Challenges in measuring CO2 dissolved in water

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Outline

1 Background

2 Experience about measuring CO2 concentration dissolved in water

3 Method
1 Background

The global C cycle of lake in diverse lakes
(by applying the ‘active pipe’ concept)

A) Arctic lake, Alaska
DIC 45%
DOC 52%
POC 3%

CO₂ 20%
downstream export 78%
(DIC 39%, DOC 37%, POC 2%)
sediment storage 2%

B) Boreal lake in non-carbonate bedrock, Sweden

CO₂ 42%
downstream export 39%
(TOC 34%, DIC 5%)

TOC 66%
DIC 34%
sediment storage 19%

DIC : dissolved inorganic carbon
DOC : dissolved organic carbon
POC : particulate organic carbon
TOC : total organic carbon

C) Open basin hard-water lake, Saskatchewan, Canada

DIC 77%
DOC 19%
POC 2%

CO₂ influx 2%
downstream export 70%
(DIC 56%, DOC 13%, POC 1%)
sediment storage 30%

D) Closed lake basin north-temperate lake, Minnesota

CO₂ 2%
CH₄ 19%
groundwater export 68%
(DIC 58%, DOC 10%)

DIC 96%
DOC 3%
POC 1%
sediment storage 11%
The produce of CO2 in lake water

Schrier-Uijl et al. 2011. Biogeochemistry
The factors that affect the CO2 concentration dissolved in water include:

1. The decomposition of sediment
2. Microbial activity
3. Respiration and photosynthesis of aquatic plants
4. The input of allochthonous carbon

CO2 is produced by respiration throughout lakes and lake sediments. (PETER CASPER et al. 2000. Biogeochemistry)
The most challenge is how to control the microbial activity when measure CO2 concentration dissolved in Lake Taihu.

(1) The biomss in water samples is rich.
(2) The water samples couldn’t be sent to lab for analysis immediately.
Sample site and water sample

Microbial activity will have a great impact on the water sample if not analyzed immediately.
2 Experience about measuring CO2 concentration dissolved in water

Add copper sulfate (\(\text{CuSO}_4\)) in water sample to control the microbial activity.

Some sediment will arise in water sample after adding 5ml \(\text{CuSO}_4(2\%)\), and it show that \(\text{CuSO}_4\) can eliminate the impact of microbial activity.

However, the CO2 concentration that measured by water equilibrium method is very high when add \(\text{CuSO}_4\) in water sample.

Whether \(\text{CuSO}_4\) can increase CO2 concentration, and if so, what about other sterilization, for example \(\text{HgCl}_2\), \(\text{CuCl}_2\) and so on?
Experiment scheme to confirm the impact of sterilization

Water sample

6 → Group A (hollow)

6 → Group B (1ml CuSO4)

6 → Group C (5ml CuSO4)

6 → Group D (0.5ml HgCl2)

3

A1, A2, A3: analyzed immediately after 5 minutes of shaking

A4, A5, A6: after 5 minutes of shaking, waited 2 days to analyze

3

B1, B2, B3: analyzed immediately after 5 minutes of shaking

B4, B5, B6: after 5 minutes of shaking, waited 2 days to analyze

3

C1, C2, C3: analyzed immediately after 5 minutes of shaking

C4, C5, C6: after 5 minutes of shaking, waited 2 days to analyze

3

D1, D2, D3: analyzed immediately after 5 minutes of shaking

D4, D5, D6: after 5 minutes of shaking, waited 2 days to analyze
The result — CO2 concentration at different treatment

A: hollow
B: 1ml CuSO4
C: 5ml CuSO4
D: 0.5ml HgCl2

1, 2, 3: Analyzed immediately after shaking 5 minutes

4, 5, 6: Wait 2 days to analyzed after shaking 5 minutes
Correlation: CO2 concentration and alkalinity

\[ y = -16.48x + 1640 \]
\[ R^2 = 0.6947 \]

\[ y = -46.98x + 4245 \]
\[ R^2 = 0.7554 \]

Data from analyzed immediately:

Data from analyzed after waiting 2 days:

Alkalinity analyzed by James
The equilibria about alkalinity and CO2 concentration

\[
\text{CO}_2, \text{ as p. p. m. of } \text{CO}_2 = 9.70 \times 10^{10} \ (\text{H}^+) \left[ \frac{\text{Alk}}{50,000} + (\text{H}^+) - \frac{10^{-14}}{(\text{H}^+)} \right] \frac{1 + 11.22 \times 10^{-11}}{(\text{H}^+)}
\]

\(\text{Alk}\) = total alkalinity, as p. p. m. of CaCO\(_3\)

(\(\text{H}^+\)) = hydrogen-ion concentration, moles per liter

A. A. HIRSCH et al. Journal of the American Chemistry Annual Meeting

- Calculate the dissolved CO2 concentration using alkalinity and pH data and compared the calculated values with the values measured by GC next step.
Table I. Comparison of Two Methods of Total Carbon Dioxide Determination

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Salinity, p.p.t.</th>
<th>pH-alkalinity method</th>
<th>Gas chromatographic method</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>0.19</td>
<td>0.20</td>
<td>0.01</td>
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<td>2</td>
<td>5.2</td>
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<td>0.41</td>
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<td>3</td>
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<td>0.76</td>
<td>0.80</td>
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<td>4</td>
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<td>1.12</td>
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<td>5</td>
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<td>1.42</td>
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<td>6</td>
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<td>7</td>
<td>31.3</td>
<td>2.05</td>
<td>2.01</td>
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<td>8</td>
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<td>2.16</td>
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<td>9</td>
<td>36.4</td>
<td>2.33</td>
<td>2.31</td>
<td>0.02</td>
</tr>
</tbody>
</table>
3 Method

1. Don’t add any sterilization, and analysis water samples as soon as possible when they are sent to lab.
2. Gas pocket

The gas to be analyzed can be transferred from the water sample to the gas pocket once sample and pretreatment are completed. Its air tightness can be checked by whether it makes it vacuum.
Some questions about gas pocket when use it measure GHGs concentration.

(1) whether it will break the balance between gas and liquid when transfer gas from sample to gas pocket, then promote the water emission gas.

(2) whether the gas pocket can save the gas for a period of time.
3. Compare the data: bottle Vs gas pocket

A1, A2, A3: measured by bottle
A4, A5, A6: measured by gas pocket
B1, B2, B3: measured by bottle
B4, B5, B6: measured by gas pocket

**tap water**

- A1
- A2
- A3
- A4
- A5
- A6

**river water**

- B1
- B2
- B3
- B4
- B5
- B6
The data of water sample measured by bottle and gas pocket respectively.

For tap water:

- **A1**: Bottle 44 μmol/L, Gas pocket 48 μmol/L
- **A2**: Bottle 52 μmol/L, Gas pocket 48 μmol/L
- **A3**: Bottle 44 μmol/L, Gas pocket 36 μmol/L

For river water:

- **B1**: Bottle 340 μmol/L, Gas pocket 320 μmol/L
- **B2**: Bottle 320 μmol/L, Gas pocket 300 μmol/L
- **B3**: Bottle 280 μmol/L, Gas pocket 260 μmol/L
4. Make a choice measure dissolve CO2 concentration

water sample → save → fridge → treat → target gas → analysis → GC

Vs

water sample → treat → target gas → save → gas pocket → analysis → GC

Vs

Alkalinity—CO2
Thank You