Statistical approach for the analysis of contaminants of emerging concern (CECs) in complex water samples during treatment processes

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1 Introduction

Non-targeted analysis
- tentative identification
- transformation products

Challenges:
Subjectivity (sample preparation, measurement, data analysis)
Analysis of trace amounts in complex matrices
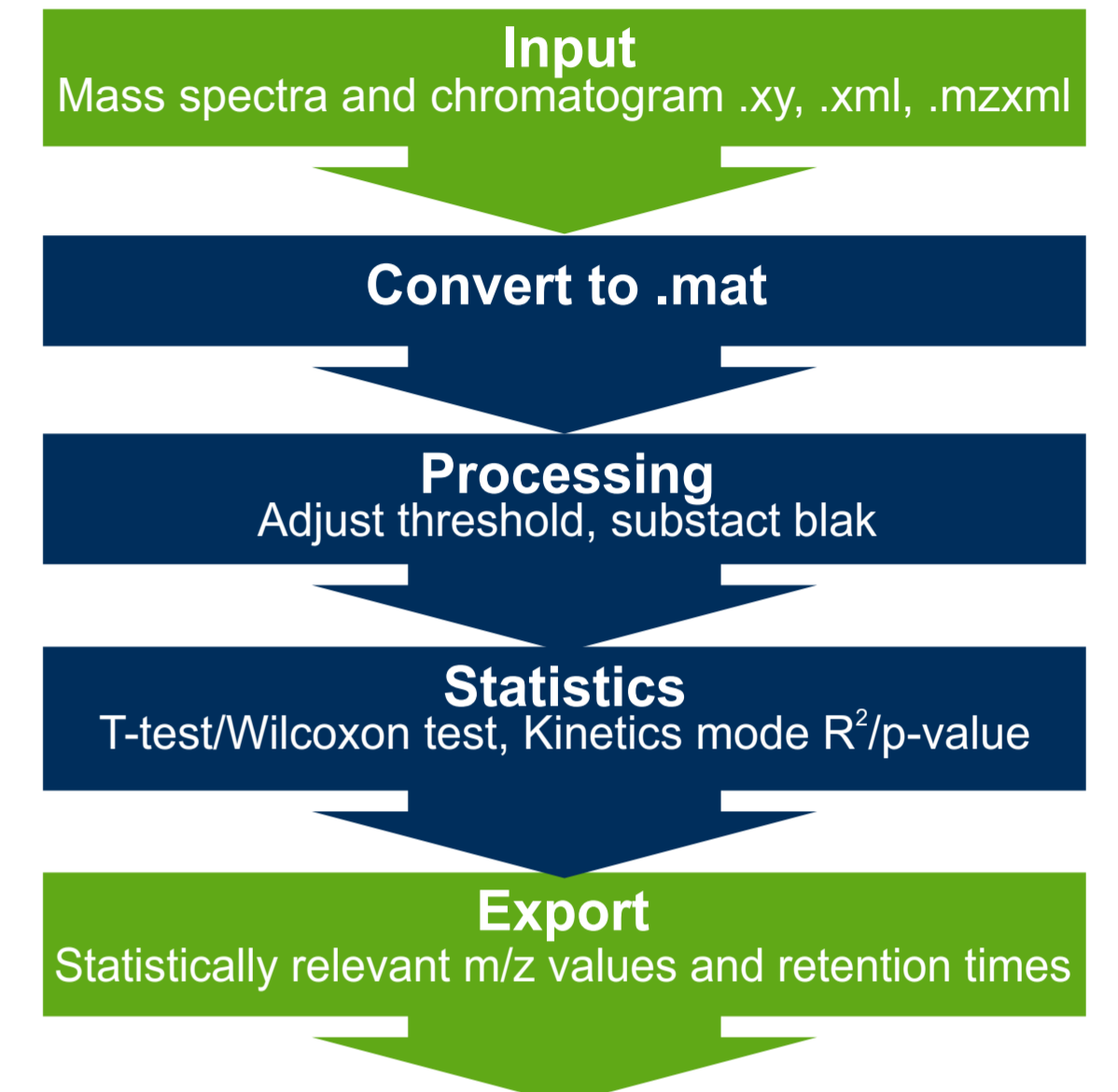Uncertainties related to the identification and quantitation of micropollutants

Statistical approach to monitor chemical changes

2 Methods

Experimental conditions

| Contaminant	Category	Conc.	Matrix	Treatment
Maprotiline	Antidepressant drug	5 ppm	Secondary treated wastewater	H_2O_2/UV
Acetamiprid	Neonicotinoid insecticide	40 ppb	Simulated river water (20 ppm fulvic acid)	UV irradiation

Analysis

- **direct infusion** mass spectrometry
- Bruker SolarixXR FT-ICR 9.4 T instrument (**sub-ppm** accuracy)
- **electrospray ionization source**
- in-house developed freeware (**SPIX**): follow **statistically relevant changes** in complex mixtures and to **model the kinetics** of the transformation products

Input
Mass spectra and chromatogram .xy, .xml, .mzxml

Convert to .mat

Processing
Adjust threshold, substact blak

Statistics
T-test/Wilcoxon test, Kinetics mode R^2/p-value

Export
Statistically relevant m/z values and retention times

3 Results: Examples of SPIX abilities on water treatment monitoring

Kinetics of maprotiline degradation in wastewater matrix

- decrease of Maprotiline: **exponential decay**, modeled with a **good fitting** by the software and **high statistical relevance**
- maximum number of transformation products, get an overview of the occurring changes.
- SPIX suggested 24 peaks ($R^2 > 0,9$), 22 of them were tentatively assessed as maprotiline-related compounds, export data
- **reagents, intermediates, and products were revealed, by optimal kinetic modeling**
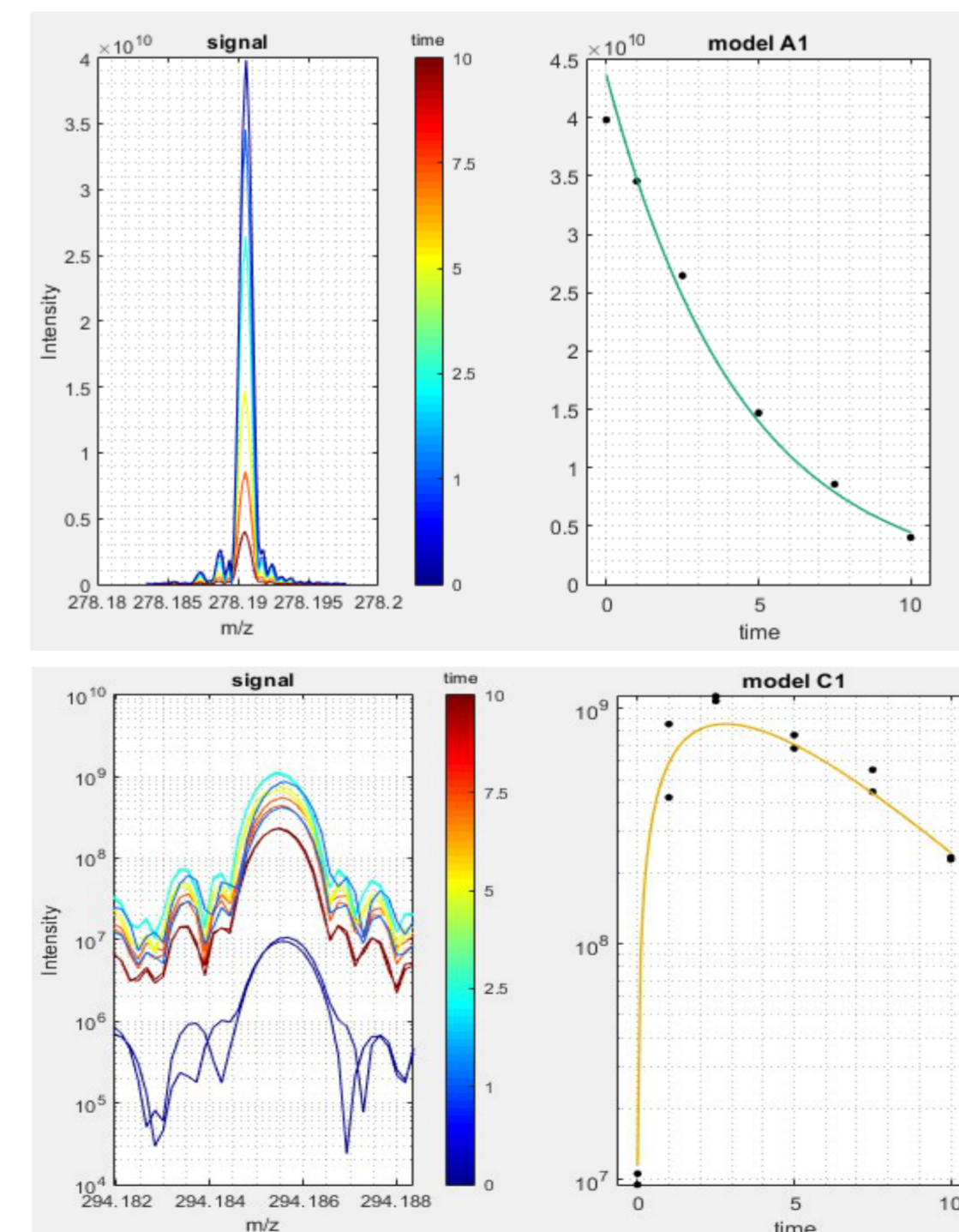
Acetamiprid in low concentrations in simulated river water

- **aim: lower the limit of detection** without pre-concentration using direct infusion mass spectrometry
- acetamiprid and possible photoproducts going through statistically relevant changes between the two conditions, detected by SPIX at **1% intensity of the base peak**
- quick and reliable way to identify the **treatment efficiency** and the **persistence** of transformation-products
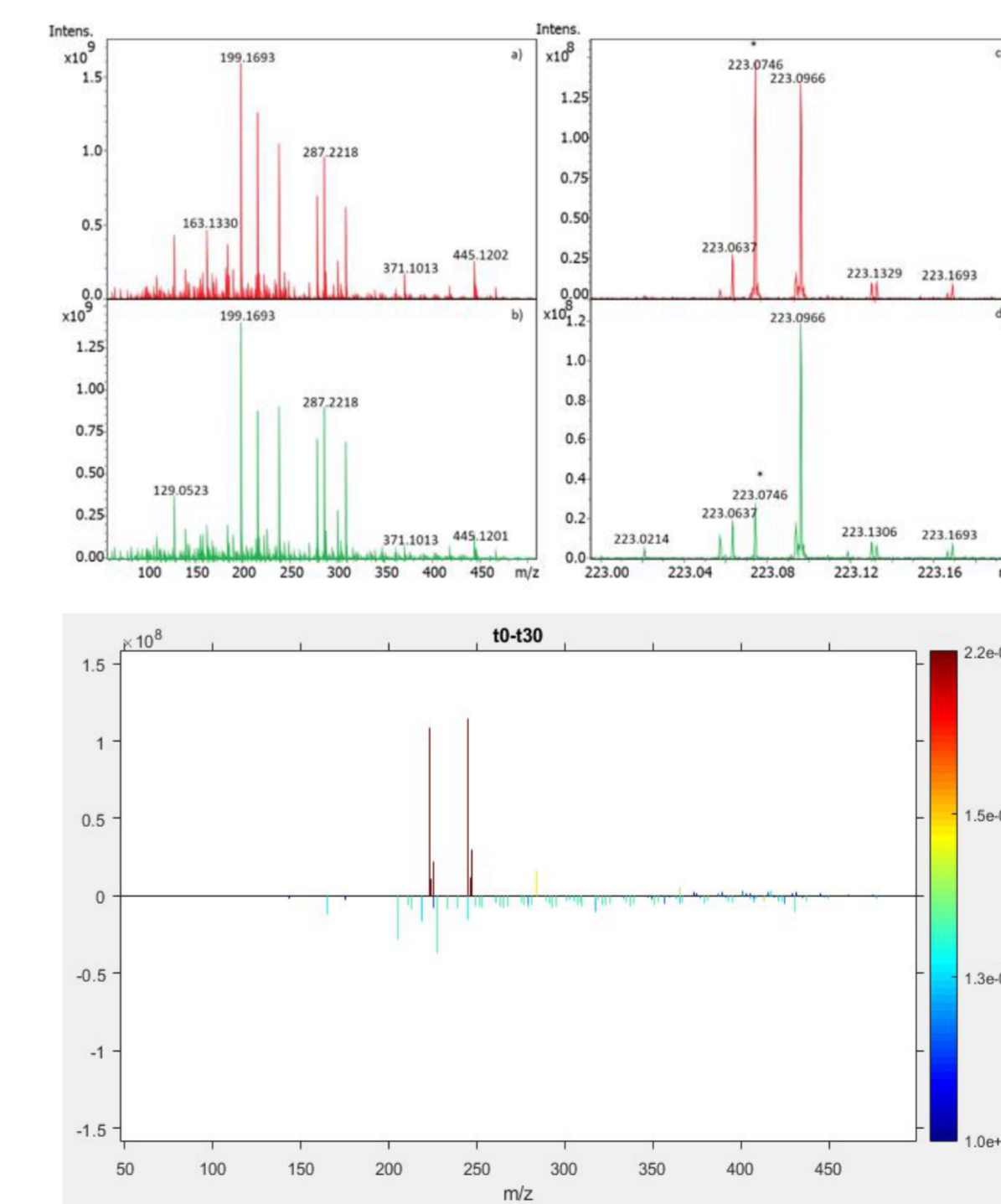
4 Conclusion

SPIX free software:
- identification of peaks in complex mixtures
- variations of peaks, even at low abundances
- an approach based on statistical relevance
- tackle subjectivity
- kinetic modeling
- export statistical description in .csv format

Acknowledgements

Download now http://spix.webpopix.org/

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