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麦秸及其烟尘中正构脂肪酸的组成

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摘要:在不同燃烧条件下对6种麦草进行焚烧,并利用GC/MS对麦秸和烟尘中的正构脂肪酸进行了测定。结果表明,烟尘中含有碳数C₈~C₃₂的正构脂肪酸。在明火烟尘中,正构脂肪酸总含量分布于1 509.3~10 543.7 mg·kg⁻¹之间,平均值为5 871.2 mg·kg⁻¹。其轻(C₈~C₁₆)、重(C₁₇~C₃₂)正构脂肪酸含量之比(L/H)为0.8~5.3,平均值为2.8; C₁₄/C₁₆、C₂₈/C₁₆、C₃₀/C₁₆等比值的平均值分别为16.5%、14.1%、11.4%。正构脂肪酸呈双峰式分布,其主峰碳数是C₁₆,次峰碳数是C₂₈或C₃₀,且具有显著的偶碳数优势。其碳优势指数(CPI)和平均碳链长度(ACL)的平均值分别为19.8和18.2。在闷烧烟尘中,正构脂肪酸的总含量为5 799.3~37 244 mg·kg⁻¹,平均值为15 838.6 mg·kg⁻¹。其L/H值介于1.2~5.6之间,平均为4.2; C₁₄/C₁₆、C₂₈/C₁₆、C₃₀/C₁₆的平均值分别为12.7%、10.1%、6.0%。闷烧烟尘中正构脂肪酸的分布模式与明火烟尘的类似,其CPI和ACL的平均值分别为24.7和17.7。总之,虽然两类烟尘和麦秸中的正构脂肪酸均具有类似的分布模式和偶碳数优势,但三者在组成上仍然存在明显的差别。这有助于识别大气气溶胶中麦秸及其燃烧排放的正构脂肪酸。

关键词:麦秸;明火燃烧;闷烧;烟尘;正构脂肪酸

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Chemical Compositions of *n*-Alkanoic Acids in Wheat Straw and Its Smoke

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Abstract: Wheat straws of six genotypes were burned under different conditions, and *n*-alkanoic acids in the straw and its smoke were measured by GC/MS. The results showed that the carbon number of the fatty acids in all the smoke ranged from C₈ to C₃₂. In the flaming smoke, the total amounts of the compounds varied from 1 509.3 to 10 543.7 mg·kg⁻¹, with a mean value of 5 871.2 mg·kg⁻¹. And the content ratio values of *n*-alkanoic acids with low carbon number (C₈ to C₁₆) to those with high carbon number (C₁₇ to C₃₂) (L/H) were between 0.8 and 5.3, with an average of 2.8. In addition, the mean values for C₁₄/C₁₆, C₂₈/C₁₆ and C₃₀/C₁₆ were 16.5%, 14.1% and 11.4%, respectively. The distribution of the compounds in the smoke was bimodal with the peak carbon number of C₁₆ followed by C₂₈ or C₃₀, and it showed an even carbon number preference. The mean values of carbon preference index (CPI) and average carbon chain length (ACL) were 19.8 and 18.2, respectively. In the smoldering smoke, the total amounts of the fatty acids were in the range of 5 799.3 to 37 244 mg·kg⁻¹, and the mean was 15 838.6 mg·kg⁻¹. Moreover, the L/H ratios varied from 1.2 to 5.6, with a mean value of 4.2. The average ratio values for C₁₄/C₁₆, C₂₈/C₁₆ and C₃₀/C₁₆ were 12.7%, 10.1% and 6.0%, respectively. The content distribution pattern of the compounds was similar to that in the flaming smoke, and the mean values of CPI and ACL were 24.7 and 17.7, respectively. In general, *n*-alkanoic acids in both wheat straw and its two types of smoke had similar distribution modes, both with even carbon number preference, but there was prominent distinction among the chemical compositions of the compounds in the straw and the smokes. This is maybe useful in identifying the organic matter from wheat straw or its smoke in the atmospheric aerosol.

Key words:wheat straw; flaming combustion; smolder; smoke; *n*-alkanoic acids

正构脂肪酸是大气气溶胶的主要有机成分之一^[1~6]。植物风化碎屑是其重要来源。农业秸秆、草、灌木、乔木等生物质在燃烧过程中会排放正构脂肪酸^[7~18]。煤、石油等化石燃料的燃烧也产生此类污染物^[19,20]。秸秆在露天焚烧过程中向大气排放了大量的烟尘^[21~23]。小麦作为我国的一种主要粮食作物,其秸秆产量在作物秸秆总产量中占有较大的比例^[24,25]。因此,麦秸燃烧活动对大气气溶胶中的正构脂肪酸有着很大的贡献。目前,虽然对不同类型生物质燃烧排放烟尘中正构脂肪酸的组成,以及排放因子进行了大量的研究,但对燃烧方式与烟

尘中正构脂肪酸组成之间的关系却关注较少^[7~18]。对我国6个品种的麦秸在不同燃烧条件下进行了燃烧试验,对麦秸及其烟尘中的正构脂肪酸开展了研究,初步探讨两者在正构脂肪酸组成上的差异,以期为识别气溶胶中麦草及其燃烧来源的正构脂肪酸提供参考。

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1 材料与方法

1.1 稜秆采集与制备

2010~2012年共采集了6个品种的小麦稜秆。扬麦10、扬麦16、烟农10等品种采自江苏；矮抗58、温六、西农979均采自河南。在制备测定稜秆中正构脂肪酸用的样品时，取适量完整的麦稜，用剪刀剪至小段，用清水冲去表面的泥土。将洁净的碎样在50℃烘烤12 h，用植物粉碎机粉碎至60目。对于焚烧用的麦秆，在室内自然风干，临烧前拣去杂物，抖去灰尘。

1.2 燃烧试验与烟尘采集

模拟稜秆的2种田间焚烧方式，明火燃烧和闷烧，在一面积为20 m²的房间内进行燃烧试验。在模拟明火燃烧时，取每种麦稜0.5 kg，自然堆放在一张铁盘上点燃。闷烧时取稜秆0.2 kg，点燃使之发烟但不产生明火^[7]。

用一台小流量(28.3 L·min⁻¹)大气颗粒物采样器(AH-200型，美国Tisch Environmental, Inc)采集排放到室内空气中的烟尘(PM₁₀)。采样器离火堆2 m，距地面1.2 m。点燃稜秆后即开始采样，每个样持续采集1 h。采样期间保持门窗关闭，以减少烟尘向外扩散。采样所用的玻璃纤维滤膜在使用前于500℃灼烧2 h，冷却后置于干燥器中在室温下平衡24 h。采样后的滤膜同样在室温下于干燥器中平衡24 h后再称重。烟尘样品用铝箔(在500℃灼烧2 h)包裹，冷冻保存。

1.3 有机物提取与测定

称取麦稜粉末4 g或者取采集了烟尘的玻璃纤维滤膜0.5~1张，每次加入二氯甲烷/甲醇混合液(2:1，体积比)10 mL，在室温下超声振荡15 min，共重复提取3次。合并提取液，以3 000 r·min⁻¹的转速离心2 min，用旋转蒸发器在40℃浓缩上清液至3 mL，再用氮吹仪在40℃吹至近干。加入2 mL 1 mol·L⁻¹的KOH甲醇/水溶液(4:1，体积比)和1 mL去离子水，在60℃皂化2 h。先后用3 mL二氯甲烷提取皂化溶液内的中性组分各3次。向剩余的皂化溶液内加入6 mol·L⁻¹稀盐酸进行酸化处理(pH=1)，共用7 mL二氯甲烷萃取其中的有机酸组分，并用氮吹仪将提取液吹至近干。以BF₃/MeOH(200 μL)在60℃对其衍生2 h。衍生液浓缩后用乙酸乙酯定容至0.5 mL。

用气质联用仪(6890N/5975GC-MS型，美国安捷伦公司)对上述衍生物进行测定。所用色谱柱为

Agilent-5MS(30 m×0.25 mm×0.25 μm)非极性石英毛细管色谱柱；载气流量1 mL·min⁻¹，汽化温度300℃，进样量1 μL(不分流)；升温程序：初始温度60℃，保持2 min，以5℃·min⁻¹升温至300℃，保持35 min。根据质量数为74的离子色谱峰面积进行外标法定量。每个样品测定一次。定量用的正十二酸甲酯~正二十四酸甲酯混合标准物质购自美国Nu Chek Prep, Inc. 以正十六酸进行了加标回收试验，回收率达70%~110%，基本符合要求。

2 结果与讨论

2.1 麦草中正构脂肪酸的组成

麦稜中含有碳数为C₈~C₃₂的正构脂肪酸(表1)。不同品种麦草中正构脂肪酸的总含量差别巨大。烟农10的总含量最高(644.9 mg·kg⁻¹)，矮抗58的最低(41.3 mg·kg⁻¹)，两者相差14.6倍。麦草中正构脂肪酸的平均总含量为335.9 mg·kg⁻¹。其低碳数(C₈~C₁₆)和高碳数(C₁₇~C₃₂)正构脂肪酸的含量之比(L/H)分布于1.3~9.2之间，其平均值为5.5。表明低碳数正构脂肪酸，尤其是正十六酸，是麦稜中正构脂肪酸的主要组分。

麦草中正十四酸与正十六酸的含量比(C₁₄/C₁₆)为6.0%~52.0%，平均为27.8%；正二十八酸与正十六酸的含量比(C₂₈/C₁₆)为1.7%~21.4%，平均为8.1%；正三十酸与正十六酸的含量比(C₃₀/C₁₆)为3.5%~11.3%，平均值为6.8%。

就含量分布模式而言，麦草中的正构脂肪酸具有双峰式分布的趋势。其主峰碳数是C₁₆，次峰碳数是C₂₈(图1)。C₉~C₃₂正构脂肪酸的偶碳数优势极为显著。其碳优势指数(CPI)介于5.8~40.3之间，平均值为20.2。C₈~C₃₂的平均碳链长度(ACL)的分布区间是15.7~19.5，平均值为17.3。

2.2 明火烟尘中正构脂肪酸的组成

在麦草明火燃烧产生的烟尘中，正构脂肪酸的组成与麦稜的类似，其碳数变化范围是C₈~C₃₂。这与前人的研究结果基本一致^[9,11]。各品种的总含量分布区间是1 509.3~10 543.7 mg·kg⁻¹，平均值为5 871.2 mg·kg⁻¹。其中最高值与最低值相差6倍，明显小于麦稜中总含量的差别。从西农979的明火烟尘中检出的正构脂肪酸单体明显少于其他5种麦稜，这是其L/H值明显偏大的原因。除此之外，在其余5种麦草的明火烟尘中L/H值分布于0.8~5.3之间，平均值为2.8。该值明显小于麦稜的L/H平均值，表明在明火燃烧过程中麦草中原有的一部

表1 麦草及烟尘中正构脂肪酸的含量和参数值¹⁾Table 1 Proxies and contents of individual *n*-alkanoic acids in wheat straw and its smoke

项目	烟农 10			温六			矮抗 58			扬麦 10			西农 979			扬麦 16		
	麦草	明火	闷烧	麦草	明火	闷烧	麦草	明火	闷烧	麦草	明火	闷烧	麦草	明火	闷烧	麦草	明火	闷烧
C ₈	39.4	127.9	77.6	46.6	39.4	50.2	0.8	73.4	98.6	81.8	73.8	3.8	519.9	540.9				
C ₉	1.1	35.1	93.9	82.7	47.1	26.1	39.3	1.1	41.8	70.3	2.5	56.6	3.9	137.2	465.1			
C ₁₀	1.6	18.8	52.5	0.5	72.8	36.3	0.6	25.5	36.4	0.7	60.7	1.8	27.1	3.8	70.1	345.5		
C ₁₁		13.9	31.2		30.8	15.4		19.4		25.7	13.6	9.3						
C ₁₂	6.6	79.1	187.8	1.9	133.5	61.3	1.6	69.8	81.3	4.3	128.2	96.8	4.5	37.5	88.0	6.1	73.9	1119.5
C ₁₃	0.6		29.5	0.3	34.1	12.4		20.0	9.3	0.3		9.1	0.5	18.8	4.0	68.5	408.5	
C ₁₄	61.6	481.4	846.7	14.2	1320.1	644.1	11.6	502.8	722.8	29.6	459.7	504.7	21.8	258.7	918.5	16.9	105.5	2721.2
C ₁₅	5.5	50.6	147.6	1.2	213.6	85.3	1.0	73.3	75.9	4.0	96.6	72.2	1.9	47.3	117.0	10.9	84.7	1118.6
C ₁₆	407.4	3357.2	9446.2	29.4	6893.1	4653.9	22.3	2010.0	3647.9	324.4	3573.8	14596.5	60.5	1088.4	9741.7	281.8	2829.1	13184.8
C ₁₇	3.1	17.6	73.6	0.3	62.0	30.1		19.7	24.8	2.8	35.1	29.4	0.7	42.3	8.7	156.9	423.0	
C ₁₈	15.6	59.0	296.3	1.3	219.1	94.2	1.2	69.9	79.3	29.2	201.2	250.4	2.2	48.8	130.1	29.4	401.4	228.5
C ₁₉	0.6															4.9	150.3	202.8
C ₂₀	9.1	24.8	95.3	0.4	88.2	36.6	0.5	31.6	37.0	6.8	71.7	64.0	0.8	19.3	71.0	14.3	250.2	875.4
C ₂₁	3.0									2.4				24.6	8.4	165.5	478.9	
C ₂₂	23.1	37.5	110.2	1.0	118.9	49.4	0.7	44.3	42.2	18.1	102.3	119.2	2.0		131.3	35.3	282.4	2279.8
C ₂₃	10.0	16.5	51.7	0.5	45.4	26.8		19.8	17.2	8.6	34.6	53.9	0.8		44.9	17.9	199.0	1318.1
C ₂₄	17.7	66.4	176.5	0.7	110.6	81.2	0.9	36.4	45.3	18.9	137.4	283.9	1.4		173.8	29.7	279.9	1959.4
C ₂₅	3.1	17.1	62.2			38.2		17.6	34.2	4.5		52.1	0.5		42.9	9.4	209.7	444.4
C ₂₆	16.1	110.7	220.9	0.5	96.8	94.5	0.5	56.7	103.3	16.3	166.3	252.2	0.8		173.3	21.6	305.6	1352.9
C ₂₇	1.6	16.5	33.3							2.9		41.7			6.8	199.7	227.2	
C ₂₈	38.6	471.8	869.8	0.7	358.0	304.6	0.4	321.8	385.4	69.5	810.1	957.0	1.0		619.7	32.9	356.7	2835.2
C ₂₉	1.3	15.6	57.8			25.6		22.5	30.0	3.3	43.1	44.8			36.1	6.5	208.2	227.8
C ₃₀	14.1	233.4	453.6		396.9	246.2		349.6	268.8	36.7	485.3	477.3			523.1	15.6	378.2	1306.9
C ₃₁																221.1	131.9	
C ₃₂	3.5	57.6	182.4		189.5	101.2		68.6	49.3	6.8	189.0	154.5			195.6	7.8	258.7	537.8
L/H	3.0	3.6	4.1	8.8	5.3	5.0	8.8	2.6	4.2	1.6	2.0	5.6	9.2	21.2	5.0	1.3	0.8	1.2
\sum	644.9	5220.0	13646.1	52.9	10543.7	6731.0	41.3	3825.4	5799.3	592.0	6736.0	18278.6	103.7	1509.3	13332.0	580.4	7392.5	37244.0
L/H																		
CPI	20.6	27.3	22.3	22.0	21.3	22.8	40.3	18.0	22.0	18.8	23.1	46.0	14.0	25.7	30.0	5.8	3.3	5.3
ACL	17.9	18.0	17.6	15.8	17.1	17.4	15.8	18.6	17.6	19.5	19.2	17.4	15.7	15.6	17.5	19.1	20.5	19.0

1) 含量单位为 mg·kg⁻¹; \sum 为正构脂肪酸总含量; L/H = (C₈ + C₉ + ... + C₁₆) / (C₁₇ + C₁₉ + ... + C₃₂); CPI = (C₁₀ + C₁₂ + ... + C₃₂) / (C₉ + C₁₁ + ... + C₃₁); ACL = (8C₈ + 9C₉ + ... + 32C₃₂) / (C₈ + C₉ + ... + C₃₂)

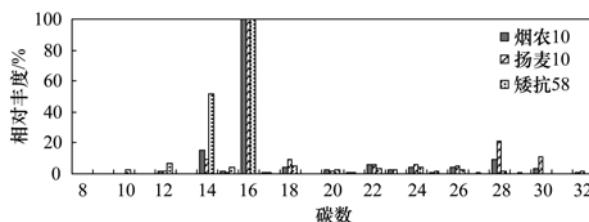


图1 麦草中正构脂肪酸的相对含量分布

Fig. 1 Abundance distribution of *n*-fatty acids in wheat straw

分低碳数正构脂肪酸发生了化学反应,或者又新生成了一部分高碳数的正构脂肪酸。

明火烟尘中 C_{14}/C_{16} 、 C_{28}/C_{16} 、 C_{30}/C_{16} 等比值与麦秸有显著的差别(图2)。明火烟尘中 C_{14}/C_{16} 的变化范围是 3.7% ~ 25.0%, 平均值为 16.5%。除了扬麦 10 外, 在其他各品种的明火烟尘中, C_{14}/C_{16} 值均小于相应的秸秆, 且二者之间的差异变化较大(0.8% ~ 29.1%)。就 C_{14}/C_{16} 值变化趋势而言, 麦秸和明火烟尘基本上是一致的。 C_{28}/C_{16} 值介于 5.2% ~ 22.7% 之间, 其平均值为 14.1%。各品种麦草的 C_{28}/C_{16} 值均小于对应的明火烟尘, 不过两者之间的变化趋势却极为相似的。 C_{30}/C_{16} 值的变化区间是 5.8% ~ 17.4%, 平均值为 11.4%, 且都大于对应的麦秸。说明在明火燃烧过程中, 麦草中的 C_{14} 和 C_{16} 更易于发生化学反应而被消耗, 而 C_{28} 和 C_{30} 则相对稳定。

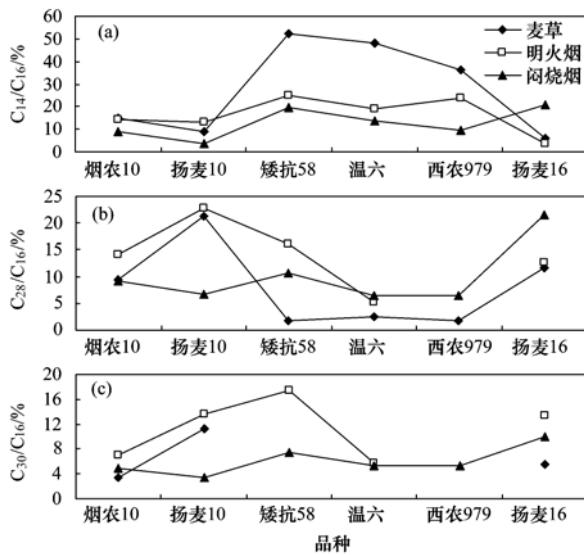


图2 麦草烟尘中3种正构脂肪酸的相对丰度变化趋势

Fig. 2 Varying tendency for values of C_{14}/C_{16} , C_{28}/C_{16} and C_{30}/C_{16} in smoke

明火烟尘中正构脂肪酸的含量分布与麦草类似, 其主峰碳数是 C_{16} , 次峰碳数是 C_{28} 或 C_{30} (图3)。这与木头燃烧排放烟尘中正构脂肪酸的分布模式有

明显的差别^[13]。其 CPI 值的变化范围为 3.3 ~ 27.3, 平均值为 19.8, 与上述麦秸的平均值十分接近; ACL 值在 15.6 ~ 20.5 之间变化, 其平均值是 18.2, 大于麦草的平均值。

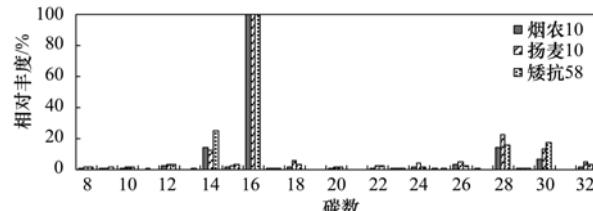


图3 麦秸明火烟尘中正构脂肪酸的相对含量分布

Fig. 3 Abundance distribution of *n*-fatty acids in flaming smoke

2.3 闷烧烟尘中正构脂肪酸的组成

与麦草和明火烟尘类似, 麦秸闷烧烟尘中正构脂肪酸的碳数分布范围也是 C_8 ~ C_{32} 。其总含量的变化区间为 5 799.3 ~ 37 244.0 mg·kg⁻¹, 平均值为 15 838.6 mg·kg⁻¹。后者是明火烟尘中平均总含量的 2.7 倍。表明闷烧过程中参与化学反应的正构脂肪酸较少, 麦秸内的大多数正构脂肪酸直接气化后转变为烟尘。其 L/H 值的变化范围是 1.2 ~ 5.6, 平均值为 4.2。此值明显小于麦秸的对应值, 而大于明火烟尘的平均值。说明虽然闷烧温度比明火燃烧的要低, 但麦秸中的部分正构脂肪酸同样发生了化学反应, 不过消耗量要低于明火燃烧过程。

闷烧烟尘中 C_{14}/C_{16} 值分布于 3.5% ~ 20.6% 之间, 其平均值为 12.7%。该值比麦草和明火烟尘的都要小。 C_{28}/C_{16} 值分布于 6.4% ~ 21.5% 之间, 平均值为 10.1%, 介于麦草和明火烟尘之间。 C_{30}/C_{16} 值分布于 3.3% ~ 9.9% 之间, 平均值是 6.0%, 明显小于明火烟尘。不同品种麦秸闷烧烟尘中 C_{14}/C_{16} 、 C_{28}/C_{16} 和 C_{30}/C_{16} 值的变化关系见图2。除了扬麦 16, 在其他 5 种麦草的闷烧烟尘中 C_{14}/C_{16} 值均低于对应的麦草和明火烟尘。在烟农 10 和扬麦 10 的闷烧烟尘内 C_{14}/C_{16} 值与对应秸秆的差别仅为 5.6% ~ 6.1%, 而矮抗 58、温六、西农 979 等品种的闷烧烟尘与秸秆的差别增大到 26.6% ~ 34.5%。不过, 其与麦秸的变化趋势总体上是一致的, 说明二者之间存在成因关系。除了扬麦 16 之外, 在其他 5 种麦草的闷烧烟尘和明火烟尘之间, C_{14}/C_{16} 值的变化趋势基本相同, 且差别变化幅度比麦草小得多(5.2% ~ 14.4%)。对于 C_{28}/C_{16} 值, 除扬麦 10 以外, 其他 5 种麦草闷烧烟尘的变化趋势与秸秆基本相似, 但与明火烟尘有明显的差别。闷烧烟尘中 C_{30}/C_{16} 值的变化趋势与明火烟尘基本相似。以上 3 个比值及其变

化趋势说明,闷烧条件下麦秸中的 C_{16} 比明火焚烧稳定,参加反应的比例更低。

与麦秸和明火烟尘的类似,闷烧烟尘中的正构脂肪酸也呈双峰式分布。其主峰碳数是 C_{16} ,次峰碳数是 C_{28} (图4)。另外,正构脂肪酸含量也表现出明显的偶碳数优势。其 CPI 的变化区间是 5.3~46.0,平均值为 24.7,远大于麦秸和明火烟尘的平均值。说明燃烧温度对烟尘中奇偶碳数正构脂肪酸的相对含量高低有显著的影响。闷烧烟尘中正构脂肪酸的 ACL 值分布于 17.4~19.0 之间,其平均值为 17.7。该值介于麦秸和明火烟尘的 ACL 平均值之间。

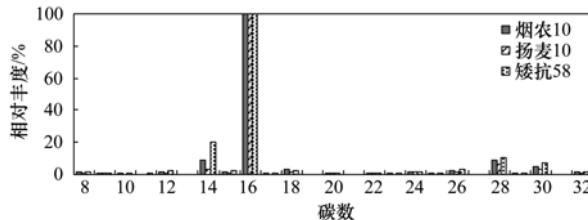


图4 麦秸闷烧烟尘中正构脂肪酸的相对含量分布

Fig. 4 Abundance distribution of n -fatty acids in smoldering smoke

3 结论

(1) 明火烟尘中正构脂肪酸的组成继承了麦草的部分特点。两者均呈以 C_{16} 为主峰碳的双峰式分布,且都具有显著的偶碳数优势。但是,明火烟尘的 ACL、 C_{28}/C_{16} 和 C_{30}/C_{16} 值均比麦草显著增大,而 L/H 和 C_{14}/C_{16} 值明显小于麦草。

(2) 闷烧烟尘中的正构脂肪酸也继承了麦草的分布模式和偶碳数优势,但其 ACL、L/H、 C_{28}/C_{16} 等值介于麦草和明火烟尘之间; C_{14}/C_{16} 值比麦草和明火烟尘都要小, C_{30}/C_{16} 值也小于明火烟尘。

(3) L/H、 C_{14}/C_{16} 、 C_{28}/C_{16} 、 C_{30}/C_{16} 等比值可用于识别大气颗粒物中麦草及其燃烧来源的正构脂肪酸。

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