

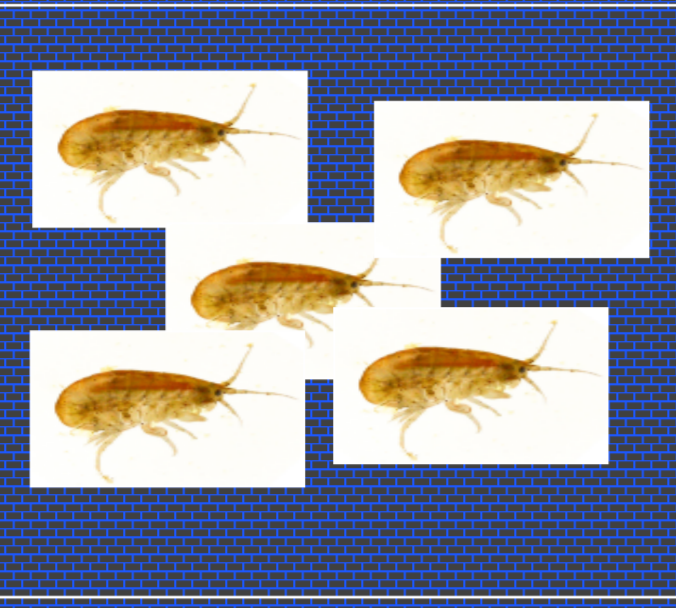


High-Resolution Mass Spectrometry for a Comprehensive Pesticide Screening in a Vulnerable Aquatic Ecosystem

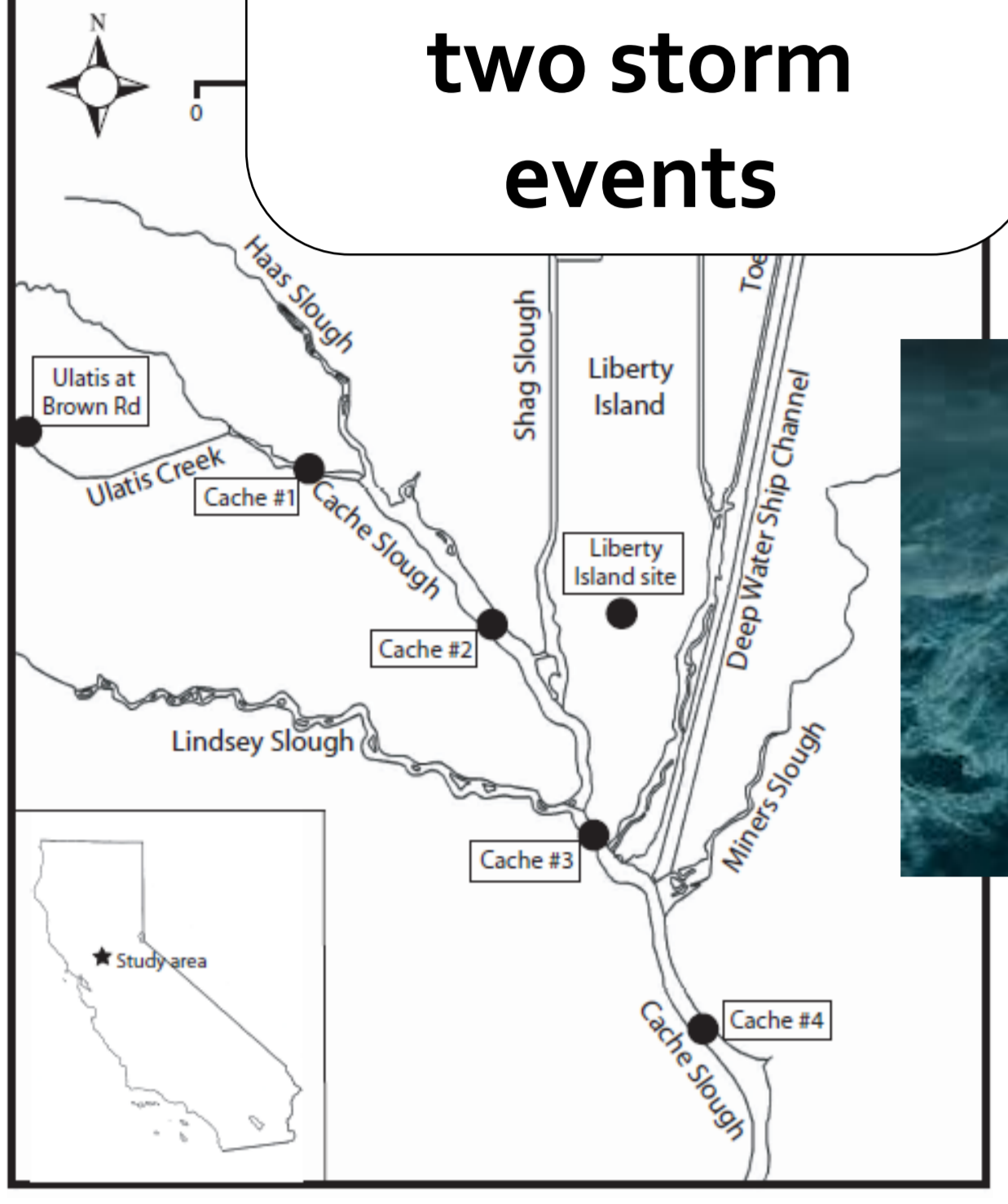
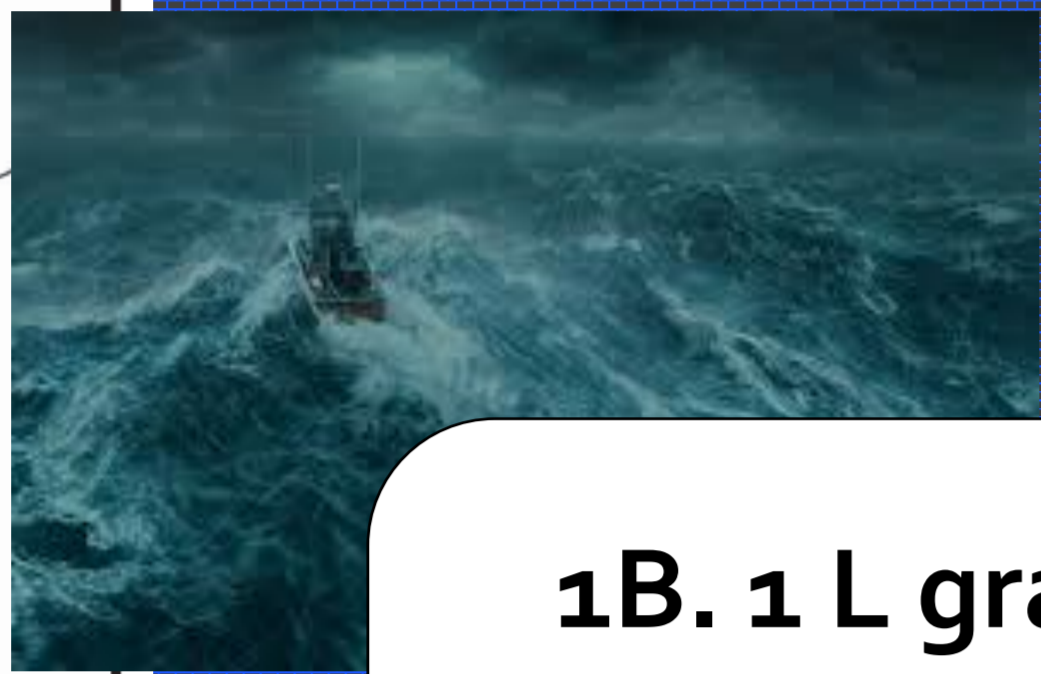
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1A. In-situ deployment of *H. azteca* during two storm events



1B. 1 L grab samples during 4 time points at 6 locations



SPE

2A. GC Target Analysis

21 targets (pyrethroids, organophosphates, fipronil)
→ 16 detected at least once. Pyrethroid concentrations: 0.1-10 ng/L, some > EC₅₀

GC-QTOF/MS (EI + NCI)

2B. GC Suspect Screening

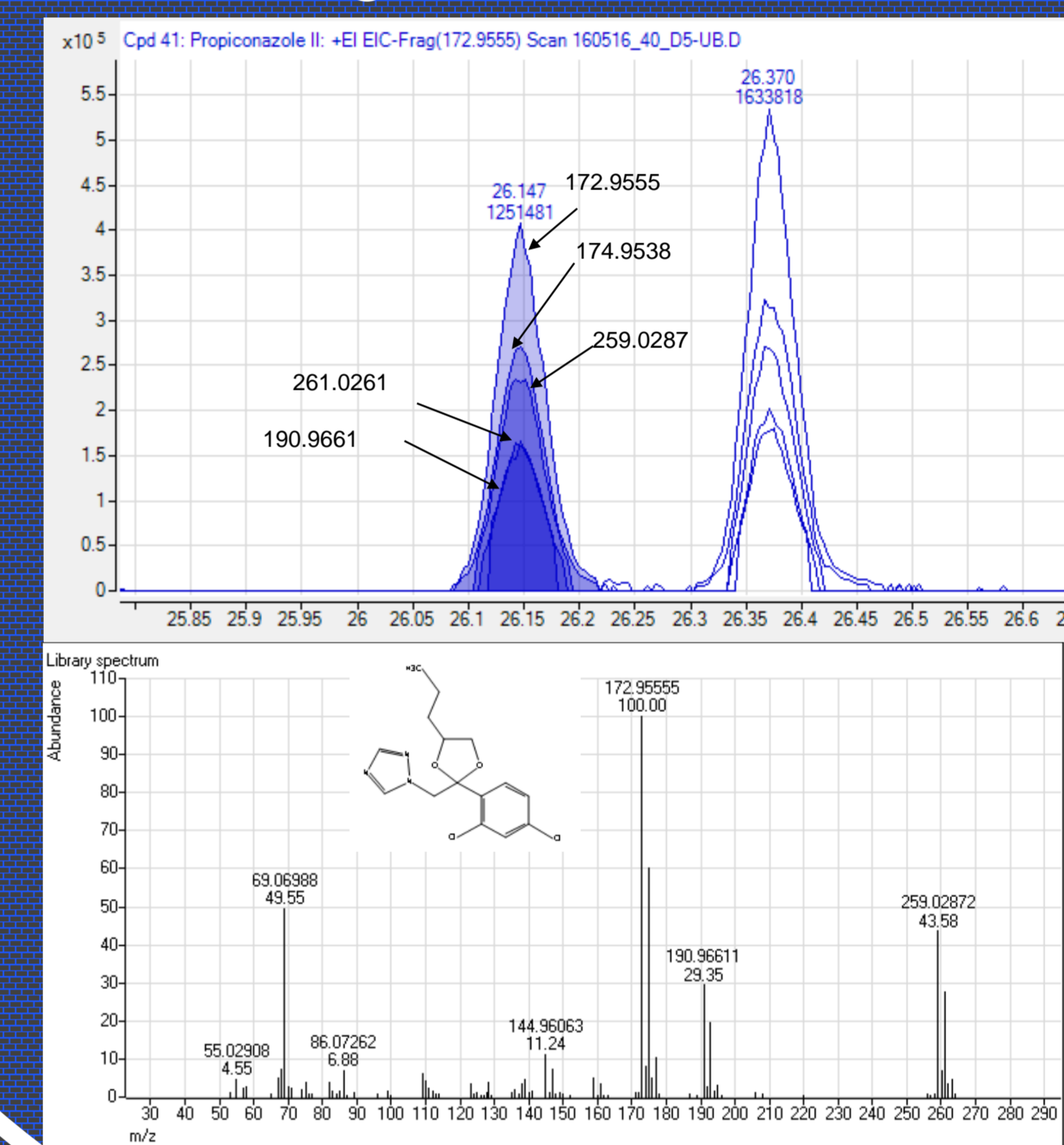
Suspect List:

Agilent Pesticide PCDL

- 750 compounds
 - accurate mass EI spectra
 - retention time (RT) availability
- Analytical method: retention time locking to match database RT

Results: 43 detected compounds (incl. dacthal, bromacil, BAM, napropamide)

Quantified: 23 with later received ref. standard



EIC of 5 confirmed fragments in environmental sample

PCDL Library EI spectra. RT in PCDL: 26.16 + 26.38

Example: Propiconazole

3A. LC Target Analysis

27 targets (herbicides, insecticides, fungicides)
→ 21 detected, max. concentrations: 800 ng/L (2,4-D), 500 ng/L (dimethoate) and 400 ng/L (boscalid) for H, I, and F

SPE

LC-QTOF/MS/MS

3B. LC Suspect Screening

Suspect List:

Agilent Pesticide PCDL (1,800 compounds)

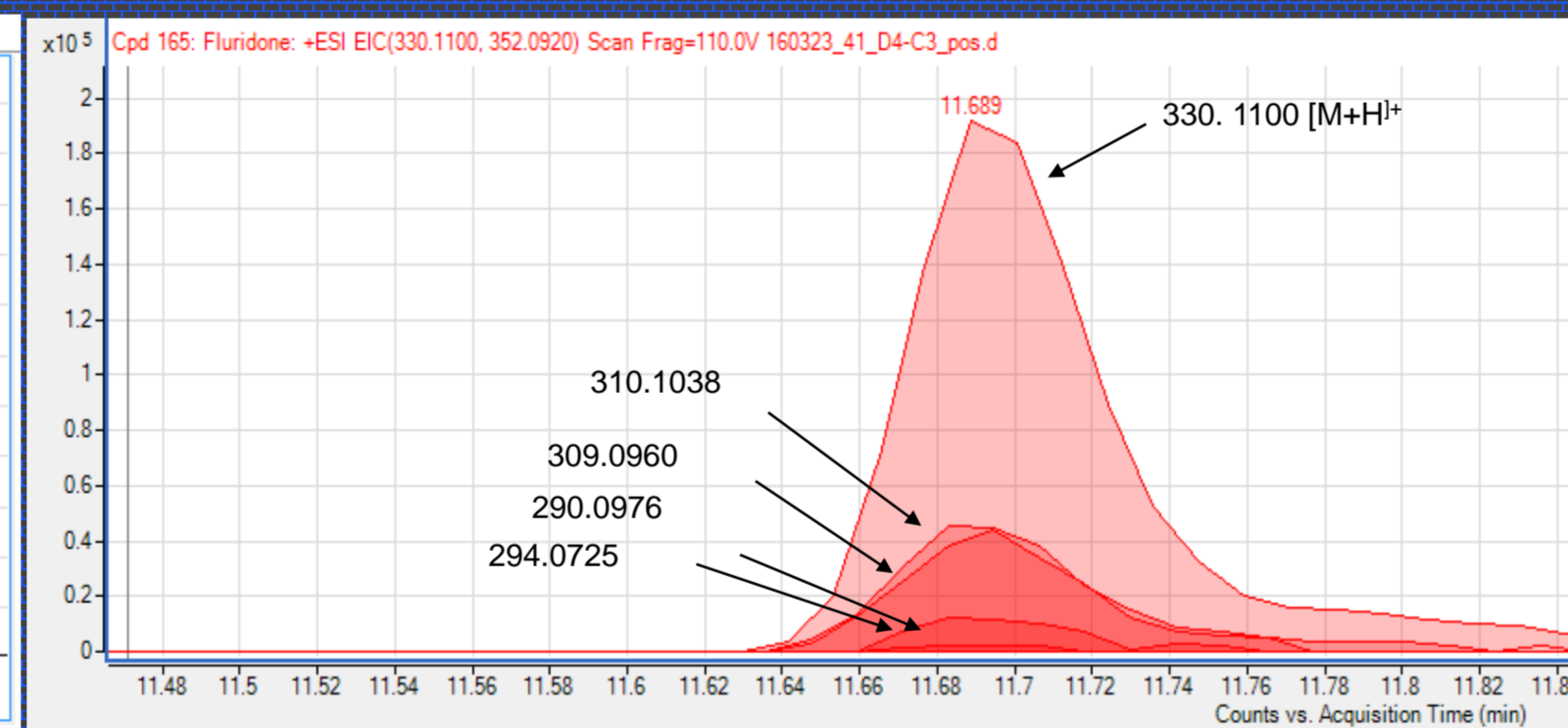
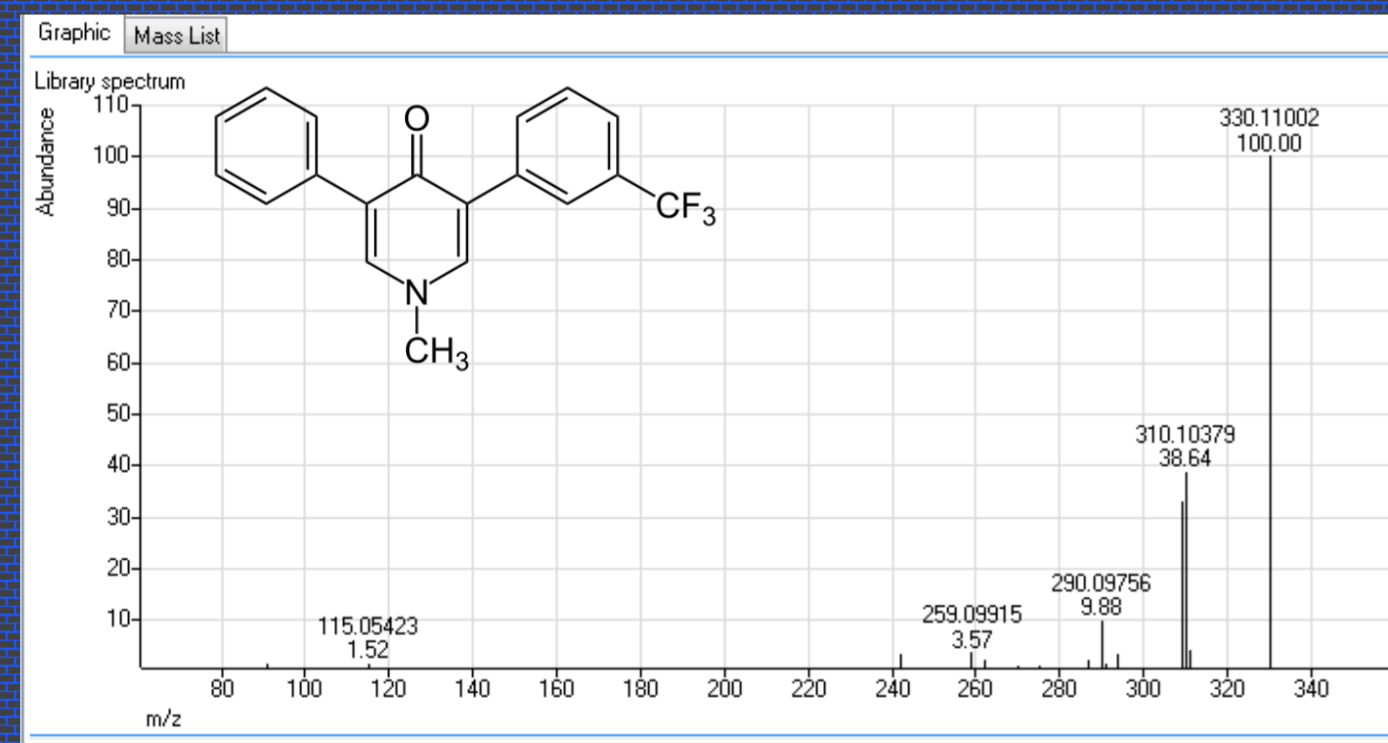
- accurate mass MS/MS spectra

Analytical method: All-Ions MS/MS, collision energy 0, 10, 20, 40 V

Results: 57 detected compounds (incl. propiconazole, norflurazone, triclopyr)

Confirmed: 18 out of 21 with ref. standard

PCDL Library ESI+ MS/MS spectra



EIC of [M+H]+ and 4 fragments of fluridone in environmental sample

Example: Fluridone

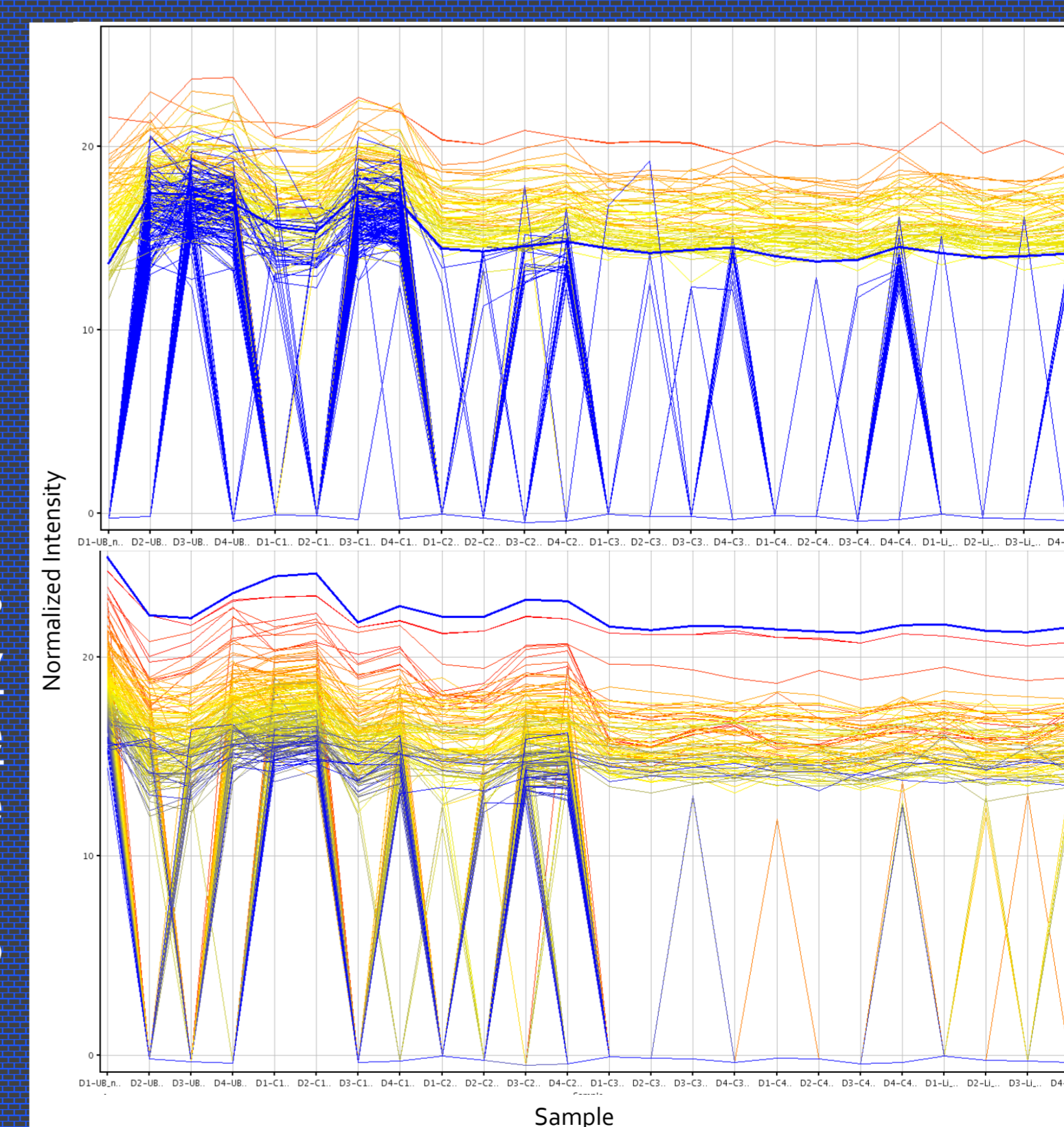
3D. Similar Feature Identification**

Indicator Compounds:

- 2,4-D (herbicide, agriculture)
- Sucralose (artificial sweetener, waste water)

212 features showing similarity to 2,4-D abundance (thick blue line) > 0.75

235 features showing similarity to sucralose abundance (thick blue line) > 0.75



Confirmed compounds with similarity >0.9:

- Dimethenamid
- Triclopyr
- Sulfentrazone
- Norflurazone

Tentatively confirmed compounds with similarity >0.9:

- Bicalutamide
- Nicothiazone
- Efavirenz

Venn Diagram showing that no feature is overlapping

3C. Transformation Product (TP) Screening

1. Prediction of TPs by Eawag-PPS*

Input: 30 parent SMILES

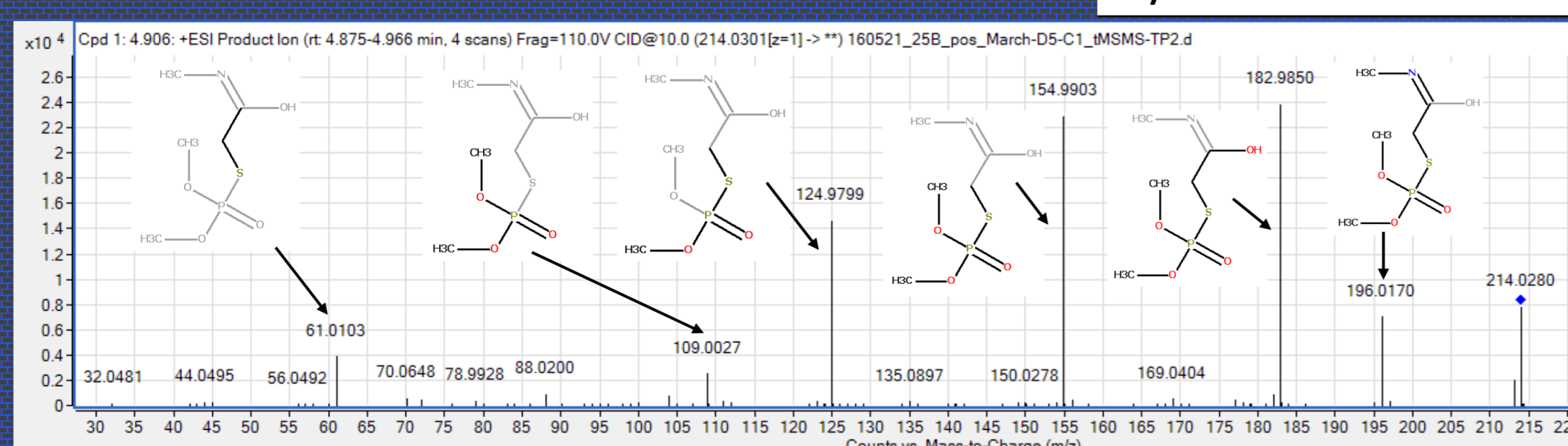
2. Find by Formula (Mass Hunter Qual): exact mass, adducts, isotope pattern, subtract blank

3. Rerun samples by targeted MS/MS

→ Fragment confirmation by MassFrontier™ and Agilent Molecular Structure Correlator (MSC)

Workflow	Number of compounds
Output Eawag-PPS:	269
Theoretically Ionizable:	192
Find by Formula Match:	13 (10 neg / 3 pos)
Tentatively confirmed by MS/MS:	4 (3 neg / 1 pos)

MS/MS spectra (CE 10) with 6 plausible fragments



Example: TP of dimethoate (omethoate)

* <http://eawag-bbd.ethz.ch/predict/>

** by Agilent Mass Profiler Professional (MPP) software

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