Comparison of Sugar Composition in Fine and Coarse Particulate Matter at Four Sites in Eastern Texas and Central Arizona

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9th ICCPA, Berkeley, CA
Sugars in Ambient PM

• Summary of 1999 National Emission Inventory by major source category (US EPA, 2001) (millions of tons / year)

<table>
<thead>
<tr>
<th>Source</th>
<th>PM$_{2.5}$</th>
<th>PM$_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Combustion for Electric Utility</td>
<td>0.13</td>
<td>0.23</td>
</tr>
<tr>
<td>On-road Vehicles</td>
<td>0.41</td>
<td>0.46</td>
</tr>
<tr>
<td>Agriculture &amp; Forestry</td>
<td>0.95</td>
<td>4.89</td>
</tr>
<tr>
<td>Agricultural burning &amp; Forest fires</td>
<td>0.87</td>
<td>1.01</td>
</tr>
</tbody>
</table>

• Sugars as primary markers for biogenic carbon associated with biomass burning and atmospheric entrainment of soil
## Sugars and Main Sources

<table>
<thead>
<tr>
<th>Main Source</th>
<th>Compound</th>
<th>Sugar Category</th>
<th>Formation and Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass Burning</td>
<td>Levoglucosan</td>
<td>Anhydrosaccharide</td>
<td>Cellulose decomposition; Established marker</td>
</tr>
<tr>
<td>Soil Organic Matter</td>
<td>Glucose</td>
<td>Monosaccharide</td>
<td>Cellulose pyrolysis</td>
</tr>
<tr>
<td></td>
<td>Sucrose</td>
<td>Disaccharide</td>
<td>Storage for fixed CO2</td>
</tr>
<tr>
<td></td>
<td>Trehalose</td>
<td>Disaccharide</td>
<td>Fungal metabolite; storage and transport carbohydrates and cell protectants against environmental stress (e.g., desiccation, frost and heat)</td>
</tr>
<tr>
<td></td>
<td>Mannitol</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sorbitol</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Arabitol</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ribitol</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Iso-erythritol</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Glycerol</td>
<td>Sugar Polyol</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **24-hr PM2.5 Samples:**
  - Every 3rd day using High-Vol air samplers at a flow rate of 1.13 m³/min, 174 samples in total
Sampling in Arizona (Jan – Apri. 2008)

- **24-hr PM2.5 and PM10 Samples:**
  - Every other day using a High-Vol air sampler at 1.13 m³/min
  - A total of 45 PM2.5 and 46 PM10 samples in parallel

- **Soil Samples:**
  - 18 agricultural soil samples, 6 native soil samples, 8 road dust samples taken in the vicinity of Higley sampling site in Jan and Apri 2008 for source study
Results and Discussion
Ambient Sugars in PM2.5

Levoglucosan

Glucose

Sucrose

Trehalose
Ambient Sugar Polyols in PM2.5

Higley

San Augustine

Clarksville

Dallas

Trehalose
Mannitol
Arabitol
Glycerol

Figures show the concentration of ambient sugar polyols (Trehalose, Mannitol, Arabitol, Glycerol) in PM2.5 for different locations over several months. The graphs illustrate the peak and trough values for each polyol at each location.
Correlation Analysis

- Strong correlation among trehalose and major sugar polyols (mannitol and arabitol);
- Weaker correlation between glycerol and trehalose, and glycerol with other major polyols – other potential source for glycerol;
- Stronger correlations for samples at the two rural sites – local biogenic sources have less influence on sugars in aerosols at the urban site than at the rural sites.

<table>
<thead>
<tr>
<th></th>
<th>Higley</th>
<th>San Augustine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trehalose</td>
<td>Mannitol</td>
</tr>
<tr>
<td>Trehalose</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Mannitol</td>
<td>0.73</td>
<td>1</td>
</tr>
<tr>
<td>Arabitol</td>
<td>0.62</td>
<td>0.84</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.12</td>
<td>0.49</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>-0.15</td>
<td>0.18</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>Clarksville</th>
<th>Dallas</th>
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<tbody>
<tr>
<td></td>
<td>Trehalose</td>
<td>Mannitol</td>
</tr>
<tr>
<td>Trehalose</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Mannitol</td>
<td>0.78</td>
<td>1</td>
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<tr>
<td>Arabitol</td>
<td>0.64</td>
<td>0.85</td>
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<tr>
<td>Glycerol</td>
<td>-0.02</td>
<td>0.06</td>
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<tr>
<td>Levoglucosan</td>
<td>-0.06</td>
<td>-0.03</td>
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</tbody>
</table>
Higley Sample – PM10 vs. PM2.5

Levoglucosan - Higley

![Graph showing PM10 and PM2.5 levels from 1/22/2008 to 4/15/2008. The x-axis represents dates, and the y-axis represents ng/m3. The graph shows fluctuations in PM10 and PM2.5 levels over time.]
Estimated compound ratio in Higley PM$_{10}$ and PM$_{2.5}$ samples using least square linear relationship:

<table>
<thead>
<tr>
<th></th>
<th>Levoglucosan</th>
<th>Glycerol</th>
<th>Glucose</th>
<th>Sucrose</th>
<th>Trehalose</th>
<th>Mannitol</th>
<th>Arabitol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$<em>{10}$/PM$</em>{2.5}$</td>
<td>0.89</td>
<td>1.04</td>
<td>2.72</td>
<td>2.57</td>
<td>2.48</td>
<td>4.27</td>
<td>1.93</td>
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</table>
Higley Sample - Correlation Analysis

Pearson’s Correlation Coefficients (PM2.5, Higley)

<table>
<thead>
<tr>
<th></th>
<th>Levoglucosan</th>
<th>Glucose</th>
<th>Sucrose</th>
<th>Trehalose</th>
<th>Glycerol</th>
<th>Erythritol</th>
<th>Arabinol</th>
<th>Mannitol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levoglucosan</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucose</td>
<td>0.17</td>
<td>1.00</td>
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<tr>
<td>Sucrose</td>
<td>-0.23</td>
<td>0.63</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Trehalose</td>
<td>-0.15</td>
<td>0.72</td>
<td>0.84</td>
<td>1.00</td>
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</tr>
<tr>
<td>Glycerol</td>
<td>0.54</td>
<td>0.46</td>
<td>-0.06</td>
<td>0.12</td>
<td>1.00</td>
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<tr>
<td>Erythritol</td>
<td>0.12</td>
<td>0.62</td>
<td>0.60</td>
<td>0.77</td>
<td>0.32</td>
<td>1.00</td>
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<tr>
<td>Arabinol</td>
<td>0.19</td>
<td>0.64</td>
<td>0.44</td>
<td>0.62</td>
<td>0.45</td>
<td>0.75</td>
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<tr>
<td>Mannitol</td>
<td>0.18</td>
<td>0.73</td>
<td>0.51</td>
<td>0.73</td>
<td>0.49</td>
<td>0.83</td>
<td>0.84</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Pearson’s Correlation Coefficients (PM10, Higley)

<table>
<thead>
<tr>
<th></th>
<th>Levoglucosan</th>
<th>Glucose</th>
<th>Sucrose</th>
<th>Trehalose</th>
<th>Glycerol</th>
<th>Erythritol</th>
<th>Arabinol</th>
<th>Mannitol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levoglucosan</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucose</td>
<td>0.10</td>
<td>1.00</td>
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<td></td>
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<tr>
<td>Sucrose</td>
<td>-0.33</td>
<td>0.42</td>
<td>1.00</td>
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<td></td>
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<tr>
<td>Trehalose</td>
<td>-0.33</td>
<td>0.38</td>
<td>0.82</td>
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<tr>
<td>Glycerol</td>
<td>0.20</td>
<td>0.20</td>
<td>0.14</td>
<td>0.15</td>
<td>1.00</td>
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<td></td>
<td></td>
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<tr>
<td>Erythritol</td>
<td>0.09</td>
<td>0.08</td>
<td>-0.14</td>
<td>-0.07</td>
<td>0.53</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arabinol</td>
<td>0.14</td>
<td>0.21</td>
<td>0.16</td>
<td>0.36</td>
<td>0.53</td>
<td>0.39</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Mannitol</td>
<td>0.01</td>
<td>0.25</td>
<td>0.30</td>
<td>0.44</td>
<td>0.25</td>
<td>0.03</td>
<td>0.77</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Higley Soil Resuspension Samples

Higley Soil - Glucose

Higley Soil - Trehalose

Higley Soil - Sucrose

Higley Soil - Glycerol

Site # with a B suffix refers to samples taken in April, others were taken in Jan
Higley Soil Resuspension Samples

Soil Samples:
- 11 – Native Soil
- 15 – Road Dust
- Others – Agricultural Soil

Ambient PM:
Data shows an enrichment of sugars in ambient PM2.5 relative to PM10
PMF Modeling Using Sugars As Molecular Markers - Texas

- 8 sugar compounds were used along with other particulate molecular markers;

- 3 factors enriched in sugar compounds were resolved to represent the contribution of wood smoke, entrainment of soil to PM$_{2.5}$
PMF Modeling Using Sugars As Molecular Markers - Texas

Relative Source Contribution to PM2.5

Dallas
- Wood Smoke: 16%
- Mobile Sources: 32%
- Meat Cooking: 13%
- Soil Entrainment: 5%
- Biogenic SOA: 9%
- Secondary Sulfate: 25%

San Augustine
- Wood Smoke: 22%
- Mobile Sources: 31%
- Meat Cooking: 3%
- Soil Entrainment: 14%
- Biogenic SOA: 4%
- Secondary Sulfate: 26%

<table>
<thead>
<tr>
<th>Source Type</th>
<th>Dallas</th>
<th>San Augustine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood Smoke</td>
<td>16%</td>
<td>22%</td>
</tr>
<tr>
<td>Soil Entrainment</td>
<td>5%</td>
<td>14%</td>
</tr>
</tbody>
</table>

- A baseline for the further expansion of sugars as tracers for soil sources in receptor modeling
Conclusions

• Much lower sugar concentrations in ambient PM2.5 in AZ than in TX;

• Biomass burning and entrainment of soils – two major sources of aerosol sugars;

• Different degree of source impact in different seasons and geographic locations;

• Smaller influence of local soil entrainment to the atmosphere at the urban/suburban sites than rural sites.

• Levoglucosan is similar in ambient PM2.5 and PM10, glucose, sucrose, trehalose and sugar polyols are more abundant in ambient PM10;
Conclusions (continued)

- Lower sugar levels in agricultural soil may indicate an alteration of soil microbial activity;

- Higher sugar contents were measured in the coarse fraction of agricultural soil particles. For native and road dusts, the fine faction contained greater sugar contents;

- Although PM2.5 soil samples have higher sugar content, ambient PM10 levels of sugars are greater than PM2.5;

- The contribution of agricultural soil entrainment and biomass burning to ambient PM2.5 can be isolated and quantified using source apportionment models with sugars as molecular markers.
Acknowledgements

- Dr. Matt Fraser
- Andrea Clements and Shagun Bhat
- Dr. Pierre Herckes
- Funding from Texas Commission on Environmental Quality and Environmental Protection Agency (STAR Program)