Characterization of PM2.5 Associated Organic Compounds of Emission Sources Collected During the California Regional PM10/PM2.5 Air Quality Study

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ABSTRACT
As part of the California Regional PM10/PM2.5 Air Quality Study (CRPAQS), PM2.5 emissions samples have been collected and analyzed to expand the current knowledge of the chemical composition and evaluate the contributions of these sources. Emission sources include on-road gasoline and diesel vehicles, off-road construction equipment, meat cooking, residential wood combustion, agricultural and prescribed burning, brake and tire wear, and petroleum production. Samples were analyzed by GC/MS methods for semi-volatile organic compounds such as polycyclic aromatic hydrocarbons, alkanes, hopanes, and after derivatization with bis(trimethylsilyl)trifluoroacetamide to convert polar compounds into their trimethylsilyl derivatives for organic acids, methoxylaed phenols, cholesterol, sitosterol, and levoglucosan. The preliminary results of these analyses for residential and agricultural wood combustion and meat cooking source samples are presented.

INTRODUCTION
Emission source samples were collected as part of the CRPAQS project. The objective of this study was to develop a more comprehensive database of the mass fractions of gaseous, semi-volatile, and particulate species for the major sources of organic and elemental carbon within the California San Joaquin Valley. These profiles will then be used to conduct receptor-oriented source apportionment to assess contributions to ambient fine particulate matter (PM2.5). Organic compounds are emitted from all combustion sources and may provide valuable information to the receptor modeling. To distinguish sources, tracer compounds must be emitted in relatively high abundance and be stable for detection in ambient samples. The chemical mass balance (CMB) model requires input of distinct chemical profiles to quantify the contributions of sources, without distinct chemical and physical properties the sources cannot be distinguished.

Polycyclic aromatic hydrocarbons (PAH) are formed during the combustion process and as such are potential tracers for various combustion emissions. Many of these compounds are found in all combustion sources but have variable proportions. Further information can be

obtained by the analysis of additional classes of compounds such as methoxylated phenols, organic acids, sterols, hydrocarbons, hopanes and levoglucosan. Many of the hydrocarbon compounds analyzed, such as normal and branched alkanes, are common to many emission sources. However, normal alkanes may provide information regarding the nature of the emission source. Biogenic emissions are reported to have an even-odd carbon number preference, but anthropogenic emissions do not show an even-odd preference.[1] Methoxylated phenols are reported to be associated with wood combustion and may aid in differentiation between soft and hard woods.[2,3] In addition, levoglucosan has been reported to be unique to wood combustion and found to be in relatively high quantities among biomass species sampled.[4-6] Cholesterol, which is found in tissues of higher animals, may aid in the apportionment of meat cooking sources.[7-9] Geochemists have used hopane and sterane compounds for the unique identification of oils and oil shale. Hopanes and steranes may provide a unique marker for mobile sources such as gasoline and diesel vehicles, due to their presence in lubricating oils.[10,11] Additional information may be gathered from the analysis of organic acids, which are emitted in high abundance relative to many of the other identifiable semi-volatile organic compounds.[12,13] These compounds are emitted in many of the combustion emissions, however unique proportions of organic acids may exist for various emission sources. To assess the importance of these and many other compounds complete organic analysis of the emission sources were conducted. The objective of this paper is to discuss the sample collection and unique semi-volatile organic compounds for the residential and agricultural wood combustion and meat cooking source samples.

EXPERIMENTAL

Sample Collection

Source samples were collected to characterize emissions from residential and agricultural combustion of biomass using a dilution stack sampler. Samples include fireplace combustion of oak, pine, almond, eucalyptus and cedar woods as well as wheat and rice straws. The Desert Research Institute (DRI) dilution stack sampler was modeled after the California Institute of Technology dilution tunnel which is described elsewhere.[14] Emissions were withdrawn isokinetically from the flue and diluted approximately 20 times with activated charcoal and HEPA filtered air. The dilution process includes rapid mixing of emissions with clean filtered air to cool the samples to ambient temperature and then the sample is swept into the residence time chamber to allow 80 seconds for equilibrium of gas and particle phase species before sampling. Samples are drawn through cyclone separators with a cut-off diameter of 2.5 μm and then pulled through the sampling devices by individual sampler vacuum pumps. The semi-volatile organic compounds were collected on Teflon-impregnated glass-fiber filters followed by PUF/XAD/PUF cartridges using a DRI fine particle/semi-volatile organic sampler.

Meat cooking emission sampling was conducted at the University of California, Riverside, College of Engineering-Center for Environmental Research and Technology (CE-CERT) commercial kitchen test facility using their standard test methods. Test methods and the CE-CERT facility are described elsewhere.[15] A brief summary of meat cooking tests conducted

for this study can be found in Goliff et al.[16] Meat cooking samples were collected using a dilution stack sampler as described above.

Organic Analysis

Several deuterated internal standards were added to each filter/PUF/XAD/PUF sample prior to extraction. The deuterated standards used include: PAH compounds ranging from naphthalene-d8 to coronene-d12; high molecular weight aliphatic hydrocarbons ranging from dodecane-d26 to octacosane-d58, cholestane-d4; and polar organics ranging from benzoic-d3 acid to cholesterol-d6. The organic analysis included extraction by two organic solvents to expand the polarity range of analytes. The filter and XAD were combined and extracted by microwave-assisted extraction with dichloromethane followed by acetone. The PUF plugs were extracted using the Soxhlet apparatus with 10% diethylether in hexane followed by acetone. These extracts were then combined and concentrated in the laboratory and then split into two fractions. The first fraction was analyzed without further alteration for PAH, alkanes, hopanes, and steranes by a GC/MS using an electron impact select ion storage (SIS) method. The second fraction was derivatized using a mixture of bis(trimethylsilyl)trifluoroacetamide (BSTFA), trimethylsilylcholorosilane (TMCS), and silylation grade pyridine to convert the polar compounds into their trimethylsilyl derivatives for analysis of organic acids, cholesterol, sitosterol, and levoglucosan. Samples were then analyzed by GC/MS using isobutane chemical ionization SIS method. All analyses were conducted using a Varian 3800 Gas Chromatograph interfaced to Varian Saturn 2000 Mass Spectrometer equipped with either a Varian 8200 Autosampler or a Varian 8400 Autosampler. A 30m CP-Sil-8 CB MS column was used for all analyses.

The choice of the derivatization reagent BSTFA for polar organics was made due to its reactivity with the hydroxyl functional group. The reaction involves a replacement of the hydroxyl hydrogen with a trimethylsilyl group. This replacement transforms organic acids, levoglucosan, and cholesterol into more non-polar and more volatile derivatives, thus enhancing the chromatography. Identification was then further enhanced by mass spectral isobutane chemical ionization, providing a soft fragmentation. A strong presence of the molecular ion (M+) was found in most spectra. In addition, the spectra of most organic acids contained a high abundance of (M-15)+ fragment ion, corresponding to a loss of methyl group. Even though the compounds reported here were all quantified using authentic standards, the soft fragmentation of these analytes provided additional evidence for positive identification. Table 1 provides a list of the polar organic compounds and the quantification ions used for identification.

Table 1 List of Polar Organics.

Compound Type	Mnemonic	Compound Name	Quantitation Ion
IS		hexanoic-d11 acid	200
Analyte	HEXAC	hexanoic acid	173, 189
Analyte	HEPTAC	heptanoic acid	203, 187
Analyte	MEMALON	methylmalonic acid	263
Analyte	GUAI	Guaiacol	181, 196
IS		benzoic-d5 acid	184, 200
Analyte	BENAC	benzoic acid	179, 195

Compound Type	Mnemonic	Compound Name	Quantitation Ion
Analyte	OCTANAC	octanoic acid	201, 289
Analyte	GLYCERO	Glycerol	309, 293
Analyte	MALEAC	maleic acid	261
IS		succinic-d4 acid	251, 267
Analyte	SUCAC	succinic acid	173, 263
Analyte	MEGUA4	4-methylguaiacol	210, 195
Analyte	MESUCAC	methylsuccinic acid	187, 349
Analyte	OTOLUIC	o-toluic acid	281
Analyte	PICAC	picolinic acid	196
Analyte	MTOLUIC	m-toluic acid	281
Recovery Std.		1,2,4-butanetriol	233, 307
Analyte	NONAC	nonanoic acid	231, 215
Analyte	PTOLUIC	p-toluic acid	281
Analyte	MEPIC36	3-, 6-methylpicolinic acid	250
Analyte	DIMEB26	2,6-dimethylbenzoic acid	295
Analyte	ETGUA4	4-ethyl-guaiacol	224, 209
Analyte	SYRI	Syringol	211, 226
Analyte	GLUAC	glutaric acid	187, 261
Analyte	MEGLU2	2-methylglutaric acid	331, 275
Analyte	DIMEB25	2,5-dimethylbenzoic acid	295
Analyte	MEGLU3	3-methylglutaric acid	275, 331
Analyte	DIMEB24	2,4-dimethylbenzoic acid	295
Analyte	DIMEB35	3,5-dimethylbenzoic acid	295
Analyte	DIMEB23	2,3-dimethylbenzoic acid	295
Analyte	DECAC	decanoic acid	245, 229
Analyte	ALGUAI4	4-allyl-guaiacol (eugenol)	221, 236
Analyte	MESYR4	4-methyl-syringol	241, 224
Analyte	DIMEB34	3,4-dimethylbenzoic acid	295
Analyte	HEXDAC	hexanedioic (adipic) acid	201, 291
Analyte	TDECEN2	trans-2-decenoic acid	243, 227
Analyte	CPINAC	cis-pinonic acid	257, 239
Analyte	MEADIP3	3-methyladipic acid	289, 305
Analyte	FGUAI4	4-formyl-guaiacol (vanillin)	225
Analyte	UNDEC	undecanoic acid	243, 259
Analyte	ISEUG	Isoeugenol	236, 221
Analyte	HEPDAC	Heptanedioic (pimelic) acid	215, 305
Analyte	ACVAN	acetovanillone	239, 223
Analyte	LAUAC	dodecanoic (lauric) acid	273, 257
Analyte	PHTHAC	phthalic acid	295
IS		Levoglucosan-U-13C6	295, 367
Analyte	LEVG	Levoglucosan	289, 361
Analyte	SYRALD	syringaldehyde	255, 327
Analyte	TDECAC	tridecanoic acid	287, 271
Analyte	ISPHAC	isophthalic acid	295, 311
Analyte	AZEAC	azelaic acid	243, 333
Analyte	MYROL	myristoleic acid	299
IS		myristic-d27 acid	328, 312
Analyte	MYRAC	myristic acid	301, 285
Analyte	SEBAC	sebacic acid	257, 347
Analyte	PDECAC	pentadecanoic acid	315, 299
Analyte	UNDECDI	undecanedioic acid	271
Analyte	PALOL	palmitoleic acid	327, 311
Analyte	PALAC	palmitic acid	329, 313
Analyte	ISSTER	isostearic acid	357, 341
Analyte	HEPTAD	heptadecanoic acid	341, 327
Analyte	UNDD111	1,11-undecanedicarboxylic acid	299
Analyte	OLAC	oleic acid	355

Compound Type	Mnemonic	Compound Name	Quantitation Ion
Analyte	ELAC	elaidic acid	355
Analyte	STEAC	stearic acid	357, 341
Analyte	DODD112	1,12-dodceanedicarboxylic acid	313
Analyte	NDECAC	nonadecanoic acid	371, 355
Analyte	DHABAC	dehydroabietic acid	373
Analyte	ECOSAC	eicosanoic acid	385, 370
Analyte	ABAC	abietic acid	375, 359
IS		cholesterol-d6	464, 448
Analyte	CHOL	Cholesterol	458, 444
Analyte	BSIT	b-sitosterol	397, 486

RESULTS AND DISCUSSION

Data presented in the following sections include a qualitative description of the most unique compounds for characterization of wood combustion and meat cooking sources samples. The data shown here have been normalized to the percent weight fraction of analyte to the total particulate carbon and to the mass concentration. Carbon measurements were made using pre-fired quartz-fiber filters and the thermal/optical reflectance (TOR) method described in detail elsewhere.[17] The total carbon concentration was chosen as a denominator to avoid controversy between various operational definitions of organic and elemental carbon. Mass concentration was also chosen as a denominator to assess the overall uncertainty. Comparisons will be made regarding these two normalization choices.

Wood Combustion

Chemical characterizations of the residential and agricultural wood combustion source samples are summarized in Figures 1 and 2. The methoxylated phenols and levoglucosan have been previously reported as unique semi-volatile compounds for biomass combustion[2,4] produced during the pyrolysis of wood lignin. The two classes of methoxylated phenols found in wood smoke are guaiacols and syringols. These compounds vary in volatility and can be found distributed between the gas and particle phases. The results reported here are analyzed from combined extracts from the filter/PUF/XAD mixed phase media. Methoxylated phenols and levoglucosan are quantitated as trimethylsilyl derivatives as described above.

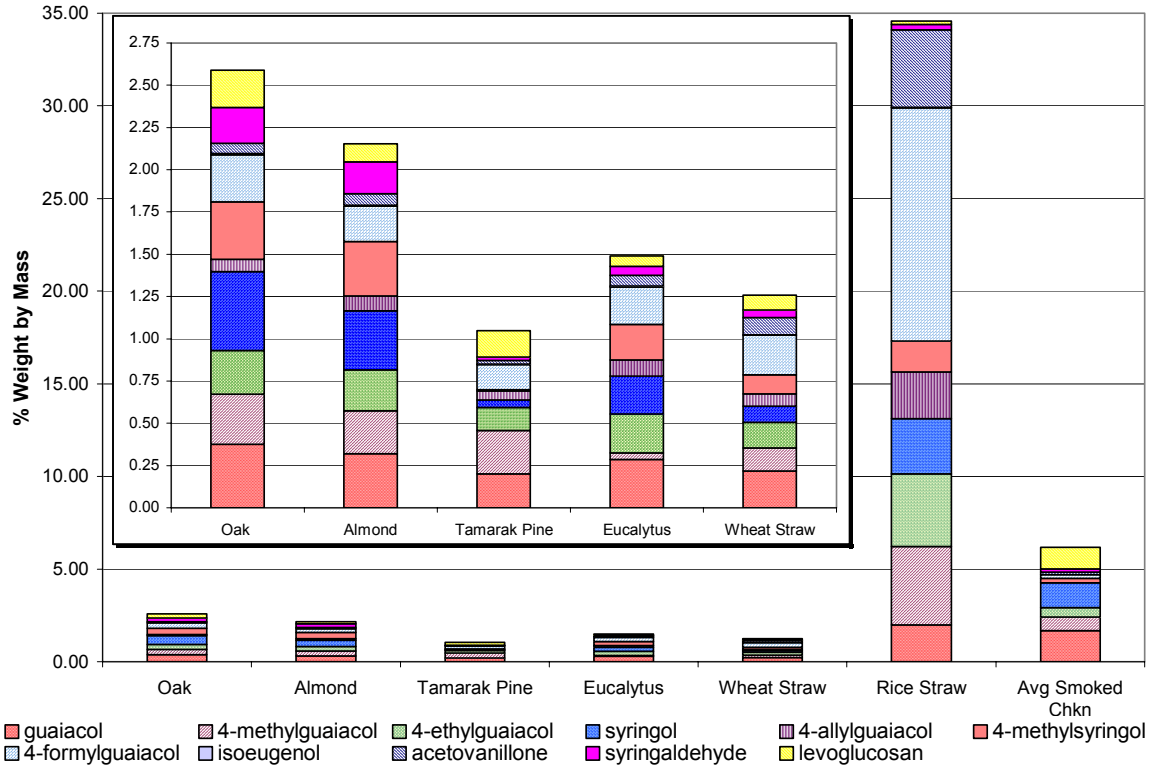
Emission of guaiacols, syringols, and levoglucosan can be seen in each of the biomass source samples. Although small amounts of syringols can be seen in each of the samples the abundance of syringols in the hardwoods and straws are much greater than abundance found in pine. This finding is consistent with results previously reported by McDonald et al. and Hawthorne et al.[2,3,18,19] Hawthorne et al. reported an average syringol value 20 times higher for hardwoods than softwoods.[2] The percent weight by total carbon for the abundance of syringol found in oak compared to Tamarak pine shown here is 13 times higher.

It has been reported that the concentration of total carbon in rice straw is lower than in other types of biomass; it has been estimated to make up only 35% of the total dry matter.[20] Rice straw has high amounts of silicon, which may account for 10-15% of the total dry mass.[20] During the fireplace combustion of this rice straw, we observed the rice straw to melt and

condense together rather than burn efficiently as other biomass. This inefficient combustion produced volatile organic compounds but did not produce much of the particulate species, compared to the other biomass types. In addition, the artifact associated with carbon measurements appears to be quite high. The total organic carbon measured by TOR accounts for 160% of the mass. The high percentage is likely a result of the difference in filter types. Measurements of mass are obtained gravimetrically from a Teflon-impregnated glass fiber filter and the carbon analysis is performed using a quartz filter. The physical properties differ between these filters, thus yielding an artifact due to the absorption of volatile organics to the quartz filter. The percent weight fractions shown here of methoxylated phenols are also quite high by comparison due to low amount of particulate mass and particulate carbon collected.

Levoglucosan, a sugar anhydride, is formed in the pyrolysis of cellulose. The mechanism of pyrolysis is described by Simoneit et al.[4] Levoglucosan, shown in Figures 1 and 2, appears to be found in all of the biomass samples and seems to be relatively consistent over the various biomass samples. The abundance of levoglucosan is shown more clearly in Figure 2, where the percent weight is shown as a function of total carbon.

Figure 1. Residential and Agricultural Biomass Combustion Characterization Normalized by Mass Concentration.

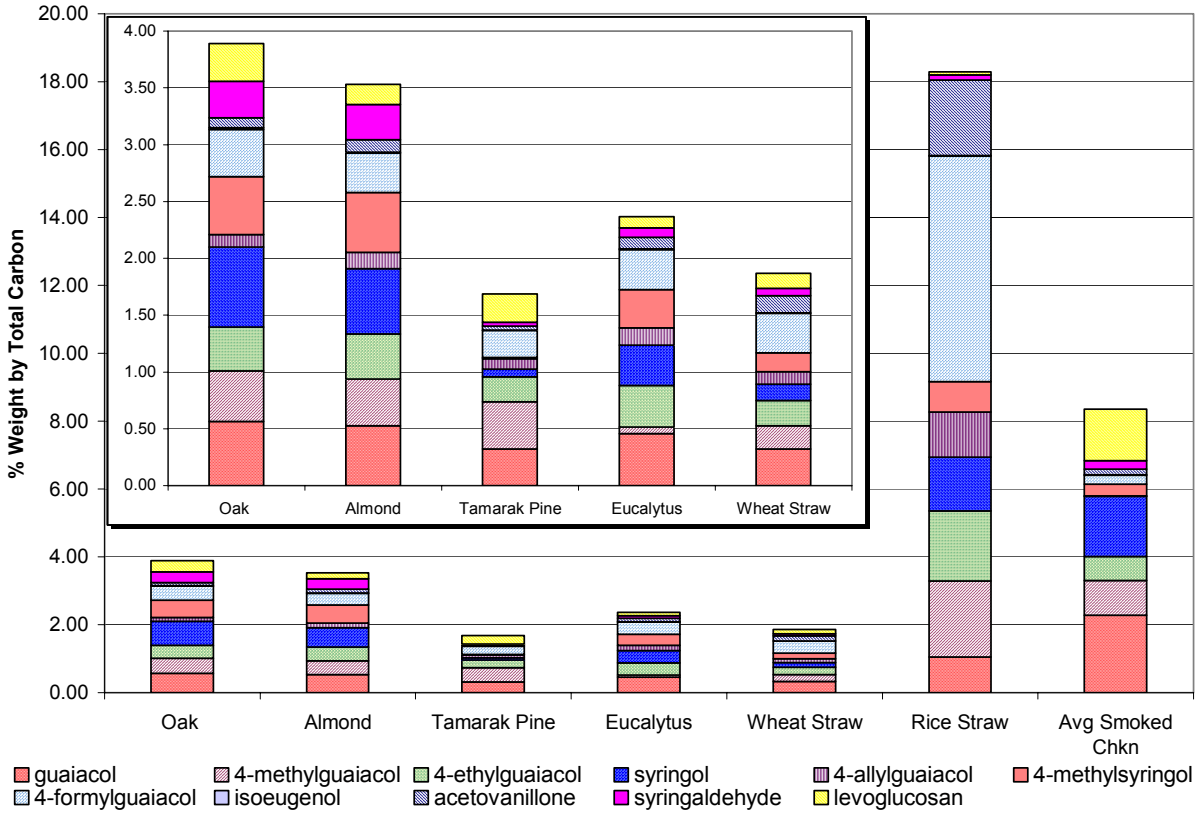


Also shown in Figures 1 and 2 is the percent weight of the methoxylated phenols and levoglucosan associated with the mesquite smoked chicken emission tests. The smoking process involves low temperature cooking by the heat produced during pyrolysis of mesquite wood. Thus, a comparison to other biomass samples may provide a better understanding of

the emissions produced. This emission sample is also discussed in the meat cooking section below.

Comparisons between the relative weight percentages by mass and by total carbon show little evidence of distinct differences as can be seen in Figures1 and 2. The most notable difference is the percent weight of the methoxylated phenols and levoglucosan for rice straw when divided by the mass concentration. The total weight fraction of these compounds is almost 35% by mass as compared to 18% by total carbon. This difference may be due to the larger total organic carbon concentration measurement than the mass concentration measurement, produced in part due to the artificial adsorption of volatile organic compounds by the quartz filter.

Figure 2 Residential and Agricultural Biomass Combustion Characterization Normalized by Total Carbon Concentration.



Meat Cooking

The chemical characterization of meat cooking source samples is summarized in Figures 3 and 4. Semi-volatile organic compounds found in meat cooking are often also found in other sources and are found in very low concentrations in the ambient atmosphere. Compounds such as cholesterol, palmitoleic acid, palmitic acid, stearic acid, and oleic acid are more

abundant in meat cooking than in most other emission sources.[7] The cholesterol and organic acids reported here are quantified as trimethylsilyl derivatives as described above.
Due to the presence of cholesterol in the body tissues of all higher animals, cholesterol may be indicative of meat cooking.[9] The abundance of cholesterol in source samples is dependent upon the type of meat and the cooking appliance.[9] Results shown here from this study indicate the highest abundance is found in chicken and hamburger that has been charbroiled or propane grilled. Values are found to be much lower for the mesquite smoked chicken and three orders of magnitude lower for the stir-fry sample. This difference is due to different cooking methods.

Other polar semi-volatile organic compounds seem to be enhanced in meat cooking samples but are not necessarily unique to these source emissions. Compounds such as palmitoleic acid, palmitic acid, stearic acid, and oleic acid are found in most of the meat cooking emission samples. The percent weight of oleic acid is quite high relative to the other organic acids for the charbroiled chicken, charbroiled hamburger, and the propane grilled chicken. Palmitoleic acid is also relatively high in the charbroiled chicken, charbroiled hamburger, propane grilled chicken, and the mesquite grilled chicken. Both of these alkenoic acids were reported to be quite abundant in charbroiled hamburger in tests conducted by Rogge et al.[7] The values shown for oleic acid are approximately 10 times higher than the palmitoleic acid values in charbroiled hamburger.[7] Weight percentage values shown here for oleic acid compared to palmitolec acid differ by a factor of 5 for charbroiled hamburger and a factor of 3 for charbroiled chicken.

Weight percentages of analytes measured in the stir-fry source sample are relatively high due to the lower total carbon emitted by the cooking type. Important organic acids here include 1,12-dodecanedicarboxylic acid, 3-methylpicolinic acid and/or 6-methylpicolinic acid (quantified together), octanoic acid, and heptanoic acid. The differences in the relative abundance of oleic acid, palmitoleic acid, and palmitic acid as compared to 1,12-dodecanedicarboxylic acid, 3-methylpicolinic acid and/or 6-methylpicolinic acid is most likely due to the type of cooking operation. Under-fire cooking emits oleic acid, palmitoleic acid, and palmitic acid in relatively high abundances, which is likely due to the drippings of the meat fat directly onto the fire, thus volatizing these compounds. Stir-fry cooking is conducted inside a hot frying pan. Thus the food products do not volatilize from dripping into the fire but may volatilize from the heat applied to the cooking surface and the mixing together of various water containing vegetables and oil. The smoked chicken emission tests are conducted using a side-by-side firebox and smoking chamber. This setup provides lower heat to the cooking chicken and thus reduces the volatilization rates of palmitoleic acid, palmitic acid, stearic acid, and oleic acid.

Differences between Figure 3 and Figure 4 are minor. The overall weight percentage is slightly higher for most samples when normalized by the mass concentration as opposed to the total carbon normalization. This may be due in part to the artificial adsorption of volatile organic compounds by the quartz filter.

Figure 3 Characterization of Meat Cooking as Percent Weight by Mass.

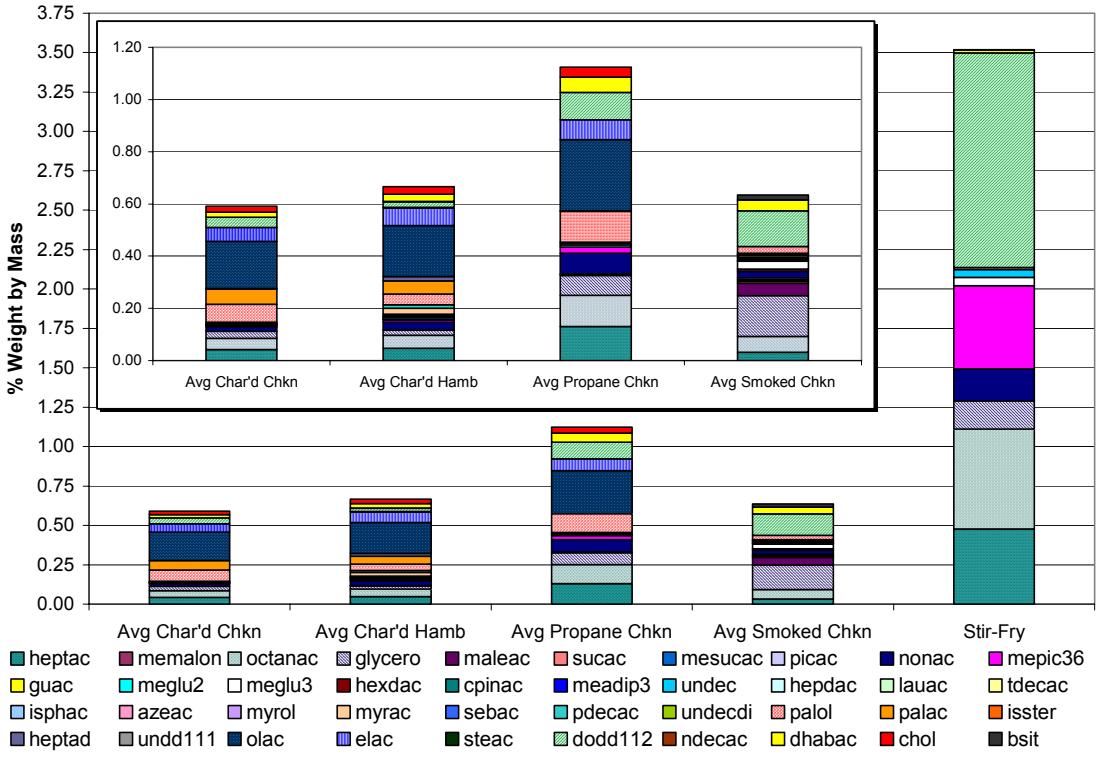
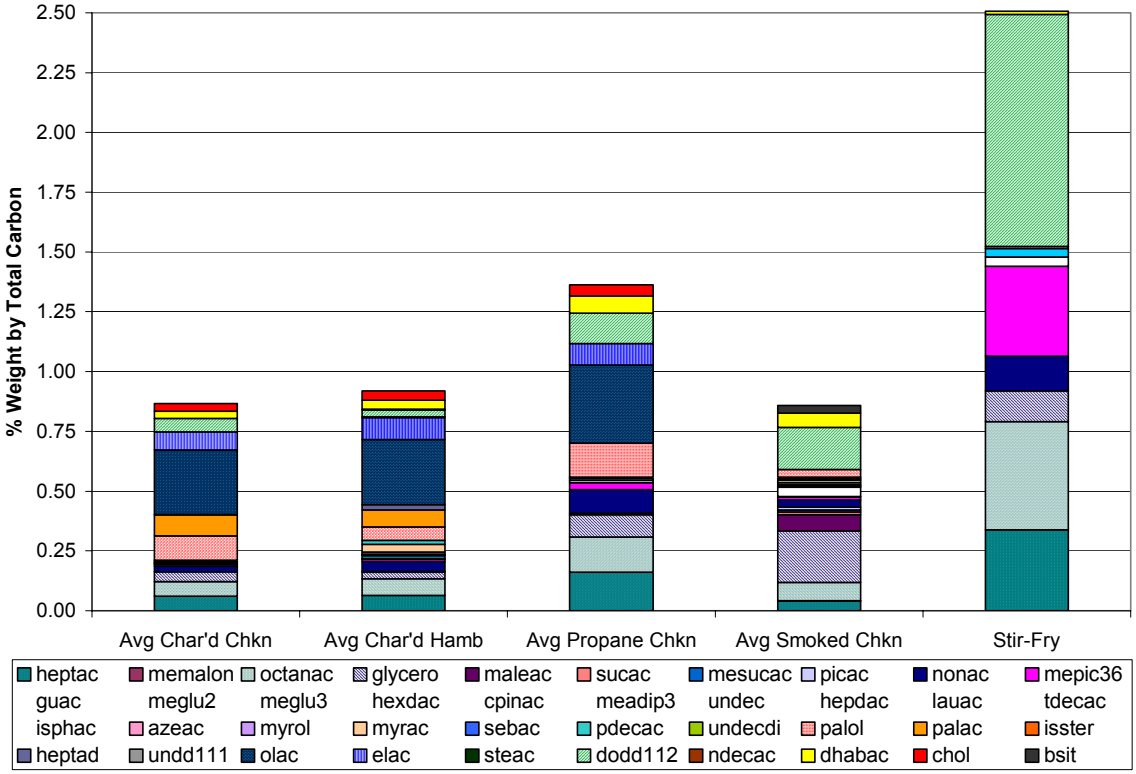


Figure 4 Characterization of Meat Cooking as Percent Weight by Total Carbon.



CONCLUSIONS

Methoxylated phenols and levoglucosan are emitted in relatively high abundance across the biomass samples including residential and agricultural combustion emission samples. The abundance of syringols differs significantly for Tamarak pine as compared to the other biomass samples. Rice straw shows much higher weight percentages of the methoxylated phenols and was found to have very low amounts of total particulate species due to low temperature combustion or melting of sample in fireplace. The amounts of volatile species were increased relative to the semi-volatile species as seen by the 160% organic carbon by mass. Mesquite smoked chicken emissions also show methoxylated phenols and levoglucosan.

Abundance of cholesterol in meat cooking source samples is low compared to the abundance of palmitoleic and oleic acid in charbroiled chicken, charbroiled hamburger, and propane grilled chicken. These emission sources have higher amounts of these organic acids than mesquite smoked chicken and the marinated beef stir-fry. Grilling by either by charcoal or propane utilizes high temperatures with a large surface area which may rapidly volatilize drippings from the meat. However, stir-fry cooking is conducted inside a hot frying pan. Thus the food products do not volatilize from dripping into the fire, but may volatilize from the heat applied to the cooking surface and the mixing together of various water containing vegetables and oil. Likewise, mesquite smoked chicken is cooked slowly by the heat generated by the smoke of mesquite combustion.

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Key Words

CRPAQS, PM 2.5, Source Emissions, Polar Organics