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ICRAPHE

4th INTERNATIONAL CONFERENCE ON RISK ASSESSMENT OF PHARMACEUTICALS IN THE ENVIRONMENT

Barcelona, 9-10 October 2023

RECLAIMED WASTEWATER: TREATMENTS AND RISK ASSESSMENT

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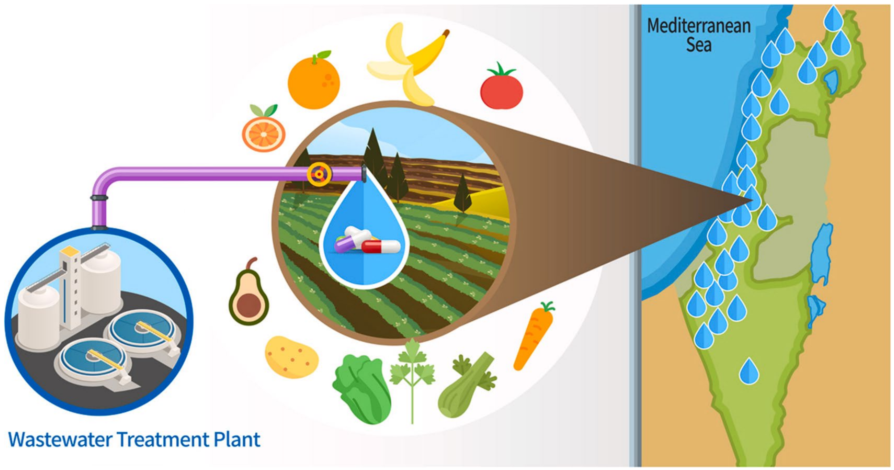
Main issues addressed




Journal of Hazardous Materials
Volume 416, 15 August 2021, 126184

Pharmaceuticals in edible crops irrigated with reclaimed wastewater: Evidence from a large survey in Israel

Evyatar Ben Mordechay, Vered Mordehay, Jorge Tarchitzky, Benny Chefetz

- ✓ Polishing treatments in reclamation facilities: CEC removal capacity
- ✓ Environmental risk residual due to CECs
- ✓ Fate of CECs in the soil
- ✓ Fate of CECs in crops
- ✓ Human and environmental risk assessment
- ✓ Some remarks

Starting point: the release of a (municipal) WWTP

WWTP of Ferrara, Italy

WWTP in Johannesburg: secondary clarifier

WWTP release in Po River, Italy

An in depth analysis of the secondary effluent

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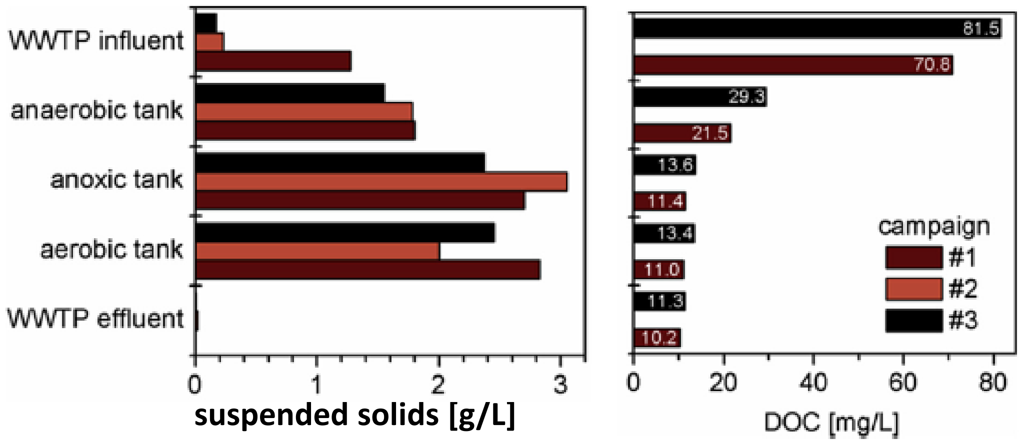
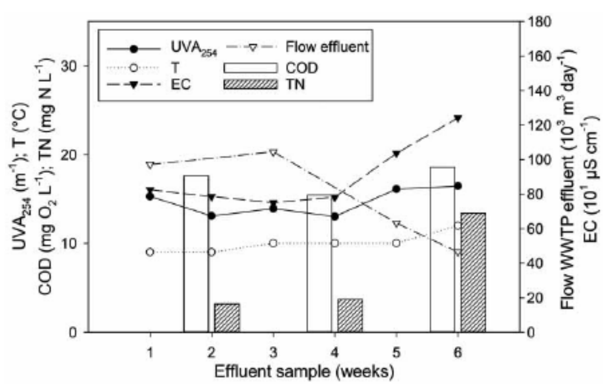
***Regulated** compounds* in the discharged effluent fulfill their legal limits

***Unregulated** compounds* may be still present in the discharged effluent



- DOC = 5-20 mg/L (much higher than the concentration of *trace organic contaminants*, namely PhCs, CECs, micropollutants MP in general)
- UV_{254} = 25-28 1/m

also: N compounds, P compounds, *E. coli*,…



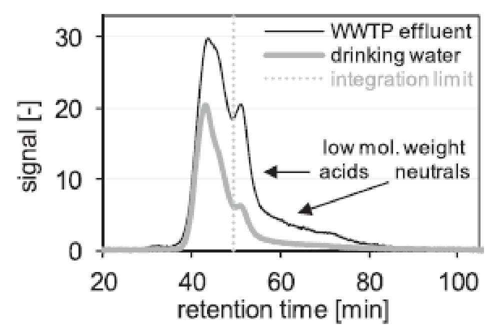


Fig. 1. LC-OCD chromatograms of the WWTP effluent and the drinking water with low molecular weight acids and neutrals indicators and corresponding integration limit.

Table 1
Characterization of differently spiked drinking waters and WWTP effluents.

	Spiking level	DOC [mg C/L]	UV_{254} [1/m]	SUVA [L/mg/m]	LMW organics concentration [mg C/L]	LMW organics UV_{254} [1/m]
drinking water	low	4.9	10.6	2.2	1.1	1.9
	med.	4.9	11.0	2.2	–	–
	high	5.0	11.8	2.4	–	–
WWTP effluent	low	10.7	25.9	2.4	4.5	9.2
	med.	10.8	26.5	2.5	–	–
	high	10.7	27.5	2.6	–	–

van Gijn et al 2022; Gutierrez et al., 2021, Zietzschmann et al.2016, Stretcher et al.,2016, Chys et al.,2017

Risk due to PhCs in a secondary effluent

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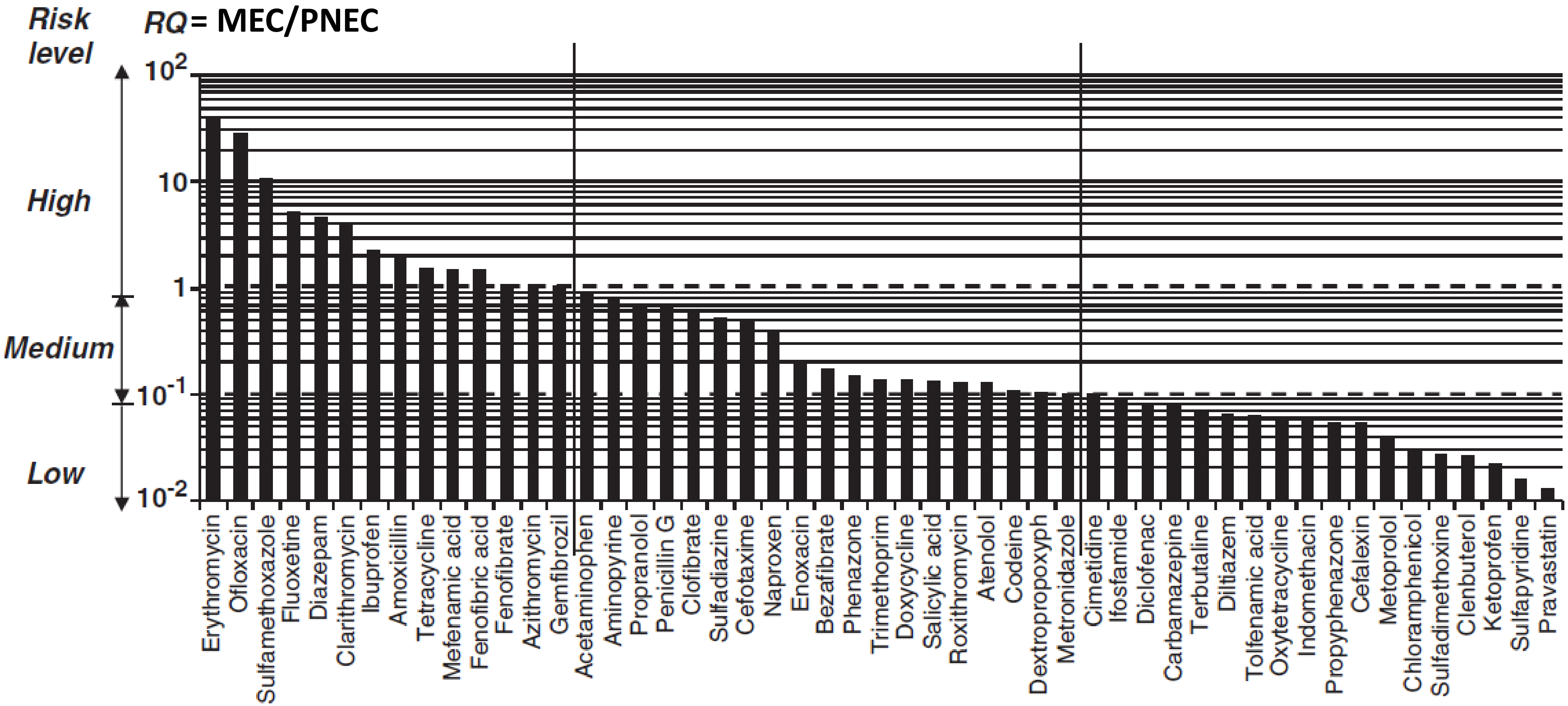
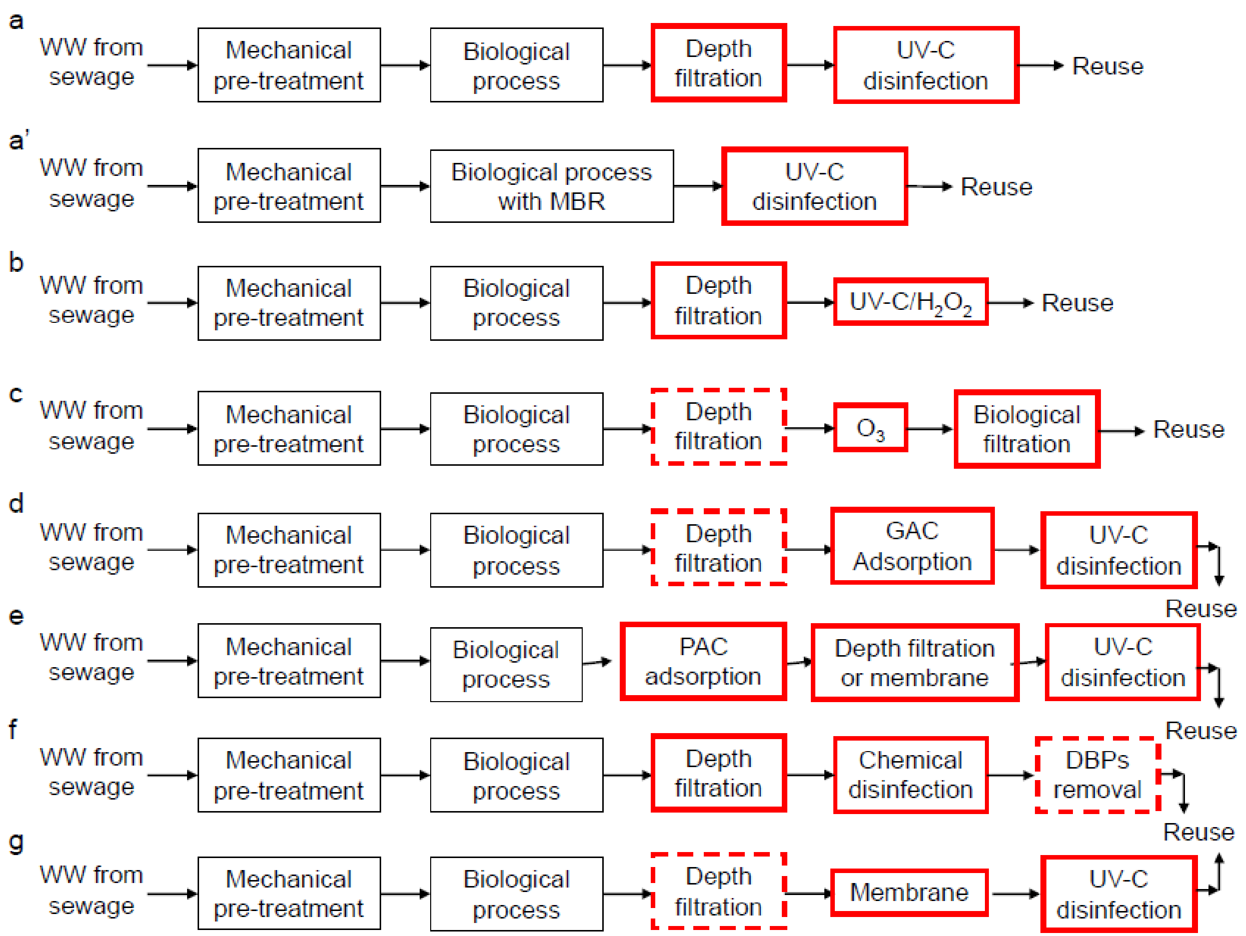


Verlicchi et al., 2012 *Stoten*

Treatment trains: different options



Advanced treatment

Process application evaluated case by case.

additional options by replacing "biological process" with "MBR" for treatment trains from "b" to "f" and by removing depth filtration.

Slow Sand Filtration (biofiltration) of a rapid filter effluent

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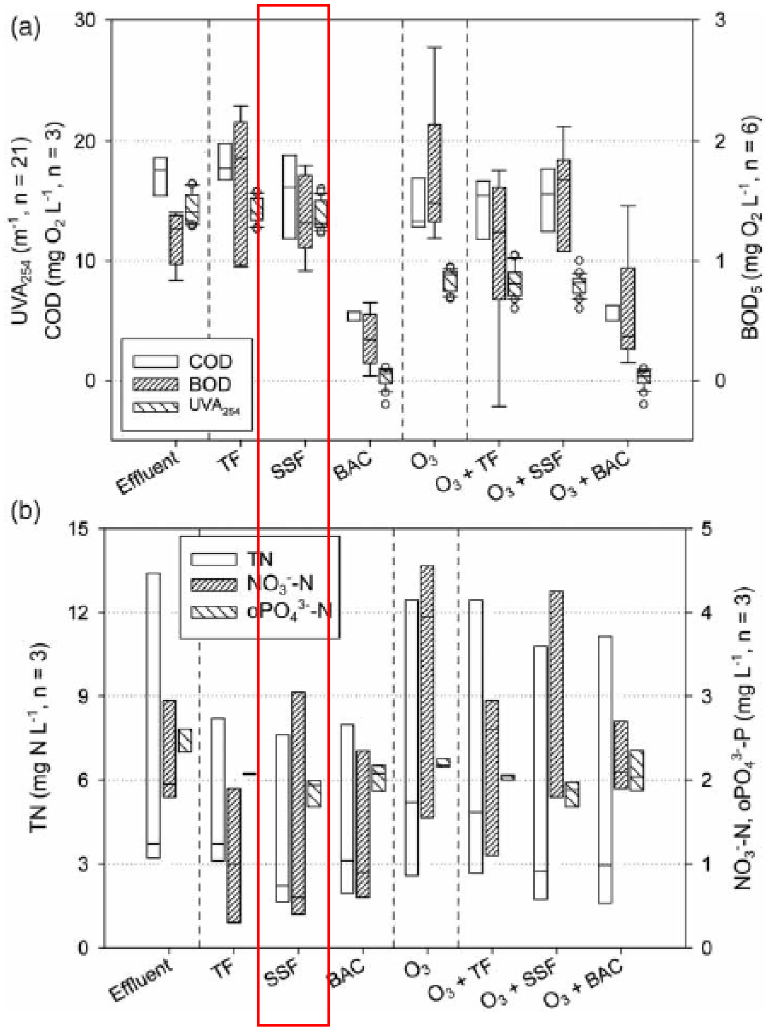
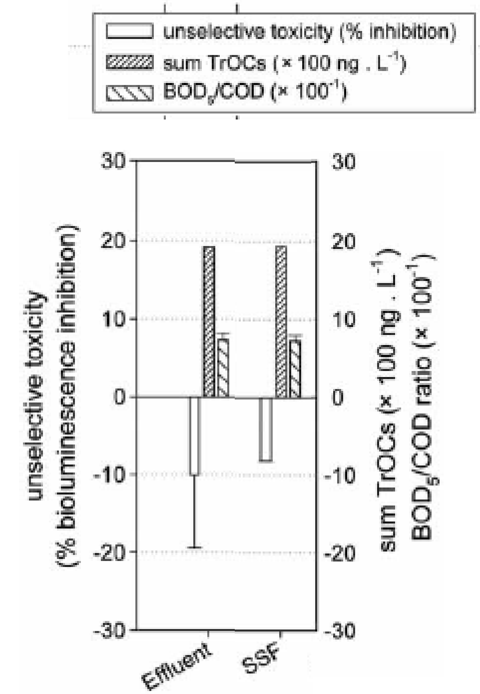


Figure 3 | Physical-chemical water characteristics before and after (combined) treatment: (a) UVA_{254} (m^{-1}), COD and BOD_5 ($mg\ O_2\ L^{-1}$) and (b) nutrients TN, NO_3^--N ($mg\ N\ L^{-1}$) and oPO_4^{3-}-P ($mg\ P\ L^{-1}$). The number of samples of each characteristic is indicated on the left or right y-axis.

TrOCs	Effluent ng. L^{-1}	SSF %
Alprazolam	3	n.r.
Amantadine	45	n.r.
Amitriptyline	35	46
Carbamazepine	487	n.r.
Ciprofloxacin	71	bdl
Diazepam	2	n.r.
Diclofenac	506	n.r.
Flumequine	5	10
Indomethacin	48	bdl
Levofloxacin	30	83
Metronidazole	24	76
Nalidixic acid	5	15
Nevirapine	8	n.r.
Paracetamol	132	51
Sulfamethoxazole	24	n.r.
Tetracycline	50	32
Trimethoprim	74	n.r.
Venlafaxine	367	n.r.

n.r. means removal efficiency < 10%;
bdl means below detection limit (< lod)



Chrys et al.,2017

Disinfection

Chlorine dioxide

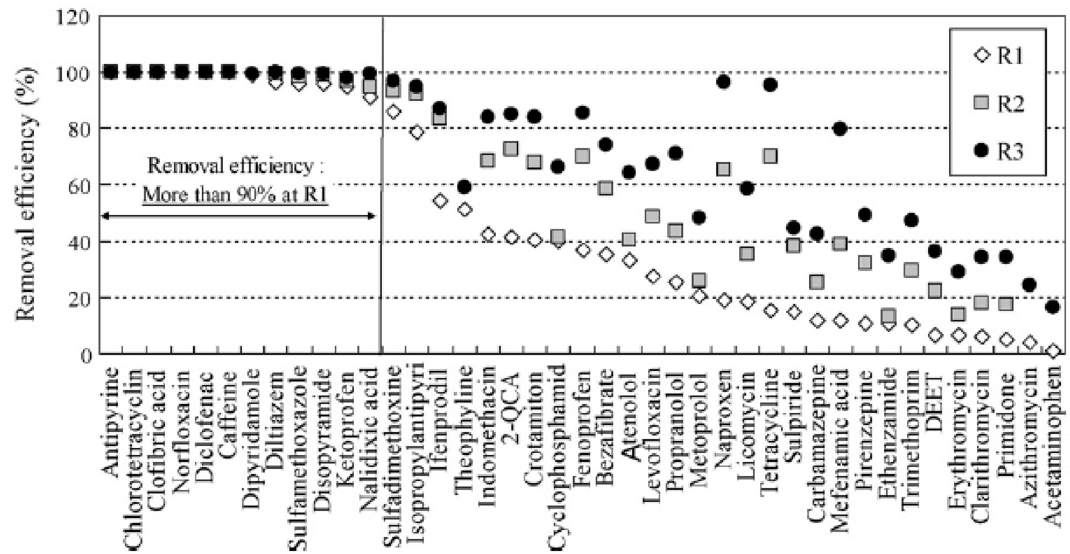
API	Outlet from MBR	60 mg/l 15 min	60 mg/l 120 min
ac-sulfadiazine	80		
ac-sulfamethoxaz.	1,100		
Amoxicillin	<5		
Atenolol	1,500	15	16
Azithromycin	1,100	430	220
Bisoprolol	34	20	19
Capecitabine	16		
Carbamazepine	2,200	2,100	1,800
Cefuroxime	<25		
Ciprofloxacine	4,800	113,000	32,000
Citalopram	750	220	210
Clarithromycin	920	410	390
Clindamycin	130	4	3
Cyclophosphamide	19		
Diclofenac	<5	1	5
Erythromycin	540		
Erythromycin deh.	780		
Fenofibrat	13		
Furosemide	5,400		
Ibuprofen	1,100		
Ifosfamide	120		
Metoprolol	1,200	1,900	1,900
MTX	<2		
Oxcarbazepine	<1		
Paracetamol	<1		
Phenanzon	190		
Propranolol	300		
Roxithromycin	180	28	22

API	Outlet from MBR	60 mg/l 15 min	60 mg/l 120 min
Sotalol	300	4	2
Sulfadiazine	23		
Sulfamethizole	45		
Sulfamethoxazole	680	520	660
Tramadol	1,200	860	440
Trimethoprim	3,200	2,100	2,200
Venlafaxin	550	250	170
Amidotrizoeacid	65,500		
Iohexol	550,000		
Iopromide	1,000,000		
Ioversol	330,000		

Nielsen et al., 2013

UV radiation *Kim et al., 2009*

3 reactors in series, a dose of 923 mJ/cm^2 each



Ozonation

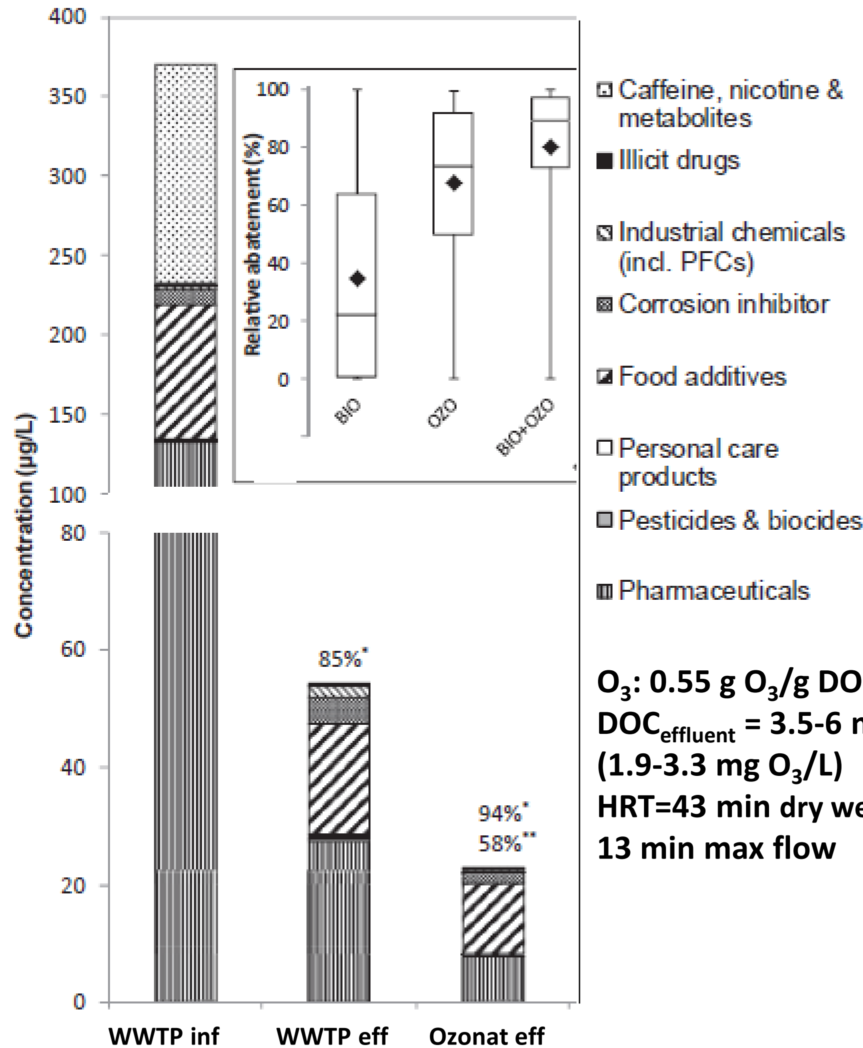
Concentrations [ng/L]

API	Outlet from MBR	Ozone 82 mg O$_3$/l 10 min	Ozone 156 mg O$_3$/l 20 min
ac-sulfadiazine	80	<5	<5
ac-sulfamethoxaz.	1,100	780	67
Amoxicillin	<5	<5	<5
Atenolol	1,500	<10	<10
Azithromycin	1,100	<5	<5
Bisoprolol	34	7.9	6.3
Capecitabine	16		<10
Carbamazepine	2,200	<5	<5
Cefuroxime	<25	<25	<25
Ciprofloxacine	4,800	650	250
Citalopram	750	45	27
Clarithromycin	920	51	12
Clindamycin	130	16	<5
Cyclophosphamide	19	9.7	<5
Diclofenac	<5	51	<5
Erythromycin	540	<20	<20
Erythromycin deh.	780	<20	<20
Fenofibrat	13	<12.5	<12.5
Furosemide	5,400	<25	<25
Ibuprofen	1,100	190	12
Ifosfamide	120	35	8.6
Metoprolol	1,200	31	17
MTX	<2	<2	<2
Oxcarbazepine	<1	<1	<1
Paracetamol	<1	<1	<1
Phenanzon	190	<10	<10
Propranolol	300	<2	<2
Roxithromycin	180	16	7.9

Nielsen et al., 2013 WST

Swiss Regulation (Micropoll strategy): suggested activated carbon and ozonation for large WWTPs; requested 80% removal for a selection of OMPs (among those listed in the act).

Removal achieved at Neugut WWTP, Switzerland (150 000 PE). **Ozonation**. Investigation on **550 MPs**



O_3: 0.55 g O_3/g DOC
$DOC_{effluent}$ = 3.5-6 mg/L
(1.9-3.3 mg O_3/L)
HRT=43 min dry weather, 13 min max flow

Bourgin et al., 2018 Water Research

Too many compounds to look after.
Removal of a subgroup under different ozone dosages (HRT 43 min)

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	0.35 ± 0.02 g O_3/g DOC			0.54 ± 0.05 g O_3/g DOC			0.67 ± 0.03 g O_3/g DOC			0.97 ± 0.07 g O_3/g DOC		
	BIO	OZO	BIO + OZO	BIO	OZO	BIO + OZO	BIO	OZO	BIO + OZO	BIO	OZO	BIO + OZO
Acesulfame	95 ± 1	39 ± 5	97 ± 1	90 ± 8	59 ± 9	96 ± 3	95 ± 1	70 ± 8	98 ± 1	88 ± 5	>90 ± 4	>99 ± 1
Aliskiren	25 ± 4	>84 ± 1	>88 ± 1	23 ± 22	>93 ± 1	>95 ± 1	7 ± 12	>81 ± 1	>82 ± 3	8 ± 11	>92 ± 3	>93 ± 2
Amisulpride[e]	2 ± 14	91 ± 1	91 ± 2	3 ± 16	>98 ± 1	>98 ± 1	−1 ± 13	>95 ± 1	>95 ± 1	3 ± 8	>98 ± 1	>98 ± 1
Atenolol	75 ± 3	70 ± 2	92 ± 1	70 ± 5	92 ± 3	98 ± 1	72 ± 5	93 ± 5	98 ± 1	71 ± 4	>93 ± 1	>98 ± 1
Atenolol acid	76 ± 2	70 ± 3	93 ± 1	72 ± 3	91 ± 3	98 ± 1	67 ± 4	>92 ± 4	>97 ± 1	69 ± 3	>98 ± 1	>99 ± 1
Azithromycin	8 ± 28	>90 ± 1	>90 ± 3	n.m.2	>54 ± 3	n.m.	25 ± 14	>88 ± 2	>91 ± 3	23 ± 15	>95 ± 1	>96 ± 1
Benzotriazole[e]	66 ± 3	52 ± 1	83 ± 1	62 ± 7	74 ± 3	90 ± 3	63 ± 6	80 ± 7	93 ± 2	64 ± 3	91 ± 4	97 ± 1
Bezafibrate	96 ± 1	>62 ± 5	>98 ± 1	>95 ± 2	>75 ± 1	>99 ± 1	>93 ± 2	n.m.1	>97 ± 1	>94 ± 1	>24[d]	>97 ± 2
Candesartan[e]	0 ± 16	63 ± 1	63 ± 6	1 ± 12	82 ± 3	82 ± 5	−24 ± 20	85 ± 6	81 ± 6	−17 ± 19	94 ± 3	93 ± 3
Carbamazepine[e]	−16 ± 12	95 ± 1	94 ± 1	−14 ± 19	>98 ± 1	>98 ± 1	−33 ± 23	>98 ± 1	>98 ± 1	−24 ± 8	>98 ± 1	>98 ± 1
Carbendazim	8 ± 18	82 ± 2	83 ± 5	−1 ± 23	>94 ± 3	>94 ± 4	7 ± 16[c]	>93 ± 5	>89 ± 8[c]	−28 ± 50	>89 ± 4	>86 ± 9
Cetirizine	6 ± 12	92 ± 1	92 ± 2	−9 ± 12	>93 ± 1	>92 ± 1	−25 ± 25	>95 ± 1	>94 ± 1	−19 ± 10	>95 ± 1	>94 ± 1
Citalopram[e]	5 ± 4[c]	91 ± 3	89 ± 4[c]	4 ± 4	>96 ± 3	>96 ± 3	−8 ± 2	>94 ± 1	>93 ± 1	4 ± 8	>97 ± 1	>97 ± 1
Clarithromycin[e]	51 ± 2	93 ± 2	97 ± 1	28 ± 19	>95 ± 1	>96 ± 1	45 ± 6	>94 ± 1	>97 ± 1	52 ± 8	>97 ± 1	>99 ± 1
DEET	96 ± 1	49 ± 9	98 ± 1	>90 ± 3	65 ± 1	>95 ± 2	97 ± 1	52 ± 18	99 ± 1	97 ± 1	70 ± 15	99 ± 1
Diclofenac[e]	22 ± 8	96 ± 1	97 ± 1	23 ± 8	100 ± 1	100 ± 1	11 ± 10	>99 ± 1	>99 ± 1	13 ± 18	>99 ± 1	100 ± 1
Diuron	0 ± 30	64 ± 2	64 ± 10	−7 ± 7	>84 ± 8	>83 ± 10	−5 ± 14	>84 ± 6	>84 ± 4	−40 ± 72[c]	>90 ± 6	>79 ± 20[c]
Eprosartan	98 ± 1	>66 ± 3	>99 ± 1	>93 ± 2	n.m.1	>97 ± 1	>97 ± 1	>67 ± 7	>99 ± 1	>88 ± 5	n.m.1	>94 ± 3
Fexofenadine	13 ± 16	83 ± 3	85 ± 6	9 ± 4	>94 ± 1	>95 ± 1	12 ± 12	>96 ± 3	>97 ± 2	−1 ± 12	>91 ± 1	>91 ± 2
Gabapentin	44 ± 10	44 ± 4	69 ± 6	43 ± 6	55 ± 4	75 ± 1	37 ± 5	63 ± 10	77 ± 6	44 ± 5	75 ± 6	86 ± 3
Hydrochlorothiazide[e]	9 ± 13	86 ± 2	87 ± 4	13 ± 9	>98 ± 2	>98 ± 2	−2 ± 17	>97 ± 3	>97 ± 2	1 ± 10	>99 ± 1	>99 ± 1
Iopromide	72 ± 5	28 ± 1	80 ± 4	70 ± 8	43 ± 3	83 ± 5	53 ± 20	53 ± 6	78 ± 8	64 ± 8[c]	65 ± 1[c]	88 ± 3[c]
Irbesartan[e]	17 ± 18	57 ± 1	64 ± 8	15 ± 15	75 ± 3	78 ± 5	2 ± 20	79 ± 4	79 ± 6	0 ± 25	89 ± 4	89 ± 1
Lamotrigine	−125 ± 31	37 ± 1	−42 ± 18	−128 ± 10	50 ± 2	−15 ± 4	−140 ± 30	57 ± 7	−3 ± 21	−132 ± 5	71 ± 6	32 ± 13
Levetiracetam	99 ± 1	>66 ± 34	100 ± 1	98 ± 1	>43 ± 36	>99 ± 1	>99 ± 1	n.m.1	100 ± 1	>99 ± 1	n.m.1	100 ± 1
Losartan	71 ± 2	93 ± 1	98 ± 1	68 ± 5	>98 ± 1	>99 ± 1	66 ± 5	>98 ± 1	>99 ± 1	67 ± 4	>98 ± 1	>99 ± 1
Mecoprop	−5 ± 2[c]	59 ± 2	56 ± 1[c]	14 ± 7[c]	77 ± 2	81 ± 4[c]	5 ± 30	82 ± 7	84 ± 5	9 ± 14[c]	>91 ± 3	91 ± 1[c]
Metoprolol[e]	41 ± 7	75 ± 2	85 ± 3	38 ± 5	94 ± 3	96 ± 2	37 ± 8	94 ± 5	96 ± 3	38 ± 4	>99 ± 1	>99 ± 1
Methylbenzotriazole[a,e]	45 ± 22	66 ± 3	81 ± 9	61 ± 4	89 ± 4	96 ± 2	2 ± 22	90 ± 1	90 ± 7	28 ± 12	98 ± 1	99 ± 1
N4-Acetyl-Sulfamethoxazole	>98 ± 1	n.m.1	>99 ± 1	>98 ± 1	n.m.1	>99 ± 1	>98 ± 1	n.m.	>99 ± 1	>95 ± 2	n.m.1	>97 ± 1
Oxazepam	5 ± 17	55 ± 1	57 ± 7	10 ± 10	73 ± 3	75 ± 5	−13 ± 22	77 ± 5	74 ± 6	−10 ± 9	88 ± 4	87 ± 3
Phenazone	n.m.2	>91 ± 1	n.m.1	n.m.2	>92 ± 1	n.m.1	n.m.2	>92 ± 1	n.m.1	n.m.2	>81 ± 4	n.m.1
Primidone	19 ± 12	48 ± 3	58 ± 5	15 ± 17	66 ± 1	72 ± 6	14 ± 14	70 ± 10	75 ± 7	−4 ± 8	86 ± 5	86 ± 5
Ranitidine	82 ± 1	>74 ± 2	>95 ± 1	79 ± 4	>80 ± 4	>96 ± 1	66 ± 16	>71 ± 2	>90 ± 5	77 ± 2	>53 ± 19	>89 ± 6
Sucralose	9 ± 20	21 ± 2	28 ± 14	13 ± 13	27 ± 1	36 ± 10	−9 ± 17	38 ± 4	32 ± 12	−4 ± 13	46 ± 4	44 ± 6
Sulfamethoxazole	55 ± 3	85 ± 2	93 ± 1	46 ± 6	>97 ± 1	>98 ± 1	31 ± 6	>97 ± 1	>98 ± 1	34 ± 2	>95 ± 3	>96 ± 2
Telmisartan	15 ± 3	66 ± 1	71 ± 1	3 ± 16	86 ± 3	86 ± 4	−24 ± 27	88 ± 5	84 ± 8	−7 ± 18	>94 ± 1	>94 ± 1
Tramadol[b]	0 ± 11	91 ± 1	90 ± 3	2 ± 7	98 ± 1	98 ± 1	−5 ± 11	>98 ± 1	>98 ± 1	−6 ± 10	>98 ± 1	>98 ± 1
Triclosan	n.m.1	n.m.1	n.m.1	n.m.1	n.m.1	n.m.1	n.m.1	>56 ± 1	n.m.1	n.m.1	n.m.1	n.m.1
Trimethoprim	>89 ± 4	>59 ± 6	>95 ± 1	85 ± 6	>61 ± 15	>95 ± 1	75 ± 6	>58 ± 4	>90 ± 1	83 ± 3	>79 ± 3	>97 ± 1
Valsartan	94 ± 1	52 ± 3	97 ± 1	93 ± 2	69 ± 3	98 ± 1	96 ± 1	68 ± 8	99 ± 1	93 ± 1	>86 ± 3	>99 ± 1
Valsartan acid	n.m.2	49 ± 1	n.m.1	n.m.2	67 ± 1	n.m.1	n.m.2	71 ± 5	n.m.1	n.m.2	76 ± 8	n.m.1
Venlafaxine[e]	4 ± 15	84 ± 2	84 ± 5	9 ± 10	>97 ± 2	>97 ± 2	−12 ± 17	>96 ± 3	>96 ± 2	1 ± 5	>96 ± 1	>96 ± 1
Average of the 12 indicator substances[e]	17 ± 8	79 ± 1	85 ± 3	20 ± 7	>91 ± 2	>94 ± 2	7 ± 8	>92 ± 3	>93 ± 2	14 ± 9	>96 ± 1	>97 ± 1

Subgroup of 43 OMPs and among these, a subgroup of **12 non-easily degradable (in bold)**

Bourgin et al., 2018 Water Research

Some considerations…

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To comply with the guidelines established by the Swiss authorities for the evaluation of advanced wastewater treatment, **12 indicator substances need to be eliminated by 80% on average over the whole treatment chain** (the bold ones in the table).

These 12 indicator substances were abated by 2-44% during biological treatment (BIO), except benzotriazole (64 ± 4%).

The average abatement increased to 85 ± 3% when the biological treatment was followed by a low specific ozone dose (0.35 g O_3/g DOC) and even **up to >94%** when the specific ozone dose was 0.54 g O_3/g DOC.

Ozonation → generation of transformation compounds and oxidation byproducts → **potential increment in the ecotoxicity**

An additional post treatment is necessary to eliminate potential ecotoxicological negative effects posed by ozonation transformation products and oxidation byproducts: sand filtration, moving bed, fixed bed, but also GAC

Bourgin et al., 2018 Water Research

Toxicity increases after ozonation

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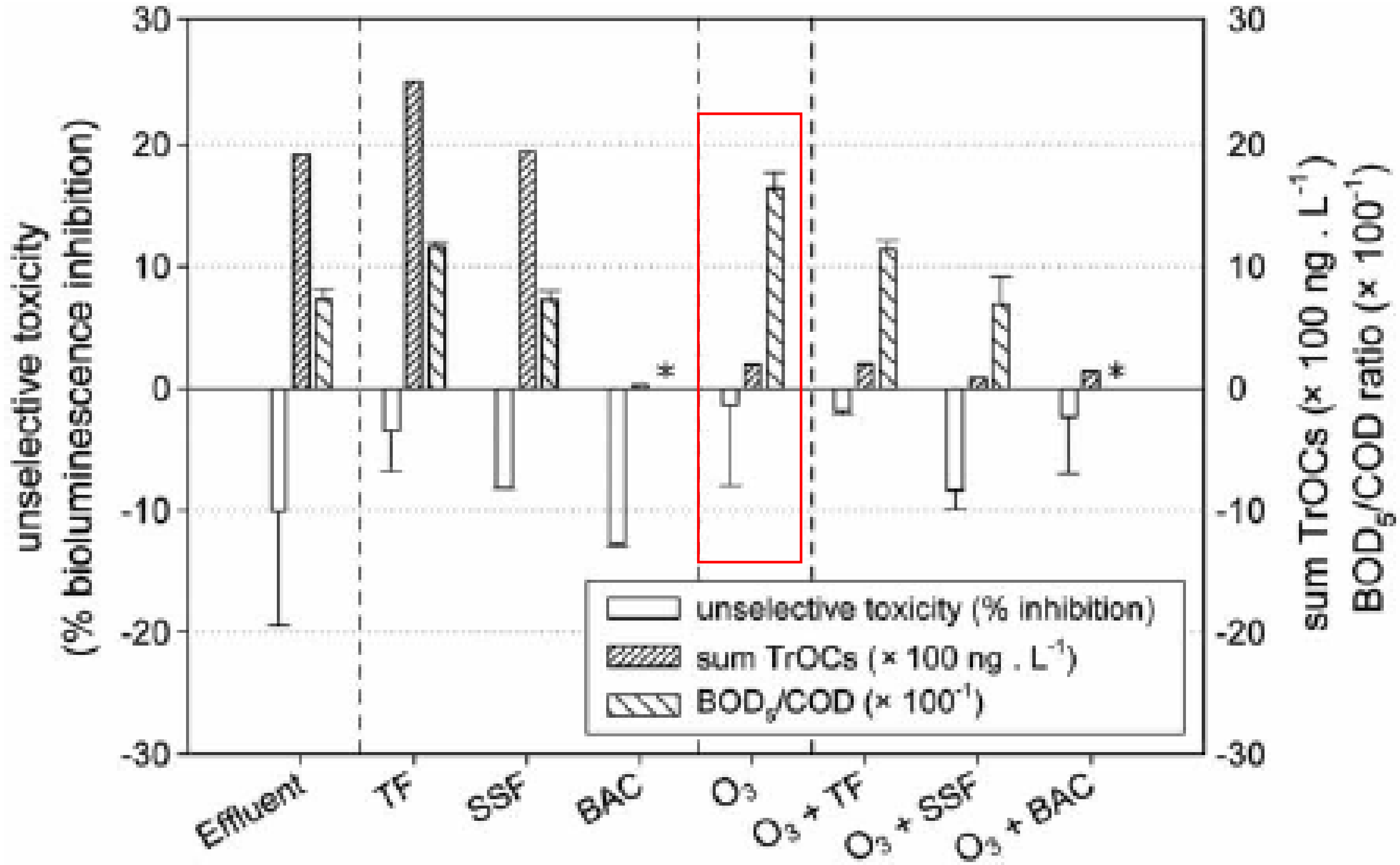

Especially for **ozonation**, an **increase of the BOD$_5$/COD ratio** (from 0.07 to 0.16) indicates **changes in the water matrix** with the formation of **smaller and more biodegradable moieties**, which have been **associated to an increased toxicity**.

Chys et al, 2017

Different treatment trains tested

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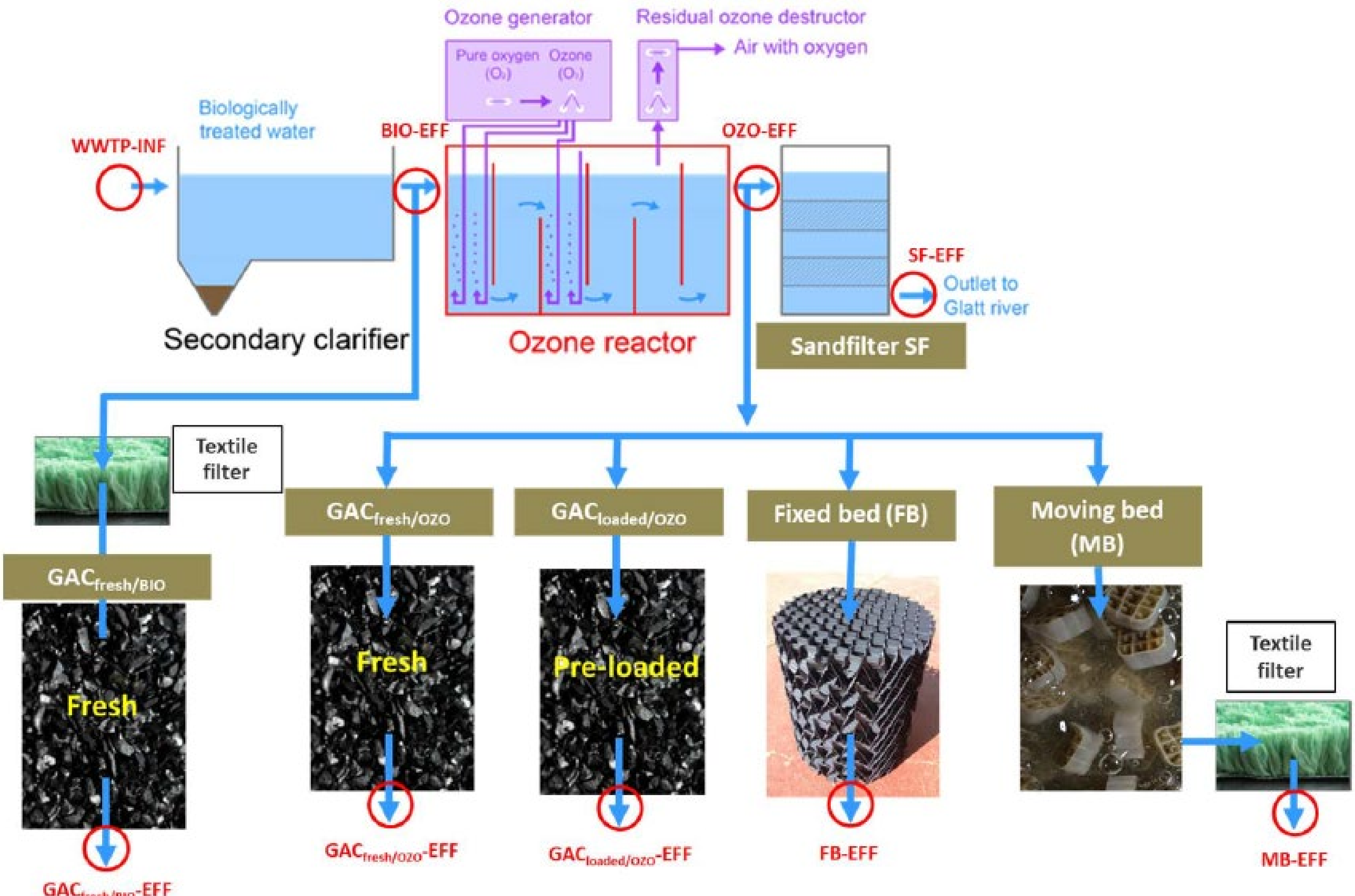

Process flow diagram of the WWTP Neugut including the full-scale ozonation reactor and various post-treatments.

Bourgin et al., 2018 Water Research

Some results

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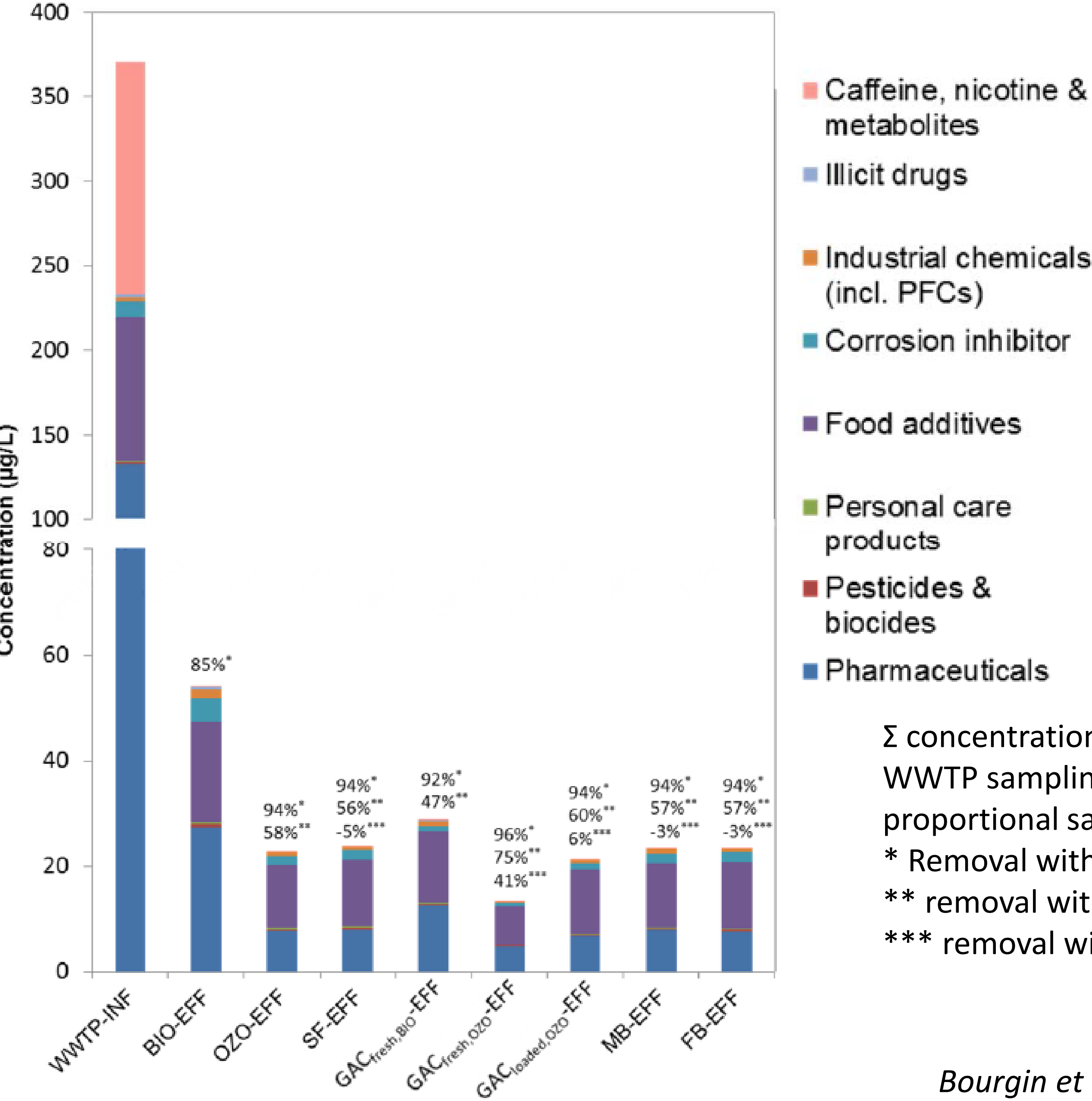

Σ concentrations of micropollutants at various WWTP sampling points; (n = 2, 48-h flow proportional samples, dose 0.55 g O_3/g DOC,

* Removal with respect to WWTP-INF

** removal with respect to BIO-EFF

*** removal with respect to OZO-EFF

Bourgin et al., 2018 Water Research

BAC and O_3

WWTP effluent

	BAC		
Flowrate (L/h)	3.62	0.91	0.37
EBCT (h)	0.33	1.32	3.21
Sulfamethoxazole	-21	88	54
Diclofenac	70	>95	>95
Trimethoprim	86	>95	92
Carbamazepine	44	76	73
Propanolol	92	>95	>95
Erythromycin	70	>95	>95
Furosemide	65	>95	>95
Clarithromycin	79	>95	>95
Sotalol	83	>95	>95
Atenolol	80	>95	94
Caffeine	68	92	NA
4 and 5 methylbenzotriazole	71	90	80
Metoprolol	63	>95	86
Dimetridazole	57	70	69
Mecoprop	45	82	67
Irbesartan	16	91	76
Benzotriazole	24	60	62
2,4-D	60	82	75
DEET	28	89	81
BAM	40	67	60

Removal in BAC filter at three flowrates. Removal in% is shown with a color scale from 0 (red) to >95 (green). NA means not analyzed.

WWTP effluent

	BAC	BO_3			O_3		
Specific ozone dose (g O_3/g TOC)	0	0.18	0.36	0.55	0.20	0.39	0.59
Absolute ozone dose (mg O_3/L)	0	2.1	4.2	6.4	3.2	6.5	9.7
Sulfamethoxazole	88	>95	>95	>95	79	>95	>95
Diclofenac	>95	>95	>95	>95	79	>95	>95
Trimethoprim	>95	>95	>95	>95	77	>95	>95
Carbamazepine	76	>95	>95	>95	67	>95	>95
Propanolol	>95	>95	>95	>95	74	>95	>95
Erythromycin	>95	>95	>95	>95	80	>95	>95
Furosemide	>95	>95	>95	>95	92	>95	>95
Clarithromycin	>95	>95	>95	>95	72	93	94
Sotalol	>95	>95	>95	>95	81	>95	>95
Atenolol	>95	>95	>95	>95	39	73	92
Caffeine	92	>95	>95	>95	41	66	87
4 and 5 methylbenzotriazole	90	>95	>95	>95	41	76	90
Metoprolol	>95	>95	>95	>95	45	79	94
Dimetridazole	70	87	>95	>95	34	66	84
Mecoprop	82	92	>95	>95	37	69	84
Irbesartan	91	>95	>95	>95	57	80	88
Benzotriazole	60	83	>95	>95	40	71	87
2,4-D	82	91	>95	>95	29	68	81
DEET	89	>95	>95	>95	34	72	84
BAM	67	76	92	>95	28	61	72

Removal in BAC, BAC+O_3 (=BO_3) process (operated at 0.91 L/h, EBCT of 1.32 h) and for O_3 without BAC as a pre-treatment (O_3). Removal in% is shown with a color scale from 0 (red) to >95 (green). TOC concentration before and after BAC filtration were 16.6 and 11.7 mg/L respectively. NA means not analyzed.

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Removal of micropollutants and ecotoxicity during combined biological activated carbon and ozone (BO_3) treatment

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Risk in the two scenarios BAC+O_3 *versus* O_3

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WWTP effluent
8.4 mg TOC/L→

RQ

	Feed	BO₃				O₃		
Ozone dose (g O_3/g TOC) >	0	0	0.18	0.36	0.55	0.20	0.39	0.59
Ozone dose mg O_3/L	0	0	1.5	3.04	4.62	1.68	3.23	5.0
Sulfamethoxazole	1.4	0.1	0.0	0.0	0.0	0.1	0.0	0.0
Diclofenac	16.5	0.0	0.0	0.0	0.0	1.4	0.0	0.0
Trimethoprim	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carbamazepine	22.4	5.0	0.2	0.2	0.2	3.1	0.5	0.2
Propranolol	2.3	0.0	0.0	0.0	0.0	0.3	0.0	0.0
Erythromycin	5.3	0.1	0.0	0.0	0.0	0.5	0.1	0.0
Furosemide	1.5	0.0	0.0	0.0	0.0	0.1	0.0	0.0
Clarithromycine	6.0	0.2	0.1	0.1	0.1	1.0	0.5	0.4
Atenolol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Caffeine	0.9	0.1	0.0	0.0	0.0	0.4	0.2	0.1
4 and 5 methylbenzotriazole	8.4	0.8	0.2	0.1	0.1	3.1	1.7	1.0
Metoprolol	0.3	0.0	0.0	0.0	0.0	0.1	0.0	0.0
Dimetridazole	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mecoprop	1.2	0.2	0.1	0.0	0.0	0.5	0.3	0.2
Irbesartan	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzotriazole	0.3	0.1	0.0	0.0	0.0	0.1	0.1	0.0
2,4-D	1.5	0.3	0.1	0.0	0.0	0.7	0.4	0.3
DEET	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
BAM	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Desphenyl chloridazon	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Van Gijn et al., 2023

UV and UV/H_2O_2

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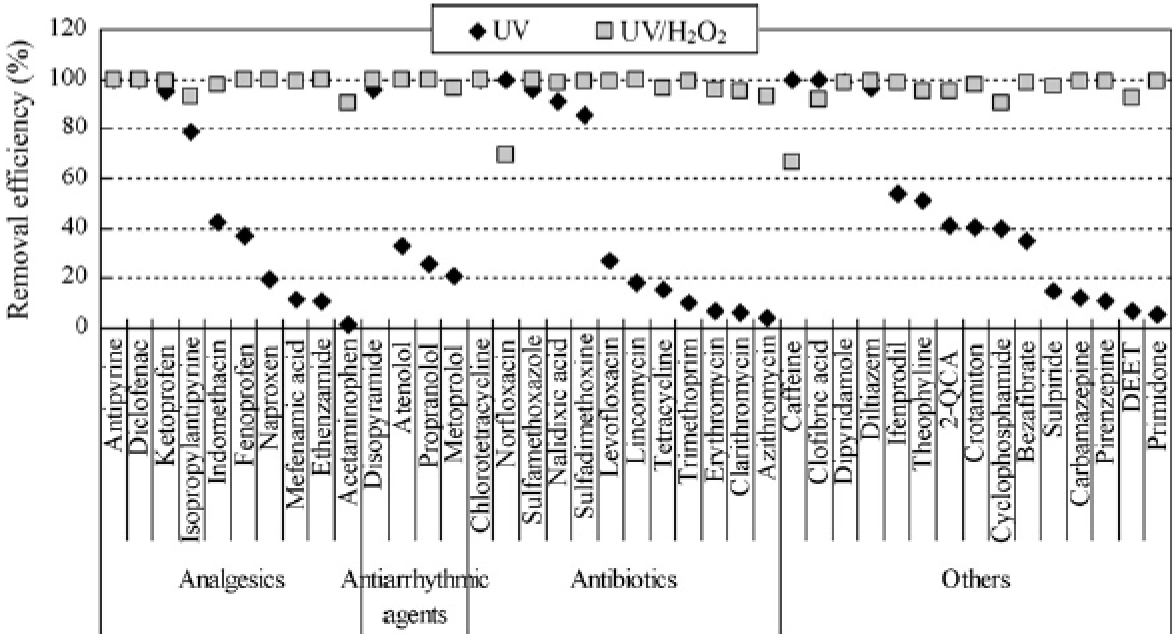

Fig. 4. Removal efficiency of the 41 pharmaceuticals detected during UV and UV/H_2O_2 processes for HRT of 5 min

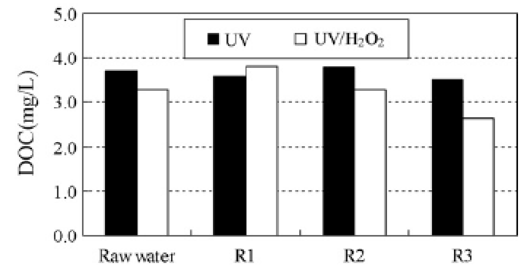

Fig. 5. Variation of DOC concentration during UV and UV/H_2O_2 processes

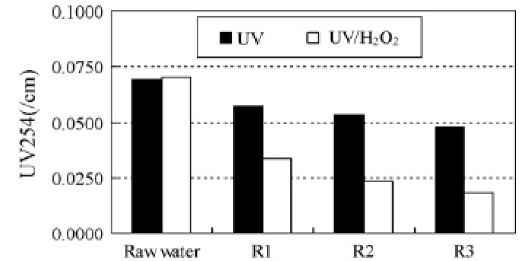

Fig. 6. Variation of UV254 during UV and UV/H_2O_2 processes.

Among 41 PhCs, 29 were not removed effectively in spite of considerable UV dose of **2768 mJ/cm²** during UV process. Therefore, **a good PhC removal can not be expected by UV** process applied for the disinfection of treated water in wastewater treatment plants because UV doses of **40–140 mJ/cm²** are usually used for **water disinfection**.

For UV/ H_2O_2 process, **90% removal efficiency could be accomplished in 39 pharmaceuticals** at UV dose of **923 mJ/cm²**. This means that it is possible to reduce UV energy required for the effective PhCs removal by the combination of H_2O_2 with UV process.

DOC and above all UV254 confirm the different removal level achieved by UV and UV/H_2O_2

Kim et al., 2009

Reclaimed water for reuse:
key (macro)factors influencing the behavior of CECs in the system water-soil-crop

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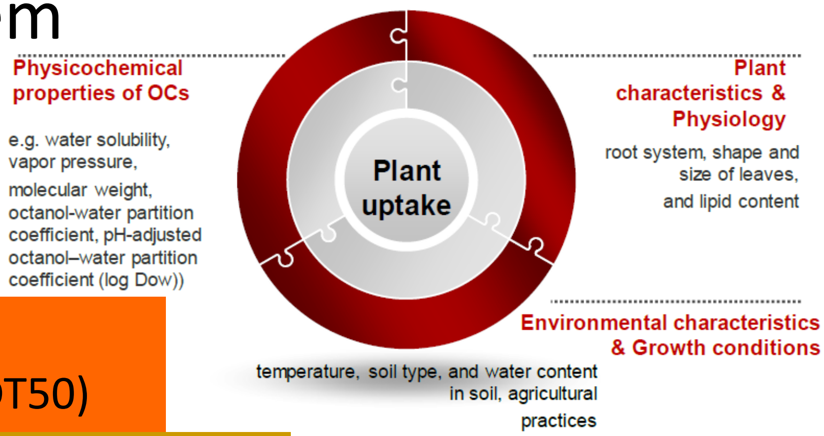

Nereus cost action. D7

CEC concentrations
CEC physico-chemical properties (LogK_{ow}, charge, DT50)

Soil properties (texture, composition, pH, cation exchange capacity, C, content, nutrient content, EC)

Ambient conditions (T, humidity, precipitation pattern)

Plant physiology (leafy vegetable, root, trees) and characteristics

Agronomical **practices**
(irrigation technology, frequency)

Duration of the reuse practice

The SOIL

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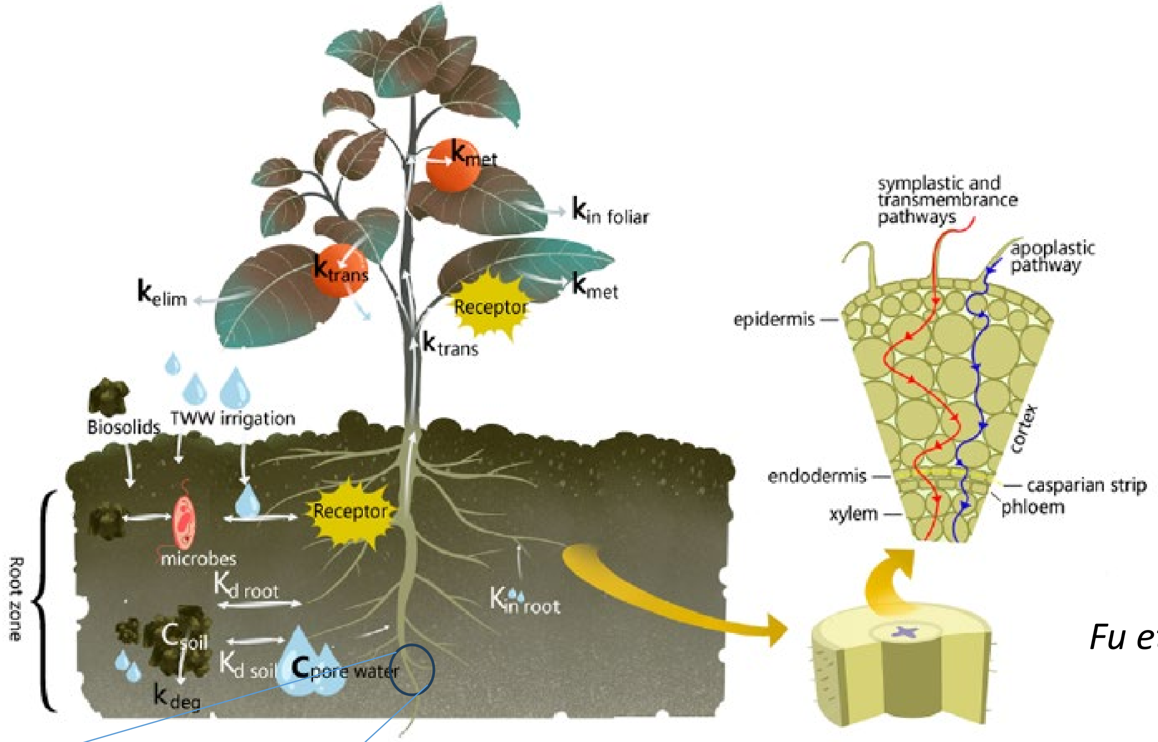
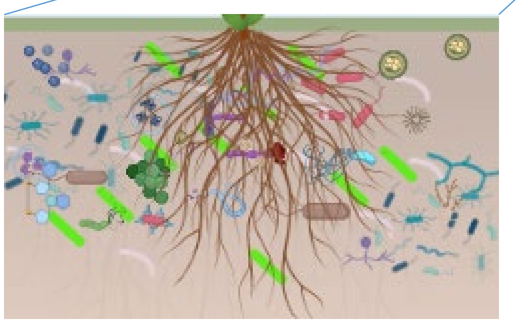


Fu et al., 2019 EST



Soil microrganisms: bacteria, actinomycetes, fungi and algae

Interactions between soil microbioma and plant on a **molecular level**.
Bacteria develop in the rhizosphere.

The processes occurring in this region control a range of reactions, regulating terrestrial carbon and other element cycles.

From: https://fruit.wisc.edu/2023/07/18/beneficial-soil-bacteria-role-in-agriculture/

CECs in the soil

CEC concentrations
CEC physico-chemical properties

Key properties to look at: related to the CEC

- Log K_{ow} (<1 → hydrophilic; >4 hydrophobic) gives a rough idea
- Charge (cationic, anionic and zwitterionic)
- DT_{50} (dissipation time= time needed to degrade 50 % of the CEC initial concentration in cropped soils; e.g. caffeine DT50= 1.5-3 d; Carbamazepine 6.4-693 d, triclosan 18-693 d)

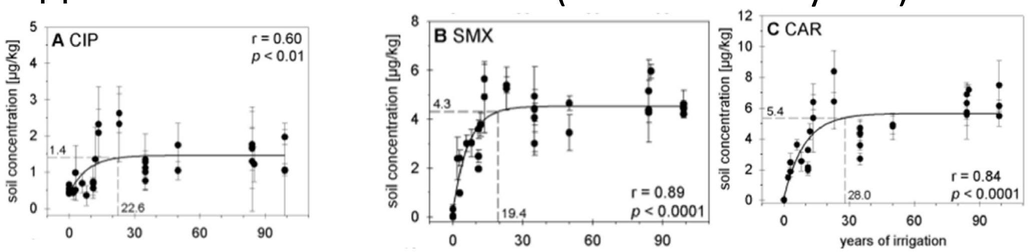
Processes

1. Sorption (→ K_d)
2. Desorption
3. Transformation processes

reducing the CEC concentration **available** for biodegradation and plant uptake.

Bioavailability of a CEC for plant or microorganisms depends on its chemical form related to the (environmental) conditions.

- ➢ Soil properties, such as the **Organic Carbon content**, can inhibit CEC biodegradation reducing their bioavailability.
- ➢ Cation Exchange Capacity, strictly related to the organic substances contents in the soil, increases with prolonged application of reclaimed water (>15 % after 4 years) and influence CEC fate.
- ➢ CECs may accumulate:



Dalkmann t al. 2012

CECs in the soil

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Soil properties (texture, composition, pH, cation exchange capacity, C, content, nutrient content, EC)

Key properties related to the **soil** to look at:

- Soil characteristics: pH, organic carbon content, humidity, cation exchange capacity, nutrient concentration, electrical conductivity
- Soil type: fine/coarse structure; clay/silt/sand contents
- Fungal mycelial network in the top soil, which favor the distribution of microbes within the soil and thus promote the distribution of bioavailable CEC to remote bacteria
- **Hydroponic cultures** have the highest bioconcentration factors due to the lack of soil partitioning. Hydroponics= worse case scenario.
- **Sand-perlite growing medium** exhibits the smallest interaction with contaminants and experimental bioconcentration factors found in crops are similar to those found with hydroponics.

(Banitz et al. 2013)

CECs in the soil?

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Environmental conditions

- Rain events (intensity, duration)
- **High T, increased wind speed, and low air humidity** increase evapotranspiration rates of plants and they increase water and nutrient uptake by plant.

(Banitz et al. 2013)

CECs in the soil: irrigation practices

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- **Drip irrigation** provides the lowest contaminant intake to crops due to the small volume of water locally distributed;
- **Sprinkling irrigation** can lead to a direct contact between dissolved CECs in RWW and the edible parts of crops.

➢ **Dissipation time** (to degrade to 50% of the initial concentration): these values can be smaller than in non cropped soil due to the presence of root exudates enhancing the activity of microorganisms in degrading CECs near the rhizosphere.

Factors affecting crop uptake

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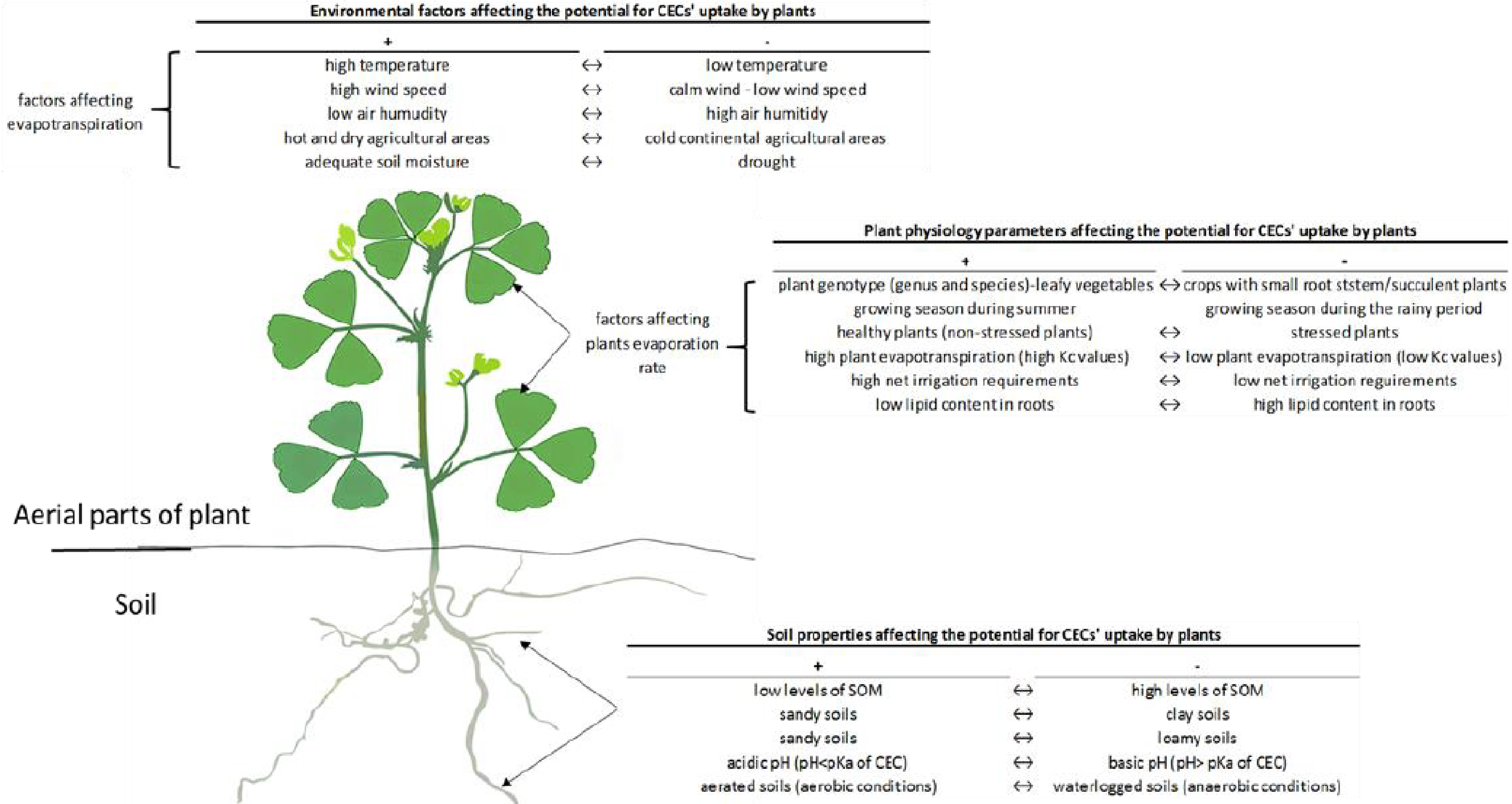


Environmental factors affecting the potential for CECs' uptake by plants

+		-
high temperature	↔	low temperature
high wind speed	↔	calm wind - low wind speed
low air humudity	↔	high air humitidy
hot and dry agricultural areas	↔	cold continental agricultural areas
adequate soil moisture	↔	drought

Plant physiology parameters affecting the potential for CECs' uptake by plants

+		-
plant genotype (genus and species)-leafy vegetables	↔	crops with small root ststem/succulent plants
growing season during summer		growing season during the rainy period
healthy plants (non-stressed plants)	↔	stressed plants
high plant evapotranspiration (high Kc values)	↔	low plant evapotranspiration (low Kc values)
high net irrigation requirements	↔	low net irrigation reguirements
low lipid content in roots	↔	high lipid content in roots

Soil properties affecting the potential for CECs' uptake by plants

+		-
low levels of SOM	↔	high levels of SOM
sandy soils	↔	clay soils
sandy soils	↔	loamy soils
acidic pH (pH<pKa of CEC)	↔	basic pH (pH> pKa of CEC)
aerated soils (aerobic conditions)	↔	waterlogged soils (anaerobic conditions)

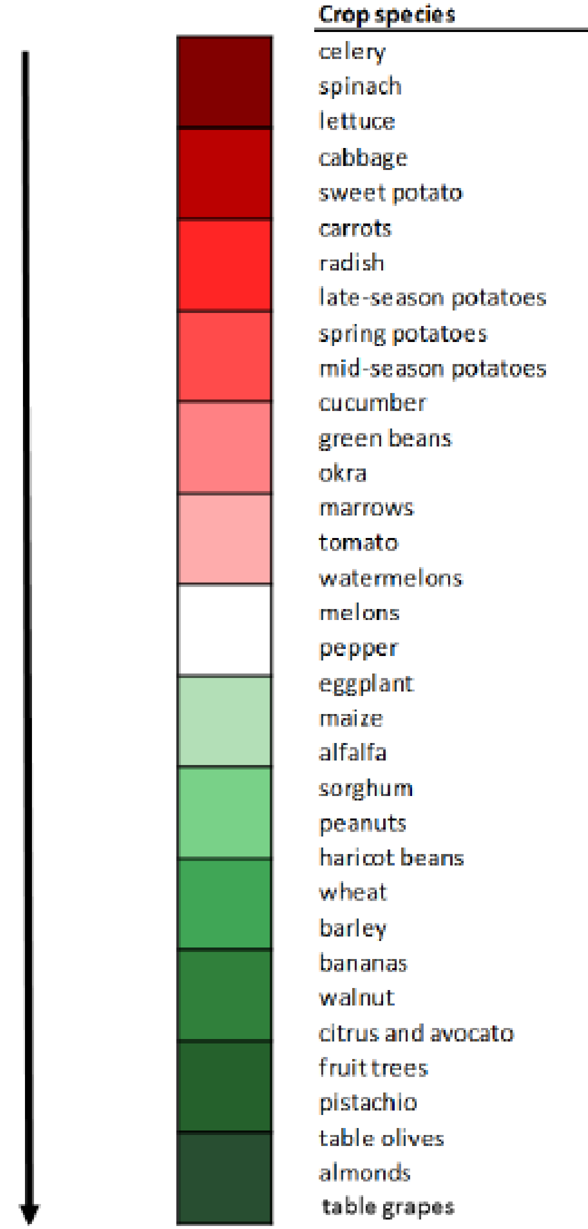
Nereus cost action. D8

Crop uptake

Crop uptake depends on

- bioavailability and bioassessibility in soil pore water near the rhizosphere (sorption to soil constituents and transformation by soil organisms reduce bioavailability);
- CEC physicochemical properties
- Soil environment: in the case of low carbon content or sandy/silty soil, a higher potential of crop uptake may occur. Lower in clay or loamy soil
- Evapotranspiration rate of crop plants, determined by climatic and plant specific values (Kc, crop coefficient) is a good indicator of the potential uptake
- Investigations carried out referring to around 100 different crops

Highest potential of crop uptake



Lowest potential of uptake

Christou et al., 2019

Crop uptake: physiology –related parameters

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Evapotranspiration rate (EVT) of crop plants, determined by climatic and plant specific values (Kc, crop coefficient) is a **good indicator** of the potential uptake:

- Crops with a **high EVT** and a **high Net Irrigation Requirements NIR** are expected to have a higher potential for CEC uptake:

Crops	ETc	NIR
	Total ETc (m^3 water/ ha/ year)	Total NIR (m^3 water/ ha/ year)
Tree crops		
Almonds	3445	3364
Bananas	12184	11340
Citrus & Avocado	8237	7615
[illegible]	[illegible]	[illegible]

- Crops grown in greenhouses and perennial crops irrigated with RWW may have a high potential uptake
- Crops growing in autumn or winter requiring less water due to rain events, or with a modest root development should have a lower potential uptake.
- Leafy vegetables may bioaccumulate greater CEC concentrations as the aboveground of the plants are edible.

Fate in the soil

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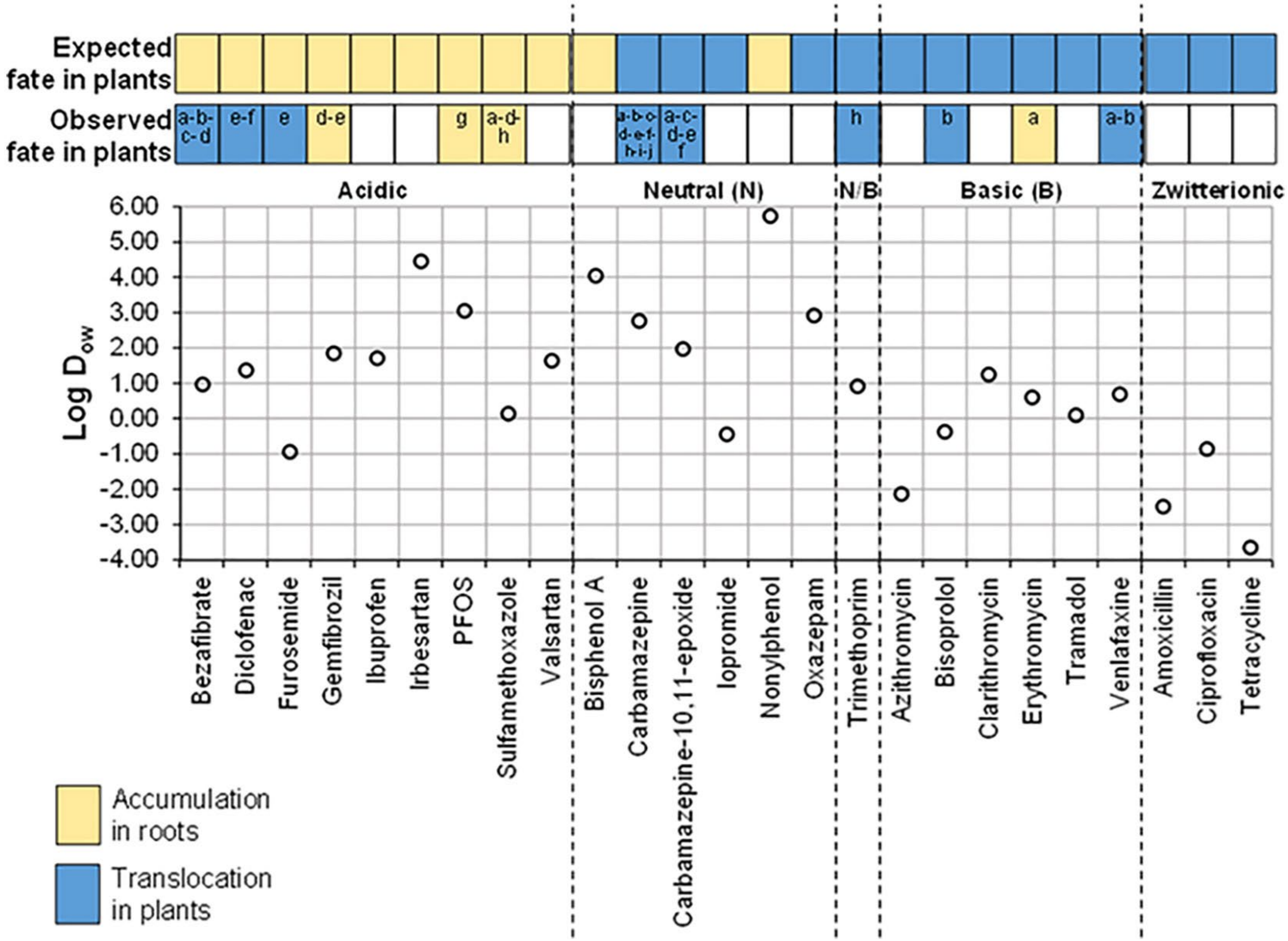

Verlicchi et al., 2023 Stoten

How to monitor the risk in soil, crop, and humans?

Selection of the most representative CECs

- *Frequency of detection (the highest!)* =f(use patterns, CEC recalcitrance)
- *Environmental concern* → DT_{50}(> 14 d e.g.), phytotoxicity, PNECsoil,..
- *Human health effects* →Thresholds of toxicological concern (TCC)
- *Uptake rate by crops*→ bioconcentration factors (RCF, LCF, FCF > 1) ratio between concentration in root and growing medium, leaf and growing medium, fruit and growing medium
- Evapotranspiration rate of the crop plant

Exemple of selection: Verlicchi et al., **Selection of indicator contaminants of emerging concern when reusing reclaimed water for irrigation — A proposed methodology,** *2023 Stoten*

Risk assessment evaluation

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- **Accepted Daily Intake** (ADI) **and Estimated Daily Intake** (EDI) (WHO 2011)
- Hazard Quotient *HQ* =EDI/ADI (HQ>0,1 high risk), evaluated for the mixture of CECs:

$$HQ_{tot} = \Sigma_i HQ_i$$

- Thresholds of toxicological concern TTC (recommended in absence of toxicity data). Based on Cramer classification tree (Cramer et al., 1978)

Structural Features	TTC (µg/day)	TTC (µg/kg-day)
Cramer Class III	90 µg/day	1.5 µg/kg-day
Cramer Class II	540 µg/day	9.0 µg/kg-day
Cramer Class I	1800 µg/day	30 µg/kg-day
Acetylcholinesterae Inhibitors (AChEIs)	18 µg/day	0.3 µg/kg-day
Genotoxic alerts	0.15 µg/day	0.0025 µg/kg-day

Verlicchi et al., 2023 Review
Verlicchi et al., 2023 Research Article

Further research

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- Selection of representative CEC, including ARB and ARGs (microbial CECs).
- Investigations on soil accumulation and uptake in different crops of organic and microbial CECs analysing specific processes as outlined in Fu et al., 2019 and other overview/discussing papers.
- Validation of predictive models available in the literature
- Evaluation of the effects of prolonged irrigation with reclaimed water in soil quality and crop uptake with regard to the selected CECs
- Environmental risk assessment of a mixture of compounds

Thank you for your attention

It's time for your questions…

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