2018 年度陈嘉庚科学奖专辑

陈嘉庚青年科学奖——地球科学奖获奖人

孙业乐

中国科学院大气物理研究所研究员, 中国科学院大学岗位教授. 2006 年获北京师范大学博士学位, 2006~2011 年先后在美国纽约州立大学、加州大学戴维斯分校和科罗拉多州立大学从事博士后研究. 目前主要从事大气气溶胶理化特性、来源和生成机制的研究, 共发表 SCI 论文 140 余篇.

相关成果名称: 中国大气复合污染的来源、形成机制及影响

孙业乐研究员系统全面地研究了以北京大城市为代表的中国大气复合污染理化特性、组分来源和形成机制. 揭示了二次粒子包括硫酸铵、硝酸铵和二次有机气溶胶、夏季光化学反应和冬季液相反应在重污染形成中的作用; 阐明了气象要素、二次粒子的快速生成及区域输送在细颗粒物快速增长中的关键作用; 定量解析了本地排放和区域输送对北京重污染形成的贡献, 并提出了一次和二次粒子演化机制概念框架模型; 率先开展了城市边界层理化结构观测和研究, 阐明了大气污染化学组分的垂直分布特征及与边界层气象的耦合作用; 定量评估了大气污染成分对不同源排放控制措施的响应机制, 支撑了我国大气污染的科学防治.

城市边界层理化结构与大气污染形成机制研究进展

孙业乐^{1,2,3}

1. 中国科学院大气物理研究所, 大气边界层物理和大气化学国家重点实验室, 北京 100029;

2. 中国科学院大学, 北京 100049;

3. 中国科学院区域大气环境研究卓越创新中心, 厦门 361021

E-mail: sunyele@mail.iap.ac.cn

2018-03-20 收稿, 2018-04-04 修回, 2018-04-08 接受, 2018-05-09 网络版发表

国家重点基础研究发展计划(2014CB447900)和国家自然科学基金(91744207)资助

摘要 自2013年《大气污染防治行动计划》实施以来,我国空气质量持续改善,但京津冀地区细颗粒物浓度仍远高于国家标准,秋冬季重污染天气仍时有发生.近些年,我国科学家在大气污染的立体探测、成因机制和来源解析、气溶胶和边界层相互作用等研究领域取得重要进展,进一步支撑了我国大气污染的科学防治和重污染天气的有效应对,然而我国当前大气污染仍面临诸多科学难题.本文简要概述了我国近些年在大气污染垂直探测方面的一些研究进展,特别是依托于北京325 m气象塔建设的城市边界层理化结构探测平台,详细论述了北京地区不同季节大气气溶胶化学组分的垂直分布特征及其与边界层物理要素的相互作用,同时基于2014年亚太经合组织峰会(APEC)和2015年纪念抗日战争胜利70周年阅兵前后的垂直观测,阐明了大气污染化学组分对区域源排放控制的响应机制.本文还针对大气细颗粒物中的二次无机组分(硝酸盐和硫酸盐)和二次有机气溶胶的生成机制以及极端霾事件的生消机制的最新研究进展进行了评述,并在最后对大气污染监测、二次无机气溶胶生成机制和有机气溶胶的分子组成和物理化学属性(相态、挥发性和氧化态等)等未来研究给出了一些建议.

关键词 大气边界层, 理化结构, 大气污染, 二次气溶胶, 生成机制

大气细颗粒物污染是我国当前面临的主要环境问题之一.细颗粒物(PM_{2.5})通过吸收和散射太阳光直接影响气候辐射强迫,也可以作为云凝结核影响云的形成和寿命^[1],细颗粒物还可对人体健康产生严重危害^[2].以高浓度细颗粒物为特征的重污染频频袭击我国华北地区,特别是秋冬季,重污染的形成过程极为迅速,往往呈现爆发性增长特征,数小时之内PM_{2.5}质量浓度可以从几十微克/立方米攀升至几百微克/立方米,造成五级及以上的严重污染^[3,4].为此,国务院2013年9月出台了《大气污染防治行动计划》,实施系列减排和大气污染防治措施,我国总体空气质量也因此得到持续改善.以北京为例,细颗粒物年

均浓度由2013年的89.5 $\mu\text{g m}^{-3}$ 降至2017年的58.0 $\mu\text{g m}^{-3}$,降幅高达35%.然而我国当前大气污染形势仍十分严峻,京津冀地区细颗粒物年均浓度仍远高于国家标准(年均值为35 $\mu\text{g m}^{-3}$),重污染天气仍时有发生,我国未来大气污染的科学防治和重污染天气的有效应对仍面临诸多挑战,特别是当前仍有诸多科学问题不明,如颗粒物爆发性增长过程中的关键大气化学和大气物理过程(如硫酸盐的生成机制),大气边界层理化结构及其与大气复合污染的相互作用等.为此,本文分析和总结了我国科学家近些年在城市边界层理化结构垂直探测、大气污染垂直分布特征及其与边界层相互作用和二次气溶胶生成机制等领域的

引用格式: 孙业乐. 城市边界层理化结构与大气污染形成机制研究进展. 科学通报, 2018, 63: 1375–1389

Sun Y L. Vertical structures of physical and chemical properties of urban boundary layer and formation mechanisms of atmospheric pollution (in Chinese). Chin Sci Bull, 2018, 63: 1375–1389, doi: 10.1360/N972018-00258

<https://engine.scichina.com/doi/10.1360/N972018-00258>

一些研究进展.

1 城市边界层理化结构探测

当前大气污染综合观测实验主要集中在地面,如珠江三角洲区域空气质量综合实验计划(PRIDE-PRD)^[5]、北京及周边地区空气质量综合观测实验(CARE-Beijing)^[6]和中国超大城市空气污染和人体健康研究(APHH-中国计划)等.我国大气污染往往呈现区域性分布特征^[7],而地面观测尤其是在大城市地区受局地排放影响较大,难以量化表征区域输送对城市空气质量的影响,同时给数值模式的验证评估带来了一定的不确定性.相反,大气污染垂直探测可以在一定程度上弥补地面观测的不足,并提供更为丰富的大气边界层物理和化学信息,如最新研究发现高层的黑碳气溶胶在抑制边界层高度发展和减弱湍流混合方面比低层黑碳更为重要^[8].在过去几十年期间,我国大气垂直观测技术取得了巨大进步^[9],目前主要包括激光雷达立体遥测、飞机航测、系留气球探测和气象塔观测等.飞机航测由于可以在短时间获得大范围区域内污染物的空间分布和垂直分布而被国内外广泛的应用^[10].如我国飞机航测发现不同气团中黑碳气溶胶的垂直分布显著不同,但在0.5~1 km之间受明显的区域输送影响^[11].Zhang等人^[12]通过分析2005和2006年春季有关粒子数谱的17次航测数据发现了3种典型的垂直分布,且与气象要素密切耦合.Chen等人^[13]则通过分析北京2007年夏季气态污染物的航测数据,揭示了山地平原风对大气污染物垂直分布的影响.上述飞机航测观测最低高度通常为约300~500 m,难以对重污染期间低层大气的垂直分布进行表征.激光雷达可以对多要素参数的垂直分布进行长期连续观测,如刘建国等人^[14]利用京津冀区域15部激光雷达同步观测结果发现北京重污染期间存在显著区域输送,主要来自西南通道(邢台-石家庄-琉璃河-北京)和东南通道(天津-永乐店-北京).然而,激光雷达数据无法表征大气污染物在输送过程中复杂的物理和化学变化,且存在一定的“探测盲区”(≈<300 m).系留气球也可对地面至1 km之间的大气污染进行探测^[15,16],但目前大部分都集中在郊区,难以在市区开展观测实验.

气象塔是研究城市边界层理化结构的重要平台,特别是靠近城市中心的北京325 m气象塔^[17]和天津255 m气象塔^[18],可以深入研究城市地区大气污染物

的垂直分布和边界层要素的耦合作用机制.北京325 m气象塔目前拥有15层气象要素(温度、湿度、风速和风向)、7层湍流、CO₂/H₂O^[19]和3层辐射长期连续观测,但独缺大气化学观测平台.为了更好地发挥大气物理和大气化学学科交叉研究优势,Sun等人^[20]于2013年在气象塔260 m高度处建设了大气化学观测平台,首次实现了地面和260 m高度处颗粒物化学组分(有机物、硫酸盐、硝酸盐、铵盐和氯化物)的同步、实时连续在线观测.Wang等人^[21]进一步发展了气象塔吊舱系统,实现了重污染天气下地面至260 m高度之间的大气污染多要素如消光系数、气态前体物、成分等的垂直精细观测.经过近些年的发展,中国科学院大气物理研究所大气边界层物理和大气化学国家重点实验室目前已经建立了基于北京325 m气象塔的完备的城市边界层理化结构探测平台(图1),平台涵盖气溶胶化学组分、光学特性、气态前体物和粒子数浓度谱等大气污染特性观测和边界层物理要素观测.

2 城市大气边界层湍流输送垂直分布特征

基于北京325 m气象塔,我国科学家针对北京城市下垫面大气边界层湍流输送垂直分布特征开展了大量的研究^[22~25].徐祥德等人^[24]早在2001年便开展了北京城市和郊区大气边界层的对比观测试验,揭示了城、郊大气边界层结构热力和动力参数的差异.研究发现,城市地区不稳定层结条件下无量纲三维风速标准差 σ_i/u_* ($i=u,v,w$)与 z'/L 之间关系在47和120 m高度上符合1/3次方率,无量纲温度方差符合-1/3次方率^[25].刘阳等人^[22]进一步分析了北京气象塔2008~2012年期间3层高度(47, 140和280 m)的湍流观测资料,讨论了城市下垫面湍流输送特征,结果发现无量纲三维风速、温度、CO₂和水汽浓度标准差在自由对流条件下符合±1/3次方率,近中性条件除温度外均维持常数不变,稳定条件下被动标量(CO₂和水汽)不随稳定度变化,三维风速和温度随稳定度增大.Guo等人^[26]分析了北京冬春季不同污染条件下城市大气边界层湍流输送效率、统计特征量、湍流谱,以及温湿湍流的非相似性等.结果发现重霾污染天气下的城市边界层常表现出显著的热力层结,即白天的对流不稳定和夜间的极端稳定,风速矢量的几何参数和湍流输送效率也随之呈现出更明显的日变化.大气边界层垂直结构可显著影响大气污染物的垂直分布^[27~29].如丁国安^[27]研究发现静稳天气以及污

图1 基于北京 325 m 气象塔的城市边界层理化结构探测平台

Figure 1 Beijing 325 m meteorological tower research platform on vertical measurements of chemical and physical properties of urban boundary layer

染日气溶胶垂直分布特征为渐缓递减型, 而冷空气过境及清洁日气溶胶垂直分布则表现为快速递减型, 该结果佐证了大气热力、动力结构以及湍流强度对气溶胶垂直分布的影响. 2014年, 国家自然科学基金委员会第十一届大气边界层研究战略研讨会^[30]明确指出我国未来大气边界层研究的第一优先领域便是重污染天气下的大气边界层结构特征及大气污染与边界层的相互作用, 特别是大气污染如何通过影响大气边界层内能量平衡和湍流动能进而改变大气稳定度的反馈机制.

3 城市大气气溶胶化学组分垂直分布特征

基于城市边界层理化结构探测平台, 孙业乐等人先后开展了多次垂直观测, 深入研究了北京城市地区化学组分的垂直分布特征, 阐明了大气污染成分对区域源排放控制的响应机制^[20,21,31~35]. 如2013年北京冬季垂直观测研究发现, 地面和高层颗粒物化学组分存在显著差异^[20]. 地面有机气溶胶平均贡献 PM_{10} 的65%, 显著高于260 m, 而硝酸盐则反之. 进

一步对气溶胶来源进行比对分析发现, 二次无机(SIA, 包括硝酸盐, 硫酸盐和铵盐)和二次有机气溶胶(SOA)在地面和260 m高度处变化趋势较为一致, 而一次气溶胶则呈现明显的垂直差异. 该结果直接佐证了本地排放和区域输送对城市不同高度处一次和二次气溶胶的影响差异, 同时也突显了地面和城市高层同步观测的重要性和必要性. Han等人^[36]通过分析天津255 m气象塔所采集的4个不同高度处 PM_{10} 样品的化学组分也发现地面一次排放源的影响随高度的增加而降低, 而受区域输送影响更大的二次组分贡献量则随高度的增加而升高. 基于2014年亚太经合组织峰会(APEC)期间的北京325 m气象塔垂直观测, Chen等人^[31]和Xu等人^[37]等发现地面和城市高层化学组分对区域源排放控制的不同响应机制. 研究发现管控前和期间颗粒物化学组分占比在260 m高度处无明显变化, 说明区域减排导致的前体物, 如 SO_2 、 NO_x 和挥发性有机物(VOCs)的同步降低对气溶胶总体化学组成并无显著影响. 相反, 地面化学组分在管控前和期间发生明显变化, 其中二次气溶胶组

分在管控期间的浓度降低高达56%~74%，但一次有机气溶胶组分(生物质燃烧、机动车和餐饮)仅降低16%~27%^[37]，说明区域减排的同时需要同步加强局地排放管控。Sun等人^[33]进一步综合比对和分析地面和气象塔垂直观测数据，揭示了区域源排放控制与

北京“APEC蓝”之间的内在关联机制(图2)。结果发现“APEC蓝”的实现主要得益于二次颗粒物组分的大幅降低，而二次粒子的降低又主要由于气态前体物的区域协同减排导致其生成和增长速率大幅降低约2~3倍所致。根据气溶胶化学组分在不同管控阶段的增

图2 APEC前和期间气溶胶化学组成变化。(a), (b) 260 m和地面的化学组分时间序列及5次污染事件的平均化学组成; (c), (d) 化学组分在260 m与地面的浓度比及每次污染事件各化学组分与平均值之间的差异^[33]

Figure 2 Aerosol particle composition before and during APEC. (a), (b) Time series of aerosol species, and average chemical composition of PM₁ for five episodes at 260 m and ground site, respectively. (c), (d) Concentration ratio of each aerosol species between 260 m and the ground site, and average difference in aerosol concentration for each episode compared to the average of all five episodes at 260 m and the ground site^[33]

长差异, Sun等人^[33]进一步构建了一次和二次气溶胶在有减排和无减排两种情境下的演化概念框架模型, 并对本地源和区域输送源进行了定量估算。结果显示, 区域输送在重污染形成过程中可贡献51%~65%。上述研究结果为《大气污染防治行动》中的京津冀区域协同减排和联防联控提供了直接科学依据。对比区域协同减排, Jiang等人^[38]和Zhang等人^[39]发现北京春节期间人为活动的降低导致一次污染物(如机动车、餐饮、燃煤等)显著降低, 但二次气溶胶浓度无明显变化甚至略有增加。一次和二次气溶胶对局地减排的不同响应机制导致春节期间细颗粒物污染水平与春节前后相当甚至略有增加, 因此, 局地污染减排对改善重污染期间的空气质量效果相对有限, 该结果也进一步佐证了重污染期间更应注重区域协同减排, 而且减排应在重污染形成之前, 通过降低前体物浓度抑制二次粒子的生成, 进而改善空气质量。

Zhao等人^[34]和Du等人^[32]随后对2015年纪念抗日战争胜利70周年阅兵前后气象塔垂直观测数据进行分析, 结果同样发现区域源排放控制可导致地面和260 m高度处颗粒物化学组分浓度降低42%~74%, 而化学组成同样发生明显变化, 其中二次无机组分贡献量从48%~52%显著降低至38%~39%显著降低, 有机物贡献量则相应增加。上述研究结果说明区域源排放控制在不同气象条件下对化学组成的影响有显著差异。Zhao等人^[34]进一步研究还发现区域源排放控制可有效降低区域性的、高度老化的二次有机气溶胶(MO-OOA), 但对局地生成的新鲜二次有机气溶胶(LO-OOA)影响较小。事实上, 通过对管控前后粒子数谱的垂直观测和比对发现, 区域源排放控制可有效降低积聚模态粒子, 进而降低总颗粒物浓度, 但对爱根模态粒子影响相对有限。相反, 空气质量改善和颗粒物浓度降低导致的凝结汇减小反而促进了新粒子事件的发生和超细粒子数浓度的增加^[32]。

4 城市边界层理化结构和成霾相互作用

重污染的形成与大气边界层密切相关。诸多研究表明气溶胶和边界层之间的正反馈作用机制是重污染形成的重要因素之一^[41~44], 特别是高浓度的细颗粒物可以大幅减少到达地表的短波辐射、感热和潜热通量, 冷却地表表面, 进而抑制边界层的发展, 降低边界层高度, 导致污染程度进一步加剧^[45]。与此相比, 边界层顶的吸收性气溶胶(如黑碳)则可以加热

上层大气, 增加边界层的逆温和抑制大气污染物的垂直扩散^[44,45]。如Ding等人^[44]研究了黑碳气溶胶在重污染发生、发展过程中与边界层要素的双向机制, 发现大气黑碳气溶胶的“穹顶效应(dome effect)”是加剧超大城市空气污染的重要因素。Zhong等人^[43]研究也发现, 气溶胶和边界层的反馈机制甚至能够解释我国华北地区PM_{2.5}爆发性增长的70%。然而上述研究大部分基于数值模式, 为更好地研究气溶胶和边界层的相互作用及其对重污染形成和演化的影响, 当前仍亟需深入开展大气污染和边界层要素的垂直观测。

基于北京325 m气象塔城市边界层理化结构探测平台, Sun等人^[20,21,31,33,34]开展了多次垂直观测实验, 深入表征了低层大气中大气污染物的垂直结构与边界层物理要素的相互作用, 如边界层高度、逆温层、相对湿度、风速和湍流等, 阐明了3种典型的边界层气象垂直结构与化学组分垂直差异的耦合机制, 包括重污染演化过程中的逆温层导致二次粒子上高下低, 重污染清除过程中的气象要素垂直差异导致地面和高层污染物清除时间差及山地平原风与北京颗粒物污染之间的相互作用(图3)。边界层气象要素(如温度和湿度)和气态前体物的垂直差异还可直接影响二次气溶胶生成速率和浓度的垂直分布。如城市高层的低温和夜间残留层高浓度O₃可促进硝酸盐的气-粒转化和N₂O₅的非均相反应生成^[46], 导致260 m高度处硝酸盐浓度高于地面^[20]。Wang等人^[21]随后分析了北京两次重污染事件过程中地面至260 m的污染和气象要素的垂直分布特征和演化规律。结果发现, 冬季重污染过程中大气污染垂直分布呈现4类典型特征(图4), 即垂直分布均匀型, 主要发生在混合层高度较高、大气混合充分的中午和下午; 下高上低递减型; 上高下低型, 主要由高空污染物输送造成的, 同时伴随着明显的风向变化; 下高上低骤降型, 通常伴随着强的逆温和不同气团之间的交汇叠加。该研究显示污染物的垂直分布与混合层高度和气象要素密切相关, 但主要受混合层高度、垂直逆温、高空输送和本地排放四个因子的影响。冬季重污染期间混合层高度低至约100~150 m, 而当前雷达遥测受盲区的影响难以对其进行准确反演^[47]。同时, 研究也发现当前化学传输模式对低层大气重污染的垂直分布模拟也存在较大偏差, 进而影响对气溶胶气候辐射强迫效应的评估。

图3 2013年冬季3次污染过程中气象要素(风向、风速、温度和湿度)的垂直分布演化以及地面和260 m测得的硫酸盐和硝酸盐的时间序列^[40]
Figure 3 Evolution of vertical profiles of meteorological variables (WS, WD, T, and RH) and mass concentrations of sulfate and nitrate at 260 m and at the ground level during three episodes^[40]

5 大气二次气溶胶生成机制

大气颗粒物(或大气气溶胶)的组成和来源异常复杂,既包含无机组分,又含有成百上千种有机化合物,既有一次直接排放(如生物质燃烧、燃煤、机动车和餐饮等),又有二次生成如硫酸盐、硝酸盐和VOCs氧化生成的二次有机气溶胶^[48]。气溶胶还在大气中不断老化,进而改变其吸湿性、挥发性和光学特性等重要性质^[49]。我国科学家在过去十几年期间针对大气气溶胶的组成、来源和形成机制开展了大量的研究^[50~59]。如研究发现,重污染期间气溶胶组成发生显著变化,其中二次无机组分如硫酸盐、硝酸盐和铵盐的贡献量显著增加,有机物则相应降低^[60~63],但二次有机气溶胶与二次无机气溶胶的贡献量仍然相当^[50]。二次气溶胶是重污染期间细颗粒物的主要成分,因此厘清二次气溶胶的生成机制是阐明重霾成因的关键。目前,二次无机组分硝酸盐和硫酸盐的主要生成机制相对较为清楚。如硝酸盐主要来自白天 NO_2 和OH自由基的光化学生成和夜间的 N_2O_5 非均

相水解反应^[64]。最新研究发现北京市区由于 N_2O_5 非均相摄取导致的夜间硝酸盐生成量高达 $24\sim 85\ \mu\text{g}\ \text{m}^{-3}$,与 HNO_3 的气粒分配生成量相当甚至更高^[65]。然而,受不同因素的影响如气溶胶化学组成、表面积和液态水等, N_2O_5 在不同环境下的摄取系数仍存在极大变率^[66~68],这也成为影响数值模式能否准确模拟硝酸盐的一个关键。由于硝酸盐通常以半挥发性硝酸铵形态存在,其大气浓度水平还受气粒平衡的显著影响。如Sun等人^[51]发现硝酸盐在冬季白天的浓度逐渐增加,主要来自光化学生成,而在夏季白天浓度则迅速降低,主要由于温度升高导致的挥发性损失^[69]。气粒分配平衡机制还可以影响硝酸盐的垂直分布,如一些垂直观测发现大气边界层内硝酸盐的贡献随高度的增加而增加^[20,70]。

大气中硫酸盐的主要生成机制已被广泛地认知^[64]。在全球范围内,云中液相反应平均贡献约80%,而其余20%则主要来自气相OH自由基氧化生成^[71]。硫酸盐的液相反应机制主要包括 H_2O_2 、 O_3 和过

图4 四类典型垂直廓线: b_{ext} 、 $b_{\text{ext}}/\text{NO}_2$ 、温度(T)、相对湿度(RH)和风速(WS)。最右列图给出了廓线3、25、33和11测得的风向。“U”和“D”分别代指吊舱系统上行和下行测得的垂直廓线。为清楚起见,一些垂直廓线进行了平移,标记为“+”或“-”^[21]

Figure 4 Four selected types of vertical profiles of b_{ext} , $b_{\text{ext}}/\text{NO}_2$, T , RH , and WS . The rightmost panels show four selected vertical profiles of WD , i.e., V3, V25, V33, and V11. “U” in the legend indicates the “up” experiments, the others are the “down” ones. For clarity, some vertical profiles were offset by certain values as indicated by “+” or “-” in the figure^[21]

渡金属的催化氧化等,各个机制的重要性则取决于溶液的酸碱性(pH),而 NO_2 氧化 SO_2 生成硫酸盐机制则通常认为并不重要。我国冬季重污染的一个典型特征是硫酸盐的快速增加,且硫氧化率(SOR ,硫酸盐中的硫在总硫中的摩尔比)随相对湿度或气溶胶液态水含量的增加成指数上升趋势^[51,62,72],说明非均相化学反应是重霾期间硫酸盐的重要生成途径^[73]。基于不同化学组分在不同相对湿度下的相关性,Sun等人^[74]估算冬季重污染期间液相反应对硫酸盐的贡献可能高达~50%。由于当前数值模式对重污染期间硫酸盐的峰值模拟通常存在严重低估,近些年科学家针对 NO_2 氧化 SO_2 机制进行了大量研究,特别是在中国富 NH_3 环境下^[40,75-79],然而该机制目前仍存在一定的争议,尤其是气溶胶表面酸碱性问题。Wang等人^[77]研究认为在高湿和富 NH_3 条件下,气溶胶表面 pH 接近7, NO_2 氧化 SO_2 是硫酸盐重要的生成途径。Cheng等人^[78]基于热力学平衡模型ISORROPIA-II^[80]估算的气溶胶表面 pH 在5.4~6.2之间,同样认为该途

径是我国冬季硫酸盐的重要生成机制。然而Guo等人^[79]和Liu等人^[40]等研究认为即使在富 NH_3 条件下,气溶胶表面仍呈酸性, pH 在4.2~4.5之间,Song等人^[81]对不同热力学平衡模型估算气溶胶酸碱性进行了综合评估,结果也显示我国华北地区气溶胶表面总体呈酸性(pH 4~5)。该研究结果说明,即使在富 NH_3 的华北地区, NO_2 氧化 SO_2 可能并非硫酸盐的重要生成途径。Li等人^[82]随后在实验室对该机制进行了研究,结果发现在 NaHSO_3 液相表面(pH 3~6), NO_2 并不能直接氧化 S(IV) 生成硫酸盐,反而生成了硝酸盐和 HONO ,据此推测, HONO/NO_2 氧化 S(IV) 可能是更为重要的生成途径。由于目前仍无法对气溶胶表面酸碱性进行实际测定,硫酸盐生成机制仍需进一步研究。随着我国大气污染防治的推进,我国二氧化硫浓度持续降低,而氮氧化物仍维持在一个较高水平,由此导致硝酸盐逐渐超越硫酸盐,成为大气细颗粒物中最重要的二次无机气溶胶^[69,83,84]。因此未来我国大气污染防治需要进一步加强 NO_x 的控制排放。

相对于二次无机气溶胶,有机气溶胶生成机制更为复杂,特别是大气中含有成百上千种有机化合物,而其分子量、官能团、吸水性等性质千差万别^[85].通常认为,大气中挥发性有机物的白天光化学氧化(如OH自由基氧化)和夜间NO₃自由基氧化是二次有机气溶胶的重要生成来源^[86~88],而最近研究发现液相反应也可能是SOA的重要生成机制^[89~92].当前二次气溶胶生成机制的研究主要依托于实验室烟雾箱模拟,定量研究不同的前体物在不同环境下的生成产率、产物及其生成机制^[93].随着质谱技术的快速发展^[94,95],我们对SOA的分子组成和生成机制的认识也有了大幅度的提高.如Ehn等人^[96]发现一些挥发性有机物如单萜烯的氧化过程可以生成大量的极低挥发性有机气体(ELVOCs),可以直接在气溶胶表面凝结生成SOA,并在新粒子生成的最初阶段起关键作用^[97].再比如实验室研究发现柴油车排放的VOCs氧化生成的SOA远高于汽油车^[98],但该结果却与外场观测结论相反^[99],造成该差异的原因目前仍然不是很清晰,但可能与研究的地区和实验室较短的氧化时间有关^[100].与实验室研究不同,外场观测更侧重二次气溶胶的总体生成机制变化.在实际大气中,

SOA的生成和老化过程主要包含官能团化(functionalization)、碎裂化(fragmentation)和聚合化(oligomerization)3种机制^[49,95,101],并对有机气溶胶的挥发性、氧化态和反应活性产生不同的影响.最新研究发现,SOA在生成的初期阶段以官能团化为主,而在随后的增长阶段则以碎裂化为主^[95],而一些挥发性有机物(如羰基化合物和酚类化合物等)的液相反应则可以生成一定量的聚合物^[92,102].最近外场观测也发现了液相反应生成SOA的大量证据^[90,103,104],如生物质燃烧排放的有机物的液相反应在欧洲地区可贡献总有机气溶胶的4%~20%^[103].我们最新的研究也发现光化学反应和液相反应对二次有机气溶胶生成和转化有明显的不同,其中光化学反应显著影响新鲜二次有机气溶胶的生成,而液相反应则主要影响低挥发性二次有机气溶胶的生成及其氧化态^[105].

二次气溶胶在重污染形成中起关键作用. Sun等人^[3,62]利用气溶胶质谱研究了典型重霾污染的生消机制,阐明了气象要素、二次粒子的快速增长及区域输送在成霾中的关键作用.研究显示,冬季极端重污染事件生消过程通常包括4个阶段(图5):气象条件转变导致的污染物协同快速增长过程;二次气溶胶持续、

图5 2015年极端霾生消过程中化学组分的变化. 饼图给出了每个阶段的平均化学组成, 方框内容则具体描述了每个事件特征^[3]

Figure 5 Evolution of aerosol chemical composition during the severe haze episode in 2015. Pie charts show the average chemical composition for each episode and the description of each episode is also included in the figure^[3]

稳定演化过程;高湿过程及硫酸盐的快速生成和干、冷的北-西北风的清除过程.气象和化学的协同影响机制是霾生消的关键,其中静稳气象(低风速、高湿和逆温)是极端霾事件形成的外因,而高污染排放和二次气溶胶的快速生成则是内因,特别是二次粒子在重污染期间的占比可高达70%.研究还进一步揭示了北京极端霾事件生消过程中的快速变化(爆发性增长和快速消除)主要由区域输送和南北气团交替所致,而硫酸盐的快速转化也起了一定作用.基于颗粒物化学组分的爆发性增长估算的区域输送贡献高达53%~70%,佐证了重污染天气下仍存在较强的区域输送^[106].

6 总结与展望

近5年,我国大气污染防治取得了重要成果,空气质量持续改善.与此同时,我国科学家在大气污染的立体探测、来源和成因机制解析、气溶胶和边界层相互作用等重要领域取得系列研究进展,进一步支撑了我国大气污染的科学防治和重污染天气的有效应对,然而我国当前大气污染仍面临诸多科学难题,也亟需开展进一步研究.

(1) 大气气溶胶化学成分的长期连续观测和垂直观测.随着大气污染防治行动计划的持续推进,我国大气污染排放未来会发生剧烈变化,细颗粒浓度持续降低,但臭氧污染问题日益突出^[107].当前数值模式虽然能够较好地模拟PM_{2.5}总浓度,但对准确模拟化学组分仍存在较大不确定性.开展长期连续观测不仅可以阐明大气污染成分对气态前体物(SO₂, NO_x和VOCs等)变化的响应机制,还可以为改进数值模式提供重要的数据验证.同时,大气污染的立体综合探测仍需进一步加强,尤其是大气气溶胶化学成分的垂直观测以及高时间分辨率、多要素、多参数的协同垂直观测,进而可以更深入地研究大气污染的垂直分布特征、输送及其与大气边界层的相互作用,同时对改进和提高数值模式在垂直方向上的模拟能力也具有重要的意义.

(2) 二次气溶胶生成机制研究.硫酸盐和硝酸盐是细颗粒中最重要的二次无机组分,但其非均相化学反应生成机制仍需进一步研究,如NO₂氧化SO₂生成硫酸盐机制仍需要更多的实验室研究进行评估,

N₂O₅的非均相摄取系数也需要开展不同环境下的广泛观测.同时,如何将上述反应机制更好地参数化至数值模式,改进和提高对二次无机气溶胶的模拟也是未来亟需开展的研究之一.

(3) 有机气溶胶的分子组成和物理化学属性研究. SOA可以通过多种途径直接或间接影响气候变化和人体健康^[108].由于有机气溶胶分子种类繁多,官能团、挥发性和氧化态等千差万别,当前数值模式对二次有机气溶胶的模拟仍存在严重低估^[108].研究发现,超过一半以上的SOA来自半挥发性和中等挥发性有机物(S/IVOCs)生成,但目前关于S/IVOCs的观测仍然相对匮乏.随着气溶胶质谱技术的发展,特别是基于软电离技术的化学电离质谱,全面表征有机气溶胶成为可能.如Hunter等人^[109]利用5种气溶胶质谱对一森林站点的有机气溶胶进行了全面表征,基本实现了挥发性、氧化态和分子量等多参数的闭合观测.结果发现S/IVOCs平均贡献了总有机碳的近三分之一,具有极大的SOA生成潜势.我国大气污染背景高,来源复杂,有机气溶胶的分子组成和老化机制远未明晰,目前也亟需联合多质谱技术,开展有机气溶胶综合观测实验,深入研究SOA的生成机制,同时更好地参数化有机气溶胶老化过程中挥发性和氧化态变化^[110],大幅改进和提高数值模式对有机气溶胶的模拟.

有机气溶胶颗粒通常认为以液相形态存在,直到最近研究才发现SOA颗粒还可以以高度黏稠的半固态或非晶玻璃状固态存在^[111-113].颗粒物相态不仅影响SOA的生成、气粒分配和多相化学反应过程等,还可以影响云凝结核和冰核的形成,以及气溶胶气候辐射强迫的准确评估. Shiraiwa等人^[114]和Li等人^[115]先后发展了分子通道模型,将有机分子化合物的挥发性、分子量和氧化态(O:C)进行了参数化,估算玻璃转化温度(T_g),并对全球SOA的相态进行了模拟.研究发现在对流层的中高层, SOA大部分以玻璃状固态存在,进而限制了SOA的气粒分配,促进冰核的形成和SOA中的毒性有机组分的长距离输送^[116].然而,目前有关气溶胶相态的观测相对缺乏,且大部分集中在地面,数值模式模拟结果难以进行很好地评估和验证,因此未来仍需要开展不同地区、不同环境和不同高度的颗粒物的相态观测.

参考文献

- 1 Boucher O, Randall D, Artaxo P, et al. Clouds and aerosols. In: Climate Change 2013: the Physical Science Basis Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge: Cambridge University Press, 2013
- 2 Nel A. Air pollution-related illness: Effects of particles. *Science*, 2005, 308: 804–806
- 3 Sun Y, Chen C, Zhang Y, et al. Rapid formation and evolution of an extreme haze episode in Northern China during winter 2015. *Sci Rep*, 2016, 6: 27151
- 4 Guo S, Hu M, Zamora M L, et al. Elucidating severe urban haze formation in China. *Proc Natl Acad Sci USA*, 2014, 111: 17373–17378
- 5 Zhang Y H, Hu M, Zhong L J, et al. Regional integrated experiments on air quality over Pearl River Delta 2004 (PRIDE-PRD2004): overview. *Atmos Environ*, 2008, 42: 6157–6173
- 6 van Pinxteren D, Brüggemann E, Gnauk T, et al. Size- and time-resolved chemical particle characterization during CAREBeijing-2006: Different pollution regimes and diurnal profiles. *J Geophys Res*, 2009, 114: D00G09
- 7 Zhao X J, Zhao P S, Xu J, et al. Analysis of a winter regional haze event and its formation mechanism in the North China Plain. *Atmos Chem Phys*, 2013, 13: 5685–5696
- 8 Wang Z, Huang X, Ding A. Dome effect of black carbon and its key influencing factors: A one-dimensional modelling study. *Atmos Chem Phys*, 2018, 18: 2821–2834
- 9 Liu W Q, Chen Z Y, Liu J G, et al. Stereoscopic monitoring technology and applications for the atmospheric environment in China (in Chinese). *Chin Sci Bull*, 2016, 61: 3196–3207 [刘文清, 陈臻懿, 刘建国, 等. 我国大气环境立体监测技术及应用. *科学通报*, 2016, 61: 3196–3207]
- 10 Heald C L, Coe H, Jimenez J L, et al. Exploring the vertical profile of atmospheric organic aerosol: Comparing 17 aircraft field campaigns with a global model. *Atmos Chem Phys*, 2011, 11: 12673–12696
- 11 Zhao D, Tie X, Gao Y, et al. *In-situ* aircraft measurements of the vertical distribution of black carbon in the lower troposphere of Beijing, China, in the spring and summer time. *Atmosphere*, 2015, 6: 713–731
- 12 Zhang Q, Ma X, Tie X, et al. Vertical distributions of aerosols under different weather conditions: Analysis of *in-situ* aircraft measurements in Beijing, China. *Atmos Environ*, 2009, 43: 5526–5535
- 13 Chen Y, Zhao C, Zhang Q, et al. Aircraft study of Mountain Chimney effect of Beijing, China. *J Geophys Res*, 2009, 114: D08306
- 14 Liu J G, Xie P H, Wang Y S, et al. Haze observation and control measure evaluation in Jing-Jin-Ji (Beijing, Tianjin, Hebei) area during the period of the Asia-Pacific Economic Cooperation (APEC) Meeting (in Chinese). *Bull Chin Acad Sci*, 2015, 30: 368–377 [刘建国, 谢品华, 王跃思, 等. APEC 前后京津冀区域灰霾观测及控制措施评估. *中国科学院院刊*, 2015, 30: 368–377]
- 15 Li J, Fu Q, Huo J, et al. Tethered balloon-based black carbon profiles within the lower troposphere of Shanghai in the 2013 East China Smog. *Atmos Environ*, 2015, 123: 327–338
- 16 Ran L, Deng Z, Xu X, et al. Vertical profiles of black carbon measured by a micro-aethalometer in summer in the North China Plain. *Atmos Chem Phys*, 2016, 16: 10441–10454
- 17 Liu X H, Hong Z X, Li J L, et al. Meteorological and chemical parameters determining the photochemical air pollution in Beijing (in Chinese). *Clim Environ Res*, 1999, 4: 231–236 [刘小红, 洪钟祥, 李家伦, 等. 北京地区严重大气污染的气象和化学因子. *气候与环境研究*, 1999, 4: 231–236]
- 18 Wang J, Zhou M, Liu B S, et al. Characterization and source apportionment of size-segregated atmospheric particulate matter collected at ground level and from the urban canopy in Tianjin. *Environ Pollut*, 2016, 219: 982–992
- 19 Cheng X L, Liu X M, Liu Y J, et al. Characteristics of CO₂ concentration and flux in the Beijing urban area. *J Geophys Res*, 2018, 123: 1785–1801
- 20 Sun Y L, Du W, Wang Q, et al. Real-time characterization of aerosol particle composition above the urban canopy in Beijing: Insights into the interactions between the atmospheric boundary layer and aerosol chemistry. *Environ Sci Technol*, 2015, 49: 11340–11347
- 21 Wang Q, Sun Y, Xu W, et al. Vertically resolved characteristics of air pollution during two severe winter haze episodes in urban Beijing, China. *Atmos Chem Phys*, 2018, 18: 2495–2509
- 22 Liu Y, Liu H Z, Wang L. The vertical distribution characteristics of integral turbulence statistics in the atmospheric boundary layer over an urban area in Beijing. *Sci China Earth Sci*, 2017, 60: 1533–1545 [刘阳, 刘辉志, 王雷. 北京城市下垫面大气边界层湍流输送垂直分布特征. *中国科学: 地球科学*, 2017, 47: 1243–1256]
- 23 Zhang M G, Hu F, Zou H, et al. An overview of recent studies on atmospheric boundary layer physics and atmospheric environment in LAPC (in Chinese). *Chin J Atmos Sci*, 2008, 32: 923–934 [张美根, 胡非, 邹捍, 等. 大气边界层物理与大气环境过程研究进展. *大*

- 气科学, 2008, 32: 923–934]
- 24 Xu X D, Ding G A, Bian L G. Beijing city air pollution observation experiment (in Chinese). *J Appl Meteorol Climatol*, 2007, 17: 815–828 [徐祥德, 丁国安, 卞林根. 北京城市大气环境污染机理与调控原理. *应用气象学报*, 2007, 17: 815–828]
 - 25 Zhou M Y, Yao W Q, Xu X D, et al. Study of the characteristics of low-level vertical dynamics and thermal characteristics of urban atmospheric boundary layer in Beijing and its relationship with concentration of pollutants (in Chinese). *Sci China Ser D: Earth Sci*, 2006, 35: 20–30 [周明煜, 姚文清, 徐祥德, 等. 北京城市大气边界层低层垂直动力和热力特征及其与污染物浓度关系的研究. *中国科学 D 辑: 地球科学*, 2006, 35: 20–30]
 - 26 Guo X, Sun Y, Miao S. Characterizing urban turbulence under haze pollution: Insights into temperature-humidity dissimilarity. *Bound-Lay Meteorol*, 2016, 158: 501–510
 - 27 Ding G A, Chen Z Y, Gao Z Q, et al. Vertical structure and dynamic characteristics of PM_{10} and $PM_{2.5}$ in the lower atmosphere in Beijing city (in Chinese). *Sci China Ser D: Earth Sci*, 2005, 35: 31–44 [丁国安, 陈尊裕, 高志球, 等. 北京城区低层大气 PM_{10} 和 $PM_{2.5}$ 垂直结构及其动力特征. *中国科学 D 辑: 地球科学*, 2005, 35: 31–44]
 - 28 Liu X H, Hong Z X, Li J L, et al. Observations of O_3 , NO and CO on Beijing meteorological tower in autumn in Beijing (in Chinese). *Prog Nat Sci*, 2000, 10: 338–342 [刘小红, 洪钟祥, 李家伦, 等. 北京气象塔秋季大气 O_3 , NO 及 CO 浓度变化的观测实验. *自然科学进展*, 2000, 10: 338–342]
 - 29 An J L, Li X, Wang Y S, et al. Measurements of atmospheric boundary layer O_3 , NO_x and CO in summer with Beijing 325 m meteorological tower (in Chinese). *Environ Sci*, 2003, 24: 43–47 [安俊琳, 李昕, 王跃思, 等. 北京气象塔夏季大气 O_3 , NO_x 和 CO 浓度变化的观测实验. *环境科学*, 2003, 24: 43–47]
 - 30 Lee X, Gao Z, Zhang C, et al. Priorities for boundary-layer meteorology research in China. *Bull Amer Meteorol Soc*, 2015, 96: ES149–ES151
 - 31 Chen C, Sun Y L, Xu W Q, et al. Characteristics and sources of submicron aerosols above the urban canopy (260 m) in Beijing, China, during the 2014 APEC summit. *Atmos Chem Phys*, 2015, 15: 12879–12895
 - 32 Du W, Zhao J, Wang Y, et al. Simultaneous measurements of particle number size distributions at ground level and 260 m on a meteorological tower in urban Beijing, China. *Atmos Chem Phys*, 2017, 17: 6797–6811
 - 33 Sun Y, Wang Z, Wild O, et al. “APEC Blue”: Secondary aerosol reductions from emission controls in Beijing. *Sci Rep*, 2016, 6: 20668
 - 34 Zhao J, Du W, Zhang Y, et al. Insights into aerosol chemistry during the 2015 China Victory Day parade: Results from simultaneous measurements at ground level and 260 m in Beijing. *Atmos Chem Phys*, 2017, 17: 3215–3232
 - 35 Zhou W, Wang Q, Zhao X, et al. Characterization and source apportionment of organic aerosol at 260 m on a meteorological tower in Beijing, China. *Atmos Chem Phys*, 2018, 18: 3951–3968
 - 36 Han S, Zhang Y, Wu J, et al. Evaluation of regional background particulate matter concentration based on vertical distribution characteristics. *Atmos Chem Phys*, 2015, 15: 11165–11177
 - 37 Xu W Q, Sun Y L, Chen C, et al. Aerosol composition, oxidation properties, and sources in Beijing: Results from the 2014 Asia-Pacific Economic Cooperation summit study. *Atmos Chem Phys*, 2015, 15: 13681–13698
 - 38 Jiang Q, Sun Y L, Wang Z, et al. Aerosol composition and sources during the Chinese Spring Festival: Fireworks, secondary aerosol, and holiday effects. *Atmos Chem Phys*, 2015, 15: 6023–6034
 - 39 Zhang Y, Sun Y, Du W, et al. Response of aerosol composition to different emission scenarios in Beijing, China. *Sci Total Environ*, 2016, 571: 902–908
 - 40 Liu M, Song Y, Zhou T, et al. Fine particle pH during severe haze episodes in Northern China. *Geophys Res Lett*, 2017, 45: 5213–5221
 - 41 Petäjä T, Järvi L, Kerminen V M, et al. Enhanced air pollution via aerosol-boundary layer feedback in China. *Sci Rep*, 2016, 6: 18998
 - 42 Quan J, Gao Y, Zhang Q, et al. Evolution of planetary boundary layer under different weather conditions, and its impact on aerosol concentrations. *Particuology*, 2013, 11: 34–40
 - 43 Zhong J, Zhang X, Dong Y, et al. Feedback effects of boundary-layer meteorological factors on cumulative explosive growth of $PM_{2.5}$ during winter heavy pollution episodes in Beijing from 2013 to 2016. *Atmos Chem Phys*, 2018, 18: 247–258
 - 44 Ding A J, Huang X, Nie W, et al. Enhanced haze pollution by black carbon in megacities in China. *Geophys Res Lett*, 2016, 43: 2873–2879
 - 45 Li Z, Guo J, Ding A, et al. Aerosol and boundary-layer interactions and impact on air quality. *Nat Sci Rev*, 2017, 4: 810–833
 - 46 Wang H, Lu K, Chen X, et al. Large particulate nitrate formation from N_2O_5 uptake in a chemically reactive layer aloft during winter time in Beijing. *Atmos Chem Phys Discuss*, 2018, 2018: 1–27
 - 47 Tang G, Zhang J, Zhu X, et al. Mixing layer height and its implications for air pollution over Beijing, China. *Atmos Chem Phys*, 2016, 16: 2459–2475
 - 48 Pöschl U. Atmospheric aerosols: Composition, transformation, climate and health effects. *Angew Chem-Int Ed*, 2005, 44: 7520–7540

- 49 Jimenez J L, Canagaratna M R, Donahue N M, et al. Evolution of organic aerosols in the atmosphere. *Science*, 2009, 326: 1525–1529
- 50 Huang R-J, Zhang Y, Bozzetti C, et al. High secondary aerosol contribution to particulate pollution during haze events in China. *Nature*, 2014, 514: 218–222
- 51 Sun Y L, Wang Z F, Fu P Q, et al. Aerosol composition, sources and processes during wintertime in Beijing, China. *Atmos Chem Phys*, 2013, 13: 4577–4592
- 52 Zhang R, Wang G, Guo S, et al. Formation of urban fine particulate matter. *Chem Rev*, 2015, 115: 3803–3855
- 53 Zhang X Y, Wang Y Q, Niu T, et al. Atmospheric aerosol compositions in China: Spatial/temporal variability, chemical signature, regional haze distribution and comparisons with global aerosols. *Atmos Chem Phys*, 2012, 12: 779–799
- 54 He K, Yang F, Ma Y, et al. The characteristics of PM_{2.5} in Beijing, China. *Atmos Environ*, 2001, 35: 4959–4970
- 55 Yang F, Tan J, Zhao Q, et al. Characteristics of PM_{2.5} speciation in representative megacities and across China. *Atmos Chem Phys*, 2011, 11: 5207–5219
- 56 Sun Y, Zhuang G, Tang A, et al. Chemical characteristics of PM_{2.5} and PM₁₀ in haze-fog episodes in Beijing. *Environ Sci Technol*, 2006, 40: 3148–3155
- 57 Zhang Y J, Zheng M, Cai J, et al. Comparison and overview of PM_{2.5} source apportionment methods (in Chinese). *Chin Sci Bull*, 2015, 60: 109–121 [张延君, 郑玫, 蔡靖, 等. PM_{2.5}源解析方法的比较与评述. *科学通报*, 2015, 60: 109–121]
- 58 Zhang R, Jing J, Tao J, et al. Chemical characterization and source apportionment of PM_{2.5} in Beijing: Seasonal perspective. *Atmos Chem Phys*, 2013, 13: 7053–7074
- 59 Zhang X Y, Sun J Y, Wang Y Q, et al. Factors contributing to haze and fog in China (in Chinese). *Chin Sci Bull*, 2013, 58: 1178–1187 [张小曳, 孙俊英, 王亚强, 等. 我国雾-霾成因及其治理的思考. *科学通报*, 2013, 58: 1178–1187]
- 60 Wang Y, Yao L, Wang L, et al. Mechanism for the formation of the January 2013 heavy haze pollution episode over central and eastern China. *Sci China Earth Sci*, 2014, 57: 14–25
- 61 Zheng G J, Duan F K, Su H, et al. Exploring the severe winter haze in Beijing: The impact of synoptic weather, regional transport and heterogeneous reactions. *Atmos Chem Phys*, 2015, 15: 2969–2983
- 62 Sun Y L, Jiang Q, Wang Z, et al. Investigation of the sources and evolution processes of severe haze pollution in Beijing in January 2013. *J Geophys Res*, 2014, 119: 4380–4398
- 63 Jansen R C, Shi Y, Chen J, et al. Using hourly measurements to explore the role of secondary inorganic aerosol in PM_{2.5} during haze and fog in Hangzhou, China. *Adv Atmos Sci*, 2014, 31: 1427–1434
- 64 Seinfeld J H, Pandis S N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. New York: Wiley, John & Sons, Incorporated, 2006
- 65 Wang H, Lu K, Chen X, et al. High N₂O₅ concentrations observed in urban Beijing: Implications of a large nitrate formation pathway. *Environ Sci Technol Lett*, 2017, 4: 416–420
- 66 Brown S S, Ryerson T B, Wollny A G, et al. Variability in nocturnal nitrogen oxide processing and its role in regional air quality. *Science*, 2006, 311: 67–70
- 67 Morgan W T, Ouyang B, Allan J D, et al. Influence of aerosol chemical composition on N₂O₅ uptake: Airborne regional measurements in northwestern Europe. *Atmos Chem Phys*, 2015, 15: 973–990
- 68 Wang X, Wang H, Xue L, et al. Observations of N₂O₅ and ClNO₂ at a polluted urban surface site in North China: High N₂O₅ uptake coefficients and low ClNO₂ product yields. *Atmos Environ*, 2017, 156: 125–134
- 69 Sun Y L, Wang Z, Dong H, et al. Characterization of summer organic and inorganic aerosols in Beijing, China with an Aerosol Chemical Speciation Monitor. *Atmos Environ*, 2012, 51: 250–259
- 70 Morgan W T, Allan J D, Bower K N, et al. Enhancement of the aerosol direct radiative effect by semi-volatile aerosol components: Airborne measurements in North-Western Europe. *Atmos Chem Phys*, 2010, 10: 8151–8171
- 71 Harris E, Sinha B, van Pinxteren D, et al. Enhanced role of transition metal ion catalysis during in-cloud oxidation of SO₂. *Science*, 2013, 340: 727–730
- 72 Elser M, Huang R J, Wolf R, et al. New insights into PM_{2.5} chemical composition and sources in two major cities in China during extreme haze events using aerosol mass spectrometry. *Atmos Chem Phys*, 2016, 16: 3207–3225
- 73 Zheng B, Zhang Q, Zhang Y, et al. Heterogeneous chemistry: A mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China. *Atmos Chem Phys*, 2015, 15: 2031–2049
- 74 Sun Y L, Wang Z, Fu P, et al. The impact of relative humidity on aerosol composition and evolution processes during wintertime in Beijing, China. *Atmos Environ*, 2013, 77: 927–934
- 75 He H, Wang Y, Ma Q, et al. Mineral dust and NO_x promote the conversion of SO₂ to sulfate in heavy pollution days. *Sci Rep*, 2014, 4: 4172

- 76 Xie Y, Ding A, Nie W, et al. Enhanced sulfate formation by nitrogen dioxide: Implications from *in-situ* observations at the SORPES Station. *J Geophys Res*, 2015, 120: 12679–12694
- 77 Wang G, Zhang R, Gomez M E, et al. Persistent sulfate formation from London Fog to Chinese haze. *Proc Natl Acad Sci USA*, 2016, 113: 13630–13635
- 78 Cheng Y, Zheng G, Wei C, et al. Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. *Sci Adv*, 2016, 2: e1601530
- 79 Guo H, Weber R J, Nenes A. High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production. *Sci Rep*, 2017, 7: 12109
- 80 Nenes A, Pandis S N, Pilinis C. ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols. *Aquat Geochem*, 1998, 4: 123–152
- 81 Song S, Gao M, Xu W, et al. Fine particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models. *Atmos Chem Phys Discuss*, 2018, 2018: 1–26
- 82 Li L, Hoffmann M R, Colussi A J. The role of nitrogen dioxide in the production of sulfate during Chinese haze-aerosol episodes. *Environ Sci Technol*, 2018, 52: 2686–2693
- 83 Wen L, Xue L, Wang X, et al. Summertime fine particulate nitrate pollution in the North China Plain: Increasing trends, formation mechanisms, and implications for control policy. *Atmos Chem Phys Discuss*, 2018, 2018: 1–27
- 84 Wang Y, Zhang Q Q, He K, et al. Sulfate-nitrate-ammonium aerosols over China: Response to 2000–2015 emission changes of sulfur dioxide, nitrogen oxides, and ammonia. *Atmos Chem Phys*, 2013, 13: 2635–2652
- 85 Atkinson R, Arey J. Atmospheric degradation of volatile organic compounds. *Chem Rev*, 2003, 103: 4605–4638
- 86 Rollins A W, Browne E C, Min K E, et al. Evidence for NO_x control over nighttime SOA formation. *Science*, 2012, 337: 1210–1212
- 87 Brown S S, Stutz J. Nighttime radical observations and chemistry. *Chem Soc Rev*, 2012, 41: 6405–6447
- 88 Ziemann P J, Atkinson R. Kinetics, products, and mechanisms of secondary organic aerosol formation. *Chem Soc Rev*, 2012, 41: 6582–6605
- 89 Ervens B, Turpin B J, Weber R J. Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): A review of laboratory, field and model studies. *Atmos Chem Phys*, 2011, 11: 11069–11102
- 90 Ge X, Zhang Q, Sun Y, et al. Effect of aqueous-phase processing on aerosol chemistry and size distributions in Fresno, California, during wintertime. *Environ Chem*, 2012, 9: 221–235
- 91 Lim Y B, Tan Y, Perri M J, et al. Aqueous chemistry and its role in secondary organic aerosol (SOA) formation. *Atmos Chem Phys*, 2010, 10: 10521–10539
- 92 Tan Y, Lim Y B, Altieri K E, et al. Mechanisms leading to oligomers and SOA through aqueous photooxidation: Insights from OH radical oxidation of acetic acid and methylglyoxal. *Atmos Chem Phys*, 2012, 12: 801–813
- 93 Hallquist M, Wenger J C, Baltensperger U, et al. The formation, properties and impact of secondary organic aerosol: Current and emerging issues. *Atmos Chem Phys*, 2009, 9: 5155–5235
- 94 Nozière B, Kalberer M, Claeys M, et al. The molecular identification of organic compounds in the atmosphere: State of the art and challenges. *Chem Rev*, 2015, 115: 3919–3983
- 95 Isaacman-VanWertz G, Massoli P, O'Brien R, et al. Chemical evolution of atmospheric organic carbon over multiple generations of oxidation. *Nat Chem*, 2018, 4: 462–468
- 96 Ehn M, Thornton J A, Kleist E, et al. A large source of low-volatility secondary organic aerosol. *Nature*, 2014, 506: 476–479
- 97 Tröstl J, Chuang W K, Gordon H, et al. The role of low-volatility organic compounds in initial particle growth in the atmosphere. *Nature*, 2016, 533: 527–531
- 98 Gentner D R, Isaacman G, Worton D R, et al. Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions. *Proc Natl Acad Sci USA*, 2012, 109: 18318–18323
- 99 Bahreini R, Middlebrook A M, de Gouw J A, et al. Gasoline emissions dominate over diesel in formation of secondary organic aerosol mass. *Geophys Res Lett*, 2012, 39: L06805
- 100 Gentner D R, Jathar S H, Gordon T D, et al. Review of urban secondary organic aerosol formation from gasoline and diesel motor vehicle emissions. *Environ Sci Technol*, 2017, 51: 1074–1093
- 101 Kroll J H, Donahue N M, Jimenez J L, et al. Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. *Nat Chem*, 2011, 3: 133–139
- 102 Sun Y L, Zhang Q, Anastasio C, et al. Insights into secondary organic aerosol formed via aqueous-phase reactions of phenolic compounds based on high resolution mass spectrometry. *Atmos Chem Phys*, 2010, 10: 4809–4822
- 103 Gilardoni S, Massoli P, Paglione M, et al. Direct observation of aqueous secondary organic aerosol from biomass-burning emissions. *Proc Natl Acad Sci USA*, 2016, 113: 10013–10018

- 104 Sun Y, Du W, Fu P, et al. Primary and secondary aerosols in Beijing in winter: Sources, variations and processes. *Atmos Chem Phys*, 2016, 16: 8309–8329
- 105 Xu W, Han T, Du W, et al. Effects of aqueous-phase and photochemical processing on secondary organic aerosol formation and evolution in Beijing, China. *Environ Sci Technol*, 2017, 51: 762–770
- 106 Li J, Du H, Wang Z, et al. Rapid formation of a severe regional winter haze episode over a mega-city cluster on the North China Plain. *Environ Pollut*, 2017, 223: 605–615
- 107 Jiang M Q, Lu K D, Su R, et al. Analysis of ozone formation mechanisms and reactivities of key VOCs in typical city clusters in China (in Chinese). *Chin Sci Bull*, 2018, 63: 1130–1141 [蒋美青, 陆克定, 苏榕, 等. 我国典型城市群臭氧形成机制和关键 VOCs 的反应活性分析. *科学通报*, 2018, 63: 1130–1141]
- 108 Shrivastava M, Cappa C D, Fan J, et al. Recent advances in understanding secondary organic aerosol: Implications for global climate forcing. *Rev Geophys*, 2017, 55: 509–559
- 109 Hunter J F, Day D A, Palm B B, et al. Comprehensive characterization of atmospheric organic carbon at a forested site. *Nat Geosci*, 2017, 10: 748–753
- 110 Donahue N M, Kroll J H, Pandis S N, et al. A two-dimensional volatility basis set-Part 2: Diagnostics of organic-aerosol evolution. *Atmos Chem Phys*, 2012, 12: 615–634
- 111 Virtanen A, Joutsensaari J, Koop T, et al. An amorphous solid state of biogenic secondary organic aerosol particles. *Nature*, 2010, 467: 824–827
- 112 Bateman A P, Gong Z, Liu P, et al. Sub-micrometre particulate matter is primarily in liquid form over Amazon rainforest. *Nat Geosci*, 2016, 9: 34–37
- 113 Reid J P, Bertram A K, Topping D O, et al. The viscosity of atmospherically relevant organic particles. *Nat Commun*, 2018, 9: 956
- 114 Shiraiwa M, Berkemeier T, Schilling-Fahnestock K A, et al. Molecular corridors and kinetic regimes in the multiphase chemical evolution of secondary organic aerosol. *Atmos Chem Phys*, 2014, 14: 8323–8341
- 115 Li Y, Pöschl U, Shiraiwa M. Molecular corridors and parameterizations of volatility in the chemical evolution of organic aerosols. *Atmos Chem Phys*, 2016, 16: 3327–3344
- 116 Shiraiwa M, Li Y, Tsimpidi A P, et al. Global distribution of particle phase state in atmospheric secondary organic aerosols. *Nat Commun*, 2017, 8: 15002

Summary for “城市边界层理化结构与大气污染形成机制研究进展”

Vertical structures of physical and chemical properties of urban boundary layer and formation mechanisms of atmospheric pollution

Yele Sun^{1,2,3}

¹ State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China;

² University of Chinese Academy of Sciences, Beijing 100049, China;

³ Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
E-mail: sunyele@mail.iap.ac.cn

Air quality in China has been continuously improved since the implementation of “Atmospheric Pollution Prevention and Control Action Plan” in 2013. However, the mass concentrations of fine particles particularly in Beijing, Tianjin and Hebei are still much higher than the National Ambient Air Quality Standard ($35 \mu\text{g m}^{-3}$ as an annual average), and severely polluted events also occur occasionally in autumn and winter seasons. In recent years, Chinese research scientists have made significant progresses in vertical measurements of air pollution, formation mechanisms and source apportionment of atmospheric aerosol, and also the interactions between aerosol and atmospheric boundary layer, which greatly support the scientific prevention and control of atmospheric pollution. Despite this, many questions on atmospheric pollution have not been well addressed yet. This paper first summarizes the recent research progresses in vertical measurements of air pollution in China, in particular, the measurements from the research platform of the Beijing 325 m meteorological tower. In addition to the routine long-term measurements of boundary layer (turbulence, CO_2 and H_2O flux) and meteorological parameters (temperature, relative humidity, wind speed and wind direction) at 7 and 15 heights, respectively, this platform can have simultaneous real-time measurements of aerosol particle composition (organics, sulfate, nitrate, ammonium, chloride, and black carbon), gaseous species (CO , SO_2 , and O_3), particle number size distributions, and optical properties (extinction and absorption coefficients) at ground level and 260 m, and also the continuously vertical measurements from ground to 260 m using the tower container equipped with specific instruments. Then, the vertical differences of aerosol composition in different seasons in Beijing, and their interactions with boundary layer are discussed. Also, the response of aerosol chemistry to regional source emission control are elucidated based on vertical measurements during the Asia-Pacific Economic Conference (APEC) summit in 2014 and the 70th anniversary parade in 2015. This paper also reviews the latest research progress on formation mechanisms of secondary inorganic aerosol (nitrate and sulfate) and secondary organic aerosol, and the life cycles of severe haze events in China. In particular, the heterogeneous formation of sulfate during severe haze episodes strongly depends on pH values of aerosol liquid water content. While techniques for direct measurements of aerosol particle pH are essential yet challenging, laboratory experiments are more needed now to prove the hypothesis of sulfate formation mechanisms. Compared with inorganic species, the formation and evolutionary mechanisms of secondary organic aerosol (SOA) are far more complex in polluted environments, and their roles in haze formation need to be better characterized. Finally, this paper lists some future recommendations for air pollution measurements (e.g., from long-term to vertical measurements in terms of significant emission changes in the near future), formation mechanism of secondary aerosol, and molecular composition and physical and chemical properties (phase, volatility, oxidation state, etc.) of organic aerosol.

atmospheric boundary layer, physical and chemical structure, air pollution, secondary aerosol, formation mechanisms

doi: 10.1360/N972018-00258