# High-Resolution Mass Spectrometry for a Comprehensive Pesticide Screening in a Vulnerable Aquatic Ecosystem
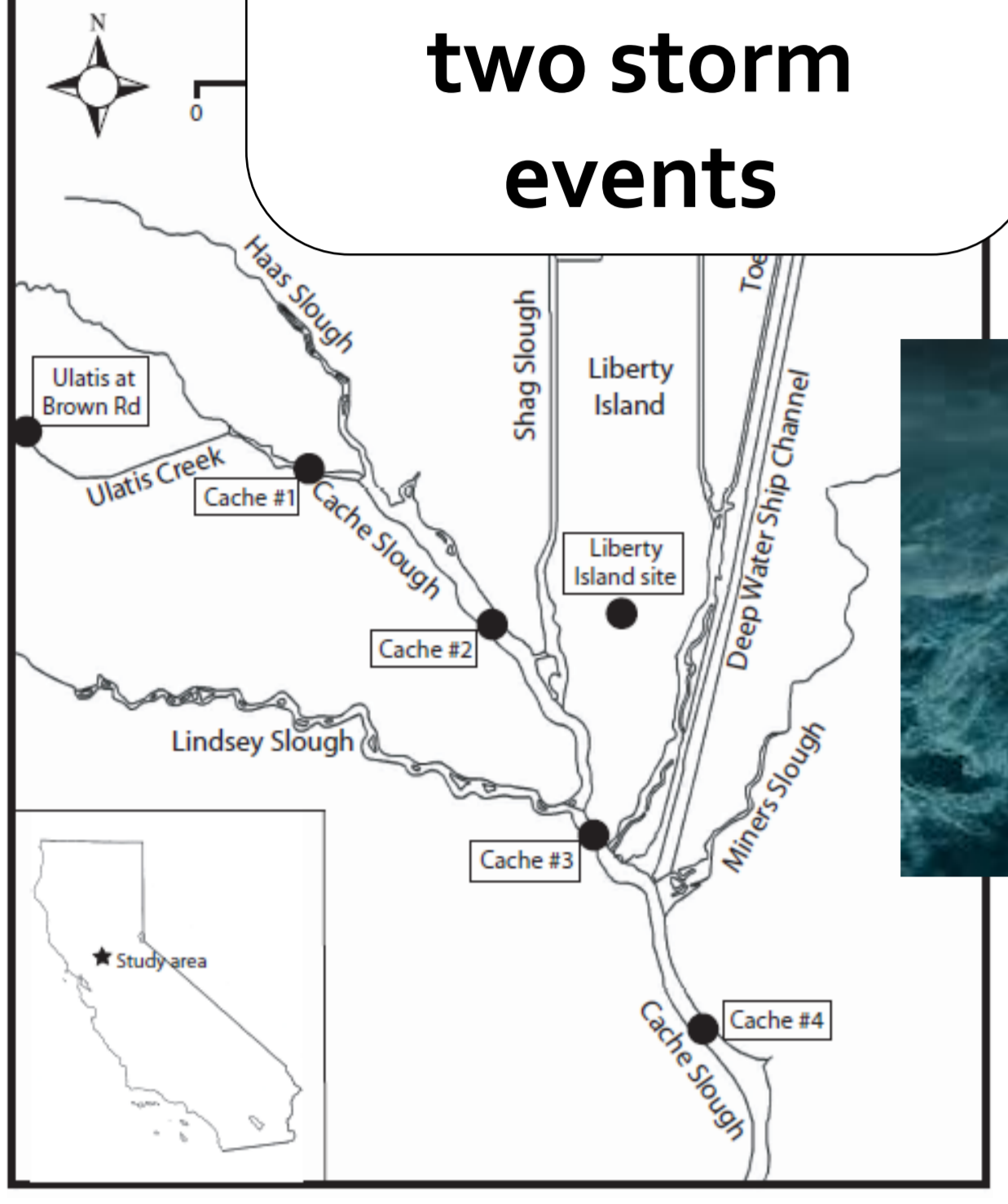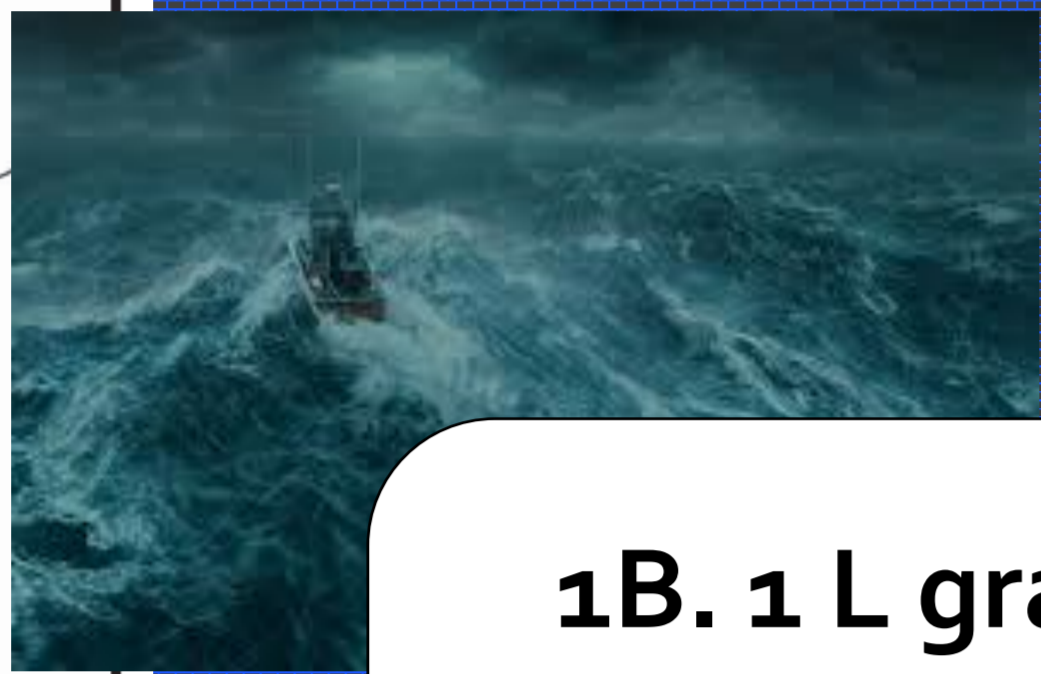
Christoph Moschet[a], S. Hasenbein[a], B. M. Lew[a], T. Anumol[b], and T. M. Young[a]

[a] Department of Civil and Environmental Engineering, UC Davis, CA, USA, [b] Agilent Technologies, Wilmington, DE, USA

cmoschet@ucdavis.edu

1A. In-situ deployment of H. *azteca* during two storm events
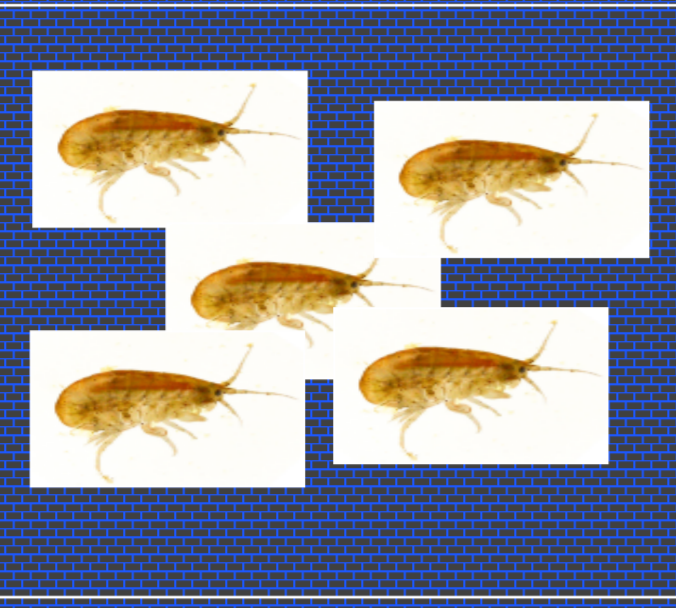
1B. 1 L grab samples during 4 time points at 6 locations

SPE

GC-QTOF/MS (EI + NCI)

LC-QTOF/MS/MS

2A. GC Target Analysis

21 targets (pyrethroids, organophosphates, fipronil)
→ 16 detected at least once. Pyrethroid concentrations: 0.1-10 ng/L, some > EC_{50}
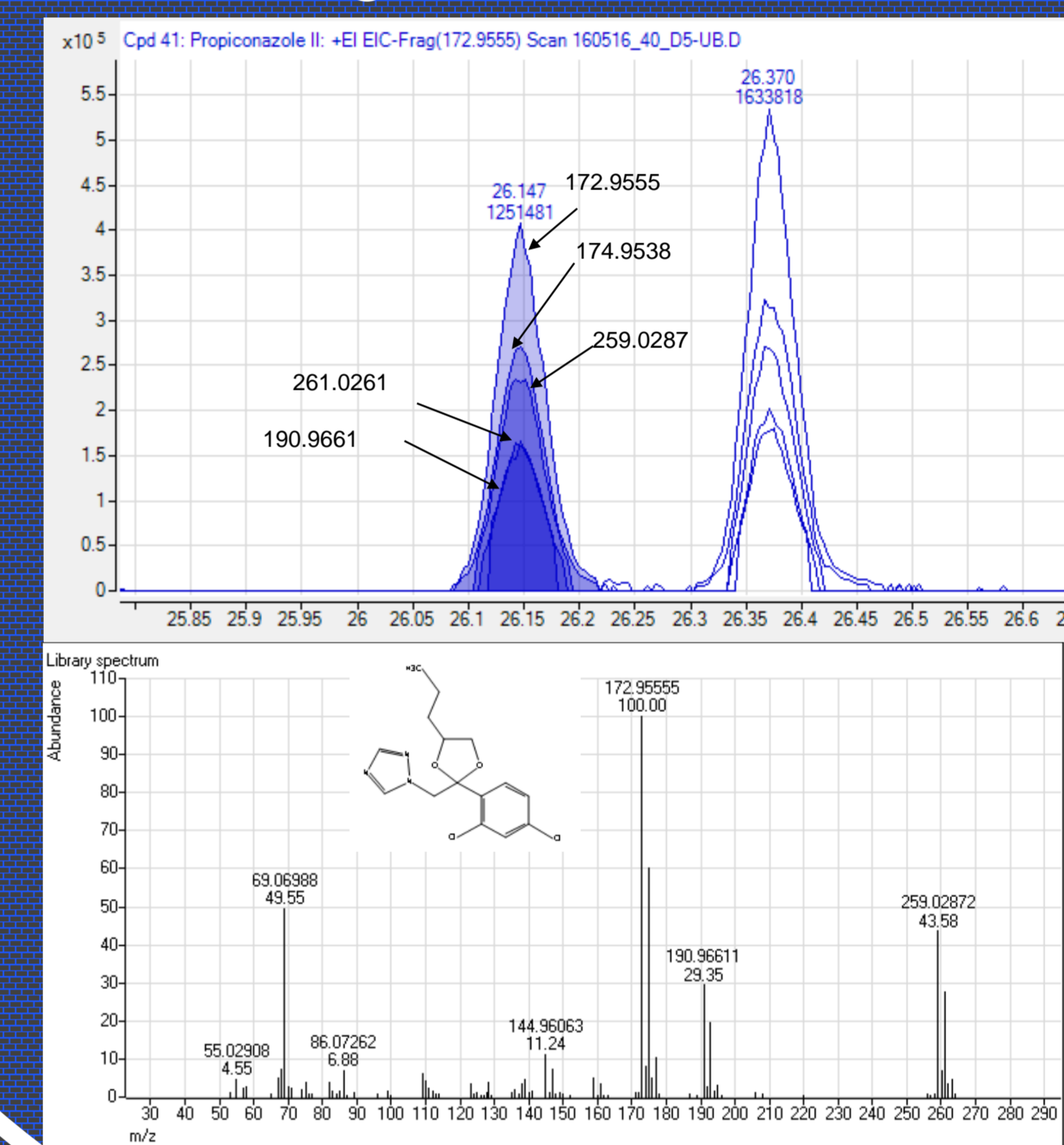
2B. GC Suspect Screening

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

3B. LC Suspect Screening

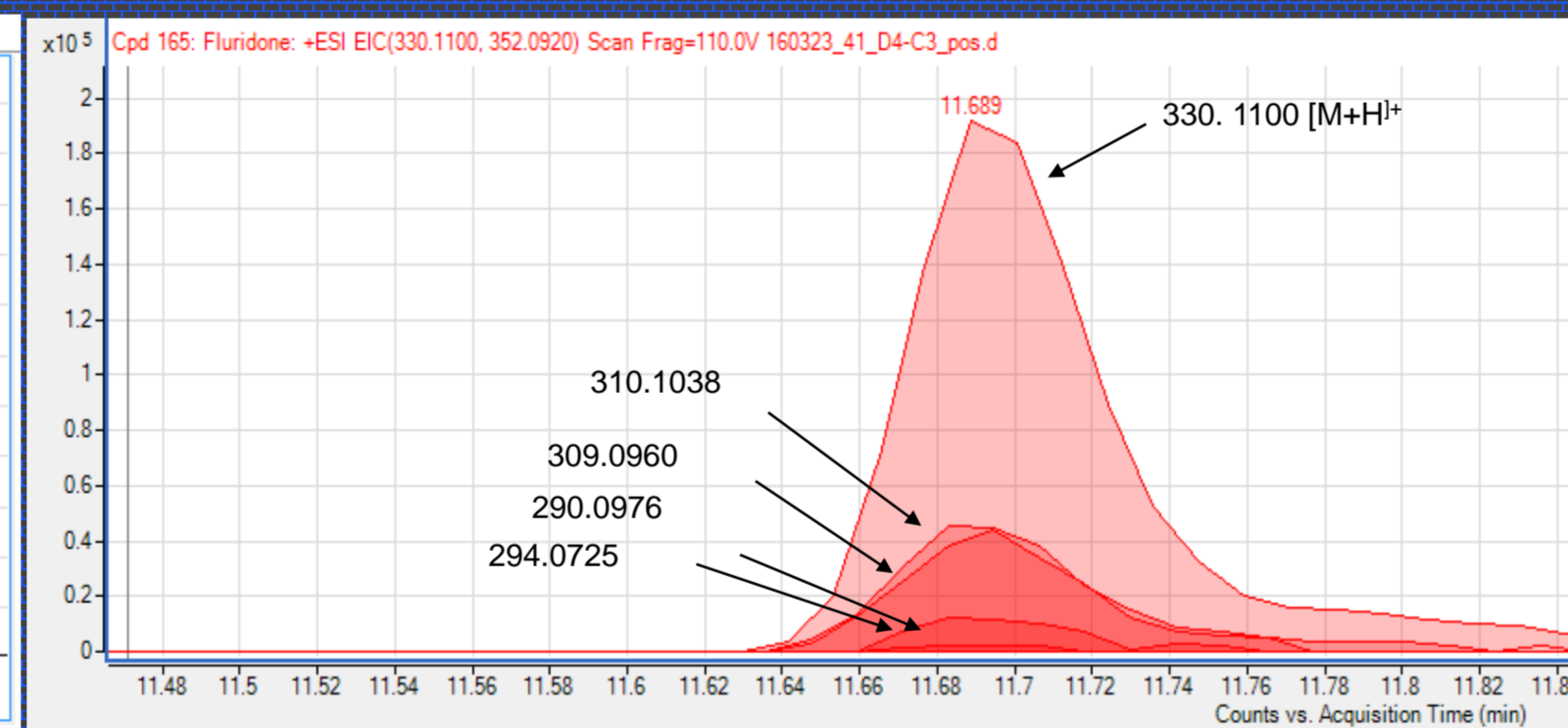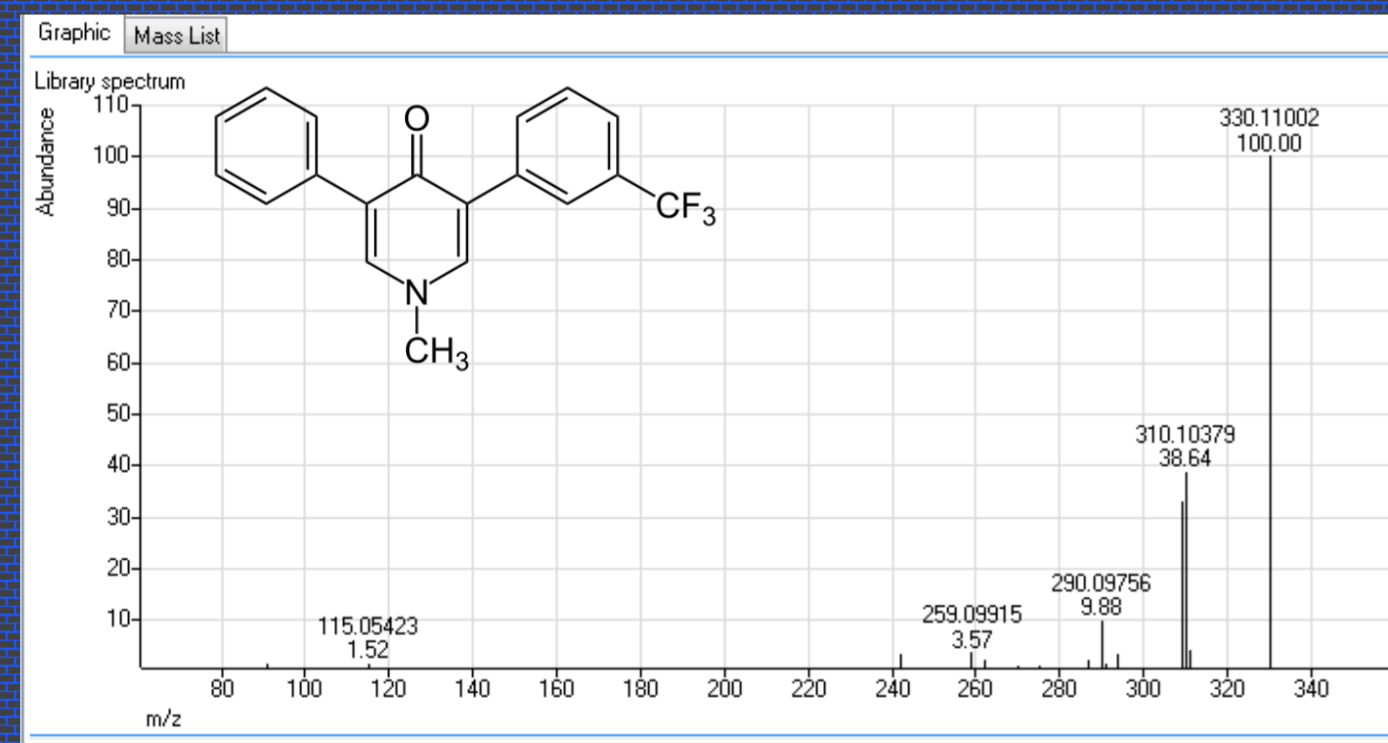**Suspect List:**
Agilent Pesticide PCDL (1,800 compounds)
- accurate mass MS/MS spectra

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
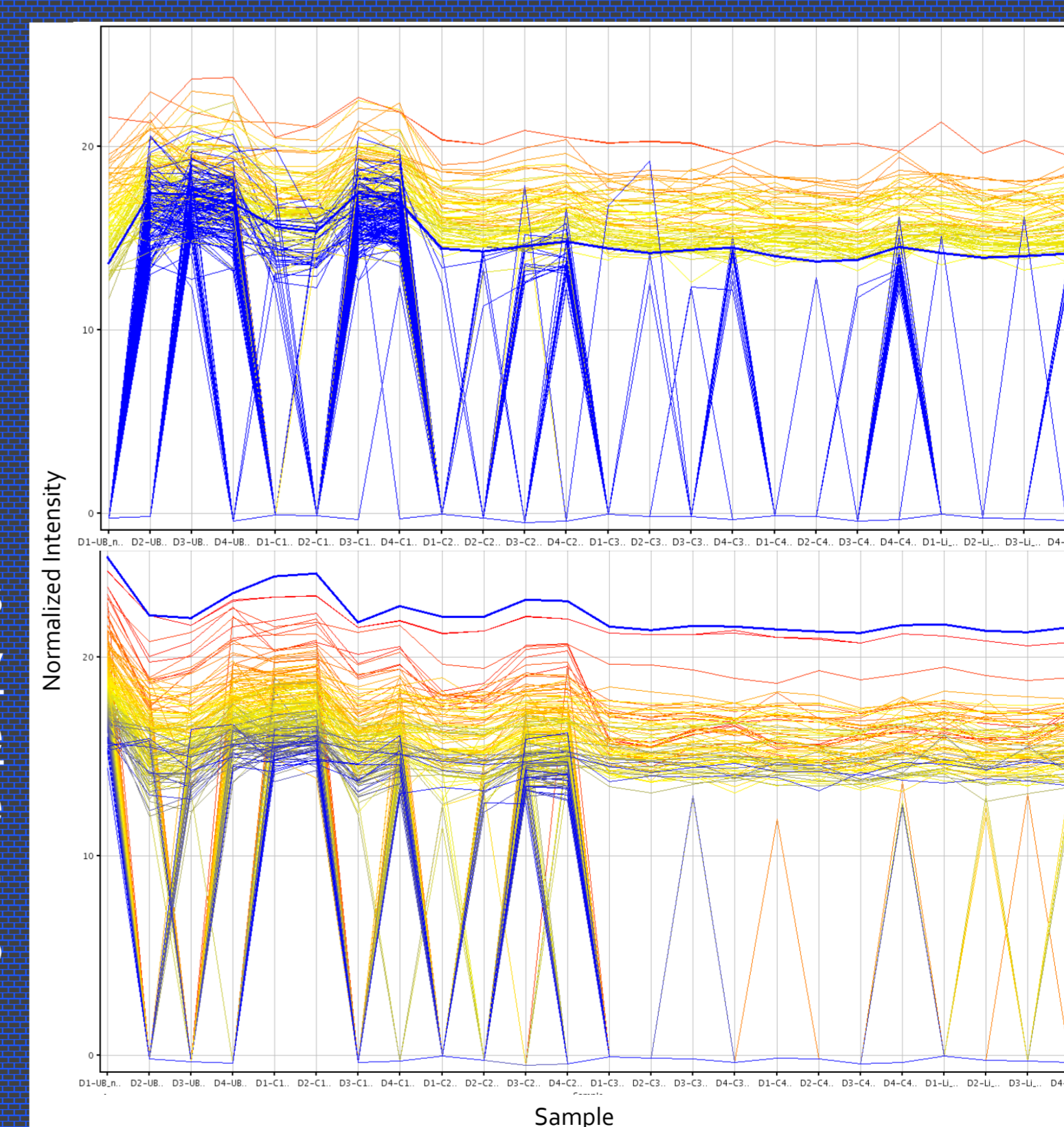
Example: Fluridone

3C. Transformation Product (TP) Screening

1. Prediction of TPs by Eawag-PPS*
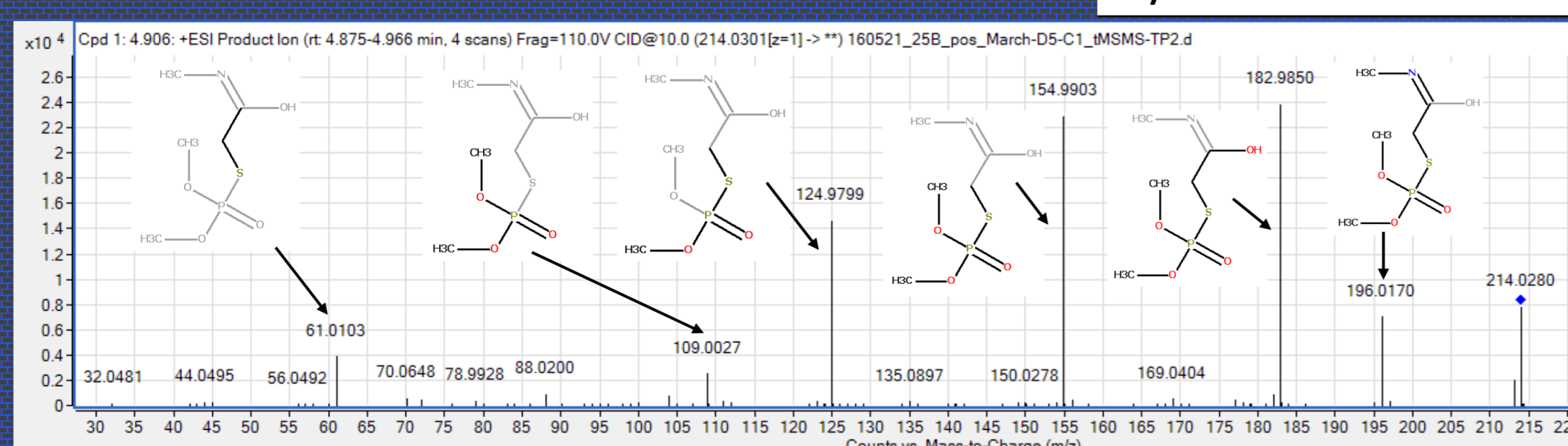Input: 30 parent SMILES

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/

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

** by Agilent Mass Profiler Professional (MPP) software