

Advanced Oxidation Processes for the Removal of Emerging Contaminants in Wastewater

Prof Chedly Tizaoui, FIChemE

Water and Resources Recovery Research (WR3) Lab

Department of Chemical Engineering

Faculty of Science and Engineering

Swansea University

E-mail: c.tizaoui@swansea.ac.uk



Platfform yr
Amgylchedd Cymru

Environment
Platform Wales

**Better Water Quality for Wales
Conference**



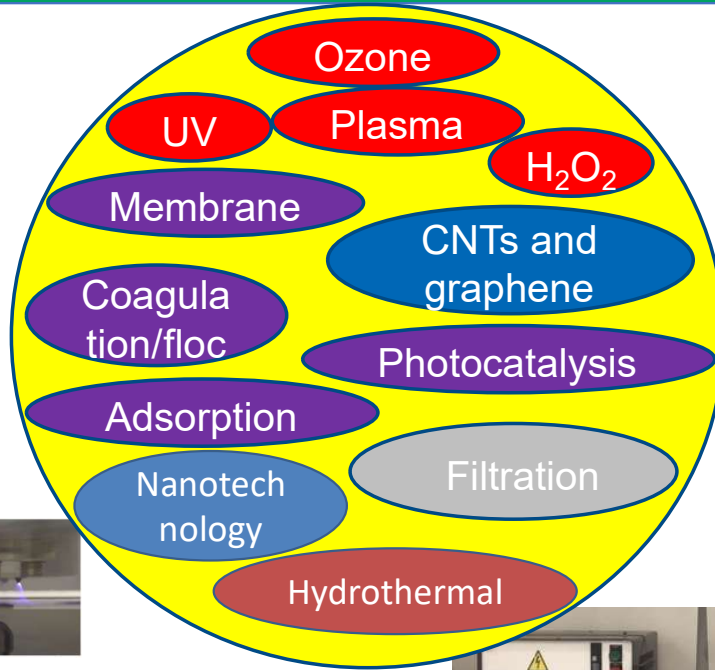
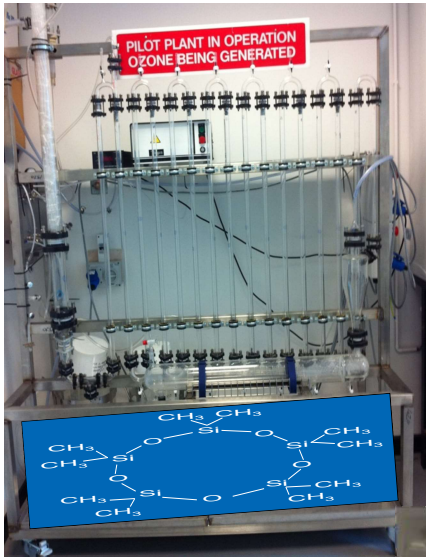
27 - 29 June 2023

Fundamental

WR3 Lab Research Interests

Applied

Novel water treatment techs; oxidation, chemical engineering, separation procs.; mass trans.; reaction kinetics



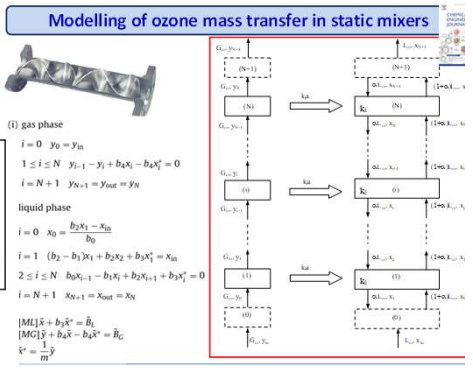
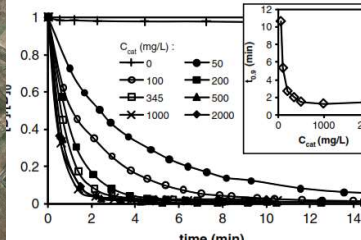
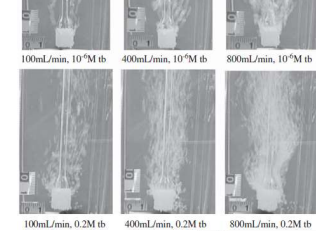
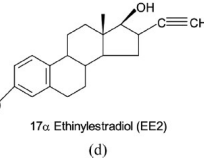
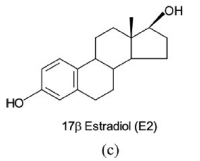
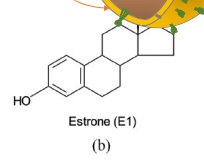
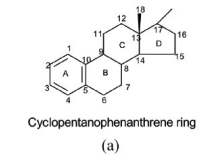
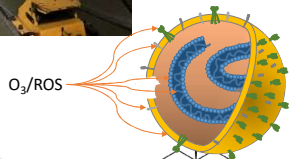
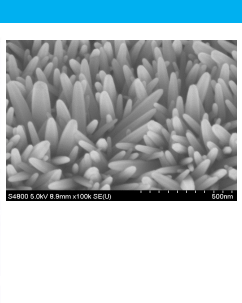
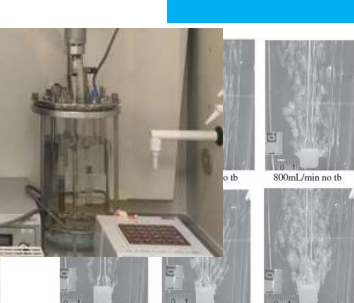
Clean water production

Water reuse

Protection of the environment

Resource recovery

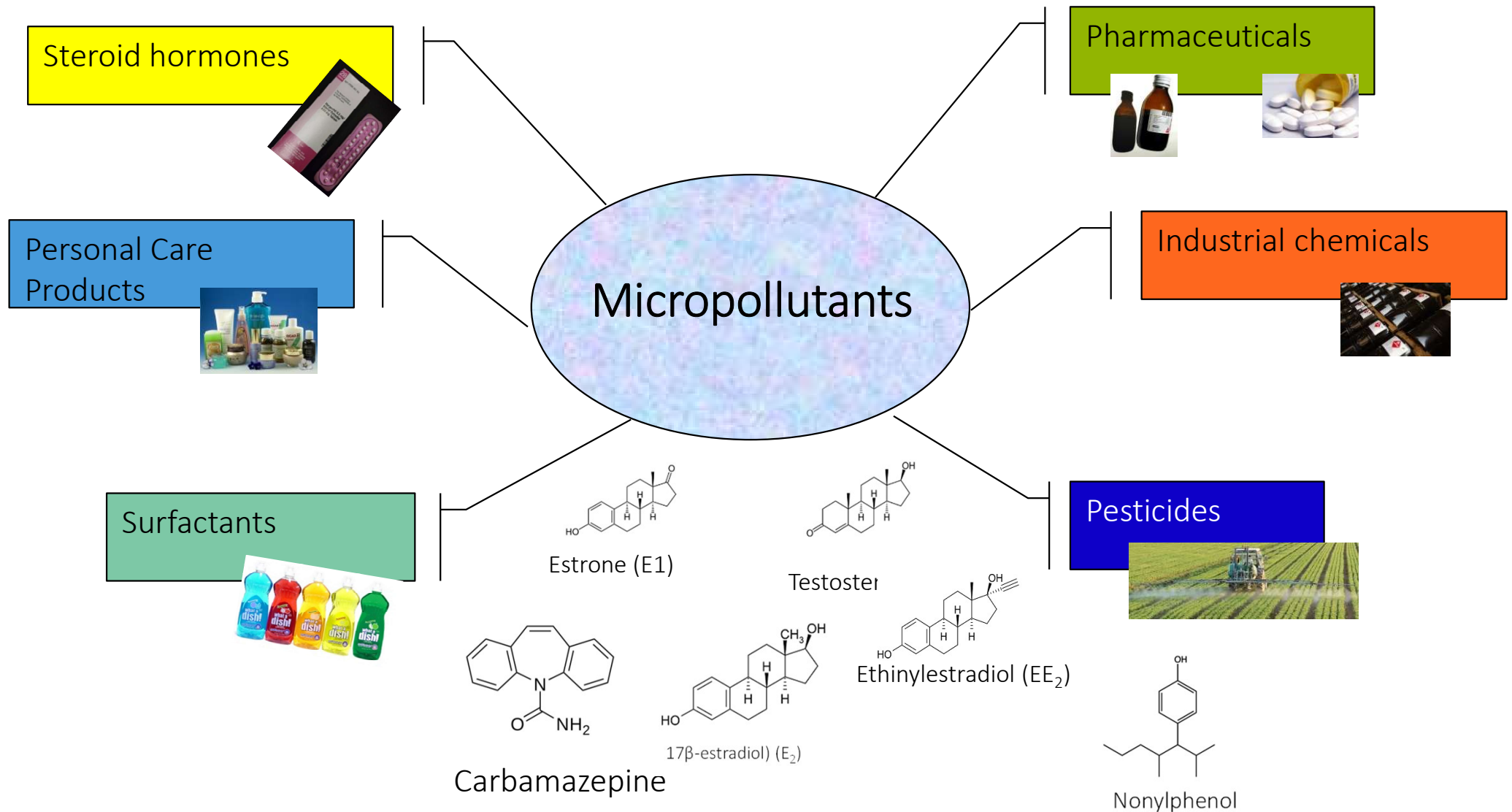
Circular Economy



Content

- Introduction (MPs and AOPs)
- Research Results on MPs removal
- Conclusions

Micropollutants (MPs)/Trace Organic compounds (TOrcs)/Emerging Contaminants (ECs)/Endocrine Disrupting Chemicals (EDCs)



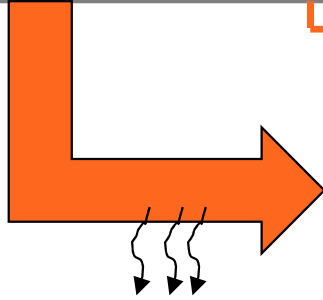
Effects: Disruption of the endocrine system, feminisation of male fish via exposure to hormones (e.g. E1, E2, EE2); learning disabilities, cancers, genital abnormalities in newborn males; Bacterial resistance caused by exposure of bacteria to antibiotics. Antimicrobial resistance → antibiotics fail to treat a number of infections.



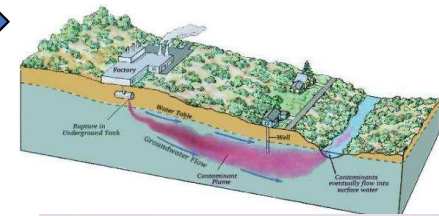
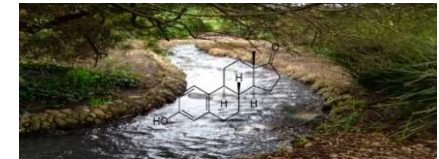
Micropollutants in the environment



- Biodegrade (e.g. aspirin)
- Partial biodegradation (e.g. penicillins)
- Persist (e.g. clofibrate, triclosan, triclocarban)

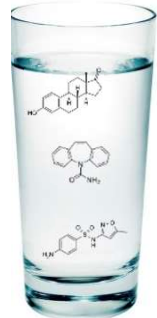


Conventional WWTPs are not designed to eliminate micropollutants.

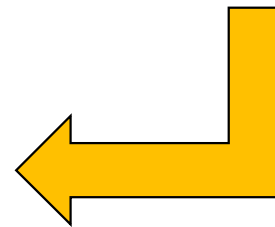


Threats to wildlife and aquatic system

>1µg/L



Problems for drinking water industry

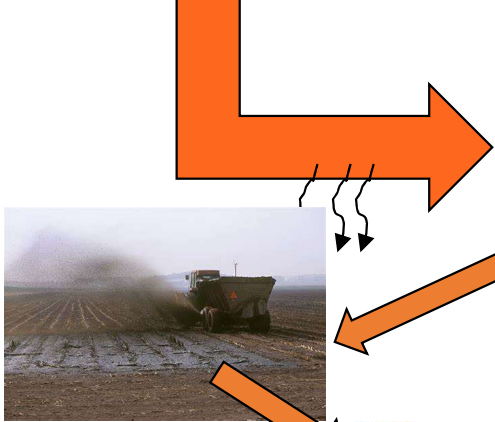




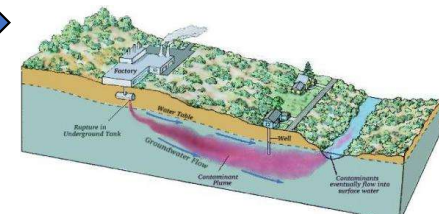
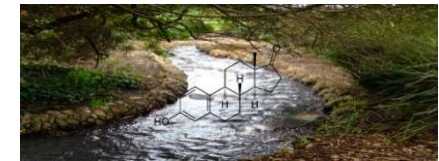
Micropollutants in our food



- Biodegrade (e.g. aspirin)
- Partial biodegradation (e.g. penicillins)
- Persist (e.g. clofibrate, triclosan, triclocarban)



Conventional WWTPs are not designed to eliminate micropollutants.



Threats to wildlife and aquatic system

Further treatment?



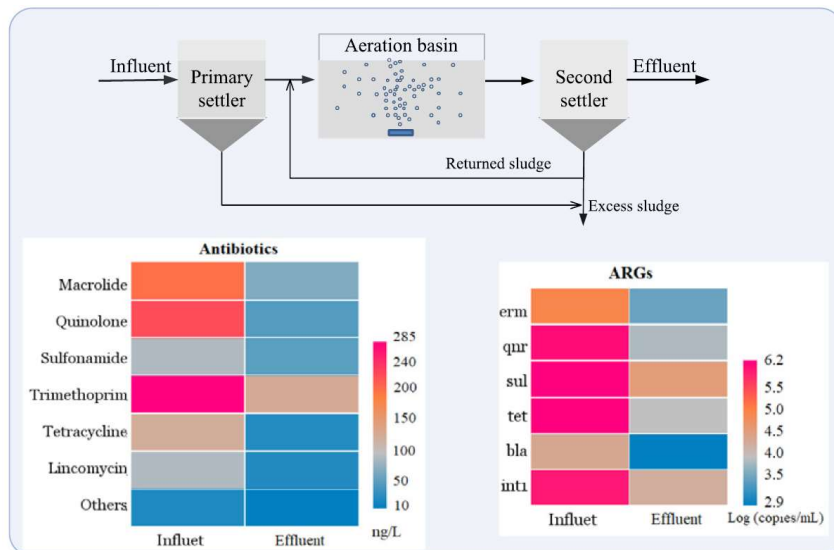
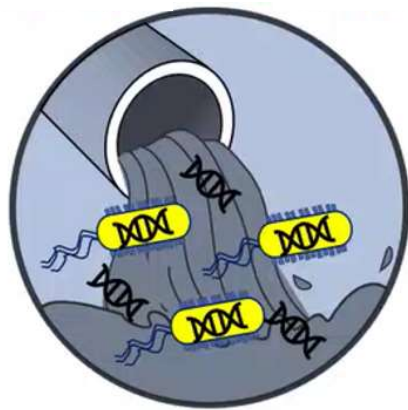
Human exposure to MPs via fruit and vegetable ~ 9.8 µg/P.week



- ☞ accumulation in food products threatening human health through the food chain
- ☞ MPs can also induce changes in plant hormone level, thus impacting plant health

Micropollutants in the environment

👉 **Wastewater treatment plants** are the main **hotspots** for the release of micropollutants and dissemination of determinants of antibiotic resistance in the environment.



Wang et al., 2020, *Science of the Total Environment*
<https://doi.org/10.1016/j.scitotenv.2020.140997>

Levin et al. **1951**. "Estrogenic, androgenic and gonadotrophic activity in wheat germ oil", *Endocrinology* 49(3): 289-301

Fisher et al. **1952**. "Estrogenic action of some DDT analogues", *Proc. Soc. Exptl. Biol. Med.* 81(2): 439-441

Tabak, H.H., and R.L. Bunch. **1970**. *steroid hormones as water pollutants*. *Developments in Industrial Microbiology*

J. Pharm. Pharmacol. **1985**, 37: 1-12

© 1985 J

SETAC PRESS

Environ. Sci. Technol. **1998**, 32, 2498-2506

REVIEW

The fate of pharmaceutical chemicals in the environment

MERVYN L. RICHARDSON AND JUDITH M. BOWRON

Thames Water Authority, New River Head, Rosebery Avenue, London EC1R 4TP

Increased demands for potable water, especially where supplies are drawn from rivers has necessitated a greater degree of water re-use. As water undertakings have to maintain the wholesome quality of potable water supplies, increasing concern is expressed over the presence of organic micro-contaminants (contaminants at $\mu\text{g litre}^{-1}$ concentrations). This study outlines some of the problems encountered assessing the risk from pharmaceutical chemicals which might enter the water from domestic and industrial sources. Analytical chemistry was of value for only a few compounds studied. However, much useful information was derived from tracing metabolic routes of the drugs and is collated in Appendix I. Biodegradation and other ecotoxicity/environmental toxicology data may be required to a greater extent in the future. Particular consideration is given to vulnerable sections of the population

ESTROGENIC ACTIVITY IN FIVE MEASUREMENT OF VITEI

JULE E. HARRIES,‡ DAVID A. SHEAHAN,† ; JOHN P. SUMPTER,‡ I

†Ministry of Agriculture, Fisheries, and Food, Remembrance Avenue, Wallingford, Oxon OX10 8BD, U.K.
‡Department of Biology and Biochemistry, Brunel University, Uxbridge, Middlesex UB8 3PH, U.K.

(Received 14 March 1998)

Abstract—It was recently demonstrated that most, if not all, effluents from sewage treatment works (STWs) are estrogenic to fish. To assess this, the estrogenic activity of effluents from five STWs at various distances downstream of the effluent entry into five rivers in England were studied. In four cases, very marked and rapid increases in their plasma vitellogenin levels of these four cases, none of the downstream sites were found to respond by synthesizing appreciable amounts of vitellogenin in the fourth river was quite different; not only did the concentration of vitellogenin in the plasma of fish did not respond by synthesizing appreciable amounts of vitellogenin in the fourth river was quite different; not only did the concentration of vitellogenin in the plasma of fish where the effluent entered. This particular river received concentrations of alkylphenolic chemicals than any of the other four rivers. This discharge comes from a very small STW, which may account for the estrogenic activity of this river. The fish which were studied were *Oncorhynchus mykiss* (rainbow trout). This discharge comes from a very small STW, which may account for the estrogenic activity of this river. The fish which were studied were *Oncorhynchus mykiss* (rainbow trout).

Keywords—Estrogen Sewage *Oncorhynchus*

Widespread Sexual Disruption in Wild Fish Cited>2500

SUSAN JOBLING,*† MONIQUE NOLAN,‡ CHARLES R. TYLER,† GEOFF BRIGHTY,§ AND JOHN P. SUMPTER†

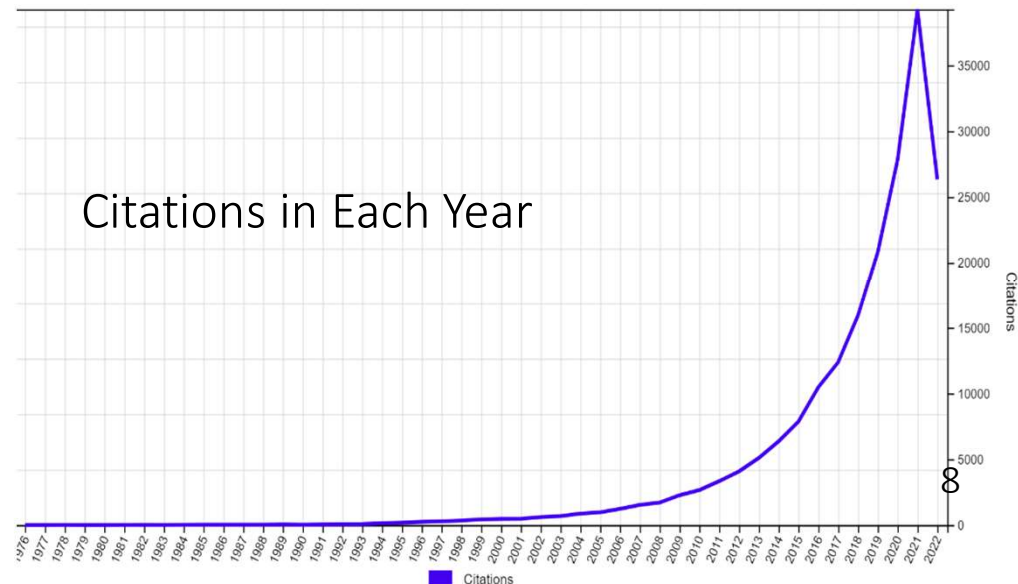
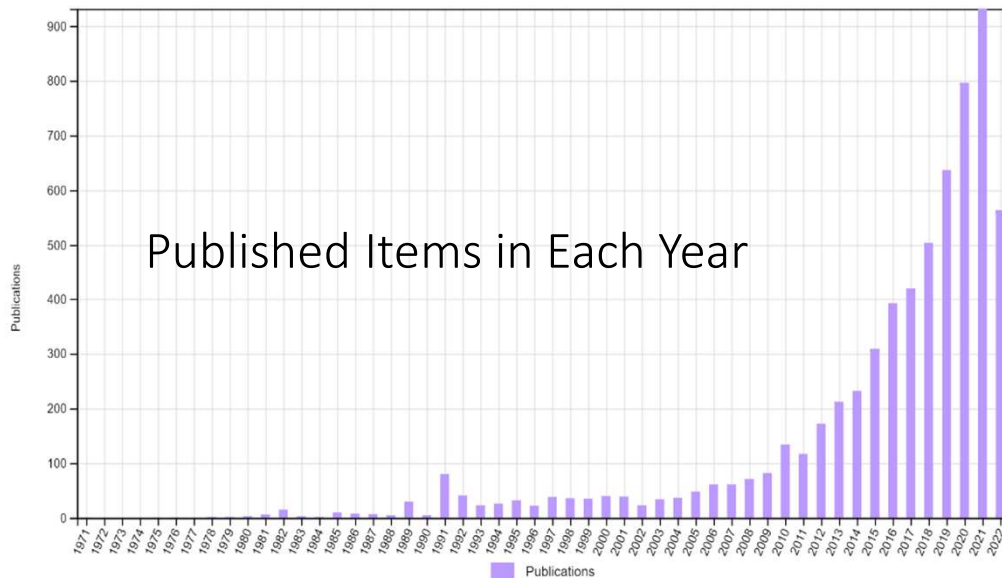
*The Fish Physiology Research Group, Department of Biology and Biochemistry, Brunel University, Uxbridge, Middlesex UB8 3PH, U.K., Environment Agency, National Fisheries Laboratory, Bromholme Lane, Brampton, Cambs PE18 8NE, U.K., and Environment Agency, National Centre for Ecotoxicology and Hazardous Substances, Hawberry Park, Wallingford, Oxon OX10 8BD, U.K.

A number of chemicals present in the environment have been shown to mimic or antagonize the actions of steroid hormones, an issue often described as "endocrine disruption/modulation". There is very little evidence, however, to support the hypothesis that exposure to endocrine-disrupting chemicals is a global environmental health problem. In this paper, we demonstrate a high incidence of intersexuality in wild populations of riverine

fish, but geographically limited, probably due to the fact that most of the chemicals that many orders of magnitude less potent counterparts, and it therefore seems likely that exposure will cause significant health effects. The critical issue is whether sufficient exposure to endocrine-modulating substances in the environment to exert adverse reproductive effects on humans. It is primarily this question that is the basis of the international conference on the environmental impact of endocrine-disrupting chemicals. While this debate has been the subject of many meetings and has received much support, the hypothesis that endocrine-disrupting chemicals are a significant human and environmental health problem is lacking (for a recent review of this conclusion seems to be due to a lack of studies on this subject and not to a lack of support for the converse hypothesis.

Rivers and estuaries throughout the world.

Micropollutants & water or wastewater



Water Policy

- New regulations will aim at controlling the discharge of ECs into the environment (e.g. *EU Watch list of Priority Substances Directive 2013/39/EU*)
- **Switzerland** is the first country that enforced control of ECs at the point source scale
- Ozone and activated carbon are the processes of choice in Switzerland¹
- Ozone was also found the cheapest option in a study of the National Demonstration Programme (UK)²

¹Audenaert, W. T. M., Chys, M., Auvinen, H., Dumoulin, A., Rousseau, D. and Hulle, S. W. H. V. (2014) (Future) Regulation of Trace Organic Compounds in WWTP Effluents as a Driver of Advanced Wastewater Treatment. *Ozone News: The Newsletter of the International Ozone Association*, 42, 17-23.

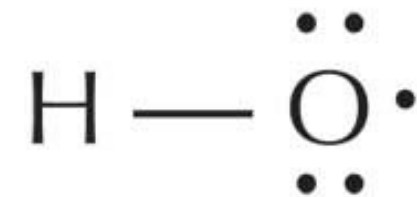
²Churchley, J., Drage, B., Cope, E., Narroway, Y., Ried, A., Swierk, T., Alexander, K. and Kanda, R. (2011) Performance of ozone for EDC removal from sewage effluent. *20th IOA World Congress - 6th IUVA World Congress. Ozone and UV Leading-edge science and Technologies*. Paris, France: International Ozone Association.

Advanced Oxidation for MPs Removal

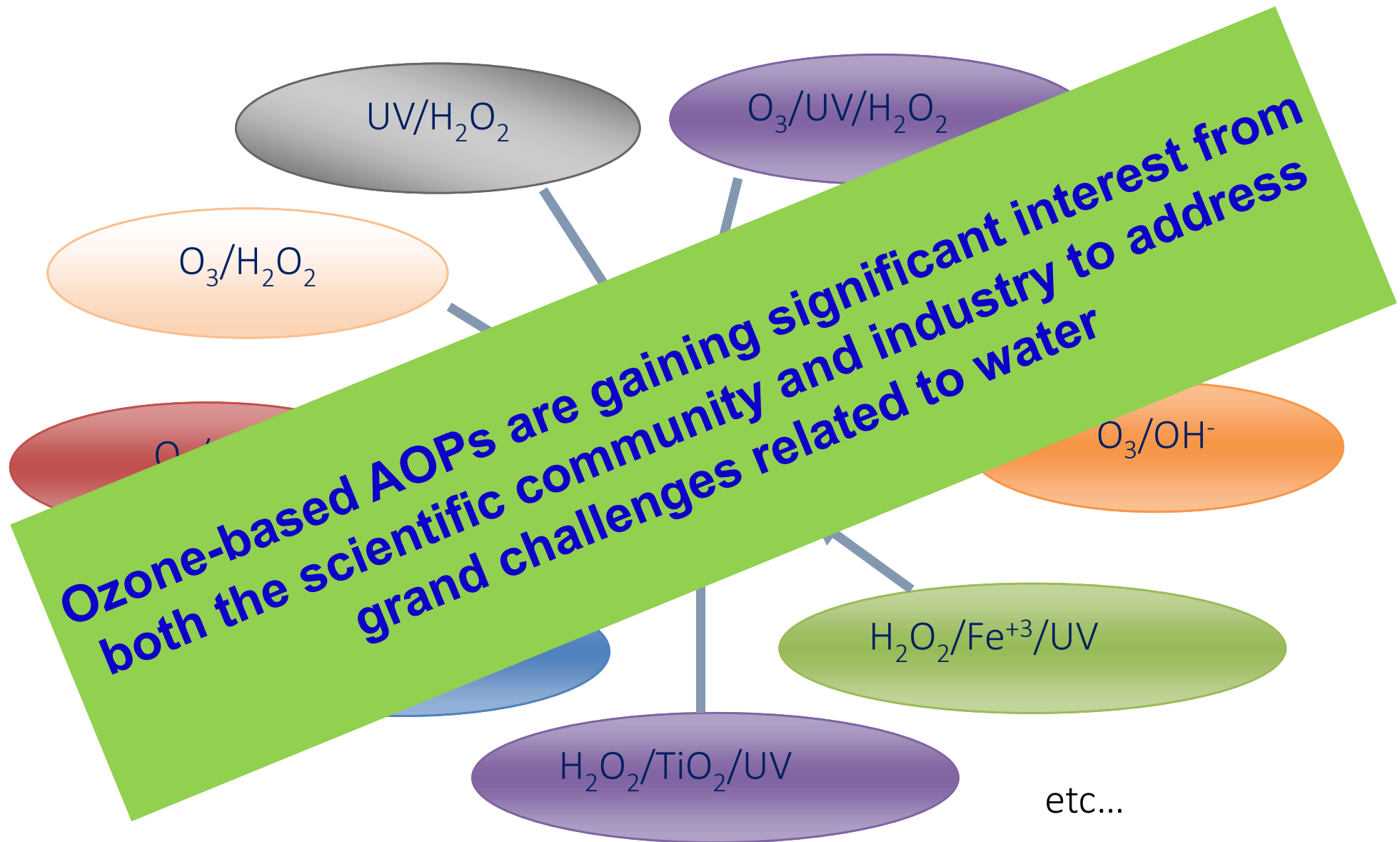
Advanced oxidation processes are processes which involve the generation of highly reactive radical intermediates, especially hydroxyl radicals $\bullet\text{OH}$, in sufficient quantity to effect water purification.

Glaze et al. (1987). "The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation." Ozone Science & Engineering **9**: 335-352.

- ☞ $\bullet\text{OH}$ is the neutral form of the hydroxide ion (HO^-)
- ☞ $\bullet\text{OH}$ can oxidise almost all organic matter
- ☞ They are short-lived (~few ns)



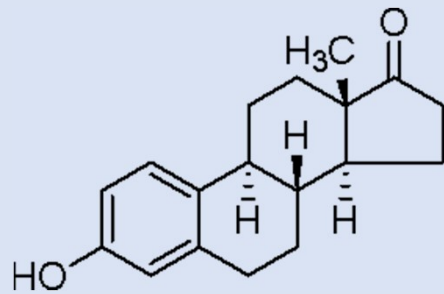
Examples of AOPs



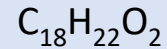
Research Results on MPs removal

Removal of E1, E2, and EE2 using the Liquid/Liquid-Ozone system

Estrogens of interest

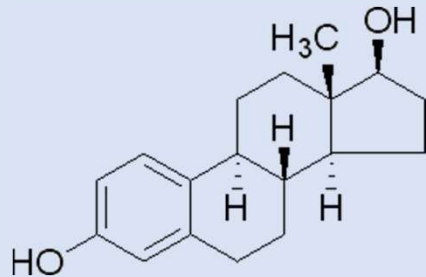


Estrone (E1)

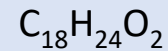


M=270.366 g/mol

- Secreted by the ovary
- Product resulting from oxidation of E2

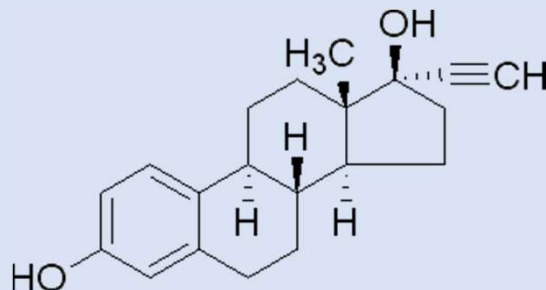


17β-estradiol (E2)

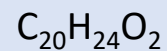


M=272.39 g/mol

- Produced by all mammals
- Binds easily with human receptor



17α-ethinylestradiol (EE2)

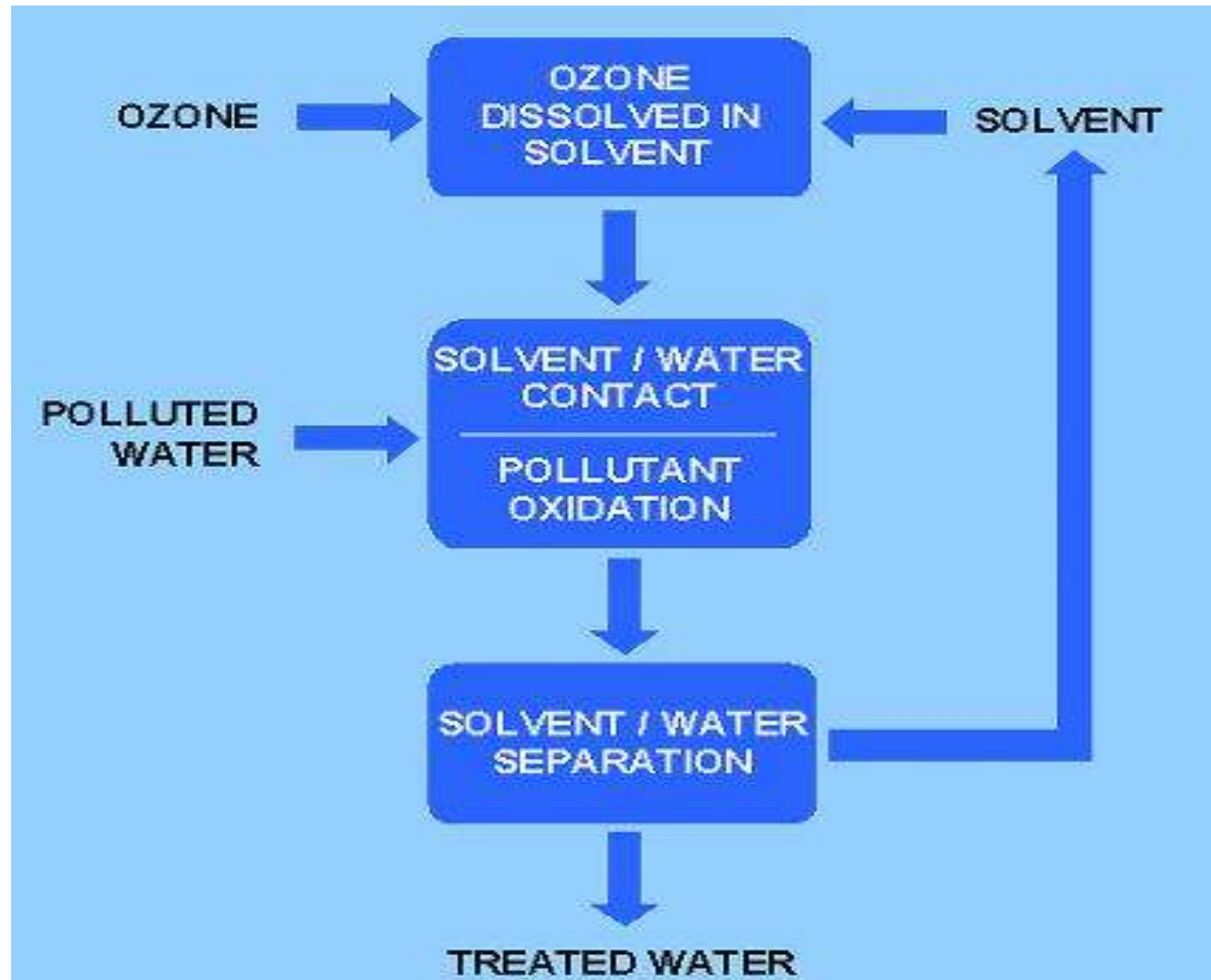


M=296.403 g/mol

- Synthetic
- Main ingredient of contraceptive pills

Removal of E1, E2, and EE2 using the Liquid/Liquid-Ozone system

The Process



Removal of E1, E2, and EE2 using the Liquid/Liquid-Ozone system



Sampling point

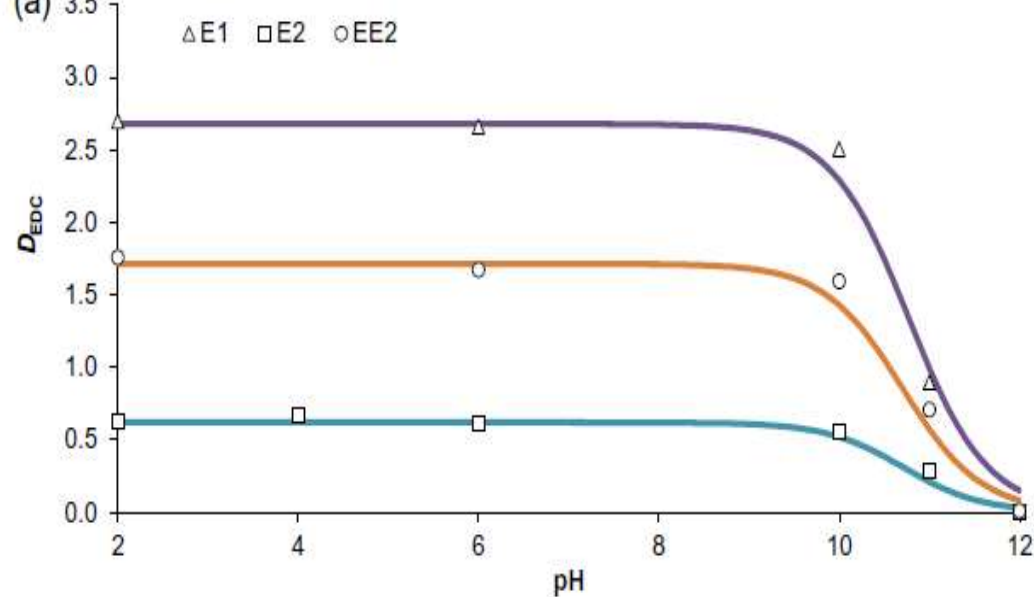
☞ Sample preservation (15 mL of a solution containing hydrochloric acid (30%) and copper nitrate (0.25 g/L) added to 5L sample).

Marley STW, Yorkshire, UK

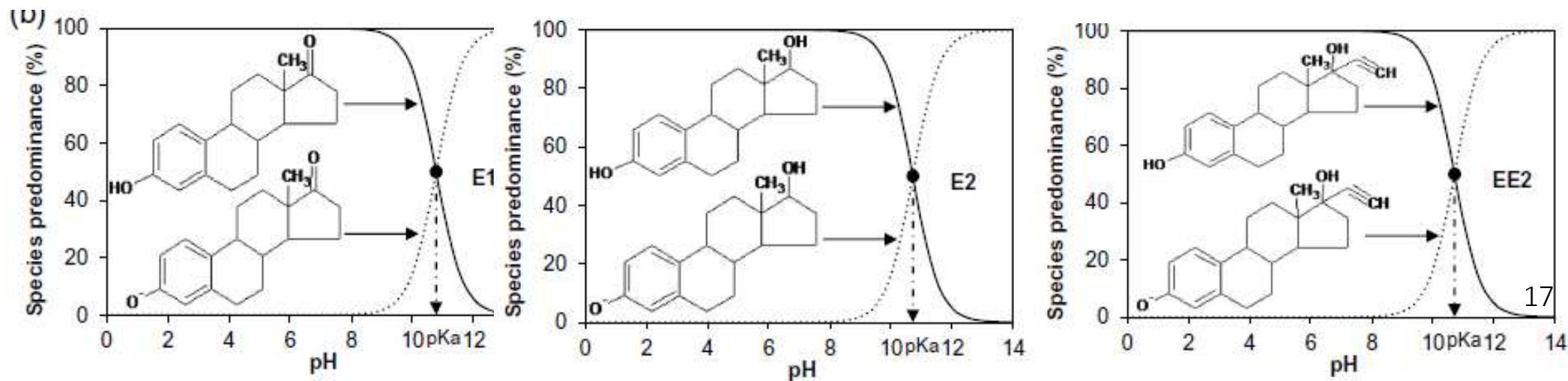
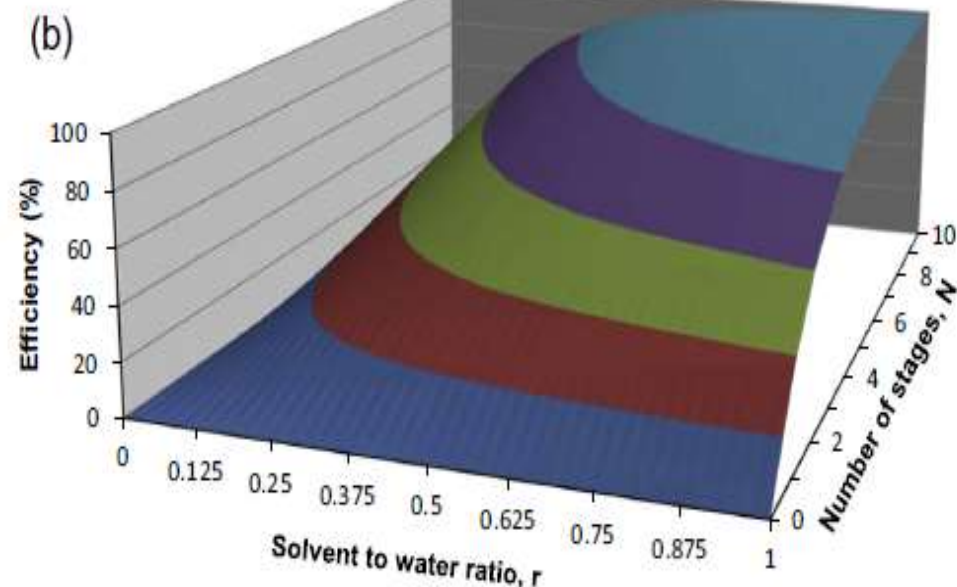
Removal of E1, E2, and EE2 using the Liquid/Liquid-Ozone system

Extraction of EDCs to the solvent

(a) Distribution coefficients

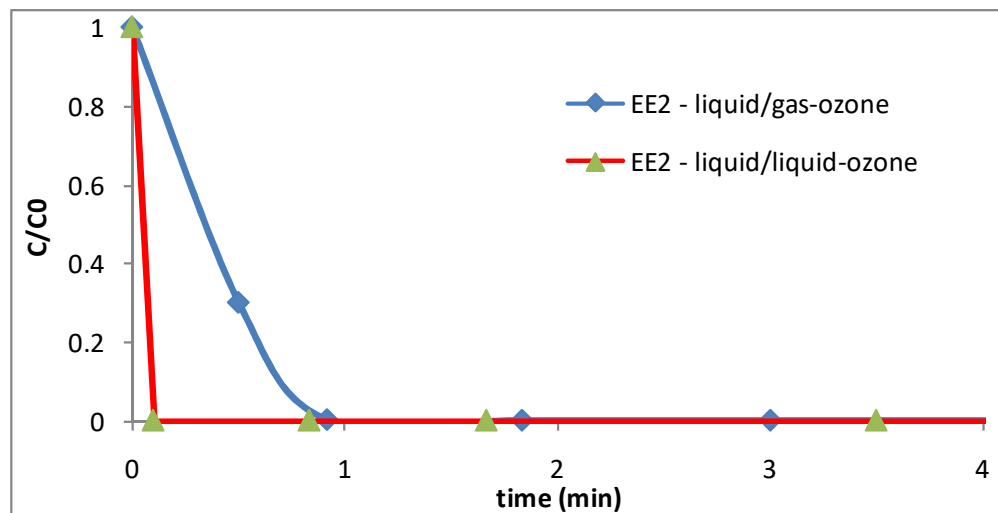
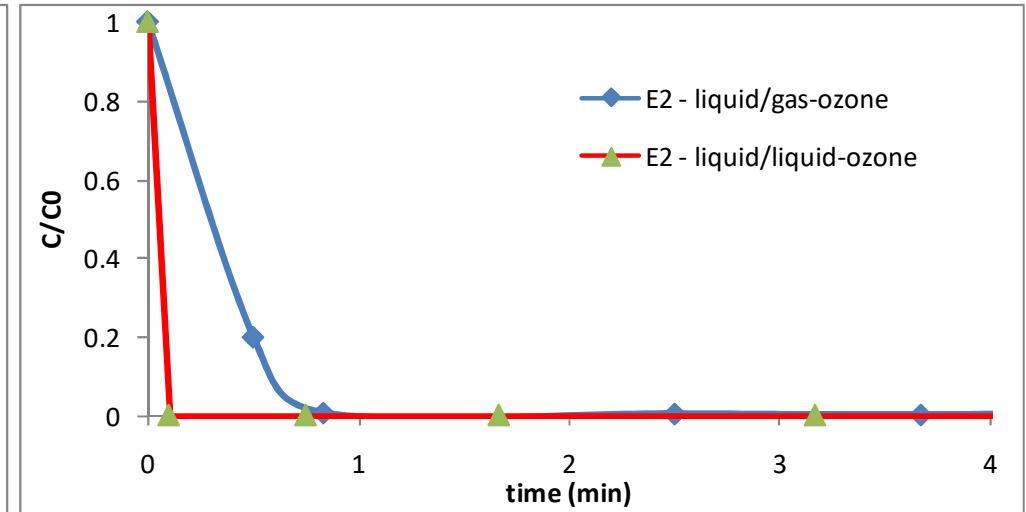
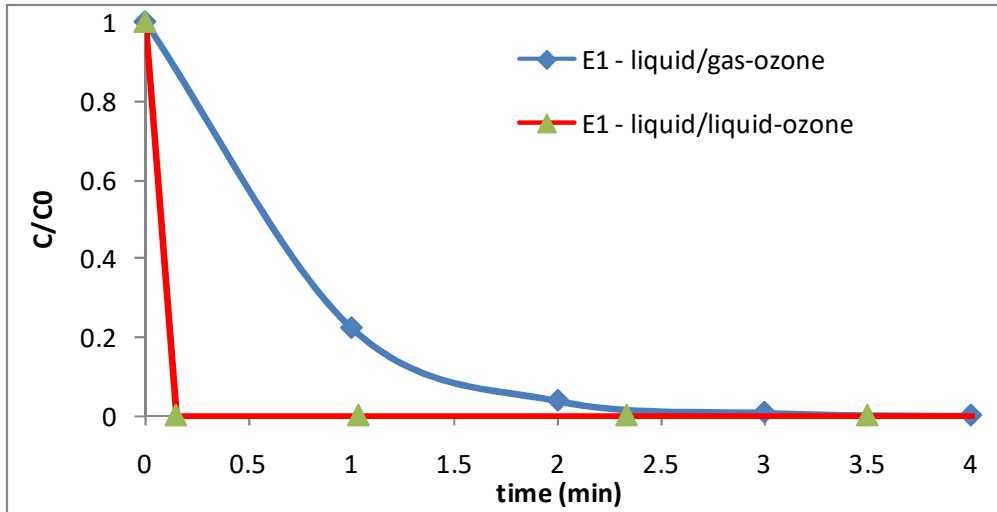


E2 removal



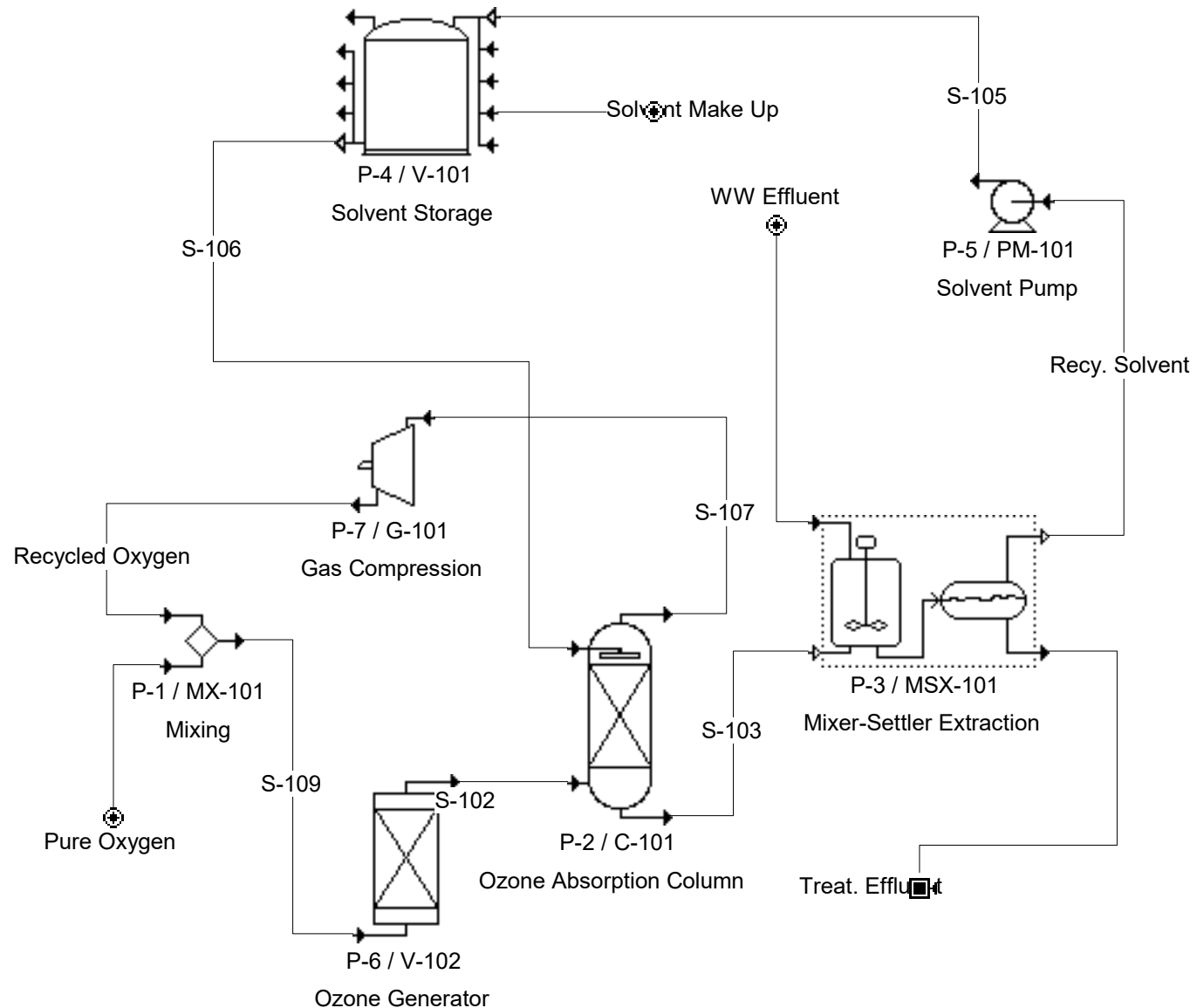
Removal of E1, E2, and EE2 using the Liquid/Liquid-Ozone system

Rates: LLO vs LGO



Removal of E1, E2, and EE2 using the Liquid/Liquid-Ozone system

Process calculation and estimation of basic operational costs (Super Pro Designer™)



Removal of E1, E2, and EE2 using the Liquid/Liquid-Ozone system

PROCESS CALCULATION AND ESTIMATION OF BASIC OPERATIONAL COSTS

Input

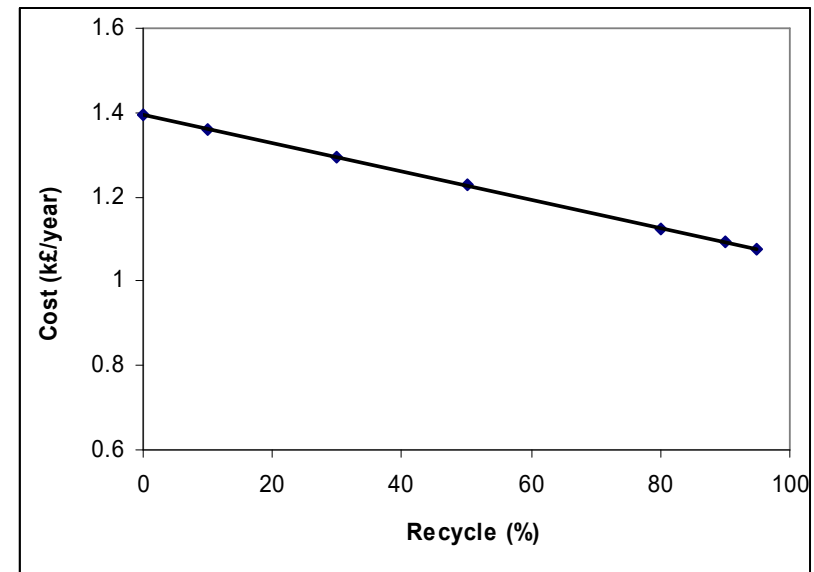
Parameter	Value
Effluent flow rate (L/s) (highest at Marley)	400
Effluent flow rate (MLD)	34.6
E1 (ng/L)	100
E2 (ng/L)	100
EE2 (ng/L)	100
Ozone gas concentration (g/m ³) NTP	100
Solvent ozone transfer efficiency (%)	95
Ozone transfer efficiency to water (%)	90
Ozone dose (mg/L)	1
Percentage solvent/water (%)	1
Solvent+ozone/water contact time (min)	1
Ozone production specific energy consumption (kWh/kg)	10
Cost unit power (£/kg)	0.1
Cost unit oxygen (£/kg)	0.1
Cost unit solvent (£/L)	7
Solvent replacement frequency/year	0.5
Contingency solvent volume ratio	0.2



Output

Parameter	Value	Value
Oxygen recycle (%) (var)	0	80
Volume of LLO contactor (m ³)	24.2	24.2
Total cost (£/ML)	0.111	0.089

(NDP (O₃ only) → cost of ~£4/ML



Removal of E1, E2, and EE2 using the Liquid/Liquid-Ozone system

Chemical Engineering Journal 262 (2015) 417–426



Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Chemical
Engineering
Journal

Removal of estrone (E1), 17 β -estradiol (E2), and 17 α -ethinylestradiol (EE2) from wastewater by liquid–liquid extraction



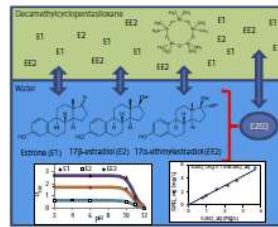
S. Ben Fredj^a, J. Nobbs^b, C. Tizaoui^{b,*}, L. Monser^a

^aAnalytical and Electrochemical Laboratory, National Institute of Applied Sciences and Technology, University of Carthage, Centre Urbain Nord, Charguâa, Tunisia
^bCentre for Water Advanced Technologies and Environmental Research, College of Engineering, Swansea University, SA2 8PP, UK

HIGHLIGHTS

- Huge concerns about occurrence of endocrine disrupting chemicals (EDCs) in water.
- EDCs have tendency to distribute to organic solvents.
- Decamethylcyclopentasiloxane was effective to extract E1, E2 and EE2.
- The distribution coefficients were not affected by pH up to pH 9.5.
- Liquid–liquid extraction was effective to remove estrogenic potency from water.

GRAPHICAL ABSTRACT



Ben Fredj, S., J. Nobbs, C. Tizaoui, and L. Monser. 2015. "Removal of estrone (E1), 17 β -estradiol (E2), and 17 α -ethinylestradiol (EE2) from wastewater by liquid–liquid extraction", *Chemical Engineering Journal* 262 pp:417-426.

Ozone: Science & Engineering, 36: 110–120
Copyright © 2014 International Ozone Association
ISSN: 0191-9512 print / 1547-6545 online
DOI: 10.1080/01919512.2013.836956



A Modified Indigo Method for the Determination of Ozone in Nonaqueous Solvents

J. Nobbs and C. Tizaoui

Centre for Water Advanced Technologies and Environmental Research (CWATER), College of Engineering, Swansea University, Swansea, SA2 8PP, United Kingdom

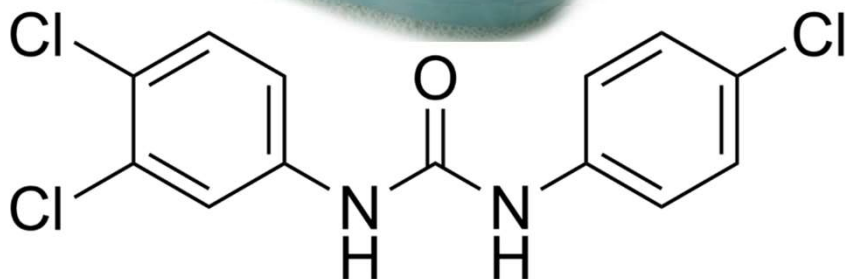
The indigo method for the analysis of aqueous ozone was modified to allow analysis of dissolved ozone in nonaqueous liquid phases. The method was tested using the solvent decamethylcyclopentasiloxane (DMS) and a vegetable oil. The

hurdles which must be overcome if the use of ozone in water treatment is going to continue to grow (Gottschalk et al. 2010). Traditionally, it has been difficult to expose contaminants of

Nobbs, J., and C. Tizaoui. 2014. "A Modified Indigo Method for the Determination of Ozone in Nonaqueous Solvents", *Ozone: Science & Engineering* 36(1): 110-120

Removal of the antimicrobial triclocarban with ozone

- Triclocarban is an antimicrobial chemical
- Used in soaps, lotions
- but, it was found:
 - Endocrine disruptor
 - Antibacterial resistance



0013-7227/08/\$15.00/0
Printed in U.S.A.

Endocrinology 149(3):1173-1179
Copyright © 2008 by The Endocrine Society
doi: 10.1210/en.2007-1067

Triclocarban Enhances Testosterone Action: A New Type of Endocrine Disruptor?

Jiangang Chen, Ki Chang Ahn, Nancy A. Gee, Mohamed I. Ahmed, Antoni J. Duleba, Ling Zhao, Shirley J. Gee, Bruce D. Hammock, and Bill L. Lasley

Center for Health and the Environment (J.C., N.A.G., B.L.L.), Department of Entomology (K.C.A., S.J.G., B.D.H.), California National Primate Research Center (N.A.G., B.L.L.), Division of Reproductive Endocrinology and Infertility, University of California, Davis, Medical Center (A.J.D.), Department of Nutrition (L.Z.), Cancer Research Center (B.D.H.), University of California, Davis, California 95616; and Department of Obstetrics and Gynecology (M.I.A., A.J.D.), Yale University School of Medicine, New Haven, Connecticut 06510

Many xenobiotics have been found in a wide range of products usually between receptor signaling systems. 3,4,4'-trichlorocarbonyl urea compounds that are used in personal care products that are found to be disrupting substances. A substantiated bioassay was used to show that urea compounds with no endocrine activity.



The latest science news,
research tidbits
and science discussion

Home | News | Discussion Forum | Books | Curiosity Shop | Features

Discussion Forum



Science Talk
What's on your mind? Discuss scientific conundrums with our motley band of bamboozled boffins in the forum.

News And Research

- [Physics](#)
- [Climate Change](#)
- [Space](#)
- [Natural World](#)
- [Health](#)
- [Technology](#)
- [All 2008 News](#)
- [All Feature Articles](#)

Sponsored Links

Search

27 April 2006

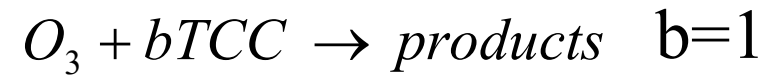
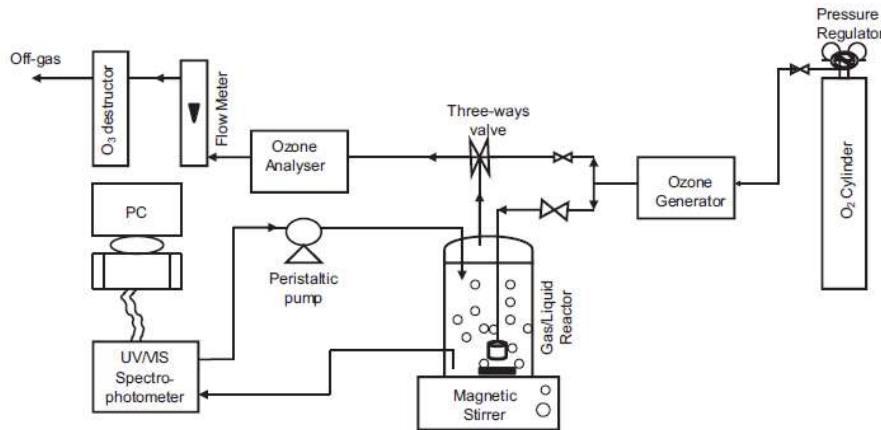
Persistence Of Triclocarban Surprises

Johns Hopkins researchers have been measuring levels of the antibacterial hand soap ingredient, triclocarban, as it passed through water treatment facilities and found that 75 percent of the ingredient washed down household drains persists during wastewater treatment. Worse still, the chemical accumulates in municipal sludge, which is later used as a fertilizer and soil conditioner for crops.

"The observed persistence of triclocarban is remarkable," said researcher Jochen Heidler. "In the [treatment] plant, the chemical contained in sludge underwent biological



Removal of the antimicrobial triclocarban with ozone

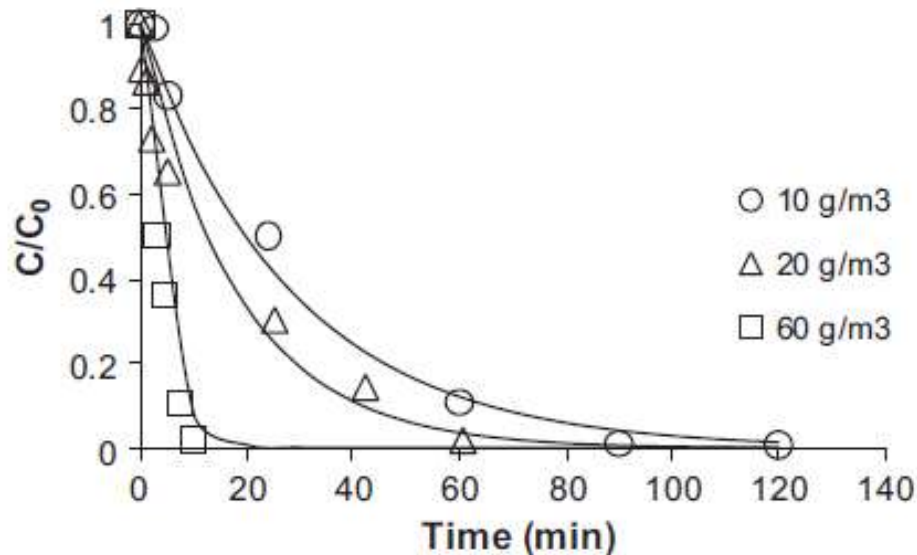


$$r_B = -\frac{1}{b} \frac{dC_B}{dt} = N_{O_3} = aC_{O_3}^* \sqrt{D_{O_3} k_2 C_B} \text{ for } 5H_a < E_i$$

$$N_{O_3} = k_L a C_{O_3}^* H_a \text{ for } 5H_a < E_i$$

$$H_a = \frac{\sqrt{D_{O_3} k_2 C_B}}{k_L} \quad E_i = 1 + \frac{C_B D_B}{b C_{O_3}^* D_{O_3}}$$

$$C_{B_0}^{0.5} - C_B^{0.5} = ba C_{O_3}^* \frac{\sqrt{k_2 D_{O_3}}}{2} t$$

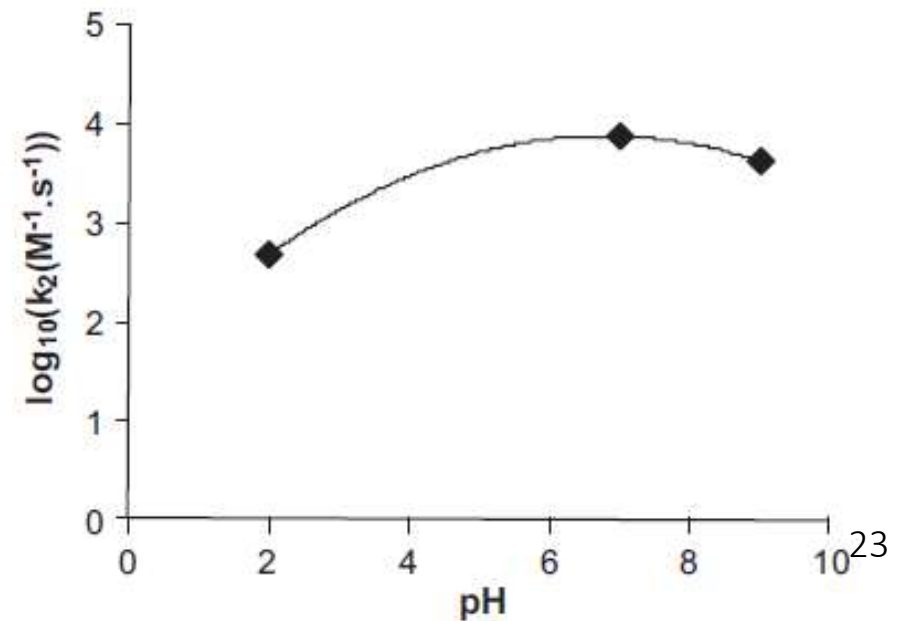


Chemical Engineering and Processing 50 (2011) 637–643

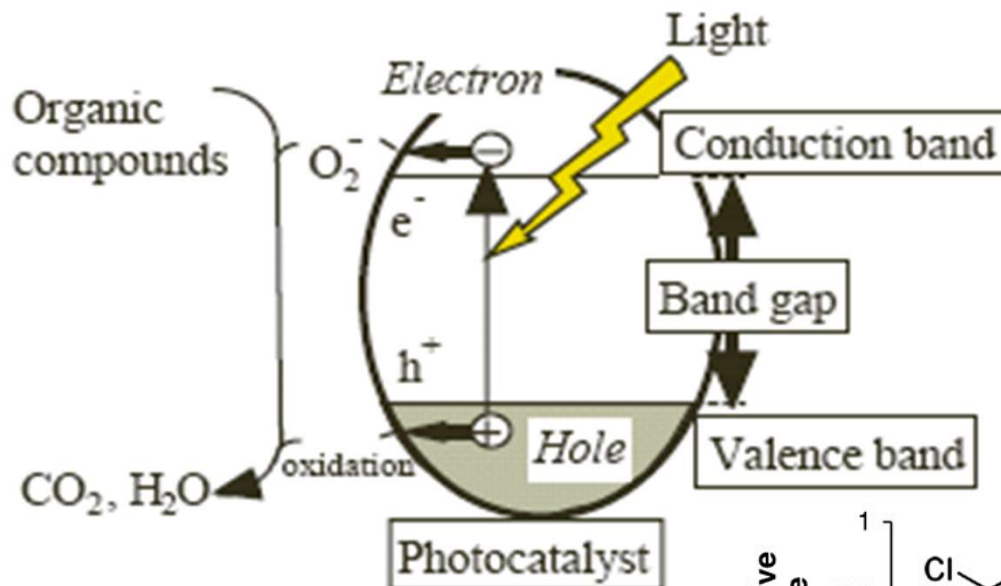
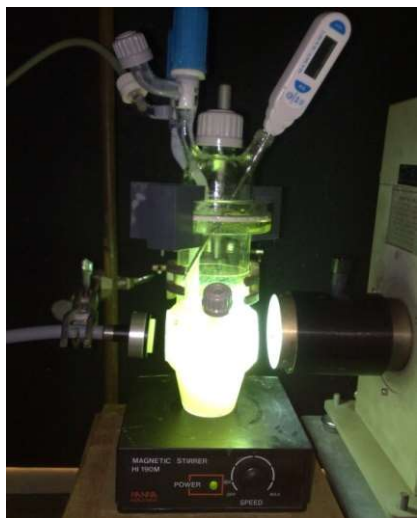


Contents lists available at ScienceDirect
Chemical Engineering and Processing:
Process Intensification

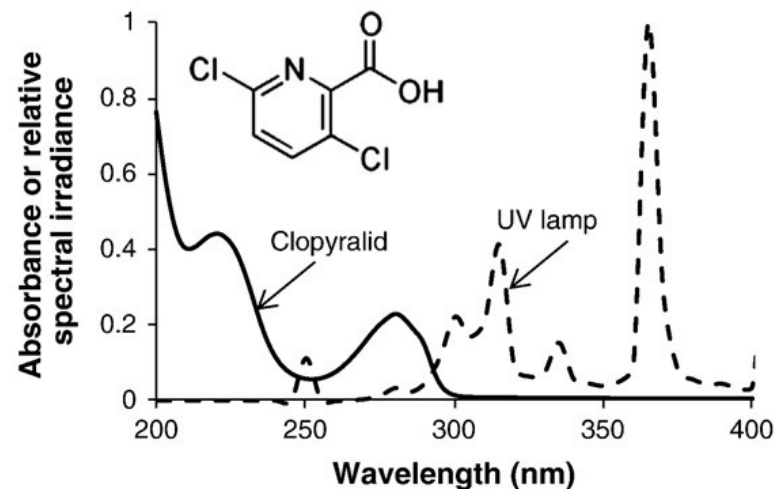
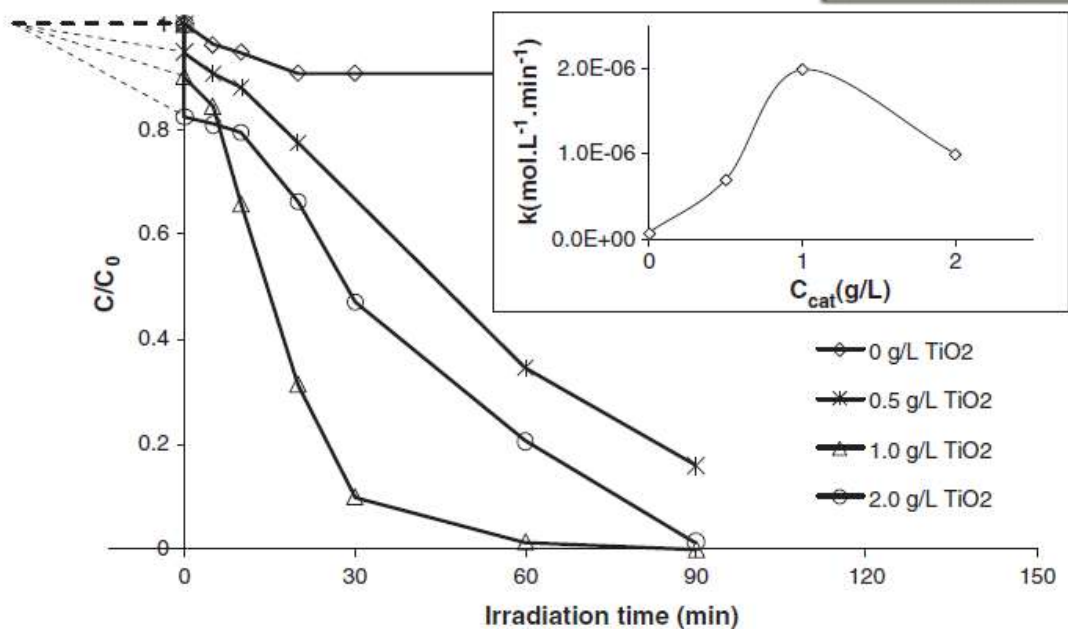
Journal homepage: www.elsevier.com/locate/cep



Photocatalysis and AOPs for the removal of the herbicide clopyralid



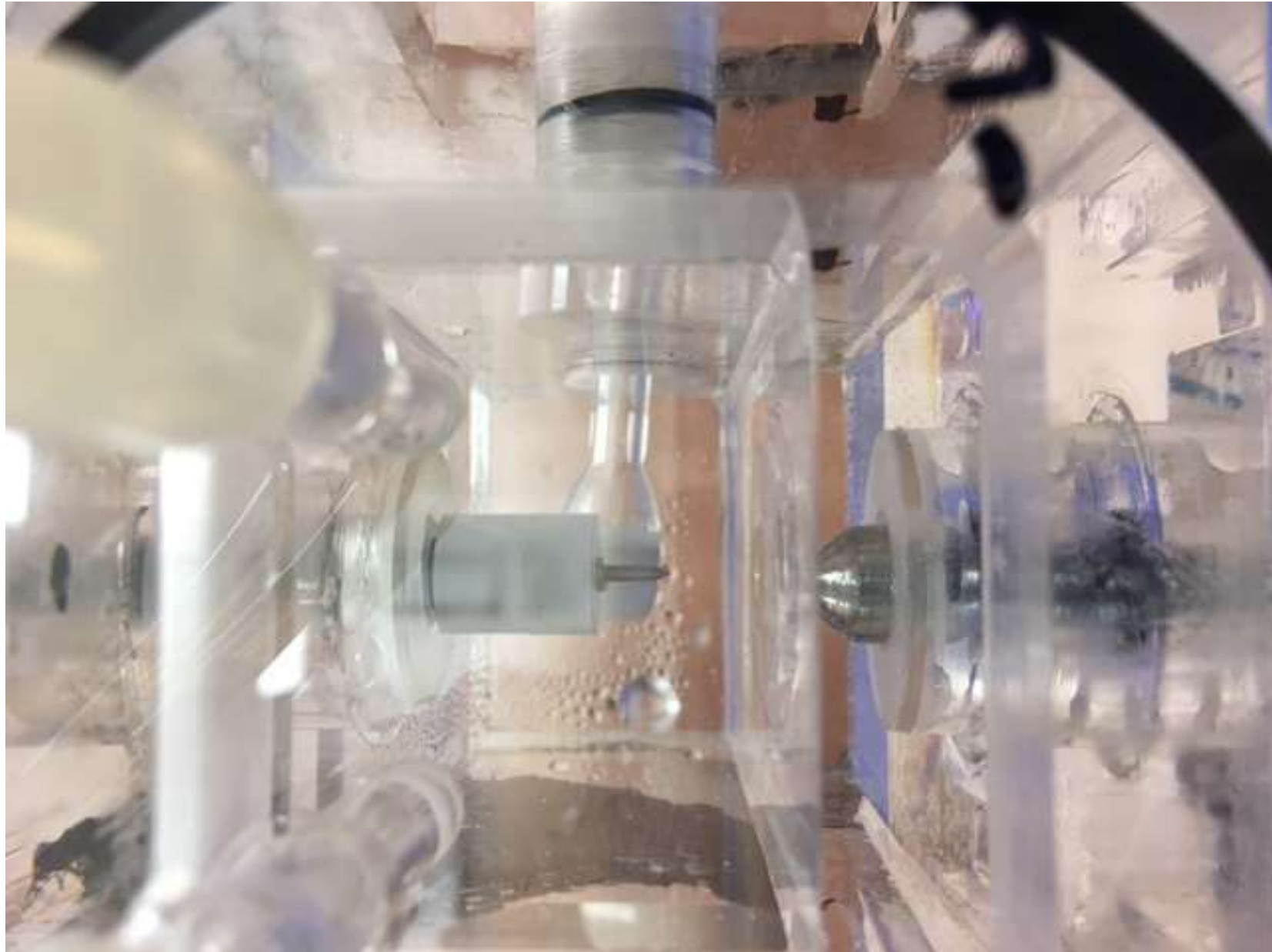
- Clopyralid is a herbicide
- Highly mobile in the environment
- Stable against hydrolysis and photolysis
- Causes contamination of groundwater and surface water



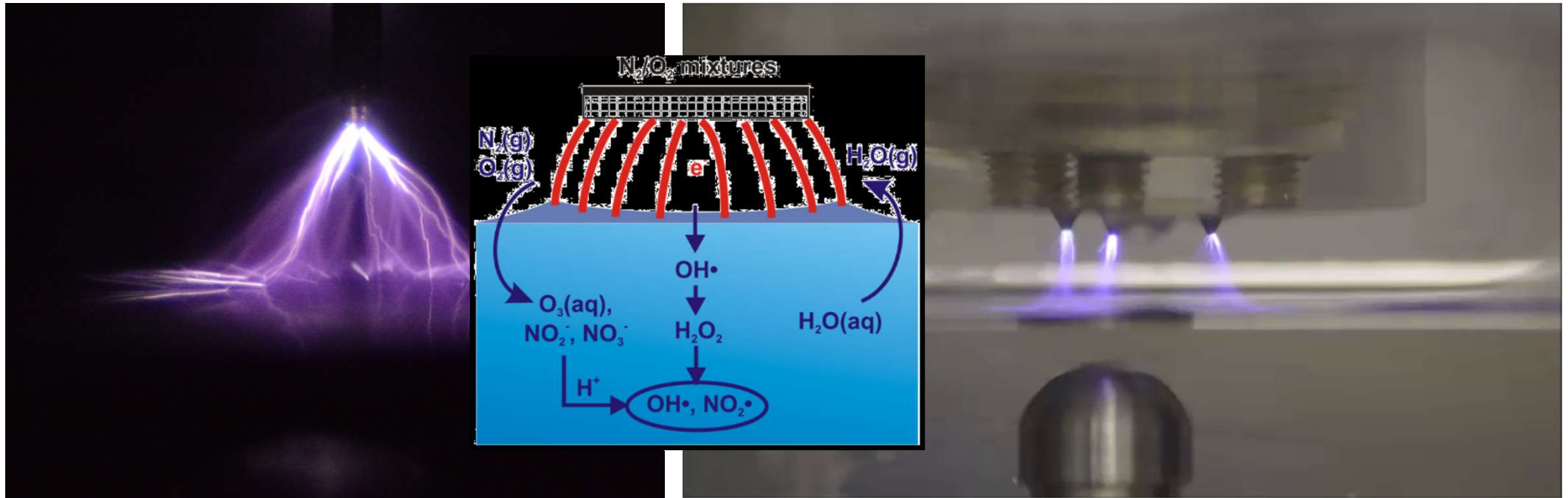
Tizaoui et al. 2011 "Heterogeneous photocatalytic removal of the herbicide clopyralid and its comparison with UV/H2O2 and ozone oxidation techniques", *Desal*, 273(1):197-204
<https://doi.org/10.1016/j.desal.2010.11.036>

Removal of clopyralid with UV/TiO₂ (C₀=0.078 mM, Power=160 W, pH=5). Inset: changes of the pseudo-zero-order rate constant vs. catalyst concentration

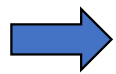
Non-thermal plasma for estrogens removal



Non-thermal Plasma



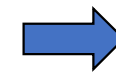
HV



high-
energy e^-
(1-10eV)

+

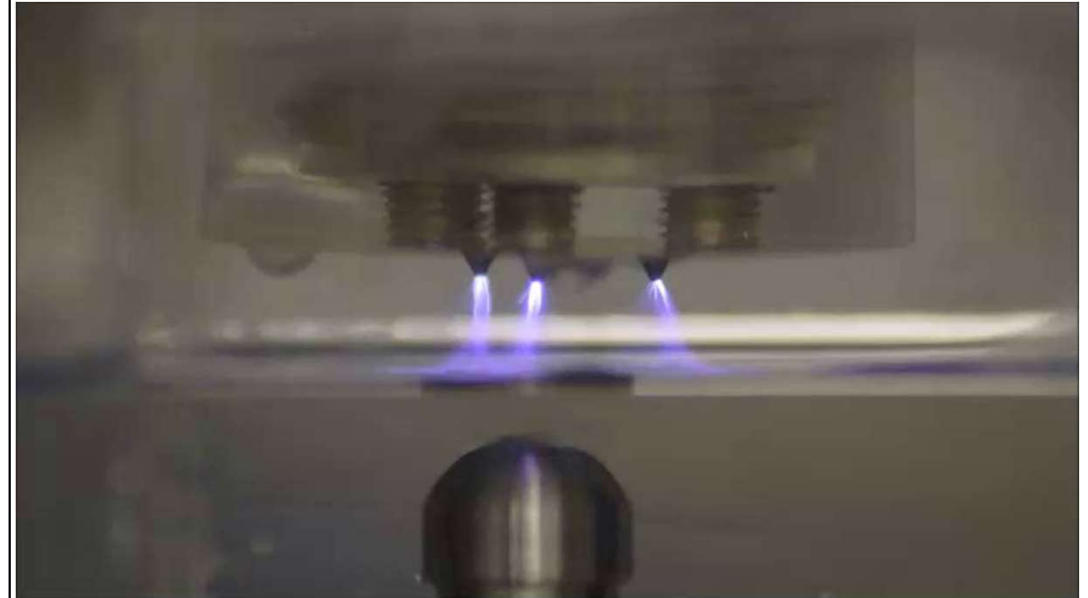
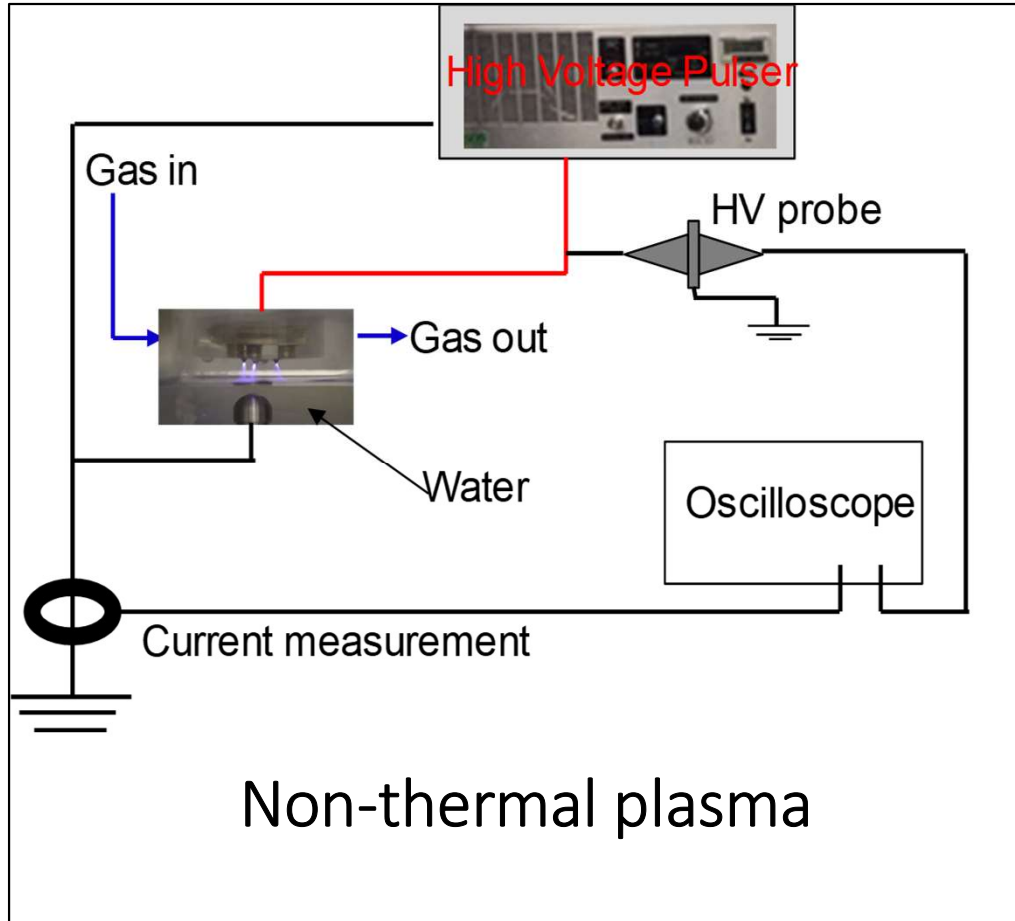
Collision
with
molecules



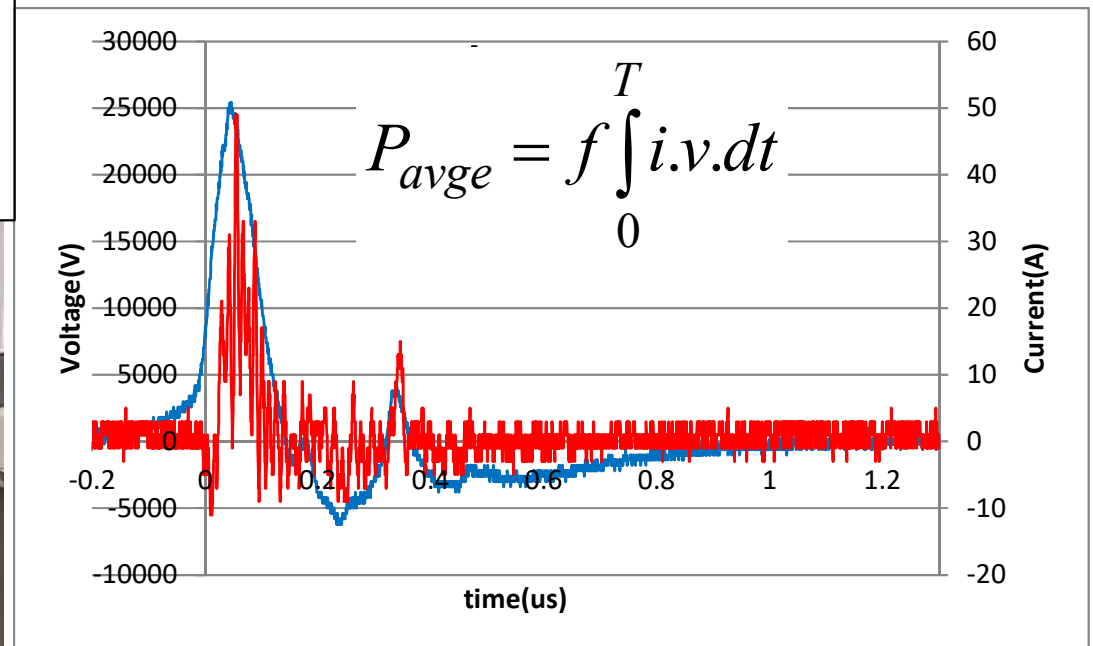
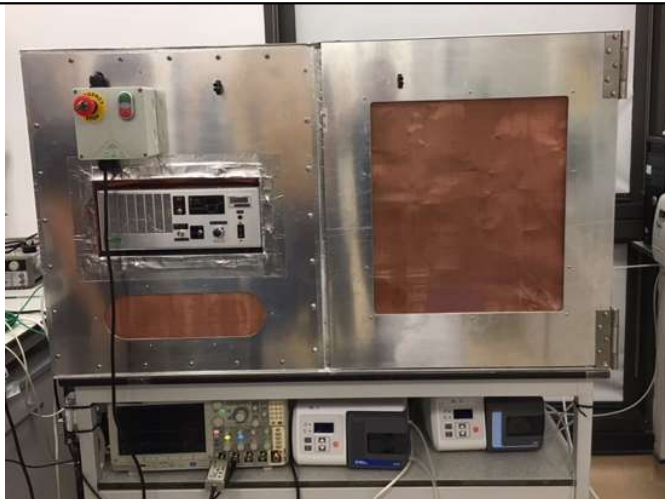
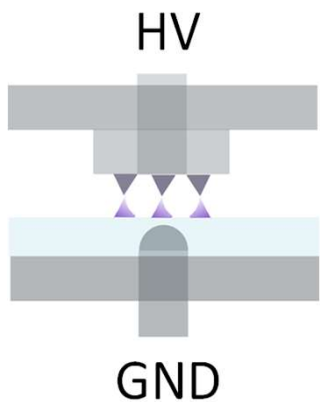
O_3 , H_2O_2 ,
 $\bullet OH$, $\bullet O$, H,
 HO_2 , NO,
US, shock
wave, UV

Plasma System

HV pulser (500 Hz var.; 30 kV var., 50ns rise time, 100 ns pulse width)

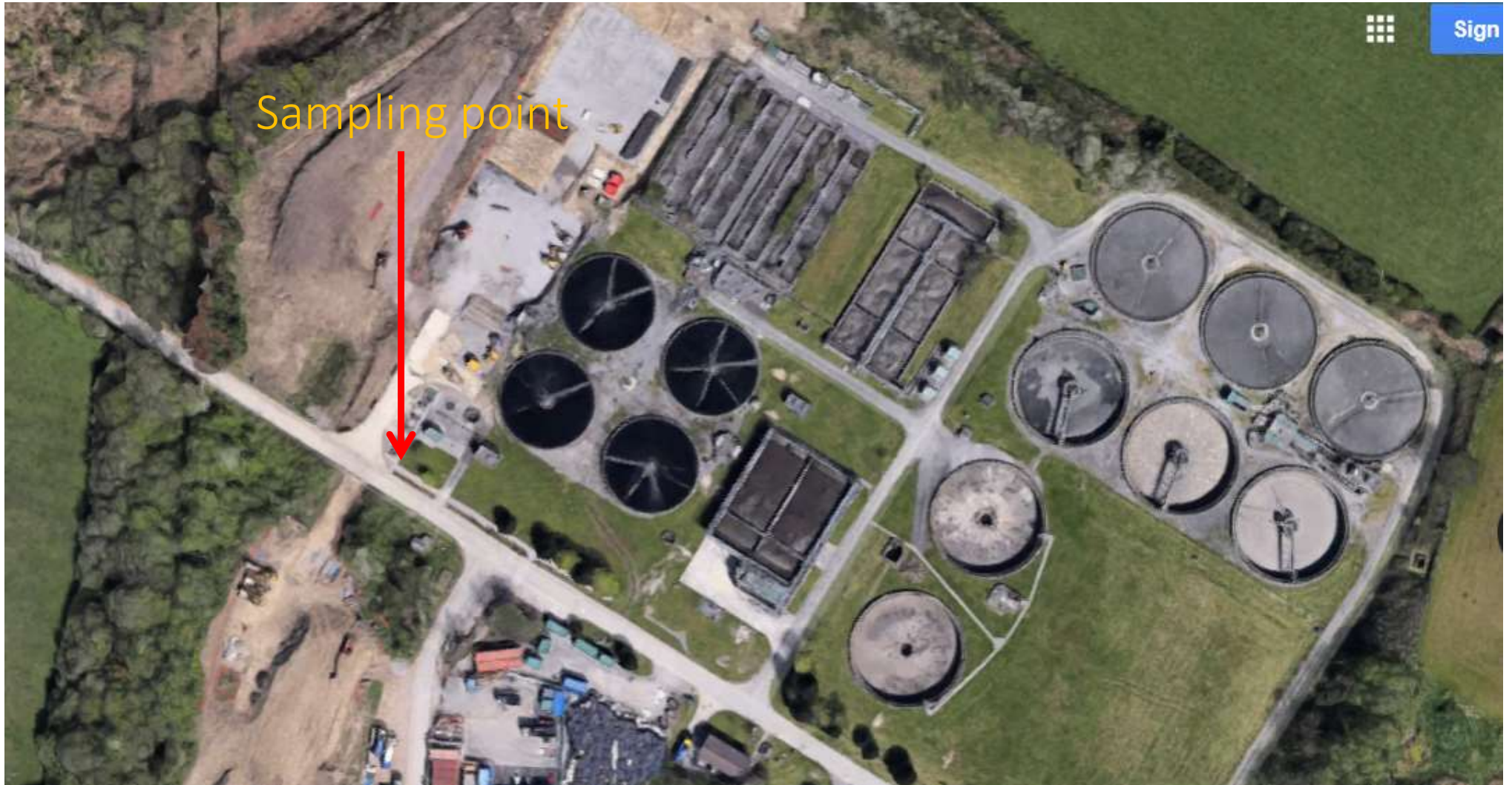


Non-thermal plasma

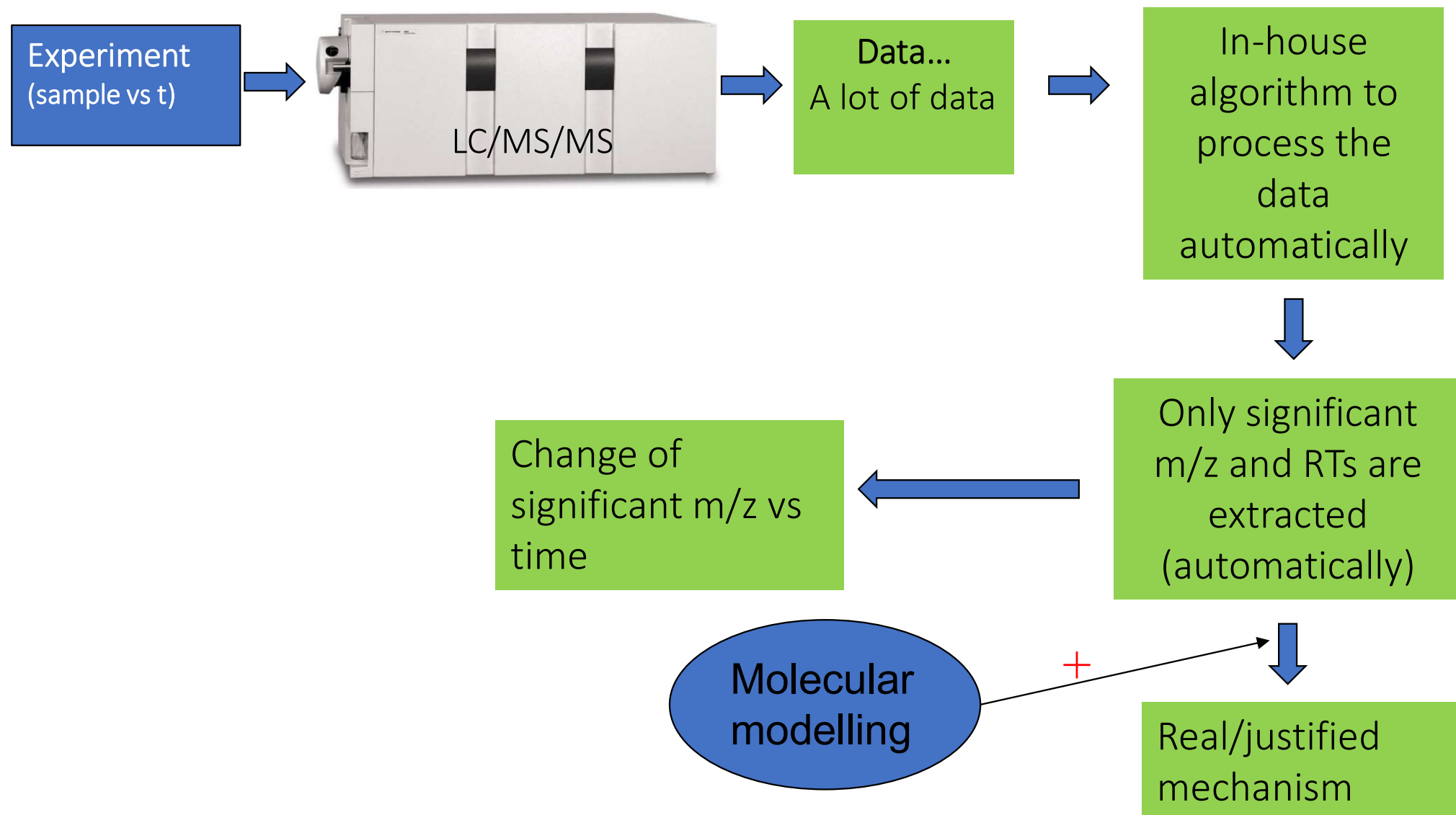


Non-thermal plasma for estrogens removal

Gowerton WWT works

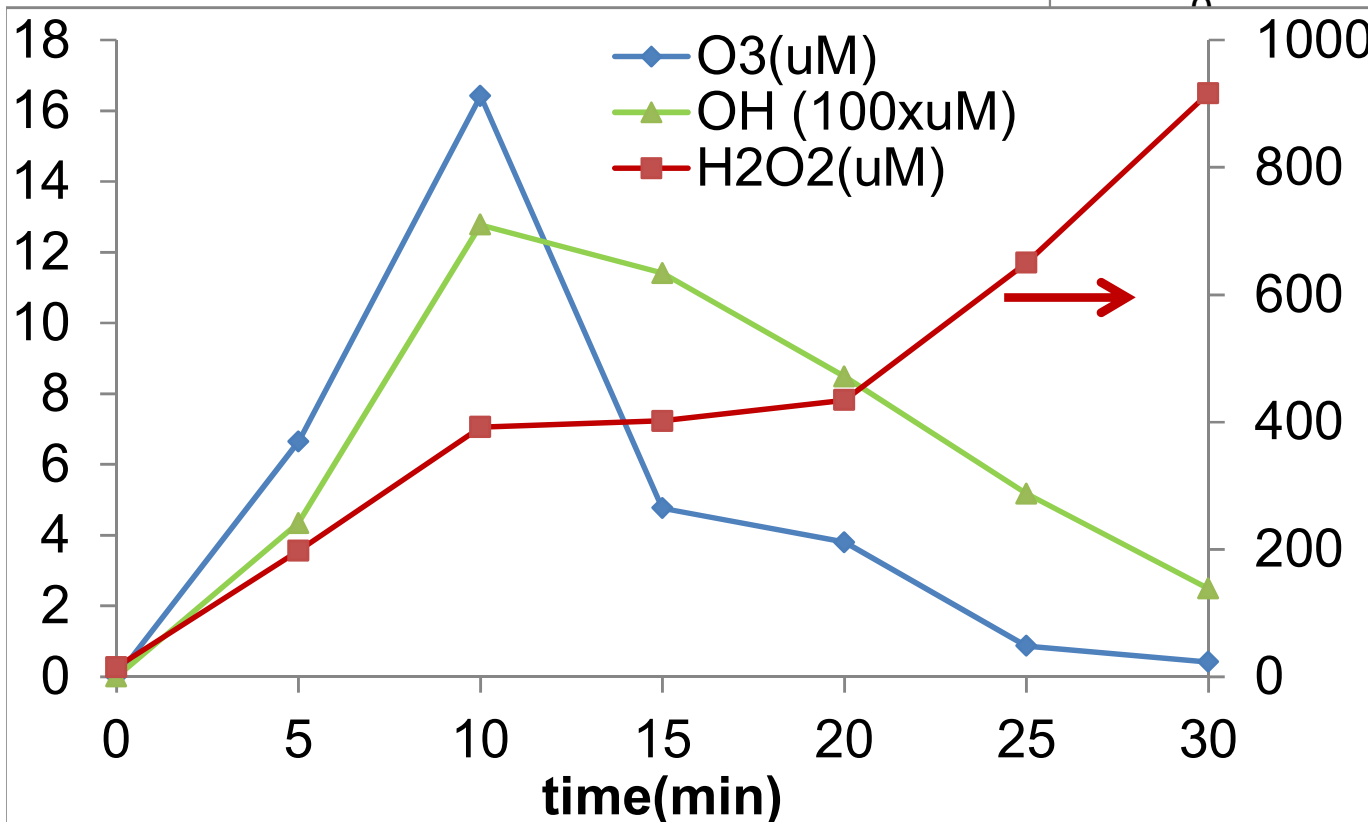
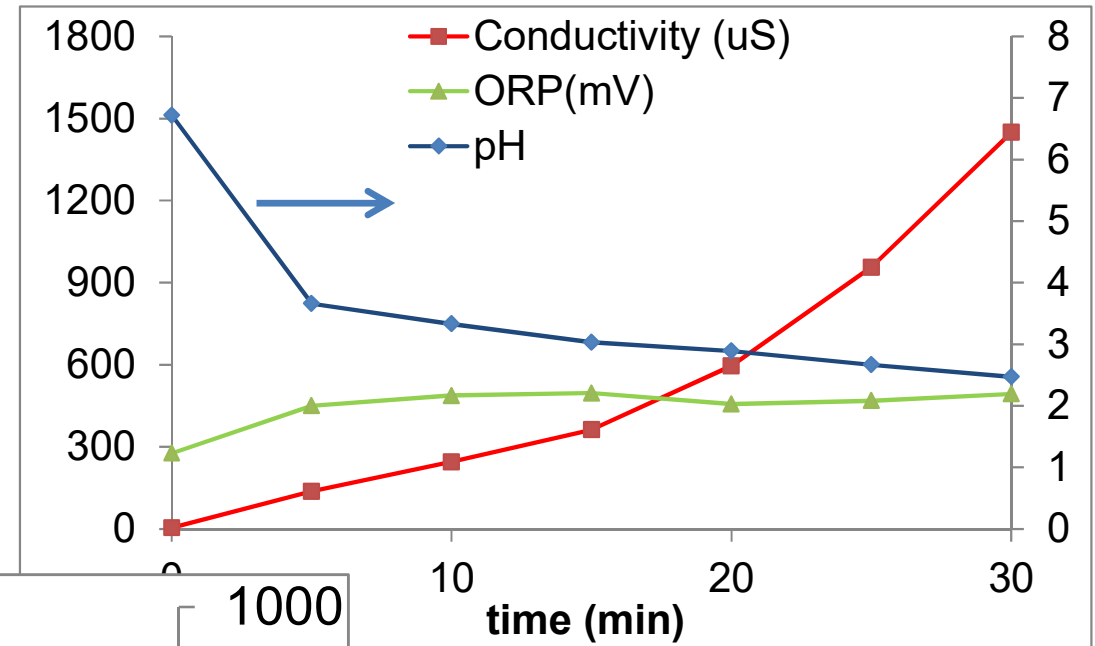


MPs degradation products – workflow



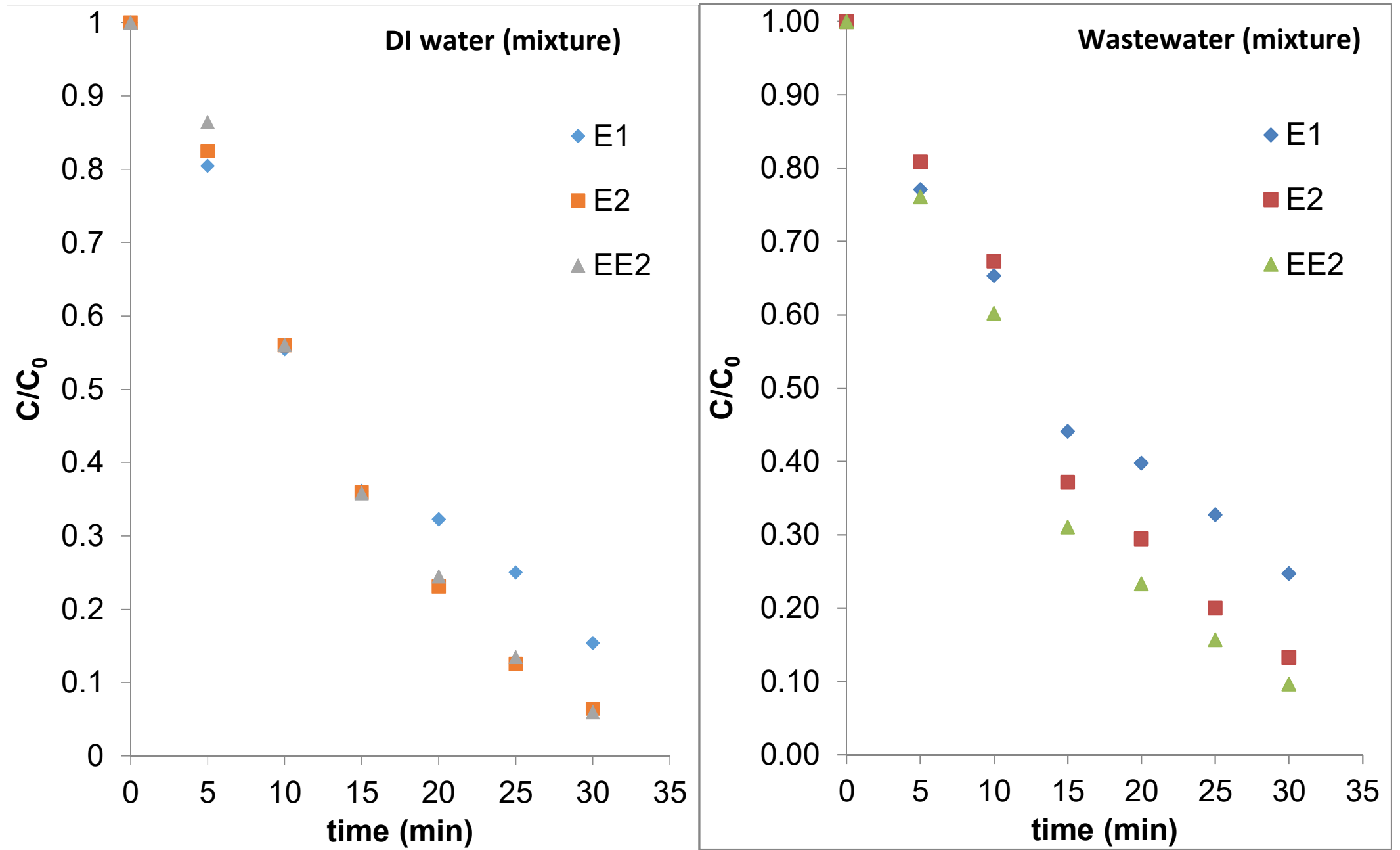
Results

Reactive species



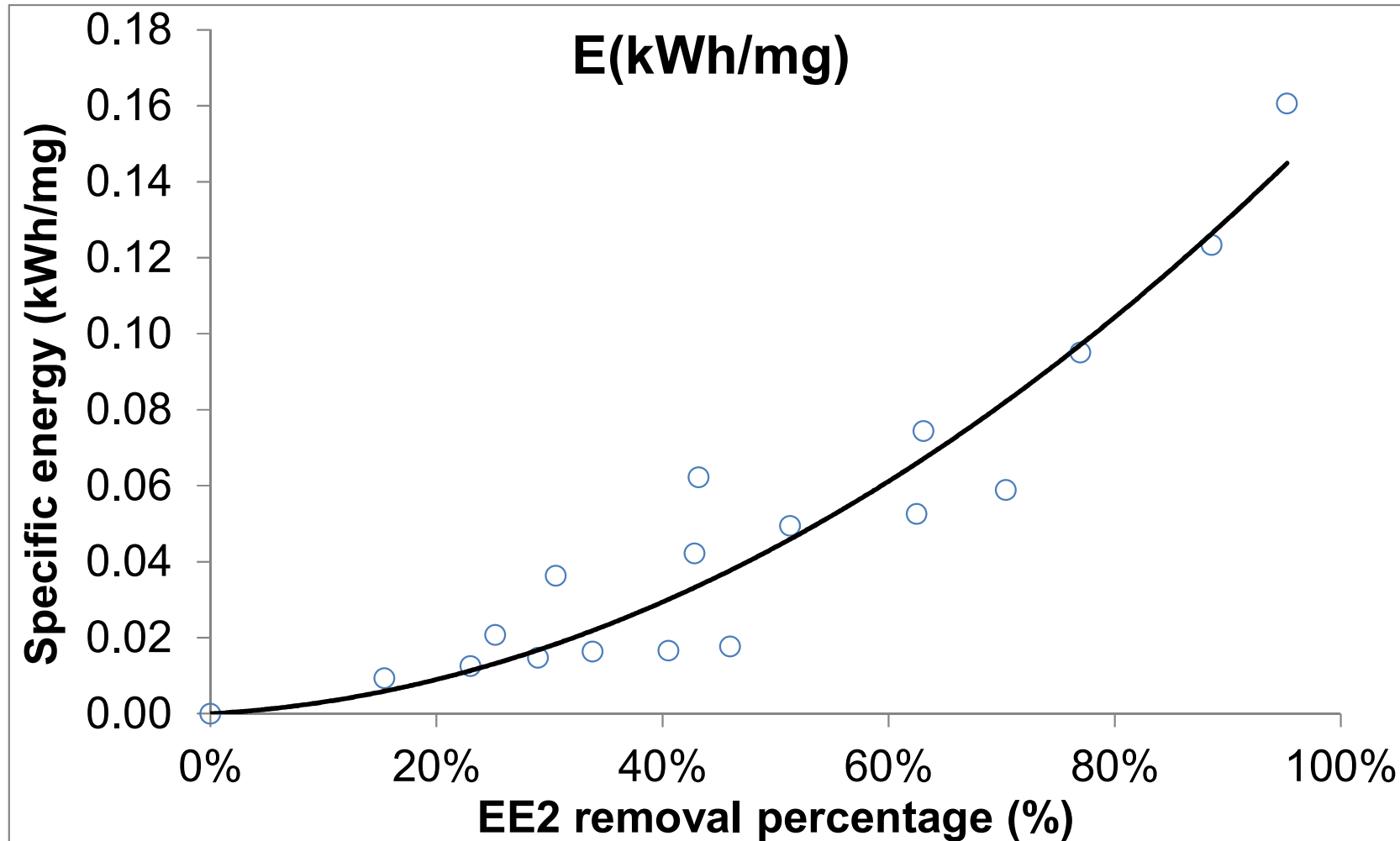
Non-thermal plasma for estrogens removal

E1+E2+EE2 (mixture)



Non-thermal plasma for estrogens removal

All in one



$O_3 \sim 0.4 \text{ kWh/mg}$

Conclusions

- AOPs are effective processes in water and wastewater treatment
- MPs (PPCPs, EDCs etc.) have **serious effects** on human health and the environment but **still largely unnoticed**
- **Regulation** is still **lacking** in this area though in recent years some regs started to emerge (e.g. 🇨🇭 Switzerland and EU “watch list”)
- Ozone-based AOPs have been found very effective to remove MPs
- LLO was effective to extract/destroy EDCs, and was cheaper than O₃ gas
- UV/TiO₂ is effective but there are issues with high UV cost and catalyst recovery/reuse
- Non thermal plasma is an emerging AOP with great potential in wastewater treatment

Acknowledgement



Y Gyfadrn Gwyddoniaeth a Pheirianeg
Faculty of Science and Engineering



Engineering and Physical Sciences
Research Council



Dŵr Cymru
Welsh Water



YorkshireWater



CANOLFAN
RAGORIAETH SBRI
SBRI CENTRE OF
EXCELLENCE



Haydale Graphene Industries plc -



ROYAL
ACADEMY OF
ENGINEERING



The University of
Nottingham

UNITED KINGDOM • CHINA • MALAYSIA



UNIVERSITY of
BRADFORD

THE
**ROYAL
SOCIETY**

Questions

Chedly Tizaoui, PhD, FIChemE, CEng

Department of Chemical Engineering

**Water and Resources Recovery Research Lab,
Faculty of Science and Engineering, Swansea**

University, Swansea, UK

e-mail: c.tizaoui@swansea.ac.uk

