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Fluxes, seasonal patterns and sources of various nutrient species (nitrogen, phosphorus and silicon) in atmospheric wet deposition and their ecological effects on Jiaozhou Bay, North China

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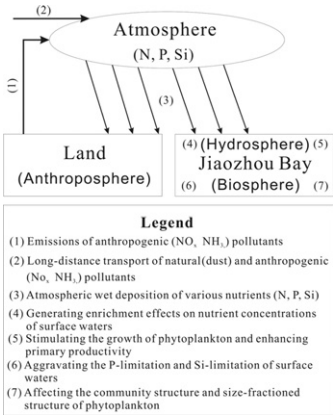
HIGHLIGHTS

- Concentrations and fluxes of various nutrient species were analyzed.
- The impacting factors of seasonal variations of nutrients in AWD were illustrated.
- DON, DOP occupied 24.3% and 62.0% of the AWD fluxes of TDN and TDP, respectively.
- AWD would aggravate the P- and Si-limitation of surface waters.
- Sudden heavy rains affect PP and community structures of phytoplankton.

GRAPHICAL ABSTRACT



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ABSTRACT

Atmospheric wet deposition (AWD) is an important pathway for anthropogenic and natural pollutants entering aquatic ecosystems. However, the study on the magnitudes and ecological effects of AWD of various nutrient species (nitrogen, phosphorus and silicon) on Jiaozhou Bay is scarce. To address these issues, in this study, wet deposition samples were collected at a coastline site along Jiaozhou Bay from June 2015 to May 2016. Dissolved inorganic nitrogen (DIN, including NH_4–N, NO_3–N and NO_2–N), dissolved organic nitrogen (DON), dissolved inorganic phosphorus (DIP, i.e. PO_4–P), dissolved organic phosphorus (DOP) and reactive silicate (SiO_3–Si) were analyzed. The volume-weighted mean (VWM) concentrations of NH_4–N, NO_3–N and DON in AWD were higher compared with those of NO_2–N, PO_4–P, DOP and SiO_3–Si. The annual influxes of NH_4–N, NO_3–N, NO_2–N, DON, DIP, DOP, and SiO_3–Si via AWD were 92.8, 54.5, 0.427, 47.5, 0.274, 0.448 and 1.73 mmol·m^{-2}·yr^{-1} respectively; NH_4–N and DOP were the dominant species for N and P, and the roles of DON and DOP in AWD could not be neglected. Significant seasonal variations were observed in concentrations and fluxes of all nutrient species owing to the effects of rainfall, the intensities of local emission sources and the long-distance transports of natural and anthropogenic pollutants. The major sources of N, Si and P in AWD were agricultural activities, soil dust and a

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Ecological effects
Jiaozhou Bay

mixing one involving both anthropogenic and natural sources, respectively. Though AWD represents relatively low percentages of external inputs for nutrients and low contribution to primary productivity (PP) of Jiaozhou Bay, large amounts of nutrient inputs originating from sudden heavy rains may enhance PP prominently, as well as aggravate P-limitation and Si-limitation and further affect phytoplankton community structures and size-fractioned structures with the quite high DIN:DIP ratios and extremely low Si:DIN ratios in AWD.

1. Introduction

Nitrogen (N), phosphorus (P) and silicon (Si) are the major biogenic elements that support primary productivity (PP) in aquatic ecosystems. With great enhancement of human activities (Chen and Mulder, 2007; Galloway et al., 2008) and natural changes (Izquierdo et al., 2012; Kang et al., 2009; Min et al., 2011), increasing amounts of airborne anthropogenic and natural nutrients (N, P and Si) are being deposited into oceans through precipitation. Atmospheric wet deposition (AWD) has been proved to be an important pathway for nutrients being transported into marine ecosystem, particularly in the coastal waters (Ayars and Gao, 2007; Duce et al., 2008; Liu et al., 2013; Martinez-Garcia et al., 2015; Paerl et al., 2002; Song, 2010). In the Yellow Sea, AWD supplies 65% and 70% of total inputs for DIN and DIP, respectively (Zhang, 1994; Zhang and Liu, 1994). The wet deposition flux of N occupies ~70% of total inputs of total nitrogen (TN) in the coastal waters of Singapore (He et al., 2011). As a result, AWD of nutrients would strongly affect the marine ecosystem by stimulating the growth of phytoplankton, promoting carbon (C) and N fixation, and eventually enhancing PP (Duce et al., 2008; Martinez-Garcia et al., 2015; Paerl et al., 2002; Srinivas and Sarin, 2013; Zou et al., 2000), even leading to eutrophication and red tide (Bergstrom et al., 2005; Zhang, 1994; Zou et al., 2000). In the open oceans such as the tropical western Pacific Ocean, the nutrients in atmospheric deposition may sustain ~10% of PP (Martino et al., 2014). In the Yellow Sea, due to minor riverine inputs, new productivity (NP) induced by TN deposition accounts for 0.3–6.7% of PP, which is higher than the values of 1.1–3.9% found in the East China Sea (Qi et al., 2013; Zhang et al., 2010). Meanwhile, dissolved inorganic phosphorus (DIP) in atmospheric deposition could account for up to 38% of NP in the eastern Mediterranean (Markaki et al., 2003). Moreover, the increase in N availability resulted by atmospheric deposition has switched parts of the Northwestern Pacific Ocean from being N-limited to P-limited (Kim et al., 2011).

Jiaozhou Bay, located in the southeastern of Shandong Peninsula and western of the Yellow Sea, is surrounded by Qingdao, Jiaozhou and Huangdao on three sides with an area of 370 km^2 and an average depth of 7 m (Fig. 1). Jiaozhou Bay is a typical semi-enclosed bay under the interactions between natural changes and human activities in northern China, which is influenced by the natural factors such as East Asia Monsoon, and the continually enhancing anthropogenic activities in coastal regions such as terrigenous pollutant emissions and mariculture etc. (Sun and Sun, 2015). Owing to the collective influences from the rapid-advancing economy, exploded population, and the frequent haze/fogs and sandstorms, the role of AWD in the inputs of terrigenous nutrients into Jiaozhou Bay may be increasingly prominent. Particularly in the recent years, the runoff and sediment discharges of the rivers around Jiaozhou Bay have been reducing gradually (Liu et al., 2005); in addition, the discharge amounts of nutrients e.g. NH_4–N, total phosphorus (TP) derived from industrial and agricultural wastewater, domestic sewage have decreased over the past few years (Qingdao Municipal Ocean and Fisheries Administration, 2014, 2015). Thus, atmospheric deposition, especially AWD, will be more significant relative to riverine input and discharge of non-point source pollution. Hence, the study on AWD of nutrients is becoming more urgent. Moreover, reversal of eutrophication in Jiaozhou Bay requires the identification of pollution sources and the reduction of nutrient inputs. However, the data on AWD concentrations, fluxes, sources, transport and ecological effects of various nutrients species (N, P and Si) in this region are quite scarce and remain uncertain, although some similar studies have been conducted in the adjacent Yellow Sea (Chung et al., 1998; Zou et al., 2000) and Qingdao City (Zhang et al., 2011).

In this paper, dissolved inorganic nitrogen (DIN, including NH_4–N, NO_3–N, NO_2–N), dissolved organic nitrogen (DON), DIP, i.e. PO_4–P (He et al., 2011), dissolved organic phosphorus (DOP), and reactive silicate (SiO_3–Si) in AWD collected at a coastal site along Jiaozhou Bay were determined, with an aim of the analysis of seasonal patterns and impacting

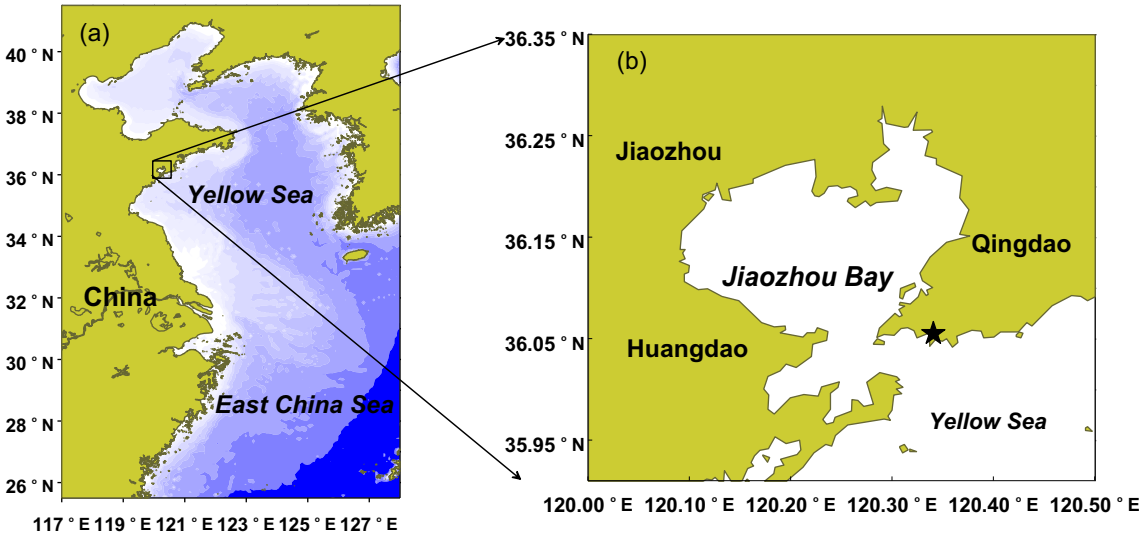

Fig. 1. The location of Jiaozhou Bay (a) and sampling site for atmospheric wet deposition (b) (★ represents the sampling site).

factors of concentrations and deposition fluxes of various nutrient species in AWD, as well as the exploration of relevant potential ecological effects on Jiaozhou Bay ecosystem. This study provided a comprehensive data set on AWD of major nutrient species into the Jiaozhou Bay, which is beneficial for the systematic calculation of the budget of nutrients in Jiaozhou Bay. Furthermore, the results will offer valuable data for assessment of the effects of inorganic and organic nutrient wet deposition on the nutrient levels, PP and the community structures of phytoplankton in Jiaozhou Bay. Eventually, this study will also provide fundamental information for the understanding of the biogeochemical cycle of biogenic elements in Jiaozhou Bay.

2. Materials and methods

2.1. Sampling

The sampling site (36°03′19.46″N, 120°20′25.11″E) (Fig. 1b) was located on the roof of a building in Institute of Oceanology, Chinese Academy of Sciences (IOCAS), where the linear distance to the nearest coastline is approximately 20 m. As the prevailing wind directions in Jiaozhou Bay are NW and SE (Sun and Sun, 2015), both of the two types of prevailing winds would pass through the sampling site, either entering or leaving the Jiaozhou Bay during the sampling period. Besides, there are no obvious obstacles and pollution sources nearby. All of those guarantee the AWD samples collected in this site represent the actual status of atmospheric wet deposition into Jiaozhou Bay to the greatest extent. An automatic sampler (DH-200, Qingdao-Shengding Inc., China) was employed and mounted at 1.5 m above the roof to prevent the impact from raised dust. A wetness detector was triggered to open the lid of the wet deposition bucket once the rain started during a rain event. After the cease of the rain, the lid was closed and the bucket was sealed to shelter the rain samples from being polluted (Cui et al., 2014). Meanwhile, the rainfall was determined by a standard rain gauge, while the snowfall was measured using a clean standard measuring cylinder when the snow samples were thawed under room temperature.

Almost all the rain and snow events were considered except some special cases when the rainfall amount was <1 mm, and the samples were excluded from the study due to the fact that the amount was insufficient for analysis (Bartoli et al., 2005). In all, 49 AWD samples (48 rainwater samples and 1 snow water sample) were collected from June 2015 to May 2016 except January 2016 when there was no precipitation.

All the AWD samples were collected immediately after each precipitation events. Then, they were filtered through nucleopore membranes (0.45 μm pore size) to remove particles. The filtrates were poured into high density polyethylene bottles and sterilized with chloroform (1 mL $CHCl_3$ per liter sample) to prevent chemical degradation by microorganisms (Zhang et al., 2012). Then the filtered samples were stored in a refrigerator at −20 °C until analysis. To minimize the loss of nutrients, all samples were determined within a month. Prior to use and after each collection, all of the containers (e.g. wet deposition buckets, polyethylene bottles, etc.) used in the sampling and analysis processes were soaked in 10% HCl solution for 3 d, and carefully rinsed with Milli-Q water (resistivity: 18.2 $M\Omega \cdot cm^{-1}$). Field blanks were collected monthly according to Guo et al. (2015) that the Milli-Q water was flushed through the sampler and was then collected as a field blank. Field blanks were treated with the same methods as samples.

2.2. Chemical analysis and quality control

To calculate the content of suspended particle matters (SPM) in rainwater and snow water, the filters were weighed before and after the filtration (continuously weighed until constant weight after being placed in a desiccator several days). Prior to the analysis, all of the samples were thawed at room temperature. Subsequently, the concentrations of NH_4–N, NO_3–N, NO_2–N, PO_4–P and SiO_3–Si were determined photometrically following the standard procedure using a continuous flow analyzer (QuAAtro, Bran-Luebbe Inc., Germany). DIN is the sum of NH_4–N, NO_3–N and NO_2–N. The detection limits for NH_4–N, NO_3–N, NO_2–N, PO_4–P, and SiO_3–Si were 0.25, 0.40, 0.01, 0.03 and 0.01 $\mu mol \cdot L^{-1}$, respectively. National standard references were used to determine the precision and accuracy of the analysis, and the precisions and recoveries for all nutrient species were better than 5% and between 95.0 and 105.1%, respectively.

A microwave-assisted persulfate oxidation method was employed to convert all N and P containing species to NO_3^- and PO_4^{3-} for the determination of TDN and TDP, respectively (He et al., 2011; Karthikeyan et al., 2009; Qi et al., 2013). Then, TDN and TDP concentrations were measured using the same methods as described above. Ethylenediaminetetraacetic acid (EDTA), quinoline, urea, NH_4Cl and $NaNO_2$ were employed as the standards to perform the standard addition tests for TDN (Chen et al., 2015), while KH_2PO_4 and organic phosphorus mixed standard material were used for the standard addition tests of TDP. The recoveries for TDN and TDP were all found to be higher than 90%. The concentrations of DON and DOP were computed by the differences of TDN and DIN, TDP and DIP, respectively. Field blanks and reagent blanks were determined in parallel to the wet deposition sample treatment by the same methods, and these blanks were all below the detection limits of the measured species, suggesting negligible contamination.

2.3. Data analysis

In this study, the concentrations of all nutrient species refer to the volume-weighted mean (VWM) concentrations. The VWM and AWD fluxes of different nutrient forms were calculated using the following formulae:

$$C_{VWM} = \sum_{i=1}^{n}(C_i \times Q_i)/\sum_{i=1}^{n} Q_i \quad (1)$$

$$F_W = 0.001 \times \sum_{i=1}^{n} C_i \times Q_i \quad (2)$$

where C_{VWM} and F_W are the VWM concentrations ($\mu mol \cdot L^{-1}$) and AWD fluxes ($mmol \cdot m^{-2}$) calculated from the n samples within a month/season/year, respectively, and n refers to the times of precipitation events in a certain period; C_i ($\mu mol \cdot L^{-1}$) and Q_i (mm) are the measured concentration and rainfall amount of individual precipitation event, respectively.

3. Results and discussion

3.1. Concentrations and temporal variability of nutrients in AWD

In this study, June–August was defined as summer, September–November was defined as autumn, and December–February and March–May were defined as winter and spring respectively. The seasonal and 1-year VWM concentrations of SPM and different nutrient species in AWD were presented in Table 1. Obviously, compared with P and Si, the N species i.e. NH_4–N, NO_3–N and DON constituted the main body of the nutrients in AWD with VWM concentrations of 107.1, 62.9 and 54.8 $\mu mol \cdot L^{-1}$, respectively. These data were notably higher than those obtained during 1988–1993 (73.3 $\mu mol \cdot L^{-1}$ for NH_4–N, 12.0 $\mu mol \cdot L^{-1}$ for NO_3–N, and 0.11 $\mu mol \cdot L^{-1}$ for NO_2–N) and 1998 (48.5 $\mu mol \cdot L^{-1}$ for NH_4–N, 24.8 $\mu mol \cdot L^{-1}$ for NO_3–N) in the coastal regions of Qingdao, Maidao and Laoshan (Zhang et al., 1999; Zhang et al., 2000; Zhang and Liu, 1994). Moreover, the results of our study were significantly higher than the values of investigation carried out in 2009–2010 (Zhu, 2011). It was reported that the overall distribution trend of N species in rainwater in the marginal sea of China was that the

Table 1
Seasonal and annual VWM concentrations of SPM ($mg \cdot L^{-1}$) and nutrients ($\mu mol \cdot L^{-1}$) in AWD in Jiaozhou Bay.

Year	Season	Volume-weighted mean concentrations									References
		SPM	NH_4–N	NO_3–N	NO_2–N	DIN	DON	DIP	DOP	SiO_3–Si	
2015–2016	Summer	8.08	161.5	86.0	0.58	248.1	67.4	0.16	0.63	0.10	This study
	Autumn	5.30	74.3	41.2	0.09	115.4	53.8	0.27	0.52	0.13	
	Winter	19.9	89.8	83.0	1.70	174.5	39.0	0.55	0.45	3.87	
	Spring	31.2	104.1	66.4	0.72	171.2	44.9	0.55	0.37	8.28	
	1-year average	12.3	107.1	62.9	0.49	170.5	54.8	0.32	0.52	2.00	
2009–2010	2-year average		54.8	36.3[a]		91.1		0.12		5.12	Zhu, 2011

[a] Refers to the sum of NO_3–N and NO_2–N.

concentrations in coastal urban areas (e.g. Qingdao, North China) were higher than those on the remote islands (Zhang et al., 2011). That implies that the anthropogenic N pollution in the air around Jiaozhou Bay is becoming more serious following the fast-advancing economy and continuous population expansion. By contrast, the concentrations of DIP and SiO_3–Si in AWD were very low, which may be partially attributed to the relative less sources and the low solubility of soil dust (Bartoli et al., 2005; Izquierdo et al., 2012). Meanwhile, the concentrations of DIP and SiO_3–Si in AWD have decreased significantly since 1980s (0.93 $\mu mol \cdot L^{-1}$ for DIP and 6.0 $\mu mol \cdot L^{-1}$ for SiO_3–Si, Zhang and Liu, 1994), indicating the emission sources and emission intensities of DIP and SiO_3–Si may have decreased over the past three decades. Nevertheless, the slight increase of DIP concentration in the present study relative to those in 2009–2010 may be related to anthropogenic influence and biomass burning. In addition, the annual VWM concentration of DOP exceeded that of DIP, thus DOP constituted the main body of P wet deposition, revealing the role of DOP in AWD may be more important than that of DIP. Unfortunately, the measurements of DON and DOP in AWD were ignored in the previous studies (Zhang and Liu, 1994; Zhu, 2011).

Fig. 2 listed the monthly variations of all the nutrient species in AWD with rainfall amount in Jiaozhou Bay, from which, distinctly monthly variations can be observed among all of nutrient species. In general, the highest monthly concentrations of nutrients can be several times the lowest values, and especially for NO_2–N and SiO_3–Si, the highest values of 1.72 $\mu mol \cdot L^{-1}$ and 11.4 $\mu mol \cdot L^{-1}$ are 2 and 3 orders of magnitude higher than the lowest values (0.04 $\mu mol \cdot L^{-1}$ and 0.07 $\mu mol \cdot L^{-1}$, respectively). On the whole, most nutrient species presented contrary variation trends with rainfall amounts that the lower concentrations occurred in the wet season (Jun.–Nov.) and the higher values appeared in the dry season (Dec.–May) (Fig. 2). This is partially ascribed to the strong dilution effects of the higher rainfall in the wet season and the longer residency time of ambient aerosols in the dry season (Qiao et al., 2015; Zhang and Liu, 1994). The long residency time may facilitate the accumulation of particles that are rich in nutrients. Similar results were also found in the southwestern United States (Sorooshian et al., 2013). It should be noted that the maximum concentrations of DON and DOP occurred in June, a month with relatively more rainfall in the wet season. Further study found that the VWM concentrations of these two organic nutrient species also had higher contents in the wet season (59.4 $\mu mol \cdot L^{-1}$ and 0.56 $\mu mol \cdot L^{-1}$, respectively) than those in the dry season (43.1 $\mu mol \cdot L^{-1}$ and 0.40 $\mu mol \cdot L^{-1}$, respectively), which was contrary to the most inorganic nutrients, revealing that there may exist quite strong emission sources in summer and autumn for DON and DOP. Similarly, the fact that the peak values of NH_4–N occurred in spring and summer (Table 1) may be associated with the volatilization of N fertilizer under relatively high temperature (Zhao et al., 2009). To sum up, rainfall amount and the intensities of local emission sources dominate the concentrations of nutrients in AWD in Jiaozhou Bay.

3.2. Fluxes and seasonal patterns of nutrients in AWD

The annual AWD fluxes of NH_4–N, NO_3–N, NO_2–N, DON, DIP, DOP and SiO_3–Si were estimated to be 92.8, 54.5, 0.427, 47.5, 0.274, 0.448, and 1.73 $mmol \cdot m^{-2} \cdot yr^{-1}$, respectively. Compared with the findings of 2009–2010 that the annual fluxes of NH_4–N, (NO_3–N + NO_2–N), DIP and SiO_3–Si were 28.3, 18.8, 0.07 and 2.56 $mmol \cdot m^{-2} \cdot yr^{-1}$, respectively (Zhu, 2011), the results of the present study are observably higher but SiO_3–Si, which indicate the fluxes and roles of AWD of N and P species have been significantly enhanced in recent years. High AWD fluxes are closely associated with high rainfall, as rainwater is the carrier of various airborne nutrients. The similar variation trends were found between rainfall and the monthly AWD fluxes of different nutrient species (Fig. 3), indicating that rainfall is a crucial contributor to the wet deposition fluxes of all nutrient species. Similar results were also found in the coastal regions of the Yellow Sea (Qi et al., 2013; Zhang et al., 1999). However, AWD fluxes of nutrients were not always in direct proportion with rainfall concertedly, especially SiO_3–Si, which possess relatively high AWD fluxes in the dry season (e.g. February, May). This is

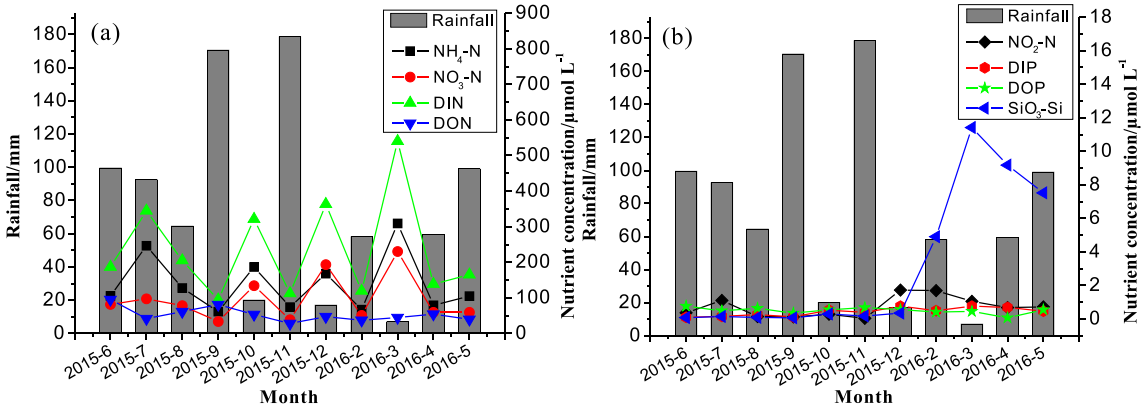

Fig. 2. Monthly variations of various nutrients species concentrations ($\mu mol \cdot L^{-1}$) in AWD with rainfall (mm) in Jiaozhou Bay. (a): NH_4–N, NO_3–N, DIN and DON; (b): NO_2–N, DIP, DOP and SiO_3–Si.

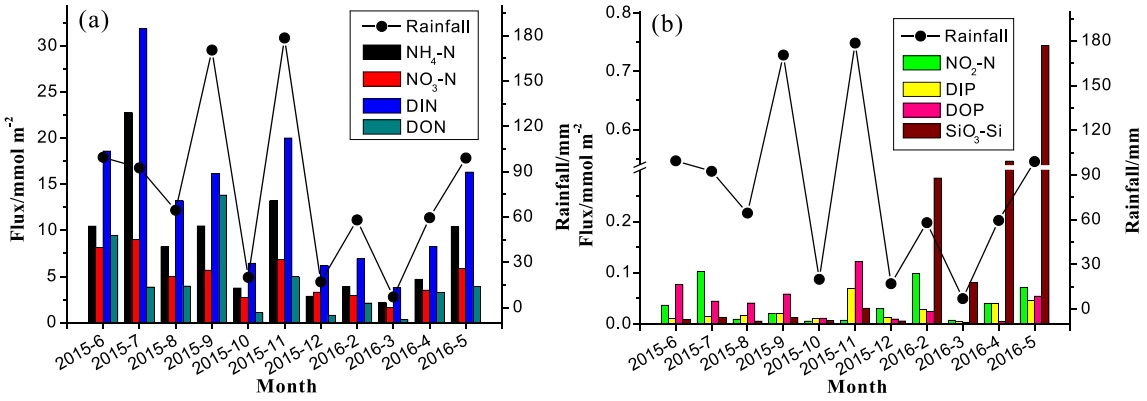

Fig. 3. Monthly variations of atmospheric wet deposition fluxes ($mmol \cdot m^{-2}$) of various nutrient species with rainfall amount (mm) in Jiaozhou Bay. (a): NH_4–N, NO_3–N, DIN and DON; (b): NO_2–N, DIP, DOP and SiO_3–Si.

coincident with the peak concentration of SiO_3–Si in the same period (Fig. 2b). Consequently, the concentration of nutrient species in AWD is also a factor affecting AWD fluxes, which in turn implies that there exists seasonal sources of SiO_3–Si. The Yellow Sea (including Jiaozhou Bay) is below the major route of East Asian dust storms affecting the interior of the Northwestern Pacific Ocean (Zhang et al., 2011), which mainly occurs in the dry season when the northwest monsoon is prevailing. Thus the AWD fluxes of DIP and SiO_3–Si were higher in the dry season than those in the wet season. The AWD of N species from the coastal urban regions of East Asia to the remote regions of the Northwestern Pacific Ocean suggests a pattern of flux consistent with regulation by emission sources and rainfall, and with species-specific character (Zhang et al., 2011), which provided support for our hypothesis.

Among the annual AWD fluxes of various nutrient species, TDN accounted for approximately 98.8% of the total nutrient wet deposition fluxes, which is higher than the value of 86.3% in Daya Bay (Chen et al., 2014). However, the percentages of AWD fluxes for P (0.37%) and Si (0.88%) were very low. In TDN fraction, DIN and DON showed a proportion of 3:1 (Fig. 4), which is different from that in Pearl River Estuary (DIN:DON = 1:1) (Fan et al., 2010), indicating DIN is the main body of N species in AWD in Jiaozhou Bay, and the wet deposition flux of DON cannot be neglected. DOP wet deposition flux exceeded DIP and accounted for 62.0% of TDP flux in this study, which is consistent with the result obtained in the coastal region of Singapore (He et al., 2011), highlighting the importance of DOP in P wet deposition. NH_4–N, NO_3–N and DON represented 47.5%, 27.9% and 24.3% of the TDN flux, respectively. For DON, the percentage was lower than the average value of 30% of DON accounting for TDN in rainwater in Qingdao coastal urban area during the years of 1997–2005 (Zhang et al., 2011), and also lower than the average contribution of DON to TDN (~30%) in 15 rural,

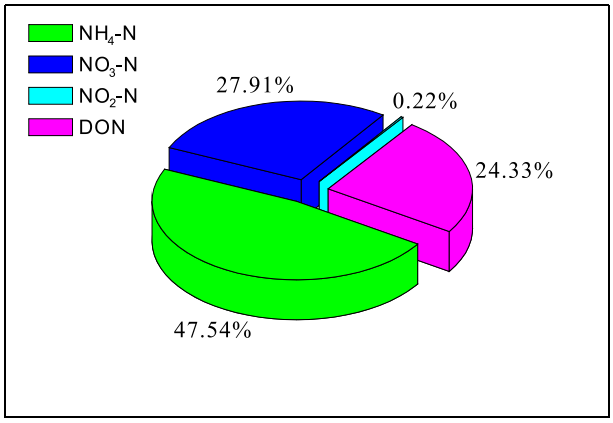

Fig. 4. The relative proportions of AWD fluxes for different N species in Jiaozhou Bay.

suburban and urban sites of China (Zhang et al., 2008). The low DON percentage in the present study may be ascribed to the differences among study periods as well as study areas. DON is a ubiquitous and important component in rainwater (Cornell et al., 1995). However, the wet deposition of DON has been ignored in the past studies (Zhang et al., 2010; Zhao et al., 2009; Zhu, 2011). With the high concentration and proportion of DON in rainwater in East Asia, particularly in the coastal zone of China (Chen et al., 2015), the AWD flux of N might have been underestimated in previous studies owing to the exclusion of DON.

During a 4-year (2003–2006) measurements in the Eastern Mediterranean, the contributions of various N species to TDN in rainwater were 31.6% for NH_4–N, 45.7% for NO_3–N and 22.7% for DON, respectively (Violaki et al., 2010). Similarly, in the Neuse River estuary, North Carolina, a fairly even distribution of NH_4–N, NO_3–N and DON (32%, 32%, and 36%, respectively) were observed (Whitall et al., 2003). All of these results are different from our study that NH_4–N was the dominating N species in AWD of Jiaozhou Bay.

3.3. Source identification of nutrients in AWD

3.3.1. Air mass backward trajectory analysis

By means of the latest HYSPLIT-4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) online transport and dispersion model developed by the U.S. National Oceanic and Atmospheric Administration (NOAA), backward air mass trajectories were established to analyze the origins of air masses passing through Jiaozhou Bay during the sampling period (He et al., 2011). Based on the meteorological data from NCEP's Global Data Assimilation System (GDAS, global, 09/2007–present), backward air mass trajectory was generated for 72 h back in time with 500 m-agl ending level (Erel et al., 2007), which is a level frequently used to guarantee the trajectory starts in the atmospheric boundary layer (ABL) (Dvorska et al., 2008). By this means, 4 representative trajectory groups were recognized and classified roughly according to the originating directions (NW, NE, SW and SE) from all the air masses trajectories during the one-year sampling period (Fig. 5).

(1) Fig. 5a: this is a typical category of continental air mass characterized with higher contents of dust (Table 2) and anthropogenic pollutants originating from the northwestern of Chinese Mainland. It passed through the arid/semiarid regions of Northwestern China and the developed areas in North China (e.g. North China Plain) with high mixing depth and reached Jiaozhou Bay. The occurrence frequency of this type of air mass was 34.7% and it occurred mainly in spring and winter during the sampling period.

(2) Fig. 5b: a category mixed with continental and marine air masses passed through the Sea of Japan and Korean Peninsula and reached the sampling site. Both anthropogenic and marine

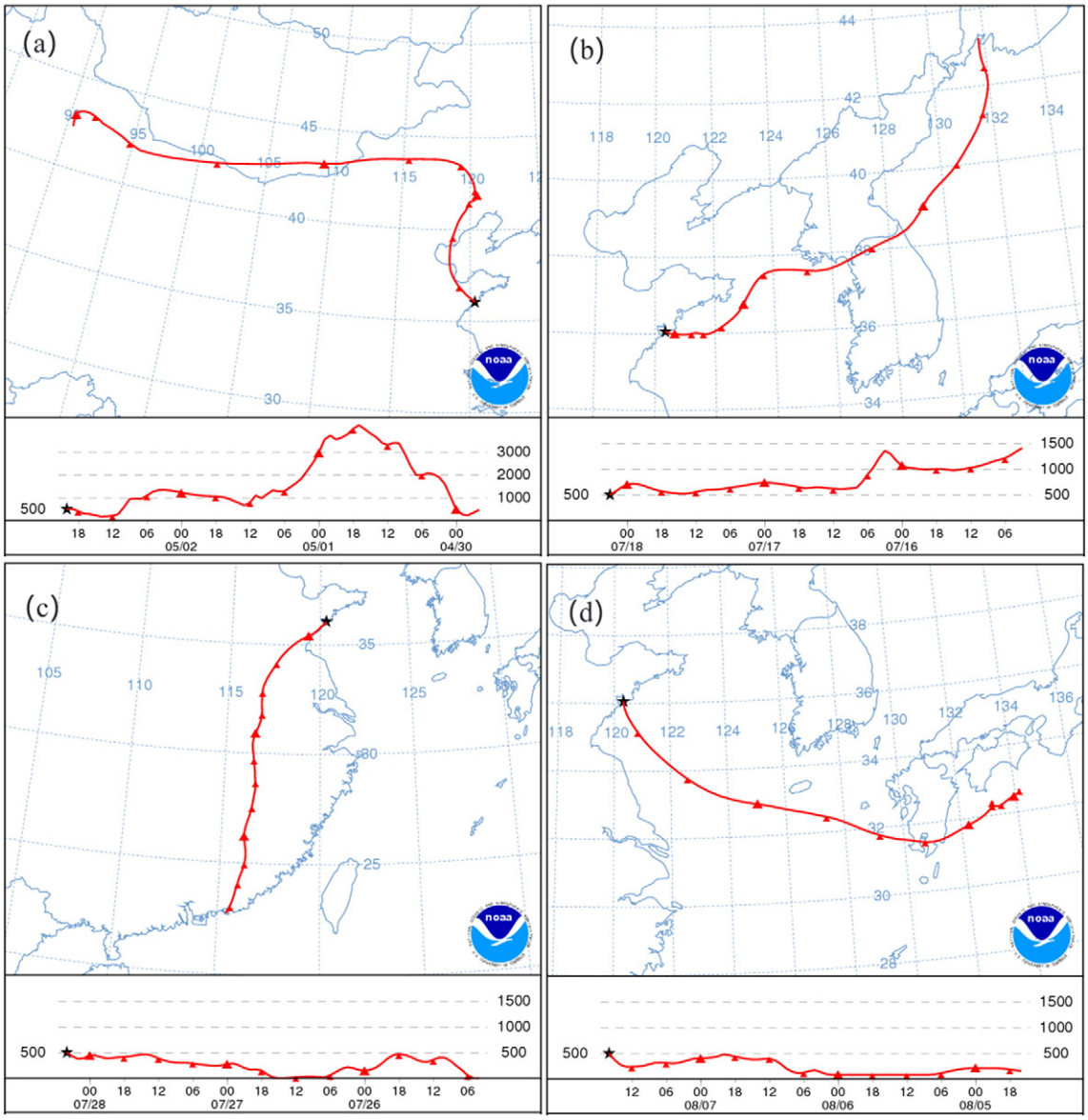

Fig. 5. Typical backward trajectories for different air masses reached the study region during June 2015–May 2016: (a) NW; (b) NE; (c) SW; (d) SE.

aerosols may affect the chemical compositions of these air masses to some degree. The occurrence frequency of this type of air mass was 14.3% and it occurred mainly in autumn in this study.

(3) Fig. 5c: this category of air mass originated from the South China Sea, passing through the South of China with lower mixing depth and reached the study area. Thus, it may also bring Jiaozhou Bay marine pollutants (e.g. exhaust emission from steamship. Beyn et al., 2015) and anthropogenic pollutants. However, it occurred fewer during the sampling period.

(4) Fig. 5d: it is a type of air mass derived from the East China Sea or Japan with highly randomness and uncertainty indirections. The extremely low mixing depth implies both anthropogenic and marine aerosols exerted strong impacts on these air masses. It was the most frequent type of air mass with an occurrence frequency of 42.8% and primarily occurred in summer and autumn.

Table 2
VWM concesntrations of SPM ($mg \cdot L^{-1}$) and nutrients ($\mu mol \cdot L^{-1}$) in AWD under the impacts of different categories of air masses.

Air mass type	SPM	VWM concentrations							
		NH_4–N	NO_3–N	NO_2–N	DIN	DON	DIP	DOP	SiO_3–Si
NW($n = 17$)	26.2	185.4	107.9	0.84	294.1	63.0	0.34	0.47	1.61
NE($n = 7$)	4.6	119.9	66.6	0.28	186.7	63.6	0.21	0.49	0.18
SW($n = 4$)	14.8	128.8	58.1	0.81	187.8	42.8	0.32	0.68	1.40
SE($n = 21$)	7.2	70.4	44.9	0.33	115.6	52.3	0.32	0.51	2.47

Note: NW, NE, SW and SE refer to the air masses during the rain events stemming from the northwestern, northeastern, southwestern and southeastern of the sampling site, respectively. The letter n represents the occurrence times of different categories of air masses.

Based on the classification above, the VWM concentrations of SPM and nutrients in AWD under the influences of different categories of air masses were calculated and the results were listed in Table 2. The rainwater under the influences of air masses stemming from NW and SW were characterized with higher concentrations of SPM, DIN, DIP and SiO_3–Si (Table 2), while the higher DON concentrations presented in the rainwater were affected by NW and NE air masses, and DOP high values were mainly affected by SW and SE air masses. These characteristics were partially in accordance with seasonal distribution of nutrient species (Table 1), based on the main occurrence seasons of

different categories of air masses mentioned above. As a result, the air masses originating from different directions probably exert great effects on the contents of nutrient species in AWD by means of the long-distance transports of pollutants from the emission sources to the study area. Surprisingly, the extremely high value of SiO_3–Si appeared in the rainwater under the influence of SE air mass. That is a complicated problem needing to be further studied.

3.3.2. Correlation analysis

Pearson correlation analysis was conducted using SPSS (version 16.0, SPSS Inc., Chicago) among the concentrations of various nutrients species and rainfall (Table 3). The varying degrees of negative correlations between rainfall and all nutrient forms proved the dilution effects of high rainfall amount on nutrient concentrations described above (Section 3.1). Previous study demonstrated wet deposition of atmospheric reactive nitrogen mostly originates from anthropogenic NH_3 and NO_x (Beyn et al., 2015). As a result, significant positive correlations were found among all N species, especially the DIN species (NH_4–N and NO_3–N), indicating anthropogenic N emissions were their common dominating sources. However, the moderate correlations between DON and DIN implies that DON may be partially derived from anthropogenic sources. Previous study indicated that DON in atmosphere may be related with the application of organic fertilizers such as livestock manure (Zhang et al., 2012). It should be noted that DON is constitutive of a variety of organic compounds, of which many originate from diverse natural and anthropogenic sources, and even some of them may stem from secondary aerosols formed by means of gas-to-particle reactions in the atmosphere (Cornell et al., 2003).

Compared to the N species, moderate correlations between P and N species were observed, suggesting DIP and DOP may have other sources in addition to human activities. However, the poor correlation between SiO_3–Si and DIN shows that SiO_3–Si is not mainly stemming from anthropogenic activities. The strong correlation between DIP and SiO_3–Si implies they may have similar sources, which is similar to the report of the tropical western Pacific Ocean (Song and Li, 1997a). Previous study has indicated continental or terrigenous origins (e.g. the dissolution of soil dusts) made significant contribution to atmospheric DIP and Si (Zhang and Liu, 1994), which can be proved by similar seasonal patterns between DIP, Si and SPM shown in Table 1. Also, some recent studies have proved atmospheric P is derived from multiple sources that combine crustal (dust), biogenic and biomass burning (Izquierdo et al., 2012; Markaki et al., 2010; Ridame and Guieu, 2002), which can be proved by the coexisting obvious correlations of DIP with DIN and SiO_3–Si in this study (Table 3).

3.3.3. NH_4–N/NO_3–N ratio

In general, NH_4–N mainly originates from agricultural activities (Beyn et al., 2015; Qiao et al., 2015), including the ammonium volatilization loss from N fertilizer, animal production and human/livestock excrements (Gu et al., 2012; Paerl et al., 2002; Zhao et al., 2009), whereas NO_3–N is regarded to be related to industrial and traffic emissions (Chen et al., 2011; Cui et al., 2014; Gu et al., 2012). Thus, NH_4–N/NO_3–N ratio is a reliable indicator for the evaluation of the relative contributions of industrial and agricultural origins to N wet deposition on the local/regional scale (Pan et al., 2012; Xu et al., 2015). If NH_4–N/NO_3–N ratio is <1 for N deposition, the industrialization of the surveyed region is high; on the contrary, the surveyed region is characterized with intensive agriculture (Zhao et al., 2009).

As expected, in this research, an average value of 2.2 for the NH_4–N/NO_3–N ratios was estimated, implying reduced N (NH_4–N) originating from agricultural production dominated N wet deposition in Jiaozhou Bay, which is consistent with the overall status in China (Xu et al., 2015). In addition, the seasonal mean values of NH_4–N/NO_3–N ratios were 1.6, 1.7, 3.3 and 1.2 in spring, summer, autumn and winter, respectively. The maximum value occurred in autumn, which corresponds to the autumn harvest and the widely use of chemical fertilizer and livestock excrement as the additional fertilizer for summer grain crops and the base fertilizer for winter wheat, respectively. Moreover, the high temperature in summer and autumn also accelerate the volatilization of NH_3 in N fertilizer (Zhao et al., 2009), revealing the contribution of agricultural activities was maximal in autumn around Jiaozhou Bay. Further, recent studies have shown that NH_3 concentration in the atmosphere was related to population, anthropogenic discharges and biological sources (e.g. the emissions from humans, sewage systems and garbage containers) (Reche et al., 2012; Yang et al., 2010), especially in summer, the volatilization of NH_3 from the aerosol phase was apparent (Reche et al., 2012). That may be also used to explain the higher content of NH_4–N in summer to some extent.

To summarize, the dominating sources of N, Si and P in AWD were local agricultural activities, soil dust and a mixing one combining anthropogenic and natural sources, respectively. In addition, the industrial emission, anthropogenic waste discharge and vehicle exhaust may be other sources of atmospheric N.

3.4. Contribution of AWD to the annual nutrient input in Jiaozhou Bay

The quite narrow mouth limits the water exchange between Jiaozhou Bay and the Yellow Sea (Sun and Sun, 2015). Consequently, the nutrient inputs via AWD would increase nutrient loads in Jiaozhou Bay undoubtedly. To illuminate the role of AWD in the total external input of Jiaozhou Bay, we compared the AWD with the point source discharge (refers to riverine input and wastewater drainage) and mariculture discharge (Table 4). The results indicated that AWD accounted for a lower percentage in the total external inputs of nutrients in Jiaozhou Bay, indicating the major source of nutrients in Jiaozhou Bay is terrigenous point source discharge (Liu et al., 2005). With respect to DIP, the percentage is similar to the result from Sun and Sun (2015) that atmospheric DIP accounts for <1% of the total input. Furthermore, the AWD

Table 3
Correlation matrix of the various nutrient species and rainfall in wet deposition.

Parameters	Rainfall	NH_4–N	NO_3–N	NO_2–N	DIN	DON	DIP	DOP	SiO_3–Si
Rainfall	1.000								
NH_4–N	−0.322*	1.000							
NO_3–N	−0.333*	0.904**	1.000						
NO_2–N	−0.221	0.406**	0.366**	1.000					
DIN	−0.336*	0.979**	0.972**	0.402**	1.000				
DON	−0.034	0.532**	0.615**	0.178	0.584**	1.000			
DIP	−0.335*	0.693**	0.790**	0.481**	0.757**	0.410**	1.000		
DOP	−0.208	0.287*	0.417**	0.210	0.356*	0.338*	0.313*	1.000	
SiO_3–Si	−0.032	0.038	0.010	0.364*	0.028	−0.011	0.327*	−0.244	1.000

* Refers to the correlation is significant at $P < 0.05$ (two-tailed).
** Refers to the correlation is significant at $P < 0.01$ (two-tailed).

Table 4
Comparison of nutrient input loads of wet deposition and point source discharge and mariculture discharge in Jiaozhou Bay.

Nutrient	Wet deposition/(mol·yr^{-1})	Point source discharge/(mol·yr^{-1})	Mariculture discharge/(mol·yr^{-1})	Wet deposition percentages in the total input loads/%
DIN	5.46×10^7	5.19×10^8	1.47×10^7	9.52
DON	1.76×10^7	2.03×10^8	–	7.98
DIP	1.01×10^5	2.18×10^7	1.16×10^6	0.44
SiO_3–Si	6.42×10^5	2.67×10^7	–	2.35

Note: The point source discharge data of N and P refer to Yang (2014) and Wang (2009); the point source discharge data of SiO_3–Si are from Liu et al. (2014), which excludes wastewater drainage; the mariculture discharge data refer to Sun and Sun (2015).

load of DIN in the present study is approximately 1.5 times that by Sun and Sun (2015), and the percentage may be doubled if the dry deposition was added. All of these suggest the contribution of atmospheric deposition to the nutrient levels in Jiaozhou Bay is enhancing gradually.

3.5. Ecological effects of nutrient input via AWD on Jiaozhou Bay

3.5.1. Enrichment effects of AWD on nutrient concentrations in Jiaozhou Bay

The above have proved that AWD is an important pathway for terrigenous N entering Jiaozhou Bay. Thus, the contributions of AWD nutrients to the surface seawater of Jiaozhou Bay were estimated based on all of the individual rain events. In this study, we suppose the nutrient deposited into Jiaozhou Bay via AWD could affect only 2 m depth of the surface water over a short period (Du et al., 2008), then the enrichment effects of AWD on the nutrient concentrations of Jiaozhou Bay can be calculated by the wet deposition fluxes of individual precipitation events divided by the depth (2 m). The nutrient inputs via AWD can increase the surface concentrations of all nutrient species in varying degrees (Table 5), of which, the average contribution of NH_4–N was the most prominent. Although the average contributions were low, the individual short-term heavy rains may result in significantly increase in nutrient concentrations of surface water. A case on July 31, 2015 showed that the contributions of the nutrient inputs via 1-h heavy rain to the concentrations of DIN, DIP and SiO_3–Si could reach 19.3%, 1.2% and 0.02%, respectively. Similar results were also found in the coastal waters of Xiamen (Du et al., 2008) and the tropical western Pacific Ocean (Song et al., 1997b). Owing to the restriction of narrow bay mouth to water exchange, the inputs of large amounts of nutrients in short-term heavy rain may increase the risk of eutrophication in Jiaozhou Bay.

3.5.2. The contribution of AWD to PP

It has been discovered that owing to the abundant nutrient inputs by wet deposition, the growth of phytoplankton could be stimulated and accelerated by rainwater (Zhang, 1994; Zhang and Liu, 1994; Zou et al., 2000). Moreover, NH_4–N is the N species assimilated in preference to NO_3–N by phytoplankton (Zou et al., 2000), which corresponding to the fact that NH_4–N is the most abundant nutrient species in wet deposition. Consequently, PP may be enhanced rapidly after the rain events (Zhang, 1994; Zou et al., 2000). Just in the East China Sea, according to the simulative results from the MM5/CMAQ model, a NP of 100–200 mmol C·m^{-2}·yr^{-1} can be triggered by the input of atmospheric total N, which occupied 1.1–3.9% of NP in the East China Sea (Zhang et al., 2010). The nutrient addition experiment conducted in the coastal Yellow Sea showed that phytoplankton species flourished and chlorophyll-*a* concentration significantly increase when rainwater was added (Zou et al., 2000).

It has been reported that the annual DOP deposition into oceans is ~0.35 Tg P·yr^{-1}, and ~10% of the DOP deposition (~0.04 Tg P·yr^{-1}) can constitute "new" P to support PP in P-limited waters (Kanakidou et al., 2012; Okin et al., 2011). Considering P-limitation for photosynthesis in Jiaozhou Bay, supposing that all of DIP and 10% of DOP could be assimilated by phytoplankton, then NP supported by AWD could be 1.38, 0.803, 1.69 and 0.631 mg C·m^{-2}·d^{-1} for spring, summer, autumn and winter respectively, according to Redfield ratio C:P = 106 (Redfield et al., 1963). That accounted for 0.48%, 0.10%, 0.68% and 0.62% of the average PP measured by Sun et al. (2005) in Jiaozhou Bay. These were lower than the percentage (14%) found in the open western Mediterranean Sea (Ridame and Guieu, 2002), where the DIP flux was high owing to the frequent Saharan dust events.

Although the average contribution of AWD to PP was low, the sudden heavy rain in the wet season may greatly stimulate the rapid growth of phytoplankton, causing the fast increase of PP in a short time. In this study, a case of sudden heavy rain event occurred on Nov. 5–6, 2015, NP triggered only by DIP in AWD could reach up to 60.6 mg C·m^{-2}·d^{-1}, accounting for approximately 25% of the average PP of Jiaozhou Bay in autumn (247.81 mg C·m^{-2}·d^{-1}, Sun et al., 2005). Moreover, the transitory peak value (7213.5 mg C·m^{-2}·d^{-1}) for PP in the east coastal region of Jiaozhou Bay in June 2003 may also be associated with the heavy rain occurred one week ago (Sun et al., 2005).

It should be noted that all of those were just a rough calculation for the NP induced by nutrient input via AWD, owing to the ecological effects of AWD on aquatic ecosystem depend not only on amounts of the nutrients, but also on the nutrient structures and compositions of the surface water to a large extent (Zhang et al., 2004). Moreover, that rainwater stimulates the growth of phytoplankton generally does not just rely on a single nutrient species but on the synthetic action of multiple major nutrients and trace elements (Zou et al., 2000).

Table 5
The enrichment effects of atmospheric wet deposition on the nutrient concentrations (μmol·L^{-1}) in Jiaozhou Bay.

Nutrients	Enrichment concentration	Average nutrient concentrations in Jiaozhou Bay	Average contribution of AWD to the surface nutrients concentrations/%
NH_4–N	0.95	8.00	13.0
NO_3–N	0.56	11.5	4.87
NO_2–N	0.0044	1.36	0.20
DIN	1.51	21.6	7.45
DON	0.48	17.11	3.27
DIP	0.0028	0.30	0.70
DOP	0.0046	0.50	0.92
SiO_3–Si	0.0177	7.00	0.02

Note: The average nutrient concentrations in the surface water of Jiaozhou Bay refer to Kang (2014) and Ding et al. (2013).

3.5.3. The effects of AWD on phytoplankton structure

On average, the molar ratios of DIN:DIP and Si:DIN were 1234 and 0.01 in AWD during the sampling period in Jiaozhou Bay, respectively, which were notably higher and lower than those in seawater of Jiaozhou Bay (69.5 and 0.34, respectively, calculated by the data in Table 5) and the Redfield ratios (16 and 1, respectively. Redfield et al., 1963), revealing the excessive input of rainwater from short-term heavy rain may intensively elevate the molar ratio of DIN:DIP and decrease Si:DIN molar ratio of surface waters in Jiaozhou Bay. For that reason, the status of P-limitation and Si-limitation in Jiaozhou Bay will be further exacerbated, which is in agreement with the studies conducted in lakes in Norway, Sweden, and Colorado, United States (Elser et al., 2009a, 2009b) and the Mediterranean Sea (Markaki et al., 2010), where the nutrient limitations were shifting from N to P owing to the

increase in anthropogenic N wet deposition. Similar result was also found in the Yellow Sea (Zou et al., 2000).

Further, the changes of nutrient structure may give rise to the succession for dominant species of phytoplankton. The long-term unbalanced N:P ratio may cause the rise of the percentage of dinoflagellate in phytoplankton (Zhou et al., 2008). Correspondingly, the probability that dinoflagellate becomes the dominant species in Jiaozhou Bay has been increasing in recent years (Sun and Sun, 2015). Besides, considering the extremely high DIN:DIP in AWD and the relative deficiency of P and Si in AWD, AWD may be responsible for the succession of the dominant species from diatom to dinoflagellate to some extent. Similar result was also found in alpine lakes of the Rocky Mountains of Colorado (USA), suggesting that sustained N deposition may have significant effects on phytoplankton communities as well as plankton-based food webs (Elser et al., 2009b). In addition, the growth of nano-phytoplankton is closely related to the high concentration of NH_4–N, while high concentration of NO_3–N may facilitate the growth of micro-phytoplankton to some degree (Sun and Sun, 2012). The fact that the percentage of micro-phytoplankton has decreased while the fact that of the nano-phytoplankton has increased since 1998 (Sun and Sun, 2012) may also be associated with the higher percentage of NH_4–N than that of NO_3–N in wet deposition. This is consistent with the incubation experiment conducted by Seitzinger and Sanders (1999). In conclusion, AWD is likely to have an impact on the community structure as well as on the size-fractioned structure of phytoplankton by shifting the nutrient regimes of the surface water in Jiaozhou Bay.

It should be noted that under an anthropogenically warmed climate, extreme precipitation events will become more frequent in the present and future over the Northern Hemisphere (Allan and Soden, 2008; Min et al., 2011). Accordingly, the inputs of nutrients, especially N, via wet deposition would be increasingly enhanced. Eventually, the status of AWD of nutrients in total external input of Jiaozhou Bay, together with their ecological effects on Jiaozhou Bay ecosystem, would be further enhanced. The indirect AWD flux, however, was not calculated owing to the deficiency of data. That is limited by the sampling technology and the complicated terrain in the drainage basin of Jiaozhou Bay. Research has shown that indirect wet deposition is approximately 2.5 multiple of the direct wet input (Whitall et al., 2003). That highlights the prominent status of the indirect import of wet deposition nutrient from watershed. Therefore, the recognition and assessment of indirect wet deposition processes and fluxes will be our research focus in the near future.

4. Conclusions

The concentrations of N species in AWD of Jiaozhou Bay during 2015–2016 were significantly higher than that in 1980s, which is opposite to the trends of P and Si concentrations. The annual AWD fluxes of NH_4–N, NO_3–N, NO_2–N, DON, DIP, DOP, and SiO_3–Si were 92.8, 54.5, 0.427, 47.5, 0.274, 0.448 and 1.73 $mmol \cdot m^{-2} \cdot yr^{-1}$, respectively. The VWM concentrations and fluxes of NH_4–N, NO_3–N and DON in AWD were relatively higher compared with NO_2–N, PO_4–P, DOP and SiO_3–Si. NH_4–N and DOP were the dominating N and P species, respectively. DON and DOP occupied 24.3% and 62.0% of TDN and TDP, respectively, revealing their roles in AWD cannot be neglected. Partially owing to the intense perturbation by human activities and meteorological factors, significant seasonal/monthly variations were observed for all nutrient species. Rainfall and the intensities of local emission sources as well as the long-distance transports of natural and anthropogenic pollutants dominated wet deposition of nutrients in Jiaozhou Bay.

The dominating source of N species in precipitation was agricultural activities (e.g. fertilization and livestock excrements, etc.), while fossil fuel combustion, anthropogenic discharge (e.g. sewage systems, etc.) and biological sources (e.g. emissions of garbage containers, etc.) may also make great contributions. By contrast, atmospheric P in Jiaozhou Bay has a complex source mixed with natural (mineral dusts) and anthropogenic sources (fossil fuel and biomass combustion), and the dissolution of soil dusts make significant contribution to the wet deposition of SiO_3–Si.

AWD occupied relatively low percentages of total external input loads of nutrients in Jiaozhou Bay. The average NP supported by the sum of DIP and bio-available DOP were 1.38, 0.803, 1.69, and 0.631 $mg\,C \cdot m^2 \cdot d^{-1}$ in spring, summer, autumn and winter, respectively. Furthermore, the average DIN:DIP and Si:DIN molar ratios in AWD were greatly deviated from Redfield ratios and the actual ratios of those in seawater of Jiaozhou Bay. However, large amounts of nutrient inputs originating from sudden heavy rainfall may stimulate the rapid growth of phytoplankton and promote the increase of PP prominently, as well as aggravate P-limitation and Si-limitation and further affect the community structures and size-fractioned structures of phytoplankton in Jiaozhou Bay. Under the dual influences from the climate change and anthropogenic activities, the contribution of AWD to the nutrient budgets and possible potential ecological effects on Jiaozhou Bay ecosystem would become increasingly apparent. Considering the importance of indirect wet deposition, the recognition and assessment of indirect wet deposition processes and fluxes will be the focus of our research in the near future.

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