

Time Integrating, Micro Flow, In-line Extraction (TIMFIE) sampler for the determination of pesticide concentrations in water

- a new quantitative tool in pollution monitoring

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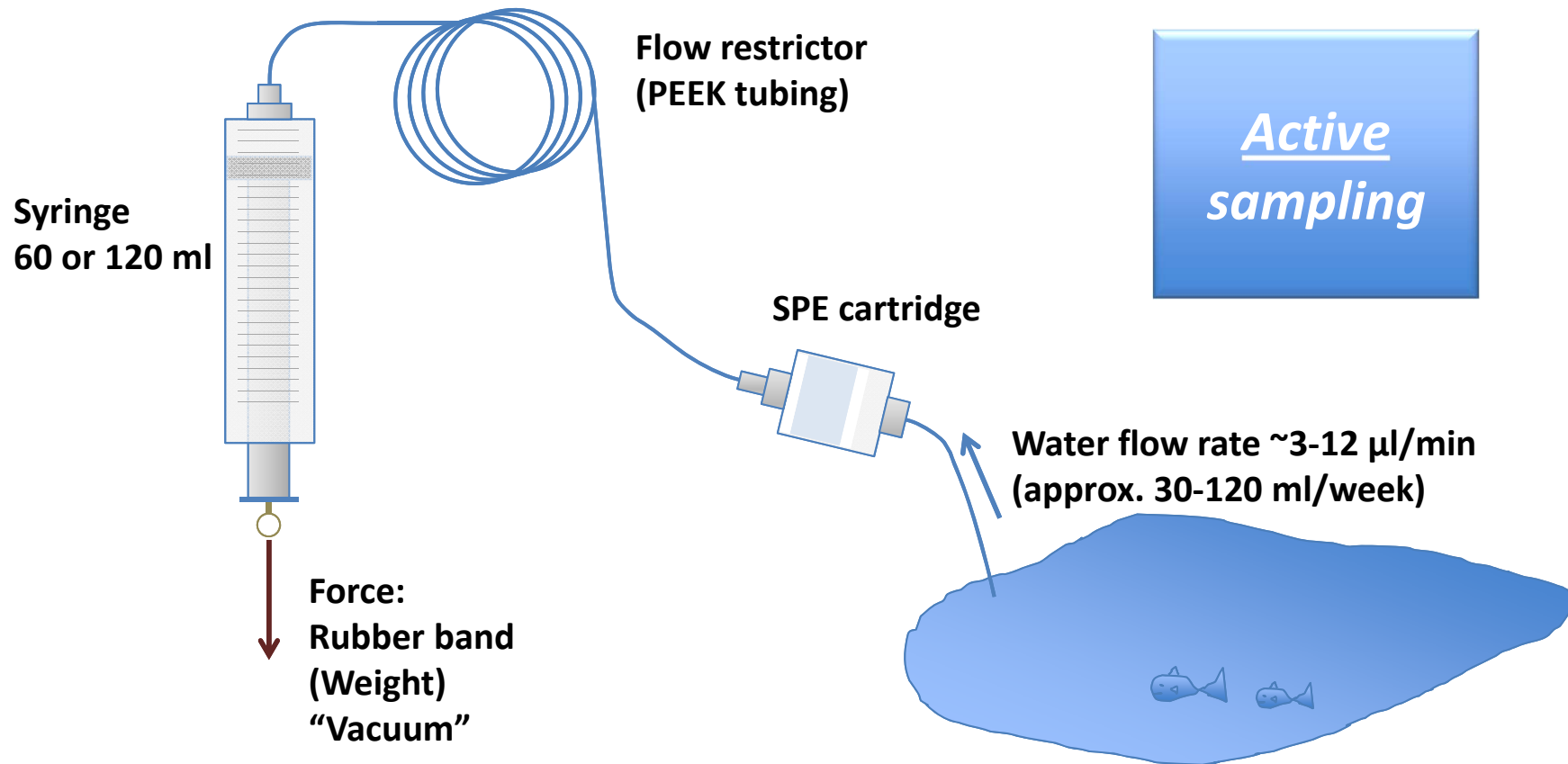
CKB

Center for Chemical Pesticides

On the wish list for a new water sampler...

1. Time integrated sampling, 1 week or more
2. Whole water analysis
3. Quantitative
4. Flexible sample volume
5. Possible to validate according to established procedures
6. Low cost (and low-tech)
7. Robust
8. Flexible - study design and compound classes
9. Easy to apply in field
10. Easy to transport and store
11. Rational handling in the analytical lab

Principle of the TIMFIE sampler



TIMFIE application in field (example)



Photo: Ove Jonsson

Inlet and SPE

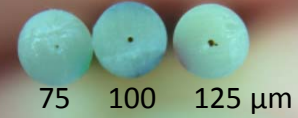
Rubber band (black)

Telescopic stick

Restrictor (beige)

Syringe

Inner diameters of restrictors

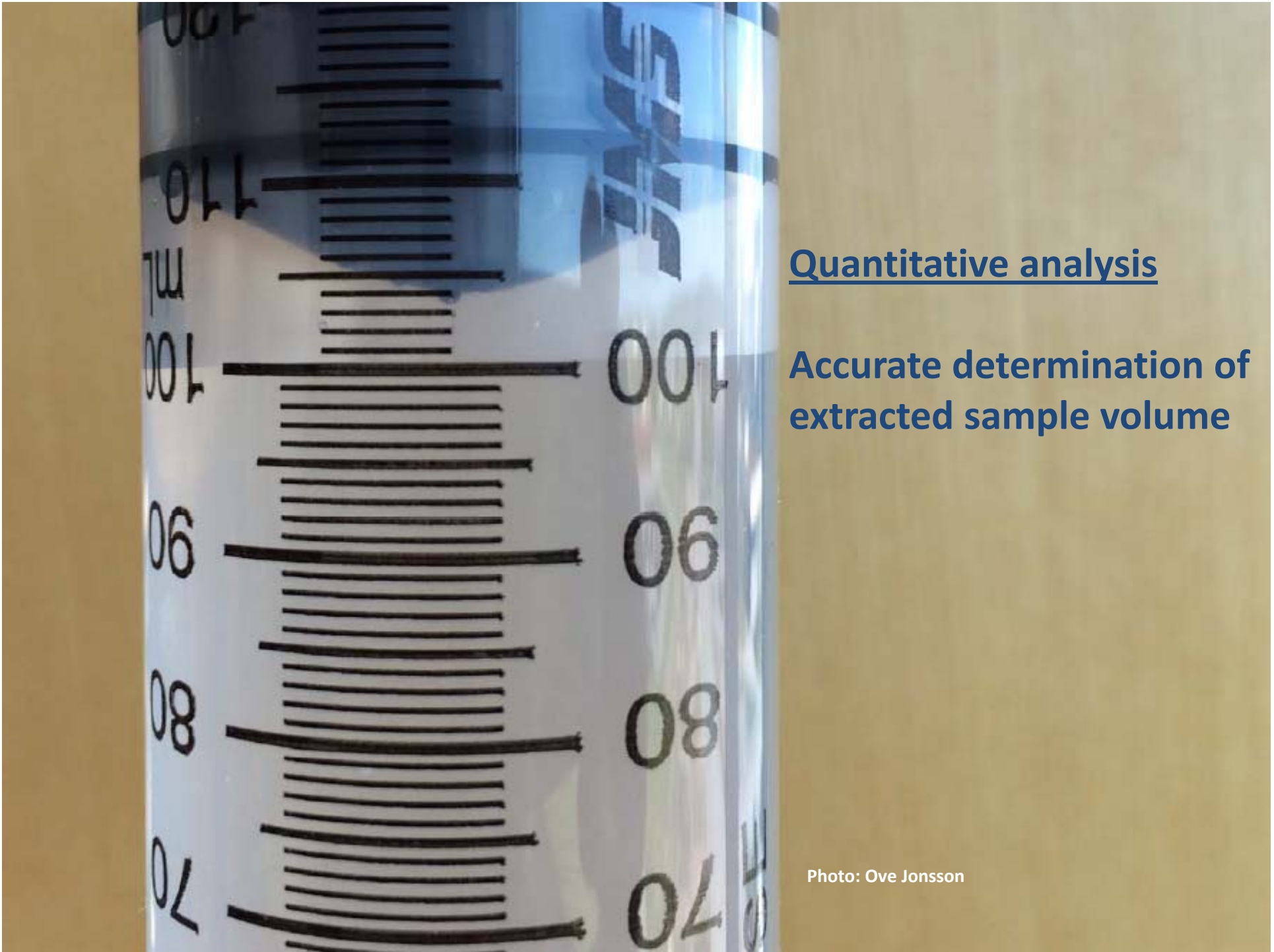


Photos: Ove Jonsson



Cut inlet tubing to a point shape to avoid stops



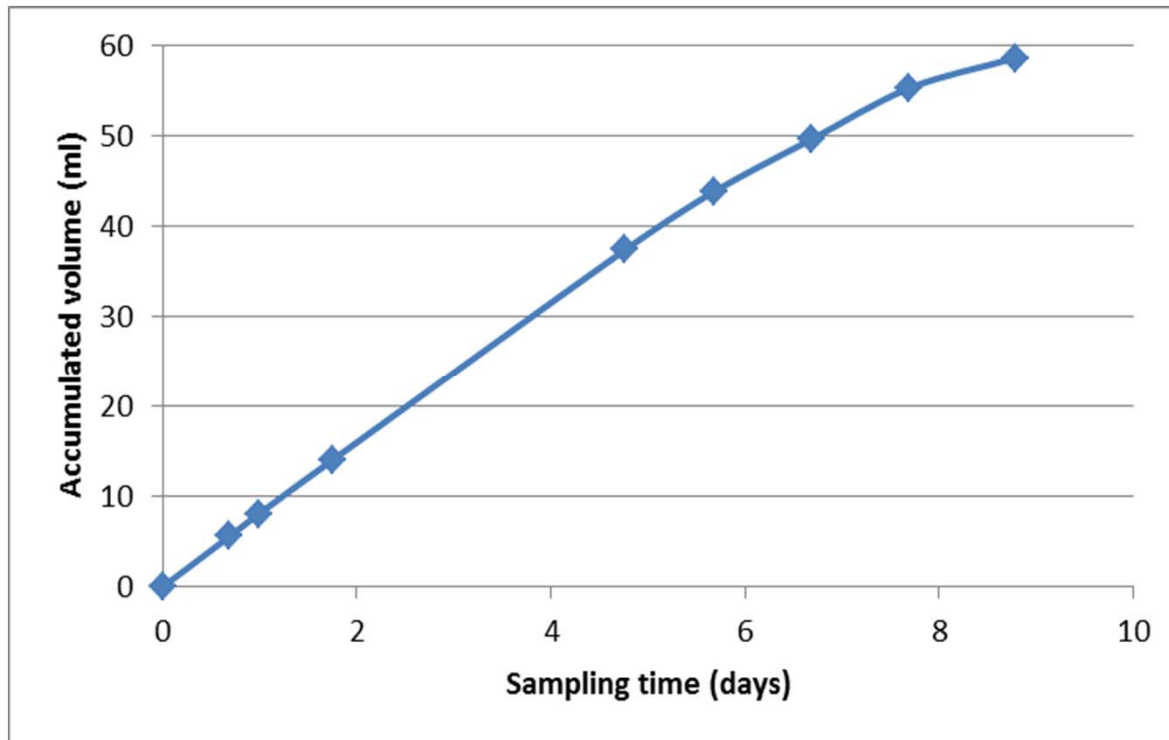


Quantitative analysis

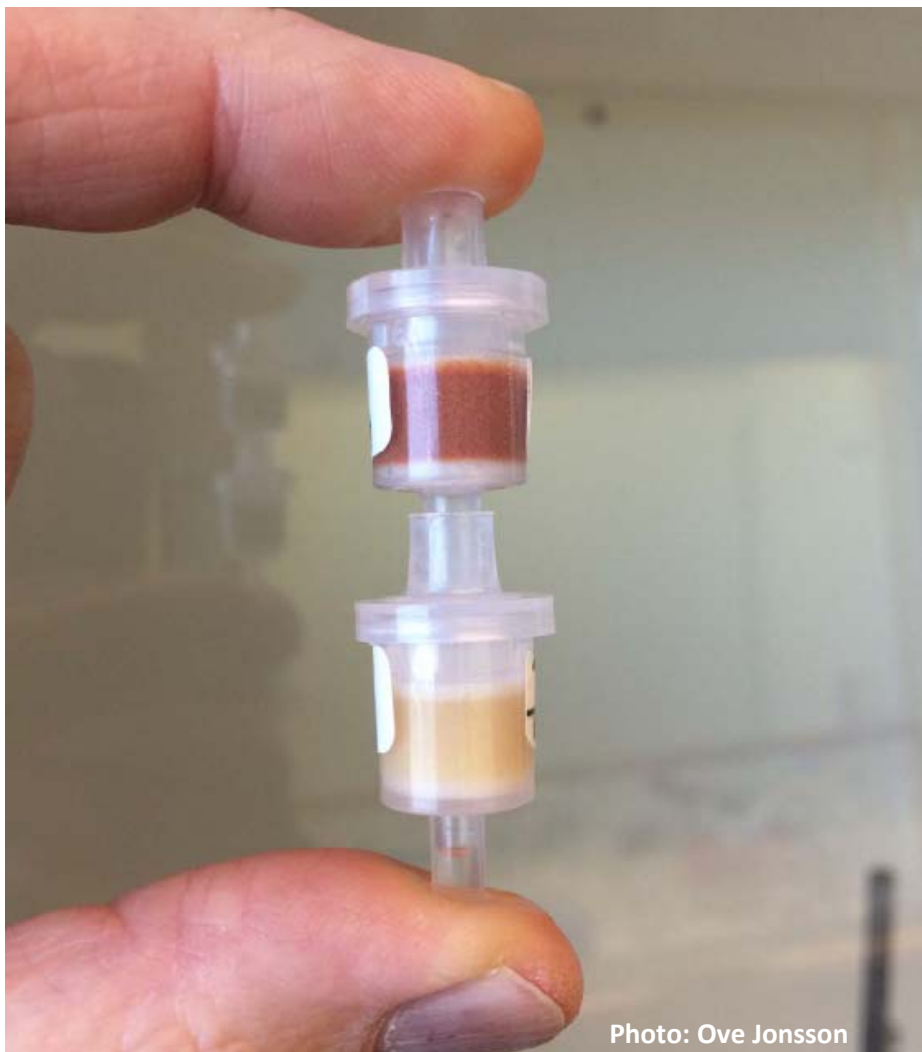
Accurate determination of extracted sample volume

Photo: Ove Jonsson

Extracted volume over time (example)



Solid Phase Extraction (SPE) possibilities



- ✓ Small SPE format
- ✓ Closed flow system
- ✓ Stack cartridges in series to extract different compound classes
- ✓ Minimized solvent consumption
- ✓ Simple, inexpensive shipping and storage

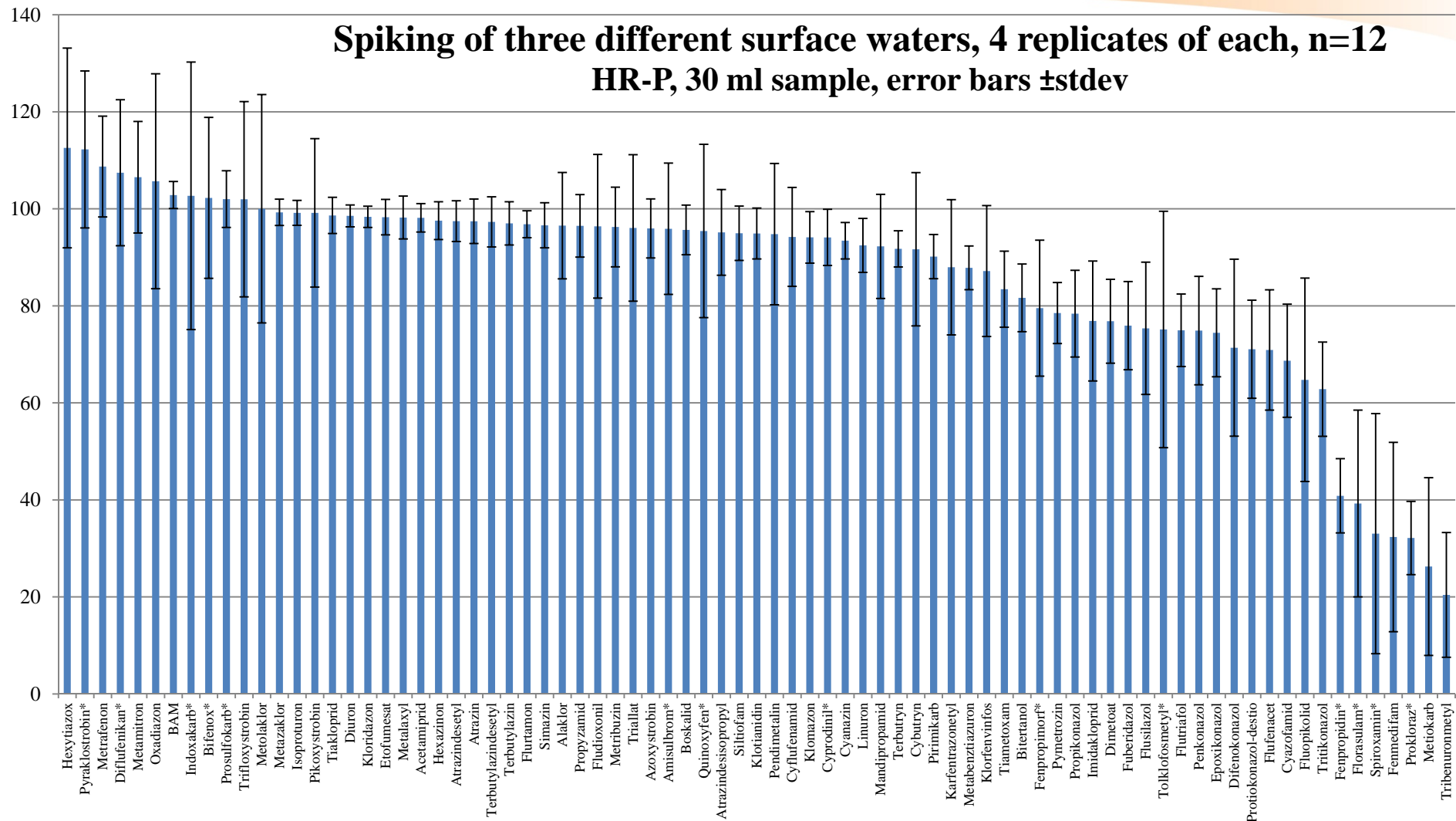
- ✓ Rational internal standard addition

Here Chromafix HR-P and HR-XA columns from Macherey-Nagel

Method validation TIMFIE LC-MS/MS(ES+)

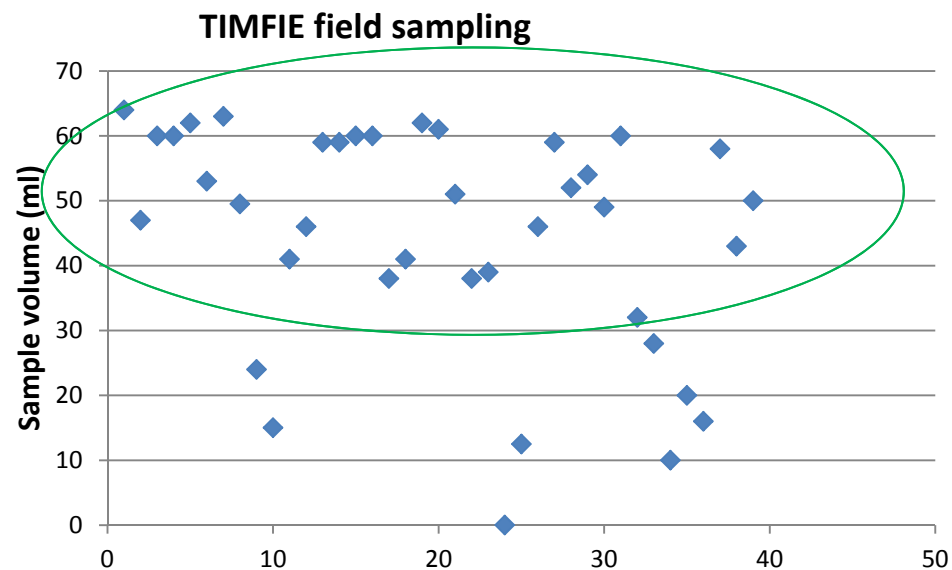
- 30 ml of water extracted on HR-P SPE (hydrophobic polymer particles)
Sample preparation
Final volume 3 ml, 0.5 ml injected on LC
- Relevant surface waters used as matrix
- Matrix blanks, system blanks
- Absolute recoveries (3 surface waters, n=4)
- Relative recoveries (to internal standards, calibration curve in buffer)
Spiking on LOD, LOQ and “high” concentration level (10 surface waters)
- Field application, 3 locations, different field personnel
- Duplicate field sampling n=9 (176 data pairs > LOQ)

TIMFIE absolute recoveries of 79 pesticides



TIMFIE field study

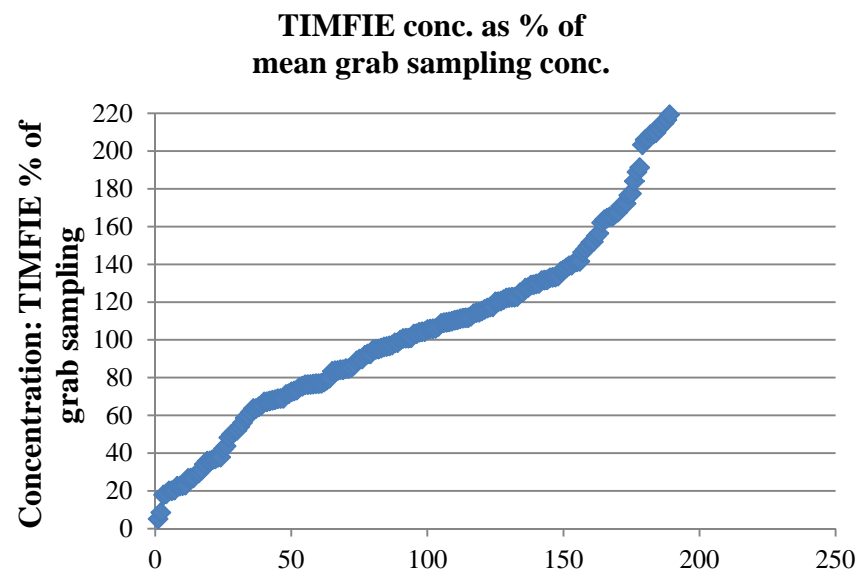
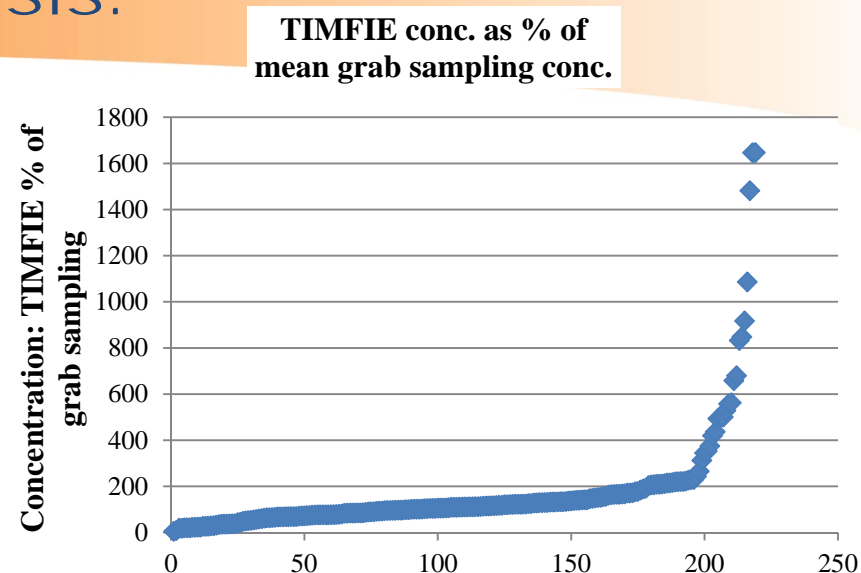
Three streams in southern Sweden, 2015
14 1-week periods sampled, May-Oct
9 duplicate sampling
In total 39 TIMFIE samples
Grab sampling start and end of week



Results from LC-MS/MS analysis:

- Including concentration values >LOQ:
TIMFIE 698 hits, grab sampling 308
On average 19 compounds/sample with TIMFIE,
9 comp/sample with grab sampling + ref. method [1]
(TIMFIE LOQ 10 times lower than
ref. method for most compounds)
- TIMFIE deviation within duplicates: $(100 * \text{diff}/\text{mean})$
Mean 18%, Median 14%, Range 0-120% (176 data pairs)
- TIMFIE conc. as percent of mean grab sampling:
Mean 168%
Range 5-1647%, (219 data pairs , >LOQ)

Zoom in:



Summary TIMFIE sampling

Pros

- Time integrated sample
- Whole water
- Quantitative
- Preconcentration
- Validation process
- Inexpensive
- Flexible, different SPE materials translate current SPE methods to TIMFIE conditions
- Small format, flexible application
- Transport and storage

Cons

- No pH adjustment
- Not all compounds will be extracted
- Restricted sample volume
- (Robustness in field)

**TIMFIE is a new
quantitative technique
that enables
time integrated
whole water sampling
for pesticide monitoring**

Acknowledgement

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Photo: Therese Nanos

Thank you
for your
time

Questions?