ACID RAIN, PROMOTING THE ACCUMULATION OF CO_2 IN SURFACE WATERS ?!

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Keywords: acid rain, elevated concentrations of aluminum, surface waters

ABSTRACT

Acid rain and increase of CO_2 concentration in atmosphere are the important problems to the global changes. In the past, people studied them separately. Someone found that lakes are sources of atmopheric CO_2,but the mechanism is not clear. In this paper, we present our investigation on this question by using chemical equilibrium model. Theoretical calculation indicates that: in the acidic range of pH<5, P_{CO_2} may change from 1×10^{-4} to 0.1 atm without altering pH value of waters due to the buffering actions of Al^{n+} and H^+; Oppositely, the pH is very sensitive to the P_{CO_2} in the neutral (pH> 5) surface waters. Therefore, we come to the conclusion that acidified surface waters may hold much more CO_2 than neutral waters. Acid rain, also promotes the accumulation of CO_2 in surface waters !

INTRODUCTION

There is increased concern over the supersaturation of carbon dioxide in the surface waters of lakes [1,2]. Processes that add and remove CO_2 occur simultaneously in the surface waters of lakes. Data on the partial pressure of carbon dioxide in the surface waters from a large number of lakes (1835) with a worldwide distribution show that only a small proportion of the 4665 samples analyzed (less than 10%) were within ±20% of the equilibrium with the atmosphere and that most samples (87%) were supersaturated. Furthermore, lakes showed an enormous range of CO_2 concentrations from 175-fold below to 57-fold above atmospheric equilibrium at the extremes. This indicates that lakes are sources rather than sinks of atmospheric CO_2. The probable reason for this excess CO_2 may be due to the large accumulation of organic matter in the tundra and its respiration in soil or lake waters [3,4]. Thermokarst and fluvial processes cause great erosion of peat and release of dissolved organic carbon (DOC) into lakes and rivers [5-7], and this C may be respired to CO_2 [8,9]. There is also direct evidence that dissolved inorganic C in ground is moving from land to lakes and rivers, movement of CO_2-charged ground waters into the river can easily account for the high P_{CO_2} observed in the river. However, this explanation is not very satisfying, because it does not consider the effect of the pH of surface waters. As we know, acid rain is a very serious problem to the global changes. One of the consequences of the acidic precipitation is that H^+ and aluminum concentrations increased in the surface waters.[10,11] In this paper, we try to link the excess CO_2 with the acid rain by considering the effects of Al^{n+} and H^+ buffering actions in acidifed surface waters. A theoretical model based on the chemical equilibrium equations is developed for evaluating the interactions of P_{CO_2} and pH. Water quality data from the literatures for about 20 sampling stations are analyzed by our model. Interesting conclusion was obtained.

THEORY

We initially make the following assumptions:

(1) the surface water studied is in equilibrium with the natural gibbsite. It is a dilute solution with low ionic strength [12];

(2) in acidic pH range, Al^{n+} and H^+ dominate the buffering system. The chemical speciation of aluminum in acidic surface waters is complicated because Al^{3+} forms complexes with OH^-, SO_4^{2-}, F^- and organic compounds.[12]

(3) $[Al^{3+}]$ can be predicted as a function of pH using an aluminum trihydroxide solubility relation. $Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$, $[Al^{3+}]=K_{sp}[H^+]^3$ [14];

(4) concentrations of Fe and Mn are very low, their reactions with ligands (F^-, SO_4^{2-}, OH^-, and organic solute) are insignificant [15];

(5) organic solutes in natural waters are presented as a triprotic acids, while two species of aluminum-organic solutes are depicted [16];

(6) no adsorption of anions was taken into account;

(7) for an open system, the following reactions controlling the CO_2 concentrations take place: (P_{CO_2} is the partial pressure of CO_2)

$$[H_2CO_3^*] = K_H P_{CO_2} \quad (1)$$
$$[HCO_3^-] = K_{C1} K_H P_{CO_2}/[H^+] \quad (2)$$
$$[CO_3^{2-}] = K_{C1} K_{C2} K_H P_{CO_2}/[H^+]^2 \quad (3)$$

By employing the electroneutrality relationship, we can write:

$$E_N = E_{N,Al-OH} + E_{N,Al-F} + E_{N,Al-SO_4} + E_{N,Al-Org} + E_{N,CO_3} + C_B - C_A + [NH_4^+] - [F^-] + [H^+] - [OH^-] \quad (4)$$

E_N is the discrepance in electroneutrality, in which contributions from various compoents $E_{N,i}$ are:

$$E_{N,Al-OH} = 3[Al^{3+}]+2[Al(OH)^{2+}]+[Al(OH)_2^+]-[Al(OH)_4^-] \quad (5)$$
$$E_{N,Al-F} = 2[AlF^{2+}]+[AlF_2^+]-[AlF_4^-]-2[AlF_5^{2-}] \quad (6)$$
$$E_{N,Al-SO_4} = [AlSO_4^+]-[Al(SO_4)_2^-] \quad (7)$$
$$E_{N,Al-Org} = [AlHOrg^+]-3[Org^{3-}]-2[HOrg^{2-}]-[H_2Org^-] \quad (8)$$
$$E_{N,CO_3} = -2[CO_3^{2-}]-[HCO_3^-] \quad (9)$$

C_B is the sum of basic cation equivalence ($2[Ca^{2+}]+2[Mg^{2+}]+[K^+]+[Na^+]$ in eq/L), C_A is the sum of acidic anion equivalence ($2[SO_4^-]+[NO_3^-]+[Cl^-]$ in eq/L).

E_N is a function of $[H^+]$, $E_N = f(H^+)$. By using Newton-Raphson method, $[H^+]$ can be calculated:

$$[H_{i+1}^+]=[H_i^+]- \frac{E_N}{\left(\frac{\partial E_N}{\partial H}\right)} \quad (10)$$

$[H^+]$ is the hydrogen ion concentration at the i th iteration and $[H_{i+1}^+]$ is the hydrogen ion concentration at the i th + 1 iteration. Equations (1-10) express the relationship of P_{CO_2} with pH in surface waters and can be used to evaluate their interactions. With fixed P_{CO_2}, pH can be given; On the other hand, P_{CO_2} can also be calculated at a fixed pH by iteration. The mass balance is:

$$C_F^T=[F^-]+[HF]+[AlF^{2+}]+2[AlF_2^+]+3[AlF_3]+4[AlF_4^-]+5[AlF_5^{2-}] \quad (11)$$
$$C_{SO_4}^T= [SO_4^{2-}]+ [AlSO_4^+] + 2[Al(SO_4)_2^-] \quad (12)$$
$$C_{Org}^T= [Org^{3-}]+[HOrg^{2-}]+[H_2Org^-]+[H_3Org]+[AlHOrg^+]+[AlOrg] \quad (13)$$

A GW-BASIC computer program was developed to perform the necessary calculation. All chemical reactions equilibrium constants are cited from literatures [12-14].

RESULTS AND DISCUSSION

Atmospheric deposition and processes occuring in the soil are responsible for the observed surface water chemistry in a catchment. [19] CO_2 partial pressure in soil is commonly much higher than atmospheric CO_2 partial pressure ($10^{-3.5}$ atm). When the solution is removed from

contact with the soil matrix and exposed to the atmosphere (that is when water enters the stream channel), two situations may be occuring for the CO_2, depending on the pH value of the surface waters. Figure 1 gives the results of the theoretical calculation of pH values as the function of C_B-C_A under various P_{CO_2} values for surface waters. We can use it to explain the influence of pH on the accumulation of CO_2 concentrations in surface waters.

(1) the surface water is in the acidic range of C_B-C_A < -200 μ eq/L, P_{CO_2} may increase from 1×10^{-4} to 0.1 atm without change of pH. Acidic conditions restrict the dissociation of CO_2 (H_2CO_3) to H^+ and HCO_3^- due to the buffering actions of Al^{m+} and H^+. This means that much more CO_2 concentrations can be accumulated in surface waters under acidic condition;

(2) CO_2 is not easy to accumulate in the surface water which is of C_B-C_A > 0 μ eq/L. Under this condition, the water is poorly buffered and small changes in CO_2 concentration can significantly affect pH. Higher P_{CO_2} needs lower pH. Otherwise, the pH of the solution will increase, causing CO_2 lost to the atmosphere.[20,21] This means that when water enters the neutral stream channel from soil, excess CO_2 concentrations can not be accumulated in surface waters due to the increase of pH.

Figure 2 depicts the " P_{CO_2} *vs.* pH " relationship for analyzing the practical sampling water quality data. The data are cited from the literatures [22-26]. The values of P_{CO_2} are calculated from pH measured. After pH > 5, P_{CO_2} is not more than 20 P_o. Conversely, P_{CO_2} increases rapidly as an exponential function at pH < 5. Lakes are a small but potential important conduit for carbon from terrestrial sources to the atmospheric sink. Acid rain, also promotes the accumulation of carbon dioxide in surface waters!

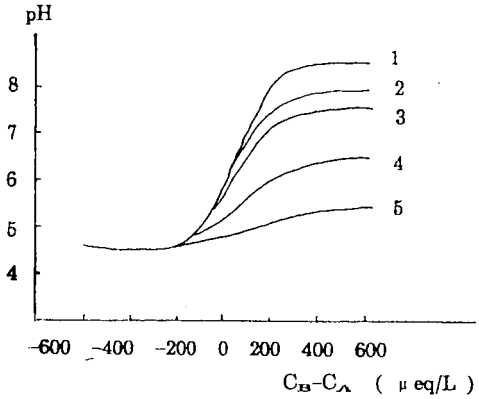

Fig.1 plot of " pH *vs.* C_B-C_A "
P_{CO_2} (atm):
1 — 1×10^{-4}, 2 — 3.16×10^{-4},
3 — 1×10^{-3}, 4 — 1×10^{-2},
5 — 1×10^{-1}

ACKNOWLEDGEMENT
This project is financed by the National Natural Science Foundation of China, Fok Ying Tung Education Foundation of Hong Kong and State Education Committee Foundation of China. The author thanks Prof.Rongshi Cheng, Hongyuang Chen, Ying Wang and Director of Smithsonian Environmental Research Center D.L.Correll for their supports and help.

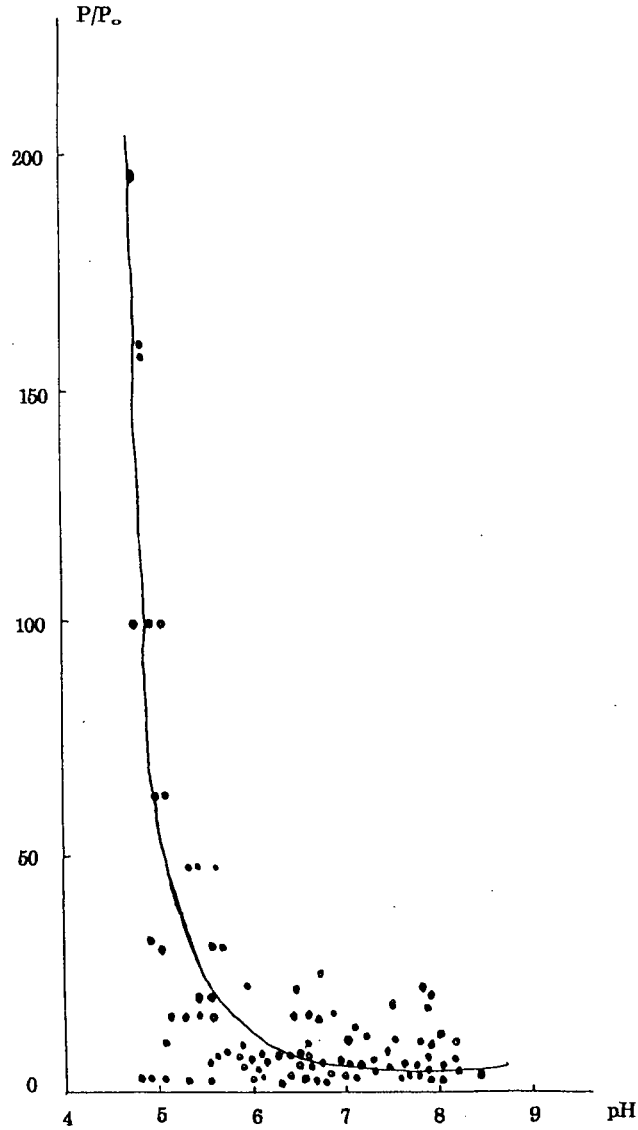

Fig.2 plot of " P_{CO_2} *vs.* pH "
($P_o = 3.16 \times 10^{-4}$ atm)

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