USGS Methods:
Water, Sediment and Colloids

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Overview of Methods

- Water
  - Separation of fractions
    - Dissolved
    - Suspended sediments
    - Sorption to containers

- Sediments
  - Bed and suspended sediments

- Colloids
  - SPME

Pyrethroids Included

- Allethrin
- Bifenthrin
- Cyfluthrin
- Cyhalothrin
- Cypermethrin
- Deltamethrin
- Esfenvalerate
- Fenpropathrin
- Fluvalinate
- Permethrin
- Resmethrin
- Sumithrin (Phenothrin)
- Tetramethrin

Separation of Sample

Sample large volume of water (100-1000 liters)

Continuous-Flow centrifuge

Suspended Sediments (> 0.4 microns)

Dissolved + Colloids (<0.4 microns)

Water Method

- 1-L sample
- Filter (0.7 μm glass fiber)
- Solid Phase Extraction (HLB cartridge)
- Bottle rinse (sorbed pyrethroids)
- Extract filter paper (suspended sediments)
- GC/MS and GC/MS/MS (ion-trap)
- Recovery 91-98%
- MDLs 2-5 ng/L

Pyrethroid Sorption

- Pyrethroids in water sorb to sampling containers (glass or plastic)
  - Up to 50%
  - Analytical and toxicological importance
- Composition of sample influences extent of sorption
  - DOC
  - Suspended sediments
  - Relative surface area of container
Container Sorption - Varying Removal

- Filtered water, 6 mg/L DOC
- Equilibrated for 24 hours
- Spiked at 200 ng/L

Water Mass Balance

- Unfiltered water, 5 mg/L DOC, 13.5 mg/L SSC
- Equilibrated for 3 days
- Spiked at 400 ng/L

Pyrethroid Sorption to Containers

- Not all pyrethroids sorb to the same degree
- Allethrin and tetramethrin sorb less
  - Lack similar functional group
- Sorption seems to be "loose association"

Pyrethroid Water Method - SPE Storage

- SPE cartridge storage
  - Dried
  - Put in freezer
- Tested HLB and C8
  - Found not degradation on either cartridge after 1 month
- Can store cartridges

Pyrethroid Sorption to Containers

- Sorption addressed for analytical purposes not for toxicity or sampling
  - Continue exploring ways to mitigate or address pyrethroid sorption
  - Need concentration organisms are exposed to
- EPA funding to develop SOP for water sampling (FY07-08)
  - Cross-sections, composite samples
  - Autosamplers

Sediment Method

- 5-10 g samples
- MASE extraction at 120 °C, 50 % moisture with DCM:MeOH (9:1)
- Matrix clean-up: Carbon/Alumina stacked cartridges
  - Eluted with DCM
- Sulfur clean-up: GPC or activated Cu
- GC/MS or MS/MS
- Recovery 80-93%
- MDLs 1-5 ng/g
Sediment Method Development

- **MASE temperature**
  - Did not achieve complete extraction with 100 °C
- **MASE solvent**
  - Started with 1:1 DCM:Acetone
  - More efficient (less matrix) with DCM; Methanol
- **Clean-up**
  - Tried 10 g Florisil
  - No significant reduction of matrix and more time consuming
  - Also took other current use pesticides into consideration

GC/MS

- **Instrument**
  - Varian
    - 3800 GC
    - Saturn 2000 MS (ion-trap)
- **Column**
  - DB-5MS
    - 30 m × 0.25 mm × 0.25 μm
- **Individual isomer peaks added; reported as total compound**
- **GC/MS/MS**
  - Increases confirmation by decreasing background
  - Does not significantly reduce MDLs

MDL Limitations

- **Instrument (ion-trap) is at sensitivity limit**
- **Sediment samples have more matrix problems**
  - Greater concern for multiple isomers
- **Cannot increase sample size (suspended sediments)**

Colloids - Separation

- Sample large volume of water (100-1000 liters)
- **continuous-flow centrifuge**
- **tangential-flow ultrafilter**
- **Suspended Sediments (> 0.4 microns)**
- **Colloids (between 1000 Daltons and 0.4 microns)**
- **"truly dissolved" (< 1000 Daltons)**

SPME

- **Solid-phase microextraction**
- **Fused silica fiber coated with appropriate stationary phase**
- **Used to measure total and bioavailable compounds**
Colloids- Measurement of Pyrethroids

• Several types of SPME
  – Headspace, liquid

• Negligible depletion SPME
  – Freely dissolved (or bioavailable) fractions
  – Only if equilibrium is not disturbed (EE of less than 5-10%)
  – Sample matrix should not disturb sorption kinetics

SPME- Parameters

• 20 mL of water

• Fiber
  – Tested 7 and 100 μm PDMS phase
  – 1 cm

• Total pyrethroids
  – Sorption onto fiber at 90 ºC for 30 min with agitation
  – Desorption at 275 ºC for 3 min

• Negligible depletion/ Bioavailable
  – Based on Liu et al., 2004, ET&C, 23, p 7-11.
  – Sorption at ambient temperature for 10 min with agitation
  – Desorption at 275 ºC for 3 min