COMPARISON OF LOW LEVEL CHLORINE MONITORING INSTRUMENTATION FOR STREAM MONITORING

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Abstract

Chlorinated wastewater has the potential to impact habitat for threatened and endangered mussels. Limited information indicates that mussel exposures to chlorine may be significant and, in some cases, exceed concentrations known to be harmful. Due to the extreme toxicity of chlorine to aquatic life, federal water quality criteria and many state standards are set at concentrations less than 20 parts per billion (ppb). Many field instruments for chlorine analysis cannot attain detection limits as low as these standards. Chlorine is also highly reactive and volatile, and the U.S. Environmental Protection Agency recommends a maximum 15 minute holding time for total residual chlorine (TRC) analysis often precludes a laboratory-based approach. This makes accurate measurement of ambient chlorine concentrations a challenge. For instream monitoring of selected wastewater in North Carolina, several portable low level (0 – 500 ppb) chlorine detection systems were laboratory- and field-tested. Results of the benchtop comparison of chlorine measurement protocols and instrumentation prompted selection of a N,N-Diethyl-p-Phenylenediamine (DPD) colorimetric method with a demonstrated method detection limit of 6 ppb. Use of this method in the field has resulted in accurate (coefficient of determination from 5-point calibration curve average 0.996) and precise (relative percent deviations for duplicate samples averaging 14%) low level measurements of TRC over a range of 6 to 300 ppb. The approach is likely to be useful for various applications including routine discharge monitoring and assessment of chlorine toxicity threats to mussels and other fauna.

Methods / Results

Lab- and field-based performance comparisons were conducted with two amperometric titrators (Fisher CI Titrimeter Model 397 and Wallace and Tiernan Series A-790) and a spectrophotometer (HACH DR/2010)¹. Though amperometric titrators performed reasonably well in the lab and the chlorine detection protocol using these systems is associated with fewer chemical interferences, they were not conducive to field use (reading unsteadiness, design limitations, inability to achieve reliable standard curves).

We selected the low-range chlorine detection DPD method using the HACH DR/2010 with a demonstrated method detection limit of 6 ppb:

1. System designed for field use (physically and functionally more stable when operated using vehicle battery power).
2. Accurate (coefficient of determination from calibration curve average 0.996) and precise (relative percent deviations for duplicates averaging 14%) measurements of TRC over a range of 6 to 300 ppb were achieved in the field.
3. Protocol does not require a high level of expertise.
4. Protocol can be modified to correct for some chemical interferences (e.g., Mn). High turbidity and color in receiving stream downstream gradients is needed to determine the extent of the stream affected.

We validated selected DPD spectrophotometric approach. Exceedences of standards found at only 2 of 15 sites over a 12 month period. TRC concentrations exceeding the NC water quality standard of 17 ppb were found in 10% of samples (range of exceedences 50 to 302 ppb) at these 2 sites. Field validation of selected DPD spectrophotometric approach was conducted sites in the habitat range of the federally-listed Carolina hellbender (Lestodon platensis) and dwarf wedgemussel (Alasmidonta heterodon). Based on 1) elevated TRC concentrations in habitat supporting federally-listed mussel species and 2) the potential for chlorine impacts to vary with stream conditions, additional study is needed to evaluate instream persistence. This approach is likely to be useful for various applications including routine discharge monitoring and assessment of chlorine toxicity threats to mussels and other fauna.

Conclusions

The DPD colorimetric low-level chlorine detection protocol is preferable to amperometric titration alternatives for field analysis (due to reliability, demonstrated ease of use, and improved field performance). Notable exceptions exist (waters characterized by high turbidity or discharges containing color).

Based on 1) elevated TRC concentrations in habitat supporting federally-listed mussels and 2) the potential for chlorine impacts to vary with stream conditions, additional study is needed to evaluate instream persistence.

References


1. Trade names are provided for information only and do not imply a government endorsement.

Table 1: Comparison of TRC detection methods

<table>
<thead>
<tr>
<th>Station</th>
<th>DPD Colorimeter</th>
<th>Amperometric Titrator 1</th>
<th>Amperometric Titrator 2</th>
<th>Field Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goose Creek at WWTP outfall</td>
<td>28.2</td>
<td>27.8</td>
<td>27.6</td>
<td>28.0</td>
</tr>
<tr>
<td>Goose Creek 100 meters below WWTP</td>
<td>27.5</td>
<td>27.3</td>
<td>27.2</td>
<td>27.5</td>
</tr>
<tr>
<td>Goose Creek 300 meters below WWTP</td>
<td>27.0</td>
<td>26.8</td>
<td>26.7</td>
<td>27.0</td>
</tr>
</tbody>
</table>

¹. Field results are provided for information only and do not imply a government endorsement.