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CENTRE FOR ENERGY
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TECHNOLOGIES

INSTITUTE OF
ENVIRONMENTAL
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Monitoring of pesticides in surface waters and methods of their elimination

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Presentation structure

1. Introduction.
2. Research objectives.
3. Selected pesticides.
4. Experimental part.
5. Result part.
6. Conclusion.

Introduction – the issue of pesticides in the environment

- The consumption of pesticides in agriculture continues to increase.
- Pesticides can pass through WWTPs in unchanged form.
- They reach the environment via diffusion routes – contamination of water sources occurs.
- Pesticides pose a risk to non-target organisms, especially invertebrates and amphibians.
- Efforts to remove them are still growing.



Introduction – the issue of invasive plants

- Invasive plants are problematic species.
- They were imported to the Czech Republic as ornamental plants and spread thanks to the rapid growth of seeds or fruits.
- They multiply quickly and crowd out native plants.
- They can change the properties of the soil and the processes that take place in the soil.
- Their removal methods are time- and financially expensive or require the use of pesticides.

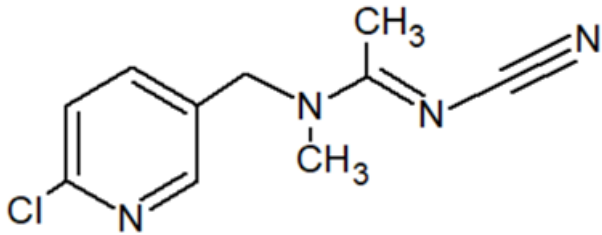


Research objectives

- Monitoring of pesticides in the environment
 - Area of research: surface water, sediment, riparian plants.
- Pesticide removal
 - Adsorption on activated carbon and composite materials.
 - Photocatalytic processes.
 - Biological degradation by *Aegagropila linnaei*, *Microalgae*, *Lemna* and *Cyanobacteria*.

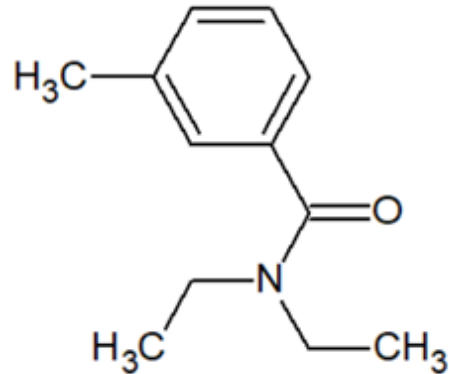
Selected pesticides

ACETAMIPRID



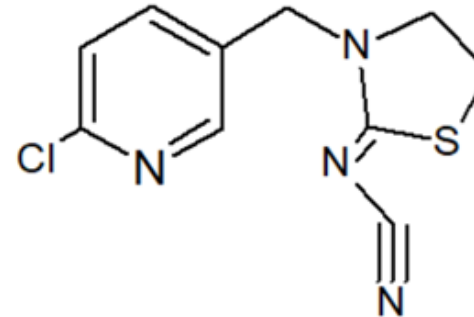
Use: vegetables, fruits, cotton and ornamental plants.

DEET



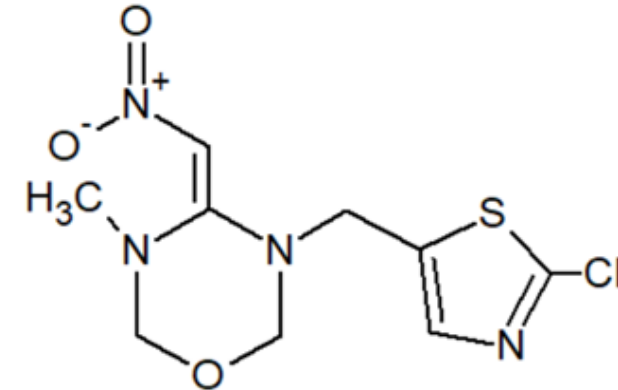
Use: as an insect repellent in concentrations of 4 - 100%.

THIACLOPRID



Use: rapeseed, cotton, stone fruits, vegetables and potatoes.

THIAMETHOXAM

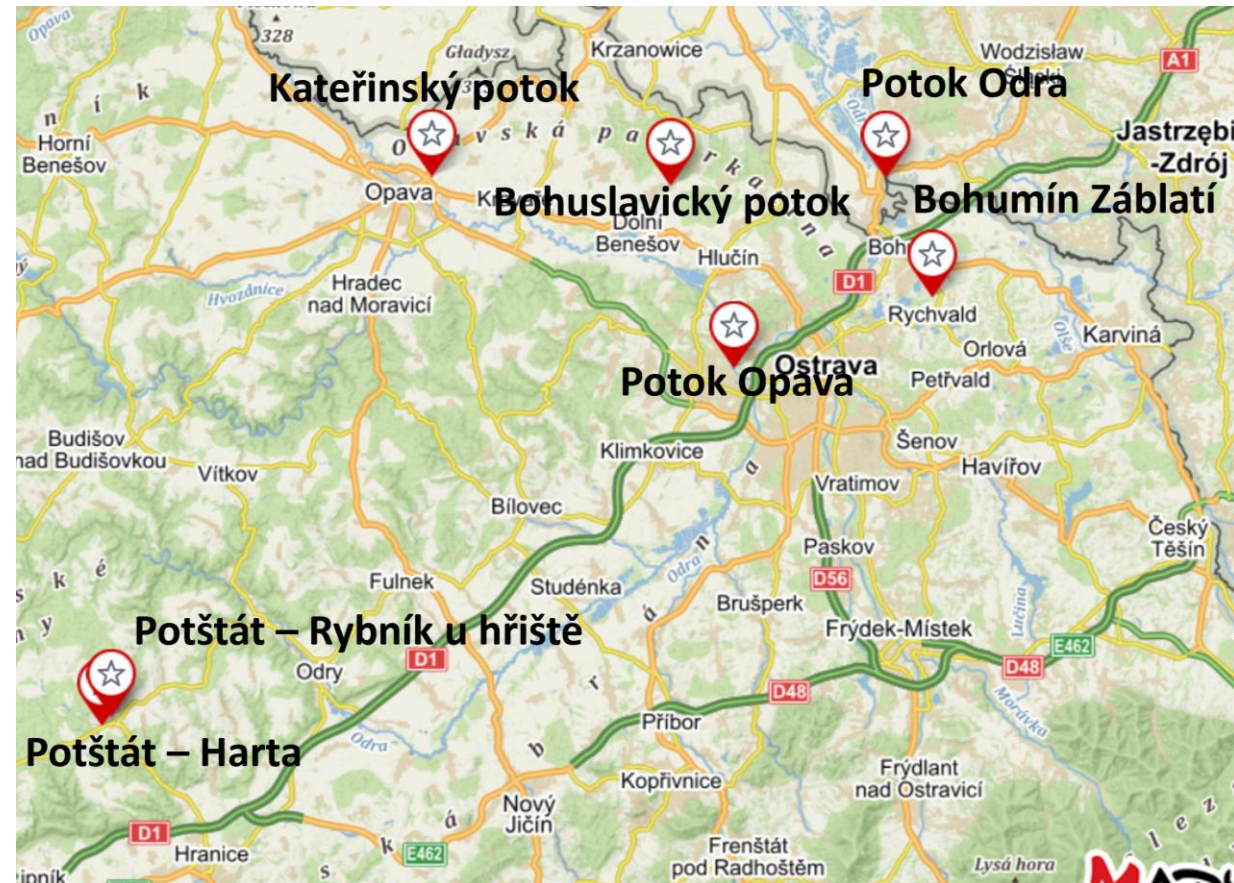


Use: corn, vegetables, rice, potatoes, peas, tobacco...

Experimental part

Monitoring of pesticides in surface waters

- Collection interval: 1x per month.
- Collecting in plastic sample boxes.
- Stored in a refrigerator at 4 °C until analysis.
- Filtration (microfilters with glass fibers).
- SPE (EnvirElut pesticides columns).
- LC-MS/MS analysis.
- Analysis of a total of 95 pesticides, of which 70 were detected.



Monitoring of pesticides in sediment

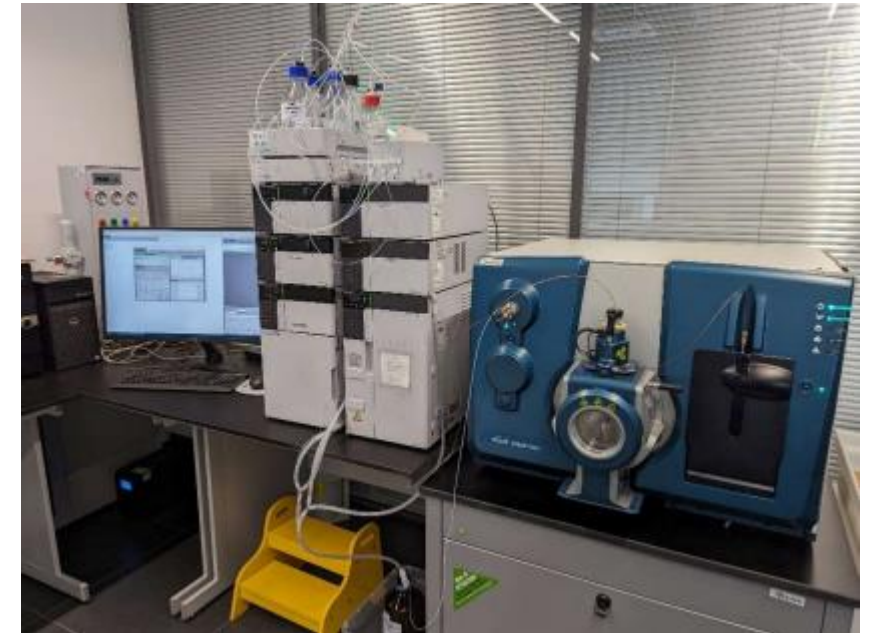
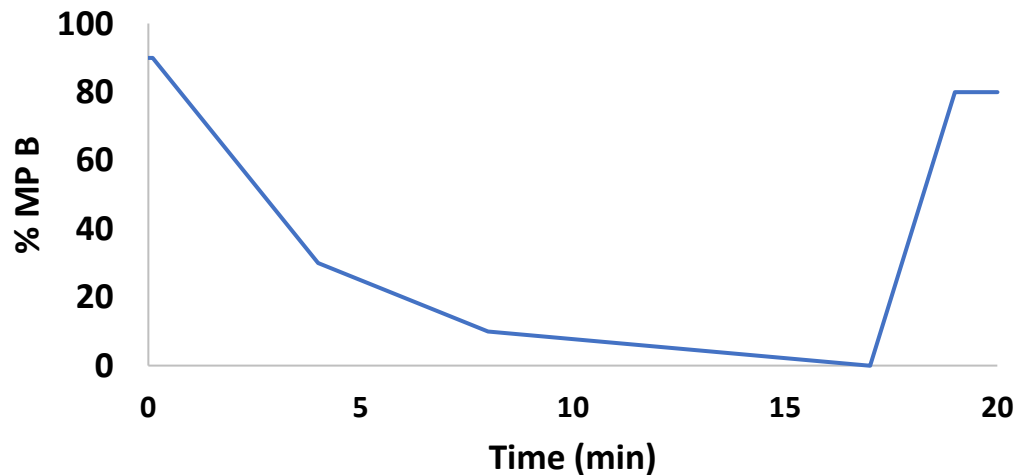
- Collection interval: 4 times a year.
- Collecting in plastic sample boxes.
- Dried to dryness at laboratory temperature.
- Processed with a modified "QuEChERS" method.
- SPE (EnvirElut pesticides columns).
- LC-MS/MS analysis.
- Analysis of a total of 95 pesticides, of which 30 were detected.



Measurement conditions on HPLC-MS/MS

- Column: Kinetex XB-C18 100A (150 x 4,6 mm; 2,6 μm).
- MP A: 5 mM ammonium formate in MeOH.
- MP B: 5 mM ammonium formate in H₂O.

Gradient MP B



Preparation of activated carbon

- Material: Invasive plants - *Reynoutria japonica* (RJ) and *Impatiens glandulifera* (IG).
- Activating agents: NaOH and H₃PO₄.
- Activation ratio: biomass/activator 1:2.
- A total of four AC activated carbons were prepared through microwave pyrolysis.
- Process time: 20 minutes.
- Power: 400 W and 600 W.
- Washed with H₂O and HCl to neutral pH.
- Ground to sizes below 0.09 mm.

Reynoutria japonica

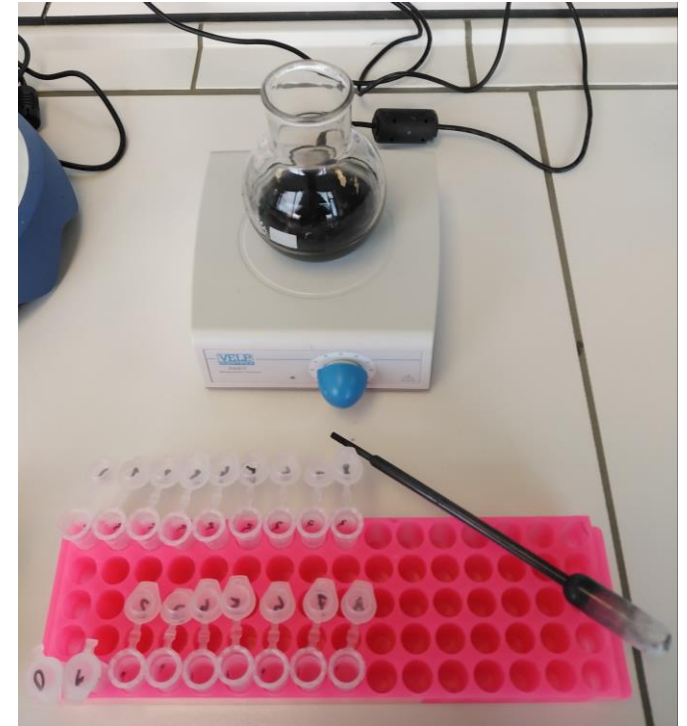


Impatiens glandulifera



Kinetic experiments

- Dosage of AC: 5 mg.
- Solution volume: 50 ml.
- Concentration of pesticide solutions: $c = 1 \text{ mg/l}$.
- Samples left on the mixer for 660 min - regular sampling.
- Samples filtered using microfilters (SWINNEX 13 mm).
- Analysis by LC-MS/MS.

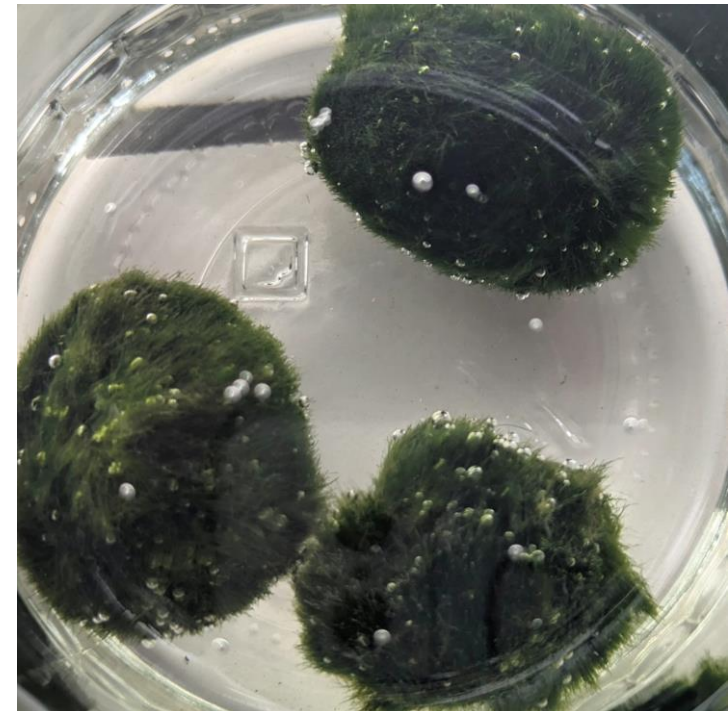


Adsorption experiments

- Dosage of AC: 5 mg.
- Solution volume: 50 ml.
- Concentration of pesticide solutions: $c = 0.01-1$ mg/l.
- The samples were left on the shaker for 220 min.
- Samples filtered using microfilters (SWINNEX 13 mm).
- Analysis by LC-MS/MS.

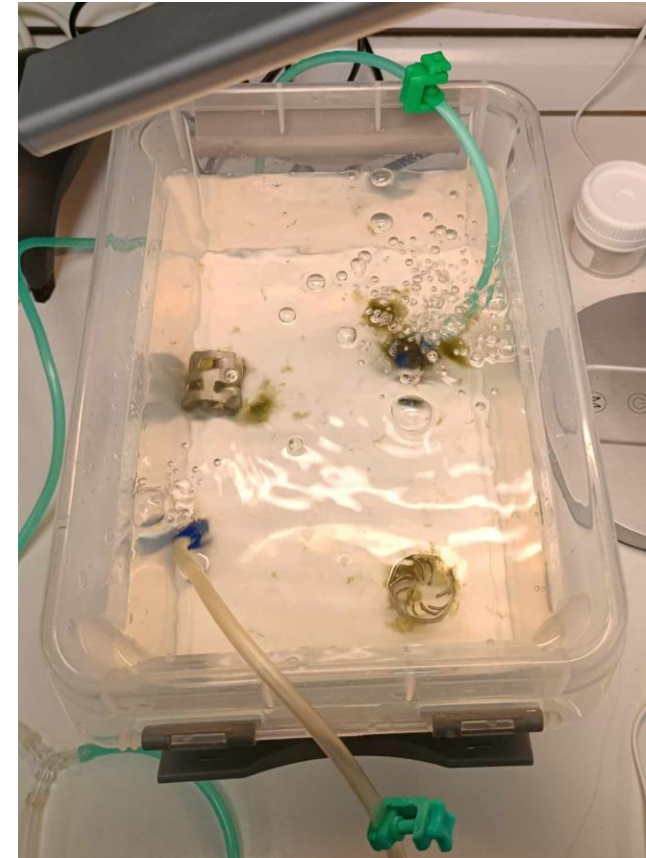
Biological degradation - *Aegagropila linnaei*

- 1x *Aegagropila linnaei*.
- Solution volume: 200 ml.
- Concentration of pesticide solutions: $c = 1 \text{ mg/l}$.
- Process time: 10 days.
- Analysis by LC-MS/MS.
- The effect of photosynthesis was also tested.



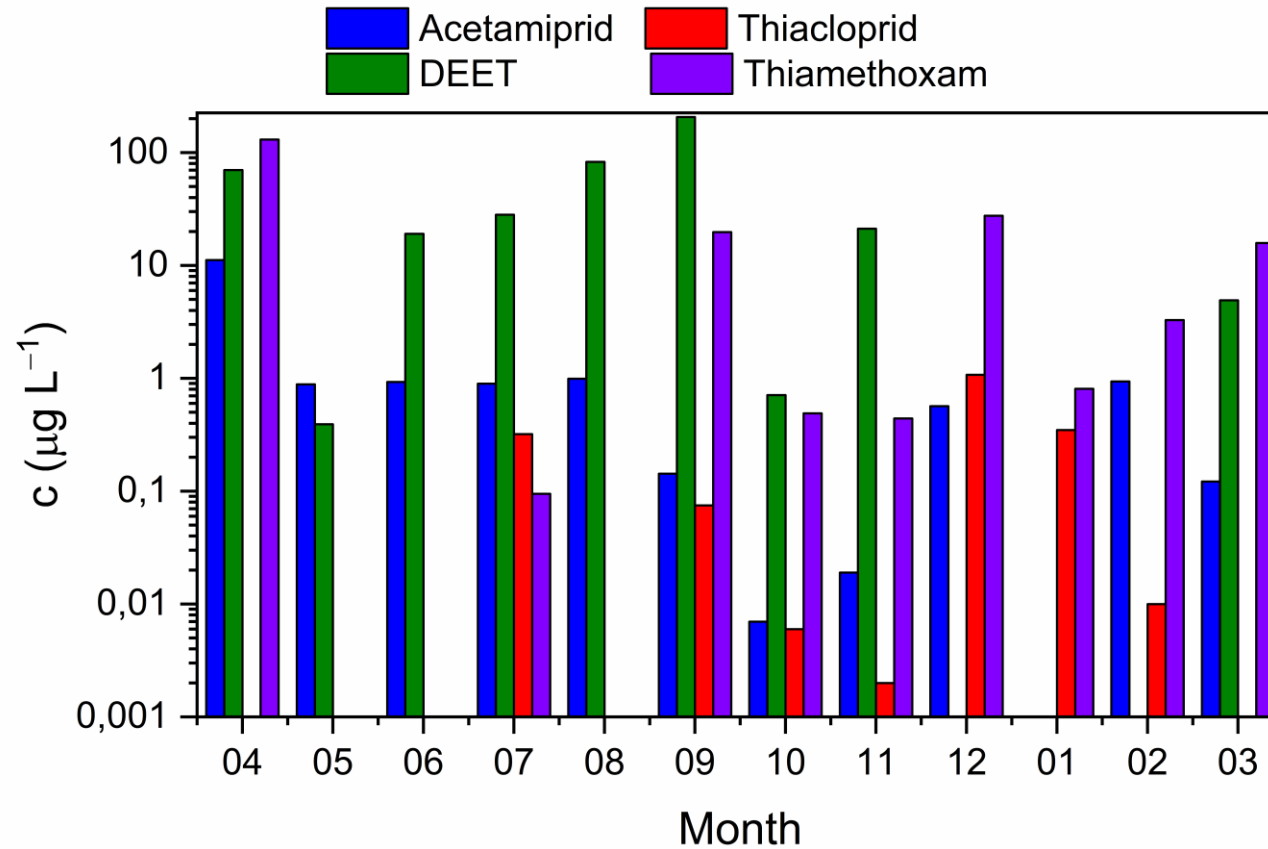
Biological degradation – *Audouinella* sp.

- Cultivation of *Audouinella* is in progress.
- Biological degradation of pesticides is in process.
- Dosage of *Audouinella*: 0.80 g.
- Solution volume: 200 ml.
- Concentration of pesticide solutions: $c = 1 \text{ mg/l}$.



Result part

Pesticides detected in the collection point "Kateřinský potok"

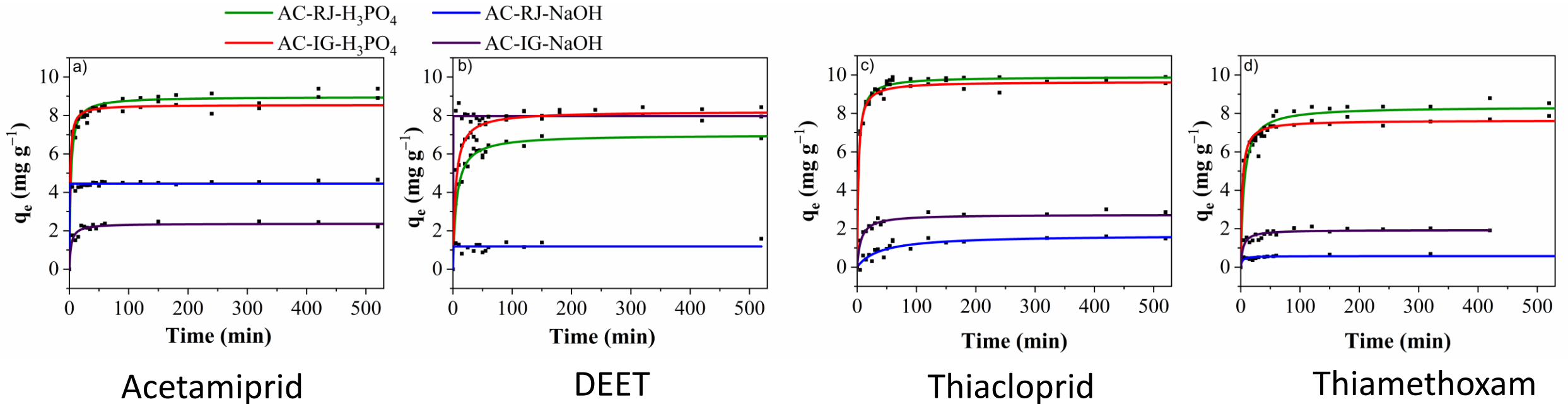


Pesticides detected in the sediment at the sampling point "Kateřinský potok"

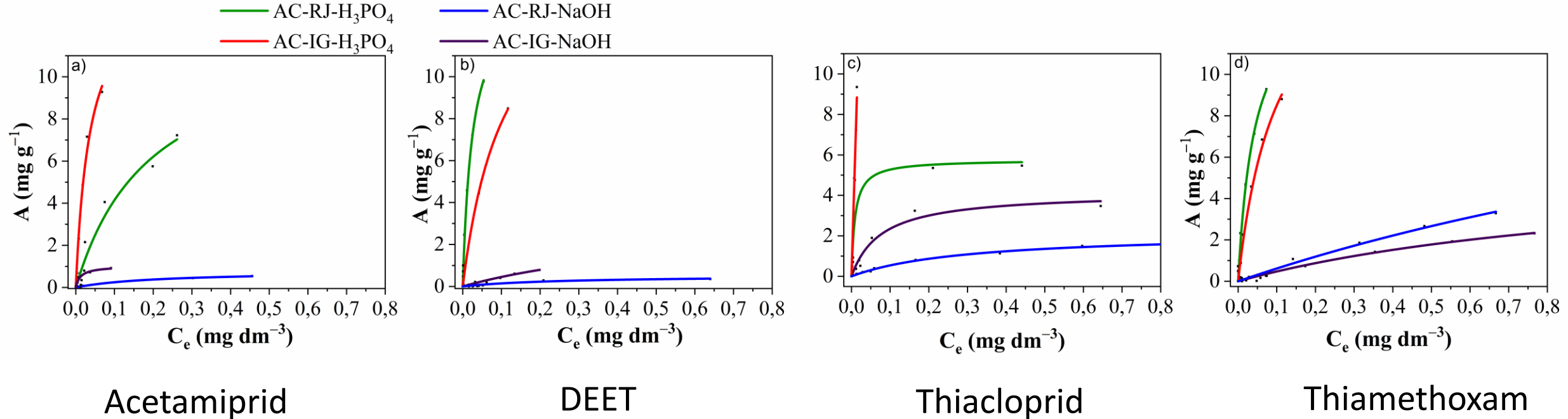
Pesticides	October	February
2,6 – Dichlorbenzoni-tril	✓	✓
Acetampirid	✓	✓
Atraton	✓	-
Bromacil	✓	✓
Cyprodinil	✓	✓
DEET	✓	✓
Desethylatrazine	✓	✓
Desmetryn	-	✓
Dichlofenthion	-	✓
Goal	-	✓
Chlorthiophos	-	✓
Chlortoluron	-	✓
Linuron	✓	-
Metamitron	✓	✓

Pesticides	October	February
Metazachlor	✓	-
Nitrothal-isopropyl	✓	✓
Oxadixyl	-	✓
Pethoxamid	✓	-
Prometon	✓	-
Propachlor	✓	-
Ro-neet	-	✓
Simazin	✓	-
Systhane	✓	-
Tebukonazol	-	✓
Terbuthylazin	✓	-
Thiacloprid	✓	✓
Thiamethoxam	✓	✓
Triadimefon	✓	✓

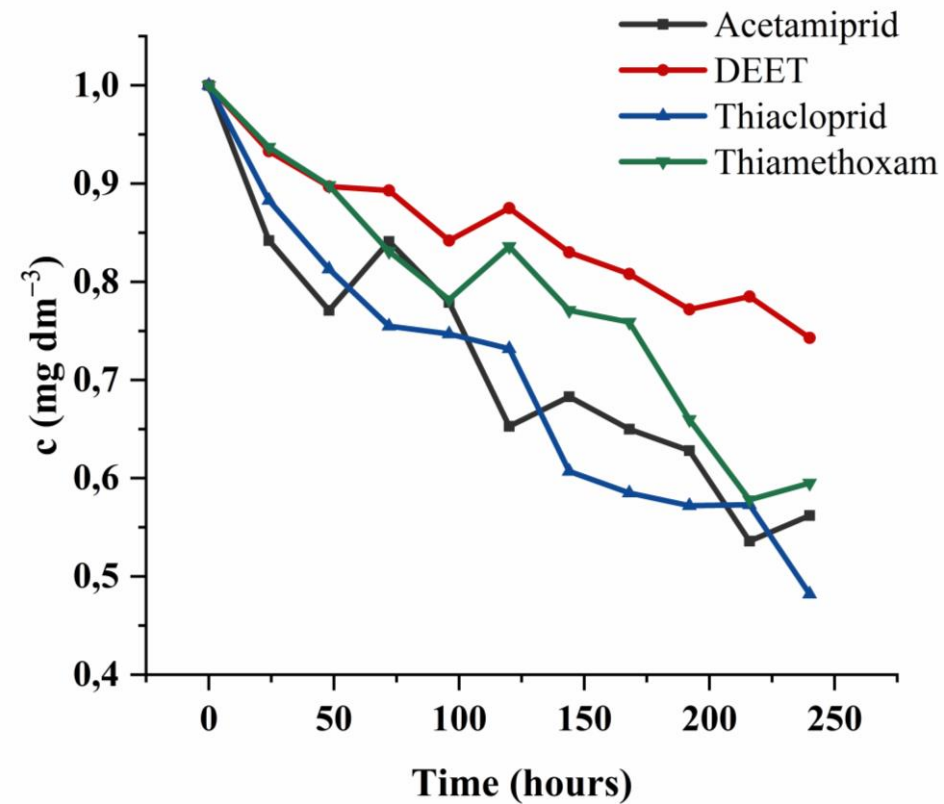
Kinetic experiments – Active carbon



Adsorption experiments – Active carbon



Biological degradation - *Aegagropila linnaei*



Conclusion

- Based on monitoring, four pesticides were selected.
- A total of four sorbents were prepared from invasive plants.
- The highest sorption capacity was shown by the sorbent from *Reynoutria japonica* and then from the *Impatiens glandulifera*, which was prepared by activation with H_3PO_4 .
- In the case of acetamiprid and thiacloprid, the best sorbent was prepared from *Impatiens glandulifera*, followed by *Reynoutria japonica*.
- The opposite was true for DEET and thiamethoxam.
- Conversely, sorbents prepared by activation with NaOH show a lower sorption capacity.
- This work shows that invasive plants appear to be suitable material for the preparation of activated carbon.
- Biodegradation tests are still in process.

Acknowledgement

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Thank you for your attention

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