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Chemical characteristics, deposition fluxes and source apportionment of precipitation components in the Jiaozhou Bay, North China



Jianwei Xing ^{a,b}, Jinming Song ^{a,b,c,*}, Huamao Yuan ^{a,b,c}, Xuegang Li ^{a,b,c}, Ning Li ^{a,b,c}, Liqin Duan ^{a,b,c}, Baoxiao Qu ^{a,c}, Qidong Wang ^{a,c}, Xuming Kang ^{a,c}

^a Key Laboratory of Marine Ecology and Environmental Sciences, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c Function Laboratory of Marine Ecology and Environmental Sciences, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266237, China

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ABSTRACT

To systematically illustrate the chemical characteristics, deposition fluxes and potential sources of the major components in precipitation, 49 rainwater and snow water samples were collected in the Jiaozhou Bay from June 2015 to May 2016. We determined the pH, electric conductivity (EC) and the concentrations of main ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺, SO₄²⁻, NO₃⁻, Cl⁻ and F⁻) as well as analyzed their source contributions and atmospheric transport. The results showed that the precipitation samples were severely acidified with an annual volume-weighted mean (VWM) pH of 4.77. The frequency of acid precipitation (pH < 5.6) reached up to 71.4%, and the mean EC value was relatively higher at $64.9 \, \mu S \, cm^{-1}$, all of which suggested a higher atmospheric pollution level over the Jiaozhou Bay. Surprisingly, NH_4^+ (40.4%), which is higher than Ca²⁺ (29.3%), is the dominant species of cations, which is different from that in most areas of China. SO_4^{2-} was the most abundant anions, and accounted for 41.6% of the total anions. The wet deposition fluxes of sulfur (S) was 12.98 kg ha⁻¹ yr⁻¹. Rainfall, emission intensity and long-range transport of natural and anthropogenic pollutants together control the concentrations and wet deposition fluxes of chemical components in the precipitation. Non-sea-salt SO_4^{2-} and NO_3^- were the primary acid components while NH_4^+ and non-sea-salt Ca^{2+} were the dominating neutralizing constituents. The comparatively lower rainwater concentration of Ca^{2+} in the Jiaozhou Bay than that in other regions in Northern China likely to be a cause for the strong acidity of precipitation. Based on the combined enrichment factor and correlation analysis, the integrated contributions of sea-salt, crustal and anthropogenic sources to the total ions of precipitation were estimated to be 28.7%, 14.5% and 56.8%, respectively. However, the marine source fraction of SO_4^2 may be underestimated as the contribution from marine phytoplankton was neglected. Therefore, the precipitation components in the Jiaozhou Bay present complex chemical characteristics under the combined effects of natural changes and anthropogenic activities.

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1. Introduction

The chemical composition of precipitation is a sensitive indicator of atmospheric pollution as the precipitation plays an efficient role in removing particles and gases pollutants from the atmosphere (Al-Khashman, 2009; Laouali et al., 2012; Liu et al., 2013; Budhavant et al., 2014; Moreda-Piñeiro et al., 2014; Niu et al., 2014; Rao et al., 2016), by means of in-cloud scavenging and below-cloud washout (Duhanyan and Roustan, 2011; Huo et al., 2012; Kajino and Aikawa, 2015; Li et al., 2011). The chemical composition of precipitation depends upon various sources such as local natural sources (e.g., sea spray, soil-derived windblown dust, suspended road dust) (Đơrđević et al., 2005; Larssen et al., 1999; Mihajlidi-Zelić et al., 2006),

anthropogenic sources (e.g., coal-combustion, vehicle exhausts, agricultural production, biomass burning) (Migliavacca et al., 2005; Lu et al., 2011; Pauliquevis et al., 2012; Zhang et al., 2012; Xiao, 2016), as well as the long-range transport of soil dust and gaseous pollutants (Gioda et al., 2013; Li et al., 2011; Li et al., 2016). Sulfur dioxide (SO₂), nitrogen oxide (NO_x) and particles, which play crucial roles in controlling the chemical characteristics and acidification or neutralization process of rainwater (Huo et al., 2012; Singh et al., 2016; Roy et al., 2016), constitute the main body of atmospheric pollutants (Lu et al., 2011; Wu et al., 2012).

Acid rain, as the most remarkable form of acid deposition, has been a serious environmental issue that perplexes the world. East Asia, particularly China, has become the third region in the world suffering from acid rain badly following Northeast America (Galloway et al., 1976; Ito et al., 2002) and Central Europe (Avila and Alarcón, 1999) over the past several decades (Sun et al., 2010). The mineral acidity in rainwater is principally associated with the strong acids H₂SO₄ and HNO₃ that

^{*} Corresponding author at: Key Laboratory of Marine Ecology and Environmental Sciences, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China. *E-mail address:* jmsong@qdio.ac.cn (J. Song).

originating from NO_x and SO₂ gaseous precursors (Laouali et al., 2012). In Northeastern China, however, the extremely high ambient sulfate concentrations are not always accompanied by corresponding high acidities of rainwater, which is owing to the high values of alkaline ions (e.g., Ca^{2+} , NH_4^+) neutralize acidity in this region (Cao et al., 2013; Wang et al., 2012; Wu et al., 2013). In addition, it is well known that acid rain has a strong impact on the aquatic ecosystem (Larssen et al., 1999; Menz and Seip, 2004), as well as on the marine biogeochemical cycle of sulfur (S) and nitrogen (N) (Song, 2010). The study on the chemical characteristics of precipitation is conductive to assessing the effects of local multiple emission sources as well as the long-range transport of gases and particles on the ecosystem. Thus, the study on precipitation chemistry has being a research focus during the last two decades.

In China, as the severe acid rain condition resulted from extremely higher emissions of SO_2 and NO_x , the study on precipitation chemical characteristics has gained unprecedented attentions from the researchers, governments and the public. In the recent decade, the studies on inorganic chemistry of precipitation at urban, suburban, rural and mountain background sites of China has been widely conducted (Aas et al., 2007; Niu et al., 2014; Qiao et al., 2015; Li et al., 2016; Xu et al., 2015; Yang et al., 2012; Lu et al., 2011; Wu et al., 2012; Wu and Han, 2015; Li et al., 2015; Xiao, 2016; Zhao et al., 2013). However, the data on precipitation chemistry of the ocean is extremely limited, especially in the coastal waters (Song et al., 1994; Song and Li, 1997; Zhang et al., 2000; Zhang et al., 2007a; Zhang et al., 2011), let along in the Jiaozhou Bay. Thus, it is urgent to gain a detailed understanding of precipitation chemistry of the coastal waters that are significantly affected by anthropogenic perturbation.

Jiaozhou Bay (35°55′-36°18′N, 120°04′-120°23′E), which adjoins the southeastern of Shandong Peninsula, North China, is located in the west of the Yellow Sea (Fig. 1a). It is a typical semi-enclosed bay surrounded by the downtown of Qingdao, Jiaozhou and Huangdao district on three sides (Fig. 1b) and is deeply affected by both the natural change and anthropogenic activities (Sun and Sun, 2015). Qingdao, the biggest industrial city in Shandong Province, suffered from acid rain badly as there are heavy emissions of SO_2 and NO_x originating from fossil fuel combustion to meet the demand of fast-developing economy (Wang et al., 2006; Zhang et al., 2011). In addition, the agricultural production around the Jiaozhou Bay is also well-developed (ODMBS, 2015). Moreover, the Yellow Sea (including the Jiaozhou Bay) lies on the main trajectory of the East Asia sand-dust affecting the Northwest Pacific Ocean (Zhang et al., 2011). Therefore, both anthropogenic activities and crustal-derived dust as well as the sea are likely to exert strong effects on the composition of the atmosphere and further to affect the chemical composition of the precipitation in the Jiaozhou Bay.

To systematically probe the precipitation chemistry in the Jiaozhou Bay ecosystem, in the present study, one-year precipitation (including rainwater and snow water) samples were collected at a shore-based site along the Jiaozhou Bay from June 2015 to May 2016. The chemical characteristics, deposition fluxes as well as temporal variation of the major inorganic ions in the precipitation were also illustrated. Further, the relative contributions of sea-salt, crustal and anthropogenic sources were calculated. This research aims to provide a preliminary understanding of the formation mechanism and influencing factors of acid rain in the Jiaozhou Bay under the combined effects of marine, crustal and anthropogenic sources.

2. Materials and methods

2.1. Study area

The area of the Jiaozhou Bay is approximately 370 km² with an average depth of 7 m. The agricultural farmland is mainly distributed on the north of the Jiaozhou Bay, while there are extensive industrial district and residential guarters distributed on the eastern and western shores. Jiaozhou Bay is located in the North Temperate Monsoon Climate Zone with an annual mean temperature of 13.2 °C and an annual mean relative humidity of 70.4%. The relative lower humidity accompanied by the lower rainfall (mean 187 mm) occurs mainly in spring and winter (dry season), owing to the influence of cold and dry northwest monsoon. In summer and autumn (wet season), however, the humidity and rainfall (mean 558 mm) are high under the dual impacts of the North Pacific subtropical high and southeast monsoon. The southeaster and easterly are the prevailing winds in spring and summer with a relative lower average wind speed of 3.5 m s^{-1} , while in autumn and winter are northwester with relative higher average wind speed of 5.6 m s⁻¹ (Sun and Sun, 2015).

2.2. Sampling, chemical analysis and quality control

The shore-based sampling site (36°03'19.46"N, 120°20'25.11"E) (Fig. 1b) for precipitation is situated on the roof of a four-story building (15 m high) in the Institute of Oceanology, Chinese Academy of Sciences, where the linear distance to the nearest coastline is approximately 20 m. There is an excellent ventilation condition and no obvious obstruction stands nearby. The samples for each precipitation event were collected by an automatic sampler (DH-200, Qingdao-Shengding Inc., China), which was mounted at 1.5 m above the roof to avoid the influence of raised dust. The lid of the sampling bucket opened and closed automatically at the onset and end of precipitation event under the control of a wetness detector, preventing wet samples from being polluted by dry deposition (Shen et al., 2012). An automatic pluviometer was



Fig. 1. Geographical locations of the Jiaozhou Bay (a) and the sampling site (b). "•" represents the sampling site.

employed to record the rainfall (precision 0.5 mm) for each rain event, while the snowfall was measured using a clean standard measuring cylinder when the snow samples were thawed at room temperature. The samples with a rainfall amount <1 mm were discarded as the amount is insufficient for analysis (Bartoli et al., 2005). All samples were collected as soon as possible once the precipitation event stops. Eventually, a total of 49 valid precipitation samples (48 rainwater samples and 1 snow water sample) were obtained from June 2015 to May 2016. Prior to use and after each collection, the sampling buckets were carefully cleaned (i.e., soaked in 20% HNO₃ for about one day and rinsed several times with Milli-Q water, resistivity: 18.2 M Ω cm⁻¹) (Al-Khashman, 2009) and dried.

In the laboratory, the pH and electric conductivity (EC) were measured at once after each collection using a Multi-function Measuring Instrument (Orion Versa Star, Thermo Fisher Inc., USA), which was calibrated by standard buffer solutions of pH 4.00 and 7.00 with an accuracy of ± 0.01 (Niu et al., 2014), and also was calibrated against a reference potassium chloride (KCl) solution for EC before each measurement (Budhavant et al., 2014). Then, all samples were filtered through pre-cleaned and pre-weighted nucleopore membranes (0.45 µm). The filtrate were divided into two aliquots loaded into precleaned polyethylene bottles. One was used for anion measurement and the other was acidified with ultra-purified HNO₃ to pH < 2 for cation measurement (Xu et al., 2015). Then, the filtrate samples were stored at 4 °C in a refrigerator for ion analysis as soon as possible. The filter membranes load with particles were dried and used to calculate the concentrations of suspended particulate matter (SPM) in precipitation.

Major anions (SO_4^{2-} , CI^- , F^-) were determined by using an ionic chromatography (Dionex ICS-90, Dionex Co., USA), while major cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) were measured using ICP-AES (Thermo's IRIS Intrepid II) according to the procedures reported by Xu et al. (2015). NO_3^- and NH_4^+ were determined photometrically following the standard procedures using a Continuous Flow Analyzer (QuAAtro, Bran-Luebbe Inc., Germany). Reagent and procedural blanks were analyzed in parallel to the sample treatment using identical procedures. Those blank values were all below the detection limits. The analytical precisions were computed from repeated measurements of standard samples of ion species, and they were found to be ~5% for all ions. Meanwhile, field blank samples were also collected, stored and measured by the same methods as the precipitation samples. The final data were the blank corrected values as field blank values were subtracted from the measured values.

2.3. Ion balance

In this study, the ion balance check proved to be reliable based on the acceptable range (15-30%) set for samples that the sum ion concentration > 100 μ eq L⁻¹ by USEPA (United State Environmental Protection Agency) (Ayers, 1995). The equivalent concentration of hydrogen ([H⁺]) can be calculated by the determined pH values for each precipitation events. While for bicarbonate (HCO_3^-) , it was theoretically estimated using the formula suggested by Kulshrestha et al. (2003) that $[HCO_3^-] = 10^{(pH-5.05)}$. The regression analysis between the sum of anions $(SO_4^{2-}, NO_3^{-}, Cl^{-}, F^{-}, HCO_3^{-})$ and sum of cations (H^+, Na^+, K^+, K^+) Ca²⁺, Mg²⁺, NH₄⁺) was presented in Fig. 2. The extremely higher coefficient of determination (0.987) demonstrated a strong correlation between sum anions and sum cations, confirming the main anions and cations were sufficient to reach a good ion balance in this study (Okay et al., 2002). Moreover, the strong linear correlation between EC and the total ion concentration (R = 0.625) indicated the determination methods were credible (Shen et al., 2012). However, the equivalence ratio of the sum anions to sum cations was <1, revealing there may be anion deficiency (Yang et al., 2012). Given that the higher vegetation coverage around the Jiaozhou Bay, especially Qingdao City, the anions deficit might be ascribed to the exclusion of organic acids from the



Fig. 2. Linear regression between sum anions and sum cations.

measurements in this research (Akpo et al., 2015), like that reported by many researchers (Tiwari et al., 2012; Xu et al., 2015; Li et al., 2016).

2.4. Data analysis

The volume-weighted mean (VWM) concentrations (μ eq L⁻¹) and wet deposition fluxes (kg ha⁻¹) of main ions in precipitation were calculated by the equations below (Akpo et al., 2015):

$$C_{\text{VWM}}\left(\mu eq \ L^{-1}\right) = \sum_{i=1}^{n} (C_i \times P_i) / \sum_{i=1}^{n} P_i$$
(1)

$$WD(kg ha^{-1}) = C_{VWM}(\mu eq L^{-1}) \times M/V \times P_t/100,000$$
(2)

where C_{VWM} is the VWM concentration, C_i (µeq L⁻¹) and P_i (mm) are the measured ion concentration and the rainfall amount of individual precipitation event, respectively. *WD* refers to the seasonal/annual wet deposition flux expressed in kg ha⁻¹, *M* is the molar mass of ion, while *V* represents the absolute value of valence of corresponding ion, and P_t (in mm) is the seasonal/annual rainfall amount. The VWM of pH was calculated from the VWM concentrations of H⁺.

Supposing that all sodium origins from marine sources, then the non-sea-salt fraction (nss) value of any particular ion can be calculated using sodium as the reference element (Keene et al., 1986) by the following equations (Das et al., 2005; Roy et al., 2016; Rao et al., 2016):

$$[ss-X] = [Na^+]_{rainwater} \times ([X]/[Na^+])_{seawater}$$
(3)

$$[nss-X] = [X] - [ss-X] \tag{4}$$

where [ss-X] and [nss-X] refer to the concentrations of sea salt (ss) component and non-sea-salt (nss) component of the ion X, respectively; $[Na^+]_{rainwater}$ and $([X]/[Na^+])_{seawater}$ are the concentration of Na⁺ in samples and the ratio of ion X and Na⁺ concentration in seawater respectively (Keene et al., 1986), $[X]_{rainwater}$ is the measured concentration of ion X in samples.

To identify the potential sources of elements in precipitation, the enrichment factor (EF) was computed by comparing the elemental ratios measured in precipitation versus the ratios of elements present in the standard seawater (Okay et al., 2002). In this study, we choose Na⁺ as the reference elements for marine origin (Safai et al., 2004; Keene et al., 1986). The calculation formula can be described as follows:

$$EF(X)_{marine} = \left[X/Na^{+} \right]_{sample} / \left[X/Na^{+} \right]_{seawater}$$
(5)

where, X refers to the concentration of concerned ion, [X/Na⁺]_{seawater} is the ratio of seawater constituent mentioned above (Keene et al., 1986).



Fig. 3. Variation of individual rainfall amount during the sampling period.

3. Results and discussion

3.1. Rainfall, pH value and EC

The total rainfall during one year period was 866 mm, which is slightly higher than the annual averaged rainfall (745 mm) of Jiaozhou Bay (Sun and Sun, 2015). The individual and seasonal distribution of rainfall was not even as most of rainfall (72%) occurred in June–November 2015 (Fig. 3), which was defined as a wet season, including summer (June–August) and autumn (September–November). Similarly, December 2015–May 2016 was defined as a dry season as there was only a small portion of rainfall. It includes winter (December–February) and spring (March–May). This was consistent with the universal distribution characteristics of rainfall amount in the Jiaozhou Bay, as described in Section 2.1.

During the study period, the pH values for the individual precipitation in the Jiaozhou Bay ranged from 3.84 to 6.91 with an annual VWM of 4.77 (Table 1). In general, the unpolluted atmosphere corresponds to a rainwater pH value of ~5.6 owing to the dissolution of natural atmospheric CO₂ in undefiled rain droplets (Charlson and Rodhe, 1982). Therefore, the pH value of 5.6 is regarded as the threshold of acid rain widely (Das et al., 2005; Roy et al., 2016; Zhao et al., 2013). From this perspective, the atmosphere in the Jiaozhou Bay has been seriously polluted, which is also supported from the pH distribution exhibited in Fig. 4. Approximately 71.4% of the samples have the pH < 5.6, and up to 53% of those samples have the pH values in the scope of 3.5-5.0, suggesting a severe acidification of precipitation in the Jiaozhou Bay. That may be mainly due to the heavy emission of anthropogenic gaseous pollutants from Qingdao and the adjacent developed regions such as Beijing, Tianjin and the North China Plain. The detailed discussion can be seen in the following Section 3.5.3. Since the VWM pH value (4.73) in autumn was relatively lower together with a portion of more than two fifths (42.6%) of the total rainfall



Fig. 4. Distribution histogram of pH ranges and the corresponding frequencies in the precipitation of the Jiaozhou Bay. The numbers on the right of column represent the frequencies of corresponding pH ranges.

amount, the yearly acid wet deposition was mainly dominated by the rainfall in this season. Compared with the annual average value in Qingdao coastal region during 1997–2005 (VWM pH 4.81) (Zhang et al., 2011), the result in the present study is slightly lower. Nevertheless, the precipitation acidity in the Jiaozhou Bay was weaker than that in the Yellow Sea (VWM pH 4.59) and the East China Sea (VWM pH 4.37) (Zhang et al., 2011). That might be due to the lesser alkaline components in rainwater of these two regions (average rainwater concentrations for NH₄⁺ and Ca²⁺ in the Yellow Sea were 63.6 and 97.3 µeq L⁻¹, respectively; while in the East China Sea, these concentrations were 34.3 and 25.3 µeq L⁻¹, respectively; Zhang et al. (2007a)) as the longer distance to the originating areas of terrestrial dust soil (Zhang et al., 1999). Moreover, no apparent correlation was observed between the pH and rainfall (Fig. 5a), reflecting the minor effect of rainfall on the acidity of precipitation.

Another index of the pollution level of the atmosphere is the EC of precipitation (Yang et al., 2012), which is strongly impacted by rainfall amount. As shown in Fig. 5b, the EC values decreased rapidly with the increase of rainfall. The details of EC during the study period as shown in Table 1 also reflects the higher atmospheric pollution level in the Jiaozhou Bay comparing with a background site at Mt. Waliguan (mean 21.26 μ S cm⁻¹. Zhang et al., 2014), Northwest China, as well as the mountainous background sites such as the Yulong Snow Mountain (mean 11.5 μ S cm⁻¹, Niu et al., 2014), Southwestern China and the North Western Himalayan (mean 5.05 μ S cm⁻¹, Tiwari et al., 2012). Meanwhile, the VWM value of EC in this study is comparable to that in Beijing (66.5 μ S cm⁻¹, Yang et al., 2012). All of these indicated a bad air quality in the Jiaozhou Bay because of the substantial emissions of anthropogenic pollutants in surrounding cities and villages.

3.2. Chemical composition and acidic deposition

The descriptive statistics of the major precipitation chemical constituents together with their non-sea-salt fractions were listed in Table 1.

Table 1

Volume-weighted mean (VWM) concentrations of major ions (µeq L⁻¹), pH values (in unit) and electric conductivity (EC, in µS cm⁻¹) together with statistical results in the precipitation in the Jiaozhou Bay.

	pН	EC	Na ⁺	K^+	Ca ²⁺	${\rm Mg}^{2+}$	NH_4^+	SO_4^{2-}	NO_3^-	Cl^{-}	F^{-}	nss-SO ₄ ²⁻	nss-Ca ²⁺	nss-Mg ²⁺	nss-K ⁺
VWM	4.77	40.2	54.7	17.2	64.1	21.9	107	93.7	62.9	66.0	2.55	87.0	61.7	9.56	16.0
Mean	5.12	64.9	87.1	22.5	166	42.4	200	205	145	100	6.09	195	163	22.7	20.6
Max	6.91	190.0	599	159	2076	381.7	1524	2094	1430	667	67.6	2021	2050	246	146
Min	3.84	5.56	6.52	0.64	3.19	2.10	13.1	13.6	0.48	4.74	0.11	8.01	2.04	0	0.07
Median	4.91	51.9	51.2	8.31	83.6	25.1	122	110.9	84.0	68.5	2.93	107	79.6	13.2	6.36
S.D.	0.83	44.9	110	37.4	315.2	57.4	250	307	213	118	10.8	298	312	36.4	36.2

S.D. refers to standard deviation.



Fig. 5. The relationships between rainfall and pH (a), rainfall and EC (b) in the precipitation of the Jiaozhou Bay.

The annual total ionic VWM concentration was up to 490.3 μ eg L⁻¹. The high standard deviations (S.D.) for all ions species indicated a larger variation range in individual precipitation event. Combined with their relative component proportions exhibited in Fig. 6, the VWM concentrations of the major ions in the precipitation (on equivalent basis) were in the order of $NH_4^+ > SO_4^{2-} > Cl^- > Ca^{2+} > NO_3^- > Na^{+-}$ > Mg²⁺ > K⁺ > F⁻, suggesting NH⁺₄, SO²⁻₄, Cl⁻, Ca²⁺ and NO⁻₃ were the dominating ions in precipitation with a percentage of over 80%, while F⁻ was the least abundant ion in wet precipitation with a VWM concentration of only 2.55 μ eq L⁻¹ and <1% of the total ions. In detail, SO_4^2 was the most abundant anion, and accounted for 41.6% of the total anions, followed by Cl^- (29.3%) and NO_3^- (27.9%). The higher proportion of Cl^- than that of NO_3^- may be due to the strong influence from sea spray, similar to the finding of Zhang et al. (2000) at Maidao, a coastal area of South Yellow Sea. For cations, NH_4^+ (40.4%) exceeded Ca^{2+} (29.3%) and became the dominant species, similar to the finding in Dalian (Zhang et al., 2012), a coastal city located in the Northeastern China. That, however, is different from most of the regions in China where Ca^{2+} is the most abundant cation in precipitation (Cao et al., 2009; Lu et al., 2011; Qiao et al., 2015; Xiao, 2016; Xu et al., 2015; Yang et al., 2012). The higher proportion of NH₄⁺ in precipitation may be closely related to the well-developed agricultural production and livestock breeding farming around the Jiaozhou Bay, especially in Oingdao (ODMBS, 2014, 2015). In contrast, Na⁺ and Cl⁻ were the principal cation and anion respectively in both the Yellow Sea and East China Sea (Zhang et al., 2007a), which is mainly due to the predominant control from the sea. The F⁻ concentration in wet precipitation of the Jiaozhou Bay was comparatively lower than that in the most China cities such as Beijing (Yang et al., 2012), Xi'an (Lu et al., 2011; Shen et al., 2012; Xiao, 2016), Chengdu (Wang and Han, 2011), Guangzhou (Cao et al., 2009) and Ya'an (Zhao et al., 2013), but similar to that in the remote Yulong



Fig. 6. Chemical composition percentages of the precipitation in the Jiaozhou Bay (based on volume-weighted mean equivalent concentrations).

Snow Mount, Southwestern China (Niu et al., 2014) and rural North Western Himalayan, India (Tiwari et al., 2012), revealing a relatively lower fluoride pollution level around the Jiaozhou Bay.

The proportions of non-sea-salt fractions for SO_4^{--} (nss- SO_4^{2--}), Ca^{2+} (nss- Ca^{2+}), Mg^{2+} (nss- Mg^{2+}) and K^+ (nss- K^+) were calculated based on formulae (3) and (4) and the data were showed in Table 1. The extremely higher proportions (92.9% for nss- SO_4^{2-} , 96.3% for nss- Ca^{2+} and 93.1% for nss- K^+) were found for those species except nss- Mg^{2+} (43.6%), which were comparable to the finding at a suburban site in the northwest coast of Spain (Moreda-Piñeiro et al., 2014), suggesting a relatively lower contribution of marine source to them despite the study area belongs to the sea. Moreover, it also implied the strong impact from anthropogenic sources and crustal sources on the chemical components of precipitation in the study area.

The annual wet deposition fluxes for the measured ions were 12.99 kg N ha⁻¹ for NH₄⁺, 12.98 kg S ha⁻¹ for SO₄²⁻, 20.30 kg ha⁻¹ for Cl⁻, 11.11 kg ha⁻¹ for Ca²⁺, 7.63 kg N ha⁻¹ for NO₃⁻, 10.90 kg ha⁻¹ for Na⁺, 2.28 kg ha⁻¹ for Mg²⁺, 5.81 kg ha⁻¹ for K⁺ and 0.42 kg ha⁻¹ for F⁻. In contrast, the deposition fluxes of SO₄²⁻, NO₃⁻ and NH₄⁺ were significantly higher than those reported at Jiuzhaigou National Nature Reserve where the anthropogenic impact is minor (annual wet deposition fluxes of SO₄²⁻, NO₃⁻, and NH₄⁺ were 8.06, 1.29 and 1.39 kg S(N) ha⁻¹, respectively) (Qiao et al., 2015), confirming the great influence of anthropogenic disturbance on wet deposition of pollutants. Such a huge amount of acidic deposition (represented by sulfur) may cause the seawater acidification (Menz and Seip, 2004), and further exert serious impact on aquatic ecosystem of the Jiaozhou Bay. Meanwhile, the eutrophication of the Jiaozhou Bay was likely to be enhanced because of the substantial input of nitrogen (expressed as NO₃⁻ and NH₄⁺) through wet deposition.

3.3. Temporal variation of concentrations and deposition fluxes of major constituents

The seasonal variations of the measured major ions and their nonsea-salt fractions together with rainfall were showed in Fig. 7. It can be seen that most of non-sea-salt species (e.g., NO_3^- , F^- , Ca^{2+} , SO_4^{2-}) exhibited the inverse variation trends with rainfall, namely the higher concentrations occurred in summer and autumn while the lower values appeared in winter and spring, which were similar to the studies in Dalian, a coastal city located in Northeastern China (Zhang et al., 2012), and northwest coast of Spain (Moreda-Piñeiro et al., 2014). In general, however, the marine origin components (e.g., Na⁺, Cl⁻) showed the similar tendency with rainfall. Specially, the highest concentrations of NH₄⁺ and nss-K⁺ occurred in summer and autumn, respectively, when the rainfall were relatively high in the study year. On one hand, these results reflect the dilution effect from much larger rainfall during wet season. On the other hand, higher amounts of particles suspended in the atmosphere are usually expected in the dry season (Niu et al., 2014). Meanwhile, lesser rainfall event during the dry season can result in



Fig. 7. Seasonal variations of major ions with rainfall in the Jiaozhou Bay. (a) all inorganic ions; (b) non-sea-salt ions.

longer residence time and accumulation of particles and gases rich in anthropogenic and crustal-derived species (Rao et al., 2016). That can obviously increase the ion concentrations of precipitation from the clear correlation between the total ion concentration and SPM exhibited in Fig. 8. Moreover, there may be potential seasonal sources for NH_4^+ and nss-K⁺. The higher temperature in summer greatly facilitates the volatilization of ammonia (Bouwman et al., 2002), combined with the larger application amount of nitrogen fertilizer in summer, which are responsible for the highest concentration of NH_4^+ over this season. Biomass burning such as straw burning brings a mass of nss-K⁺ into the air in autumn, a harvest season for the Northern China, and thus greatly promotes the increase of concentration of K⁺.

Rainfall amount is proved to be a great contributor of wet deposition flux because of the total ion wet deposition fluxes in four seasons demonstrated a similar variation trend with seasonal rainfall as shown in Fig. 9. The inconsistent episodes between individual species and rainfall might be ascribed to the different seasonal sources of them. Overall, the higher ionic wet deposition during the wet season suggested the predominance function of rainfall amount. Simultaneously, the seasonal emission intensity also plays an important role in controlling the wet deposition fluxes of major chemical components in the Jiaozhou Bay.

3.4. Acid neutralization

3.4.1. The type of acid precipitation

The equivalent ratio of nitrate to non-sea-salt sulfate $[NO_3^-]/[nss-SO_4^2^-]$ is widely used to evaluate the type of acidity in precipitation (Tuncer et al., 2001; Yang et al., 2012). The average ratios of $[NO_3^-]/[nss-SO_4^2^-]$ for all precipitation events in this study was 0.85 ± 0.59 , which is more than twice of that estimated in Beijing during 2001–2005 (Yang et al., 2012) and Newark in the East Coast of US (Song and Gao, 2009). These comparisons suggest that despite the precipitation



Fig. 8. Correlation between total ionic concentration and SPM in the precipitation.

acidity was still controlled by the excessive emission of SO_2 (i.e., sulfur acid type), the role of NO_3^- that deriving from NO_x discharged by motor vehicles cannot be neglected in the Jiaozhou Bay. In addition, it is anticipated that the impact of NO_x on the precipitation chemistry would be greatly enhanced along with the opening of the Jiaozhou Bay Cross-sea Bridge, and the precipitation acidity may be in turn dominated by the excessive emission of NO_x (i.e., nitric acid type) in the future. This inference is supported by the study in Beijing (Yang et al., 2012) as well as by the decreasing atmospheric concentration of SO_2 but increasing atmospheric NO_x concentration in Qingdao (QDMBS, 2014).

3.4.2. Acid neutralization indicators

In general, the acidity of rainwater depends mainly on the relative abundance of the dominant acids (i.e., H_2SO_4 , HNO_3 and organic acids) and alkaline materials (e.g., NH_3 , $CaCO_3$) as well as on the neutralization reactions among them (Niu et al., 2014). Thus, the existing concentrations of main acidic or alkaline ions such as SO_4^{2-} , NO_3^{-} , NH_4^{+} and Ca^{2+} are the representative of these acid/neutralization species mentioned above (Xu and Han, 2009). This conclusion also can be proved by the significant correlations between ($nss-Ca^{2+}+NH_4^{+}$) and ($nss-SO_4^{2-}+NO_3^{-}$), as well as between pH and ($nss-Ca^{2+}+NH_4^{+}$) - ($nss-SO_4^{2-}+NO_3^{-}$) (defined as neutralization capacity (NC)) exhibited in Fig. 10a, b, respectively. Niu et al. (2014) also found similar results in rainwater in the Yulong Snow Mountain.

Considering nss- SO_4^{2-} and NO_3^{-} are the two main acidic constituents in rainwater, Fractional Acidity (FA), an index reflecting acidity neutralization capacity by alkaline components in rainwater can be estimated using the following formula suggested by Balasubramanian et al. (2001) based on equivalent concentration:

$$FA = [H^+] / \left(\left[nss - SO_4^{2-} \right] + [NO_3^{--}] \right)$$
(6)

where, the equivalent concentration of H⁺ ([H⁺]) is calculated by pH value. Generally, if FA value is <1, indicating the acidity of rainwater has not been completely neutralized by alkaline substances in the atmosphere. However, if this value is equal to 1, it is considered that the acidity of rainwater produced by these strong acids is not be neutralized at all (Cao et al., 2009; Tiwari et al., 2012). The mean FA value for all precipitation episodes in the present study was 0.13 ± 0.17 , revealing that ~13% of the acidity had not been neutralized by alkaline components. This value is lower than that in Ya'an, Southwestern China, a typical city that suffering from severe acid with a VWM pH value as low as 4.03 and a acid rain frequency of up to 79% (Zhao et al., 2013).

Another indicator used to reflect the neutralizing capacity of different alkaline species in precipitation is neutralization factor (NF). It can be calculated by the equation as follows (Moreda-Piñeiro et al., 2014; Roy et al., 2016):

$$NF_X = [X] / \left(\left[nss - SO_4^{2-} \right] + [NO_3^{--}] \right)$$

$$\tag{7}$$



Fig. 9. Seasonal patterns of wet deposition fluxes of major ions in the Jiaozhou Bay, (a) all determined ions; (b) non-sea-salt ions.

where [X] refers to the concerned ions such as NH_4^+ , nss- Ca^{2+} , nss- K^+ and nss- Mg^{2+} , because of the role of Na⁺, Cl⁻, and other sea-salt (ss) species (e.g., ss- SO_4^{2-} , ss- Ca^{2+} , ss- Mg^{2+} and ss- K^+) in either acid production or neutralization is negligible as they exist in the form of sea salt (Possanzini et al., 1988; Budhavant et al., 2014). The ionic unit used in this equation is μ eq L⁻¹.

The NFs for the ions above were showed in Table 2. It can be seen that NH_4^+ displayed the highest NF value followed by nss-Ca²⁺, and the NF value for nss-Mg²⁺ was the lowest, suggesting that NH₃ exceeded CaCO₃ and became the principal compound that neutralize the acidic components. That is similar to the study in Bhubaneswar (Das et al., 2005), India and Ya'an (Zhao et al., 2013), Southwestern China, but is different from the cases reported in Northern China such as Xi'an (Lu et al., 2011; Shen et al., 2012) and three non-urban sites of Hebei Province (Wu et al., 2016), where Ca^{2+} was the principal neutralization substance in wet precipitation. The likely causes for this consequence are the large emissions from fertilizer application, biomass burning and animal breeding in surrounding agricultural regions around the Jiaozhou Bay. This opinion was partially supported from the studies at a rural site in the east coast of India (Das et al., 2005) and a semi-rural site in Ya'an (Zhao et al., 2013). In addition, it is worth noting that the particles rich in CaCO₃ play a dominant role in neutralization process of rainwater in Northern China (Cao et al., 2013; Wu et al., 2016). Thus, the relatively deficient of Ca^{2+} in this study may partially explain the high acidity in the precipitation, which is consistent with the results reported in Ya'an (Li et al., 2016) and Beijing (Xu et al., 2015).

3.5. Source apportionment

3.5.1. Enrichment factor (EF)

In general, an element is considered to be concentrated or diluted relative to the reference source with an EF value much >1 or much smaller than 1 (Zhang et al., 2007b; Cao et al., 2009). According to

formula (5), the calculated EFs for K⁺, Ca²⁺, Mg²⁺, Cl⁻ and SO₄²⁻ were presented in Table 3. The EF_{marine} of Cl⁻ was closely approximate to 1, revealing the main source of Cl⁻ was of marine origin. Similarly, the EF_{marine} of Mg²⁺ was a little >1, suggesting marine sources contribute to most of Mg²⁺ in wet precipitation in the Jiaozhou Bay. However, the higher EF_{marine} for SO₄²⁻ clearly proved its non sea salt sources. The same is true for K⁺ and Ca²⁺.

3.5.2. Relative source contribution

Generally, nss-SO₄²⁻, NH₄⁺, NO₃⁻ and F^- are considered to be originated mostly from anthropogenic emissions (e.g., chemical fertilizer and manure application, fossil fuel combustion, automobile exhausts and production of brick and tiles from clay with high fluoride contents) (Larssen et al., 1999; Wang and Han, 2011; Wu et al., 2012; Zhang et al., 2012; Zhu et al., 2016). In addition, Na⁺ and Ca²⁺ are usually regarded as the indicator elements of sea salt (Safai et al., 2004; Keene et al., 1986) and crust (Taylor, 1964), respectively. nss-Mg²⁺ is commonly originated from suspended soil dust (Lu et al., 2011), while nss-Cl⁻ and nss-K⁺ are mostly considered to be of various anthropogenic sources (Xu and Han, 2009; Moreda-Piñeiro et al., 2014). For these reasons, three main categories of origins (i.e., anthropogenic, crustal and sea salt sources) for the precipitation components in the Jiaozhou Bay can be summarized, supposing that the contributions from volcanic and other natural sources are negligible. The relative contributions from these three reservoirs can be reflected by the chemical compositions of precipitation (Das et al., 2005; Safai et al., 2004). The relative contributions of sea salt, crustal and anthropogenic sources to the total precipitation components can be calculated by formulae (3) and (4) and the following formulae:

 $\text{SSF} = (\text{Na}^+ + \text{ss-Cl}^- + \text{ss-SO}_4^{2-} + \text{ss-Ca}^{2+} + \text{ss-Mg}^{2+} + \text{ss-K}^+) / \sum ion \times 100$

(8)



 Table 2

 Neutralization factors (NFs) for ions in precipitation in different study areas.

Region	$NF(NH_4^+)$	$NF(nss-Ca^{2+})$	NF(nss-K ⁺)	NF(nss-Mg ²⁺)
Jiaozhou Bay ^a	0.72	0.42	0.11	0.07
Beijing ^b	0.60	0.60	-	0.13
Xi'an ^c	0.35	0.70	-	0.06
Bhubaneswar ^d	0.70	0.44	0.07	0.15
Ya'an ^e	0.71	0.40	0.13	0.05

^a This study.

^b Yang et al. (2012).

^c Lu et al. (2011).

^e Zhao et al. (2013).

$$%CF = \left(nss-Ca^{2+} + nss-Mg^{2+}\right) / \sum ion \times 100$$
(9)

$$%AF = 100 - %SSF - %CF$$
 (10)

where SSF, CF and AF represent sea-salt fraction, crust fraction and anthropogenic source fraction, respectively. Here, \sum ion includes all the determined ions but H⁺ and HCO₃⁻, and the calculation were based on VWM equivalent concentrations.

The integrated contributions of sea-salt, crustal and anthropogenic sources to the total ion concentration of precipitation were estimated to be 28.7%, 14.5% and 56.8%, respectively. Overall, anthropogenic source controls the precipitation composition of the Jiaozhou Bay, indicating the great effects of anthropogenic activities on the atmospheric environment of coastal waters.

However, it should be noted that the contribution of marine source to SO_4^{2-} might be underestimated in the method mentioned above, as the omission of the contribution from marine phytoplankton (biogenic emission). The dimethylsulfide (DMS), produced by phytoplankton could form SO_2 by means of the reaction with hydroxyl radical, and then further form SO_4^{2-} (Liu et al., 1997). Previous study proved that the contribution of biogenic sulfur in the North Yellow Sea was estimated to range from 1.2% to 11.5% (Yang et al., 2009). Furthermore, the sea-air fluxes of DMS in the Jiaozhou Bay was 1.70–1.79 µmol m⁻² d⁻¹ (Liu et al., 1997), which is an important source that should not be neglected. Although the method used in this study has some limits, it still provided a rough quantitative estimation for the relative source contributions of sea salt, crustal and anthropogenic sources. Therefore, further studies on this issue are necessary.

3.5.3. Backward trajectory analysis of air mass

As an important tool to recognize the potential sources and transport routes of air pollutants and precipitation clouds, air mass backward trajectory analysis was performed using the Hybrid-Single Particle Integrated Trajectory Model (HYSPLIT 4) (Avery et al., 2006; Wu et al., 2012), provided by the Air Resource Laboratory of National Oceanic and Atmospheric Administration (NOAA) (Stein et al., 2015; Rolph, 2016). For each precipitation episode, 72-h backward trajectories were established at 500 m, 1000 m and 3000 m height above ground level over the sampling site (Wu et al., 2012; Wu and Han, 2015).

 Table 3

 Enrichment factors for precipitation components relative to seawater (on equivalent basis).

	K^+/Na^+	Ca^{2+}/Na^{+}	Mg^{2+}/Na^+	Cl^-/Na^+	$\mathrm{SO}_4^2-/\mathrm{Na}^+$
Seawater ratio	0.022	0.044	0.227	1.16	0.121
Rainwater ratio	0.314	1.172	0.401	1.206	1.711
EF _{marine}	14.3	26.6	1.77	1.04	14.1

Based on the origin areas and transport directions, four categories of air masses were recognized from the entire trajectories (Fig. 11), and their associated occurrence frequencies, precipitation chemistry parameters were listed in Table 4.

It can be seen that the precipitation events during the sampling period were dominated by the air-mass from northwest (NW) and southeast (SE) (Table 4), which is corresponded to the climate characteristics of the Jiaozhou Bay as mentioned in Section 2.1. The air mass comes from the NW direction is characterized by the highest values of pH, EC, total ion concentration as well as the highest concentrations for almost all ions except for K⁺, which is due mainly to this category of air mass originating from the arid/semiarid desert region of Central Asia, and arrives at the study area passing through the North China, an area with advanced industry, agriculture and dense population. The relatively higher contents of soil dust in the air-mass neutralize the acidity of precipitation, and various natural and anthropogenic pollutants cause the higher concentrations of precipitation components. In contrast, the air-masses deriving from SE direction (e.g., coastal area of Southeastern China, Japan and Western Pacific) characterized with the lowest pH, EC and total ion concentration, as well as with the lowest crustal-derived component (i.e., Ca^{2+}) contents, which was considered to be one of the causes for the highest acidity in the precipitation affected by this category of air-mass. The moderate pH, EC and ion concentrations in the air-masses from the northeast and southwest directions might be owing to the joint impacts from natural and human sources. Besides, the lower occurrence frequencies of these two types of air-masses have made their effects on the chemical composition of the precipitation in the Jiaozhou Bay to be neglected. In conclusion, the air-masses originating from NW and SE directions controlled the source of the precipitation components in terms of long-range transport in the Jiaozhou Bay during the sampling period.

It should be noted that the long-range transport of air-mass only represent the in-cloud scavenging process. Nevertheless, the data listed in Table 4 reflected an integrated process combined with both in-cloud and below-cloud scavenging. For this reason, it is worth mentioning that although the long-range transport of air-mass would have strong effects on the chemical composition of precipitation, the local emission intensity of atmospheric pollutants and weather conditions (mainly means rainfall) can still play the dominant roles. That might explain the inconsistence between the levels of certain ion species and the origin and transport pathway of air-masses. For example, the lowest pH in the precipitation under the effect of SE air-mass (Table 4) may be mostly ascribed to the acidic precursors emitted from local industry and traffic. On this occasion, below-cloud scavenging likely to be more important than in-cloud scavenging.

4. Conclusions

The pH values of precipitation in the Jiaozhou Bay were ranged from 3.84 to 6.91 with an annual volume-weighted mean (VWM) pH of 4.77, and the frequency of acid rain (the occurrence frequency of precipitation events with a pH < 5.6) was up to 71.4%. The severe acidification of precipitation reflects the serious air pollution level, which also can be proved by the comparatively higher electric conductivity (EC) (mean 64.9 $\mu S~cm^{-1}$). $NH_4^+,$ $SO_4^{2-},$ $Cl^-,$ Ca^{2+} and NO_3^- were the major species in precipitation with a percentage of over 80%. NH₄⁺ (40.4%), which exceeded Ca^{2+} (29.3%), became the dominant species of cations, which is different from that in most areas of China. SO_4^{2-} was the most abundant anions, and accounted for 41.6% of the total anions. The wet deposition fluxes of sulfur (S) was 12.98 kg ha⁻¹ yr⁻¹. Such huge amounts of deposition fluxes of S may lead to seawater acidification of the Jiaozhou Bay. Rainfall, emission intensity and long-range transport of natural and anthropogenic pollutants govern the concentrations and wet deposition fluxes of chemical components. The type of acid rain in the Jiaozhou Bay was sulfur acid type. The significant correlation between $(nss-Ca^{2+} + NH_4^+)$ and $(nss-SO_4^{2-} + NO_3^-)$ and the calculated

^d Das et al. (2005).



Fig. 11. Typical air mass trajectories classified into four categories for precipitation events from four defined directions during the sampling period. a. Northwest (NW); b. Northeast (NE); c. Southwest (SW); d. Southeast (SE).

neutralization factors both indicated that NH_4^+ and $nss-Ca^{2+}$ were the main neutralizing constituents. NH_4^+ showed stronger capacity of acid neutralization than $nss-Ca^{2+}$, which may be ascribed to the developed agricultural production around the Jiaozhou Bay. However, the comparatively lower rainwater concentration of Ca^{2+} in the Jiaozhou Bay than that in other regions in Northern China, where Ca^{2+} is the primary acid neutralizing substance, likely to be a cause for the strong acidity of

precipitation. The integrated contributions of sea-salt, crustal and anthropogenic sources to the total ions of precipitation were estimated to be 28.7%, 14.5% and 56.8%, respectively. Note that the marine source fraction of SO_4^2 – may be underestimated owing to the neglected contribution from marine phytoplankton. It is obvious that the composition of precipitation in the Jiaozhou Bay exhibits complex chemical characteristics under the combined effects of natural and anthropogenic sources.

Table 4

VWM mean of pH (in unit), EC (in µS cm⁻¹) and major ion concentrations (in µeq L⁻¹) in the precipitation under the influences of the four categories air-masses.

	Frequency	pН	EC	\sum ions	Na ⁺	K^+	Ca ²⁺	${\rm Mg}^{2+}$	NH_4^+	SO_4^{2-}	NO_3^-	Cl ⁻	F^{-}
NW ^a	34.7%	5.05	59.8	832	99.9	10.8	129	38.8	185	154	108	101	5.19
NE ^b	14.3%	4.99	38.3	374	47.5	7.46	51.0	21.4	20.1	101	66.6	57.4	1.94
SW ^c	8.2%	4.94	40.8	447	33.1	9.41	53.8	13.6	129	107	58.1	39.8	2.89
SE ^d	42.8%	4.66	32.4	360	40.5	22.2	40.8	16.4	70.4	66.0	44.9	57.0	1.49

^a Northwest direction.

^b Northeast direction.

^c Southwest direction.

^d Southeast direction.

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