*Activity 2 of Output 3.1.2*

*—Monitoring and acquisition of data about atmospheric nutrients and heavy metals in the Yellow Sea*

# Deliverable 12-1:

# Atmospheric deposition of Nutrients and Heavy Metals over the Yellow Sea

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# Contents

# Atmospheric deposition of Nutrients and Heavy Metals over the Yellow Sea

## 1. Background and Objectives

The Yellow Sea is an important part of the world's oceans and the key to the survival of the residents along the Yellow Sea coast. However, the lack of understanding of the ecosystem of the ocean in the past and the lack of effective management and coordination of the environment and resources have triggered a series of problems such as the decline of biological resources, the decline of biodiversity and the degradation of environment and ecosystem, serious water pollution in coastal waters. These have posed a tremendous threat to the sustainable development.

There are many ways for pollutants to enter the ocean, such as river input, direct sewage discharge, mariculture pollution, air-sea exchange, and so on. In the past 30 years of research, the role of the atmosphere in transporting man-made and natural source pollutants to the ocean has proved to be significant. Globally, atmospheric deposition input is generally equivalent to or even greater than the riverine input of some pollutants in the coastal waters (GESAMP, 1989; Duce et al., 1991), especially in the open sea atmospheric deposition is the most important entry route for pollutants from human activities in the open sea area far from the land. The substances transported to the sea are mineral dust, plant residues, heavy metals, nitrogen compounds from combustion and fertilization, pesticides, and a range of industrial and synthetic organic compounds.

Among all kinds of pollutants, nitrogen and phosphorus are the key nutritional components. Excessive inputs of nitrogen and phosphorus nutrients may change the structure of nutrients in water, cause eutrophication, destroy the structure of biological communities and may trigger deterioration of marine ecological environment such as red tide, which seriously affect the coastal ecological balance and its functions,

especially in the summer. For example, annual atmospheric nitrogen deposition brought about 10% of Japan's seawater productivity， in summer and autumn the number could reach up to 25% (Kang et al., 2010). It was found that the value of N/P in the atmosphere is generally high. For example, the value of N/ P in the dry deposition in the northern Atlantic Ocean is generally greater than 30 and in some areas over 1000 (Baker et al., 2007; Dentener et al., 2006). In fact, higher value of DIN and N/P in dry-wet deposition of the atmosphere contributes significantly to new productivity in the low nutrient sea area and mitigates nitrogen or phosphorus limitation in the water (Baker et al., 2007; Zhang et al., 2007). Studies done by (Markaki Z, 2010) on the Mediterranean Sea showed that the DIN / DIP increased gradually from west to east in wet deposition, and a trend that was consistent with the trend of DIN / DIP in seawater corresponding to the sea area, indicating that atmospheric wet deposition can directly affect DIN / DIP in seawater.

Heavy metals are another important source of atmospheric pollutants which can cause significant structural changes in marine ecosystems. Through the atmospheric transmission, heavy metal pollutants generated by human activities enter into the sea. Some can bring substances beneficial to the growth of marine plankton such as iron (Duce et al., 1991). While other elements (such as Cu, Pb, etc.)will have toxic effects on phytoplankton (Adina et al., 2009). In many offshore waters, metal elements coming from atmospheric precipitation can account for a significant proportion of the total input. In the English Channel, heavy metal elements coming from atmospheric dry and wet deposition accounted for 20.70% of the total input. In the North Sea, V, Cr, Ni, Cu, Zn and Pb coming from atmospheric deposition reached 560,1300, 650, 690, 3500 and 1970 tons, contributing 28%, 29% and 57% of the total input of Cu, Zn and Pb, respectively(Deboudt et al., 2004; Injuk et al., 1998; Sakata et al., 2008; Williams et al., 1998). In some areas such as the East China Sea and the eastern Mediterranean, the nitrogen and phosphorus coming from atmospheric deposition accounts for a considerable proportion of new productivity. The concentrations of lead, copper and

zinc in aerosol observed in Qingdao in 2006 were 2.3 times of those in the 1990s. The calculated dry deposition fluxes of copper and lead to the Yellow Sea are higher than those of the North Sea in the early 1990s. And the value is nearly a magnitude higher (Lammer et al., 2006).

Overall, studies on atmospheric nutrients and heavy metals in the Yellow Sea have been carried out since a few years ago, but the number of studies has declined in the last decades, especially about heavy metals and precipitation in the Yellow Sea. Therefore, it is necessary to pay attention to the heavy metals and nutrient components importing into the Yellow Sea from the atmosphere-based. So, there are two objectives of this study: 1. Improve the method for assessing the deposition flux of marine atmospheric pollutants, which has been given in the previous report ; 2.Estimate the total amounts of nitrogen and phosphorus from atm.-based sources in the Yellow Sea, which will be described in this reports.

# 2. Air quality status in typical coastal cities along the Yellow Sea in China

## 2.1 Data Sources

The AQI pollution index the six pollutant mass concentration data of two typical coastal cities were obtained from the data center of $PM_{2.5}$ real-time monitoring network (http://www.pm25china.net/). The two typical cities are Rongcheng City and Rizhao City in Shandong Province.

## 2.2 Analysis of air quality in typical coastal cities

The air quality parameters of Rizhao City and Rongcheng City are shown in Fig.2-1 and Fig.2-2. The average concentration of $PM_{2.5}$, $PM_{10}$, $SO_2$, $NO_2$, CO, $O_3$ in Rizhao City in 2017 was 47 μ g/m$^3$, 87 μ g/m$^3$, 14 μ g/m$^3$, 37 μ g/m$^3$, 0.81mg/m$^3$, 69 μ g/m$^3$ respectively. The average concentration of $PM_{2.5}$, $PM_{10}$, $SO_2$, $NO_2$, CO, $O_3$ in

Rongcheng City in 2017 was 24 μ g/m$^3$, 51, 9 μ g/m$^3$, 14 μ g/m$^3$, 0.66mg/m$^3$, 84 μ g/m$^3$, respectively. At the same time, it can be seen that the air quality in summer and autumn was better than that in autumn and winter.

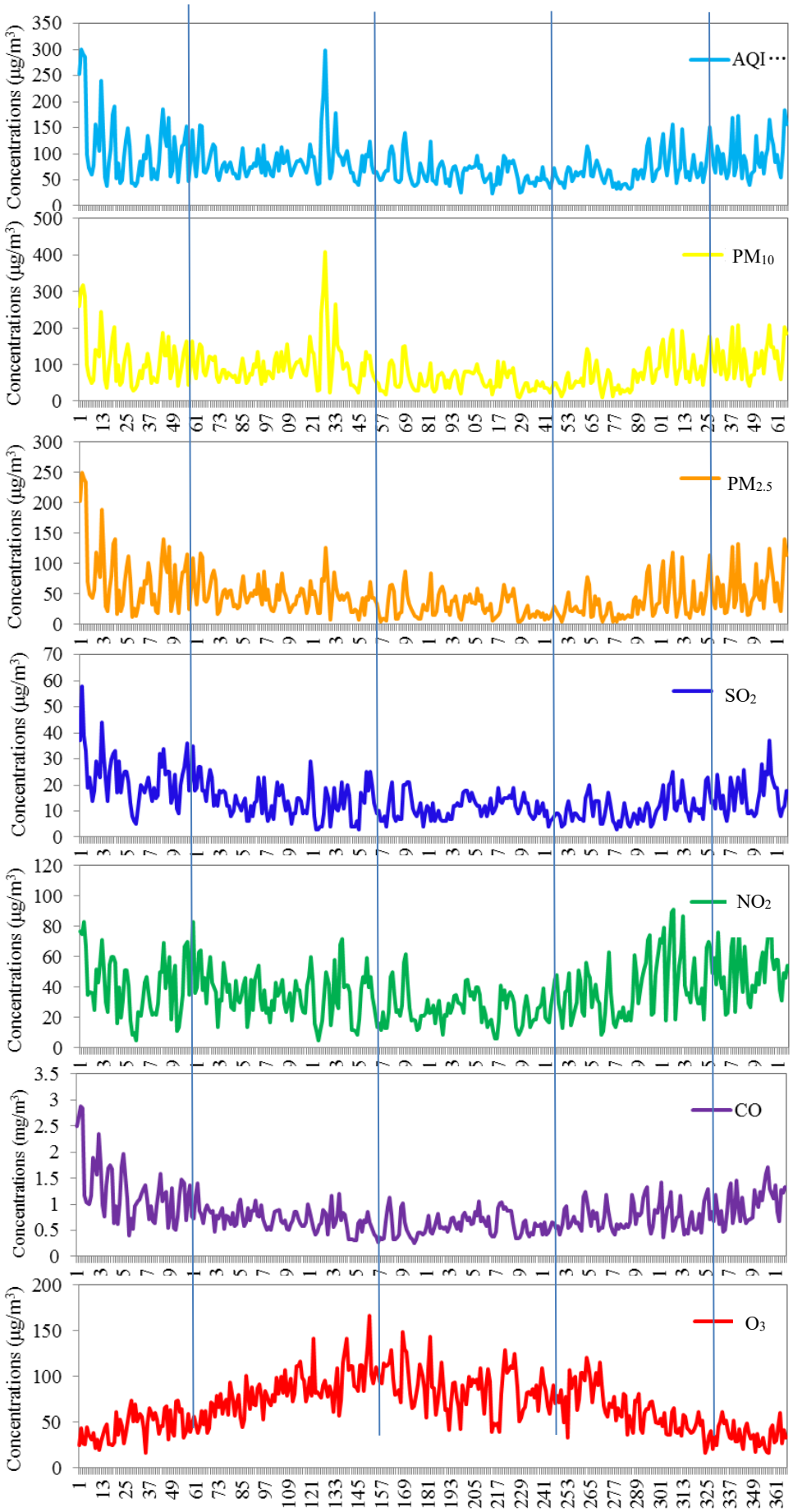
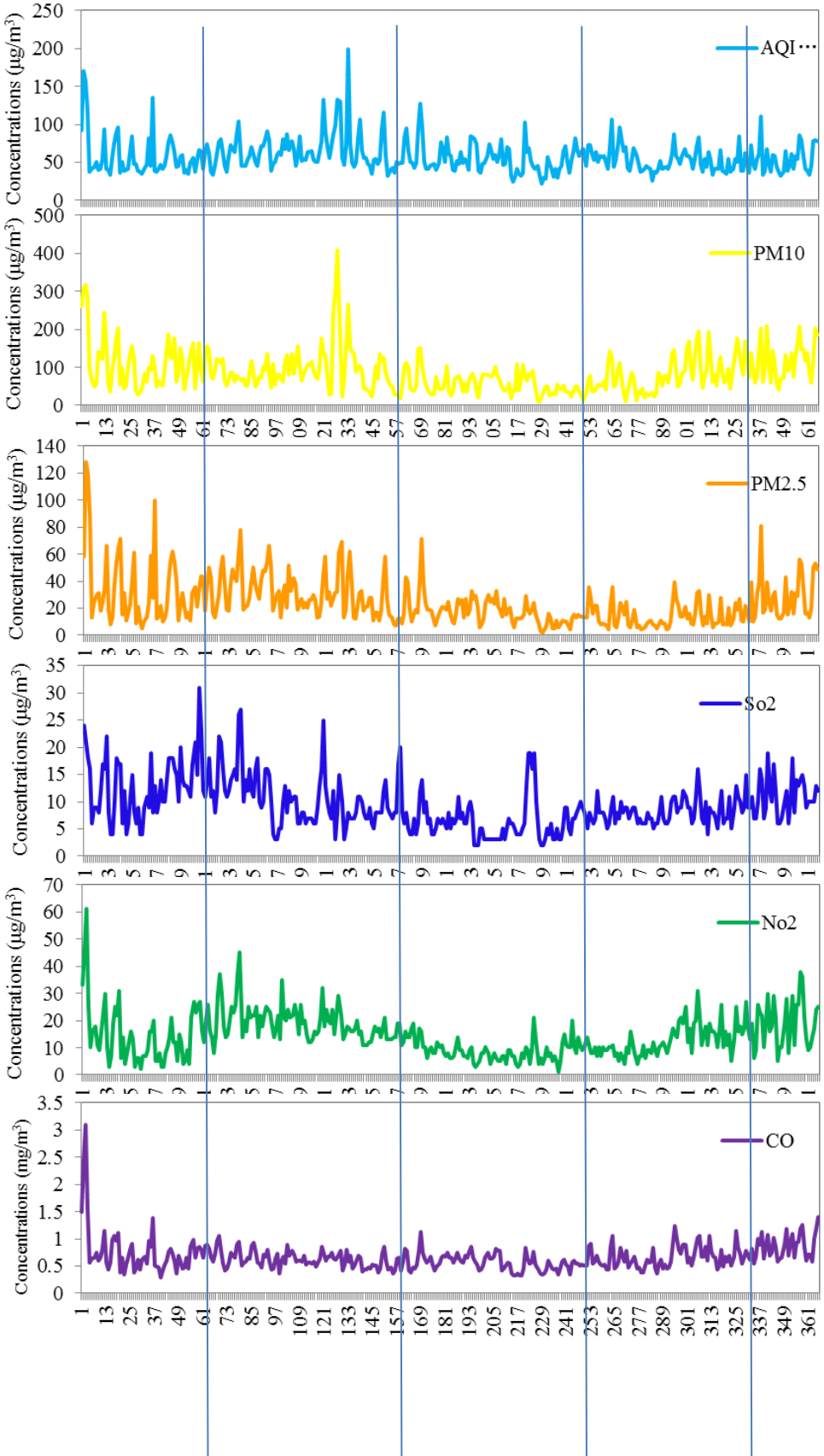


Fig.2-1 Air pollution situation in Rizhao City，Shandong Province in 2017



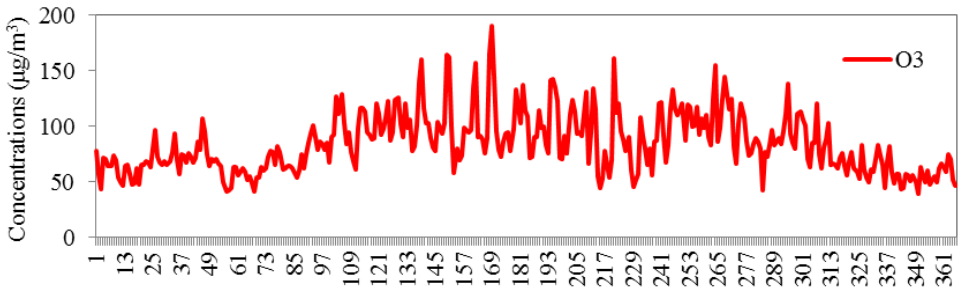



Fig.2-2 Air pollution situation in Rongcheng City Shandong Province in 2017

Table.2-1 Air quality status of Rizhao City and Rongcheng City in 2017

| | | Index of AQI | $PM_{2.5}$ | $PM_{10}$ | $SO_2$ | $NO_2$ | CO | $O_3$ |
|---|---|---|---|---|---|---|---|---|
| **Rizhao** | Average | 81 | 47 | 87 | 14 | 37 | 0.81 | 69 |
| | Max | 300 | 249 | 409 | 58 | 107 | 2.88 | 166 |
| | Min | 24 | 4 | 10 | 3 | 5 | 0.26 | 17 |
| **Rongcheng** | Average | 58 | 24 | 51 | 9 | 14 | 0.66 | 84 |
| | Max | 199 | 128 | 282 | 31 | 61 | 3.09 | 190 |
| | Min | 22 | 2 | 11 | 2 | 1 | 0.29 | 40 |

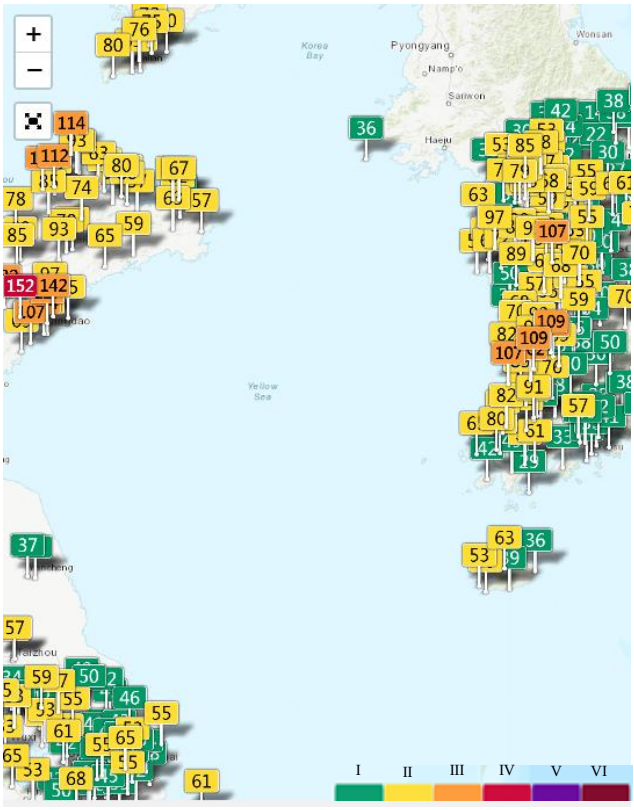



Fig.2-3 Air pollution in major cities around the Yellow Sea

(http://aqicn.org/map/world/cn/)

It can be seen from the statistical result in Table 2-1 and Table 2-2 that the air quality of the two typical cities along the Yellow Sea coast in 2017 was good, the proportion of excellent and quantitative grades in the Rizhao city was over 78%, and Rongcheng City, even reaches more than 95% in Rongcheng City, showing the results of China's comprehensive air pollution control in recent years. More worthwhile, there were no server pollution and most serious pollution in Rongcheng. Rongcheng's air quality is significantly better than that of Rizhao, which is related to the size of the city on the one hand, and is also related to the urban industrial structure and environmental protection measures on the other hand.

We intercepted the real-time air quality index map at a certain moment from the World Air Pollution Network (http://aqicn.org/map/world/cn/) and found that although the air quality in China's inland areas is poor, the air quality in the eastern coastal cities is significantly better than that in the inland, even the air quality of the city in most

cities on the west coast of the Yellow Sea is almost the same to those on the east coast of the Yellow Sea (see Fig. 2-3).

Table.2-2 Air quality status of Rizhao City and Rongcheng City in 2017

| Areas | | Excellent | Good | Light pollution | Moderate pollution | Severe pollution | Most serious pollution |
|---|---|---|---|---|---|---|---|
| Rizhao | Spring | 6.5% | 71.0% | 16.1% | 4.3% | 1.1% | 1.1% |
| | Summer | 38.0% | 56.5% | 5.4% | - | - | - |
| | Autumn | 23.3% | 61.1% | 13.3% | 2.2% | - | - |
| | Winter | 13.3% | 43.3% | 25.6% | 12.2% | 4.4% | 1.1% |
| | **Annual** | **20.3%** | **58.1%** | **15.1%** | **4.7%** | **1.4%** | **0.5%** |
| Rongcheng | Spring | 23.7% | 68.8% | 6.5% | 1.1% | – | – |
| | Summer | 55.4% | 42.4% | 2.2% | - | – | – |
| | Autumn | 47.8% | 51.1% | 1.1% | - | – | – |
| | Winter | 55.6% | 38.9% | 3.3% | 2.2% | – | – |
| | **Annual** | **45.5%** | **50.4%** | **3.3%** | **0.8%** | **–** | **–** |

## 3. Dry deposition of Nutrients and heavy metals over the Yellow Sea

There are two forms of atmospheric pollutant deposition, namely dry deposition and wet deposition, which are collectively referred to as total deposition. In this section, we mainly discuss the dry deposition. Dry deposition refers to the atmospheric deposition process without precipitation, which generally includes diffusion (gaseous and vaporous), Brownian motion (<2μm) and gravity deposition (>2μm). The dry deposition has a long duration and a wide range of influences, and the input of pollutants in the sea can't be ignored (Loughner et al., 2016; Zhang et al., 2010). The atmospheric dry deposition process is controlled by many factors such as the physical and chemical

properties of pollutants, meteorological conditions and characteristics of underlying surface, and the estimation of flux is difficult. In the first report of this study, the evaluation method of dry deposition flux is given. The main framework is as follows:

$$F_d = V_d * C * t \quad (1)$$

Where

$F_d$——Dry deposition fluxes of atmospheric pollutants；

$V_d$——Dry deposition velocities of atmospheric aerosol pollutants；

$C$——Average concentration of contaminated components in atmospheric TSP during the evaluation period；

$t$——Calculating time.

Here, deposition velocity is an important parameter. The values recommended by (GESAMP ) are generally adopted. However, it is usually low (Shahin et al., 2000). In fact, the velocities are greatly affected by particle size distribution (Kong et al., 2014; Kang et al., 2010).

## 3.1 Size distribution of Nutrients and heavy metals in aerosol

In order to obtain the dry deposition velocities of nutrients and heavy metal in atmospheric aerosols particles in the Yellow Sea, aerosol samples of different particle sizes were collected around the Yellow Sea and the characteristic of size distributions of nutrients and heavy metals in aerosol were obtained.

### 3.1.1 Sampling stations

Different particle size aerosol sampling station was located at Penglai Station, on the edge of the Yellow Sea. There is no large pollution source within 10 km around this station and was one of the excellent sites of China's marine atmospheric monitoring which can represent the atmospheric conditions in the north China Sea very well.

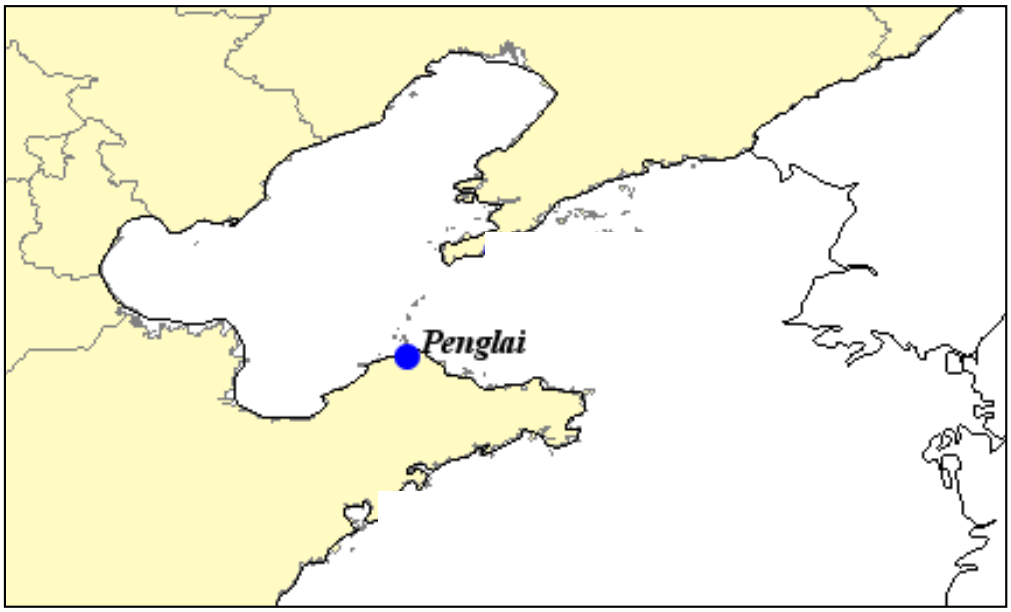



Fig.3-1 Location of sampling station of Penglai.

Fig.3-2 Sampling station of Penglai.

### 3.1.2 Sampling method

Anderson 8-stages aerosol sampler (made in US Tisch (TE-20-800)) installed with Quartz membrane was used to collect different particle size aerosol samples. The cut-points of eight stages include >10 μm, 9.0–10 μm, 5.8–9.0 μm, 4.7–5.8 μm, 3.3–4.7 μm, 2.1–3.3 μm, 1.1–2.1 μm, 0.65–1.1 μm, 0.43–0.65 μm and <0.43 μ m, with the sampling flow rate 28.3L/min. In October 2015, January 2016, May 2016, and July 2016, twelve sets of samples representing autumn, winter, spring and summer were collected, three sets per season. The cumulative sampling time for each sample was about 60–72 hours.

### 3.1.3 Analysis Methods

The nitrogen and phosphorus components in the sample were measured with standard colorimetric method in nutrient continuous flow analyzer (SEAL-AA3). And the heavy metals were measured with ICP-MAS (Agilent 7500ce).

Table 3-1 Target analytes and analysis methods

| No. | items | analysis methods |
|---|---|---|
| 01 | Nitrate-nitrogen | Standard colorimetric method in nutrient continuous flow analyzer (SEAL-AA3) |
| 02 | Nitrite-nitrogen | Standard colorimetric method in nutrient continuous flow analyzer (SEAL-AA3) |
| 03 | Ammonium-nitrogen | Standard colorimetric method in nutrient continuous flow analyzer (SEAL-AA3) |
| 04 | Phosphate | Standard colorimetric method in nutrient continuous flow analyzer (SEAL-AA3) |
| 05 | Cu, Pb, Zn, Cd, As | ICP-MAS (Agilent 7500ce) |

### 3.1.4 Size distribution of Nutrients and heavy metals in aerosol

For aerosol particle size samples, the particle size interval is not uniform, so the concentration of a component in each particle size range cannot directly reflect the size distribution characteristics of the component. In order to express its distribution law more objectively, this report uses the mass concentration distribution function q to describe it.

$$q = dC / d\lg D \approx \Delta C / \Delta \lg D.$$

Where，$\Delta C$ is the mass concentration of the components in the particle size interval; $\Delta \lg D$ is the difference between the upper and lower particle diameters of the corresponding particle size interval. The size distributions of various components in different seasons were shown in Fig.3-3~ Fig.3-11.

It can be seen from the particle size distributions of the contaminated components in aerosols that most of the components peaked in the particle size range of 9~10μm except for ammonia nitrogen. Because the particle size span of 9~10μm is small, a certain amount of pollutants in this particle size segment can lead to a higher value of ΔC / ΔlgD. However, ammonia nitrogen did not show obvious peak in particle size section of 9~10μm, and it can be seen that the proportion of ammonia nitrogen in the atmospheric aerosol was very low. It is fully demonstrated that $NH_4^+$-N in atmospheric particulates is mainly derived from the secondary conversion of $NH_3$ with other components in the air, which is confirmed in both chromatographic analysis and single particle analysis (Li et al., 2013; Xu et al., 2016). At the same time, we can see that ammonia nitrogen was distributed in the fraction with particle size less than 1μm, so mainly distributed in fine particles is the most important particle size distribution characteristic of ammonia nitrogen in atmospheric aerosol.

The remaining components showed at least two peaks in the coarse particles and fine particles，which shows that except for ammonia nitrogen, the sources of other pollutants are more complicated, ranging from one-time pollution components with coarser particle size to secondary pollution components with finer particle size.

Take nitrate nitrogen for an example, the peak of fine particles was formed in a similar way to ammonia nitrogen, deriving from the secondary conversion of polluting gases in the atmosphere. However in the summer and autumn, there was a significant peak enhancement in the range of 2.1~4.7μm, which is an obvious phenomenon in marine aerosols. Some studies showed that marine aerosols could help the removal of certain atmospheric pollutants in coastal areas, and may be an important source of atmospheric nitrate aerosols (Yao and Zhang, 2012). The sol background is also called the "chlorine loss" phenomenon of aerosols. In the offshore atmosphere, the relative humidity is relatively high, and the NOx emitted from the city forms a NaCl-NOx-$H_2O$ (steam)-gas system with the sea salt aerosol and water vapor in the air, then form a non-volatile nitrate, which is the final removal mechanism of $HNO_3$ and NOx in the atmosphere. Mamane and Gottlieb (Mamane, 1992) found that under laboratory simulation conditions, the amount of nitrate formed on sea salt aerosols was increased by about 5 times when exposed to ultraviolet light, indicating that the formation of nitrate by heterogeneous reaction on the surface of sea salt aerosol under sunlight exposure may be an important process for the removal of NOx from the atmosphere in coastal areas. Due to the large proportion of sea salt aerosol in the atmospheric environment in summer and autumn, and the strong sunlight in summer and autumn, the photochemical reaction is also more active than the winter and spring, which causes the ratio of NOx to NO3-aerosol in summer and autumn to be higher than the rest of the season. The gas-particle conversion relationship caused by the loss of aerosol chlorine is as follows:

$$NaCl(d)+NOx(g)\rightarrow NaCl(d)+N(\text{Ⅱ},\text{Ⅳ})(d)$$

$$NaCl(d)+NOx(g)\rightarrow NaNO_3(d)+HCl(g)$$

$$2NaCl(p)+H_2SO_4(g)\rightarrow Na_2SO_4(p)+2HCl(g)$$

$$NaCl(p)+HNO_3(g)\rightarrow NaNO_3(p)+HCl(g)$$

$$NaCl(d)+(NH_4)_2SO_4(d)\rightarrow Na_2SO_4(d)+2NH_4Cl(d)$$

$NaCl(d)+(NH_4)_2SO_4(d)\rightarrow Na_2SO_4(d)+2NH_3(g)+2HCl(g)$

$NaCl(d)+NH_4NO_3(d)\rightarrow NaNO_3(d)+NH_4Cl(d)$

$NaCl(d)+NH_4NO_3(d)\rightarrow NaNO_3(d)+NH_3(g)+HCl(g)$

Where, d-droplet； g-gas； p-particle

The remaining components are also due to the fact that they are mostly composite sources, resulting in a complex particle size distribution of pollutants and multiple peaks. Crust dust, biomass burning, vehicle exhaust emissions, industrial sources, etc. are potential sources. The characteristics of human activities and surface pollution sources in the region through which atmospheric pollutants are transported will have an important impact on size distribution of pollutants in atmospheric aerosols in Penglai. Pb mainly comes from mining, smelting, automobile exhaust, various paints, coating, batteries, coal, and lead-containing in “three waste of industries”, etc.. Cd mainly comes from mining, non-ferrous metal smelting, electroplating, batteries, paint production, etc.. As mainly comes from mining, smelting, decolorizing agents in the glass industry, chemical pharmaceuticals, and production of chemical fertilizers and pesticides. Zn in the atmosphere comes from waste incineration, motor vehicle exhaust, coal-fired fly ash, thermal power generation, steel smelting, rubber tire wear, incinerators, coal-fired boilers, smelting furnaces. Cu is mainly derived from motor vehicle emissions and non-ferrous metal smelting (Gu J., 2012). It can be seen that these sources include both primary and secondary pollution, both coarse and fine.

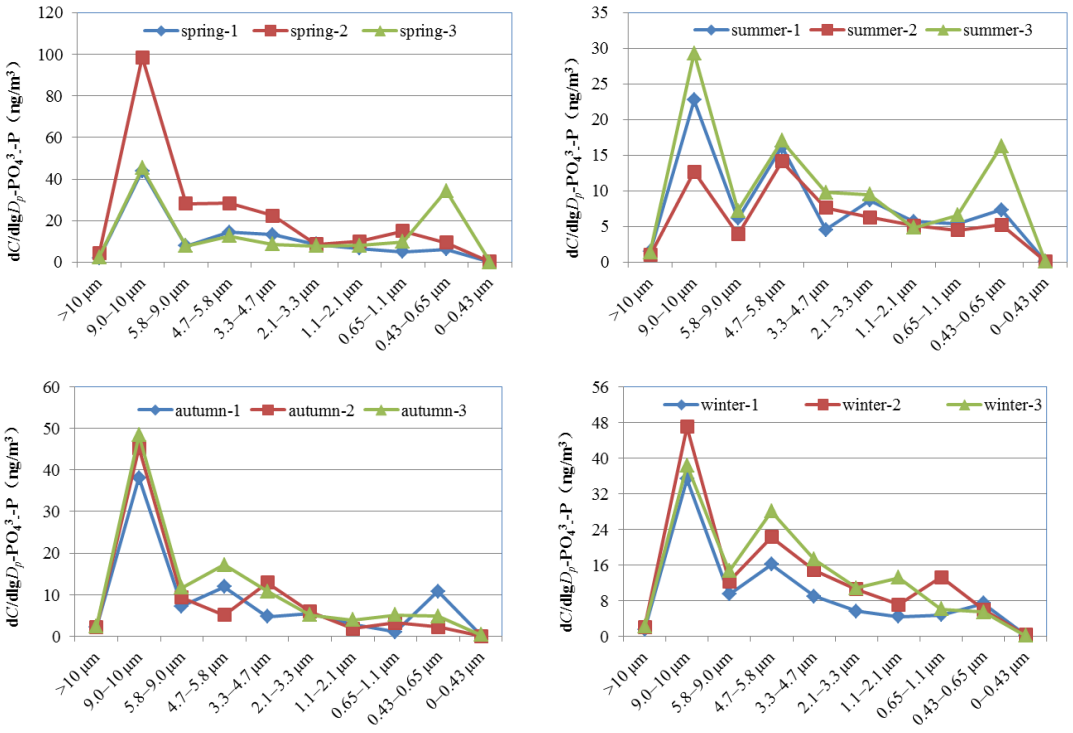



Fig.3-3 Size distribution of phosphate in aerosols in Penglai

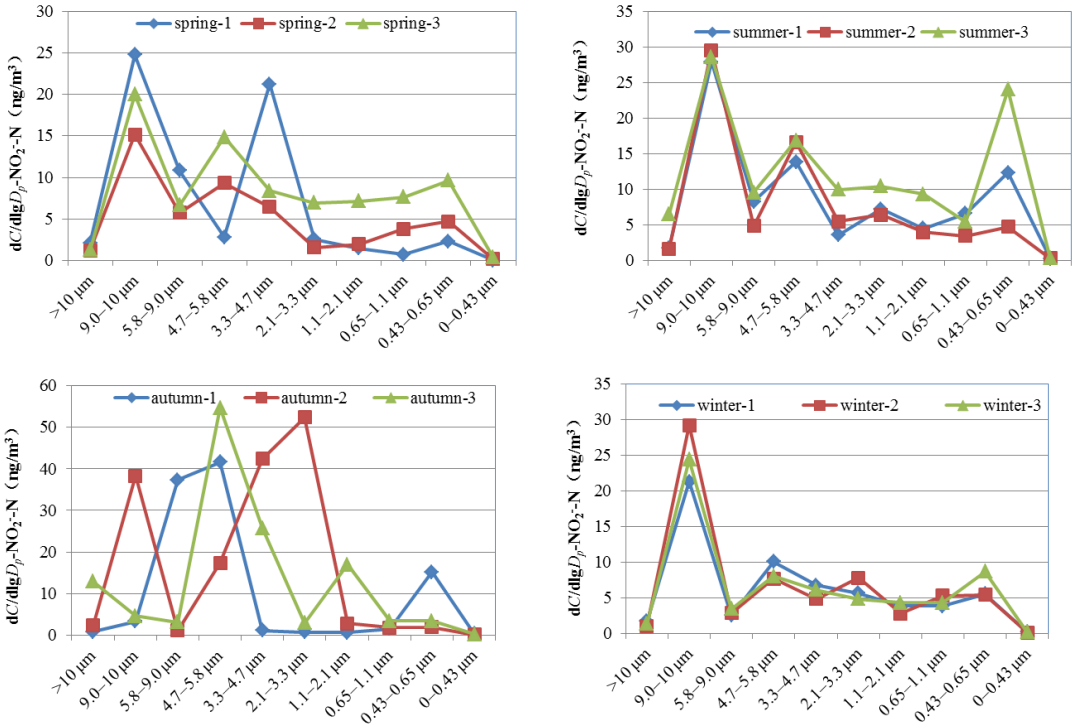



Fig.3-4 Size distribution of nitrite-nitrogen in aerosols in Penglai

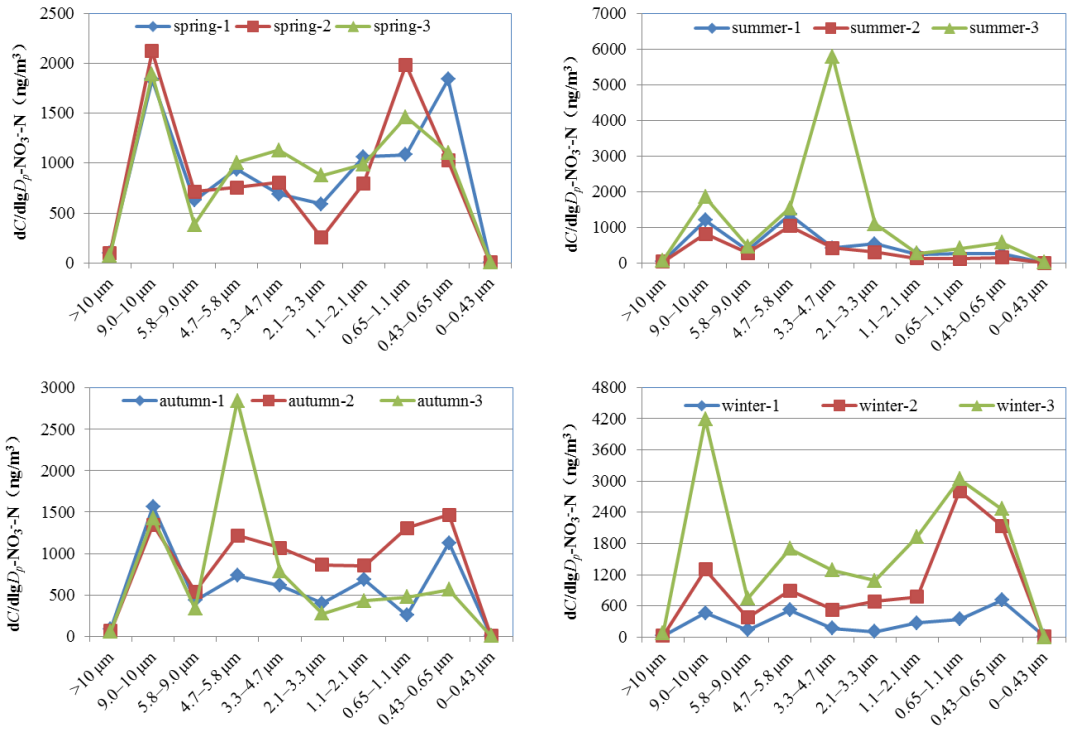



Fig.3-5 Size distribution of nitrate-nitrogen in aerosols in Penglai

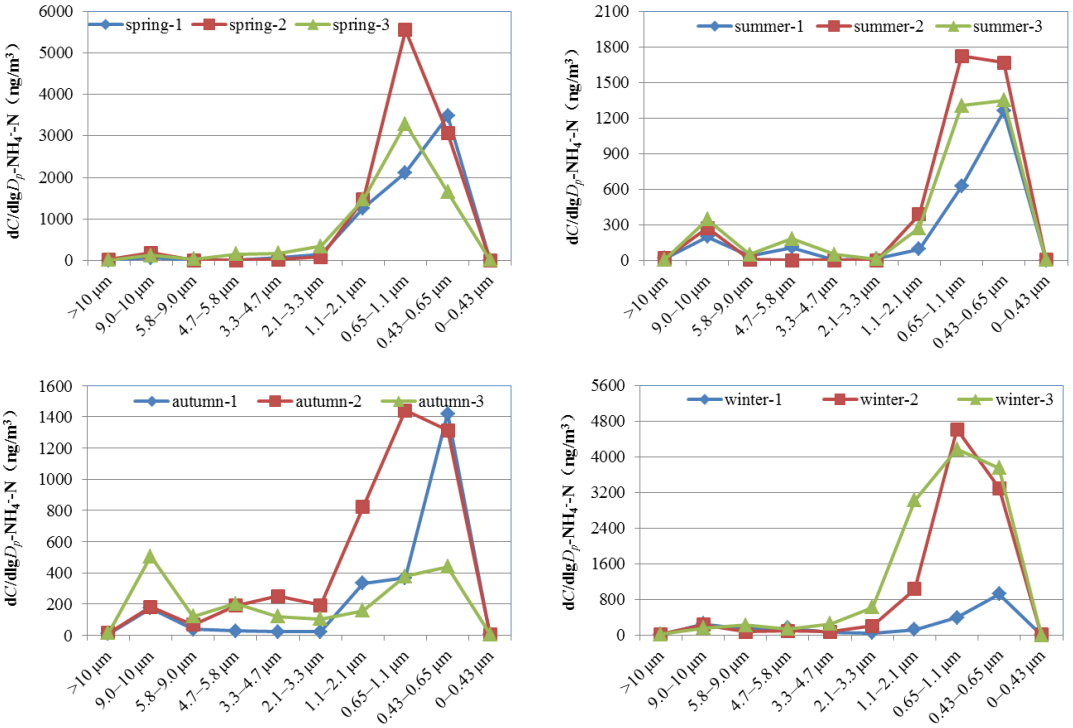



Fig.3-6 Size distribution of ammonium-nitrogen in aerosols in Penglai

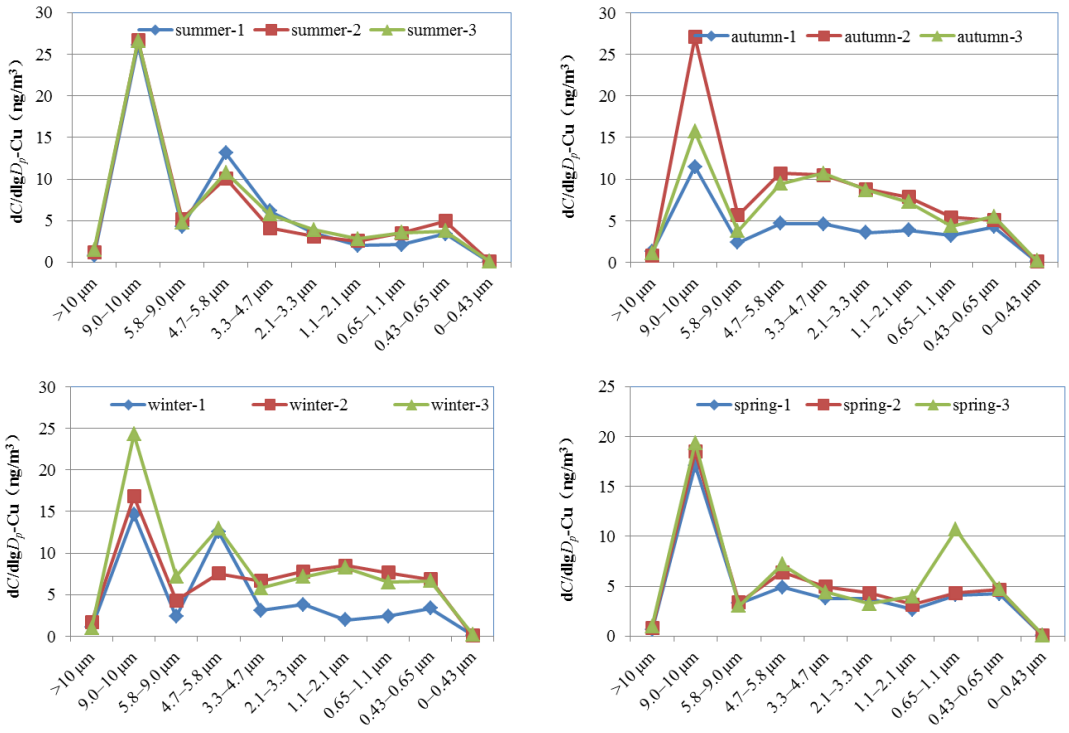



Fig.3-7 Size distribution of Cu in aerosols in Penglai

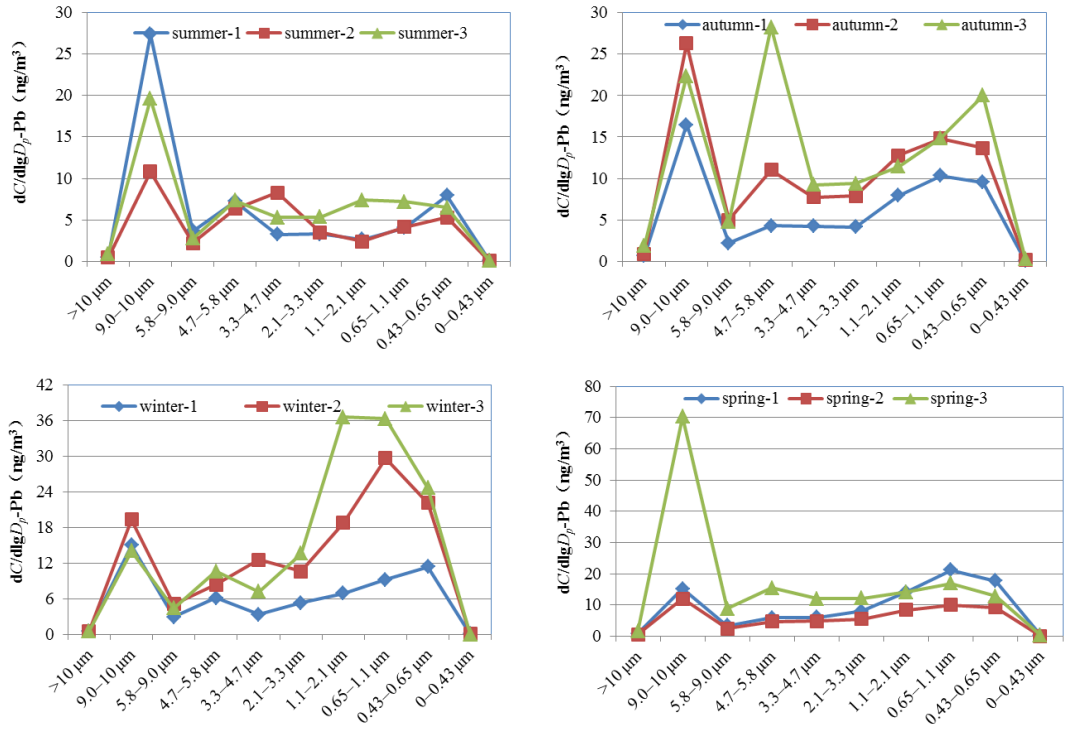



Fig.3-8 Size distribution of Pb in aerosols in Penglai

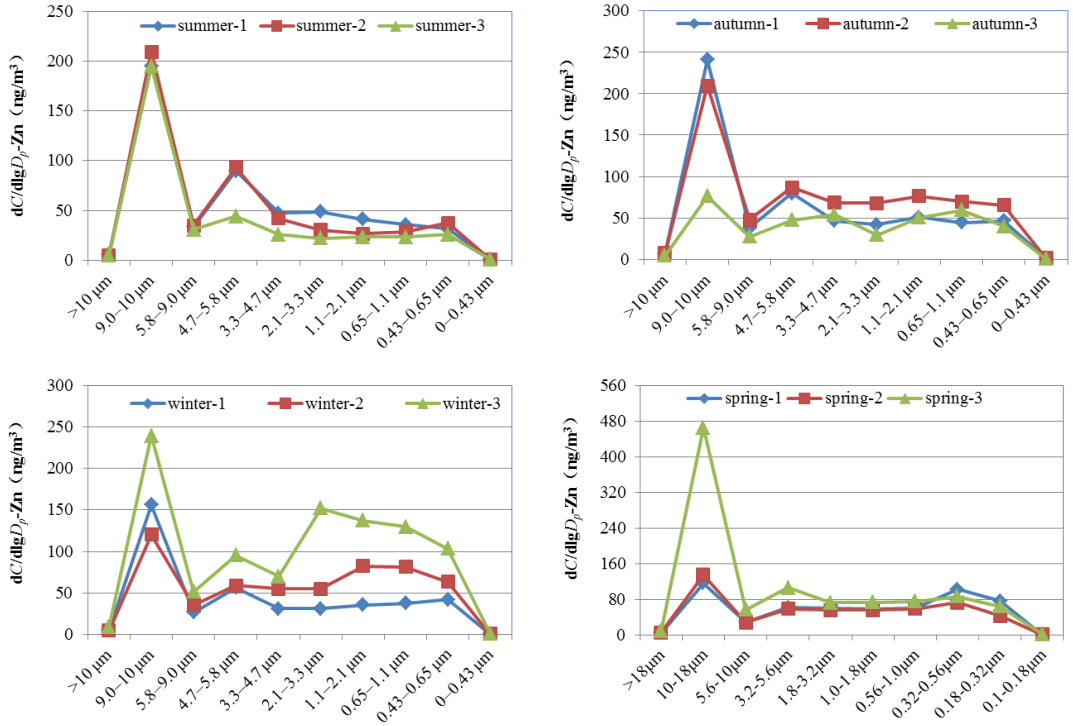



Fig.3-9 Size distribution of Zn in aerosols in Penglai

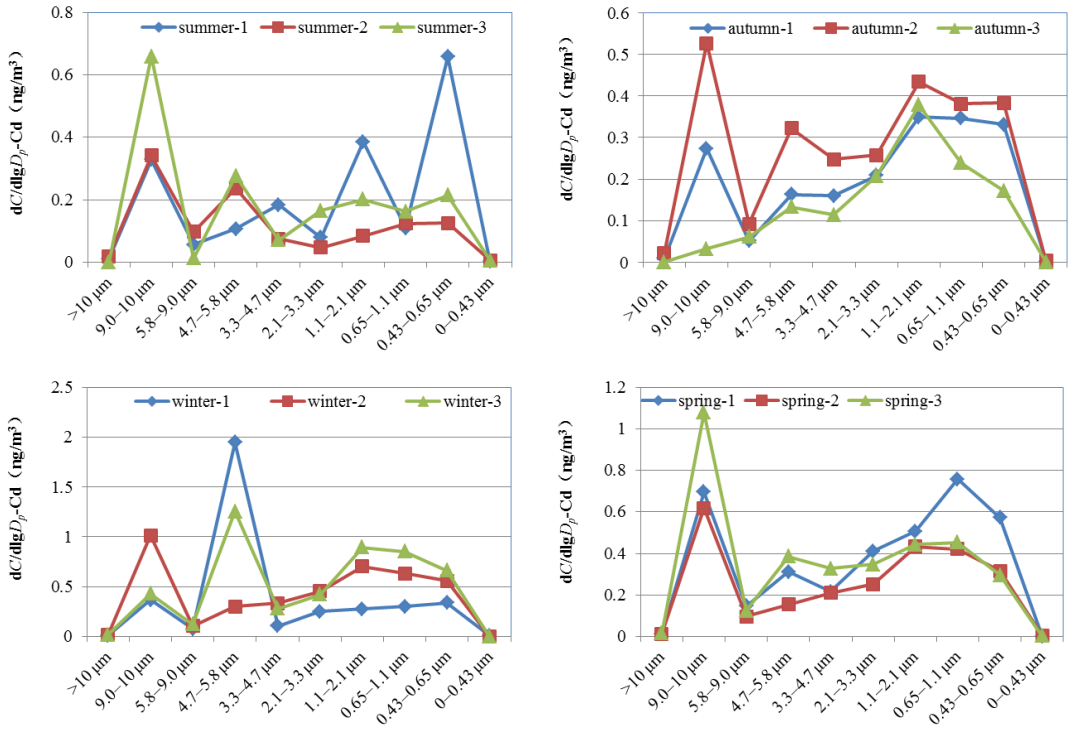


Fig.3-10 Size distribution of Cd in aerosols in Penglai

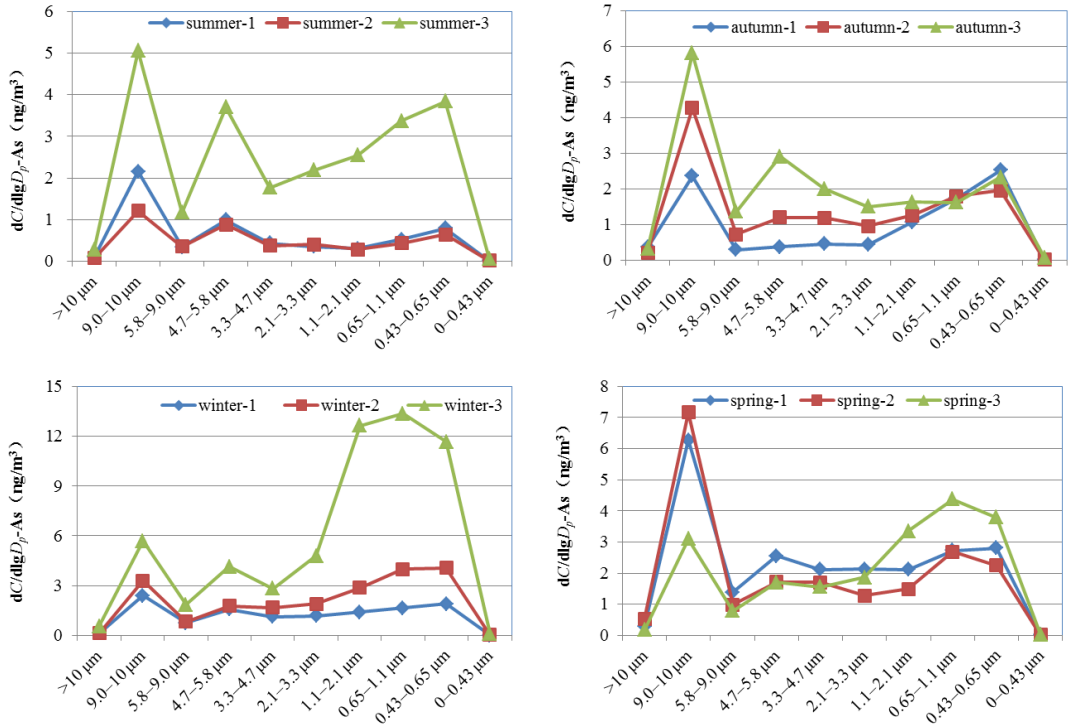



Fig.3-11 Size distribution of As in aerosols in Penglai

## 3.2 Dry deposition velocities of various components

The Willimas Modle (Williams, 1982) which is suit for the natural water surface was improved in ①Wet particle growth effect ②Broken surface coverage ③Broken surface transmission coefficient by referring to methods such as Qi (Qi et al., 2005) and Wang Zejie (2006).

The dry deposition velocities of atmospheric particulate matter of different particle sizes per day is obtained by importing the relative humidity RH (%), wind speed (m/s), air temperature (K), air pressure (Pa) and the sea surface temperature extracted from the satellite data were input into the improved Williams model. The dry deposition velocities of atmospheric particles with different particle sizes were obtained daily. The average value of different seasons and the whole year were obtained, then the deposition rate of various components in atmospheric TSP were calculated according to the following formula.

The $V_{dn}$ of different particle sizes of atmospheric particles in different seasons is obtained. The settlement rate of N/P components in atmospheric TSP in different seasons of Qinhuangdao coastal waters is calculated according to the following formula:

$$V_d = V_{d1} * I_1 + V_{d2} * I_2 + \ldots + V_{dn} * I_n$$

Where

$V_d$——Deposition velocity of pollutant components in TSP(cm/s)；

$V_{dn}$——Deposition velocity of atmospheric particulate matter on the *n*-th particle size obtained by the Williams model(cm/s)；

$I_n$——Proportion of pollutant components in atmospheric aerosols at the nth particle size (%).

The deposition velocities in total suspended particulates were showed in table 3-2. It can be seen that the deposition velocities of component with higher proportion in

coarse particle were higher than those with higher proportion fine particle. The velocities of $PO_4^{3-}$P, $NO_2^-$N and Cu were greater than 1.0 cm/s, with the value 1.461 cm/s, 1.637 cm/s and 1.111 cm/s, respectively. The velocities of $NO_3^-$-N, Zn and As were greater than 0.8 cm/s and less than 1.0 cm/s, with the value 0.837 cm/s, 0.825 cm/s, and 0.831 cm/s, respectively. And the velocities of $NH_4^+$-N, Pb and Cd were less than 0.7 cm/s, with the value 0.310 cm/s, 0.676 cm/s, and 0.514 cm/s, respectively. It can be concluded that the proportion of aerosol pollutants in fine particles has little effect on the dry deposition velocity, while the proportion of coarse particles may be the most important factor.

Table 3-2 Dry deposition velocities of various components (cm/s)

| Components | Spring | Summer | Autumn | Winter | **Annual** |
|---|---|---|---|---|---|
| $NO_3^-$N | 0.813 | 1.071 | 0.925 | 0.549 | **0.837** |
| $NH_4^+$-N | 0.175 | 0.356 | 0.414 | 0.296 | **0.310** |
| $NO_2^-$N | 1.558 | 1.729 | 1.828 | 1.431 | **1.637** |
| $PO_4^{3-}$P | 1.445 | 1.230 | 1.863 | 1.303 | **1.461** |
| Cu | 1.002 | 1.075 | 1.038 | 1.332 | **1.111** |
| Pb | 0.657 | 0.471 | 0.703 | 0.880 | **0.676** |
| Zn | 0.747 | 0.723 | 0.811 | 1.024 | **0.825** |
| Cd | 0.501 | 0.481 | 0.443 | 0.630 | **0.514** |
| As | 0.864 | 0.554 | 1.009 | 0.899 | **0.831** |

## 3.3 Trends of Nutrients and heavy metals in TSP

In this section, another parameter for estimating the dry deposition flux should be discussed, namely, the content of nitrogen and phosphorus in aerosols.

### 3.3.1 Data Sources

There are 5 stations around the Yellow Sea. TSP samples were collected in four seasons every year from 2011. The data derived from the operational monitoring data of the marine and environmental protection departments of the P.R. China.

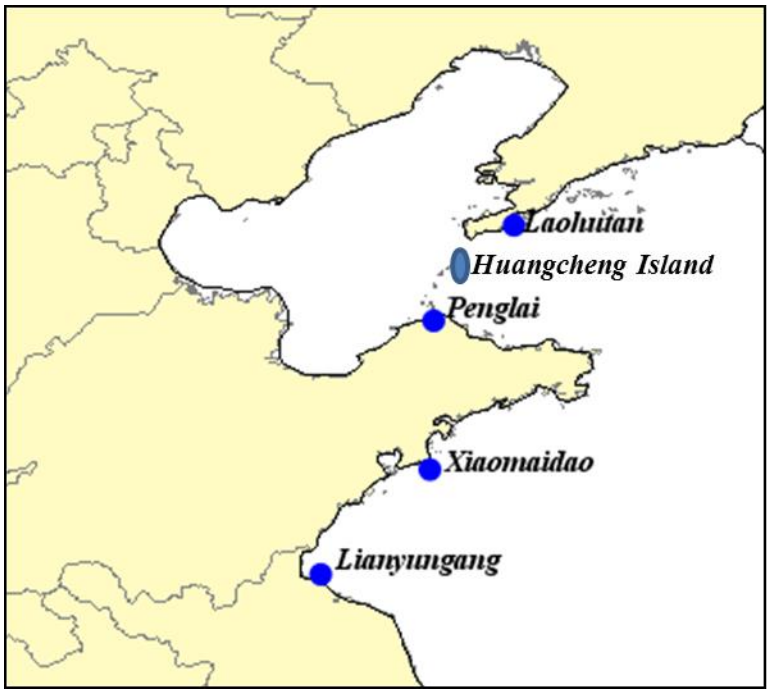



Fig.3-12 Atmospheric sampling station along the Yellow Sea coast

### 3.3.2 Trends of nutrients and heavy metals in aerosol along the Yellow Sea

Here, taking the average contents of inorganic nitrogen, copper and lead in five stations as an example, the trends of atmospheric pollutants along the Yellow Sea were discussed.

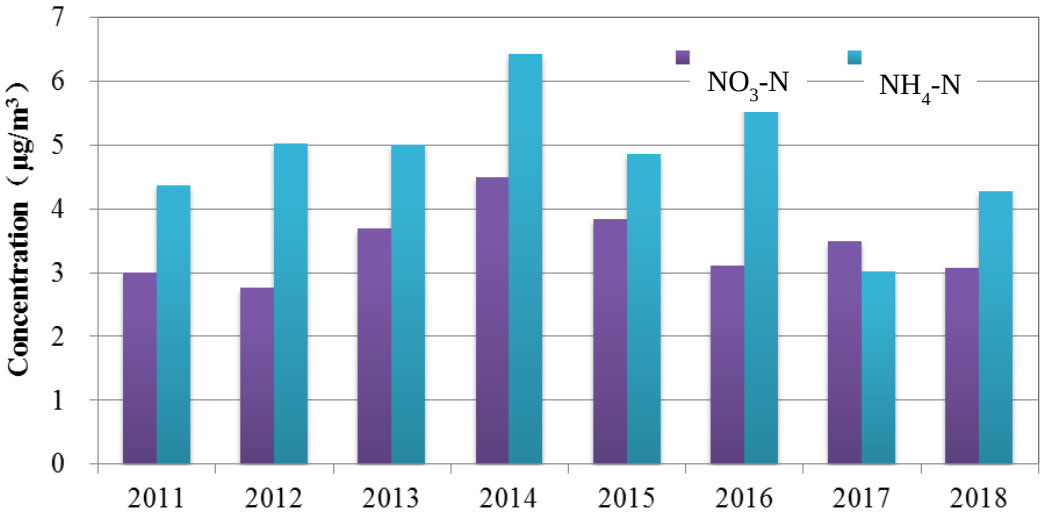



Fig.3-13 Trends of inorganic nitrogen in aerosols over the Yellow Sea coast from 2011

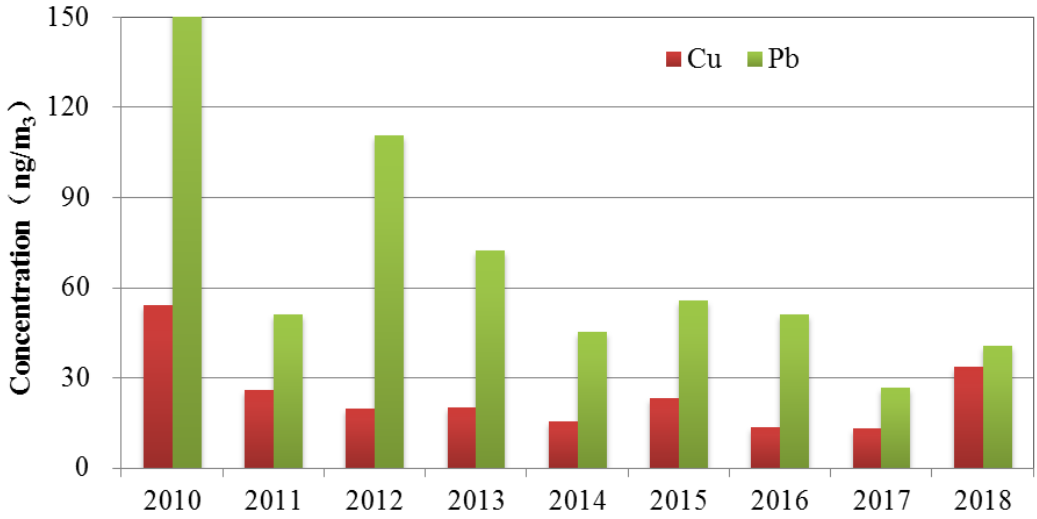



Fig.3-14 Trends of copper and lead in aerosols over the Yellow Sea coast from 2011

Taking 2014 as a turning point，the inorganic nitrogen in aerosols along the Yellow Sea coast has increased first and then decreased year by year since 2011. The concentration of inorganic nitrogen in the aerosol was 6.5~10.9 μg/m$^3$. In general, the content of ammonia nitrogen in atmospheric aerosols over the Yellow Sea coast is higher than that of nitrate nitrogen (except for that in 2007). As for heavy metals, the contents of copper and lead in atmospheric aerosols all showed the highest value in 2010, then showed a downward trend in general, minimized in 2017, however,

increased slightly in 2018. The concentration of copper and lead in the aerosol was 13.0~53.9 ng/m$^3$.and 26.7~185.5 ng/m$^3$, respectively. The content of lead in atmospheric aerosols over the Yellow Sea coast is higher than that of copper.

## 3.4 Dry deposition of Nutrients and heavy metals over the yellow sea

### 3.4.1 Calculation area division

The actual monitoring results of our study about the content of pollutants in the atmosphere are mostly located near the shore, but in fact the actual situation in the central and eastern shores of the Yellow Sea will be somewhat different from the western shores. In order to reflect the differences in pollutant concentrations in different regions when calculating the deposition flux, we divide the Yellow Sea into three regions: the western part of the Yellow Sea, the central part of the Yellow Sea, and the eastern part of the Yellow Sea, with the areas of 83600, 22800, 68400km$^2$, respectively.

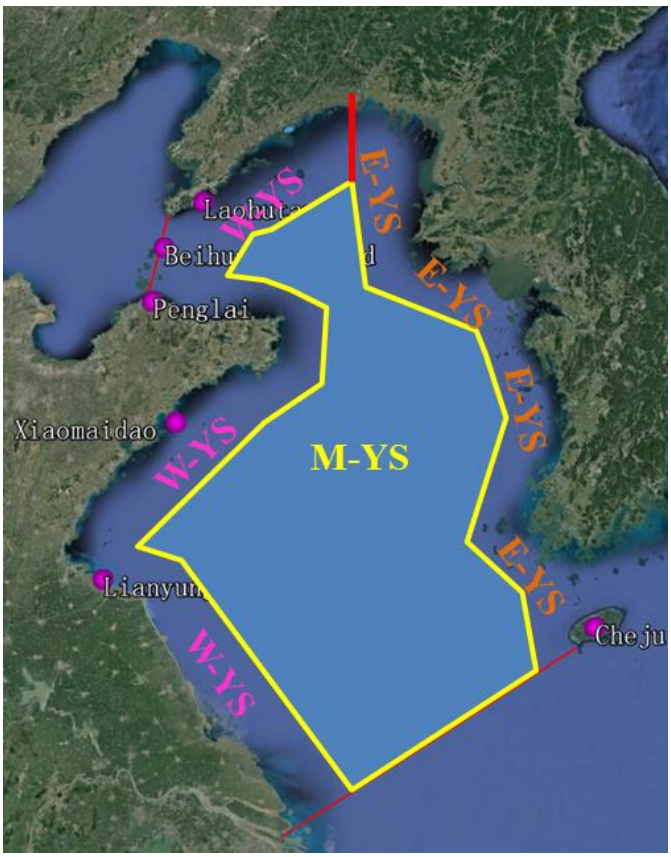



Fig.3-14 Yellow Sea Division Schematic (the western part of the Yellow Sea (W-YS), the central

part of the Yellow Sea (M-YS), and the eastern part of the Yellow Sea (E-YS))

### 3.4.2 Method description

The concentration of N&P in W-YS is taken from the monitoring results in China in 2017, and the concentration of inorganic nitrogen in E-YS is taken from the monitoring results in Jeju Island in 2017, the concentrations of inorganic nitrogen in M-YS were estimated based on a large number of navigational monitoring data collected in the literature. And the concentration of heavy metals in E-YS and M-YS were estimated according to the ratio coefficient of the measured data of Jeju Island and the western part of the Yellow Sea.

Nutrients and heavy metals dry deposition flux over the Yellow Sea can be calculated based on the concentration，velocities and the area of each region as the the following formula:

$$F_d=0.864V_d*C*A*t$$

Where

$F_d$——Dry deposition of contaminated components (kg)；

$V_d$——Deposition velocity of pollutant components in TSP (cm/s)；

$C$——Concentrations of atmospheric particulate matter on the particle size obtained by the Williams model ( μ g/m$^3$)；

$A$——Areas of the calculation regions (km$^2$);

$t$——Calculation time (d).

### 3.4.3 Results

The estimation results of pollutant concentrations in atmospheric aerosols in different regions of the Yellow Sea were shown in Table 3-3. And the estimation results of dry deposition amounts of atmospheric pollutants in different regions were showed in table 3-4.

In 2017, the dry deposition of atmospheric inorganic nitrogen in the Yellow Sea was about 304,382 tons. The dry deposition amount of nitrate nitrogen was 227,543 tons, which is the most important component in the dry deposition of inorganic nitrogen, accounting for 74.8%; followed by ammonia nitrogen, the dry deposition amount was 72,927 tons, accounting for 24.0%; the least deposition is nitrite nitrogen. The dry deposition amount was only 3,913 tons, accounting for less than 2%. The dry deposition amount of $PO_4$-P over the Yellow Sea in 2017 was relatively low compared with that of nitrogen, with the value of 2558 tons/yr. The dry deposition amount of Cu, Pb, Zn, Cd and As was 1982 tons/yr, 1973 tons/yr, 6753 tons/yr, 35 tons/yr, 356 tons/yr, respectively. Among them, the dry deposition amount of Zn was the highest, while the the dry deposition amount of Cd was the lowest.

At the same time, it can be found that the dry deposition amount of components with high concentration in the atmosphere is not necessarily high. For example, the concentration of copper in the atmosphere was lower than that of lead, and the dry deposition amount of copper to the sea was 1982 tons, which was higher than tthat of lead, with value of 1793 tons. The reason is that the deposition velocities is different, lead in the atmospheric particles is more distributed on fine particles and can be suspended in the atmosphere for a longer time.

Table 3-3 Estimation results of pollutant concentrations in atmospheric aerosols in different regions of the Yellow Sea

| Components | W-YS | M-YS | E-YS |
|---|---|---|---|
| **$NO_3$-N (μg/m$^3$)** | 3.10 | 2.07 | 1.92 |
| **$NH_4$-N (μg/m$^3$)** | 2.82 | 1.88 | 1.19 |
| **$NO_2$-N (ng/m$^3$)** | 27.25 | 18.17 | 16.92 |
| **$PO_4$-P (ng/m$^3$)** | 23.43 | 12.32 | 11.47 |
| **Cu (ng/m$^3$)** | 23.87 | 12.56 | 11.69 |

| | | | |
|---|---|---|---|
| **Pb (ng/m$^3$)** | 35.47 | 18.66 | 17.37 |
| **Zn (ng/m$^3$)** | 109.50 | 57.60 | 53.62 |
| **Cd (ng/m$^3$)** | 0.91 | 0.48 | 0.44 |
| **As (ng/m$^3$)** | 5.74 | 3.02 | 2.81 |

Table 3-4 Estimation results of dry deposition amounts of atmospheric pollutants in different regions of the Yellow Sea (t/yr)

| Components | W-YS | M-YS | E-YS | All the Yellow Sea |
|---|---|---|---|---|
| **$NO_3$-N** | 68390 | 124407 | 34746 | **227543** |
| **$NH_4$-N** | 23053 | 41936 | 7938 | **72927** |
| **$NO_2$-N** | 1176 | 2139 | 597 | **3913** |
| **$PO_4$-P** | 902 | 1295 | 362 | **2558** |
| **Cu** | 699 | 1003 | 280 | **1982** |
| **Pb** | 632 | 907 | 253 | **1793** |
| **Zn** | 2382 | 3417 | 954 | **6753** |
| **Cd** | 12 | 18 | 5 | **35** |
| **As** | 126 | 180 | 50 | **356** |

## 4. Wet deposition of Nutrients and heavy metals over the Yellow Sea

Atmospheric wet deposition refers to the process of dissolving or flushing water-soluble gaseous or particulate nitrogen-phosphorus pollutants by the rain and snow to the ground under the action of gravity.

## 4.1 Data Sources

Eight-nine rain samples were collected in Beihuangcheng Island, Penglai, Xiaomaidao and Lianyungang in 2017. The data derived from the operational monitoring data of the marine and environmental protection departments of the P.R. China.


Fig.4-1 Four rainwater sampling stations along the Yellow Sea coast

## 4.2 Method description

The wet deposition is usually determined by the amount of precipitation and the concentration of the material in the rainwater. The time and space are relatively concentrated, so the wet deposition flux is also easy to measure.

Generally, the wet deposition flux ($F_w$) is the sum of the product of the pollutant concentration and the precipitation in each precipitation during the research. The calculation formula is as follows:

$$F_{\mathrm{w}}=\sum_{i=1}^{n}\left(I_i C_i\right)\times A\times 10^{-3}$$

Where

$F_w$——Wet deposition fluxes of atmospheric pollutants (kg);

$I_i$——Rainfall of the i-th rainfall, mm;

$A$——Areas of the calculation regions ($km^2$);

$C_i$——Concentration of contaminated components in the i-th precipitation (μg/L).

However, not all the samples of each rainfall event can be collected. In this case, the rainfall samples which can be collected can be weighted and averaged according to the rainfall to obtain the weighted average concentration. Then average concentration is multiplied by the total amount of rainfall during the evaluation period. Thus the wet deposition fluxes of atmospheric pollutants can be calculated as follow formula:

$$F_{\mathrm{w}}=\frac{\sum_{i=1}^{n} I_i C_i}{\sum_{i=1}^{n} I_i} I_{\mathrm{yr}}\times A\times t\times 10^{-3}$$

Where

$F_w$——Wet deposition fluxes of atmospheric pollutants (kg);

$I_i$——Rainfall of the i-th rainfall (mm);

$C_i$——Concentration of contaminated components in the i-th precipitation, (mg/L);

$I_{yr}$——Rainfall of Annual rainfall (mm);

$A$——Areas of the calculation regions ($km^2$).

Considering that the Yellow Sea has a large span from south to north, in order to obtain the representative average rainfall, the rainfall in the North Yellow Sea takes Dalian's annual average rainfall (620mm) as a reference, and the South Yellow Sea takes Shanghai's annual average rainfall (1200mm). For reference, the average of the two is the average annual rainfall (910mm) along the Yellow Sea. However, the rainfall in the outside sea is often different from the near-shore rainfall. Here we refer to the European OSPAR to calculate rainfall outside sea using 70% rainfall at the near-shore site.

Through reviewing a large amount of literature, we found that the concentration of pollutants in atmospheric aerosols is similar to that in dry deposition, and the concentration of pollutants in rainfall in the central part of the ocean also decreases with increasing offshore distance. Therefore, we also refer to the method mentioned in 3.4.1 to divide the study area into three areas, and estimate the content of pollutants in the central Yellow Sea by reference to the proportional coefficient method in 3.4.2. Because the actual measurement data of heavy metal content in the precipitation of the East China Sea was not obtained, we used the ratio of nutrients in the precipitation of Jeju Island to the west bank of the Yellow Sea to estimate the concentration of heavy metals in the precipitation on the east coast of the Yellow Sea.

## 4.3 Results

### 4.3.1 Average concentration of pollutants weighted by rainfall

The average concentrations weighted by rainfall for various pollutants in the four stations in 2017 were shown in Fig. 4-2~ Fig. 4-7.

As can be seen from the figure, among the four sites, the contents of various pollutant components were the highest in the rainwater of Qingdao Xiaomai Island in 2017. Followed by Beihuangcheng Island, except for the content of phosphate, copper and cadmium in the rainwater, which was the third place among the four stations, the content of the remaining 6 pollutants was the second among the four stations. Overall, the contents of pollutants in the rainwaters of Lianyungang and Penglai were lower than

those of Xiaomai Island and Beihuangcheng Island. The content of cadmium and four nutrients (nitrate-nitrogen, nitrite-nitrogen, ammonia-nitrogen, phosphate) in the rainwater of Lianyungang Station was lower than that of Penglai Station, while the content of heavy metals (copper, lead, zinc, arsenic) in Penglai Station was lower than that of Lianyungang Station.

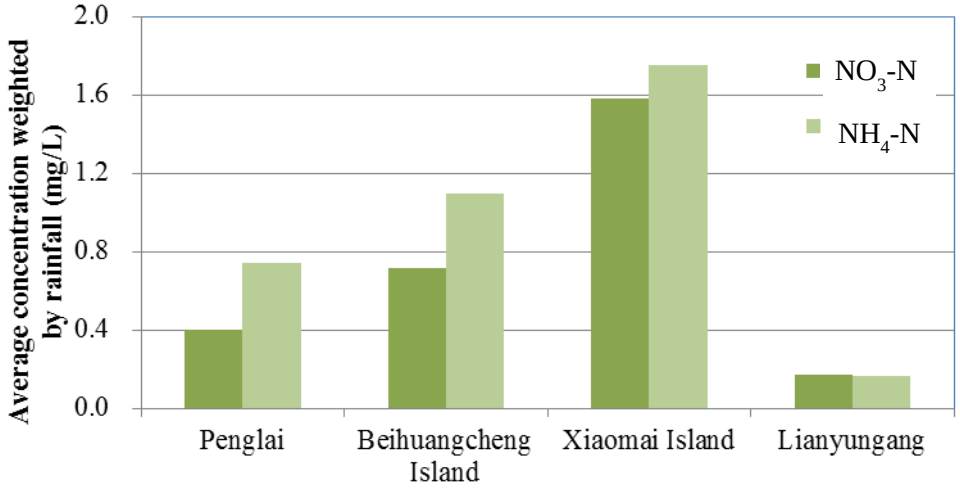



Fig.4-2 Average concentration of $NO_3$-N and $NH_4$-N weighted by rainfall along the Yellow Sea in 2017

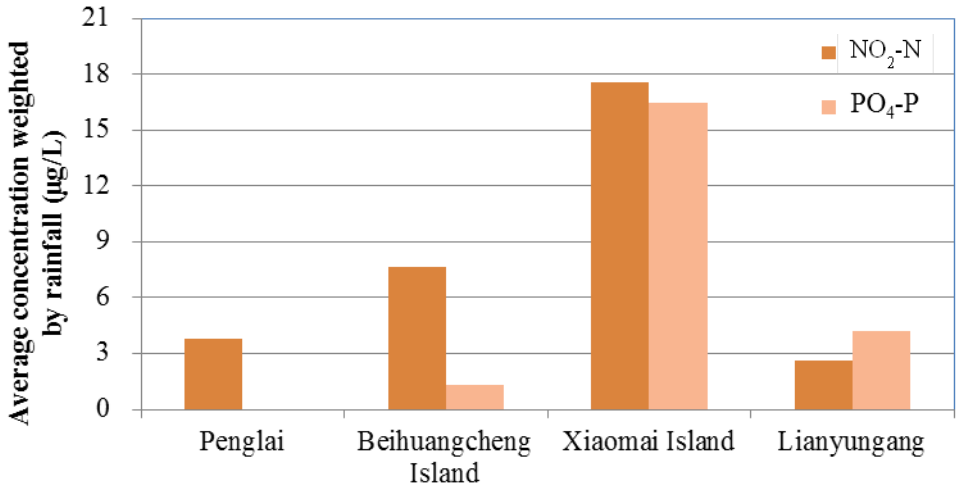



Fig.4-3 Average concentration of $NO_2$-N and $PO_4$-P weighted by rainfall along the Yellow Sea in 2017

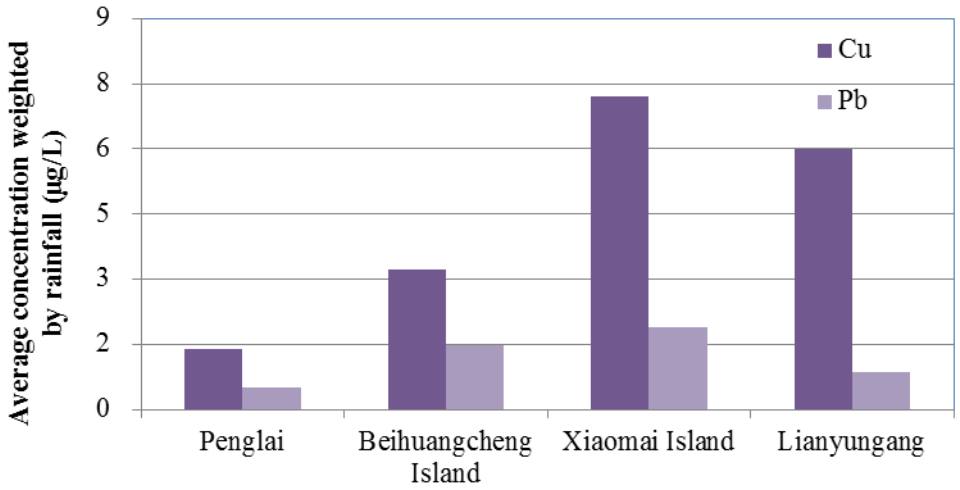



Fig.4-4 Average concentration of Cu and Pb weighted by rainfall along the Yellow Sea in 2017

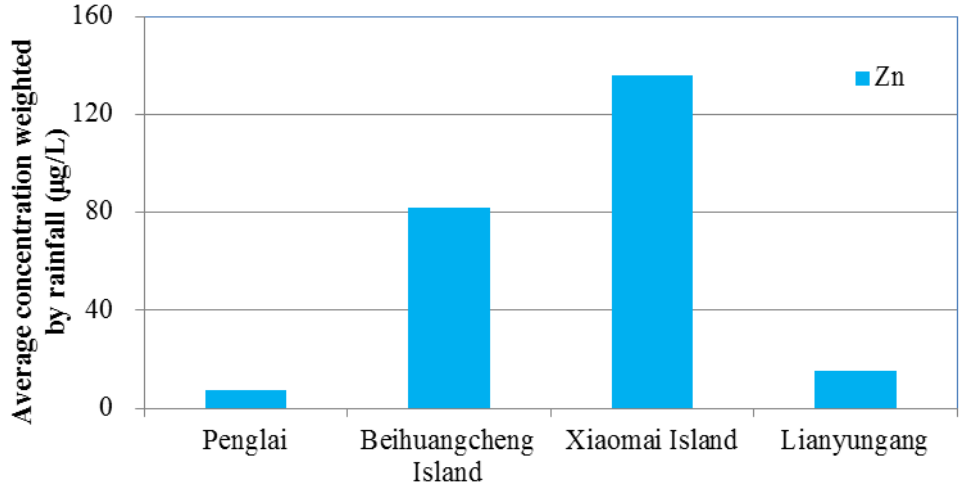



Fig.4-5 Average concentration of Zn weighted by rainfall along the Yellow Sea in 2017

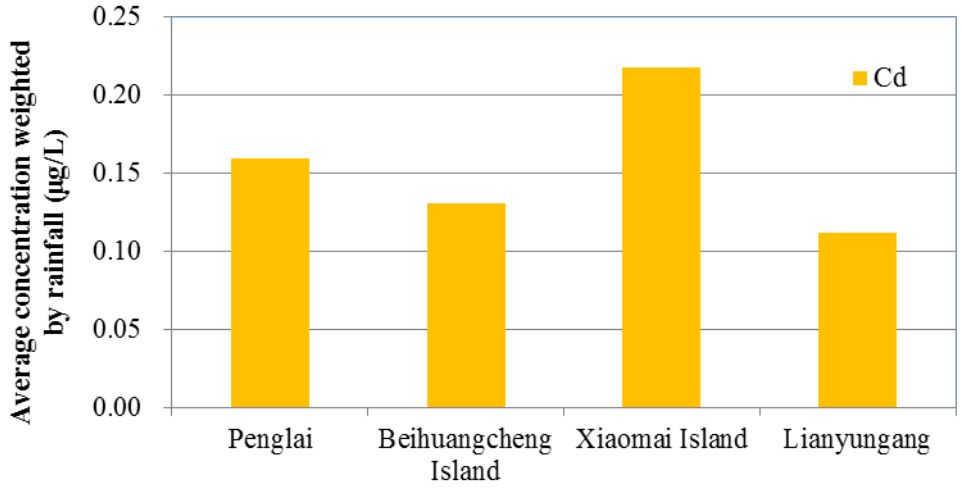



Fig.4-6 Average concentration of Cd weighted by rainfall along the Yellow Sea in 2017

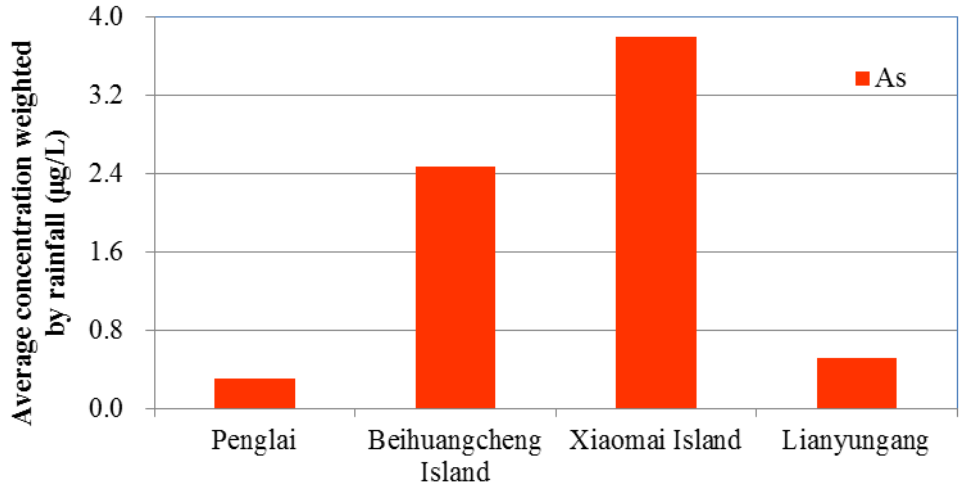



Fig.4-7 Average concentration of Cd weighted by rainfall along the Yellow Sea in 2017

Table 4-1 Estimation results of pollutant concentrations in precipitations in different regions of the Yellow Sea in 2017

| Components | W-YS | M-YS | E-YS |
|---|---|---|---|
| **$NO_3$-N (mg/L)** | 0.72 | 0.48 | 0.56 |
| **$NH_4$-N (mg/L)** | 0.94 | 0.63 | 0.54 |
| **$NO_2$-N (μg/L)** | 7.91 | 5.27 | 6.13 |

| | | | |
|---|---|---|---|
| **$PO_4$-P (μg/L)** | 5.51 | 2.90 | 3.37 |
| **Cu (μg/L)** | 4.45 | 2.34 | 2.72 |
| **Pb (μg/L)** | 0.91 | 0.48 | 0.56 |
| **Zn (μg/L)** | 60.10 | 31.61 | 36.77 |
| **Cd (μg/L)** | 0.15 | 0.08 | 0.09 |
| **As (μg/L)** | 1.77 | 0.93 | 1.08 |

From the average concentration of pollutants weighted by rainfall along the west coast of the Yellow Sea (see Table 4-1), the concentrations of the four nutrient components—nitrate-nitrogen, ammonia-nitrogen, nitrite-nitrogen and active phosphate are 0.72 mg/L, 0.94 mg/L, 7.91μg/L and 5.51μg/L respectively. Ammonia-nitrogen and nitrate-nitrogen were still important components in rainwater inorganic nitrogen, and phosphorus content in rainwater was relatively low. Comparing the ratio of ammonia-nitrogen to nitrate-nitrogen in rainwater and the ratio of that in the aerosol in the same period, we can find that the ratio of $NH_4$-N/ $NO_3$-N (1.31) in rainwater is greater than that in aerosol (0.91), indicating that the dissolution efficacy and removal efficacy of precipitation to ammonia-nitrogen in the atmosphere was greater than that of nitrate-nitrogen. The concentrations of five heavy metals−Cu, Pb, Zn, Cd and As are 4.45μg/L, 0.91μg/L, 60.10μg/L, 0.15μg/L and 1.77μg/L respectively. Zinc is the most concentrated heavy metal element in rainwater, followed by copper and arsenic, and again lead and cadmium.

### 4.3.2 Wet deposition amounts of atmospheric pollutants over the Yellow Sea

Based on the content of pollutants in the rainwater we calculated the wet deposition of nutrients and five heavy metals in the atmosphere of the Yellow Sea with the method mentioned in section 4.2. The estimated results are shown in Table 4-3.

Table 4-2 Estimation results of wet deposition amounts of atmospheric pollutants in different regions of the Yellow Sea in 2017(t/yr)

| Components | W-YS | M-YS | E-YS | All the Yellow Sea |
|---|---|---|---|---|
| **$NO_3$-N** | 54506 | 91906 | 57025 | 203437 |
| **$NH_4$-N** | 71498 | 120557 | 55014 | 247068 |
| **$NO_2$-N** | 602 | 1014 | 629 | 2245 |
| **$PO_4$-P** | 419 | 557 | 346 | 1322 |
| **Cu** | 339 | 450 | 279 | 1068 |
| **Pb** | 69 | 92 | 57 | 219 |
| **Zn** | 4572 | 6080 | 3772 | 14425 |
| **Cd** | 12 | 16 | 10 | 37 |
| **As** | 135 | 179 | 111 | 425 |

From the estimation results of wet deposition amounts of atmospheric pollutants over the Yellow Sea, the wet deposition amounts of the four nutrient components—nitrate-nitrogen, ammonia-nitrogen, nitrite-nitrogen and active phosphate were 203437 tons/year, 247068 tons/year, 2245 tons/year and 1322 tons/year respectively. Ammonia-nitrogen and nitrate-nitrogen were important components in rainwater inorganic nitrogen, and phosphorus content in rainwater was relatively low. Different from dry deposition, the wet deposition of ammonia nitrogen was greater than that of nitrate nitrogen. The wet deposition amounts of five heavy metals−Cu, Pb, Zn, Cd and As were 1068 tons/year, 219 tons/year, 14425 tons/year, 37 tons/year and 425 tons/year respectively.

# 5. Total deposition of Nutrients and heavy metals over the Yellow Sea

The pollutants in the atmosphere settle into the sea in the form of dry and wet sedimentation, also known as full settlement. This chapter will combine the evaluation results of dry and wet deposition to explore the relationship between atmospheric deposition and Yellow Sea pollution.

## 5.1 Method for estimating total deposition

The total deposition can be available (obtained) by adding the atmospheric dry deposition and the wet deposition. The calculation method of the total marine subsidence into the sea flux is shown in formula：

$$F_t=F_d+F_w$$

Where

$F_t$——Total deposition amount of atmospheric pollutants;

$F_d$——Dry deposition amount of atmospheric pollutants；

$F_w$——Wet deposition amount of atmospheric pollutants.

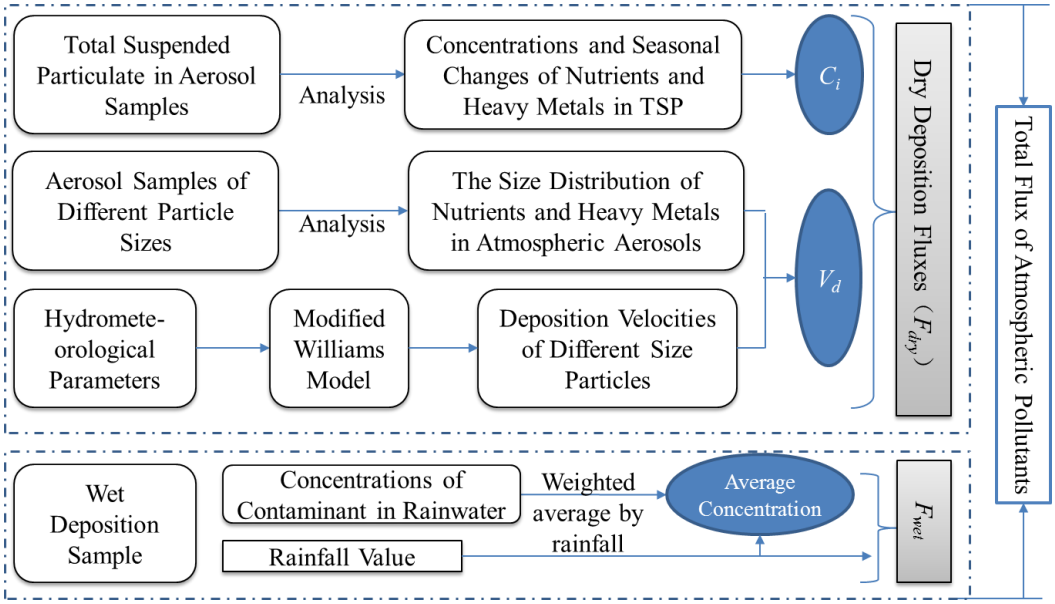



Fig. 5-1 Frame of the total deposition flux assessment method

## 5.2 Results

Total deposition amounts of atmospheric pollutants over the Yellow Sea were shown in Table 5-1. Total deposition amounts of atmospheric pollutants in different regions of the Yellow Sea were shown in Table 5-2.

Table 5-1 Total deposition amounts of atmospheric pollutants over the Yellow Sea in 2017(t/yr)

| Components | Dry deposition of the Yellow sea | Wet deposition of the Yellow sea | Total deposition of the Yellow sea |
|---|---|---|---|
| **$NO_3$-N** | 227543 | 203437 | **430979** |
| **$NH_4$-N** | 72927 | 247068 | **319996** |
| **$NO_2$-N** | 3913 | 2245 | **6158** |
| **$PO_4$-P** | 2558 | 1322 | **3881** |
| **Cu** | 1982 | 1068 | **3050** |

| | | | |
|---|---|---|---|
| **Pb** | 1793 | 219 | **2011** |
| **Zn** | 6753 | 14425 | **21178** |
| **Cd** | 35 | 37 | **72** |
| **As** | 356 | 425 | **781** |

Table 5-2 Total deposition amounts of atmospheric pollutants in different regions of the Yellow Sea in 2017(t/yr)

| **Components** | **W-YS** | **M-YS** | **E-YS** | **Total deposition of the Yellow sea** |
|---|---|---|---|---|
| **$NO_3$-N** | 122895 | 216312 | 91771 | **430979** |
| **$NH_4$-N** | 94551 | 162493 | 62952 | **319996** |
| **$NO_2$-N** | 1778 | 3154 | 1227 | **6158** |
| **$PO_4$-P** | 1322 | 1852 | 707 | **3881** |
| **Cu** | 1038 | 1453 | 559 | **3050** |
| **Pb** | 701 | 999 | 310 | **2011** |
| **Zn** | 6954 | 9497 | 4727 | **21178** |
| **Cd** | 24 | 33 | 15 | **72** |
| **As** | 260 | 359 | 161 | **781** |

The calculation of the total deposition shows that input amounts of the four nutrient components—nitrate-nitrogen, ammonia-nitrogen, nitrite-nitrogen and active phosphate into the Yellow Sea from atmosphere-based were 430979 tons/year, 319996 tons/year, 6158 tons/year and 3881 tons/year respectively. Ammonia-nitrogen and

nitrate-nitrogen were important components, and phosphorus was relatively low. The total deposition of nitrate-nitrogen was greater than that of ammonia-nitrogen. The total deposition amounts of five heavy metals−Cu, Pb, Zn, Cd and As were 3050 tons/year, 2011 tons/year, 21178 tons/year, 72 tons/year and 781 tons/year respectively.

## 5.3 Discussions

### 5.3.1 Proportion of dry deposition amount to wet deposition amount

In order to understand the different contributions of dry and wet deposition to the total atmospheric deposition of various pollutants, the proportion of dry deposition amount to wet deposition amount were analyzed (see Fig. 5-2).

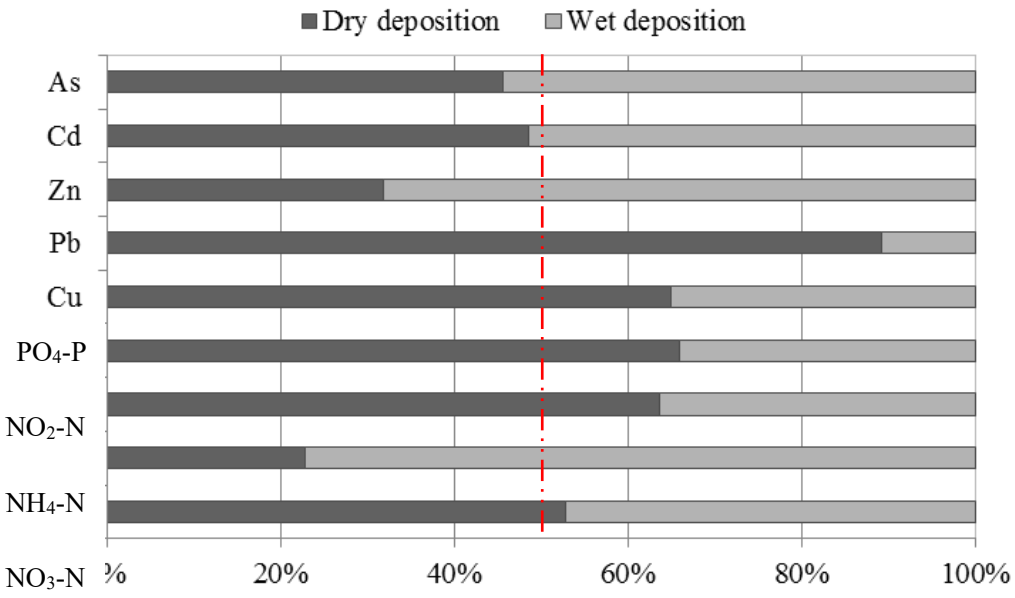



Fig. 5-2 Proportion of dry deposition amount to wet deposition amount over the Yellow Sea in 2017

The contributions of dry deposition to the total deposition of nitrate-nitrogen, nitrite-salt, nitrogen-activated phosphate, copper and lead were greater than those of wet deposition, especially lead, which accounts for 89.1% of total deposition. However, the contributions of wet deposition to the total deposition of ammonia-nitrogen, zinc, cadmium and arsenic were greater than those of dry deposition, especially ammonia,

which accounts for 67.2% of total deposition. For the nine pollutants as a whole, the contribution of dry and wet deposition was comparable, which was comparable to the conclusion of the global ocean assessment. In recent years, a large number of regional simulation results and mass balance calculations have made people realize that atmospheric dry deposition and wet deposition are almost important equally (Garland, etc., 1978； Fowler, etc., 1978).

### 5.3.2 Comparison with the amount of pollutants input into the river

In the previous chapters we calculated the total amount of nutrients and heavy metals transported through the atmosphere to the Yellow Sea. However, what is the role of atmospheric deposition in the input of pollutants in the Yellow Sea?

In this section, we compare the atmospheric input with the input of the river on the west coast of the Yellow Sea. Here, we mainly target the coastal waters in the western part of the Yellow Sea. The data on pollutant input from rivers comes from the operational monitoring of the former State Oceanic Administration of the People's Republic of China in 2017, including 71 major rivers along the Yellow Sea and the Yangtze River.

It is worth mentioning here that the Yangtze River, although it flows into the East China Sea in principle, but as the world's third largest river, the amount of pollutants it transports to the sea will not be limited to the local East China Sea, and will have a certain impact on the coastal waters of the Qidong coast of Jiangsu Province. In the spring, autumn and winter, the surface Yangtze River dilute water expansion is basically restricted to the Yangtze River estuary, Hangzhou Bay and Zhoushan waters, which is mainly affected by the coastal stream in northern Jiangsu. However, in the autumn and winter, the Yangtze River dilute water is strong along the coast of Zhejiang, and the spring flooding water only reaches the southern waters of Zhoushan. In the summer, due to the prevailing wind direction, it is affected by the Ekman effect of the wind. After the Yangtze River flows into the East China Sea, it is deflected to the south. Due to the

southerly wind and the tide-induced Stokes drifting, some of the Yangtze River diluted water expanded to the south Yellow Sea along the coast of the North Jiangsu (Wu et al., 2014; Yan et al., 2015; Wang et al., 2012). As can be seen from Figure 5-3, about one-fourth of the pollutants from the Yangtze River in July-October can affect the western coastal waters of the Yellow Sea (W-YS). Therefore, from the whole year, up to 15% of the pollutants in the Yangtze River are imported into the western coastal waters of the Yellow Sea (W-YS).Therefore, we calculate the amount of various pollutants entering the offshore of the Yellow Sea through rivers, including the amount of pollutants entering the sea through 71 major rivers monitored along the West Bank of the Yellow Sea and the 15% of the Yangtze River carrying pollutants into the sea in 2017 (see Table 5-3).

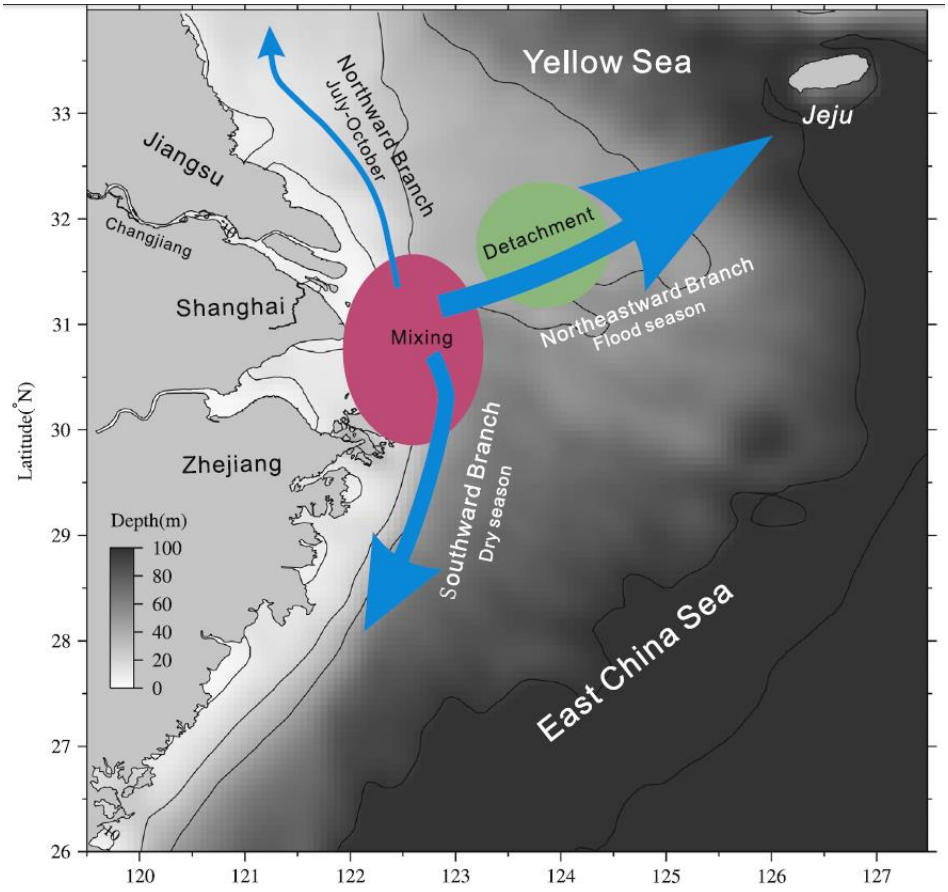



Fig. 5-3 Schematic map of the major patterns of the Changjiang plume (Wu et al., 2014).

Arrows signify the three major plume branches. The purple patch represents the mixing-active region. The green patch is the detached plume region.

Table 5-3 Comparison of atmospheric deposition and river input over the Western Yellow Sea in 2017(t/a)

| Components | | Atm.-based | River-input |
|---|---|---|---|
| **Inorganic nitrogen (DIN)** | $NO_3$-N | 122895 | **203907** |
| | $NH_4$-N | **94551** | 6301 |
| | $NO_2$-N | **1778** | 1292 |
| | Sum of inorganic nitrogen | **219224** | 211500 |
| **Phosphorus** | $PO_4$-P | 1322 | **23069** |
| **Heavy metals** | Cu | **1038** | 219 |
| | Pb | **701** | 21 |
| | Zn | **6954** | 436 |
| | Cd | **24** | 4 |
| | As | 260 | **292** |

It can be found that the nitrate-nitrogen input into the western Yellow Sea from the atmosphere accounted for the highest proportion (56.1%) of inorganic nitrogen, while the nitrate-nitrogen carried by the river into the sea accounts for an absolute proportion of inorganic nitrogen (96.4%), which was a significant difference between the two. At the same time, by comparison, it was found that the amount of ammonia-nitrogen input into the western Yellow Sea was significantly higher than that from the atmosphere (the river input was 1.7 times the atmospheric input), but the ammonia-nitrogen input from the atmosphere was higher than that of the river (the atmospheric input was 15 times the input of the river). The total amount of inorganic nitrogen input by the atmosphere and river to the western part of the Yellow Sea was equivalent. The amount of active

phosphate input into the western Yellow Sea was significantly higher than that from the atmospheric (the river input was 17.5 times the atmospheric input). It can be seen that the input effect of the river on ocean phosphorus was significant. Among the five heavy metals, the atmospheric input of arsenic was equivalent to that of river input, and the atmospheric input of the other four heavy metals of copper, anterior, zinc and cadmium was significantly higher than that of river input (the atmospheric input is 4.7 times, 34.2 times, 15.9 times, and 5.4 times of the river input, respectively), it can be seen that the atmosphere has a significant contribution to the input of heavy metals in the ocean.

The above is the overall analysis conclusion of the coastal waters in the western part of the Yellow Sea. However, if the regional division is more detailed, the areas such as the near-shore waters of the Yangtze River estuary, the river input role will occupy an absolute high proportion, and the atmospheric input effect will be significantly reduced. On the contrary, in the middle of the Yellow Sea, the effect of atmospheric deposition on the central Yellow Sea is more important due to the lack of direct input of rivers. Therefore, the contribution of atmospheric pollutants to the input of pollutants to the sea will have different results depending on the specific conditions of the region.

### 5.3.3 Seasonal variation of atmospheric deposition

In order to understand the seasonal variation of atmospheric deposition, we discussed the single-site deposition flux of nutrients at Penglai Station.

The results showed that the wet deposition fluxes of nutrients were the largest in summer, related to the most rainfall in summer. The dry deposition fluxes were greater in winter and spring than in summer and autumn, due to the high concentration of nitrogen and phosphorus in the terrestrial atmosphere in winter and spring. The total deposition fluxes of N&P were the highest in summer and lowest in autumn. This may be related to the high incidence of red tides in summer. At the same time, due to the highest rainfall in the Yellow Sea and coastal areas during the year, the runoff of rivers entering the Yellow Sea is also rapidly increasing, further increasing the pollution input

pressure to the Yellow Sea. The solution to the ecological environment problems in the Yellow Sea depends on the joint efforts of the countries along the Yellow Sea, not only controlling the total amount of pollutants, but also paying attention to the seasonal changes in pollution input, and taking targeted countermeasures to protect the health of the Yellow Sea marine ecosystem effectively.

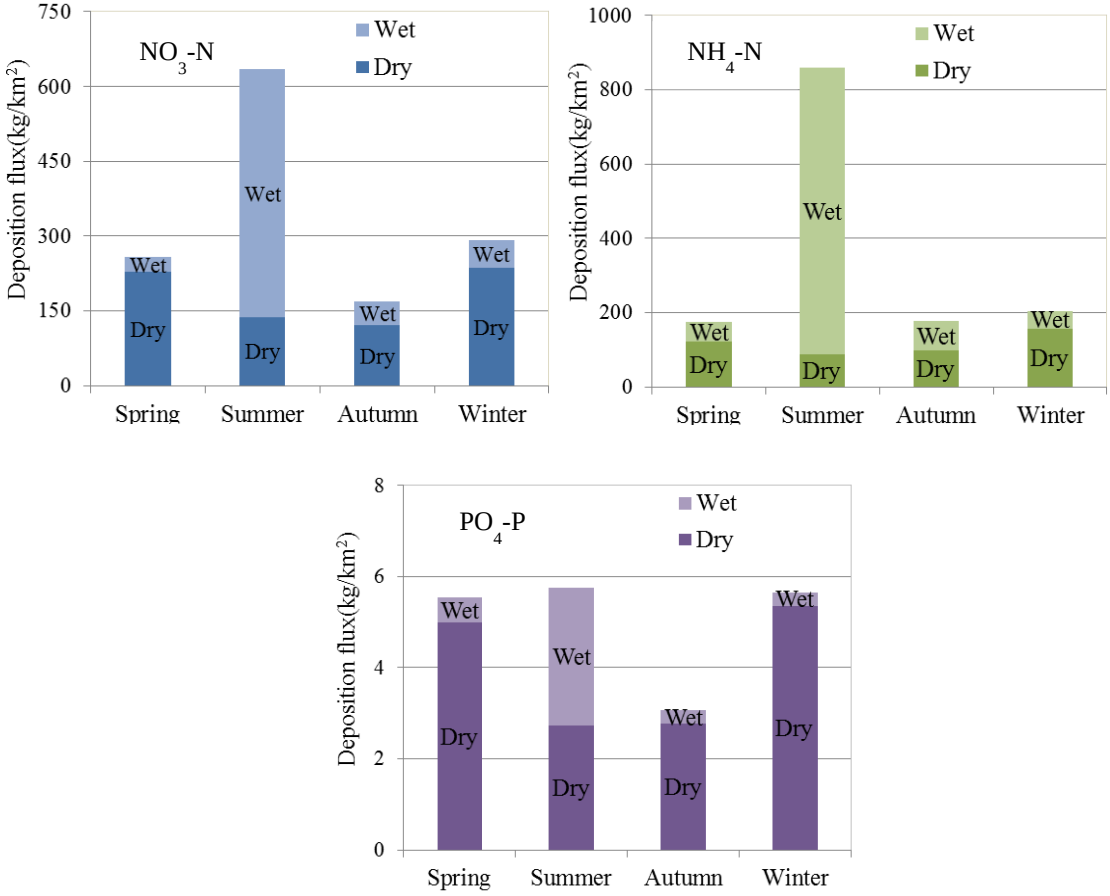



Fig. 5-4 Seasonal distribution of atmospheric nitrogen and phosphorus deposition fluxes at a single site in the Yellow Sea in 2017

## 6. Conclusions and recommendations

1) The air quality of the two typical cities along the Yellow Sea coast in 2017 was good, the proportion of excellent and quantitative grades in the Rizhao city was over

78%, and Rongcheng City, even reaches more than 95% in Rongcheng City, showing the results of China's comprehensive air pollution control in recent years.

2) The proportion of aerosol pollutants in fine particles has little effect on the dry deposition velocity, while the proportion of coarse particles may be the most important factor. The ammonia nitrogen in the atmospheric particles of the Yellow Sea is more distributed on the fine particles, while the nitrate nitrogen, phosphate and heavy metal components have certain amount both in the coarse and fine particles. The velocities of $PO_4^{3-}$P, $NO_2^-$N , $NO_3^-$-N, Cu, Zn, As, $NH_4^+$-N, Pb and Cd were 1.461 cm/s, 1.637 cm/s. 0.837 cm/s, 1.111 cm/s, 0.825 cm/s, 0.831 cm/s, 0.310 cm/s, 0.676 cm/s and 0.514 cm/s respectively.

3) Trends of nutrients and heavy metals in aerosol along the Yellow Sea was: Taking 2014 as a turning point， the inorganic nitrogen in aerosols along the Yellow Sea coast has increased first and then decreased year by year since 2011. The contents of copper and lead in atmospheric aerosols all showed the highest value in 2010, then showed a downward trend in general, minimized in 2017.

4) In 2017, the dry deposition of atmospheric inorganic nitrogen in the Yellow Sea was about 304,382 tons. Nitrate nitrogen was the most important component in the dry deposition of inorganic nitrogen, accounting for 74.8%, followed by ammonia nitrogen (24.0%). The dry deposition amount of $PO_4$-P over the Yellow Sea in 2017 was relatively low compared with that of nitrogen, with the value of 2558 tons/yr. The dry deposition amount of Cu, Pb, Zn, Cd and As was 1982 tons/yr, 1973 tons/yr, 6753 tons/yr, 35 tons/yr, 356 tons/yr, respectively.

5) Among the four sites, the contents of various pollutant components were the highest in the rainwater of Qingdao Xiaomai Island in 2017, followed by Beihuangcheng Island. The content of nutrients in the rainwater of Lianyungang Station was lower than that of Penglai Station, while the content of heavy metals (copper, lead, zinc, arsenic) in Penglai Station was lower than that of Lianyungang Station.

6) The wet deposition amounts of the four nutrient components—nitrate-nitrogen, ammonia-nitrogen, nitrite-nitrogen and active phosphate were 203437 tons/year, 247068 tons/year, 2245 tons/year and 1322 tons/year respectively. Different from dry deposition, the wet deposition of ammonia nitrogen was greater than that of nitrate nitrogen. The wet deposition amounts of five heavy metals-Cu, Pb, Zn, Cd and As were 1068 tons/year, 219 tons/year, 14425 tons/year, 37 tons/year and 425 tons/year respectively.

7) Input amounts of nitrate-nitrogen, ammonia-nitrogen, nitrite-nitrogen and active phosphate into the Yellow Sea from atmosphere-based were 430979 tons/year, 319996 tons/year, 6158 tons/year and 3881 tons/year, respectively. The total deposition amounts of five heavy metals-Cu, Pb, Zn, Cd and As were 3050 tons/year, 2011 tons/year, 21178 tons/year, 72 tons/year and 781 tons/year respectively. For the nine pollutants as a whole, the contribution of dry and wet deposition was comparable, which was comparable to the conclusion of the global ocean assessment.

8) The total amount of inorganic nitrogen input by the atmosphere and river to the western part of the Yellow Sea was equivalent. The amount of ammonia-nitrogen input into the western Yellow Sea was significantly higher than that from the atmosphere, but the ammonia-nitrogen input from the atmosphere was higher than that of the river. The input effect of the river on ocean phosphorus was significant, while the atmosphere has a significant contribution to the input of heavy metals in the ocean.

9) From the perspective of seasonal changes, the total deposition fluxes of nutrients were highest in summer and lowest in autumn. This may be related to the high incidence of red tides in summer.

**10) Recommendations:**

◆ Establish a marine atmospheric monitoring network for the Yellow Sea. Comprehensive planning and deployment of marine atmospheric monitoring stations in countries along the Yellow Sea, relying on existing shore base stations, strengthening

the monitoring of maritime atmosphere obtaining more representative data on marine atmospheric pollutant deposition.

◆ Jointly with the countries along the Yellow Sea, jointly carry out analysis on the source of marine pollution (including the analysis of atmospheric pollution sources in the Yellow Sea), so as to effectively resolve cross-border pollution disputes and propose effective countermeasures.

◆ The comprehensive remediation of the ecological environment in the Yellow Sea requires a more detailed division of the region. Take into account the regional characteristic, focus on land-based pollution in important estuaries, consider land-source, atmospheric deposition and maritime sources in the remaining coastal waters, focus on the atmospheric source in the open sea, and then propose targeted regional solutions.

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