我国北方城市冬季$PM_{2.5}$暴增机制及相关液相反应

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提 纲

1. 冬季雾霾期硫酸盐的快速增长
   (1) 北京西安外场观测
   (2) 实验室烟雾箱模拟
2. 沙尘暴期二次粒子
   (1) 硝酸铵
   (2) 二次有机气溶胶
3. 区域生物质燃烧
   (1) 无机盐
   (2) 有机酸

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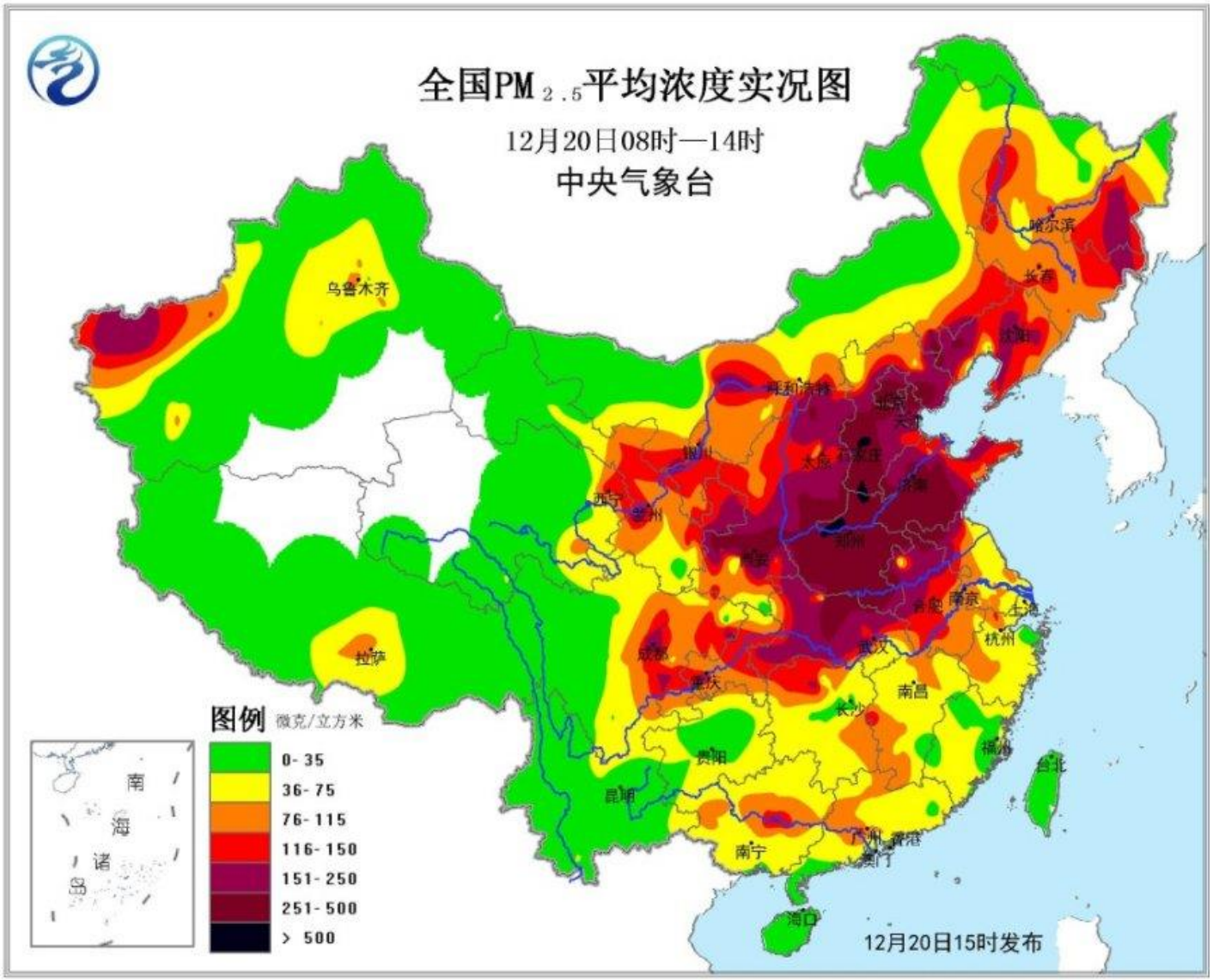
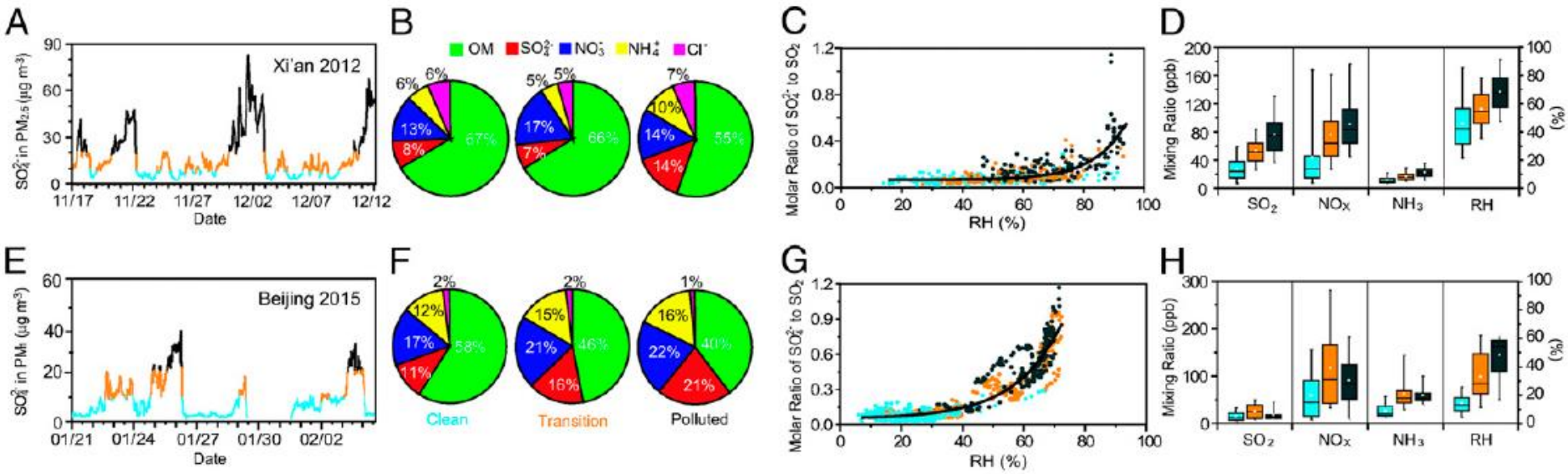


西安和北京冬季灰霾期间硫酸盐形成与演化 (Wang et al., PNAS 2016)



(1) 清洁期： 有机物为主，污染期：无机盐为主

(2) 西安有机物含量高于北京

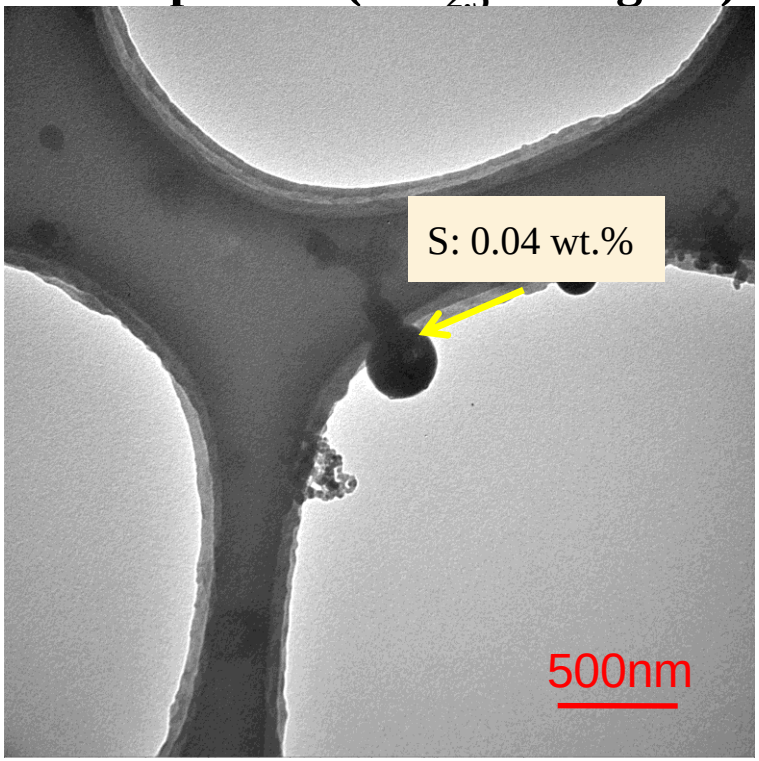
(3) 硫酸盐随着相对湿度的增加而呈指数型增长

(4) 北京SO2可在更低相对湿度下转化成硫酸盐

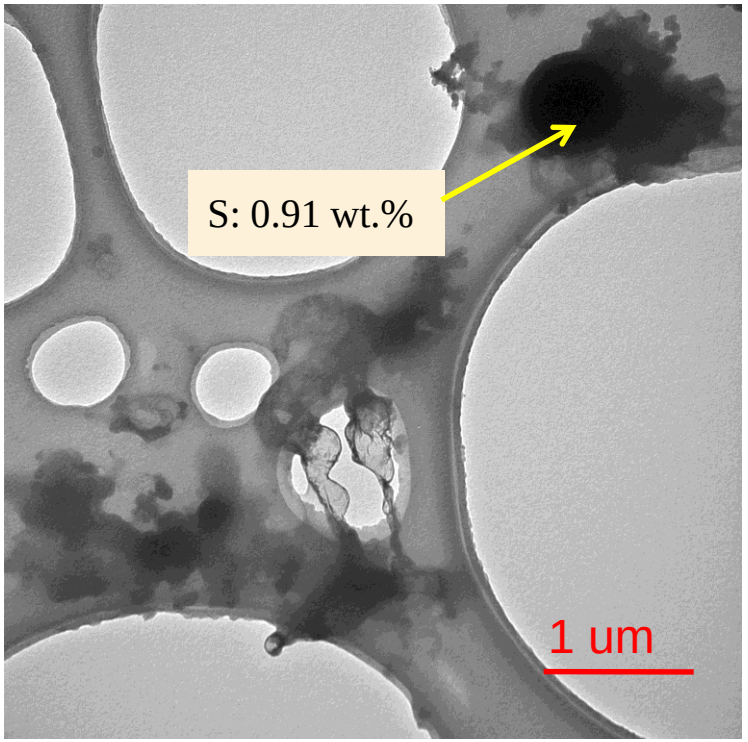
(5) 重污染期间伴随着高浓度SO2,NOx, NH3以及高相对湿度

扫描电镜分析

Clean period ($PM_{2.5}$<75 ug/m^3)



Hazy period ($PM_{2.5}$>200 ug/m^3)



(1) The content of sulfur in particles, which is SO_4^{2-}, is around 20 times higher on hazy days in comparison with that in clean periods;

(2) Most of the aerosols on hazy days are liquid

Again indicating the aerosol aqueous phase formation of sulfate in haze episodes

$$OH + SO_2 + M \rightarrow HO_2 + \text{Sulfate}$$

气相反应机制

液相反应机制

$$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H^+ + H_2O \quad (M4)$$

$$SO_2 + O_3 + H_2O \rightarrow SO_4^{2-} + 2H^+ + O_2 \quad (M5)$$

$$HSO_3^- + O_3 \rightarrow SO_4^{2-} + H^+ + O_2 \quad (M6)$$

$$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2 \quad (M7)$$

$$SO_2 + H_2O + 0.5O_2 + Fe(III)/Mn(II) \rightarrow SO_4^{2-} + 2H^+ \quad (M8)$$

$$HSO_3^- + CH_3OOH \rightarrow SO_4^{2-} + H^+ + CH_3OH \quad (M9)$$

$$HSO_3^- + CH_3COOOH \rightarrow SO_4^{2-} + H^+ + CH_3COOH \quad (M10)$$

(Wang et al., JGR 2014)

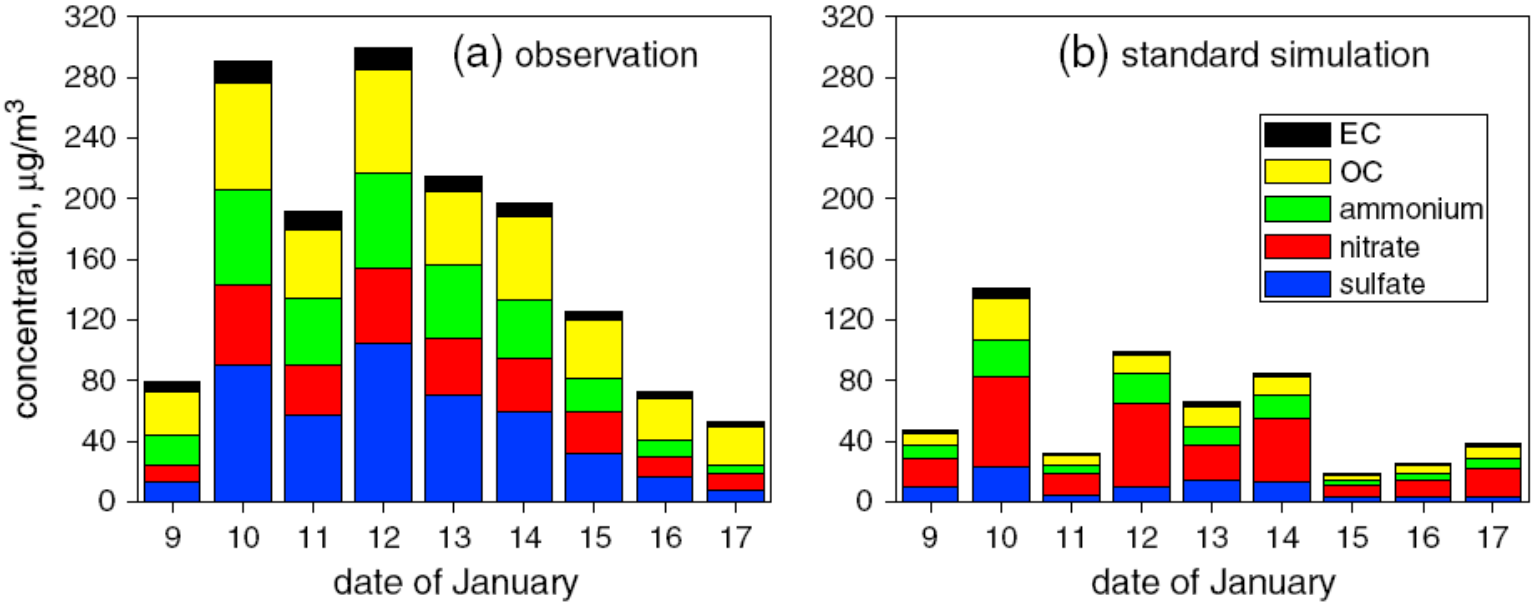


Table 2. A Summary of All the Simulations in This Study

Simulation Name	Description
Standard simulation	Model standard simulation with the 2013 inventory
DoubleSO_2 run	SO_2 emissions from the standard simulation are doubled over NC and reduced by 30% over SC. Changes are applied uniformly throughout January.
Emission_run	Total monthly emissions of SO_2, OC, and EC (anthropogenic portions only) from the standard run are increased by 100% over NC; SO2 emissions over SC are reduced by 30%; NO*x* and NH3 emissions are the same as those in the standard run. The meteorology correction factors are applied on a day-to-day basis to emissions of SO_2, NO*x*, NH_3, OC, and EC over NC.
Gamma_run T1	Emissions are the same as in the emission_run; $\gamma = 10^{-4}$ when RH = 50%, $\gamma = 10^{-3}$ when RH = 50%; γ increases linearly with RH from 50% to 100% (equation (2)).
Gamma_run T2	Emissions are the same as those in the emission_run; $\gamma = 10^{-3}$ when RH = 50%, $\gamma = 10^{-2}$ when RH = 50%; γ increases linearly with RH from 50% to 100% (equation (2)).
Gamma_run T3	Emissions are the same as those in the emission_run; $\gamma = 10^{-2}$ when RH = 50%, $\gamma = 10^{-1}$ when RH = 50%; γ increases linearly with RH from 50% to 100% (equation (2)).

西安2012年冬季高时间分辨率滤膜采样分析显示：过渡金属铁锰氧化不重要

Table S1. Gaseous and PM pollutants and meteorological parameters during Xi'an 2012

	Clean		Transition		Polluted	
	Mean	Range	Mean	Range	Mean	Range
I. Gaseous pollutants (ppb)						
SO_2	28±17	1.0–86	54±22	17–191	78±31	16–203
NO_X	44±49	5.0–264	76±51	15–300	92±39	25–245
O_3	7.4±7.0	0.0–26	4.1±4.7	0.4–11	4.1±2.4	0.6–9.6
NH_3	12±7.4	4.7–67	17±7.7	7.6–35	23±8.3	9.3–61
HONO	1.3±1.0	0.2–5.4	2.1±1.3	0.2–6.5	2.7±1.8	0.3–10
II. Inorganic ions, Fe, Mn and organic matter in $PM_{2.5}$ ($\mu g\ m^{-3}$)						
SO_4^{2-}	5.9±2.2	2.3–10	14±4.4	10–20	38±14	20–83
NO_3^-	8.7±4.9	1.4–25	16±6.7	3.8–35	33±10	12–55
Cl^-	4.0±3.7	0.0–22	9.8±5.1	2.4–28	14±6.3	2.6–34
NH_4^+	4.0±2.2	0.8–11	10±3.7	5.1–18	25±7.7	3.2–44
Na^+	3.6±3.2	0.2–8.4	4.5±3.2	0.5–17	4.2±2.7	0.5–17
K^+	1.3±0.7	0.3–4.1	3.1±1.2	1.3–7.0	4.6±1.4	1.8–8.3
Mg^{2+}	0.2±0.1	0.1–0.7	0.3±0.1	0.0–0.7	0.3±0.1	0.0–0.8
Ca^{2+}	1.6±1.0	0.3–6.3	2.4±1.2	0.0–5.3	2.3±1.2	0.2–5.9
Total ions	29±13	6.8–63	60±19	34–97	121±32	65–199
Fe ($\mu g\ m^{-3}$)	0.82±0.29	0.37–1.13	1.51±0.70	0.60–3.0	1.76±0.66	0.79–2.79
Mn ($\mu g\ m^{-3}$)	0.04±0.04	0.00–0.10	0.11±0.08	0.04–0.35	0.15±0.07	0.08–0.29
Water-soluble Fe ($ng\ m^{-3}$)	1.5±2.1	0.0–6.1	4.6±3.9	0.0–14	16±5.1	7.3–23
Water-soluble Mn ($ng\ m^{-3}$)	10±2.1	3.8–20	21±8.7	11–40	41±16	17–70
Organic matter (OM)	35±15	7.0–70	99±33	38–163	177±39	116–288
pH	6.70±1.40	4.43-11.0	6.04±1.24	4.16-8.03	6.96±1.33	4.14-8.16
III. $PM_{2.5}$ and meteorological parameters						
$PM_{2.5}$ ($\mu g\ m^{-3}$)	43±18	8.0–74	139±65	76–613	250±120	101–839
T (^{O}C)	5.7±4.1	-2.0–17	4.1±4.0	-2.3–11	4.1±4.4	-3.1–14
RH (%)	46±18	14–94	56±17	26–93	68±14	41–93
Visibility (km)	8.9±3.4	3.2–17	6.1±2.8	2.4–12	3.2±1.1	1.4–7.2

实验室反应瓶模拟：大气中O_2没有效应

Table S3. Detection of sulfate formation in the reaction cell

Experimental run	SO_2 (350 ppm)	NO_2 (350 ppm)	Water	3 wt % NH_3	Integrated sulfate desorption peak area (x 10^6 cps)
1 (3)	In N_2	In N_2	√	x	6.8±2.6
2 (3)	In N_2	In N_2	x	√	11.0 ±4.3
3 (1)	In air	In air	√	x	6.5
4 (1)	In air	In air	x	√	10.0

The symbols "√" and "x" indicate whether a water or NH_3 solution was used and not used in the exposure, respectively. The number in parenthesis on the right column denotes the number of repeating experiments.

确认：无光照条件下：

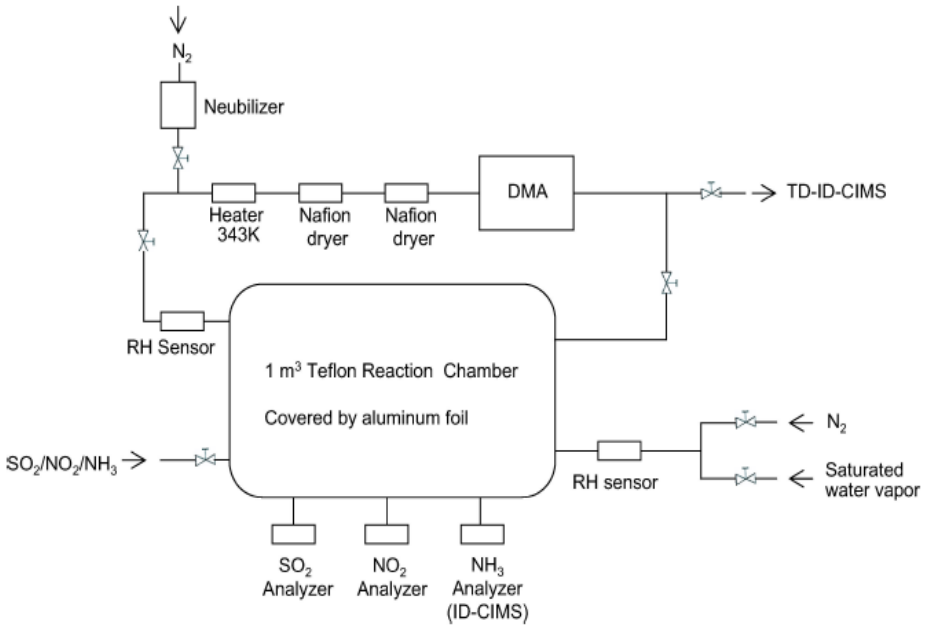
(1)二氧化氮可以快速液相氧化二氧化硫，生成硫酸盐

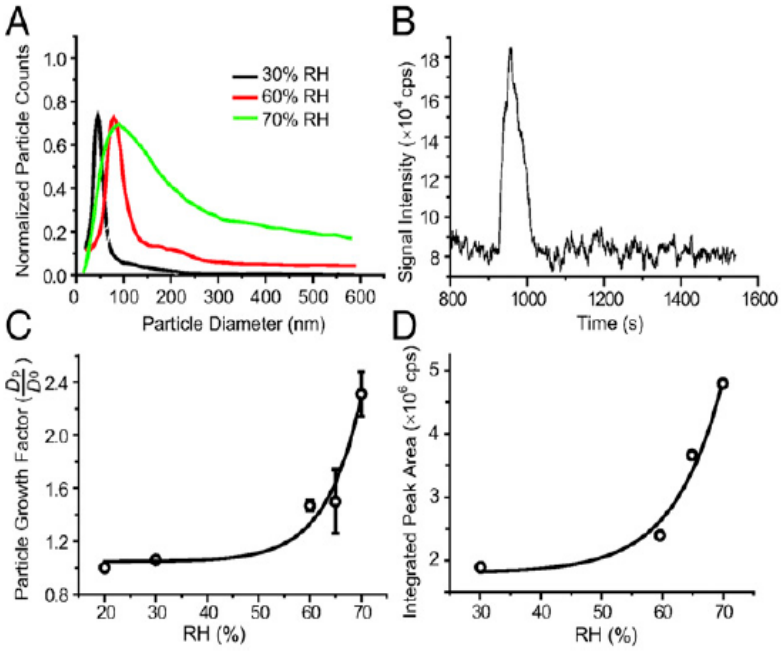
(2)氨气可促进上述反应进行

(3)在此非均相反应过程中，大气中氧气没有作用

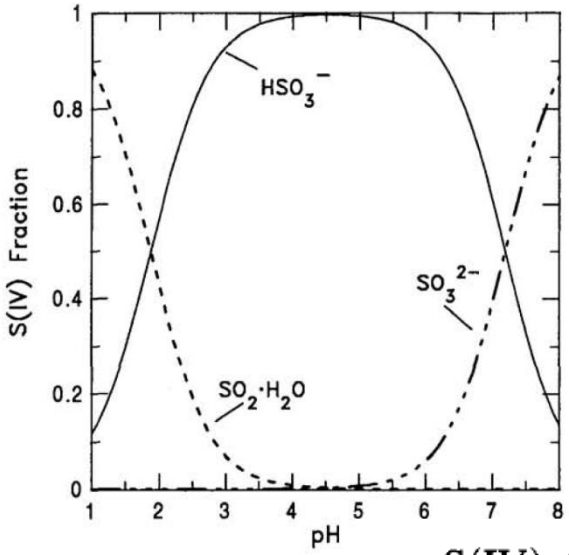
烟雾箱模拟：纳米粒子上液相SO_2+NO_2氧化(重要)

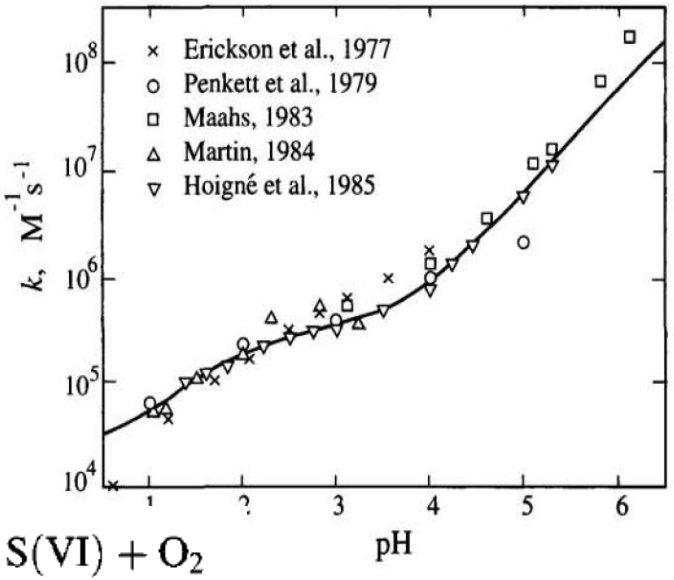
1立方米烟雾箱，通入二氧化硫、二氧化氮、氨气和水汽（调节相对湿度）, 45 nm seed (草酸）
1个小时后，用仪器检测硫酸盐的浓度，发现：
当二氧化硫、二氧化氮、氨气、>60%相对湿度四个条件同时满足时，硫酸盐才能形成，并且与相对湿度成指数增长关系；
没有氨气是看不到硫酸盐的信号，





二氧化硫氧化形成硫酸盐颗粒物酸度是关键，氨气对酸度起着决定性作用





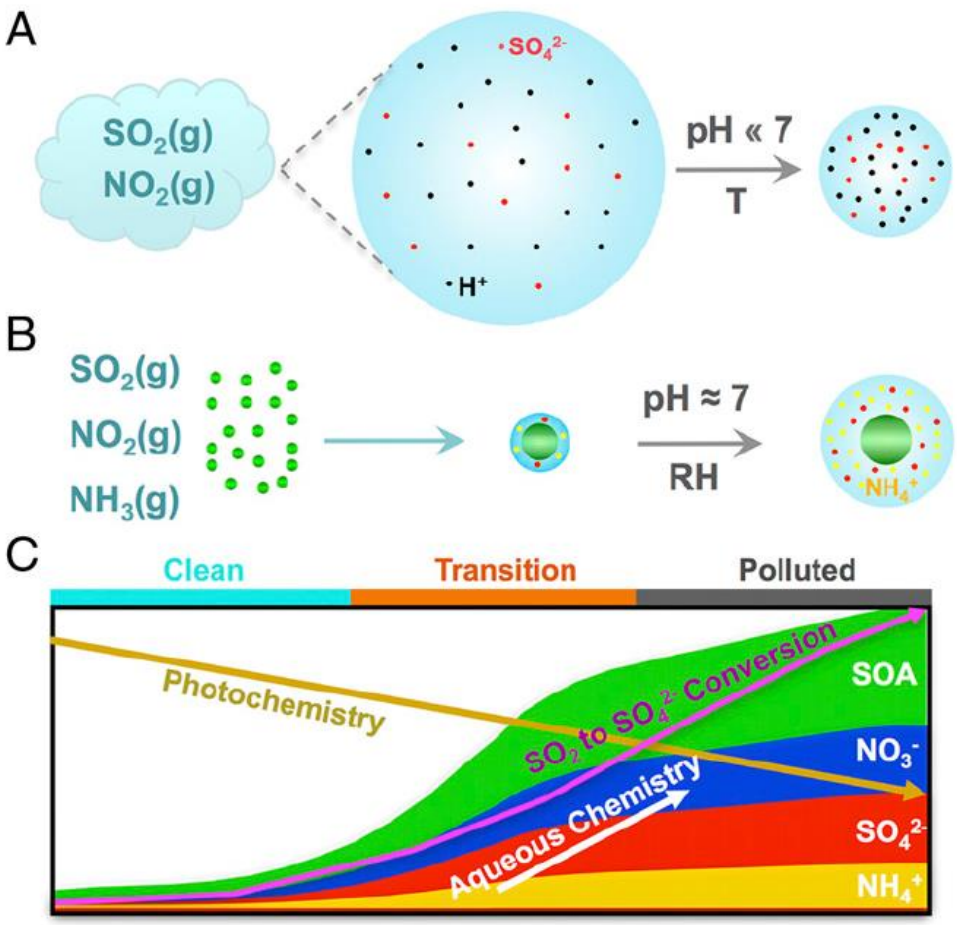
$$S(IV) + O_3 \rightarrow S(VI) + O_2$$

$$R_0 = -\frac{d[S(IV)]}{dt} = (k_0[SO_2 \cdot H_2O] + k_1[HSO_3^-] + k_2[SO_3^{2-}])[O_3] \qquad (7.80)$$

with $k_0 = 2.4 \pm 1.1 \times 10^4\ M^{-1}\ s^{-1}$, $k_1 = 3.7 \pm 0.7 \times 10^5\ M^{-1}\ s^{-1}$ and, $k_2 = 1.5 \pm 0.6 \times 10^9\ M^{-1}\ s^{-1}$. The activation energies recommended by Hoffmann and Calvert (1985) are based on the work of Erickson et al. (1977) and are $46.0\ kJ\ mol^{-1}$ for k_1 and $43.9\ kJ\ mol^{-1}$ for k_2.

(Seinfeld and Pandis., 1998)

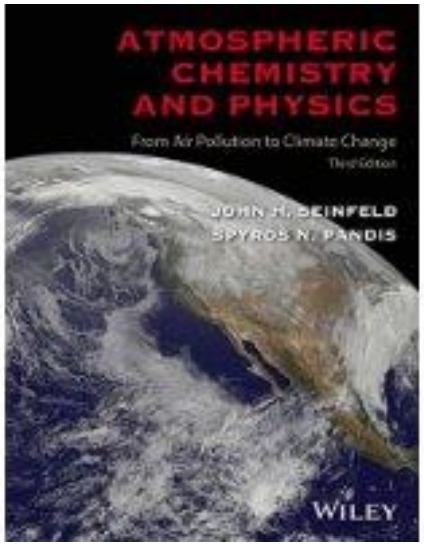
Wang et al., PNAS 2016：伦敦雾与中国霾



$$SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq) + 2HONO(g) \quad (A)$$

$$2NH_3(g) + SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow 2NH_4^+(aq) + SO_4^{2-}(aq) + 2HONO(g) \ (B)$$

本项工作的重要性



We see that under these conditions oxidation by dissolved H_2O_2 is the predominar pathway for sulfate formation at pH values less than roughly 4–5. At pH $\geq$ 5 oxidation b O_3 starts dominating and at pH 6 it is 10 times faster than that by H_2O_2. Also, oxidation c S(IV) by O_2 catalyzed by Fe and Mn may be important at high pH, but uncertainties in th rate expressions at high pH preclude a definite conclusion. Oxidation of S(IV) by NO_2 unimportant at all pH for the concentration levels above.

----Seinfeld and Pandis "*Atmospheric Chemistry and Physics*"

tion process with enforced NH_3 and NO_2 control measures. In addition to explaining the polluted episodes currently occurring in China and during the 1952 London Fog, this sulfate production mechanism is widespread, and our results suggest a way to tackle this growing problem in China and much of the developing world.

M. Molnia, 1995年
大气化学诺贝尔奖得主

On Sep 27, 2016, at 12:03 PM, Molina, Mario <mjmolina@ucsd.edu> wrote:

Hi Renyi,

Sorry it has taken so long to respond. It turns out I had a couple of urgent projects to finish here at our study center, and they took longer than anticipated.

Anyhow, I am working on the Sulphur paper, and I agree that it is an important piece of work on atmospheric chemistry. And yet, given the various commentaries by the reviewers I

灰霾成因论文（Wang et al., PNAS 2016）受到李克强总理、全国政协副主席罗富和等国家领导人高度关注，设立总理基金

周卫健院士建议攻克雾霾形成机理 李克强：谁攻克，重奖谁！

2017-03-10 | 【大 中 小】【打印】【关闭】

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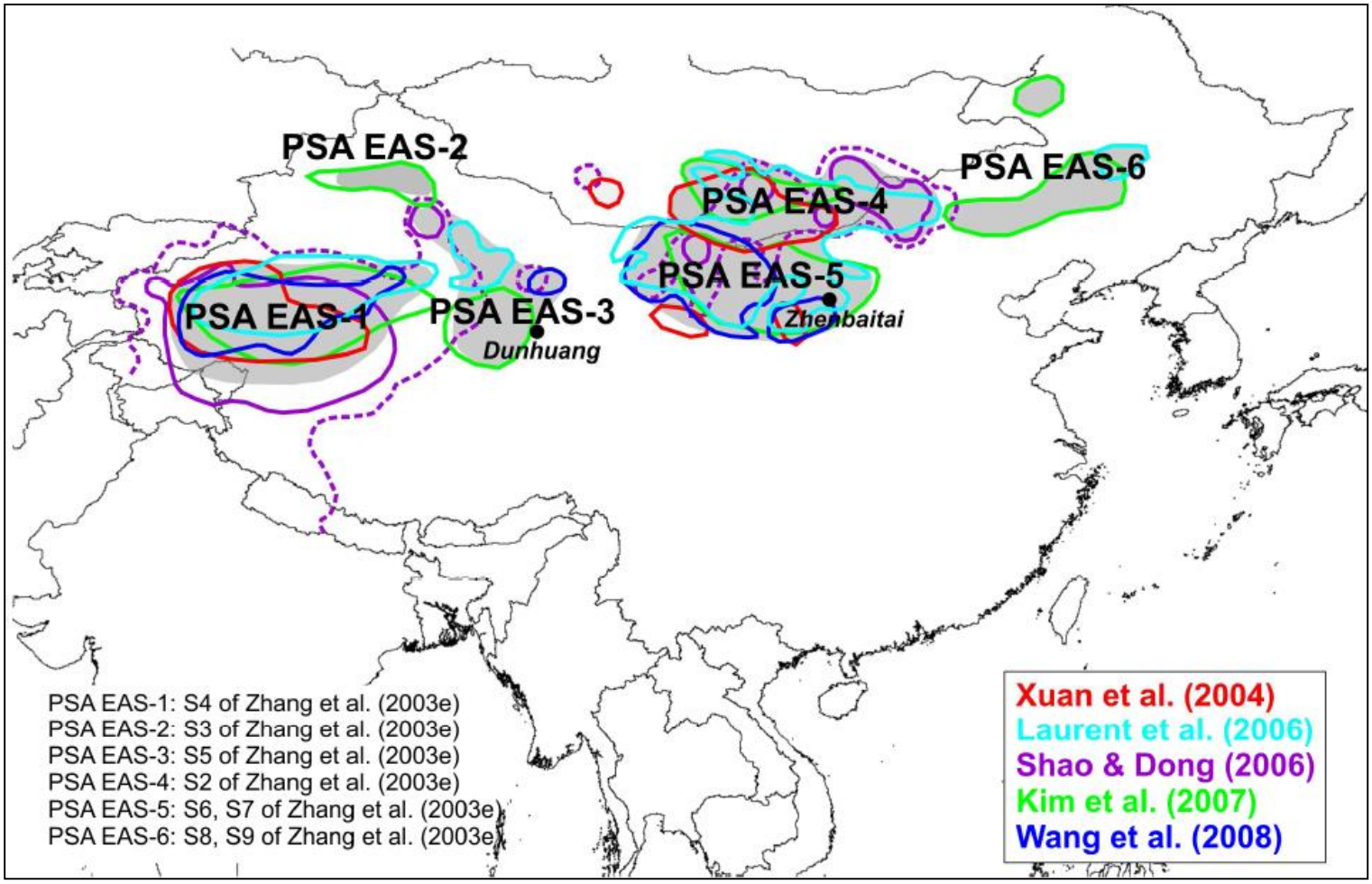
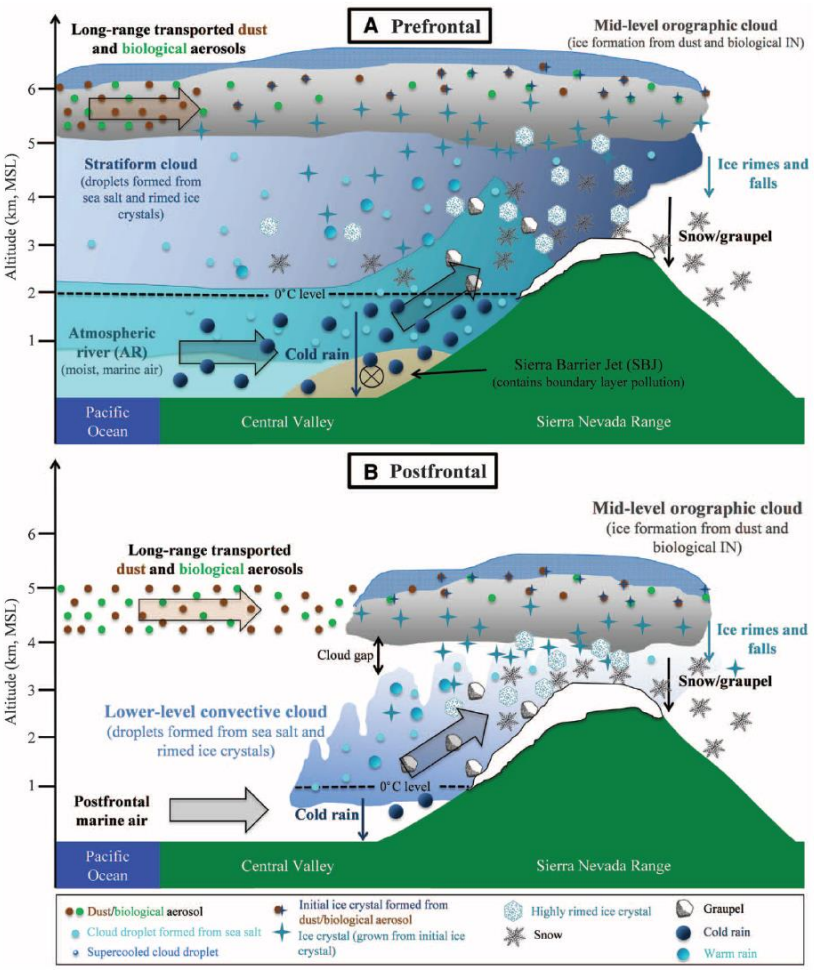
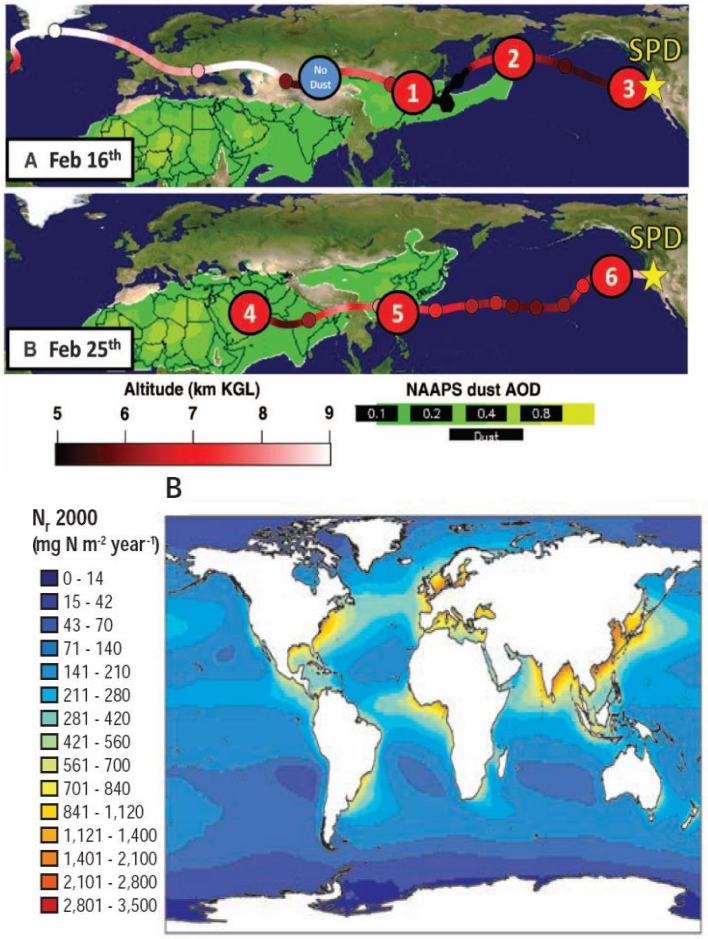


Taklamakan and Gobi desert areas are the major dust source regions of east Asia, releasing more than 800Tgyr^{-1}

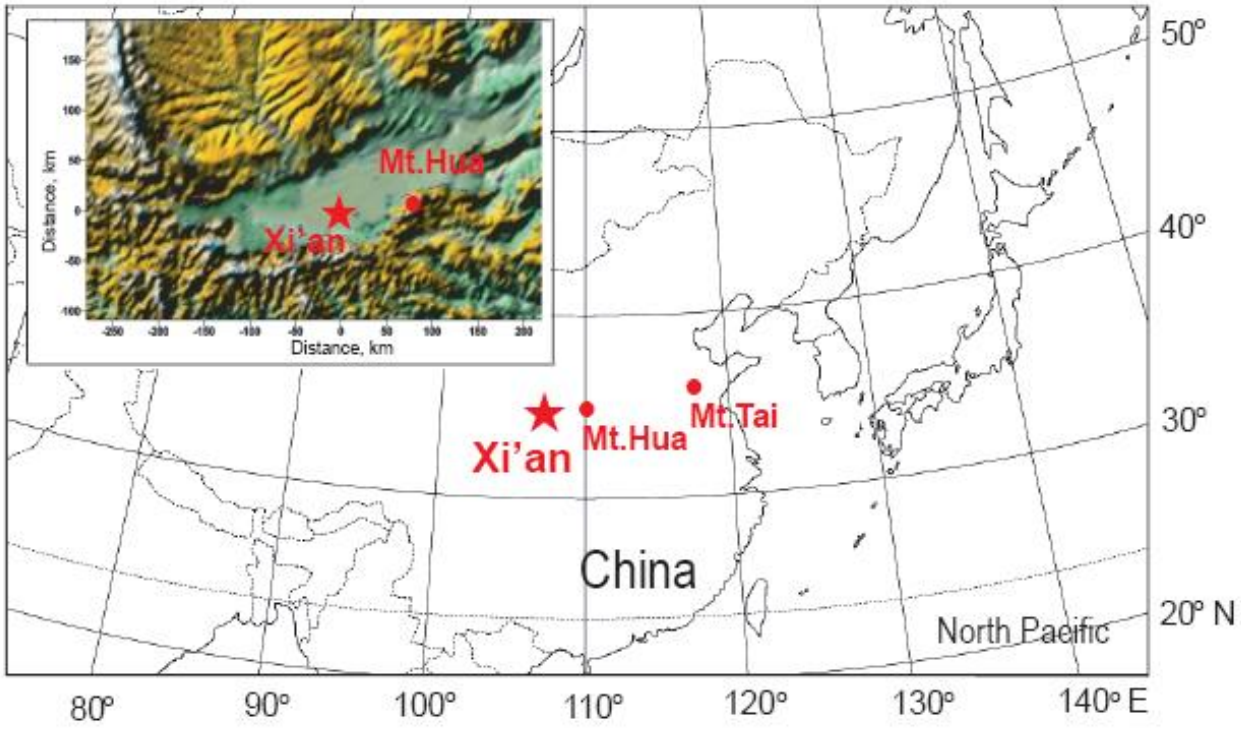
2. 沙尘暴期二次粒子



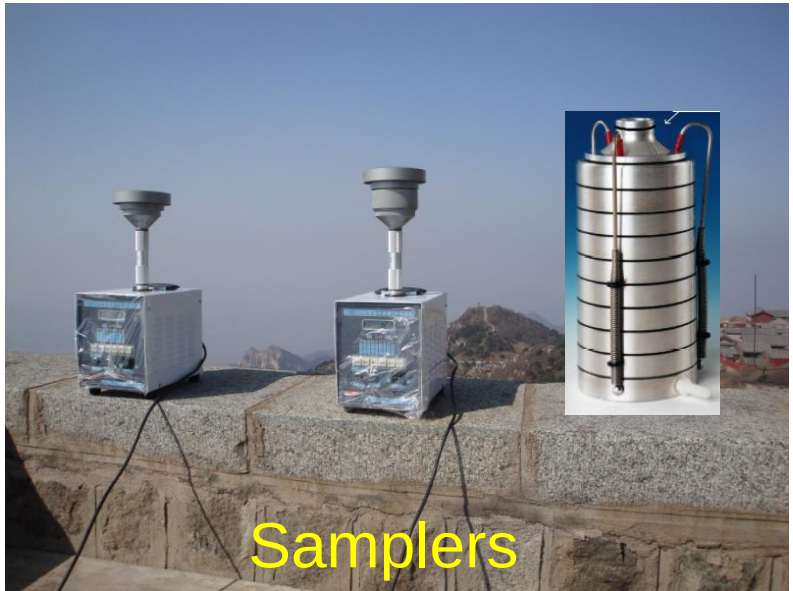
(Creamean et al. Science, 2013)



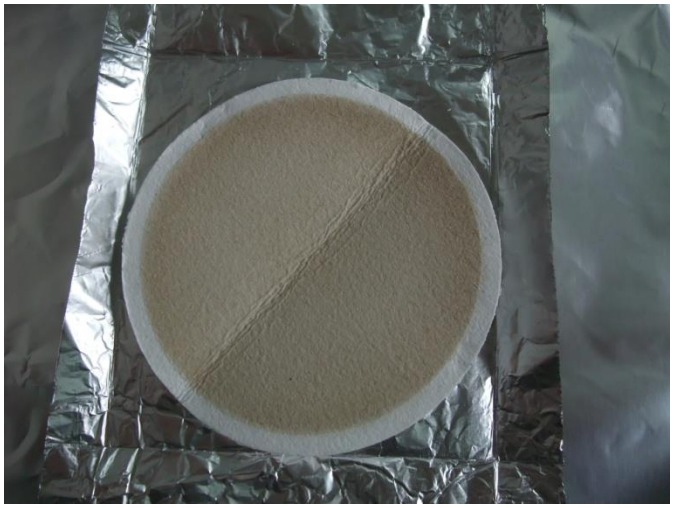
(Duce et al. Science, 2008)


Mt.Hua
Xi'an
Distance, km
Distance, km
Xi'an
Mt.Hua
Mt.Tai
China
North Pacific
50°
40°
30°
20° N
80°
90°
100°
110°
120°
130°
140° E

Sampling sites



(i) Xi’an



(ii) Mt. Hua

(iii) Mt. Tai

I. Non-event days (Spring 2009)

Xi’an

Mt. Hua

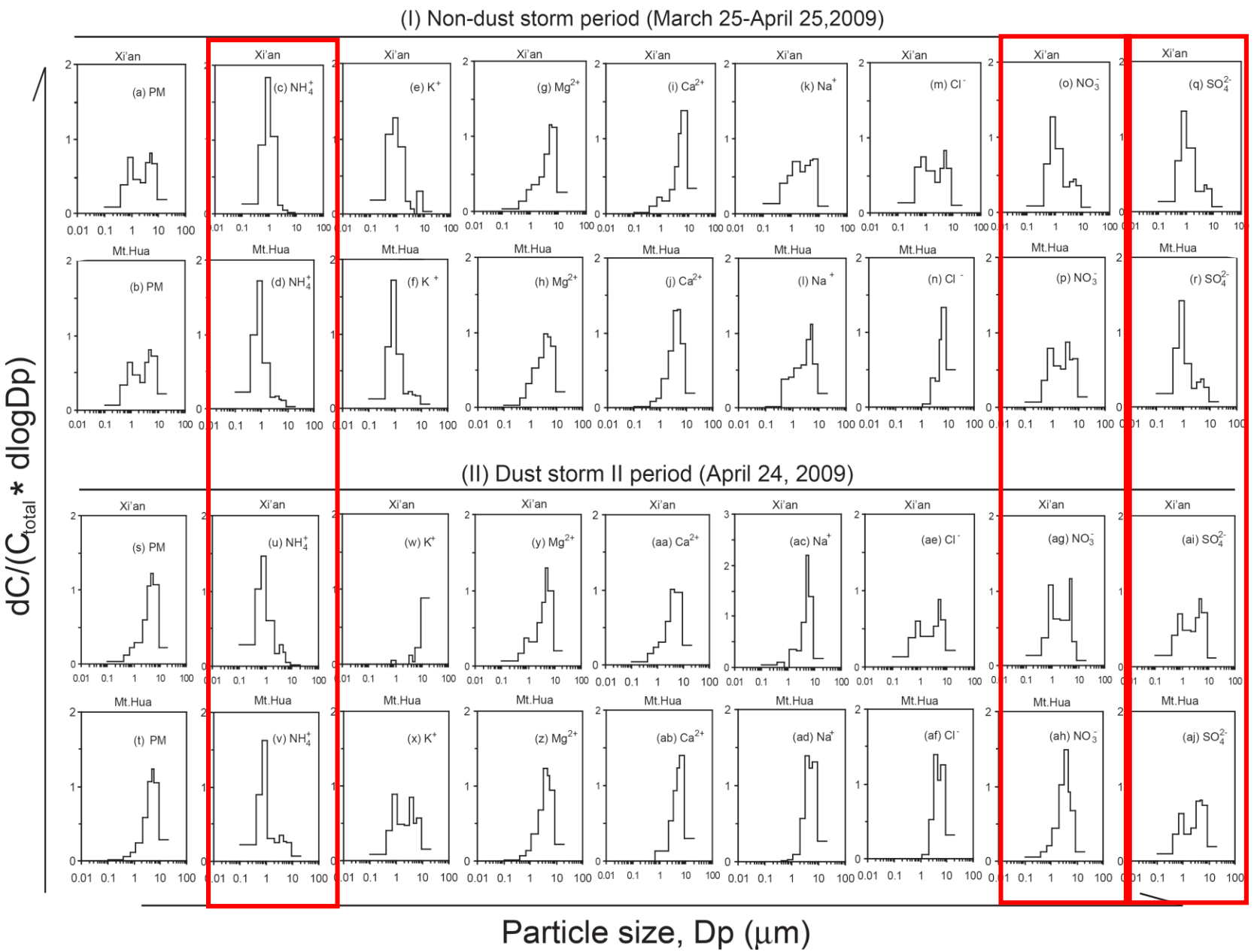
Mt. Tai

II. Dust storm day(April 24, 2009)

Xi’an

Mt. Hua

Mt. Tai



(Wang* et al., Atmos .Chem. Phys. 2013)

Heterogeneous reactions in Xi'an during the DS II event

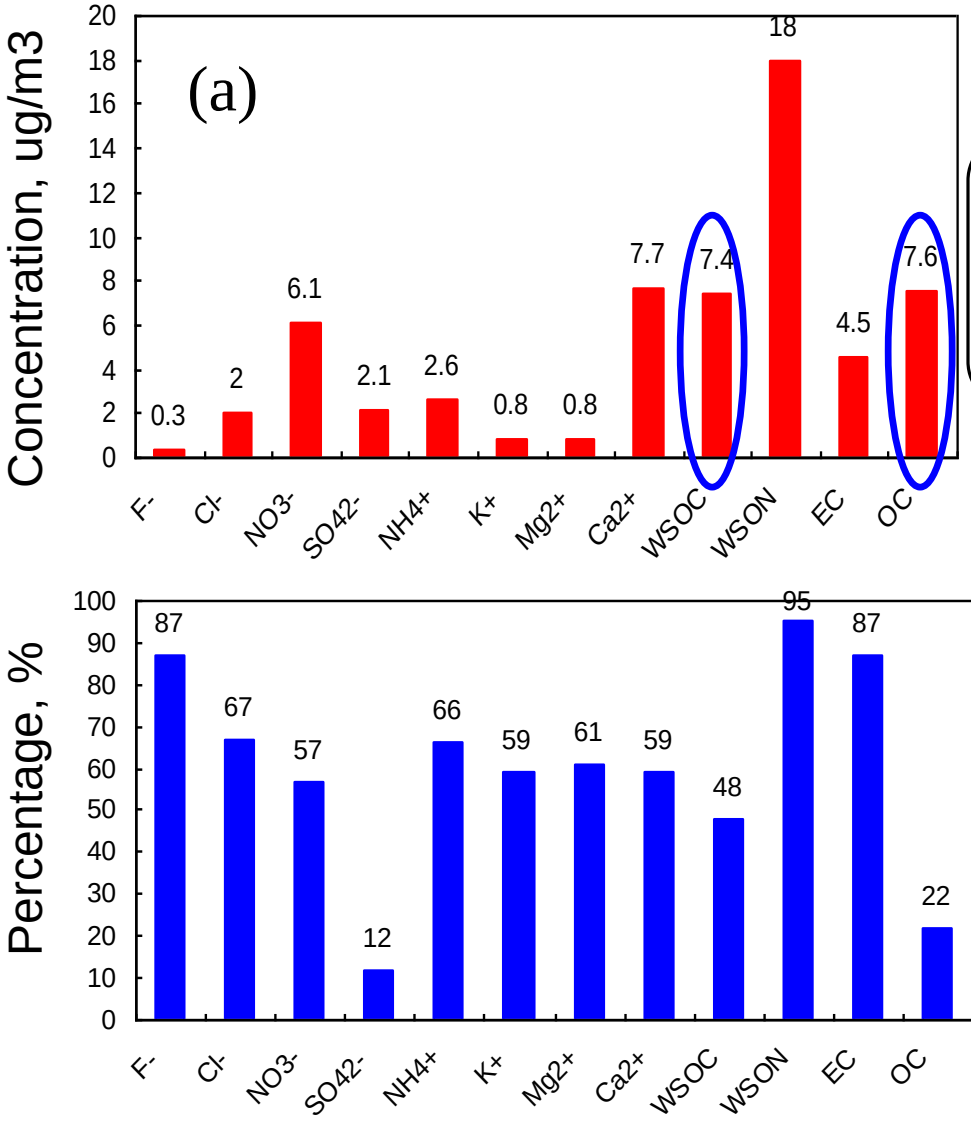
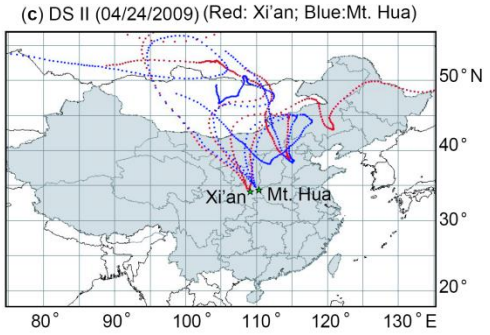


Fig. 8 Productions of pollutants from local sources in Xi'an



Reaction rates, $cm^3 molecules^{-1} s^{-1}$

$NO_2 + OH \rightarrow HNO_3$ $\quad k_{17} = 8(-12)$

$SO_2 + OH \rightarrow --- \rightarrow H_2SO_4$ $\quad k_{18} = 6(-13)$

"$SO_2 + H_2O_2 + CLOUD \rightarrow H_2SO_4$" $\quad k_{19} = 6(-16)$

Rodhe & Crutzen, Tellus 33 (1981)

Contribution from local sources due to heterogeneous reactions

NO_3^- 6.1ug/m^3, 57%

SO_4^{2-} 2.1ug/m^3, 12%

WSOC 7.4 ug/m^3, 48%

WSON 18 ug/m^3, 95%

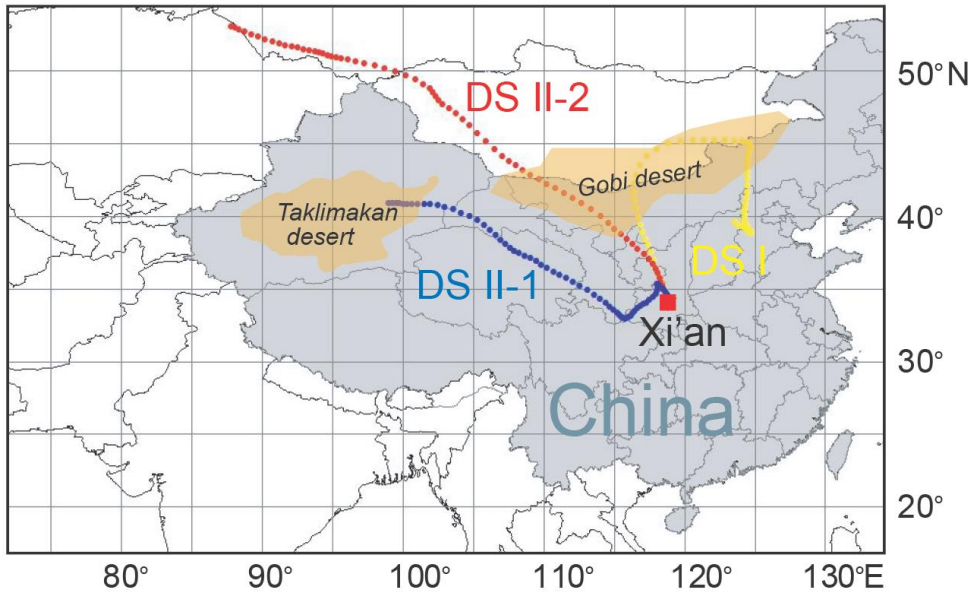
Contribution by long-range transport

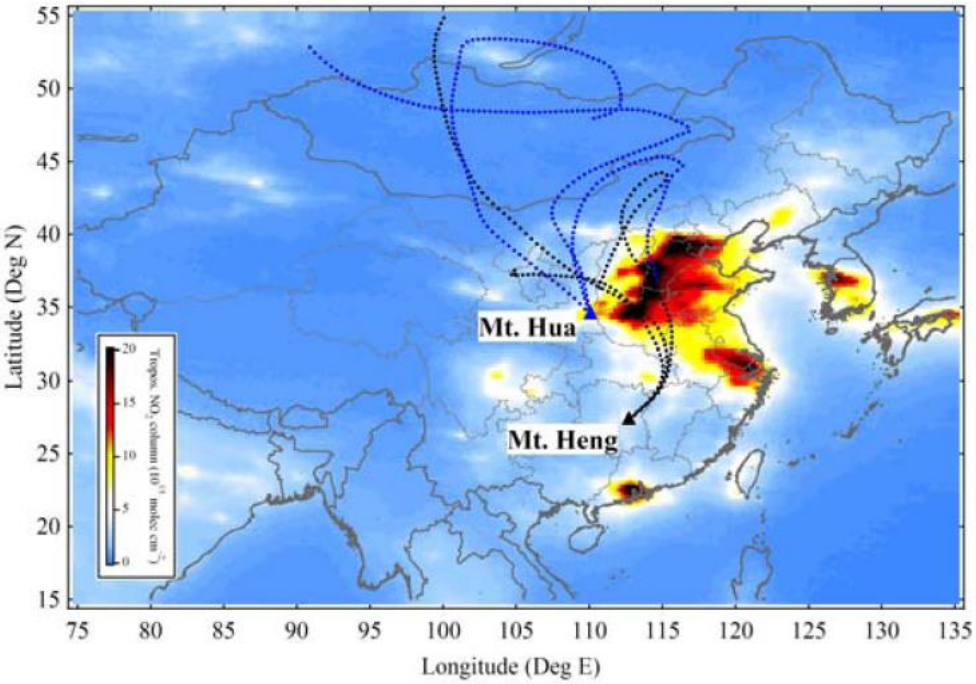
NO_3^- 4.6ug/m^3, 43%

SO_4^{2-} 15.4ug/m^3, 88%

WSOC 8.5 ug/m^3, 52%

WSON 2 ug/m^3, 5%





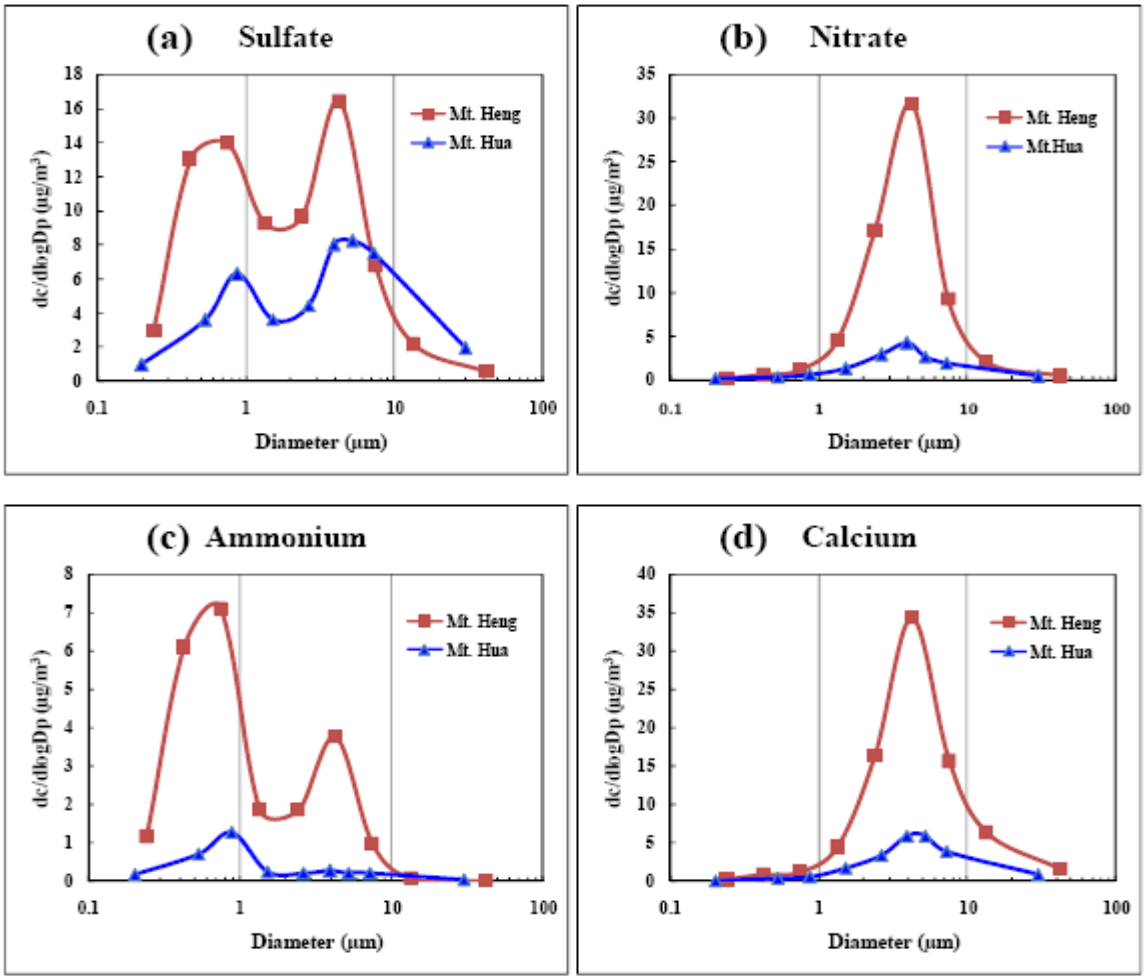
(Nie et al, Atmos. Chem. Phys. 2012)

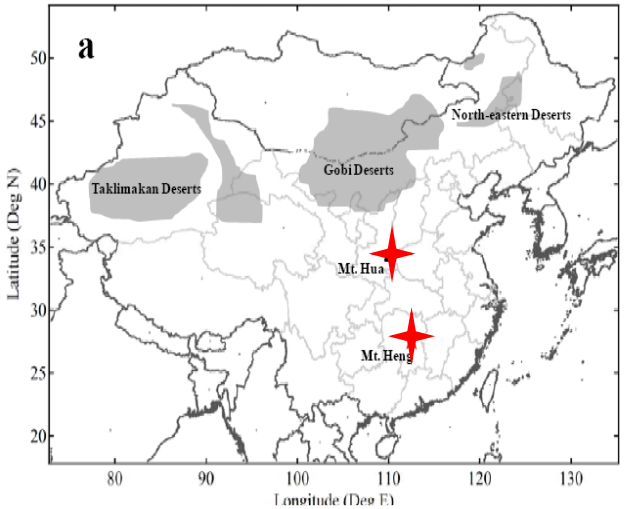
'SP-equivalent concentrations[a] of dicarboxylic acids, keto-carboxylic acids, ls, and other species during dust storm events in Xi'an, Central China

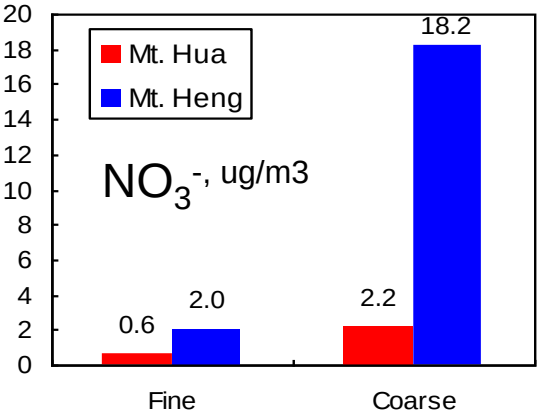
	DSI	DSII-1	DSII-2
I. Dicarboxylic acids, ng m^{-3}			
Oxalic (C_2)	1511	539	365
Malonic (C_3)	163	241	230
Succinic (C_4)	200	117	93
Glutaric (C_5)	50	19	19
IV. Inorganic ions, μg m^{-3}			
F^-	0.1	1	1
Cl^-	19	6	2
NO_3^-	22	9	4
SO_4^{2-}	32	28	17
NH_4^+	2	1	1
Na^+	6	26	32
K^+	3	1	1
Mg^{2+}	2	2	1
Ca^{2+}	11	27	9
Subtotal	97	100	67
V. Other species, μg m^{-3}			
WSOC[b]	38	46	38
WSIC[b]	27	28	13
Particle mass (PM)	682	1144	2406

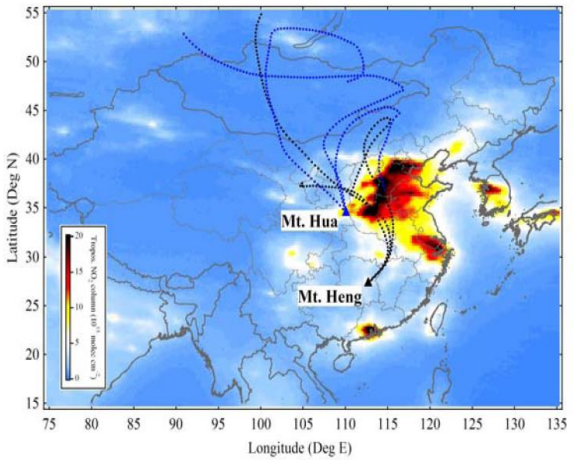
(Wang et al., Atmos. Environ., 2015)

Enhanced heterogeneous formation of NO_3^-





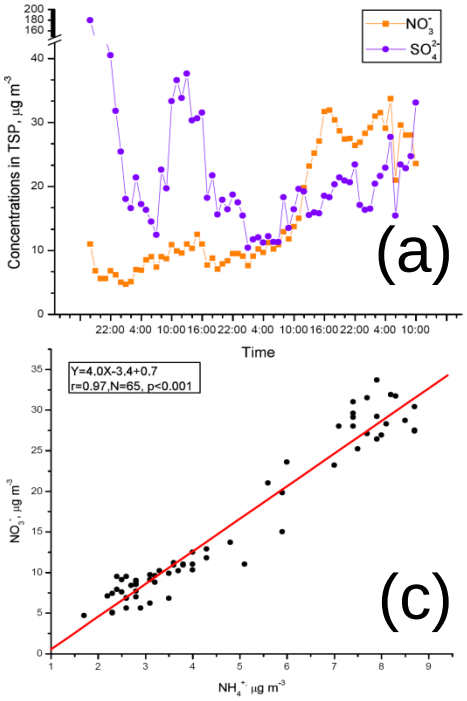


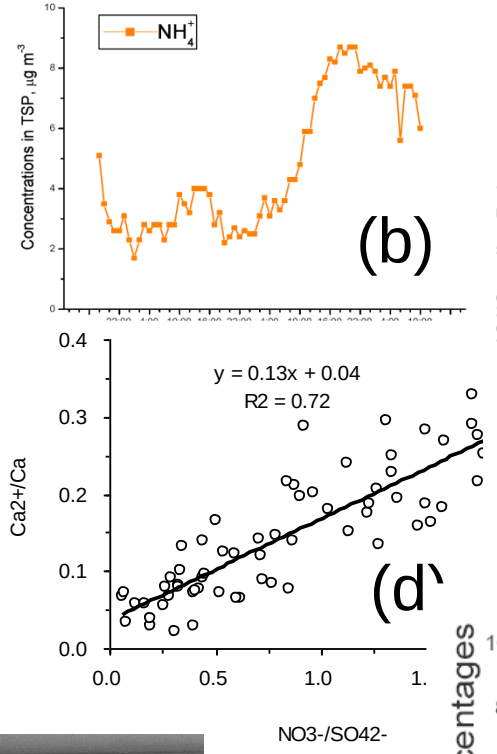


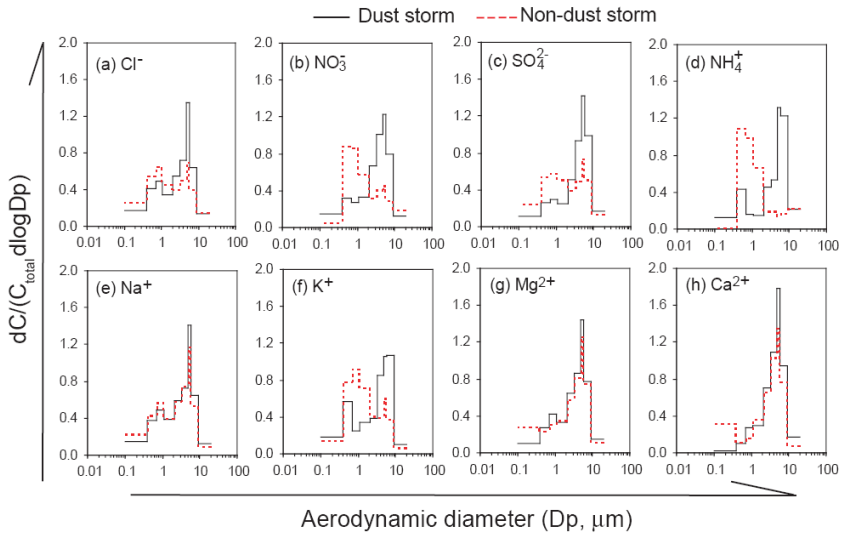
PM>1 $\frac{NO_3^-}{SO_4^{2-}}$ Mt. Hua 0.34
Mt.Heng 1.4

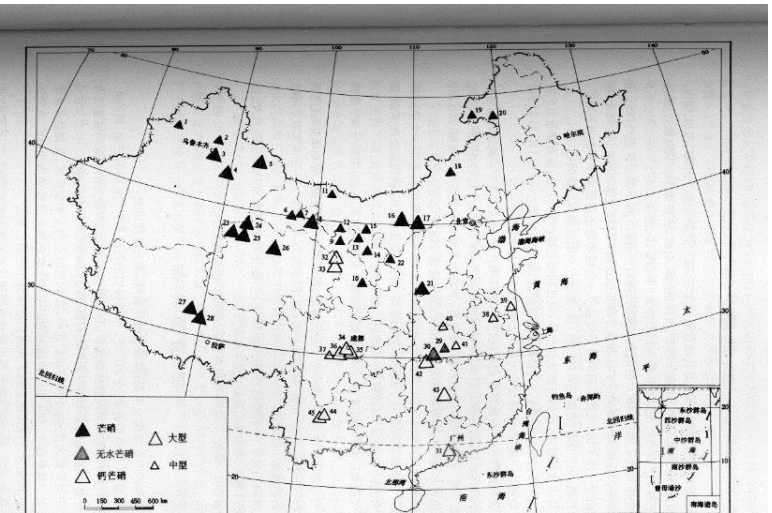
(Nie et al., Atmos. Chem. Phys., 2012)

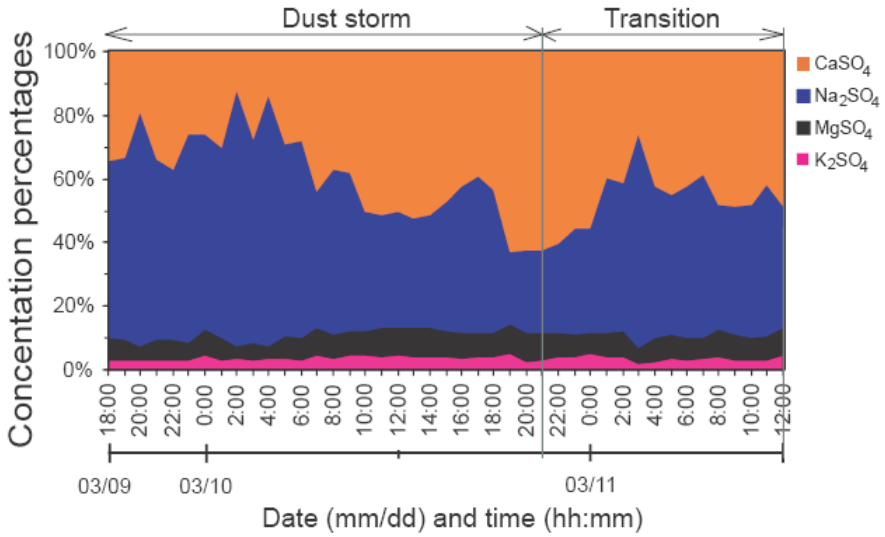
SO_4^{2-}, NO_3^- and NH_4^+ 小时浓度变化 （2013年西安沙尘暴期间, March 9-12, 2013 ）









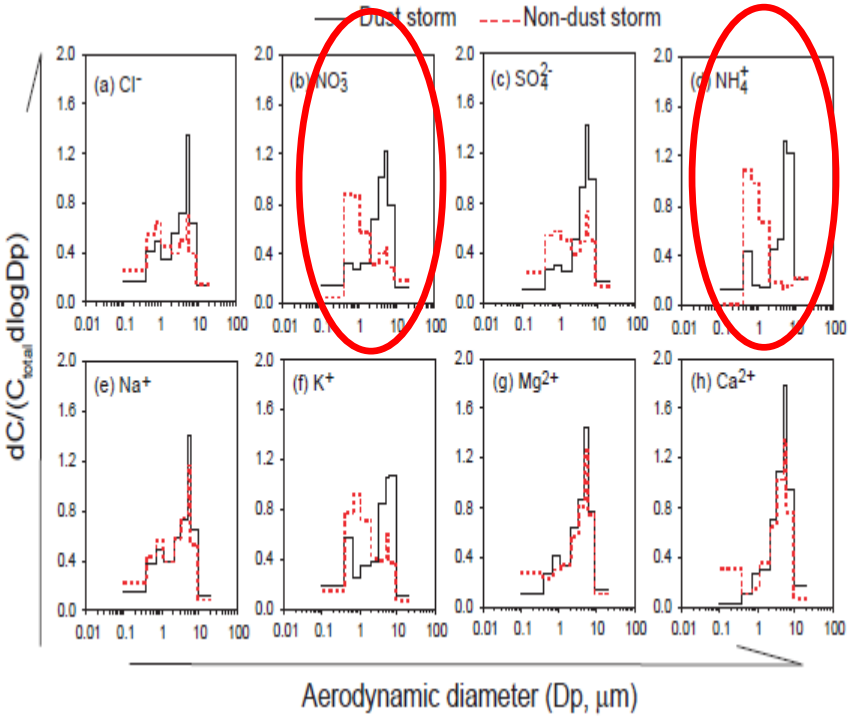


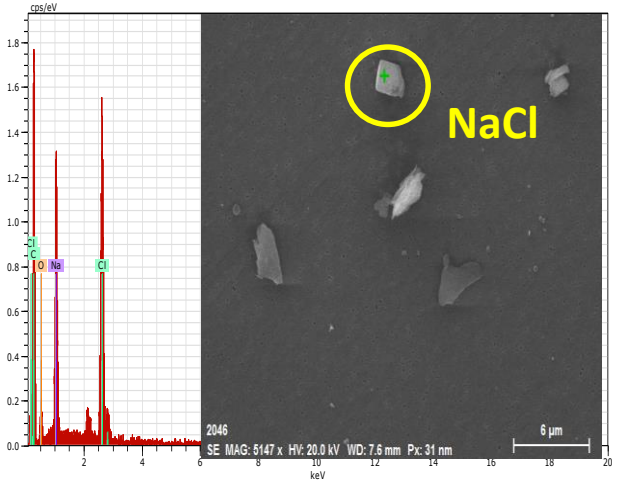
(Wang et al. 2014, Atmos. Chem. Phys.)

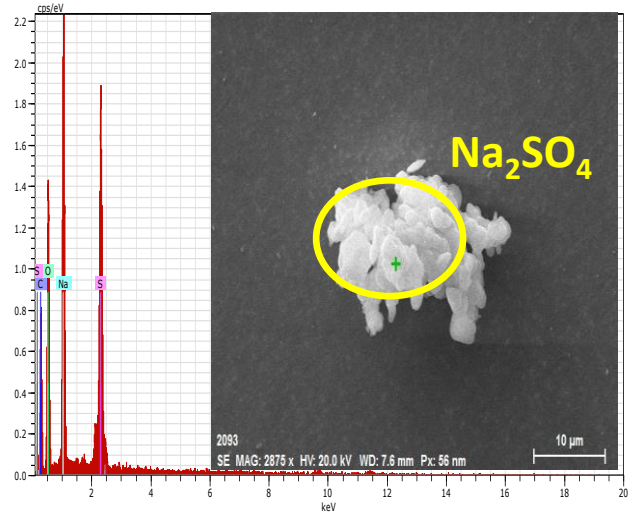
硝酸铵

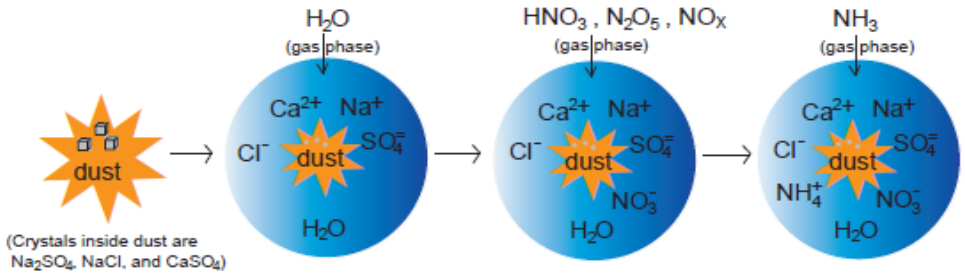
(Wang et al., ACP 2014, AE 2105,)

(Zhang, Wang, et al., Chem. Rev. 2015)



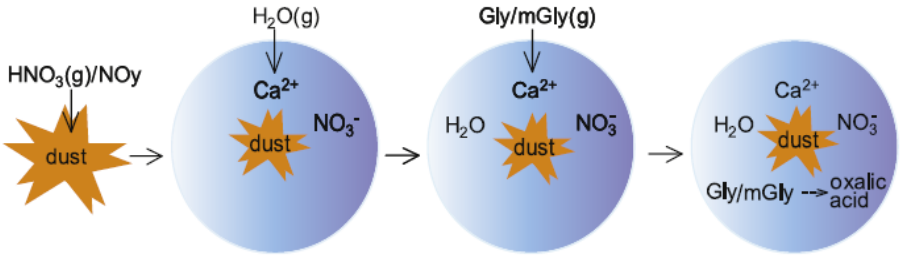


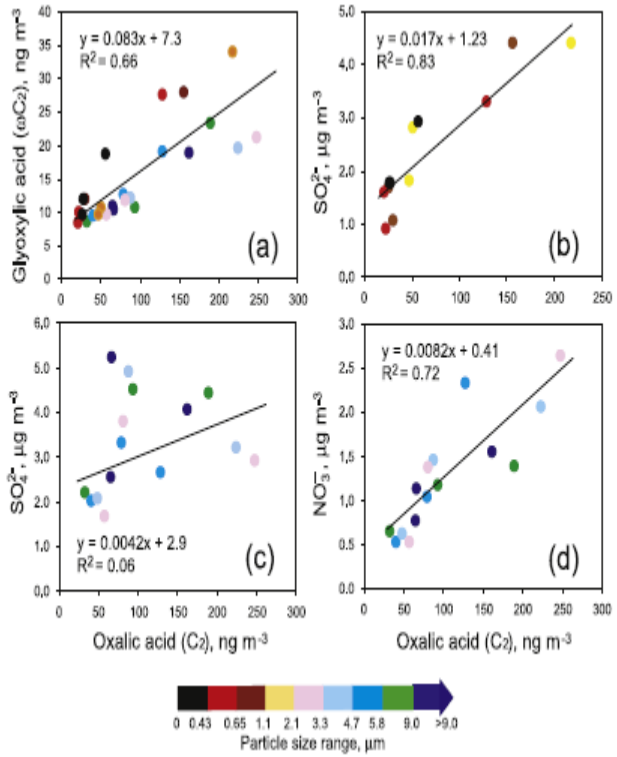


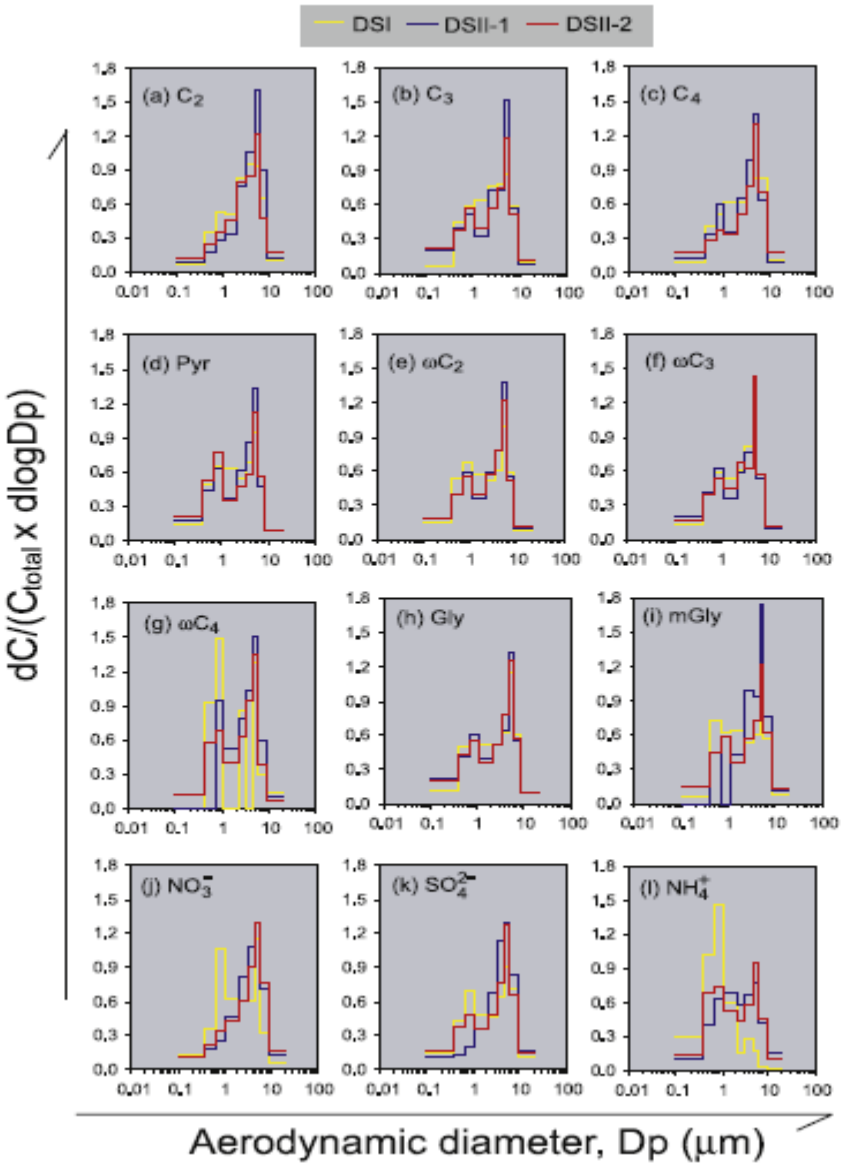


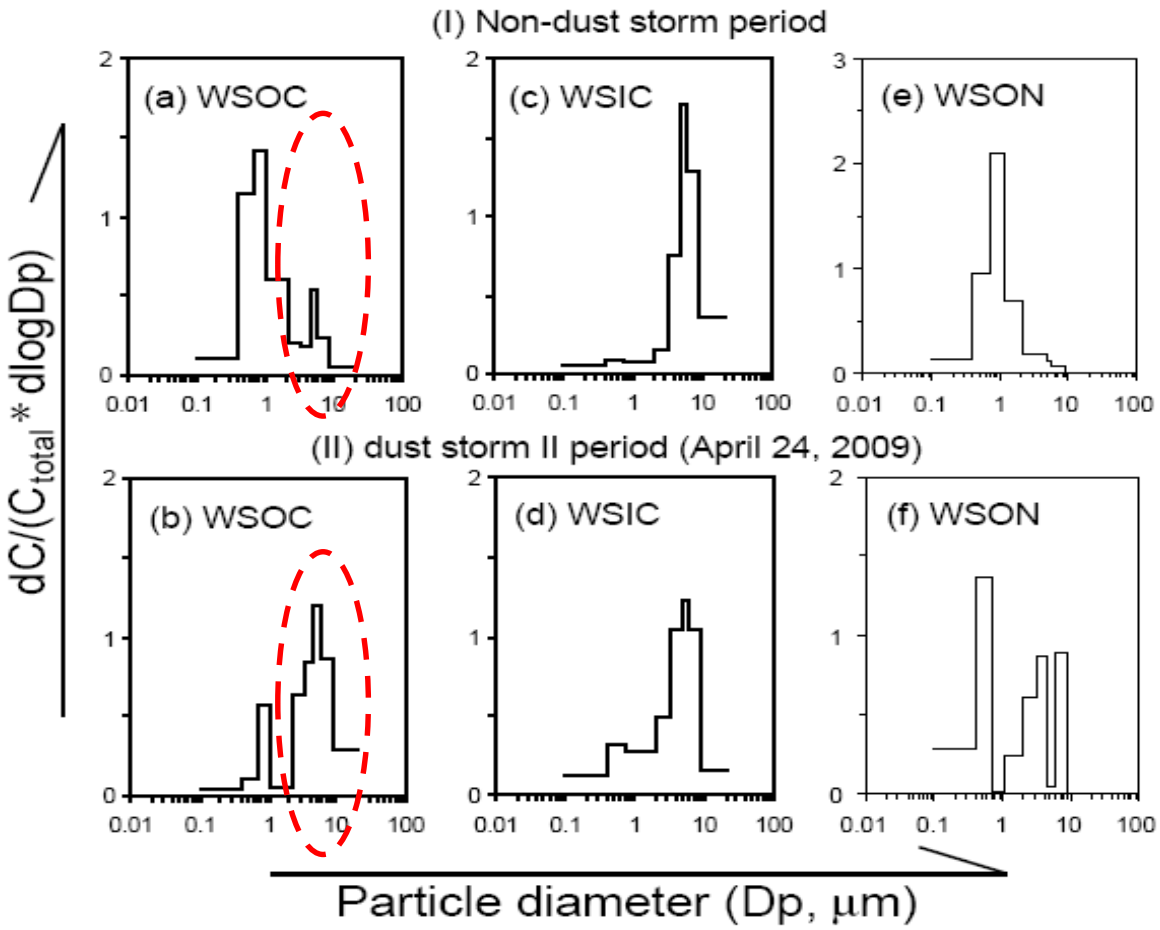
沙尘表面二次有机气溶胶

(Wang et al., ACP 2014, 2017; AE 2105,)
(Zhang, Wang, et al., Chem. Rev. 2015)









	F^-	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	WSOC	EC	OC
Concentrations of species from local sources, $\mu g\,m^{-3}$	0.3	2.0	6.1	2.1	2.6	0.8	0.8	7.7	7.4	4.5	7.6
Relative abundance to the total in PM_{10}, %	87	67	57	12	66	59	61	59	48	87	22

(Wang* et al., Atmos .Chem. Phys. 2013)