Yale 耶鲁大学-南京信息工程大学大气环境中心

Yale-NUIST Center on Atmospheric Environment

Challenges in measuring CO2 dissolved in water

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Video conference of YNCenter

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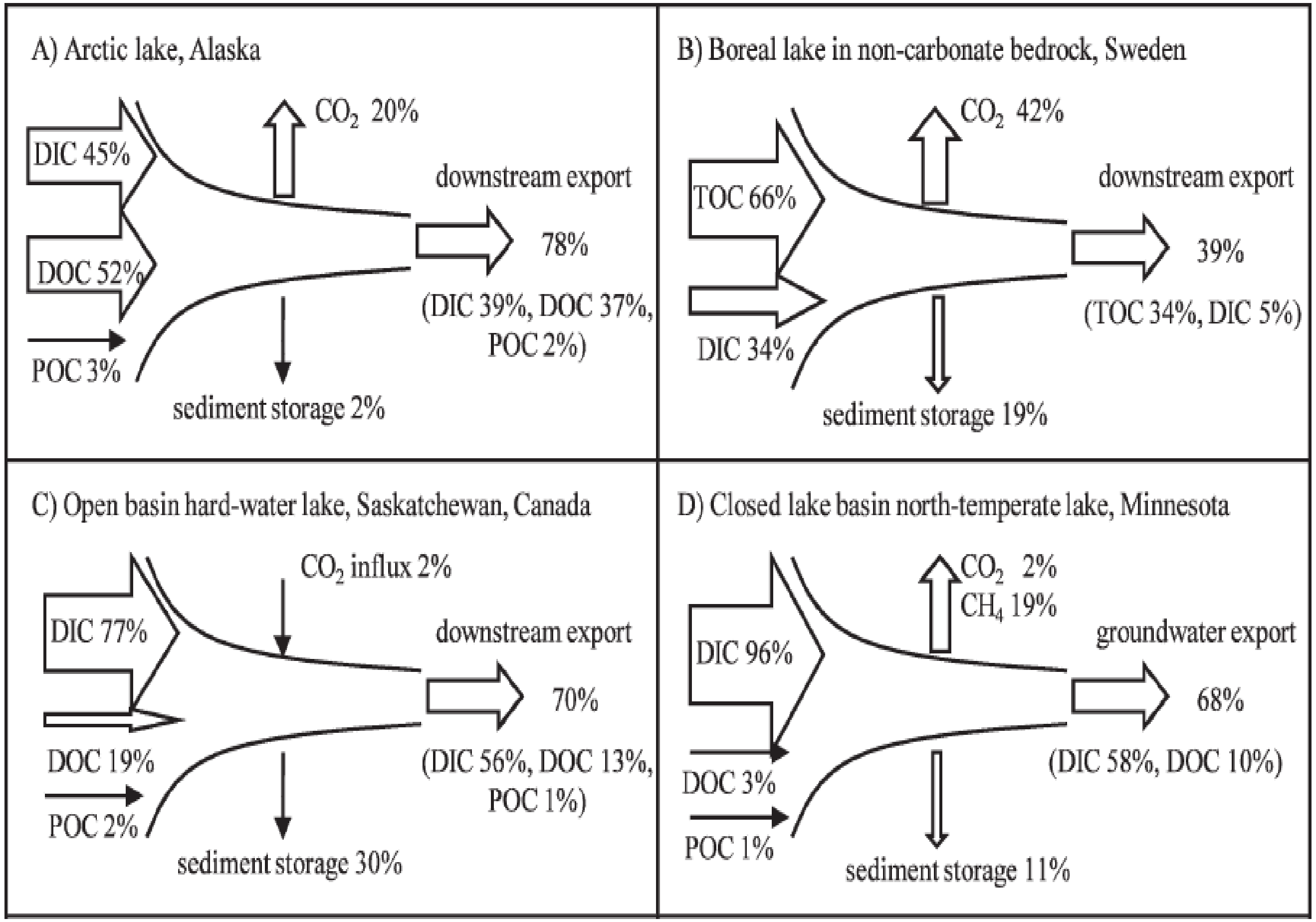
◆Outline

- **1 Background**
- **2 Experience about measuring CO_2 concentration dissolved in water**
- **3 Method**

◆1 Background

- The global C cycle of lake in diverse lakes

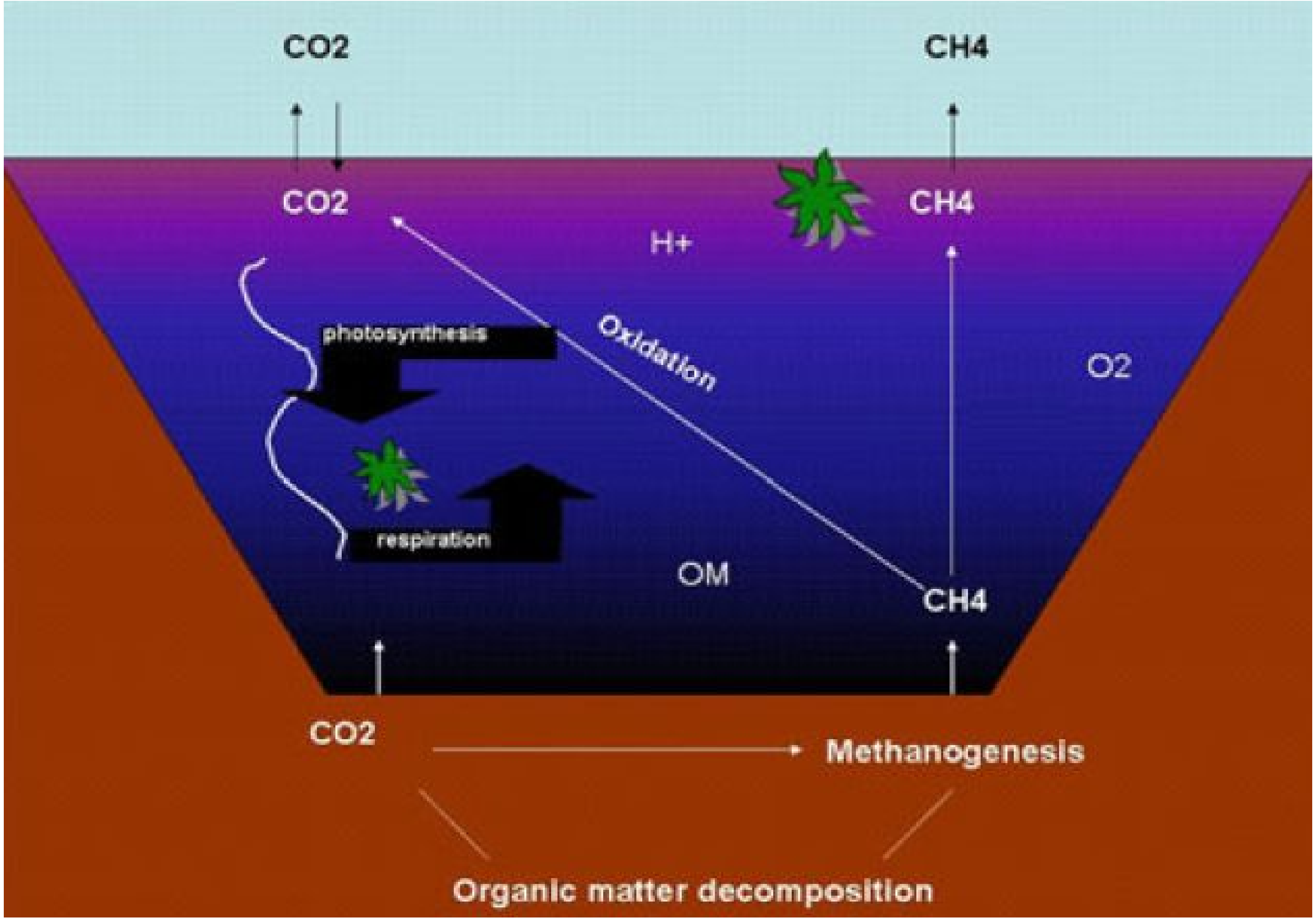
(by applying the 'active pipe' concept)



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

Lars J. Tranvik et al. 2009 .Limnol. Oceanogr

- The produce of CO2 in lake water



Schrier-Uijl et al. 2011. Biogeochemistry

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- The factor affect the CO_2 concentration dissolved in water

(1) the decomposition of sediment

(2) microbial activity

(3) respiration and photosynthesis of aquatic plants

(4) the input of allochthonous carbon

- CO_2 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 samlpes is rich.

(2) The water samples couldn’t be sent to lab for analysis immediately.

Sample site and water sample

contain

phytoplankton

zooplankton

organic matter

cyanobacteria

Microbial activity will have a great impact on the water sample if not analyzed immediately.

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◆2 Experience about measuring CO2 concentration dissolved in water

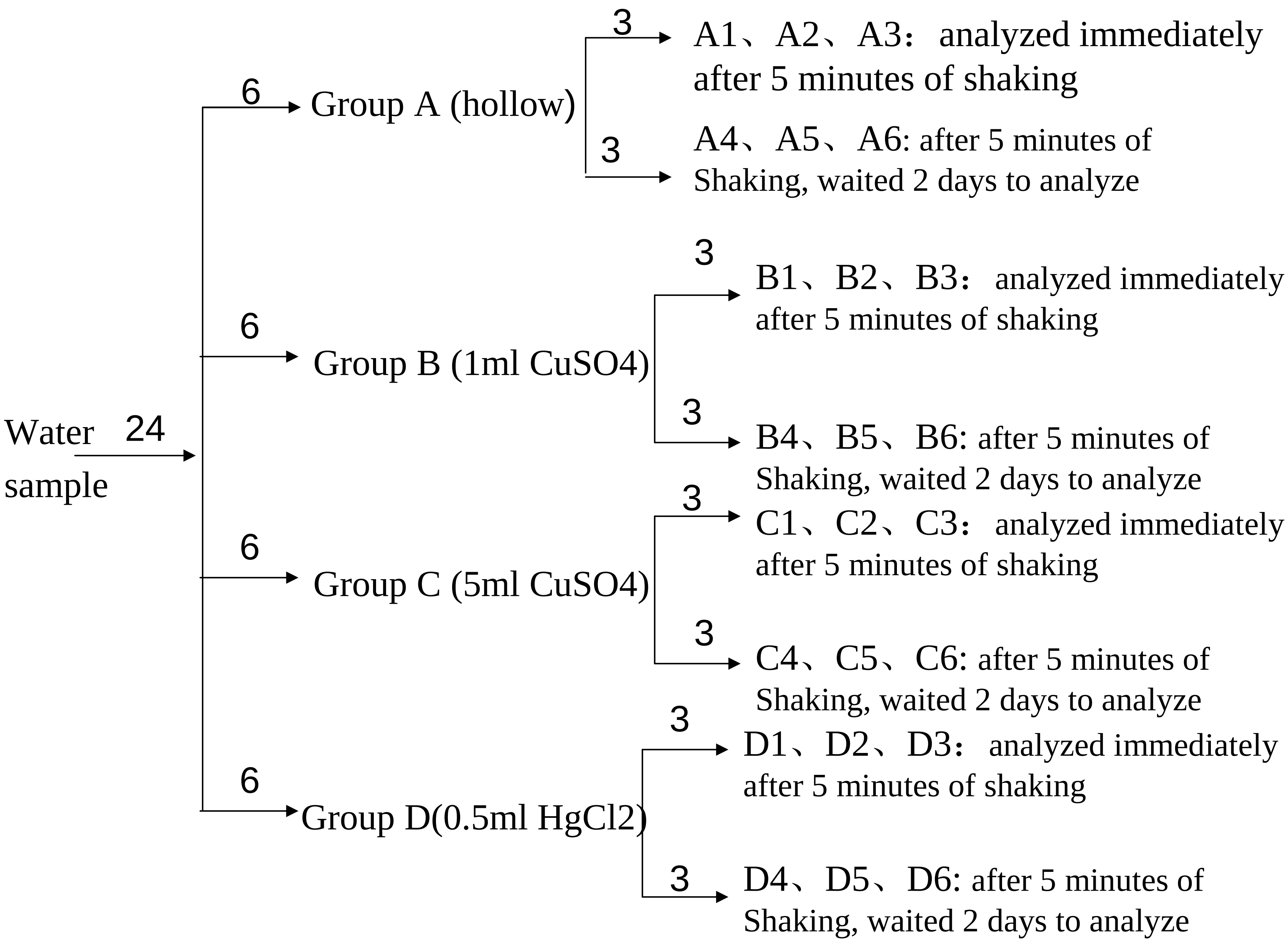
- Add **copper sulfate**（$CuSO_4$) in water sample to control the microbial activity.

Some sediment will arise in water sample after adding 5ml $CuSO_4$(2%), and it show that $CuSO_4$ can eliminate the impact of microbial activity.

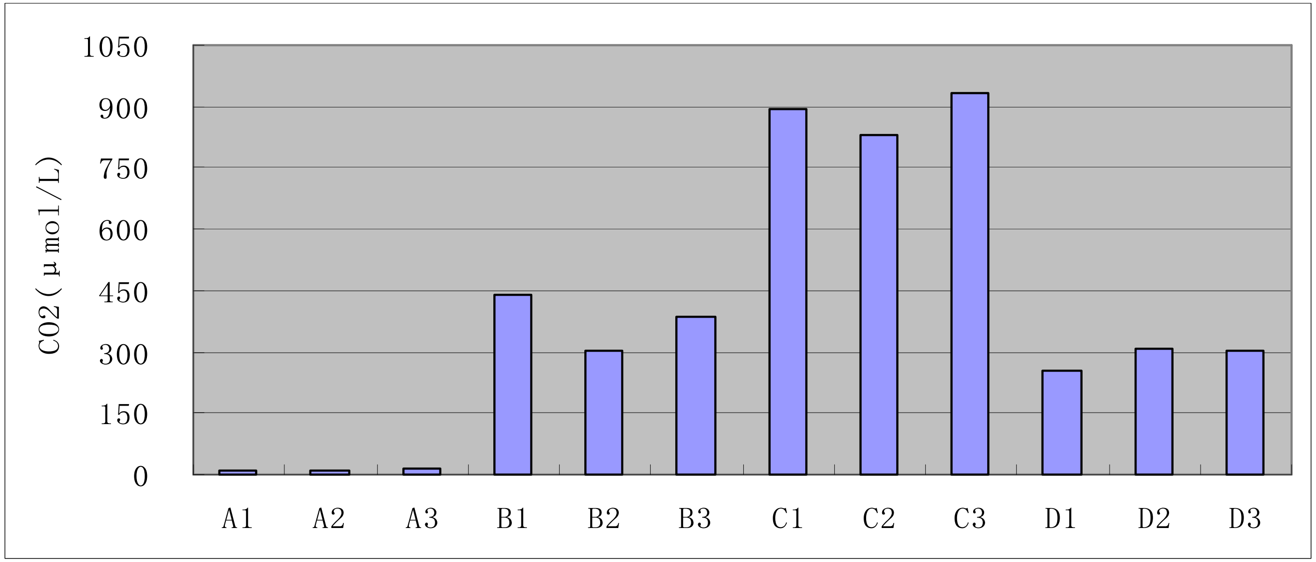
However， the CO2 concentration that measured by water equilibrium method is very high when add $CuSO_4$ in water sample.

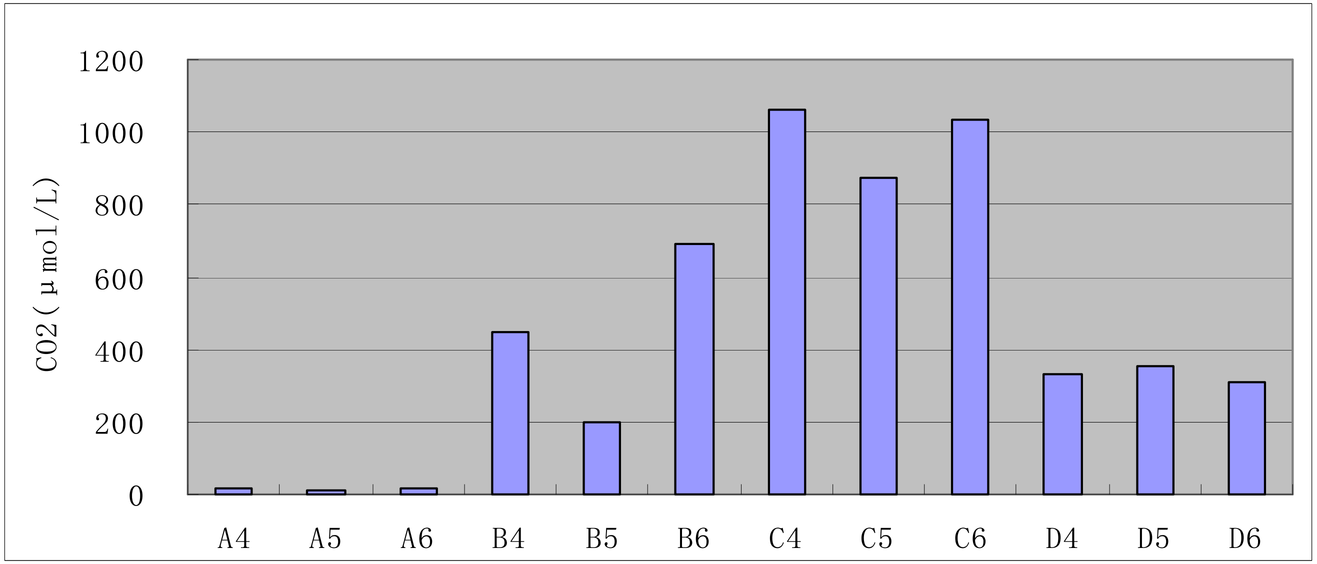
Whether $CuSO_4$ can increase CO2 concentration ,and if so, what about other sterilization, for example $HgCl_2$、$CuCl_2$ and so on ?

● Experiment scheme to confirm the impact of sterilization



● The result — CO_2 concentration at different treatment



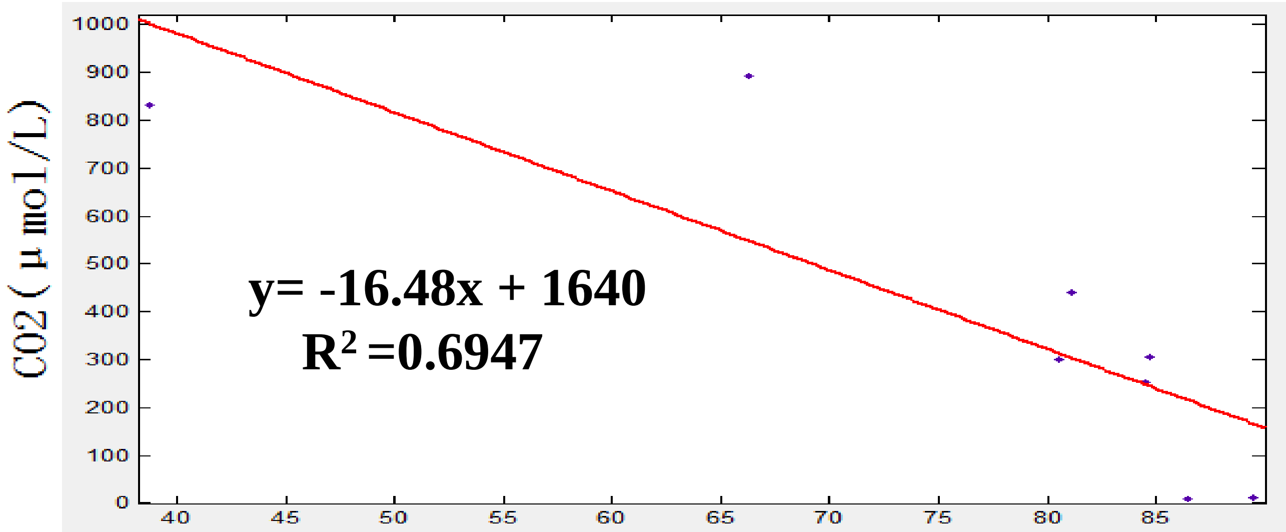


A: hollow
B: 1ml $CuSO_4$
C: 5ml $CuSO_4$
D: 0.5ml $HgCl_2$

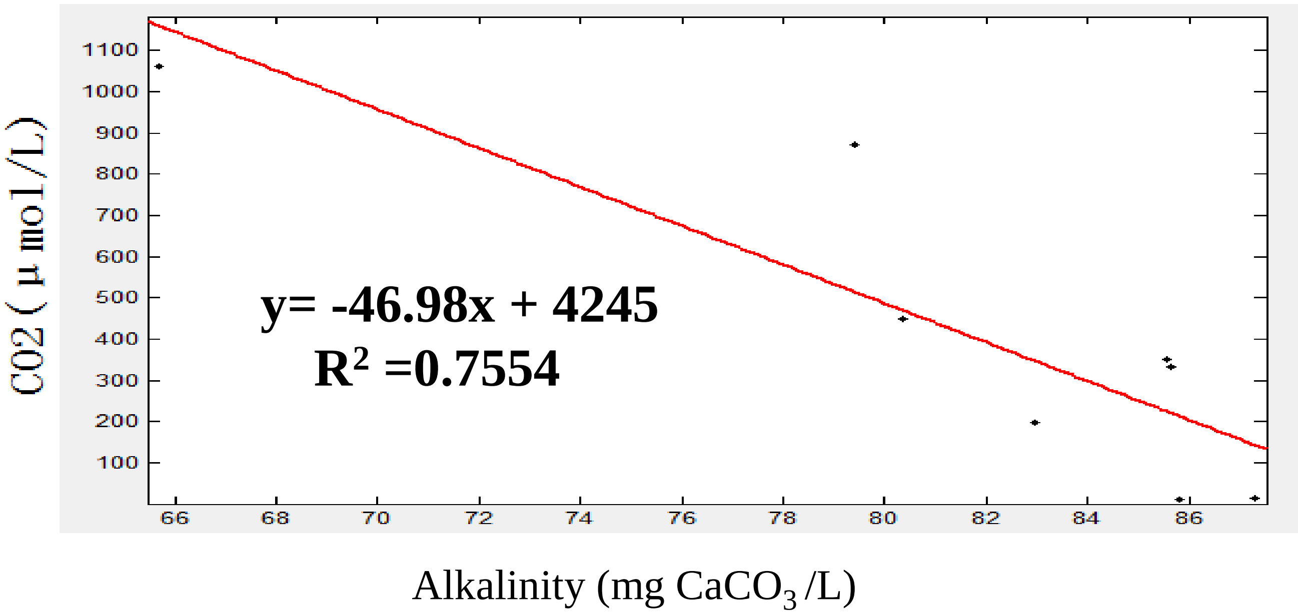
1、2、3:
Analyzed immediately after shaking 5 minutes

4、5、6:
Wait 2 days to analyzed after shaking 5minutes

Correlation: CO2 concentration and alkalinity



data from analyzed immediately



data from analyzed after waiting 2 days

alkalinity analyzed by James

- **The equilibria about alkalinity and CO2 concentration**

$$CO_2,\ \text{as p. p. m. of } CO_2 = 9.70 \times 10^{10}\,(H^+)\,\frac{\left[\dfrac{Alk}{50{,}000} + (H^+) - \dfrac{10^{-14}}{(H^+)}\right]}{1 + \dfrac{11.22 \times 10^{-11}}{(H^+)}}$$

Alk = total alkalinity, as **p.** p. m. of $CaCO_3$
(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

Sample number	Salinity, p.p.t.	Total carbon dioxide, m*M* per liter: pH-alkalinity method	Gas chromatographic method	Difference
1	2.0	0.19	0.20	0.01
2	5.2	0.43	0.41	0.02
3	10.3	0.76	0.80	0.04
4	15.5	1.10	1.12	0.02
5	21.1	1.44	1.42	0.02
6	26.4	1.75	1.76	0.01
7	31.3	2.05	2.01	0.04
8	33.8	2.19	2.16	0.03
9	36.4	2.33	2.31	0.02

Journal of the American Chemistry Annual Meeting

◆3 Method

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

sample

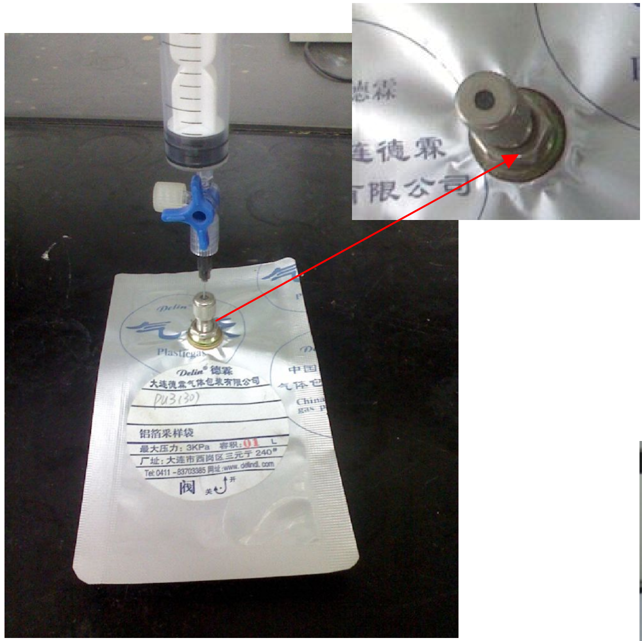
underwater 20cm

save

analysis

2. Gas pocket

The gas to be analyzed can be transfer from water sample to gas pocket once sample and pretreatment completed.



Its air tightness can be checked by whether make it vacuum.

water sample

transfer →

gas pocket

- 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.

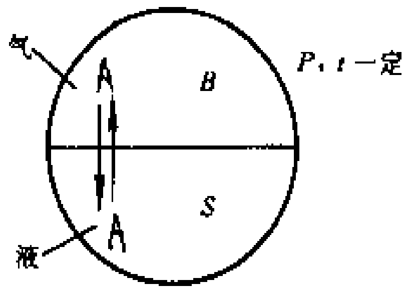
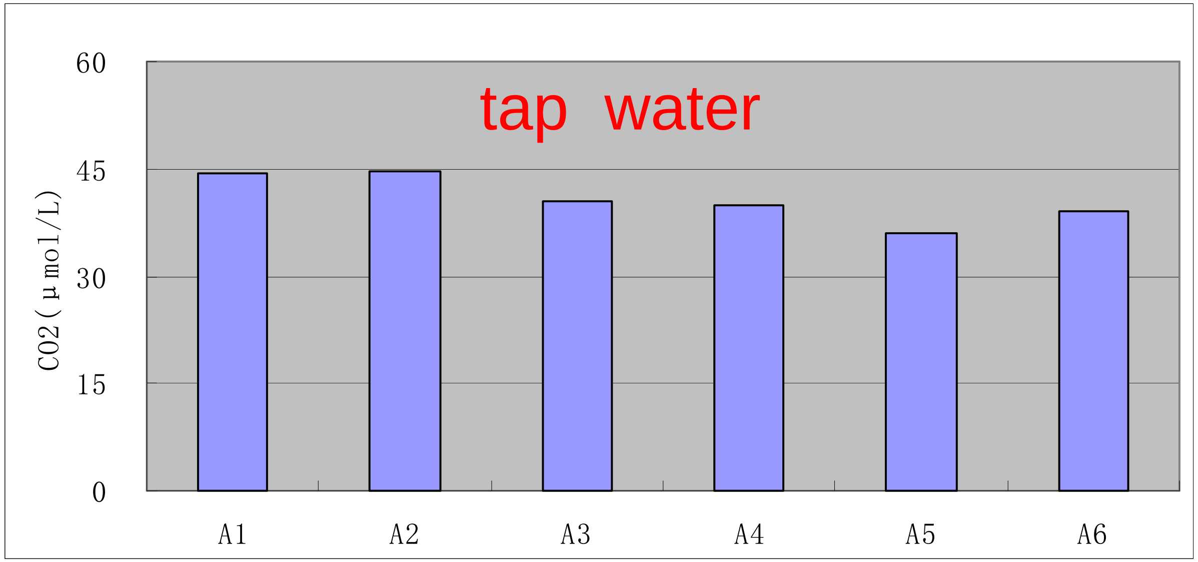


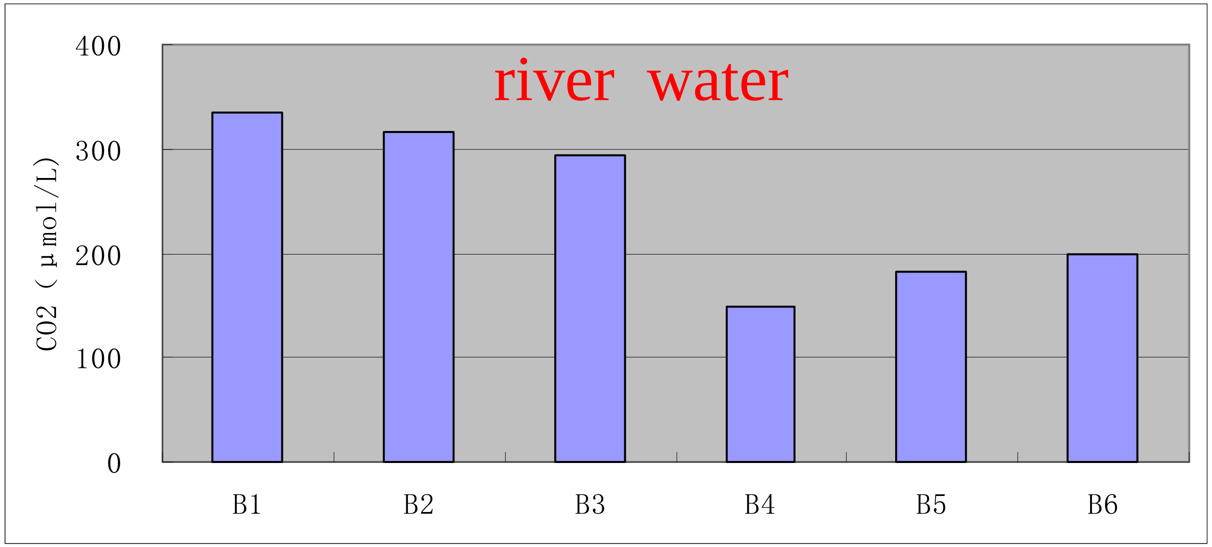
图 5-2 气液平衡

3 .Compare the data: bottle Vs gas pocket



A1、A2、A3:
measured by bottle

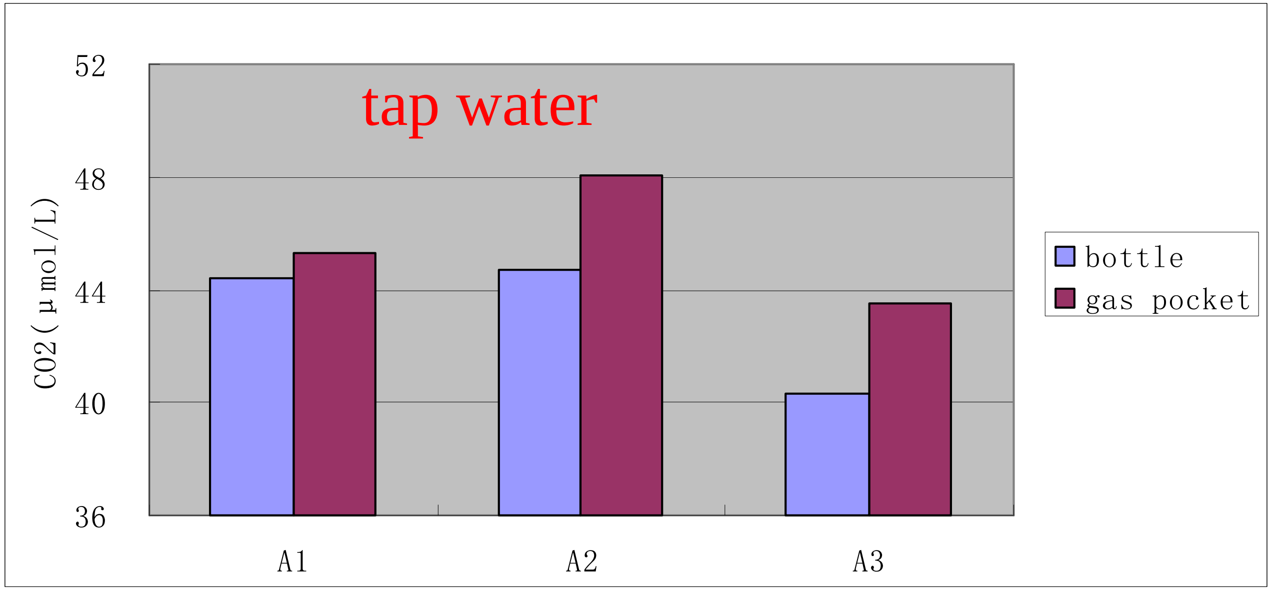
A4、A5、A6:
measured by gas pocket

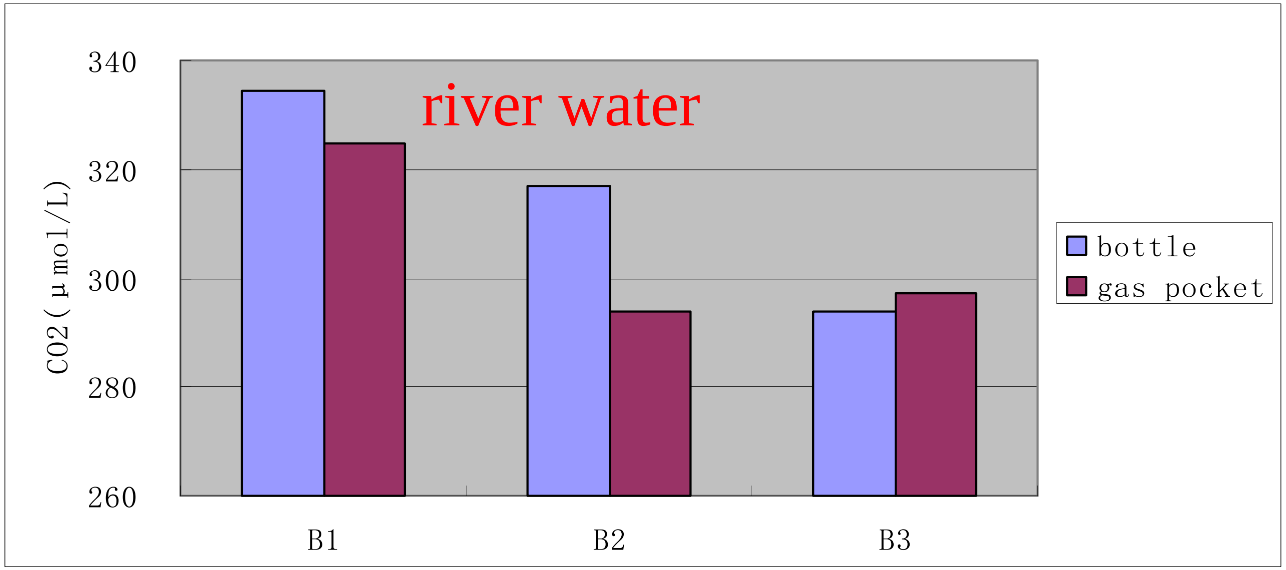


B1、B2、B3:
measured by bottle

B4、B5、B6:
measured by gas pocket

- The data of water sample measured by bottle and gas pocket respectively





- **4. Make a choice measure dissolve CO2 concentration**

water sample $\xrightarrow{\text{save}}$ fridge $\xrightarrow[\star\text{wait}]{\text{treat}}$ target gas $\xrightarrow{\text{analysis}}$ GC

Vs

water sample $\xrightarrow{\text{treat}}$ target gas $\xrightarrow{\text{save}}$ gas pocket $\xrightarrow[\star\text{wait}]{\text{analysis}}$ GC

Vs

Alkalinity—CO2

Thank You