Screening of surface water samples for contaminants in an industrialized area of Luxembourg using non-targeted LC-HRMS and open-source data processing

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INTRODUCTION

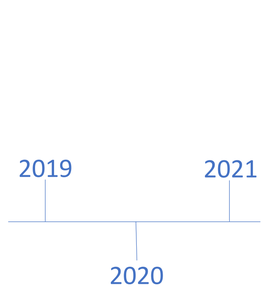
Environmental samples can provide rich information about human activities in a given area. Especially in *industrialized areas* there is an increasing need to look at chemicals endangering *human health* and that of the surrounding ecosystem. In this work the focus is on *surface water* samples from the river Chiers, which is located in the so-called *Minette* region, a highly industrial region in the southwest of *Luxembourg* (see Figure 1).

OBJECTIVES

- Retrospective analysis of river water samples
- Identification of *emerging contaminants* and their *transformation products*
- Better understanding of possible industrial influences on the aquatic environment
- Input for eventual *LuxTIME* project-based sampling campaigns

METHODS

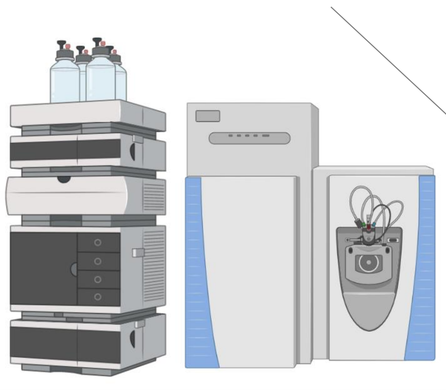
***Figure 1**: River Chiers in the Minette region*



Water samples (22)

***Conditioning:** 2xACN/2xH_2O*
***Sample Loading:** 1 L, 30 mL/min*
Washing (2xH_2O), Drying
***Elution:** Cyclohexane/ACE/4x ACN*
Drying Steps
***Resuspension:** 2 mL ACN/H_2O (10/90)*
Filtration

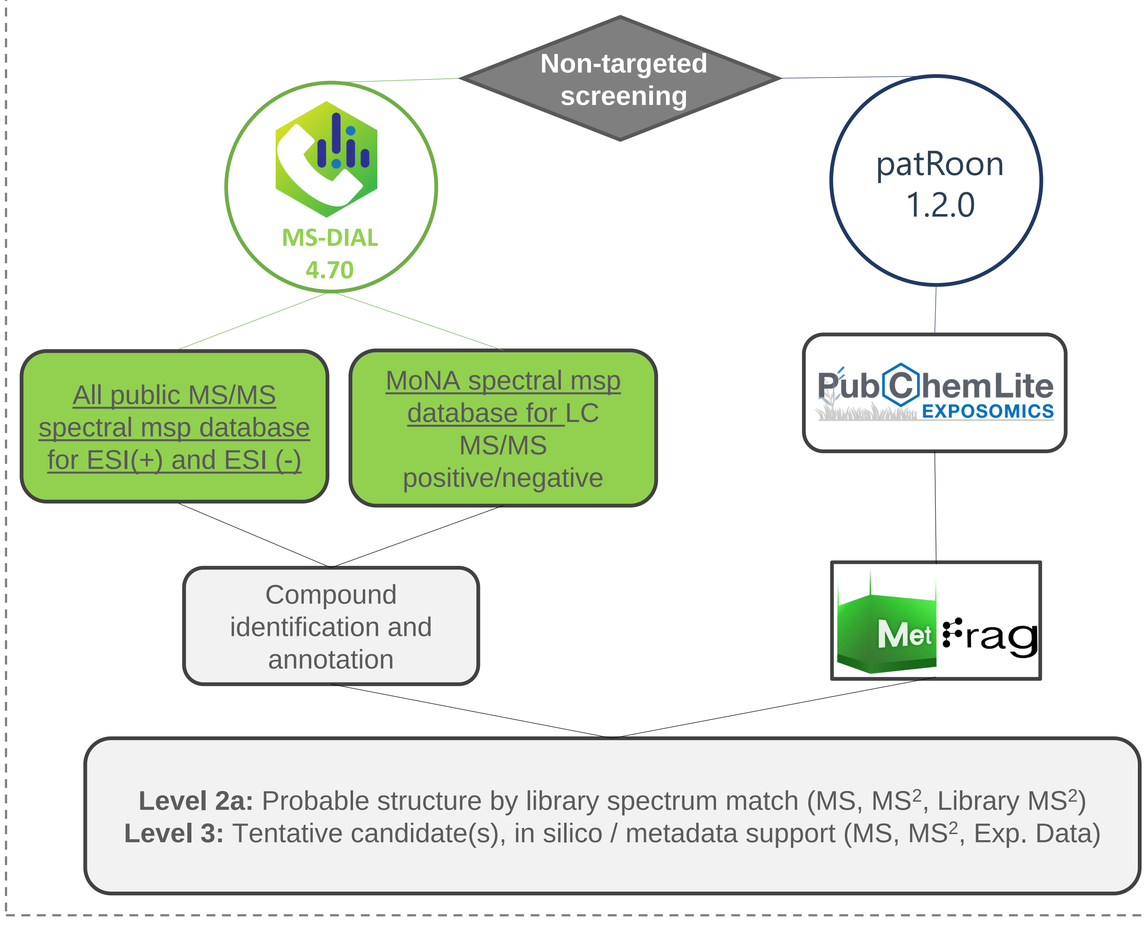
Solid Phase extraction



LC-MS (Q Exactive HF) analysis

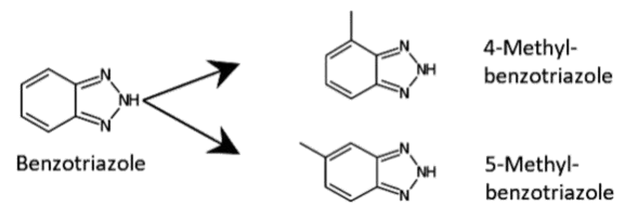
***Column:** Waters Acquity UPLC BEH C_{18} column (Reversed Phase)*
***Mobile Phase A:** MeOH*
***Mobile Phase B:** H_2O/0.1% FA (10/90, v/v)*
***Ionization mode:** ESI (+) and ESI (-)*

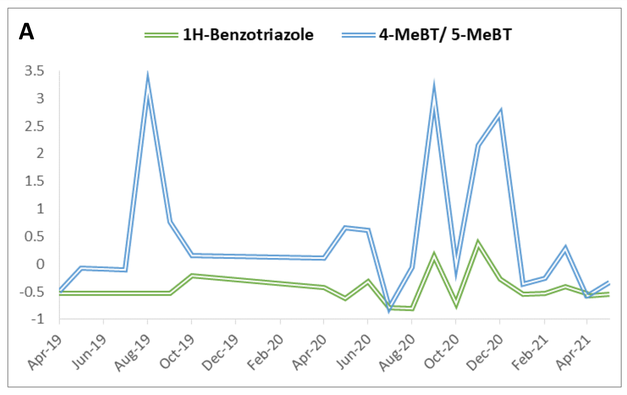
DATA ANALYSIS



RESULTS AND DISCUSSION

- Time trends at Chiers reveal interesting patterns in *parents* and *transformation products (TPs)*, shown in Figure 2A (Benzotriazole; corrosion inhibitors) and B (Venlafaxine; pharmaceutical).





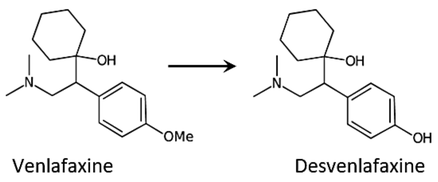


***Figure 2:** Time trends (peak intensities) of identified transformation products and their parent compounds measured in ESI(+). All values are standardized* $[z = \frac{x-\mu}{\sigma}]$.
***A:** The corrosion inhibitors 4- or 5- Methylbenzotriazole (MeBT) and their parent 1H-Benzotriazole. **B:** The antidepressant Venlafaxine and its transformation product Desvenlafaxine.*

Annotations

ESI (+)			ESI (-)		
2019	*2020*	*2021*	*2019*	*2020*	*2021*
286	126	132	130	30	30

92 overlapping compounds — 26 overlapping compounds

52 — MoNA score > 0.9 — 8

- All water samples contained the same *52 chemicals* in ESI (+) relevant for *exposomics*
- Several *industry-related* compounds were found, typical for the industrial Minette region (focus of *LuxTIME* project).

***Table 1:** Overview of use information for the 52 Level 2a hits from ESI(+)*

Use	# Level 2a hits
Flame retardants	2
Agricultural	6
Food additives	6
Adhesives	3
Corrosion inhibitors	2
Cosmetics	6
Pharmaceuticals	40
Others	9

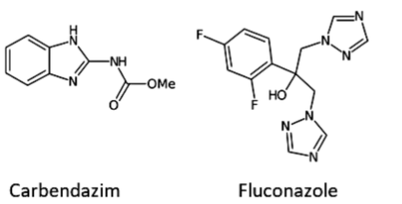


***Figure 4:** Structures of several tentatively identified agrochemicals (level 2a), not authorized for use in Luxembourg. Examples of pharmaceuticals and corrosion inhibitors are in **Figure 2**.*

***Figure 3:** Heatmap showing the peak intensities of all 52 chemicals identified at level 2a in positive mode in 2019, 2020 and 2021. The cell colour represents the peak intensity or chemical level in the sample (dark red=high). All values were standardized per compound and year to compensate for intensity and method differences. 9 transformation products (blue) could be found and 4 of the according parent compounds (green).*

CONCLUSION

Several features indicating *environmental pollution* of surface waters over three years were identified using *non-targeted* workflows. Further work is ongoing to confirm the identity, concentration, origin and relevance (effects) of the tentatively identified chemicals.

REFERENCES

1. Krier J, Singh RR, Kondić T, et al. *Environment International*. 2022;158:106885. DOI:10.1016/j.envint.2021.106885
2. Dummer NM. Rev Environ Sci Biotechnol. 2014;13(1):53-61. DOI:10.1007/s11157-013-9318-y
3. Kruve lab. Accessed August 9, 2021. https://kruvelab.com
4. Schymanski EL, Jeon J, Gulde R, et al. Environ Sci Technol. 2014;48(4):2097-2098. DOI:10.1021/es5002105
5. Helmus et al (2021). patRoon. J. Cheminformatics. DOI: 10.1186/s13321-020-00477-w
6. Ruttkies, Schymanski et al. (2016) DOI: 10.1186/s13321-016-0115-9

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