

The TIMFIE sampler - A new time-integrating, active sampling device for quantitative monitoring of pesticides in whole water

Time-Integrating, Micro Flow, In-line Extraction (TIMFIE)

Ove Jonsson

Swedish University of Agricultural Sciences
Department of Aquatic Sciences and Assessment



ove.jonsson@slu.se

CKB

Center for Chemical Pesticides

Swedish pesticide monitoring program



4 monitoring catchments ●
Surface + ground water
Time integrating sampling

Two rivers
Grab sampling

Sediments in all 6 locations

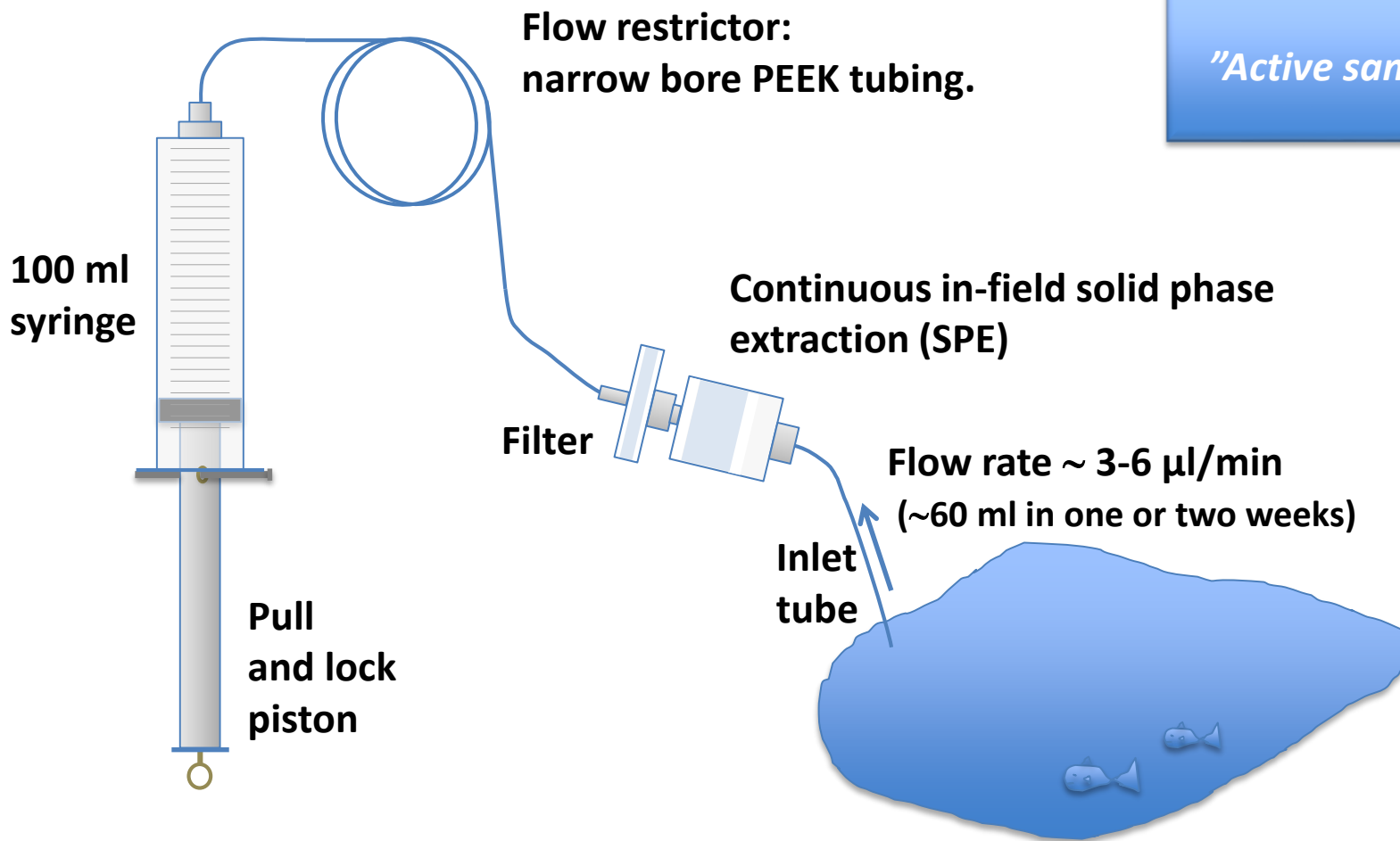
Air + rain (south west)
Air + rain (remote)

Information on pesticide
use by farmers

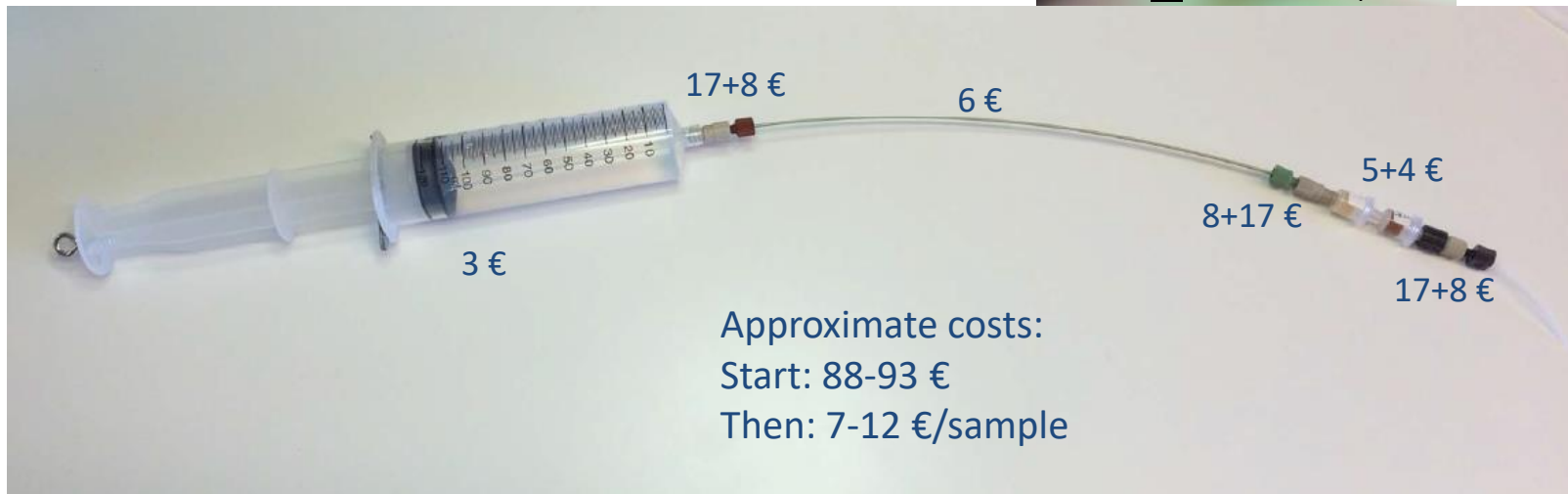
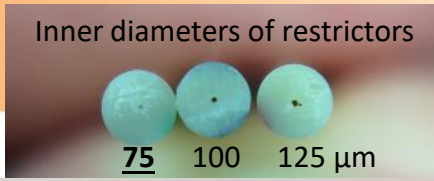
Pesticide fate

- Pesticide concentration in surface water will vary significantly over time
- Grab sampling will not give a fair estimate of mean concentration (or maximum peak concentrations)
- Time integrating sampling needed

Principle of the TIMFIE sampler



Consumables



Photos: Ove Jonsson



Cut inlet tubing to a point shape to avoid stops



TIMFIE field application (examples)



Photo: Roland Persson




Photo: Torbjörn Hansson, Grön Kompetens AB

Two weeks sampling



Changes in water level



Winter sampling (Sweden) entire sampler
below surface to avoid freezing.
TIMFIE mounted on a fishing-rod.

Photo: Torbjörn Hansson, Grön Kompetens AB



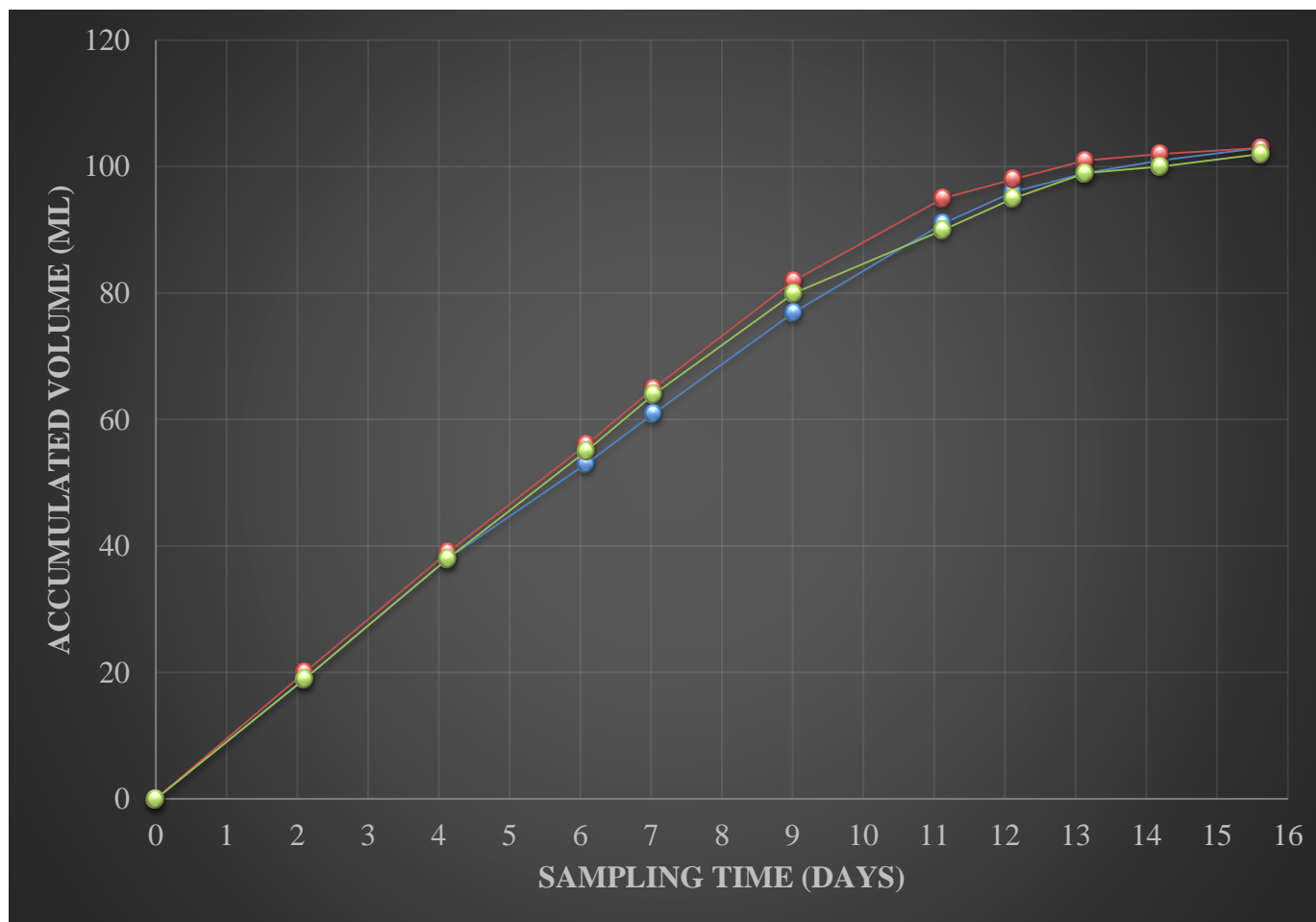
Photo: Torbjörn Hansson, Grön Kompetens AB



Quantitative analysis

Accurate determination of extracted sample volume

Extracted volume over time (example)



Linear range 0-80 ml
 $R^2=0.999$

Sample volume
between 30-80 ml
is preferred

LOD and LOQ
defined with 30 ml
sample

SPE possibilities

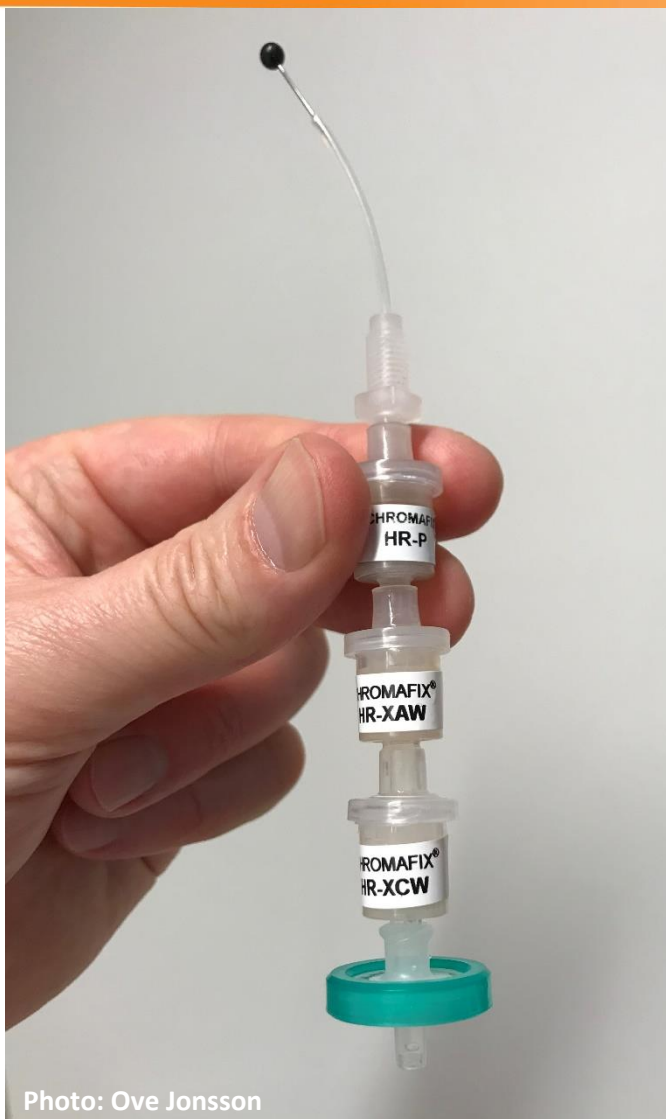
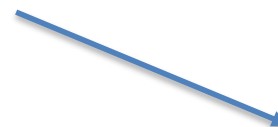


Photo: Ove Jonsson

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

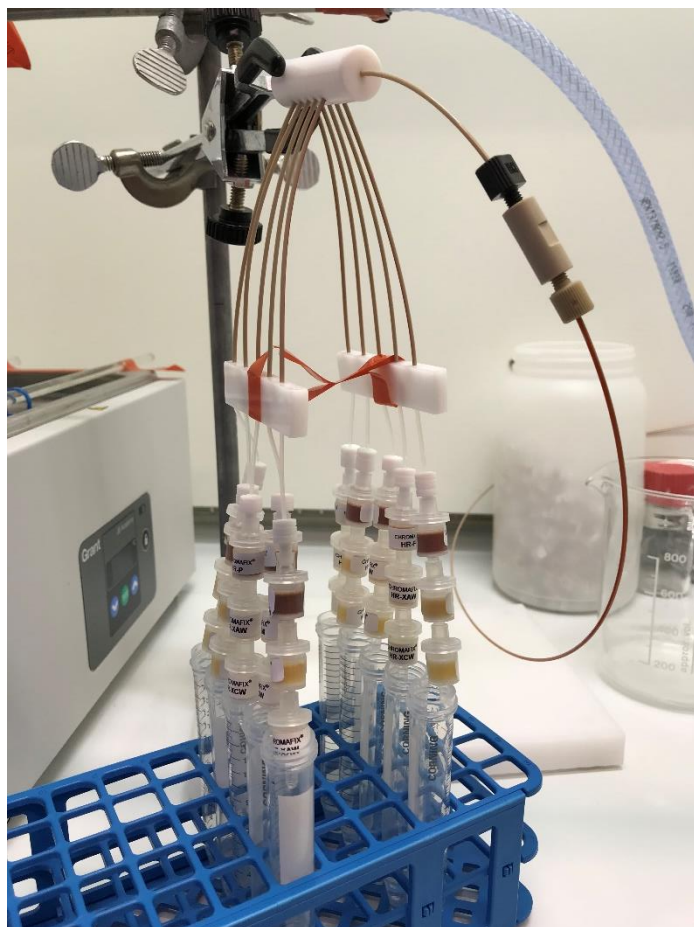
- ✓ Rational internal standard addition



Chromafix HR-P,
HR-XAW and
HR-XCW columns
from Macherey-Nagel

Automation: Conditioning of SPE columns, 10 in parallel

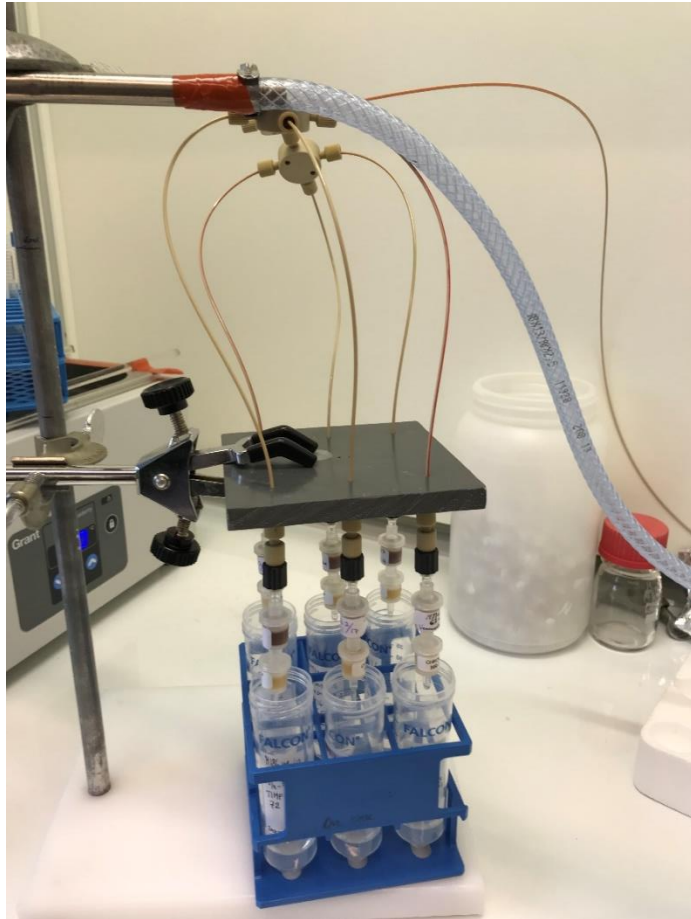
MeOH followed by H₂O



Quaternary pump 1100 (refurbished)
with handheld controller

Automation: Elution of SPE columns, 6 in parallel

Methanol, acetone, (ethyl acetate) and methanol with NH₃



Evaporation in water bath at 40°C and N₂ flow.
50 µl DMSO as a keeper

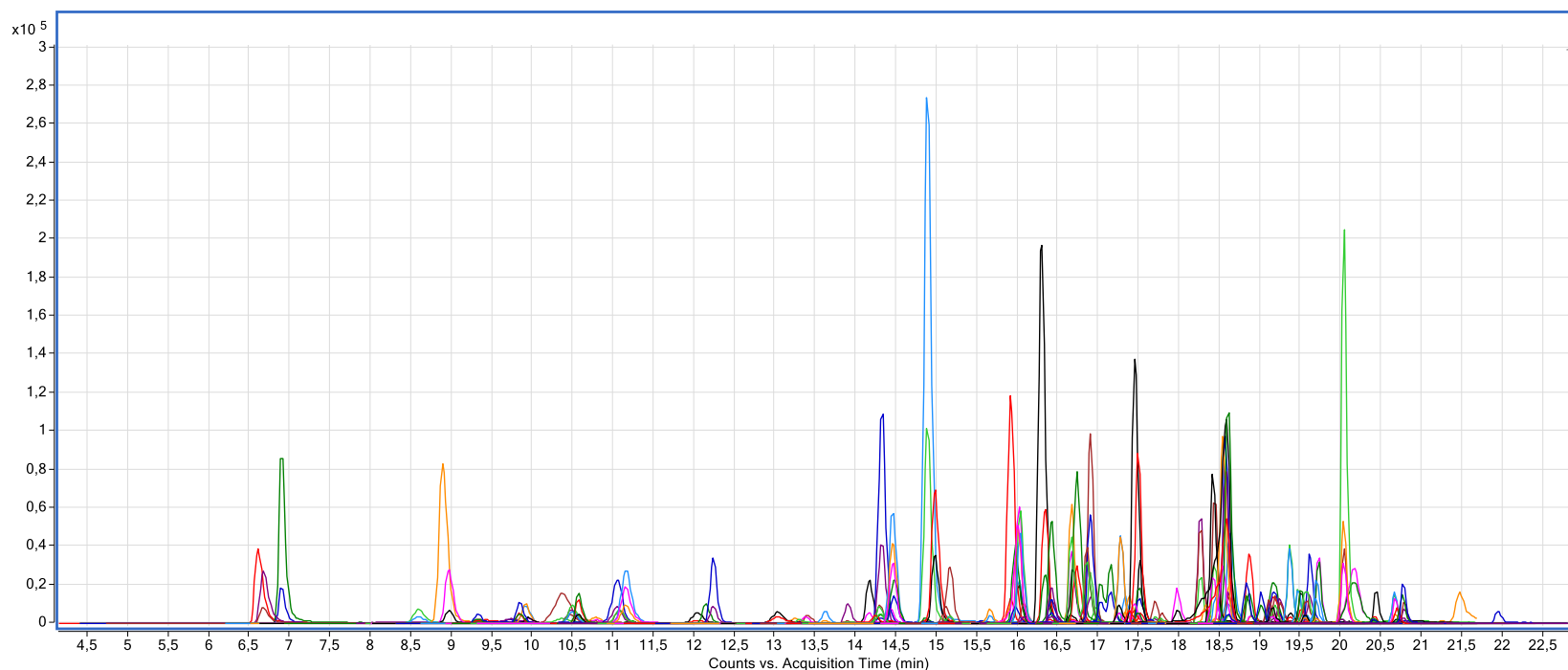
Dissolve in 3 ml ammonium acetate buffer at pH 5
Inject 0.5 ml

On-line SPE-HPLC-MS/MS (6470)

500 μ l water sample or TIMFIE extract injected



On-line SPE-LC-MS/MS (ES+) chromatogram (TIC), example ~100 compounds studied in this multimethod

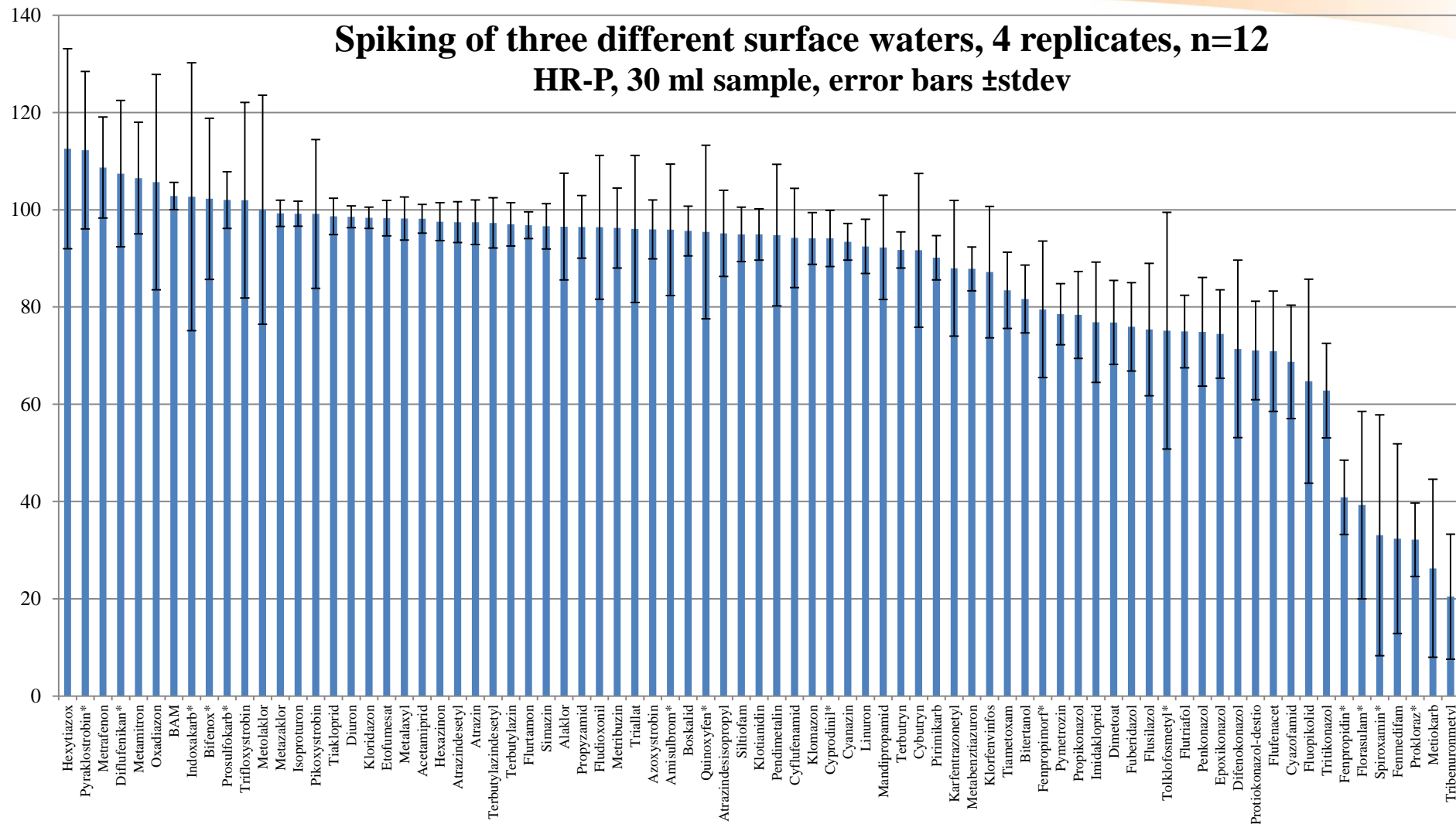


TIMFIE method validation LC-MS/MS(ES+)

- 30 ml of water extracted on HR-P SPE (hydrophobic polymer particles)
IS -> wash -> dry -> elute -> evaporate -> reconstitute
Final volume 3 ml, 0.5 ml injected on LC-MS/MS
- Relevant surface water used as matrix
- Matrix blanks, solvent 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 study, 3 locations, different field personnel
- Duplicate field sampling n=9

TIMFIE absolute recoveries of 79 pesticides

Spiking of three different surface waters, 4 replicates, n=12
HR-P, 30 ml sample, error bars \pm stdev



TIMFIE field study

Three streams in southern Sweden,
2015

1-week periods sampled, May-Oct

9 duplicate sampling

In total 39 TIMFIE samples

Grab sampling start and end of week

TIMFIE vs grab sampling + accredited method

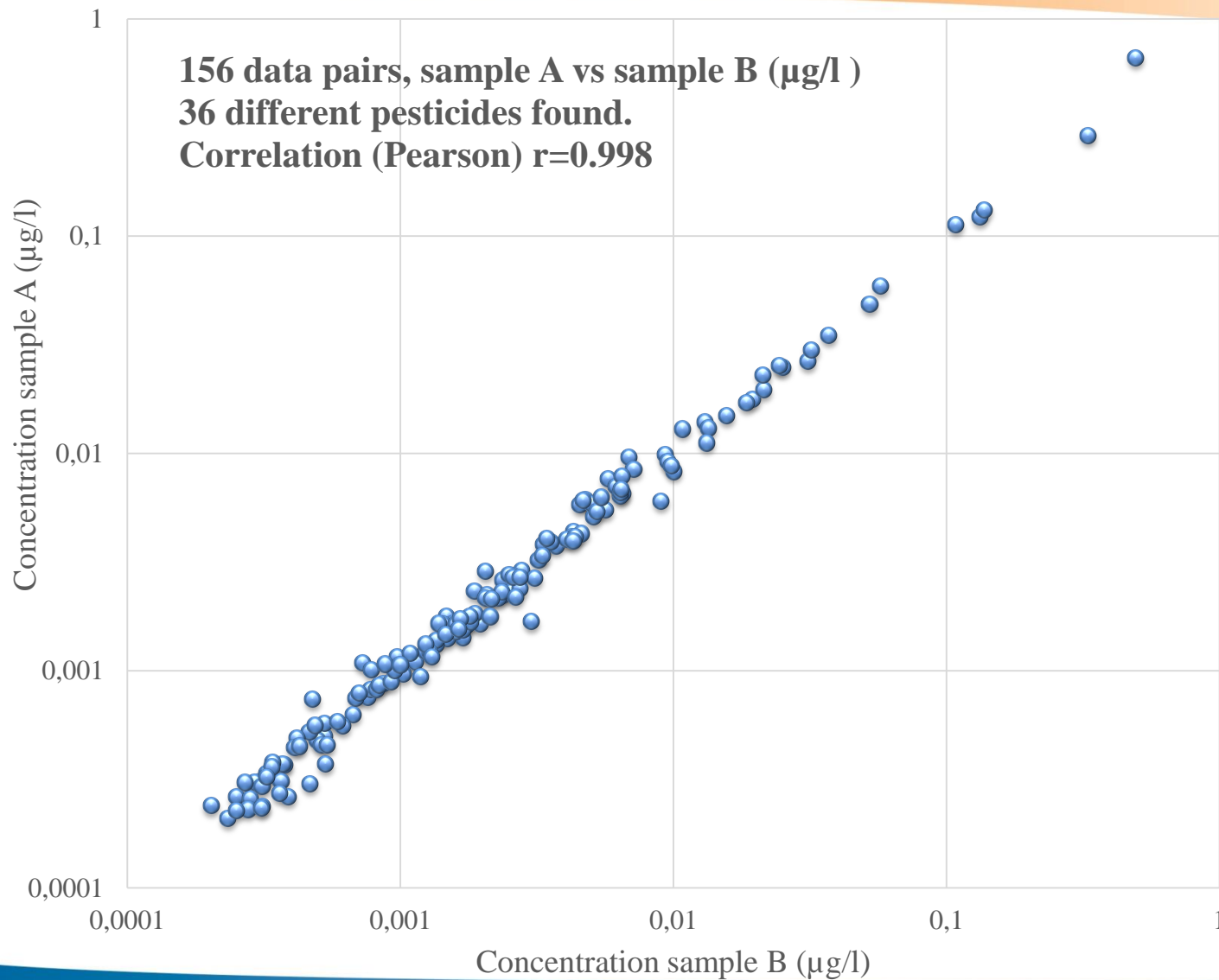
Including concentration >LOQ:

TIMFIE 698 hits, grab sampling 308 hits

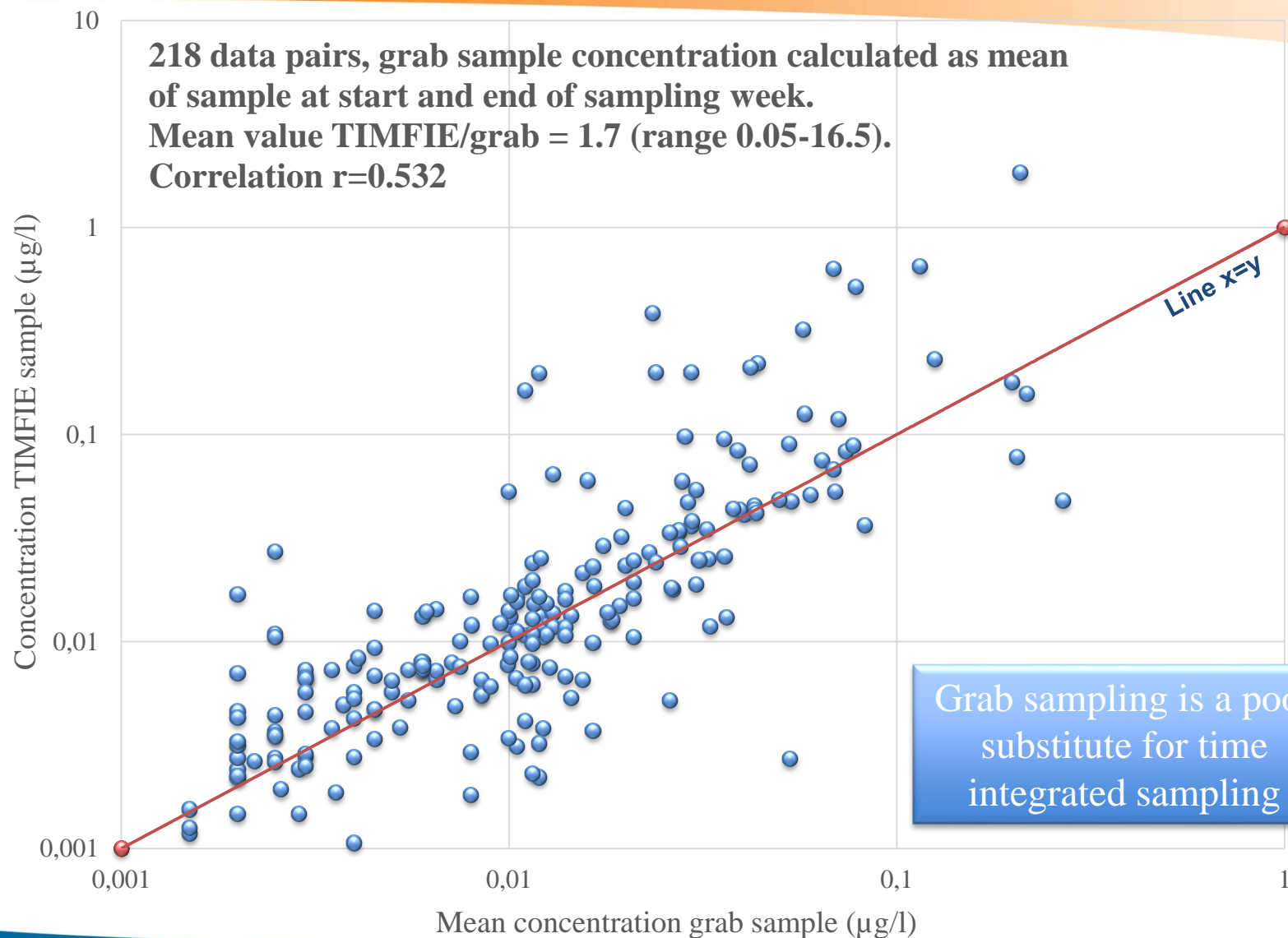
On average 19 compounds/sample with TIMFIE,
9 comp/sample with grab sampling and ref. method¹

(TIMFIE LOQ 10 times lower than
reference method for most compounds)

TIMFIE Duplicate field sampling



TIMFIE vs grab sampling



Summary TIMFIE sampling

Pros

- Time integrated sample 1-2 weeks
- Whole water
- Quantitative
- Pre-concentration
- Validation process according to established procedures
- Flexible, different SPE materials
Translate current SPE methods to TIMFIE conditions
- Small format, flexible application
- Transport and storage
- Inexpensive
- Use syringe water for further analysis?

Cons

- No pH adjustment
- Restricted sample volume

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

Acknowledgement

Swedish EPA and the Centre for Chemical Pesticides for financial support

Elin Paulsson SLU for performing most of the LC-MS/MS runs and analysing the massive amount of data generated

Henrik Jernstedt SLU for practical discussions

Jenny Kreuger, CKB and SLU, for support and scientific discussions

Nils-Åke Johansson and Anette Andrén are acknowledged for performing parts of the field sampling



Photo: Therese Nanos

Thank you
for your
time!