大气边界层内挥发性有机物的垂直观测方法及应用进展

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摘要 总结分析了大气边界层内挥发性有机物(VOCs)的主要垂直观测方法与应用进展,着重对高层建筑、系留气球、载人飞机、无人机和激光雷达等不同平台的VOCs垂直观测技术进行介绍,并对不同VOCs垂直观测平台的优缺点和主要应用场景进行归纳总结。同时,较为系统地总结了大气边界层内VOCs垂直观测的主要应用进展,着重对VOCs垂直分布特征的关键影响因素、排放通量计算、排放清单验证、光化学臭氧生成机制的垂直分布特征,以及夜间边界层内VOCs氧化降解的垂直分布特征等方面进行归纳总结。目前对于环境大气中VOCs化学过程的研究主要以地面观测数据为主,而获取大气边界层内关键VOCs组分浓度的垂直分布数据是深入解析区域大气二次污染成因机制的重要前提。

关键词 大气边界层, 挥发性有机物, 垂直观测, 二次污染

挥发性有机物(VOCs)是环境大气中的重要痕量气体组分,许多VOCs组分除了本身是有毒有害物质之外,还是大气二次污染物(如臭氧和二次有机气溶胶(SOA)等)的重要前体物^[1,2]。近年来,为了有效控制区域性大气复合污染,中国政府和相关机构制定了严格的污染物排放管控措施,环境大气中一次污染物(如氮氧化物(NO_x)和二氧化硫等)的浓度水平不断下降^[3]。但已有报道表明,环境大气中的VOCs浓度水平在近年来并未得到有效控制,甚至出现不断升高的趋势^[4,5]。因此,深入理解各类VOCs组分在环境大气中的时空分布规律及其化学转化机制是制定有效大气污染管控措施的重要前提。

以往的研究主要着重分析地面大气中不同VOCs组分的浓度水平与变化规律、排放来源解析和化学转化机制等^[6-8],以及不同VOCs组分对二次污染物(如臭

氧和SOA)的生成影响与贡献等,而对于VOCs在大气边界层内的垂直研究报道则相对较少。有研究表明,受到区域污染源位置和排放强度、湍流扩散、水平输送和大气化学过程等因素的综合影响,VOCs在大气边界层内的垂直方向上并非均匀混合,而是呈现出显著的分布波动,且不同VOCs物种的垂直梯度变化特征也存在显著差异^[9,10]。此外,在大气垂直混合过程中,VOCs在边界层中上部大气中的氧化降解产物可以被输送至地面,影响地面环境大气中的二次污染物浓度水平^[11]。因此,深入理解各类VOCs物种分布特征与主要氧化降解通道的垂直分布差异是解析区域二次污染形成机制的关键,但是这都需要以有效可靠的VOCs垂直观测数据为基础。

截至目前,能够准确量化分析VOCs浓度的仪器设备(包括离线和在线分析设备)通常十分昂贵,且较为笨

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重,难以像其他常规污染物监测设备一样进行广泛配置^[12]。此外,由于许多VOCs物种的化学活性较高,且在环境大气中的浓度水平较低,加之垂直方向上的VOCs浓度测量难度较大,导致VOCs垂直分布的研究难度进一步加大。尽管如此,目前已有国内外学者和研究人员使用多种平台和分析设备在许多国家和地区开展过VOCs垂直观测实验(图1),但不同平台或观测设备(技术)的优缺点差异较大,获取VOCs垂直观测数据的质量和应用场景也不尽相同(图2)^[13]。本文对目前主要使用的VOCs垂直观测平台(技术)的发展状况进行总结分析,并对VOCs垂直观测数据在大气环境领域中的应用进行总结与展望。

1 挥发性有机物垂直观测方法

1.1 高层建筑物和气象梯度观测塔

利用高层建筑物或气象梯度观测塔为依托平台是目前较为普遍采用的VOCs垂直观测方法。高层建筑物主要指在城市区域中用于商业办公、旅游观光或广播等具有较高高度的高楼,在其上面采集的大气样本能够反映城市近地面大气中的VOCs垂直分布特征^[14]。气象梯度观测塔通常多建造于城郊或森林地区,可用于监测区域环境大气的气象参数或关键污染物浓度的垂

直分布结构^[15]。

利用高层建筑物和气象梯度观测塔获取VOCs垂直分布数据,其观测方法已经较为成熟,且观测成本相对较低。与其他观测方法相比,操作简单,只需要选定满足条件的高层建筑物即可;此外,它能够作为长期观测平台,并且可以配置相对较为全面的观测仪器。但是,高层建筑物和气象塔的最大观测高度通常有限,无法有效获取大气边界层上部大气中VOCs浓度的长期有效观测数据;此外,高层建筑物或气象塔的空间位置固定,其观测数据的空间代表性有限^[13]。

高层建筑物和气象塔上的VOCs浓度获取主要分为离线和在线观测两种方式。离线观测方法是在建筑物的不同高度上使用各种采样工具获取空气样本。目前普遍使用的VOCs采样工具主要包括泰德拉(Tedlar)袋、苏玛罐和2,4-二硝基苯肼(DNPH)采样管等^[13]。获取空气样本之后,在实验室条件下使用相关分析仪器(如气相色谱-火焰离子化检测器/质谱(GC-FID/MS))进行定性与定量分析,获取各类VOCs组分浓度的垂直分布数据。除了离线观测之外,目前已有一些研究以气象塔为依托平台,采用在线分析设备(如质子转移反应质谱仪 PTRMS))获取大气边界层内VOCs浓度的垂直分布数据^[16]。基于高层建筑或气象塔的VOCs在线垂直观测技术大致可以分为三类:(1)在不同高度平台上直接

图1 世界范围内开展VOCs垂直观测点位图

Figure 1 Locations of VOCs vertical observation sites around the world

图 2 (网络版彩色)大气边界层内VOCs垂直观测平台^[13]

Figure 2 (Color online) Vertical observation platform of VOCs in the planetary boundary layer^[13]

配置分析仪器。该方法能够连续获取VOCs浓度的垂直梯度观测数据,但其搭建和运营维护成本十分高昂。(2)将分析仪器配置在垂直移动平台(如吊篮和电梯等)。该方法能够获取VOCs浓度的垂直廓线数据,但通常仅在专业气象塔上应用于加强观测,且运营维护成本同样较高。(3)在不同高度上布设采样管路,将样本气体通入放置在地面的分析仪器,通过切换不同高度上的样本气体进入分析仪器,获取VOCs浓度的垂直分布数据^[17]。该方法能够长期获取VOCs浓度的高时间分辨率垂直观测数据,但是考虑到使用的采样管路较长,通常仅用于测量黏性较小的VOCs物种浓度。

1.2 系留气球

系留气球通常是以填充氢气的气球(或飞艇)作为观测平台,搭载采样设备或在线分析仪器获取大气边界层内VOCs浓度的垂直观测数据。系留气球通过绳索与地面控制设备(如电动绞车)连接,通过调节绳索的收放进行垂直观测作业。

系留气球比较显著的优点是,能够提供一个相对较为稳定的观测平台来探索边界层内VOCs的垂直演化^[18],并且其观测高度通常优于建筑物(或气象塔)^[19];此外,与高层建筑物和气象塔观测相比,系留气球观测点位的选择更加灵活^[20]。但是,基于系留气球的VOCs

垂直观测方法也存在一些不足,这主要体现在系留气球的升降作业需要较为宽阔的场地支撑,并且难以在建筑物较多和人群密集区域进行作业。此外,系留气球在进行升降作业时容易受天气情况变化的影响。

在已有报道中,系留气球平台主要使用苏玛罐和固体吸附剂离线采样方式获取VOCs浓度的垂直分布数据^[21]。当使用固体吸附剂获取环境样本时,其采样流量通常难以准确控制。对此,有研究提出可以使用氟氯烃(CFC)和四氯化碳(CCl_4)内标法提高样本采集效率和测量精度^[22]。除了离线方式之外,也有研究将系留气球作为采样管路的升降平台,通过系留气球平台调节管路采样口的高度位置,与配置在地面的分析仪器结合,在线获取VOCs浓度的垂直分布数据^[23]。并且该方法已经被成功用于奥地利INNOX-2006实验中的VOCs测量^[23]和西班牙巴塞罗那天然源VOCs通量观测实验^[24]。受到系留气球有效载重和采样管路自身强度等因素的限制,基于系留气球平台的VOCs在线垂直观测方法能够获取观测数据的空间高度有限,其应用也相对较少。

1.3 载人飞机平台

载人飞机观测主要指,使用载人飞行器(包括直升机和直翼飞机等)搭载VOCs采样装置或在线分析仪器,

获取目标VOCs物种浓度的垂直分布数据^[25]。载人飞机平台的续航时间较长,并且能够获取较大空间尺度上的VOCs浓度数据^[26],因此观测数据更加具有区域空间代表性,已经在国外被广泛应用于VOCs的垂直观测研究中。图3为北美地区已经开展过的基于载人飞机平台的VOCs观测实验航迹汇总^[25]。

载人飞机的有效载荷大,除了可以搭载VOCs分析仪器之外,还能够同时配置其他大气观测设备(如气象参数和其他大气化学组分测量设备等)^[27],获取较为全面的观测数据集。截至目前,载人飞机平台在VOCs垂直观测研究中的应用较为广泛,但也存在一些不足。比如,载人飞机通常使用化石燃料驱动,其尾气排放可能会对测量结果造成干扰^[28,29];此外,载人飞机对观测场地(如机场和空域等)和后勤补给的要求较高,并且飞机的使用和运营维护成本同样较高^[13]。

在以往研究中,载人飞机平台主要使用离线采样方式,获取环境大气中各类VOCs组分浓度的垂直分布数据^[13]。并针对载人飞机平台特点(巡航速度高和气流扰动大等特点),专门开发了相应的VOCs离线采样与分析技术^[30-34],以提升样本采样效率与分析结果的可靠性。此外,由于载人飞机平台的高载重特性,也可以直接搭载在线分析仪器(如PTRMS),在线获取VOCs浓度的垂直分布数据。根据已有报道,国外研究已经使用载人飞机搭载VOCs在线分析仪器对区域烟羽来源特征及化学变化^[35]、VOCs通量测量^[36]、地面VOCs测量^[37]和边界层内VOCs大气寿命^[38]等开展过广泛研究。与机载离线采样分析方法类似,VOCs在线测量设备容易受高空气流扰动和湿度垂直变化等因素的影响。目前许多研究人员也致力研发更加稳定可靠和小型便捷的机载VOCs在线分析仪器。

图3 北美地区基于载人飞机的VOCs测量航迹图^[25]

Figure 3 Flight tracks of aircraft for VOCs observation over North America^[25]

1.4 无人机平台

无人机平台以无人驾驶飞行器(包括固定翼和多旋翼等)为依托,通常使用离线分析方法获取大气边界层内VOCs物种浓度的垂直分布数据^[39,40]。随着民用无人机产业的快速发展,许多性能优异(载荷大、续航时间长和操控稳定度高等)且价格低廉的中小型无人机被广泛用于大气监测领域,获取边界层内各类大气参数的垂直分布数据^[41]。无人机是近些年来较为热门的大气垂直观测平台,基于无人机平台的各种优异性能,其在大气垂直观测领域有广阔的应用前景。

无人机平台的优点在于其机动灵活性较高,能够在复杂环境中使用^[42],对后勤保障和观测场地的要求较低,且其使用成本也相对低廉^[43]。使用电池驱动的无人机可以有效避免燃油废气排放对VOCs观测样本可能造成的污染,提高观测数据的可靠性^[44-46]。虽然无人机平台具有较好的操控性和灵活机动性,但也存在诸多因素限制。首先,受当前电池技术发展的限制,无人机的续航时间仍然不足,有效载重较小,并且续航时间随附加设备重量的增加而急剧下降^[47],严重限制了一个航次中能够有效获取的观测样本数量。其次,无人机平台主要使用离线分析方法获取VOCs物种浓度的垂直分布数据,数据的时空分辨率通常较低^[48]。最后,包括我国在内的许多国家对民用小型飞行器的使用具有较为严格的管控,空域申请难度较大,很大程度上限制了无人机平台在大气环境检测领域中的广泛应用与发展。

当前而言,离线采样分析是无人机平台获取大气VOCs数据的最主要手段,离线采样方式同样还是以苏玛罐、Tedlar袋和吸附管等工具为主。此外,也有一些研究专门设计了针对无人机平台的VOCs观测技术或方法^[49-51]。比如,Zhou等人^[49]研发的空气检测传感器(Kolibri)是应用于无人机上的低成本检测传感器,它包括VOCs和颗粒物采集器以及黑炭分析仪。Chen等人^[50]设计用于无人机平台的苏玛罐采集系统,这种无人机有效载荷1 kg,能满足250 m以下采样需求。

1.5 遥感技术

遥感技术可以分为卫星遥感和地面遥感。地面遥感技术主要使用激光雷达遥感(lidar)和差分吸收光谱技术(DOAS)。卫星遥感是借助传感器对远距离环境辐射和反射的电磁波信号进行收集与处理^[52]。激光雷达遥感是向目标发射激光束,将反射信号与发射信号比

较并适当处理, 获取VOCs浓度的垂直分布数据^[53~55].

遥感技术作为长期稳定的监测手段, 能及时反馈地球大气中关键VOCs组分浓度的时空分布信息. 例如, 卫星遥感能够检测到乙二醛和甲醛的垂直柱浓度, 并且能够监测全球范围内VOCs浓度空间分布的实时变化^[56]. 但由于各类遥感技术的原理不同, 空气中的颗粒物和大气水汽等能对遥感信号造成干扰, 因此遥感技术的准确性受到限制^[57]. 此外, 使用遥感技术测量的VOCs种类受到限制, 目前遥感技术主要用于对流层大气中甲醛、乙二醛和一些芳香烃的测量^[58,59].

卫星遥感能长期监测大范围空间内的VOCs变化特征^[60], 常与模型计算结果进行对比分析, 以提高模拟结果的准确性^[61]. 比如, 借助卫星平台的高空间分辨率遥感数据, 研究人员能够有效分析区域燃烧源相关VOCs的排放清单并加以验证^[62]; DOAS通常用于测量区域甲醛和乙二醛的垂直柱浓度, 研究关于它们的大气化学过程^[63]; LiDAR不仅能测量VOCs, 也能测量气溶胶消光系数和臭氧浓度等多种大气痕量组分浓度的垂直分布数据, 为研究整个大气边界层内的VOCs化学过程提供更加充足的数据支撑^[64].

本节主要对现在大气环境领域中主要使用的5种VOCs垂直观测技术进行了简要介绍与分析, 不同观测方式的优缺点及其主要适用场景如表1所示.

2 VOCs垂直观测的应用进展

获取VOCs垂直分布数据的主要目的是, 解析大气边界层内不同VOCs组分理化特性的垂直分布特征及其环境效应. 因此, 本文对VOCs垂直观测数据在其垂直分布结构分析、排放通量测量、排放清单验证、臭氧生成敏感性分析和夜间VOCs氧化降解机制分析等五方面的研究进展进行总结分析.

2.1 VOCs垂直分布特征与关键影响因素

对于使用任何方式开展VOCs垂直观测实验而言, 分析VOCs物种的垂直分布特征及其关键影响因素通常是获取垂直观测数据之后的首要工作. 受到大气化学活性和地面排放源结构差异等因素的影响, 不同VOCs物种在边界层内的垂直分布结构也存在差异. 已有研究表明, 大气边界层内VOCs物种浓度的垂直分布结构与变化规律主要受以下三方面因素的影响.

(1) 地面污染源排放类型和排放强度影响. 地面VOCs主要来源可以分为天然源(如森林、海洋和农业

表1 各类VOCs垂直观测平台的优缺点汇总

Table 1 Summary of the advantages and disadvantages of the VOCs vertical observation platforms

垂直观测技术	优点	缺点
高层建筑物/ 高塔	测量成本低; 运营成本低; 适合长期稳定观测	受地理位置限制; 受建筑物最高高度限制
系留气球/ 飞艇	可以长期观测; 测量高度较高; 观测高度和场地选择灵活	不适合在城市地区测量; 受天气情况影响显著
载人飞机	测量范围大; 测量高度高; 载重大, 即可离线, 也可在线观测	使用与运营成本高; 边界层内观测样本较少; 飞机排放影响测量结果
无人机	灵活性高; 适用各种复杂地形条件; 观测和运营成本低; 适合长期观测	续航能力短; 有效负载低; 受空域管制影响显著
遥感技术	测量范围广; 测量分辨率高; 可作为长期观测平台	测量VOCs种类少; 测量数据的不确定性较高

相关排放等)^[65]和人为源(如工厂和机动车排放等)^[66]. 源排放类型分为移动源和固定源: 移动源(如机动车)影响地面VOCs浓度^[67]; 固定源除了影响地面VOCs浓度^[68]外, 也影响VOCs垂直分布^[69~71]. 如Wada等人^[69]发现富士山上的VOCs垂直分布结构受到周边森林排放VOCs影响; Zhang等人^[71]发现上海机动车排放高浓度的苯, 导致地面200 m内出现多个峰值. 当区域地面污染源排放结构存在显著差异时, 关键VOCs物种和其他污染物(如NO_x和一氧化碳等)的垂直分布结构也出现显著的空间分布差异^[72], 在区域污染物输送和大气化学过程的联合作用下, 导致边界层内不同VOCs物种浓度的垂直分布结构不同.

(2) 垂直湍流混合和水平输送影响. 垂直湍流混合包括大气边界层的发展与演变过程、垂直机械湍流混合(垂直风切变)和垂直热力湍流混合等^[73], 边界层过程能够显著影响VOCs浓度的垂直分布结构^[74]. 大气边界层的垂直混合^[75]、夜间逆温层的出现^[76]以及城市热岛^[77]等能够显著影响近地面大气的稳定状态, 进而影响边界层内VOCs浓度的垂直分布结构. 污染气团的水平输送主要受风速、风向和地面排放源空间布局等因素的影响, 风速风向^[78]影响VOCs覆盖范围, 污染气团的水平输送是影响高空VOCs浓度垂直剖面结构的重要原因^[79,80].

(3) 垂直空间尺度上的大气化学过程影响. 大气边

界层内VOCs浓度的垂直分布结构除了受大气物理过程(湍流传输和沉降等)的显著影响外,各类VOCs物种在垂直传输过程中的化学转化也是影响其垂直分布和变化的关键因素^[81]。在大气边界层内,VOCs主要与OH自由基和臭氧等大气氧化剂发生反应而被清除^[82],当大气氧化剂在垂直方向上出现不均匀分布时,各类VOCs物种在不同高度上的化学反应进程也显著不同。此外,不同VOCs物种的化学活性差异显著(主要体现在与OH自由基化学反应速率上),同样导致其在垂直方向上的浓度分布差异^[83]。已有研究表明,随着VOCs在垂直输送过程中的不断消耗,大气边界层内的VOCs浓度随高度增长主要呈现显著的下降趋势^[84]。

2.2 VOCs排放通量测量

地面VOCs排放通量的测量通常使用气象梯度观测塔^[81]、系留气球^[85]或载人飞机平台^[86]完成。VOCs排放通量计算方法主要有边界层梯度法、涡度相关法、质量守恒法以及模型计算。其中边界层梯度法和涡度相关法为直接测量方法,质量守恒法和模型计算为间接通量估算^[21]。

边界层梯度法根据同一时段不同高度上的VOCs物种浓度,计算不同VOCs物种的排放通量,多个垂直剖面的计算结果被证实更加具有区域代表性^[85];边界层梯度法测算VOCs排放通量通常依托气象塔和系留气球平台,离线采样和在线测量数据均可以使用。如Mo等人^[87]利用广州塔不同高度上的离线分析数据计算广州城区不同VOCs物种的排放通量;涡度相关法根据一个高度上VOCs浓度的高频(通常为10 Hz)在线观测数据,结合三维风速信息,计算区域不同VOCs物种的排放通量。涡度相关法测算VOCs排放通量通常依托高塔和载人飞机平台,如Acton等人^[88]和Squires等人^[89]利用气象塔测量计算了北京城市地区的VOCs排放通量;Yuan等人^[27]和Karl等人^[90]分别依托载人飞机平台测算了美国海恩斯维尔地区天然气和加利福尼亚地区VOCs排放通量。此外,载人飞机除了可以使用涡流相关法测算VOCs排放通量,也可以结合模型计算,如de Gouw等人^[35]采集了美国伊利诺伊州迪凯特上风向和下风向的VOCs数据,利用盒子模式计算区域VOCs通量。

2.3 区域VOCs排放清单验证

垂直观测除了能够应用于测算VOCs排放通量外,还可用于验证区域VOCs的源排放清单,包括对VOCs

排放总量验证、对VOCs来源贡献验证和对VOCs空间分布验证等。通过垂直观测进行区域排放源清单验证,观测点位高度不同,气团混合程度不同,能够表征VOCs排放特征的空间区域也显著不同;相对于地面点位观测(包括城市站点、远郊站点、农村站点和背景站点等)而言,观测点位远离地面的空间位置越高,污染物在气团中的混合程度越高,受局地排放源和地形地势的影响越小,观测数据的空间区域代表性越好^[70,72]。此外,VOCs排放源具有显著的空间分布差异,因此在评估源排放清单时,需要根据重点关注物种的主要排放特征,选择合适的观测方式和观测地点。比如,研究人员通常在远郊或森林地区使用系留气球、飞机和气象塔等平台的观测数据评估天然源VOCs排放清单^[69,91-93],在城市区域通常使用高塔平台的观测数据评估工业源和交通源排放清单^[94,95]。

验证区域VOCs排放清单是研究区域VOCs排放特征和变化规律的重要工作。根据需要重点评估的VOCs物种,选择合适的垂直观测技术和测量平台,获取VOCs物种浓度的垂直观测数据。然后,结合使用受体模型或三维空气质量模式,采用“自下而上”(bottom-up)方法,分析区域环境大气中各类VOCs物种的排放贡献。比如,Hu等人^[96-98]利用明尼苏达大学公共无线电通讯塔为平台,使用PTR-MS获取VOCs物种浓度的长期观测数据,结合使用戈达德地球观测系统模型的化学传输模式(GEOS-Chem),对所使用源排放清单中的甲醇、丙酮、异戊二烯、C6~C8芳香烃等物种的来源与排放强度进行验证与评估。Mo等人^[87]利用广州塔不同高度上的VOCs观测数据,采用混合层梯度法计算了广州城市区域不同VOCs物种的排放通量,并与已有研究中的排放清单进行对比,发现现有清单对城市区域地面VOCs(尤其是C2~C5烷烃)的排放通量存在严重低估。Mao等人^[99]利用中国科学院大气物理研究所(北京)气象铁塔的垂直观测数据,采用主成分分析方法对不同高度上的VOCs来源进行解析,也能达到验证区域排放源清单的目的。此外,VOCs垂直观测数据还可以用于验证VOCs组分的空间分布,包括对生物燃料燃烧烟羽在空中扩散过程^[100]、甲醛在大气中的空间分布等^[101]。这能够为研究大气中VOCs的传输与转化及其环境效应提供有力支撑。

2.4 光化学臭氧生成敏感性的垂直分布机制研究

VOCs和NO_x是对流层大气中臭氧的重要前体物,

并且臭氧浓度变化与之存在显著的非线性响应关系^[102,103], 当大气中VOCs和NO_x浓度比例发生显著变化时, 光化学臭氧生成敏感性也随之发生变化^[104]. 也有研究表明, 臭氧生成敏感性除了呈现出显著的水平空间分布差异外, 在边界层内也同样呈现垂直分布差异. 图4为已有研究中给出的边界层内臭氧生成敏感性变化示意图^[105]. 由于缺乏充足的VOCs垂直观测数据, 已有研究主要使用大气化学模式开展边界层内臭氧生成敏感性的垂直分布研究, 但是相关研究结论还未有充足的观测事实支撑^[106~108]. 因此, 充分了解大气边界层内光化学臭氧生成敏感性的垂直分布机制, 及其对地面环境大气中臭氧变化的影响与贡献, 是深入解析区域臭氧污染形成机制的重要前提, 但获取充足有效的VOCs垂直观测数据是基础.

除了空间分布差异, 光化学臭氧生成敏感性也存在显著的时间分布特征^[109]. 因此, 使用在线垂直观测技术获取长时间内具有较高时间分辨率的VOCs垂直分布数据, 是研究大气边界层内臭氧生成敏感性垂直分布的重要基础. 此外, 随着边界层高度增加, 光照条件更加有利, 地面环境大气中的VOCs和NO_x浓度虽然较高, 但有效光照强度不足, 因此一些VOCs随高度的增加而更加有利于臭氧生成^[110]. 目前, 我国许多地区均面临严重的臭氧污染问题, 获取高时间分辨率的VOCs垂直分布数据, 解析大气边界层内光化学臭氧生成敏感性的垂直分布特征, 及其对地面环境大气中臭氧浓度变化的贡献与影响机制, 是制定有效污染防治措施的重要前提.

2.5 夜间边界层内VOCs氧化降解过程的垂直分布研究

目前对VOCs氧化降解过程的垂直观测研究更多是基于白天时段内的观测数据, 而对于夜间边界层内VOCs化学过程的研究报道则相对较少. 与白天边界层结构不同, 夜间边界层更稳定, 地面辐射冷却产生的逆温在很大程度上抑制了VOCs在近地面大气中垂直方向上的输送与扩散. 但是, 也有研究表明^[111], 尽管夜间时段内的大气稳定度较高, 但许多大气化学组分(例如臭氧和NO₃自由基等)在垂直方向上的传输作用仍然显著. 如图5所示, 在白天时段内, VOCs主要与OH自由基反应而逐步降解^[112]. 而在夜间时段内, VOCs主要参与NO_x化学循环^[113], 与臭氧和NO₃自由基反应, 生成有机硝酸酯和含氧挥发性有机物(OVOCs)等. 该过程在夜

图4 (网络版彩色)VOCs与臭氧生成敏感性关系图^[105]. BLH, 边界层高度; RH, 相对湿度; TMP, 温度

Figure 4 (Color online) The relationship between VOCs and ozone generation sensitivity^[105]. BLH, boundary layer height; RH, relative humidity; TMP, temperature

间残留层大气中更为显著^[114].

夜间VOCs垂直分布研究难点在于, 缺乏有效垂直观测数据和难以模拟的夜间边界层过程. 虽然夜间VOCs氧化过程的垂直分布研究已有一定进展^[115], 但夜间边界层和残留层内VOCs氧化降解过程对地面环境空气质量的潜在影响仍需开展深入研究. 此外, 由于NO_x和五氧化二氮在环境大气中的测量难度较大^[116], 并且对某些关键VOCs物种的降解机制尚不完全清晰, 导致对夜间VOCs化学过程的认知仍然存在显著不足^[117]. Brown等人^[118]和Osthoff等人^[119]在北美洲和亚洲等地开展过多次夜间VOCs垂直观测研究, 并总结了夜间自由基化学, 为研究夜间大气化学过程提供了部分理论依据和数据支撑^[117]. 此外, 除了夜间大气的垂直输送作用之外, VOCs在夜间残留层中的氧化降解产物能够在白天时段内随着边界层的扩展而被输送至地面, 进而影响地面环境大气中的臭氧和SOA等二次污染物的生成与浓度水平. 因此, 使用在线垂直观测技术获取夜间大气边界层内各类VOCs物种的高时间分辨率垂直观测数据, 研究残留层大气中关键活性VOCs物种的主要氧化降解通道, 及其关键氧化产物对白天地面大气中主要二次污染物的生成影响, 同样是制定区域大气二次污染的重要工作.

3 总结与展望

本文对目前研究中主要使用的VOCs垂直观测平台(技术)进行了简要总结与分析, 各种垂直观测平台的优缺点各异, 但在实际环境大气观测中均有重要应用. 随着VOCs质谱分析技术的快速发展, 大气边界层内VOCs的垂直观测逐渐以离线采样分析转变为在线测

图5 (网络版彩色)昼夜大气化学循环示意图^[112]

Figure 5 (Color online) Schematic of the atmospheric chemical cycles in both day and night^[112]

量分析为主, 观测数据的时间分辨率更高, 能够有效量化分析的VOCs物种更多. 此外, 随着无人机技术的快速发展, 基于无人机平台的VOCs垂直观测与分析技术在大气环境监测领域具有较好的应用前景. 与传统地面观测数据相比, 大气边界层内的VOCs垂直观测数据有助于深入解析区域地面VOCs来源贡献, 分析各类VOCs物种在整个大气边界层内的化学行为, 及其对地面环境空气质量的影响机制, 为区域大气二次污染防治和空气质量管理措施的制定提供有效支撑.

此外, 随着我国空气污染治理强度的不断加大, 一次排放污染物的环境浓度水平不断下降, 以VOCs为主

要前体物的二次污染物(如臭氧和SOA等)已经逐渐成为影响许多区域空气质量持续改善的重要大气污染组分. 在未来大气污染防治和环境空气质量预警与预报工作中, 实时有效且充足可靠的VOCs垂直观测数据必不可少, 但是目前已有的观测技术或方法还难以快速提供多点位、多物种VOCs浓度的垂直观测数据. 因此, 应该着重发展轻型便捷且便宜可靠的VOCs在线分析仪器, 使其既能够作为常规设备应用于高塔平台, 也能够有效应用于无人机和系留气球等灵活度较高的垂直观测平台, 以满足研究和业务人员对高时间分辨率VOCs垂直观测数据的需求.

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Summary for “大气边界层内挥发性有机物的垂直观测方法及应用进展”

Progress on the vertical observation methods of volatile organic compounds and their applications within the atmospheric boundary layer

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Volatile organic compounds (VOCs) are important trace gases in the troposphere that play vital roles in the formation of secondary air pollutants such as ozone and organic aerosol components. An in-depth characterization of the spatiotemporal variability, particularly in three-dimensions, of VOCs in the atmospheric boundary layer is an essential prerequisite for understanding the formation mechanisms of regional pollution episodes. However, vertically resolved VOCs measurements are seldom made during field campaigns due to the limitation of available observation techniques. This review summarizes the progress in vertical observation of VOCs and their applications to the atmospheric boundary layer, focusing on the introduction of platforms for vertical measurement techniques for VOCs, including high-rise buildings, tethered balloons, aircraft, unmanned aerial vehicles (UAVs), and remote sensing. All of these platforms have been used in previous studies and have their respective advantages and disadvantages. High-rise buildings are generally characterized by low altitudes and fixed locations but could serve as long-term platforms for both online and offline VOCs measurements. Tethered balloons, generally used for offline VOCs measurements, have flexible launch locations and altitude ranges. Aircraft can provide platforms for both offline and online VOCs measurements over large spatial scales, but aircrafts are not suitable for long-term observations because of their high operating cost. Similar to tethered balloons, UAVs are used for offline VOCs measurements, while they are much more flexible in utilization and can be launched in complex environments. However, small payload, short flight duration, and availability of airspace are key factors that limit the wide application of UAVs in the field of environmental monitoring. Remote sensing platforms (including ground-based and space-based techniques) could provide vertical measurements of several VOCs species over large temporal and spatial scales. However, the vertical VOCs profiles provided by remote sensing techniques are frequently characterized by large uncertainty. With the rapid development of VOCs measurement techniques (such as UAVs and proton-transfer-reaction time-of-flight mass spectrometry), future studies are expected to obtain vertical VOCs observations with higher spatiotemporal resolutions as well as lower operating costs. Vertical observations of VOCs concentrations could provide valuable opportunities for a thorough analysis of VOCs emissions and variation of their related chemical processes within the atmospheric boundary layer. Therefore, this review also summarizes the progress in applications of vertical VOCs observations in the atmospheric boundary layer, focusing on introducing the key factors influencing VOCs vertical distribution patterns, determination of VOCs emission fluxes, evaluation and calibration of VOCs emission inventories, investigation of the vertical distribution of photochemical ozone production sensitivity, and the vertical distribution of VOCs degradation mechanisms at night. At present, vertical observations are predominantly used to identify impacts of transport and boundary-layer dynamics on the vertical distributions of different VOCs species and to estimate speciated VOCs emissions. However, the vertical variability of the oxidation and degradation mechanisms for different VOCs species and the environmental effects of this variability have been reported in only a few studies. More effort should be made to elucidate how the interactions between VOCs chemistry and vertical transport affect the formation and concentration of secondary air pollutants at ground level. In summary, there is an urgent need to obtain reliable vertical observations of key VOCs species in the atmospheric boundary layer for better investigating the formation mechanisms of regional atmospheric pollution.

planetary boundary layer, volatile organic compounds, vertical distribution, secondary pollution

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