Analytical challenges for the analysis of biocides in aqueous and solid environmental matrices

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Environmental monitoring of biocides in Europe - from prioritisation to measurements
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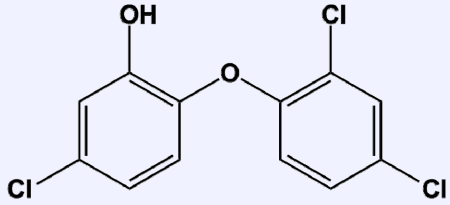
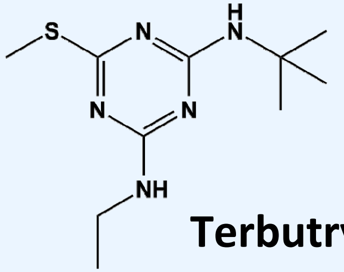
Biocides – main groups

- Disinfectants and general biocidal products
  e.g. Human hygiene biocidal products



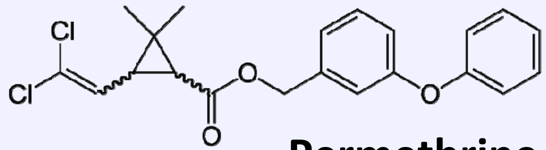
Triclosan

- Preservatives
  e.g. film preservatives

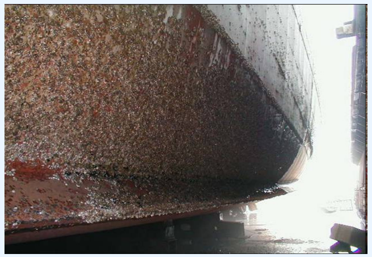


Terbutryn

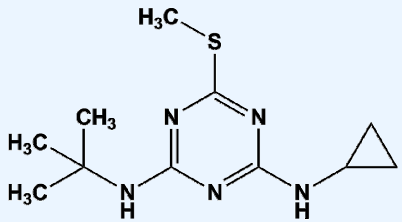
- Pest control, e.g. insecticides



Permethrine



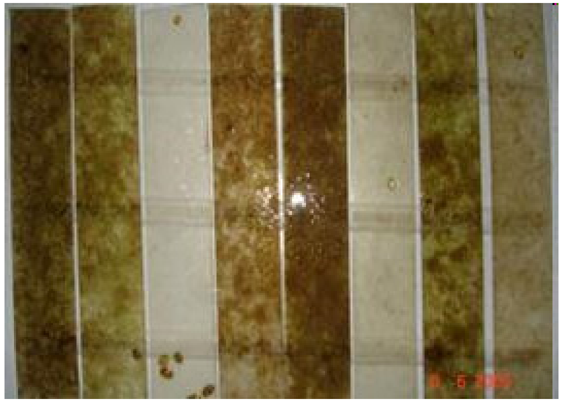
- Other biocidal products, e.g. antifouling



Cybutryne (Irgarol)

Biocides – Ecotoxicity

Periphyton



Mohr et al. (2008), *Aquatic Toxicol.*, 90(2), 109-120

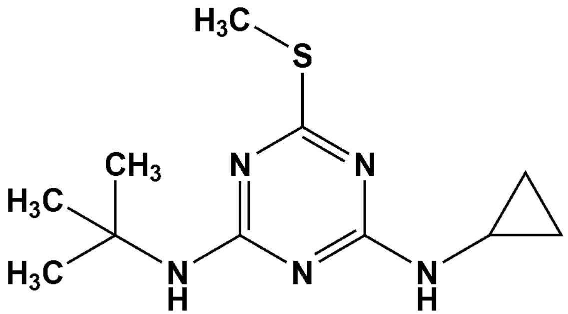
EC_{50} = 340 ng/L
EC_{10} = 10 ng/L

Myriophyllum verticillatum

Mohr et al. (2009), *Environ. Sci. Technol.*, 43, 6838-6843

EC_{50} = 210 ng/L

→ proposed
AA-EQS: 2.5 ng/L



Example: Irgarol

Copepods

Mohr et al. (2008), *Aquatic Toxicol.*, 90(2), 109-120

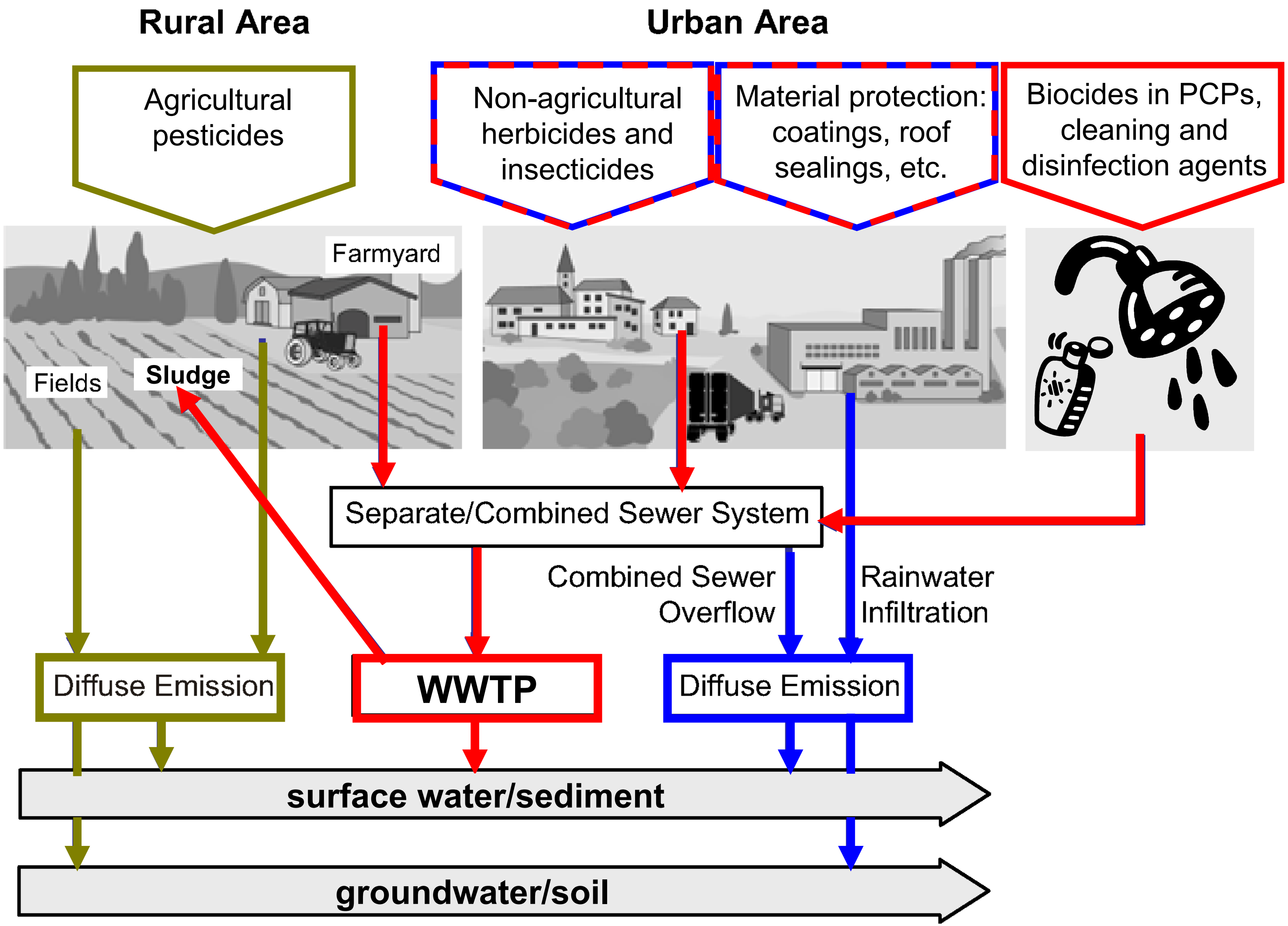
EC_{50} = 90 ng/L

Radix balthica

Oehlmann and Watermann (2005), UBA Dessau

EC_{10} = 32 ng/L

Emission routes of biocides



adapted from Gerecke et al. (2002), 48, 307-315

Analytical requirements

- Broad compound spectrum with different physico-chemical properties

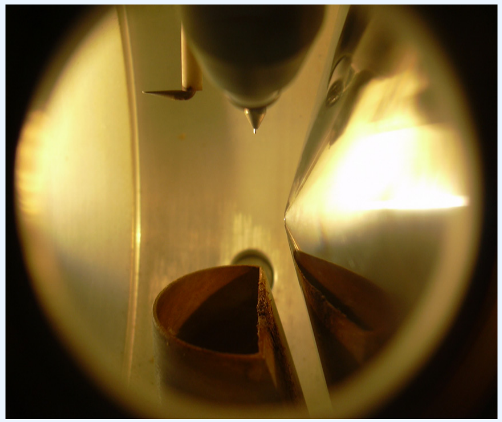
  positively charged: *climbazole, imazalil* **negatively charged:** *mecoprop, 2,4-D*

  polar: *carbendazim* (log K_{OW} = 1.5) **non-polar:** *triclocarban* (log K_{OW} = 5.1)

- Complex matrices (surface water, wastewater, sludge, sediment)
- Sensitivity and reproducibility (**e.g. LOQ Irgarol < 2.5 ng/L**)
- High throughput

➡ ***Methods based on LC Tandem MS detection***

➡ ***Problem: Matrix effects***
→ often severe ion suppression using ESI



ESI source

Reduction and compensation of matrix effects

Reduction:

Sample preparation:

- Enrichment volume for SPE
- SPE cartridge
- SPE cartridge wash step
- Clean-up

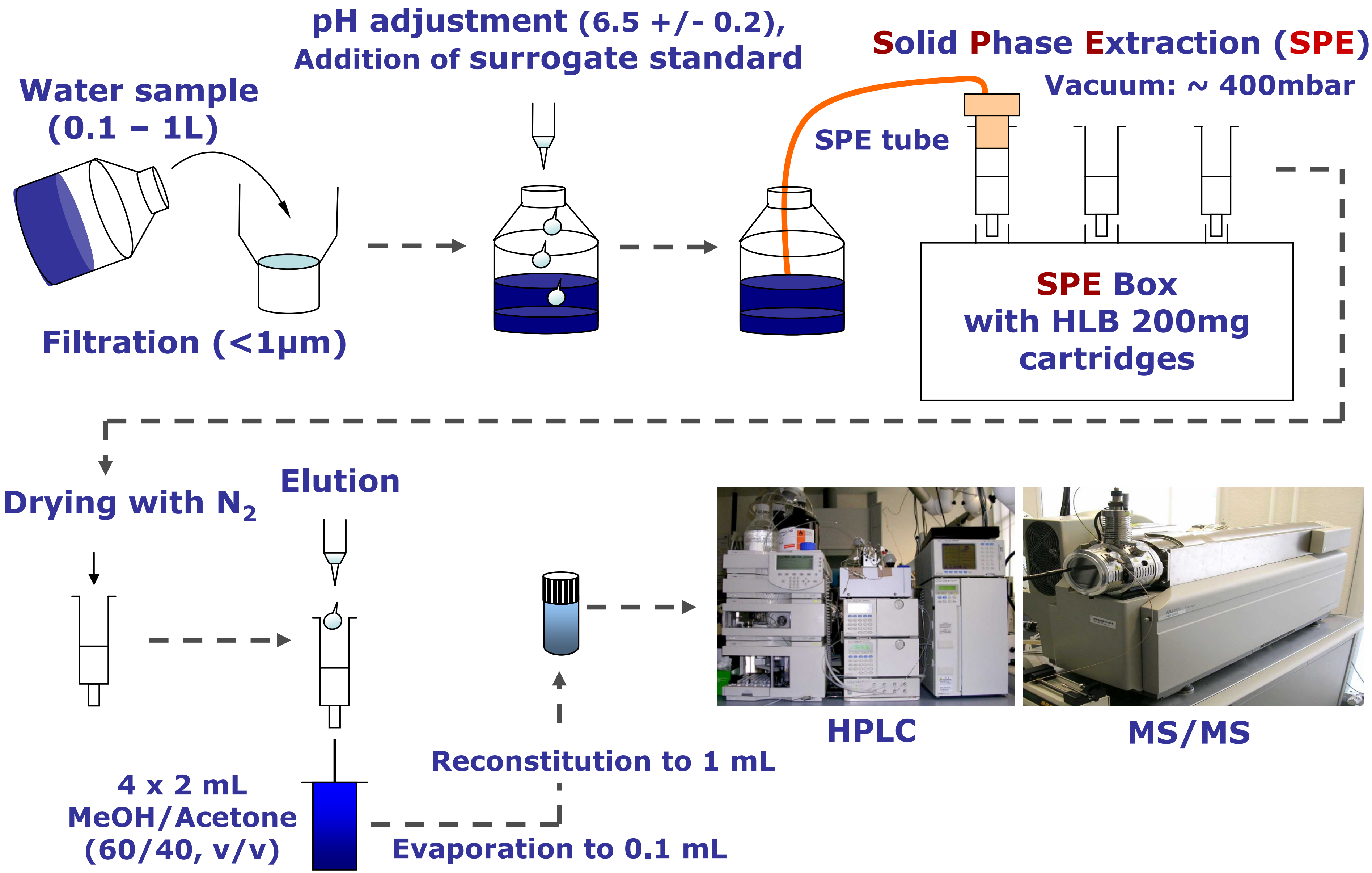
LC-MS/MS:

- Injection Volume
- Chromatographic conditions
- Flow rate to MS (split)
- **Ionization source (APCI *vs.* ESI)**

Compensation:

- Use of labeled surrogate standards (isotope dilution technique)
- Use of standard addition

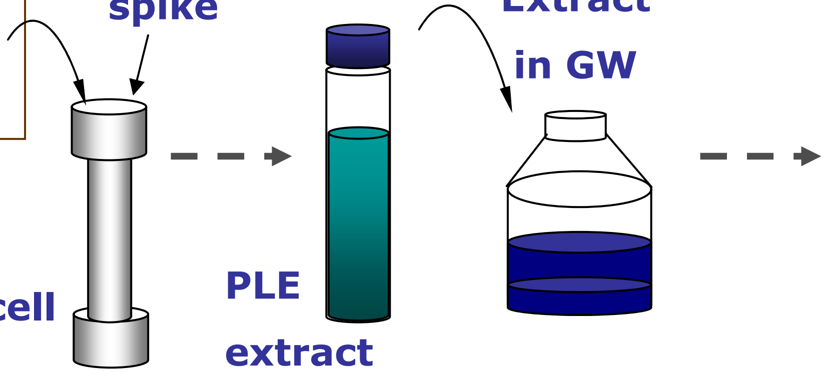
Analytical method – water samples



Analytical method – solid samples

Freeze-dried sediment ~ 1g

Surrogate standard spike



PLE cell

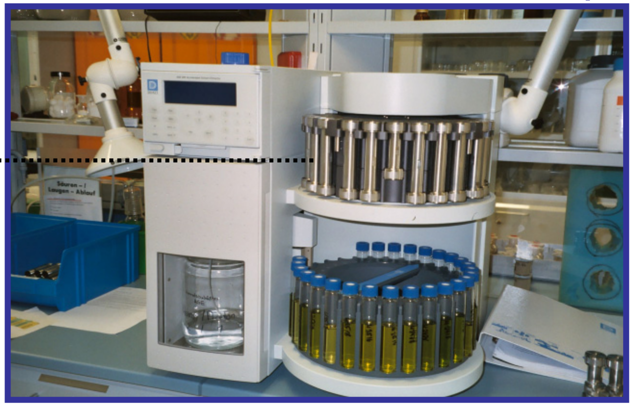
PLE extract

Extract in GW

SPE clean-up, HLB

Measurement with LC-MS/MS

Pressurized Liquid Extraction (PLE)



ASE Parameter: 80°C/100bar

Different extraction solvents

Method performance

~ 45 biocides and pesticides, + benzothiazoles and polar UV-filters

- Isothiazolones (e.g. Benzisothiazolone, BIT, Octylisothiazolone, OIT)
- Imidazole fungicides (e.g. climbazole, imazalil)
- Triazole fungicides (e.g. propiconazole, tebuconazole)
- Carbamate fungicides (e.g. carbendazim, IPBC)
- Phenyl urea herbicides (e.g. diuron, isoproturon)
- Triazines (e.g. terbutryn, irgarol)
- Bacteriocides (e.g. triclosan, triclocarban)
- Insecticides (e.g. DEET, imidacloprid)

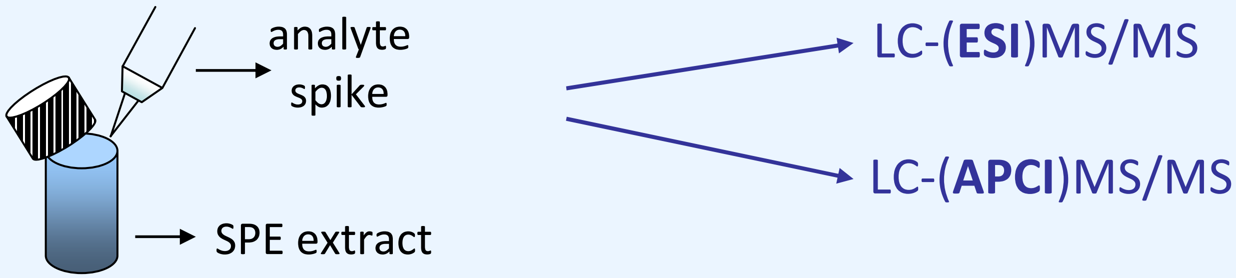
Matrix: groundwater, surface water, wastewater, partly for sludge, sediments and soils

$LOQ_{surface\ water}$: **0.5 – 50 ng/L, Accuracy: 80-120%, Precision < 25%**

Determined for every analytical run and matrix!!

Determination of matrix effects

Post-extraction spike

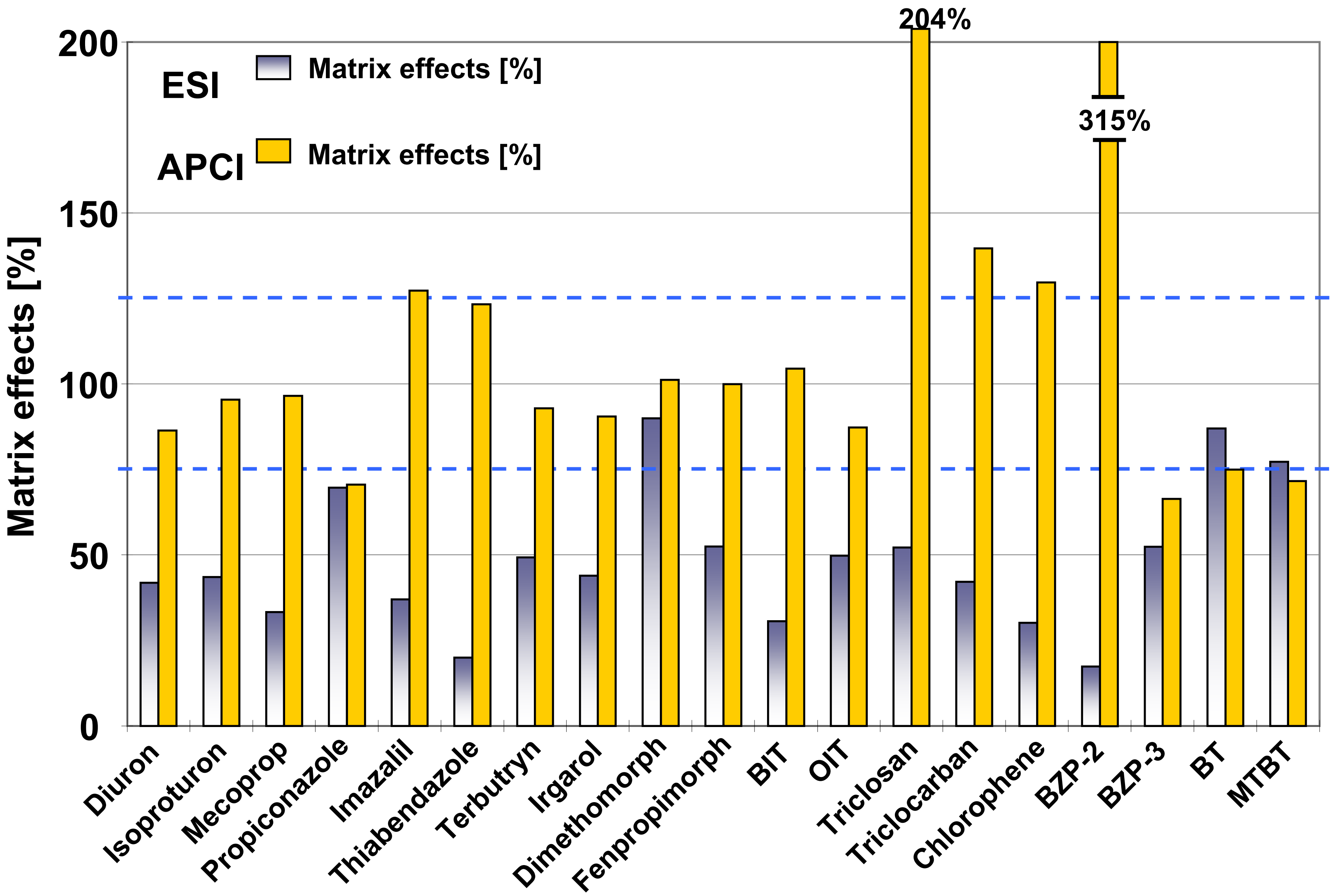


Matrix effect (ME)

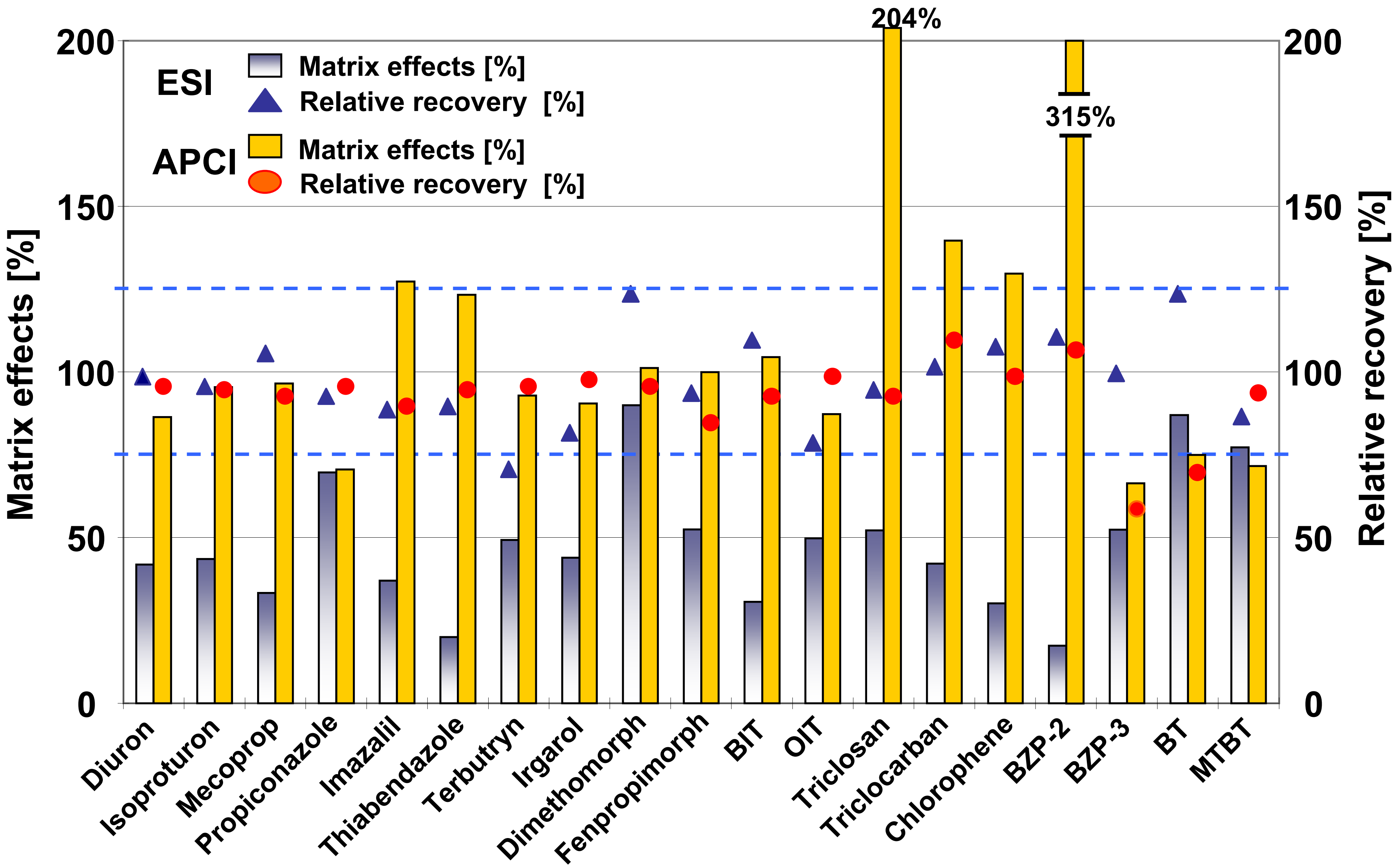
= Absolute recovery of a post-extraction spike

$$ME(\%) = \frac{\text{peak area}_{\text{post-extraction spike}} - \text{peak area}_{\text{blank}}}{\text{peak area}_{\text{external standard}}} \bullet 100$$

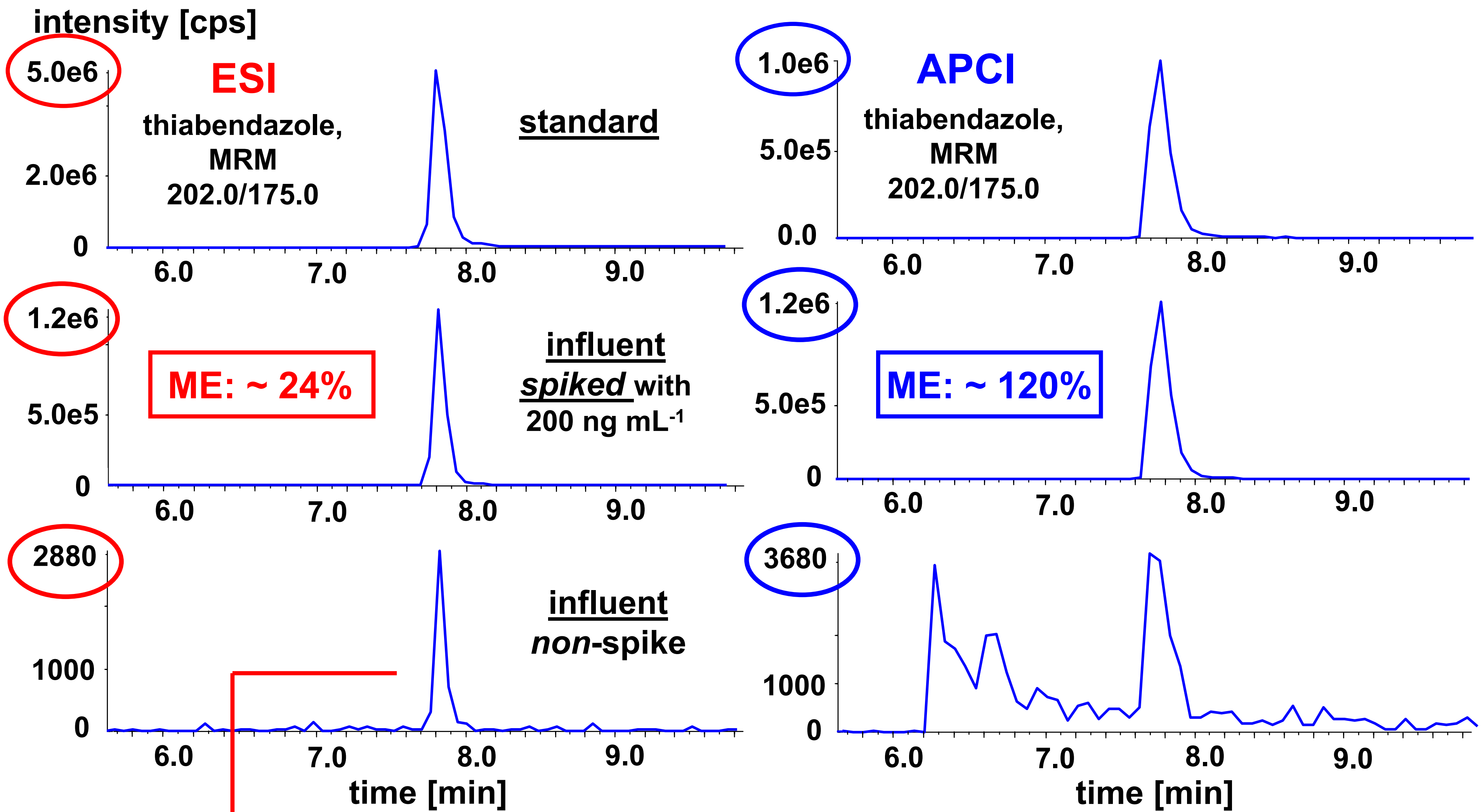
Matrix effects (raw wastewater)



Relative Recovery



Example: Thiabendazole



S/N = 35, ~ 4 ng/L

→ **LOQ ~ 1 ng/L**

S/N = 9, ~ 4 ng/L

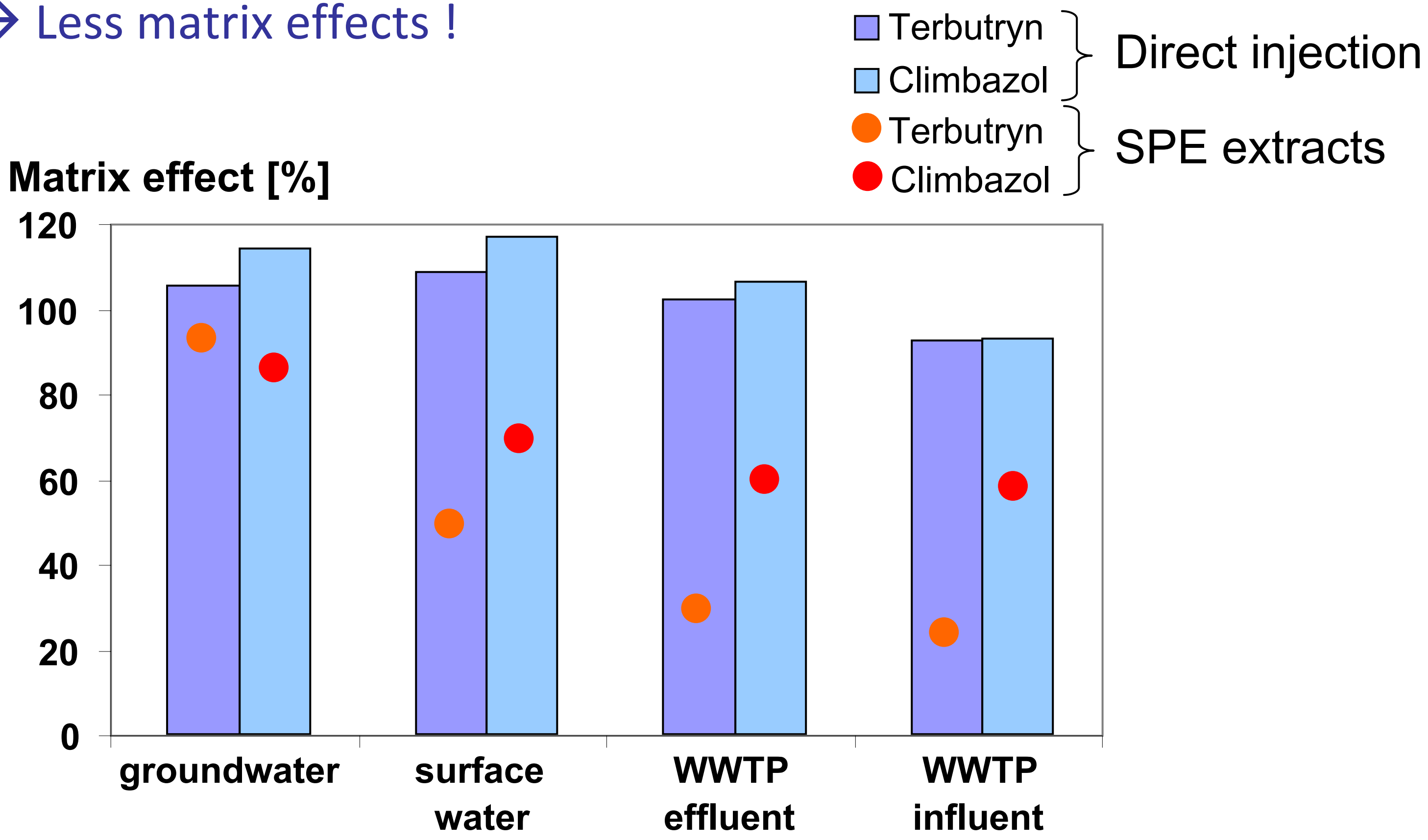
→ **LOQ ~ 5 ng/L**

Direct injection

No enrichment prior to measurement with an API 5500 Tandem MS

→ No losses during SPE, High Throughput

→ Less matrix effects !



→ Possible drawbacks: Higher LOQs, higher blank values

Extraction of solid samples

Many biocides are predominantly sorbed:

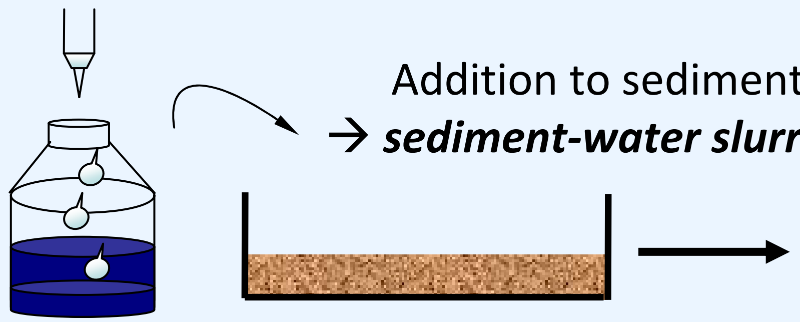
Quarternary ammonium compounds (QACs), triclosan, triclocarban, chlorophene, many conazoles (e.g. climbazole, ketoconazole, miconazole), etc.

→ Analysis in particulate matter, sediments, biota, soils and sludge is required

→ Challenge: Extractability depends on the physico-chemical properties of the compounds (e.g. charge, K_{OW}, etc.) and the properties of the solid matrix (cation exchange capacity, pH, TOC, etc.) → *no certified reference materials*

Spiking of analytes to *non-polluted* groundwater

Preparation of reference material



Addition to sediment
→ ***sediment-water slurry***

Evaporation at 30°C

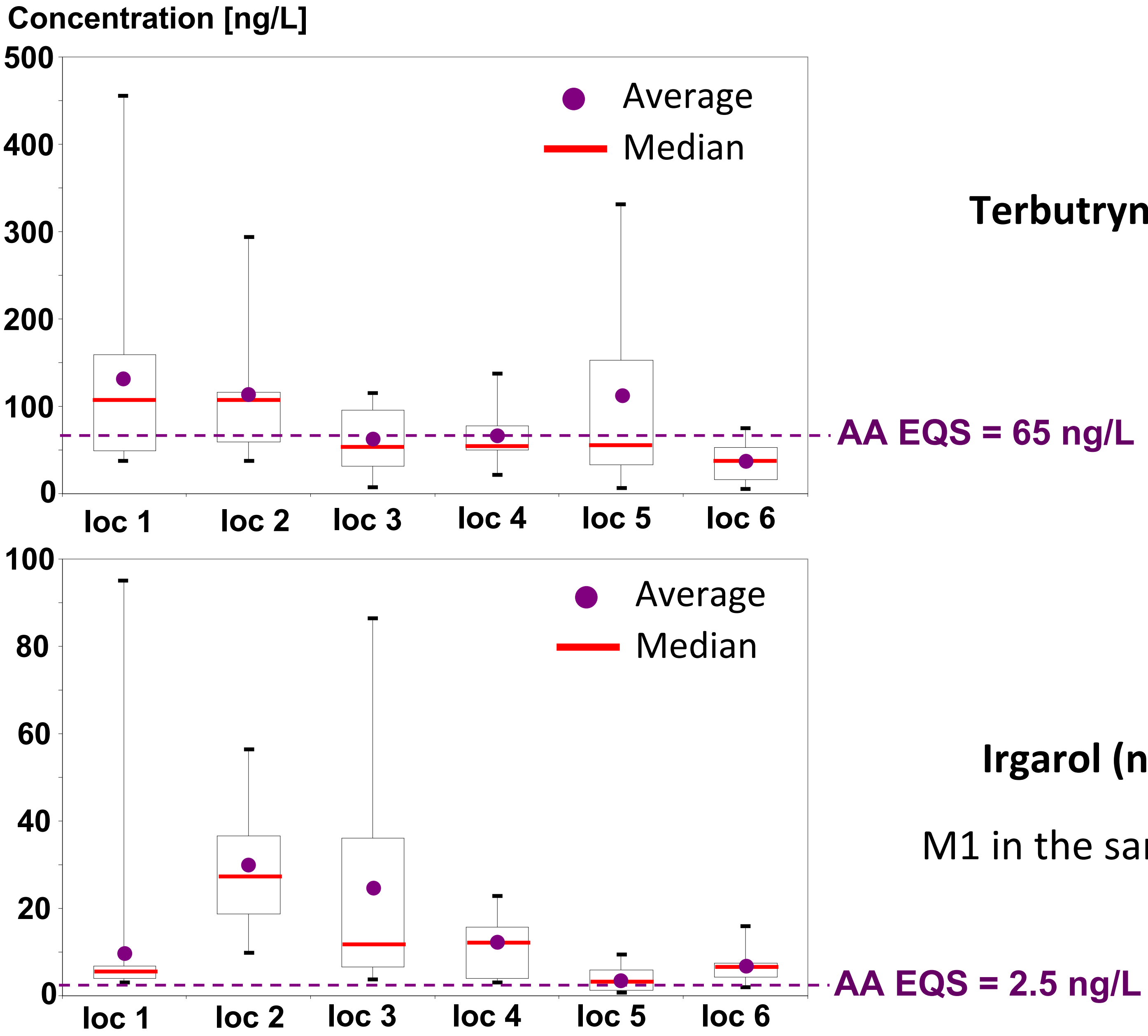
Extraction of solid samples

Recovery [%] of climbazole using self-prepared reference materials

	$MeOH/H_2O$	MeOH	MeOH/Acetone
soil	**79**	**60**	**32**
sediment	**78**	**51**	**8**
sludge	**50**	**71**	**20**

Recovery using freeze-dried soil spiked with climbazole directly prior to extraction with MeOH/acetone: **~ 100 %**

Concentration variability



Terbutryn (n = 11)

Irgarol (n = 11)

M1 in the same conc. range

Conclusions

Many biocides can be determined simultaneously in various environmental matrices down to the low ng/L and ng/g level. Ionization by ***APCI*** can be a valuable alternative, especially if labeled ***surrogate standards*** are missing

*

A compensation of ***matrix effects*** is the prerequisite for analytical accuracy and reproducibility.

*

The ***relative recoveries*** and the ***LOQs*** should be determined for each sample series and each sample matrix.

*

Extraction methods for solid matrices should be validated for each individual matrix (e.g. soils, sediments, sludge, biota). Self-prepared reference materials are an option for testing extractability.

*

A sufficient ***time resolution for sampling*** is crucial for assessing annual average and maximum concentrations of biocides


Thank you for your attention
Questions ?