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城市植物挥发性有机化合物排放与臭氧相互作用及其机制

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摘要: 近地面臭氧(O_3)已成为继 $PM_{2.5}$ 后影响我国空气质量的一种重要二次污染物。随着氮氧化物浓度的持续下降和气候变暖的加剧, 城市 O_3 的形成对挥发性有机化合物的浓度更加敏感。近年来城市绿色空间显著增长, 植物源挥发性有机化合物(BVOCs)排放和浓度逐年增加。针对 BVOCs 与近地面 O_3 之间复杂的交互作用, 从植物 BVOCs 的特性与作用出发, 综述了不同因素尤其是 O_3 浓度增加对树木生理状态及 BVOCs 排放速率的影响, 定量分析了已有研究中 O_3 对不同植物异戊二烯和单萜烯排放速率的影响, 以及 BVOCs 对 O_3 形成的贡献, 总结了 BVOCs 与 O_3 相互作用研究领域存在的不足。未来亟需加强的研究包括: (1) 城市树种 BVOCs 排放因子的实测, 建立物种的排放速率数据库, 优化模型参数, 提升精细尺度 BVOCs 排放量估算模型精度; (2) 多种环境因子, 比如污染物浓度、温湿度等对城市植物 BVOCs 排放的交互作用和综合影响的研究; (3) 植物 BVOCs 对 O_3 形成贡献的定量研究, 及其对植物抗污染能力的影响, 为城市建设中的树种选择及减轻城市 O_3 污染提供理论依据和借鉴。

关键词: 植物源挥发性有机化合物(BVOCs); 臭氧; 城市植物; 异戊二烯; 单萜烯

The interactions and mechanisms between biogenic volatile organic compounds emissions and ozone concentrations in urban areas: A review

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Abstract: In China, surface ozone (O_3) has become a major secondary pollutant as the fine particulate pollution problem was largely addressed. As nitrogen oxide concentrations continue to decline and climate warming intensifies, urban ozone formation becomes more sensitive to VOC emissions. With the continuous increase of urban green space in recent years, the emissions of Biogenic Volatile Organic Compounds (BVOCs) have also increased, and thus played an increased role in ozone formation. This paper presented a comprehensive review of the interactions and mechanisms between BVOCs emissions and ozone concentrations in urban areas. We first reviewed the current states and trends in the response of plant

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physiological state and BVOCs emission rate to environmental stress, especially the elevated O_3 concentration, with a particular emphasis on previous studies that focused on the effects of O_3 on isoprene and monoterpene emission rates of various plants. We then summarized the role of BVOCs plays in O_3 formation. Based on the review of the existing studies, we found a few knowledge gaps and identified several priorities for future research: (1) studies on quantifying the BVOCs emission rate of different urban tree species to build a more comprehensive database for BVOCs emission rate that can be used to optimize the parameters of BVOCs emissions models, and thereby to improve the precision of the fine-scale BVOCs emission estimation; (2) Exploring the interaction and comprehensive influence of various environmental factors on BVOCs emissions from urban plants, such as pollutant concentration, temperature, and humidity; (3) Quantifying the contribution of plant BVOCs to O_3 formation and its effect on plant resistance to air pollution, which aims to provide a theoretical basis and reference for the selection of tree species for urban greening and the reduction of urban O_3 pollution.

Key Words: biogenic volatile organic compounds; ozone; urban plants; isoprene; monoterpene

我国众多城市存在近地面臭氧(O_3)浓度超标问题, O_3 已成为继 $PM_{2.5}$ 后影响我国空气质量的另一种重要二次污染物,在部分城市已经成为首要污染物^[1-2]。近地面 O_3 作为一种强氧化剂不仅会影响农业生产,对人体健康也会产生较大的危害^[3], O_3 浓度增加会导致过早死亡人数增加^[4]。 O_3 的生成与其前体物挥发性有机化合物(VOCs)、氮氧化物(NO_x)浓度及其比例密切相关^[1,5]。近年来我国 NO_x 排放控制卓有成效,而 VOCs 排放量巨大,其来源构成复杂,减排难度较大,使得 VOCs 与 NO_x 减排比例失衡,是造成 O_3 污染加剧的重要因素^[6-7]。因此, O_3 污染调控需注重 VOCs 和 NO_x 的协同控制,尤其是加大 VOCs 的减排力度。

VOCs 是易挥发碳氢化合物的总称,主要释放源包括人为源和植物源。植物源挥发性有机化合物(BVOCs)是指植物器官(叶、花、果实等)通过次生代谢途径合成的低沸点、挥发性强的不同种类碳氢化合物总称^[8-9]。据统计,全球植物释放的 VOCs 种类有 30000 多种^[10],年排放量约占全球挥发性有机化合物年排放总量的 90%,远超人为源挥发性有机化合物(AVOCs)的年排放量^[11]。因此,BVOCs 对 O_3 形成的贡献不容忽视^[12]。

BVOCs 对 O_3 形成的贡献,在城市地区受到高度关注。虽然在城市地区 BVOCs 的排放低于 AVOCs^[13],但 BVOCs 的化学活性较高,可以被羟基氧化并影响大气的氧化能力^[14]。受城市复杂环境影响,异戊二烯在城市中产生 O_3 的效率是在农村地区的两倍,随着 NO_x 排放的逐年减少,城市建成区内部绿地排放的异戊二烯对城市地区 O_3 形成的贡献超过来源于非城市地区传输的异戊二烯^[7]。此外,城市中促进植物释放 BVOCs 的环境条件,比如城市高温,也会促进 O_3 的生成^[15],从而加剧 O_3 污染。例如,受城市热岛效应影响,市中心较高的空气温度会导致更高水平的 BVOCs 释放,进而导致 O_3 浓度升高,而随着全球气候变暖,这种效应会进一步增强^[16]。热浪期间, O_3 浓度经常会升高,达到或超过世卫组织设定的 O_3 暴露阈值^[16-19]。近年来,随着城市居民对人居环境改善需求的增加,城市增大了生态建设的力度,城市绿色空间增长显著,城市绿地的增长速度甚至超过了城市人口的增长速度^[20]。随着城市绿地的增加,城市 BVOCs 的排放也呈现逐年增加的趋势^[21-22],有可能对城市中 O_3 的生成带来更大的影响。尤其是,城市绿化过程中不合理的植物选择、配置可能会进一步增加 BVOCs 的排放^[23],从而加剧 O_3 污染^[7]。

BVOCs 与 O_3 之间具有复杂的相互作用关系。BVOCs 是近地面 O_3 形成的重要前体物,对 O_3 的生成有较大的贡献。其中占比较高的异戊二烯类与单萜类化合物具有较高的化学反应活性,能与 O_3 反应,影响大气的氧化性质。已有研究显示,植物释放的 BVOCs 对近地面 O_3 生成的贡献不容忽视。与此同时,植物本身具有一定的吸收 O_3 的能力,可以通过气孔和非气孔机制吸收 O_3 以改善环境空气质量。BVOCs 通过叶子细胞间隙和植物外部环境空气中的气相化学反应,在去除 O_3 方面也发挥着关键作用^[24]。在 O_3 胁迫下,不同城市植物的 BVOCs 排放会如何变化?如何影响 O_3 生成?回答这些问题对于城市树种的优化配置非常重要。围绕上

述问题,本文从植物 BVOCs 的特性与作用出发,综述了 BVOCs 和 O_3 两者之间的相互作用与机制研究的最新进展,进而分析了相关研究存在的不足和未来亟需加强的研究,以期为建设中的树种选择及减轻城市 O_3 污染提供理论依据和借鉴。

1 BVOCs 的种类、作用及特性

根据 BVOCs 的特性,将其分为 4 类^[11],其对植物生理及人体健康均具有重要的作用。此外, BVOCs 具有很高的化学反应活性,对流层大气化学过程起到重要的作用。尤其是占比较高的异戊二烯和单萜烯,对近地面 O_3 的形成有较高的贡献,有许多研究对其合成机理及特性进行了探究。

1.1 BVOCs 的种类及作用

Guenther 等^[11]学者依据 BVOCs 的化学结构、活性以及其在大气中的滞留时间等特性将其分为 4 类:异戊二烯类、单萜类(α -蒎烯、 β -蒎烯、柠檬烯等)、其他活性 VOC(甲基丁烯醇(MBO)、乙烯醛、有机酸、羰基化合物等)、其他次活性 VOC(甲醇、乙醇、丙酮等)。其中异戊二烯类与单萜类化合物占比较高,且具有很高的化学反应活性,在对流层大气化学过程中具有重要作用。相较于异戊二烯类和单萜类化合物,另外两类 VOC 在大气中的滞留时间更久,在典型的对流层条件下,其他活性 VOC 的寿命小于一天,而其他次活性 VOC 的寿命大于一天^[11]。BVOCs 对植物生理及人体健康均具有重要的作用。

BVOCs 对植物的生理生态具有重要的影响。除丙酮、甲醇等作为代谢废物排放到体外, BVOCs 是植物体内重要的信号传递物质,在植物的生长、繁殖、发育、抵御生物胁迫和非生物胁迫等方面具有重要作用^[25-26];植物释放的单萜类物质能够防御昆虫及哺乳动物的取食^[27],防御以昆虫为载体的细菌和植物体内潜在的致病菌的侵害^[25],能够引诱害虫天敌和传粉昆虫;异戊二烯能够保护植物免受高温和强光的伤害^[28]。

BVOCs 对人体健康也具有重要影响。随着对 BVOCs 生理和生态作用的认识,人们开始研究 BVOCs 与人体健康之间的关系^[29]。近年来, BVOCs 的提取、分离和鉴定等方面取得了突破性进展, BVOCs 对人体健康的作用从机理上得到了证实。一方面, BVOCs 具有抗菌、抑菌,消除疲劳、促进安眠,提神醒脑,解除紧张状态等作用^[30-33]。比如,蜡菊(*Helichrysum araxinum*)对葡萄球菌分离株有一定的抑菌活性^[34],而针叶树释放的 BVOCs 能使人体处于放松状态,缓解紧张情绪。另一方面,部分 BVOCs 对人体有害,过量吸入可能会引起肺部疾病,损伤中枢神经系统,甚至致癌致畸^[32]。例如,实验表明,珍珠梅鲜花和暴马丁香鲜花释放的 BVOCs 对小鼠的学习记忆能力、探索性、兴奋性及运动性有抑制作用^[33]。

由于 BVOCs 具有高反应活性,其在对流层大气化学过程中起到十分重要的作用,具体包括:(1)增加了近地面 O_3 的浓度^[35]。BVOCs 是 O_3 形成的前体物之一,能够与 NO_x 以及 O_3 的光解产物发生光化学反应形成 O_3 ,研究表明,与 AVOCs 相比, BVOCs 的 O_3 形成潜能约占一半^[14],对近地面 O_3 的形成具有较高的贡献。(2)通过与大气中的 O_3 、羟基自由基等氧化性物质的反应形成次级有机气溶胶(SOA)^[36],同时减小了大气的还原性^[28]。SOA 的形成影响地球系统的辐射平衡,且增加大气中云凝结核的浓度^[37]。大气还原性的减小,使甲烷等温室气体滞留时间延长;(3)增加偏远地区的酸沉降^[38]。BVOCs 在 NO_x 存在下可被氧化形成各种寿命相对较长的有机硝酸盐,在被分解前可进行远距离运输,以造成偏远地区的酸沉降及 NO_x 的远距离运输;(4)影响 CO 形成从而影响全球碳循环^[28]。光化学反应是大气中 CO 的重要来源之一,而 CO 是影响羟基自

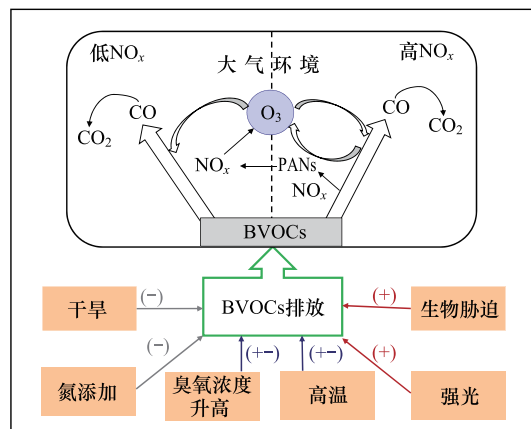


图1 BVOCs 排放对环境因素的响应及其与 O_3 相互作用

Fig.1 BVOCs emissions responses to environmental stress and its interaction with O_3

BVOCs: 植物源挥发性有机化合物 Biogenic volatile organic compounds

由基浓度的重要微量气体之一, BVOCs 参与光化学反应影响 CO 形成, 从而影响碳循环^[38]。

1.2 典型 BVOCs 的合成机理及特性

异戊二烯及单萜烯是主要的两类 BVOCs, 其中异戊二烯全球年排放量占全球植物总 BVOCs 年排放量的近一半, 单萜约占十分之一^[11]。除占比较高外, 这两类化合物的反应活性较强, 具有较高的 O₃ 生成潜力。有许多研究对两者的合成机理及特性进行探究, 异戊二烯合成主要采用甲羟戊酸 (MVA) 途径和丙酮酸/磷酸甘油醛 (MEP) 途径^[39-40], 单萜类化合物仅通过甲羟戊酸途径合成^[41]。除合成途径不同外, 两者的排放机制也存在差异, 异戊二烯在叶绿体内即时合成即时排放^[42], 仅在白天排放, 晚上排放量基本为零, 而部分单萜烯合成后可存储在特殊器官中。因此异戊二烯的释放速率与光合有效辐射 (PAR) 关系密切, 光照影响腺嘌呤核苷三磷酸 (ATP)/二甲基烯丙基二磷酸酯 (DMAPP) 的合成, 间接控制异戊二烯合成酶的活性, 随着光照的增强, 异戊二烯的释放速率迅速增加^[43]。而叶片内单萜合成酶的活性受光强的影响较小, 多数试验表明, 晚上单萜烯的排放量变化不明显^[44], 但罗勒烯的释放速率受 PAR 影响强烈^[42]。近期有研究表明部分植物合成单萜类也受光照影响^[45]。

温度是影响植物释放异戊二烯与单萜烯的另一重要因素, 温度通过增强合成酶的活性, 升高 BVOCs 蒸气压, 以及降低扩散路径的阻力, 提高释放速率^[41], 当温度升高至一定程度后, 其速率会下降^[46-48]。相比于异戊二烯, 温度对单萜烯的影响更大, 两者之间呈较好的指数关系^[49]。

异戊二烯和单萜烯是最常见的植物源挥发性有机化合物, 在生产甲基乙烯基酮 (MVK)、甲基丙烯醛 (MACR)、羟基氢过氧化物 (ISOPOOH)、甲醛 (HCHO) 等主要的化学氧化剂的过程中起着重要的作用^[50]。O₃ 的形成潜力一定程度上取决于 VOCs 的反应活性, 不同化合物的反应活性不同。异戊二烯是 66 种 VOC 中羟基自由基 ·OH 反应活性最高的^[51], 其反应活性比是 AVOCs 苯的 22 倍^[51-52]。当气温超过 30℃ 时, 异戊二烯的 ·OH 反应活性是苯的 443 倍^[51]。在夏季与秋季的白天, 植物源异戊二烯浓度高于人为源异戊二烯, 同时白天残留的异戊二烯为夜间贡献了很大一部分, 残留的大部分是生物源的异戊二烯^[53]。在城市环境中, 植物源异戊二烯与人为源异戊二烯协同作用下, 对近地面 O₃ 的形成有更高的贡献^[14], 因此需要进一步关注 BVOCs 的释放。

2 影响植物释放 BVOCs 的主要因素

不同植物在不同环境中释放 BVOCs 的速率与组分不同, 与环境的差异及植物的遗传变异有关^[54]。影响植物释放 BVOCs 的内部因素主要包括: 树种、树龄、叶龄、芽期、花期等; 环境因素主要包括光照、温度、湿度、氮素、二氧化碳、生物胁迫、O₃ 等。随着 O₃ 污染的加剧, 其对植物释放 BVOCs 的影响受到广泛的关注。

2.1 影响植物释放 BVOCs 的内部因素

不同植物释放 BVOCs 的速率、组分差别很大。排放 BVOCs 的树种主要是落叶树种和针叶树种如栎属、杨属、柳属、桉属、云杉属等^[55-58]。其中柳属、杨属、栎属的大部分种类异戊二烯的排放高, 而桦属、松属等多为萜烯类化合物释放者^[59-60]。部分属不同种植物 BVOCs 释放速率也存在差异, 通过测量柳属 4 个不同品种柳树的 BVOCs 排放, 发现 4 个品种柳树的异戊二烯、单萜烯、倍半萜的释放速率均存在差异^[54]。

单个植物的不同发育阶段也会对 BVOCs 的释放有一定影响, 相较于成熟阶段, 小麦在衰老阶段的 BVOCs 总排放量增加了两倍^[61]。树龄、叶龄、是否处于花期等因素也影响植物 BVOCs 的释放。幼苗比成熟植株更脆弱, 因此会释放更多 BVOCs 以提高存活率, 未成熟叶片的总挥发物浓度高于成熟叶片^[62], 且植物幼叶相较于成熟叶有更高的 BVOCs 排放速率, 由于新枝叶较薄的表皮厚度会导致较高的排放速率^[63-66]。成年树相较于幼树有更高的排放速率, 而排放的 BVOCs 组分是相似的^[54, 65]。是否处于开花期同样会影响植物的 BVOCs 排放速率, 美国皂荚 (*Gleditsia triacanthos*)、海棠 (*Malus spectabilis*) 等植物开花期的总单萜排放速率高于开花后, 通过自然气体和气溶胶排放模型 (MEGAN) 模拟发现, 春季开花期间花卉的 BVOCs 排放量约占该研究区总单萜的 11%^[67]。

2.2 影响植物释放 BVOCs 的环境因素

植物释放 BVOCs 受到许多环境因素的影响。光照和温度影响大部分植物 BVOCs 的释放速率^[68],主要通过影响合成酶的活性影响 BVOCs 的排放,与植物节律也有一定的关系^[69]。增温一般对植物 BVOCs 的释放具有促进作用,由于瞬时温度效应,随着气温升高,能显著增加植物释放的萜烯类化合物浓度^[66],但如果植物长期受高温胁迫,可能会影响植物的防御能力^[70],从而降低植物的萜烯类化合物释放。例如,生长季增温增加了挪威云杉针叶中单萜烯的浓度,但随着云杉的生长,单萜烯排放速率下降^[71]。光照则主要影响异戊二烯合成酶的活性,随着光照的增强,异戊二烯的排放速率显著升高,除罗勒烯外,大部分单萜烯的排放受光照的影响较小。

食草^[72]、真菌或细菌感染^[73-74]等生物胁迫及干旱^[75]、重金属^[76]等非生物胁迫均会诱导植物释放绿叶挥发物(GLVs),GLVs 是构成 BVOCs 中的重要组成部分,植物在受到机械损伤^[77]和生物胁迫时几乎立即释放 GLVs 以防御草食动物的啃食和病原体的侵入,并对细菌和真菌产生直接的毒性作用^[78]。减少食草动物的啃食显著降低植物 BVOCs 的排放量^[70]。

此外,湿度、氮素、二氧化碳等因素均对植物释放 BVOCs 有一定的影响。不同植物受湿度的影响不同,部分树种释放速率随着环境湿度增加而逐渐增加^[79-80],但有些树种对环境湿度的变化不敏感,甚至随着湿度的增加而降低;Caser 等^[81]研究发现干旱胁迫会调节丹参体内与 BVOCs 有关基因的表达,特别是引起倍半萜产量的增加。施氮对植物 BVOCs 释放的影响结果存在较大不确定性^[82],叶面施氮与土壤施氮对植物 BVOCs 释放的影响不同^[83],如对于马尾松(*Pinus massoniana* Lamb.),土壤施氮能显著增加总 BVOCs 排放量,而叶面施氮无显著影响。目前研究表明,施氮对植物 BVOCs 的影响具有化合物特异性^[49],已有研究显示叶片氮素浓度与植物叶片异戊二烯释放呈显著正相关^[84],但对于萜烯类物质的影响较为复杂,大部分研究结果显示氮添加显著降低植物萜烯类物质的释放^[85-87]。然而,Carriero 等^[88]关于苏格兰松(*Pinus sylvestris*)的研究表明,氮添加对于萜烯类物质的作用并不一致^[89],氮添加对蒎烯有显著抑制作用,但能刺激己醛、DMNT((E)-4,8-二甲基-1,3,7-壬三烯)等 BVOCs 的释放。二氧化碳对 BVOCs 释放的影响,目前不同研究结果不同,存在一些争议,有部分研究显示高浓度二氧化碳可以促进部分植物 BVOCs 的排放,但一些研究表明高浓度二氧化碳熏蒸可以抑制 BVOCs 的排放,也有研究显示 BVOCs 对二氧化碳浓度变化不敏感^[50,90-92]。环境因子除影响叶片 BVOCs 的释放外,部分环境因子对根际 BVOCs 的释放也有影响^[71],例如氮添加、变暖会减少了苏格兰松(*Pinus sylvestris*)根际 BVOCs 的排放总量^[93];单次暴露的动物啃食会增加根际 BVOCs 的排放,但长期胁迫下,相较往年会减少根际 BVOCs 的排放^[94]。

近年来,随着近地面 O₃ 浓度的增加,越来越多的研究关注 O₃ 浓度增加对植物、环境、人体健康等的影响, O₃ 的峰值浓度不仅会导致叶片损伤和抑制植物生长,还会影响包括 BVOCs 在内的次生代谢产物的合成和释放^[8]。由于 BVOCs 对大气光化学过程的重要影响以及 O₃ 与 BVOCs 之间复杂的相互作用关系, O₃ 胁迫对植物 BVOCs 释放的研究受到日益广泛的关注。

2.3 O₃ 对植物 BVOCs 排放的影响

通过对已有文献进行检索,获取 O₃ 单因子及复合因子胁迫相关研究,通过式(1)将对照组与实验组的速率进行比较分析,得到 BVOCs 速率增减的比例(图 2)。结果显示, O₃ 胁迫产生的抑制作用在异戊二烯释放上更明显,对于单萜烯的释放更多为促进作用。

$$R = \frac{E_e}{E_c} - 1 \quad (1)$$

式中, R 表示 BVOCs 速率增减的比例, E_e 表示实验组速率, E_c 表示对照组速率。

高浓度的 O₃ 暴露通常会抑制异戊二烯,但不同树种的抑制不同。例如,在高浓度 O₃ 刺激下,番茄(*Solanum lycopersicum* L. var. Tiny Tim.) BVOCs 释放量显著增加^[95],高浓度 O₃ 刺激并不影响白松(*Pinus halepensis* L.)释放 BVOCs^[96]。而我国长三角地区落叶阔叶林的异戊二烯排放量由于 O₃ 暴露受到抑制^[5]。

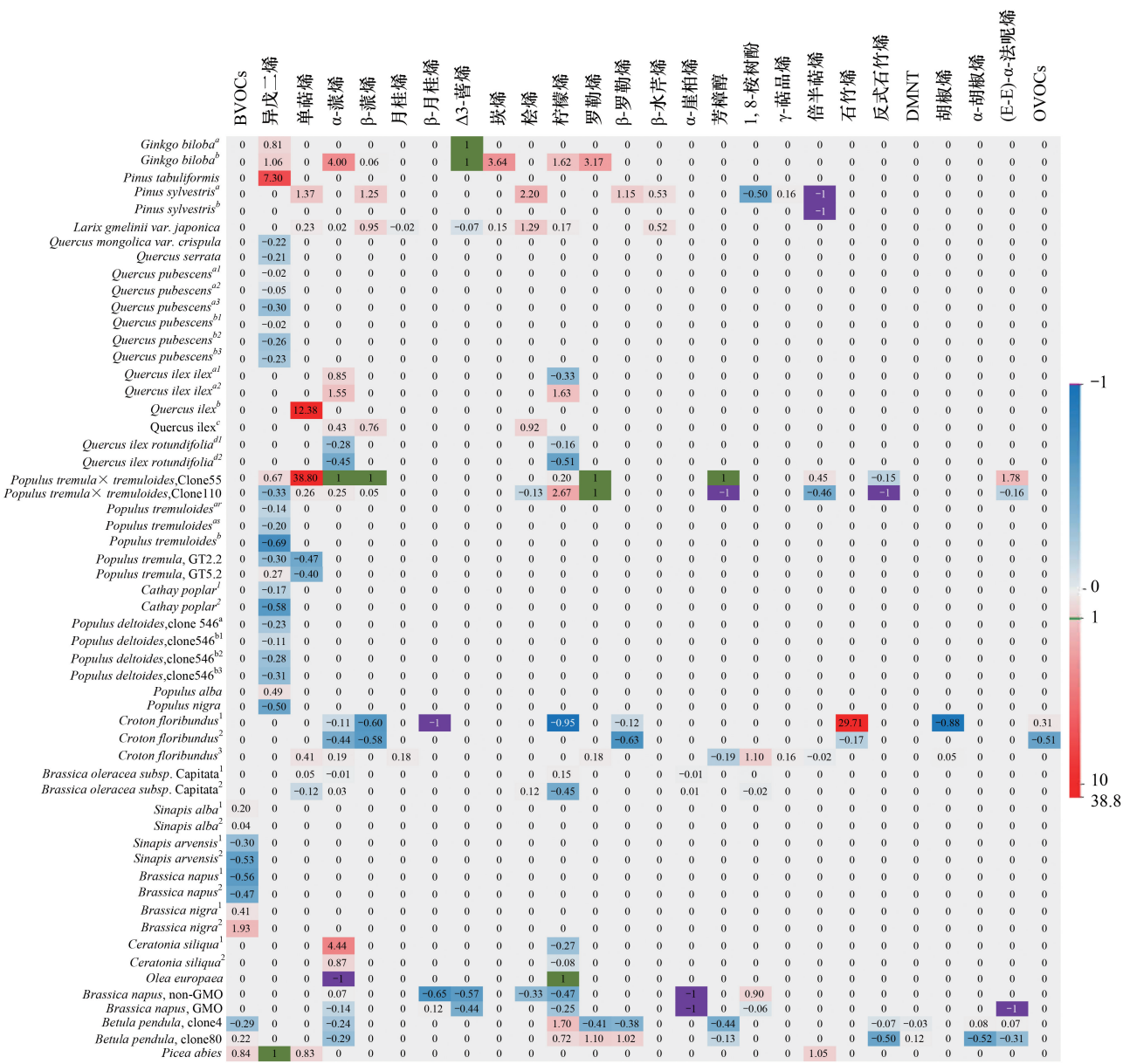


图2 O₃对不同植物 BVOCs 排放速率的影响

Fig.2 The effects of ozone on BVOCs emission rates among species

图中数字为 BVOCs 速率增减的比例,数字-1 表示对照组检测到排放,实验组未检测到排放;数字 1 表示对照组未检测到排放,实验组检测到排放;角标:r-O₃耐受种,s-O₃敏感种;字母区分多篇文献中的同一物种;数字区分 O₃浓度,数字越大浓度越大。涉及的植物物种学名、拉丁名及文献来源见表 1;DMNT:(E)-4,8-二甲基-1,3,7-壬三烯;OVOCs:其他挥发性有机化合物

植物对 O₃不同的响应主要取决于植物释放的 BVOCs 类型^[97],O₃暴露浓度、时间^[98—99],植物类型^[100—101],以及植物叶片的不同生长阶段^[102]等因素。短期 O₃暴露与长期 O₃暴露对植物 BVOCs 释放的影响不同。玫瑰花卉的倍半萜烯释放速率在急性 O₃暴露下增加,而长期暴露使其单萜烯与倍半萜烯释放速率均下降,受合成酶底物的限制^[103],且在长期暴露下植物将 BVOC 排放改为含氧和反应性较低的化合物。某些植物在长期 O₃熏蒸条件下会促进异戊二烯的排放,高浓度 O₃刺激其防御机制。单萜排放对长期暴露于 O₃的敏感性较低,对急性暴露应激反应较大^[104],由于其合成后存储在植物中。春季,O₃浓度升高降低了挪威云杉(*Picea abies*)和苏格兰松(*Pinus sylvestris*)地上部分 BVOCs 的排放量,因为植物的休眠恢复受到抑制^[105];夏季的结果与之相

反,两个物种地上部分的 BVOCs 的排放都随着 O₃的增加而增加,此时,O₃诱导的单萜烯释放是主要的挥发性防御反应。此外,O₃还会增强变暖对植物 BVOCs 排放的刺激作用,植物通过加快发育增加了合成萜烯类化合物的能力,以保护植物免受高浓度 O₃胁迫的影响^[66]。

已有部分研究对 O₃影响异戊二烯排放的生理生化机制进行了探究。O₃会破坏/抑制 BVOCs 合成酶活性从而影响 BVOCs 的释放,通过影响叶片表皮蜡的生物合成,从而影响 BVOCs 的释放,但 O₃还可能影响植物的信号转导途径,从而诱导 BVOCs 的产生^[106]。在低每小时臭氧浓度超过 40nmol/mol 部分的积累值(AOT40)下,随着 O₃暴露的增加,异戊二烯的排放量有一定的增长,但随着 O₃暴露的增加,异戊二烯的排放量总体呈线性下降,这可能是由氧化防御机制引起的^[5,107]。O₃暴露可能导致胞间二氧化碳的增加,并增加产生异戊二烯所需的磷酸烯醇丙酮酸盐的消耗,从而降低异戊二烯的排放速率^[98]。异戊二烯排放的减少也可能是由于抑制了蛋白质合成的表达和活性^[108]。

表 1 实验植物基本信息
Table 1 Basic information of experimental plants

物种 Species	重复次数 Repetitions	文献来源 References	物种 Species	重复次数 Repetitions	文献来源 References
银杏 <i>Ginkgo biloba</i> L.	3,4	[97,109]	黑芥 <i>Brassica nigra</i>	5,4	[100—101]
油松 <i>Pinus tabulaeformis</i> Carr.	3	[97]	长豆角 <i>Ceratonina siliqua</i>	3	[100]
多花巴豆 <i>Croton floribundus</i>	3	[110]	油橄榄 <i>Olea europaea</i>	3	[100]
野甘蓝 <i>Brassica oleracea</i> subsp. Capitata	5(8)	[111]	冬青栎 <i>Quercus ilex</i>	3,6,4	[100,112—113]
蒙古栎 <i>Quercus mongolica</i> var. <i>crispula</i>	4	[114]	<i>Quercus ilex rotundifolia</i>	3	[100,115]
枹栎 <i>Quercus serrata</i>	4	[114]	杂交杨 <i>Populus tremula</i> × <i>tremuloides</i> (Clone55,Clone110)	4	[108,115—116]
柔毛栎 <i>Quercus pubescens</i>	4,5	[99,117]	白杨树 <i>Populus tremuloides</i> (271;42E)	3,30 *	[108,116]
白杨 <i>Populus alba</i>	4	[118]	杂交落叶松 <i>Larix gmelinii</i> var. <i>japonica</i> × <i>Larix kaempferi</i>	3	[119]
黑杨 <i>Populus nigra</i>	4	[102]	垂枝桦 <i>Betula pendula</i> Roth (Clone4;Clone80)	4	[120]
美洲黑杨 <i>Populus deltoides</i> (clone 546)	3,3	[98,121]	青杨 <i>Cathay poplar</i>	3	[122]
白芥 <i>Sinapis alba</i>	5	[101]	欧洲云杉 <i>Picea abies</i>	4(24)	[123]
野芥 <i>Sinapis arvensis</i>	5	[101]	欧洲山杨 <i>Populus tremula</i> (GT2.2;GT5.2)	4	[124]
欧洲白菜 <i>Brassica napus</i>	5,3(4)	[101,125]	苏格兰松 <i>Pinus sylvestris</i> L.	4(18),4(18)	[49,87]

括号内表示每次重复的植物棵数,若无标注则表示每次重复为一株植物,*表示该实验中测量了 30 片叶子的排放速率

3 植物 BVOCs 排放对 O₃的影响

植物 BVOCs 是 O₃形成的前体物之一,对近地面 O₃的生成及其远距离运输具有一定的作用,且其可作为植物抵抗 O₃胁迫的保护剂,并帮助清除大气中的 O₃。目前,部分城市绿地的平均 BVOCs 排放强度高于郊区森林^[126],部分地区地表 O₃浓度随归一化植被指数(NDVI)增加呈逻辑斯蒂增长,BVOCs 是植被良好地区 O₃浓度高的原因^[127]。

BVOCs 能够通过与 NO_x 反应以及与 O₃的光解产物反应等途径直接和间接增加近地面 O₃浓度。当大气中 NO_x 浓度较高时不利于 O₃的形成,而植物释放的 BVOCs 增加了大气中 VOC 的浓度,使得 VOC/NO_x 趋向最佳生产区,增加近地面 O₃浓度。BVOCs 还能与 O₃光解产物反应,使 O₃光解产生的羟基自由基快速氧化为过氧自由基,一氧化氮转化为二氧化氮,从而增强 O₃的形成^[128],影响大气的还原性。模型模拟显示夏季 BVOCs 对 O₃形成的贡献高达 16%—20%^[22],在热浪期间甚至高达 60%^[17]。与 AVOCs 相比,异戊二烯的排放量占 O₃形成潜能(OFP)的一半(49.5%)^[14]。

异戊二烯的氧化产物在 O₃远距离生成中起到一定作用,其能与 NO_x 反应产生有机硝酸盐,其中一种为过

氧乙酰硝酸酯(PAN)^[53],是光化学烟雾的主要成分,在低温下比较稳定,但在较高温度下又能分解形成NO_x。因此在温度较低的高海拔地区产生的PAN能在下降到温度较高的低海拔地区之前被远距离运输,之后又被分解,使得NO_x被远距离运输,导致远距离O₃的产生^[129—130]。

此外,植物存在气孔及非气孔的O₃沉积^[131],当城市树木暴露在由土壤不透水性和根系器官的约束引起的干旱胁迫下,气孔活性损伤时,树冠内的气孔活动减弱,会发生额外的非气孔O₃沉积过程^[131]。夏季柑橘树可以利用气孔和非气孔机制吸收O₃来改善果园的空气质量^[24]。吸收的O₃可在细胞间隙累积,会导致壁细胞氧化,对光合器官造成损伤,使植物的光合作用和生理代谢技能受到限制,对生长速率、生物量的积累有不利影响,加速植物的衰老^[132]。而异戊二烯可以作为羟基自由基的清除剂以及作为光合作用膜和大分子免受氧化损伤的保护剂^[133—134],单萜可以代替光呼吸,作为高温下产生的活性氧的清除剂,以防止高温下的光损伤^[135]。在同时具有高温和高O₃浓度的条件下,BVOCs可作为抗氧化剂,通过抑制O₃或活性氧,稳定对高温和高O₃浓度敏感的膜^[66,134],在压力条件下维持性能,并帮助清除大气中的O₃^[118]。

4 研究展望

植物具有滞尘^[136]、净化空气、涵养水源、固碳释氧,消除疲劳、减轻压力等作用。城市绿地在缓解城市环境问题、改善人居环境等方面发挥着不可替代的作用。随着城市居民对人居环境质量要求的不断提高,增加城市绿色空间已成为城市生态建设的一个重要组成部分。但植物释放的BVOCs也有一些不容忽视的负面影响^[137],不合理的树种选择和配置导致植物释放的BVOCs增加,进而加剧雾霾和O₃污染。

BVOCs对植物、人体及环境的作用已取得较大的进展。随着分离、提取技术的进步,其对植物本身及人体健康的作用进一步得到验证。在城市居民对人居环境质量要求提高的背景下,BVOCs与环境之间的相互作用备受关注。BVOCs对近地面O₃、次级有机气溶胶等二次污染物形成具有重要贡献,不断有学者提出新的模型方法以更精确估算BVOCs排放量,但不同植物对污染的抗性不同,其BVOCs的释放会受到环境因子的影响。因此,需要加强排放估算模型的本地化,深入探究环境胁迫对BVOCs释放影响的内部机理机制,充分考虑植物BVOCs排放水平及其抗性之间的平衡。具体来说,包括以下几个方面:

(1)加强本地树种BVOCs排放因子的实测及精细化尺度BVOCs排放量估算。我国植被覆盖面积广且物种丰富,部分树种的排放速率会随着经纬度等的变化发生改变^[138—140],因此建立本地物种的排放速率数据库尤为重要。早期测量多限于异戊二烯和单萜烯,且多采用静态封闭式采样法,会导致较大的误差。随着技术的发展,目前多采用动态封闭式采样法,可以进一步提升精度^[141]。而目前关于BVOCs排放量估算的研究中,由于树种排放速率的缺失,部分研究可能会选择同科属植物替代,或基于粗糙的植被空间分布仅考虑优势树种,会导致BVOCs的估算结果产生较大的误差。

(2)进一步探究城市中常见树种BVOCs释放对复合胁迫的响应。已有研究多基于单一环境条件和单一物种水平的比较,而在城市环境中的植物BVOCs释放受到复合因素的影响。关于复合作用的研究较少,且各研究结果存在差异^[116,142]。O₃浓度升高和增温对欧洲山杨异戊二烯排放的影响依据基因型的不同而异,但在田间暴露环境下发现O₃浓度升高和增温对挪威云杉的异戊二烯排放没有显著影响,对单萜烯和倍半萜烯排放的影响更显著^[123]。在O₃和二氧化碳对异戊二烯排放的复合影响研究,也得到了相似的结果^[109]。此外,随着全球气候变化,极端天气的增加,是否会影响BVOCs的释放也亟待研究。综上,需进一步探究复合胁迫对植物BVOCs排放的影响及其内在机理。

(3)平衡树种的生态系统服务与其BVOCs排放对O₃生成的贡献。城市景观建设中,对树种选择与配置时,除了满足生态、景观等功能外,还需考虑植物对环境和人体身心健康的潜在的负面影响。植物BVOCs会一定程度上加剧O₃形成,但BVOCs也是植物抵御环境胁迫的保护剂,高排放树种相较于低排放树种能更好抵御O₃等环境胁迫,更好的适应城市环境,并提供更多的生态系统服务。如何选择合适的树种,优化其配置,从而减少其负面影响,提升其生态系统服务,亟需开展更多的研究。

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