PPCP Quality Assurance/Quality Control: Lessons Learned

NWRI/MWD/OCWD Project

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PPCPs – QA/QC: Lessons Learned

- Background/Overview
  - Analytical Methods
  - Detection Reporting levels
  - QA/QC protocols
  - Reporting criteria
- Experience/Findings
- Summary and Recommendations

Overview of Analytical Methods at MWD

- **Solid phase extraction**
  - **500 mL sample concentrated to 1 mL extract**
- **Liquid chromatography/tandem mass spectrometry (LC/MS/MS)**
- **14 polar and non-volatile PPCPs**
- **Gas chromatography/mass spectrometry (GC/MS)**
- **20 volatile and semi-volatile PPCPs**

Method Detection/Reporting Levels

- **MDL**
  - **7 replicates of organic pure water samples fortified with PPCPs at or near MDL**
  - **MDL=3.14 x SD**
- **MRL**
  - **3 times the MDL**
  - **Practical and routinely achievable quantitation level**
  - **LC/MS/MS method: 1-10 ng/L**
  - **GC/MS method: 10-50 ng/L**

Analytical Methods/MRLs at OCWD

- **Solid phase extraction**
  - **Pharmaceuticals and phenols: 500 mL sample concentrated to 1 mL**
  - **Hormones: 1 L sample concentrated to 1 mL**
- **LC/MS/MS**
  - **11 pharmaceuticals: MRLs range from 1-50 ng/L**
  - **9 hormones: MRLs at 10 ng/L**
  - **8 phenols: MRLs range from 1,000-10,000 ng/L**

Isotope Dilution

- Used for LC/MS/MS to compensate for matrix effects
- Ensure high-quality data, especially with complex matrices
- MWD:
  - 13 of 14 PPCPs are analyzed by isotope dilution
- OCWD
  - Pharmaceuticals method: by isotope dilution
  - Hormones method: to be done by isotope dilution
  - Phenols method: to be done by isotope dilution

QA/QC Protocols: Sample Collection and Preservation

- Amber glass bottles
- Sodium azide as biocide
- Ascorbic acid as quenching agent
- Field blanks
- Samples are extracted within 2 weeks of collection

QA/QC Protocols: QA/QC Samples

- Method blanks: potential contamination from analytical procedures
- Duplicates to assess precision
- Matrix spikes to assess accuracy
- Calibration: 5-point calibration curve; continued check standards
- Inter-laboratory QA samples

Criteria for Data Reporting

- Check duplicated samples
  - 20% relative percent difference
- Check matrix spikes
  - 70-130% spike recovery (except for TCEP)
- Check method blanks and field blanks
  - Only report levels at least twice that in the blanks
- Check historical data where applicable
- Re-analyze when needed

Experience/Findings: MWD

- Relative percent difference for duplicates
  - Average 2-8%
  - Range 0-24%
- Spikes recoveries
  - Average 87-114%
  - Range 53-145%
- Field blanks
  - 10 of 86 field blanks with low levels (1-18 ng/L) of sulfamethoxazole
  - Levels much lower than corresponding samples (4-1,295 ng/L)

Field Blanks: April to September, 2008

Sampling Event	Sampling sites	Number of sites with field blanks	Analyte in field blanks and levels (ng/L)	Same analyte in corresponding samples and levels (ng/L)
1	11	11	None	---
2	13	6	Sample 1: SMX*, 17 Sample 2: SMX, 18 Sample 3: SMX 6	Sample 1: SMX, 332 Sample 2: SMX, 148 Sample 3: SMX 87
3	7	6	SMX, 2	SMX, ND (<1)
4	11	11	None	---
5	13	13	Sample 1: SMX, 10 Sample 2: SMX, 13 Sample 3: SMX 14 Sample 4: SMX, 3	Sample 1: SMX, 431 Sample 2: SMX, 410 Sample 3: SMX 128 Sample 4: SMX 1295
6	8	8	SMX, 1.5	SMX, 4
7	10	10	None	---
8	13	13	SMX, 1.3	SMX, 10
9	8	8	None	---

***SMX=sulfamethoxazole**

Experience/Findings: OCWD

- Relative percent difference for duplicates
  - Average 0-14%
  - Range 0-50%
- Spikes recoveries
  - Average 80-107%
  - Range 52-119%

Analytes Prone to Analytical Difficulties

- Sulfamethoxazole
- Erythromycin
- Ciprofloxacin
- Caffeine
- Carbamazepine
- Ibuprofen

Inter-laboratory QA/QC

- **Split samples on a regular basis with OCWD and SNWA**
  - **Round Robin Test from March to April 2008**
  - **Encountered problems from April to June when OCWD used Restek standard solution with inaccurate concentrations**

Results Comparison: MWD and OCWD

- Overall 88% of the results have <30% relative percent difference
  - 42 samples collected from July to October, 2008
  - 8-9 common analytes each time
- Analytes with >30% relative percent difference
  - Caffeine, sulfamethoxazole, primidone, triclosan, carbamazepine, Ibuprofen, DEET

Results Comparison: MWD and SNWA

- Overall 87% of the results have <30% relative percent difference
  - 8 samples collected in June and September, 2008
  - 15 common analytes each time
- Analytes with >30% relative percent difference
  - Caffeine, sulfamethoxazole, triclosan, diclofenac, TCEP, gemfibrozil, Bisphenol A, DEET

Summary

- **Major Challenges**
  - **Ultra trace levels**
  - **No standard methods available**
  - **Large sample volume (2-4 L per sample)**
- **QA problems**
  - **Low levels in field blanks**
  - **Some analyte are prone to analytical difficulties**
- **Our experience validated analytical methods developed by Shane Snyder**
  - **EPA method 1694 / USGS method**
  - **Water Research Foundation project 4167**

Recommendations

- QA/QC is essential for analysis of PPCPs
  - Sample preservation
  - Duplicates and Matrix spikes
  - Method blanks and field blanks
- Isotope dilution is needed to ensure accuracy of data
- Use multiple laboratories as QC checks
  - In case of different results, further investigation is needed (analytical methods, standards, QC, etc.)

Questions?

List of Analytes: GC/MS (MWD)

Class	Compound	Use
Industrial By-Product	Anthracene	PAH
	Benzo[a]pyrene*	PAH
Pesticide	Triazines: Atrazine, Cyanazine, Cyprazine, Propazine, Simazine	Pesticides
	Atrazine-Desethyl	Atrazine Degradate
	Atrazine-Desisopropyl	Atrazine Degradate
	g-BHC (Lindane*)	Pesticide
	DDD	”
	Methoxychlor	”
Personal Care Product	Bisphenol A*	Material used to make plastics
	DEET	Insect Repellent
	Nonylphenol*	Surfactant
	Octylphenol*	”
	Parabens (butyl, ethyl, methyl, propyl)	Antibacterial

*Suspected EDCs

List of Analytes: LC/MS/MS (MWD)

Class	Compound	Use
Pharmaceutical	Carbamazepine	Anti-seizure
	Diclofenac	Anti-inflammatory
	Dilantin	Anti-epileptic
	Primidone	Anti-seizure
	Gemfibrozil	Anti-cholesterol
	Ibuprofen	Pain killer
	Sulfamethoxazole	Antibiotic
Personal Care Product	Triclosan*	Antibacterial
	Caffeine	Stimulant
	TCEP	Flame retardant
Hormone	Ethynylestradiol*	Birth control
Pesticide	Atrazine*	Herbicide
	Diuron	”
	Linuron	”

List of Analytes: LC/MS/MS (OCWD)

Class	Compound	Use
Pharmaceutical	Acetaminophen	Analgesic
	Azithromycin	”
	Carbamazepine	Anti-seizure
	Ciprofloxacin	Antibiotic
	Gemfibrozil	Anti-cholesterol
	Ibuprofen	Pain Reliever
	Primidone	Anti-seizure
	Sulfamethoxazole	Antibiotic
Personal Care Product	Bisphenol A*	Material used to make plastics
	Caffeine	Stimulant
	DEET	Insect Repellant
	4-Nonylphenol*	Surfactant
	Nonylphenol Ethoxylates*	”
Personal Care Product	Octylphenol*	Surfactant
	Tetrabromo-bisphenol A	Flame Retardant
	Triclosan*	Antibiotic
Hormone	Diethylstilbestrol*	Synthetic Estrogen
	Epitestosterone*	Hormone
	Estradiol (17-a)*	”
	Estradiol (17-b)*	”
	Estriol*	”
	Estrone*	”
	Ethynylestradiol*	Birth Control
	Progesterone*	Hormone
	Testosterone*	”
Pesticide	Pentachloro-phenol	Fungicide
	4-Phenylphenol	”
	Trichlorophenol	”

Method Comparison

Summary	MWD	EPA 1694	USGS
Number of Analytes	33	74	14
Type of Analytes	PPCPs, including one flame retardant, Bisphenol A, etc.	PPCPs; not including flame retardants, Bisphenol A, etc.	PPCPs; not including flame retardants, Bisphenol A, etc.
Method Description	SPE followed by GC/MS; SPE followed by LC/MS/MS	SPE, followed by LC/MS/MS	SPE, followed by LC/MS
Matrix Applicable	Water	Water, Soil, Sediment, Biosolids	Water
MRLs (ng/L)	1-50	2-500	15-100
Preservatives	Ascorbic acid, sodium azide	80 mg/L sodium thiosulfate	None; filtered
Isotope Dilution	Used for 13 of 14 LC analytes	Used for 18 Analytes	No
Holding Studies	Yes	No	Yes
Inter-laboratory Comparison	Yes	No	No
Potential Issues	---	Accuracy due to matrix effects; Range of precision and accuracy 5-200 %	Accuracy due to matrix effects (range of recovery 2-138%); MS/MS not used