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Chemical composition of precipitation in Shenzhen, a coastal mega-city in South China: Influence of urbanization and anthropogenic activities on acidity and ionic composition

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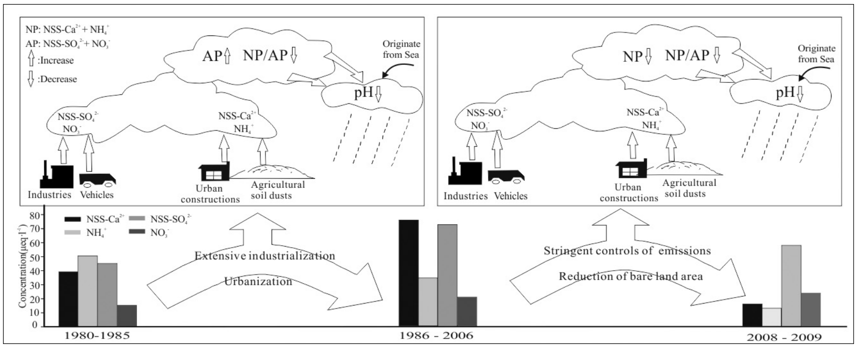
HIGHLIGHTS

- Rainwater chemical composition was studied for one year period in Shenzhen, a coastal mega-city in South China.
- The low NP/AP, ΔpH and NF value indicates that neutralization capacity of base cations was weak.
- Changes in anthropogenic activities at different stages of urban development can lead to synergistic changes in the chemical characteristics of atmospheric precipitation.
- The decline of alkaline species inputs could be an important reason for the acid rain situation in Shenzhen.

GRAPHICAL ABSTRACT



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ABSTRACT

Rainwater samples from Shenzhen in south China were collected over the period of a year, and the chemical compositions were measured with the main purpose of understanding the acidification of rainwater and the controlling factors. The pH value of precipitation ranged from 3.72 to 6.77, with a volume-weighted mean (VWM) value of 4.29, and the acid rain frequency was 97%. The VWM concentrations of anions and cations followed the order of $SO_4^{2-} > Cl^- > NO_3^-$ and $Na^+ > Ca^{2+} > NH_4^+ > Mg^{2+} > K^+$, respectively. Air mass back-trajectory and positive matrix factorization analyses indicated that sources of ions in rainwater were mainly from sea salt, soil dust and anthropogenic activities. Compared with other areas in China, the rainwater of Shenzhen has the lowest values of the NP/AP, ΔpH and NF values of Ca^{2+} and NH_4^+, indicating that the lack of the capacity for neutralization could be the main reason for the severe acid rain problem. It is noteworthy that the rain acidification tendency is obvious, and the pH value has reduced by 1.0 units since the 1980s. Based on a comparison of the chemical compositions of the rainwater from different historical periods, the NO_3^- concentration was found to have increased consistently, whereas the NH_4^+ concentration maintained a decreasing trend since 1980. On the other hand, the nss-SO_4^{2-} and nss-Ca^{2+} concentrations increased after 1980 and then decreased after 1994. Meanwhile, the decreasing pH was accompanied by a decreasing NP/AP ratio. These results suggest that the changes in human activities at different stages of urban development can lead to a synergistic change in the chemical characteristics of

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precipitation. Both an increase in the acidic species emissions (especially NO_X) due to rapid economic development and a decrease in the alkaline ions concentration due to urbanization have resulted in the rain acidification tendency in Shenzhen.

1. Introduction

As a global environmental problem, acid deposition can affect the soil, aquatic ecosystems, forests, and human health (Menz and Seip, 2004; Rice and Herman, 2012). China has become the third acid deposition region after North America (Barrie and Hales, 1984; Heuer et al., 2000; Ito et al., 2002) and Central Europe (Al-Momani et al., 1995; Avila and Alarcon, 1999) because of the increase in its economic development and energy consumption. According to the China Environmental Bulletin (2015), most Chinese cities suffered from acid rain, and approximately 100 out of 480 Chinese cities had an acid rain frequency that exceeded 25%, and 61 of them had an acid rain frequency that exceeded 50% in 2015. Moreover, despite the reportedly lower concentrations of the acidic species SO_4^{2-} and NO_3^- in the southern region of China compared to those in the northern region (Zhang et al., 2007b; Xiao et al., 2013; Zhao et al., 2013), the areas that are seriously affected by acid deposition are located mainly in developed cities in South China.

The composition of rainwater depends on the particulate or gaseous atmospheric constituents that are emitted locally or are transported from distant sources by natural or anthropogenic sources (Larssen and Seip, 1999; Migliavacca et al., 2005; Lu et al., 2011; Gioda et al., 2013). In recent decades, the rapid economic growth and urbanization in China have been accelerated by industrial development and urban construction, which has led to increased usage of fossil fuels, decreased agricultural activities and decreased open land (Tang et al., 2010; Xiao et al., 2013). Thus, urbanization and anthropogenic activities have had significant impacts on the acidity and chemical compositions of rainwater. Most studies on the acid deposition in South China have focused on the distribution of pH and the causes of acid rain (Zhao et al., 1988; Tu et al., 2005; Cao et al., 2009; Wang and Han, 2011). Few studies have been published regarding the impact of urbanization and anthropogenic activities on the precipitation acidity and neutralization in South China. Moreover, although a national control measure known as the Two Control Zone (TCZ) was enacted in 1998 with the aim to reduce acid rain and SO_2 emission, areas in southern China are still suffering from severe acid deposition (Liu et al., 1998; Zhang et al., 2007b). Therefore, the precipitation acidity and the chemical composition and their relationship with urbanization are still serious environmental problems of major concern in China.

Shenzhen is located in the Pearl River Delta region in South China, which is one of the most developed regions and is noted for its rapid urbanization and economic development. It became the first Special Economic Zone in China in 1980 and has been transformed from an agricultural area into an international mega-city over the past decades. The GDP of Shenzhen reached 2.24 trillion RMB in 2017 with its aggregate economic volume ranking fourth in Chinese cities, and the population increased from 330,000 to 12,530,000. Rapid economic growth over the past few decades has been accompanied by deteriorated air pollution (Huang et al., 2010; Zhang et al., 2008). The pH of the precipitation in Shenzhen showed a significant decreasing trend during the period 1986–2006 (Huang et al., 2008b). The aim of this paper is to probe the acidity and chemical composition of precipitation, to identify the possible sources of chemical species, to explore changes of the relationship between the acidity and chemical composition, and, finally, to gain an understanding of the causes of the rain acidification tendency in Shenzhen, which is a representative area to study the acidification of precipitation as a result of intense anthropogenic activities and fast urbanization.

2. Methods

2.1. Location and sampling

Shenzhen (22°27′-22°52′ N, 113°46′-114°37′ E), which is adjacent to the South China Sea, is located in the southern region of Guangdong Province and has an area of 1997 km^2 (Fig. 1). The city features a subtropical monsoon climate with a mean annual temperature of 22.4 °C and an annual rainfall of 1933 mm. The wind blows from the south and the east and brings abundant rainfall to the region. Most of the rainfall events occur during summer, while other seasons are relatively cool and dry. The rainwater samples were collected in the Daya Bay Eco-station (22°33′ N; 114°31′ E) of Shenzhen. A total of 59 rainwater samples were collected from June 2008 to May 2009. The total precipitation of the rainfall events that were measured for this study was 1715 mm, which accounted for approximately 74% of the total precipitation of the sampling period. The rainwater samples were collected from the beginning of each rain event using a polyethylene bucket with a polyethylene lid. It was located approximately 120 cm above the roof of a building in the Daya Bay Eco-station. Prior to use, the collector and container were pre-cleaned with hydrochloric acid (2–3 M) and were rinsed thoroughly with Milli-Q water. To prevent contamination by dry deposition, the collector was covered by a lid, which was removed just before the onset of rainfall.

2.2. Sample analyses

Water chemistry analyzing was conducted in the hydrochemistry and environmental laboratory at the Institute of Geology and Geophysics, Chinese Academy of Sciences. The pH values were measured immediately after sample collection at the sampling site with a portable pH metre (HANNA HI98129, Italy). The rainwater samples were then filtered through 0.22 μm Millipore membrane filters using a pre-cleaned Nalgene filter apparatus, and the filtrate was separated into two aliquots. One was stored directly in a 50 ml pre-cleaned polyethylene bottle for the determination of anions, while the other was acidified with ultra-purified nitric acid to a pH <2 and was stored in a pre-cleaned 200 ml polyethylene bottle for the determination of cations. The concentrations of the major anions (NO_3^-, SO_4^{2-} and Cl^-) were measured by using ionic chromatography (Dionex DX-120, USA), and the concentrations of the major cations (Na^+, Ca^{2+}, Mg^{2+} and K^+) were determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES) (IRIS Intrepid II XSP, USA). The NH_4^+ concentration was determined by spectrophotometry using the Nessler method. A reagent and procedural blanks were determined in parallel to the sample treatment, and the analytical precision was better than ±5%. The volume-weighted mean (VWM) of ionic constituents in rainwater was calculated as $X_{VWM} = (X_1P_1 + X_2P_2 + \ldots\ldots + X_nP_n) / (P_1 + P_2 + \ldots\ldots + P_n)$, where X_i is the concentration of the ions, P_i and n are the rain amount for each rainy event (in mm) and the total number of rainfall events, respectively (Sequeira and Lai, 1998). The equivalent ratio of the total anions to total cations (Σanions/Σcations) has been regarded as an indicator of the completeness of the measured major constituents (Al-Khashman, 2005). Data are generally considered to be acceptable if the ratio is within the range of 1 ± 0.25 (Keene et al., 1986). The ratio in the present study is 1.05, which suggested that all of the major components in the sampled rainwater were identified and measured for discussion.

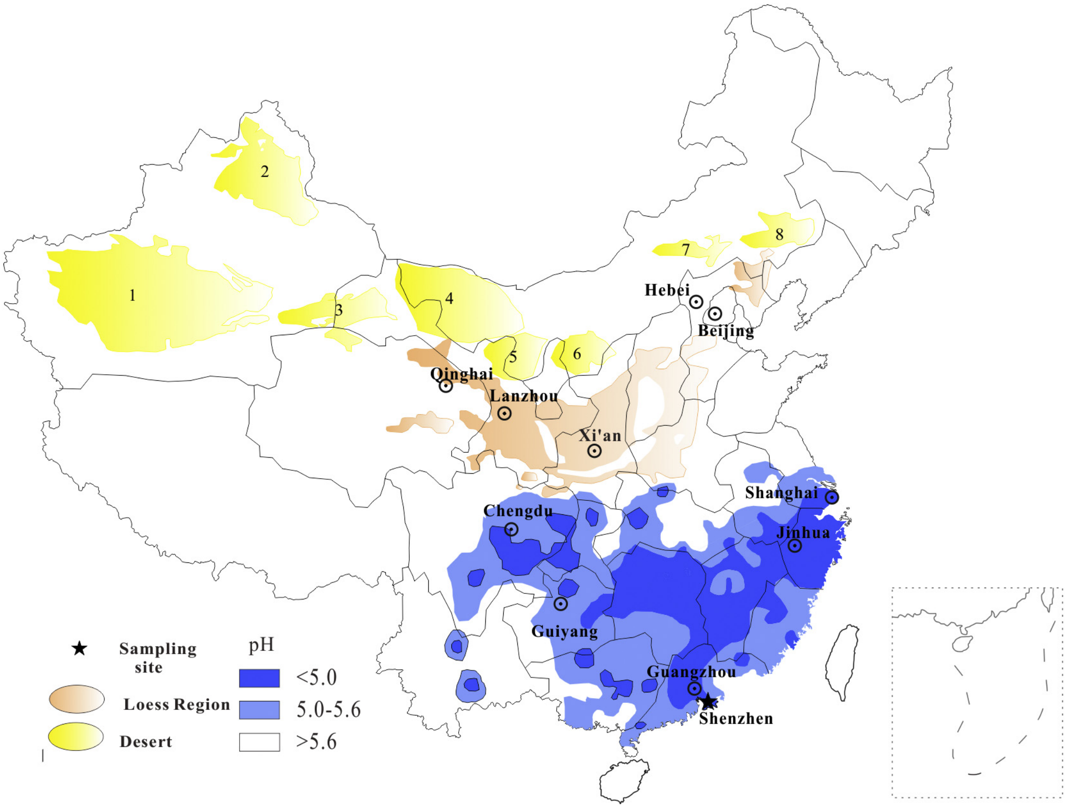

Fig. 1. Sketch map showing the location of the sampling site (Shenzhen) and other areas and the distribution of desert and loess areas and precipitation acidity during 2008 in China. 1. Taklimakan Desert; 2. Gurbantonggut Desert; 3. Kumtag desert; 4. Badain Jaran Desert; 5. Tengger desert; 6. Muus Desert; 7. Hunshandake Desert; 8. Khorchin Desert. This map is modified after Xu and Han (2009).

3. Results

3.1. Chemical composition

The pH value, the major ions concentration, the calculated VWM concentration and the statistical analyses are presented in Table S1, and the annual percentage distribution of the ionic compositions in rainwater are presented in Fig. 2, respectively. These charts show that the concentrations of the ionic species in the precipitation decreased in the order of $SO_4^{2-} > H^+ > Cl^- > Na^+ > NO_3^- > Ca^{2+} > NH_4^+ > Mg^{2+} > K^+$. The most abundant anion was SO_4^{2-}, with a VWM concentration of 59.3 μeq l^{-1}, which accounted for 46% of the total anions. Cl^- was another abundant anion, with a VWM concentration of 45.9 μeq l^{-1}, which accounted for 36% of the total anions. Among the cations, H^+ and Na^+ were predominant. The VWM concentrations of H^+ and Na^+ were 51.7 and 36.4 μeq l^{-1}, accounting for 38% and 27% of the total cations, respectively. In addition, the VWM concentrations of Ca^{2+} and NH_4^+ appeared to be low in the precipitation, with the values of 18.1 and 14.7 μeq l^{-1}, respectively.

3.2. pH of rainwater

Due to the dissolution of atmospheric CO_2 in rain droplets, the natural rainwater in a clean atmosphere is considered to be weakly acidic, with the reference level of 5.6 (Charlson and Rodhe, 1982). Precipitation with a pH lower than 5.6 was considered to be acid rain. The pH of the collected rainwater varied from 3.72 to 6.77 with the VWM value of 4.29. The percentage frequency distribution of the pH for the rainwater samples is plotted in Fig. 3. Approximately 14% of the rainwater samples with pH < 4.0, and 93% of the rainwater samples with pH < 5.0 indicate a severe acid rain problem in the study area. The pH of precipitation is generally determined by the types and relative proportions of acids and bases in the solution. The rainwater acidity can be regulated by the relative contributions of the basic components (e.g., nss-Ca^{2+}, NH_4^+) and the acidic components (e.g., nss-SO_4^{2-}, NO_3^-) (Fujita et al., 2000; Larssen and Carmichael, 2000). Compared with other areas in

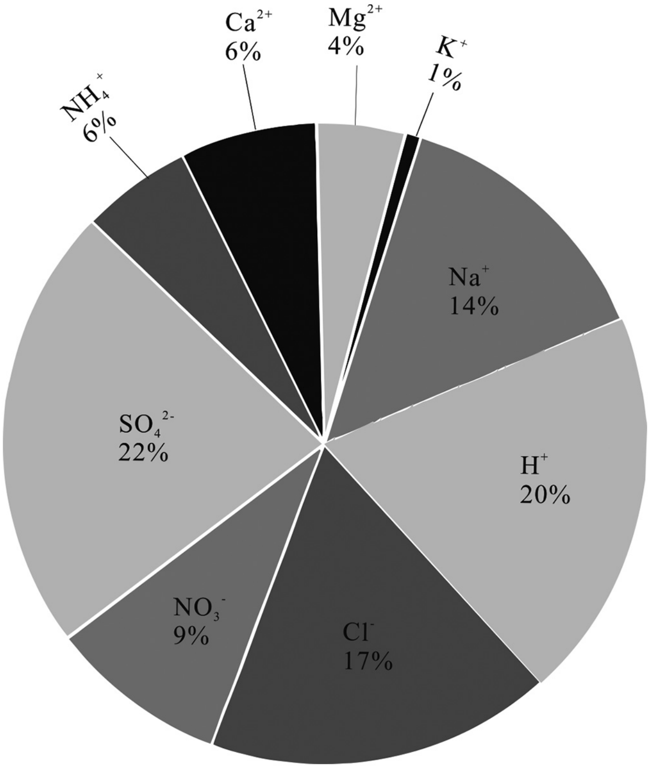

Fig. 2. Chemical composition percentages of rainwater in Shenzhen.

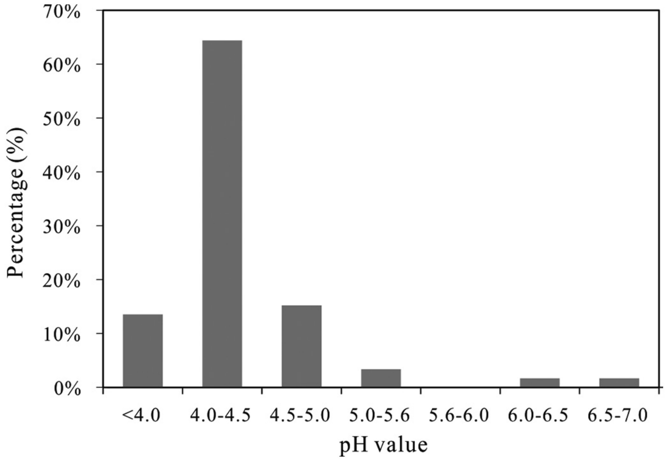

Fig. 3. Frequency distribution of the pH values of rainwater in Shenzhen during the sampling period.

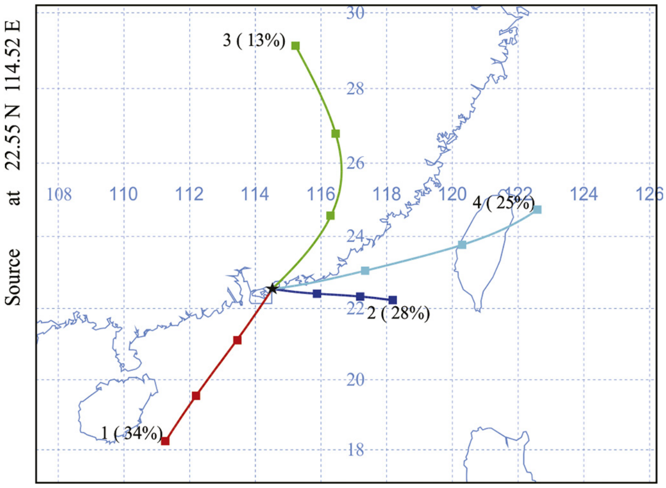

Fig. 4. Mean directions of air masses during the sampling period in Shenzhen.

China (Table 1), the pH value and the concentrations of NO_3^- and SO_4^{2-} of rainwater in Shenzhen were the lowest. Meanwhile, the basic ionic concentrations (Ca^{2+} and NH_4^+) of the rainwater were also the lowest. Thus, it is obvious that the content of acidic components is not the only reason for the low pH value of rainwater in Shenzhen.

3.3. Seasonal variation of the chemical composition

Due to the influence of the monsoon climate, the precipitation happens mainly during the rainy season (April–August). The seasonal VWM concentrations of the major ions are depicted in Table 2. There were obvious seasonal differences in the VWM concentrations of ionic components. All of the VWM concentrations of the major ions were higher in the dry season (DS) than in the rainy season (RS). The accumulation effect of particulate matter and the weak dilution effect of rainfall during the DS due to less rainfall could be the reason for the relatively higher ionic concentrations of rainwater in the DS. In addition, there was no obvious seasonal variation in the VWM pH value (RS = 4.31, DS = 4.12).

4. Discussion

4.1. Sources of major ions

4.1.1. Trajectory analysis

The potential source regions of air that may affect the chemical composition of rainwater can be determined from the air mass back trajectories (Huang et al., 2008a; Wu et al., 2016). The back-trajectories were calculated and clustered at the sampling site by using the NOAA HYSPLIT4 Model and the GDAS meteorological data obtained at 1000 m above ground level. Four major trajectory clusters were classified for Shenzhen during the sampling period (Fig. 4). Most of the air masses came from southwest, east and northeast and passed through areas of the South China Sea and the Pacific Ocean. These air masses were clean and contained a large amount of moisture, which brings a great quantity of rainfall to the sampling site. The back-trajectory analysis indicates that the proportion of chemical components that were derived from continent in the precipitation was the lowest among all the

Table 1
Comparison of pH and major ions concentration (in μeq l^{-1}) at Shenzhen with other areas in China.

Area	pH	Cl^- (μeq l^{-1})	NO_3^- (μeq l^{-1})	SO_4^{2-} (μeq l^{-1})	NH_4^+ (μeq l^{-1})	Ca^{2+} (μeq l^{-1})	Mg^{2+} (μeq l^{-1})	K^+ (μeq l^{-1})	Na^+ (μeq l^{-1})	References
Shenzhen	4.29	45.9	23.7	59.3	14.7	18.1	11.8	1.98	36.4	This study
Guangzhou	4.49	86.8	53.4	163	70.6	104	17.0	32.9	55.0	Cao et al. (2009)
Shanghai	4.49	58.3	49.8	200	80.7	204	29.6	14.9	50.1	Huang et al. (2008a)
Jinhua	4.54	8.51	31.2	95.2	81.1	47.9	3.45	4.73	6.27	Zhang et al. (2007b)
Beijing	5.32	67.8	139	270	174	291	38.5	6.69	8.51	Xu et al. (2012)
Hebei	5.29	67.6	130	230	88.1	273	84.7	14.9	18.2	Wu et al. (2016)
Qinghai	7.10	48.8	48.1	84.0	161	314	37.9	69.2	96.6	Zhang et al. (2003)
Lanzhou	7.70	27.9	74.4	208	57.2	886	46.5	7.26	12.3	Xu et al. (2009)
Xi'an	6.64	38.7	129	490	230	426	36.6	13,8	31.1	Lu et al. (2011)
Chengdu	5.10	8.90	156	213	151	197	16.2	6.60	1.40	Wang and Han (2011)
Guiyang	4.90	9.80	39.6	238	77.0	218	18.6	11.1	1.80	Han et al. (2011)

Table 2
Seasonal variations of the VWM concentrations of the major ions in the rainwater from Shenzhen.

Season	Rainfall (mm)	pH	Cl^- (μeq l^{-1})	NO_3^- (μeq l^{-1})	SO_4^{2-} (μeq l^{-1})	NH_4^+ (μeq l^{-1})	Ca^{2+} (μeq l^{-1})	Mg^{2+} (μeq l^{-1})	K^+ (μeq l^{-1})	Na^+ (μeq l^{-1})
Rainy season	1535	4.31	43.7	21.8	56.1	14.5	17.2	11.0	1.84	34.3
Dry season	180	4.12	64.2	39.9	86.8	16.1	25.6	18.5	3.13	54.6

contributors. Meanwhile, due to the wetter weather and the high vegetation coverage in southern China, the soil dust contribution for the alkaline components to atmosphere was considered to be very limited (Wang, 1994; Wang and Wang, 1995). Thus, the alkaline constituent contribution that originated from both the remote transport of soil dust and the local soil are considered to be less important compared to the impact of human activities, which could be the dominant factor controlling the alkaline species content in the precipitation as well as the rain acidity.

4.1.2. Source contributions

Sea salts, terrestrial dust, anthropogenic emissions and biogenic material were recognized as the main contributors for ions in precipitation (Roy and Negrel, 2001; Chetelat et al., 2005; Négrel et al., 2007;Zhang et al., 2007a). The chemical compositions of rainwater are used to reflect the relative contribution of the elements from these reservoirs (Safai et al., 2004). The positive matrix factorization (PMF) has been used to examine the potential sources of elements in precipitation (Anttila et al., 1995; Juntto and Paatero, 2010; Dumka, 2016). The PMF analysis requires only concentration data and the associated uncertainties of the precipitation samples (Hopke, 2016). Here, US EPA's PMF version 5.0 was applied to identify the possible sources of the ionic species in rainwater. Three factors provided good fits to the data based on the distributions of scaled residuals and the physically interpretable source contribution profiles. The chemical stacked source profiles extracted by PMF 5.0 are provided in Fig. 5. The uncertainty values that are associated with ionic species were calculated using the method described by Anttila et al. (1995).

As Fig. 5 shows, factor 1 (F1) represents the sea salt. The contributions of Mg^{2+} (69.1%), Cl^- (79.8%) and Na^+ (86.3%) were high, which implied the influence of marine aerosols. Factor 2 (F2) explains 80.4% of the Ca^{2+}. This factor can be interpreted as the contributions from dusts (including both natural and anthropogenic inputs). Inorganic species (SO_4^{2-}, NO_3^- and NH_4^+) were important constituents in Factor 3

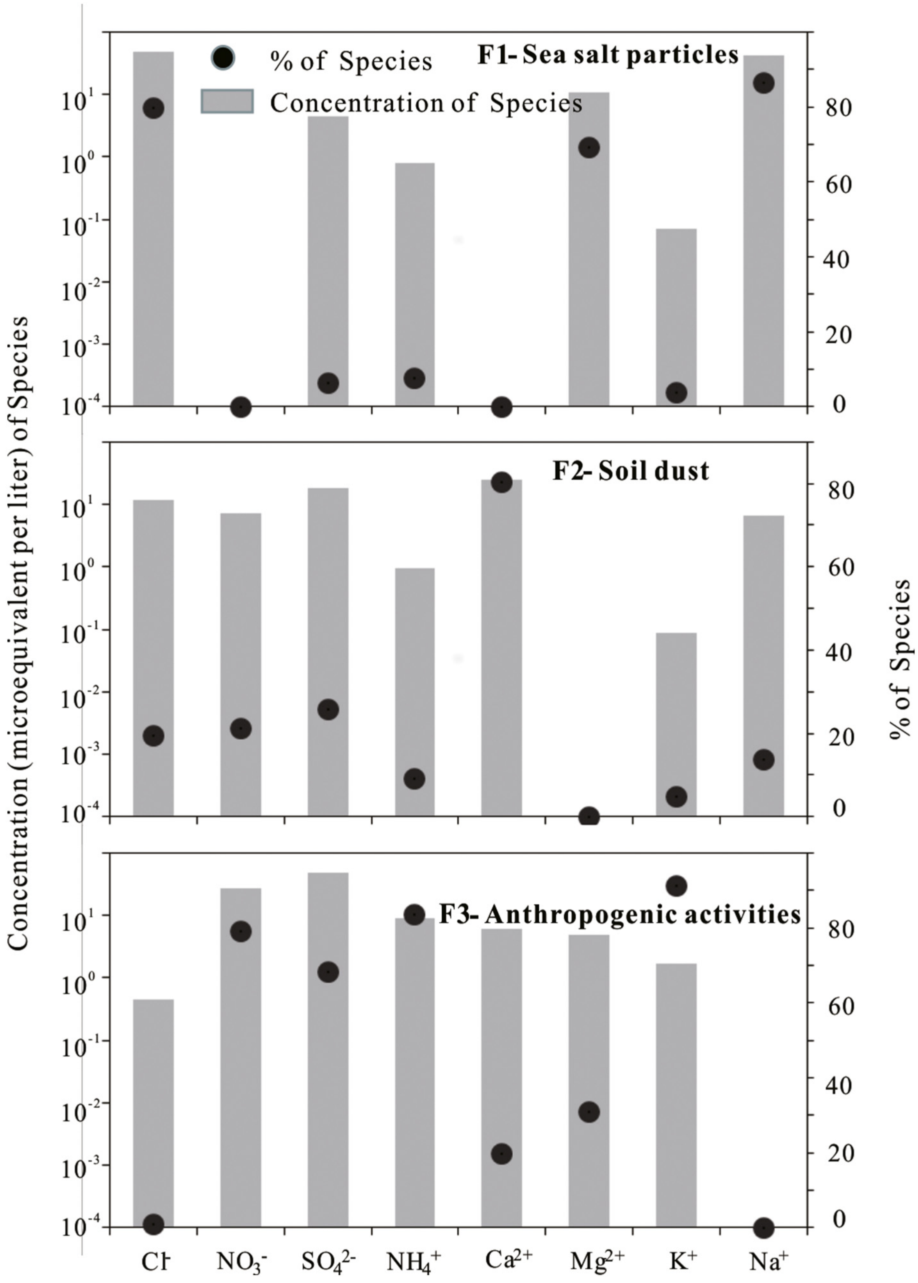

Fig. 5. PMF-extracted source profile of chemical constituents in rainwater. Points represent the contributions of a factor to the total species concentrations.

(anthropogenic activities), with high explained variations of SO_4^{2-} (66.8%), NO_3^- (75.9%), and NH_4^+ (75.4%). These species are markers of secondary aerosol particles [NH_4NO_3 and $(NH_4)_2SO_4$] that formed from the oxidation of SO_X and NO_X (Rao et al., 2016). SO_4^{2-} and NO_3^- originate mainly from the combustion of fossil fuel, while NH_4^+ originates from agricultural activity and biomass burning (Dentener and Crutzen, 1994; Zhao and Wang, 1994; Zhang et al., 2012).

4.2. Controlling factors of acidification

4.2.1. Acid neutralization

In general, the acidity of rainwater is controlled mainly by the concentration of acidic ions (e.g., NO_3^- and SO_4^{2-}). As discussed above, the rainwater from Shenzhen has the lowest pH value compared with that of other areas in China (Table 1). However, the concentrations of NO_3^- and SO_4^{2-} are also the lowest. This indicates that the content of acidic ions is not the main reason for the low pH value of rainwater in Shenzhen. Previous studies have pointed out that the rainwater acidity can also be affected by the contents of basic ions (Ca^{2+} and NH_4^+) in the rainwater (Larssen and Carmichael, 2000; Wang et al., 2002; Wang et al., 2012; Wu et al., 2013; Wu et al., 2016). The rainwater acidity and the relationship between the acidic and basic components can reflect the intensity of neutralization. To assess the neutralization capacity of the basic components, the ratio of the neutralizing potential to the acidifying potential (NP/AP) was employed as suggested by Fujita et al. (2000):

$$NP/AP = \left[nss{-}Ca^{2+} + NH_4{}^{+}\right] / \left[nss{-}SO_4{}^{2-} + NO_3{}^{-}\right] \tag{1}$$

where the value of [nss-Ca^{2+} + NH_4^+] is considered to be the neutralizing potential (NP), and [nss-SO_4^{2-} + NO_3^-] is considered to be the acidifying potential (AP). The non-sea salt (NSS) values of different ionic species were calculated from the measured element concentrations by using sodium as the reference element and assuming that all sodium is derived from marine sources (Keene et al., 1986). Non-sea-salt fraction ion concentrations were given by $NSS_X = [X]_{rainwater} - [Na^+]_{rainwater} \times ([X] / [Na^+])_{seawater}$, in which X denotes the measured ion.

The calculated results of nss-Ca^{2+}, nss-SO_4^{2-}, NP, AP and NP/AP of rainwaters in Shenzhen and other areas in China are presented in Table 3. The equivalent ratio of the NP/AP of the rainwater from cities in northwest China (Qinghai = 3.91, Lanzhou = 3.36) was obviously higher than that of other regions, which reflects the intense neutralization capacity of the basic components (mainly $CaCO_3$) that were derived from soil dusts in northwest China (Wang and Wang, 1995; Huang et al., 2009; Xu et al., 2009). However, the equivalent ratio of NP/AP in Shenzhen was the lowest, with the value of 0.40, which indicated that the basic components were not sufficient to neutralize the acidity of the rainwater.

Table 4
The value of neutralization factor (NF) of rainwater from Shenzhen and other areas in China.

Area	NF(Ca^{2+})	NF(NH_4^+)	NF(Mg^{2+})	NF(K^+)
Shenzhen	0.21	0.19	0.05	0.02
Guangzhou	0.48	0.34	0.02	0.15
Shanghai	0.83	0.33	0.07	0.06
Jinhua	0.38	0.65	0.02	0.04
Beijing	0.71	0.43	0.09	0.02
Hebei	0.76	0.25	0.23	0.04
Qinghai	2.57	1.34	0.13	0.56
Lanzhou	3.15	0.20	0.16	0.02
Xi'an	0.69	0.37	0.05	0.02
Chengdu	0.53	0.41	0.04	0.02
Guiyang	0.78	0.28	0.07	0.04

To determine the degree of neutralization of the acidity, ΔpH is computed as:

$$\Delta pH = pH - pAi \tag{2}$$

where pAi is the estimated pH. The pAi equals the measured pH when no neutralization has occurred (Hara et al., 1995), and the pAi can be calculated by the following equation:

$$pAi = -\log\left[nss{-}SO_4{}^{2-} + NO_3{}^{-}\right] \tag{3}$$

Thus, the differences (ΔpH) between the measured pH and the estimated pH (pAi) can be taken as the evaluation index of the acid-neutralization capacity. The calculated results of pAi and ΔpH are presented in Table 3. Compared with the calculated data from other areas in China, the ΔpH of rainwater from Shenzhen was also the lowest. The ΔpH of rainwater from Shenzhen is only 0.18, which reflects a very weak neutralizing capacity of the basic cations in the rainwater.

To evaluate the neutralization percentage of basic cations in rainwater, the neutralization factor (NF) was calculated by the following equation (Possanzini et al., 1988):

$$NF_{Xi} = [X_i] / \left(\left[nss{-}SO_4{}^{2-}\right] + [NO_3{}^{-}]\right) \tag{4}$$

where X_i is the chemical composition of interest, with all of the ions expressed in μeq l^{-1}. The NF values of Ca^{2+}, NH_4^+, Mg^{2+} and K^+ in the rainwaters of Shenzhen and other areas in China are presented in Table 4. The NF values of Ca^{2+}, NH_4^+, Mg^{2+} and K^+ in the rainwater of the study area are only 0.21, 0.19, 0.05 and 0.02, respectively. Compared with other cities in China, the NF values of Ca^{2+} (NF(Ca^{2+})) and NH_4^+ (NF(NH_4^+)) in the rainwater of Shenzhen were the lowest, which indicated the weak neutralization resulting from the deficiency of alkaline constituents. Based on the calculated results of the NP/AP, ΔpH and NF

Table 3
The value of NP, AP, NP/AP and ΔpH of rainwater from Shenzhen and other areas in China.

Area	Shenzhen	Guangzhou	Shanghai	Jinhua	Beijing	Hebei	Qinghai	Lanzhou	Xi'an	Chengdu	Guiyang
nss-Ca^{2+} μeq l^{-1}	16.5	102	202	47.6	291	272	310	885	425	197	218
nss-SO_4^{2-} μeq l^{-1}	54.9	156	194	94.4	269	228	72.3	207	486	213	238
NP	31.2	172	283	129	465	360	471	943	655	348	295
AP	78.6	210	244	126	408	358	120	281	615	369	277
NP/AP	0.40	0.82	1.16	1.02	1.14	1.01	3.91	3.36	1.06	0.94	1.06
pH	4.29	4.49	4.49	4.54	5.32	5.29	7.10	7.70	6.64	5.10	4.90
pAi	4.11	3.68	3.61	3.90	3.39	3.45	3.88	3.55	3.21	3.43	3.56
ΔpH	0.18	0.81	0.88	0.64	1.93	1.84	3.22	4.15	3.43	1.67	1.34

nss-Ca^{2+} = $[Ca^{2+}]_{rainwater} - [Na^+]_{rainwater} \times ([Ca^{2+}] / [Na^+])_{seawater}$; nss-$SO_4^{2-}$ = $[SO_4^{2-}]_{rainwater} - [Na^+]_{rainwater} \times ([SO_4^{2-}] / [Na^+])_{seawater}$; NP/AP = [nss-$Ca^{2+}$ + NH_4^+] / [nss-SO_4^{2-} + NO_3^-]; pAi = −log [nss-SO_4^{2-} + NO_3^-]; ΔpH = pH − pAi.

(Ca^{2+}) and NF(NH_4^+) in the rainwater, the lack of a neutralization capacity could be the main reason for the severe acid rain in Shenzhen.

4.2.2. Temporal variations of the acidity and ions concentration

Shenzhen became the first special economic zone in China in 1980. It has undergone tremendous changes during the past several decades, transforming from an agricultural area into a cosmopolitan metropolis. During the development process, the rainwater pH value of Shenzhen has shown a significant downward trend since the 1980s. To understand the causes of the historical rapid decrease of rainwater acidity, we compiled the data from previous studies and compared the rainwater chemistry composition in Shenzhen among three contrasting different periods (1980–1985, data from Yang et al., 1996; 1986–2006, from Huang et al., 2008b; 2008–2009, this study) (Fig. 6).

The rainwater pH value of Shenzhen decreased from 5.22 in the period 1980–1985 to 4.29 during the period 2008–2009 (Fig. 6). The concentration of NO_3^- showed an increasing tendency accompanied by the continuously decreasing rainwater pH, which indicated that the contribution of HNO_3 to the rainwater acidity continues to increase. According to the Statistic Yearbook of Shenzhen (2009), there are a large number of chemical and motor industries and power plants located in Shenzhen and its surrounding areas. The total number of factories has reached approximately 10,000 and the number of vehicles reached 1,450,000 in 2009. As an important precursor of HNO_3, the emission of NOx from fossil fuel combustion during extensive industrialization and urbanization is regarded as an important factor of the increasing rainwater acidity in Shenzhen. Compared with the period of 1980–1985, the concentration of nss-SO_4^{2-} in the rainwater increased by 63% during the period 1986–2006 (Fig. 6). This is attributed mainly to the growing emissions of SO_2 during the economic booming (Wang and Xu, 2009). However, the concentration of nss-SO_4^{2-} dropped by approximately 21% during the period 2008–2009, compared with that of the period 1986–2006. According to Huang et al. (2008b), the concentration of SO_4^{2-} in the rainwater reached its peak in 1994. The nss-SO_4^{2-} concentration reduction may be attributed mostly to the emission control policy. To suppress the development of acid rain, China issued the “Atmospheric Pollution Prevention and Control Act of the People's Republic of China” in 1995 (Tang et al., 2010). Moreover, a more stringent control measure known as the “Two Control Zone” was enacted in 1998, with the aim to reduce acid rain and the SO_2 emission.

Among the alkaline ions, the concentration of NH_4^+ in the rainwater showed a significant decreasing trend (Fig. 6). According to the ammonia emission inventory, the main ammonia emitters are agricultural activities, while the ammonia contribution of human activities and industries to the atmosphere are minor in Shenzhen (Yin et al., 2010; Huang et al. 2012). Therefore, the decrease of agricultural activities during extensive urbanization may be the main cause of the continuous decrease of NH_4^+ concentration (Huang et al., 2008b). The concentration of nss-Ca^{2+} increased by 96% during the period 1986–2006, compared with the period 1980–1985 (Fig. 6). The concentration of nss-Ca^{2+} in the rainwater also reached its peak in 1994 (Huang et al., 2008b). The substantial increase of nss-Ca^{2+} in this period may have resulted from intense urban construction activities, e.g., cement factories, buildings, thermal power plants, traffic, etc. Larssen and Carmichael (2000) reported the Ca^{2+} deposition in China and argued that the southern region is not heavily influenced by the soil dust that is transported from deserts and loess soils in northern China, but the influence of locally emitted dust (e.g., due to agriculture, construction, fly ash) in the southern region should be considerable. Compared with the period 1986–2006, the concentration of nss-Ca^{2+} decreased by 79% during the period 2008–2009 (Fig. 6). According to the Statistic Yearbook of Shenzhen in 2007 (Shenzhen Statistical Bureau, 2007), the concentration of total suspended particulates in ambient air shows a descending trend. The decrease of the nss-Ca^{2+} concentration in the rainwater could be attributed to the stringent controls of industrial and urban dust emissions and the reduction of bare land area during urbanization (Tu et al., 2005; Huang et al., 2008b).

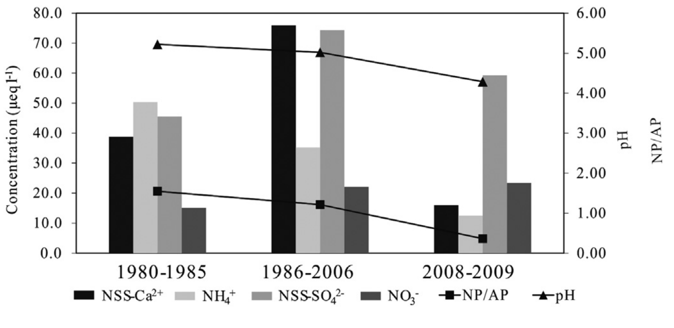

Fig. 6. Temporal variations of the pH value, the equivalent ratio of NP/AP, the acidic and alkaline ion concentrations during three different periods in Shenzhen. (1980–1985, data from Yang et al., 1996; 1986–2006, from Huang et al., 2008b; 2008–2009, this study).

The equivalent ratio of NP/AP showed decreasing trend during the three periods (Fig. 6), which reflected a decline in the contribution of alkaline species to precipitation relative to acidic species. Meanwhile, the pH values also showed a decreasing trend over the same time period. The good correlation between them ($R^2 = 0.99$) suggests that the acidification of the precipitation in Shenzhen was related to the reduced neutralizing capacity. Therefore, in addition to the increase of acidic ions (nss-SO_4^{2-} and NO_3^-) emissions due to rapid economic development, the decline of alkaline ions (nss-Ca^{2+} and NH_4^+) inputs due to urbanization and environmental protection measures could be another important mechanism for the acidification of precipitation in Shenzhen.

4.2.3. Comparison with other regions in China

From Tables 1 and 3, the acidic ions (nss-SO_4^{2-} and NO_3^-) concentrations of rainwater from Shenzhen, Guangzhou, Jinhua and Shanghai in southeast China are much lower than those of rainwater from Xi'an, Lanzhou, Beijing and Hebei in northern China, but their rainwater acidity levels are higher. Meanwhile, their alkaline ions (nss-Ca^{2+} and NH_4^+) concentrations are also much lower than those of rainwater from northern China. This indicates that the neutralization of alkaline ions has an important impact on the acidity of rainwater besides the content of acidic ions. The pH values of the rainwater in these areas have a similar tendency as the NP/AP ratios (Fig. 7), which confirms that the acidity of precipitation would be more or less neutralized by alkaline ions. The ΔpH values of the rainwater varied significantly and showed a descending trend, as follows: Lanzhou > Xi'an > Qinghai > Beijing > Hebei > Chengdu > Guiyang > Shanghai > Guangzhou > Jinhua > Shenzhen (Table 3). The NP/AP ratios and ΔpH decreased from the northwest to the southeast coastal area (Fig. 1), which indicated that the neutralizing capacity of basic cations decreased from the inland area to the coastal area in China. According to previous studies, the basic cations in the precipitation in northern China mostly come from alkaline substances in soil dusts that have been transported from deserts and semi-arid areas (Zhao et al., 1988; Xu and Han, 2009; Wang et al., 2012; Wu et al., 2013). However, for southeast China, where the climate regime is more humid than that of northern China, the soil is relatively wet, and the surface dust is not readily incorporated into the air. Hence, it is reasonable to infer that the contribution of the neutralizing components from soil dusts in northwest China is higher than that of southeast China (Huang et al., 2009). Meanwhile, the pH values of rainwater from these areas show a good positive correlation with the ΔpH value, with $R^2 = 0.96$ (Fig. 8). This further suggests that variations of precipitation pH in China were strongly influenced by the neutralizing capacity of alkaline constituents. In addition to the soil particles that were derived from the deserts and semi-arid areas of the continent, calcium is also emitted into the atmosphere through combustion processes and city infrastructure. Ammonia arise mainly from anthropogenic inputs, such as chemical fertilizer, livestock, and energy consumption. Therefore, even the soil environment and the sources of these alkaline

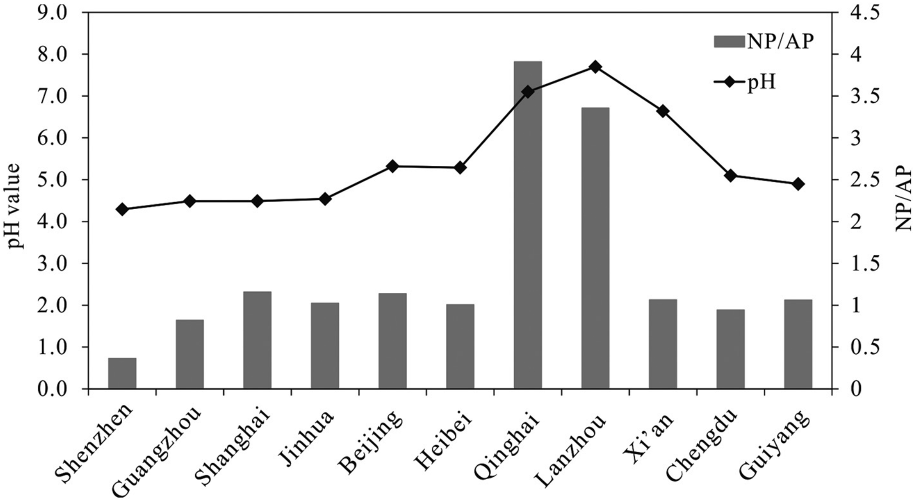

Fig. 7. Variations of the pH and the NP/AP ratio of precipitation in Shenzhen and other regions in China.

substances in China are variable, and a reduction of the neutralizing capacity due to the decrease of alkaline substances that resulted from natural and/or anthropogenic activity inputs is regarded as one of the main causes of the acidification of precipitation in Chinese cities.

Lateritic red soils and yellow soils are dominant in these regions, with a low Ca^{2+} concentration and a low buffering capacity (Tao et al., 2002). It is noteworthy that the ecosystem is relatively vulnerable because of the low soil buffering capacity in southeast China. Thus, the rapid acidification of precipitation will increase the potential for ecological and environmental risks. Serious environmental problems (water and soil acidification, release of potentially toxic aluminium, soil degradation, etc.) could occur there if rain acidification continues to increase due to the increase of acidic species emissions and the decrease of the neutralizing capacity. It is worthwhile to conduct further exploration on this topic.

5. Conclusions

Noted for its rapid urbanization and economic development, Shenzhen represents the typical changing course of the atmospheric environment of Chinese cities, especially in south China. The acidity and chemical composition of precipitation in Shenzhen were analysed between June 2008 and May 2009. The rainwater was typically acidic (with a VWM pH of 4.29), and 93% of the rainwater had a pH < 5.0, indicating a serious acid rain situation in the study area. Compared with other areas in China, values of the NP/AP ratio, ΔpH, NF(Ca^{2+}) and NF (NH_4^+) of the rainwater from Shenzhen were all the lowest, indicating a poor neutralization capacity due to deficiency in alkaline constituents in the rainwater. Based on the historical data analysis, the precipitation in Shenzhen has undergone rapid acidification since the 1980s. The precipitation pH showed a decreasing trend, from the value of 5.22 during the period 1980–1985 to 4.29 during the period 2008–2009. Meanwhile, the concentration of NO_3^- in the rainwater showed a continuously increasing tendency. Compared with the period of 1980–1985, the concentration of nss-SO_4^{2-} in the rainwater also increased by 63% and 30% during the periods 1986–2006 and 2008–2009, respectively. The increase of acidic species (nss-SO_4^{2-} and NO_3^-) emissions due to rapid economic development is one of the causes of rain acidification in Shenzhen. Meanwhile, with stringent controls on industrial and building dust emissions, the reduction of bare land area and agricultural activities due to urbanization processes in recent decades, the input of alkaline ions (nss-Ca^{2+} and NH_4^+) to the rainwater is decreasing. Compared with the period 1986–2006, the concentration of nss-Ca^{2+} decreased by 79% during the period 2008–2009. The concentration of NH_4^+ in the rainwater has maintained a decreasing trend since the 1980s. Therefore, the decrease of the neutralizing capacity could be a nonnegligible mechanism for the severe acid rain situation in Shenzhen.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.01.096.

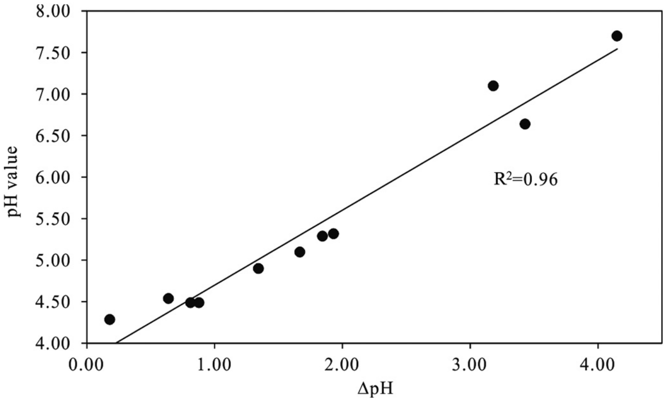

Fig. 8. Relationship between the measured pH and ΔpH for the rainwater of Shenzhen and other regions in China.

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