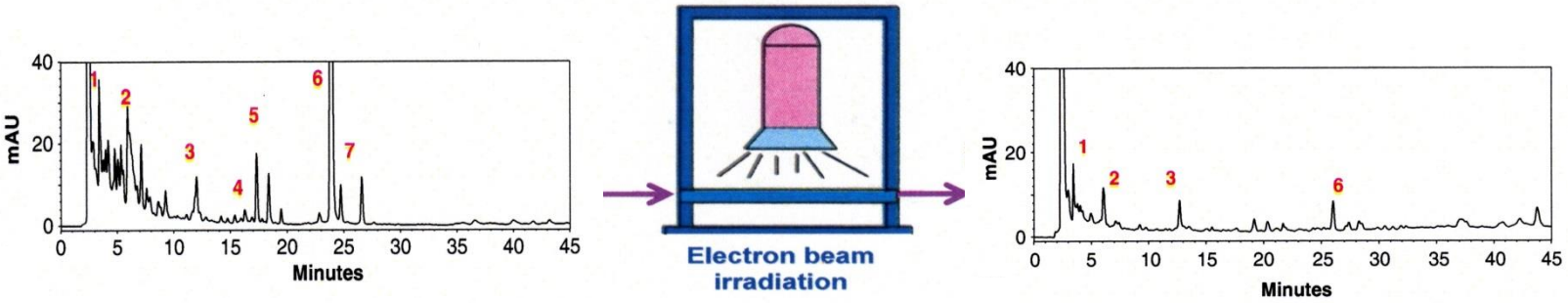

Application of Electron Beam Irradiation in Remediation of Wastewaters

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EuCARD²

Warsaw, 2016

Removal of Organic Pollutants at Wastewater Treatment Plants

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

Pharmaceuticals (and metabolites) detected in world wide 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

Main Purposes of Radiolytic Degradation of Organic Pollutants

- Decomposition to inorganic non-toxic species
- Degradation to less toxic species
- Degradation to biodegradable species

Early Works on γ-Irradiation of Pesticides

Pesticide	Matrix	Authors	
Alidrin	Organic solvents, corn oil, lard	Carp et al.,	1972
Aldrin, endrin,heptachlor epoxide	Potatoes	J.M.Solar et al.,	1971
Aldrin, dieldrin,	Hexane	Ceurvels	1974
heptachlor, lindane			
Atrazine	Water	Buchlotz et al.,	1977
Chlordane	Hexane	Vollner and Korte	1974
Disulfoton, phorate	Water, solvents	Grant et al.,	1969
Hexachlorocyclohexane	Propanol	Hamada et al.,	1981
Lindane	Hexane	Vollner, Korte	1974
	Water	Cappadona et al.,	1975
Malathion, parathion, tetradifon	Hexane	Lippold et al.,	1969
Malathion	Paper strips, wheat	Cogburn, Mahany	1969
Mirex	Duck eggs	Lane et al.,	1976
	Fish	Cin and Kroger	1982
DDT	Water, wastes	Cappadona et al.,	1975
	Solvents, fatty esters	Lepine et al.,	1991
	Onion	Bachman et al.,	1982
	Water	Shastri, Rao	1980
	Propanol	Sherman et al.,	1971
	Oyster homogenates	Hallab	1968

Taken from: F. L. Lepine, J. Agric. Food Chem., 39 (1991) 2112

Decomposition of Pharmaceuticals in Environmental Samples by Ionizing Radiation

Antibiotic Tetracycline

Cho, Chonbuk National University Korea,	*Bull. Environ. Contam. Toxicol. 2010*
Cooper et al., University of California, Irvine,	*Chemosphere 2010*

Ciprofloxacin

Cooper et al., University of California, Irvine,	*Appl. Catal. B-Environ., 2010*

β-Blockers

Cooper et al., Univrsity of California, Irvine,	*Environ. Sci. Technol., 2008*

Nitroimidazoles

Rivera-Utrilla et al., University of Granada,	*Water Res., 2009*

Cefaclor (antibiotic)

Chang et al., Kunsan National University, Korea,	*Chemosphere 2008.*

β-Lactam antibiotics

Cooper et al., University of California, Irvine,	*J. Phys. Chem. A, 2008*

Sulfa drugs

Cooper et al., University of California, Irvine,	*J. Phys. Chem. A, 2007*

β-Estradiol (steroid hormone)

Taguchi et al., Takasaki Res. Center, Gunma, Jap.,	*Radiat. Phys. Chem., 2004.*

Fibrate Pharmaceuticals

Cooper et al., University of California, Irvine,	*J. Phys. Chem. A, 2009*

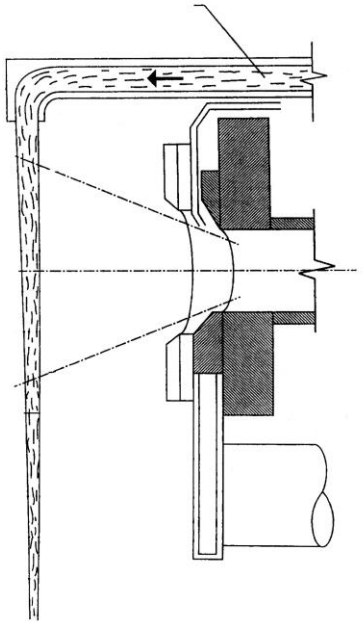
Diclofenac

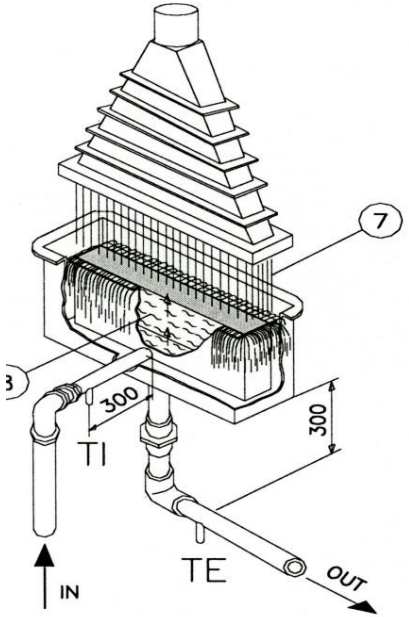
Jones, North Carolina University, Releigh	*Ph.D. Thesis., 2007*
Liu et al., Nanjing University, China,	*Environ. Sci.Poll. Res., 2011*
Homlok et al., Institute of Isotops, Hungary	*Chemosphere, 2011*
Kimura et al., Japan Atomic Energy Agency	*Radiat.Phys.Chem., 2012*
Bojanowska-Czajka et al., INCT, Warsaw	*Enviorn. Sci. Poll. Res., 2015*

EB Irradiation Flow-through Installations

Cascade configuration for Miami EB research facility

Kurucz et al., 1995



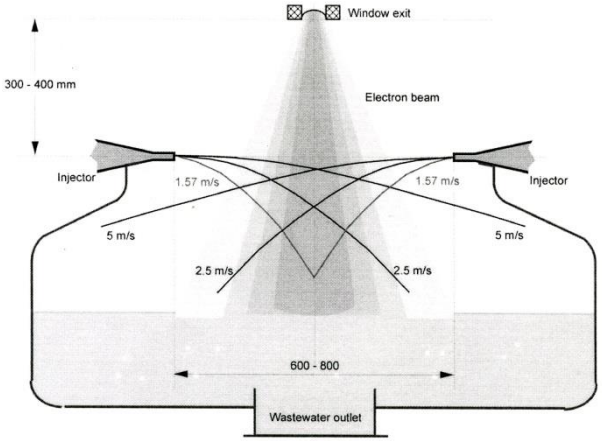


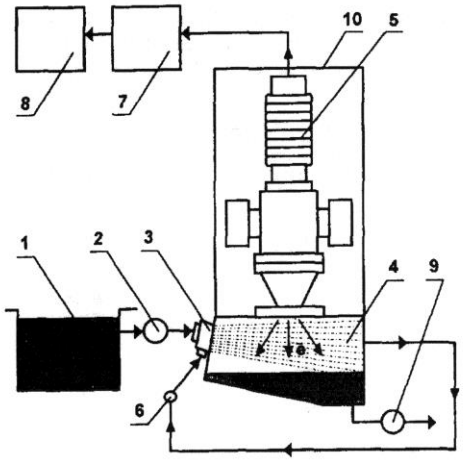
Overflow-type configuration from IPEN, Sao Paulo

Duarte et al., 2002

Two opposite nozzles configuration

Pikaev et al., 2001





Combined EB/ozone installation with aerosol flow from Russia

Pikaev et al., 1997

Irradiation Facilities Currently Used in INCT

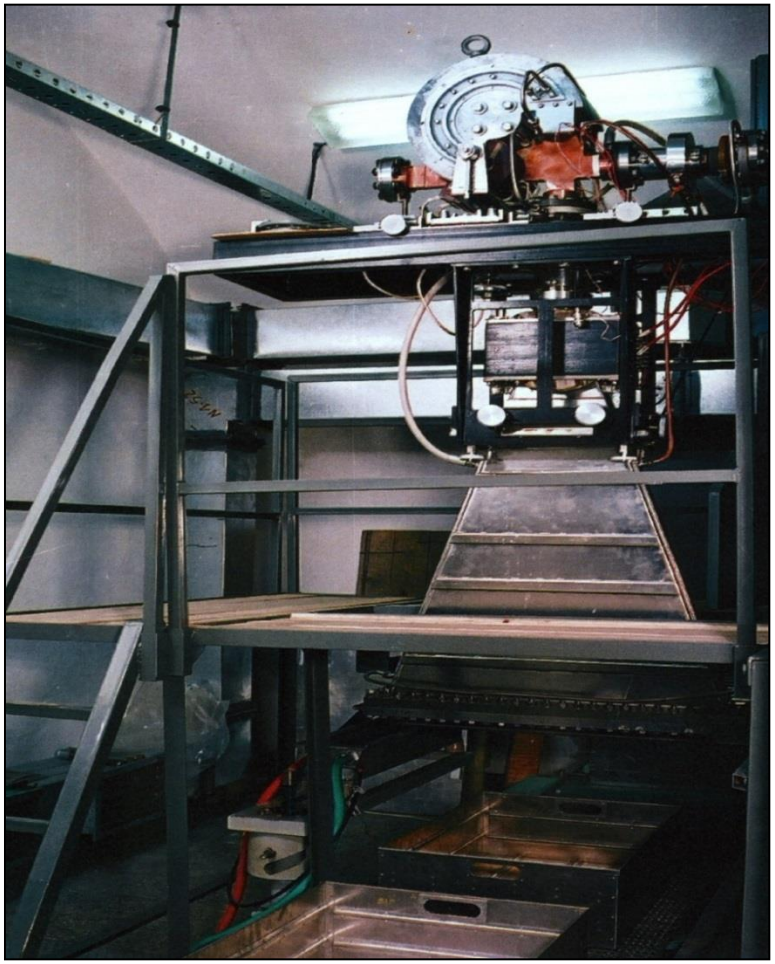
^{60}Co-sources

γ-Source „Issledovatel”

Samples are irradiated in 300 mL Winkler’s bottles used for oxygen measured (tightly closed, with zero volume head space)

Dosimetry is performed with Fricke dosimeter based on Fe(II) oxidation

Gamma Chamber 5000, ~4 kGy/h



Electron beam accelerator
Elektronika 10/15
(energy 10 MeV, beam power 15 kW; conveyor speed 0.3 – 7 m/min)

Main Groups of Organic Pollutants Decomposed using Ionizing Radiation

- Halogenated alkanes and alkenes
- Aromatic hydrocarbons
- Phenol and chlorinated phenols, nitrophenols
- Pesticides
- Polychlorinated biphenyls
- Detergents, perfluorinated surfactants
- Hormones, antibiotics and other pharmaceuticals
- Dyes

Environmental Pollutants of Waters and Wastewaters Examined in INCT for Radiolytic Removal

Industrial pollutants	Pesticides	Pharmaceuticals	Mycotoxins
Chlorophenols	2,4-D	Diclofenac	Aflatoxin B_1
Biphenol A	MCPA	Carbamazepine	
Perfluorinated surfactants	Dicamba		
	Carbendazim		
	Parathion		
	Chlorfenvinfos		

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

Radiolytic Removal of Organic Compounds Involving Different Reactive Products of Water Radiolysis

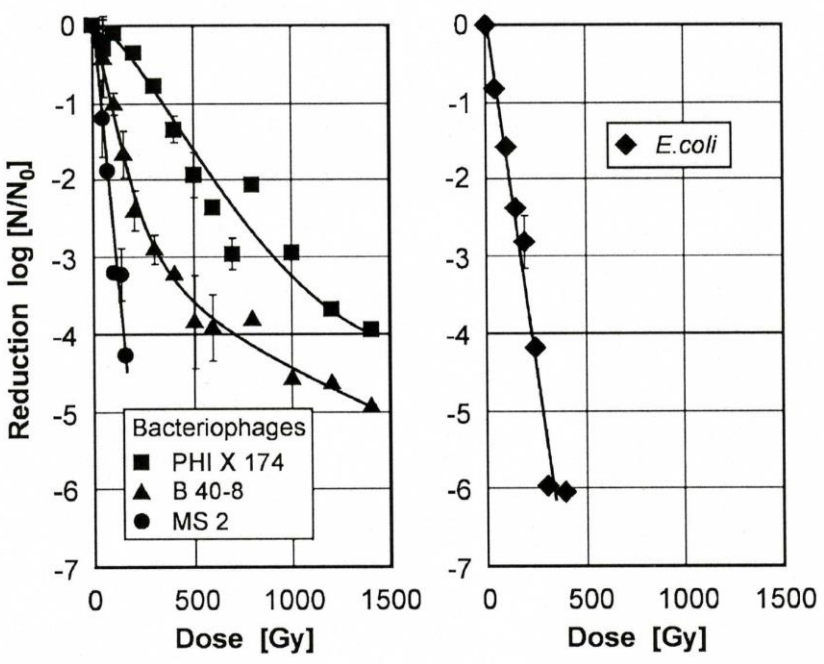
Compound	Bimolecular rate constants ($M^{-1}s^{-1}$ ($\times 10^{y}$))			Relative importance of species (%)		
	•OH	e^-aq	H•	•OH	e^-aq	H•
Target organic compounds						
MTBE	2	0.0175	0.0001	99	1	0
Trichloroethylene	2.9	1.9	NF	61	39	0
Tetrachloroethylene	2	1.3	5	46	29	25
Benzene	7.6	0.009	0.91	97	0.1	3
Toluene	5.1	0.011	2.6	90	0.1	10
Ethyl benzene	7.5	NF	NF	100	0	0
o-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	2.8	NF	NF	100	0	0

Cooper et al., Radiat. Phys. Chem. 65 (2002) 451

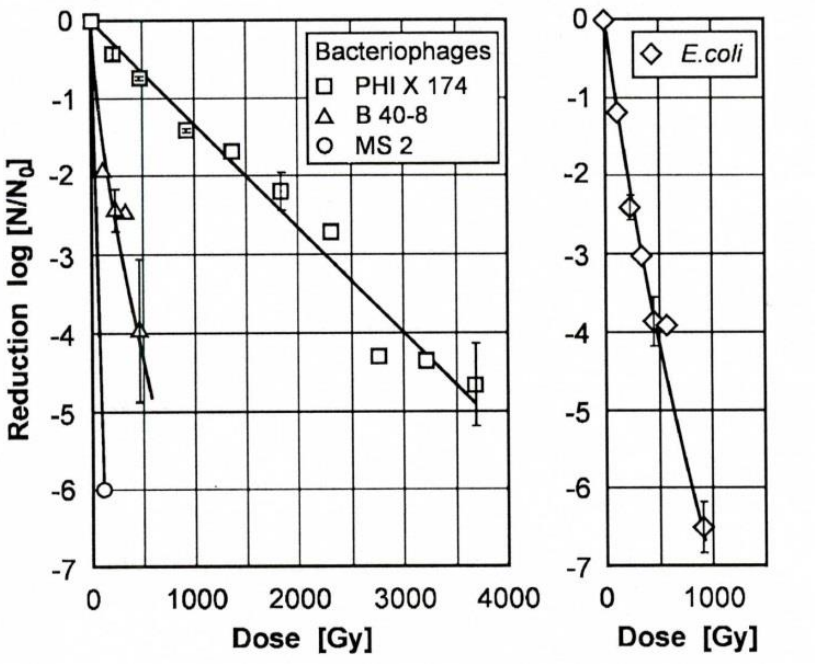
Water Disinfection by Radiation Processing – Dose-rate Effects

Selected bacteriophages and *E.coli* suspended in tap water (1 x 10^6 microorganisms/mL) were irradiated and different inactivation sensitivity was observed

Gamma irradiation



EB irradiation



Evident dose-rate effect was observed for PHI X 174 phage, and also *E. coli*

Gehringer et al., Appl. Radiat. Isotop., 58 (2003) 651

Dose Rate Effect for Decomposition of Perchloroethylene (PCE) in Water

No alternative for ozone to eliminate the disadvantage caused by dose rate effect

Table 1
Conversion of solvated electrons into OH free radicals

Reaction	Bimolecular reaction rate constant
$O_3 + e^-_{aqu} \rightarrow O_3^- \overset{+H^+}{\rightarrow} OH + O_2$	$k = 3.8 \times 10^{10}$ l/mol s
$O_3 + OH \rightarrow HO_2 + O_2$	$k = 1.1 \times 10^{8}$ l/mol s
$H_2O_2 + e^-_{aqu} \rightarrow OH + OH^-$	$k = 1.2 \times 10^{10}$ l/mol s
$H_2O_2 + OH \rightarrow H_2O + HO_2$	$k = 2.7 \times 10^{7}$ l/mol s
$N_2O + e^-_{aqu} \rightarrow OH + N_2 + OH^-$ almost inert against OH attack	$k = 9.1 \times 10^{9}$ l/mol s

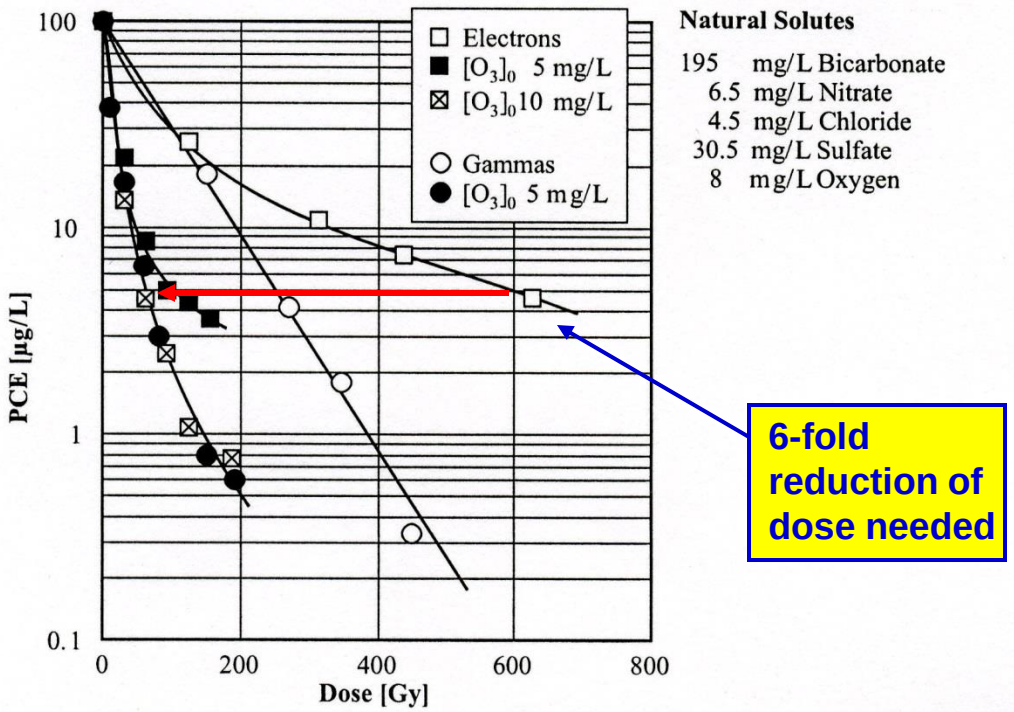


Fig. 6. Effect of ozone addition on the radiation-induced PCE decomposition in tap water.

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

Scavengers - Rate-Constants ($M^{-1}s^{-1}$)

for reactions of main products of water radiolysis with common radical scavengers in waters and wastewaters

Compound	$^{\bullet}OH$	e_{aq}^-	$^{\bullet}H$
O_2	NR	1.9×10^{10}	$< 1.0 \times 10^6$
HCO_3^-	8.5×10^6	$< 1.0 \times 10^6$	$< 1.0 \times 10^6$
CO_3^{2-}	3.9×10^8	3.9×10^5	NR
Cl^-	3.0×10^9	$< 1.0 \times 10^6$	$< 1.0 \times 10^5$
NO_2^-	1.1×10^{10}	3.5×10^6	7.1×10^8
NO_3^-	NR	9.7×10^9	1.4×10^6
DOC	2.0×10^8	NR	NR

DOC- dissolved organic carbon, NR- non-reacting

Buxton et al., G.V.,
Critical review of rate constants for reaction of hydrated electrons, hydrogen atoms and hydroxyl radical (˙OH/H˙-) in aqueous solution.
J. Phys. Chem. Ref. Data 17 (1987) 512

Kinetic modeling of Radiolytic Degradation of Pollutants

CCl_4 decomposition by EB irradiation at different initial concentrations

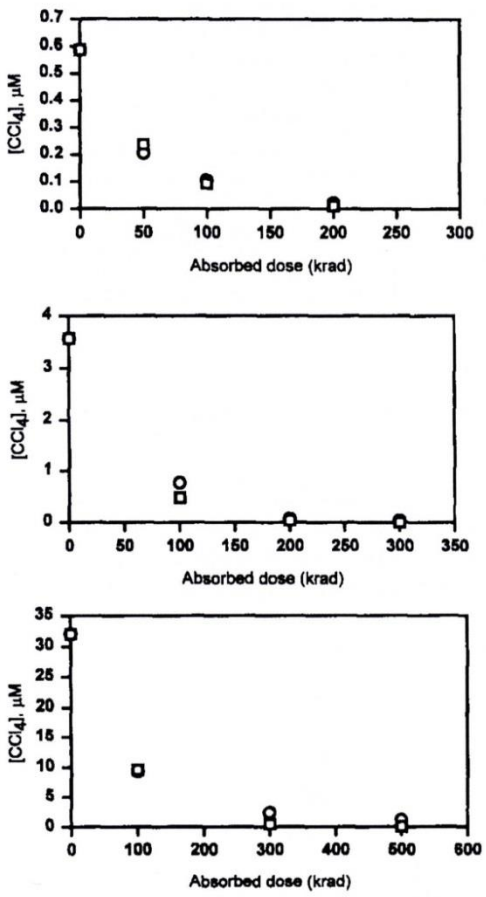
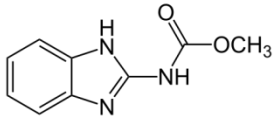


Fig. 1. Carbon tetrachloride removal from aqueous solution (pH 9) as a function of absorbed dose at three influent concentrations (○—experimental, □—model). Rate constant for $CCl_4 + e^-_{aq}$ is ($k = 1.3 \times 10^{10}$) obtained from literature.

Mak, Cooper et al., Wat. Res., 31(1997) 219

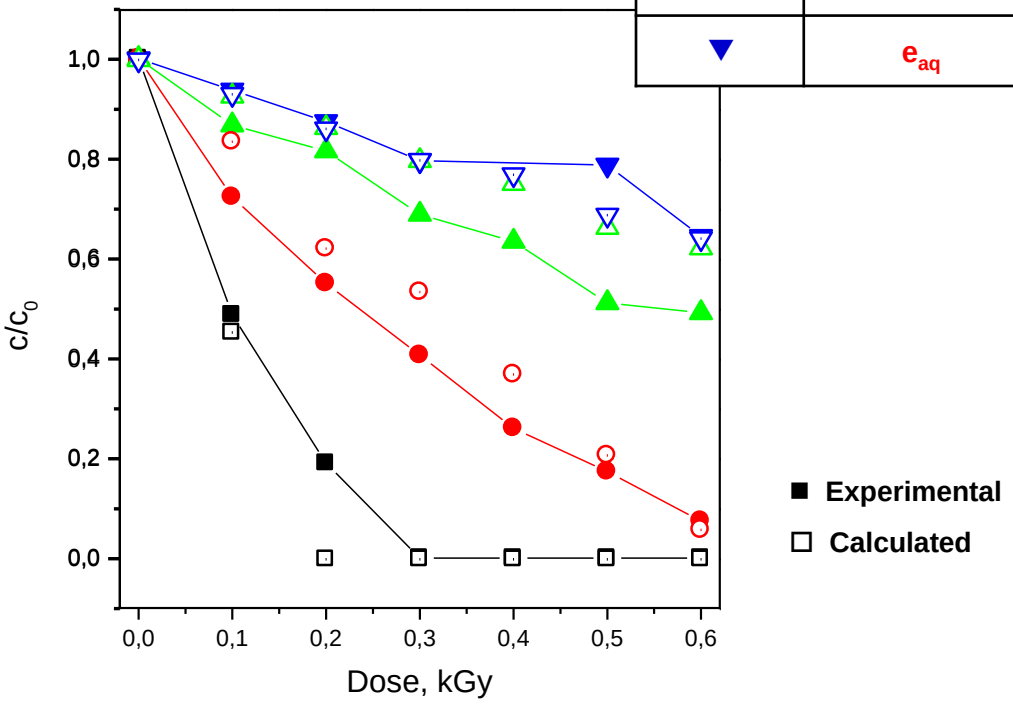
Modelling of Irradiation of Pesticide Carbendazim in Different Radical Scavenging Conditions



Methyl *1H*-benzimidazol-2-yl-carbamate (Carbendazim)

Irradiation conditions

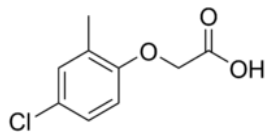
Symbol	Predominated radicals
■	•OH
●	•OH, HO_2•,O_2•-
▲	•H
▼	e_{aq}



γ – Irradiation of 100 μM aqueous solution of carbendazim

Bojanowska-Czajka, et al., J. Radional. Nucl. Chem., 289 (2011) 303

γ-Radiolytic Decomposition of Pesticide MCPA

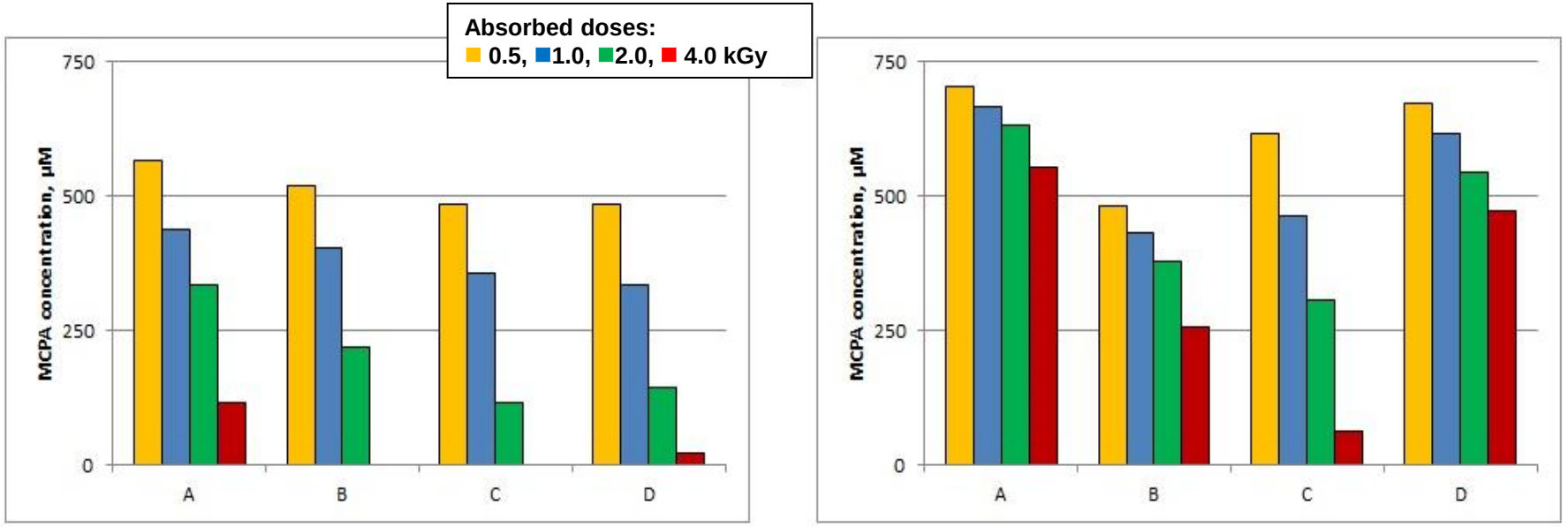


(4-Chloro-2-methyl-phenoxy) acetic acid **MCPA**

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

Synthetic aqueous solutions 750 μM MCPA containing 90 g/L chloride

Industrial wastewater from production of MCPA containing 750 μM MCPA



A – pH 7, aerated (•OH, $O_2^{\bullet -}$, $HO_2^{\bullet}$)
B – pH 0.5, aerated (*like in non-treated wastewater*)
C – pH 0.5, aerated, containing 4.8 mM H_2O_2
D – pH 7, aerated, containing 4.8 mM H_2O_2

The most effective conditions

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

Figures of Merit of γ-Radiolytic Decomposition of Selected Organic Pollutants

Compound	Examined concentration, mg/L	Reaction rate constant, $M^{-1}\ s^{-1}$ (with •OH radicals)	Radiation yield G_o μM J^{-1} (at dose, kGy)	Dose constant, kGy^{-1}	$D_{0.9}$ kGy (dose required for 90% decomposition)
Parathion	15	$4.2 - 9.7 \times 10^9$	0.136 (0.2)	1.76	1.31
Bisphenol A	6.9	6.9×10^9	0.141 (0.1)	7.19	0.32
Aflatoxin B1	10	not found	0.506 (0.02)	9.33	0.25
Diclofenac	10	12×10^9	0.147(0.2)	6.02	0.38
Ibuprofen	10	$6.7 - 10 \times 10^9$	0.163 (0.2)	7.02	0.33
Carbamazepine	10	$2.0 - 9.7 \times 10^9$	0.109 (0.2)	4.37	0.53

Chemo-radiation yield, μM J^{-1} $\quad G = [(C_0 - C_D)\ 6.02 \times 10^{23}] / [D \times 6.46 \times 10^{16}]$

C – concentration, M

D – absorbed dose, Gy

Dose constant , K_{obs}, kGy^{-1} $\quad$ Slope of plot – ln (C_D/C_0) vs. D

Radiation dose required for 90% decomposition, $D_{0.9}$, kGy

$$D_{0.9} = \ln 10 / K_{obs}$$

γ-Radiolytic Decomposition of Pesticide MCPA

Figures of merit calculated for processes of decomposition of MCPA by gamma radiation in synthetic aqueous solutions and **industrial wastewater** from MCPA production, which were carried out in different conditions of irradiation.

G_0 – chemo-radiation yield ($\mu M\ J^{-1}$) ;
$D_{0.9}$ – dose required for 90% decomposition of target species (kGy)

Irradiated solution	Aerated solution of pH 7.0		Aerated solution of pH 0.5		Aerated solution, pH 7.0, with 4.8 mM H_2O_2	
	G_0	$D_{0.9}$	G_0	$D_{0.9}$	G_0	$D_{0.9}$
500 μM MCPA aqueous solution	0.262	3.13	0.278	2.69	0.446	1.77
750 μM MCPA aqueous solution with 90 g/L chloride	0.237	5.06	0.296	3.81	0.339	2.66
Industrial wastewater containing 750 μM MCPA	0.059	32.0	0.342	10.0	0.099 (0.171)*	20.9 (3.70)*

*) Data for irradiation in aerated waste sample of pH 0.5 with added 4.8 mM H_2O_2

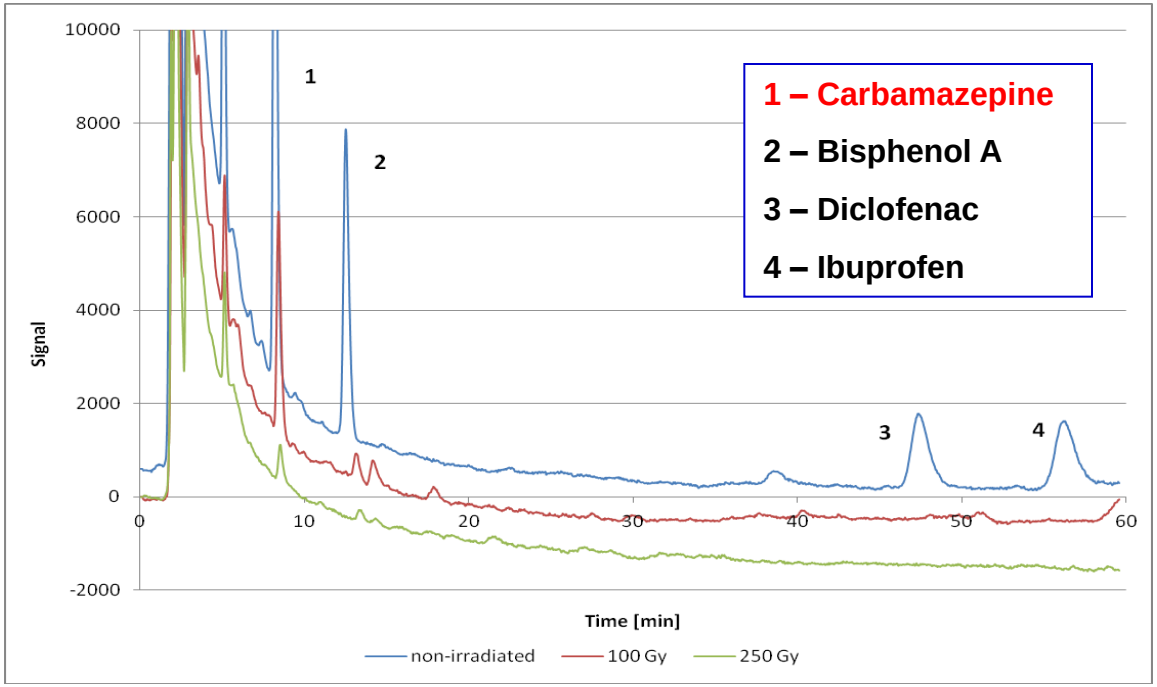
Essential effects of:
- pH of irradiated solution
- Presence of chloride
- Addition of H_2O_2

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

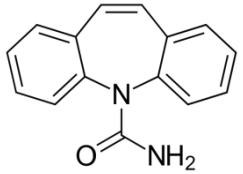


1 – Carbamazepine

2 – Bisphenol A

3 – Diclofenac

4 – Ibuprofen



5*H*-dibenzo[*b*,*f*]aze-pine-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

Bojanowska-Czajka et al., Environ. Sci. Pollut. Res., 22 (2015) 20255

Radiolytic Decomposition of Pharmaceutical Carbamazepine

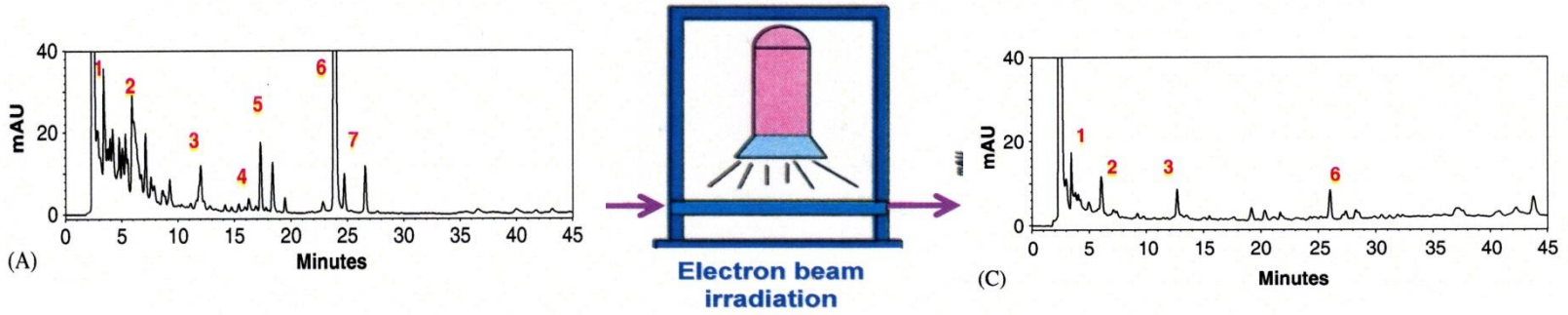
Figures of merit for processes of decomposition of carbamazepine (CBZ) by ionizing radiation in synthetic aqueous solutions and spiked natural waters and wastewaters of different origin

G_0 - chemo-radiation yield ($\mu M\ J^{-1}$);
$D_{0.9}$ – dose required for 90% decomposition of target species (kGy)

Initial CBZ concentration	Irradiated solution	Conditions of irradiation (type of radiation)	G_0, $\mu M\ J^{-1}$	$D_{0.9}$, kGy	Reference
42.3 nM (10 ppb)	Aqueous CBZ solution	Aerated solutions (γ)	0.390	0.071	*Bojanowska-Czajka et al., 2015*
	River water spiked with CBZ		0.302	0.192	
	Hospital waste spiked with CBZ		0.132	0.650	
5.0 mM (1.18 ppm)	Wastewater after treatment with activated sludge	pH 7.45; aerated (γ)	0.020	0.294	*Kimura et al., 2012*
212 mM (50 ppm)	Aqueous CBZ solution	N_2 saturated solutions (EB)	0.261	1.03	*Zeng et al., 2014*
	Surface water spiked with CBZ		0.196	1.66	

Bojanowska-Czajka et al., Environ. Sci. Pollut. Res., 22 (2015) 20255
Kimura et al., Radiat. Phys. Chem., 81 (2012) 1508
Zheng et al., J. Radioanal. Nucl. Chem., 302 (2014) 139

CONCLUSIONS



Results obtained in several pilot plants and also in this study indicate, that radiolytic degradation may serve as attractive and cost-effective AOP for the degradation of organic pollutants

The cost-effectiveness of radiolytic degradation of pollutants depends mostly on type of organic pollutants, matrix of irradiated samples and also on their initial concentration and presence of scavangers of radicals

In cost-effective conditions the complete mineralization of organic pollutants is practically not observed, but rather degradation to easier biodegradable, less-toxic species

Due to extremaly high dose-rate the EB-based radiolytic processes are much faster than any other AOPs

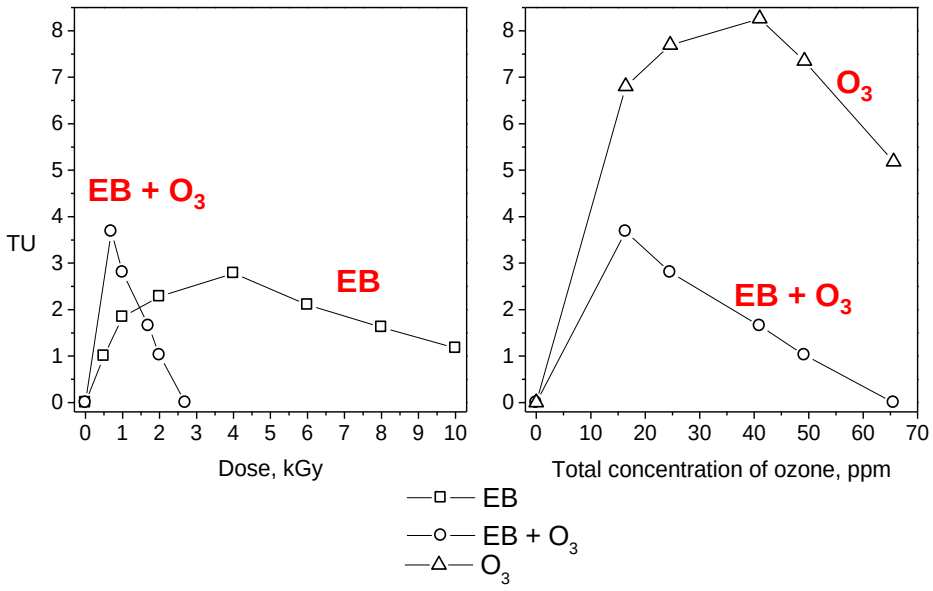
The cost-effectiveness of the radiolytic degradation may be improved by carrying them in the presence of ozone or hydrogen peroxide

But…..

Microtox Toxicity Changes Observed for Radiolytic Decomposition of 2,4-D Pesticide in Aerated Solutions

Ground water spiked with 500 μM 2,4-D

EB irradiation without and with ozone

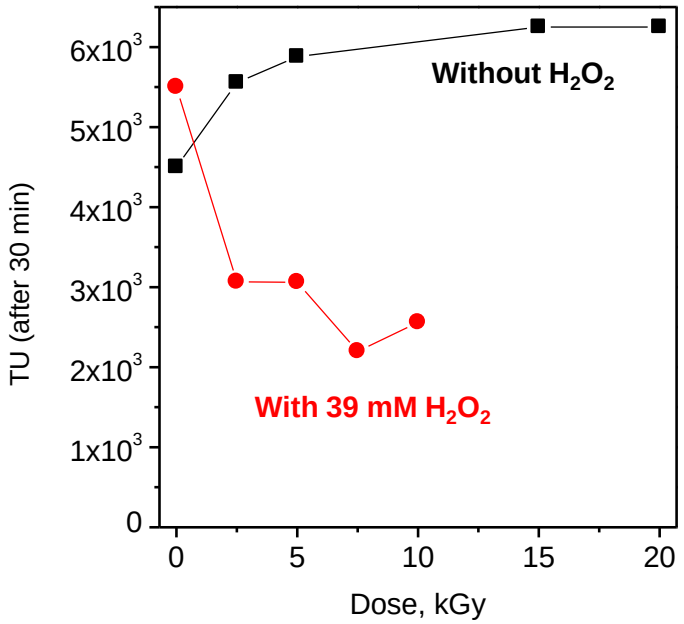


TU = 100 / EC_{50} (15 min)

The combined process EB/O_3 gives better reduction of total toxicity than separate EB or O_3 treatment.
The positive effect of addition of H_2O_2 is evident only in doses up to 2 kGy

Industrial wastes from 2,4-D production

Irradiation with and without H_2O_2



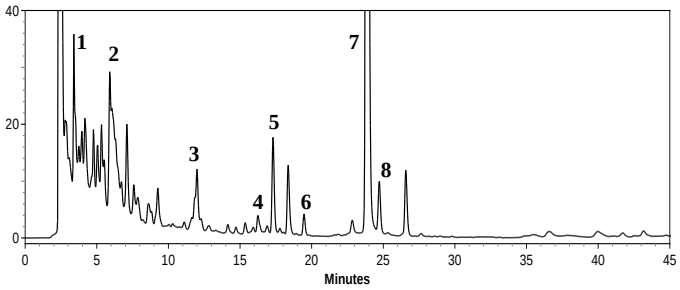
TU = 100 / EC_{50} (30 min)

Addition of 39 mM H_2O_2 reduces toxicity during γ-irradiation of industrial waste from 2,4-D production

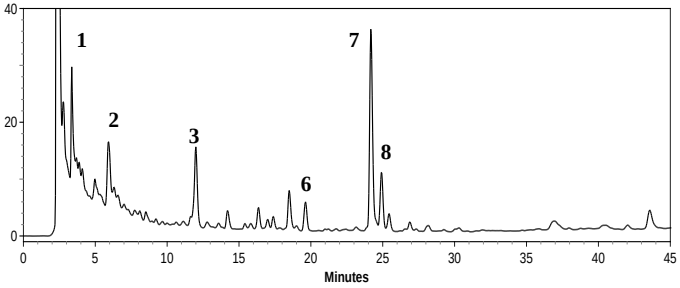
γ-Radiolytic Degradation of MCPA in Industrial Waste

MCPA

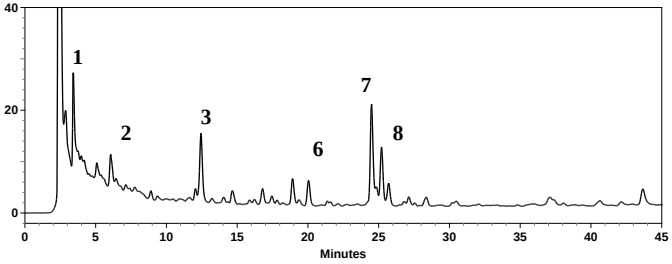
Wastewater prior to the irradiation



5 kGy



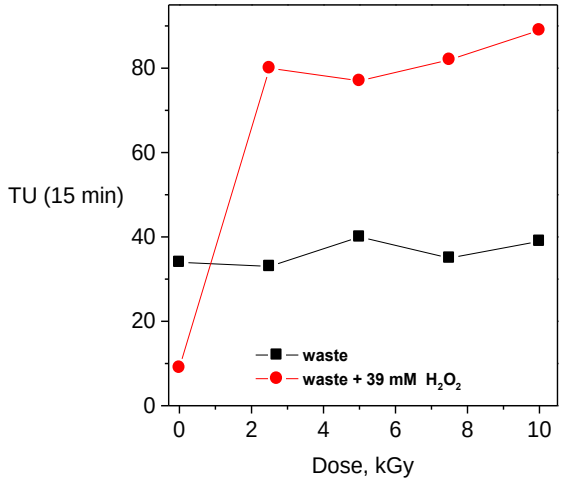
10 kGy



In contrary to irradiation of pure MCPA solutions, the addition of H_2O_2 affects positively the yield of pesticide decomposition

The reason of the toxicity increased in the presence of hydrogen peroxide is formation of more toxic semi-products

Changes of toxicity

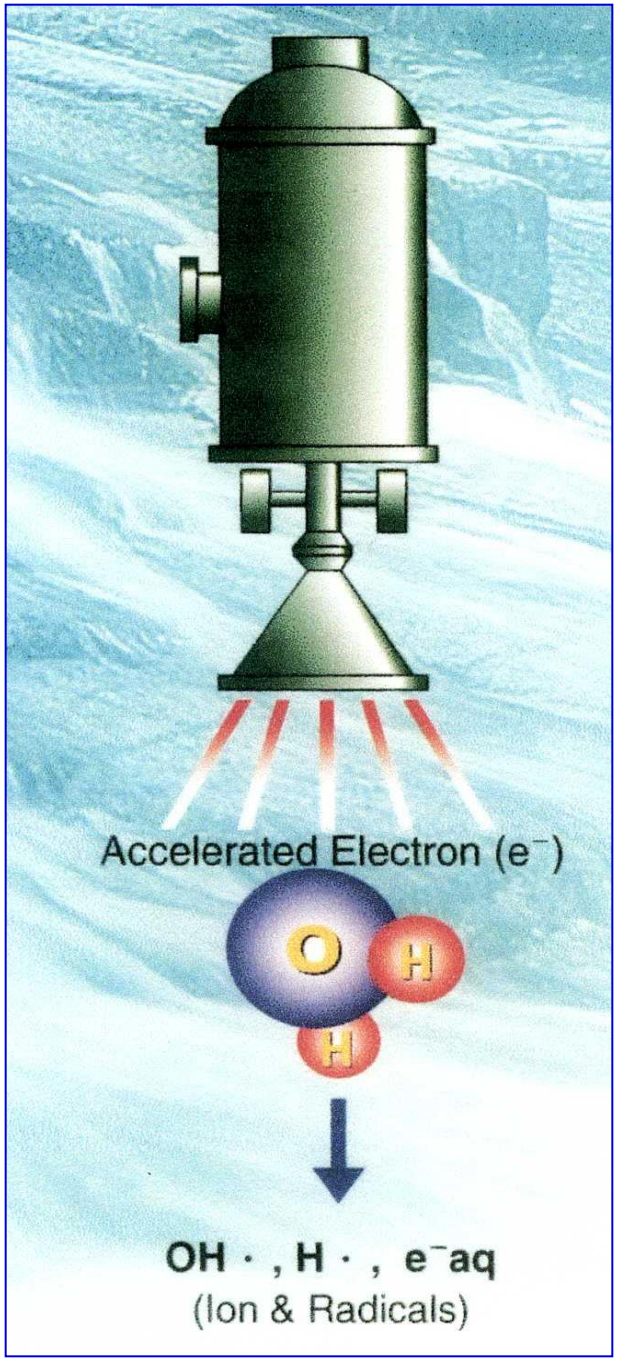


Initial concentration of MCPA 0.5 g/l, pH 1.5

Excess of H_2O_2 removed by sodium thiosulphate

Microtox® toxicity EC_{50} of selected phenolic compounds (ppm)

MCPA (4-chloro-2-methylphenoxyacetic acid)	75.6
MPA (methylphenoxyacetic acid)	300
o-Cresol	38.4
2-chloro-6-methylphenol	63.2
4-chloro-2-methylphenol	1.5
Methylhydroquinone	0.3



Can Radiation Chemistry Supply a Highly Efficient, Economical Process Alternative for Organics Removal from Wastewater?

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

System	$^{\bullet}OH$	e^{-}_{aq}	$^{\bullet}H$
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

Significant Advantage of Radiation Technologies

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

Economic Comparison – Effect of Ozonation

for the reduction of 120 ppb trichloroethylene to 5 ppb in groundwater by EB irradiation with and without ozone

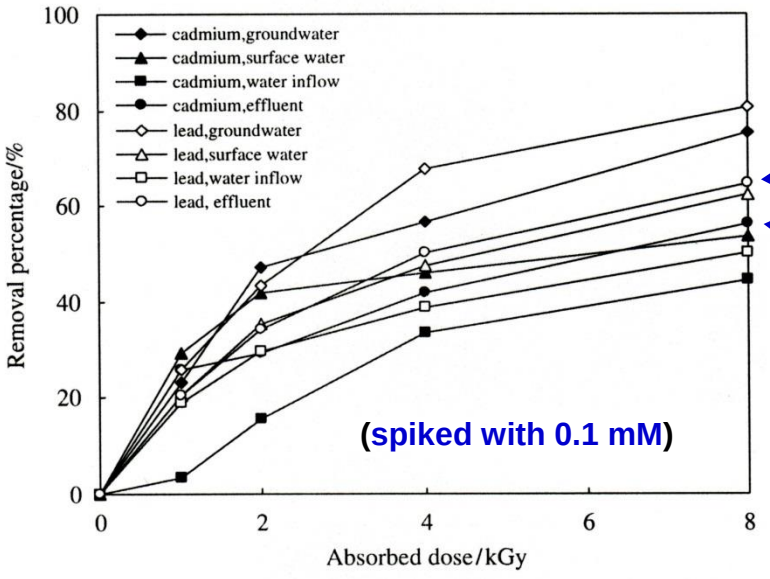
Cost	EB Electron beam irrad. 370 Gy ≡ 146 m^3/h	EB + O_3 Ozone-Electron beam irrad. (3 ppm O_3 + 45 Gy) ≡ 1200 m^3/h
Capital requirement (in 1000 US $ units)		
• 25 kW electron beam accelerator (incl. auxiliary equipment, transport, installation, building and vault)	1200	1200
• Ozone generator	-	270
• 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

Removal of selected metals from industrial effluents using EB treatment

Removed element	Initial concentration ,g/L	Removal at given absorbed dose, %		
		20 kGy	100 kGy	500 kGy
Al	11	63.6	97.8	97.8
Cr	2	97.3	99.6	99.6
Fe	21	96.2	99.9	99.9
Zn	2	99.95	99.95	99.5
Co	0.42	96.2	96.2	99.8

Ribeiro et al.,
Radiat. Phys. Chem. 71 (2004) 423



Guo et al., Radiat. Phys. Chem., 77 (2008) 1021

γ-Radiolytic removal of Cd and Pb from waters and wastes (~ 60% at 8 kGy)

Pb in effluent

Cd in effluent

Gamma irradiation-induced removal of Cd^{2+} and Pb^{2+} by reducing species under different conditions followed pseudo-first-order kinetic model.

Cd^{2+} and Pb^{2+} removal was facilitated in low solution pH, low dissolved oxygen concentration and the presence of sodium carbonate, while inhibited by adding EDTA to solution.

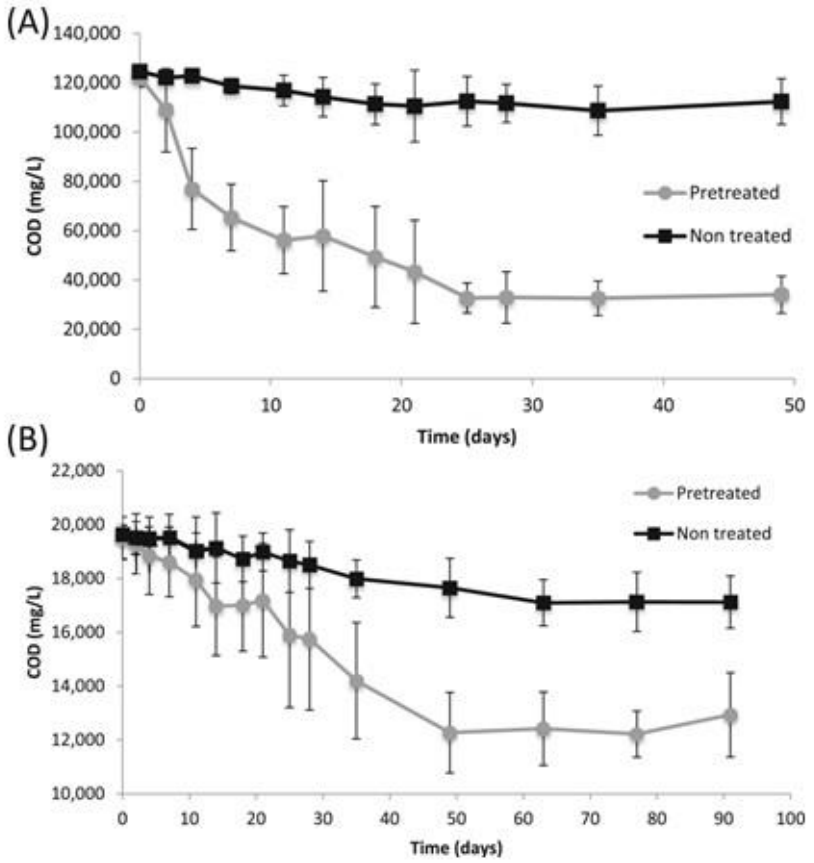
Hybrid - Biological, EB and Nano Fe(0) Treatment of Recalcitrant Metalworking Fluids

They are chemically complex yet defined and consist of base mineral oils, emulsifiers and surfactants, corrosion inhibitors, extreme pressure agents, friction reducing agents, foam inhibitors and biocides, making subsequent treatment challenging.

Effect of electron beam pre-irradiation of toxic recalcitrant industrial wastewater (metalworking fluids) on COD removal

Concentrated fresh fluids

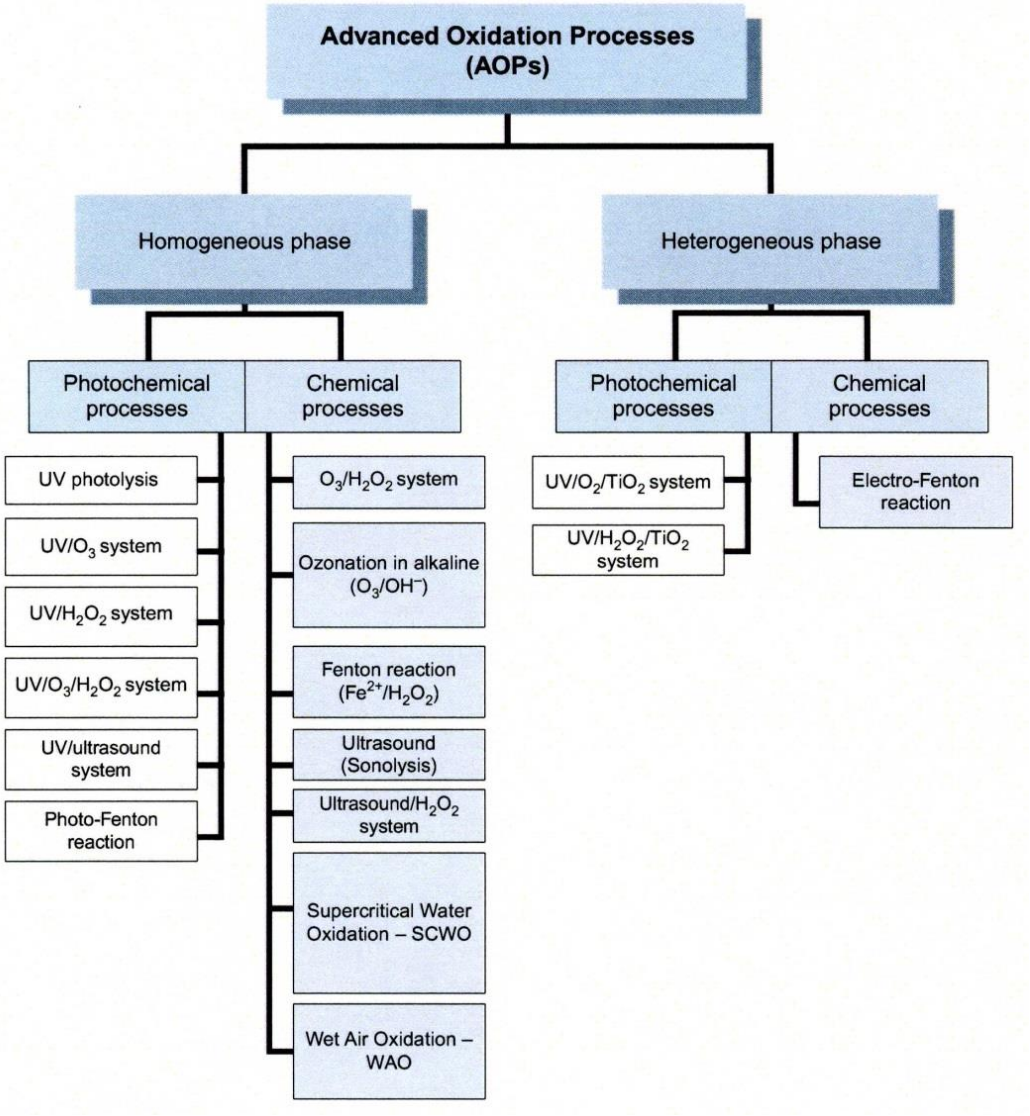
Exhausted metalworking fluids



Thill et al., University of Oxford, Water Res. 93 (2016) 214

Advanced Oxidation Processes

Chemical degradation via oxidative radical (*e.g.* •OH) generation

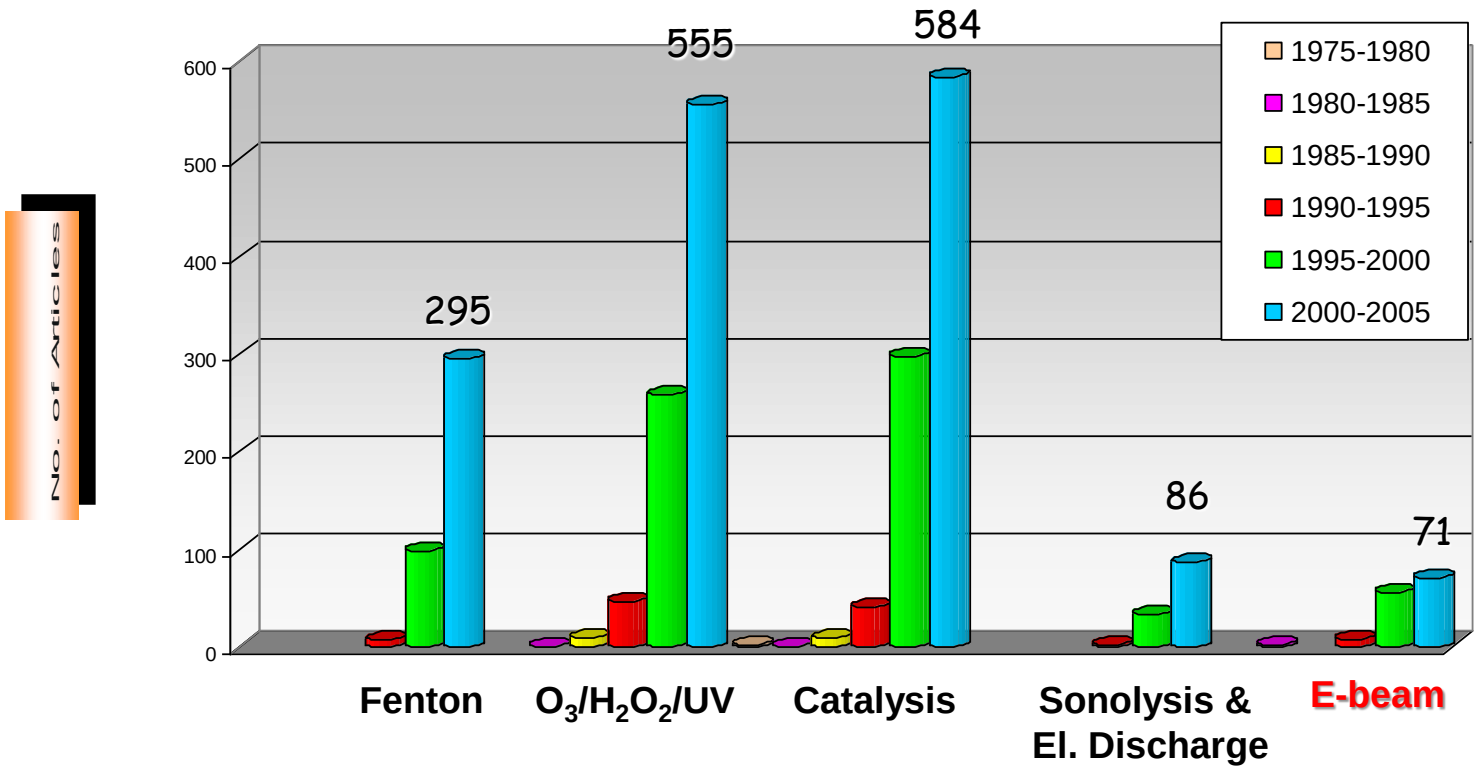


Bin, Sobera-Madej, Ozone Sc. Eng., 34 (2012) 136

AOPs Articles by Methods
(up to 2005)

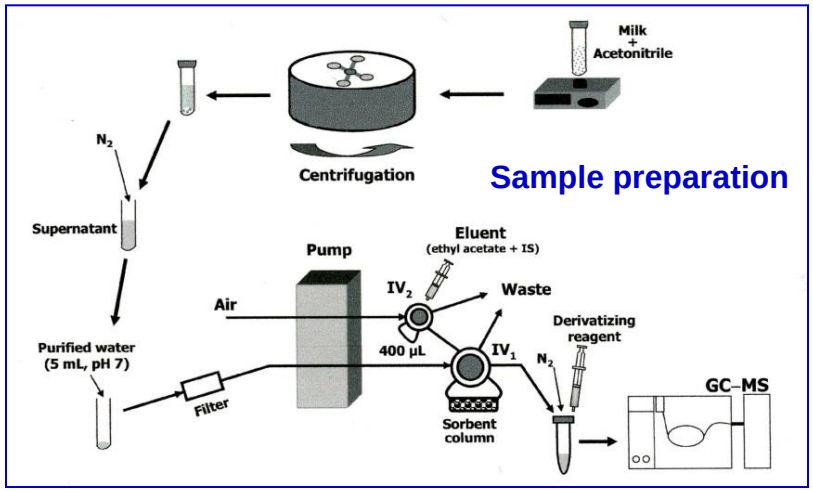
Total number of articles
4 153

AOP	1975-1980	1980-1985	1985-1990	1990-1995	1995-2000	2000-2005
Fenton				7	98	295
$O_3/H_2O_2/UV$		1	9	47	258	555
Catalysis	2	1	9	40	298	584
Sonolysis & El. Discharge				2	33	86
E-beam		2		8	56	71



Emmi, IAEA RCM , Vienna, 2006

GS/MS of Pharmaceuticals in Milk Samples



Determined pharmaceuticals

milk sample	pharmacologically active substance	concentration found (μg/kg)
human breast 1	triclosan	0.16 ± 0.01
	17α-ethinylestradiol	0.035 ± 0.002
human breast 2	ibuprofen	0.37 ± 0.02
	triclosan	0.25 ± 0.02
	estrone	0.055 ± 0.004
	17β-estradiol	0.54 ± 0.03
	17α-ethinylestradiol	0.045 ± 0.003
human breast 3	naproxen	1.9 ± 0.1
	estrone	0.17 ± 0.01
	17β-estradiol	0.49 ± 0.03
goat (whole)	none	
goat (half-skim)	niflumic acid	0.085 ± 0.005
	flunixin	0.095 ± 0.006
powdered 1–2	none	

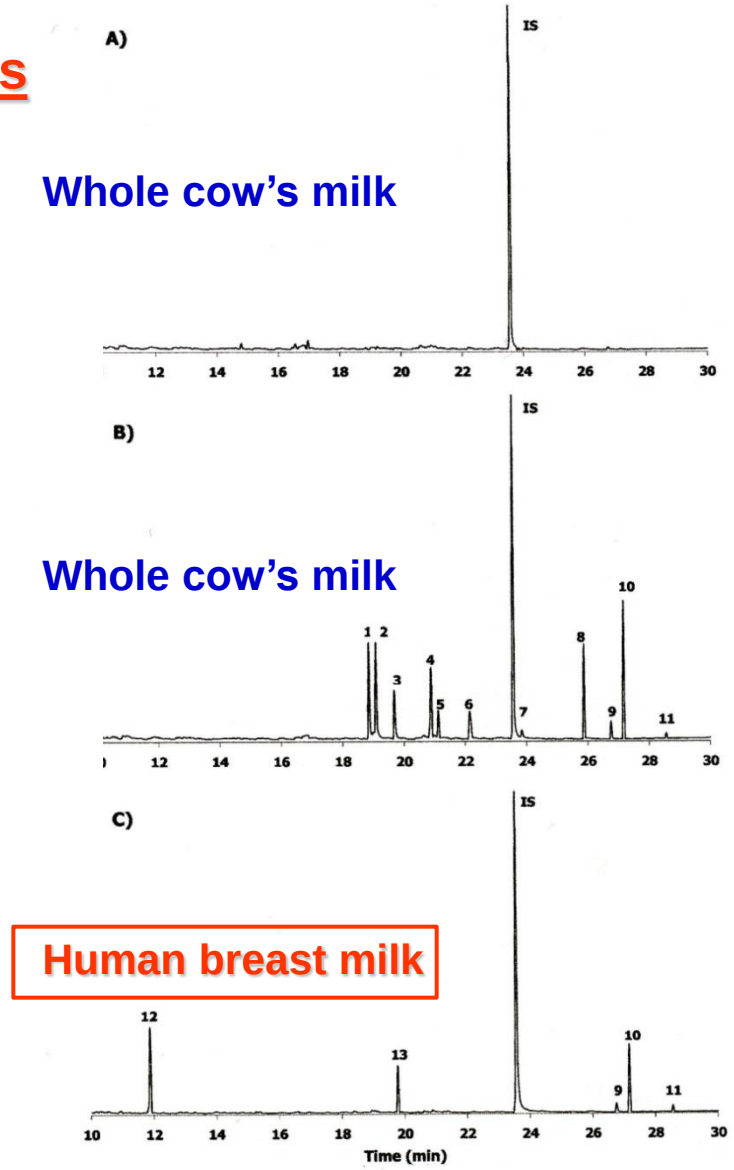


Figure 2. GC-MS chromatograms in the SIM mode for whole cow's milk samples 1 (A) and 3 (B) and human breast milk sample 2 (C) (see Tables 4 and 5). Peaks: (1) niflumic acid; (2) naproxen; (3) flunixin; (4) ketoprofen; (5) pyrimethamine; (6) diclofenac; (7) phenylbutazone; (8) florfenicol; (9) estrone; (10) 17β-estradiol; (11) 17α-ethinylestradiol; (12) ibuprofen; (13) triclosan; (IS) internal standard.

Azzouz et al., J.Agric.Food Chem., 59 (2011) 5125

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