Application of Automated Systems for Clean Composite Sampling

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Importance of Data Quality

- Data used to monitor regulatory compliance
- Trace metal data may easily be compromised by contamination in sampling and analysis
- Use of clean techniques in sampling and analysis is critical to obtaining representative and accurate data
Evolution of Clean Metals Sampling System

- In recognition of need for collecting clean metals, state suspended final effluent metals monitoring for 2 years
- Delay provided time to develop clean sampling techniques & analytical procedures
- HRSD developed a sampling system which could provide representative automated composite samples for trace metals
Pro’s and Con’s of System

- **Advantages:**
  - Reduces sample handling & potential contamination
  - Decreases labor and expendable equipment costs

- **Disadvantages:**
  - Large footprint
  - Use in collection of dissolved metals can be controversial
Dissolved Metals Controversy

- 40 CFR 136 – Table II
  - “Samples should be filtered immediately on-site before adding any preservative for dissolved metals”
  - “Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection. When the use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is complete”
How do states handle this?

- Most states seem to incorporate 40 CFR 136 Table II language directly into regs – some do not specifically address issue while others, interpret the language to preclude the use of automated samplers for the collection of dissolved metals

- At least one state indicates that “samples for dissolved metals must be filtered at time of collection or within 24 hours of collection and prior to preservation”
Effect of Collection on DS Metals

- Study designed to specifically address collection method and its affect on dissolved metals
- Also addressed automated collection of mercury using EPA 1631 and the use of alternate container compositions
- Examined effect of prolonged delay between the end of the composite and sample splitting
Study Difficulties

- Needed to obtain quantifiable numbers
- Needed to sample from free-flowing effluent source so metals states would not artificially achieve equilibrium
- Needed consistent sample source so that manual aliquots and automated aliquots were collected from same slug of effluent
Study Plan

- Automated aliquots collected using our clean sampling system
- Intermediate samples kept on ice for duration of composite period
- Manual aliquots collected using our clean system for grab samples
- Wastewater collected in flow-through barrel – influent and effluent valves closed 15 minutes prior to aliquot collection to allow volume to thoroughly mix
Dissolved Copper

<table>
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<tr>
<th>Treatment Plant</th>
<th>Manual Aliquots</th>
<th>Automated Aliquots - 24 hrs</th>
<th>Automated Aliquots - 48 hrs</th>
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<td>10</td>
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</tbody>
</table>
Dissolved Nickel

Treatment Plant

Manual Aliquots
Automated Aliquots - 24 hrs
Automated Aliquots - 48 hrs

Concentration (µg/L)

1 2 3

1.5 2.0 2.5 3.0
Dissolved Mercury

- Manual Aliquots - Teflon
- Automated Aliquots - 24 hrs
- Automated Aliquots - 48 hrs

Treatment Plant

Concentration (ng/L)
Conclusions

- Though the power of the test comparing the 3 plants was low, the individual plant results indicate that there is no difference in dissolved metals concentrations in samples collected via automated and manual aliquots.
- Differences in concentrations seemed to relate more to sampling and analytical variability – there were no evident trends.
- Plan to conduct several more rounds of data collection at the same plants to yield more conclusive data.