Eutrophication Cause Determination Protocol

Water Resources Advisory Committee

October 25, 2017

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Intended Use of the Protocol

➢ Follow-up to Aquatic Life Use (ALU) Impairment Decision Made with an Appropriate DEP Assessment Protocol

➢ Listing Nutrients – Eutrophication as A Cause of ALU Impairment Under Category 5 of the Integrated Report

➢ Streams With a Drainage Area of Up to 350 mi²
Definition of Stream Eutrophication

Eu = “Well” and Troph = “Nourished”

- Process by Which Nutrient Enrichment
- Stimulates the Growth of Plants & Algae
- Alters the Quant & Qual of Organic Matter Available as Food for Stream Organisms
- Modifies Stream Ecosystem Metabolism
Stream Ecosystem Metabolism

➢ Biophysical Process of How Energy in the Form of Organic Matter is:

• Acquired from External Sources
• Produced In-Stream via Photosynthesis
• Utilized By Stream Organisms via Respiration
Technical Foundation of the Protocol

Odum’s Open-Water Diel DO Method of Measuring Stream Ecosystem Metabolism (Odum 1956)

\[ \frac{\Delta O_2}{\Delta t} = P - R - K - A \]

➢ Photosynthesis:

\[ 6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{\text{Light Energy}} \text{C}_6\text{H}_{12}\text{O}_6 \text{ (Organic Matter)} + 6\text{O}_2 \]

➢ Respiration:

\[ \text{C}_6\text{H}_{12}\text{O}_6 \text{ (Organic Matter)} + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{Energy} \]
Protocol Uses Diel DO Swings as Indicator of Metabolic Conditions

- Photosynthesis Rates are Light-Dependent and Fluctuate on Diel (Daily) Cycle
- Photosynthesis $\uparrow$DO
- Respiration $\downarrow$DO
- Amplitude of Diel DO Swings Reflect P and R Rates and Overall Ecosystem Metabolic Conditions
Protocol Uses Diel DO Swings as Indicator of Metabolic Conditions

- Amplitude of Diel DO Swings are Compared to the Swings of Reasonably Healthy Streams (Benchmark Values)

- Diel DO Swings > Benchmark Values Indicate that Eutrophication has Substantially Altered Stream Metabolic Conditions, and

- Nutrients-Eutrophication are Determined to be A Cause of ALU Impairment
Data Used to Develop the Protocol

- Continuously Monitored DO, pH, & Temp (Readings every ½ Hour)
- March - April – May Timeframe
- 2013 thru 2016 Sample Seasons
- TP and TN Approximately Monthly
- At Least One Benthic Chl-a Sample at Most Stations
- One Macro IBI Sample at Each Station
Sample Stations & EPA Nutrient Ecoregions

- 59 Stations
- 66 Samples
Efforts to Account for Natural Variability

March - April - May Timeframe
- Pre or Early Leafout / Shading
- Insect Emergence

Monthly
- Daylight Duration
- Water Temperature
- Stream Q / Velocity Scour
Efforts to Account for Natural Variability

Drainage Area Size Categories

- $<50 \text{ mi}^2$ and $50 - 350 \text{ mi}^2$
- 6D-200 Macro Protocol
- Water Depth and Volume
- Turbidity
- Irradiance of Benthic Periphyton
Quantification of Diel DO Conditions

- **Diel DO Swing** = Daily DO Max – DO Min

- **Only Use Days With at Least 75% of the Day Monitored** (Minimum of (36) ½-Hr Readings)

![Graph showing diel DO conditions](image)

- **Diel DO Max** = 18.4 mg/l
- **Diel DO Min** = 8.8 mg/l
- **Diel DO Range (Swing)** = 18.4 – 8.8 = 9.6 mg/l

1 Day (48) ½ Hour Readings
Diel DO Swings Summarized by Month

- 75th Percentile Value of Diel DO Swings Recorded Within a given Month
- Minimum of Half the Month with Diel DO Swing Values
- 1,340 ½-Hour DO Readings
- 28 Days
Benchmark Sample Screening Criteria

➢ ALU Attaining Streams With Macroinvertebrate IBI Score ≥53

➢ Mean TP, TN, and Benthic Chl-a Values Could Not Be Statistical Outliers
  • \([Q1 - (1.5 \times IQR)]\) or \([Q3 + (1.5 \times IQR)]\)

➢ Benchmark Values Represent the Upper Threshold of Photosynthesis and Respiration Rates of Reasonably Healthy Streams
Benchmark Sample Stations

➢ 29 Stations
➢ 33 Samples
Monthly p75 Diel DO Swing Benchmark Values

Diel DO Swing Benchmark Values

- March: (n=14) 4.6
- April: (n=17) 4.9
- May: (n=18) 4.2

- March: <50 mi²: 2.4
- April: ≥50 mi²: 3.1
- May: <50 mi²: 3.5

Pennsylvania Department of Environmental Protection
### Application of Benchmarks to Entire Dataset (N=66)

<table>
<thead>
<tr>
<th></th>
<th>Aquatic Life Use Attaining</th>
<th>Aquatic Life Use Impaired</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Exceedance of Any Monthly Diel DO Swing Benchmark Value</td>
<td>36</td>
<td>7</td>
</tr>
<tr>
<td>Exceedance of One or More Diel DO Swing Benchmark Values</td>
<td>3</td>
<td>20</td>
</tr>
</tbody>
</table>

**Cause of ALU Impairment:**

*Nutrients - Eutrophication*
Application of Benchmarks to Entire Dataset (N=66)

- **ALU Attaining**
  - (n=21) (n=15)
  - ALU Attaining w Excessive DO Swings

- **ALU Impaired**
  - (n=2) (n=1)
  - Cause: Other
  - (n=5) (n=2)
  - Cause: Eutrophication
  - (n=15) (n=5)
The Magnitude of Diel DO Swings Reflect:

- Stream Photosynthesis Rates
- Ecosystem Respiration Rates
- Overall Ecosystem Metabolic Conditions
Additional Analyses to Confirm Accuracy of Assumption (N=59)

➢ Reasonable to Assume that Diel DO Swings Reflect Photosynthesis and Respiration Rates (Overall Metabolic Conditions)

➢ 7 ALU Impaired Samples With **Cause:** Other to Establish a Clear Gradient of Trophic Conditions

➢ Relationships Between DO and pH Swings
Photosynthesis and Respiration Influences Both DO and pH on a Diel Cycle

➢ Photosynthesis:

\[6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{\text{Light Energy}} \text{C}_6\text{H}_{12}\text{O}_6 \text{ (Organic Matter)} + 6\text{O}_2\]

➢ Respiration:

\[\text{C}_6\text{H}_{12}\text{O}_6 \text{ (Organic Matter)} + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{Energy}\]

➢ \(\Delta \text{CO}_2 \rightarrow \Delta \text{DIC pH Buffer System} \rightarrow \Delta \text{pH}\)

Removal of \(\text{CO}_2\) during photosynthesis shifts equilibrium (higher pH)

\[
\begin{align*}
\text{CO}_2\text{(gas)} & \leftrightarrow \text{CO}_2\text{(aq)} + \text{H}_2\text{O} \\
& \leftrightarrow \text{H}^+ + \text{HCO}_3^- \\
& \leftrightarrow 2\text{H}^+ + \text{CO}_3^{2-}, \text{ and } \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{OH}^- 
\end{align*}
\]

Addition of \(\text{CO}_2\) during respiration shifts equilibrium (lower pH)
Photosynthesis and Respiration Influences Both DO and pH on a Diel Cycle

➢ Photosynthesis: \( \uparrow \text{DO} \), \( \downarrow \text{CO}_2 \) and \( \uparrow \text{pH} \)

➢ Respiration: \( \downarrow \text{DO} \), \( \uparrow \text{CO}_2 \) and \( \downarrow \text{pH} \)

➢ If Photosynthesis and Respiration Are Driving Diel DO Swings, There Should Be a Relationship Between the Magnitude of Diel DO and Diel pH Swings
Photosynthesis and Respiration Influences Both DO and pH on a Diel Cycle

➢ If DO and pH Swings Are Not Correlated:
• DO Swings Are Not Driven by Photosynthesis
• Heterotrophic System

➢ If DO and pH Swings Are Correlated:
• DO Swings Are Driven by Photosynthesis
• Autotrophic System
Heterotrophic System: Diel DO and pH Relationship Hyner Run

**Hyner Run 2016 Clinton Co (Eco VIII, 26.6 mi²)**

- ALU Attaining
  - Macro IBI = 100
  - Mean Chl-a = 24 mg/m²
  - Mean TP = 0.010 mg/L
  - Mean TN = 0.26 mg/L
Heterotrophic System: Diel DO and pH Relationship Hyner Run

Hyner Run 2016 (March – May Data)
Diel DO Swing – Diel pH Swing
\[ r = 0.059, \quad p = 0.575 \]

➢ No Correlation DO & pH
➢ Photosynthesis Not Driving DO Swings
➢ Predominantly Heterotrophic

Hyner Run 2016 Clinton Co
(Eco VIII, 26.6 mi²)

- Organic Matter (Energy) from Outside Source Not In-Stream Photosynthesis
Autotrophic System: Diel DO and pH Relationship Beaver Run

Beaver Run 2016 Chester Co
(Eco IX, 5.0 mi²)

- ALU Attaining
- Macro IBI = 73
- Mean Chl-a = 190 mg/m²
- Mean TP = 0.028 mg/L
- Mean TN = 1.00 mg/L
Beaver Run 2016 (March – May Data)
Diel DO Swing – Diel pH Swing
\[ r = 0.915, \quad p = 0.000 \]

Beaver Run 2016 Chester Co
(Eco IX, 5.0 mi²)

- Strong Correlation DO & pH
- DO Swings Driven by Photosynthesis
- **Predominantly Autotrophic**
  Organic Matter (Energy) from In-Stream Photosynthesis
<table>
<thead>
<tr>
<th>DO Swings Driven by Photosynthesis (Based on DO–pH Swing Correlation r-Value)</th>
<th>General Trophic Category</th>
<th>Excessive Diel DO Swings (Relative to Protocol Benchmark Values)</th>
<th>Nutrient-Trophic Status Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>Heterotrophic</td>
<td>No</td>
<td>Oligotrophic (9)</td>
</tr>
<tr>
<td>Yes</td>
<td>Autotrophic</td>
<td>No</td>
<td>Mesotrophic (30)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yes</td>
<td>Eutrophic (20)</td>
</tr>
</tbody>
</table>

Cause of ALU Impairment: Nutrients – Eutrophication (n=20)
Trophic Status (Small Streams)

- Heterotrophic = Oligotrophic
- Autotrophic Split Based on ECD Protocol Results
- Autotrophic with Excessive DO Swings = Eutrophic
- Autotrophic w/o Excessive DO Swings = Mesotrophic
Water Temperature Influences Stream DO Levels on a Diel Cycle

- Diel DO and Temp Relationships Support Assumption that DO Swings Reflect Stream Photosynthesis Rates

- Water Temp $\uparrow$ DO Solubility $\downarrow$

- Water Temp Fluctuates on a Diel Cycle and Peaks in Afternoon and Cools Throughout the Evening and Early-Morning Hours

- The Strength of the Relationship Between Diel DO Swings and Diel Temp Swings Reflects the Influence of Temp on DO Swings
Trophic Status (Small Streams)

- Heterotrophic = Oligotrophic
- Autotrophic Split Based on ECD Protocol Results
- Autotrophic with Excessive DO Swings = Eutrophic
- Autotrophic w/o Excessive DO Swings = Mesotrophic
Trophic Status (Large Streams)

Large Streams (≥ 50 mi²)

- (n=1 Sample)
- (n=15 Samples)
- (n=5 Samples)

Diel Swing Correlation Coefficient (r)

<table>
<thead>
<tr>
<th>DO - pH</th>
<th>DO - Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligotrophic</td>
<td></td>
</tr>
<tr>
<td>Mesotrophic</td>
<td></td>
</tr>
<tr>
<td>Eutrophic</td>
<td></td>
</tr>
</tbody>
</table>

Pennsylvania Department of Environmental Protection
Time of Day Diel Max DO Reflects Trophic Status

- Water Temp $\uparrow$ DO Solubility $\downarrow$
- If DO Swings are Driven by Temp, Max DO Should Occur Near Time of Min Temp
Time of Diel DO Max Hyner Run (Oligotrophic)

- **Hyner Run 2016 Clinton Co**
  - Time of Max DO = Min Temp
  - DO Swings Driven by Temp Not Photosynthesis
  - Predominantly Heterotrophic
    Organic Matter (Energy) from Outside Source Not Photosyn
Time of Diel DO Max Beaver Run (Mesotrophic)

Beaver Run 2016 Chester Co

- **Time of Max DO 2-3 Hours After Min Temp**

- **DO Swings Driven by Photosynthesis and Water Temp**

- **Predominantly Autotrophic**
  Organic Matter (Energy) from Photosynthesis
Indian Cr (Rt 63) 2014 Montgomery Co

- Time of Max DO Close to **Time of Max** Temp (Min Solubility)
- Excessive DO Swings Driven by Photosynthesis
- Autotrophic: **Eutrophic**
Time-of-Day of Max DO by Trophic Status (Small Streams)

Small Streams (<50 mi²) March - May

- Oligotrophic (n=8 Samples)
- Mesotrophic (n=15 Samples)
- Eutrophic (n=15 Samples)

Hour of Day (Sample Median)

- Temp
- Min DO
- Max Temp
- Attn - Hetero
- Attn - Auto
- Imp: Eutro - Auto

12 Noon
Time-of-Day of Max DO by Trophic Status (Large Streams)

Large Streams (≥ 50 mi²) March - May

- Oligotrophic (n=1 Sample)
- Mesotrophic (n=15 Samples)
- Eutrophic (n=5 Samples)

Hour of Day (Sample Median)

- Temp Min DO Max Temp Max
  - Attn - Hetero
  - Attn - Auto
  - Imp:Eutro - Auto
Second Critical Assumption of the Protocol

- Excessive Diel DO Swings Indicate that:
  - Degraded Ecosystem Health is Linked to Nutrient Enrichment and the Eutrophication Process

- Land Use, Nutrient, Benthic Chl-a, and Benthic Macroinvertebrate IBI Data Support this Assumption
Mean Total Phosphorus by Trophic Status

- **Oligotrophic**
  - (n=8)
  - (n=1)

- **Mesotrophic**
  - (n=15)
  - (n=15)

- **Eutrophic**
  - (n=15)
  - (n=5)

The graph shows the mean total phosphorus (TP) in mg/l across different trophic statuses and area sizes. The data points indicate lower TP levels in oligotrophic and mesotrophic conditions compared to eutrophic conditions.
Mean Total Nitrogen by Trophic Status

- **Oligotrophic**
  - (n=8)
  - <50 mi²: Attn - Hetero
  - ≥50 mi²: Attn - Auto

- **Mesotrophic**
  - (n=15)
  - <50 mi²: Attn - Hetero
  - ≥50 mi²: Attn - Auto

- **Eutrophic**
  - (n=15)
  - <50 mi²: Imp: Eutro - Auto
  - ≥50 mi²: Imp: Eutro - Auto
Mean Benthic Chlorophyll-a by Trophic Status

- **Oligotrophic**
  - (n=7)
  - (n=1)

- **Mesotrophic**
  - (n=13)
  - (n=13)

- **Eutrophic**
  - (n=11)
  - (n=5)

The diagram shows the mean benthic chlorophyll-a (mg/m²) by trophic status and area (<50 mi² or ≥50 mi²) for different attention criteria: non-auto (Hetero) and auto (Auto). The Eutrophic category has the highest mean values compared to Oligotrophic and Mesotrophic categories.
➢ Protocol Uses Diel DO Swings as an Indicator of Stream Photosynthesis & Ecosystem Respiration Rates

➢ Excessive Diel DO Swings Indicate the Eutrophication Process has Substantially Altered Stream Metabolic Conditions and Eutrophication Is Identified as A Cause of ALU Impairment

➢ The Results of the Protocol are Supported by Analysis of:
  • DO-pH and DO-Temp Relationships
  • Time-of-Day of Max DO
  • Mean Benthic Chl-a, TP, TN Values
  • Watershed Land Use Composition
Questions

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