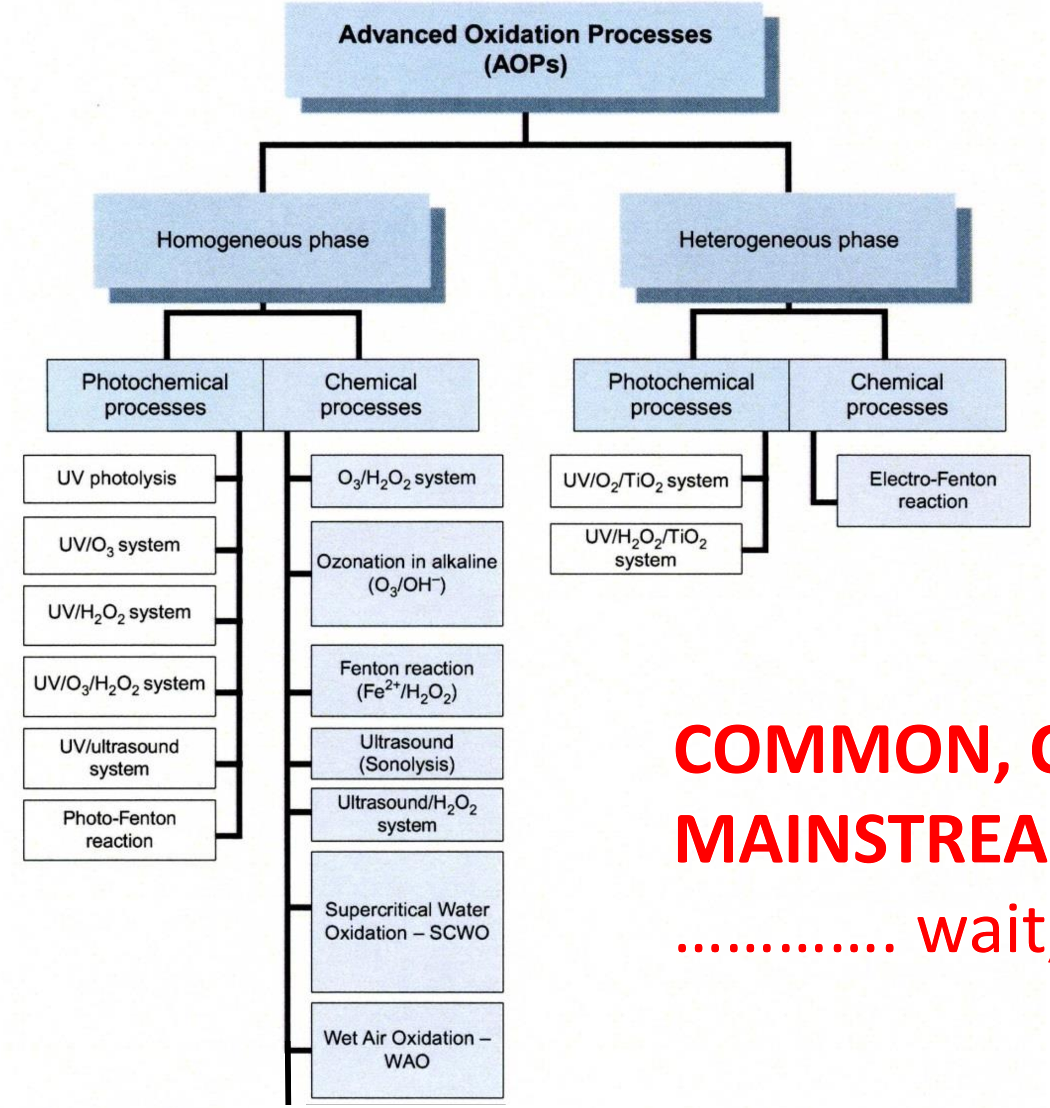

Advanced Oxidation Processes (AOPs)

- Homogeneous phase
  - Photochemical processes
    - UV photolysis
    - UV/O_3 system
    - UV/H_2O_2 system
    - UV/O_3/H_2O_2 system
    - UV/ultrasound system
    - Photo-Fenton reaction
  - Chemical processes
    - O_3/H_2O_2 system
    - Ozonation in alkaline (O_3/OH^-)
    - Fenton reaction (Fe^{2+}/H_2O_2)
    - Ultrasound (Sonolysis)
    - Ultrasound/H_2O_2 system
    - Supercritical Water Oxidation – SCWO
    - Wet Air Oxidation – WAO
- Heterogeneous phase
  - Photochemical processes
    - UV/O_2/TiO_2 system
    - UV/H_2O_2/TiO_2 system
  - Chemical processes
    - Electro-Fenton reaction

COMMON, CURRENT AOPs

MAINSTREAM CLASSIFICATION

…………. wait, something's missin'!

Bin, Sobera-Madej, Ozone Sc. Eng., 34 (2012) 136

Advanced Oxidation Processes Classification

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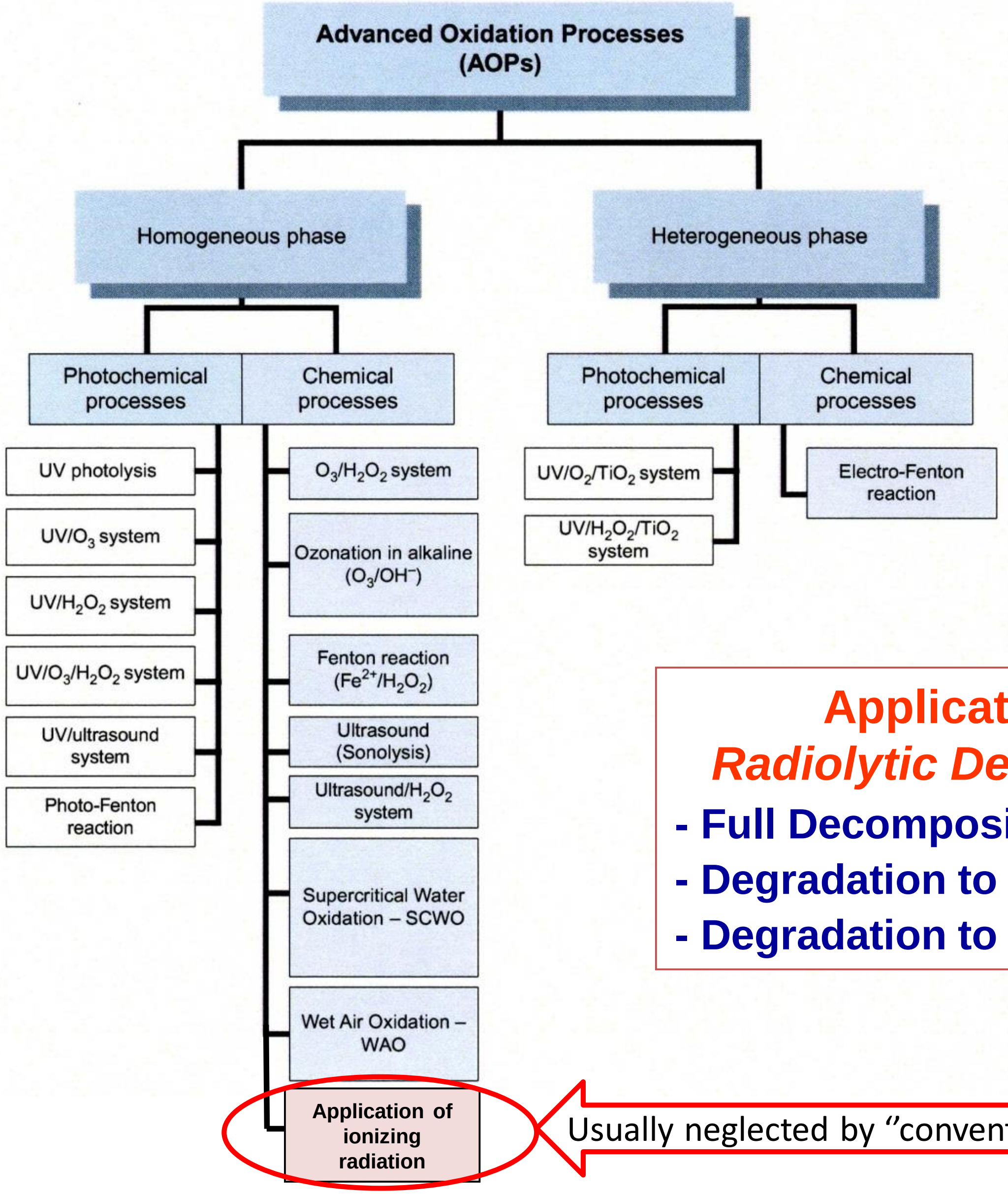

Advanced Oxidation Processes (AOPs)

Homogeneous phase

- Photochemical processes
  - UV photolysis
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  - UV/O_3/H_2O_2 system
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  - Supercritical Water Oxidation – SCWO
  - Wet Air Oxidation – WAO
  - **Application of ionizing radiation**

Heterogeneous phase

- Photochemical processes
  - UV/O_2/TiO_2 system
  - UV/H_2O_2/TiO_2 system
- Chemical processes
  - Electro-Fenton reaction

Formation of free radicals and molecular products:

e^-_{aq}, H•, HO•, HO_2•, OH^-, H_3O^+, H_2, H_2O_2

BOTH OXYDATIVE AND REDUCTIVE

AO(R)P

ADVANCED OXYDATION & REDUCTION PROCESS

Application of Ionizing Radiation for *Radiolytic Degradation* of Organic Pollutants:

- **Full Decomposition to non-toxic species (inorganic)**
- **Degradation to less toxic species**
- **Degradation to more easily biodegradable species**

Usually neglected by ''conventional'' water literature, except by radiation chemists

Bin, Sobera-Madej, Ozone Sc. Eng., 34 (2012) 136

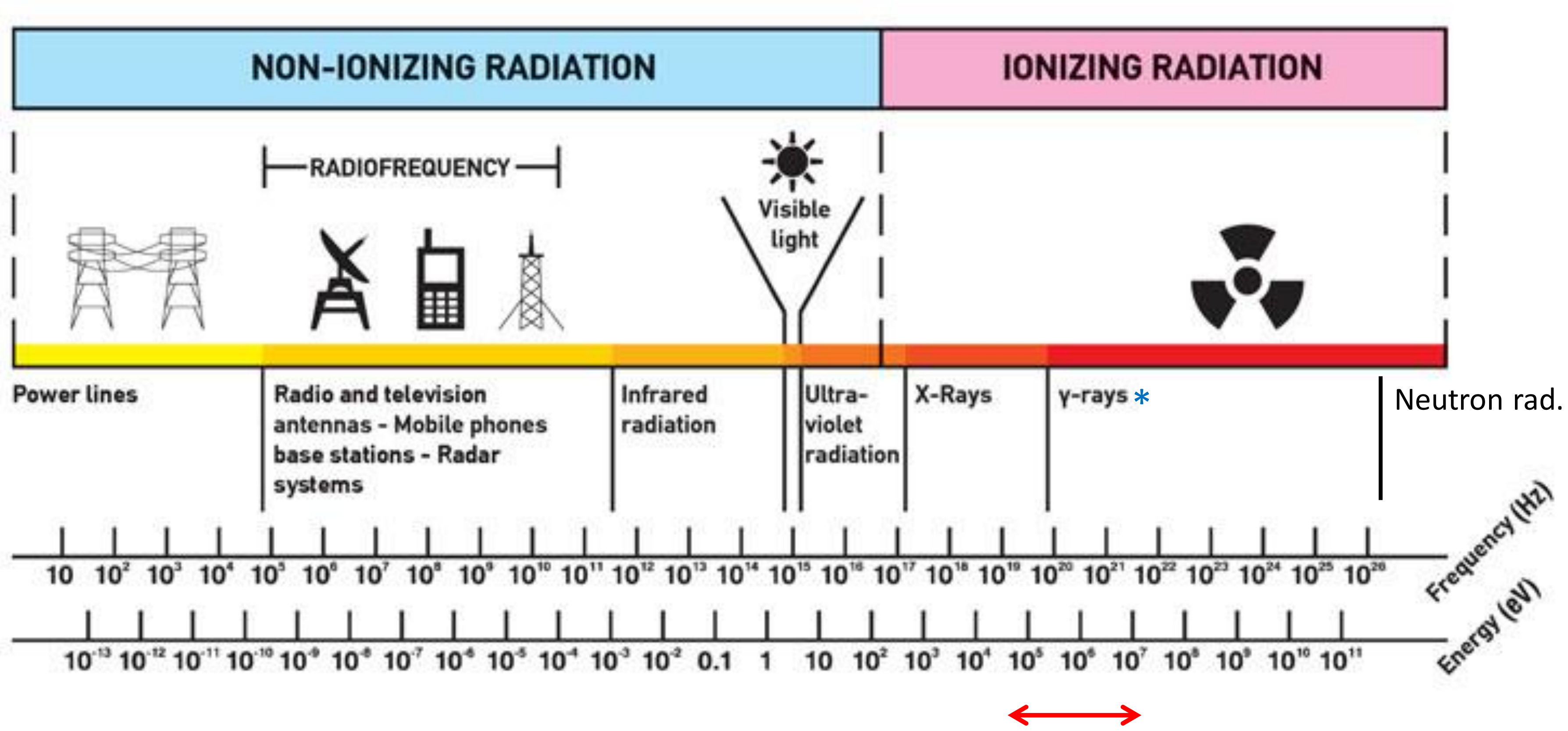
RADIATION ?

NOT REALLY…

RADIATION: NON-IONIZING vs. *IONIZING*

non-ionizing: cannot break chemical bonds but may vibrate atoms

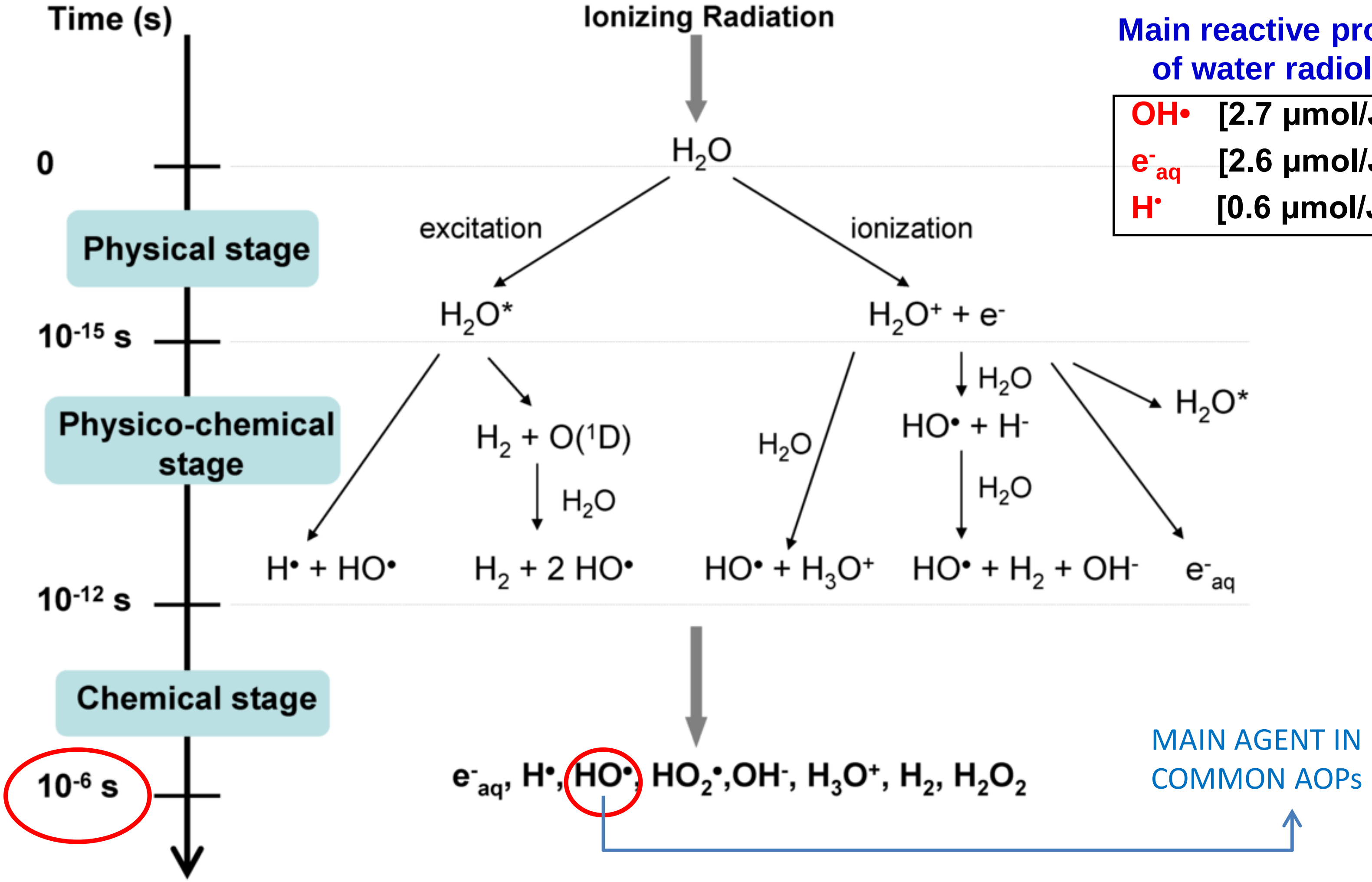
ionizing: can turn atoms into ions by causing loss of electrons



- **γ-Radiation: most penetrating form of radiation (except neutron).**

usually from ^{60}Co source, identical effects can be obtained from electron beam (EB) with additional “practical” advantages

ADVANCED OXYDATION & REDUCTION PROCESSES BY IONIZING RADIATION OCCUR EXTREMELY FAST



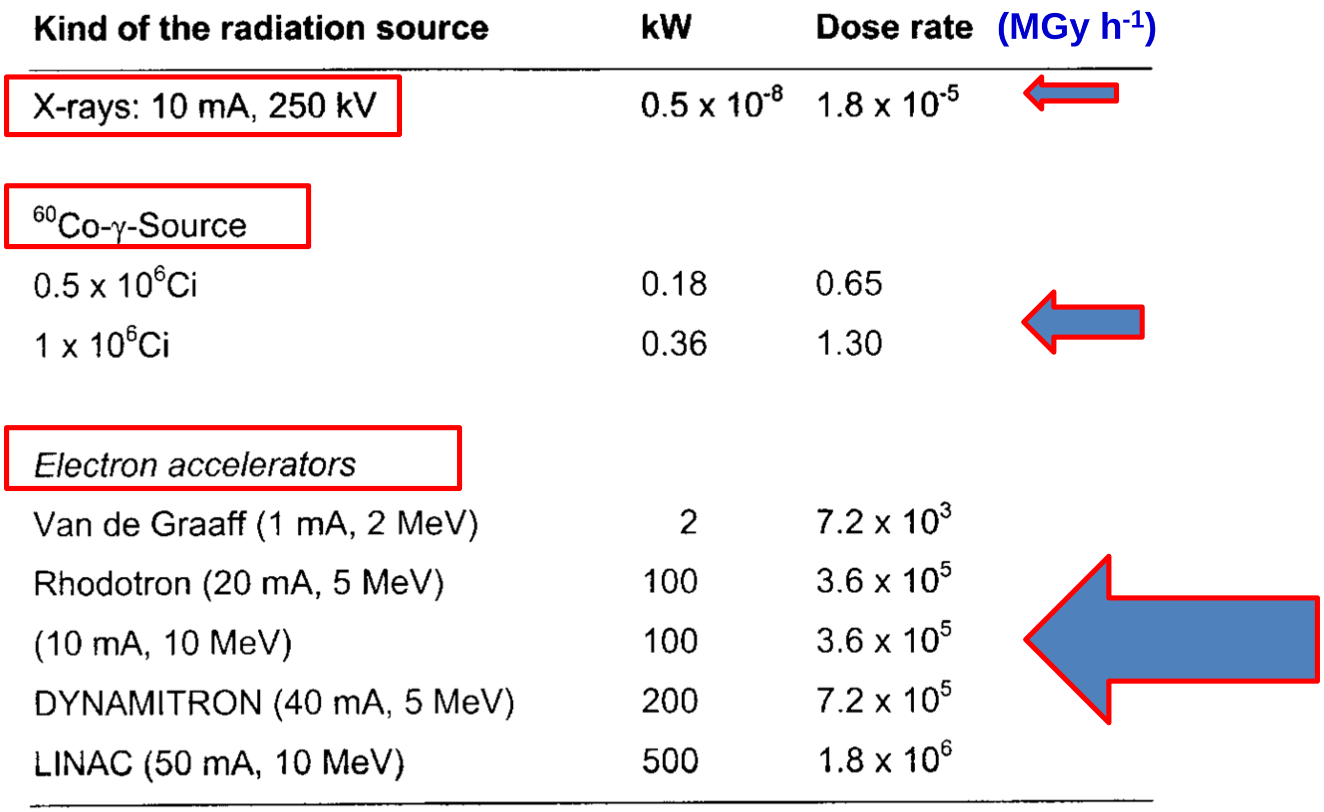
Main reactive products of water radiolysis

$OH^\bullet$	[2.7 µmol/J]
e^-_{aq}	[2.6 µmol/J]
$H^\bullet$	[0.6 µmol/J]

RADICALS AND MOLECULAR REACTANTS ALSO REVERT EQUALLY FAST TO THE ORIGINAL STATE (WATER) IF NO ORGANIC MOLECULES/SCAVENGERS ARE PRESENT IN SOLUTION. NO TRACE OF RADIOLYSIS (ENERGY OR RADIATION) IS LEFT IN THE SOLUTION.

S. La Caer, Water 3 (2011) 235

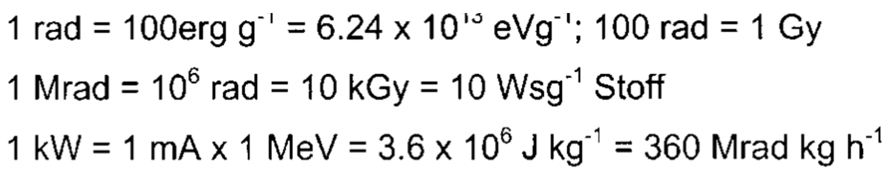
Dose Rates achievable by Different Radiation Sources



Kind of the radiation source	kW	Dose rate (MGy h^{-1})
X-rays: 10 mA, 250 kV	0.5×10^{-8}	1.8×10^{-5}
^{60}Co-γ-Source		
0.5×10^{6}Ci	0.18	0.65
1×10^{6}Ci	0.36	1.30
Electron accelerators		
Van de Graaff (1 mA, 2 MeV)	2	7.2×10^{3}
Rhodotron (20 mA, 5 MeV)	100	3.6×10^{5}
(10 mA, 10 MeV)	100	3.6×10^{5}
DYNAMITRON (40 mA, 5 MeV)	200	7.2×10^{5}
LINAC (50 mA, 10 MeV)	500	1.8×10^{6}

10 kGy absorbed dose produce 2.9 mM $^{\bullet}$OH radicals

Dose Units



1 rad = 100erg g^{-1} = 6.24×10^{13} eVg^{-1}; 100 rad = 1 Gy

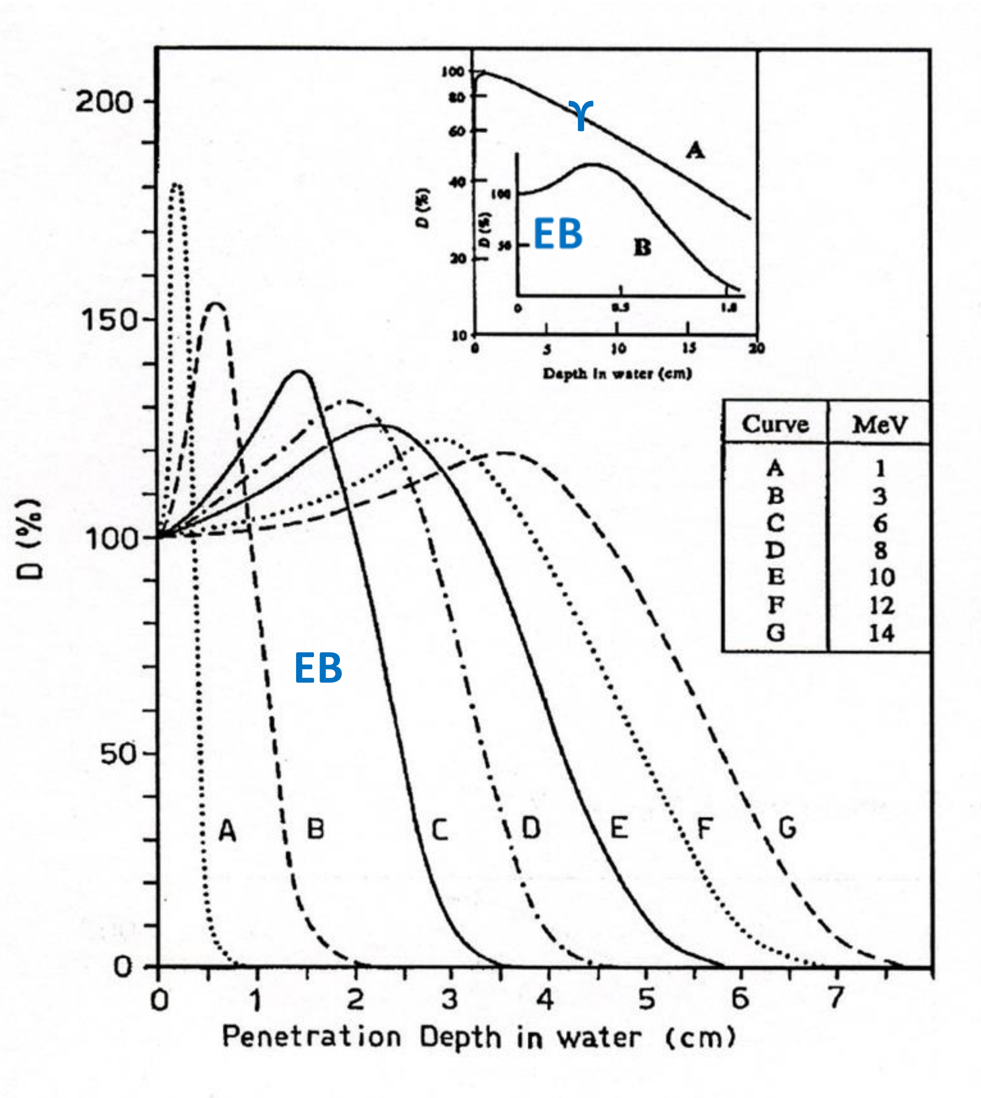
1 Mrad = 10^{6} rad = 10 kGy = 10 Wsg^{-1} Stoff

1 kW = 1 mA x 1 MeV = 3.6×10^{6} J kg^{-1} = 360 Mrad kg h^{-1}

Getoff, Radiat, Phys. Chem., 65 (2002) 437.

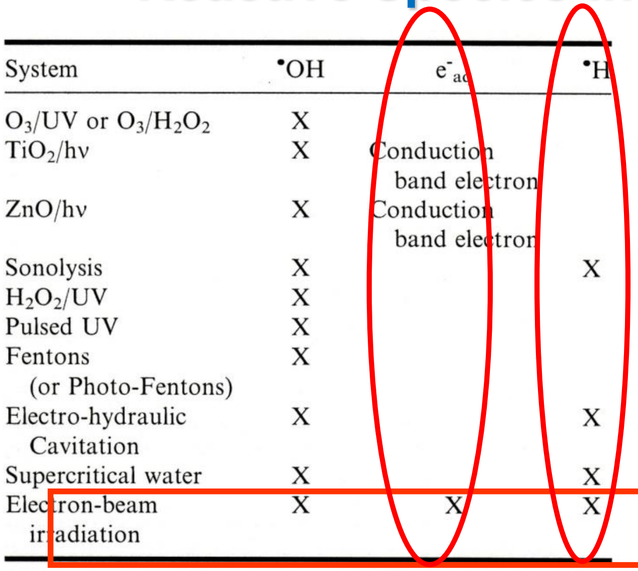
Comparison of Types of Radiation Used for Degradation of Pollutants

Electron beam (EB)	γ-Radiation from ^{60}Co source
Advantages	
High energy	High penetration depth
High dose rate	Lower cost than EB accelerators
Switch on and off operation	
Most efficient source of $OH^{\cdot}$	
Disadvantages	
High cost	Continuous operation
Low penetration depth	Careful protection needed against radiation
	Most radiation absorbed by shielding
	Decreasing activity in time
	Low social acceptance



Getoff, Radiat. Phys. Chem., 65 (2002) 437

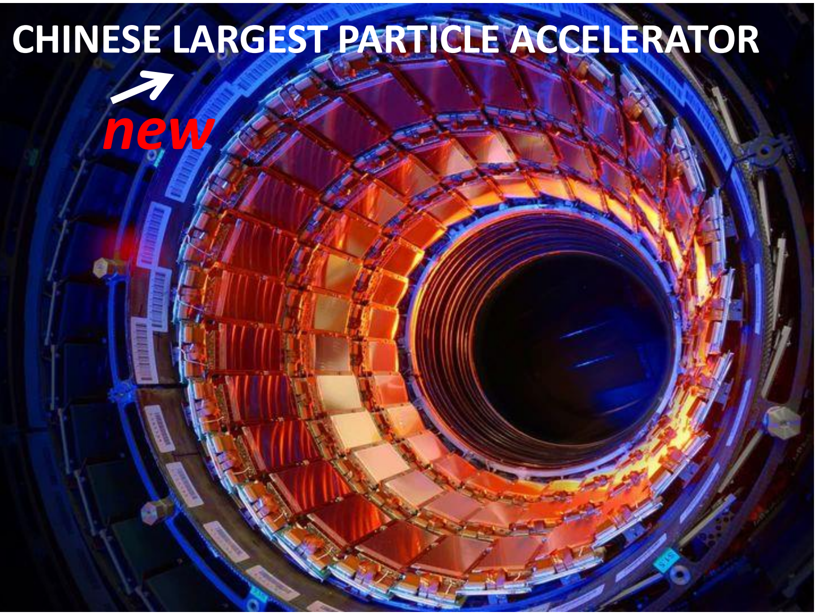
Advanced Oxidation/Reduction Processes and Reactive Species Involved in Destruction of Organic Pollutants



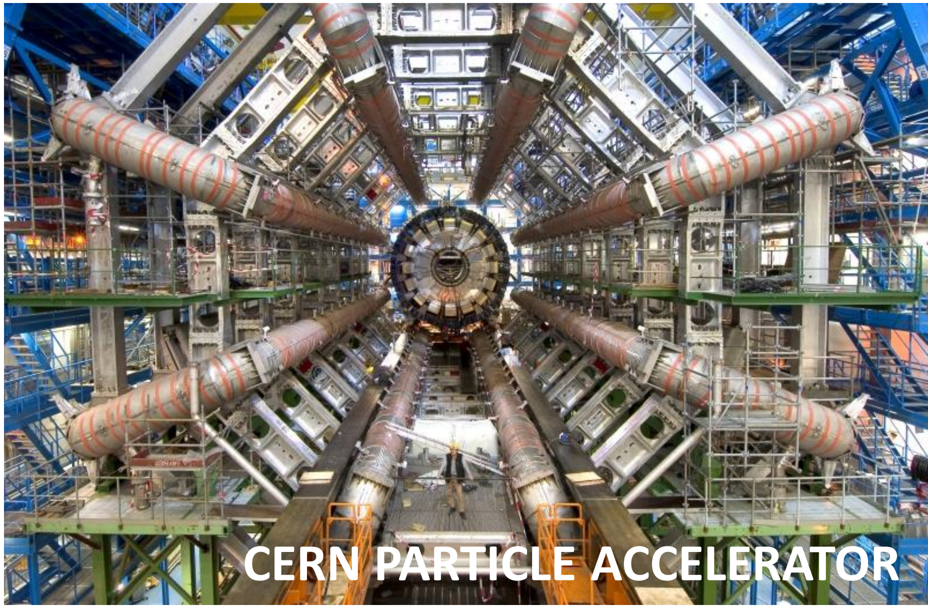
System	•OH	e^-_{aq}	•H
O_3/UV or O_3/H_2O_2	X		
TiO_2/hν	X	Conduction band electron	
ZnO/hν	X	Conduction band electron	
Sonolysis	X		X
H_2O_2/UV	X		
Pulsed UV	X		
Fentons (or Photo-Fentons)	X		
Electro-hydraulic Cavitation	X		X
Supercritical water	X		X
Electron-beam irradiation	X	X	X

Cooper et al., Ozone Sci. Technol., 30 (2008) 58

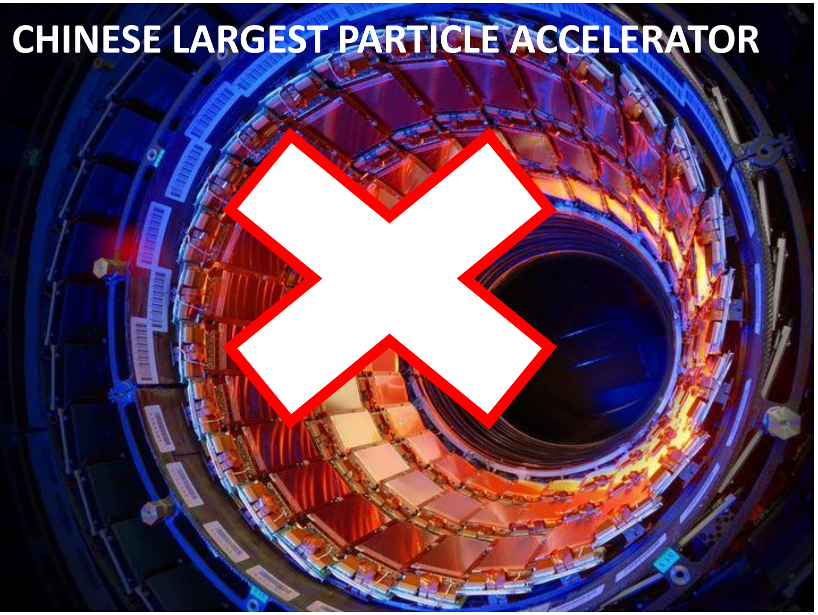
Compound	Bimolecular rate constants ($M^{-1}s^{-1}$ 10^9)			Relative importance of species (%)		
	•OH	e^-_{aq}	•H	OH	e^-_{aq}	•H
Target Organic Compounds*						
MTBE	2	0.0175	0.0001	99	1	0
Trichloroethylene	2.9	1.9	NF	61	39	0
Tetrachloroethylene	2	1.3	5	46	29	25
Benzene	7.6	0.009	0.91	97	01	3
Toluene	5.1	0.011	2.6	90	0.1	10
Ethylbenzene	7.5	NF	NF	100	0	0
α-Xylene	6.7	NF	2	94	0	6
Chloroform	0.054	11	0.073	0.4	99	0.1
$CHBrCl_2$	NF	21	NF	0	10	0
$CHBr_2Cl$	NF	20	NF	0	10	0
Bromoform	0.11	26	1.9	0.5	97.5	2
Ethylenedibromide	0.26	14	NF	2	98	0
DBCP	0.73	NF	NF	100	0	0
NDMA	0.33	NF	NF	100	0	0
Atrazine	2.6	NF	NF	100	0	0
Simazine	208	NF	NF	100	0	0
Natural Scavenging Compounds**						
O_2	NR	19	<0.001	no data available		
HCO_3^-	0.0085	<0.001	<0.001			
CO_3^{2-}	0.39	0.00004	NR			
Cl^-	3	<0.001	<0.00001			
NO_2^-	11	0.0035	0.71			
NO_3^-	NR	9.7	0.0014			
DOC	0.2	NR	NR			

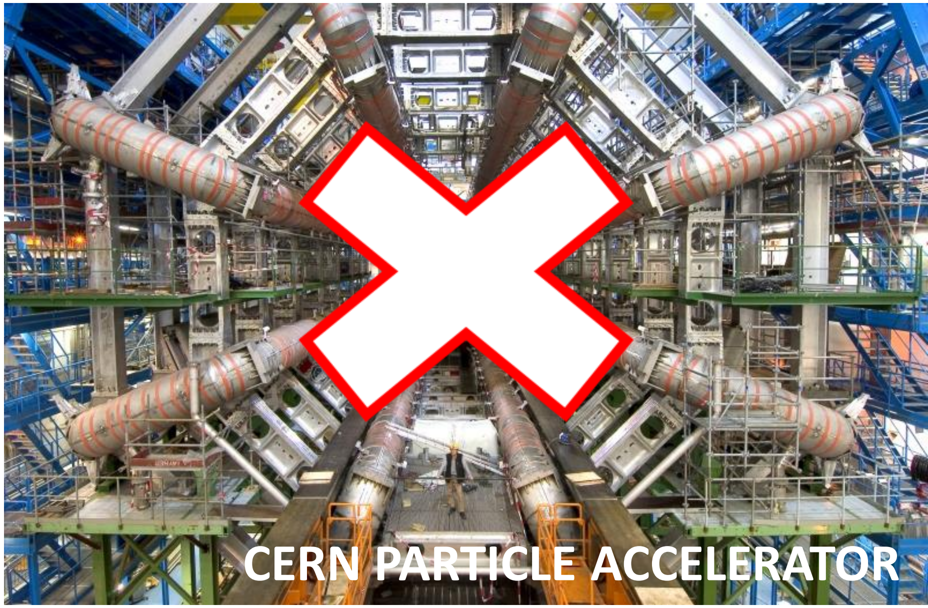

CHINESE LARGEST PARTICLE ACCELERATOR

new


CERN PARTICLE ACCELERATOR

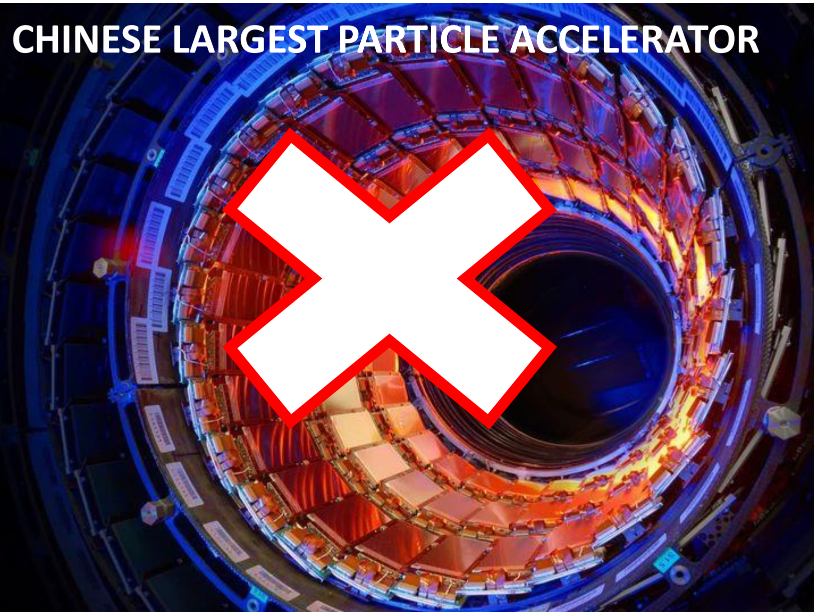
WHAT IS AN ELECTRON ACCELERATOR (E-BEAM)?

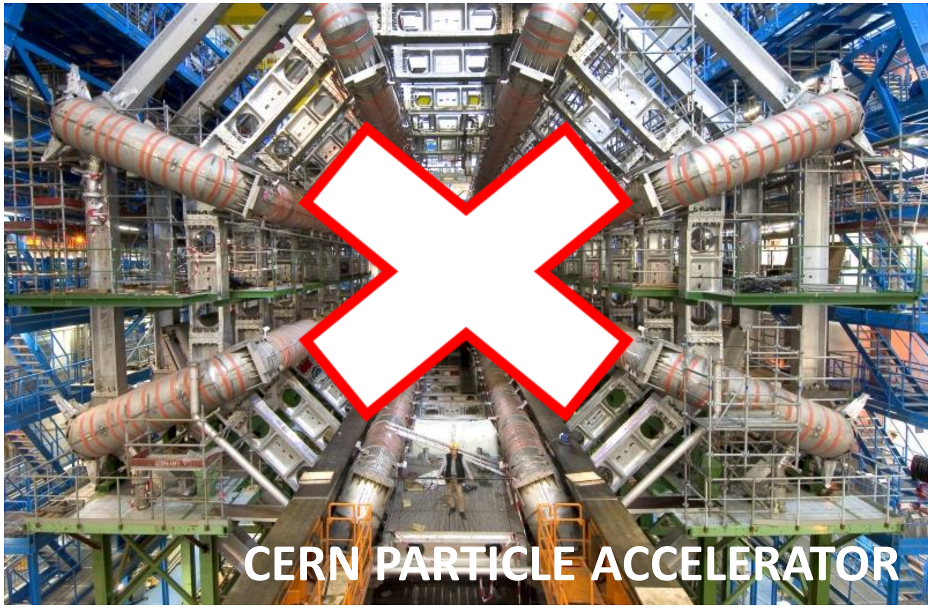

CHINESE LARGEST PARTICLE ACCELERATOR


CERN PARTICLE ACCELERATOR

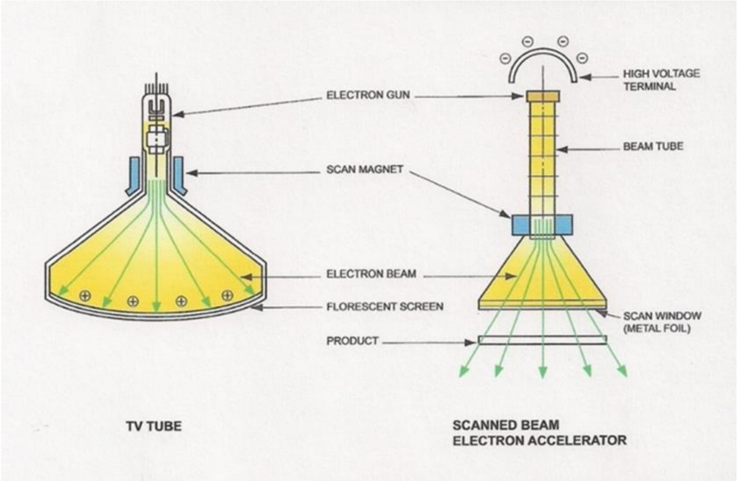
WHAT IS AN ELECTRON ACCELERATOR (E-BEAM)?

(YOUTUBE ONLINE VIDEO)

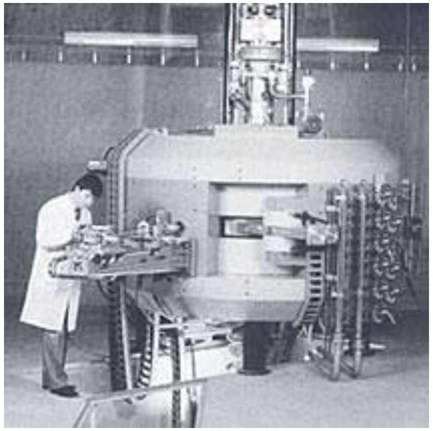




WHAT IS AN ELECTRON ACCELERATOR (E-BEAM)?



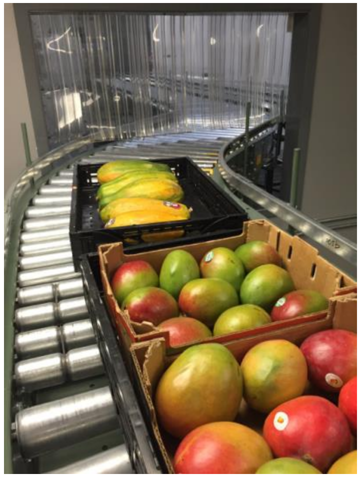
BASICALLY, A LARGE TV TUBE!!!



1950’s Electron accelerator

2000’s E-BEAM to treat 10000 m^3/d Textile Wastewater in S. Korea

E-Beam for sterilization of aseptic packaging (food/medical)

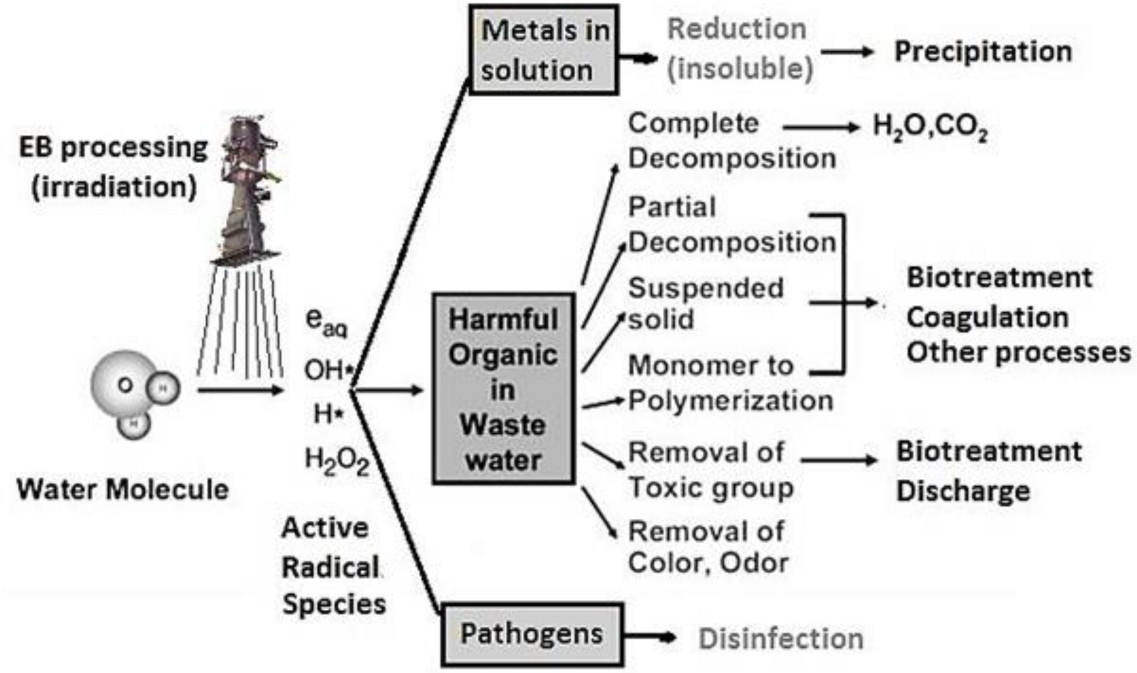


E-Beam for food sterilization

Present day US-Postal service: E-Beam for suspected anthrax-contaminated post sterilization

Present day compact E-Beam for communications cable processing

E-BEAM APPLICATION TO WATER & WASTEWATER



EB processing (irradiation)

Water Molecule

e_{aq}
OH•
H•
H_2O_2

Active Radical Species

Metals in solution → Reduction (insoluble) → Precipitation

Harmful Organic in Waste water

Complete Decomposition → H_2O,CO_2

Partial Decomposition
Suspended solid
Monomer to Polymerization
→ Biotreatment
Coagulation
Other processes

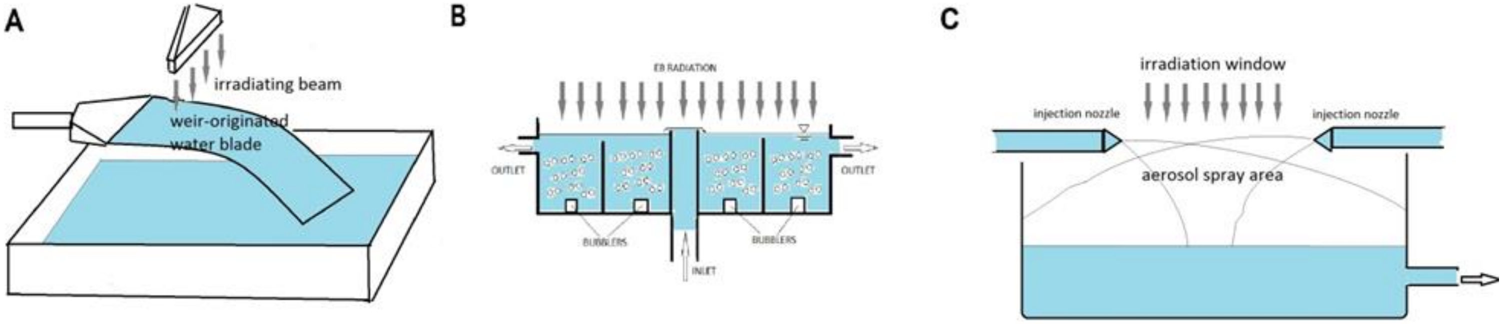
Removal of Toxic group → Biotreatment
Discharge

Removal of Color, Odor

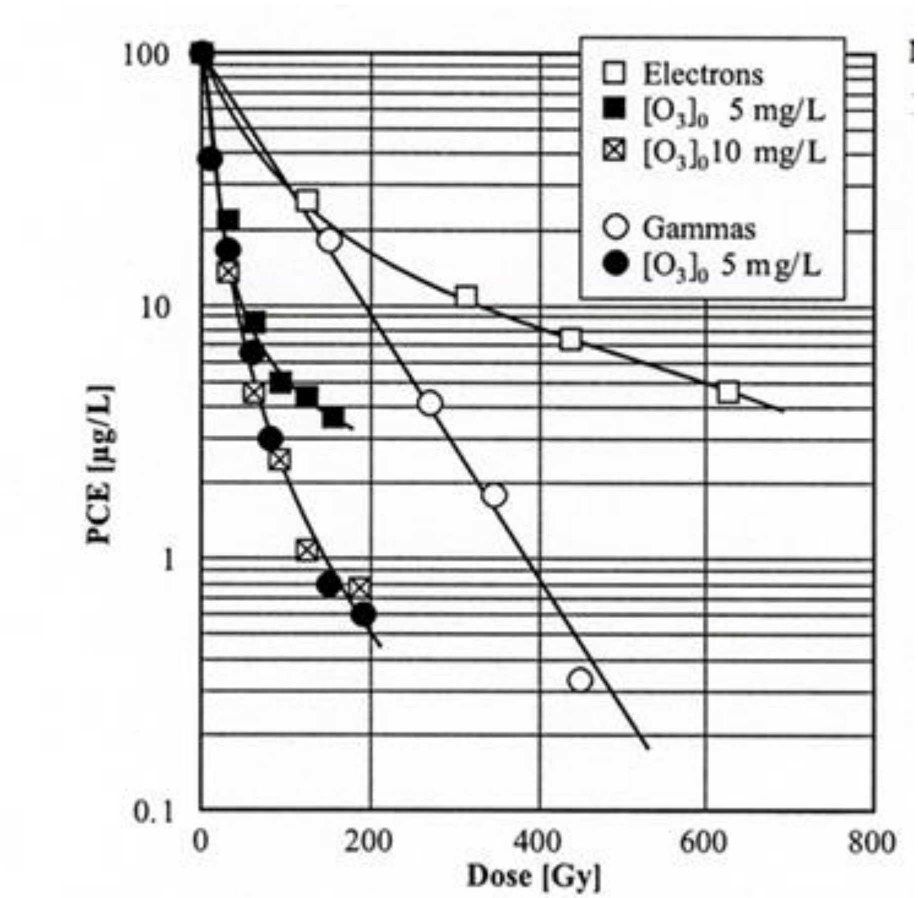
Pathogens → Disinfection

FLEXIBLE, ADAPTABLE TO OBJECTIVES, EASILY INTEGRATED WITH OTHER EXISTING PROCESSES

STREAM IRRADIATION MODES

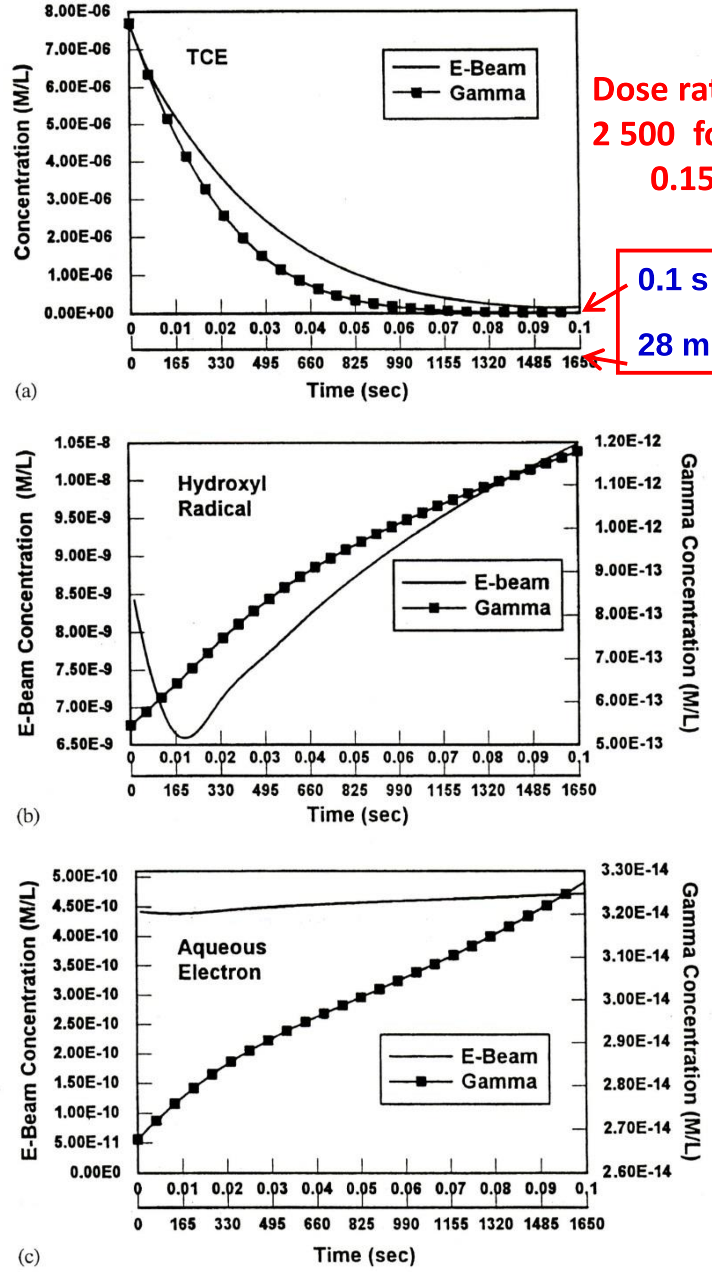


APPLICATIONS: Comparison of EB and γ Irradiation – Dose-rate Effects



Variable dose-rate effect for EB, gamma, alone or plus O_3

Gehringer, Eschweiler, Radiat. Phys. Chem., 65 (2002) 379



Dose rates (Gy)
2 500 for EB
0.15 for γ

0.1 s (EB)

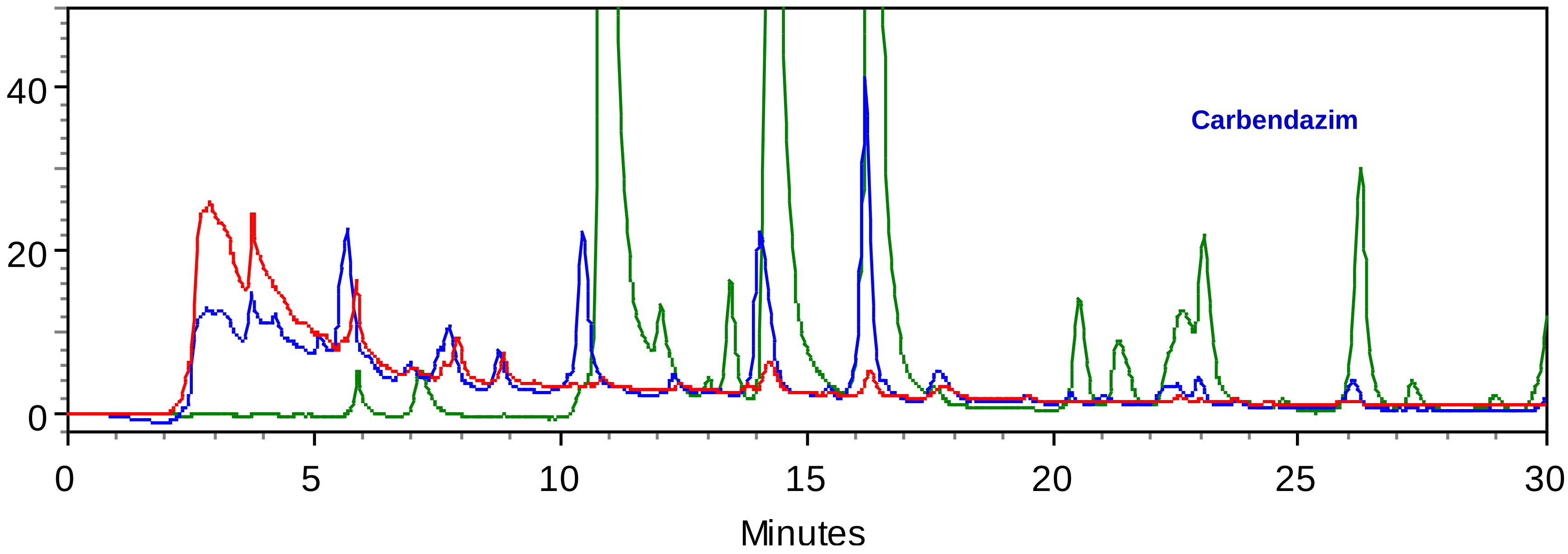
28 min (γ)

Kurucz et al., Radiat. Phys. Chem. 65 (2002) 367

Irradiation of Industrial Wastes from Production of Carbendazim

HPLC chromatograms for 1:20 diluted industrial wastes from production of carbendazim irradiated with electron beam:

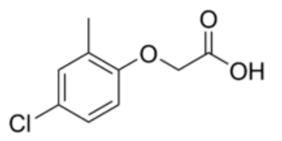
- **prior to the irradiation (green)**
- **irradiated with 26 kGy dose (blue)**
- **irradiated with dose 52 kGy (red)**



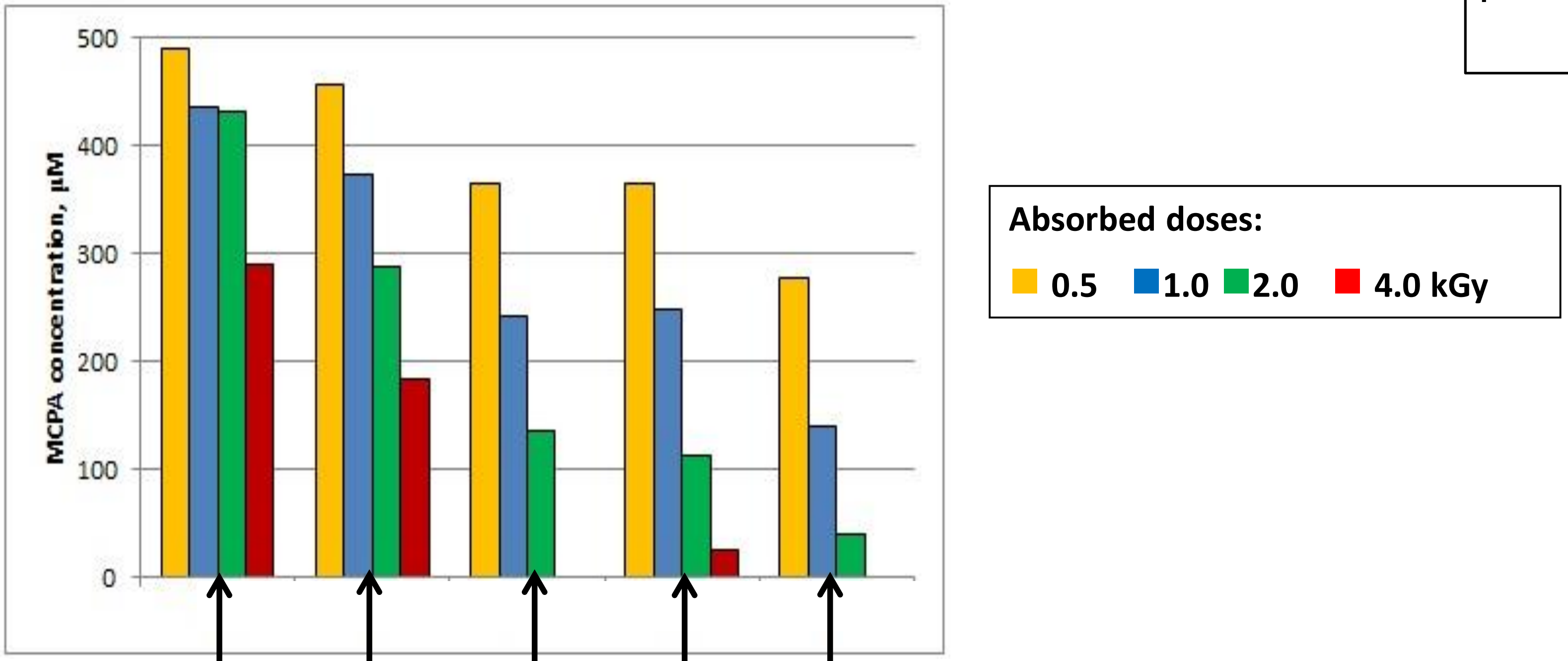
γ-Irradiation of MCPA Pesticide

Changes of MCPA concentration in aqueous solutions determined by HPLC after γ-irradiation with different doses and in different chemical conditions

Initial MCPA concentration 500 μM



(4-Chloro-2-methyl-phenoxy) acetic acid
MCPA



pH 7, aerated with 4.8 mM H_2O_2 ($^{\bullet}OH$, $O_2^{-\bullet}$, $HO_2^{\bullet}$)

pH 7, aerated ($^{\bullet}OH$, $O_2^{-\bullet}$, $HO_2^{\bullet}$)

pH 7, N_2O saturated ($^{\bullet}OH$)

pH 1.5, Ar saturated with *t*-butanol ($^{\bullet}H$)

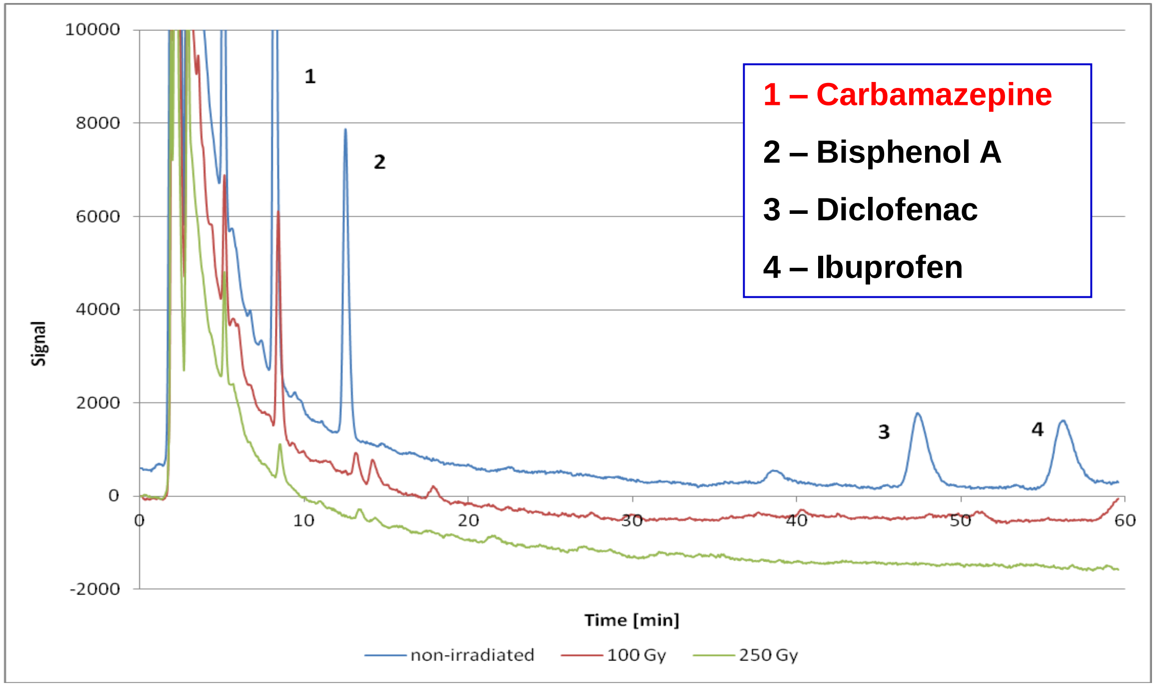
pH 7, Ar saturated, with *t*-butanol (e_{aq}^{-})

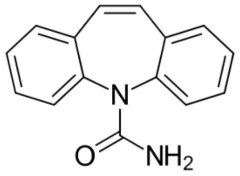
Bojanowska-Czajka, Trojanowicz et al.,
Radiat. Phys. Chem. 76 (2007) 1806

γ-Irradiation of River Water Sample Spiked with Pharmaceuticals

Water sample from river Vistula in Warsaw, spiked with 10 ppb of each analyte

500 mL spiked sample preconcentrated on Oasis HBL (Waters), eluted with 2 mL methanol – prior to and after γ-irradiation at different doses





5*H*-dibenzo[*b*,*f*]azepine-5-carboxamide
Carbamazepine

Non-irradiated
Irradiated with 100 Gy
Irradiated with 250 Gy

RP-HPLC with UV detection at 220 nm, column KROMASIL-100 C18, 25 cm, 5 µm, 4 mm

Isocratic elution with 50% 0.6 mM KH_2PO_4, 30% acetonitrile, 20% methanol, pH 4

S. Borowiecka, M.Sc. Thesis, Univerrsity of Warsaw, 2013

Experimental Factors Determining the Yield of Radiation-Induced Degradation of Organic Pollutants

- Molecular structure of decomposed pollutant
- Kind and energy of radiation, absorbed dose and dose-rate
- Effect of presence of radical scavengers
- Initial concentration of target pollutant
- pH of irradiated solutions
- Content of dissolved oxygen in irradiated solutions
- Synergistic effect of radiation and the presence of ozone or H_2O_2

THE MECHANISMS ARE THE SAME AS FOR ALL OTHER RADICALS-BASED AOPs, PAST, PRESENT AND FUTURE!

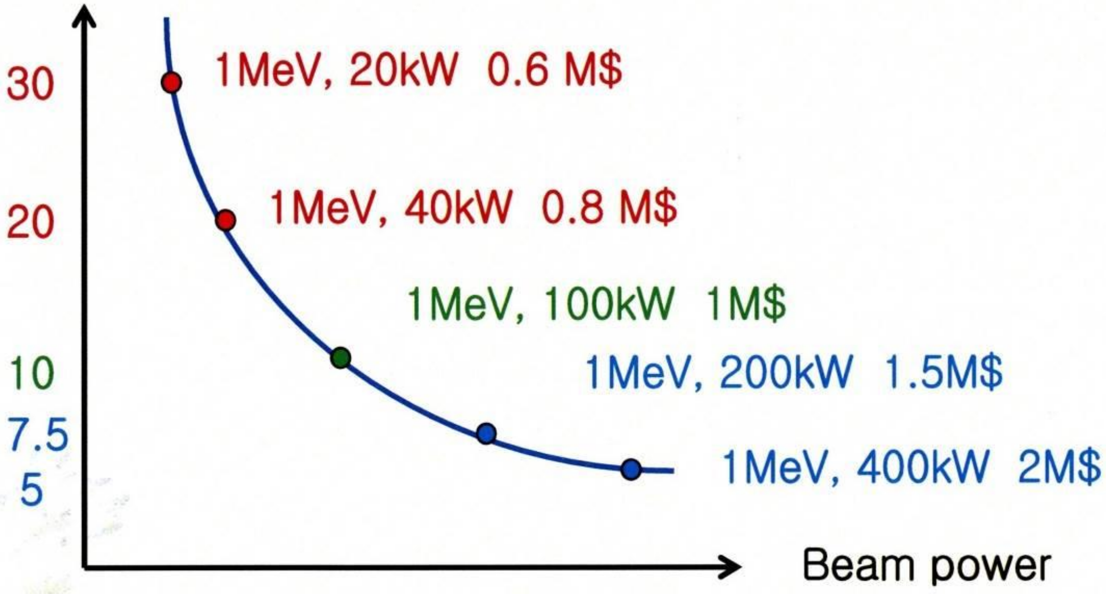
… only, faster…

Comparison of Advanced Oxidation Technologies

Characteristic	**UV / H_2O_2 Homogeneous Process**	**UV / TiO_2 Heteogeneous Process**	**Electron Beam Process**
Wavelength, nm	200-300	< 385	-
Quantum yield per $^{\bullet}OH$ radical generated	1.0	0.04 – 0.08	-
Moles $^{\bullet}OH$ per 1 kWh	**1.4**	0.087	**1.0**
Requires added chemicals?	Yes – H_2O_2 at >25 ppm	No	No
Energy needed **EE/O (kWh / m^3)**	< 3 for most pollutants	> 50 for most pollutants	< 3 for most pollutants
Phenol 500 μM	**3.6**	**336**	**1.5**
Methylene Blue 10 μM	**0.63**	**16.4**	**0.60**
Separtion needed after treatment?	No	Yes, if TiO_2 suspension is used	No
Capital cost	Moderate	Moderate	High

Bolton, Cooper et al., J. Adv. Oxid. Technol., 3 (1998) 174

Cost for Unit Power Using Electron Acceleraters (US $/W)



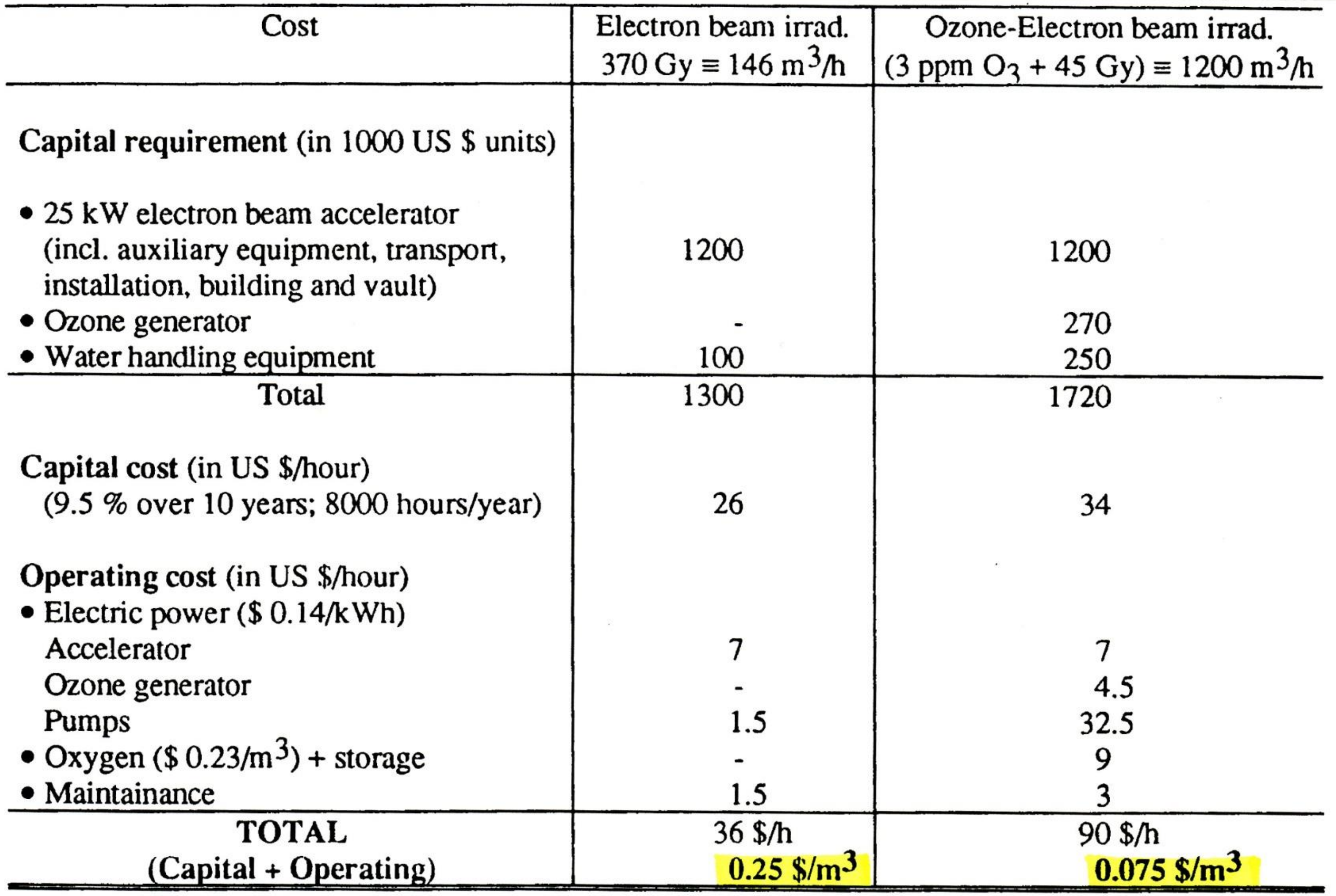
Beam Power	20kW	40kW	100kW	200kW	400kW	1MW
Total Cost (M$)	0.6	0.8	1.0	1.5	2	2.2*
Unit Cost ($/W)	30	20	10	7.5	5	2.2

*BUT… does **SIZE** matters?*

B. Han, EB-Tech, Daejeon, Korea, 2013

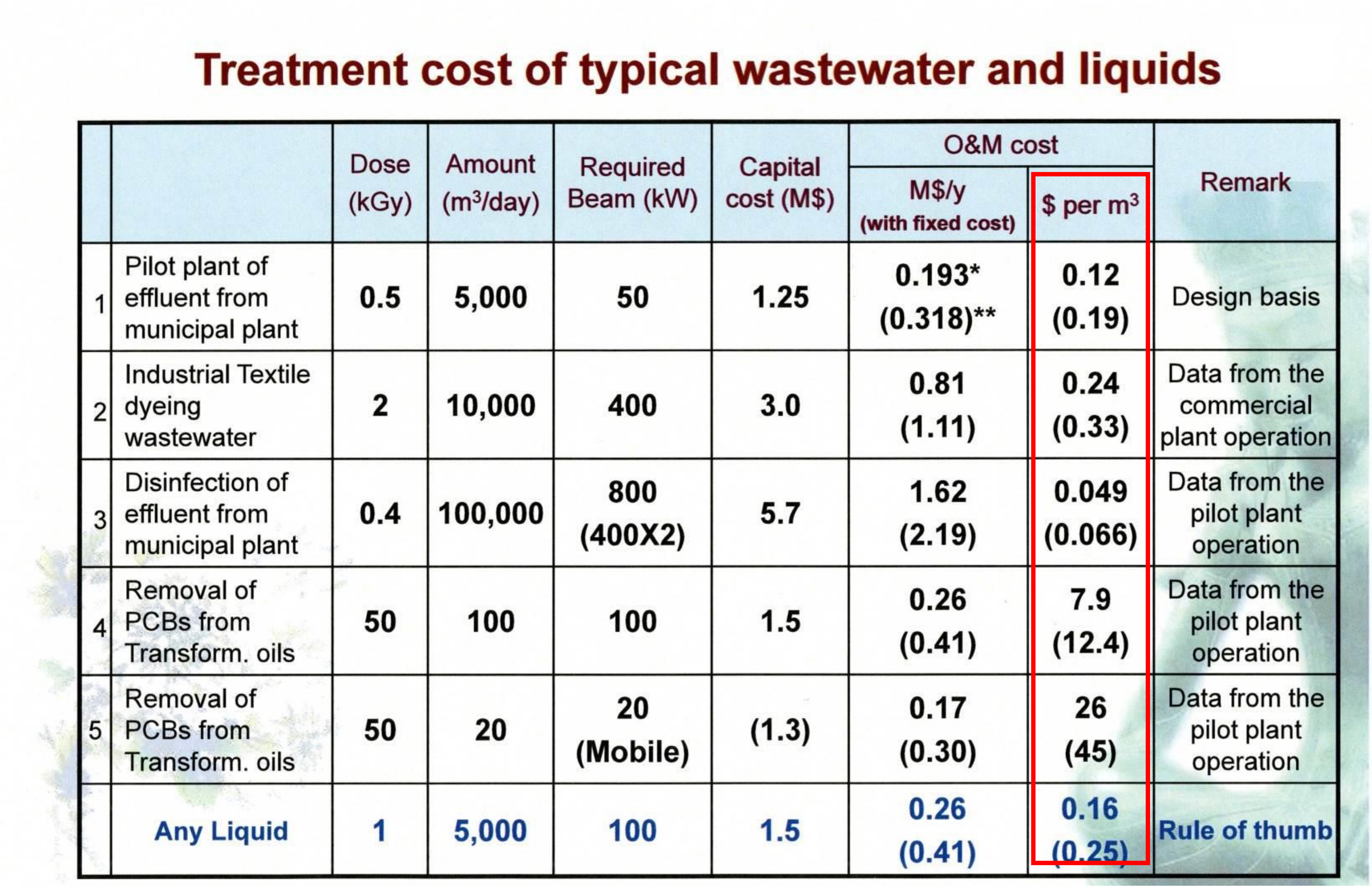
RESULTS…… Economic Comparison

for reduction of 120 ppb trichloroethylene to 5 ppb in GW by EB irradiation with and w/out ozone



	EB	EB + O_3
Cost	Electron beam irrad. 370 Gy ≡ 146 m^3/h	Ozone-Electron beam irrad. (3 ppm O_3 + 45 Gy) ≡ 1200 m^3/h
Capital requirement (in 1000 US $ units)		
• 25 kW electron beam accelerator (incl. auxiliary equipment, transport, installation, building and vault)	1200	1200
• Ozone generator	-	270
• Water handling equipment	100	250
Total	1300	1720
Capital cost (in US $/hour) (9.5 % over 10 years; 8000 hours/year)	26	34
Operating cost (in US $/hour)		
• Electric power ($ 0.14/kWh)		
Accelerator	7	7
Ozone generator	-	4.5
Pumps	1.5	32.5
• Oxygen ($ 0.23/m^3) + storage	-	9
• Maintainance	1.5	3
TOTAL (Capital + Operating)	36 $/h **0.25 $/$m^3$**	90 $/h **0.075 $/$m^3$**

Gehringer et al., Seibersdorf, Austria,
Radiat. Phys. Chem., 46 (1995) 1075



Treatment cost of typical wastewater and liquids

		Dose (kGy)	Amount (m^3/day)	Required Beam (kW)	Capital cost (M$)	O&M cost		Remark
						M$/y (with fixed cost)	$ per m^3	
1	Pilot plant of effluent from municipal plant	**0.5**	**5,000**	**50**	**1.25**	**0.193*** **(0.318)****	**0.12** **(0.19)**	Design basis
2	Industrial Textile dyeing wastewater	**2**	**10,000**	**400**	**3.0**	**0.81** **(1.11)**	**0.24** **(0.33)**	Data from the commercial plant operation
3	Disinfection of effluent from municipal plant	**0.4**	**100,000**	**800** **(400X2)**	**5.7**	**1.62** **(2.19)**	**0.049** **(0.066)**	Data from the pilot plant operation
4	Removal of PCBs from Transform. oils	**50**	**100**	**100**	**1.5**	**0.26** **(0.41)**	**7.9** **(12.4)**	Data from the pilot plant operation
5	Removal of PCBs from Transform. oils	**50**	**20**	**20** **(Mobile)**	**(1.3)**	**0.17** **(0.30)**	**26** **(45)**	Data from the pilot plant operation
	Any Liquid	**1**	**5,000**	**100**	**1.5**	**0.26** **(0.41)**	**0.16** **(0.25)**	**Rule of thumb**

O&M – operation and maintenance(?)

B. Han, EB-Tech, Daejeon, Korea, 2013

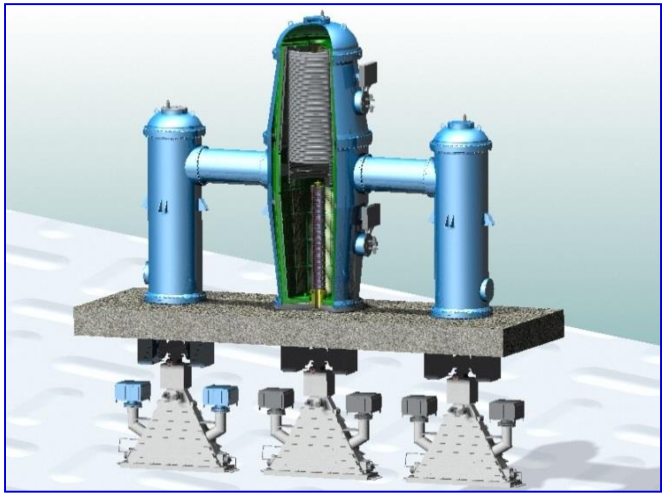
Industrial Plant for Treating Wastewater from Dyeing Process

- Decrease the amount of chemical reagent up to 50%
- Improve the efficiency of biological treatment by 30%
- Decrease the retention time in biological treatment facility

Characteristics of Industrial Plant

- Maximum flow rate of 10,000 m^3/day with one 1 MeV, 400 kW accelerator
- Combined with existing biological treatment facility

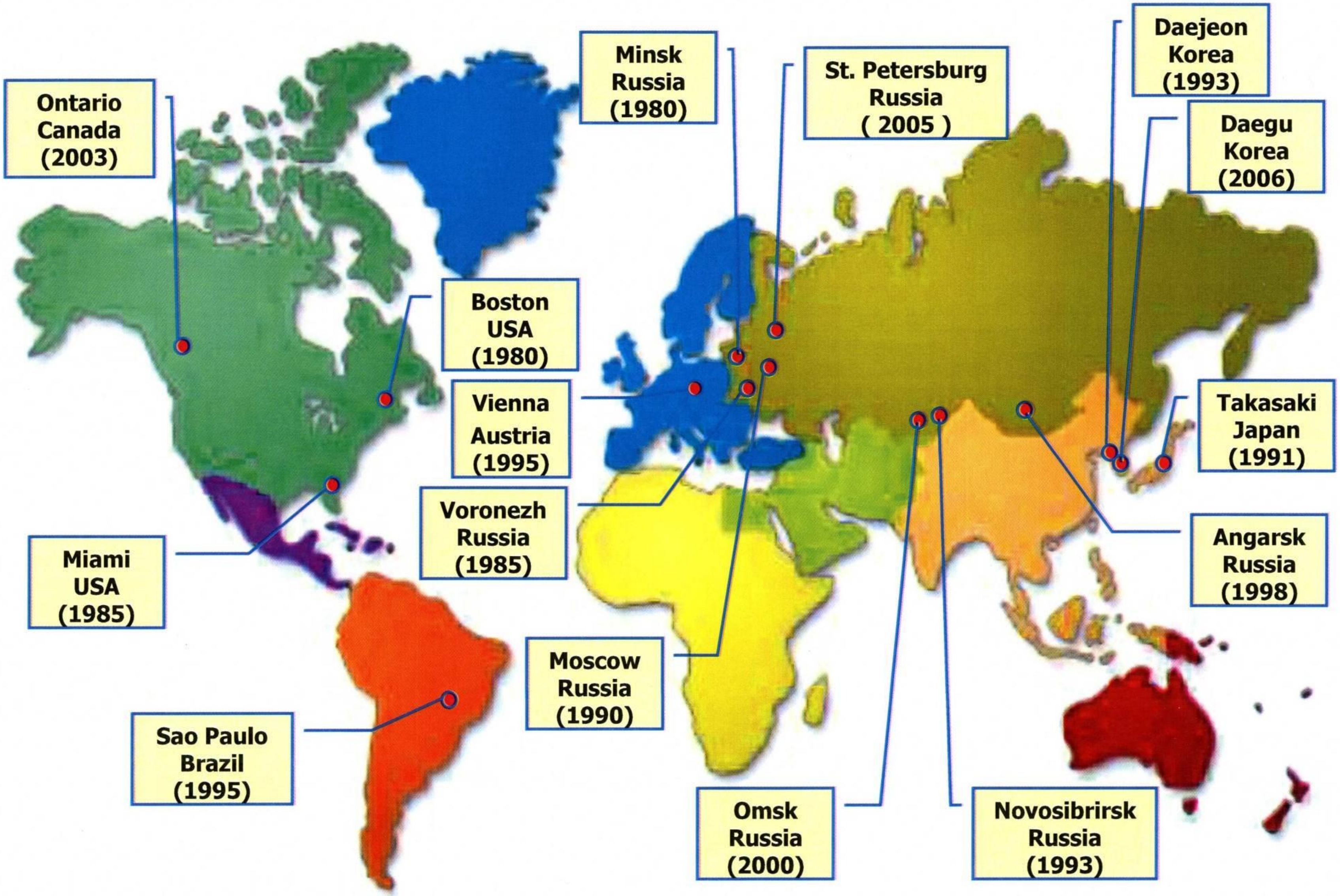
ELV-12 Accelerator:	
Energy :	0.6 - 1.0 MeV
Beam power:	400 kW
Beam current:	500 mA



Irradiators : 3 (0~200 mA)
Window width: up to 2 m
Double extraction window
Discharge protection
High frequency scanning

B. Han, EB-Tech. Co., Korea, IAEA RCM Vienna, 2006

Radiation processing of water treatment plant



B. Han, EB-Tech, Daejeon, Korea

CONCLUSIONS

Results obtained in several pilot plants indicate, that radiolytic degradation may serve as attractive and cost-effective AO(R)P for the degradation of organic pollutants (and NOT ONLY…)

The cost-effectiveness of radiolytic degradation of pollutants depends mostly on type of organic pollutants and also on their initial concentration and presence of radical scavangers in solution

EB efficacy is not affected by water turbidity or suspended solids, BUT is affected by the water matrix and the number of its components

In cost-effective conditions complete mineralization of organic pollutants, although possible, is usually not pursued in practice, but rather degradation to easier biodegradable, less-toxic species is obtained

Due to extremely high dose-rate achievable, EB-based radiolytic processes are much faster than gamma, x-rays or any other AOPs

Cost-effectiveness of the radiolytic degradation may be improved by carrying them in the presence of ozone or hydrogen peroxide that increase the radicals production of the process

CONCLUSIONS (II)

Initial capital investment is the major cost factor in radiolytic treatment, however, Electron Accelerators costs are constantly reducing due to ongoing important industrial applications

Despite the results obtained in several pilot plants indicate, radiolytic processes are still seen with **skepticism** by water reseachers and professionals

The **cost-effectiveness** of radiolytic degradation of pollutants is still to be proved over with real-life, long term applications

EB processing **can be combined** with traditional processes to achieve the best results with less effort and costs.

Thank you for your attention!

and, just a minute …

A few openings are still available for the Summer School

“Energy and material recovery from water & wastes for sustainable urban metabolism”

held at Villa Grumello (Lake Como) 21-25 August 2017.

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Prof. Gustaf Olsson, Sweden
Prof. David Vaccari, USA
Prof. Grietje Zeeman, The Netherlands

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