Data Usability Part 2: Data Validation Needs To Be More Than Just A Checklist

National Environmental Monitoring Conference 2016
Orange County, California

August 11, 2016

James J. Mc Ateer, Jr., QA/QC Solutions, LLC
and
Polly S. Newbold, ddms, inc.

Outline

- Introductory Comments
- Sampling & Analysis Concerns
- Data Verification & Validation Issues
- DQA, Usability, & Uncertainty
- Chemical Forensics/Source Tracing
- Litigation
- Closing Thoughts and Q&A

Just a Thought…

Once you have knowledge of something, you simply cannot not do something about it, because to do otherwise is…

Introductory Comments

- Chemical data used for several purposes:
  - Delineating nature and extent of contamination
  - Verifying cleanup or "clean" closure
  - Evaluating if there are potential risks
- QA/QC processes and procedures must be established, implemented, and followed
- Implement *Systematic Planning*
- Follow the scientific method

Introductory Comments, cont.

Our work must be:

- **Scientifically meaningful**
- **Valid**
- **Usable**
- **Legally admissible and defensible**

Introductory Comments, cont.

- Let's not forget:
  - How much uncertainty is acceptable in the decision-making process?
  - How much of a chance are you willing to take?
  - "Sound science" is essential
  - It's about value added service!

Remember, all QC measurements may be acceptable, but the data may not be usable for it's intended purpose(s)!

A Reminder To Myself

The Devil is in the Details!

Do I really know what I'm doing and why?

Don't forget the "BIG" picture!

Sampling & Analysis

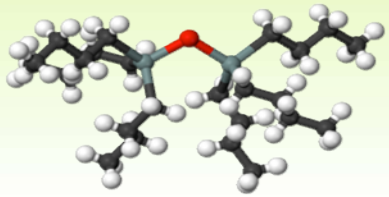
Data Do Not Support the Conceptual Site Model!

Must Be Laboratory Error!

Total uncertainty is often attributable to where & how samples are collected, the matrix (heterogeneity and interference matters), and the analytical method(s) selected

Matrix Effect?: Example 1

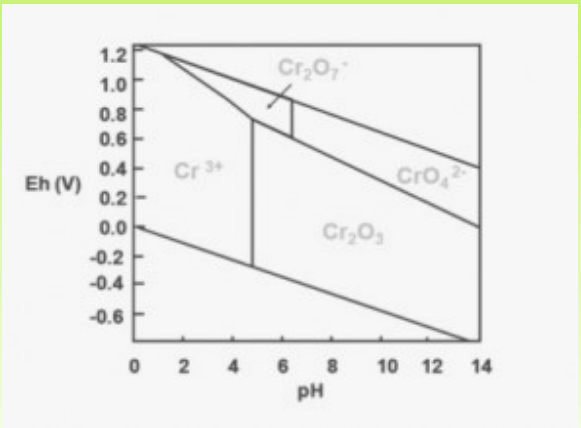
- **Butyltins in Sediment:**
  - Initially total butyltins ~6,200 ug/kg
  - Re-analysis at ~4.7 ug/kg
  - All QC measurements acceptable
  - Qualitative and quantitative criteria met
  - So use only the lowest results, right?
  - Was this just lab error or something else?



https://commons.wikimedia.org/wiki/File:Tributyltin-oxide-3D-balls.png

Matrix Effect: Example 2

- **Cr^{+6} in Groundwater:**
  - MS/MSD recoveries usually 0% to <10%
  - SRM and LCS recoveries always very good
  - All other QC measurements in control
  - Data previously always rejected
  - So what's the problem?
  - No need to reject data
  - Don't forget mass balance!



http://brooksapplied.com/?s=chromium

Data Verification and Data Validation

Verify and Re-Verify &
Review Instrument Printouts!

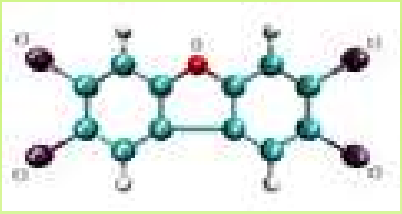
Do a reality check and ask does the data make sense?

Do a Reality Check (and Verify)

- **PCDD/Fs:**

http://commons.wikimedia.org/wiki/File:Dioxine_pcdd.png

  - Data was used and conclusions made
  - Did not look good for PRP
  - Quick look at data did not make sense
  - Requested lab printouts
  - Major database errors!
  - PCDD/F contamination minor
  - Simple, but $$$ wasted



http://commons.wikimedia.org/wiki/File:Furane_pcdf.png

Chromatograms Do Tell a Story

- **PCBs (and more):**
  - PCBs in surface soil and groundwater
  - "Expert" says soil contaminated water
  - Highly weathered A1260 in soil, but relatively unweathered A1016/A1242 in water
  - Soil and water contamination two separate issues (and very explainable too)
  - Soil different story…Tech. Grade Chlordane much bigger issue…look at chromatogram!
  - More to tell here…

DQA, Usability, and Uncertainty
&
Chemical Forensics/Source Tracing

There Are Many Valid Ways To Scientifically To Meet DQOs

Must think about effect most cost-effective way to answer DQOs and ensure acquisition of most useful quality data

Organochlorine Pesticide Data Bias

- GC/ECD vs. HRGC/MS/MS
  - GC/ECD most common (e.g., USEPA 8081B)
  - Historically used to compare data sets
  - Good sensitivity with relatively clean extracts
  - Suffers from well-documented limitations:
    - Interferences (non-target compounds)
    - Elevated detected concentrations
    - Often elevated RLs & false negatives/positives

GC/ECD vs. HRGC/MS/MS, cont.

- Used archived samples (stored frozen at -20°C); holding times slightly >1 yr.
- Most background noise and interferences 'filtered' due to tandem MS and MRM
- More definitive analyte identification
- Use of isotopically-labeled standards increases precision and accuracy
- Achieve detection levels up to 20 times lower (or more) than typically achieved by GC/ECD
- Overall, greater sensitivity and selectivity

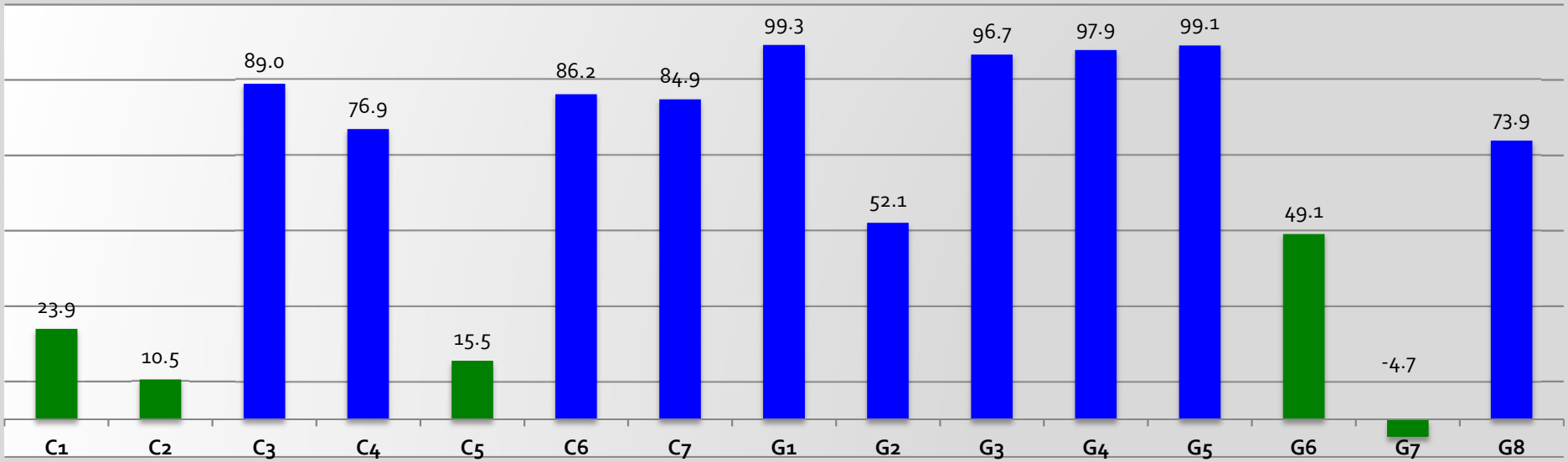
Subsurface Sediment (Core) Results

- 100% of 2,4'-DDT results by GC/ECD have RLs of 97 to 20,000 times greater than HRGC/MS/MS
- 71% of 2,4'-DDD results by GC/ECD are 1 to 70 times greater than HRGC/MS/MS for detects
- 2,4'-DDE results are comparable, with one RL at 320 times greater than HRGC/MS/MS
- 100% of 4,4'-DDT results by GC/ECD have RLs of 410 to 12,900 times greater than HRGC/MS/MS
- Two 4,4'-DDT high detected concentrations by GC/ECD, but not supported by HRGC/MS/MS
- 4,4'-DDD results by GC/ECD mixed; five results biased low; higher concentration by HRGC/MS/MS

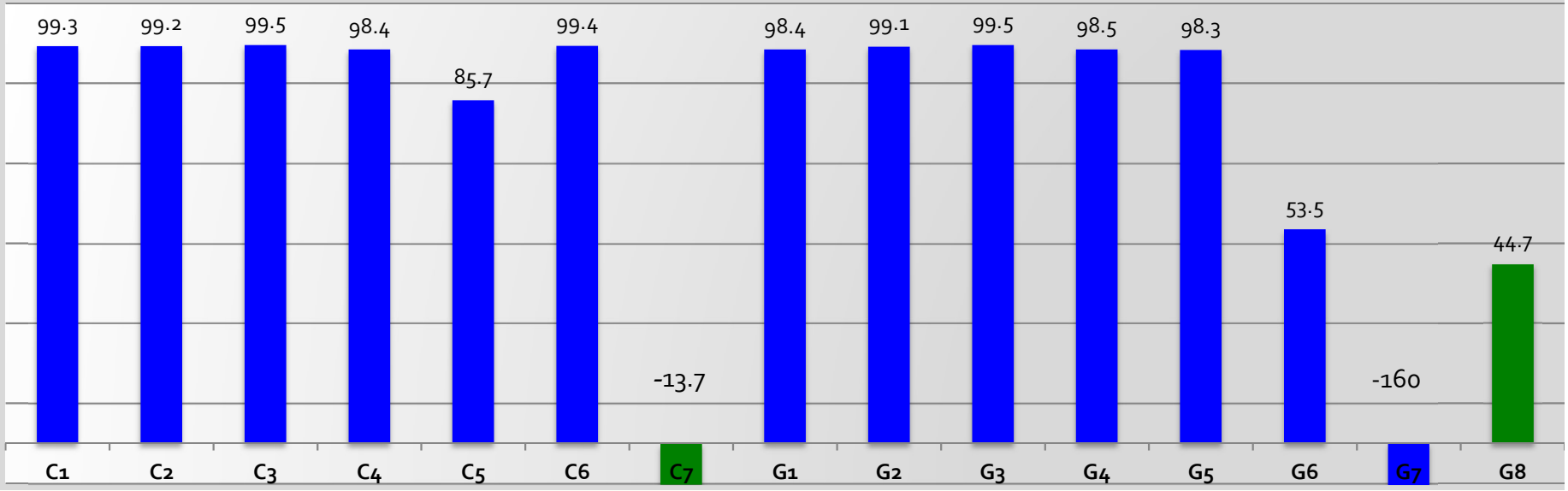
Subsurface Sediment (Core) Results.

- 4,4′-DDE results by GC/ECD mixed; three results biased low; higher concentrations by HRGC/MS/MS
- 2,4′ and 4,4′-DDx results by GC/ECD show positive bias in 4 of 7 samples (concentrations from 7 to 9 times greater than HRGC/MS/MS concentration
- 90% of Σ Chlordane results by GC/ECD show positive bias with concentrations from 7 to 220 times greater than HRGC/MS/MS concentration
- Presence of PCBs (and PHCs?) biasing results
- Non-target compounds likely interferences?

% Difference Total DDx (GC/ECD vs. HRGC/MS/MS)



% Difference Total Chlordanes (GC/ECD vs. HRGC/MS/MS)



- Key Points:
  - GC/ECD not always best choice
  - Complex matrices are always difficult
  - HRGC/MS/MS "relatively" inexpensive
  - Extent of bias could be significant
  - Effect on overall DQA (interpretation) and usability of data (decisions made)
  - Larger degree of overall uncertainty
  - This bias is not a new issue!

Differentiate COI's: Past vs. Present

- PCP & Wood Preserving Treatment
  - Former superfund site
  - On-going wood pole treatment with PCP
  - Need to differentiate former from potential new contamination (PCP is dominant COI)
  - Routine analyses will be inadequate
  - Historical contamination problematic
  - Find alternative analytical scenario

PCP Wood Preserving Treatment, cont.

- Take proactive approach
- Conduct baseline survey (SVOCs, PCP, PCDD/Fs, and full-scan PHCs)
- Identify unique marker chemicals
- Conduct "marker" study
- Be cost effective and meet DQOs (and legal)

PHC Assessment Methodology

Full-scan GC/MS - Tentatively Identified Compounds

m/z 85 and m/z 113: *n*-Alkanes & Iso-Alkanes + Isoprenoids

m/z 83: Alkylcyclohexanes

m/z 134: C_4-Alkylbenzenes

m/z 123: Bicyclanes (i.e., Bicyclic Sesquiterpanes)

m/z 191: Tri-, Tetra-, and Pentacyclic Terpanes (i.e., Sesquiterpanes)

m/z 127: Steranes

Histogram for selected alkylbenzenes, alkylated PAHs, alkylated biphenyls, alkylated biphenyls/dibenzofurans, alkylated benzothiophenes, and steranes

PCP Wood Preserving Treatment, cont.

- **Multiple lines-of-evidence needed:**
  - Differentiate historical vs. possible future COCs
  - What unique "marker" compounds present?
  - Compare PHC & PCDD/Fs results
  - Review SICPs, mass chromatograms, etc.
  - Confirm absence/presence of co-solvent (i.e., BBP) with PCP

PCP Wood Preserving Treatment, cont.

- **Results of Marker Strategy:**
  - Can differentiate existing site contamination from a potential future release of current working solution
  - BBP may be a very unique "chemical marker"
  - The PHC & PCCD/F profiles may be most useful
  - The data and information must be considered in its proper context to draw meaningful conclusions
  - All "tools" should be considered to provide a reasonable interpretation about "source"

Litigation

Does Sound Science Really Matter or is it only Perception?

A few thoughts

Litigation (a very sensitive issue)

- Limited QA review? It's already over.
- It's not so much what you did do, but what you did not do that will be the problem!
- Daubert…
- Legally admissible data?
- Are all of the *T's* crossed and *I's* dotted?

Litigation, cont.

- Create doubt!
- Lies, Damn Lies, and Statistics!
- You must provide more evidence!
- Nothing is 100%!
- Weight of evidence is the best we can do!

Closing Thoughts

The confidence in the decisions we make are only as good as the quality of the data that we use!

Even if all DQO, PQOs, and MQOs have been met, the data may not be suitable for their intended purpose(s). Remember, garbage in is still garbage out.

Closing Thoughts:

- We need to provide value added service(s)
- Do it right the first time
- Get "team" involved during initial planning and implement systematic planning
- Use tiered approaches
- Data verification, data validation, and QA must be more than a "checklist" approach

Closing Thoughts, cont.

- Conduct a DQA and usability evaluation
- Do "*reality check*" – does it all make sense?
- The data must support the decisions made
- Always use the scientific method!
- Always ask yourself, am I willing to put my reputation on the line?

Closing Thoughts, cont.

- Make sure the "end-product" is:
  - Scientifically meaningful
  - Valid
  - Usable
  - Legally admissible and defensible
- Speculation is not Science!!!
- Remember, we can always do better!

Acronyms

- BBP– Butyl Benzyl Phthalate
- COIs – Chemicals of Interest
- DQA – Data Quality Assessment
- DQO – Data Quality Objective
- GC/ECD- Gas Chromatography/Electron Capture Detection
- HRGC/MS/MS – High Resolution Gas Chromatography/Mass Spectrometry/Mass Spectrometry
- MQO – Measurement Quality Objective
- PCB – Polychlorinated Biphenyl
- PCP– Pentachlorophenol
- PCDD – Polychlorinated dibenzo-*p*-dioxin
- PCDF – Polychlorinated dibenzofuran
- PAHs – Polycyclic Aromatic Hydrocarbons
- PHC – Petroleum Hydrocarbon
- PQO – Project Quality Objective
- QA/QC – Quality Assurance/Quality Control
- RLs – Reporting limits
- SVOCs – Semivolatile Organic Compounds

Acknowledgements

- TNI, NEMC, and the USEPA
- You, the audience, for your patience and attention
- Individuals in the QA "realm" worldwide
- Regulators I have worked with in my career
- Laboratories I've worked throughout my career
- My client(s)

DISCLAIMER

The views and opinions expressed in this presentation are those solely of the presenters and do not reflect the opinions, official policy, or position of any client or regulatory agency.

Thank you!

Questions?

Contact Information

James J. Mc Ateer, Managing Member

QA/QC Solutions, LLC
Tel: 503.763.6948
email: jjmcateer@msn.com