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Agroscope

Analysis of pesticides in soil: Observations from one year routine

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Agroscope

22. November 2023

5th Swiss Pesticide Residue Workshop

www.agroscope.ch | gutes Essen, gesunde Umwelt



Overview

Action Plan Plant Protection Products

Action 6.3.3.7: Development of a Monitoring Program for PPP Residues in soil

Sampling

National Soil Monitoring Network (NABO)

Analysis

Agroscope / Method Development and Analytics / Environmental Analytics



Origin of samples

Switzerland

- Arable farming





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- Urban parks





Origin of samples

Switzerland

- Arable farming
- Grassland
- Special cultures (vineyards, orchards, vegetables)
- Forests
- Urban parks
- Remote undisturbed areas (national park)





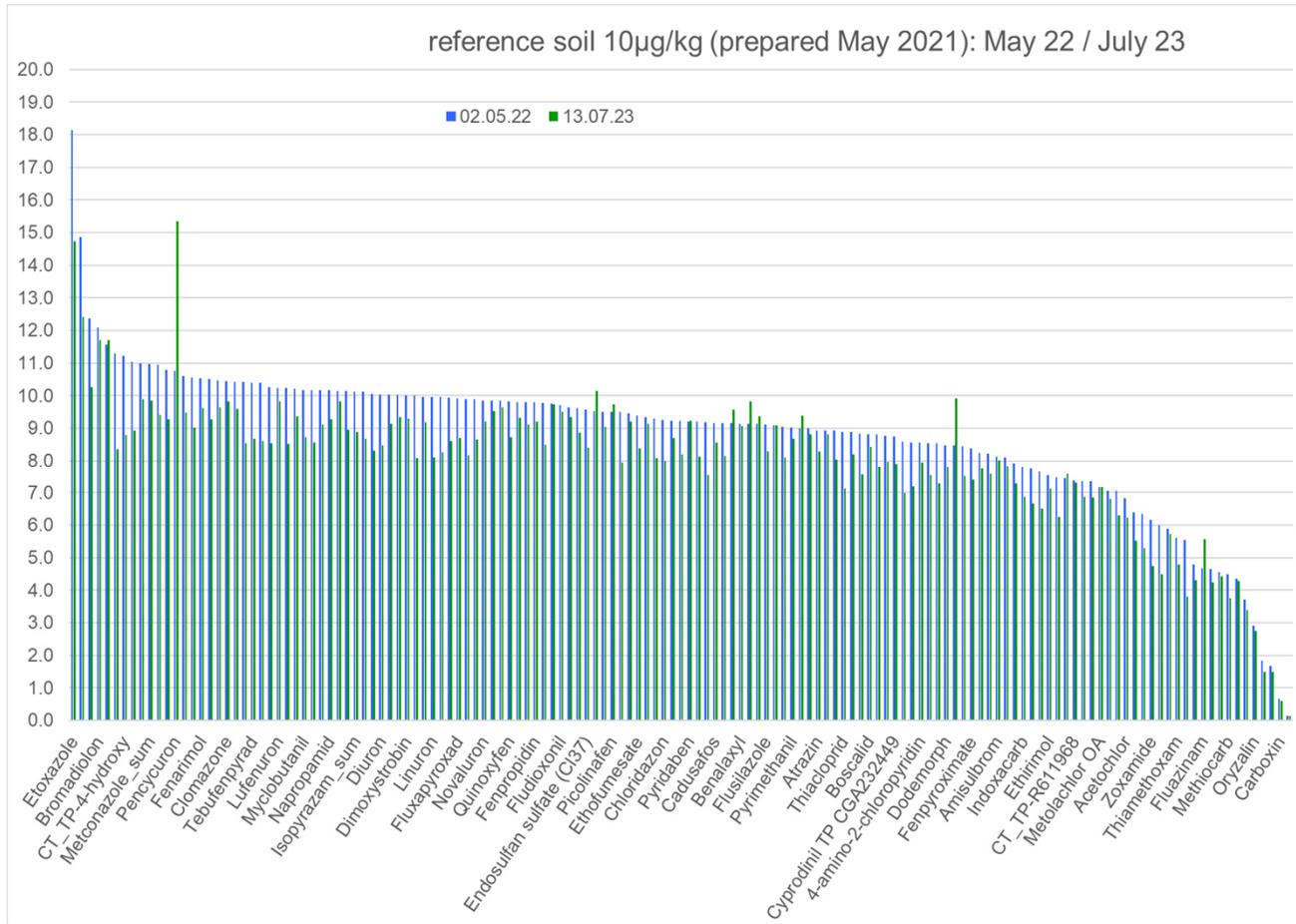
Goals

- Sensitive determination of PPP in soil samples
Median LOQ: 0.2µg/kg d.w.
- Robust extraction method for a broad selection of pesticides
- Applicable to the majority of Swiss soils (c_{OC} 1-5%)
- Strong emphasis on quality assurance and quality control
- **ALLOVER GOAL:**
 - 1st: Filling the knowledge gap with data**
 - 2nd: Basis for further actions within AP-PPP**



Outcomes I

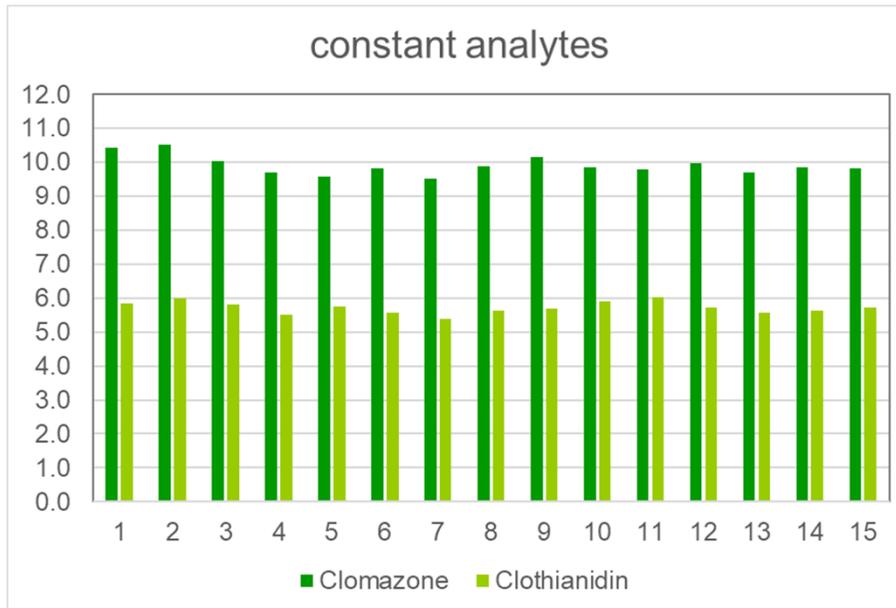
- Reference soil: stability





Outcomes I

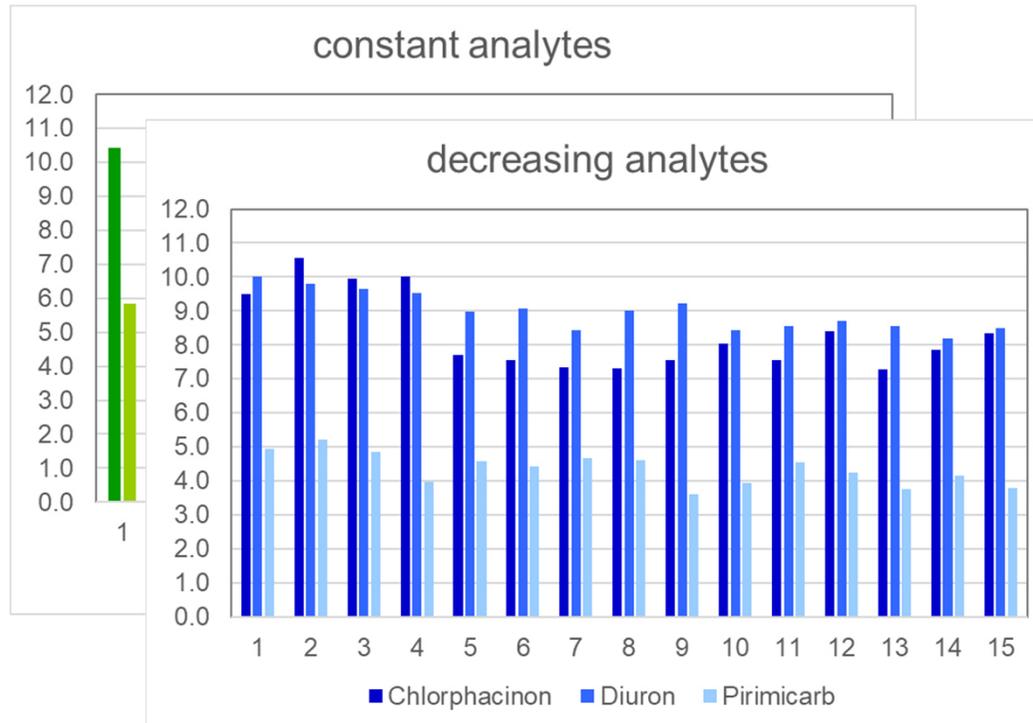
- Reference soil: timeline from July 2022 – July 2023





Outcomes I

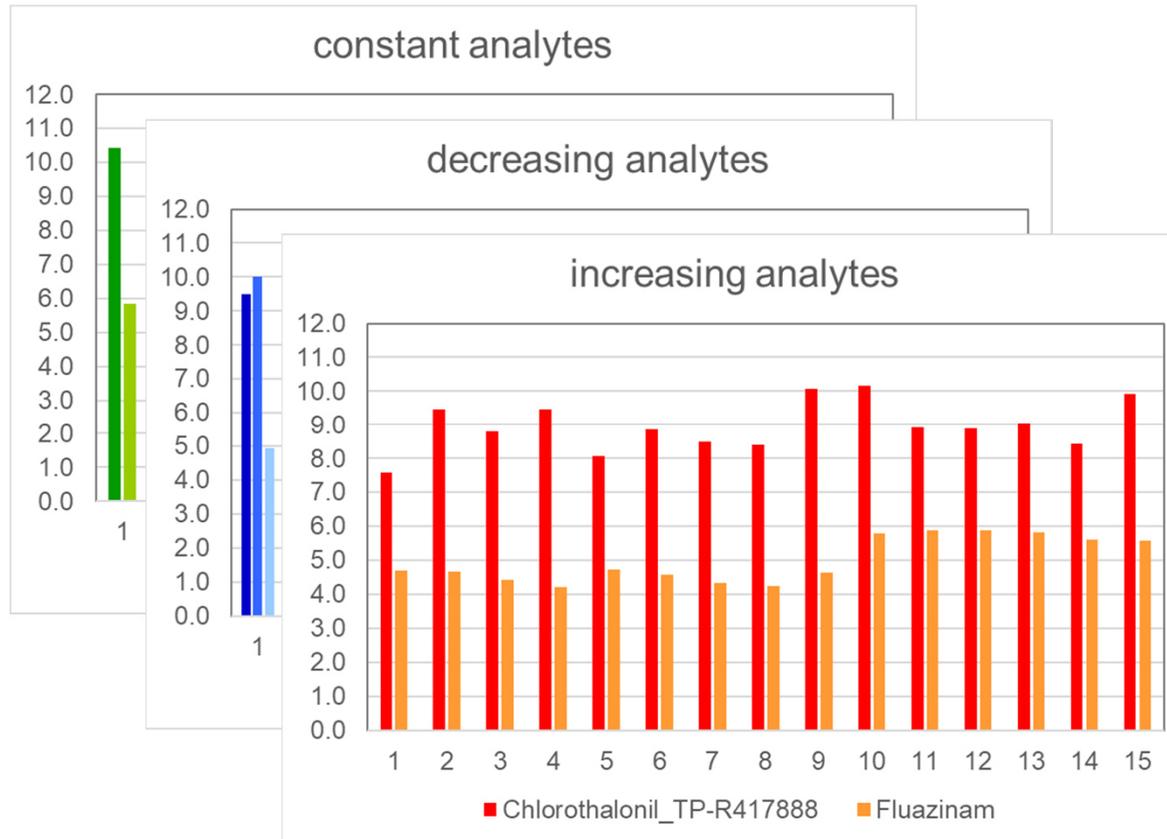
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Outcomes I

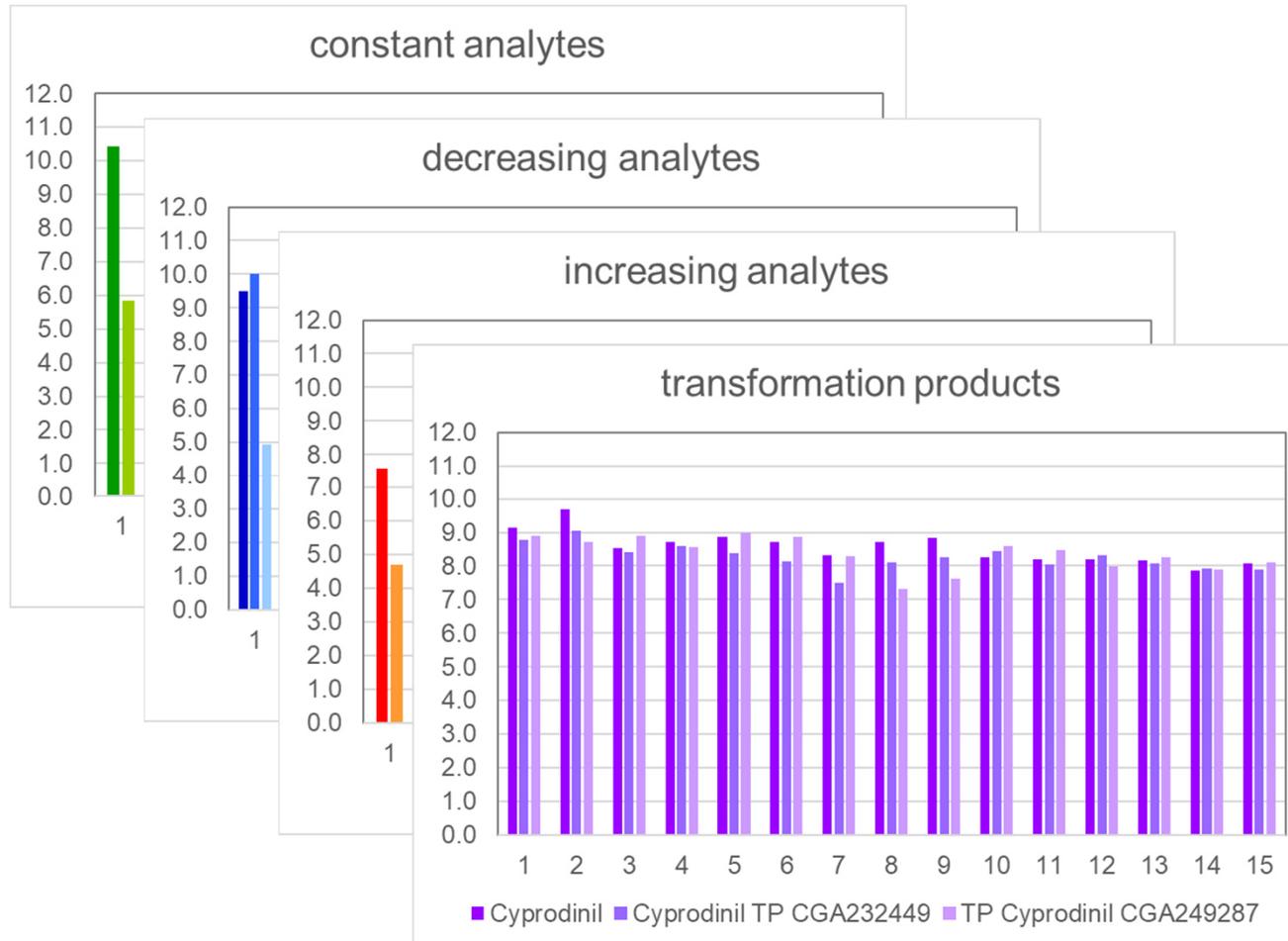
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Outcomes I

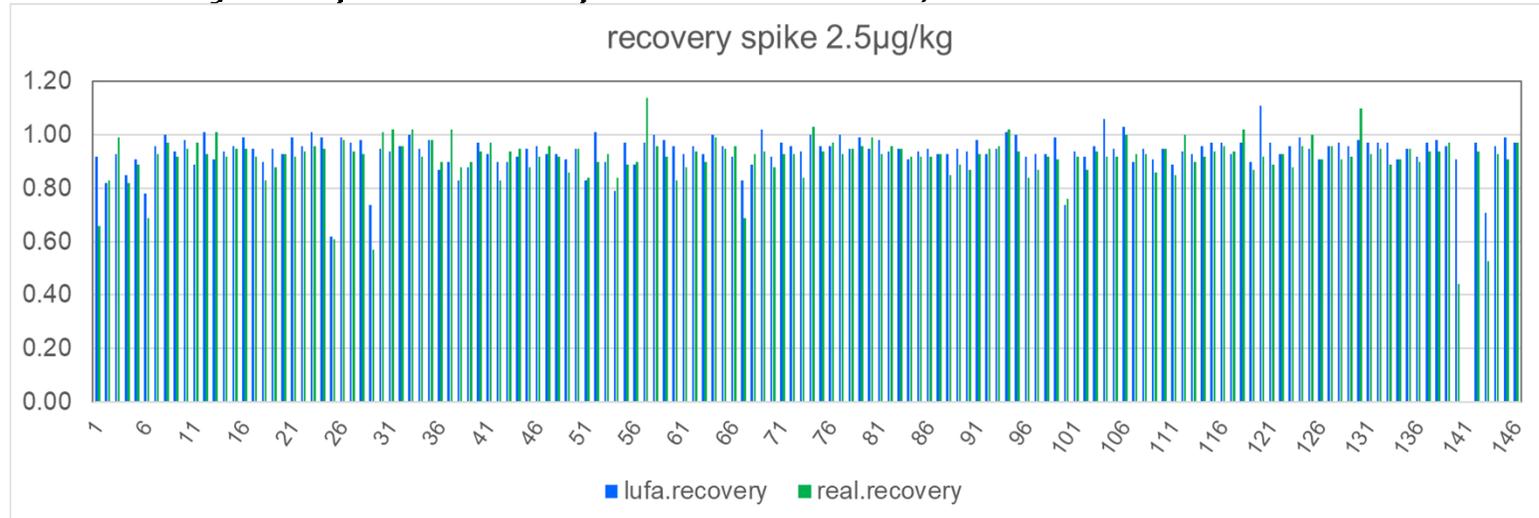
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Outcomes II

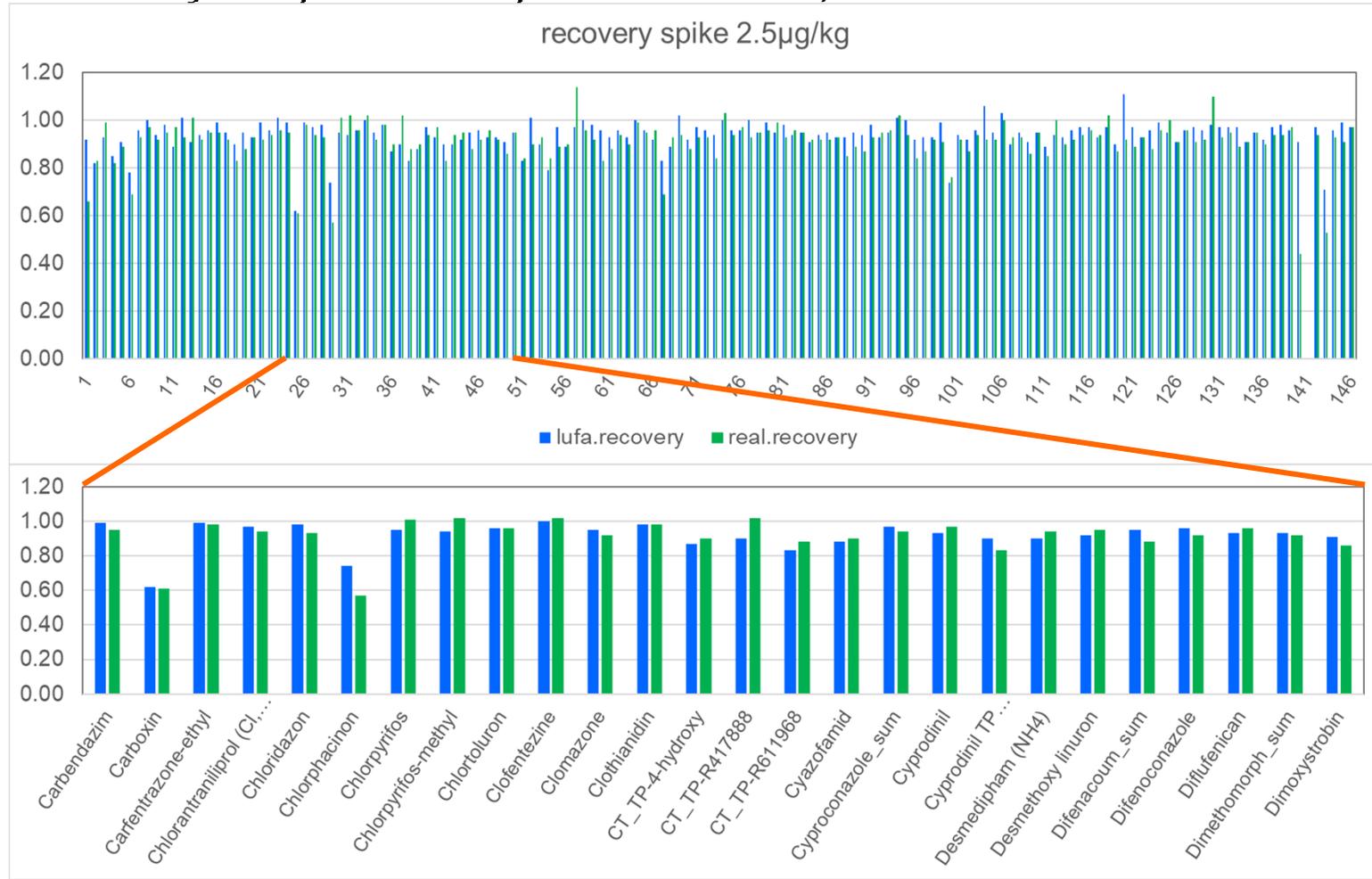
Recovery of spiked samples: Serie 76, June 2023





Outcomes II

Recovery of spiked samples: Serie 76, June 2023





Outcomes III

- Limited stability of stock solutions V1 and V2 force us to dilute them always freshly from stock solution V0

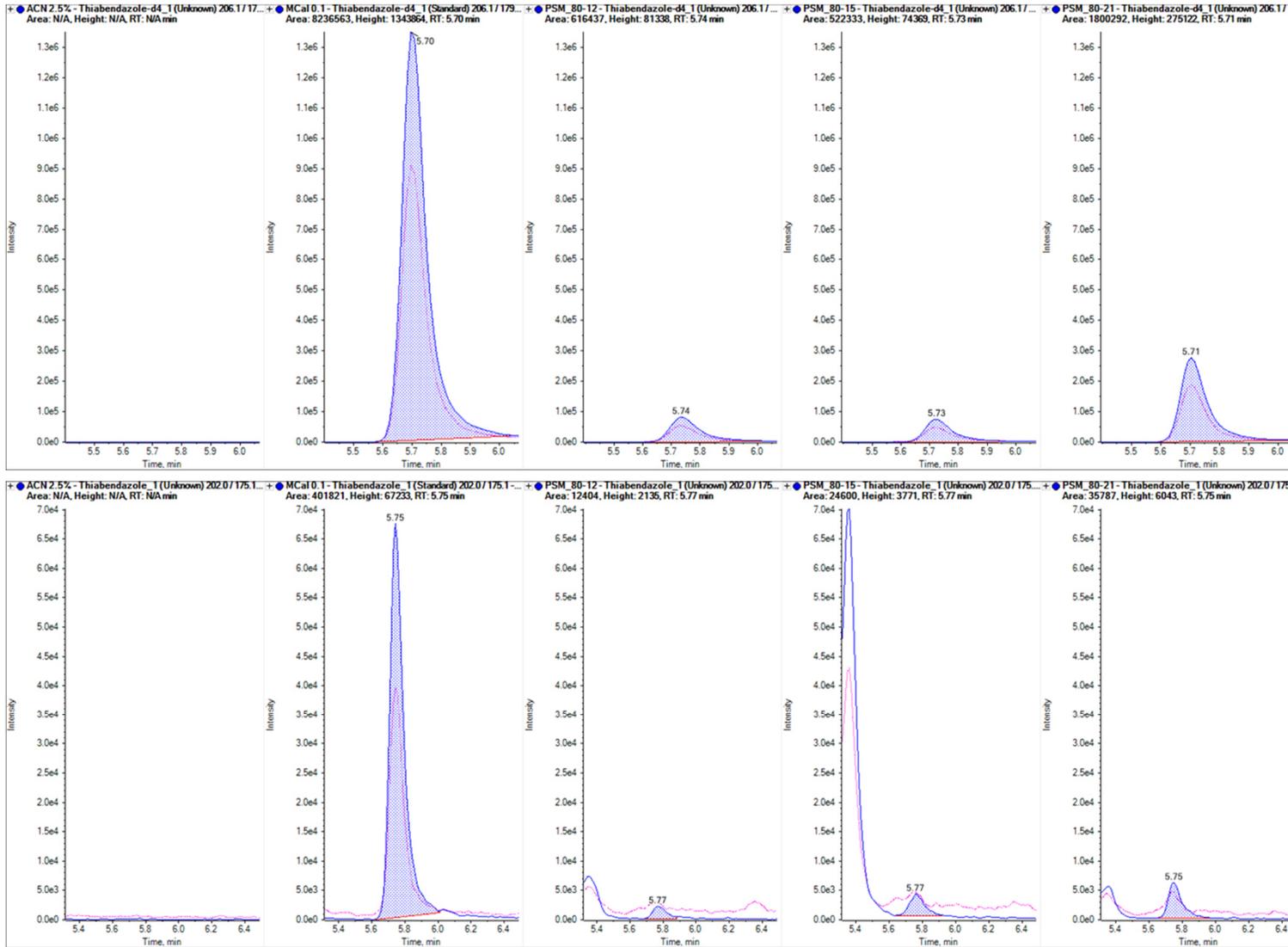
$$V0 = 250\mu\text{g/L} \quad V1 = 25\mu\text{g/L} \quad V0 = 2.5\mu\text{g/L}$$

Phenmedipham, Desmedipham, Pencycuron, Terbutylazin, Zoxamide, ...

- 30% of all samples need reextraction and remeasurement due to high analyte concentrations caused by :
 - a. short timeframe between PPP application and soil sampling
 - b. permanent crops, repeated use of the same active agents
 - c. narrow linear range of Mass Spectrometer (Sciex 5500)
- Low sample throughput (280 samples per year)

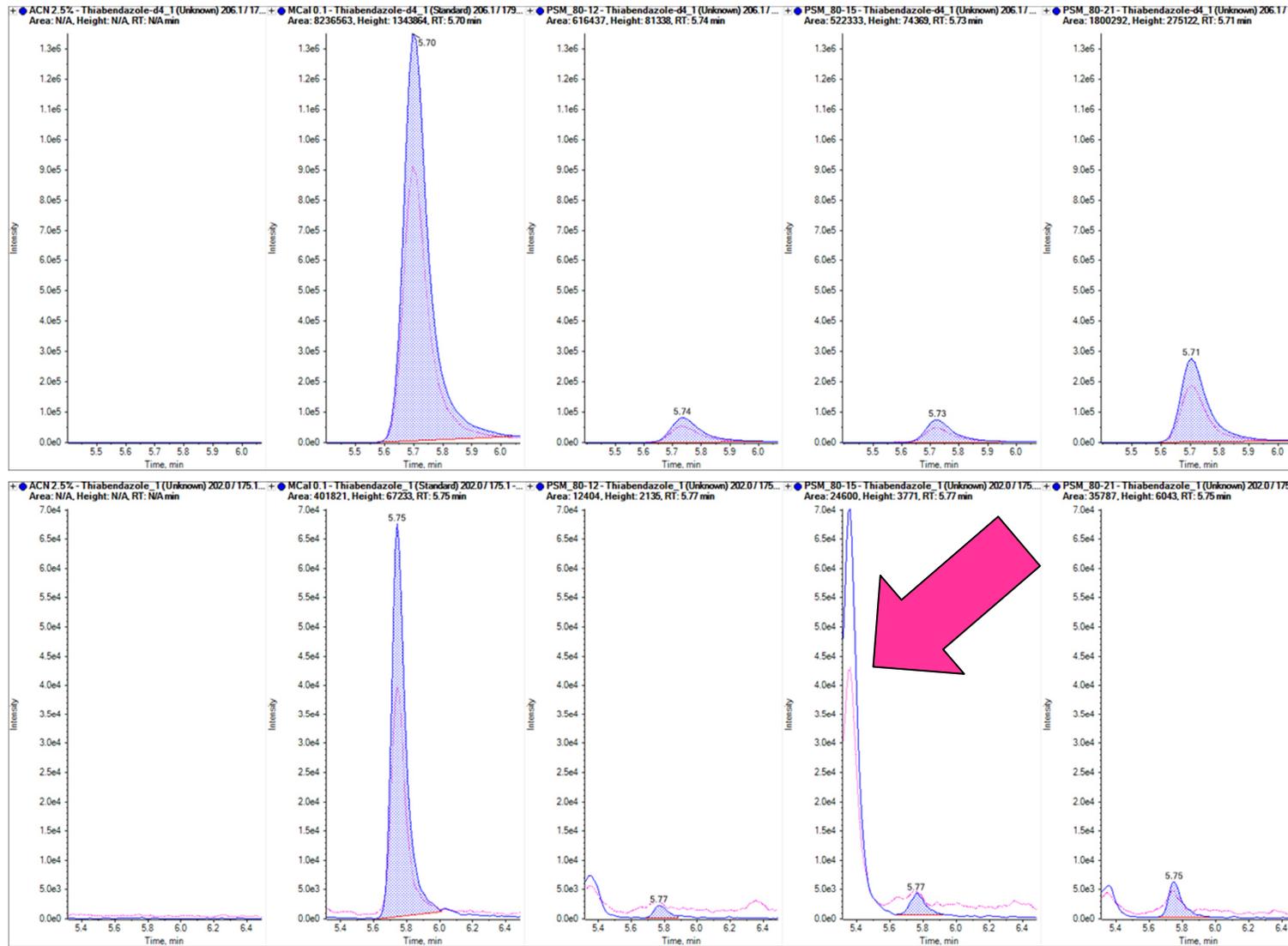


Question to the audience





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Danke für Ihre Aufmerksamkeit

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Agroscope gutes Essen, gesunde Umwelt
www.agroscope.admin.ch





Sample treatment

5g soil, dried 40°C, sieved 2mm

Spiking with ILIS, spiking with analytes (if necessary), prewetting

Optimized Quechers extraction by the aid of ultrasound, salt addition, centrifugation

Transfer extract without further treatment into LC vial

LC-MS/MS

Data analysis and control



LC-MS/MS method

Phenomenex Kinetex Biphenyl 100Å, 100 x 4,6mm, 5µm
Gradient with water and methanol containing 5mM NH₄COO
Flow: 0.750 ml/min, 29min, 35°C

146 Analytes

95 structure identical isotope labelled internal standards (ILIS)
(residuary 51 compounds got assigned ILIS)
→482 MRMs

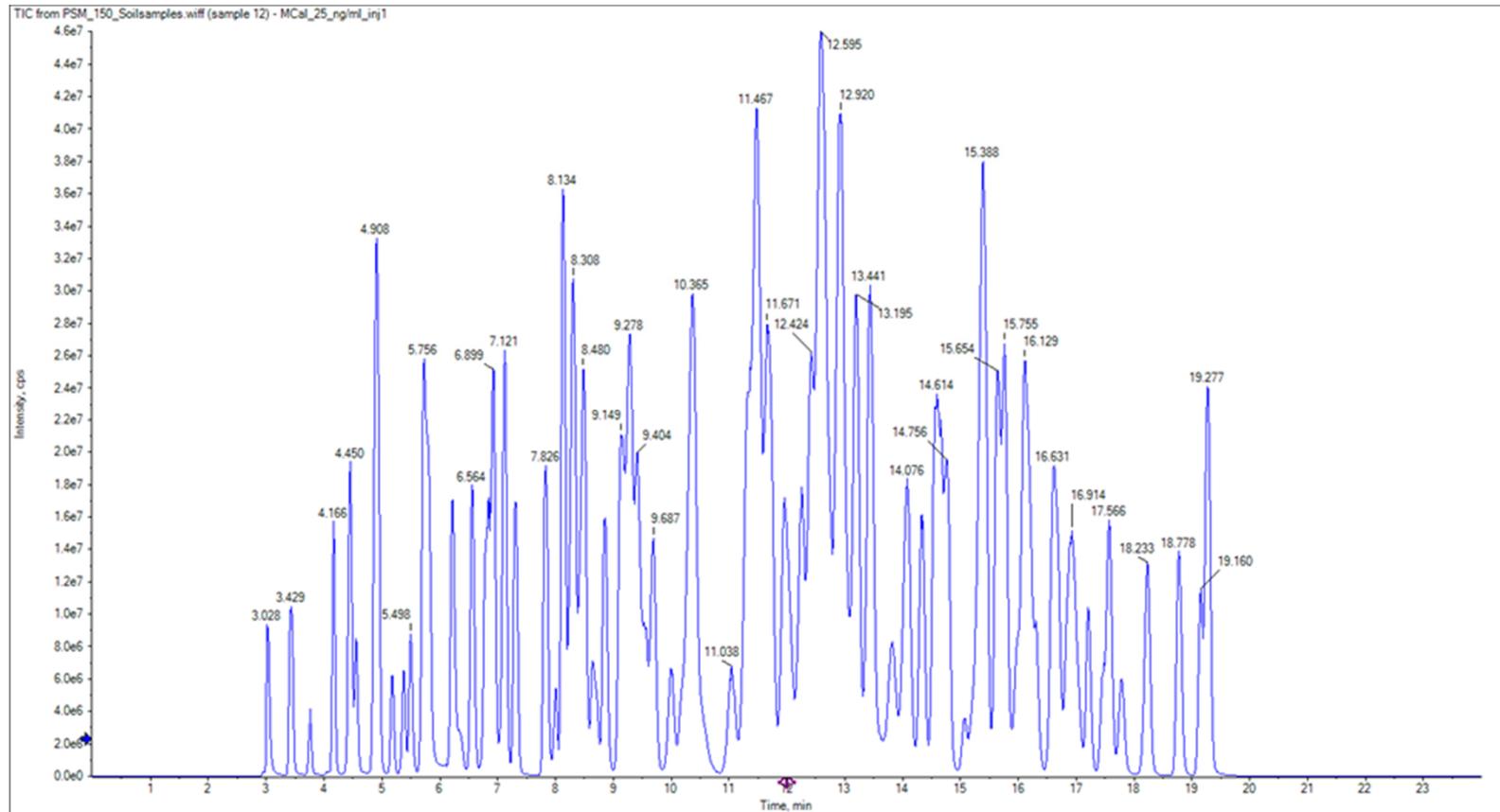
System: PAL RTC / Agilent 1290 / Sciex QT5500

Literature:

Anal. Bioanal. Chem. 2023, 415 (24), p. 6009 - 6025



Outcomes I





Outcomes II

- Strong emphasis on quality assurance and quality control
 - reference soil
 - KLZ Pesticide Mix LC-MS
 - blanks (sand, soil)
 - two replicates from last series
 - two spiked samples (matrix and randomly chosen sample)
 - matrix matched calibration standards
- Extensive number of calibration points with dual measurements of two calibration levels
 - stability check of the instrument
 - review of the quantitation limits