大气化学中有关同位素领域的若干问题

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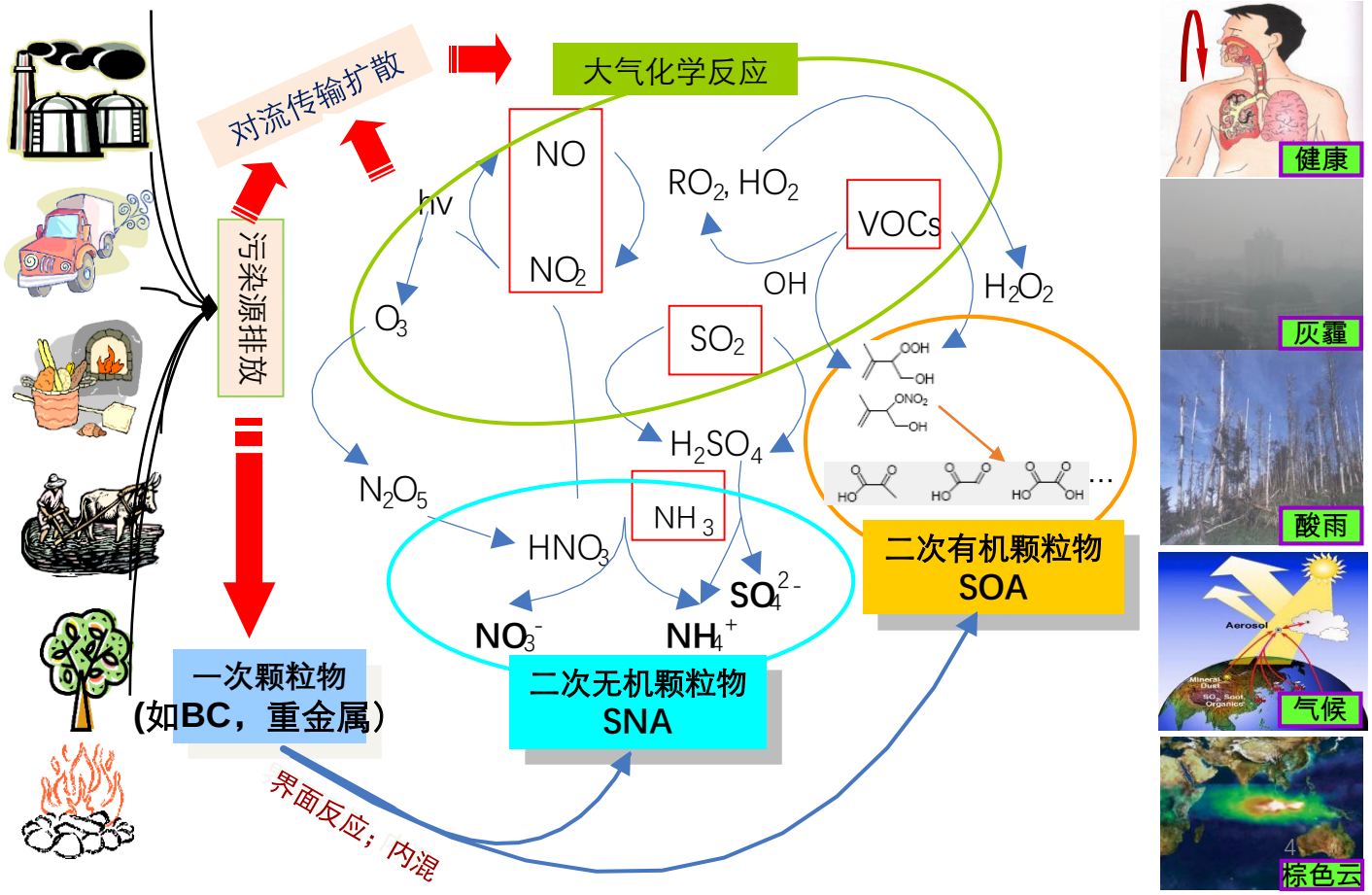
暨中国生态学学会陆生网栖生态专业委员会2017年学术年会

提纲

- 背景
- 主要技术问题
- 主要科学问题
- 发展方向
- 成果

大气化学：组分耦合关联，影响复杂多样



From Li Weijun

硫酸盐争议-化学

经典形成机制：

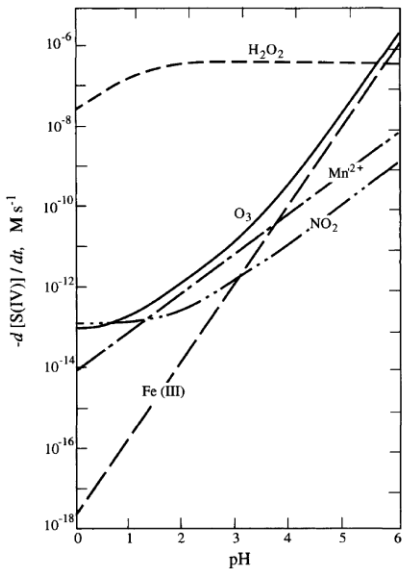


FIGURE 7.19 Comparison of aqueous-phase oxidation paths. The rate of conversion of S(IV) to S(VI) as a function of pH. Conditions assumed are $[SO_2(g)] = 5$ ppb; $[NO_2(g)] = 1$ ppb; $[H_2O_2(g)] = 1$ ppb; $[O_3(g)] = 50$ ppb; $[Fe(III)] = 0.3\,\mu M$; $[Mn(II)] = 0.03\,\mu M$.

oxidation rates in $\mu M\,h^{-1}$ for the different paths at 298 K for the conditions

$[SO_2(g)] = 5$ ppb	$[H_2O_2(g)] = 1$ ppb
$[NO_2(g)] = 1$ ppb	$[O_3(g)] = 50$ ppb
$[Fe(III)(aq)] = 0.3\,\mu M$	$[Mn(II)(aq)] = 0.03\,\mu M$

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

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

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

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

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

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

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

我国学者提出的NO_2氧化新机制：

$$2NH_3(g) + SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow$$

$$2NH_4^+(aq) + SO_4^{2-}(aq) + 2HONO(g)$$

Wang et al., PNAS, 2016.

硫酸盐争议-同位素

反应机制：运用O, S, N, Fe和Mn同位素技术，探讨硫酸盐形成机制

（1）那种反应通道占主导？各自贡献大下？

（2）是竞争关系还是协同关系？

（3）上述不同反应通道在我国不同区域的相对贡献？

追溯来源

（1）运用传统S, N同位素技术，研究燃煤电厂、钢铁厂以及民用燃煤、生物质燃烧、烟花燃放等释放的SO_2与NO_x的同位素特征及其对硫酸盐的贡献

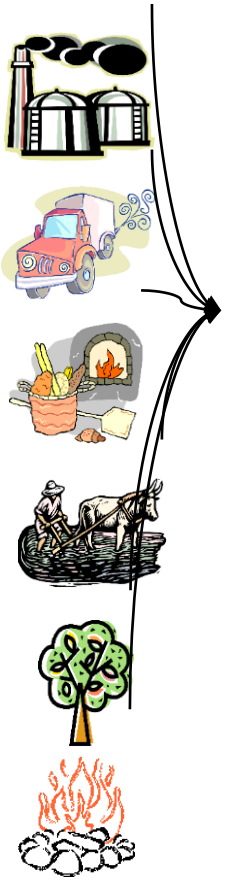
（2）运用非传统重金属Fe/Mn同位素技术，探讨人为排放（冶金与交通）与自然沙尘对大气雾霾期Fe/Mn的贡献大小，识别雾霾期气溶胶重金属来源

主要技术与科学问题

排放源

同位素质量分馏
同位素非质量分馏
传统与非传统同位素

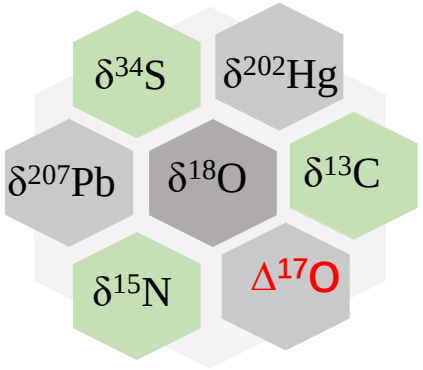
末端值



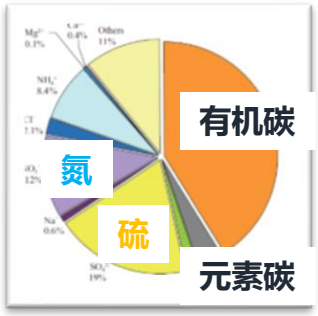
一次颗粒物
反应活性气体

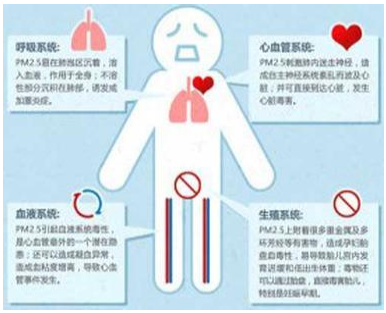
大气物理过程
大气化学过程

环境、气象因素



主要技术问题

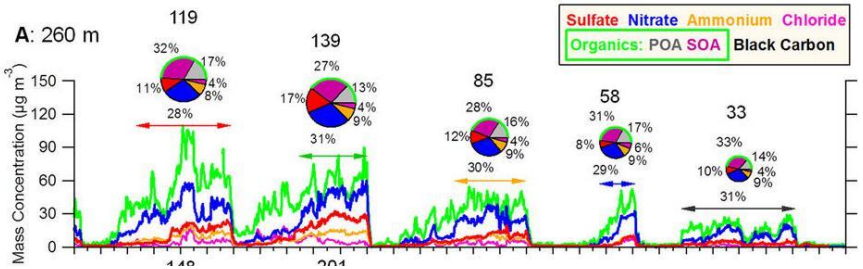




成分复杂！

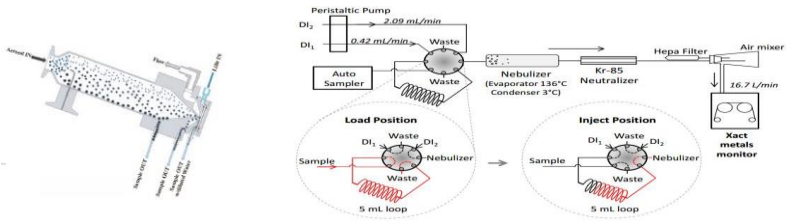
主要组分（OC, SO_4^{2-}, NO_3^-)形成雾霾
痕量组分（PAHs, Hg, Pb）危害健康

变化快速！



Sun et al., SR, 2016.

颗粒物污染的爆发性产生演化
需要同位素高时间分辨率监测



二次转化！

气体-颗粒物同步采样的必要性
采样方案的设计及检出限问题

主要技术问题

如何利用（多）同位素约束模型（如受体模型PMF或大气化学模型）的源解析结果

PMF模拟源贡献

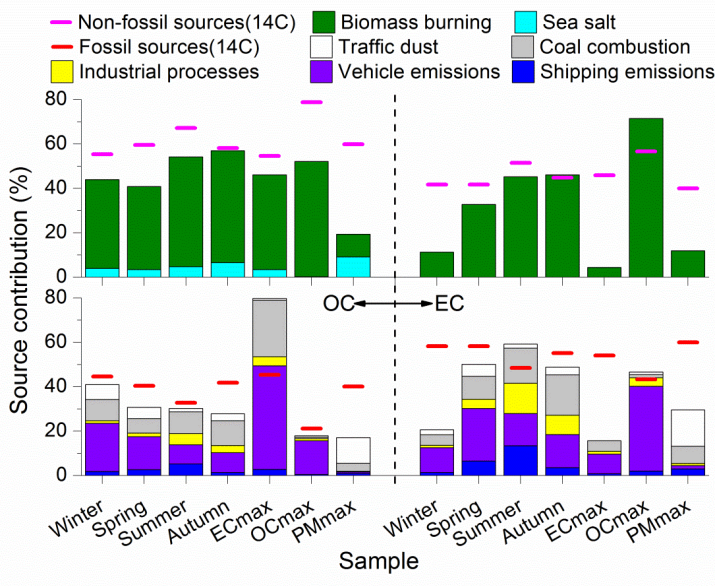
化石源贡献：∑(煤燃烧+交通源+工业过程+船舶排放)/监测浓度

生物源贡献：∑(生物质燃烧+海盐) /监测浓度

未考虑源：扬尘、交通尘

→ ^{14}C实测结果

(PMF-^{14}C值)>0➔代表错误源归类



PMF-^{14}C值(%)

	OC		EC	
	化石源	生物源	化石源	生物源
冬季	-10	-11	-40	-31
春季	-15	-18	-14	-9
夏季	-4	-13	9	-6
秋季	-17	-1	-10	1
EC_{max}	34	-8	-38	-42
OC_{max}	-4	-27	2	15
PM_{max}	-34	-41	-47	-28

主要科学问题1： SO_4^{2-}生成途经

ENVIRONMENTAL Science & Technology

Article

pubs.acs.org/est

Oxidation of Gas-Phase SO_2 on the Surfaces of Acidic Microdroplets: Implications for Sulfate and Sulfate Radical Anion Formation in the Atmospheric Liquid Phase

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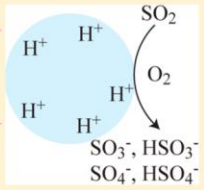
ABSTRACT: The oxidation of $SO_2(g)$ on the interfacial layers of microdroplet surfaces was investigated using a spray-chamber reactor coupled to an electrospray ionization mass spectrometer. Four major ions, HSO_3^-, $SO_3^{\bullet-}$, $SO_4^{\bullet-}$ and HSO_4^-, were observed as the $SO_2(g)/N_2(g)$ gas-mixture was passed through a suspended microdroplet flow, where the residence time in the dynamic reaction zone was limited to a few hundred microseconds. The relatively high signal intensities of $SO_3^{\bullet-}$, $SO_4^{\bullet-}$, and HSO_4^- compared to those of HSO_3^- as observed at pH < 3 without addition of oxidants other than oxygen suggests an efficient oxidation pathway via sulfite and sulfate radical anions on droplets possibly via the direct interfacial electron transfer from HSO_3^- to O_2. The concentrations of HSO_3^- in the aqueous aerosol as a function of pH were controlled by the deprotonation of hydrated sulfur dioxide, $SO_2{\cdot}H_2O$, which is also affected by the pH dependent uptake coefficient. When $H_2O_2(g)$ was introduced into the spray chamber simultaneously with $SO_2(g)$, HSO_3^- is rapidly oxidized to form bisulfate in the pH range of 3 to 5. Conversion to sulfate was less at pH < 3 due to relatively low HSO_3^- concentration caused by the fast interfacial reactions. The rapid oxidation of $SO_2(g)$ on the acidic microdroplets was estimated as



SCIENCE ADVANCES | RESEARCH ARTICLE

ENVIRONMENTAL SCIENCE

Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China

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Fine-particle pollution associated with winter haze threatens the health of more than 400 million people in the North China Plain. Sulfate is a major component of fine haze particles. Record sulfate concentrations of up to ~300 μg m^{-3} were observed during the January 2013 winter haze event in Beijing. State-of-the-art air quality models that rely on sulfate production mechanisms requiring photochemical oxidants cannot predict these high levels because of the weak photochemistry activity during haze events. We find that the missing source of sulfate and particulate matter can be explained by reactive nitrogen chemistry in aerosol water. The aerosol water serves as a reactor, where the alkaline aerosol components trap SO_2, which is oxidized by NO_2 to form sulfate, whereby high reaction rates are sustained by the high neutralizing capacity of the atmosphere in northern China. This mechanism is self-amplifying because higher aerosol mass concentration corresponds to higher aerosol water content, leading to faster sulfate production and more severe haze pollution.

INTRODUCTION

Persistent haze shrouding Beijing and the North China Plain (NCP) during cold winter periods threatens the health of ~400 million people living in a region of ~300,000 km^2. Characteristic features of the winter haze in ering the gas phase and cloud/fog chemistry, there is still a large gap between modeled and observed sulfate (Fig. 1C). Adding an apparent heterogeneous process with sulfate production rates that scale with aerosol surface area and RH can greatly improve model predictions

PNAS

CrossMark click for updates

Persistent sulfate formation from London Fog to Chinese haze

Gehui Wang[a,b,c,d,e,1], Renyi Zhang[c,d,f,2], Mario E. Gomez[c,d,g], Lingxiao Yang[c,h], Misti Levy Zamora[c], Min Hu[f], Yun Lin[c], Jianfei Peng[c,f], Song Guo[c,f], Jingjing Meng[a,b,i], Jianjun Li[a,b], Chunlei Cheng[a,b,i], Tafeng Hu[a,b], Yanqin Ren[a,b,i], Yuesi Wang[j], Jian Gao[k], Junji Cao[a,b], Zhisheng An[a,b,i], Weijian Zhou[a,b,m], Guohui Li[a,b], Jiayuan Wang[a,b,i], Pengfei Tian[c,n], Wilmarie Marrero-Ortiz[c,d], Jeremiah Secrest[c,d], Zhuofei Du[f], Jing Zheng[f], Dongjie Shang[f], Limin Zeng[f], Min Shao[f], Weigang Wang[c,o,p], Yao Huang[a,b,i], Yuan Wang[q], Yujiao Zhu[c,r], Yixin Li[c], Jiaxi Hu[c], Bowen Pan[c], Li Cai[c,s], Yuting Cheng[a,b,i], Yuemeng Ji[c,t], Fang Zhang[c,i], Daniel Rosenfeld[c,u], Peter S. Liss[c,v], Robert A. Duce[c], Charles E. Kolb[c,w], and Mario J. Molina[a,2]

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Contributed by Mario J. Molina, October 9, 2016 (sent for review July 8, 2016; reviewed by Zhanqing Li and Sasha Madronich)

Sulfate aerosols exert profound impacts on human and ecosystem ... and there have been high SO_2 emissions from combustion of coal

SCIENTIFIC REPORTS

OPEN

High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production

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Hongyu Guo[1], Rodney J. Weber[1] & Athanasios Nenes[1,2,3,4]

High levels of ammonia (NH_3) have been suggested to elevate ambient particle pH levels to near neutral acidity (pH = 7), a condition that promotes rapid SO_2 oxidation by NO_2 to form aerosol sulfate concentration consistent with "London fog" levels. This postulation is tested using aerosol data from representative sites around the world to conduct a thorough thermodynamic analysis of aerosol pH and its sensitivity to NH_3 levels. We find that particle pH, regardless of ammonia levels, is always acidic even for the unusually high NH_3 levels found in Beijing (pH = 4.5) and Xi'an (pH = 5), locations where sulfate production from NO_2 is proposed. Therefore, major sulfate oxidation through a NO_2-mediated pathway is not likely in China, or any other region of the world (e.g., US, Mediterranean) where the aerosol is consistently more acidic. The limited alkalinity from the carbonate buffer in dust and seasalt can provide the only likely set of conditions where NO_2-mediated oxidation of SO_2 outcompetes with other well-established pathways. The mildly acidic levels associated with excessive amounts of ammonia can promote high rates of SO_2 oxidation through transition metal chemistry, this may be an alternative important aerosol chemical contributor to the extreme pollution events.

我国高硫酸盐成因复杂-仍迫切需要

Discovery and measurement of an isotopically distinct source of sulfate in Earth's atmosphere

Gerardo Dominguez, Terri Jackson, Lauren Brothers, Burton Barnett, Bryan Nguyen, and Mark H. Thiemens*

Persistent sulfate formation from London Fog to Chinese haze

PNAS

September 2, 2008
vol. 105 no. 35
Masthead (PDF)
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November 29, 2016
vol. 113 no. 48
Masthead (PDF)
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多硫和三氧同位素为硫酸盐不同来源和生成途径提供定量的限制条件！

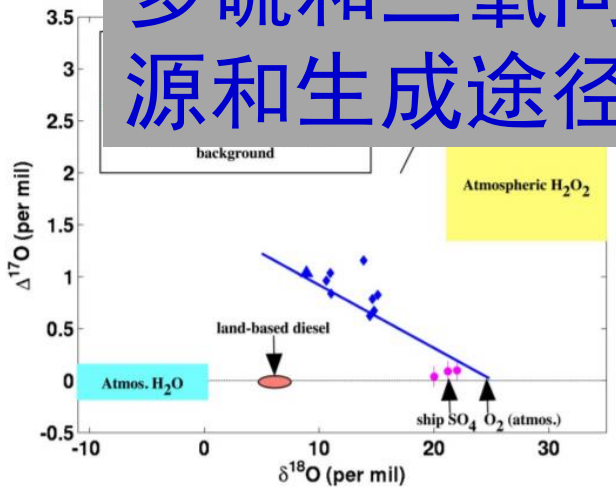
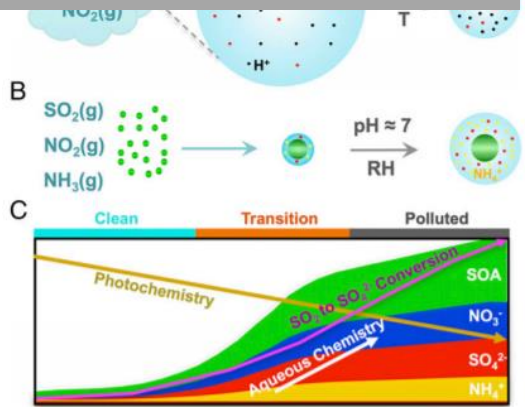
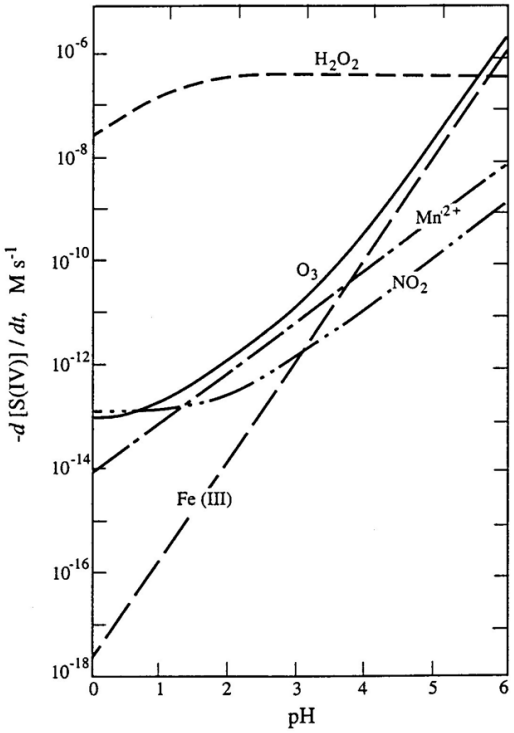


Fig. 2. A summary of potential sources of oxygen in aerosol sulfate found in the atmosphere.



主要科学问题1： SO_4^{2-}生成途经

由SO_2到SO_4^{2-}转化的途经如何真正区分



Atmospheric sulfate	Oxidants	Sulfate $\Delta^{17}O$
SO_2 oxidation (secondary)	O_3 (aq)	~ +10
	H_2O_2 (aq)	~ +0.9
	×OH, ×HO_2 (gas or aq)	~0
	O_2 + metal ions	~0
	organic peroxides	?
	NO_2	?
Primary sulfate	O_2	~0
Physical removal of SO_2 + surface oxidation	probably H_2O, O_2	~0

主要科学问题1： SO_4^{2-}生成途经

SO_4^{2-}的高维同位素提供了潜在解决方案

SO_4^{2-}

$\delta^{18}O$
$\Delta^{17}O$
$\delta^{34}S$
$\Delta^{33}S$
$\Delta^{36}S$

主要科学问题2： NO_3^-生成途经

土壤

$\delta^{15}N\text{-}NO_x$

燃煤

$\delta^{15}N\text{-}NO_x$

机动车

$\delta^{15}N\text{-}NO_x$

生物质燃烧

主要科学问题2： NO_3^-生成途经

$NO+O_3 \rightarrow NO_2+O_2$ (R_1)

$NO_2+h\nu \rightarrow NO+O$ (R_2)

$O+O_2 \rightarrow O_3$ (R_3)

$NO_2+OH \rightarrow HNO_3$ (R_4)

$NO_2+O_3 \rightarrow NO_3+O_2$ (R_5)

$NO_2+NO_3 \rightarrow N_2O_5$ (R_6)

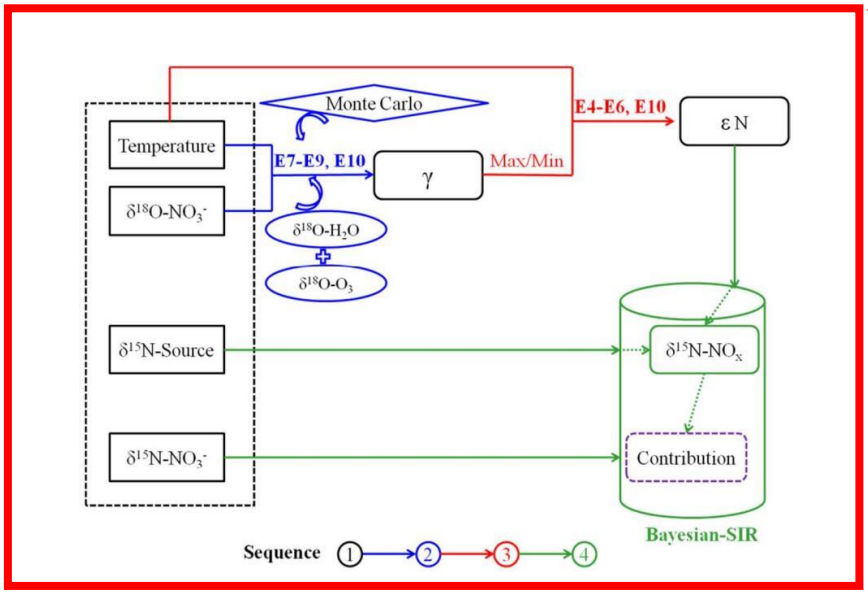
$N_2O_5+H_2O \rightarrow 2HNO_3$ (R_7)

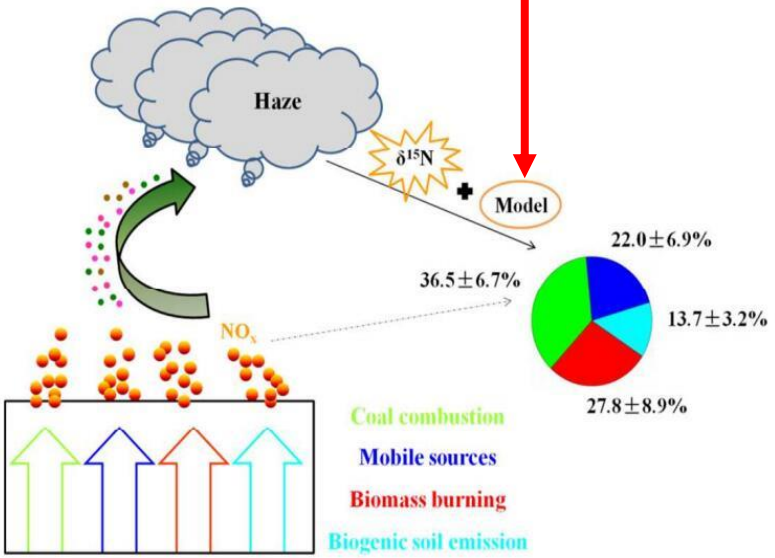
$$\varepsilon N = \gamma \times \varepsilon(\delta^{15}N-NO_3^-)_{OH} + (1-\gamma)\times\varepsilon(\delta^{15}N-NO_3^-)_{H_2O}$$
$$= \gamma \times \varepsilon(\delta^{15}N-HNO_3)_{OH} + (1-\gamma)\times\varepsilon(\delta^{15}N-HNO_3)_{H_2O}$$

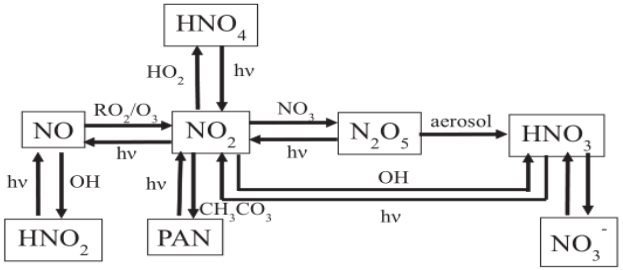
Walters, et al., GCA, 2015.

Walters, et al., GRL, 2016.

主要科学问题2： NO_3^-生成途经

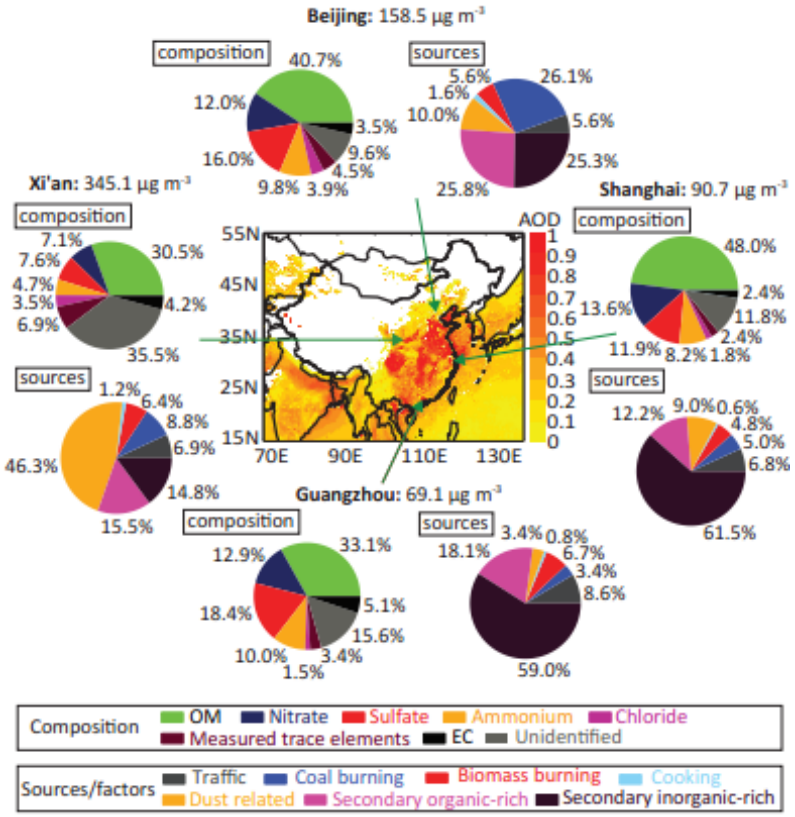






Zong et al., EST, 2017.

主要科学问题2： NO_3^-生成途经



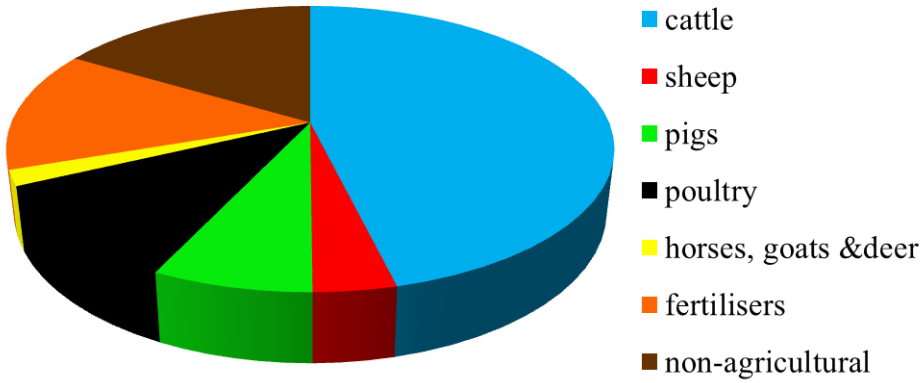
Huang et al., Nature, 2014.

生成途经在时空上存在大的差异

是否可以组织全国性的研究网络

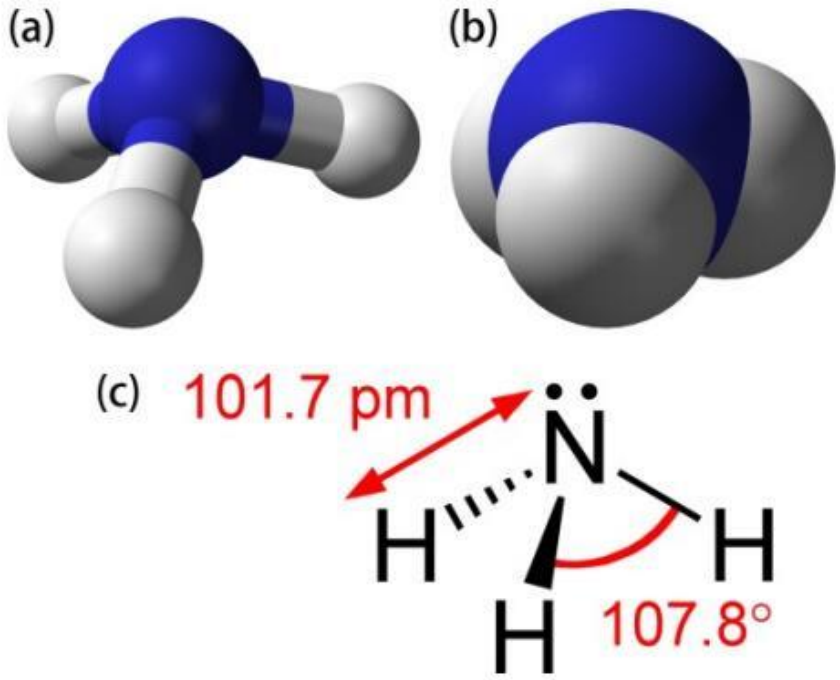
主要科学问题3： NH_3的来源

中国的非农业氨排放重要吗？



在英国，非农业源氨占到全国氨总排放量的15%

主要科学问题3： NH_3的来源



本地化源谱构建

除**N**外, **H**是否可以提供溯源信息

主要科学问题3： NH_3的来源

由NH_3到NH_4^+转化的同位素分馏如何定量

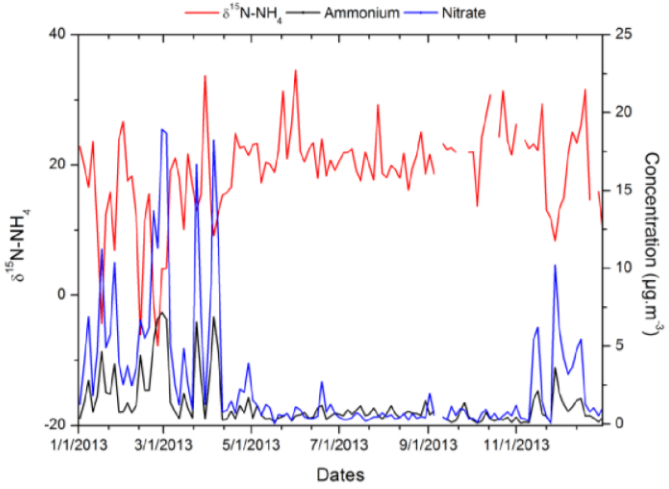
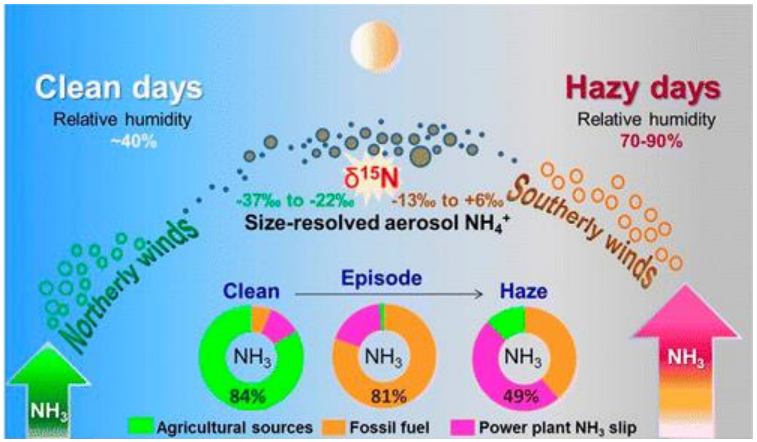


Figure 1. Temporal evolution of nitrate and ammonium concentrations, anti-correlated with $\delta^{15}N\text{-}NH_4$ in Grenoble (France).



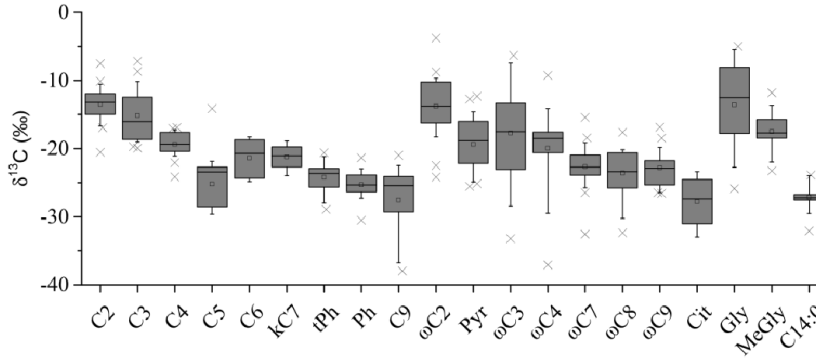
Pan et al., EST, 2016.

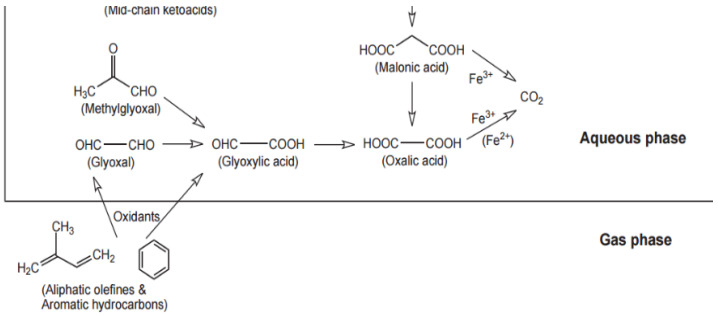
法国：高的NH_4^+，低的同位素，与农业活动有关

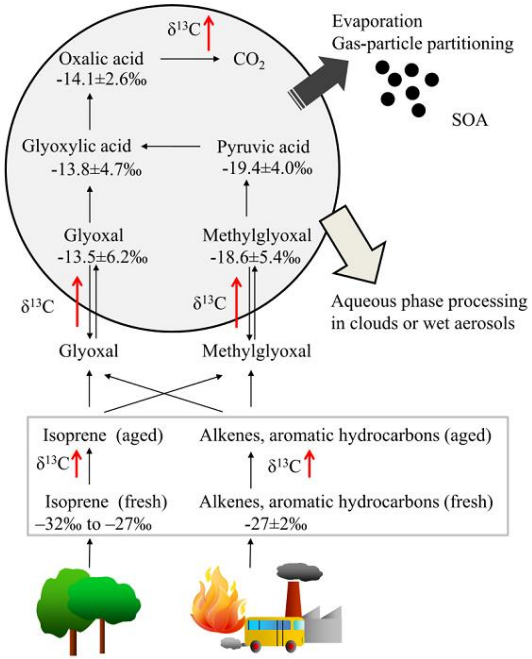
中国：高的NH_4^+，高的同位素，与化石燃料燃烧有关

主要科学问题4： 有机气溶胶的化繁为简

气固分配过程中同位素指示的潜在应用



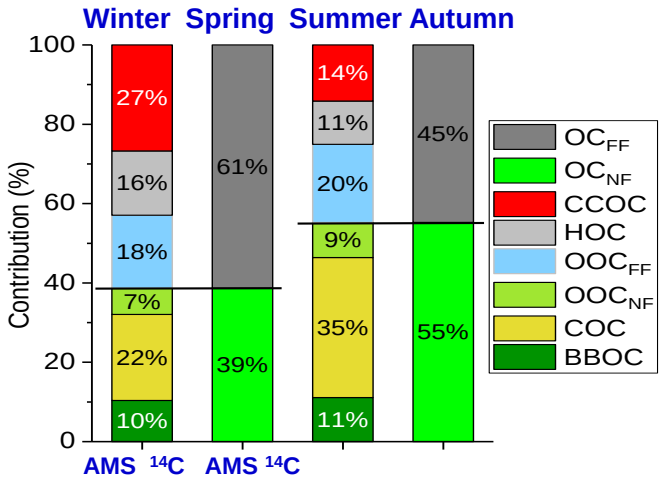


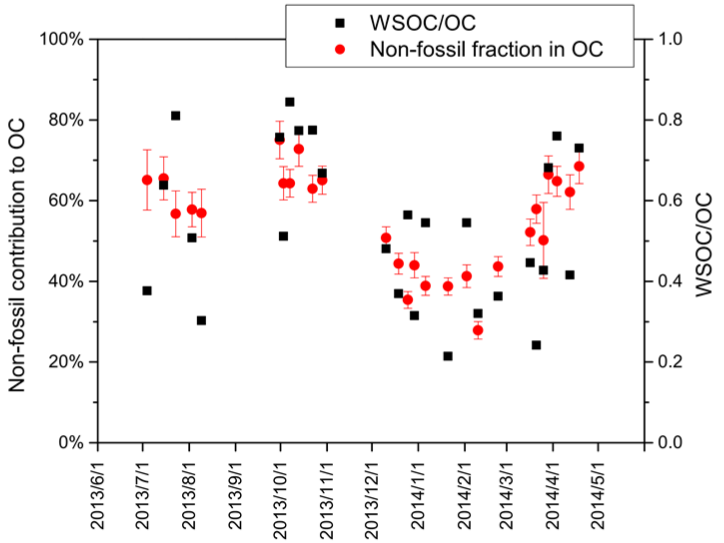


Zhang et al., JGR, 2016.

主要科学问题4： 有机气溶胶的化繁为简

单体同位素分析(CSIA)应用于复杂痕量有机物的必要性
是否仅关注有机气溶胶中的主要组分和PAHs总体即可?

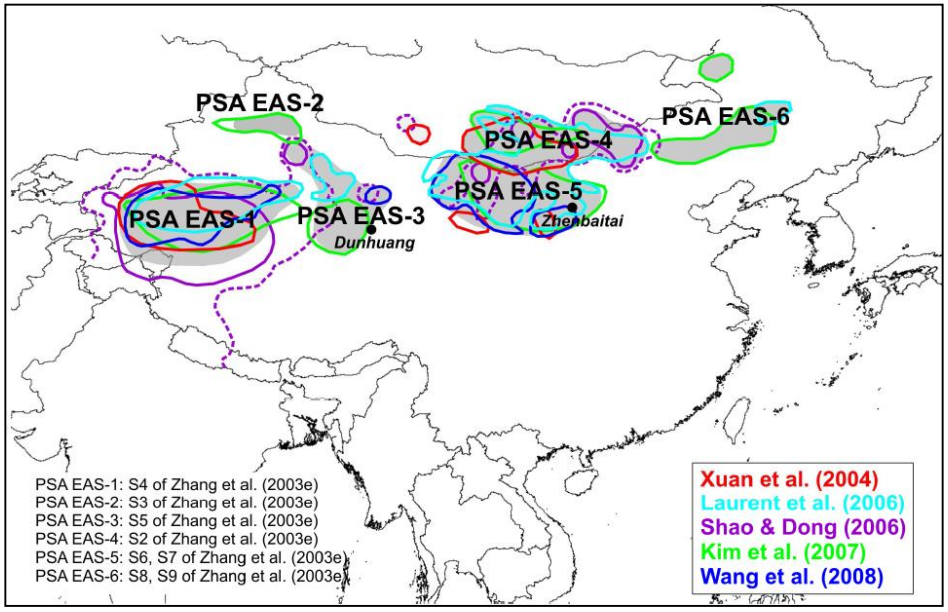




Zhang et al., EST, 2017.

主要科学问题5： 重金属

重金属问题由来已久，为什么现在强调其对雾霾形成作用



主要科学问题5： 重金属

重金属对灰霾起多大作用，作用的方式是什么

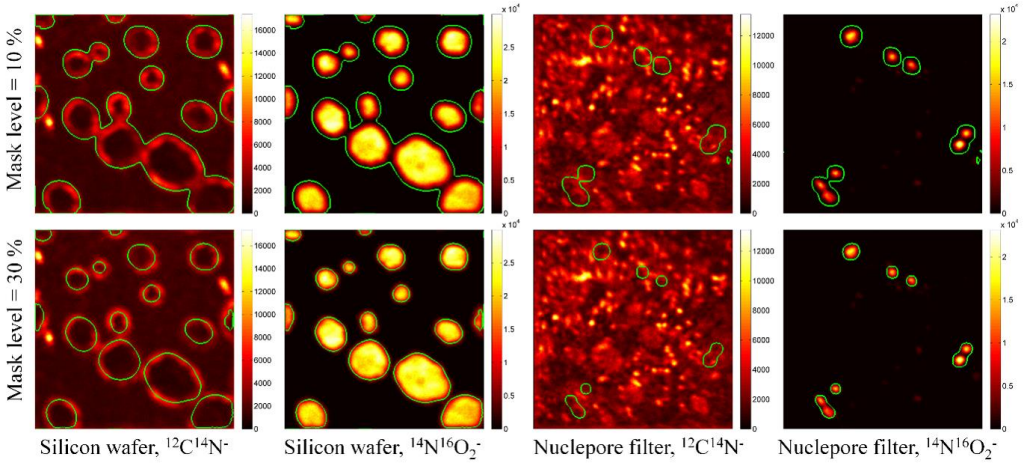
数浓度和质量浓度、粒径和化学组分加以区分

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

主要科学问题3： 重金属

NanoSIMS（纳米二次离子质谱技术）提供颗粒物的微观视野



Li et al., IJMS, 2015, in preparation.

未来发展方向

- 同位素源谱
- 非传统稳定同位素与传统同位素的联合
- 稳定同位素非质量分馏
- 宏观到微观与微观到宏观的结合
- 空间格局（大气化学过程受到具有特殊地域特色的气象条件影响）