Connecting innovative water reuse technologies with the Food Industry
January 17, 2020, Athens, Greece

Wastewater reuse: effect of advanced oxidation processes on contaminants of emerging concern

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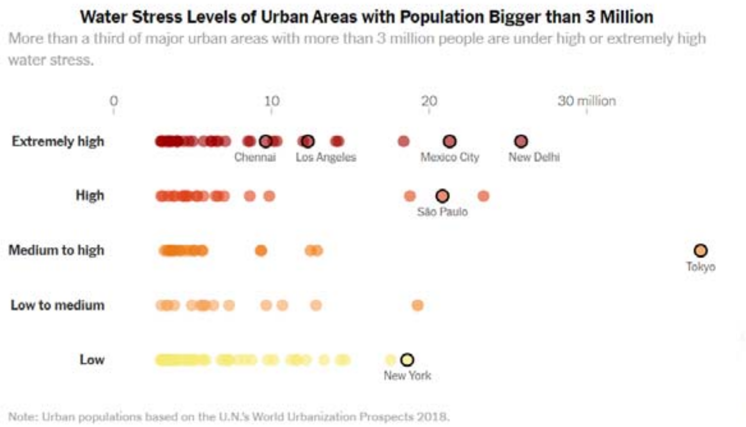
Summary

- Water scarcity and wastewater reuse
- Contaminants of emerging concern: chemical and biological
- European Regulation
- Advanced treatment of urban wastewater by Advanced Oxidation Processes (AOPs)
  - ✓ Effects on (chemical) CECs and antibiotic resistance
- Conclusions/take home messages/pending questions

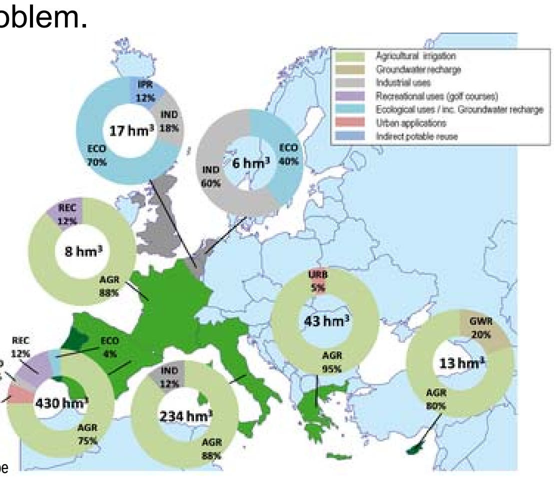
Water scarcity and wastewater reuse



A Quarter of Humanity Faces Looming Water Crises, Sengupta S. and Cai W., Aug. 6th, 2019, The New York Times

Water scarcity and wastewater reuse

- Wastewater reuse is a possible solution to address water scarcity problem.



Status of water reuse in Europe

DEMOWARE final summary report (2017), Source: (Hochstrat, Wintgens, Melin, & Jeffrey, 2006) Data from EUREAU survey and AQUAREC results www.aquarec.org)

Contaminants of emerging concern (CECs)

- Safe wastewater reuse
- Challenges in wastewater treatment
- Contaminants of emerging concern (CECs):
  - ✓ pollutants occurring at ng-µg/L concentrations in water and wastewater;
  - ✓ antibiotics, antibiotic resistant bacteria (ARB) and other mobile genetic elements occurring in water and wastewater and may contribute to antibiotic resistance (AR) transfer.

Contaminants of emerging concern

- Pharmaceuticals

- Antibiotic resistance determinants (A, ARB, ARGs)
- Personal care products

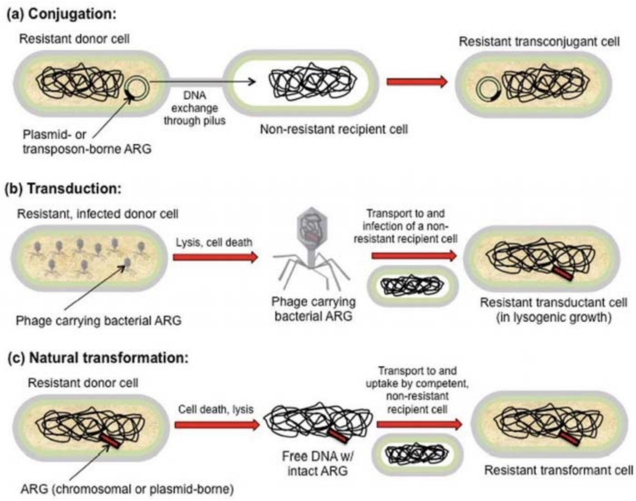
- Pesticides

- Nanoparticles

Antibiotic resistance

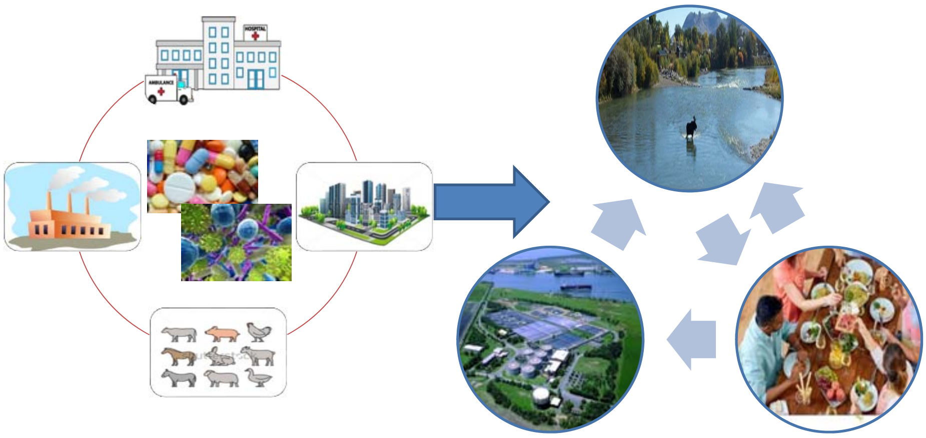
- Antibiotic resistance (AR) has become an ongoing clinical and public health issue of concern worldwide (WHO 2014).
- UWWTPs are hotspots for the release of AR determinants (antibiotics (A), ARB and ARGs) into the environment
- No specific regulations for controlling the release of A/ARB/ARGs into the environment through UWWTPs effluents

AR transfer mechanisms



Dodd 2012. J. Environ. Monit. 14, 1754-1771

Contaminants of emerging concern



Wastewater reuse

- EU minimum quality standards for wastewater reuse…
  - ✓… JRC report

Table 1 Reclaimed water quality criteria for agricultural irrigation.

Reclaimed water quality class	Indicative technology target	Quality criteria				
		E. coli (cfu/100 ml)	BOD_5 (mg/l)	TSS (mg/l)	Turbidity (NTU)	Additional criteria
Class A	Secondary treatment, filtration, and disinfection (advanced water treatments)	≤10 or below detection limit	≤10	≤10	≤5	*Legionella* spp.: <1,000 cfu/l when there is risk of aerosolization in greenhouses. Intestinal nematodes (helminth eggs): ≤1 egg/l when irrigation of pastures or fodder for livestock.
Class B	Secondary treatment, and disinfection	≤100	According to Directive 91/271/EEC	According to Directive 91/271/EEC	-	
Class C	Secondary treatment, and disinfection	≤1,000	According to Directive 91/271/EEC	According to Directive 91/271/EEC	-	
Class D	Secondary treatment, and disinfection	≤10,000	According to Directive 91/271/EEC	According to Directive 91/271/EEC	-	

Wastewater reuse

- EU minimum quality standards for wastewater reuse…
  - ✓SCHEER and EFSA scientific advices on JRC report


TECHNICAL REPORT

APPROVED: 22 May 2017

Request for scientific and technical assistance on proposed EU minimum quality requirements for water reuse in agricultural irrigation and aquifer recharge

European Food Safety Authority (EFSA),

Ana Allende, Damià Barceló Culleres, Rosina Gironés Llop, Arlette Laval, Lucy Robertson, Maria Teresa da Silva Felício, Andrea Gervelmeyer, Luisa Ramos Bordajandi, Ernesto Liebana

The European Food Safety Authority recommends that: … and (10) critical discussion on the importance of the uptake and accumulation of chemical contaminants, including compounds of emerging concern and disinfectant by-products, and the possible consequences for human and animal health, is included.


Available online at www.sciencedirect.com

ScienceDirect

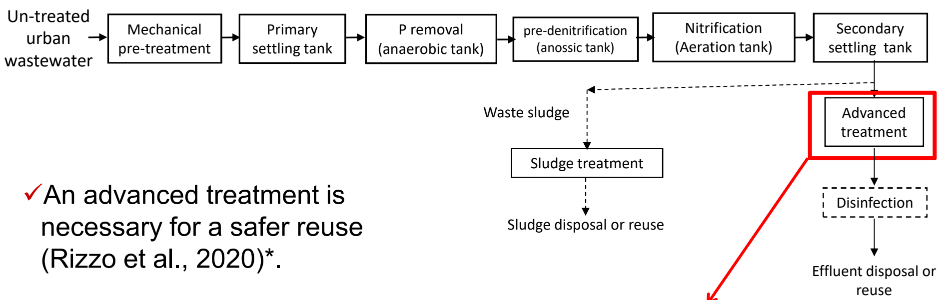
Current Opinion in Environmental Science & Health

Proposed EU minimum quality requirements for water reuse in agricultural irrigation and aquifer recharge: SCHEER scientific advice

Luigi Rizzo[1], Renate Krätke[2], Jan Linders[3,a], Marian Scott[4], Marco Vighi[5] and Pim de Voogt[6,7]

In the opinion of the SCHEER, the report inadequately addresses (i) contaminants of emerging concern (CECs), (ii) antibiotic resistance spread through urban wastewater treatment plants' (UWWTPs) effluents, and (iii) possible risks associated with disinfection and/or advanced treatment of urban wastewater (e.g. formation of disinfection by products and related toxicity). Therefore the SCHEER is of the opinion that, in its current form, the minimum quality requirements proposed provide insufficient protection both to environmental and human health.

Urban wastewater treatment



✓An advanced treatment is necessary for a safer reuse (Rizzo et al., 2020)*.

- Filtration (F)
- (F +) adsorption
- F + membranes
- (F +) AOPs

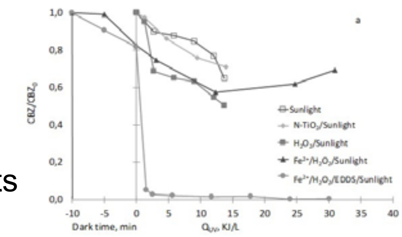
*Best available technologies and treatment trains to address current challenges in urban wastewater reuse for irrigation of crops in EU countries. Science of The Total Environment 136312, in press, https://doi.org/10.1016/j.scitotenv.2019.136312

Advanced oxidation processes (AOPs)

- ✓AOPs promote the formation of radical species (e.g., HO•) that can effectively (i) degrade/oxidize organic and inorganic contaminants in water/wastewater as well as (ii) inactivate microorganisms.
- ✓Homogeneous photo-driven AOPs (e.g., UV/H_2O_2, photo Fenton ($UV/H_2O_2/Fe$)) have more chance to be used as advanced/tertiary treatment in urban WWTPs compared to heterogeneous photocatalytic processes, in the short term;
- ✓Artificial light can be replaced by sunlight to save energy costs

Effect of AOP type on CECs: (solar)photo Fenton

- Acidic Vs neutral conditions
- UV- Vs Solar-photo Fenton
- Mild conditions Vs chelating agents



Maniakova et al., 2020. Sep. Pur. Tech. 236, 116249

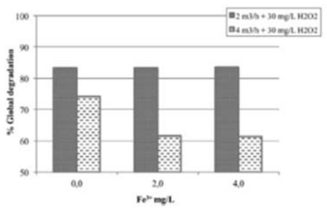
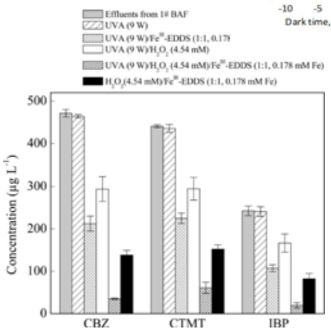


Fig. 3 – Percentage of global micropollutants removal by photo-Fenton (natural pH), with different iron additions (0, 2, 4 mg L^{-1}).

De la Cruz et al., 2013. Water Res. 47, 5836.



Dong et al., 2019. Chem. Eng. J. 366, 539.

Effect of AOP type on CECs: UV/PMS* and UV/PS*

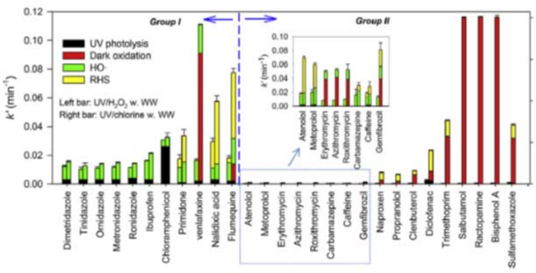
*persulphate (PS) and peroxymonosulphate (PMS)

Pollutant	Source water	Pollutant concentration	Oxidant concentration	Wavelength (nm)	pH	Reaction time (h)	Degradation* (%)	References
Sulfamethazine	Milli-Q water	0.02 mM	0.2 mM PS	254	6.5	0.75	~90%	[61]
Antipyrine	Milli-Q water	0.0265 mM	0.52 mM PS	253.7	7.2	1	~80%	[62]
Sulfamethazine	Milli-Q water	0.02 mM	0.2 mM PS	254	6.5	0.75	96.5	[61]
Atenolol	Milli-Q water	0.02 mM	0.08 mM PMS	254	7	0.5	> 80	[63]
Tetramethylammonium hydroxide	Reverse osmosis water	1.1 mM	100 mM PS	254	2	2.17	100	[64]
Perfluorooctanoic Acid	Secondary effluent	0.15 mM	15 mM PS	254	7.1	8	> 80%	[65]
2-Methylisoborneol	River water	0.238 µM	10 µM PS	254	7.0	0.14	> 90	[66]
Ciprofloxacin	Milli-Q water	50 µM	1 mM PS	254	7	1	100	[67]
Methyl paraben	Milli-Q water	32.8 µM	1 mM PS	254	6.5	1.5	98.9	[68]
Diiodoacetic acid	Deionized water	1.5 µM	60 µM PS	254	7	3	n.a.	[69]
Chloramphenicol	Deionized water	31 µM	0.25 mM PS	254	6.07	1	100	[70]
		30 µM	1 mM PS	254	7	2	~67%	
2,4-Di-tert-butylphenol	Deionized water	5 mg L^{-1}	1 mM PS	253.7	7.0	0.5	85.6	[71]
Haloacetonitriles	Milli-Q water	2 µM	0.2 mM PS	254	6	3	99.8	[72]
Oxcarbazepine	Ultrapure water	20 µM	1 mM PS	253.7	11	2	~84	[73]
Oxytetracycline	Milli-Q water	40 µM	1 mM PS	254	7	10	100	[74]
Sulfamethoxazole	Milli-Q water	23.69 µM	1 mM PS	254	5.85	n.a.	~97%	[75]
	Milli-Q water	23.69 µM	1 mM PMS	254	6.24	n.a.	~97%	
Sulfamethoxazole	Deionized water/ surface water	20 µM	1 mM PS	254	8	2	100%	[76]
Lindane	Milli-Q water	3.43 µM	0.25 mM PMS, 0.25 mM Fe^{2+}	254	3	12	78.4	[77]
Lindane	Milli-Q water	3.43 µM	0.25 mM, PMS	254	5.8	3	~90	[78]
Azathioprine	Milli-Q water	3.3 µM	0.1 mM PS	254	0.5	1.5	87	[79]
2-Chlorophenol	Milli-Q water	0.2 mM	10 mM PS	365	4	1.5	100	[80]
3-Chlorophenol	Milli-Q water	0.2 mM	10 mM PS	365	4	1.5	100	
4-Chlorophenol	Milli-Q water	0.2 mM	10 mM PS	365	4	1.5	100	
Di-(2-ethylhexyl) phthalate	Reverse osmosis water	10 mg/L	2 g L^{-1} PMS	n.a.	7	2	100	[81]
Sulfamerazine; sulfamethizole; sulfachloropyridazine	Ultrapure water	0.2 µg/L	1.0 mg L^{-1} PMS	254	7.5	0.5	100%	[82]
Sucralose	Deionized water	0.126 mM	3.78 mM PMS	254	7.0	1	> 95% (TOC)	[83]

* Represents the removal efficiency.

Ultraviolet-activated PS and PMS for the degradation of emerging contaminants (Wang and Wang, Chemical Engineering Journal 334 (2018) 1502–1517)

Effect of AOP type on CECs: UV/free chlorine



Comparison of k_0 of selected PPCPs in wastewater by the UV/chlorine and UV/H2O2 processes at pH 7. The inset shows the k_0 of 7 PPCPs by the two processes with the enlarged view of y axis scale. Conditions: [PPCP]0 =1 mg/L, [chlorine]0 = [H2O2]0 = 50 mM, [EfOM]0 =3.5 mg/L

Guo et al., 2018. Water Res. 147, 184-194

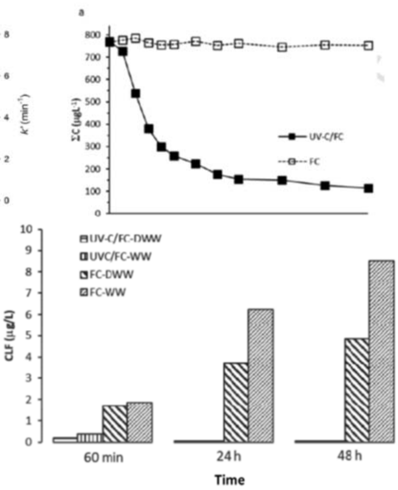
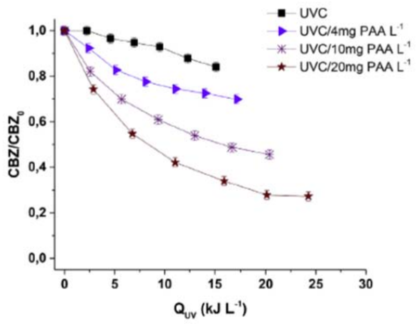


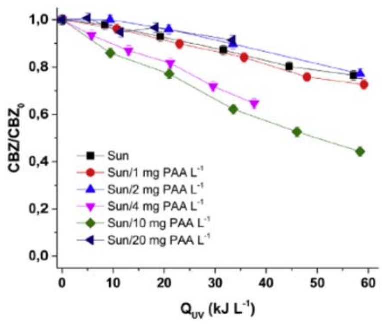
Fig. 2. Effect of UV-C and UV-C/FC (

Chloroform formation after FC and UV-C/FC treatment, respectively: comparison between the end of the treatment (60 min) and 24 h and 48 h post-treatment incubation

Cerreta et al., in press Water Research 169, 115220, https://doi.org/10.1016/j.watres.2019.115220

Effect of AOP type on CECs: sunlight/ Vs UV/PAA





Rizzo et al., 2019. Water Research 149, 272-281

Effect of AOPs type on CECs: oxidation interm. and toxicity

Maniakova et al., . Separation and Purification Technology, in press, https://doi.org/10.1016/j.seppur.2019.116249

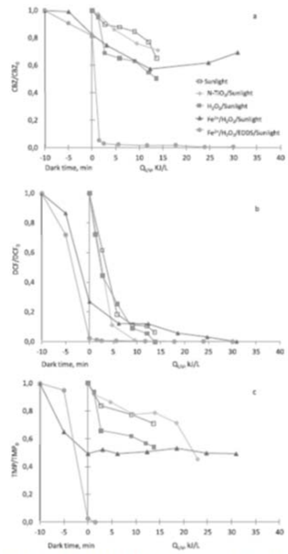


Fig. 3. Degradation of CBZ (a), DCF (b) and TMP (c) by sunlight, N-TiO_2/sunlight; H_2O_2/ sunlight (50 mg/L); photo Fenton (C_{Fe}^{3+} = 0,1 mM (5,6 mg/L); C_{H2O2} = 50 mg/L); photo-Fenton with EDDS (C_{Fe}^{3+} = 0,1 mM (5,6 mg/L; C_{EDDS} = 0,2 mM (58 mg/L); C_{H2O2} = 50 mg/L) processes in WW.

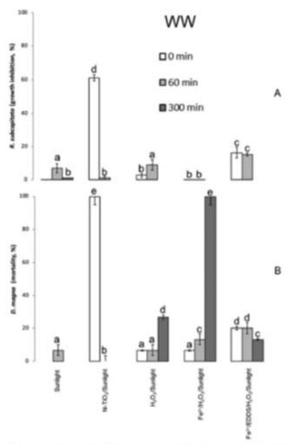


Fig. 5. . Toxicity of CECs solutions (CBZ, TMP and DCF at 200 µg/L initial concentration each one) treated with solar driven AOPs assessed considering *R. subcapitata* (A) and *D. magna* (B) in WW; letters (a–e) indicate significant statistical difference (α = 0.05) according to Tuckey's test.

Effect of AOPs on CECs: oxidation interm. and toxicity

Advanced treatment of urban wastewater by ozonation

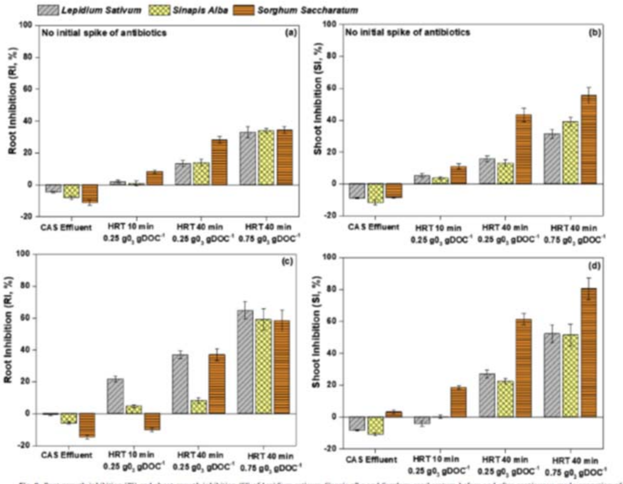


Fig. 8. Root growth inhibition (RI) and shoot growth inhibition (SI) of *Lepidium sativum*, *Sinapis alba* and *Sorghum saccharatum*, before and after continuous mode ozonation of wastewater samples, as collected or spiked at 100 μg L^{-1}, using the selected experimental conditions: 0.25 gO$_3$ gDOC^{-1} and HRT of 10 min; 0.25 gO$_3$ gDOC^{-1} and HRT of 40 min; and 0.75 gO$_3$ gDOC^{-1} and HRT of 40 min. Experimental conditions: Matrix: secondary treated effluents; pH 7.3–7.8; T = 24 ± 1 °C.

Iakovides et al., Water Research 159 (2019) 333-347

Effect of AOPs on CECs: CECs uptake in crops

Advanced treatment of urban ww by sunlight/H2O2

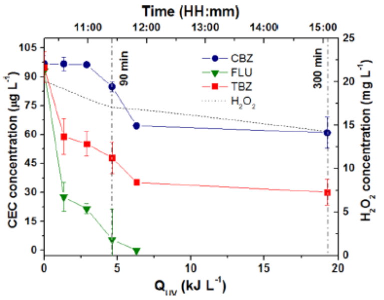


Figure 2. H_2O_2/sunlight degradation of the three CECs (carbamazepine (CBZ), flumequine (FLU), and thiabendazole (TBZ)) [H_2O_2 dose = 20 mg L^{-1}] and hydrogen peroxide concentration.

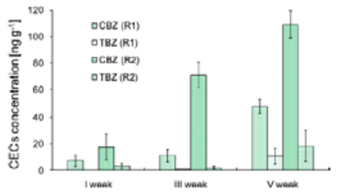


Figure 3. Carbamazepine (CBZ) and thiabendazole (TBZ) uptake by lettuce leaves during the experimental study. R1 refers to UWTP effluent treated within 5 h of H_2O_2/sunlight and then used as irrigation water; R2 refers to UWTP effluent treated within 90 min of H_2O_2/sunlight and then used as irrigation water.

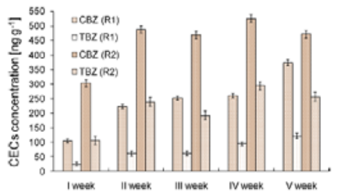
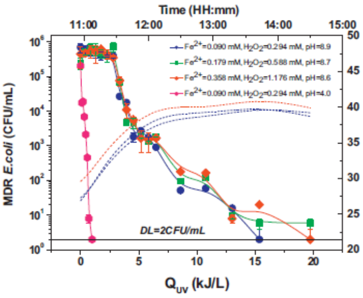


Figure 4. Carbamazepine (CBZ) and thiabendazole (TBZ) accumulation/deposition on top soil during the experimental study. R1 refers to UWTP effluent treated within 5 h of H_2O_2/sunlight and then used as irrigation water; R2 refers to UWTP effluent treated within 90 min of H_2O_2/sunlight and then used as irrigation water.

Ferro et al., 2015. Environmental Science and Technology 49, 11096−11104.

Can AOPs effectively control AR spread?

Effect of AOP type on AR

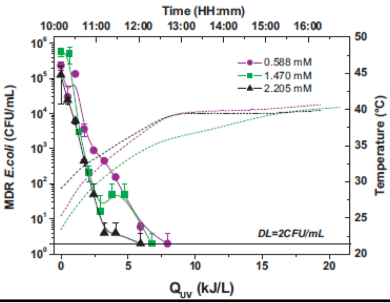


(a)

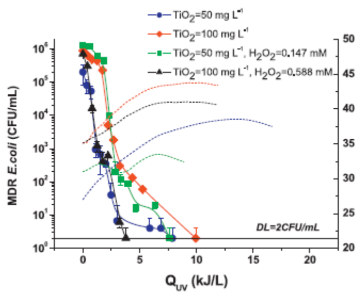
Ferro et al., 2015. Applied Catalysis B: Environmental 178, 65-73

Solar photo Fenton (a), sunlight/H_2O_2 (b), sunlight/TiO_2 and sunlight/TiO_2/H_2O_2 (c).

Inactivation of multi-drug resistant *E. coli* strain

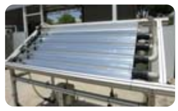


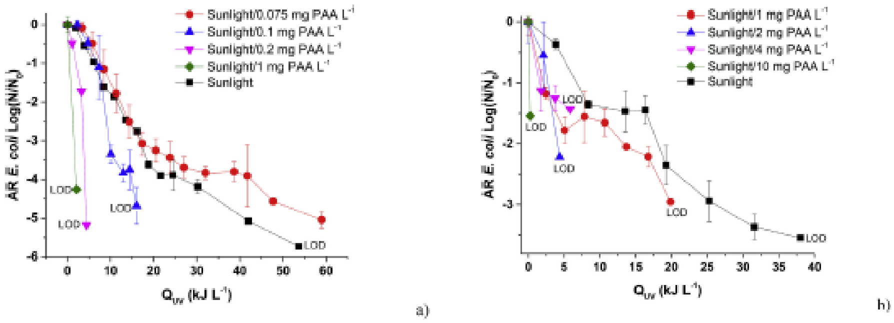
(b)



(c)

Effect of AOP type on AR: Sunlight/PAA

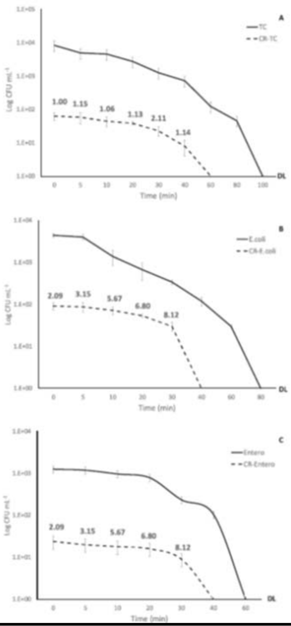




Inactivation of AR E. coli by sunlight/PAA in CPC: effect of initial PAA concentration in GW (a) and WW (b).

Rizzo et al., 2019. Water Research 149, 272-281

Effect of AOP type on AR: solar photo Fenton



Effect of solar photo-Fenton process in raceway pond reactors at neutral pH on antibiotic resistance determinants in secondary treated urban wastewater

Fiorentino et al., 2019. Journal of Hazardous Materials 378, 120737, https://doi.org/10.1016/j.jhazmat.2019.06.014

Effect of AOP type on AR: sunlight/ Vs UV/H2O2

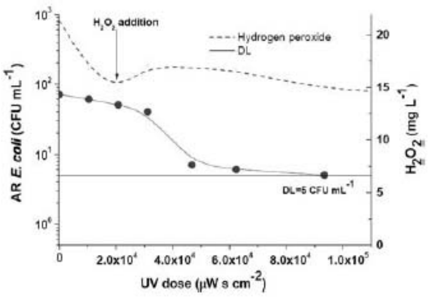


Fig. 1. Antibiotic resistant *E. coli* inactivation by UV/H_2O_2 process.

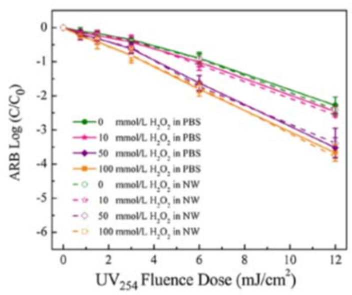


Fig. 7. *P. aeruginosa* inactivation under UV irradiation (λ = 254 nm) and H_2O_2 addition.

Guo et al. 2017, Journal of Hazardous Materials 323, 710–718

Ferro et al., 2016. Science of The Total Environment 560–561, 29–35.

Effect of AOP type on AR: intra- Vs extra-cellular

Ferro et al., 2016. Science of The Total Environment 560–561, 29–35.

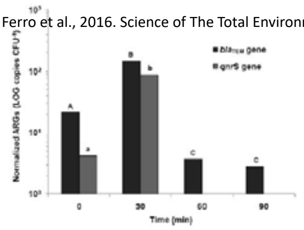


Fig. 4. Concentrations of ARGs in intracellular DNA as a function of treatment times of UV/H_2O_2 process. A, B, C, a, b, indicate significantly ($p < 0.05$) different groups of normalized ARGs (Log copies CFU^{-1}) among the investigated treatment times.

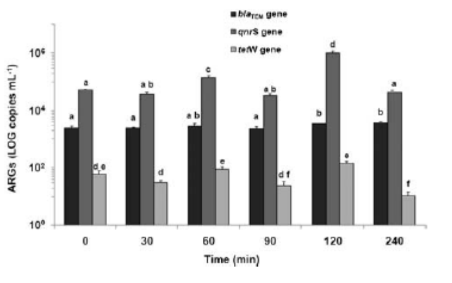


Fig. 5. Concentrations of ARGs in total DNA as a function of treatment times of UV/H_2O_2 process. a, b, c, d, e, f indicate significantly ($p < 0.05$) different groups of ARGs (Log copies mL^{-1}) among the investigated treatment times.

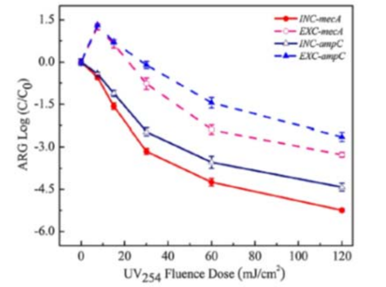


Fig. 12. Effect of TiO_2 thin film on ARGs removal under UV irradiation (λ = 254 nm) in PBS. Error bars are standard error of the mean. INC = intracellular. EXC = extracellular.

Guo et al. 2017, Journal of Hazardous Materials 323, 710–718

Effect of AOP type on AR: heterogeneous photocatalysis

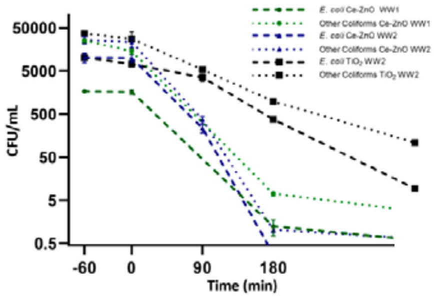


Figure 7. Inactivation of *E. coli* and other coliforms Conditions: 750 mL of WW photocatalyst coated discs with 36 W UVA.

Zammit et al., 2019. Catalysts 9, 222; doi:10.3390/catal9030222

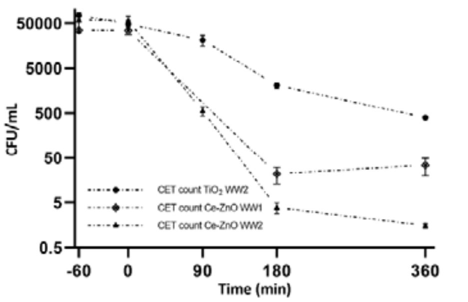


Figure 8. Inactivation of *P. aeruginosa*. Conditions: 750 mL of WW and 380 cm^2 photocatalyst coated discs with 36 W UVA.

ANSWER project, Marie Sklodowska-Curie Innovative Training Network (H2020-MSCA-ITN- 2015/675530), 2015-2019.

ANSWER

Effect of AOP operating conditions on AR: UV/PMS

Hu et al. 2019, Chem. Eng. J. 368, 888–895

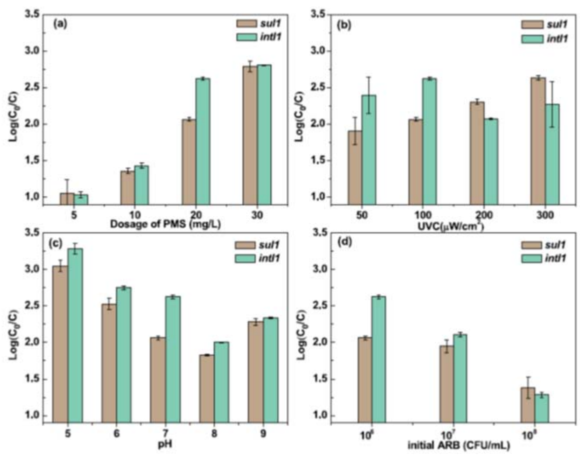


Fig. 6. Impact factors on the removal of target ARGs during UVC/PMS ((a) PMS dosage; (b) UVC intensity (50, 100, 200, 300 $\mu W/cm^2$: 30, 60, 120, 180 mJ/cm^2; (c) pH; (d) initial ARB concentration).

Effect of AOPs on AR

- ✓Most of the studies have been focused on the inactivation of specific bacterial indicators (e.g., *E. coli*)…
- ✓but disinfection processes and specifically AOPs can reduce the total amount of bacterial cells only to some extent…

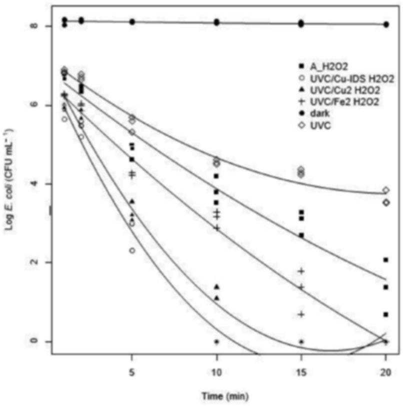


Fig. 5. *E. coli* inactivation by photo-Fenton processes, UV-C/H2O2, UV-C and H2O2. The behaviour of E. coli in absence of treatment is also included (control test in dark).

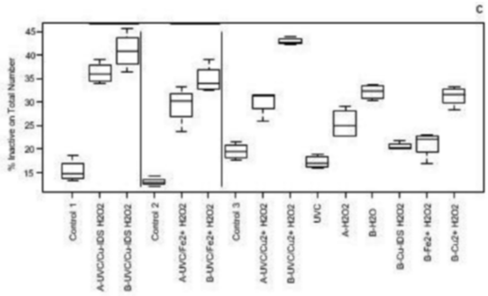


Fig. 6c. Effect of different processes on bacterial population measured by flow cytometry: proportion of inactive cells (C).

Fiorentino et al., 2018. Water Research 146, 206-215,

Effect of AOPs on AR

- ✓…. they can select for the bacterial population (Alexander et al., 2016)…
- ✓… and result in genetic mutation too (Fiorentino et al., 2017)…

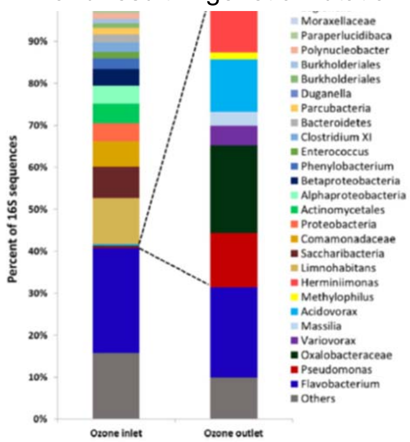


Fig. 3. Classification by 16S rRNA Illumina Amplicon Sequencing before and after ozone application. Only those genera containing ≥1% of sequences are displayed.

Alexander et al., 2016 Sci. Total Environ. 559, 103–112

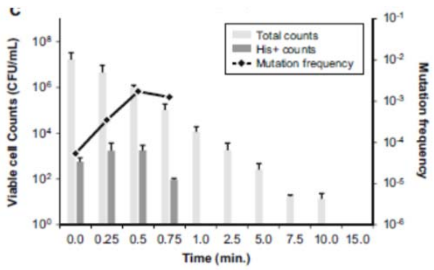


Fig. 2 Effect of TiO_2/UV process on the inactivation and the formation of mutants for three different initial cell loads of strain TA102: 10^9 (**a**), 10^8 (**b**), and 10^7 (**c**) CFU mL^{-1}. *Error bars* represent standard deviation from three independent experiments

Fiorentino et al., 2017. Environmental Science and Pollution Research 24, 1871–1879.

- ✓… thus potentially affecting AR spread

Conclusions/take home messages/pending questions

- ✓AOPs can effectively reduce CECs in secondary treated urban wastewater however, due to the formation of oxidation intermediates…
- ✓….toxicity should be monitored to find the right time to stop the process and make treated ww less toxic.
- ✓AOPs can inactivate different bacteria but, in doing so, they also select for bacterial population …
- ✓…will this finally affect antibiotic resistance transfer and spread?
- ✓The effect of AOPs on ARGs depends on the AOP, target ARGs, ww characteristics and operating conditions, which may be not sustainable at full scale …
- ✓…further work is needed to evaluate if AOPs can effectively control antibiotic resistance spread.

Acknowledgements

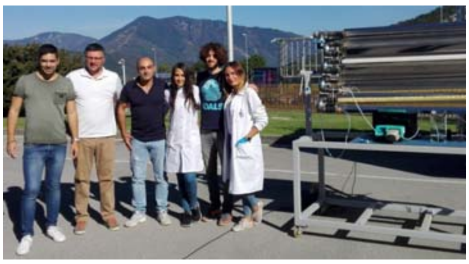
University of Salerno (UNISA)

DICIV
Teresa Agovino
Giusy Cerreta
Giovanna Ferro
Antonino Fiorentino[1]
Gulnara Maniakova
Ian Zammit

DIIn
Giusy Iervolino
Olga Sacco
Diana Sannino
Vincenzo Vaiano

DCB
Stefano Castiglione
Maurizio Carotenuto
Angela Cicatelli
Raffaele Cucciniello
Francesco Guarino
Giusy Lofrano
Antonio Proto

UNINA
Marco Guida
Giovanni Libralato



IRSA-CNR
Gianluca Corno
Andrea Di Cesare
Ester Eckert
Giuseppe Mascolo
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