

US EPA ARCHIVE DOCUMENT

Using Carbohydrates as Molecular Markers for Agricultural and Native Soils

Matt Fraser

currently: Rice University

starting August 15th: Arizona State

matthew.fraser@asu.edu



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

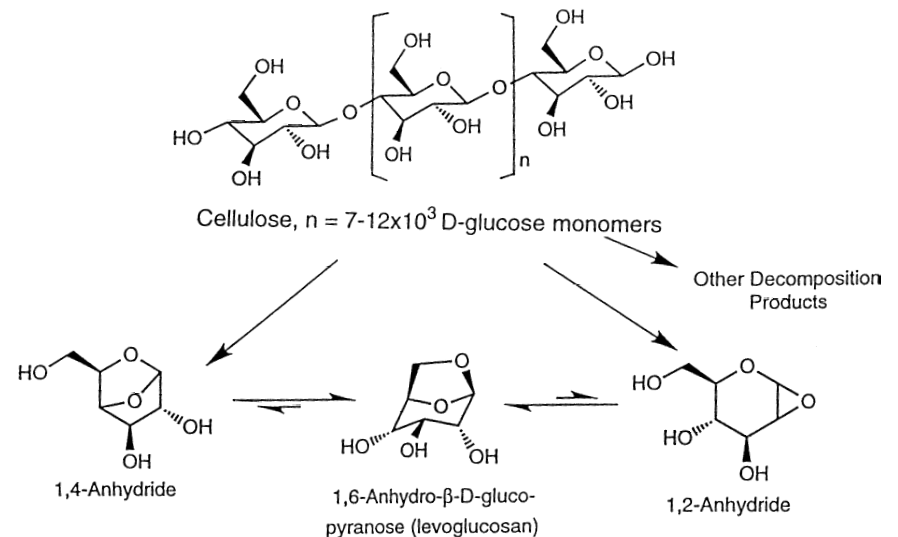
- Sugars are known components of soils and have been measured in ambient particles
- Presence of sugars in ambient PM potentially from:
 - soil resuspension
 - biomass burning



Sources of Aerosol Sugars: Biomass Burning

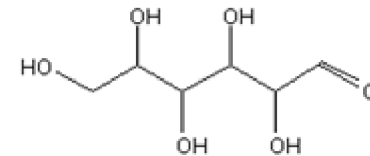
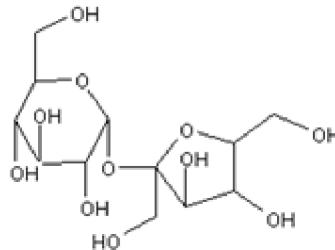
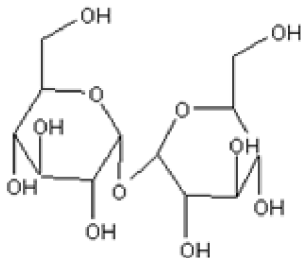
- Wood combustion – decomposition of main components of wood (cellulose, hemicellulose and lignin);

- 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 hydrolytic 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 marker
SOM	Glucose	Monosaccharide	Cellulose pyrolysis
	Sucrose	Disaccharide	Storage for fixed CO ₂
	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 PM_{2.5} 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



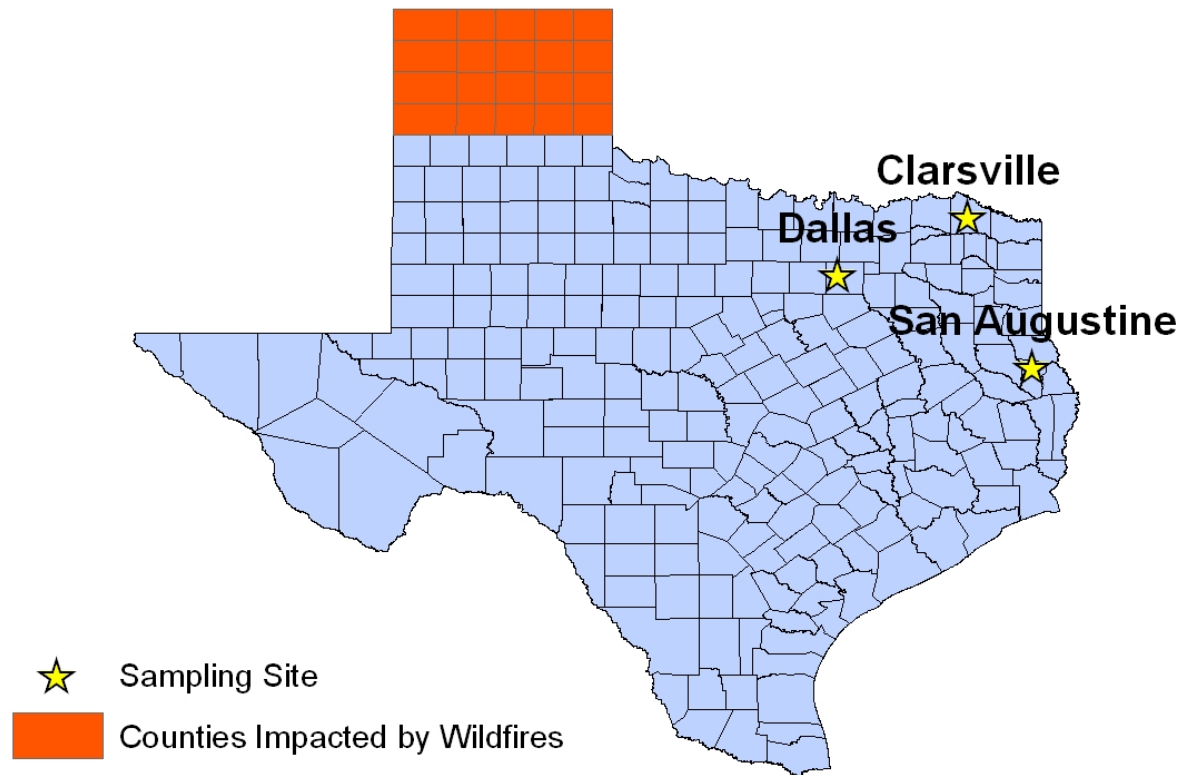
Texas Field Sampling

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 m³/min
- A total of 174 filter samples

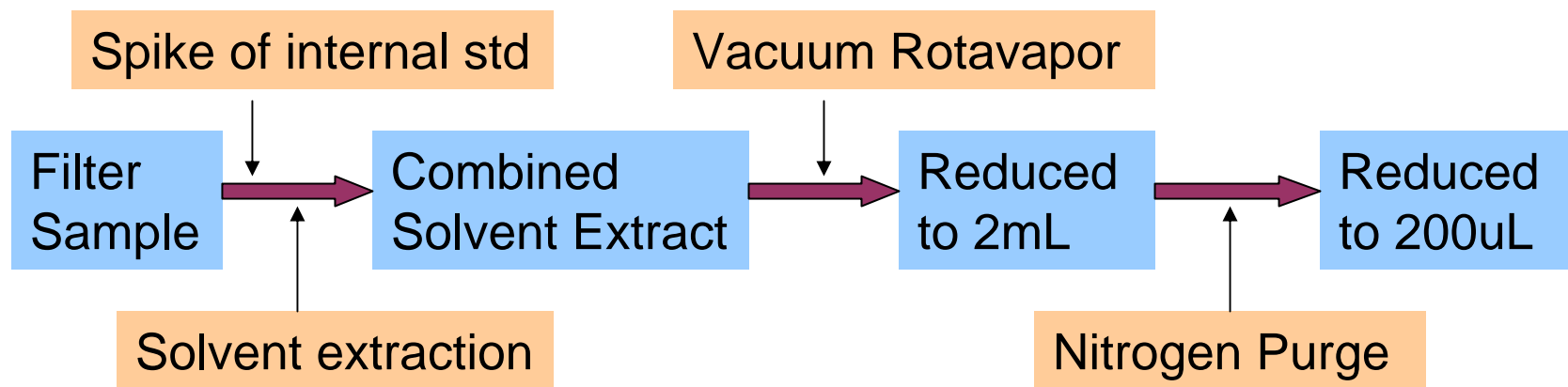
■ Soil Samples

- 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



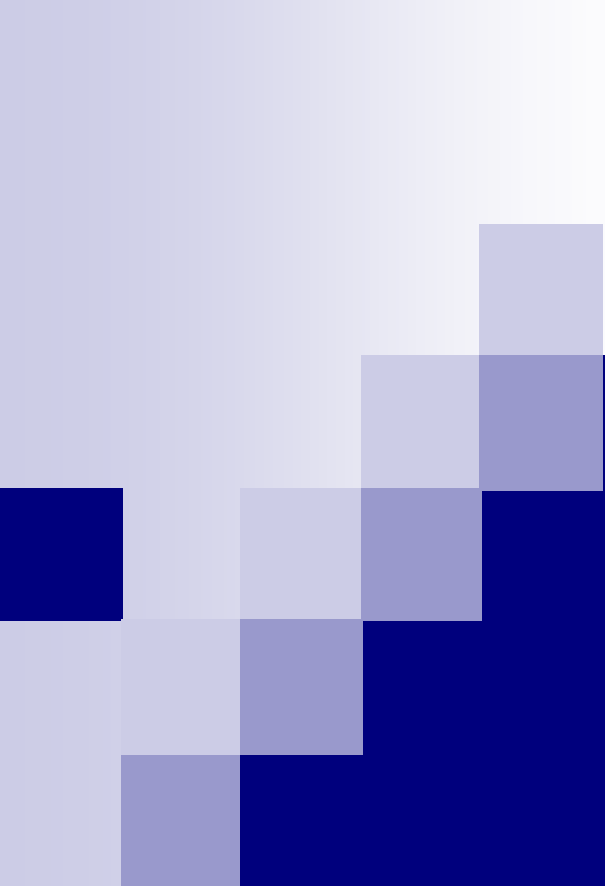
Sample Analysis

■ Derivatization of the sample extract

- BSTFA (99%)+TMCS(1%) and pyridine
- 70°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

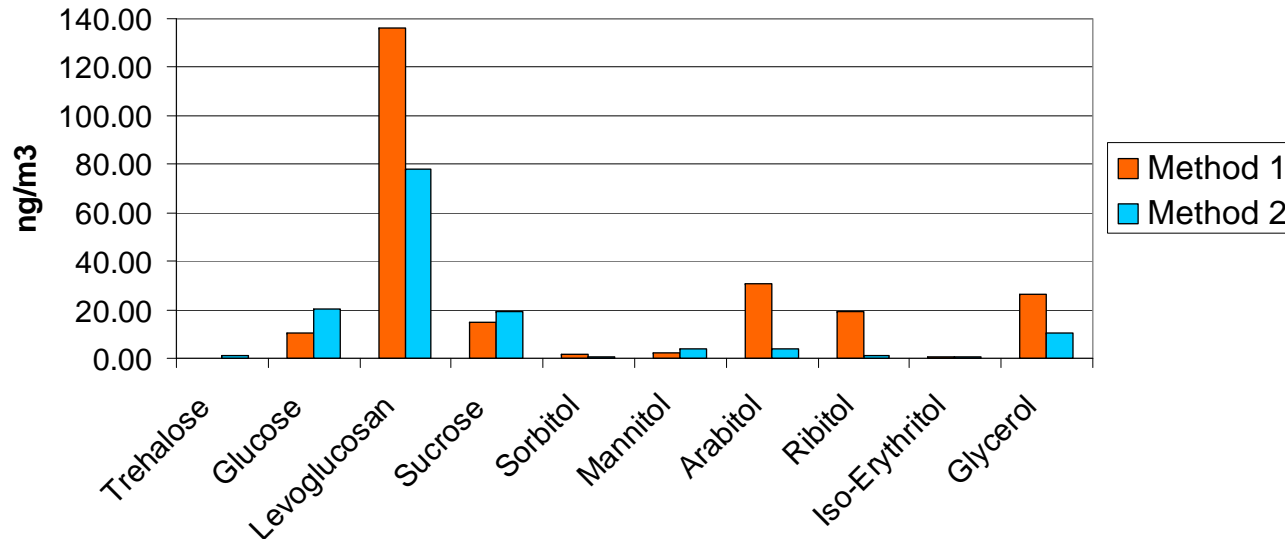


Results and Discussion

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

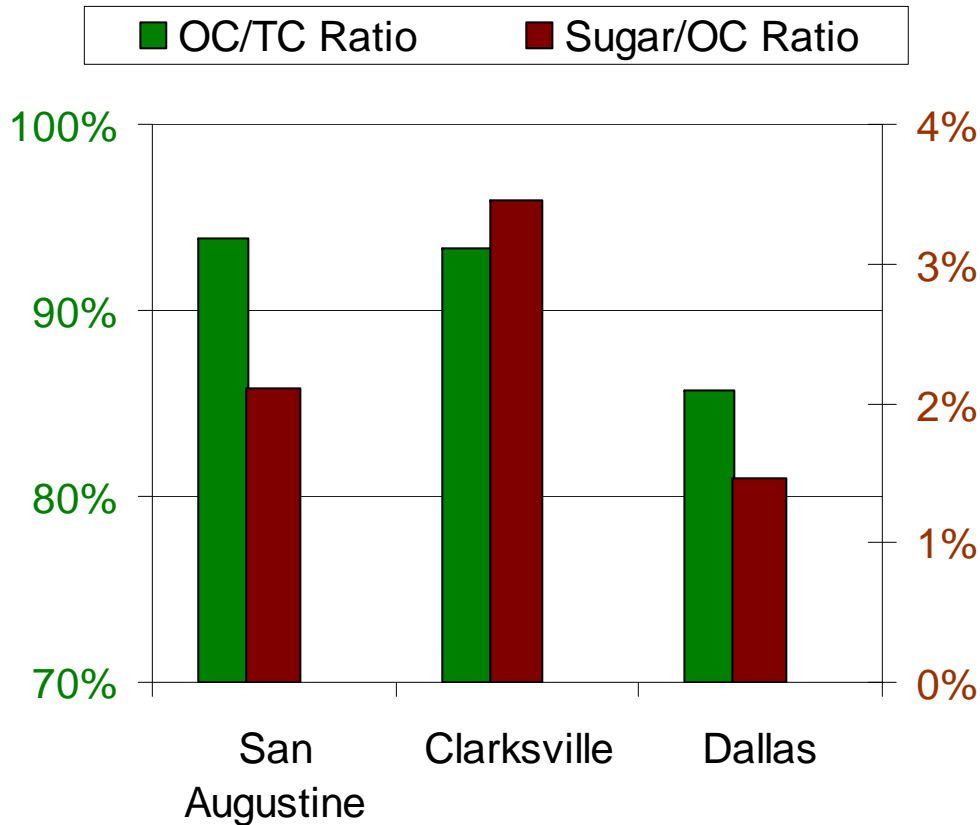
Comparison of Sugar Concentrations Calculated Using Two Extraction Methods



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

OC, TC and Total Sugars

Mean OC/TC & Sugar/OC Ratio



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

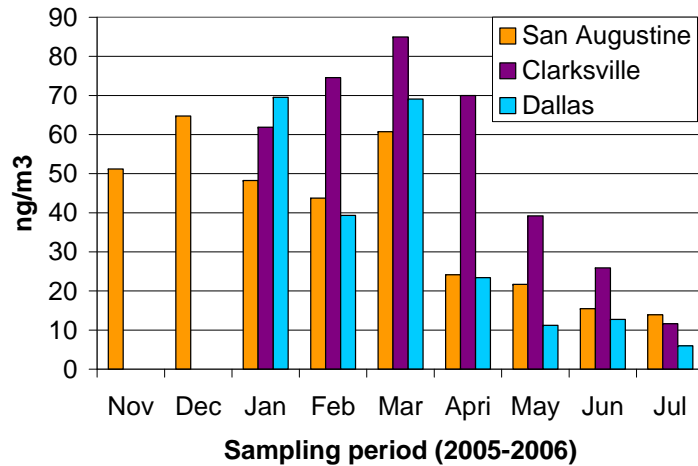
Range for all samples	22 - 164 ng/m ³
Average at San Augustine (Rural)	68 ng/m ³
Average at Clarksville (Rural)	117 ng/m ³
Average at Dallas (Urban)	55 ng/m ³

- 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

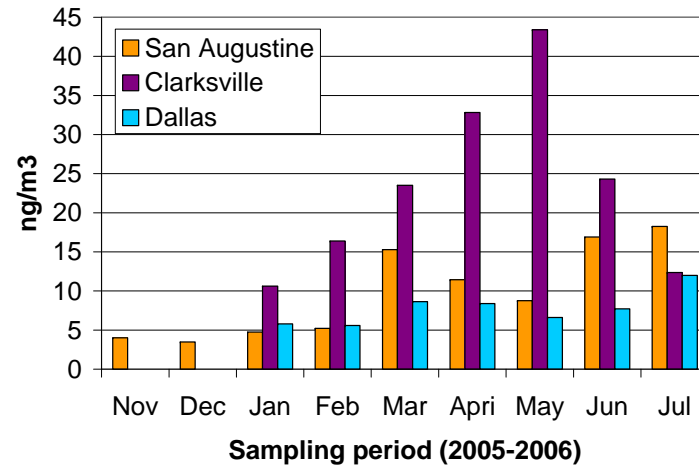
14-82% of TSM

Levoglucosan

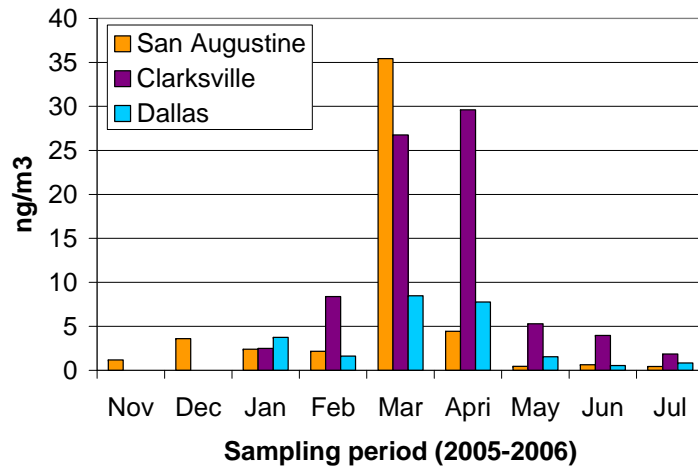


Glucose

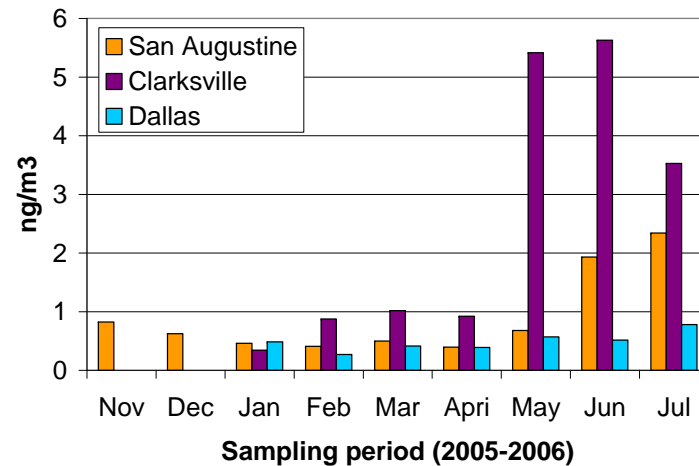
5-39% of TSM



Sucrose

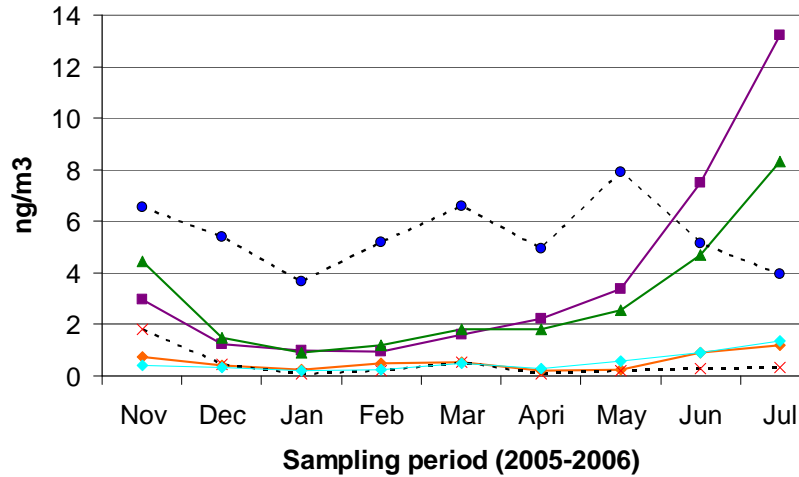


Trehalose

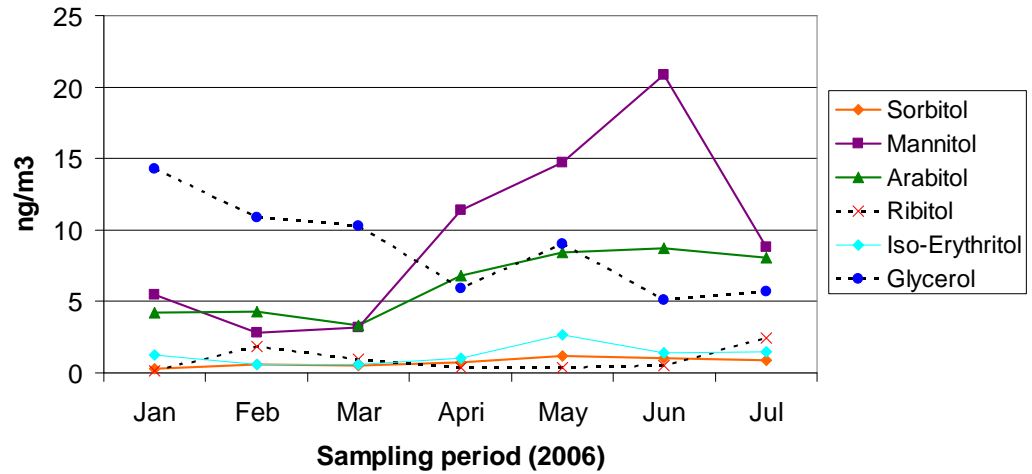


Sugar Concentrations

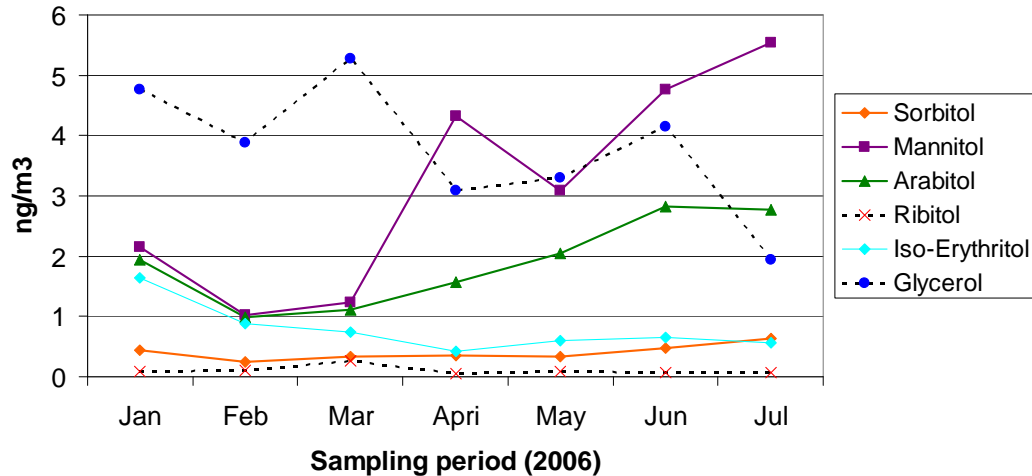
(a) Sugar Polyols - San Augustine



(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

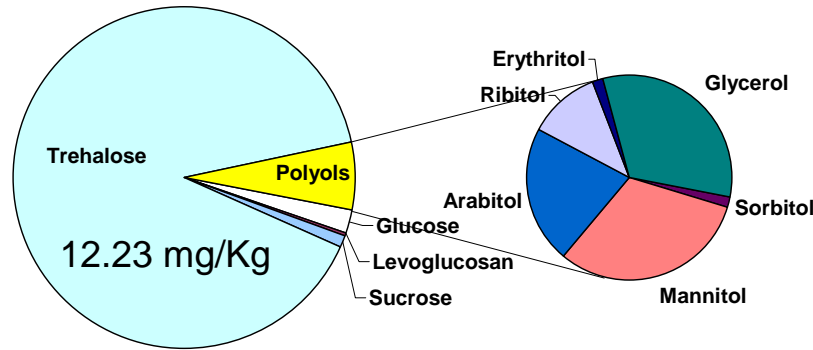
Sample Date	San Augustine	Clarksville	
	7/7/2006	6/27/2006	8/29/2006
Glucose	0.31	0.68	5.31
Levoglucozan	0.03	0.05	0.23
Sucrose	0.17	0.17	0.22
Trehalose	12.23	37.46	40.35
Sorbitol	0.01	0.02	0.07
Mannitol	0.27	0.15	0.61
Arabitol	0.19	0.10	0.14
Ribitol	0.10	0.07	0.08
Iso-Erythritol	0.01	0.01	0.00
Glycerol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

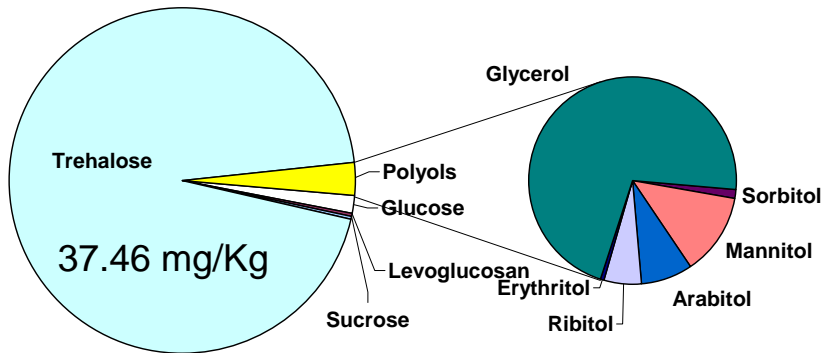
Soil Sugar Compositions

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

Total Sugars:
13.60 mg/Kg

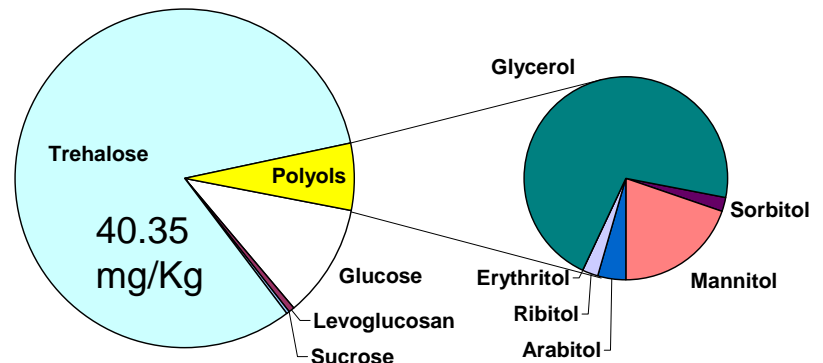


(b) Sugar Composition in Soil - Clarksville
(6/27/2006)



Total Sugars: 39.52 mg/Kg

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



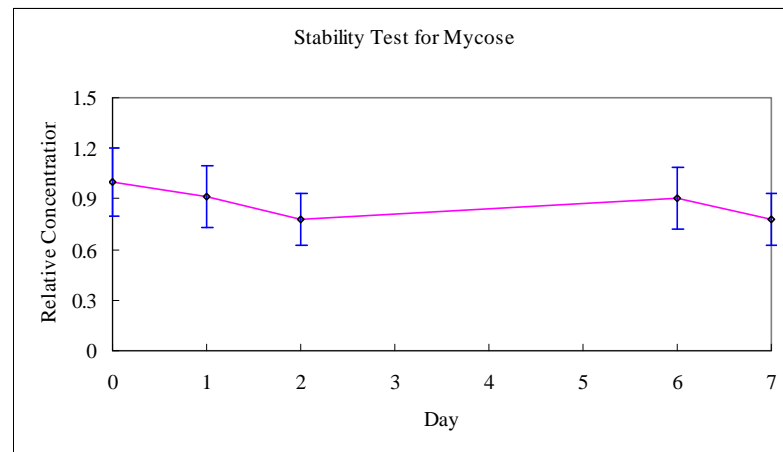
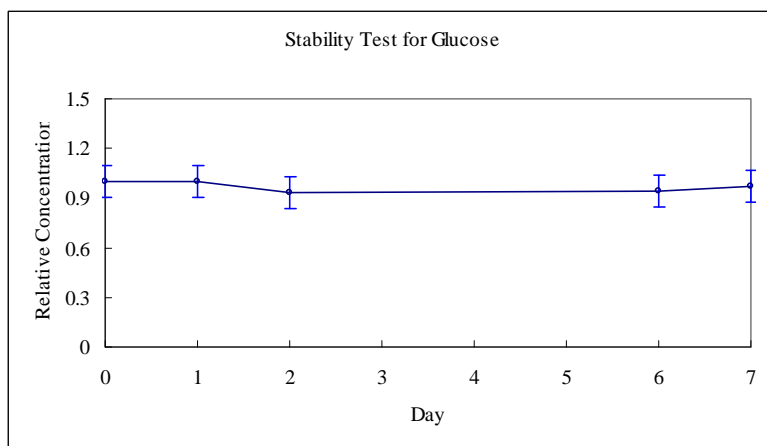
Total Sugars: 49.24 mg/Kg

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 ($\text{pH} = 2$) in the presence of ammonium sulfate and sulfuric acid
- Continuously bubbled air through solution for 7 days and exposed to sunlight



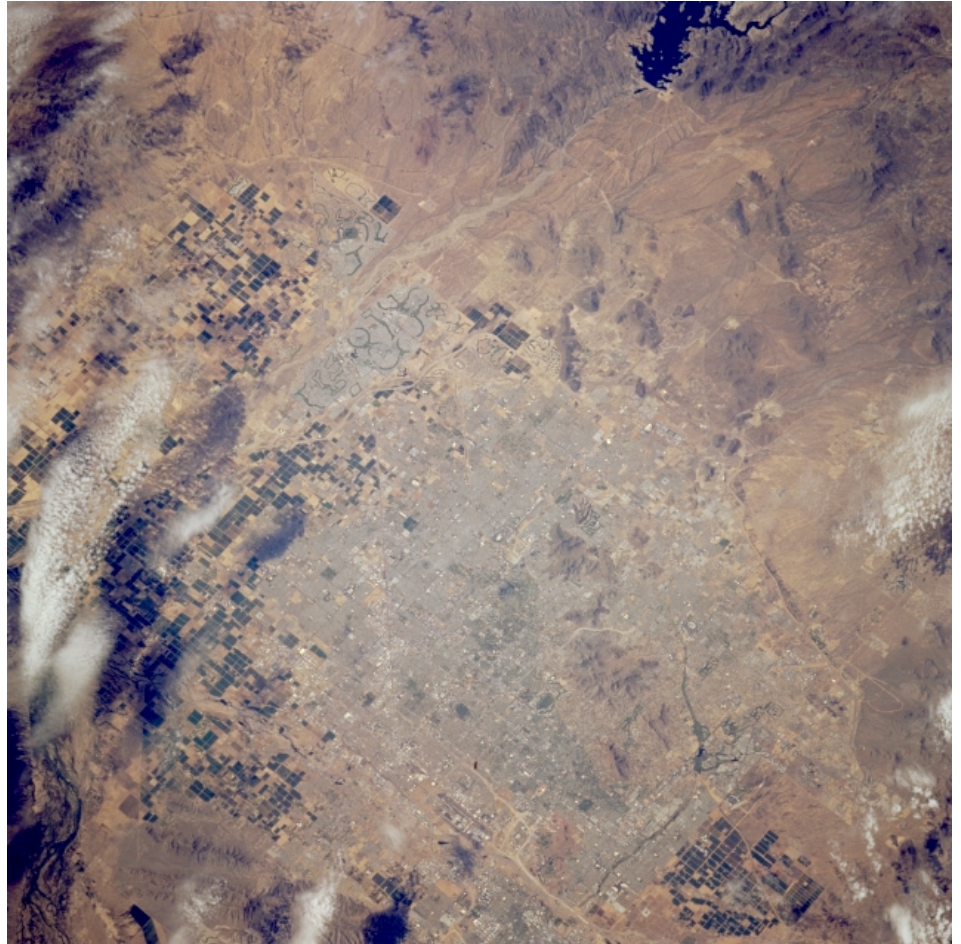
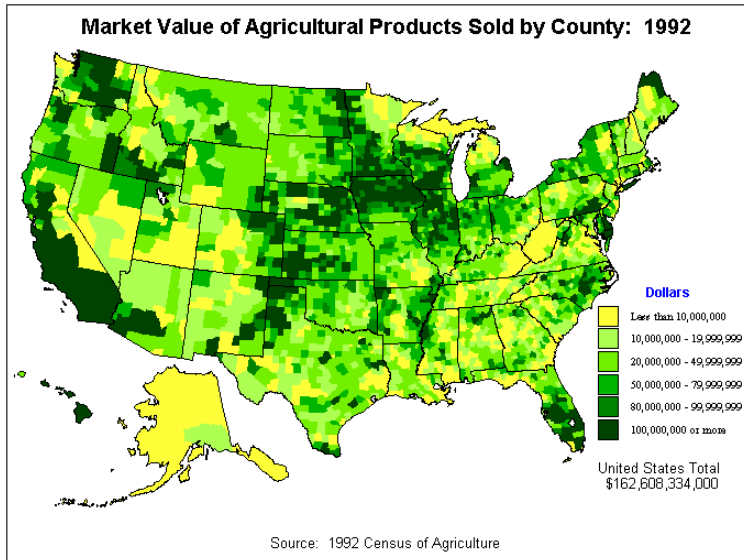
Future Work



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