

## Alkaline rains on the Tibetan Plateau and their implication for the original pH of natural rainfall

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[1] Natural rains are generally considered as weakly acidic. Long-term measurement in the Tibetan capital city, Lhasa, reveals that alkaline rain is also natural. For the last 3 years the volume-weighted mean pH of rainwater is 7.5. Earlier observation shows even higher average pH values, such as 8.36 in the 1987–1988 period. The major cause of alkaline rain is the alkaline and soil-borne continental dusts in this semiarid area. Bicarbonate is the dominant anion in the water samples. The analysis also shows that the rainwater in this city contains few pollutants, compared with other places in the world. Measurements carried out in two additional industrial cities on the northern and northeastern Tibetan Plateau, Xining and Germu, demonstrate how fast human activities such as industrial development may increase rainwater acidity. In a period of 13 years the rainfall pH value of Germu has dropped from 8.03 to 6.8, representing a manyfold increase of the  $H^+$  concentration. Such an increase was caused by rising contents of  $NO_3^-$  and  $SO_4^{2-}$  in the atmosphere. On the basis of the measurements on the Tibetan Plateau, evidence from other places around the world, and the experiments and calculation, the authors believe that the original pH of natural rainwater in arid and semiarid areas on this planet should be weakly alkaline because of the influence of alkaline dusts.

*INDEX TERMS:* 0335 Atmospheric Composition and Structure: Ion chemistry of the atmosphere (2419, 2427); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 9320 Information Related to Geographic Region: Asia; *KEYWORDS:* Tibetan Plateau, alkaline rain, rainwater chemistry, aerosol, atmosphere

### 1. Introduction

[2] The Tibetan Plateau has an average elevation of 4000–5000 m and a vast area of 2.5 million  $km^2$ . The plateau in China spreads across two regional governances, the entire Tibetan Autonomous Region and much of Qinghai Province; the latter includes the northeastern part of the plateau and the basins between the Mount Qilian and the Kulun Mountains. Across extensive areas on the plateau surface, average annual temperature ranges from  $-4^\circ C$  to  $10^\circ C$ , and the average annual precipitation ranges from 50 mm to 600 mm, which is controlled by the Indian monsoon. Low relative humidity (30–50%), high intensity of solar radiation (140–240  $kcal\ cm^{-2}$ ), and high potential evaporation (1500–2500 mm) are additional climatic characteristics of the plateau [*Tibetan Expedition Team of Chinese Academy of Science*, 1984]. Because of its remoteness, poor accessibility, and political sensitivity, the investigation of rainwater pH and chemistry in the Tibetan Autonomous Region has never been carried out. The Qinghai Province started a few annual rainwater pH measurements in the late 1980s without further analysis. The continuous monitoring

program started in 1992 and 1994 in Xining and Germu, respectively. During the last decade the Tibetan region has experienced rapid economic development. The capital city of the Tibetan Autonomous Region, Lhasa, has doubled its population, from 0.15 to 0.3 million. However, it remains largely a tourist city with little industry. Germu and Xining are the two largest and most industrialized cities in Qinghai Province; they are also on the plateau and have one third of the total population of the province. Germu is an important logistic station to Tibet, and it is here that the railway to Tibet ends. Its population tripled between 1988 and 1999, from 0.1 to 0.3 million. Many heavy industrial plants have been built around this city in the last 15 years, including oil refineries, metal smelters, and chemical industries. Xining, the capital city of Qinghai Province, has also had a fast pace of industrialization. The city's population has doubled during the last 10 years up to the current 1.6 million. The industrialization on the plateau has consequently led to air pollution. Therefore the monitoring of precipitation chemistry here is urgently needed.

### 2. Methodology

[3] The first author started the rainwater measurement during 1987–1988. The study locations were focused on

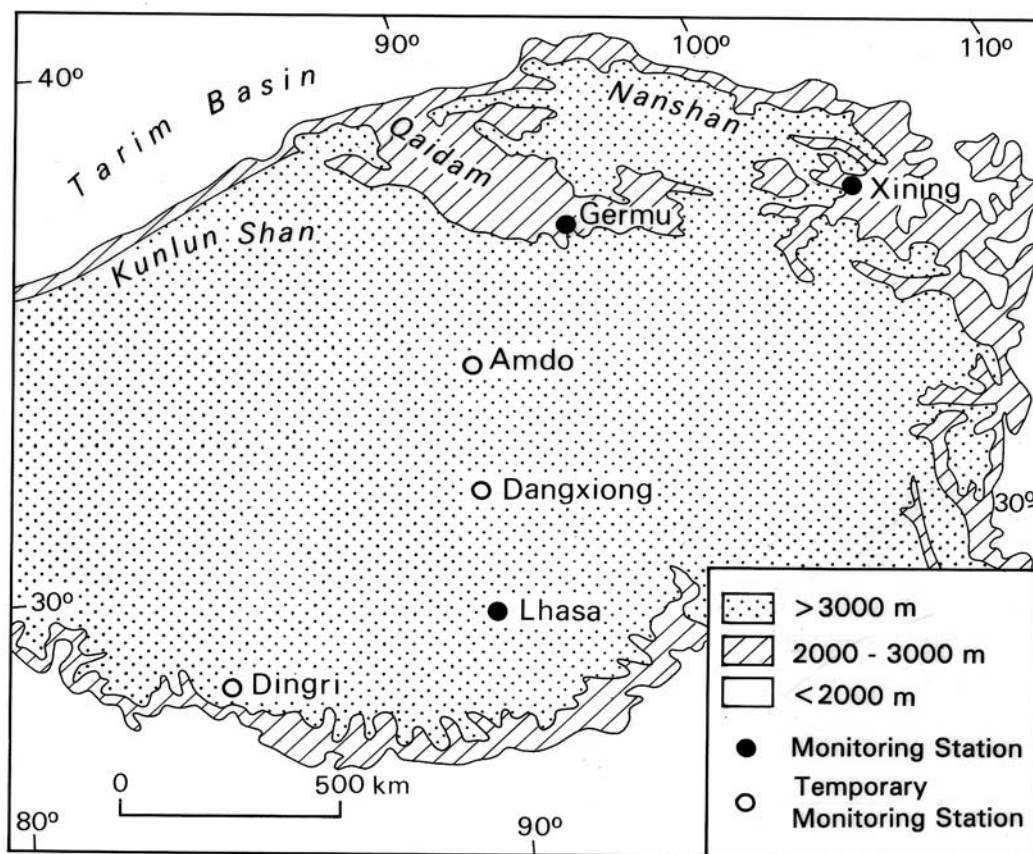


Figure 1. Tibetan Plateau and locations of the rainwater monitoring stations.

sites along an expedition route in the Tibetan Autonomous Region. A more recent research project has been carried out from 1997, with the support of Tibetan and Qinghai local scientists and meteorological stations (Figure 1). The project used meteorological stations in Lhasa (3658 m above sea level (asl), Germu (2807 m asl), and Xining (2295 m asl) to measure rainwater pH and other relevant factors, including conductivity, temperature, rainfall amount, wind speed and direction, relative humidity, and atmospheric pressure. The precipitation samples were taken by bulk collectors and were measured in the meteorological station laboratories immediately after each precipitation event for pH, conductivity, and temperature. The samples were then well sealed and carried to the University of Hong Kong and the Chinese State Key Laboratory of Environmental Geochemistry in Guiyang for chemical analysis. The content of  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Fe$ ,  $Mn$ ,  $NH_4^+$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ , and  $HPO_4^{2-}$  in the samples were analyzed by ion chromatography with the HP LC 1100 and ICP ZEISS PLASMA-QUANT110 immediately after the sample bottles were unsealed, because of the need to consider the partial pressure difference of  $CO_2$  and other gases between high and low altitudes. However, the concentration of  $HCO_3^-$  had to be determined by titration because there is no available instrumental technique. The bulk sampling and analytical programs were mainly based on *World Meteorological Organization* [1974] recommendations for precipitation sampling and analysis with some modifications according to local laboratory conditions and environmental

characteristics of the plateau. Atmospheric  $CO_2$  partial pressure and total suspended particulates were measured during the 1997, 1998, and 1999 research periods. Although different models of equipment for the measurement of pH, conductivity, and chemical concentration of rainwater were used in two separate research periods, the authors believe that the measurement results should be comparable because each of the instruments was carefully calibrated before its use.

### 3. Results

[4] The results of pH measurement for every precipitation event in Lhasa from 1997 to 1999 indicate that the Tibetan precipitation is basically alkaline (Figure 2), with a volume-weighted mean (VWM) of 7.5. Only one sample has a pH value of 5.2. The pH of precipitation has no significant correlation with its conductivity ( $r = 0.119$ ), rainfall amount ( $r = -0.023$ ), and wind speed ( $r = -0.033$ ) and directions. There also is no obvious correlation between the rainfall amount and conductivity ( $r = -0.02$ ). The measurements during 1987–1988 show that the pH value at 8.37 for the VWM (Table 1) was even higher when compared with the 1997–1999 observations. The measurements presented in Table 1, for three other towns of the Tibetan Autonomous Region, Dangxiong, Amdo, and Dingri, show a slower decrease of pH values during the last 12 years compared to Lhasa, possibly because of the remoteness of the towns and the lack of development. Measurements made in two

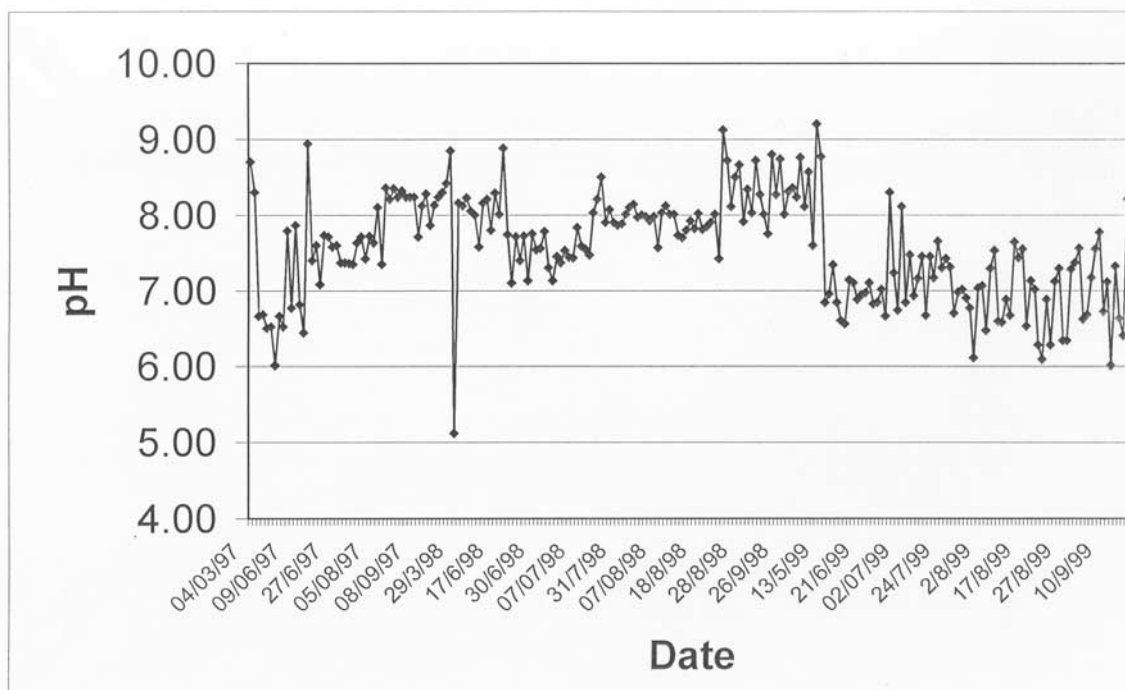


Figure 2. The pH variation of precipitation of Lhasa City, 1997–1999.

industrial cities in Qinghai Province reveal the fastest decline of rainfall pH values, with VWM values having dropped below 7 in 1992 and 1995 for Xining and Germu, respectively.

[5] Rainfall chemical analysis, which is presented in Table 2, demonstrates the background changes of atmospheric chemistry at different periods and places on the plateau, which correspond with the pH changes reported in Table 1. There were low concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in the rainfall samples of Lhasa, and their contents are similar to those measured at some remote islands of the world [Galloway *et al.*, 1982], although they demonstrate an increase in the 1997–1999 period. The samples from Dingri, Amdo, and Dangxiong, although limited in number, also show similar composition and quantities of chemical components to those of Lhasa. The 1999 samples of Xining were seriously polluted. Table 2 shows that  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  in the rainwater of Xining increased greatly in the

1990 and 1999 samples compared to those of 1987–1988, and high concentrations of  $\text{F}^-$  were found in the 1999 samples, which may be related to metal smelting and brick plants in the city. Table 2 also indicates that basically  $\text{Ca}^{2+}$  is the dominant cation species and that  $\text{HCO}_3^-$  is the major anion species in all samples. The average ratios of  $\text{Cl}^-/\text{Na}^+$  in the three cities vary between 0.20 and 0.76, and the ratios of  $\text{Na}^+$  to  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{SO}_4^{2-}$  are not similar to those of seawater. Therefore the rainfall chemistry on the internal plateau is mainly controlled by continental soils with scant contribution from marine aerosols. These soils are commonly of saline and alkaline types, with a typical pH range of 6–10 in the Tibetan area [Land Resource Bureau of Tibetan Government, 1994]. Such soils commonly contain base-forming cations,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , and free soluble salts, which could contribute alkaline particulates to the atmosphere. Fe, Mn,  $\text{HPO}_4^{2-}$ , and  $\text{Br}^-$  are present in trace quantities in the samples, which are within the range of a

Table 1. Volume-Weighted Mean of the Precipitation pH Values on the Tibetan Plateau<sup>a</sup>

Location	Elevation, m	Precipitation, mm	Conductivity, $\mu\text{s cm}^{-1}$	1986	1987–1988	1990	1992	1993	1994	1995	1996	1997	1998	1999
Lhasa	3658	443	32	NE	<b>8.37 (15)</b>	NE	NE	NE	NE	NE	NE	<b>7.61</b>	<b>7.95</b>	<b>6.97</b>
Dangxiong	4000	400	50	NE	<b>7.97 (7)</b>	NE	NE	NE	NE	NE	NE	NE	NE	7.98 (1)
Amdo	4700	400	125	NE	<b>8.78 (3)</b>	NE	NE	NE	NE	NE	<b>8.34 (2)</b>	NE	NE	7.2 (1)
Dingri	4300	322	81	NE	<b>7.64 (3)</b>	NE	NE	NE	NE	NE	NE	<b>7.84 (7)</b>	<b>8.32 (5)</b>	
Germu	2807	50		<b>8.04 (12)<sup>b</sup></b>	<b>7.99 (6)</b>	NE	NE	NE	<b>7.10</b>	<b>6.88</b>	<b>6.91</b>	<b>6.59</b>	<b>6.46</b>	<b>7.21 (3)<sup>c</sup></b>
Xining	2295	350		7.96 <sup>d</sup>	<b>7.83 (11)</b>	7.41 <sup>e</sup>	<b>6.30</b>	<b>6.69</b>	<b>6.56</b>	<b>7.32</b>	<b>7.09</b>	<b>7.09</b>	<b>6.65</b>	<b>7.12 (11)<sup>c</sup></b>

<sup>a</sup> Numbers in parentheses indicate the numbers of the sampled rainfall events in non-whole-year monitoring. Bold numbers are volume-weighted mean of measured rainfall events in the year. NE indicates no examination.

<sup>b</sup> Source is Hu and Wu [1989].

<sup>c</sup> Sampling took place from January to June.

<sup>d</sup> Source is Ni and Gao [1989].

<sup>e</sup> Source is Wang [1993].

**Table 2.** Volume-Weighted Mean of Chemical Concentration ( $\mu\text{eq L}^{-1}$ ) of Precipitation on the Tibetan Plateau<sup>a</sup>

Location	Year	Sample Number	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>
Lhasa	1987–1988	14	12.59	61.73	145.88	18.30	15.51	21.49	NE	2.27	2.10	251.78	NE
Lhasa	1998–2000	15	9.82	9.75	198.77	11.76	8.70	21.55	U	7.28	6.11	222.8	0.40
Other places in Tibet	1998–2000	4	10.25	12.14	93.18	10.35	14.85	2.85	U	1.69	6.01	136.96	0.12
Germu and Xining	1988	6	36.15	23.88	149.25	30.37	11.62	11.62	NE	8.16	7.92	263.40	NE
Germu and Xining	1990–2000	7	69.17	96.56	314.31	37.90	160.61	48.77	2.41	48.08	84.01	534.29	46.62

<sup>a</sup>NE indicates no examination; U indicates undetectable.

few  $\mu\text{g L}^{-1}$  or are undetectable, hence their contents have not been reported here.

#### 4. Analyses and Implications

[6] In many scientific literatures, natural rain is considered as weakly acidic [e.g., *Howells*, 1990; *Meszaros*, 1992; *Miller*, 1998; *Merritts et al.*, 1998]. This is based on measurements from remote oceanic islands and also the theoretical calculation of potential acidity. The original acidity of natural rain is calculated by using CO<sub>2</sub> partial pressure in the atmosphere at sea level or by using CO<sub>2</sub> plus other natural trace gases, which gives pH values of  $\sim 5.6$  [*Likens and Bormann*, 1974] or  $\sim 5.0$  [*Galloway et al.*, 1982; *Charlson and Rodhe*, 1982], respectively. Because high altitude can lower  $p\text{CO}_2$ , it is necessary to measure it on the plateau. The CO<sub>2</sub> partial pressure of the Tibetan atmosphere for 123 measurements in the sampling areas ranges from 0.00030 to 0.00019 atm. The lowest value of  $p\text{CO}_2$ , which is about a half of that at sea level, may reduce rainwater pH values by only 0.1 units based on the attainment of chemical equilibrium between rainwater and atmospheric partial pressure. Such a small decrease of pH indicates that the lower  $p\text{CO}_2$  on the plateau is an insignificant contributor to the high pH of rainfall observed in Tibet.

[7] Two distinctive facts, which are often omitted in our knowledge of the original state of natural rains, are that acid rain monitoring started after the Earth's industrialization and that the results therefore only indicate the polluted state of the atmosphere perhaps, even at remote locations as evidenced by long-range transport of pollutants [*Miller*, 1980]. Moreover, the theoretical calculation of "natural" rainfall pH did not consider that the atmosphere not only consisted of gases but also of alkaline particles. The particles of natural origin could buffer weakly acidic precipitation leading to pH values higher than 5.6 in many places, especially in arid and semiarid areas where there are plenty of alkaline dusts [*Berner and Berner*, 1987; *Sequeira* 1993]. *Hedin and Likens* [1996] have pointed out the importance of atmospheric dusts in neutralizing the acidic air pollutants, and the reduction of atmospheric dust release has aggravated the acid rain problem. The dusts derive from surface soils in the area. Such soils commonly contain base-forming cations, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, and free soluble salts, which could contribute alkaline particulates to the atmosphere. In addition, calcification is the major soil formation process in semiarid and arid regions, which produces abundant calcite (CaCO<sub>3</sub>). The wind-blown dusts mobilized from these soils

are usually  $>2.5 \mu\text{m}$  in diameter, that is, mainly of the coarse aerosol type that can be effectively and rapidly scavenged by the rainfall washout process. Between rainfall episodes the atmospheric loading of soil-borne particulates could be quickly replenished. With limited rainfall the washout effect is equivalent to the first-rain fraction of other wetter areas, which tend to have a higher pH than the later fractions [*Tuncel and Unmgor*, 1996].

[8] In Lhasa city, long-term and constant alkaline precipitation, which has rarely been reported in the literature, can be regarded as the original state of precipitation in arid and semiarid areas before industrialization. The decrease in pH values from the 1987–1988 period to the 1997–1999 period is mirrored by its population and vehicle growth. Both SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in bulk deposition at Lhasa have tripled in time, compared to the early monitoring. However, NO<sub>3</sub><sup>-</sup> has increased quicker than SO<sub>4</sub><sup>2-</sup> because vehicles and domestic energy mainly depend on oil. Such development in the two industrial cities, Germu and Xining, is more obvious, with pH values having decreased below 7. SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> have largely increased in Germu and Xining since the 1990s because of the fast growth of heavy industry and the development of the Qaidam Basin oil field. Rainfall chemistry of these two cities followed such changes very closely. In 1992–1993, when many small ferrosilicate smelting plants were built along the Xining River valleys, the NO<sub>x</sub> content in air rose to 0.067 mg m<sup>-3</sup>, SO<sub>4</sub><sup>2-</sup> rose to 0.115 mg m<sup>-3</sup>, and TSP rose to 1.036 mg m<sup>-3</sup> during the winter period [*Wang*, 1993]. The average pH of rainfall in Xining declined in tandem with development and rather drastically from 7.41 in 1990 to 6.66 (1992), 6.86 (1993), and 6.77 (1994). During the 1995–1996 period the Qinghai government enforced environmental regulations and closed many seriously polluting plants around Xining, and SO<sub>2</sub> emissions were reduced by nearly a half of those in the previous year. The rainfall VWM pH swiftly increased from 6.56 in 1994 to alkaline (7.32 and 7.09 in 1995 and 1996, respectively). Although the 1998–2000 samples in Qinghai (Table 2) were heavily polluted, the natural dusts buffered the acids from anthropogenic sources so that acid rain could not be formed.

[9] On the basis of the preceding observations made on the Tibetan Plateau, we postulate that the original acidity of natural rains in many arid and semiarid areas should have been changed from alkaline to acidic since industrialization. To support this hypothesis, a number of approaches have been adapted, including using evidence from different areas of China and other places around the world, theoretical analysis and calculation, and laboratory experiments. Com-

pared to southern Chinese cities with serious acid rain problems, the emission rates of gaseous pollutants in Xining are higher. Nevertheless, there were no serious acid rain problems in Xining. In the heavy industrial cities located in the north and northeast of China, which are usually in semiarid areas or influenced by northwesterly winds, with higher air pollutant emission rates and concentrations, pH values of rainfall are always higher than those of the light industrial cities in southern China with wet subtropical climates [Zhao and Sun, 1986; Huang and Zhao 1987]. The spatial distribution maps for the 1997 and 1998 precipitation pH in China show that the areas with a pH higher than 7 occupy all of China's arid and semiarid areas, about half of the total Chinese territory (Nanjing Institute of Environmental Sciences, Annual report of environment, available at <http://www.nies.org>, 2000). Compared with the measurements of 1982 and 1983, the area with pH higher than 7 has decreased in the 1990s [Wang and Wang, 1995].

[10] Occasional, short-term and seasonal alkaline precipitation events have been observed from previous monitoring in many arid places, such as Israel and India and arid and semiarid areas of the United States, Africa, Spain, and other sites along the world's desert belts. Such events have been associated with African air trajectories and local dusts [Subramanian and Saxena, 1980; Felly and Liljestrand, 1983; Khemani et al., 1985; Mamane, 1987; Mamane et al., 1987; Avila and Alarcon, 1999; Goni et al., 2001]. In these areas the reason that long-term and constant alkaline rains have not been published may be due to the fact that the measurements were carried out in cities and after industrialization when the acid rain problem had already entrenched itself, and hence average  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  contents in rainwater are usually higher than those of Tibet and the early Qinghai measurements and of the global background locations [Galloway et al., 1982]. Alternatively, shortage of long-term alkaline rain records could be accounted for by the taking of short-term measurements perhaps because of financial constraints or because of the absence of a serious acid rain problem. Actually, the calculated mean pH values of rainfalls from most parts of the western United States were alkaline during the 1950s and 1960s [Liljestrand and Morgan, 1979], when there was a lack of direct measurement of pH. A most interesting case is that of the rainwater pH in Chembur, a highly industrialized area in the Bombay region, which was reported as being acidic (4.8) from 1974 to 1980, and which turned to a pH of 6–7 in response to effective pollution control measures [Khemani, 1993]. In fact, the precipitation pH values in all arid and semiarid lands around the world are generally higher than those of the surrounding wet areas in both industrialized and nonindustrialized areas.

[11] Another approach to certify our hypothesis is the calculation of the buffering ability of the bases from arid soils in rainwater. On the basis of a series of conditions described by Charlson and Rodhe [1982] pertaining to pH values of cloud water, a calculation has been conducted to determine how much  $\text{CaCO}_3$ , which is the major component of the dusts in arid areas, a sample will have to contain in order to raise cloud water pH to 7 (Table 3). The concentration range of  $\text{CaCO}_3$  given in Table 3 or an equivalent base cation can easily be found in most rainfall around the world. Morgan [1982] also indicated that a

**Table 3.** Calculated  $\text{CaCO}_3$  Concentration Required to Buffer a Liter of "Natural Rainwater" to the Alkaline Condition (pH = 7)

Natural Rain System <sup>a</sup>	"Original pH" Value	Required $\text{CaCO}_3$ , $\text{mg L}^{-1}$
Whole of the system	4.6	1.12
Absence of $\text{NH}_3$ , $\text{SO}_4^{2-}$ and $\text{SO}_2$	5.6	0.38
Absence of $\text{NH}_3$ (and $\text{NH}_4^+$ )	4.4	1.33
Absence of $\text{NH}_3$ and $\text{SO}_4^{2-}$	5.5	0.42
Absence of $\text{SO}_4^{2-}$	6.2	0.43

<sup>a</sup>The natural rain system represents a possible cloud in a remote, unpolluted area. The assumption is as follows:  $T = 5^\circ\text{C}$ ;  $L = 0.5 \text{ g m}^{-3}$  liquid cloud water;  $\text{CO}_2 = 340 \text{ ppmv}$ ;  $\text{SO}_2 = 100$  parts per trillion by volume;  $(\text{NH}_3 + \text{NH}_4^+) = 0.13 \text{ } \mu\text{g m}^{-3}$  as  $\text{NH}_3$ ;  $(\text{SO}_4^{2-})_{\text{aerosol}} = 1.0 \text{ } \mu\text{g m}^{-3}$ ; all dissolved in cloud [Charlson and Rodhe, 1982].

solution with  $10 \text{ } \mu\text{eq L}^{-1}$  dissolved  $\text{CO}_2$  and a pH of 5.7 has only  $10 \text{ } \mu\text{eq L}^{-1}$  of base-neutralizing capacity to prevent the raising of the pH of the solution up to 7.6. This calculation also implies that current rains in the world would have been much more acidic if there were no base alkali in the atmosphere.

[12] Consequent to the preceding observations it is important to check alkaline dust availability in the atmosphere. Generally, dust content on the Tibetan Plateau is not less than  $50 \text{ } \mu\text{g/m}^3$ . This value is also the lower limit of dust content for semiarid and arid areas. According to this low limit a liter of rainwater will contain 100 mg of dust in the rainout process when a cubic meter of cloud contains 0.5 g of water. During the washout process the rainwater will scavenge more dust. The atmospheric dusts on the Tibetan Plateau contain >20% by weight of  $\text{CaCO}_3$  in our samples. Therefore rainwater in arid and semiarid areas can get enough alkaline material from the atmosphere to buffer "natural rainwater" to an alkaline condition.

## 5. Conclusion

[13] In conclusion, on the basis of evidence from the world and the above calculations, plus the observations from Tibet, it is believed that the original precipitation of arid and semiarid regions in the world should be alkaline, which echoes the chemistry of soil-borne aerosols. Because of slow industrialization, low population density, and high altitude on the plateau the original alkaline state of rainwater chemistry of Lhasa city in the 1987–1988 period was largely preserved. The recent measurements reported herein for Tibet and other arid and semiarid areas only represent the situation after development and associated pollution. Because 33.5% of the Earth's land surface is occupied by arid and semiarid regions and dust transportation by global atmospheric circulations has influenced the precipitation pH of many areas (G. R. Carmichael and R. Arndt, Baseline assessment of acid deposition in northeast Asia, available at <http://www.nautilus.org/papers/energy/carmichaelESENAY1.html>, 2000), the change of precipitation from alkaline to acidic and the neutralization effect of dusts on rainfall pH cannot be ignored. The environmental consequences that are the result of such a change in precipitation pH in fragile arid and semiarid regions remain unknown and need to be investigated as soon as possible. This research also suggests that rainwater pH cannot be used as a sole indicator for air pollution in

arid and semiarid regions and that  $\text{HCO}_3^-$  measurement, which is not commonly adopted in acid rain measurement, is very important in less polluted areas.

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