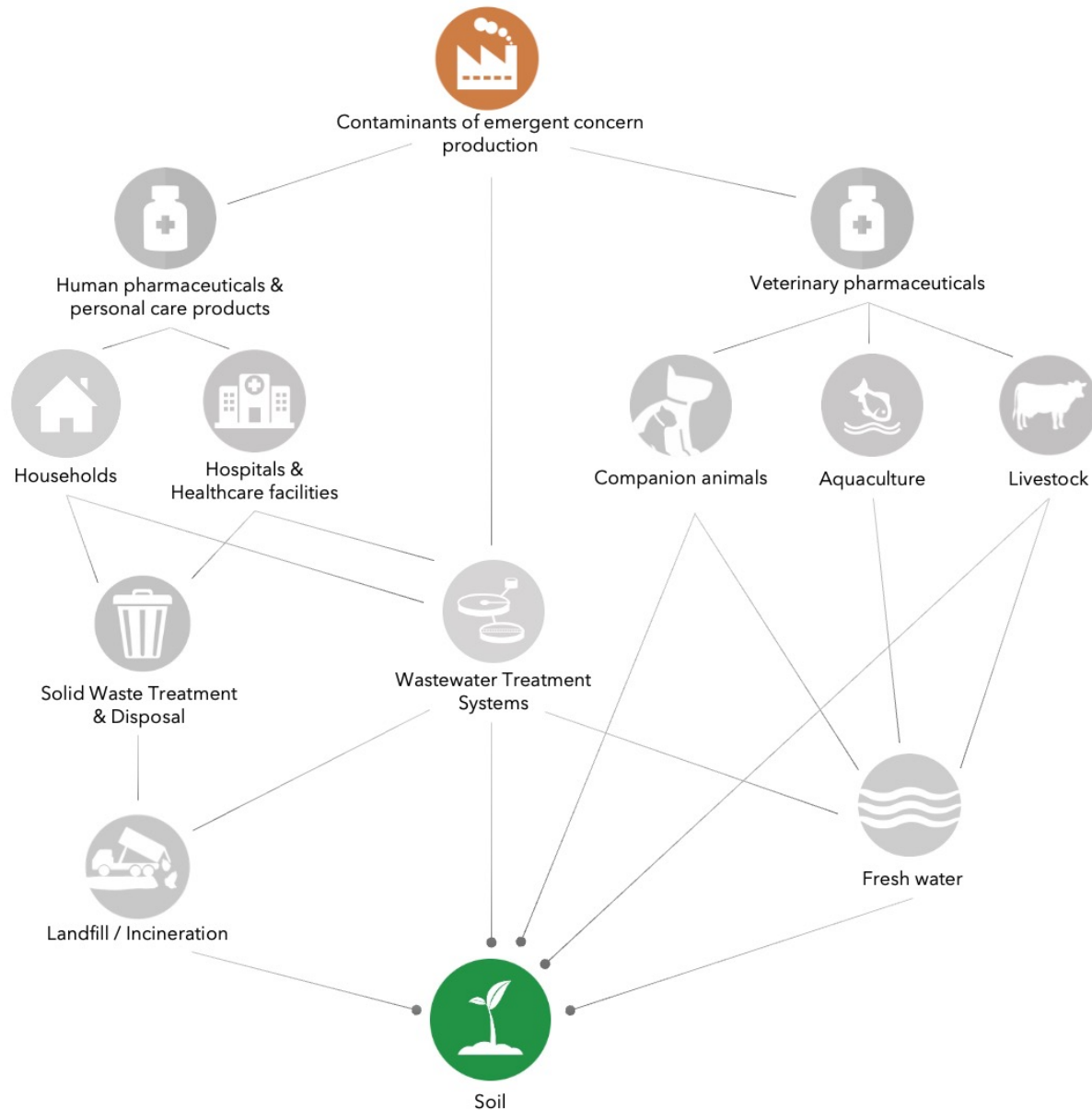


UNCOVERING ELECTROCHEMICAL REMOVAL MECHANISMS IN THE REMEDIATION OF EMERGING ORGANIC CONTAMINANTS FROM A CLAY SOIL

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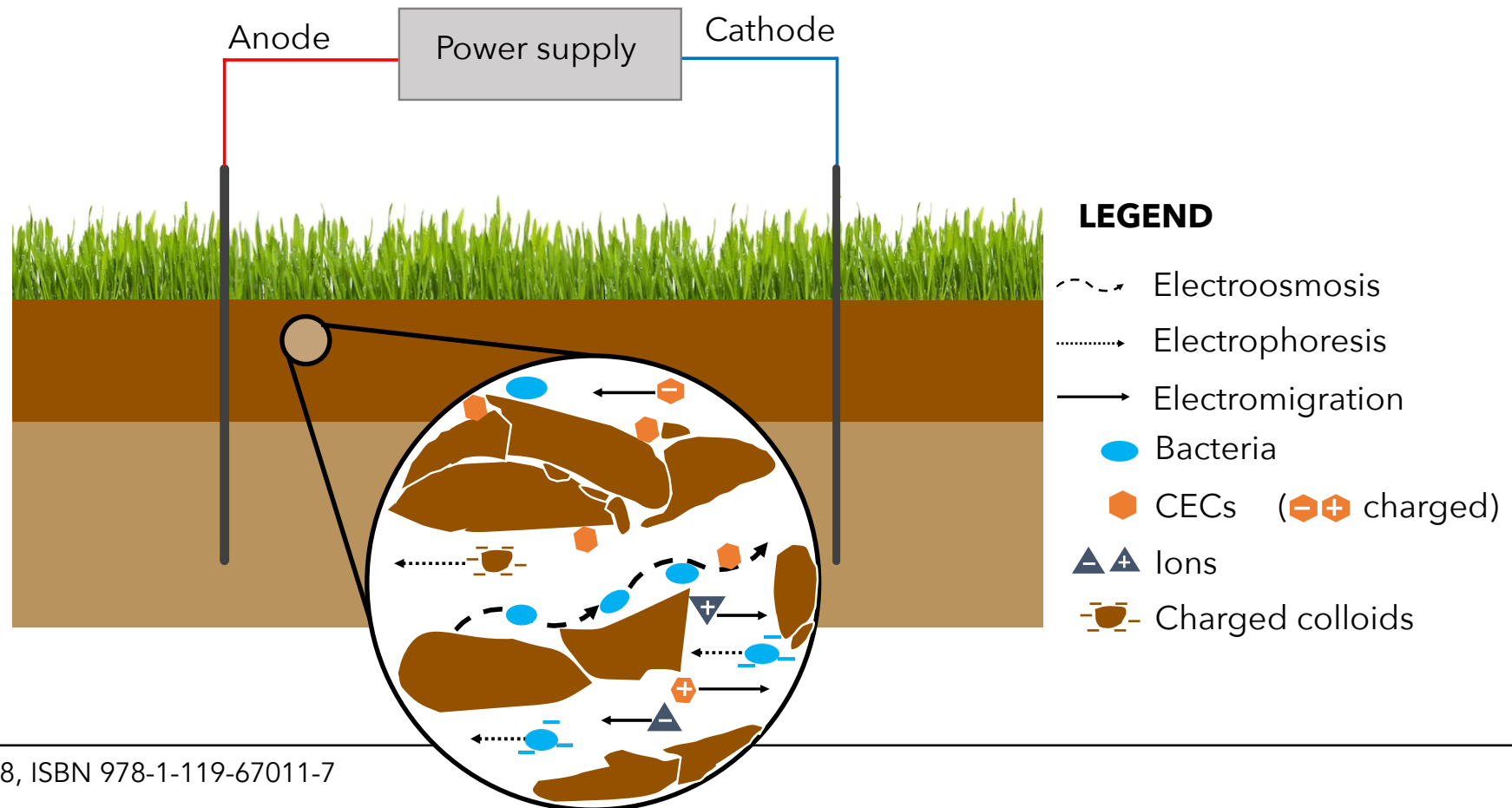


CONTAMINANTS OF EMERGENT CONCERN

Are chemical compounds that have been detected in drinking water, wastewater, and the aquatic environment.

Pharmaceuticals and personal care products and endocrine-disrupting chemicals are included in the CECs

EK-BIOREMEDIATION



EK-BIOREMEDIATION

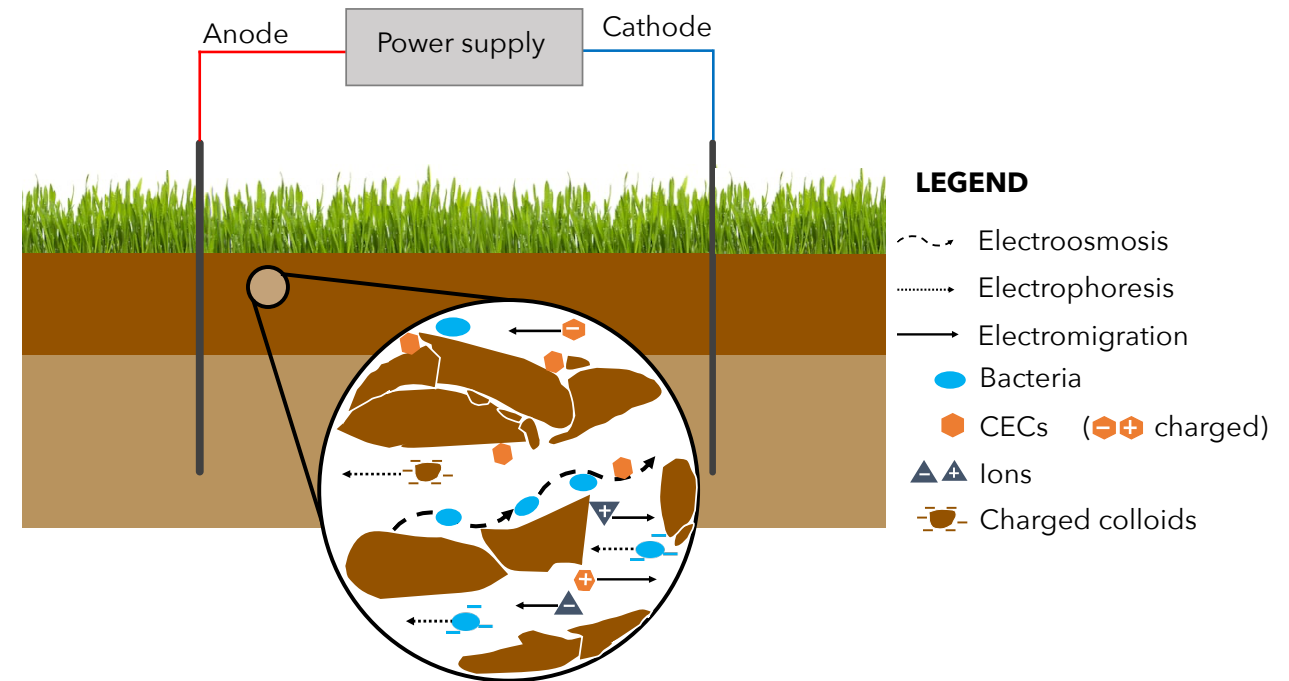
EK transport processes can be used to promote enhance bioremediation at mild conditions:

- **EK-Biostimulation**
 - Increase bioavailability of contaminants and naturally occurring nutrients and electron acceptors.
 - Allow the addition and delivery of nutrients, electron acceptors and surfactants into contaminated zones to increase bioavailability of limiting substances.
- **EK-Bioaugmentation**
 - To transport of bacterial population to specific zones where indigenous community is not adapted .

AIM

Use EK to promote a faster CECs decay and reduce the environmental risk associated to the spread of these contaminants.

- Improve bioremediation
- Promote electro-chemical degradation
 - Near the anode, the contaminants will suffer both direct and indirect oxidation, whereas in the cathode, they will only undergo indirect oxidation
 - Soil particles may act as micro-electrodes (due to the double layer), inducing redox reactions further away from the electrodes



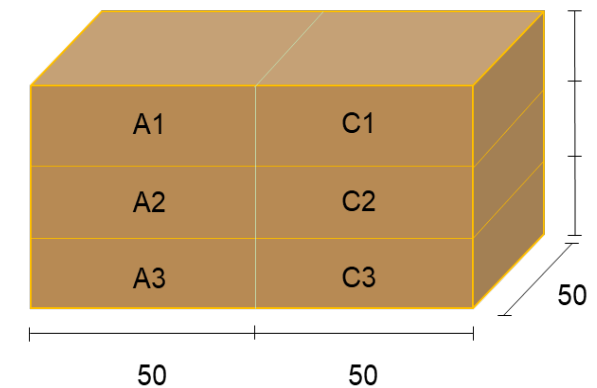
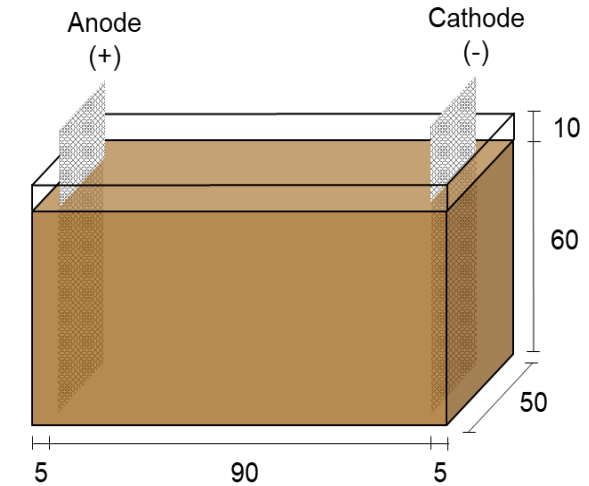
EK INFLUENCE ON CECs (BIO)DEGRADATION

Aim: Assess EK degradation mechanisms and its influence on the biodegradation of 10 CECs

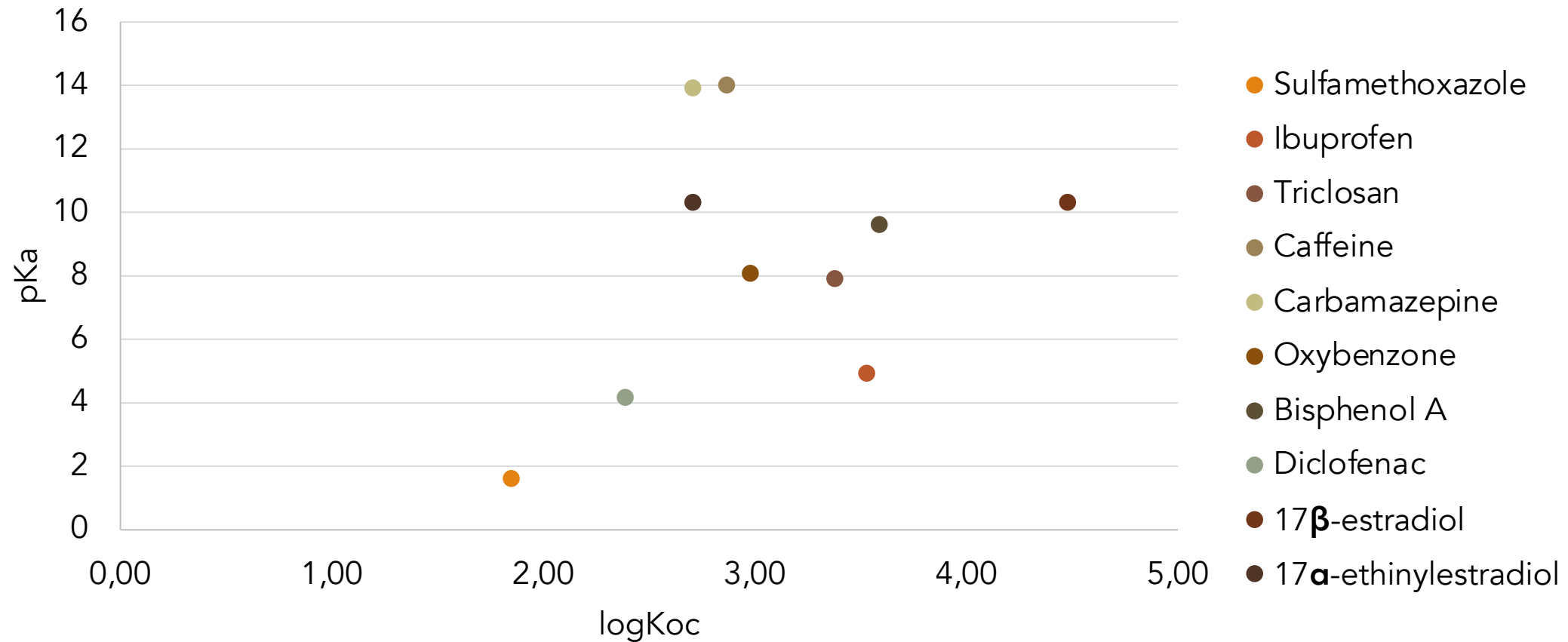
1. Changes in soil physico-chemical parameters
2. CECs decay (mobilization)

@20 mA, ON/OFF 12 h

- EK in with and without soil microbiota, conducted for 4 days
- EK in Biotic conditions, conducted for 4, 8 and 16 days



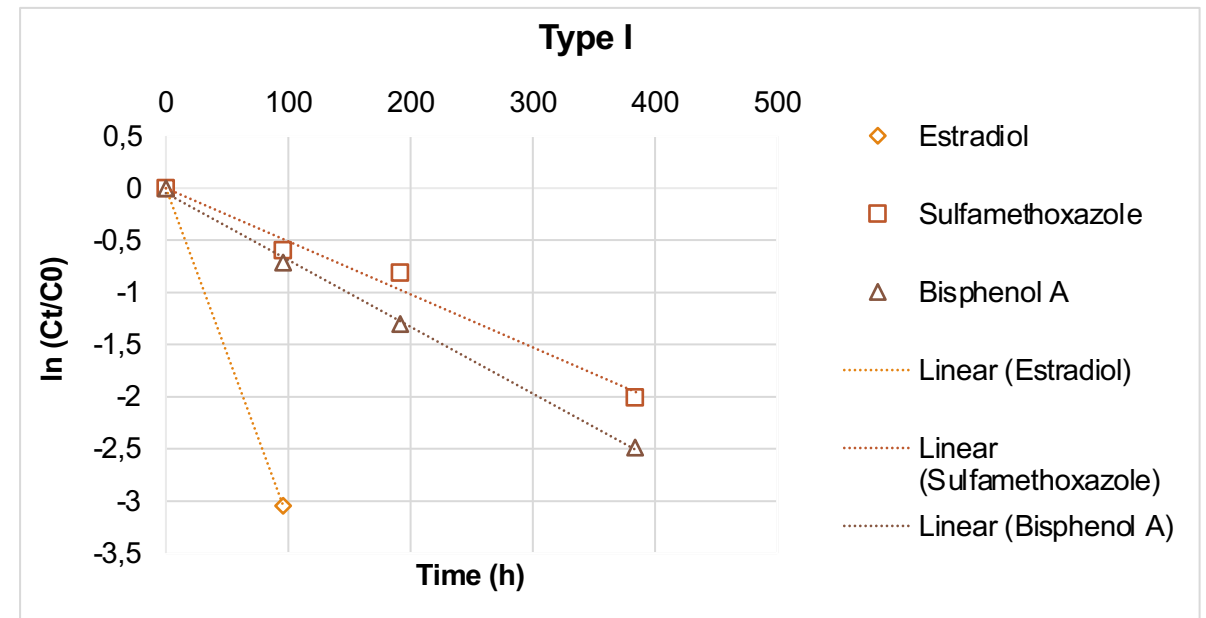
CECs SPIKED TO THE SOIL



BIODEGRADATION ALONG 16 DAYS

Type I – decay $\geq 80\%$, $t_{1/2} \leq 8$ days

- E2, SMX and BPA.



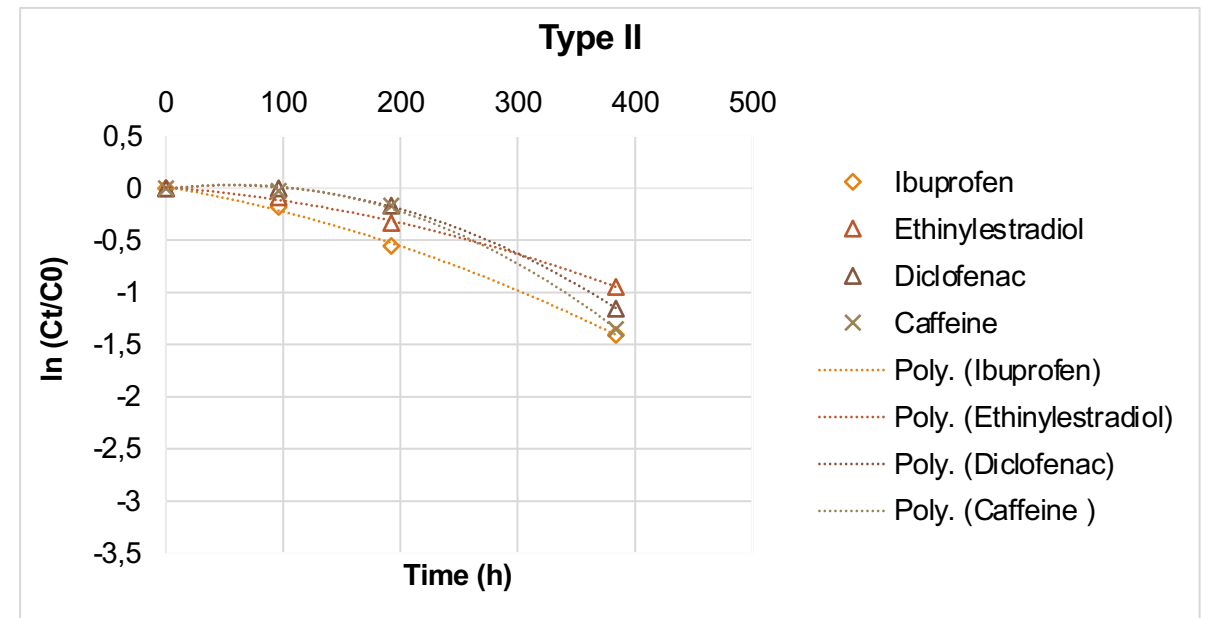
BIODEGRADATION ALONG 16 DAYS

Type I – decay $\geq 80\%$, $t_{1/2} \leq 8$ days

- E2, SMX and BPA.

Type II – $50\% \leq \text{decay} < 80\%$, $8 \text{ days} \leq t_{1/2} < 16$ days:

- IBU, EE2, DCF and CAF.



BIODEGRADATION ALONG 16 DAYS

Type I – decay $\geq 80\%$, $t_{1/2} \leq 8$ days

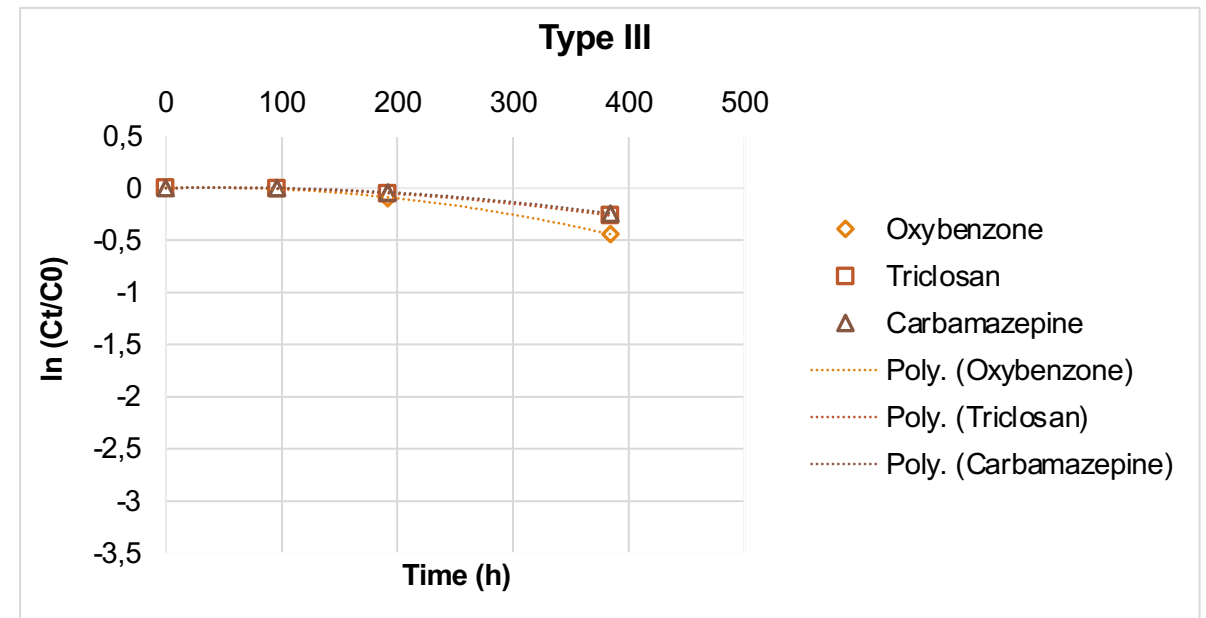
- E2, SMX and BPA.

Type II – $50\% \leq \text{decay} < 80\%$, $8 \text{ days} \leq t_{1/2} < 16$ days:

- IBU, EE2, DCF and CAF.

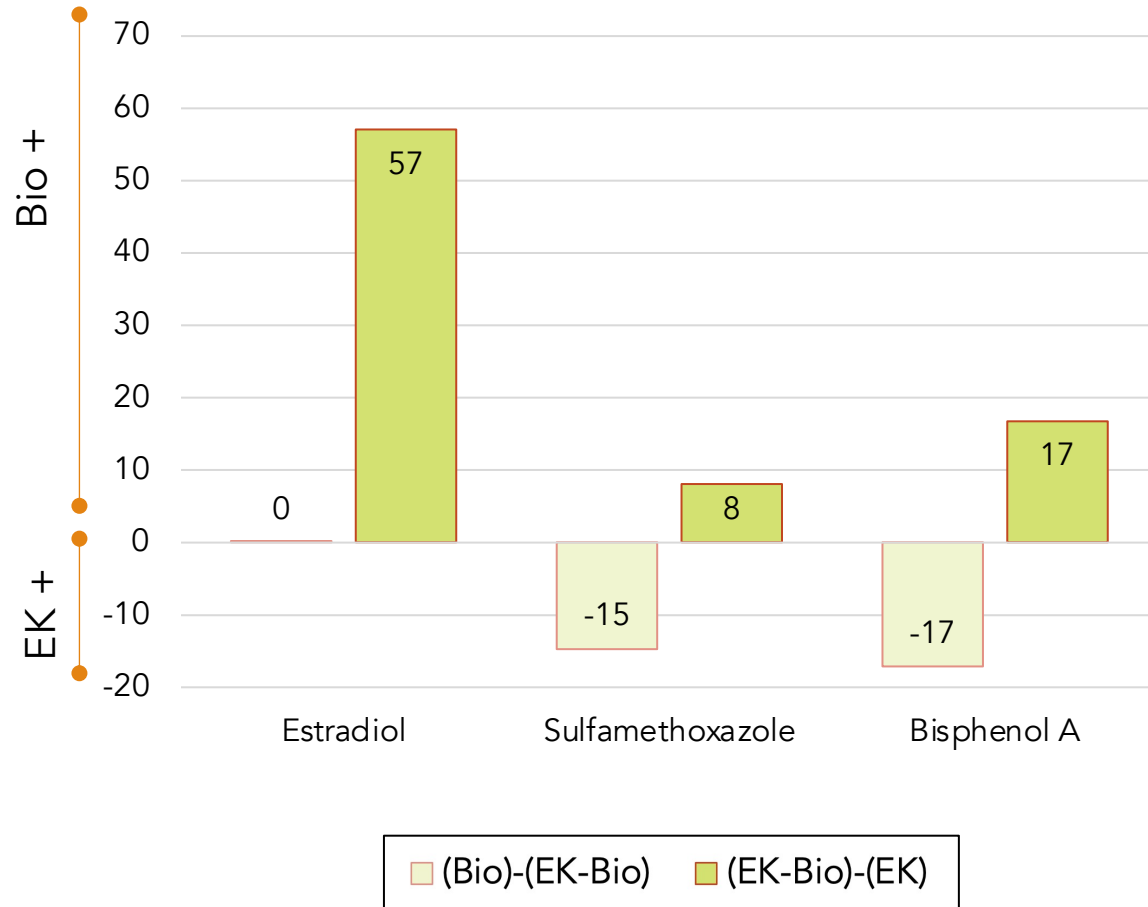
Type III – decay $\leq 50\%$, $t_{1/2} \geq 16$ days:

- OXY, TCS and CBZ.



EK APPLIED IN BIOTIC AND ABIOTIC CONDITIONS – SHORT-TERM

Difference CECs decay at day 4 (%)

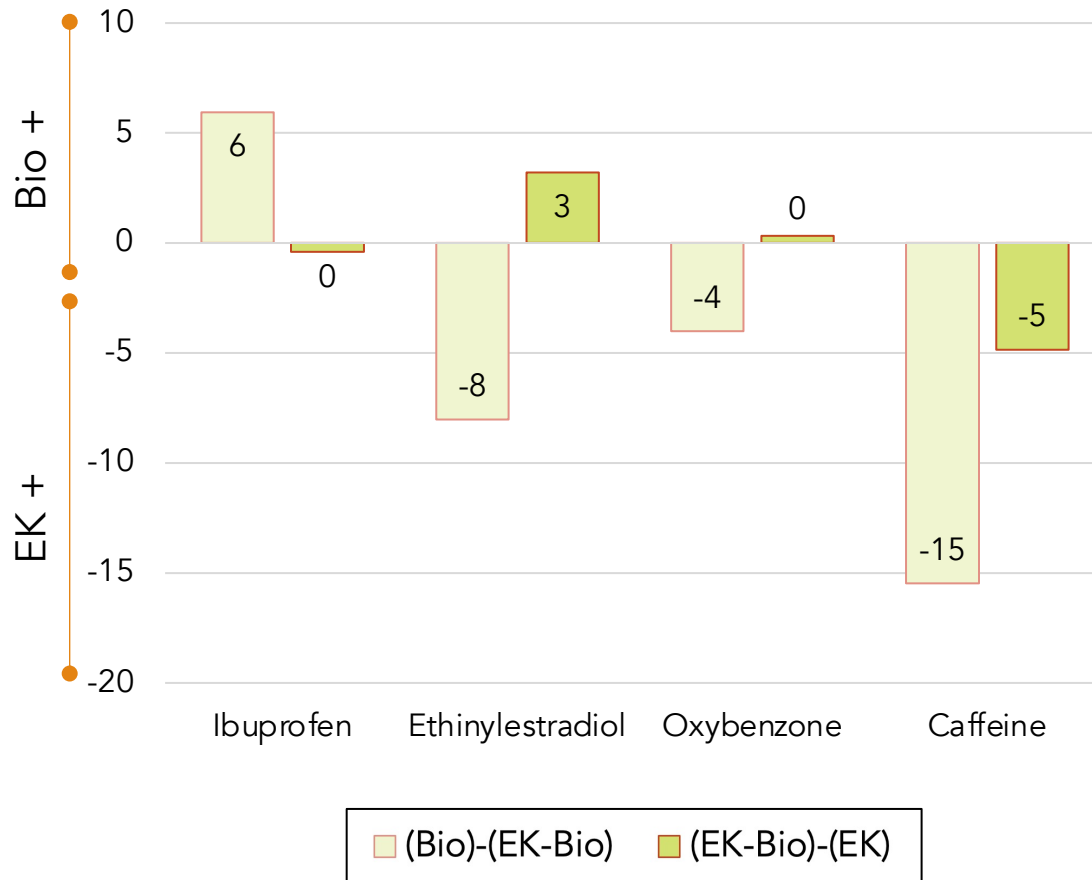


Type I decay mechanisms hypothesis:

- E2 → Biodegradation
- SMX → EK enhanced biodegradation
- BPA → EK enhanced biodegradation

EK APPLIED IN BIOTIC AND ABIOTIC CONDITIONS – SHORT-TERM

Difference of CECs decay at day 4 (%)

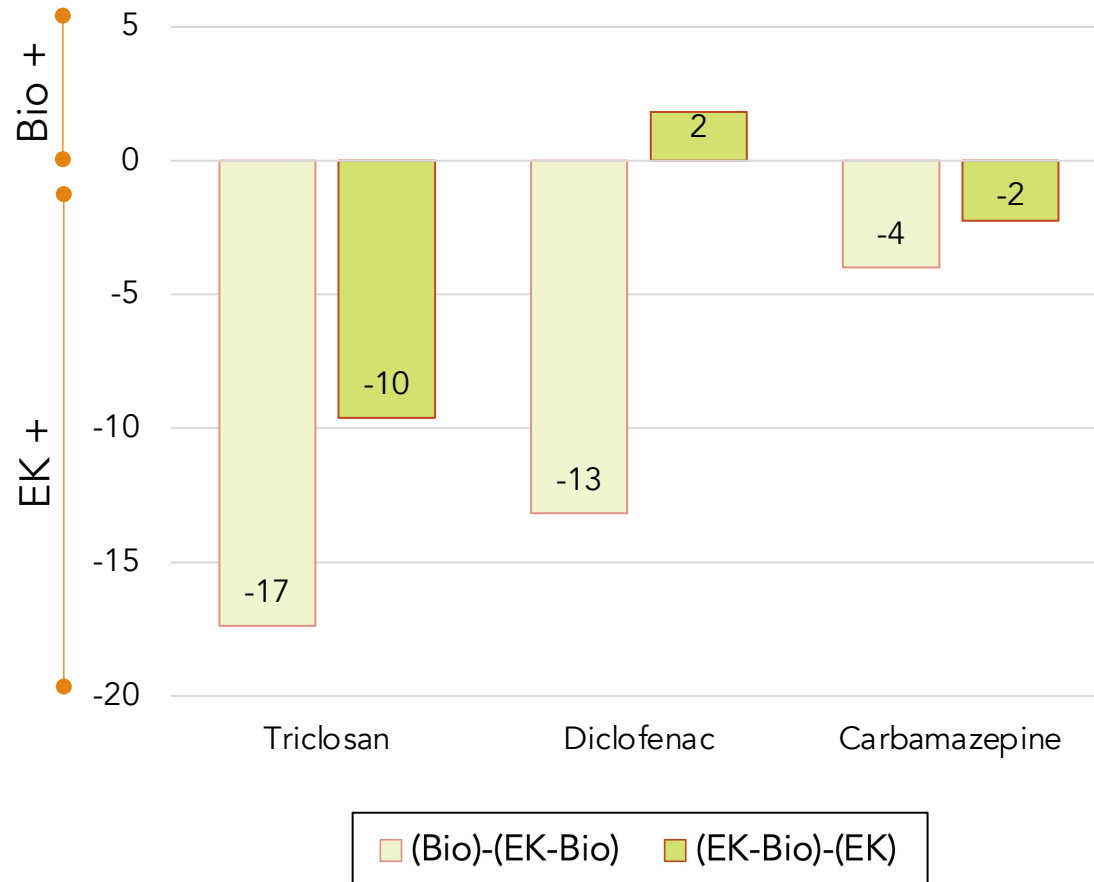


Type II decay mechanisms hypothesis:

- IBU → enhanced biodegradation and/or electro-chemical degradation
- EE2 & OXY → Enhanced biodegradation and/or electro-chemical degradation
- CAF → Electro-chemical degradation

EK APPLIED IN BIOTIC AND ABIOTIC CONDITIONS – SHORT-TERM

Difference CECs decay at day 4 (%)



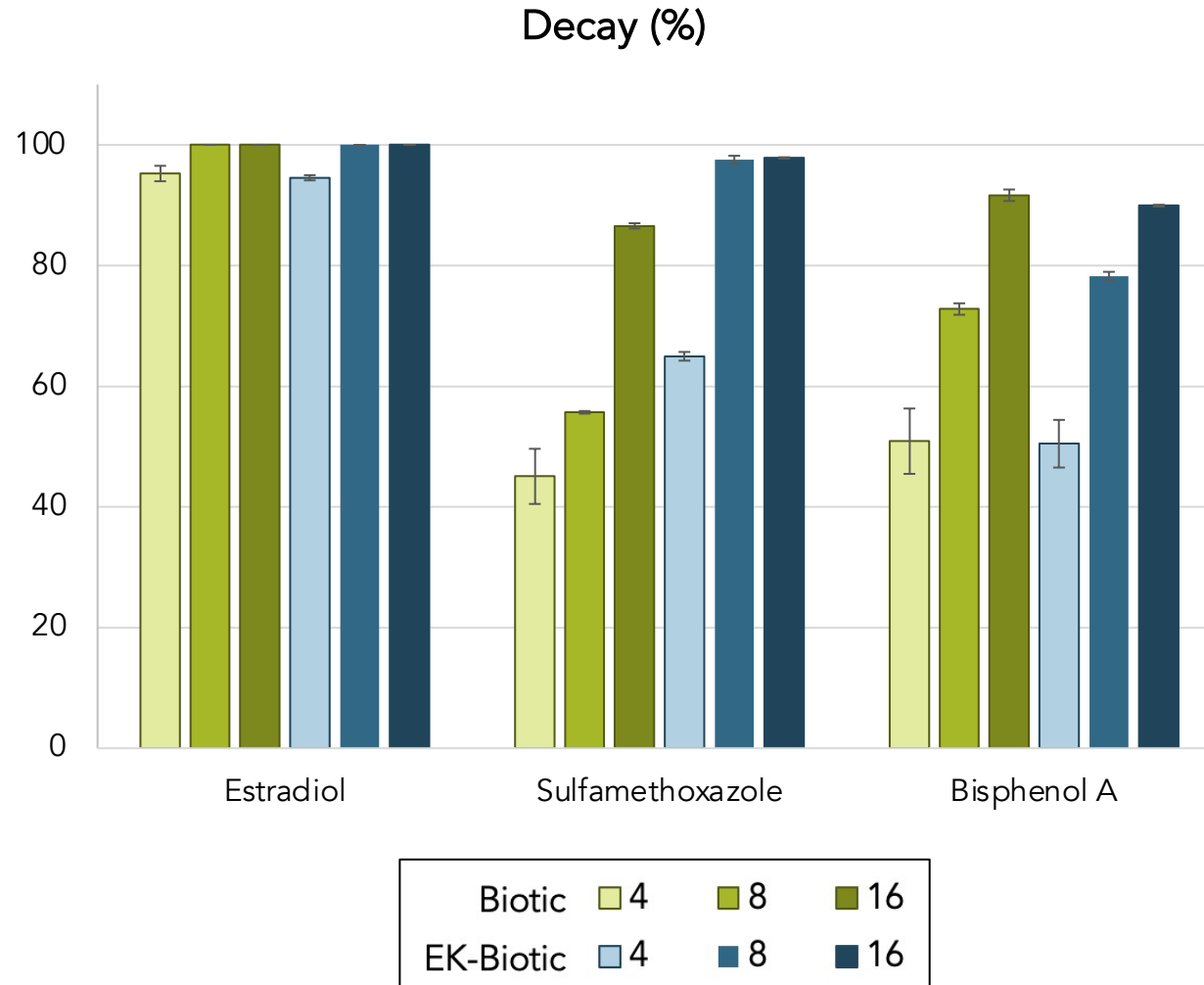
Type III decay mechanisms hypothesis:

- TCS, DCF → Enhanced biodegradation and electro-chemical degradation
- CBZ → Almost null removal, difficult to predict

INFLUENCE OF HIGHER CURRENT INTENSITY IN THE SOIL pH ALONG TIME

		Biotic			EK-Biotic		
Section	Layer	4d	8d	16d	4d	8d	16d
Anode	A1	8.33	7.66	7.76	7.27	6.61	5.86
	A2	8.33	7.63	7.83	7.31	6.47	4.85
	A3	7.38	7.65	7.75	7.11	6.40	4.31
Cathode	C1	8.39	7.38	7.87	8.94	8.48	9.38
	C2	8.30	7.45	7.85	9.35	9.19	10.33
	C3	8.27	7.71	7.91	9.53	9.69	10.51

EK APPLIED IN BIOTIC CONDITIONS – LONG TERM

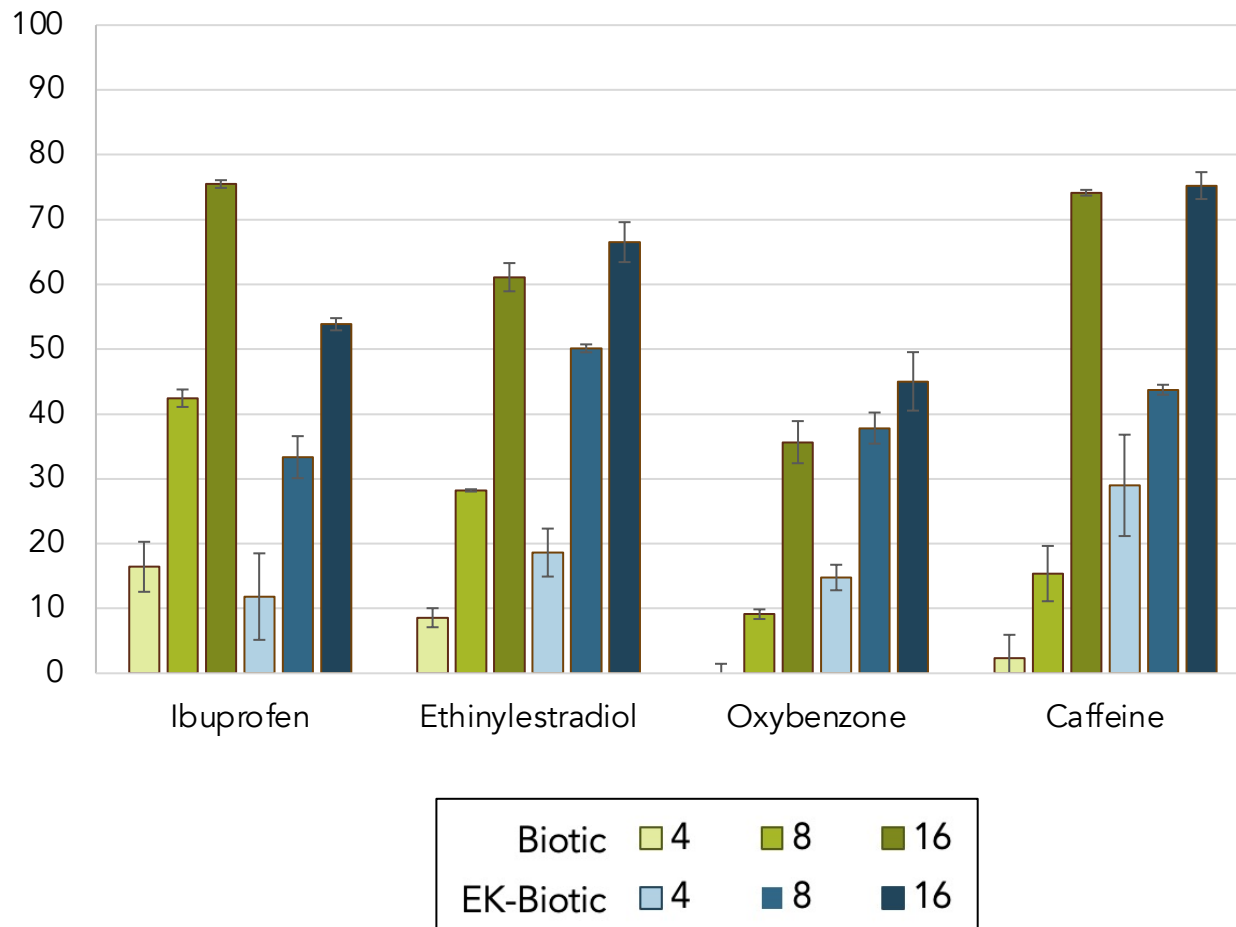


Type I ($t_{1/2} \leq 8$ days) decay mechanisms hypothesis:

- E2 → Biodegradation
- SMX → EK enhanced biodegradation
- BPA → ~~EK enhanced biodegradation~~

EK APPLIED IN BIOTIC CONDITIONS – LONG TERM

Decay (%)



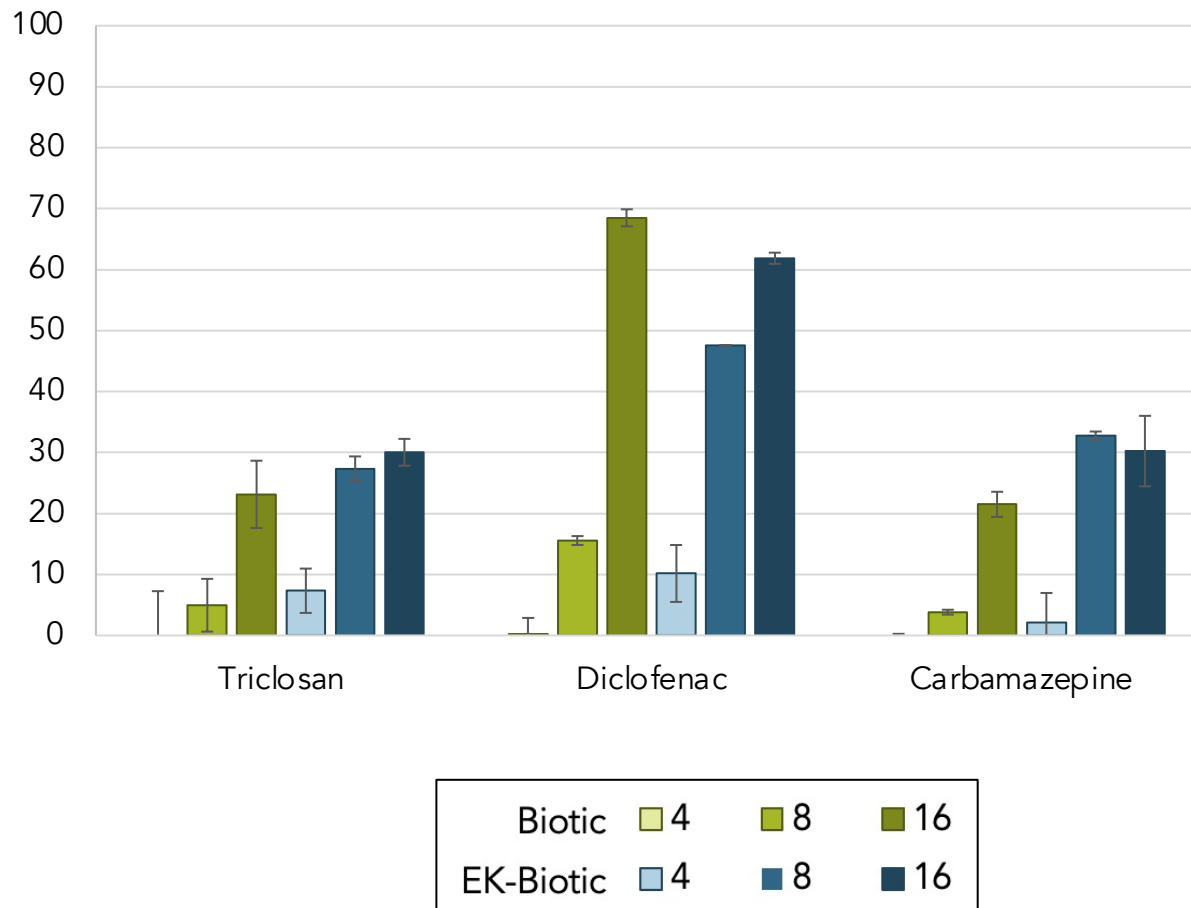
Type II (8 days $\leq t_{1/2} < 16$ days) decay mechanisms hypothesis:

- IBU → enhanced biodegradation and/or electro-chemical degradation
- EE2 & OXY → Enhanced biodegradation and/or electro-chemical degradation
- CAF → Electro-chemical degradation

EK negatively affected IBU decay after day 4
 EK only improved EE2, OXY & CAF decay till day 8

EK APPLIED IN BIOTIC CONDITIONS – LONG TERM

Decay (%)



Type III ($t_{1/2} \geq 16$ days) decay mechanisms hypothesis:

- TCS, DCF & CBZ → Enhanced biodegradation and electro-chemical degradation



EK improved TCS, DCF and CBZ decay till day 8

CECs DISTRIBUTION AFTER 16 DAYS

Day	Soil section	CEC									
		E2	SMX	BPA	IBU	EE2	OXY	DCF	TCS	CAF	CBZ
Biotic	A1		60	50	60	49	49	51	47	50	48
	A2										
	A3										
	C1		40	50	40	51	51	49	53	50	48
	C2										4
	C3										
EK-Bio	A1		100	42	100	44	39	87	47	44	39
	A2										1
	A3										
	C1			58		56	56	13	53	56	55
	C2						5				6
	C3										

EK LONG-TERM APPLICATION

- The decreased CECs decay after day 8 in the EK-Biotic comparing to the Biotic treatment, is partially explained by a decrease in the biodegradation contribution due to community inhibition promoted by the changes in the soil pH, and redox potential, gas composition, nutrients depletion in the vicinity of the electrodes (due to electro-migration).
- The low electro-chemical degradations obtained can be due to
 - (i) decreased CECs solubilization as the pH decreases in the anode side;
 - (ii) decreased electro-osmotic flow.
 - (iii) hindering of fenton-like reactions (that lead to the production of $\bullet\text{OH}$ radicals) as the pH increases in the cathode side.

SHOULD EK BE USED (IN THESE CONDITIONS) TO REMEDIATE SOILS CONTAMINATED WITH CECs?

The results obtained support the application of EK to accelerate the CECs removal in the first 8 days, after which longer EK application negatively impacted the removal of most CECs.

Considering that CECs may reach the soil if treated wastewater is used for irrigation, EK assisted remediation should be applied for *short* periods and its design should be guided by the irrigation regime used.

Thank you for the attention!



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