

The buffering effects of aquatic sediments against acidic deposition



Liao Bohan, Tang Hongxiao

Research Center for Eco-Environmental Sciences, Chinese
Academy of Sciences, Beijing 100085, China

Abstract— The cation exchange and the chemical weathering are two important processes for sediments to buffer the acidification of surface waters. In this paper, for sediments these two processes have been studied. The relationship between BEC of sediments and ANC of the surface waters and the weathering characteristics of sediments were discussed. The buffering effect and mechanism of sediments against acidic deposition have also been studied. The results show that BEC of sediments are positively correlative to ANC of the surface waters; the chemical weathering rate of sediments can be expressed as $R = k \times [H^+]^m$.

Keywords: acidic deposition; sediment; surface water; cation exchange; chemical weathering.

1 Introduction

The affection of acidic deposition on natural waters would result in a series of chemical processes taking place in sediments to buffer acidic transformation. Chemical weathering of rocks and minerals is a key factor which mitigates acidic deposition and affects water chemistry (Schnoor, 1986). Under the affection of acidic deposition, a fast cation exchange and a slow chemical weathering would take place in sediments. The two processes supply cations and alkalinity to the water systems and produce important buffering effects against acidic deposition to reduce the acidity of waters.

In this paper, the processes of cation exchange and chemical weathering of sediments in some water systems of southwestern China have been studied. According to the results of experiments, we discussed the correlation between the base exchange capacity (BEC) of sediments and the acid neutralizing capacity (ANC) of the surface waters. The chemical weathering characteristics of sediments in an acidic environment, and the buffering effects and mechanism of sediments against acidic deposition have been also studied.

2 Experiments

Sediment and surface water samples were collected in field in southwestern China. The pH values of surface waters were measured in field by a potable pH-meter. ANC of the surface waters were measured by acid titration with an automatic titrator.

Sediments were air dried first, then dried at 60 °C, and passed through a 100 mesh screen, the exchangeable cations of sediments were extracted by 1.0 mol/L ammonium acetate. Sediments were soaked in diluted HNO₃ solutions with various pH values, and chemical weathering experiments were carried out under stirring and closed conditions.

The surface waters, the extractions, and the weathering solutions were all filtrated through 0.2 μm membrane. The concentrations of cations of these solutions were measured by a Jarrell-Ash 1155v ICP Spectrometer.

3 Results and discussion

3.1 The cation exchange of sediments

When acidic deposition falls into natural waters, H⁺ from the deposition will consume the ANC of water systems. Sediments adsorb H⁺ from and release cations to the waters through the process of cation exchange. The process would compensate ANC of the waters and buffer the effects of acidic deposition. It can be expressed by the following general formula:



where Meⁿ⁺ stands for K⁺, Na⁺, Ca²⁺, Mg²⁺ and so on. Base exchange capacity (BEC), as an important index of sediments, reflects the content of exchangeable cations in sediments and could be considered as a symbol of the capacity of base exchange. The larger the BEC value of a sediment, which means there are more exchangeable K⁺, Na⁺, Ca²⁺, Mg²⁺, the larger the capacity of cation exchange with H⁺ ions and the larger the ability to buffer acidic deposition. ANC of natural waters have been widely used to evaluate the buffering ability of natural waters to acidification (Schindler, 1989; Bricker, 1989), therefore, BEC of sediments should be correlated in some extent with ANC of the waters.

Fig. 1 shows in our experiments that BEC of sediments are remarkably positively correlative to ANC of the surface waters at $p=0.01$,

$$\text{BEC (sed., meq/100g)} = 17.9 \times \text{ANC (aq., meq/L)} - 5.80, r(26) = 0.863$$

which means that the water system with the sediment of large BEC would have a large ANC and a large ability to buffer acidic deposition. Perhaps BEC of sediments, just as ANC of the water bodies, may be used as a sort of index to evaluate the ability of water systems against the acidification.

The regression analysis of the contents of exchangeable cations in sediments and the concentrations of cations in the water phases showed that the amount of

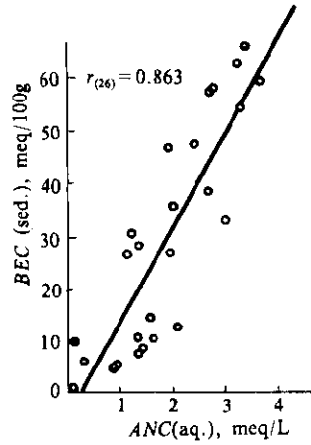


Fig. 1 Correlation between ANC of surface waters and BEC of the sediments

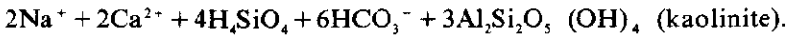
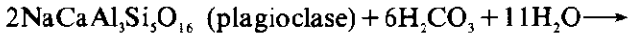
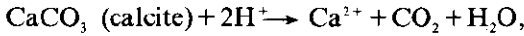
Table 1 Correlative coefficients of cations in sediments and in the surface waters

$\text{Me}^{n+} (\text{sed., mol/kg}) - a \times \text{Me}^{n+} (\text{aq., mol/L}) + b$			
Me^{n+}	a	b	$r(26)$
K^+	-117	28.5	-0.323
Na^+	0.973	0.600	0.497
Ca^{2+}	127	-23.6	0.800
Mg^{2+}	29.6	1.45	0.673

exchangeable Ca^{2+} , Mg^{2+} , Na^+ in sediments are positively correlated to the concentration of respective cations in the water phases at $p=0.01$, but there is no remarkable correlation between the two kinds of K^+ ions (Table 1). Obviously, the system whose sediment phase has higher contents of exchangeable Ca^{2+} , Mg^{2+} , Na^+ , would have higher concentrations of these cations in solution. The order of correlative coefficients is $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$, conforming to that of concentrations in waters from this area. In fact, the quality of a natural water system would be closely correlated with the composition of mineral phase through the chemical weathering process.

3.2 The chemical weathering of sediments

Under the effects of acidic deposition, minerals of sediments consume H^+ ions and release cations such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} to buffer the acidification of waters by the process of chemical weathering. For example, the chemical weathering reactions of calcite and plagioclase can be expressed respectively by the following equations:



The main cations released from sediments are K^+ , Na^+ , Ca^+ , Mg^{2+} , which account for above 95% of the total amount of released cations. Therefore the sum of the four cations (M_4) may be taken as the total amount of released cations from sediments approximately.

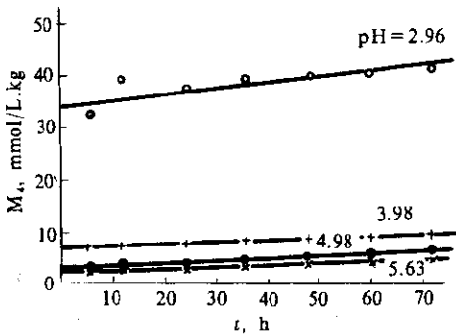


Fig. 2 Relationship between M_4 and time of chemical weathering at various pH values

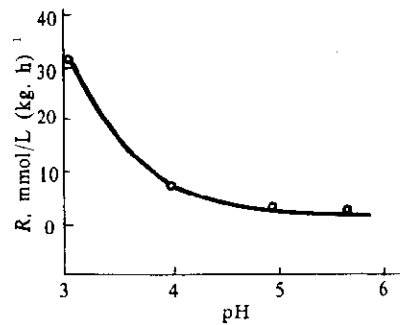


Fig. 3 Relationship between R of sediments and pH of the surface waters

In Fig. 2, it is shown that the total amount of cations released from sediments increased linearly with the experimental weathering time. Meanwhile, the chemical weathering process of sediments became stronger and more rapid with the increasing of acidity of solution. The rates (R) of chemical weathering at various pH can also be obtained from Fig. 2 and plotted in Fig. 3.

Fig. 3 shows the logarithmic relationship between the chemical weathering rates of sediments and the pH values of solution:

$$\lg R = -m \times \text{pH} + k' = m \times \lg[H^+] + k', \quad (1)$$

therefore, R could be expressed by the acidity of water system as:

$$R = k \times [H^+]^m, \quad (2)$$

where k is the rate constant of chemical weathering, m is a constant ranging from 0 to 1. Furrer and Stumm (Furrer, 1986) consider that the rate of weathering is controlled by chemical surface reactions and the relationship between the weathering rate of a pure mineral and the H^+ concentration of the solution can be expressed as $R_H = k_H [H^+]^x$, where k_H and x have the same meanings as k and m in our Expression (2) respectively. Sediments consist of various kinds of minerals including primary and secondary. If the chemical weathering of all minerals take place simultaneously, the total rates of chemical weathering of the sediments should also be controlled by the chemical surface reactions and the Expression (2) would still be valid only when the constants k and m are compositive.

Because the chemical weathering of sediments releases cations and supplies to ANC to the water systems, the weathering rate of sediments should also be related to ANC. The water system, in which sediment has a larger R value, should have a larger ANC and a stronger ability to buffer acidic deposition. The results of our weathering experiments are listed in Table 2.

Table 2 Relationship between R of sediments and ANC of the water systems

Sample	No.	1	2	3	4	5	6
ANC aq., meq/L		3.36	2.78	2.69	2.20	2.00	1.35
R , mmol/ L. kg. h	pH=3.0	144	80.5	74.2	55.2	41.6	35.2
	pH=4.0	80.8	44.5	32.3	30.6	17.5	10.7
	pH=5.0	45.3	24.6	14.1	16.9	7.37	3.24
	pH=6.0	25.4	13.6	6.13	9.36	3.10	0.98

Comparing the amount of consumed H^+ (H) with the total amount of released cations (M_+) during the process of experimental chemical weathering of sediments, we also found an linear relationship between H and M_+ as plotted in Fig. 4, and expressed as Equation (3):

$$M_+(\text{meq/L, kg}) = 0.982 \times H(\text{meq/L, kg}) + 71.2,$$

$$r(23) = 0.704. \quad (3)$$

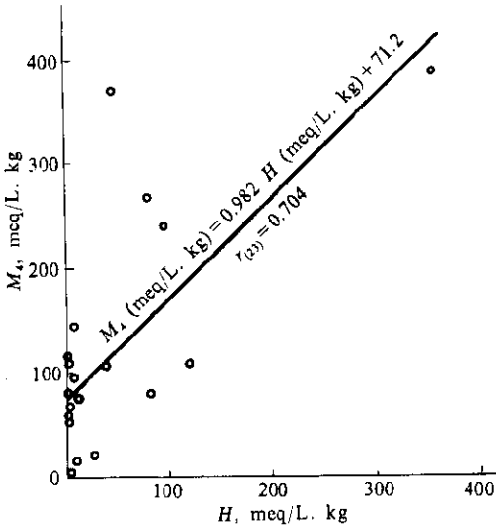


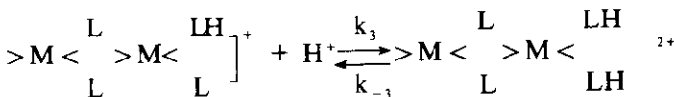
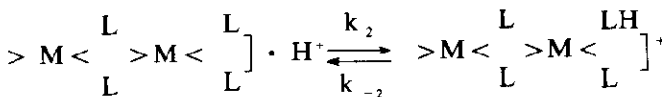
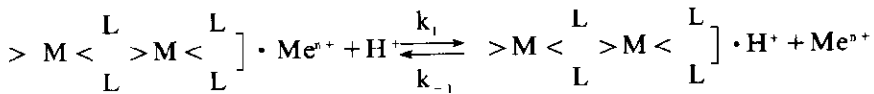
Fig. 4 Relationship between consumed H^+ (H) and released cations (M_4) during the chemical weathering of sediments

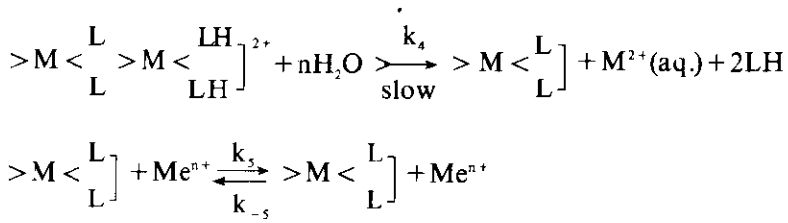
The slope term of the linear expression is nearly equal to 1.0, which means that sediments release one equivalent of cations to the surface waters when they consume the same amount of H^+ ions in the solution during the process of chemical weathering. This would be one of the ways that sediments buffer the acidification of water systems. The value of b (e. g., 71.2) may be the amount of cations released from the sediment surface before the chemical weathering begins.

3.3 The buffering mechanism of sediments against acidic deposition

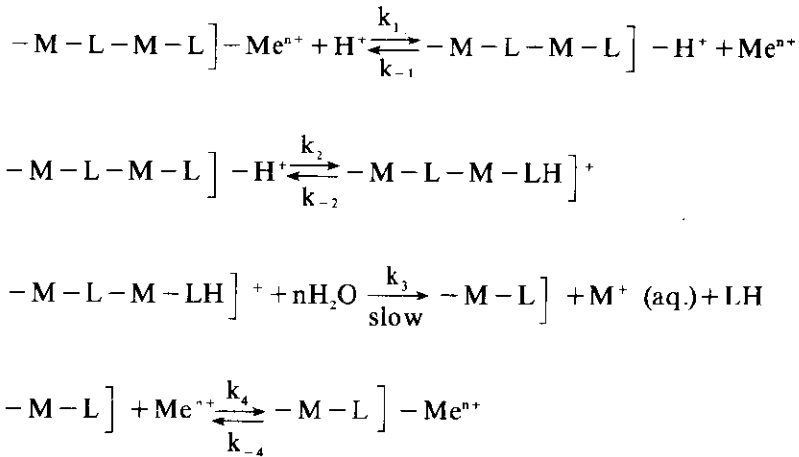
As above described, under the affection of acidic deposition, sediments consume H^+ from and release cations to the surface waters to buffer the acidification through two processes—the cation exchange and the chemical weathering. The cation exchange reaction is as faster process; on the other hand, the chemical weathering reaction is a slower process and is controlled by the chemical surface reactions. Therefore, it can be suggested that the buffering mechanism of sediments against acidic deposition would be expressed as the following patterns:

The minerals containing calcium and magnesium in sediments





The minerals containing potassium and sodium in sediments



where $\Big]$ expresses the surface of minerals, Me the cations sorbed on the surface of minerals, M the metal ions in minerals, L the anions and ligands in minerals.

Sediments consist of various minerals containing calcium, magnesium, potassium, and sodium; therefore, the buffering mechanism of sediments against acidic deposition might include these two patterns simultaneously. The first step is a fast cation exchange reaction that H^+ ions from acidic deposition substitute for the exchangeable cations sorbed on the surface of minerals in sediments. The following steps belong to the chemical weathering reaction, including the sorption of H^+ ions to anionic groups on the surface of minerals, the desorption of cations from the surface, the reformation of the surface of minerals in sediments and so on. May be the desorption of cations from the surface of minerals is a slow reaction that controls the rate of chemical weathering of sediment.

4 Conclusion

It is clear that aquatic sediments can buffer the acidification of surface waters by

the processes of cation exchange and chemical weathering. These two processes display in the buffering mechanism of sediments against acidic deposition. Our experimental results show that BEC of sediments, which determine the cation exchange capacity, are positively correlative to ANC of the surface waters; the chemical weathering rate of sediments can be expressed as $R = k \times [H^+]^m$.

References

- Bricker OP, Rice KC. *Environ Sci Technol*; 1989; 23 (4):379
Furrer G, Stumm W. *Geochimica et Cosmochimica Acta*, 1986; 50:1847
Schnoor JL, Stumm W, Schiweiz Z. *Hydrol*, 1986; 48 (2) : 171
Schindler DW, Kasian SEM, Hessein RH. *Environ Sci Technol*, 1989; 23 (5):573

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