Using Carbohydrates as Molecular Markers for Agricultural and Native Soils

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Overview

- Introduction and Background
- Research Objectives
- Texas Field Sampling
- Results and Discussion
- Future Work

Introduction and Background

PM2.5 and Sources

- Summary of 1999 National Emission Inventory by major source category (US EPA, 2001)

Source	PM2.5 (millions of tons per year)
Fuel Combustion for Electric Utility	0.13
On-road Vehicles	0.23
Agricultural & Forestry	0.95
Agricultural Fires & Forest Wildfires	0.33

Sugars as Molecular Markers

- Sugars are known components of soils and have been measured in ambient particles

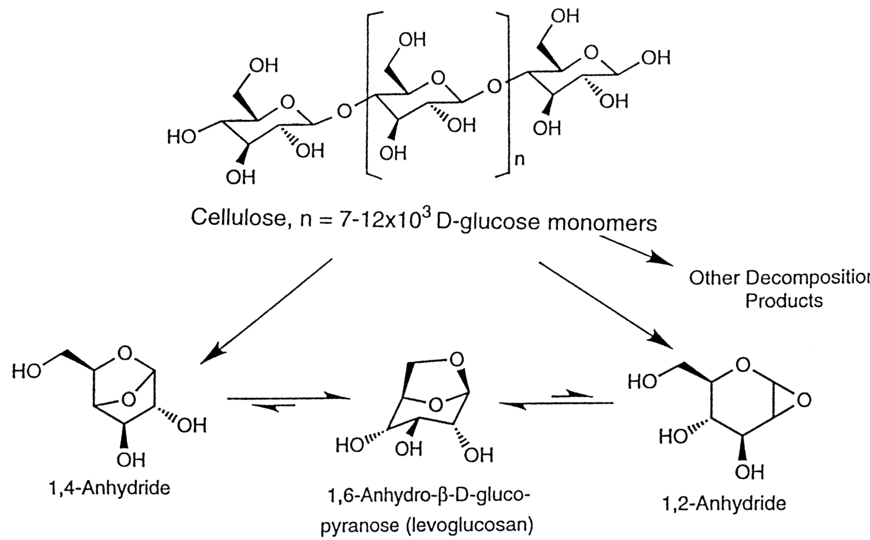
- Presence of sugars in ambient PM potentially from:

  - soil resuspension

  - biomass burning

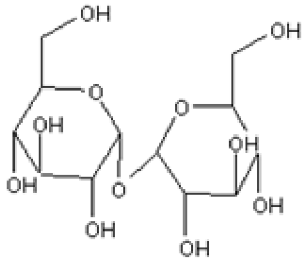
Sources of Aerosol Sugars: Biomass Burning

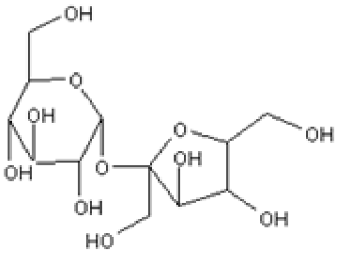
- Wood combustion – decomposition of main components of wood (cellulose, hemicellulose and lignin);
- Key tracers for PM originating from biomass burning:
  - levoglucosan
  - mannosan and galactosan

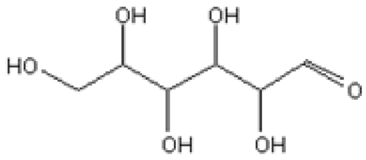


Sources of Aerosol Sugars: Soil Organic Matter (SOM)

- SOM includes plant litter, animal and microbial residues, lipids, carbohydrates, peptides, cellulose, lignin, and humic material
- Complex carbohydrates undergo oxidative, enzymatic and hydolytic degradation into simple sugars
- Total sugars constitute ~10% on average of SOM
- Major sugar content: trehalose, sucrose, glucose, etc.







Target Sugars for Marker Studies

Main Source	Compound	Sugar Category	Formation and Description
Biomass Burning	Levoglucosan	Anhydrosaccharide	Cellulose decomposition; Established maker
SOM	Glucose	Monosaccharide	Cellulose pyrolysis
	Sucrose	Disaccharide	Storage for fixed CO2
	Trehalose	Disaccharide	Fungal metabolite; storage and transport carbohydrates and cell protectants against environmental stress (e.g., desiccation, frost and heat)
	Mannitol	Sugar Polyol	
	Sorbitol		
	Arabitol		
	Ribitol		
	Iso-erythritol		
	Glycerol		

Agricultural Soils vs. Native Soils

- Enrichment of Agricultural Soils

  Addition of organic material through augmentation or tilling practices to improve soil properties

- Development of specific markers for agricultural soils to separate the contribution from agricultural processes to ambient PM

Research Objectives

Research Objectives

- Optimize the analytical procedure for quantification of sugars in aerosols and soils
- Collect samples of PM2.5 and PM10 plus local soils (native, agricultural) for sugar quantification
- Perform laboratory stability tests to investigate the atmospheric stability of potential markers
- Calculate the contribution of agricultural and native soils to ambient PM in different regions

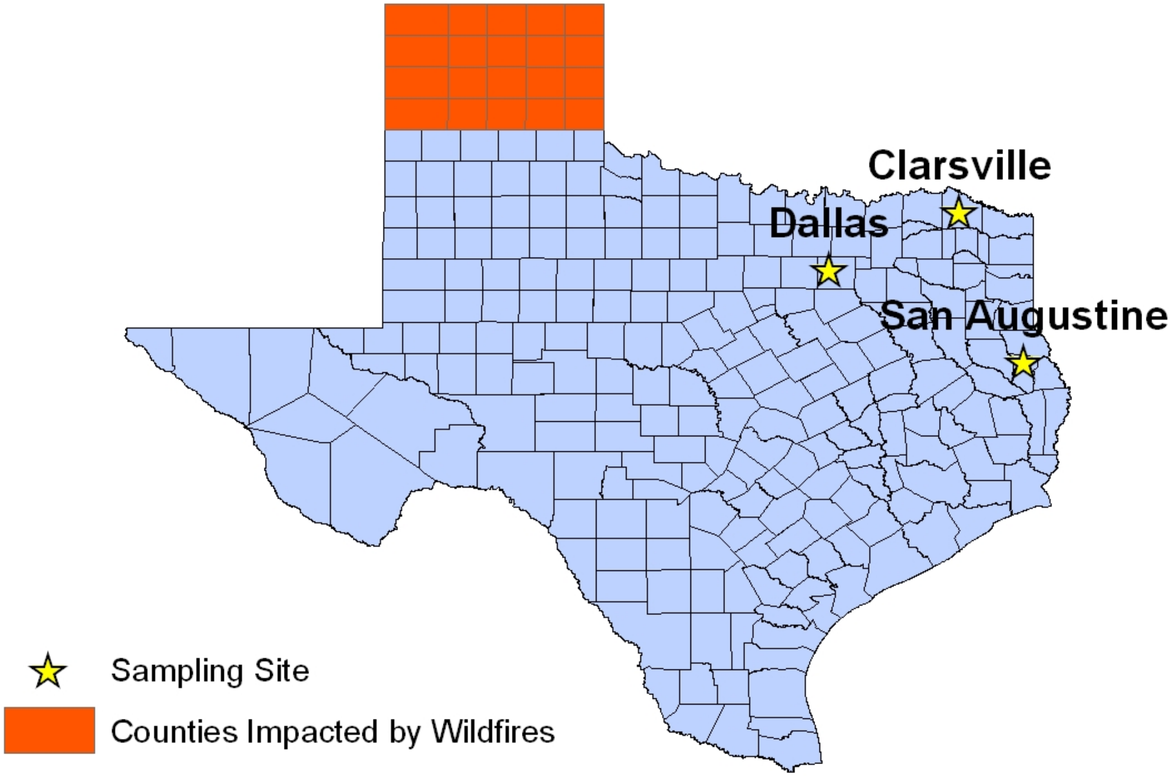
Texas Field Sampling

Two purposes:

- collect PM and soil for extraction optimization
- evaluation of seasonal variability of sugars

Sampling Sites

- Two rural sites and one urban site in Texas
- Sampling Period: Nov. 2005 – Jul. 2006
- Wildfire Events: Nov. 2005 – Apr. 2006



Sample Collection

- ***PM2.5 Samples***

- Pre-baked quartz fiber filter
- High-Volume air sampler
- Sample every 3rd day for 24 hrs
- Flow rate: 1.13 m^3/min
- A total of 174 filter samples

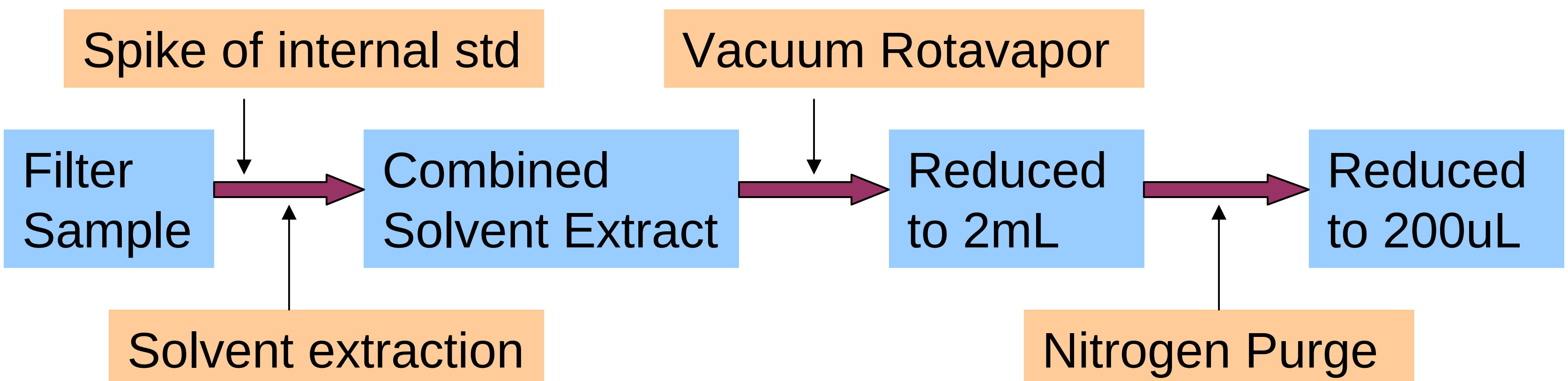
- ***Soil Samples***

- Surface soil samples (0-5cm depth) in the vicinity of the two rural sampling sites

Sampling Site	Sample Date
San Augustine	Jul. 7, 2006
Clarksville	Jun. 27 and Aug. 29, 2006

Sample Extraction

Method 1	2-30ml aliquots of hexane and 3-30ml of 2:1 benzene: isopropanol	100 samples
Method 2	3-15ml aliquots of dichloromethane and 3-15ml of methanol	174 samples



Sample Analysis

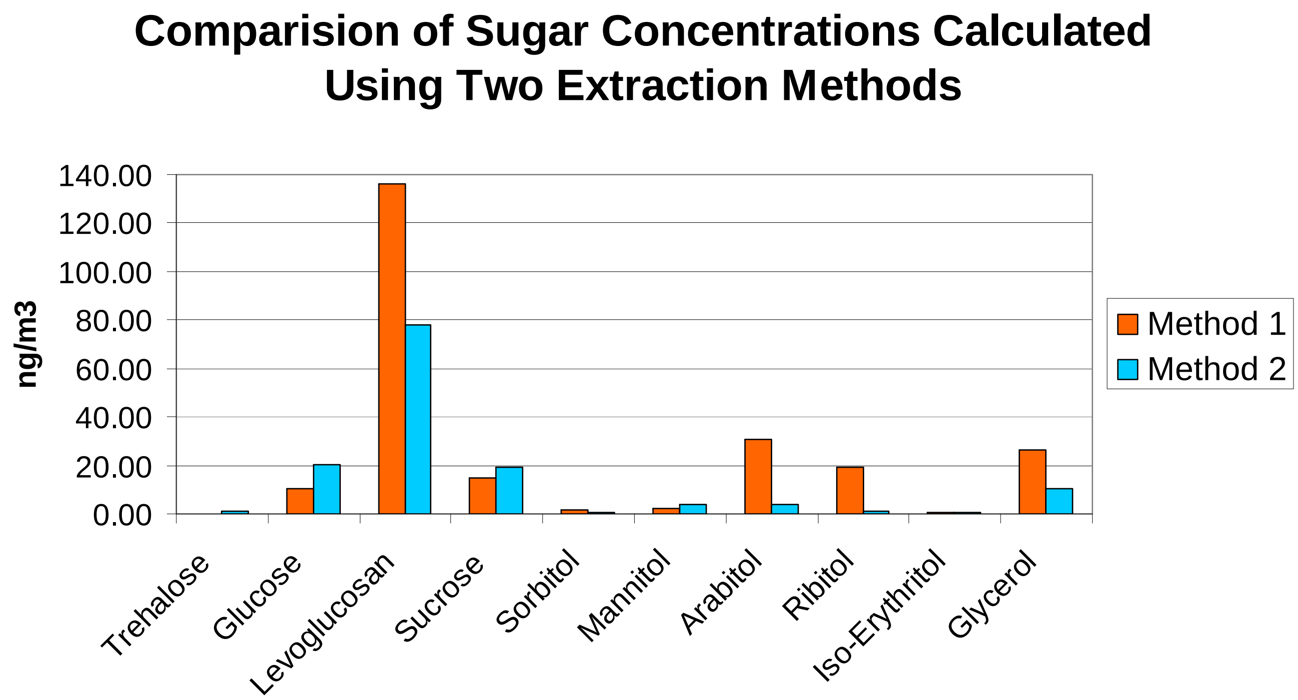
- Derivatization of the sample extract
  - BSTFA (99%)+TMCS(1%) and pyridine
  - 70^{o}C for 3 hrs

- GC-MS analysis
  - HP-5 MS capillary column
  - sugar identified by its unique retention time and specific mass fragmentation pattern
  - compounds quantified using TIC (total ion current) peak area and converted to compound mass
  - ambient concentration determined using extraction efficiency from isotopically labeled glucose

Results and Discussion

Comparison of Two Extraction Methods

	San Augustine		Clarksville		Dallas	
	Method 1	Method 2	Method 1	Method 2	Method 1	Method 2
Recovery (%)	23.73 ± 8.57	81.22 ± 3.61	NA	76.49 ± 7.22	13.47 ± 6.59	77.73 ± 4.66
RSD (%)	111.54	19.45	NA	29.56	144.78	22.60



Method 1	2-30ml aliquots of hexane and 3-30ml of 2:1 benzene: isopropanol
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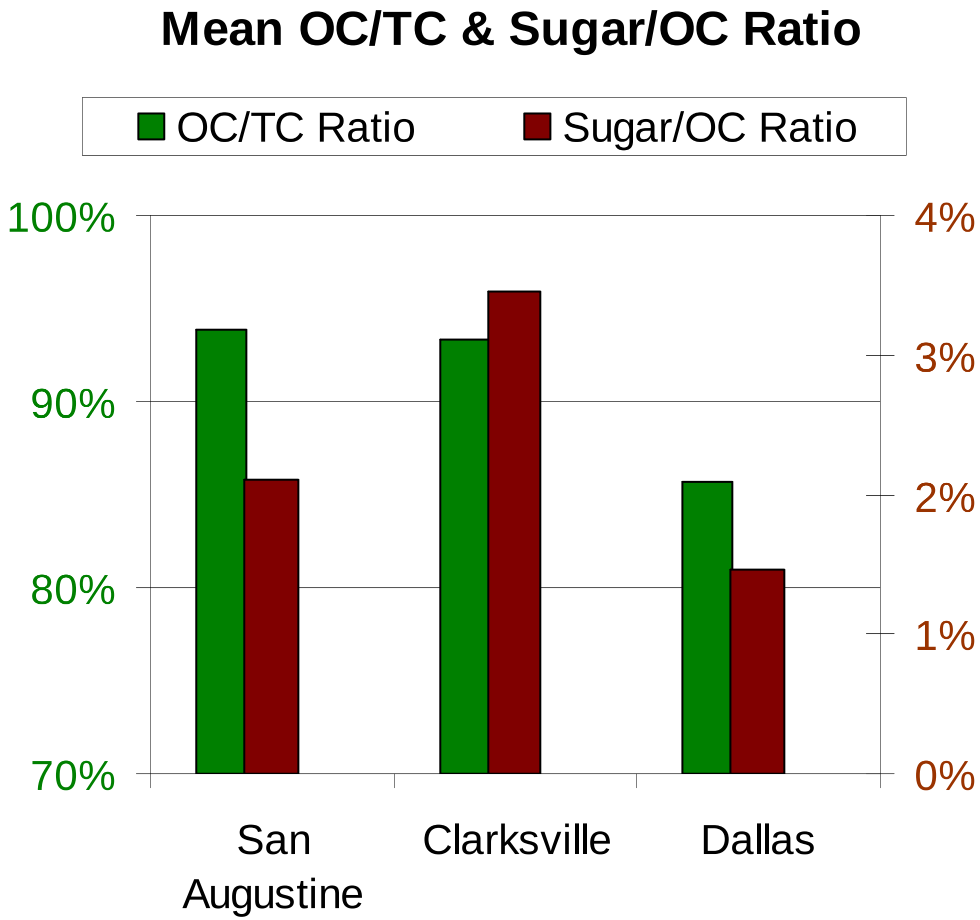
OC, TC and Total Sugars



OC/TC Ratio:

A larger contribution of OC to TC at rural locations compared to the urban location, as urban areas are more impacted by EC rich urban sources

Sugar/OC Ratio:

Biomass burning and soil organic matter as a bigger source of aerosol organic carbon content in rural places

Total Sugar Concentrations

- Total Sugar Concentrations

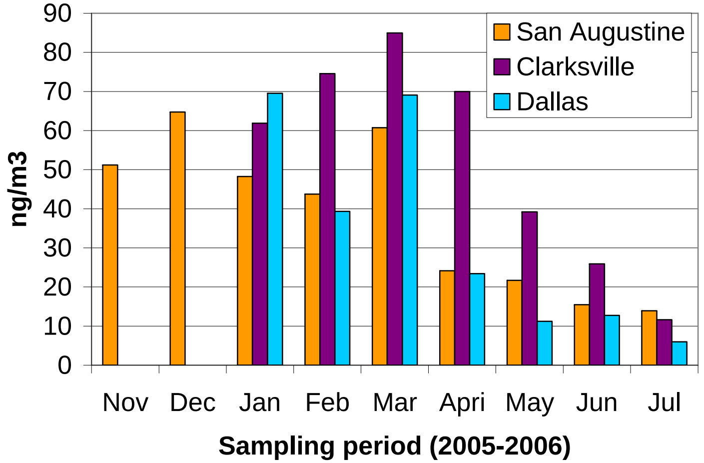
Range for all samples	22 - 164 ng/m^3
Average at San Augustine (Rural)	68 ng/m^3
Average at Clarksville (Rural)	117 ng/m^3
Average at Dallas (Urban)	55 ng/m^3

- Lower contribution from SOM at the urban location;
- Higher total sugar concentrations at Clarksville than San Augustine;
- Higher total sugar concentrations were observed from Jan to Apr 2006, parallels the agricultural tilling practices and major wildfires

Sugar Concentrations – Seasonal Variation

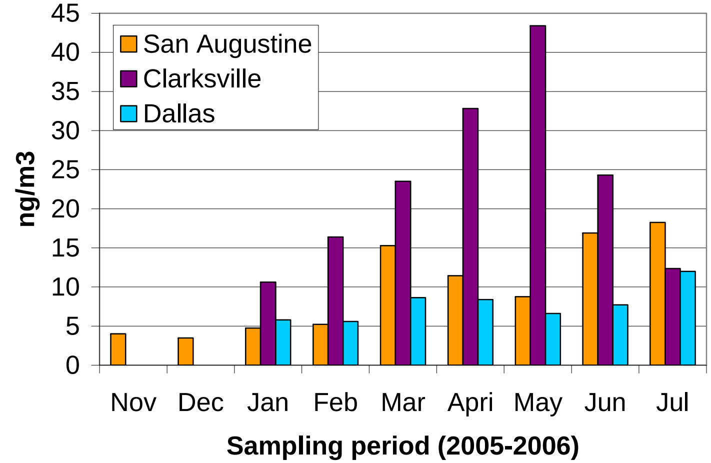
14-82% of TSM

Levoglucosan

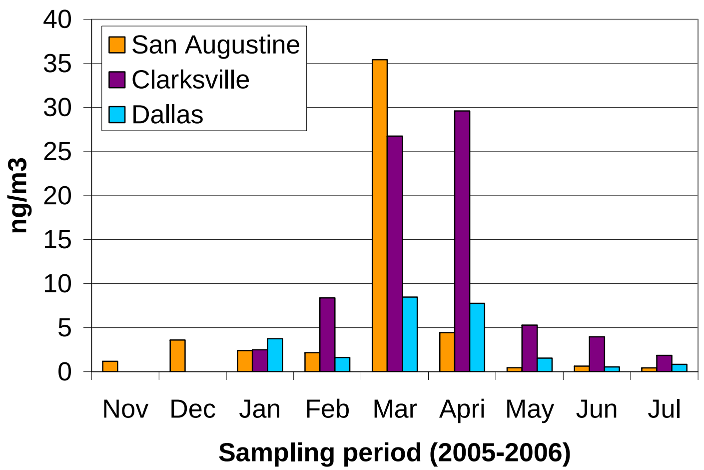


Glucose

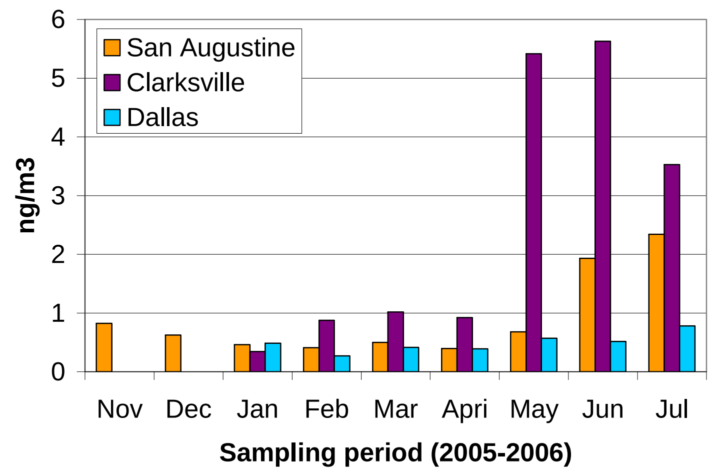
5-39% of TSM



Sucrose

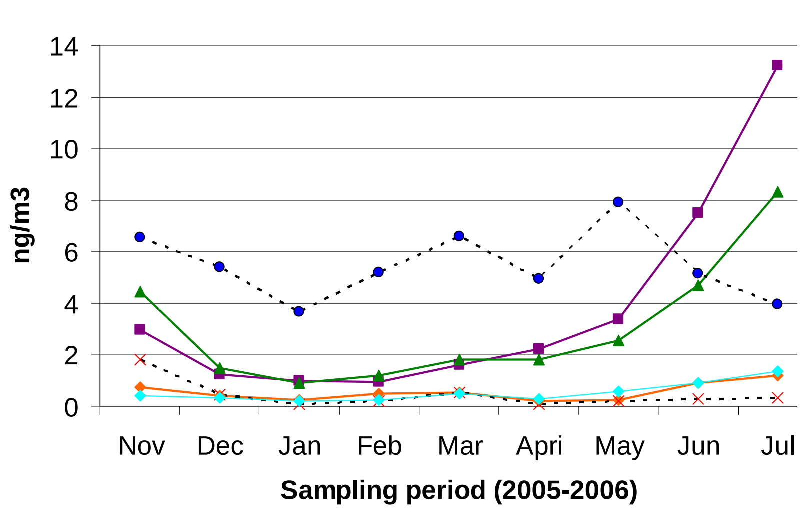


Trehalose

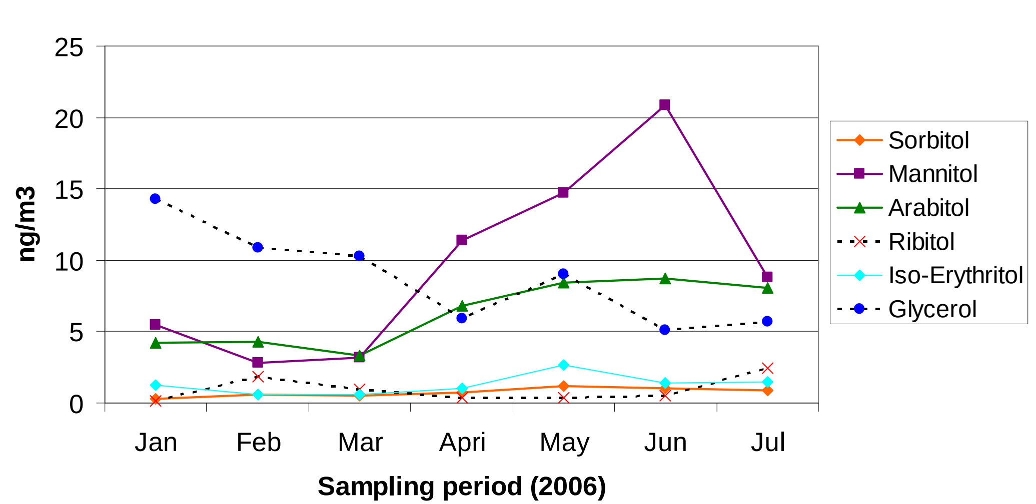


Sugar Concentrations

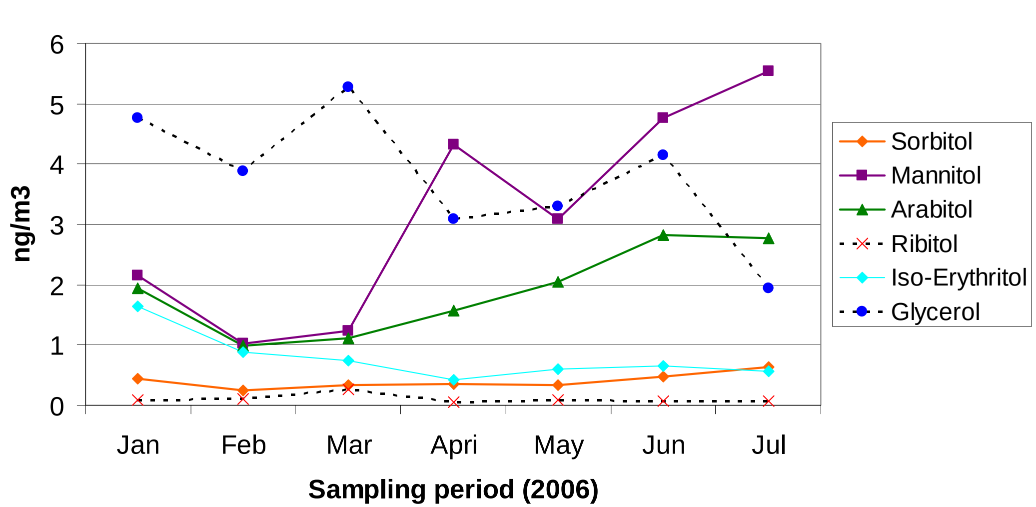
(a) Sugar Polyols - San Augustine



(b) Sugar Polyols - Clarksville



(c) Sugar Polyols - Dallas



Correlation Analysis

- Clarksville

	Trehalose	Glucose	Levoglucosan	Sucrose	Sorbitol	Mannitol	Arabitol	Ribitol	Iso-Erythritol	Glycerol
Trehalose	1									
Glucose	0.51	1								
Levoglucosan	-0.06	0.24	1							
Sucrose	-0.08	0.38	0.38	1						
Sorbitol	0.64	0.57	0.04	0.02	1					
Mannitol	0.78	0.63	-0.03	0.06	0.78	1				
Arabitol	0.64	0.59	0.03	0.05	0.90	0.85	1			
Ribitol	-0.01	-0.28	-0.06	-0.11	0.21	-0.18	0.24	1		
Iso-Erythritol	0.60	0.51	0.11	-0.07	0.63	0.71	0.71	-0.14	1	
Glycerol	-0.02	0.28	0.26	0.00	0.14	0.06	0.23	0.05	0.19	1

- Strong correlation between trehalose and major sugar polyols (mannitol, arabitol and sorbitol);
- 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

Soil Sugar Compositions

- Sugar concentrations in mg/kg

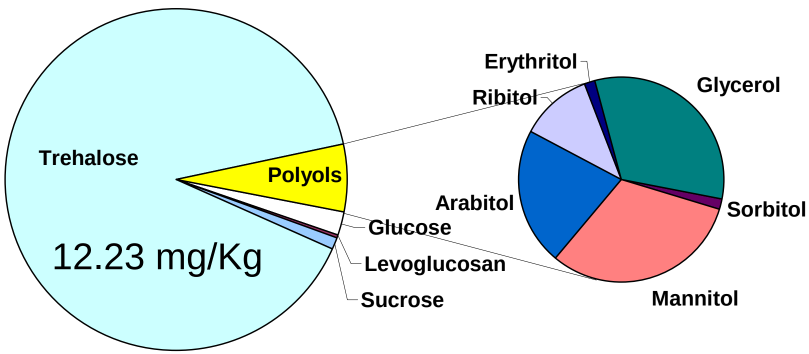
	San Augustine	Clarksville	
Sample Date	**7/7/2006**	**6/27/2006**	**8/29/2006**
Glucose	**0.31**	**0.68**	**5.31**
Levoglucosan	**0.03**	**0.05**	**0.23**
Sucrose	**0.17**	**0.17**	**0.22**
Trehalose	**12.23**	**37.46**	**40.35**
Sorbitol	**0.01**	**0.02**	**0.07**
Mannitol	**0.27**	**0.15**	**0.61**
Arabitol	**0.19**	**0.10**	**0.14**
Ribitol	**0.10**	**0.07**	**0.08**
Iso-Erythritol	**0.01**	**0.01**	**0.00**
Glycerol	**0.28**	**0.84**	**2.22**
Total	**13.30**	**38.85**	**43.92**

A lower soil organic content in San Augustine soils; consistent with measured aerosol sugar concentrations – SOM as a key source

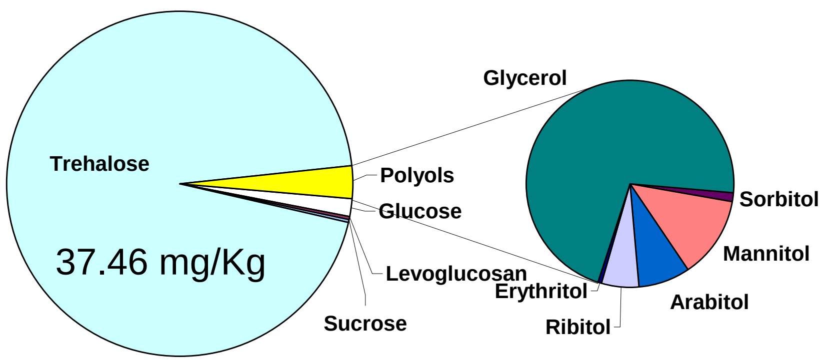
Soil Sugar Compositions

(a) Sugar Composition in Soil - San Augustine (7/7/2006)

Total Sugars: 13.60 mg/Kg

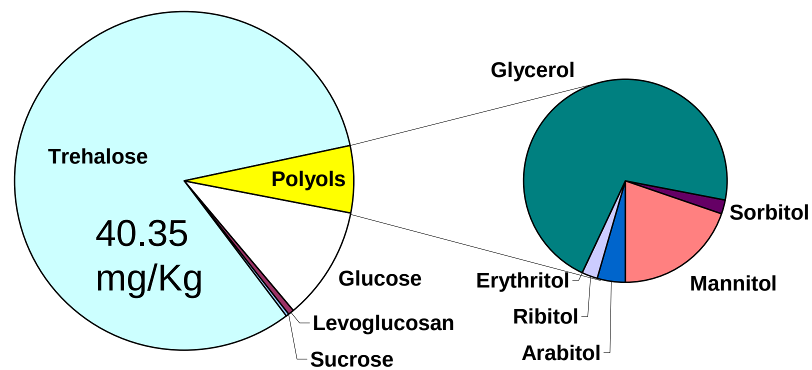


(b) Sugar Composition in Soil - Clarksville (6/27/2006)



Total Sugars: 39.52 mg/Kg

(c) Sugar Composition in Soil - Clarksville (8/29/2006)



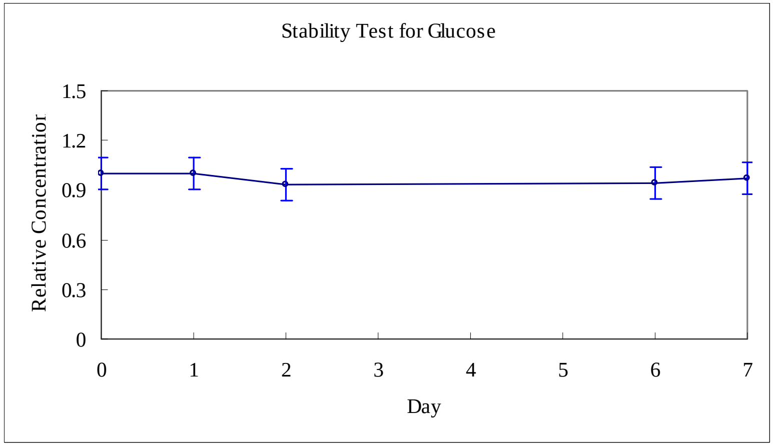
Total Sugars: 49.24 mg/Kg

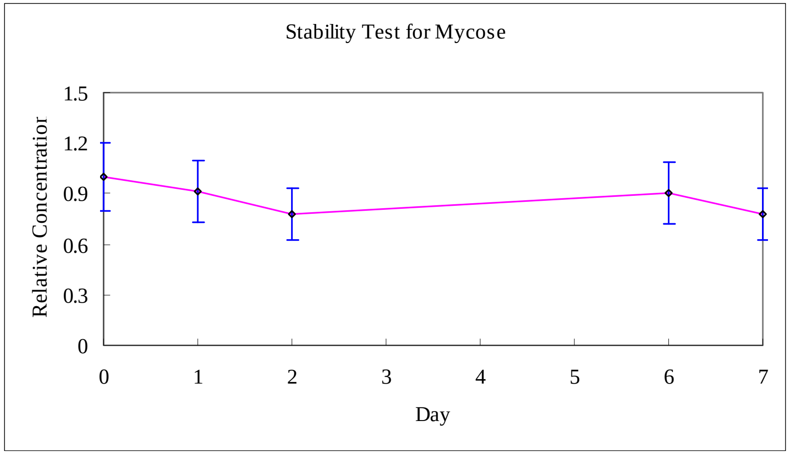
Potential Molecular Markers

Potential Marker	Source
Sucrose	Soil inputs in spring
Trehalose	Soil inputs in summer and fall
Mannitol	
Arabitol	
Sorbitol	
Glycerol	Agricultural burning residues from soil

- Present in both aerosols and soils, with specific relative concentrations that vary by season;
- Almost uniquely coming from soil and associated microbiota
- Validation of this proposal needs more future work

Laboratory Stability Tests





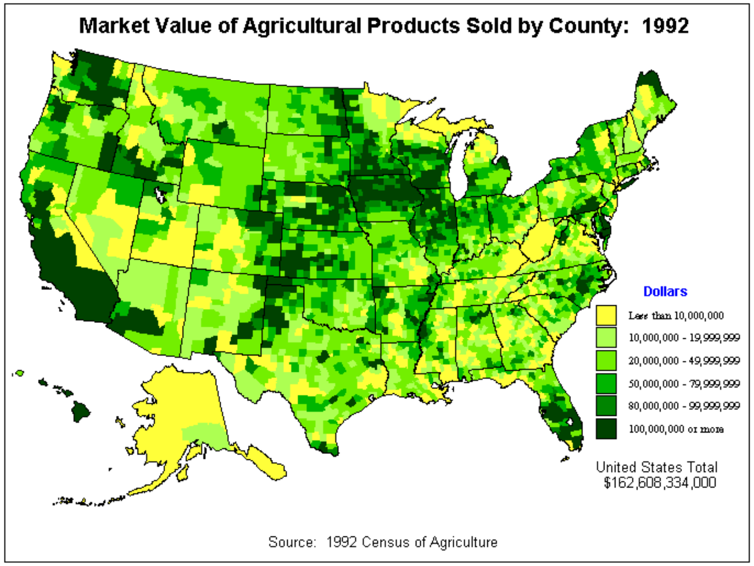
- Aqueous stability under acidic conditions (pH = 2) in the presence of ammonium sulfate and sulfuric acid
- Continuously bubbled air through solution for 7 days and exposed to sunlight

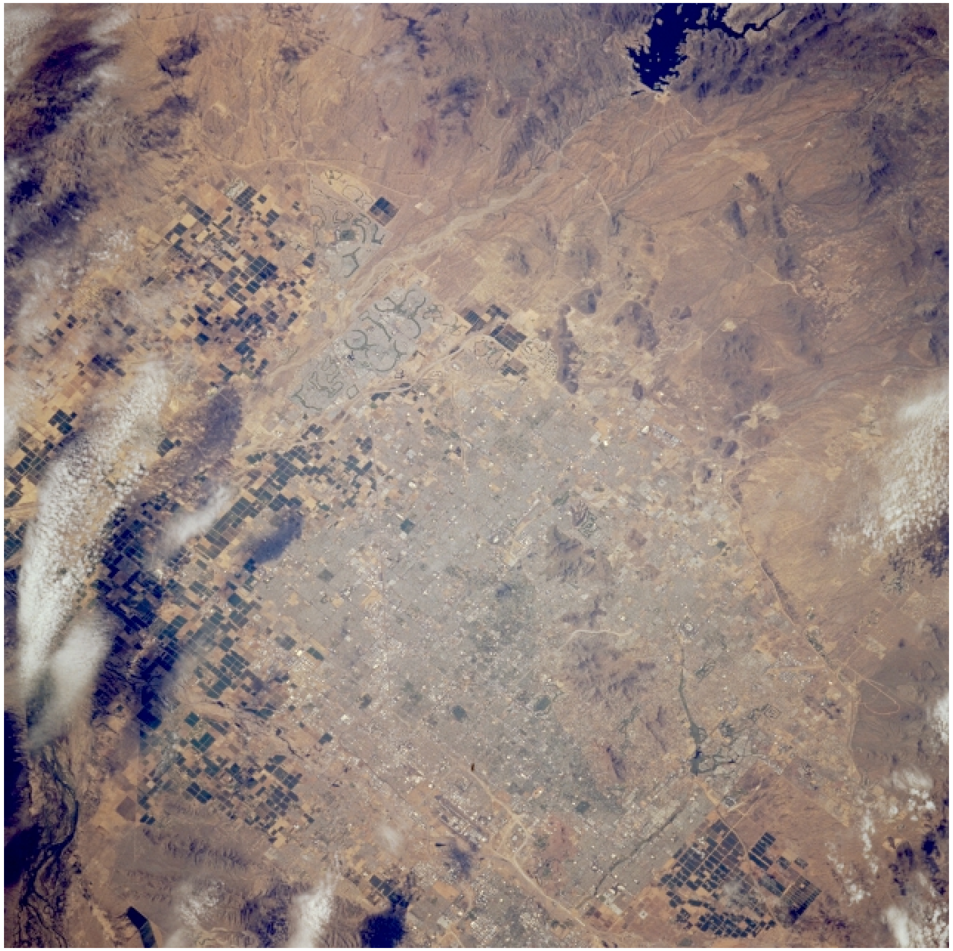
Future Work

Future Work

- Field experiment in a region more directly impacted by intensive agricultural activities
- More complete characterization of local soils, PM10 and PM2.5
- More representative stability tests

Future Work : Phoenix Sampling





Acknowledgements

- EPA for funding
- Shagun Bhat (Ph.D. 2007) now at Environ
  - Coordinated field sampling program
- Yuling Jia (M.S. 2007) continuing for Ph.D.
  - Performed extraction efficiency and sugar characterization from PM samples