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长春秋季生物质燃烧对 PM2.5 中 WSOC 吸光性的影响

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摘要: 为探究长春秋季生物质燃烧对 $PM_{2.5}$ 中水溶性有机碳 (water-soluble organic carbon, WSOC) 吸光性的影响,于 2017 年 10 ~11 月进行 $PM_{2.5}$ 样品采集,对 $PM_{2.5}$ 中碳质组分、糖类化合物和 WSOC 的光吸收特征参数进行分析. 研究表明: 长春秋季 $PM_{2.5}$ 中 WSOC、有机碳 (organic carbon,OC)、元素碳 (elemental carbon,EC) 的平均浓度分别为 (10. 12 ± 3. 47)、(17. 07 ± 5. 64) 和 (1. 34 ± 0. 75) μ g·m⁻³,二次有机碳 (secondary organic carbon,SOC) 对 OC 的平均贡献率为 38. 93%. 长春秋季总糖浓度为 (1 049. 39 ± 958. 85) η g·m⁻³,其中作为生物质燃烧示踪剂的脱水糖含量 (左旋葡聚糖、半乳聚糖和甘露聚糖) 在总糖中占比为 91. 69%,糖类相关性分析结果显示生物质燃烧源为长春秋季大气中糖类物质的主要贡献源. 糖类物质的相关性分析及 3 种脱水糖的特征比值研究显示,作为长春秋季大气主要污染源的生物质燃烧的类型是硬木和作物残渣的燃烧. 长春秋季 WSOC 的光吸收波长指数 (AAE) 为 5. 75 ± 1. 06,单位质量吸收效率 (MAE) 为 (1. 23 ± 0. 28) η g·g⁻¹,表明生物质燃烧对 WSOC 吸光性具有重要影响. 利用生物质燃烧特征源参数量化计算生物质燃烧对 WSOC 浓度的贡献达 58. 82%,对总 WSOC 光吸收的贡献达 40. 92%.

关键词:水溶性有机碳(WSOC);糖;左旋葡聚糖;生物质燃烧;吸光性

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Effect of Biomass Burning on the Light Absorption Properties of Water Soluble Organic Carbon in Atmospheric Particulate Matter in Changchun

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Abstract: To investigate the effect of biomass burning in Changchun in autumn on the absorbance of water-soluble organic carbon (WSOC) on $PM_{2.5}$, $PM_{2.5}$ samples were collected from October to November 2017. The light absorption characteristics of WSOC, carbonaceous components, and carbohydrate content in $PM_{2.5}$ were analyzed. The study showed that the average concentrations of WSOC, organic carbon (OC), and elemental carbon (EC) in $PM_{2.5}$ in Changchun were (10. 12 ± 3. 47), (17. 07 ± 5. 64), and (1. 34 ± 0. 75) μ g·m⁻³, respectively; the average contribution rate of secondary organic carbon (SOC) to OC was 38. 93%. The total sugar concentration in Changchun is (1049. 39 ±958. 85) ng·m⁻³, of which the content of anhydroglucose (L-glucan, galactan, and mannan), as a biomass burning tracer in total sugar, was 91. 69%. The results of sugar correlation analysis showed that biomass combustion was the main source of contribution to carbohydrates in the autumn of Changchun. The light absorption wavelength index of WSOC in autumn was 5. 75 ± 1.06, and the unit mass absorption efficiency was (1. 23 ± 0. 28) m²·g⁻¹, indicating that biomass combustion has an important influence on WSOC absorbance. The biomass combustion characteristic source parameter was used to quantify the contribution of biomass burning to WSOC concentration, which was found to be 58. 82%, while the contribution to total WSOC light absorption was 40. 92%.

Key words: water-soluble organic carbon (WSOC); sugar; levoglucosan; biomass burning; absorbance

大气有机气溶胶对于大气能见度、气候变化和人体健康有着复杂且重要的影响,因此其受到广泛的关注和研究.水溶性有机碳(water-soluble organic carbon, WSOC)是气溶胶有机碳(organic carbon, OC)的重要组成部分,占 OC 的 20% ~ 70% [1]. WSOC可以改变气溶胶的吸湿性并影响云凝结核的形成,从而影响气候变化 [2]. WSOC 的来源相当广泛,生物质燃烧、化石燃料燃烧、机动车尾气排放以及大气颗粒物表面的多相化学反应等都是 WSOC的来源 [3]. 近年来研究表明,生物质燃烧是 WSOC的来源 [3]. 近年来研究表明,生物质燃烧是 WSOC

的一个重要贡献源^[4,5],生物质燃烧产生的大量棕色碳(BrC)在短波区对于气溶胶的总光吸收有相当大的贡献,BrC 在辐射强迫和全球气候变化中具有重要作用^[6],对于 WSOC 吸光性的研究可以很好地

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表征 BrC 的吸光特性[7].

糖类化合物是大气中分布非常广泛的有机物质,是大气颗粒物来源非常有说服力的指示物,也是生物质燃烧和土壤再悬浮的重要示踪物^[8]. 左旋葡聚糖(levoglucoan)由于其特异性、光化学稳定性、释放量大等特点,被公认、且被广泛用作生物质燃烧示踪物^[9,10]. Fabbri等^[11]利用燃烧实验证实左旋葡聚糖、甘露聚糖、半乳聚糖之间的比值可以用来区分野外和室内生物质燃烧. Simoneit等^[8]的研究表明,这3种脱水糖的排放因子随温度的变化情况类似,它们的比值不随燃烧温度不同而显著改变,这表明3种脱水糖之间的比值可以用来指示生物质燃料类型.

有研究表明我国 OC 质量浓度表现出明显的季 节性变化,秋季受生物质燃烧的影响显著^[12,13]. Lu 等[14]通过调查 1996~2010 年中国的一次源碳质气溶 胶排放,发现用于供暖及烹饪的燃煤和生物质燃烧是 中国人为排放 OC(69%)和元素碳(elemental carbon, EC)(51%)的主要贡献源. Cheng 等[15]首次阐述了北 京冬季和夏季水溶性有机碳(WSOC)的光学特性,并 研究了几种不同生物质燃烧产生的 EC 的质量吸收 效率(MAE)特征. Du 等[16]利用正定矩阵因子法 (PMF)用生物质燃烧因子计算了 WSOC 的 MAE,结 果显示在 365 nm 处生物质燃烧产生的 WSOC (WSOC_{BB})贡献了总WSOC光吸收量的58%.李栋梁 等[17]对东北地区生物质燃烧的相关研究表明,秋季 农作物收成后东北地区会有大量秸秆燃烧. 东北三江 平原地区在受生物质燃烧影响时期,生物质燃烧对 PM, 5中 WSOC 的贡献率超过 70% [18]. 吴瑕等 [19] 对 长春秋季大气有机气溶胶组成及来源的研究表明,生 物质燃烧是长春秋季有机气溶胶的主要贡献源.

生物质燃烧对大气污染的影响十分显著,了解生物质燃烧对 WSOC 的浓度和吸光性的贡献能力以及燃烧源的类型特征对于环境监管和改善空气质量非常重要.本研究对长春秋季 PM_{2.5}的碳质组分污染特征以及 WSOC 的光学特征进行分析,并利用对生物质燃料类型的探讨,对长春 WSOC_{BB}在总 WSOC的质量浓度及光吸收的贡献进行了量化,更加深入地认识了长春大气颗粒物的光学性质和生物质燃烧的污染特征,以期为大气化学特征研究以及长春大气环境污染治理提供参考.

1 材料与方法

1.1 样品采集

本研究采样点位于吉林省长春市中国科学院东 北地理与农业生态研究所内,周围无明显污染物排 放源及障碍物,能比较好地反映采样点区域大气污 染的状况. 采样时间为 2017 年 10 月 10 日至 2017 年 11 月 9 日,每个样品连续采集 23.5 h,共采集 30 个 $PM_{2.5}$ 样品. 采样仪器是流量为 1. 05 $m^3 \cdot min^{-1}$ 的 KC-1000 大气颗粒物采样器. 采样前将石英滤膜 (PALL)用锡纸包好放在马弗炉中 450℃高温灼烧 6 h,以去除石英滤膜中残留的有机物. 灼烧后冷却,并在干燥皿中室温平衡 48 h 后用微电子天平 (BSA124S,德国 Sartorius)称重. 采样后样品放置于 -18℃的冰箱中保存.

1.2 分析方法

使用微电子天平称量采样前后滤膜的质量,通 过前后质量差和采样体积计算出大气中 PM,5的质 量浓度. 使用总有机碳分析仪(TOC,德国 Elementar)测定 WSOC 的质量浓度,其预处理方法 为:用18 mm 打孔器取一片样品放于15 mL玻璃瓶 中,加入10 mL超纯水冰浴超声振荡30 min,超声萃 取后用针式滤器(0.22 µm)过滤到进样瓶中待测. 使用离子色谱(ICS-5000 + ,美国 Thermo)测定糖类 物质的质量浓度,分离系统采用的色谱柱为 Dionex CarboPac™ MA1 分析柱(4×250 mm)和 Dionex CarboPac™MA1 保护柱(4×250 mm). 其预处理方 法为:用20 mm 打孔器取四片样品放于30 mL 塑料 瓶中加入10 mL 超纯水超声振荡30 min(放冰袋), 萃取后用针式滤器(0.22 μm)过滤到进样管中待 测. OC 和 EC 的测定使用美国 Sunset Lab 公司 Model-4 型全半自动连续式分析仪. 得到滤膜样品中 WSOC 吸收光谱的方法是将 WSOC 萃取液通过长光 程吸收池(LWCC-2000,美国 World Precision Instrument) 并利用光纤光谱仪(USB4000-UV-VIS-ES,美国 Ocean Optics)测定样品的紫外吸收系数, 其中光源采用双重氘和卤钨光源(DT-MINI-2-GS, 美国 Ocean Optics).

1.3 AAE 及 MAE 值计算

利用采集到的 WSOC 吸收光谱,可以得到提取 液对不同波长光导致的衰减(ATN),以 700 nm 处的 ATN 作为吸收基线扣除,通过公式(1)计算实际大气中的光吸收强度(Bap,Mm⁻¹)^[12]:

$$Bap = (ATN_{\lambda} - ATN_{700}) \cdot \frac{V_1}{V_a \cdot L} \cdot \ln(10) \qquad (1)$$

式中, ATN_{λ} 由光谱仪直接测量; V_{1} 为提取液的体积 (mL); V_{a} 为 $PM_{2.5}$ 样品的采样体积(L);L 为吸收光路长度(m).

Angstrom 指数(AAE)表征 BrC 的吸光能力和吸光特性随波长变化的程度,如式(2).

$$Bap_{\lambda} = K \cdot \lambda^{-AAE}$$
 (2)

式中, Bap_{λ} 为 WSOC 在波长 λ 处的光吸收强度;K

为常数,AAE 通过公式(2)拟合指数曲线得到.

WSOC 的单位质量吸收效率(MAE, $m^2 \cdot g^{-1}$), 计算公式如下:

$$MAE = \frac{Bap_{\lambda}}{c_{WSOC}}$$
 (3)

式中, c_{WSOC} 为 WSOC 的浓度($\mu g \cdot m^{-3}$).

本研究中,为排除其它物质的干扰,选择 λ = 365 nm 处的光学参数作为 WSOC 的 Bap、AAE 及 MAE 值表征.

1.4 生物质燃烧贡献的计算

生物质燃烧产生的 WSOC(WSOC_{BB})对总 WSOC的贡献采用 Yan 等^[20]的计算公式:

$$\frac{\text{WSOC}_{BB}}{\text{WSOC}} = \frac{(\text{levoglucoan/WSOC})_{\text{ambient}}}{(\text{levoglucoan/WSOC})_{\text{source}}}$$
(4)

同时,使用下式 $^{[20]}$ 计算 $WSOC_{BB}$ 在波长 365 nm 处对总 WSOC 光吸收的贡献:

$$f = \frac{\text{MAE}_{365} \cdot \text{WSOC}_{BB}}{\text{Bap}_{365}} \times 100\%$$
 (5)

式中,f 是 WSOC_{BB} 对总 WSOC 光吸收的贡献率; WSOC_{BB}为公式(4)与 WSOC 浓度乘积; MAE₃₆₅为选择源样品的特征值; Bap₃₆₅是样品中 WSOC 在波长365 nm 处的吸光系数.

2 结果与讨论

2.1 PM_{2.5}中碳质组分污染特征

采样期间,长春 PM_{2.5}秋季平均浓度为(72.36±34.62) μg·m⁻³,低于我国环境空气质量(GB 3095-2012)日平均二级标准浓度限值 75 μg·m⁻³,与李栋梁等^[17]在 2014 年对于东北三省主要城市的研究中PM_{2.5}水平较为接近.以国家环境空气质量二级标准限值来划分清洁天与污染天,在采样期间污染天数14 d,超标率46.67%,污染天PM_{2.5}平均浓度超过99

μg·m⁻³,超过清洁天的 2 倍. 本研究测得长春地区 秋季 $PM_{2.5}$ 中 WSOC 平均浓度为 (10. 12 ± 3. 47) μg·m⁻³, OC 平均浓度为 (17. 07 ± 5. 64) μg·m⁻³, EC 平均浓度为 (1. 34 ± 0. 75) μg·m⁻³. 如图 1 所示,在采样期间,长春地区的 OC、EC 与 WSOC 的浓度变化在 11 月 2 日前均有较大幅度变化且变化情况同步,在 11 月 2 日后变化均趋于稳定. OC、EC 与 WSOC 浓度变化趋势一致说明三者具有较为一致的排放源. 利用 OC/EC 的最小比值法可以计算 $PM_{2.5}$ 中的二次有机碳 (SOC) 含量 [21,22]:

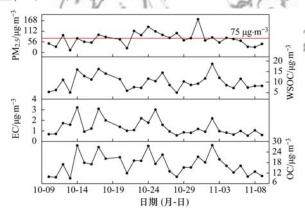


图 1 PM_{2.5}、WSOC、EC 与 OC 随时间变化情况

Fig. 1 Changes in $PM_{2.5}$, WSOC, EC, and OC over time during the study period

表 1 我国部分城市大气 PM_{2.5}中碳质组分浓度特征

Table 1 Concentration characteristics of carbonaceous components in atmospheric in some cities of China

| 研究地点 | 时间 | OC /μg·m ⁻³ | EC /μg·m ⁻³ | SOC /µg·m ⁻³ | SOC/OC /% | 文献 |
|------|---------|---------------------------|---------------------------|----------------------------|--------------|--------|
| 长春 | 2017 年秋 | 17. 07 ± 5. 64 | 1. 34 ± 0. 75 | 6. 38 ± 4. 77 | 38. 93 | 本研究 |
| 上海 | 2015 年秋 | 3. 95 | 1.87 | 1.51 | 36. 13 | [23] |
| 南京 | 2015 年秋 | 11.30 | 1. 10 | 5. 30 | 51. 90 | [24] |
| 济南 | 2015 年冬 | 18.1 ± 9.5 | 7.6 ± 3.6 | 8. 2 | 45 | [21] |
| 贵阳 | 2013 年秋 | 14.70 | 2. 31 | 6. 89 | 46. 40 | [25] |
| 北京 | 2010 年秋 | 20. 20 | 10. 20 | _ | _ | [26] |

2.2 WSOC 中的糖类

在 PM_{2.5}样品中检测到 12 种糖类物质,分别为 左旋葡聚糖、半乳聚糖、甘露聚糖、甘露醇、阿拉伯糖 醇、苏糖醇、甘露糖、葡萄糖、山梨糖醇、海藻糖、半乳 糖和木糖醇,糖类物质的月平均质量浓度如图 2 所 示. 总糖平均浓度为(1049.39 ±958.85) $ng \cdot m^{-3}$,浓度范围为 66.68 ~ 3805.17 $ng \cdot m^{-3}$,总糖质量占 $PM_{2.5}$ 的质量分数为1.45%.本研究检测到的糖类化合物分为3类(脱水糖、糖醇和糖),其中脱水糖的含量最为丰富,占到总糖比例的91.69%.左旋葡聚

糖是含量最丰富的一种脱水糖,它占到脱水糖总量的 90.23%. 糖醇占到总糖含量的 6.62%,其中甘露醇含量最高. 糖占到总糖含量的 1.69%,其中甘露糖含量最高.

脱水糖包括左旋葡聚糖及其两种同分异构体(半乳聚糖和甘露聚糖),由纤维素和半纤维素热解产生,被广泛应用作为生物质燃烧的示踪剂^[27].脱水糖在总糖比例中超过90%,本研究中总糖、脱水糖和左旋葡聚糖的浓度水平均明显高于北京、上海和柳州等城市的秋季水平(图3),甚至高于典型北方城市西安的冬季水平(图3)^[27~30],长春秋季大气气溶胶受生物质燃烧的影响可能非常严重.根据图4中糖类物质的日变化情况可以发现,甘露醇、甘露聚糖、半乳聚糖和左旋葡聚糖的变化趋势非常相似,这代表着它们具有相似的来源.为了更好地研究长春大气颗粒物中糖类化合物的组成特征及来源,本研究对大气样品中12种糖类物质进行相关性分析(表2).

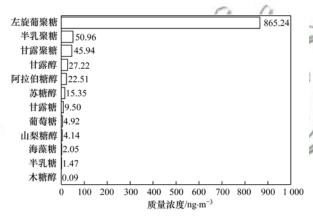


图 2 12 种糖类化合物月平均质量浓度

Fig. 2 Monthly average mass concentrations of twelve carbohydrate compounds

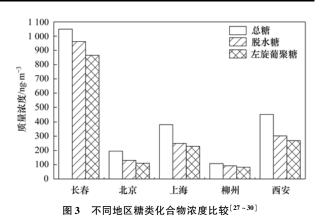


Fig. 3 Comparison of carbohydrate concentration in different regions

脱水糖之间在 0.01 水平上显著相关, 左旋葡聚 糖与甘露聚糖和半乳聚糖的相关系数 (R^2) 为 0.82 和 0.87.甘露聚糖与半乳聚糖的相关系数为 0.96. 说明3种脱水糖来源相同,为生物质燃烧. 苏糖醇、 山梨糖醇、甘露醇和甘露糖均与3种脱水糖在0.01 水平上显著相关,相关系数分布在 0.61~0.98 之 间,表明除生物质燃烧外,苏糖醇、山梨糖醇、甘露醇 和甘露糖亦有其他来源,如植物和动物的新陈代谢 排放以及土壤再悬浮[31]. 木糖醇、阿拉伯糖醇和半 乳糖在 0.01 水平上显著相关,在日变化趋势中(图 4),3种糖类物质在10月24日后浓度水平较稳定, 几乎无波动,不受生物质燃烧的影响,因此木糖醇、 阿拉伯糖醇及半乳糖来源相似,土壤再悬浮是它们 最大的影响源. 海藻糖与葡萄糖的平均质量浓度低 于5 ng·m⁻³,与其它糖类几乎无相关性,原因可能 是受长春当地植作物种类及其生长特性的影响.海 藻糖广泛存在于细菌、真菌和海藻中,在高温、高寒 以及干旱等恶劣环境中的植物表层也大量存在[11], 葡萄糖是维管植物中最常见的单糖[32]. 长春秋季维 管植物较少也并无气候恶劣地域,因此长春秋季海

表 2 糖类物质相关性分析1)

Table 2 Correlation analysis of carbohydrates

| | 左旋 葡聚糖 | 半乳聚糖 | 甘露聚糖 | 甘露醇 | 阿拉伯 糖醇 | 苏糖醇 | 甘露糖 | 葡萄糖 | 山梨糖醇 | 海藻糖 | 半乳糖 | 木糖醇 |
|-------|-----------|----------|----------|----------|-----------|----------|----------|-------|----------|-------|----------|----------|
| 左旋葡聚糖 | 1 | 0. 87 ** | 0. 82 ** | 0. 86 ** | 0.37 * | 0. 71 ** | 0. 80 ** | -0.15 | 0. 63 ** | 0.11 | 0.38* | 0. 39 * |
| 半乳聚糖 | | 1 | 0. 96 ** | 0. 98 ** | 0.30 | 0. 80 ** | 0. 93 ** | -0.26 | 0. 61 ** | 0.02 | 0.36 | 0. 37 * |
| 甘露聚糖 | | | 1 | 0. 94 ** | 0.33 | 0. 80 ** | 0. 91 ** | -0.13 | 0. 65 ** | 0.03 | 0. 37 * | 0.32 |
| 甘露醇 | | | | 1 | 0.27 | 0. 76 ** | 0. 94 ** | -0.25 | 0. 59 ** | 0.00 | 0.32 | 0.38 * |
| 阿拉伯糖醇 | | | | | 1 | 0. 66 ** | 0. 29 | -0.04 | 0. 47 * | 0. 17 | 0. 62 ** | 0. 55 ** |
| 苏糖醇 | | | | | | 1 | 0. 78 ** | -0.08 | 0. 77 ** | 0.08 | 0. 51 ** | 0.35 |
| 甘露糖 | | | | | | | 1 | -0.17 | 0. 69 ** | -0.03 | 0. 28 | 0. 27 |
| 葡萄糖 | | | | | | | | 1 | -0.05 | -0.28 | 0.07 | -0. 10 |
| 山梨糖醇 | | | | | | | | | 1 | 0. 27 | 0. 20 | 0.09 |
| 海藻糖 | | | | | | | | | | 1 | 0.00 | 0. 16 |
| 半乳糖 | | | | | | | | | | | 1 | 0. 59 ** |
| 木糖醇 | | | | | | | | | | | | 1 |

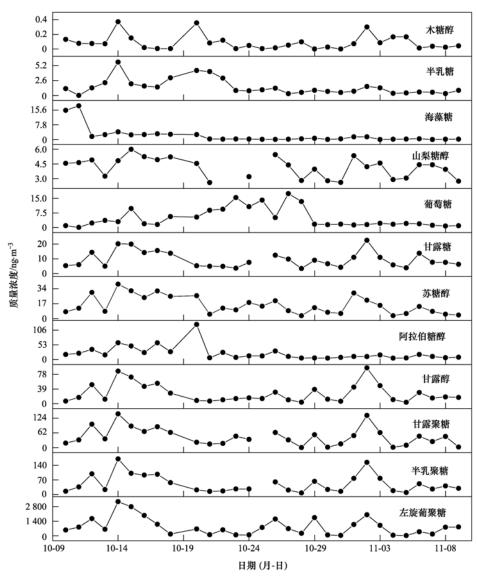


图 4 12 种糖类物质浓度日变化情况

Fig. 4 Diurnal changes of twelve carbohydrates

藻糖与葡萄糖的质量浓度较低,与其它糖类相关性也较差符合事实.综上,作为生物质燃烧示踪剂的脱水糖在总糖中的比例达91.69%,并且苏糖醇、山梨糖醇、甘露醇和甘露糖等糖醇也受生物质燃烧的影响.除部分含量极低的糖醇来源土壤悬浮外,生物质燃烧源是长春秋季大气中糖类物质的主要贡献源,大气气溶胶受生物质燃烧影响严重.

2.3 生物质燃烧类型

不同类型的生物质燃烧排放的左旋葡聚糖、甘露聚糖与半乳聚糖的比例存在差异,因此左旋葡聚糖、甘露聚糖和半乳聚糖之间的比值可以有效地识别生物质燃料类型[11,32].本研究参考王鑫彤等[33]对不同生物质燃烧产生的脱水糖类化合物比例的研究结果,将长春秋季 PM_{2.5}中脱水糖之间浓度比值与之对比.如表 3 所示,长春秋季左旋葡聚糖/甘露聚糖(L/M)、左旋葡聚糖/半乳聚糖(L/G)和左旋葡聚

糖/(甘露聚糖 + 半乳聚糖)[L/(M+G)]比率分别为 35.99、16.75 和 9.22、3 个特征值均与硬木和作物残渣燃烧排放的脱水糖特征比值相近. 长春有林地 26.5 万 hm²,森林组成以东亚阔叶林为主,硬木储量庞大,农村地区用林木烹饪及取暖现象普遍. Cao等[34]的研究表明水稻和小麦等 C3 作物的燃烧为东北三江平原地区生物质燃烧的主要贡献源,而长春的主要农作物与三江平原相似. 因此,结合长春的林业及农业的生产情况,长春大气中生物质燃烧源的主要类型是硬木和作物残渣的燃烧.

2.4 WSOC 吸光性参数

 Bap_{365} 是 WSOC 在 365 nm 处的光吸收强度,长春秋季 $PM_{2.5}$ 样品中 WSOC 的 Bap_{365} 平均值为 (13. 33 ± 5. 87) Mm^{-1} ,根据 Bap_{365} 与 OC、WSOC 和左旋葡聚糖相关性分析(图 5),发现在研究期间长春大气 OC、WSOC 与 Bap_{365} 的相关性指数分别为

表 3 不同生物质燃烧排放的糖类化合物比例[33]

Table 3 Proportion of carbohydrates emitted from

| hurning | of | different | hiomace | |
|---------|----|-----------|---------|--|

| | U | | |
|---------|------------------|-------|---------|
| 比例 | 比例范围/% | 生物质类型 | 本研究比例/% |
| | 2.4~5.8 | 软木 | |
| L/M | 10.7 ~ 83.4 | 硬木 | 35.99 |
| | $12.7 \sim 60.7$ | 作物残渣 | 33.77 |
| | 2.0 ~ 33.3 | 草 | |
| | 3.4 ~ 40.5 | 软木 | |
| L/G | 3.6 ~84 | 硬木 | 16.75 |
| L/ G | 12.7 ~884.5 | 作物残渣 | 10.75 |
| | 3.4 ~ 15.2 | 草 | |
| | 1.5 ~ 5.1 | 软木 | |
| L/(M+G) | 7.9 ~ 20.3 | 硬木 | 9.22 |
| | 6.4 ~ 52.4 | 作物残渣 | 9.22 |
| | 1.7~8.9 | 草 | |
| • | | _ | _ |

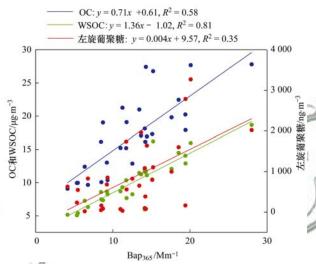


图 5 Bap₃₆₅与 OC、WSOC 和左旋葡聚糖的相关性

Fig. 5 Correlation between Bap365, OC, WSOC, and levoglucosan

0.58 和 0.81,表明 OC 和 WSOC 中含有大量水溶性 棕色碳. 与翟晓瑶等[18] 对东北三江平原生物质与非生物质燃烧时期 WSOC 吸光特性的研究对比,长春秋季左旋葡聚糖与 Bap₃₆₅的相关性指数低于三江平原生物质燃烧时期数值(0.91),高于非生物质燃烧时期数值(0.09),说明长春秋季大气 WSOC 的光吸收强度受生物质燃烧影响的同时还可能受其它来源的影响. AAE 表示吸光特性随波长变化的程度,二次转化形成的有机气溶胶(SOA)的光吸收对波长的依赖性较强,新、老 SOA 的水萃取液 AAE 值分别在7.00 和 4.70 左右[35];受煤燃烧和生物质燃烧影响时的 AAE 值约为 3.50[36].本研究中,长春地区WSOC的 AAE 值在 2.86~7.33 之间分布,平均值为5.75±1.06,长春地区秋季 WSOC的 AAE 显著受生物质燃烧和 SOA 的影响.

MAE 值表征单位质量 WSOC 的吸光能力,排放源不同的 WSOC 其 MAE 值不同. 有报道指出,生

物质燃烧源 MAE 值为 1. 19 $\text{m}^2 \cdot \text{g}^{-1}$, 柴汽油机动车排放源为 1. 33 $\text{m}^2 \cdot \text{g}^{-1}$, 混合性一次源为 2. 89 $\text{m}^2 \cdot \text{g}^{-1[16]}$. 本研究计算所得长春秋季 MAE 平均值为(1. 23 ± 0. 28) $\text{m}^2 \cdot \text{g}^{-1}$, 长春地区秋季 WSOC的MAE 值受生物质燃烧源影响较大,WSOC_{BB} 对WSOC的吸光性有重要影响.

2.5 生物质燃烧对 WSOC 光吸收效率的贡献

本研究中对长春秋季的糖类物质及吸光参数的 讨论表明,生物质燃烧源对 WSOC 的贡献和吸光性 具有重要影响. 为定量描述生物质燃烧对 WSOC 的 浓度和光吸收的影响,本研究引用公式(4)和(5)计 算 WSOC RR 对总 WSOC 浓度和光吸收的贡献. 由前 文研究可知, L/M、L/G和L/(G+M)的数值均与 稻草燃烧及硬木燃烧的特征数值接近,长春秋季生 物质燃烧源的主要类型是水稻残渣和硬木. 因此采 用稻草燃烧和木材燃烧的(levoglucoan/WSOC)source 及 MAE₃₆₅ 的平均值作为本研究的 (levoglucoan/ WSOC) $_{\rm source}$ 和 MAE $_{365}$ 的特征值. 根据 Du 等 $^{[16]}$ 以及 Ding 等[37] 使用稻草及木材的燃烧实验结果显示, 使 用稻草和小麦秸秆燃烧的(levoglucoan/WSOC)source 比率为 0.17, MAE₃₆₅ 为 0.80 m²·g⁻¹; 使用木材燃烧 的(levoglucoan/WSOC) source 比率为 0.1, MAE₃₆₅ 为 $0.97 \text{ m}^2 \cdot \text{g}^{-1}$. 计算结果显示, 生物质燃烧对 WSOC 的平均贡献率为 58.82%, WSOC RR 在波长 365 nm 处 对总 WSOC 光吸收平均贡献率为 40.92%. 长春秋 季大气中大部分的 WSOC 来源于一次生物质燃烧 源,并且该区域中生物质燃烧产生了丰富的水溶性 棕色碳,生物质燃烧是长春秋季 WSOC 吸光性的主 要影响源.

3 结论

(1)本研究测得长春秋季 $PM_{2.5}$ 平均质量浓度为(72.36 ± 34.62) $\mu g \cdot m^{-3}$, WSOC 平均质量浓度为(10.12 ± 3.47) $\mu g \cdot m^{-3}$, OC 平均质量浓度为(17.07 ± 5.64) $\mu g \cdot m^{-3}$, EC 平均质量浓度为(1.34 ± 0.75) $\mu g \cdot m^{-3}$, SOC 的平均质量浓度为(6.38 ± 4.77) $\mu g \cdot m^{-3}$, SOC 对 OC 的贡献率为 38.93%.

(2)长春秋季 PM_{2.5}中共检测 12 种糖类物质, 总糖浓度为(1049. 39 ± 958. 85) ng·m⁻³, 脱水糖(左旋葡聚糖、半乳聚糖、甘露聚糖) 在总糖中占比为91. 69%, 3 种脱水糖之间显著相关; 并且苏糖醇和甘露糖等 4 种糖/糖醇与脱水糖的相关性均超过0. 61(P<0.01). 研究表明生物质燃烧是长春秋季大气中糖类物质的主要贡献源, 长春生物质燃烧情况严重;通过生物质燃烧类型分析并结合长春当地

的农林生产情况,发现长春大气中生物质燃烧的主要类型是硬木和作物残渣的燃烧.

- (3) 长春秋季 $PM_{2.5}$ 中 WSOC 的 Bap_{365} 值为 (13. 33 ± 5. 87) Mm^{-1} , AAE 值为 5. 75 ± 1. 06, MAE 值为 (1. 23 ± 0. 28) $m^2 \cdot g^{-1}$, WSOC_{BB} 对 WSOC 吸光性有重要影响; 利用生物质燃烧特征源参数量化计算生物质燃烧对长春秋季 WSOC 的贡献为 58. 82%, WSOC_{BB} 对总 WSOC 光吸收的贡献为 40. 92%, 研究区域内生物质燃烧产生了丰富的水溶性棕色碳, 生物质燃烧是长春秋季 WSOC 吸光性的主要影响源. 参考文献:
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