Variability of Low Phosphorus Analytical Measurement

Phosphorus measurements at very low concentrations have been tested and found to be unreliable. Recent work (e.g., by Coeur d’Alene, ID, City of Spokane, WA, and the City of Las Vegas, NV) demonstrated that phosphorus analytical measurements at very low levels (20 µg/L) are highly variable. Stricter phosphorus discharge requirements are significantly challenging the capabilities of wastewater facilities and accredited laboratories to measure low phosphorus concentrations in the effluent. The major issue associated with low phosphorus measurements appears related to the sample matrix and the digestion methodologies. This WERF study determined the reliability of current phosphorus analysis methodologies, documents current certification programs, and describes enhanced monitoring and management of phosphorus removal at low levels.

The results of the study showed a significant variability in phosphorus measurements at concentrations ranging from 3 µg/L to 20 µg/L. Total phosphorus measurements in the 18 MΩ water quality samples and wastewater effluent samples and orthophosphate measurements in wastewater effluent samples, showed a large variability. However, orthophosphate measurements in the 18 MΩ water quality samples showed insignificant variability.

The results demonstrated that as the concentration of phosphorus increases, the variability decreases. A large variability in measurements of phosphorus at low level (< 50 µg/L) was observed even when laboratories followed standard procedures.

The digestion methods and the samples matrix seem to play a central role in the low phosphorus analytical measurements. The presence of some components or substances in the matrix and reagents may have caused negative and positive interferences in the results. Wastewater tertiary effluent and 18 MΩ deionized water were the matrices used in this study. The digestion methods used for total phosphorus determination include perchloric acid, nitric acid-sulfuric acid, and persulfate oxidation methods.

The ascorbic method is followed by all participating laboratories and was successfully used for the determination of orthophosphate.

This study provides important information on the capability of wastewater treatment facilities and commercial laboratories to measure low levels of phosphorus accurately and reliably.

Benefits

- Documents methods to analyze phosphorus in wastewater and associated detection limits.
- Shows high variability in total phosphorus measurements in treated effluent from datasets analyzing the accuracy of measuring orthophosphate and total phosphorus at very low concentrations in clean water and effluent.
- Verifies that high quality, consistent laboratory QA/QC protocol is fundamental to successful phosphorus (P) measurement at very low levels.
- Raises important questions about permit limits and the ability of utilities to comply with these low limits as measurements to very low limits (<20 µg/L TP) will inherently vary.

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Table 1 summarizes commonly used phosphorus analytical methods to measure total phosphorus (TP) and orthophosphate (OP), with the minimum detection limit (MDL) for each method.

**Phosphorus Analysis Testing**

Ten laboratories were selected to conduct TP and OP analysis in two different sample matrices. Twelve samples (six duplicates) were prepared in the laboratory and shipped to all 10 laboratories for testing. Each laboratory used its preferred method. Samples were deionized water or effluent from the wastewater treatment plant. Some were spiked with phosphorus, and some diluted with filtered lake water to reduce effluent P concentrations.

As the phosphorus concentration went down, it became more difficult to reach the target or “true” value in the high quality DI water and in the wastewater tertiary effluent. These results were used to evaluate the performance of the laboratories as a group for OP analysis. Similar results were obtained with total phosphorus measurements.

### Table 1. Summary of Commonly Used Phosphorus Analytical Methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Total Phosphorus</th>
<th>Orthophosphate</th>
<th>MDL (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadomolybdophosphoric Acid</td>
<td>√</td>
<td>√</td>
<td>200</td>
</tr>
<tr>
<td>Stannous Chloride</td>
<td>√</td>
<td>√</td>
<td>3</td>
</tr>
<tr>
<td>Flow Injection Analysis Orthophosphate</td>
<td>√</td>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td>Manual Digestion &amp; Flow Injection Analysis</td>
<td>√</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>In-line UV/Persulfate Digestion &amp; FIA</td>
<td>√</td>
<td>√</td>
<td>7</td>
</tr>
<tr>
<td>Persulfate Method for Determination of TP</td>
<td>√</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>I-2601-90 (Automated-segmented flow)</td>
<td></td>
<td>√</td>
<td>10</td>
</tr>
<tr>
<td>Kjeldahl Digestion Method</td>
<td>√</td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

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**CONTRACTOR**

Lazaro Eleuterio, Ph.D., P.E.
JB Neethling, Ph.D., P.E., BCEE
HDR Engineering, Inc.

**TECHNICAL REVIEW COMMITTEE**

Mario Benisch, MS, P.E.
Dave Clark, P.E.
Steve Reiber, Ph.D.
Alan W. Wells, Ph.D.
HDR Engineering, Inc.
April Gu, Ph.D.
Northeastern University
Dan Fischer
City of Las Vegas Water Pollution Control Facility
Dave Moss, P.E.
Spokane County Utilities
H. David Stensel, Ph.D., P.E., BCEE
University of Washington
Scott Smith, Ph.D.
Wilfrid Laurier University

**ISSUE AREA TEAM**

James L. Barnard, Ph.D., P.E., BCEE
Black and Veatch

Charles B. Bott, Ph.D., P.E., BCEE
Hampton Roads Sanitation District (formerly with Virginia Military Institute)

Robbin W. Finch
City of Boise, ID

Joseph A. Husband, P.E., BCEE
Malcolm Pirnie, Inc.

Gary R. Johnson, P.E., BCEE
Environmental Operating Solutions, Inc.

Ephraim S. King
Rao Surampalli, Ph.D., P.E., BCEE

James Wheeler, P.E.
U.S. Environmental Protection Agency

Carl M. Koch, Ph.D., P.E., BCEE
Greeley and Hansen, LLC

Michael McGrath, P.E., BCEE
Fairfax County, VA

Sudhir Murthy, Ph.D., P.E.
District of Columbia Water and Sewer Authority (DC Water)

Tung Nguyen
Sydney Water Corporation

Denny S. Parker, Ph.D., P.E.
Brown and Caldwell

Matt Ries, P.E.
Water Environment Federation

G. David Waitley, P.E.
Hampton Roads Sanitation District

Kenneth N. Wood, P.E.
DuPont Company

Heng Zhang, Ph.D., P.E.
Metropolitan Water Reclamation District of Greater Chicago

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City of Las Vegas Water Pollution Control Facility, Nevada
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**Contributing Laboratories:**

Analytical Sciences Laboratory – Holm Research Center, University of Idaho
City of Coeur d’Alene, Idaho WWTP Laboratory
City of Las Vegas, Nevada Environmental Division Laboratory
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