REACTIVE MATERIALS FOR ENHANCED REMOVAL OF ORGANIC MICROPOLLUTANTS IN CONSTRUCTED WETLANDS

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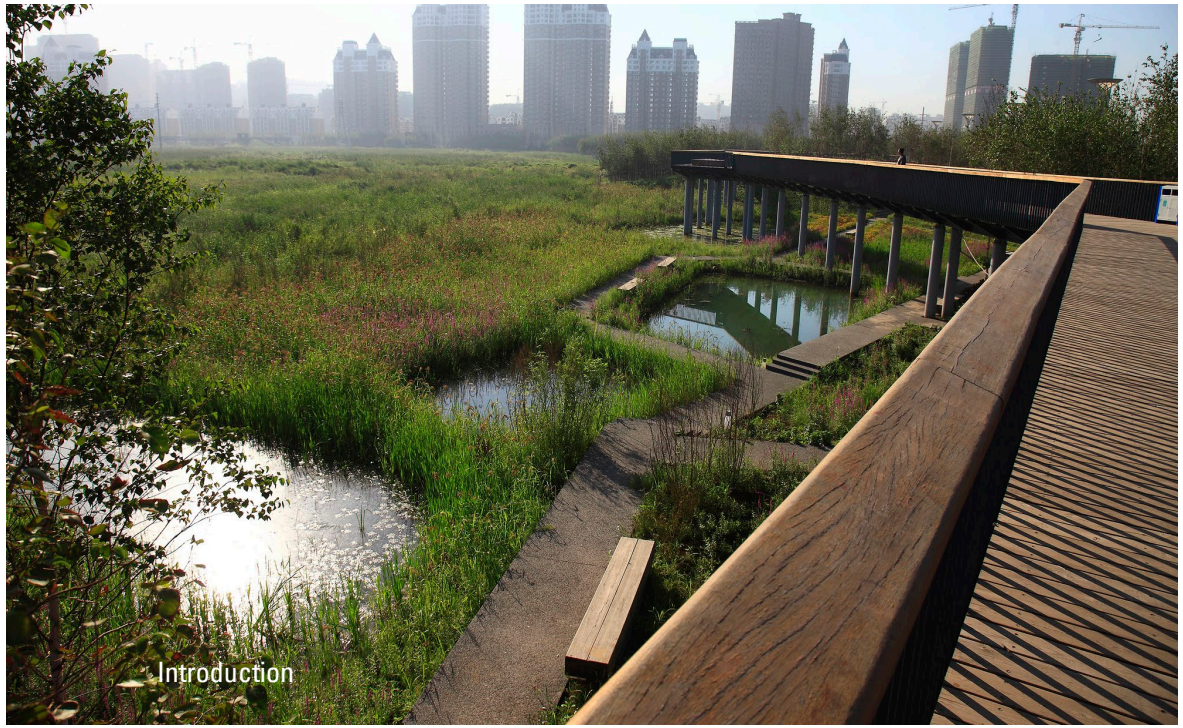
Faculty of Environmental Sciences

CAN CONSTRUCTED WETLANDS PROVIDE A SUSTAINABLE SOLUTION WHERE CONVENTIONAL METHODS FALL SHORT?

As regulations tighten and awareness grows, research increasingly highlights the need for tertiary treatments, like **constructed wetlands**, to effectively remove **micropollutants**.

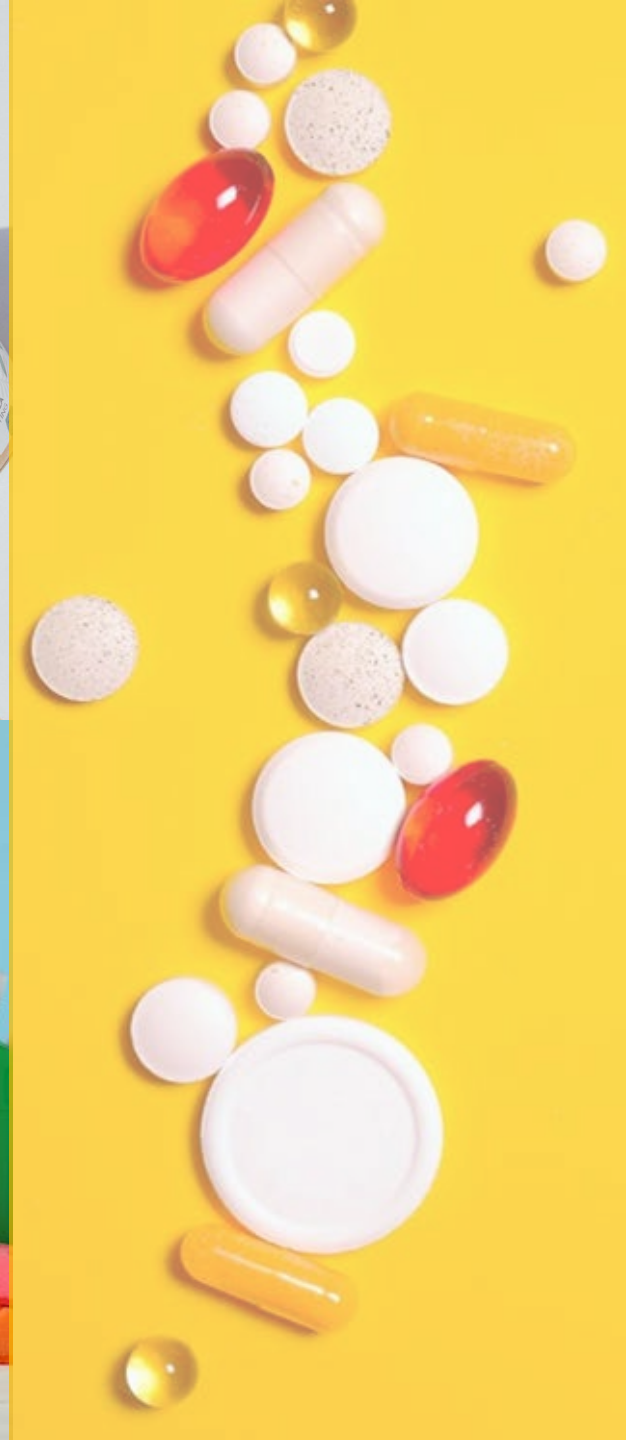


CONSTRUCTED WETLANDS

✓ Suspended solids, bulk organics (BOD_5, COD), and nutrients.

Compounds of emerging concern (CECs) or potentially harmful viral pathogens.

Implementation and rapid removal costs, scalability, environmental regulations, weather conditions, physicochemical, and biochemical properties.

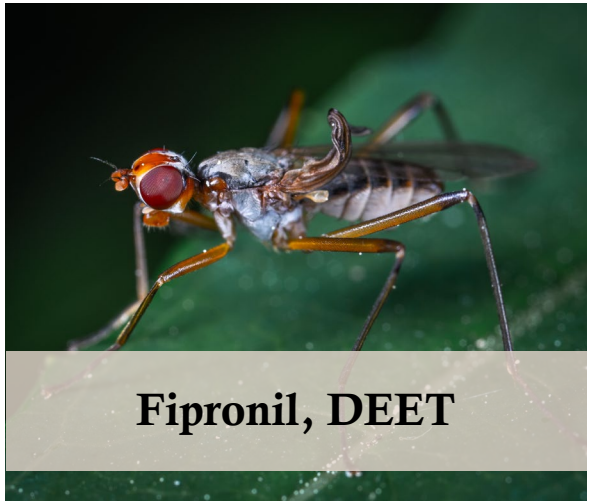


COMPOUNDS OF EMERGING CONCERN

- **The EU Water Framework Directive (Directive 2000/60/EC)**
  - **The EU Watch List concerning CECs -** identify and monitor potential pollutants in surface water, including CECs.
- **Revised Urban Wastewater Treatment Directive**
  - Pharmaceuticals, industrial compounds, pesticides, food additives and sweeteners, personal care and hygiene products, stimulants.
- Persistency, mobility, and toxicity.
- Scarce or insufficient quality monitoring data.

Diclofenac, Ibuprofen, Metformin, Carbamazepine

Bisphenol S, Benzotriazole



Fipronil, DEET

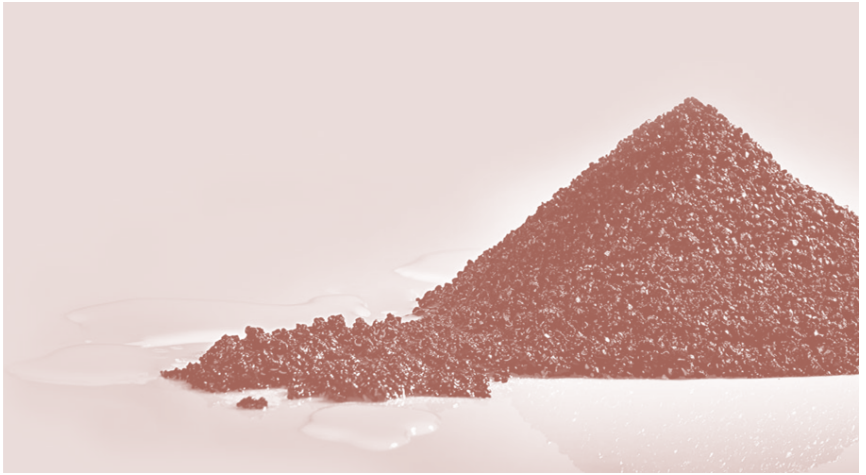
Triclosan, Climbazole

Acesulfame, Saccharin

Caffeine

IRON HYDROXIDE AND MANGANESE OXIDES

- **Fe hydroxides and Mn oxides can retain organic chemicals**
  - Large specific surface area, high redox properties, and ability to participate in various chemical and biological reactions
- **Limitations**
  - The complexity of CECs/selectivity, the reactivity of MnOx and FeOx with CECs, has been poorly studied, including loss of sorption capacity in anaerobic conditions, toxicity, and long-term performance.

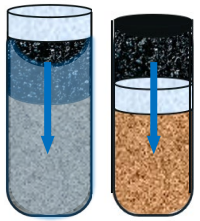


OBJECTIVES

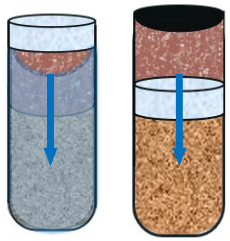
- Evaluate the impact of Fe hydroxide and Mn oxide on the removal of organic micropollutants by vertical flow CWs treating **household wastewater.**
- Test different working conditions
  - Aerobic (unsaturated) and **anaerobic/anoxic (saturated)** conditions
  - Presence and absence of plants
  - **Increased number of micropollutants**

EXPERIMENTAL SETUP - SAMPLING

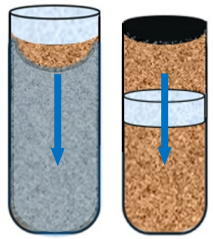
MnOx – unP – Sat/unSat



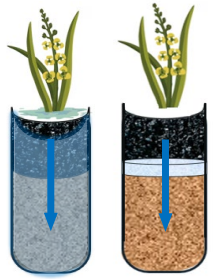
FeOx – unP – Sat/unSat



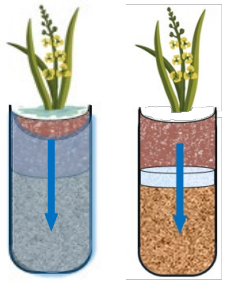
Sand – unP – Sat/unSat



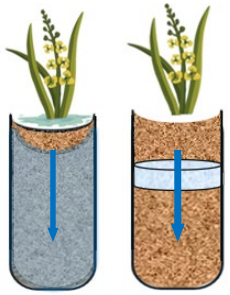
MnOx – unP – Sat/unSat



FeOx – P – Sat/unSat



Sand – unP – Sat/unSat

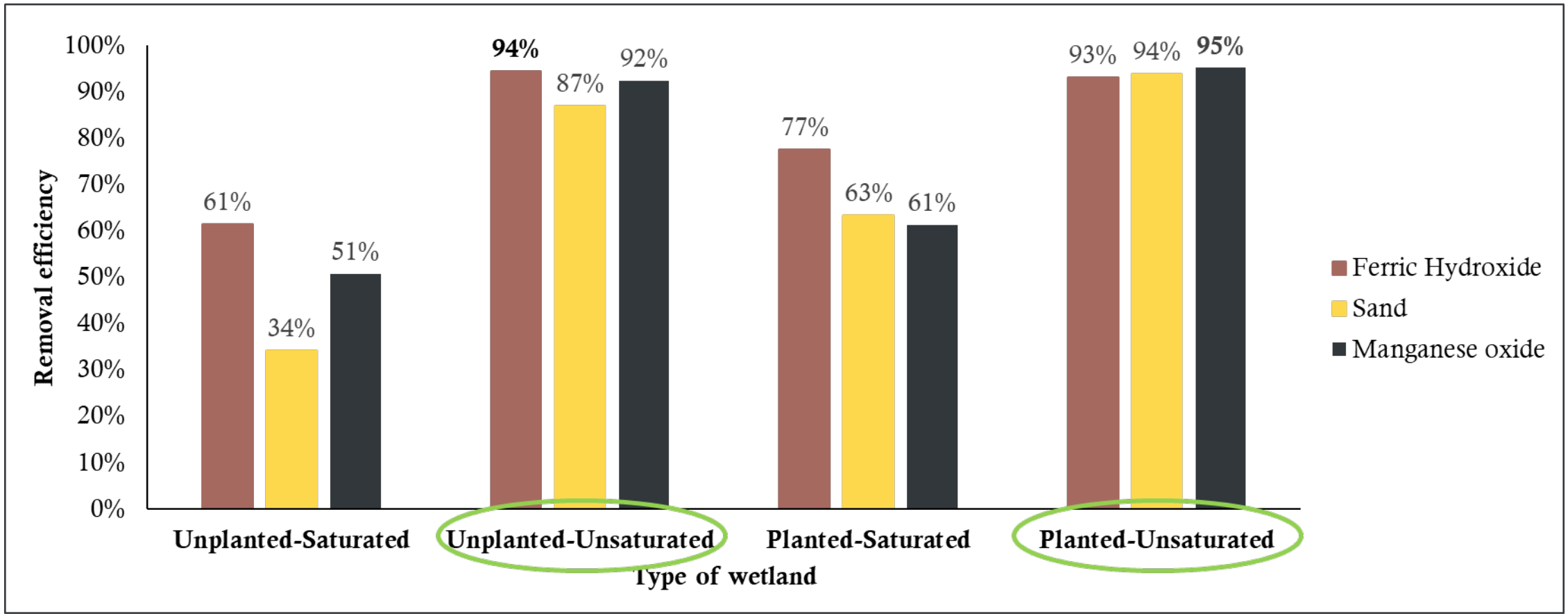


3 **different substrates**, **aerobic/anaerobic–anoxic** conditions, **presence** and **absence** of plants

12 different treatments

Working conditions	
Type of flow	Down flow vertical
Influent flow	0.4 L/dose
Hydraulic loading	0.013 m^3/m^2
Influent	Synthetic household wastewater
Duration	July – December 2024
Substrate Material	70% sand, 30% FeOx (GEH) / 30% MnOx (G-1) with sand 1:1
Macrophyte	Yellow Iris (Iris pseudacorus)
Sampling frequency	7 - 8 days (once a weekly)
Parameters	pH, EC, N-NH_4, F, Cl, N-NO_2, Br, N-NO_3, PO_4, SO_4, TC, TOC, IC, TN, metals (23), micropollutants (31)

OVERALL REMOVAL EFFICIENCIES

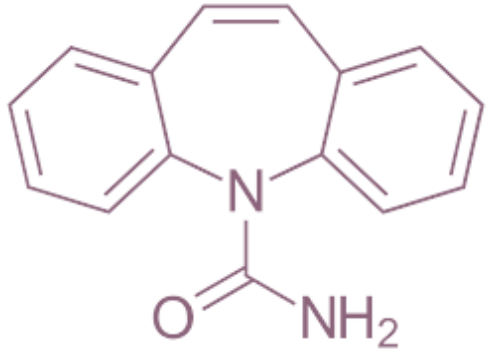


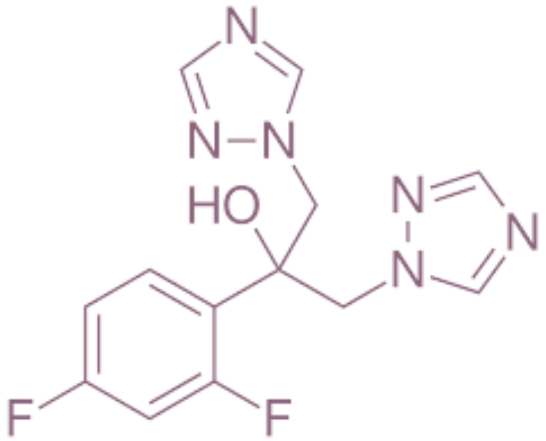
REMOVAL OF MICROPOLLUTANTS

Types of wetlands	FeOx-unP-Sat	FeOx-unP-unSat	FeOx-P-Sat	FeOx-P-unSat	Sand-unP-Sat	Sand-unP-unSat	Sand-P-Sat	Sand-P-unSat	MnOx-unP-Sat	MnOx-unP-unSat	MnOx-P-Sat	MnOx-P-unSat
Carbamazepine	≤ 0%	≤ 0%	6.2%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%
Fluconazole	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%
Lamotrigine	≤ 0%	1.8%	10.8%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%	≤ 0%

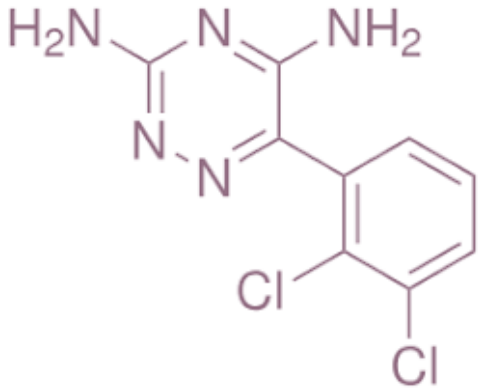
REMOVAL OF MICROPOLLUTANTS

Types of wetlands
Carbamazepine
Fluconazole
Lamotrigine





← Persistent compounds



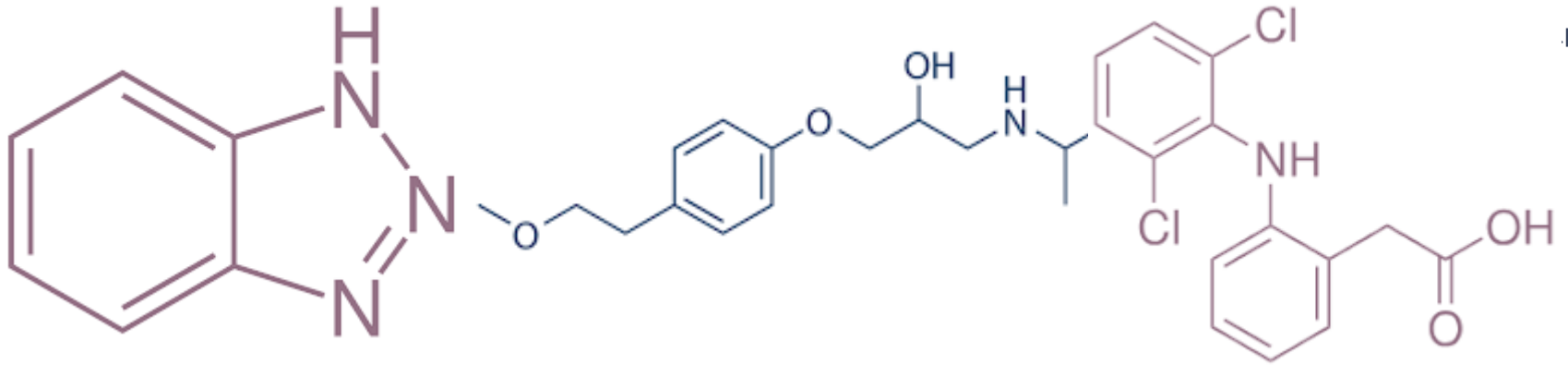
REMOVAL OF MICROPOLLUTANTS

Types of wetlands	FeOx-unP-Sat	FeOx-unP-unSat	FeOx-P-Sat	FeOx-P-unSat	Sand-unP-Sat	Sand-unP-unSat	Sand-P-Sat	Sand-P-unSat	MnOx-unP-Sat	MnOx-unP-unSat	MnOx-P-Sat	MnOx-P-unSat
Benzotriazol	48.4%	71.9%	86.3%	82.0%	2.2%	63.4%	51.7%	78.0%	17.7%	56.0%	43.2%	68.1%
*Diclofenac	30%	52%	13%	30%	-3%	19%	2%	15%	99%	84%	95%	94%
Fipronil	94.8%	94.0%	92.5%	80.5%	77.1%	45.5%	81.4%	56.8%	62.1%	45.2%	59.4%	51.9%
Furosemide	41%	34%	19%	39%	29%	24%	5%	39%	65%	46%	36%	75%
Gemfibrozil	≤ 0%	78.0%	41.8%	91.2%	≤ 0%	39.8%	13.7%	94.2%	≤ 0%	79.0%	9.5%	94.2%
Hydrochlorothiazide	24.7%	10.8%	27.7%	-13.5%	23.6%	≤ 0%	≤ 0%	≤ 0%	46.3%	13.8%	18.9%	28.9%
Ibuprofen	≤ 0%	95.0%	42.4%	95.0%	-22.3%	95.0%	37.5%	95.0%	-19.3%	95.0%	32.7%	95.0%
Ketoprofen	46.5%	98.7%	17.3%	99.4%	43.4%	69.2%	10.3%	99.4%	38.3%	92.6%	0.1%	98.5%
Metoprolol	53.7%	68.6%	85.6%	67.5%	40.7%	43.8%	88.1%	80.0%	50.7%	46.1%	50.6%	63.9%
*Sulfamethoxazole	91.4%	37.9%	99.7%	40.8%	39.3%	86.2%	84.4%	49.6%	33.1%	60.7%	32.5%	54.8%

REMOVAL OF MICROPOLLUTANTS

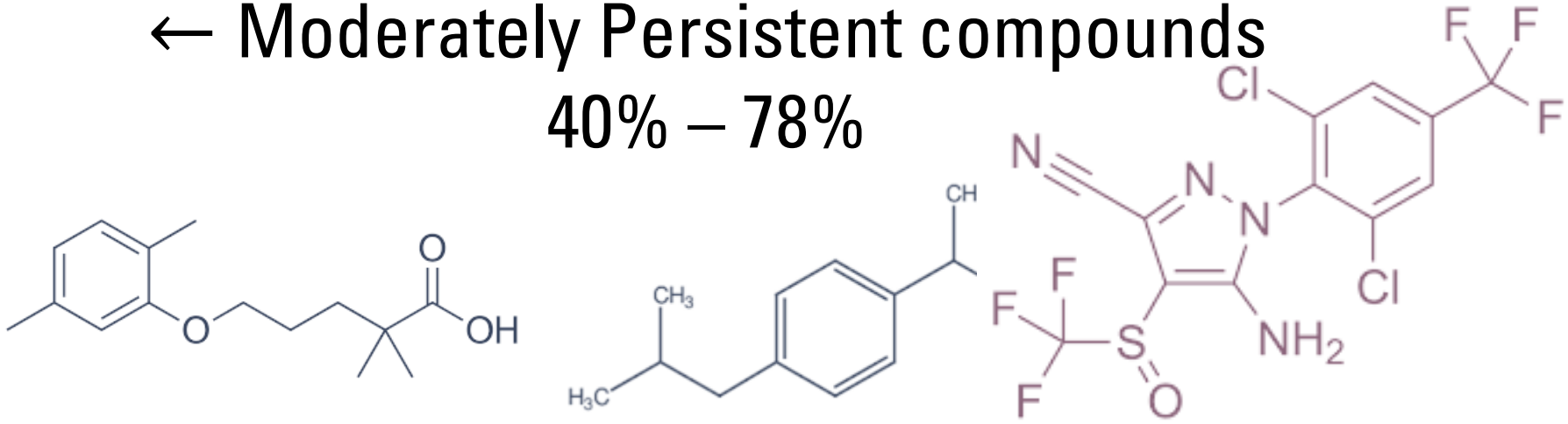
Types of wetlands

- Benzotriazol
- Diclofenac
- Fipronil
- Furosemide
- Gemfibrozil
- Hydrochlorothiazide
- Ibuprofen
- Ketoprofen
- Metoprolol
- Sulfamethoxazole



← Moderately Persistent compounds

40% – 78%



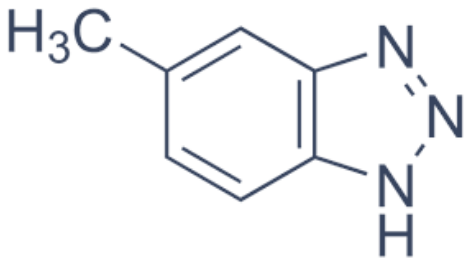
REMOVAL OF MICROPOLLUTANTS

Types of wetlands	FeOx-unP-Sat	FeOx-unP-unSat	FeOx-P-Sat	FeOx-P-unSat	Sand-unP-Sat	Sand-unP-unSat	Sand-P-Sat	Sand-P-unSat	MnOx-unP-Sat	MnOx-unP-unSat	MnOx-P-Sat	MnOx-P-unSat
5-methylbenzotriazole	58.1%	**97.0%**	90.0%	**98.9%**	≤ 0%	**95.6%**	61.0%	**98.9%**	10.1%	**96.7%**	62.9%	**98.9%**
Acetaminophen	64.6%	**99.0%**	83.7%	**99.0%**	41.2%	**99.0%**	78.3%	**99.0%**	99.0%	**99.0%**	99.0%	**99.0%**
Bisphenol S	96.7%	**96.7%**	71.9%	**99.2%**	99.2%	**93.7%**	99.2%	**99.2%**	99.2%	**91.9%**	98.2%	**99.2%**
Caffeine	69.5%	**98.0%**	93.6%	**98.0%**	59.8%	**98.0%**	89.4%	**98.0%**	82.3%	**98.0%**	95.2%	**98.0%**
Chloramphenicol	95.1%	**95.1%**	95.1%	**95.1%**	95.1%	**95.1%**	95.1%	**95.1%**	95.1%	**95.1%**	95.1%	**95.1%**
Climbazole	95.6%	**95.6%**	95.6%	**95.6%**	26.4%	**95.6%**	95.6%	**95.6%**	95.6%	**95.6%**	95.6%	**95.6%**
DEET	12.6%	**94.6%**	28.5%	**98.7%**	0.3%	**95.5%**	24.6%	**98.7%**	3.9%	**94.4%**	81.1%	**98.7%**
Metformin	89.4%	**95.9%**	82.7%	**95.9%**	52.4%	**88.4%**	65.5%	**93.2%**	48.7%	**95.9%**	63.2%	**95.9%**
Methylparaben	98.5%	**98.5%**	98.5%	**98.5%**	98.5%	**98.5%**	98.5%	**98.5%**	98.5%	**98.5%**	98.5%	**98.5%**
o-desmethylvenlafaxine	80.5%	**73.5%**	72.2%	**77.5%**	39.2%	**69.2%**	74.8%	**79.9%**	97.8%	**97.8%**	97.8%	**97.8%**
Oxybenzone	87.7%	**87.7%**	87.7%	**87.7%**	87.7%	**87.7%**	87.7%	**87.7%**	87.7%	**87.7%**	87.7%	**87.7%**
Saccharin	73.7%	**96.6%**	≤ 0%	**96.6%**	24.1%	**96.6%**	-29.6%	**96.6%**	50.5%	**96.6%**	44.1%	**96.6%**
Triclosan	96.3%	**96.3%**	96.3%	**96.3%**	91.5%	**96.3%**	96.3%	**96.3%**	96.3%	**96.3%**	96.3%	**96.3%**

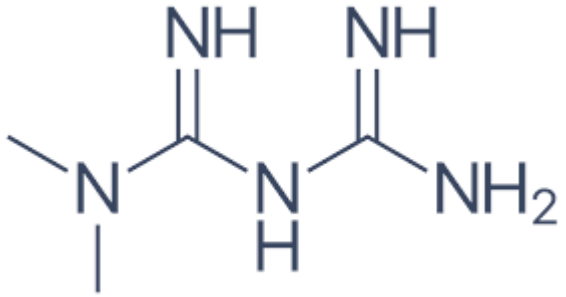
REMOVAL OF MICROPOLLUTANTS

Types of wetlands

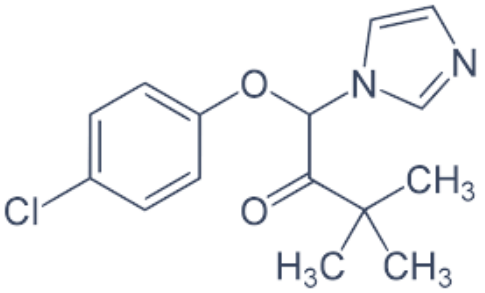
- 5-methylbenzotriazole
- Acetaminophen
- Bisphenol S
- Caffeine
- Chloramphenicol
- Climbazole
- DEET
- Metformin
- Methylparaben
- o-desmethylvenlafaxine
- Oxybenzone
- Saccharin
- Triclosan



5-methylbenzotriazole



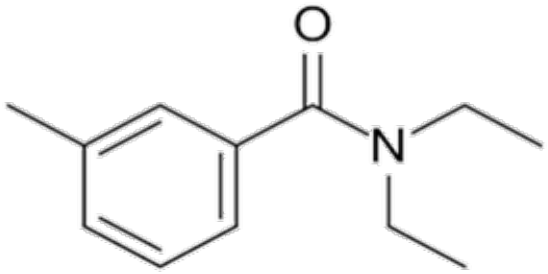
Metformin



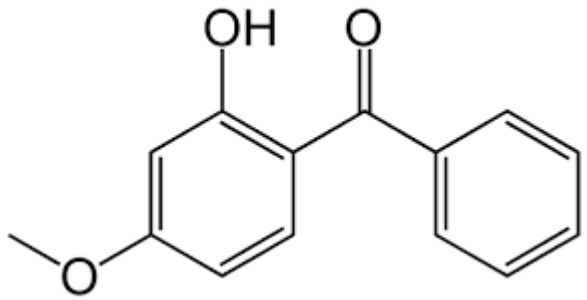
Climbazole

← Effectively removed compounds

79% – 100%

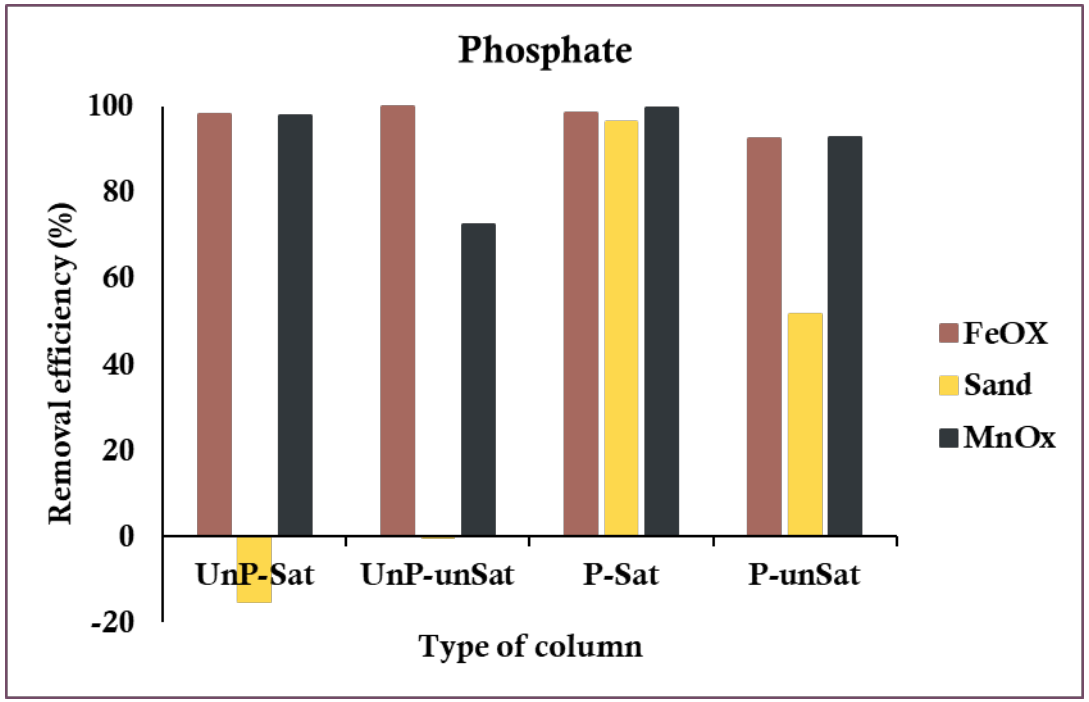


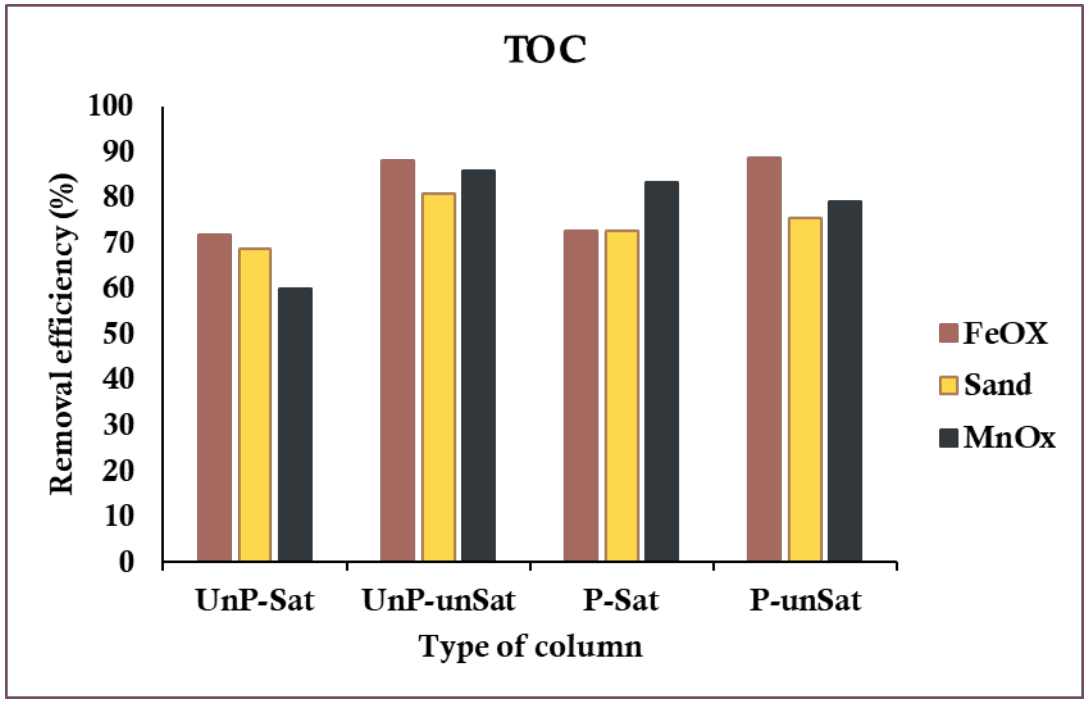
DEET



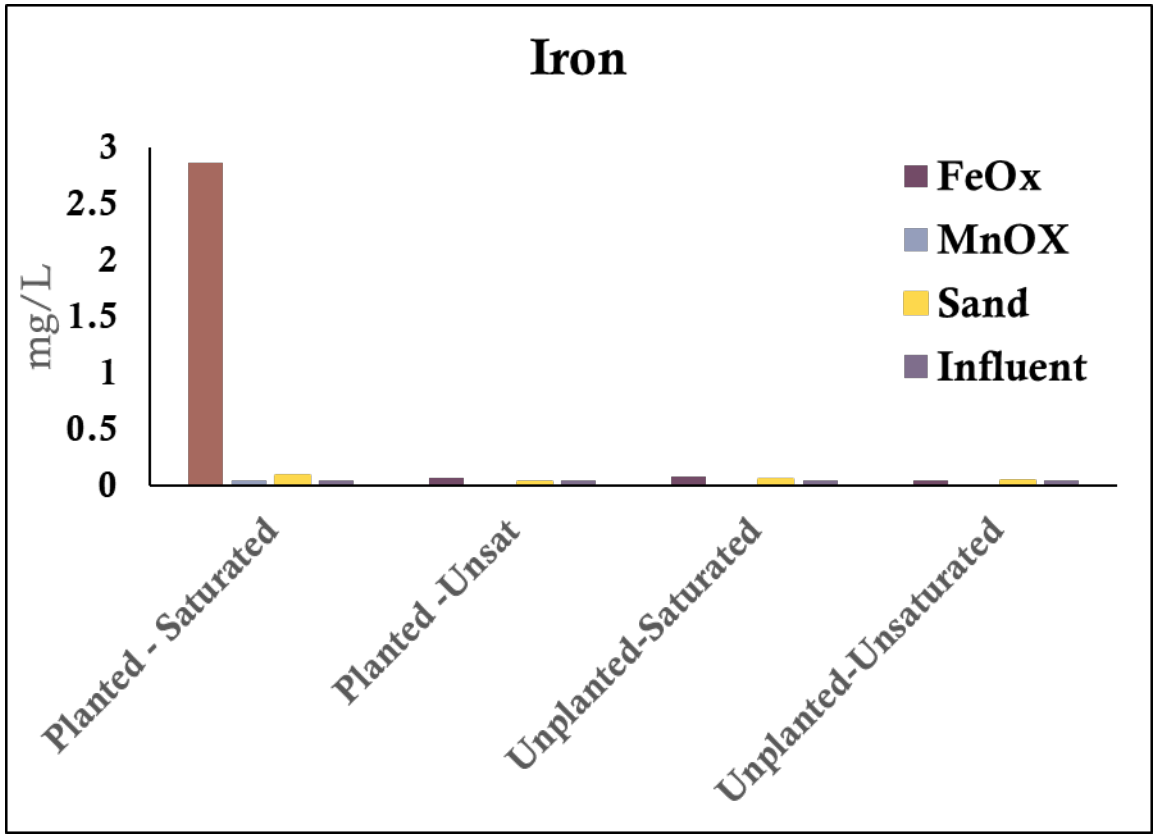
Oxybenzone

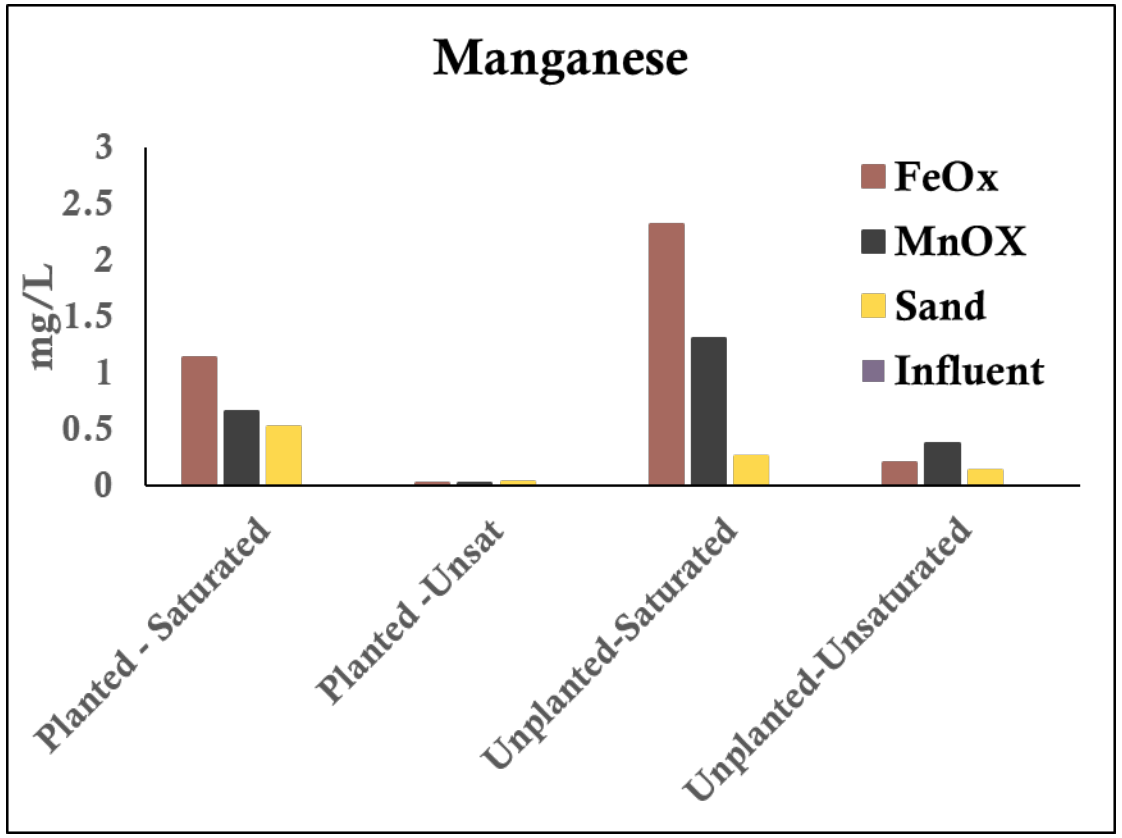
NUTRIENTS REMOVAL





METAL LEACHING





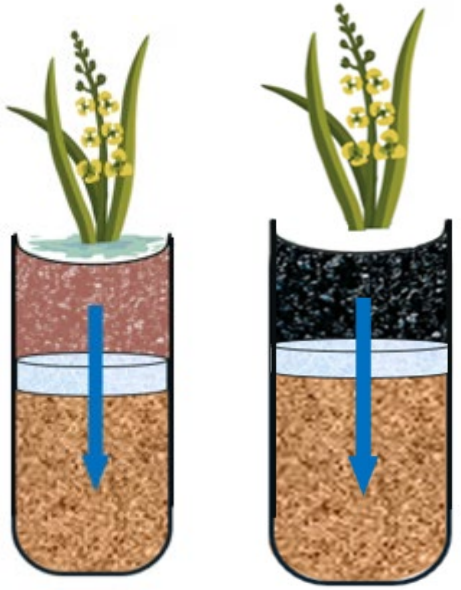
CONCLUSIONS

Enhancing wastewater treatment plants aims to minimize the release of micropollutants; for that, amendments to constructed wetlands were tested by exposing them to different working conditions.

More effective removal of most selected compounds, ranging from **87% to 95%,** under **unsaturated planted** conditions. Prominent examples of compounds reacting under saturated and unsaturated conditions with **iron hydroxides** are **sulfamethoxazole** and **fipronil**.

The removal of pollutants can be enhanced by adsorption and other processes (reaction with Fe^{+2})**Oxidation by manganese oxides**, can be observed by some compounds such as **diclofenac**.

MnOx – P – unSat



FeOx – unP – unSat

FURTHER RESEARCH

ACKNOWLEDGMENT

Project

- Reactive Interfaces for Degrading Contaminants of Emerging Concern and Pathogenic Viruses in Constructed Wetlands" from NSF and Czech Science Foundation (project No. 24-14297L)

QUESTIONS?

THANK YOU!

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