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Atmospheric deposition of nitrogen and phosphorus over the Yellow Sea

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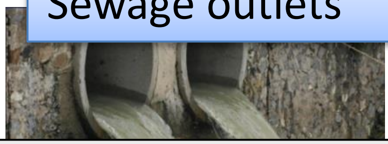
Outline

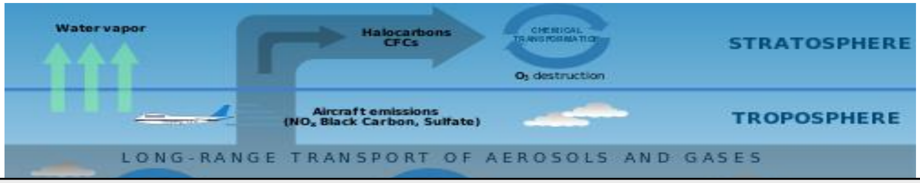
- ☐ Background and objectives
- ☐ Dry deposition of N&P over the Yellow Sea
- ☐ Wet deposition of N&P over the Yellow Sea
- ☐ Totlal deposition over the Yellow Sea

1.1Background

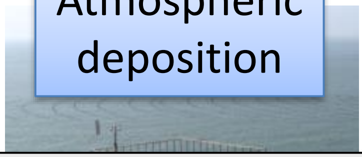
- The role of the atmosphere in transporting man-made and natural pollutants to the ocean was significant. (Duce R.A., et al., 1991; Teruya Maki, et al., 2016)
- Excessive inputs of nitrogen and phosphorus may cause changes in the structure of nutrients in the ocean. (Gao H.W., et al. ,2002; Bikkina Srinivas, 2013)
- What about the Yellow Sea?

Sewage outlets



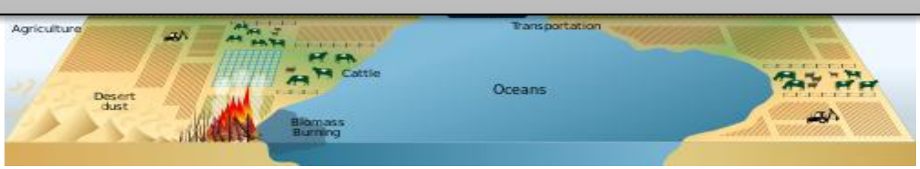


Atmospheric deposition



1.2 Objectives

- Improve the method for estimating atmospheric dry deposition flux.
- Estimate the total amounts of nitrogen and phosphorus from atm.-based sources in the Yellow Sea.



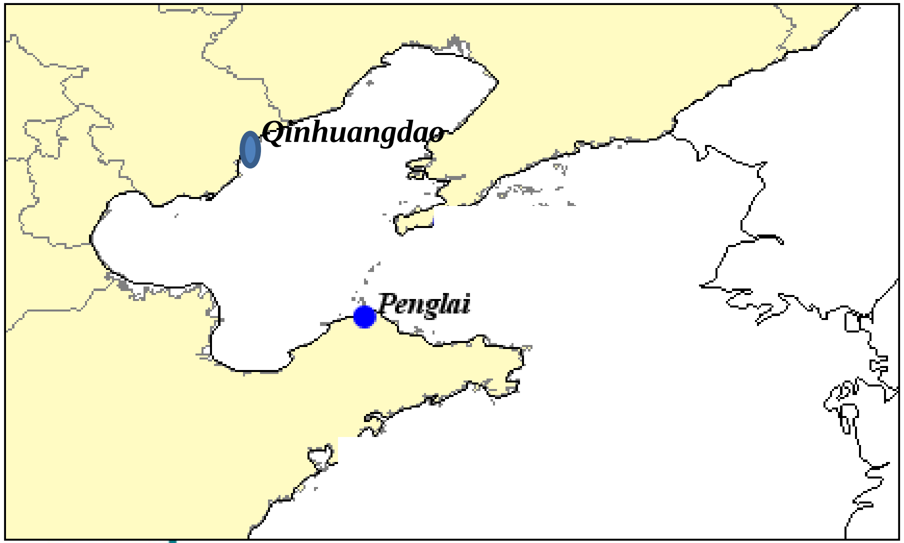
2.Atmospheric dry deposition of N&P

$$F_d = V_d * C$$ **(Hsu, et al., 2010)**

——V_d , deposition velocities of atmospheric particulate pollutants.

- The values recommended by international organizations (GESAMP)are generally adopted. However, it is usually low **(Shahin, 2000)** .
- **Related to the particle size distribution （Kang et al., 2010; Kong et al., 2014)**

2.1 Size distribution of nitrogen and phosphorus in aerosol



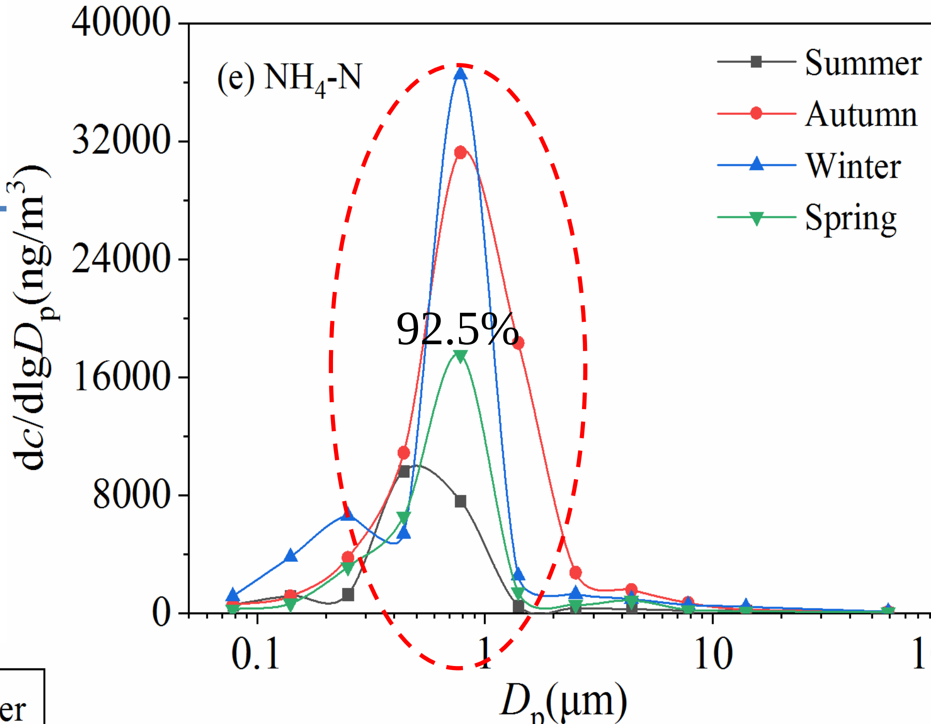
Two sites;

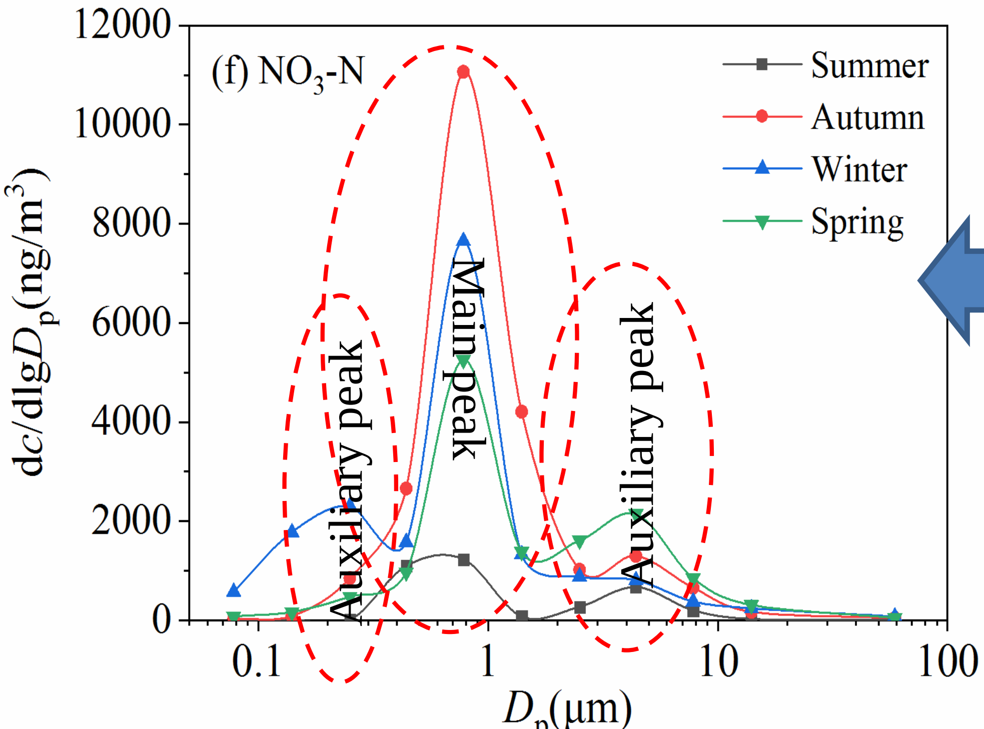
Four seasons , 2015~2016;

MSP MOUDI-110R-400 (11stages, 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1, 0.056μm) .

2.1 Size Distribution

More than 92.5% of NH_4^+-N was concentrated in the fine particle mode below 1.8μm, derived from secondary transformation.





The main peak of NO_3—N was in the accumulating mode (0.56~1.0μm, 0.32~0.56μm). And the main peak in autumn was most obvious（due to haze day）

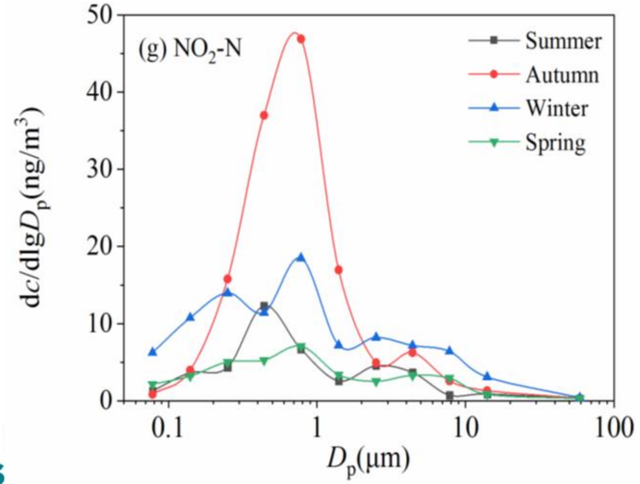
Auxiliary peak was in the coarse mode (3.2~5.6 μm)in spring, summer and autumn ,while in the condensed mode in winter .

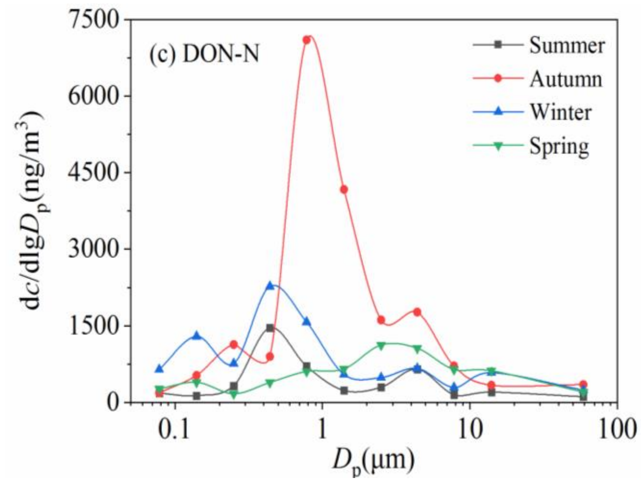
2.1 Size Distribution

- NO_2—N

  Overall, it also showed a bimodal or multimodal distribution.

- Size distribution of DON was the most complex due to the complex sources：Industrial and agricultural production, urban waste treatment, soil, animal and plant excretion（ZHENG L.X.， 2007）,photochemical reaction, and so on （Cape et al., 2011）。

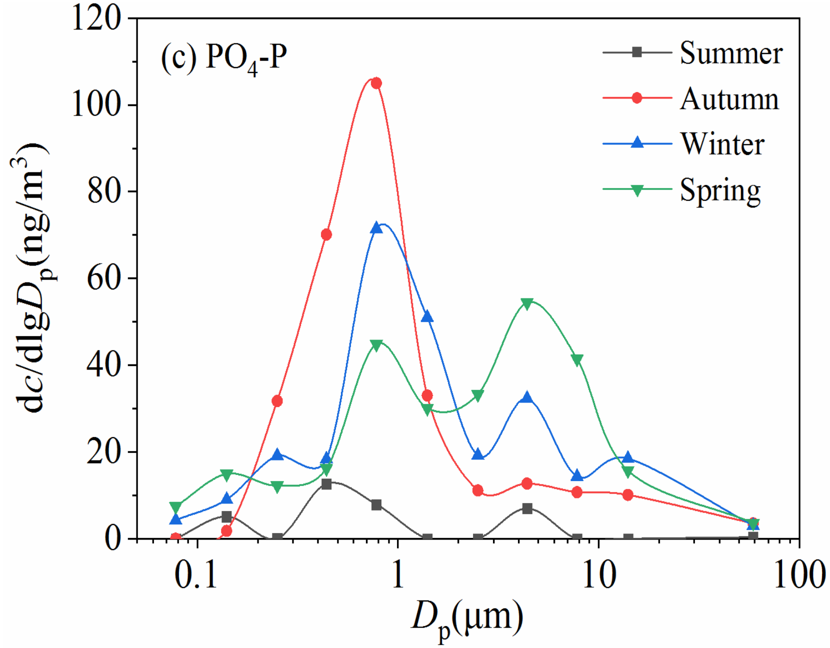




2.1 Size Distribution

DIP

- In summer, there were three peaks, two of which were in accumulating mode （0.32~0.56 and 0.10~0.18 μm), the third was in coarse mode(3.2~5.6μm)。
- In winter, two peaks appeared , in each of the coarse mode and fine particle mode.
- In spring, the highest peak appeared in the coarse mode(3.2~5.6μm),which was due to the dust weather(Baker et al., 2006; Maoi et al., 2003)
- In autumn ,there was single peak, more than 70% was in the accumulating mode(0.056~1.0μm), indicating the influences of the haze weather.



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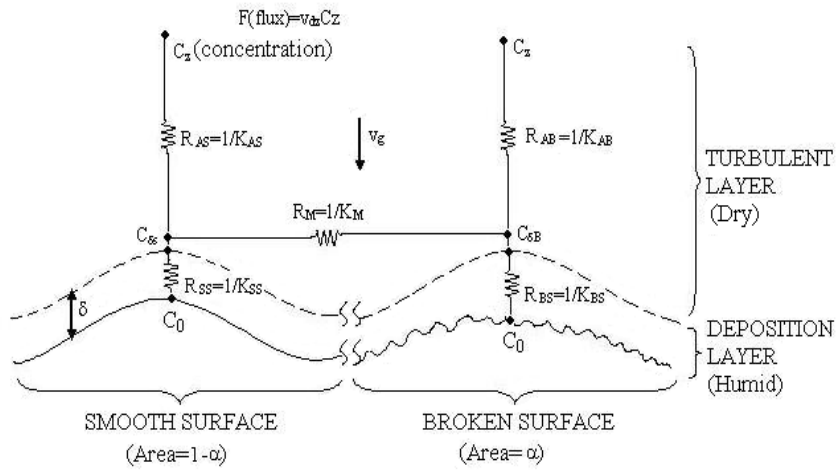
2.2 Willimas Modle

■ Model improvement

The Williams model was improved by referring to methods such as Qi et al. (2005) and Wang Zejie (2006). Improve: ①Wet particle growth effect ②Broken surface coverage ③ Broken surface transmission coefficient



A model for the dry deposition of particles to natural water surface（Williams，1982）

$$v_d = (A/B)\left[(1-\alpha)(K_{ss}+v_{gw}) + \frac{K_m\alpha(K_{bs}+v_{gw})}{K_m+\alpha(K_{ab}+K_{bs}+v_{gw})}\right] + \frac{\alpha(K_{bs}+v_{gw})\alpha(K_{ab}+v_{gd})}{K_m+\alpha(K_{ab}+K_{bs}+v_{gw})} \quad (1)$$

$$A = K_m[(1-\alpha)K_{as} + \alpha K_{ab} + v_{gd}] + (1-\alpha)(K_{ss}+v_{gd})\alpha(K_{ab}+K_{bs}+v_{gw}) \quad (2)$$

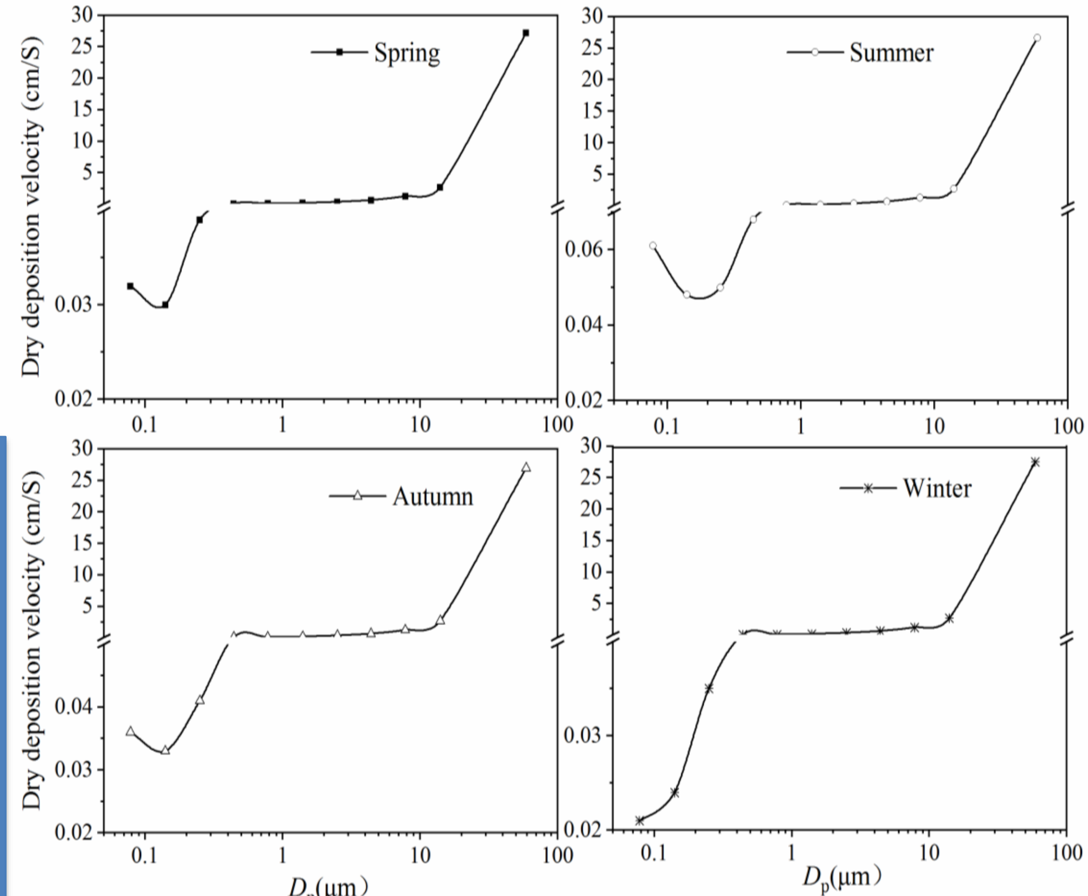
$$B = K_m[(1-\alpha)(K_{as}+K_{ss}) + \alpha(K_{ab}+K_{bs}) + v_{gw}] + (1-\alpha)(K_{as}+K_{ss}+v_{gw})\alpha(K_{ab}+K_{bs}+v_{gw}) \quad (3)$$

2.3 Dry deposition velocities

■ Deposition velocities of atmospheric particle with different sizes

➢ The deposition velocities of fine particles less than 1.8 μm varies little, while increases rapidly as the particle size continues to increase.

It can be concluded that the proportion of aerosol pollutants in fine particles has little effect on the dry deposition velocities , while the proportion of coarse particles may be the most important factor.



Variation of atmospheric deposition velocities with particle size in different seasons

2.3 Dry deposition velocities

- **Dry deposition velocities of nitrogen and phosphorus components in TSP(cm/s)**

Components	Spring	Summer	Autumn	Winter	annual
PO_4^{3-}-P	1.631	1.455	1.196	1.366	1.414
NO_2^--N	0.899	0.741	0.420	0.629	0.670
NO_3^--N	0.662	0.608	0.391	0.546	0.546
NH_4^+-N	0.338	0.327	0.250	0.273	0.297
DTP-P	1.932	1.687	1.458	1.891	1.732
DTN-N	0.776	0.659	0.493	0.581	0.629

- On the whole, the deposition velocities of P are greater than N (the proportion of coarse particles is large)
- Most deposition velocities were the highest in spring and the lowest in autumn.

2.3 Dry deposition velocities

■ Comparison with other regions and

The results were comparable with those obtained by the six-stage particle size division method based on the Slinn model, and follow the general conclusion that the NO_3^--N deposition velocities is higher than the NH_4-N.

Barnegat Bay	0.34	0.19	-	-	-	-	Slinn Model estimation based on size distribution(6 stages)	Gao, Y., 2002
Mediterranean Sea	-	-	-	-	2.1~2.7	-	Estimated method based on the glass bead system	Markaki et al., 2003
Jiaozhou Bay	0.23~0.54	0.09~0.24	0.05~0.55	0.15~0.22	0.2~0.68	0.33~1.18	Substitute surface method	Xing, 2018
The Yellow sea the Bohai Sea	0.546	0.297	0.67	0.629	1.414	1.732	Willimas Model estimation based on size distribution (11 stages)	This study

The deposition velocities obtained in our research are smaller than those in the East China Sea and Atlantic Ocean, higher than those calculated with WRF-Chem model.

2.3 Dry deposition velocities

■ Method validation

We have verified the method by collecting the dust using the surrogate surface method.

表 2 模型模拟沉降速率结果与代用表面实测值比较

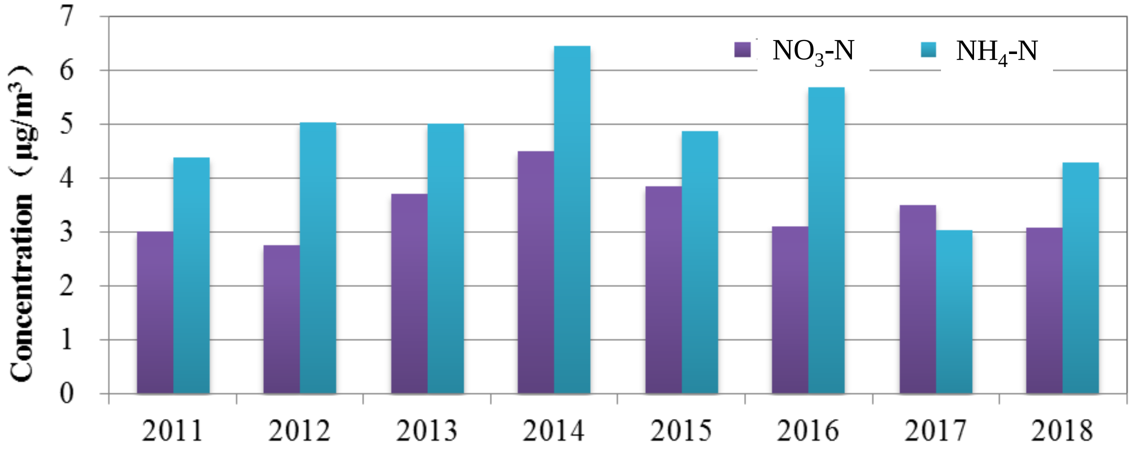
Sample number	Method	Deposition velocity（cm/S）				
		PO_4^{3-}-P	NO_3^--N	NH_4^+-N	TP	TN
D20151102-1113	Modeled	0.825	0.48	0.252	0.962	0.485
	Measured	0.651	0.381	0.234	1.474	0.731
D20150824-0831	Modeled	1.271	1.558	0.506	1.289	0.587
	Measured	1.197	1.136	0.475	2.064	1.625
D20160421-0429	Modeled	2.04	0.604	0.389	1.417	0.711
	Measured	0.946	0.908	0.128	0.675	0.32
D20160112-0129	Modeled	1.218	0.39	0.295	0.768	0.177
	Measured	1.478	0.676	0.188	0.947	0.107

- ✓ **About 75% of the components, the difference were within 1 time, and the rest were within 2 times, which were acceptable.**
- ✓ **It showed that the method was reasonable and effective.**

2.4 Trends of inorganic nitrogen in TSP

- **5 stations**
- **TSP samples were collected in four seasons every year 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/m³.



Trends of inorganic nitrogen in aerosols over the Yellow Sea coast from 2011

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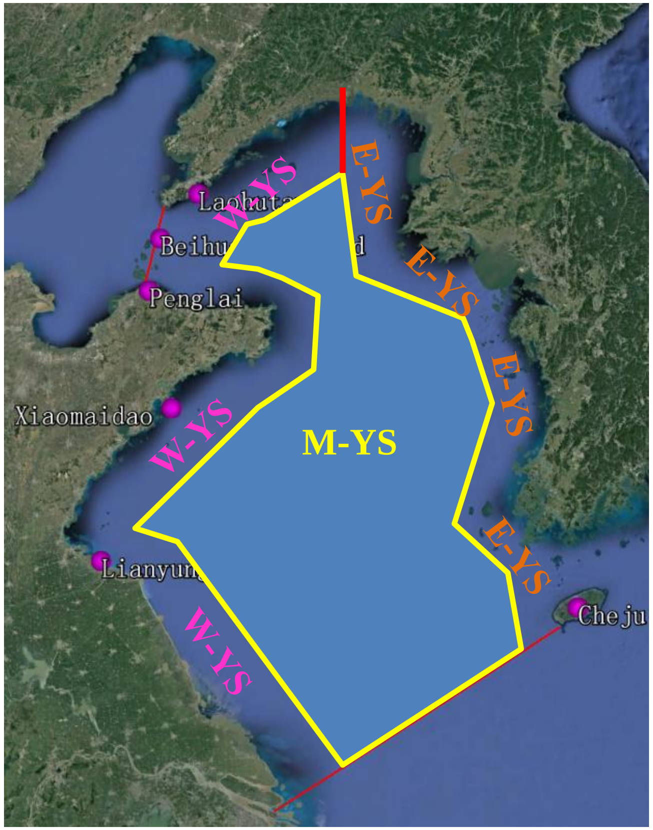
2.5 Dry deposition of N &P



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

—V_d is taken from the results in the section 2.3 above.

N&P in aerosol in different areas of the Yellow Sea in 2017

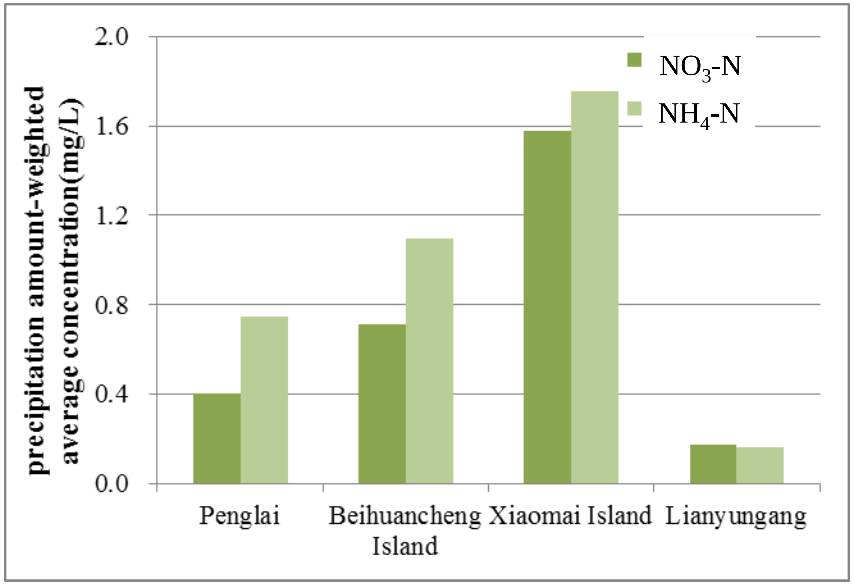
	W-YS	M-YS	E-YS
NO_3-N（μg/m^3）	3.10	2.07	1.92
NH_4-N（μg/m^3）	2.82	1.88	1.19
NO_2-N（ng/m^3）	18.34	12.24	11.39
PO_4-P（ng/m^3）	23.43	12.32	11.47
area（km^2）	83600	228000	68400

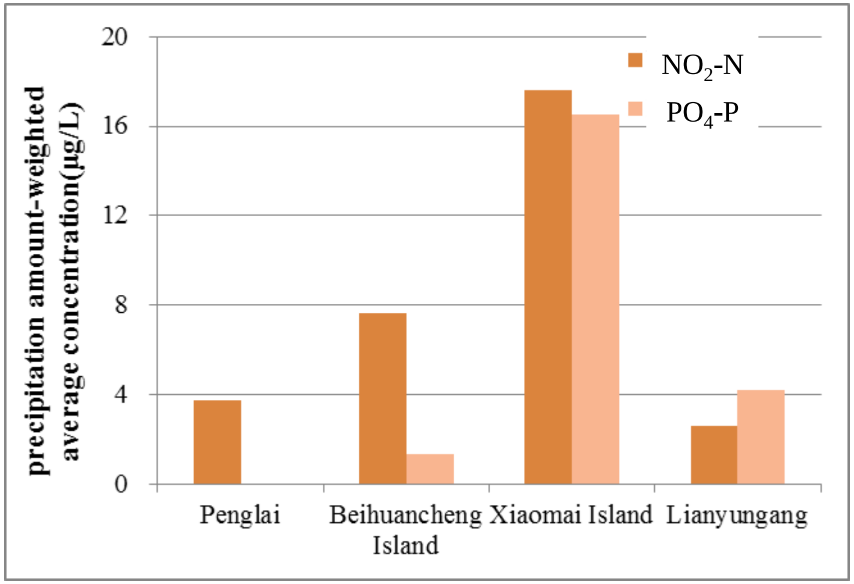
Dry deposition of N&P over the Yellow Sea in 2017(t/a)

	W-YS	M-YS	E-YS	Yellow Sea
NO_3-N	44613	81154	22666	148433
NH_4-N	22086	40177	7605	69869
NO_2-N	324	589	165	1078
PO_4-P	873	1253	350	2476

3.Atmospheric wet deposition of N&P

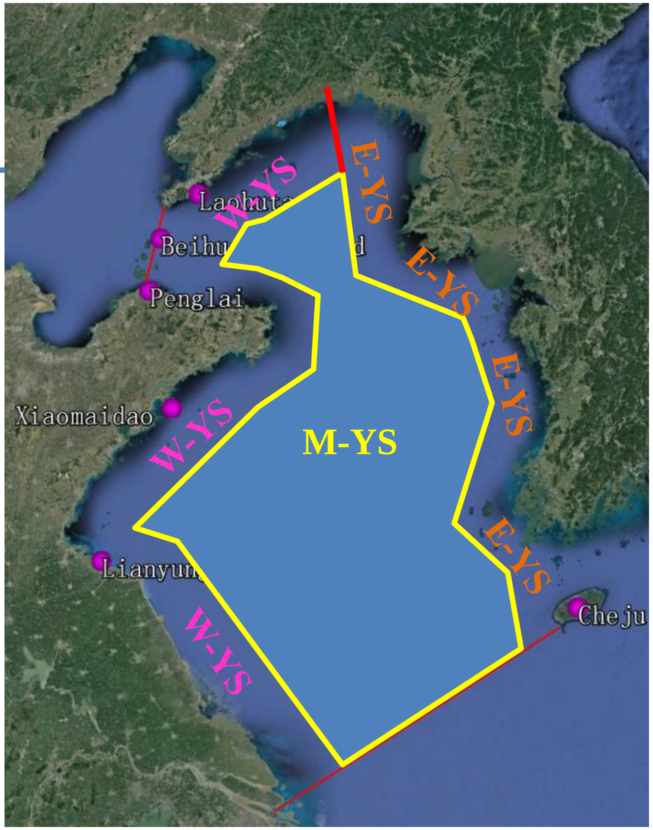
89 rain samples were collected in 4 stations in 2017 .





Average concentration weighted by rainfall in 2017

3.Atmospheric wet deposition of N&P



N&P in the rain in different areas of the Yellow Sea in 2017

	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
Area（km2）	83600	228000	68400
Rainfall (mm)	910	843.5	1500

$$F_w = C_M * I * A$$

—F_W, atmospheric wet deposition
— C_M, average concentration weighted by rainfall
— I, annual rainfall
— A, area of the region

Wet deposition of N&P over the Yellow Sea in 2017(t/a)

	W-YS	M-YS	E-YS	All 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

4.Total deposition of N&P

$$F_t = F_d + F_w$$

Atmospheric total deposition of N&P over the Yellow Sea in 2017(t/a)

	Dry deposition	Wet deposition	Total deposition
NO_3-N	148433	203437	351869
NH_4-N	69869	247068	316937
NO_2-N	1078	2245	3323
PO_4-P	2476	1322	3798

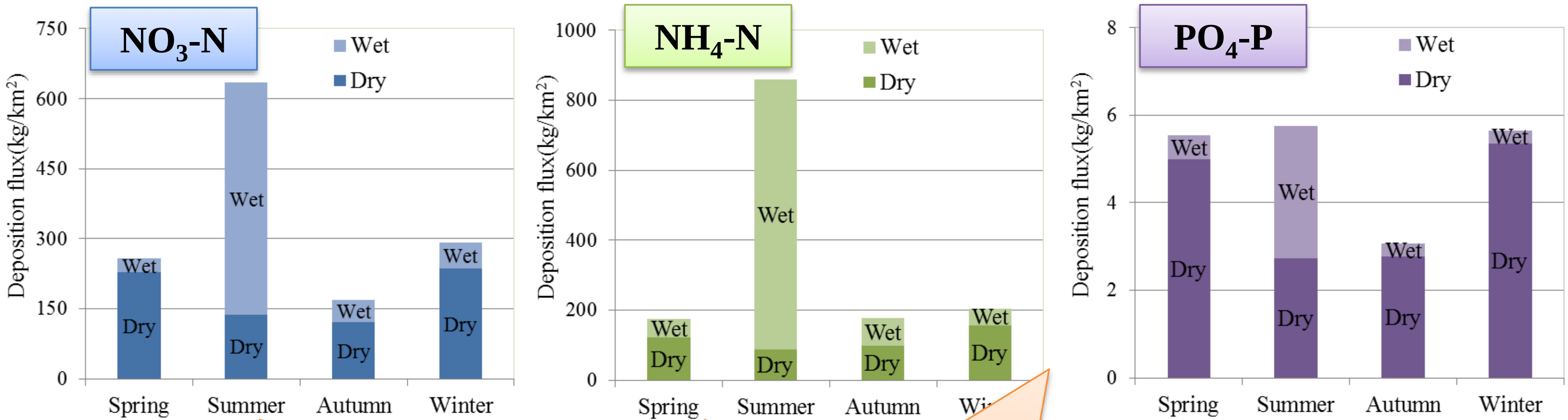
Comparison of atmospheric deposition and river input over the Western Yellow Sea in 2017(t/a)

W-YS	atm.-based	river-input
NO_3-N	99118	87629
NH_4-N	93584	52162
NO_2-N	926	7664
PO_4-P	1293	19476

- The atmospheric wet deposition of nitrogen and phosphorus in the Yellow Sea was higher than that of dry deposition in 2017.
- In the western part of the Yellow Sea， the nitrogen input from atmosphere has exceeded the input from the river, while the input from atmospheric of phosphorus is not obvious.

4.Total deposition of N&P

■ Seasonal variation of atmospheric



Single-site dry and w… deposition fl… itrog… osphorus i… different seasons

Is this related to the high incidence of red tides in summer?(to be solved)

- The wet dep… …o the most rainfall in summer
- The dry deposition fluxes … …nd … …han in summer and autumn, due to the high concentra… of nitrog… and phosphorus in the terrestrial atmosphere in winter and spring.
- The total deposition fluxes of N&P were highest in summer and lowest in autumn.

Conclusion

The proportion of aerosol pollutants in coarse particles was the most important factor effecting the dry deposition velocities.

The atmospheric wet deposition of nitrogen and phosphorus over the Yellow Sea was higher than that of dry deposition. The total deposition fluxes of N&P were highest in summer and lowest in autumn.

In the western part of the Yellow Sea，the nitrogen input from atmosphere exceeded the input from the river, while the input from atmospheric of phosphorus was not obvious.

Thank you for your attention!

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