© 2008

Harmonie A. Hawley

ALL RIGHTS RESERVED

POLAR ORGANIC COMPOUNDS IN FINE PARTICULATE MATTER IN THE NJ-NY-CT TRANSPORTATION CORRIDOR

by

HARMONIE A. HAWLEY

A dissertation submitted to the

Graduate School—New Brunswick

Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

For the degree of

Doctor of Philosophy

Graduate Program in Civil & Environmental Engineering

Written under the direction of

Dr. Monica A. Mazurek

And approved by

_____

_____

_____

_____

_____

New Brunswick, NJ

October, 2008

ABSTRACT OF THE DISSERTATION

POLAR ORGANIC COMPOUNDS IN FINE PARTICULATE MATTER IN THE NJ-NY-CT TRANSPORTATION CORRIDOR

By HARMONIE A. HAWLEY

Dissertation Director:

Dr. Monica A. Mazurek

Fine particulate matter has been associated with adverse health effects, reduced visibility, haze and global climate change. Controlling sources of fine particles in urban and rural airsheds requires detailed knowledge of emission sources, including temporal and spatial distributions. Currently, about 20% of the organic mixtures associated with fine particles can be determined quantitatively as individual chemical species. Some compounds can be related to the emission source based on the chemical profile of that source, and are designated as molecular markers.

Nonpolar and moderately polar molecular markers are used to apportion airborne fine particles to sources. Polar organic compounds are not well characterized in airsheds due to a wide range of chemical properties that introduce analytical complexity and difficulty. Consequently, emission sources that introduce polar carbonaceous matter into the atmosphere are not well understood and not effectively controlled. High performance liquid chromatography and gas chromatography-mass spectrometry were evaluated to determine the optimal method for characterizing polar organic compounds in fine particulate matter samples. Gas chromatography-mass spectrometry was chosen due to its capability to analyze a large range of chemical properties in one analysis.

Samples were studied from metropolitan New York City area from six receptor locations, including upwind and downwind sites in NY, NJ and CT from May 2002 to February 2007. The results indicated spatial and seasonal trends for the molecular markers. Statistical analysis demonstrated seasonal variations of wood smoke at two sites (Wesport, CT and Bronx, NY), meat charbroiling at only one site (Bronx, NY), and levulinic acid at three sites (Westport, CT, Bronx, NY and Pinnacle State Park, NY). When the samples were grouped as urban and rural areas the statistical analysis showed there was no spatial or seasonal trend in levoglucosan, total n-alkanols or levulinic acid. Wood smoke was higher for the NYC metropolitan and suburban sites than for the rural sites and found year-round. The levoglucosan, total n-alkanols, cholesterol, cis-pinonic acid and levulinic acid normalized to elemental carbon did show statistical differences between urban and rural sites, indicating the sites were influenced by local emission sources and meteorological conditions.

Acknowledgements

At this time I would like to acknowledge my advisor Dr. Monica A. Mazurek for all of her help. I would also like to acknowledge Dr. Min Li with whom I worked closely in the lab, and also, staff members Patti Atkins and Claire Belisle and undergraduates Majad Ullah, Joe Savoly and Joe Narcisso. Drs. Stephen R. McDow and Rachelle Duvalle from the U.S. EPA provided help and advice throughout the project.

I would like to acknowledge the following people who helped with sample collection and provided important STN data: H. Dirk Felton and Oliver Rattigan from New York State Department of Environmental Conservation in Albany, NY; Lee Alter and John Graham from the Northeast States for Coordinated Air Use Management in Boston, MA; Thomas McKenna and Charles Pietarinen from New Jersey Department of Environmental Protection in Trenton, NJ; Alan Lester and Steve Bailey from Connecticut Department of Environmental Protection in Hartford, CT; and Sania W. Tong Argao from the Human Exposure and Atmospheric Sciences Division, National Exposure Research Laboratory in Research Triangle Park, NC.

The New York State Energy Research and Development Authority (NYSERDA) Contract 7616 and the Northeast States for Coordinated Air Use Management (NESCAUM) provided funding for this research. Additional support was provided by the National Science Foundation Atmospheric Chemistry Grant ATM-0120906 and by the United States Environmental Protection Agency STAR Program, Office of Research and Development grant number RD-83216501. I thank Linda Schanz of Agilent Technologies for use of the 1200 HPLC instrument.

Table of Contents

1. Introduction 1

2. Literature Review 8

2.1. Analytical Equipment (Chromatography and Spectrometry) 8

2.2. Molecular Markers 12

2.3. Wood Smoke 13

2.3.1. The Process of Cellulose Combustion 14

2.3.2. Emission Tests 16

2.3.3. Molecular Markers for Biomass Burning 19

2.3.4. Case Studies 25

2.4. Biogenic Sources 31

2.4.1. Emission Tests 31

2.4.2. Case Studies 34

2.5. Meat Charbroiling 37

2.5.1. Emission Tests 38

2.5.2. Case Studies 39

2.6. Biogenic Oxidation Products 41

2.6.1. Reaction Experiment 41

2.6.2. Case Studies 42

2.7. Low Molecular Weight Highly Oxidized Acids 43

2.7.1. Reaction Experiments 44

2.7.2. Case Studies 45

3. Methodology 49

3.1. Materials 49
3.1.1. High Performance Liquid Chromatography (HPLC) 49
3.1.2. Gas Chromatography-Mass Spectrometry (GCMS) 50
3.1.3. Miscellaneous Lab Equipment 51
3.2. Methodology 52
3.2.1. HPLC with DNPH Derivatives 52
3.2.2. GCMS with BSTFA-TMS Derivatives 55
3.2.3. Standard Preparation 56
3.3. Method Development 59
3.3.1. HPLC and Monolithic Column 59
3.3.2. Aromatic and Oxoacids with DNPH Derivatives on HPLC with Monolithic Column 64
3.3.3. GCMS with BSTFA-TMS Derivatives 65
3.3.4. Optimal Method 67
3.4. Application to Ambient Samples 70
4. Results 79
4.1. Wood smoke Markers 79
4.2. Biogenic Sources 99
4.3. Meat Charbroiling 110
4.4. Biogenic Oxidation Product 116
4.5. Low Molecular Weight Highly Oxidized Acids 122
4.6. $PM_{2.5}$ Mass Balance 129
5. Discussion 133

5.1. Comparison to Other Studies 133
5.1.1. Wood smoke 133
5.1.2. Plant Waxes 138
5.1.3. Meat Charbroiling 144
5.1.4. Biogenic Oxidation Products 146
5.1.5. Low Molecular Weight Highly Oxidized Acids 148
5.2. Emission Estimates 152
5.2.1. Wood Smoke 153
5.2.2. Meat Charbroiling 157
5.3. Comparison to EC and OC 159
5.3.1. Wood smoke 160
5.3.2. Biogenic Sources 168
5.3.3. Meat Charbroiling 175
5.3.4. Biogenic Oxidation Product 182
5.3.5. Low Molecular Weight Highly Oxidized Acids 189
5.4. Comparison to $PM_{2.5}$ 196
5.4.1. Wood Smoke 196
5.4.2. Biogenic Sources 200
5.4.3. Meat Charbroiling 204
5.4.4. Biogenic Oxidation Product 207
5.4.5. Low Molecular Weight Highly Oxidized Acids 211
6. Context 215
6.1. Conclusion 215

6.2. Key Scientific Questions 218

6.3. What can be done to lower emissions? 220

6.3.1. Reduction Strategies for Woodsmoke Emissions 221

6.3.2. How could charbroiling emissions be reduced? 222

6.4. Future Recommendations 223

7. References 226

Appendices 236

Appendix A: HPLC Monolithic Columns Calibration Curves 237

Appendix B: GCMS quantification ions 255

Appendix C: GCMS Calibration Curves 256

Appendix D: GCMS Ambient Detection Limits 280

Appendix E: Filter Composite Scheme 282

Appendix F: SOAP 2002-2007 Ambient Data 293

Appendix G: Blank data 310

Appendix H: Statistical Analyses (descriptive statistics and outlier tests) 320

Appendix I: Statistical Analyses (Anova tables) 341

Appendix J: $PM_{2.5}$ Mass Balances 382

Appendix K: Ambient EC and OC Data Comparisons 409

Appendix L: EC normalized ambient data anova tables 419

Appendix M: $PM_{2.5}$ normalized molecular markers 435

Curriculum Vita 440

Table of Tables

Table 2-1 Wood smoke emission tests[1] 21

Table 2-2 Wood smoke emission tests (continued)[1] 22

Table 2-3 Sugars as molecular markers for wood smoke 23

Table 2-4 Additional molecular markers for wood smoke 24

Table 2-5 U.S. ambient levoglucosan concentrations[1] 30

Table 2-6 Phytosterols as molecular markers for biogenic sources 33

Table 2-7 n-Alkanols as molecular markers for biogenic sources 33

Table 2-8 Soil composition in ng compound/g-soil Rushdi et al. (2006) (ND=Not detected) 37

Table 2-9 Cholesterol chemical characteristics 39

Table 2-10 Chemical properties of cis-pinonic acid 42

Table 2-11 Low molecular weight highly oxidized acids (adapted from Hawley and Mazurek, 2008) 45

Table 3-1 GCMS settings 51

Table 3-2 BSTFA derivative optimization for subsequent sample analysis 56

Table 3-3 Sucrose Solvent Experiments 57

Table 3-4 Compound information 58

Table 3-5 Organic phase influence on carbonyl separation 60

Table 3-6 Effect of organic and flow rate changes on carbonyl separation 61

Table 3-7 Carbonyl statistical data (adapted from Hawley and Mazurek, 2008b) 62

Table 4-1 Statistical summary of levoglucosan in ng/m^3 for SOAP 2002-2003 and SOAP NY 83

Table 4-2 Summary of ANOVA results for SOAP 2002-2007 86

Table 4-3 Statistical information on total sugars, ng/m^3, for SOAP 2002-2003 and SOAP NY 90

Table 4-4 Statistical information for dehydroabietic acid, ng/m^3, for SOAP 2002-2007. 94

Table 4-5 Statistical summary of total n-alkanols, ng/m^3, in SOAP 2002-2003 and SOAP NY 100

Table 4-6 Statistical summary of total phytosterols, ng/m^3, in SOAP 2002-2007 106

Table 4-7 Statistical summary of cholesterol, ng/m^3, in SOAP 2002-2007 113

Table 4-8 Statistical summary of cis-pinonic acid, ng/m^3, in SOAP 2002-2007 118

Table 4-9 Statistical summary of levulinic acid, ng/m^3, in SOAP 2002-2007 128

Table 5-1 U.S. winter time levoglucosan concentrations 136

Table 5-2 U.S. summer levoglucosan concentrations..... 137

Table 5-3 Winter comparison of n-alkanol and sterol biogenic molecular markers..... 140

Table 5-4 Winter time fine PM cholesterol comparison..... 145

Table 5-5 Summer time cholesterol concentrations..... 146

Table 5-6 Average summertime concentrations of cis-pinonic acid 147

Table 5-7 Estimated influence of wood smoke on OC 156

Table 5-8 Comparison of OC normalized levoglucosan..... 164

Table 5-9 Summary of ANOVA results for normalized molecular markers for SOAP 2002-2007 195

Table of Figures

Figure 1-1 NAAQS attainment status 3

Figure 3-1 Sample reaction of 2,4-DNPH with an atmosphericcarbonyl compound 55

Figure 3-2 Sample reaction of BSTFA with levoglucosan 56

Figure 3-3 TIC of nine sugars, three with α and β isomers, and the internal standard at an injected mass of 10 ng (this study) 67

Figure 3-4 Mass spectral data of levoglucosan extracted from the above chromatogram (this study) 67

Figure 3-5 SOAP 2002-2007 sampling locations 72

Figure 3-6 Example input for ANOVA analysis 76

Figure 3-7 Example output of ANOVA analysis (levoglucosan in Bronx, NY SOAP NY) 76

Figure 4-1 Levoglucosan at Chester, NJ (SOAP 2002-2003) 81

Figure 4-2 Levoglucosan in Elizabeth, NJ (SOAP 2002-2003) 81

Figure 4-3 Levoglucosan in Queens, NY (SOAP 2002-2003) 82

Figure 4-4 Levoglucosan in Westport, CT (SOAP 2002-2003) 82

Figure 4-5 Levoglucosan in Bronx, NY (SOAP NY) 85

Figure 4-6 Levoglucosan in Pinnacle State Park, NY (SOAP NY) 85

Figure 4-7 Sugar profiles in Chester, NJ (SOAP 2002-2003) 87

Figure 4-8 Sugar Profiles in Elizabeth, NJ (SOAP 2002-2003) 88

Figure 4-9 Sugar Profiles in Queens, NY (SOAP 2002-2003) 88

Figure 4-10 Sugar Profiles in Westport, CT (SOAP 2002-2003) 89

Figure 4-11 Sugar profiles in Bronx, NY (SOAP NY) 91

Figure 4-12 Sugar Profiles in Pinnacle State Park, NY (SOAP NY) 91

Figure 4-13 Dehydroabietic acid in Chester, NJ (SOAP 2002-2003) 92

Figure 4-14 Dehydroabietic acid in Elizabeth, NJ (SOAP 2002-2003)..... 93

Figure 4-15 Dehydroabietic acid in Queens, NY (SOAP 2002-2003) 93

Figure 4-16 Dehydroabietic acid in Westport, CT (SOAP 2002-2003) 94

Figure 4-17 Dehydroabietic acid in NY (SOAP NY)..... 95

Figure 4-18 Total n-alkanols in Chester, NJ (SOAP 2002-2003)..... 101

Figure 4-19 Total n-alkanols in Elizabeth, NJ (SOAP 2002-2003)..... 102

Figure 4-21 Total n-alkanols in Queens, NY (SOAP 2002-2003)..... 102

Figure 4-21 Total n-alkanols in Westport, CT (SOAP 2002-2003) 103

Figure 4-22 Total n-alkanols in Pinnacle State Park, NY (SOAP NY)..... 104

Figure 4-23 Total n-alkanols in Bronx, NY (SOAP NY) 104

Figure 4-24 Phytosterols in Chester, NJ (SOAP 2002-2003)..... 107

Figure 4-25 Phytosterols in Elizabeth, NJ (SOAP 2002-2003)..... 107

Figure 4-26 Phytosterols in Queens, NY (SOAP 2002-2003)..... 108

Figure 4-27 Phytosterols in Westport, CT (SOAP 2002-2003)..... 108

Figure 4-28 Phytosterols in Pinnacle State Park, NY (SOAP NY) 109

Figure 4-29 Phytosterols in Bronx, NY (SOAP NY) 109

Figure 4-30 Cholesterol in Chester, NJ (SOAP 2002-2003) 110

Figure 4-31 Cholesterol in Elizabeth, NJ (SOAP 2002-2003) 111

Figure 4-32 Cholesterol in Queens, NY (SOAP 2002-2003) 111

Figure 4-33 Cholesterol in Westport, CT (SOAP 2002-2003) 112

Figure 4-34 Cholesterol in Pinnacle State Park, NY (SOAP NY)..... 114

Figure 4-35 Cholesterol in Bronx, NY (SOAP NY) 115

Figure 4-36 cis-Pinonic acid in Chester, NJ (SOAP 2002-2003) 119

Figure 4-37 cis-Pinonic acid in Elizabeth, NJ (SOAP 2002-2003) 119

Figure 4-38 cis-Pinonic acid in Queens, NY (SOAP 2002-2003) 120

Figure 4-39 cis-Pinonic acid in Westport, CT (SOAP 2002-2003) 120

Figure 4-40 cis-Pinonic acid in NY (SOAP NY) 121

Figure 4-41 Oxoacids in Chester, NJ (SOAP 2002-2003) 123

Figure 4-42 Oxoacids in Elizabeth, NJ (SOAP 2002-2003) 124

Figure 4-43 Oxoacids in Queens, NY (SOAP 2002-2003) 124

Figure 4-44 Oxoacids in Westport, CT (SOAP 2002-2003) 125

Figure 4-45 Oxoacids in Pinnacle State Park, NY (SOAP NY) 127

Figure 4-46 Oxoacids in Bronx, NY (SOAP NY) 127

Figure 4-47 Summer $PM_{2.5}$ Mass Balance for SOAP NY 130

Figure 4-48 Winter $PM_{2.5}$ Mass Balance for SOAP NY 130

Figure 5-1 Estimated percent of OC from wood smoke in NYC area (SOAP 2002-2003) 155

Figure 5-2 Estimated percent OC from wood smoke in NY (SOAP NY) 155

Figure 5-3 Estimated Percent of OC from meat charbroiling in NYC area (SOAP 2002-2003) 159

Figure 5-4 Estimated percent OC from meat charbroiling in NY (SOAP NY) 159

Figure 5-5 Levoglucosan normalized to OC for the NYC area (SOAP 2002-2003) 161

Figure 5-6 Levoglucosan normalized EC in the NYC area (SOAP 2002-2003) 161

Figure 5-7 Levoglucosan normalized to OC in NY (SOAP NY) 163

Figure 5-8 Levoglucosan normalized to EC in NY (SOAP NY) 163

Figure 5-9 Levoglucosan versus OC in the urban NYC area (SOAP 2002-2003) 165

Figure 5-10 Levoglucosan versus OC in the NYC area (SOAP 2002-2003) 165

Figure 5-11 Levoglucosan versus EC in the urban NYC area (SOAP 2002-2003)..... 166

Figure 5-12 Levoglucosan versus EC for the NYC area (SOAP 2002-2003) 166

Figure 5-13 Levoglucosan versus OC in NY (SOAP NY) 167

Figure 5-14 Levoglucosan versus EC in NY (SOAP NY) 167

Figure 5-15 Total n-alkanols normalized to OC in the NYC area (SOAP 2002-2003).. 169

Figure 5-16 Total n-alkanols normalized to EC in the NYC area (SOAP 2002-2003) .. 169

Figure 5-17 Total n-alkanols versus OC in the urban NYC area (SOAP 2002-2003) ... 170

Figure 5-18 Total n-alkanols versus OC in the NYC area (SOAP 2002-2003)..... 171

Figure 5-19 Total n-alkanols versus EC in the urban NYC area (SOAP 2002-2003).... 171

Figure 5-20 Total n-alkanols versus EC in the NYC area (SOAP 2002-2003) 172

Figure 5-21 Total n-alkanols normalized to OC in NY (SOAP NY) 173

Figure 5-22 Total n-alkanols normalized to EC in NY (SOAP NY) 173

Figure 5-23 Total n-alkanols versus OC in NY (SOAP NY) 174

Figure 5-24 Total n-alkanols versus EC in NY (SOAP NY)..... 174

Figure 5-25 Cholesterol normalized to OC in the NYC area (SOAP 2002-2003) 176

Figure 5-26 Cholesterol normalized to EC in the NYC area (SOAP 2002-2003)..... 176

Figure 5-27 Cholesterol versus OC in the urban NYC area (SOAP 2002-2003) 177

Figure 5-28 Cholesterol versus OC in the NYC area (SOAP 2002-2003) 178

Figure 5-29 Cholesterol versus EC in the urban NYC area (SOAP 2002-2003)..... 178

Figure 5-30 Cholesterol versus EC in the NYC area (SOAP 2002-2003)..... 179

Figure 5-31 Cholesterol normalized to OC in NY (SOAP NY) 180

Figure 5-32 Cholesterol normalized to EC in NY (SOAP NY)..... 180

Figure 5-33 Cholesterol versus OC in NY (SOAP NY) 181

Figure 5-34 Cholesterol versus EC in NY (SOAP NY) 181

Figure 5-35 cis-Pinonic acid normalized to OC in the NYC area (SOAP 2002-2003) .. 183

Figure 5-36 cis-Pinonic acid normalized to EC in the NYC area (SOAP 2002-2003)... 183

Figure 5-37 cis-Pinonic acid versus OC in the urban NYC area (SOAP 2002-2003).... 184

Figure 5-38 cis-Pinonic acid versus OC in the NYC area (SOAP 2002-2003)..... 184

Figure 5-39 cis-Pinonic acid versus EC in the urban NYC area (SOAP 2002-2003) 185

Figure 5-40 cis-Pinonic acid versus EC in the NYC area (SOAP 2002-2003) 185

Figure 5-41 cis-Pinonic acid normalized to OC in NY (SOAP NY)..... 186

Figure 5-42 cis-Pinonic acid normalized to EC in NY (SOAP NY) 187

Figure 5-43 cis-Pinonic Acid versus OC in NY (SOAP NY)..... 188

Figure 5-44 cis-Pinonic acid versus EC in NY (SOAP NY) 188

Figure 5-45 Levulinic acid normalized to OC in the NYC area (SOAP 2002-2003)..... 190

Figure 5-46 Levulinic acid normalized to EC in the NYC area (SOAP 2002-2003) 190

Figure 5-47 Levulinic acid versus OC in the urban NYC area (SOAP 2002-2003)..... 191

Figure 5-48 Levulinic acid versus OC in the NYC area (SOAP 2002-2003)..... 191

Figure 5-49 Levulinic acid versus EC in the urban NYC area (SOAP 2002-2003)..... 192

Figure 5-50 Levulinic acid versus EC in the NYC area (SOAP 2002-2003) 192

Figure 5-51 Levulinic acid normalized to OC in NY (SOAP NY)..... 193

Figure 5-52 Levulinic Acid normalized to EC in NY (SOAP NY)..... 193

Figure 5-53 Levulinic acid versus OC in NY (SOAP NY) 194

Figure 5-54 Levulinic acid versus EC in NY (SOAP NY) 194

Figure 5-55 Levoglucosan normalized to $PM_{2.5}$ in the NYC area (SOAP 2002-2003) .. 196

Figure 5-56 Levoglucosan versus $PM_{2.5}$ in the urban NYC area (SOAP 2002-2003) 197

Figure 5-57 Levoglucosan versus $PM_{2.5}$ in the NYC area (SOAP 2002-2003) 198

Figure 5-58 Levoglucosan normalized to $PM_{2.5}$ in NY (SOAP NY) 199

Figure 5-59 Levoglucosan versus $PM_{2.5}$ in NY (SOAP NY) 200

Figure 5-60 Total n-alkanols normalized to $PM_{2.5}$ in the NYC area (SOAP 2002-2003) 201

Figure 5-61 Total n-alkanols versus $PM_{2.5}$ in the urban NYC area (SOAP 2002-2003) 202

Figure 5-62 Total n-alkanols versus $PM_{2.5}$ in the NYC area (SOAP 2002-2003) 202

Figure 5-63 Total n-alkanols normalized to $PM_{2.5}$ in NY (SOAP NY) 203

Figure 5-64 Total n-alkanols versus $PM_{2.5}$ in NY (SOAP NY) 204

Figure 5-65 Cholesterol normalized to $PM_{2.5}$ for the NYC area (SOAP 2002-2003)..... 205

Figure 5-66 Cholesterol versus $PM_{2.5}$ in the urban NYC area (SOAP 2002-2003) 205

Figure 5-67 Cholesterol versus $PM_{2.5}$ in the NYC area (SOAP 2002-2003) 206

Figure 5-68 Cholesterol normalized to $PM_{2.5}$ in NY (SOAP NY) 207

Figure 5-69 Cholesterol versus $PM_{2.5}$ in NY (SOAP NY) 207

Figure 5-70 cis-Pinonic acid normalized to $PM_{2.5}$ in the NYC area (SOAP 2002-2003)208

Figure 5-71 cis-Pinonic acid versus $PM_{2.5}$ in the urban NYC area (SOAP 2002-2003). 209

Figure 5-72 cis-Pinonic acid versus $PM_{2.5}$ in the NYC area (SOAP 2002-2003) 209

Figure 5-73 cis-Pinonic acid normalized to $PM_{2.5}$ in NY (SOAP NY) 210

Figure 5-74 cis-Pinonic acid versus $PM_{2.5}$ in NY (SOAP NY) 211

Figure 5-75 Levulinic acid normalized to $PM_{2.5}$ in the NYC area (SOAP 2002-2003).. 212

Figure 5-76 Levulinic acid versus $PM_{2.5}$ in the urban NYC area (SOAP 2002-2003) ... 212

Figure 5-77 Levulinic acid versus $PM_{2.5}$ in the NYC area (SOAP 2002-2003) 213

Figure 5-78 Levulinic acid normalized to $PM_{2.5}$ in NY (SOAP NY) 214

Figure 5-79 Levulinic acid versus $PM_{2.5}$ in NY (SOAP NY) 214

List of Equations

Equation 1 54

Equation 2 56

Equation 3 69

Equation 4 73

Equation 5 74

Equation 6 74

Equation 7 75

Equation 8 154

Equation 9 157

Equation 10 157

Equation 11 157

List of Acronyms

ANOVA	Analysis of Variance
BDL	Below the detection limit
BF_3	Boronitrifluoride
BSTFA-TMS	N,O-bis(Trimethylsilyl)triflouroacetamide with Trimethylchlorosilane
CARB	California Air Resource Board
CMB	U.S. EPA Chemical Mass Balance version 8.2 computer model
CT	Connecticut
DNPH	2,4-dinitrophenylhydrazine
EC	Elemental Carbon
EPA	United States Environmental Protection Agency
GC FID	Gas Chromatography Flame Ionization Detectoion
GCMS	Gas Chromatography Mass Spectrometry
HPLC	High Performance Liquid Chromatography
IQR	Interquartile Range
LCMS	Liquid Chromatography Mass Spectrometry
ND	Not detected
NJ	New Jersey
NY	New York
NYC	New York City, NY
OC	Organic Carbon
Oxoacids	Oxygenated Acids
PFBHA	O-(2,3,4,5,6-pentafluorobenzyl)-hydroxyamine
PM	Particulate Matter
$PM_{2.5}$	Particles with a diameter less than 2.5 μm
RRF	Relative Response Factor
RSD	Percent relative standard deviation
SCAQMD	South Coast Air Quality Management District
SOA	Secondary Organic Aerosol
SOAP	Speciation of Organics for Apportionment of $PM_{2.5}$
SOP	Standard Operating Procedure
STN	U.S. EPA Speciation Trends Network

1. Introduction

Airborne particulate matter (PM) is composed of a complex mixture of chemicals which have a wide array of properties, including molecular weight and polarity. Fine particulate matter is composed of particles with a diameter of 2.5 μm or less. Fine PM, or $PM_{2.5}$, contains sulfate, nitrate, ammonium, metals, elemental carbon and organic compounds. The organic compounds are not characterized fully because the carbonaceous material consists of hundreds of organic chemicals with varying properties such as water solubility, volatility and molecular weight. Coarse PM is defined as having a diameter between 2.5 and 10 μm and consists of materials typical of the earth's crust and grinding processes (for example dust and metals) (NARSTO, 2003).

Atmospheric polar organic compounds can originate from a variety of sources, in particular from motor vehicle exhaust, biogenic sources, wood smoke and secondary organic aerosol formation from primary emissions (Simoneit and Mazurek, 1982; Simoneit, 2002; Rogge et al., 1991; Rogge et al., 1993b; Rogge et al., 1994; Rogge et al., 1997; Schauer et al., 1996; Schauer et al., 1999; McDonald et al., 2003; Fine et al., 2001; Fine et al., 2002). Polar organic compounds comprise the organic carbon (OC) fraction along with moderately polar to nonpolar chemicals (NARSTO, 2003; Medeiros et al., 2006; Simoneit et al., 2004). The polar fraction is of great interest in atmospheric chemistry and source apportionment applications since this fraction is highly water-soluble and is thought to influence PM solubility and condensation of atmospheric water vapor, impacting local, regional and global atmospheric processes. Therefore, understanding the sources and atmospheric abundances of polar organic compounds and

the magnitude of manmade emissions of these compounds to the troposphere are important for improving atmospheric chemistry and climate models.

The United States Environmental Protection Agency (EPA) set National Ambient Air Quality Standards (NAAQS) for ground level $PM_{2.5}$ as an annual average of 15 $\mu g/m^3$ and a daily average of 65 $\mu g/m^3$ (the average is a 3-year running average). Carbonaceous aerosol is a component of $PM_{2.5}$ which consists of hundreds of organic chemicals with varying properties (Mazurek, 2002; Simoneit, 2002; Rogge et al., 1993b; Li et al., 2005). Understanding the sources contributing to the carbonaceous aerosol is important in order to implement effective air quality control strategies to be in attainment status with the NAAQS (Zheng et al., 2007; Gorin et al., 2006; Mazurek, 2002). Managing PM requires understanding both anthropogenic and natural sources to determine which sources are manageable and which are not. If a state is found in non-attainment with the NAAQS the state must develop a State Implementation Plan (SIP) that describes how the state will meet the NAAQS in the years to come (NARSTO, 2003; EPA, 2004). Figure 1-1 indicates the attainment areas for the United States as set by the EPA (EPA, 2004).

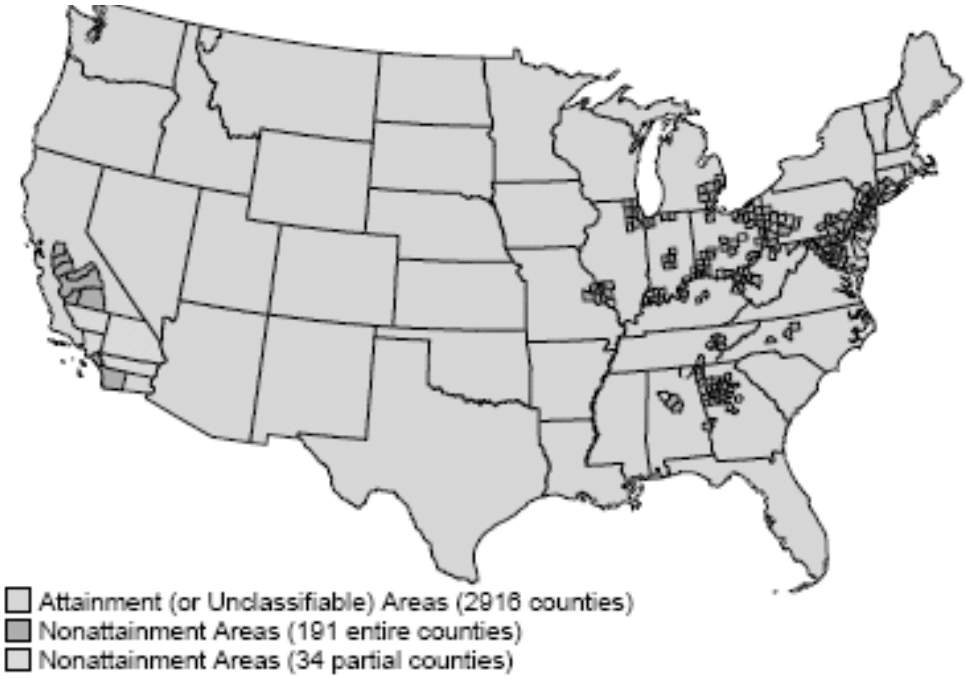


Figure 1-1 NAAQS attainment status

The northeastern United States has many areas that are in nonattainment status as specified by the NAAQS (NARSTO, 2003; EPA, 2004). The nonattainment areas are generally located in the vicinity of urban centers, such as Washington D.C., Boston, MA, Philadelphia, PA and New York City, NY. The study area of this project, New York City, is a highly populated area. It is a transportation corridor for the northeastern US and contains several airports and marine ports.

Adverse health impacts have been associated with elevated levels of PM mass (Shepherd, 2003; Dockery, 2001). Fine particles appear to be more potent than the coarse particles. The fine particles can move further into the respiratory tract and may be of chemical compositions that more readily induce adverse health effects than coarse particles.

Haze is a common problem caused by air pollution because particles can absorb or reflect visible light causing interferences resulting in attenuation of light. Highly water soluble gases and particles (e.g., polar organic compounds, sulfate and nitrate salts) absorb atmospheric water vapor producing fine particles that scatter or absorb light (NARSTO, 2003). Haze is a current problem in some urban areas, such as New York City, Atlanta, Chicago, and Los Angeles. It is a regional problem also, for example in the Rocky Mountains of the United States (Shepherd, 2003).

Aerosols are believed to impact global climate change; however it is unclear as to what dominates: the cooling effect by increasing cloud coverage or the warming effect by absorbing aerosols (Breon, 2006; Anderson et al., 2003; MacCracken, 2008; Ghan and Schwartz, 2007). Aerosols lead to the formation of numerous and smaller cloud droplets which cause brighter clouds that reflect solar radiation causing a net cooling effect. In areas such as the Indian Ocean and Amazon Basin, airborne particles, particularly those with black carbon from incomplete combustion can absorb solar energy, warm the environment and inhibit cloud formation (Breon, 2006; Karl and Trenberth, 2003; MacCracken, 2008; Ghan and Schwartz, 2007). Aerosols typically have a life on the order of several days to weeks whereas green house gases such as carbon dioxide can remain in the atmosphere for centuries (Breon, 2006; Karl and Trenberth, 2003). The impacts of particles on climate are not well understood due to difficulty in measuring the chemical composition of aerosols as well as the spatial and temporal differences in aerosol composition (Karl and Trenberth, 2003).

Chemical fingerprints for emission sources can be used to trace ambient air pollutants from sources and thus determine where the pollution is originating. Source

emission tests are conducted in order to determine which organic molecular markers are appropriate for that source. Hydrocarbons from biogenic and anthropogenic emissions have been characterized extensively, however data on the polar organic components of aerosols is limited (Simoneit, 2002; Rogge et al., 1993b; Li et al., 2005).

In a general sense there are two types of particulate matter: manageable and unmanageable sources. Manageable sources are sources that can be managed or controlled. These typically are primary pollutants from industrial (stationary) sources and motor vehicles (mobile sources). Unmanageable sources either cannot be determined or cannot be controlled, such as volcanic eruptions and biomass emissions from land and marine environments (Shepherd, 2003).

The NARSTO Assessment report "Particulate Matter Science for Policy Makers" (NARSTO, 2003) listed areas of priority research to determine methods to effectively manage air pollution and to reduce emissions. The priority research area was determining the organic chemical composition of fine PM from anthropogenic and biogenic sources to estimate the relative source contributions. These data indicate sources could be controlled to reduce emissions with improved engineering solutions. A second research priority area was evaluating fine PM for secondary organic aerosols to gain an understanding of the contribution of reaction products. A third research priority was identifying the seasonal variations in the chemical composition of fine PM necessary for the development of control strategies (Pandis, 2003; Blanchard, 2003).

Key Scientific Questions

This dissertation research was motivated and structured on the following major science questions.

How can polar organic compounds be measured in atmospheric fine particulate matter? Is there potential analytical equipment that could quantify the compounds without a derivitization technique?

What is the contribution of wood smoke to the atmosphere in the New York City (NYC) area? The abundance of wood smoke markers could help in the determination of whether or not this could be a manageable source to reduce fine PM.

Is meat charbroiling a significant cause of fine aerosols in the NYC area? Cooking operations have the ability to retrofit their operations to lower emissions however the source is questionable as a significant contributor to such pollution.

What is the contribution of vegetative detritus to this highly urbanized area? This would be characterized as an unmanageable source but it is important to understand that areas that cannot be controlled could still contribute fine PM into the atmosphere. The significance of such a contribution could aid in the development of SIPs.

What secondary organic aerosol markers, found in smog chamber experiments, can be seen in urban and regional background sites in the northeastern United States? What is the estimated primary versus secondary contribution based on molecular markers?

The methods and tasks that will be used to answer these questions are described in the following two sections. The results from the analysis are provided in the remaining sections of this thesis. The appendices provide additional information that was used to answer these key scientific questions.

2. Literature Review

The literature review aims to provide an overview of past and current studies on the analysis of polar organic compounds in fine PM. The literature review is separated in two main sections. The first section evaluates two forms of chromatography, liquid and gas, and the use of mass spectrometers as quantifiable tools. The second section begins by describing how to use molecular markers to determine air pollution sources. The remaining literature review describes emission tests to determine source specific molecular markers and case studies for wood smoke, biogenic sources, meat charbroiling and secondary organic aerosols.

2.1. *Analytical Equipment (Chromatography and Spectrometry)*

High performance liquid chromatography (HPLC) is applicable to nonvolatile samples and is considered to be efficient and selective for moderately to highly polar organic compounds with reverse phase LC conditions (i.e., nonpolar column, polar eluent). HPLC, however, is less compatible with mass spectrometer (MS) detectors than gas chromatography (GC) and it has no detector equivalent to the versatility of the GC flame ionization detector (FID). Reversed phase HPLC, where the stationary phase is nonpolar and the mobile phase is polar, currently is the most common analysis method for polar organic compounds. HPLC uses high-pressure pumps to pump the mobile phase (a polar liquid) through tubing into which the sample is injected and carried to the column to separate individual chemicals from the mixture, then carried to the detector. The mobile phase can be run in an isocratic mode, meaning the solvent composition

remains the same throughout the analysis, or with a gradient elution in which the mobile phase composition is changed throughout the analysis. Mobile phases usually are water and an organic (methanol, acetonitrile or tetrahydrofuran). There are many variations of detectors for HPLC, among the more common are the ultraviolet absorption or UV/Vis detectors (either fixed or variable wavelength), photodiode array, fluorescence, electrochemical detector (ECD), evaporating light-scattering detector (ELSD) and conductivity detector (Miller, 2005). There are more options with HPLC thus making the method development more complicated, especially for complex mixtures.

HPLC chromatographic separation typically is achieved with a packed particulate column. Packed columns can lose up to 30% of the volume due to voids that do not aid in separation (Jacoby, 2006). Smaller sized particles can reduce the loss of volume; however it increases the backpressure which can destroy the column. A newer column technology, referred to as monoliths, is one-piece porous solids. Research has shown that monolithic columns achieved separation faster than traditional columns and in some cases, had better resolution, were more stable and had a longer life. The monolithic columns produce much lower backpressure, one-third to one-fourth of the backpressure of the traditional columns (Jacoby, 2006).

The organic polymer-based monoliths are better for separating large particles, such as proteins, nucleic acids and synthetic polymers whereas silica-based monoliths are better for separation of smaller molecules. The porous silica rods are prepared then functionalized with a bonded carbon chemistry (C8 or C18) which creates the reversed-phase chromatographic column used with HPLC (Svec and Huber, 2006).

In order to examine the monolithic column as an analytical tool for environmental analysis, a set of well-characterized carbonyl compounds was chosen. The analysis of carbonyls using 2,4-dinitrophenylhydrazine (DNPH) has been in existence for several decades. There are other derivative methods for carbonyl analysis including photometric and fluorometric methods, however they tend to be selective for formaldehyde and are not applicable to other aldehydes. Therefore, the use of DNPH was used in this work. DNPH derivatives are detected typically with UV/Vis or fluorescence detectors after chromatographic separation with HPLC. Chromatographic separation has been obtained using reversed phase C18 columns and mobile phases consisting of water and one or two organics, primarily, methanol, acetonitrile or tetrahydrofuran. The DNPH derivatives are detected usually at a wavelength near 360 nm. The main interference with the DNPH derivatization is ozone which can react with the DNPH; in order to avoid this ozone scrubbers are used before derivatization (Vogel et al., 2000). Atmospheric carbonyl compounds originate from anthropogenic and biogenic sources as well as reaction intermediates from the oxidation of hydrocarbons. Carbonyl compounds also can act as precursors to organic acids and oxidants in the atmosphere. Some carbonyls are toxic to living organisms (Levart and Veber, 2001). Derivatizing samples can be done via several methods. DNPH-coated solid sorbent cartridges, impingers containing DNPH and diffusion scrubbers are the most popular techniques. Recently, researchers evaluated using cryotraps to collect the air sample followed by derivatization with promising results (Levart and Veber, 2001).

Gas chromatography (GC) is used for the analysis of volatile chemicals; GC is compatible with mass spectrometry (MS), uses a small sample volume and is considered

efficient, selective and widely applicable to environmental samples. A disadvantage to GC is the samples must be volatile; however there are many nonvolatile chemicals that can be made volatile through derivatives (Miller, 2005). In general terms a GC works by injecting the sample through a septum, where it is transported by the carrier gas through the column and into the detector (Miller, 2005). The GC is heated typically as three zones, the injector, the column and the detector. The most common detector, which was used in this study, is the flame ionization detector (FID) with the carrier gas being helium. Another common detector is the electron capture detector (ECD) with the carrier gas consisting of dry nitrogen (Miller, 2005).

The retention time in the GC analytical column characterizes a given compound when compared to a standard, however for positive identification in a complex mixture, mass spectral data is crucial. In MS, also referred to as mass selective detectors (MSD), the analytes are ionized, sometimes fragmented, then sent to a mass analyzer; the ion current generated (also referred to as the abundance) is plotted versus the mass/charge ratio (m/z , where usually z is 1). Thus, the m/z value becomes m and the value is the mass of the compound. The ion current is specific to the chemical, or groups of chemicals, and can be confirmed with standards. The MS has three main parts, the ionization chamber (or the ion source), the analyzer and the detector. The ion source can be several designs. The most common, and the oldest, is electron impact (EI), which is primarily in GCMS. In EI high energy (70 EV) electrons are released from a heated filament (usually tungsten) which strike the analyte molecules causing ionization. MS with HPLC is different than in GCMS and has “soft” ionization processes. The LC mobile phase is used in the ionization process which does not happen in GCMS because

the carrier gas is inert and is not involved in analyte ionization. The mobile phase from the HPLC is sent to a nebulizer and vaporized, then ionized with a source, the most common of which are thermospray ionization (TSI), electrospray ionization (ESI) and atmospheric pressure ionization (API). These produce adducts which are added to the compound; ESI uses H^+ so the $m/z = (MW + zH^+)/z$ and may also form dimers, trimers and polymers with the analyte and solvent molecules. Both ESI and API can form other adducts such as sodium ion (Na^+) replacing the H^+ with a mass addition of 23. The next stage is the analyzers, the most common of which are quadrupoles and ion traps. The MS, however, does not have a retention time; that valuable piece of information comes from the chromatography (Miller, 2005). Thus the chromatography and the spectrometry are useful in conjunction with each other to determine if an unknown compound in a sample is the target organic compound.

2.2. *Molecular Markers*

Sources of atmospheric aerosols are determined by correlating them with molecular markers, or indicator compounds, that are emitted from a source (Simoneit and Mazurek, 1982; Mazurek, 2002; Schauer et al., 1996). Fine particulate matter is particles with a nominal diameter less then 2.5 μm ($PM_{2.5}$) consisting of a complex mixture of organic chemicals which have a wide array of properties including molecular weight and polarity. Fine aerosols vary throughout the atmosphere spatially, temporally, in abundance and chemically in their complex mixtures. Currently about 20% of the organic mixtures can be determined quantitatively as individual species which leaves 80% which could be used to indicate new sources or potential chemical agents harmful to human health. Thus, it is necessary to try to extract this chemical information from the

PM complex mixtures to better understand the potential health impacts and to engineer technologies that would improve air quality (Mazurek, 2002).

Polar organic compounds have heteroatoms such as O, N, S or P. Polar organics are more soluble in organic solvents, including water vapor. Research is showing that increasing polarity of a compound might cause an increase in the uptake of these particles by the respiratory system causing adverse health effects (Mazurek, 2002). Polar organic compounds have not been well-characterized due to analytical difficulties, and therefore, need to be researched.

Organic components of PM can be emitted either directly as primary emissions or though reactions as secondary organic aerosols (Brown et al., 2002). A good tracer for an emission source should be stable in the atmosphere for the length of time it takes to get from the source to the sampler, the compound needs to be emitted in a large enough quantity to be detectable by analytical measurement techniques, and the compound or the emission pattern of several compounds should be unique to the source (Rogge et al., 1991).

2.3. *Wood Smoke*

Biomass burning is a primary source of particulate matter that can reduce visibility or become a reactant in atmospheric chemistry (Simoneit, 2002). Wood is burned for residential heating (also called a biofuel) and by forest fires (prescribed or natural). Denver, CO estimated that 20 to 30% of the total fine particle matter during winter is from wood combustion (Rogge et al., 1998). Los Angeles, CA showed that 14% of the year round fine particulate matter is due to biomass combustion and in the

winter upwards of 30% is from biomass combustion (Rogge et al., 1998). Wood smoke particles are mainly in the inhalable size range and can be mutagenic (Nolte et al., 2001).

Sugar compounds can be used to determine sources of organic carbon in the atmosphere. Levoglucosan is a product of biomass combustion, which has been found over the ocean indicating its stability during long-range transport (Simoneit, 2002; Medeiros et al., 2006). Glucose is a monosaccharide that is present in vascular plants and is a carbon source for soil microorganisms such as bacteria and fungi (Simoneit, 2002; Medeiros et al., 2006). Mycose is present in microorganisms which can be used as a reserve carbohydrate and stress protectant (Simoneit, 2002). As mycose is present in only a few higher plants it is a good indicator of soil microorganism impact on regional aerosol. Dehydroabietic acid is released in large quantities from soft wood combustion and in minor amounts from hard wood combustion (Medeiros et al., 2006; Simoneit, 2002). Water-soluble potassium was suggested as tracer for wood smoke; however potassium has many other sources which would need to be accounted for in mass balance models which is difficult (Simoneit, 2002).

2.3.1. The Process of Cellulose Combustion

Biomass burning, found as woodsmoke in atmospheric fine PM, is based on burning wood which consists of some form of lignins, cellulose and fillers (Simoneit, 2002; Simoneit et al., 1993; Simoneit et al., 1999). Cellulose is a long linear chain of 7,000 to 12,000 D-glucose monomers; cellulose molecules organize into longer parallel fiber structures. Hemicellulose is a mixture of polysaccharides from glucose, mannose, galactose, xylose and arabinose. The lignins are composed of coumaryl, coniferyl and sinapyl alcohols and anisyl, vanillyl, and syringyl nuclei. The fillers are tannins, terpenes

and other compounds (Simoneit, 2002). Wood combustion begins as the constituents heat up then volatize (low-molecular weight biomarkers via steam-distillation with water content in wood), hydrolyze, oxidize, dehydrate and pyrolyze as the temperature increases.

Cellulose decomposes in two ways depending on the temperature. At temperatures below 300 °C, a char forms (Simoneit, 2002; Simoneit et al., 1993; Simoneit et al., 1999). At temperatures greater than 300 °C the cellulose goes through bond cleavage, fission and disproportionation reactions forming anhdyro sugars and volatile products. These anyhdro sugars can be used as source tracers for wood smoke. The 1,6-anhydride of glucose, called levoglucosan or 1,6-anhydro-β-D-glucopyranose, is a significant tracer of cellulosic combustion as it is for the most part unique to this single source and shows no decay in ambient conditions for at least 8 hours (Simoneit, 2002). Although other carbohydrates can produce levoglucosan upon burning, the temperatures used for cooking, baking and toasting are not high enough to pyrolize carbohydrates to levoglucosan, thus these activities are not significant sources (Simoneit, 2002).

Pyrolysis degradation products of lignin are coumaryl, vanillyl and syringyl moieties (Simoneit, 2002; Simoneit et al., 1993). The molecular-level breakdown components are as phenols, aldehydes, ketones, acids and alcohols. Pine wood (a soft wood) smoke is dominated by vanillin and vanillic acid with lesser amounts of syringic and anisic acid detected (Simoneit, 2002). Hard woods, such as oak, are dominated by syringaldehyde and syringic acid with lesser amounts of vanillyl moieties. Grass smoke is dominated by p-anisaldehyde and p-anisic acid with lesser amounts of coumaryl, vanillyl and syringyl moieties (Simoneit, 2002; Simoneit et al., 1993).

2.3.2. Emission Tests

A number of studies were conducted on the emission rates of biomass combustion. The emission rates of polar compounds of interest are shown in Table 2-1 and Table 2-2. Fine et al. (2001) conducted source tests on woods grown in the northeastern United States for organic compound characterization of $PM_{2.5}$ emitted from wood combustion. The study burned six species of wood separately in a conventional masonry oven. Each test lasted between 82 and 136 hours and burned 5 to 7 kg of wood. The emission samples were collected with standard dilution samplers followed by cyclone samplers at a flow rate of 10 L/min to collect fine pm samples on a quartz fiber filter. The filters were extracted and analyzed by GCMS. The six species of trees, as well as the polar compounds of interest, are listed in the following table. The emission rates of fine particles ranged from 2.7 to 11.4 grams per kg of wood burned, depending on wood variety, dryness, and combustion conditions. The average emission rate was 5.3 grams of $PM_{2.5}$ per kg of wood burned, which is less than the U.S. EPA emission factor of 17.3 grams of $PM_{2.5}$ per kg of wood burned. Levoglucosan accounted for between 3% and 12% of the total organic compound mass emissions. Dehydroabietic acid was emitted as a dominant marker by the gymnosperm species (softwoods) (Fine et al., 2001). This marker is a thermally-altered product from abietic acid, a major component of pine wood resin.

Fine et al. (2002) conducted source tests for fine particulate matter on six wood varieties common to the southern United States following the same procedure as Fine et al. (2001). In these emissions tests 5 to 12 kg of wood were burned per test for 81 to 202 minutes. The average emission rate of fine particulate matter was 4.3 grams of $PM_{2.5}$ per

kg of wood, with a range of 1.6 to 6.8 g/kg. Levoglucosan accounted for 3% to 16% of the organic compound mass emitted during the tests. The $PM_{2.5}$ mass emission rate was 4.3 g per kg of wood burned (Fine et al., 2002). The tree species studied and the polar organic compounds of interest are shown in Table 2-1.

Rogge et al. (1998) evaluated three different woods, pine, oak and synthetic log, to determine the chemical constituents of the particulate matter in the smoke. Each type of wood was burned separately in a brick fireplace for about 3 hours for 12.5 to 20 kg of wood to simulate home heating use. The synthetic log, however, was burned according to the manufacturer's instructions. Although this study did not target levoglucosan it did look for resin acids, phytosterols and a suite of other organic compounds. The natural woods combusted contained only small amounts of n-alkanes, n-alkanals, or n-alkanols with no preference for odd numbered n-alkane carbons, which is the opposite of what is typically found in leaf waxes. The resin acid, dehydroabietic acid, was found in the pine and not in the oak, as expected. The phytosterol, β-sitosterol, was found in the pine and oak smoke. Table 2-2 shows the results of the target compounds.

Schauer et al. (2001) conducted source tests on three kinds of trees: conifers (e.g. gymnosperm trees such as pine, "softwood") and two deciduous trees (angiosperm species oak and eucalyptus, "hardwood"). The wood varities were burned separately in a residential fireplace. Fine particulate matter was collected about 5 meters above the chimney outlet. The pinewood was burned over 189 minutes and weighed 17.2 kg, 15.4 kg of oak were burned over 165 minutes and 18.9 kg of eucalyptus were burned over 218 minutes. The pinewood emitted 9.5 g fine particles per kg of wood burned, where 56% was organic carbon and 1.4% elemental carbon. The oak emitted 5.1 g fine particles per

kg of wood burned, where 59.1% was organic carbon and 3.2% elemental carbon. The eucalyptus emitted 8.5 g fine particles per kg of wood burned, where 43.7% was organic carbon and 2.6% was elemental carbon. Levoglucosan accounted for 18% to 31% of the fine particle mass emitted. Table 2-2 shows the values obtained for each of the three woods as grams levoglucosan emitted per kg of wood burned.

Nolte et al. (2001) also burned pine, oak and eucalyptus woods to determine the mass emission rates of polar organic compounds from these tree species. The tests were conducted in a residential fireplace and collected with a dilution sampler and a cyclone separator with a cutoff diameter of 2 μm and collected on quartz fiber filters. Levoglucosan was the most abundant compound in all the source tests. Its analogues, galactosan and mannosan (also anhydrous sugars), also were present. The monosaccharides glucose, xylose and mannose and the disaccharides maltose and sucrose, also were present however all were measured at lower mass emission rates than levoglucosan. The pinewood showed larger quantities of lignin products derived from coniferyl alcohol (i.e. vanillic acid) whereas the two hard woods (oak and eucalyptus) showed more syringyl compounds. Table 2-2 shows selected results from the Nolte et al. (2001) study.

Research also was conducted on other biomass materials (cellulosic) similar to wood. Hays et al. (2005) evaluated the combustion of wheat and rice in order to simulate agricultural field burning. The combustion tests where done in the same manner as Fine et al. (2001) and Fine et al. (2002) and the results were likewise reported as mg compound per gram of OC. In general the fine PM emissions were lower in agricultural burns compared to wildfires. Levoglucosan was present in the samples and the sugar

monomers were the most abundant class of compounds found. The levoglucosan values were within a factor of 2 to the wood combustion estimates (rice was about 126.5 mg per gram OC and wheat was about 100.0 mg per gram OC). Though levoglucosan was present in both agricultural and wood tests the difference in the distribution of organic chemicals may allow for separation of these two classes of biomass combustion in aerosol samples. The location of the study may also differentiate what biomass is burned because only certain regions burn crops. Finally, Simoneit et al. (2005) studied source emission tests on landfill garbage and found levoglucosan as a component. Therefore, garbage, specifically containing paper and cardboard, combustion would be expected to produce significant levoglucosan emissions as PM from low temperature burning (i.e., fireplaces, boilers, woodstoves, open fires).

2.3.3. Molecular Markers for Biomass Burning

Levoglusocan (1,6-anhydro-β-$_D$-glucopyranose) is produced from cellulose combustion and has a high resistance to environmental degradation (i.e. to photolysis in the atmosphere). This compound is not a molecular marker for direct emissions of fine particles from biogenic sources as cellulose is found in relatively low concentrations in leaves (Jordan et al., 2006). Herckes et al. (2006) collected PM samples of different size fractions at Yosemite National Park, CA during the summer of 2002. The samples were analyzed for levoglucosan and it was found in all. Levoglucosan was present mainly in the submicron size fraction, which also was where dehydroabietic acid was found. The authors observed that levoglucosan partitioned primarily into the fine fractions, which is typical of combustion derived PM, and was less significant in the coarse PM fraction (> 10 μm nominal diameter), which is derived from natural materials such as resuspended

soil and larger fragments from vegetation and airborne biota. Levoglucosan was tested for its stability in water and in acid, with the pH approximately 2 (Simoneit et al., 2004). The recoveries were greater than 99% after 1, 3, 5 and 15 days.

Other suggestions for wood smoke tracers are for isotopically "contemporary" carbon (C-14) and nonmineral potassium. However, these chemical tracers are not unique to wood smoke as they can also be emitted in particulate matter from meat cooking, refuse incineration, abrasion of leaf surfaces, sea salt and resuspended soil and road dust (Fine et al., 2002; Simoneit, 2002). Studies have tested for PAHs as tracers for wood smoke; however these are not specific to wood smoke nor do they appear to be as dominant as levoglucosan (Rogge et al., 1998; Schauer et al., 2001; Nolte et al., 2001). Retene was proposed as a tracer for wood smoke; however there are several problems with this choice. Retene is found primarily in coniferous woods and it is semivolatile with a high vapor pressure making it difficult to quantify (Nolte et al., 2001). A suite of sugars, with levoglucosan as the most important, were chosen as molecular markers for wood smoke for this study. Table 2-3 illustrates the sugars and provides several important chemical characteristics. Additional molecular markers, particularly organic acids, are shown in Table 2-4.

Table 2-1 Wood smoke emission tests[1]

Reference	Fine et al. (2001)						Fine et al. (2002)					
Source	Red Maple	Red Oak	Paper Birch	White Pine	Hemlock	Balsam Fir	Yellow Poplar	White Ash	Sweet-gum	Mockernut Hickory	Loblolly Pine	Slash Pine
Compound	mg/g-OC emitted						mg/g-OC emitted					
Levoglucosan	108.51	168.25	109.54	52.33	95.45	81.45	156.22	98.97	127.99	159.18	36.37	46.94
Galactosan	nd	3.527	nd	1.291	2.472	2.582	2.925	nd	nd	3.533	nd	nd
Mannosan	3.29	4.75	1.31	9.01	25.57	17.39	14.65	7.68	6.96	6.44	8.02	9.57
Xylose												
Mannose												
Glucose												
Sucrose												
Maltose												
Vanillic Acid	0.25	3.79	0.33	0.42	1.63	2.99	1.66	1.29	1.02	4.01	0.48	0.62
Syringic Acid	nd	4.93	nd	nd	nd	nd	4.35	1.02	2.14	3.06	nd	nd
Tetracosanol												
Hexacosanol												
Octacosanol												
Triacontanol												
Cholesterol												
Campesterol												
Stigmasterol	nd	0.43	nd	nd	nd	0.21	1.53	0.69	nd	0.57	nd	nd
β-sitosterol	0.79	6.37	0.65	0.31	2.51	4.98	2.15	4.26	1.34	3.81	0.21	0.12
dehydroabietic acid							nd	nd	nd	nd	12.33	6.62

[1] Empty cells indicate no reported values for that compound; nd = not detected

Table 2-2 Wood smoke emission tests (continued)[1]

Reference	Nolte et al. 2001			Rogge et al., 1998			Schauer et al., 2001		
Source	Oak	Eucalyptus	Pine	Pine wood	Oak wood	Synthetic log	Pine	Oak	Eucalyptus
Compound	µg/g	µg/g	µg/g	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
Levoglucosan	673	1490	1380				1375	706	1940
Galactosan	30	24	108						
Mannosan	39	42	340						
Xylose	0.1	1.1	nd						
Mannose	0.2	0.7	1.5						
Glucose	0.5	0.8	0.7						
Sucrose	0.3	0.2	0.2						
Maltose	2.8	5.0	11						
Vanillic Acid	3.5	6.8	8.5						
Syringic Acid	5.7	22	nd						
Tetracosanol	2.9	0.7	2.9						
Hexacosanol	3.1	4.1	nd						
Octacosanol	0.1	5.9	nd						
Triacontanol	nd	0.6	nd						
Cholesterol	1.6	2.2	1.7						
Campesterol	0.4	nd	nd						
Stigmasterol	0.6	nd	nd						
β-sitosterol	9.5	12	7.4	45.50	9.94	nd			
dehydroabietic acid				37.23	5.60	nd	43.6	2.07	0.424

Table 2-3 Sugars as molecular markers for wood smoke

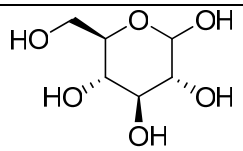
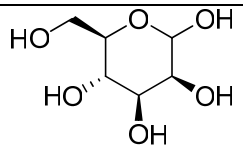
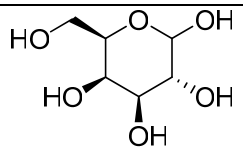
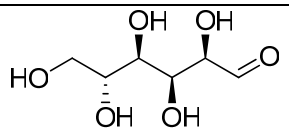
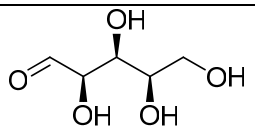
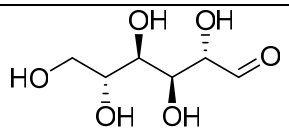
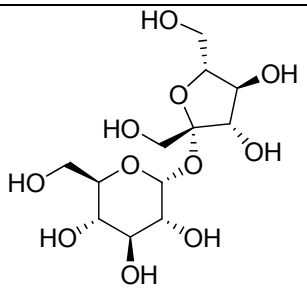
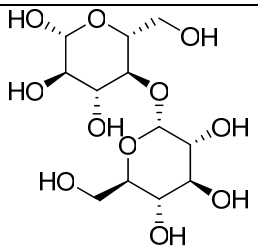
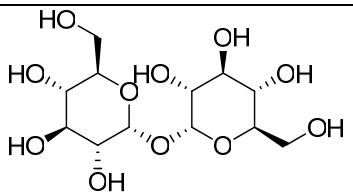
Compound	CAS no.	MW, g/mol	Formula	Structure
Levoglucosan	498-07-7	162.14	$C_6H_{10}O_5$	
Mannopyranose	14168-65-1	162.14	$C_6H_{10}O_5$	
Galactopyranose	644-76-8	162.14	$C_6H_{10}O_5$	
Glucose	50-99-7	180.16	$C_6H_{12}O_6$	
Xylose	58-86-6	150.13	$C_5H_{10}O_5$	
Mannose	3458-28-4	180.16	$C_6H_{12}O_6$	
Sucrose	57-50-1	342.30	$C_{12}H_{22}O_{11}$	
Maltose	6363-53-7	342.30	$C_{12}H_{22}O_{11}$	
Trehalose (Mycose)	6138-23-4	342.30	$C_{12}H_{22}O_{11}$	

Table 2-4 Additional molecular markers for wood smoke

Compound	CAS no.	MW, g/mol	Formula	Structure
Dehydroabietic Acid	514-10-3	302.45	$C_{20}H_{30}O_2$	
Vanillic Acid	121-34-6	168.15	$C_8H_8O_4$	
Syringic Acid	530-57-4	198.17	$C_9H_{10}O_5$	
Anisic Acid (4-Methoxybenzoic Acid)	100-09-4	152.15	$C_8H_8O_3$	
Catechol	120-80-9	110.11	$C_6H_6O_2$	

2.3.4. Case Studies

Medeiros et al. (2006) collected bulk aerosols over the Howland Experimental Forest, Maine, USA from May to October 2002; each sample was collected continuously for two weeks. The samples were extracted in dichloromethane:methanol (2:1 volume:volume), derivitized and analyzed using GCMS. In summer 2002 a large wildfire broke out in Canada and the smoke plumes were transported to the northeastern U.S. impacting the samples collected in this study. Glucose was the dominant sugar found in the Maine study site with concentrations ranging from 3.1 to 50 ng/m^3. Galactose, mannose, and fructose were other monosaccharides present in the summer, but on a much lower scale. Fructose was present in the spring, but decreased through the summer. Mycose, also known as trehalose, was the most abundant disaccharide generated as excreta by soil microbiota, indicating a soil input to the atmosphere. Levoglucosan increased about ten times during the samples affected by the smoke plume (Medeiros et al., 2006).

Jordan et al. (2006) used high-volume samplers to collect 24-hour PM_{10} samples in Launceston, Tasmania, Australia. Seventeen samples were collected from May 13, 2002 to August 2, 2002 and May 26, 2003 to September 9, 2003 (winter) and January 25 and 26, 2003 and January 16, 2004 (summer). The average levoglucosan concentration in the PM_{10} samples over both sets of winter samples was 5.2 μg/m^3 with a range of 1.41 μg/m^3 and 16.0 μg/m^3. In the summer the average was 0.26 μg/m^3 with a range of below the detection limit (BDL) to 0.47 μg/m^3. The high value was found during a bushfire. It is important to note that PM_{10} samples, as discussed in the previous two case studies, are not directly comparable to $PM_{2.5}$ samples as they can be heavily influenced by soil

particles. Levoglucosan is produced by combustion of cellulosic materials and partitions into the fine fraction rather than the coarse PM fraction.

Table 2-5 summarizes the U.S. case studies which quantified levoglucosan in fine PM samples. Nolte et al. (2001) measured fine PM samples at three sites in the San Joaquin Valley of California from December 5, 1995 to January 6, 1996. The sites were located at the Kern Wildlife Refuge (rural), Bakersfield (urban) and Fresno (urban). The samples were collected with a high-volume dichotomous sampler on quartz fiber filters. The samples were derivitized with BSTFA and analyzed on a GCMS. Levoglucosan was present even in urban sites exceeding concentrations of 2000 ng-m^{-3} which could make it one of the most abundant single organic compounds in particulate matter in the atmosphere. Other sugars also were identified; however the concentrations were much lower than levoglucosan. Lignin breakdown products were found mainly in the urban sites where residential fireplaces were common. The n-alkanols and sterols quantified were found to be higher in the ambient samples than in source tests for wood combustion. This finding indicated there were other possible sources for the n-alkanols and sterols, namely vegetative detritus and plant wax detritus.

Gorin et al. (2006) collected daily $PM_{2.5}$ samples at five sites in Fresno, CA from December 24, 2003 to January 15, 2004. High-volume collectors with a flow rate of 1.13 m^3/min ran for 20 hours a day collecting samples on quartz fiber filters. The samples were analyzed for levoglucosan, galactosan and mannosan with high-performance anion exchange chromatography coupled with pulsed amperometric detection. The average $PM_{2.5}$ concentration was 30 μg/m^3. Coarse samples also were collected to determine which fraction contained the majority of levoglucosan. The results showed 90% of the

total levoglucosan was present in the fine PM fraction. Other significant results related to the $PM_{2.5}$ samples from the Gorin et al. (2006) study in Fresno, CA in the California Central Valley found the levoglucosan concentration ranged from not detected (nd) to 1900 ng/m^3 with an average of 600 ng/m^3. Other studies in Fresno, CA, however, found wintertime levoglucosan concentrations as high as 7.59 μg/m^3 in 1995 (Gorin et al., 2006) and 4.05 μg/m^3 in 2000 (Gorin et al., 2006). The estimated contribution of wood combustion to $PM_{2.5}$ was approximately 18%; the estimated contribution of wood smoke to OC was approximately 41% for the 2003-2004 study (Gorin et al., 2006).

Brown et al. (2002) conducted a study at Big Bend National Park, Texas located along the Rio Grande River and borders the United States and Mexico. $PM_{2.5}$ samples were collected from July 1, 1999 to October 31, 1999 using a cyclone sampler with a sample volume of 160 m^3 onto 102 mm quartz fiber filters. The sugar anhydride concentrations (galactosan and mannosan) can be seen in Table 2-5. The authors used the source profile from Fine et al. (2001) to estimate that 1.5% of the total organic matter was from wood smoke. Levoglucosan was found in one sample; however retene and vanillin also were found and are present in wood smoke. The authors found the PM samples to be acidic, and postulated an environment conducive to levoglucosan destruction by acid-catalyzed hydrolysis after collection on the filter (Brown et al., 2002).

Zheng et al. (2007) collected daily $PM_{2.5}$ samples in Atlanta, GA from July 3, 2001 to August 4, 2001 (summer) and January 2 to 31, 2002 (winter) on quartz fiber filters which were extracted and analyzed by GCMS. The seasonal average of levoglucosan is shown in Table 2-5. The summer concentration varied from 14.22 to 67.3 ng/m^3 with an average of 45.6 ng/m^3. The winter concentration of levoglucosan

varied from 67 ng/m^3 to 909 ng/m^3 with an average of 433.4 ng/m^3. A chemical mass balance model was implemented to estimate source contributions. The authors found in summer, wood smoke accounted for less than 0.07 μg/m^3 of the measured fine particle OC mass. In the winter, however, the wood smoke contributed 2.14 ±1.03 μg/m^3 of the OC mass. The increase in wood smoke contributions between seasons was consistent with winter activities, such as fireplaces and prescribed burning (Zheng et al., 2007).

Engling et al. (2006) presented the results from a study on fine atmospheric particulate matter at two sites in Yosemite National Park, CA from July 14, 2002 to September 5, 2002. The samples were composited on a weekly basis; however some values were reported for individual days when it was especially hazy. Over the study period levoglucosan was found in samples from below detection to 50 ng/m^3. Dehydroabietic acid was found from 3 ng/m^3 to 17 ng/m^3; the high values occurred in the same week for both compounds (values extracted from Figure 3 in Engling et al., 2006). The individual days also were recorded during that time period where levoglucosan was found as high as 234 ng/m^3. The time period was characterized by a regional smoke plume from wildfires in Oregon and California. Biomass burning contributions to OC were determined using source profiles from other studies. The authors estimated the OC mass from wood smoke to be as high as 65% with a low value of 0.51% and an average over the study period of 20.6% (Engling et al., 2006).

He et al. (2006) collected fine PM samples in Beijing, China for three seasons: summer (July 25 to August 5, 2002), autumn (October 27 to November 3, 2002) and winter (January 3 to January 10, 2003). The $PM_{2.5}$ mass concentrations were 66 μg/m^3 in summer, 78 μg/m^3 in autumn and 77 μg/m^3 in winter. The organic carbon mass fractions

in the total fine $PM_{2.5}$ mass were 24% in summer, 50% in autumn and 51% in winter. The average levoglucosan concentrations for each season were 34 ng/m^3 in summer, 117 ng/m^3 in autumn and 78 ng/m^3 in winter. The maximum value present in the fall was consistent with the practice of agricultural burning (straw, plants, corn stover) (He et al., 2006).

Fine particulate matter samples were collected in four cities in India for four seasons: Delhi (spring, summer, autumn, winter), Kolkata (spring, summer, autumn, winter), Mumbai (spring, autumn, winter), and Chandigarh (summer) (Chowdhury et al., 2007). The levoglucosan concentrations in ng/m^3 for Delhi were 1027 (spring), 210 (summer), 1774 (autumn), and 5258 (winter). In Kolkata the levoglucosan concentrations in ng/m^3 were 336 (spring), 75 (summer), 474 (autumn), and 5492 (winter). In Mumbai the levoglucosan concentrations in ng/m^3 were 75 (spring), 392 (autumn), 908 (winter). In Chandigarh the average levoglucosan concentration was 140 ng/m^3. The last site was added in order to obtain measurements in an upwind, background site from the urban centers. The levoglucosan concentrations indicated biomass burning due to home heating in the winter and rice agricultural burning in the fall (Chowdhury et al., 2007).

Table 2-5 U.S. ambient levoglucosan concentrations[1]

Reference	Nolte et al. 2001			Gorin et al. 2006	Zheng et al. (2007)		Brown et al. (2002)	Engling et al. (2006)
Location (sampling period)	San Joaquin Valley, CA (12/5/1995-1/6/1996)	Bakersfield, CA (12/5/1995-1/6/1996)	Fresno, CA (12/5/1995-1/6/1996)	Fresno, CA (12/25/03-1/15/04)	Atlanta, GA (7/3/2001-8/4/2001)	Atlanta, GA (1/2/2002-1/31/2001)	Big Bend National Park, TX (7/12/1999-10/19/1999)	Yosemite National Park, CA (7/14/2002-9/5/ 2002)
Compound	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Levoglucosan	106	2390	2980	600	45.60	433.41	0.09	0 to 50
Galactosan	4.1	96	144				0.01	
Mannosan	7.0	171	322				0.02	
Xylose	0.7	9.1	17					
Mannose	4.5	9.3	13					
Glucose	5.4	10	15					
Sucrose	0.9	4.0	3.2					
Maltose	nd	3.2	4.0					
Vanillic Acid	0.3	7.4	11					
Syringic Acid	0.2	12	13					
Tetracosanol	1.6	11.9	18					
Hexacosanol	8.9	44	61					
Octacosanol	1.2	8.6	11					
Triacontanol	1.2	2.4	2.3					
Cholesterol	3.5	9.9	7.0					
Campesterol	nd	nd	0.8					
Stigmasterol	nd	2.0	nd					
β-sitosterol	0.5	23	20					

[1] empty cells indicate that no value was reported.

2.4. *Biogenic Sources*

Leaf surfaces of plants typically consist of a lipophilic surface layer (epicuticular waxes) that contains hydroxy fatty acids (Simoneit et al., 1981). Waxlike lipids protrude from this layer acting act as a protective barrier from dessication. Leaves also can act as deposition sites for other airborne organic material (natural and man-made), which can be resuspended into the air. Leaves emit organic compounds due to surface abraision (when the leaves rub against each other), from wind-induced mechanical shear or from aging (Rogge et al., 1993). Epicuticular waxes on plant surfaces consist of four common phytosterols: cholesterol, campesterol, β-sitosterol and stigmasterol. In urban atmospheres cholesterol can be emitted from cooking meat as well, and in higher quantities (Simoneit et al., 1981). Therefore, the phytosterols are used as molecular markers for biogenic emissions. Phytosterols maintain their structural specificity making the compounds good candidates for molecular markers of biogenic products in the air (Simoneit et al., 1981).

2.4.1. Emission Tests

Rogge et al. (1993) conducted source testing by collecting leaves from 62 plant species and compositing them (inorganic species and total masses are presented in Hildemann et al., 1991). The samples were agitated to release organic matter from the leaves and the fine aerosol was collected, extracted and analyzed. Samples consisted of freshly picked vegetation (live, green samples) and dead vegetation from the same species. Even number n-alkanol homologs were a major component of leaf waxes, specifically the C_{26} and C_{28} n-alkanols were the most abundant markers in the emission

source study. Hexacosanol was emitted at a rate of 8224 μg/g-green leaves and 2069 μg/g-dead leaves. Octacosanol was emitted at a rate of 15484 μg/g-green leaves and 7294μg/g-dead leaves. Triacontanol was emitted at a rate of 1060 μg/g-green leaves and 4325 μg/g-dead leaves. Small amounts of PAHs were found, however motor vehicle markers, hopanes and steranes, were not found (Rogge et al., 1993). No organic carbon or fine aerosol mass emission rates were reported from the study; therefore, the marker mass to OC and fine PM mass could not be calculated (Hildemann et al., 1991).

Simoneit and Mazurek (1982) conducted two source tests on biogenic inputs to the atmosphere. The sources had various plant materials in each composite to gain a representative sample; the plant material was extracted by repeated dipping in dichloromethane and analyzed with GC or GCMS. The markers are reported as the total for each class with the one of most interest being the alcohol fraction which reported the major sterols (cholesterol, β-sitosterol, campesterol, stigmasterol). The grass vegetation sample contained 370 μg/g-dry weight of the total alcohols measured where as the mixed Sierra vegetation sample contained 1680 μg/g-dry weight. Based on the information from the source tests two sets of compounds were chosen as molecular markers for biogenic contributions to fine PM. The first set was the phytosterols; Table 2-6 illustrates these compounds and several chemical characteristics. The second set of compounds was the n-alkanols as shown in Table 2-7.

Table 2-6 Phytosterols as molecular markers for biogenic sources

Compound	CAS no.	MW, g/mol	Formula	Structure
β-Sitosterol	83-46-5	414.7	$C_{29}H_{50}O$	
Campesterol	474-62-4	400.69	$C_{28}H_{48}O$	
Stigmasterol	83-48-7	412.7	$C_{29}H_{48}O$	

Table 2-7 n-Alkanols as molecular markers for biogenic sources

Compound	CAS no.	MW, g/mol	Formula
	Structure		
Tetracosanol	506-51-4	354.65	$C_{24}H_{50}O$
Hexacosanol	506-52-5	382.71	$C_{26}H_{54}O$
Octacosanol	557-61-9	410.76	$C_{28}H_{58}O$
Triacontanol	593-50-0	438.81	$C_{30}H_{62}O$

2.4.2. Case Studies

Simoneit and Mazurek (1982) studied multiple locations throughout California and Oregon to gather information on biogenic contributions to fine aerosols in rural areas. The markers were reported as the total ambient mass concentration for each compound class. The alcohol fraction reported was the major sterols (cholesterol, β-sitosterol, campesterol, stigmasterol). The combined fine and coarse fractions ("total" suspended PM) samples were extracted in dichloromethane and analyzed with GC or GCMS. The samples taken over the western USA indicated rural sites were dominated by compounds emitted from vegetation compared to urban sites. The ambient mass concentrations of the alcohols did not show a distribution pattern. For example high (2016 ng/m^3) and (1930 ng/m^3) concentrations were found in the urban and rural study areas depending on season and meteorological conditions (Simoneit and Mazurek, 1982). It is important to note the samples were extracted in dichloromethane, which is effective for nonpolar and slightly polar compounds but not the polar and water-soluble organic species. In this study, cholesterol was not screened as a marker within the rural and urban samples and limited information was presented on the distribution of the phytosterols. Therefore, the presence of cholesterol was not determined. This sterol is a molecular marker for meat charbroiling emissions and has been measured in fine PM collected in later field studies of urban airsheds (Engling et al., 2006; Rogge et al., 1993b).

Fine aerosol samples were collected weekly from July, 2002 to September, 2003 on the southwest coast of Terceira Island, Azores, Portugal in the northeastern Atlantic Ocean. The $PM_{2.5}$ mass fluctuated from 5 to 86 μg/m^3 with an average of 21.4 μg/m^3. The average OC concentration was 0.329 μg/m^3 and the average EC was 0.043 μg/m^3.

The series of n-alkanols measured from C_{12} to C_{30} showed a dominant even carbon number preference where C_{26} was typically the dominant n-alkanol. This homolog distribution indicated waxes from terrestrial higher plants because marine lipids contributed from marine algae, bacteria and phytoplankton souces generally have n-alkanol homolog distribution from C_{14} to C_{18}. The reported concentration was for total n-alkanols with a range of 0.75 to 18.61 ng/m^3 and an average of 3.47 ng/m^3. Cholesterol ranged from 0.002 to 0.209 ng/m^3. Cholesterol can be emitted from cooking operations, but on this island in the Eastern Atlantic Ocean, the dominant source was thought to originate from marine microbiota which biosynthesize cholesterol. β–sitosterol ranged from 0.010 to 1.139 ng/m^3. The vascular plant wax lipids found at Terceira Island were from a continental source and were dominant in the summer and in the autumn, then decreased in the winter months (Alves et al., 2007).

He et al. (2006) collected fine PM samples in Beijing, China as previously described. The average β-sitosterol concentration was 1.8 ng/m^3 in the summer, 11 ng/m^3 in the autumn and 7.1 ng/m^3 in the winter. The high in autumn was attributed to agricultural burning which peaked in fall.

Fine particulate matter samples were collected in four cities in India for four seasons as previously described. The only phytosterol measured was stigmasterol. The stigmasterol concentrations in ng/m^3 for Delhi were 77 in the spring, 29 in the summer, 164 in autumn and 296 in winter. In Kolkata the stigmasterol concentrations in ng/m^3 were 50 in the spring, 22 in the summer, 37 in the autumn and 300 in the winter. In Mumbai the stigmasterol concentrations in ng/m^3 were 10 in the spring, 143 in the autumn and 35 in the winter. In the summer Chandigarh had an average stigmasterol

concentration of 60 ng/m^3. Stigmasterol can be used to identify cow dung smoke. Low-income households use cow dung for heating and cooking purposes. It was possible some of the stigmasterol levels were contributed from residential heating and cooking activities using manure as fuel (Chowdhury et al., 2007).

Rushdi et al. (2006) collected soil samples from 7 locations in Kuwait City, Kuwait in February, 2004. The soils were sieved and particles less than 125 μm were evaluated for organic material. The higher molecular weight n-alkanols (C28, C30) were found more frequently and at higher concentrations than the lower molecular weight n-alkanols (C24, C26). Table 2-8 summarizes the locations and the concentrations of the compounds of interest. The even numbered *n*-alkanols were dominant, indicating vascular plant wax inputs. The dominant phytosterol was sitosterol. Cholesterol was found in the urban locations of the study and, therefore, indicates emissions from cooking activities (Rushdi et al., 2006). This emission source is discussed later in this chapter. Although the study by Rushdi et al. (2006) did not provide emission data because the the ratios of the marker compounds in the soil to fine PM was not known, the article is a good indicator of how the biogenic markers from resuspended soils can influence air quality.

Table 2-8 Soil composition in ng compound/g-soil Rushdi et al. (2006) (ND=Not detected)

Compound	Highway	Market place	Park	Bus Station	Side walk	Sea Front	Sand Dune
Tetracosanol	ND	ND	54	ND	17	ND	ND
Hexacosanol	ND	ND	172	347	62	ND	ND
Octacosanol	ND	1340	597	407	220	201	71
Triacontanol	ND	1189	992	670	294	260	100
Cholesterol	0	ND	146	289	ND	ND	ND
Campesterol	0	ND	152	ND	ND	ND	ND
Stigmasterol	0	ND	165	286	ND	ND	ND
Sitosterol	504	ND	340	347	121	ND	ND

Bulk aerosols were collected in a conifer forest in central continental Greece from July 20, 1997 to August 12, 1997 resulting in 19 samples. The samples were analyzed for a homologous series of n-alkanols ranging from C_{10} to C_{35}. The samples showed even carbon number predominance, with the most common being C_{26}, C_{28} and C_{30} (Pio et al., 2001). This pattern indicates biosynthesis from natural sources (i.e. specific enzymatic pathways in vegetation which produce the epicuticular plant waxes) (Mazurek and Simoneit, 1984). The total n-alkanols ranged from 31 to 179 ng/m^3, with the highest individual species reaching 24 ng/m^3. The authors did not report which homolog was the most abundant compound. The samples contained the phytosterols, sitosterol and cholesterol, however the concentrations were not listed (Pio et al., 2001).

2.5. *Meat Charbroiling*

Cholesterol is the molecular marker for meat charbroiling because it appears to be distinct to meat charbroiling. This marker does not have other significant sources and it is quantifiable in ambient samples (Rogge et al., 1991; Raloff, 1991; Schauer et al.,

1999). Cholesterol can be emitted from some plants, however at lower amounts than meat charbroiling (Simoneit and Mazurek, 1982; Simoneit et al., 1981). Cholesterol is found in the fats or oils of animals (Rogge et al., 1991). In order to reduce the addition of fine aerosols from meat charbroiling commercial restaurants could filter and capture the particles from these sources (Raloff, 1991).

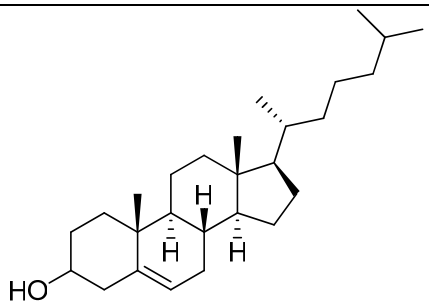
2.5.1. Emission Tests

Rogge et al. (1991) conducted emission tests on hamburger meat to collect fine particulate samples from charbroiling the meat over natural gas and frying the meat. The meat was cooked for about ten minutes for each meat patty. The study tested two kinds of meat: regular with about 21% fat and extralean with about 10% fat. Cholesterol was emitted from frying meat a rate of 7.1 mg per kg of meat fried. Charbroiling extralean meat emitted 26.5 mg of cholesterol per kg of meat charbroiled. Charbroiling regular meat emitted 72.7 mg of cholesterol per kg of meat charbroiled. Cholesterol was one of the more source specific compounds found in the study; the other targeted compounds could come from a variety of sources. Cholesterol, therefore, is the compound of choice to use as a molecular marker because it is unique to meat cooking. Hildemann et al. (1991) collected the filters used in the Rogge et al. (1991) study and reported the fine aerosol mass captured as 40 g/kg charbroiled regular hamburger, 7 g/kg charbroiled extralean meat and 1 g/kg fried meat. The study also reported that organic carbon weight percent of the fine aerosol mass was between 68% and 73% for an average of 70.5 % OC of the fine aerosol mass (Hildemann et al., 1991).

Schauer et al. (1999) conducted source tests on frozen and thawed hamburgers consisting of 114 grams of meat per patty and 20% fat. The hamburgers were charbroiled

for about 8.5 minutes for frozen patties and about 5 minutes for thawed patties. The organic analysis of the fine particulate matter emitted from the meat charbroiling resulted in 3,970 μg of cholesterol per kg of meat cooked. In addition, nonanal was emitted at 32,700 μg per kg of meat cooked, 163,000 μg of hexadecanoic acid (palmitic acid) per kg of meat cooked and 214,000 μg of 9-octadecenoic acid (oleic acid) per kg of meat cooked as the most dominant organics emitted. The fine aerosol mass emitted was 18.8 grams per kg of meat and the organic carbon weight percent was 33.8% (Schauer et al., 1999). The Rogge et al. (1991) study reported fine aerosol mass values about twice as high as those reported by Schauer et al. (1999). A reason for this could be the cooking time because Rogge et al. (1991) cooked the meat for about ten minutes where as Schauer et al. (1999) cooked the meat for only five minutes (Schauer et al. 1999). Table 2-9 illustrates cholesterol and several common properties.

Table 2-9 Cholesterol chemical characteristics

Compound	CAS no.	MW, g/mol	Formula	Structure
Cholesterol	57-88-5	386.65	$C_{27}H_{46}O$	

2.5.2. Case Studies

Fine particulate matter samples were collected as 24-hour daily samples for three weeks in July, 2001. The samples were collected at two sites in the Los Angeles, CA area: Azusa and downtown Los Angeles. The samples were composited by the day of the week, thus the total number of samples was 7. Cholesterol was found every day of the

week. The concentrations were less than 1 ng/m^3 in Azusa and in Los Angeles. The trend showed an increase in cholesterol in the later part of the week, Thursday and Friday, at both sites. Levoglucosan also increased in the later part of the week, Thursday and Friday, at both sites. Levoglucosan in Azusa ranged from 1 to 9 ng/m^3 and in Los Angeles ranged from less than 1 to 5 ng/m^3. This correlation was related to outdoor meat cooking (charcoal grills) in the summer (Lough et al., 2006).

Zheng et al. (2007) collected daily $PM_{2.5}$ samples in Atlanta, GA from July 3, 2001 to August 4, 2001 (summer) and January 2 to 31, 2002 (winter) on quartz fiber filters which were extracted and analyzed on a GCMS. The seasonal average of cholesterol was 0.71 ng/m^3 in the summer with a range of 0.20 ng/m^3 to 1.53 ng/m^3. The seasonal average in the winter was 0.89 ng/m^3 with a range of 0.22 ng/m^3 to 2.26 ng/m^3 (Zheng et al., 2007).

Engling et al. (2006) presented the results from a study on fine atmospheric particulate matter at two sites in Yosemite National Park, CA from July 14, 2002 to September 5, 2002. The samples were composited on a weekly basis. The cholesterol at Turtleback Dome ranged from 0.055 ng/m^3 to 0.450 ng/m^3 and was estimated to account for about 3% of the OC mass (Engling et al., 2006).

He et al. (2006) collected fine PM samples in Beijing, China as previously described. The average cholesterol concentration was 0.17 ng/m^3 in the summer, 2.9 ng/m^3 in the autumn and 1.8 ng/m^3 in the winter.

Rogge et al. (1993b) collected fine PM samples at five urban locations in southern California in 1982 and analyzed the samples for cholesterol. West Los Angeles had a yearly average of 2.7 ng/m^3, Pasadena had a yearly average of 1.9 ng/m^3 and San Nicolas

Island was detected but less than 0.10 ng/m^3. Downtown Los Angeles and Rubidoux had yearly averages of cholesterol below the detection limit. A subset of the samples was reported by Rogge et al. (1991). Rogge et al. (1991) analyzed the monthly fine PM samples taken in Los Angles, CA and reported for one month, October of 1982. The results showed that the fine aerosol cholesterol level was 14.6 ng/m^3 in the urban area of West Los Angeles, CA. This concentration was the highest monthly concentration found in the study (Rogge et al., 1993b).

2.6. *Biogenic Oxidation Products*

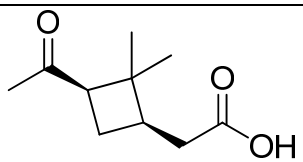
Monoterpenes, in particular α-pinene, are emitted by trees and shown to undergo photooxidation with ozone (O_3) and the OH radical to form cis-pinonic acid (Cheng et al., 2004). This section describes the reaction experiment which determined cis-pinonic acid as a reaction product followed by ambient concentrations quantified in field studies. Oxidation reaction products are commonly referred to as secondary organic aerosols (SOAs).

2.6.1. Reaction Experiment

Smog chamber experiments measured oxygenated species in particulate matter from the oxidation of monoterpenes, α-pinene and β-pinene run separately with O_3 (Yu et al., 1999). The experiments operated at temperatures between 32 °C and 37 °C. Seed particles were added as nucleation sites and 2-butanol was added as an OH radical scavenger. The initial monoterpene concentration ranged from 50 to 110 ppb by volume (a concentration of about 50,000 ng/m^3). Pinonic acid, the reaction by-product species, was listed as percent yield, where percent yield was defined as change in organic aerosol

mass produced divided by amount of hydrocarbon reacted. Pinonic acid had a molar percent yield of 0.15 % from β-pinene. The molar percent yield from α-pinene was higher than for β-pinene with a value of 1.5%. In conclusion, pinonic acid can be a molecular marker for the SOAs formed by reactions of monoterpenes from biogenic sources with ozone (Yu et al., 1999). Table 2-10 illustrates common chemical properties of cis-pinonic acid.

Table 2-10 Chemical properties of cis-pinonic acid

Compound	CAS no.	MW, g/mol	Formula	Structure
cis-Pinonic Acid	61826-55-9	184.23	$C_{10}H_{16}O_3$	

2.6.2. Case Studies

Cheng et al. (2004) collected 24-hour fine PM samples at five sites in the Lower Fraser Valley in Canada near the Pacific Coast. The samples from the forest and traffic tunnel were collected twice per day from August 6 to 10, 2001 and from August 9 to 14, 2001, respectively. The urban park, rural area and forest/urban mixed site were sampled twice per day from August 15 to 20, 2001 and August 24 to 30, 2001. The samples were separated into day and night periods. Cis-pinonic acid at the forest location peaked during the day; the average concentration was 11.1 ng/m^3 with a range of 1.6 to 44.2 ng/m^3. The tunnel varied from below the detection limit (BDL) to 6.5 ng/m^3, with an average of 1.1 ng/m^3 of cis-pinonic acid. At the urban park the concentration of cis-pinonic acid ranged from 0.3 to 20.4 ng/m^3 with an average of 5.9 ng/m^3. The forest-urban mixed site ranged from 1.3 to 42.1 ng/m^3 with an average of 9.7 ng/m^3. The rural site ranged from 0.6 to 46.5 ng/m^3 with an average cis-pinonic acid concentration of 7.3

ng/m^3. All of the sites, except for the traffic tunnel, showed an increase in cis-pinonic acid during the day and a decrease through the night, indicating photochemical production of the marker during daylight and loss during nighttime. The traffic tunnel had a fairly consistent concentration of cis-pinonic acid. The authors concluded that monoterpene oxidation was an important source of carbonaceous PM produced via photochemical oxidation of reactive volatile organic compounds emitted from vegetation in the Lower Fraser Valley (Cheng et al., 2004).

Sheesley et al. (2004) collected fine PM samples from November, 2001 to December, 2002 at the Seney National Wildlife Refuge in remote northern Michigan. The pinonic acid marker was present in spring, peaked in summer and decreased through fall. In the month of July, the pinonic acid peaked to around 14 ng/m^3 (value interpolated from Figure 2 in Sheesley et al., 2004). In September the second highest concentration was found, just over 4 ng/m^3. The study demonstrated a significant component of the airborne particulate matter was biogenic SOAs (Sheesley et al., 2004).

Bulk aerosols were collected in a conifer forest in central continental Greece from July 20, 1997 to August 12, 1997 resulting in 19 samples as previously described. Pinonic acid was found with a maximum concentration around 1 ng/m^3 (Pio et al., 2001).

2.7. *Low Molecular Weight Highly Oxidized Acids*

The low molecular weight, highly oxidized acids are formed by photooxidation reactions of primary emissions of volatile organic compounds (VOCs) in the atmosphere. Species, such as pyruvic acid and glyoxylic acid, are products of oxidation of aromatic compounds (Ortiz et al., 2006). Degradation of organic compounds with nitrogen oxide (NO_x) also is possible (Kleindienst et al., 1999).

2.7.1. Reaction Experiments

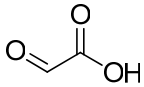
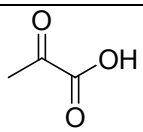
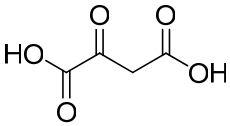
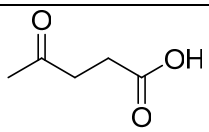
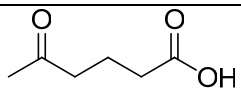
Smog chamber experiments studied the reaction of anthropogenic hydrocarbons (toluene, p-xylene and 1,3,5-trimethylbenzene) with NO_x. The hydrocarbon concentrations were about 50 ppb as carbon and the NO_x was less than 1 ppb. Seed particles, ammonium sulfate, were added to create particulate matter to simulate ambient conditions. The secondary organic carbon yield is defined as the aerosol organic carbon concentration divided by the change in hydrocarbon concentrations. For toluene this value was 0.87%, for p-xylene this value was 0.60% and for 1,3,5-trimethylbenzene this value was 0.22%. The individual SOAs were not determined, however the study indicated aromatic hydrocarbons may react with NO_x (Kleindienst et al., 1999).

Smog chamber experiments were studied to characterize oxygenated products of toluene and NO_x in the particulate phase. The initial conditions were 9.5 ppm toluene as carbon, 150 ppb NO_x and 150 ppb NO. The experimental conditions represented a toluene level over two orders of magnitude higher than those present in U.S. urban atmospheres. Glycolic acid and pyruvic acid were both found, however neither was quantified (Kleindienst et al., 2004).

Kawamura et al. (1996) suggested a pathway to the photo-oxidation of organic compounds in the atmosphere. Even in remote regions anthropogenic, polluted air can be transported from densely populated, urban areas, which provides the organic material that is oxidized. Another likely source of organic precursors is surface lipids released from sea spray and bursting bubbles. The marine surface lipid layer is produced from living microbiota and decayed organic surfactant material from marine organisms. Atmospheric photooxidation of marine lipids could eventually generate pyruvic acid and

glyoxylic acid and finally degrade to oxalic acid. The biogenic inputs from phytoplankton could degrade to 3-oxopropanoic acid and 4-oxobutanoic acid which then degrade to oxalic acid (Kawamura et al., 1996). Table 2-11 lists the low molecular weight highly oxidized acids chosen for evaluation in this study based on a literature review (Hawley and Mazurek, 2008).

Table 2-11 Low molecular weight highly oxidized acids (adapted from Hawley and Mazurek, 2008)

Oxo-acid	CAS no.	MW, g/mol	Formula	Structure	pKa
glyoxylic acid (2-oxo-acetic acid, α-ketoacetic acid; glyoxalic acid)	298-12-4	74	$C_2H_2O_3$		2.61 ± 0.54
pyruvic acid (2-oxo-propanoic acid, α-ketopropionic acid)	127-17-3	88.06	$C_3H_4O_3$		2.65 ± 0.54
oxalacetic acid (2-oxo-butanedioic acid, 2-ketosuccinic acid)	328-42-7	132.07	$C_4H_4O_5$		1.25 ± 0.32
levulinic acid (4-oxo-pentanoic acid, 4-ketovaleric acid)	123-76-2	116	$C_5H_8O_3$		4.78 ± 0.17
4-acetylbutyric acid (5-oxo-hexanoic acid, 5-ketohexanoic acid)	3128-06-1	130.14	$C_6H_{10}O_3$		4.63 ± 0.10

2.7.2. Case Studies

Samples were collected in Alert, Canada (Arctic region) weekly from July, 1987 to June, 1988 (Kawamura et al., 1996). Glyoxylic acid was the most abundant oxocarboxylic acid in the winter and into spring. 4-oxobutanoic acid was the highest of

all oxoacids in the summer. The mean concentration ± the standard deviation of glyoxylic acid was 1.7 ± 2.4 ng/m^3, 3-oxopropanoic acid was 0.07 ± 0.05 ng/m^3, 4-oxobutanoic acid was 0.35 ± 0.24 ng/m^3, 5-oxopentanoic acid was 0.02 ± 0.02 ng/m^3, and pyruvic acid was 0.13 ± 0.13 ng/m^3. Glyoxylic acid showed a gradual increase in late winter with a peak in March and then it decreased through the summer and fall. The highest concentration in March was over 50 times higher than the background concentrations in the summer. The authors suggested the glyoxylic acid was produced in the weak solar radiation during the transport of polluted air from the south to the north (Kawamura et al., 1996).

Samples were collected in Saitama City, Japan about 30 km northwest of, and downwind of, Tokyo for 5 days between August 2, 2003 and August 11, 2003 for 4 periods of 5.5 hours each day (Ortiz et al., 2006). The average concentration of fine particulate phase pyruvic acid was 156 ng/m^3 and the gaseous phase average was 6 ng/m^3. The maximum fine particulate phase concentration was around 280 ng/m^3 and the minimum about 50 ng/m^3. Average fine particulate phase glyoxylic acid concentration was 58 ng/m^3 and the gaseous phase average was 29 ng/m^3. The maximum fine particulate phase concentration was about 140 ng/m^3 and the minimum about 10 ng/m^3 (these values interpolated from Figure 5 in Ortiz et al., 2006). In general the diurnal variation of the two compounds had the maximum concentrations present in the morning, a drop in the afternoon and the minimum concentrations present at night. The authors concluded because the molecular structures of pyruvic acid and gloxylic acid were similar, the observed diurnal concentrations also were similar as expected since the UV radiation intensity and production and scavenging mechanisms were likely the same. The

two oxoacids partitioned into the particulate phase over the gaseous phase (Ortiz et al., 2006).

Wang et al. (2006) collected marine aerosol samples (size fraction not specified) over the western Pacific and the southern ocean from November 22, 1994 to February 11, 1995. In the southern ocean glyoxylic acid ranged from 0.08 to 0.36 ng/m^3; 3-oxopropanoic acid ranged from BDL to 0.01 ng/m^3; 4-oxobutanoic acid ranged from BDL to 0.03 ng/m^3; and pyruvic acid ranged from 0.01 to 0.06 ng/m^3. In the western Pacific Ocean the concentration of glyoxylic acid ranged from 0.02 to 3.9 ng/m^3; 3-oxopropanoic acid ranged from BDL to 0.24 ng/m^3; 4-oxobutanoic acid ranged from BDL to 0.31 ng/m^3; and pyruvic acid ranged from BDL to 0.74 ng/m^3. Glyoxylic acid was the predominant ketoacid found in the samples. In general, the amount of ketoacids over the southern ocean was 5 times less than found in the western Pacific Ocean. The highest concentrations of ketoacids were found in samples collected closest to continents. The results indicated transport of urban plumes from continental source regions could impact the atmospheric chemistry in marine atmospheres (Wang et al., 2006).

Edney et al. (2003) collected samples in Research Triangle Park, NC, USA in summer 2000. The location was semi-rural with biogenic and anthropogenic emission sources. The study determined qualitatively the presence of glyoxylic acid and pyruvic acid in the fine aerosol samples. Quantitative work was not conducted in the study. The solvents used to extract the organic compounds were methylene chloride and acetonitrile (Edney et al., 2003).

Sampere and Kawamura (1996) collected 14 rainwater samples in the western Pacific Ocean between September 19, 1992 and October 25, 1992. Pyruvic acid and

glyoxylic acid were the most abundant ketoacids in the rainwater with average concentrations of 11.9 and 12.2 μg/L, respectively. 3-oxopropanoic acid, 4-oxobutanoic acid, 5-oxopentanoic acid, and 6-oxohexanoic acid ranged in average concentrations from 0.43 to 3.08 μg/L. These ketoacids may be intermediate products in the oxidation of primary organics to dicarboxylic acids, in particular oxidation to oxalic acid. Pyruvic acid and glyoxylic acid were found in eastern Pacific Ocean water at a depth of 20 m at concentrations of 20 and 5 μg/L, respectively. The two acids are common intermediates in biochemical oxidation-reduction pathways, common organic matter synthesis and degration in plants and animals (marine and terrestrial). Therefore, pyruvic and glyoxylic acid may be introduced directly into the atmosphere by sea spray and bubble busting (Sampere and Kawamura, 1996). Although this study focused on rainwater samples as opposed to aerosols, it demonstrated the presence of organic acids in the atmosphere providing evidence these highly polar organic acids partition to cloud water or rainwater.

3. Methodology

The methodology chapter is separated into several sections. The first section describes the materials used to conduct the experiments. The experimental work compared two forms of chromatography and which chromatography was the optimal choice to measure polar organic compounds in atmospheric fine PM. The final section describes the ambient samples, the collection and analysis procedures.

3.1. *Materials*

This section describes the materials used to complete experiments for this research. The first two sections are the analytical equipment needed to quantify molecular markers. The remaining section describes the miscellaneous equipment used for this research.

3.1.1. High Performance Liquid Chromatography (HPLC)

The HPLC was an Agilent series LC1200 with a UV-Vis diode array detector (part number G1315B). The instrument was equipped with a binary pump (part number G1312A), a micro-vacuum degasser (part number G137913) and a standard autosampler which can hold a maximum of 100 sample microvials (part number G1329A). The mobile phases consisted of HPLC grade water with 10% tetrahydrofuran in pump A and the organic phase was methanol with 10% tetrahydrofuran in pump B. The HPLC used a thermostated column compartment set to 40 °C (part number G1316A). The software version was the Agilent 1200 series LC Chemstation. The column was a Phenomenex (Torrance, CA) Onyx C8 monolithic column (part number CHO-7647) sized 100 X 4.6 mm. The column was equipped with an Onyx C-18 monolithic guard cartridge (part

number KJO-7651) sized 5 mm X 4.6 mm. At the time of this study a C8 monolithic guard cartridge was not available. The HPLC grade water was collected from a Millipore RiOs™ system that takes tap water and sends it through a pretreatment pack to remove particles and free chlorine followed by two reverse osmosis filters. The water was stored in a reservoir then sent to a Milli-Q™ Element A10 dispensing unit equipped with a Quantum™ EX cartridge (Bedford, MA). The methanol was Burdick and Jackson HPLC grade methanol with an assay of 99.9+% (Muskegon, MI). The tetrahydrofuran was HPLC grade with an assay of 99.0 % from Fisher Scientific (Fairlawn, NJ).

HPLC chromatographic separation is achieved typically with a packed particulate column. New column technology, referred to as monoliths, consists of one-piece porous solids. Monolithic columns allow for fast chromatographic separation using high flow rates at a relatively low back pressure (Jacoby, 2006). The organic polymer based monoliths are better for separating large particles, such as proteins, nucleic acids and synthetic polymers whereas silica based monoliths are better for separation of smaller molecules. The porous silica rods are prepared then functionalized with a bonded carbon chemistry (C8 or C18), which creates the reversed-phase chromatographic column used with HPLC (Svec and Huber, 2006; Jacoby, 2006).

3.1.2. Gas Chromatography-Mass Spectrometry (GCMS)

The GCMS was a Shimadzu QP-2010 instrument equipped with a flame ionization detector (FID) and a quadrupole mass spectrometer (MS) detector. The autosampler handled up to 100 microvials and used a 10 µL syringe for sample injection which delivered 1 µL of the standard or sample. The carrier gas was helium. The GC settings are shown in the Table 3-1. A column oven was programmed to achieve

compound separation within the organic extract mixture. The initial column oven temperature was 50.0 °C, the injection temperature was 280.0 °C and was run in splitless mode. The total flow was 14.0 mL/min, however the column flow was 1.0 mL/min. The MS ion source temperature was 225.0 °C with an interface temperature of 260.0 °C. The MS source was switched on after 7 minutes to allow for the flow of solvent and reagents to pass through the system without ionization. If the solvent went into the MS and was ionized it would saturate the filament, which would then shut down the MS unit. The scan speed was 1428 Daltons/sec and scanned from m/z values of 40.0 to 650.0. The column was a J&W Scientific DB-1701 with a length of 30 m, inner diameter of 0.25 mm, film thickness of 0.25 μm and temperature limits of -20 °C to 280 °C.

Table 3-1 GCMS settings

Rate	Temperature, °C	Hold Time, minutes
None	50.0	3.00
20.0	150.0	3.00
4.0	280.0	57.0

3.1.3. Miscellaneous Lab Equipment

The analytical scale for preparing quantitative standards was an Adventurer™ scale with a capacity of 210 grams ± 0.0001 gram. The glassware used was Class A glassware that had been annealed in an oven at 550 °C for 8 hours. The standards were prepared around 1,000 parts per million (ppm) typically in 25 mL volumetric flasks which were TC 20 °C ± 0.03 mL; the 10 mL volumetric flasks were TC 20 °C ± 0.02 mL and used when needed. All transfer pipettes and beakers also were annealed at 550 °C for 8 hours. The chemical scoopers were cleaned with laboratory soap, dried and rinsed in solvent several times immediately prior to use. Glass syringes of varying sizes were

cleaned by rinsing at least ten times prior to and after each use with one or two solvents, typically dichloromethane and acetone. A Scientific Industries Vortex-Genie 2 Model G-560 (Bohemia, NY) was used to mix stock solutions when shaking by hand did not work adequately. Glassware was cleaned, if necessary, by sonication in several solvents with a VWR Scientific Products Aquasonic Model 250T (West Chester, PA). A Pierce Reacti-Therm heating module capable of heating from 30 °C to 150 °C equipped with a Pierce Reacti-Vap™ evaporating unit was used for condensing samples under N_2 gas (part numbers 18870 and 18780, respectively). The heating module also was used to heat standards if needed. The high temperature oven used to bake glassware and filters at 550 °C for 8 hours was a Blue M industrial oven. Additionally, a lower temperature oven (50-150 °C), Fisher Scientific Isotemp Oven (Fairlawn, NJ) was used to dry glassware and to bake the samples to complete N,O-bis(Trimethylsilyl)trifluoro-acetamide (BSTFA) derivitization. Autosampler vials were manufactured by Waters Corporation® and consisted of 12 x 32 mm glass screw top vials with PTFE/silicone septa (part number 18600384C; Milford, MA).

3.2. *Methodology*

The methodology is separated into three sections. The first section discusses the HPLC. The second section describes the GCMS. The final section discusses the optimal method for quantifying polar organic compounds in ambient samples.

3.2.1. HPLC with DNPH Derivatives

Derivatization techniques can be used to transform a non-quantifiable compound into a compound that can be detected with current analytical methods and instruments.

The analysis of volatile carbonyls using 2,4-dinitrophenylhydrazine (DNPH) with a UV-Vis detector has been in existence for several decades; particularly for a set of 13 carbonyl compounds which has become a standard set by the EPA and California Air Resource Board (CARB). The standard mixture is referred to as the CARB standard in this report which can be purchased as a standard solution already derivatized (Supelco, Bellefonte, PA). These compounds are listed on the EPA list of Hazardous Air Pollutants (HAPs).

In order to test the use of a monolithic silica column for environmental analysis, the carbonyl standard was chosen because there is published chromatographic information for comparison purposes. Trials were conducted on the gradient of the organic phase and the flow rate to optimize the full separation of all 13 carbonyl standard compounds. In order to determine if the monolithic silica column performed as well as traditional packed columns, the purchased CARB standard was run to make full five to seven point calibration curves with 10 duplications of each level run on the HPLC. Seven different mass levels were run on the HPLC, however not all compounds were detected at the lower mass levels. Therefore, seven levels were run to ensure that all compounds had at least five levels for its calibration curve. The stock solution was 3 ng/μL so the different calibration levels were determined using different injection volumes as depicted in the following equation (Hawley and Mazurek, 2008b).

$$Stock\ 3\frac{ng}{\mu L} * injection\ volume, 1\mu L = 3\ ng$$

Equation 1

The oxoacids used as markers for secondary organic aerosols (for example pyruvic acid and glyoxalic acid) are not detectable with UV-Vis so a DNPH derivative was used to convert the C=O to a DNPH to detect them with the detector as illustrated in Figure 3-1. This was accomplished by spiking a Waters Sep-Pak® DNPH-Silica Cartridge (part number WAT037500, Milford, MA) with the compound and eluting it. The cartridges are traditionally used to capture gaseous carbonyl compounds, in particular the 13 compounds found in the CARB standard, in the air and convert them to stable derivatives. In this case, the cartridge was slowly spiked with a liquid standard. The hold up volume of the cartridge was 700 μL so less then that was added to the cartridge while the bottom cap was still on. The cartridges were eluted with 4 to 5 mL of acetonitrile and condensed with N_2 gas until the desired concentration or volume was obtained (Hawley and Mazurek, 2008b). To ensure that this derivatizing method operated properly 3 carbonyl compounds found in the CARB standard were chosen as the tests, one with an early retention time, one with a middle retention time and one with a late retention time. The underivatized compound was added to the cartridge using the aforementioned procedure then run on the HPLC to ensure that a derivative was formed. The derivative was formed so the experiments were continued.

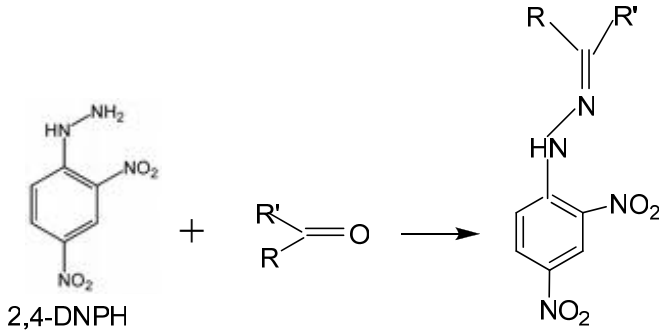


Figure 3-1 Sample reaction of 2,4-DNPH with an atmosphericcarbonyl compound

3.2.2. GCMS with BSTFA-TMS Derivatives

GCMS analysis of atmospheric polar organic compounds can be accomplished with derivatization (Medeiros et al., 2006). An approach for highly polar organic compounds uses N,O-bis(Trimethylsilyl)triflouroacetamide with Trimethylchlorosilane (BSTFA-TMS) derivatization which adds trimethyl silyl groups as ethers by replacing the –OH alcohol group. The derivatization was carried out by blowing down the samples to dryness under N_2 gas followed by adding the derivatizing agents from a glass syringe in the appropriate concentrations. The vials were kept under a stream of pure N_2 gas during chemical addition. The samples were capped under N_2 gas to prevent atmospheric water vapor from entering the vial and reversing the reaction. To complete the reaction the vials were baked, with the caps on and the vials standing up right, for at least 30 minutes at 60 °C. This technique is highly sensitive to water, including humidity in the air, and great care needs to be taken not to expose these samples to any water or the derivitizing agent will be quenched. Tests were conducted on levoglucosan to determine the best variations of derivitizing agent and solvent as shown in Table 3-2. BSTFA with 1% TMS was purchased as 100 µL ampules from Supelco (Bellefonte, PA), the anhydrous pyridine was purchased as 1 mL bottles from Fluka (Steinheim, Germany) and the anhydrous

hexane was purchased as 250 mL bottles with crown caps from Fluka (Steinheim, Germany) that were discarded after one use and about two months of use respectively (the hexane and pyridine were obtained through Sigma). The final concentrations of the standards were determined with the following equation. Figure 3-2 is a sample chemical reaction between BSTFA and levoglucosan.

$$C_{final},\ ppm\ (\frac{ng}{\mu L}) = C_{standard},\ ppm * V_{standard},\ \mu L * \frac{1}{V_{derivitizing\ agents},\ \mu L}$$

Equation 2

Table 3-2 BSTFA derivative optimization for subsequent sample analysis

Final Concentration, ppm	µL BSTFA added	µL Hexane	µL Pyridine	Peak Result in GCMS Plot
42 Levoglucosan	20	50	50	Slight shouldering
42 Levoglucosan	20	70	30	Slight shouldering
42 Levoglucosan	20	80	20	Some shouldering
42 Levoglucosan	20	100	20	Optimum

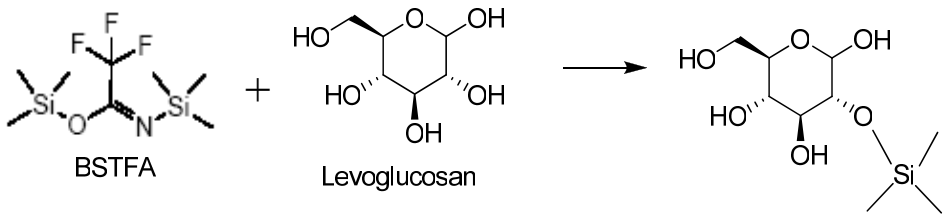


Figure 3-2 Sample reaction of BSTFA with levoglucosan

3.2.3. Standard Preparation

Standard solutions were made from chemical stocks that were diluted into high purity solvent. Several standard compound groups needed some testing to determine the appropriate solvent to use with the chemicals. As the sugars needed to be derivitized in the absence of water making those in water was inappropriate for this application. First tetrahydrofuran was tried by simply adding some sucrose crystals to volumetric flasks and filling with solvent; the crystals did not dissolve. Then the flasks were heated at

approximately 70 °C with no change in the results. However, when water was added the sucrose dissolved. As the goal was to use as small a volume of water as possible, trials were done to determine the lowest volume of water that could dissolve the sucrose into tetrahydrofuran. Five milligrams of sucrose were added to each of four five-milliliter volumetric flasks with a spatula. The water was added using an Eppenderf volumetric pipette with a range of 100 to 1,000 μL. The volumetric flask was then filled with tetrahydrofuran using a transfer pipette. Based on Table 3-3, the lowest amount of water needed was 250 μL of water per 5 mg of sucrose. This same procedure was used for all the sugars in this study. Initially, a spike of standard was run through the analytical equipment to determine the characteristic retention time and the mass spectra for the individual compounds, if applicable. Once these were determined, methods development continued to create a chromatographic method that could separate the desired compounds from one another, and separate the early eluting derivatization reagents.

Table 3-3 Sucrose Solvent Experiments

Water, μL	% Water	Result
100	2	A lot of undissolved sucrose
150	3	Some undissolved sucrose
250	5	No sucrose left
400	8	No sucrose left

The standard for the n-alkanols was made at about 1,000 ppm in dichloromethane, however it needed to be heated in the Reacti-Therm to 60 °C for 45 minutes to completely dissolve the solids. All other standard solutions were readily dissolved into the solvent as shown in Table 3-4. All standard solutions were stored in baked-out glass vials with crimp tops wrapped in Teflon tape. The vials were stored in side of plastic storage containers to make sure they were standing upright in the freezer set to 4 °C.

Table 3-4 Compound information

Chemical	Solvent	Concentration, ng/uL (ppm)	Manufacturer
Cholesterol	Methylene Chloride	1000	Aldrich
Levoglucosan	Ethanol	1000	Sigma
Sucrose	Tetrahydrofuran with 5% Water	1020	Fluka (Aldrich)
Mannose	Tetrahydrofuran with 5% Water	1000	Fluka (Aldrich)
1,6-Anhydro-β-D-Mannopyranose	Tetrahydrofuran with 5% Water	1000	Sigma
1,6-Anhydro-β-D-Galactopyranose	Tetrahydrofuran with 5% Water	1000	Sigma
Glucose	Tetrahydrofuran with 5% Water	1008	Fluka (Aldrich)
D(+)-Xylose	Tetrahydrofuran with 5% Water	1000	Biochemika (Aldrich)
D(+)-Maltose	Tetrahydrofuran with 5% Water	1016	Biochemika (Aldrich)
Hexacosanol	Methylene Chloride	1000	Chemika
Tetracosanol	Methylene Chloride	1060	Fluka (Aldrich)
Octacosanol	Methylene Chloride	1104	Sigma
Triacontanol	Methylene Chloride	1036	Biochemika (Aldrich)
Vanillic Acid	Tetrahydrofuran	1020	Fluka (Aldrich)
Dehydroabietic Acid	Tetrahydrofuran	968	Spectrum
D(+) Trehalose (Mycose)	Tetrahydrofuran with 5% Water	1008	Biochemika (Aldrich)
cis-Pinonic Acid	Tetrahydrofuran	1015	Aldrich
4-Methoxybenzoic Acid (Anisic Acid)	Tetrahydrofuran	1000	Aldrich
Syringic Acid	Tetrahydrofuran	1044	Fluka (Aldrich)
Catechol	Tetrahydrofuran	1000	Fluka (Aldrich)
β-Sitosterol	Methylene Chloride	870	Sigma
Stigmasterol	Methylene Chloride	990	Sigma-Aldrich
Campesterol	Methylene Chloride	702	Sigma
Glyoxylic Acid	Acetonitrile	1003	Aldrich
Pyruvic Acid	Acetonitrile	1000	Aldrich
Oxalacetic Acid	Acetonitrile	1000	Aldrich
4-Acetylbutyric Acid	Acetonitrile	1000	Aldrich
Levulinic Acid	Acetonitrile	1000	Aldrich

3.3. *Method Development*

3.3.1. HPLC and Monolithic Column

The monolithic silica column performed well providing good separation and consistent peak areas and retention times. The set of chemicals used to test the monolithic column was a standard set of carbonyl compounds used for the analysis of gaseous carbonyl compounds (Doughty et al., 1995; EPA, 1996; California Air Resource Board, 2006). These compounds were chosen because there is published data on HPLC analysis methods to which this method was compared. The first step to creating a baseline separation method was to evaluate the responses due to organic gradient changes with the mobile phase. To accomplish this task the flow rate was held constant at 0.8 mL/min. The second step was to evaluate the effect of flow rate on carbonyl compound separation; the flow rates were varied from 0.8 to 1.5 mL per minute. Finally, changes in organic concentration and flow rate gradients were evaluated. Table 3-5 shows the four trials associated with organic gradient changes and the resulting carbonyl elution. The gradient from Trial 2, 4.6% per minute, produced the best results from these trials indicating that a slower gradient resulted in better peak resolution. The percent of organic phase appeared to influence carbonyl separation on a monolithic column.

Table 3-5 Organic phase influence on carbonyl separation

Trial	Initial Conditions	Gradient, % B/min	End Conditions	Run Time, min	Result
1	50% B for 6 minutes	5.0	100 % B	15	11 peaks eluted
2	40% B for 2 min	4.6	100 % B	15	12 peaks, better shape
3	30% B for 2 min	5.4	100 % B	15	12 peaks, shape worse
4	30% B for 0 min	4.7	100 % B	15	Peaks were not well defined

The next step was to evaluate the effect of flow rate on the separation of carbonyls. In order to do this the gradient, 4.6 % B per minute, and conditions from trial 2 were used but the flow rate was changed.

The flow rate was set to 1.5 mL/min. All 13 standard peaks were found in the chromatogram, however the peaks were broader and the first peak eluted at about 2 minutes. The solvent inflection also was about 2 minutes so a retention time later than that was desired. The flow rate was slowed to 1.1 mL/min which resulted in 13 peaks and better resolution of the peaks. The retention time of the first compound also was late enough not to be influenced by solvent changes. These results indicated the flow rate had a large effect on the resolution of the chromatogram. If it was too slow the compounds did not elute and if it was too fast, resolution was lost.

Now, both the flow-rate and the gradient were changed to determine the optimal conditions for carbonyl analysis. Table 3-6 describes the eight trials conducted to determine the optimal HPLC with a monolithic column method. The table is divided into trial numbers. The first row of each trial is the first set of conditions and the second line is the conditions following the first line. The run time of the first row is given and the run time on the second line is the total run time of the trial method. The results indicated

that changing the flow rate during the analysis run did not aid in carbonyl resolution. The eighth trial resulted in full elution of the peaks, without broad peaks or shouldering. This method was the final method that was used to create calibration curves of the carbonyl standard and to compare against other methods to test the monolithic column for environmental analysis (Hawley and Mazurek, 2008b).

Table 3-6 Effect of organic and flow rate changes on carbonyl separation

Trial	Initial Conditions	Gradient, % B/min	Flow Rate, mL/min	End Conditions	Run time, min	Result
1	40	6.0	0.8	70	5.0	12 peaks resolved
	70	4.0	1.1	100	12.5	
2	40	5.0	0.8	70	6.0	12 peaks resolved
	70	4.0	1.1	100	13.5	
3	40	4.6	0.8	70	6.5	12 peaks resolved
	70	4.6	1.1	100	13.0	
4	40	4.6	0.8	70	6.5	12 peaks resolved
	70	3.6	1.1	100	14.8	
5	40	3.6	0.8	70	8.3	13 peaks resolved
	70	3.6	1.1	100	16.6	
6	40	2.8	0.8	70	10.7	13 peaks resolved
	70	2.8	1.1	100	21.4	
7	40	2.8	1.4	100	21.4	13 peaks resolved
8	40	3.6	1.4	100	16.7	Full elution, good peak shape

Appendix A provides the raw data and calibration curves created from these experiments. Method precision for the C8 monolithic column with HPLC protocol was evaluated by creating 5 to 7 point calibration curves for each compound using the carbonyl standard mixture. The linear correlation coefficient (R^2) values ranged from 0.999 to 0.980 for the calibration curves. These values indicate small measurement variance between the replicate injections for the peak area (y variable) versus the injected mass of each standard compound (x variable) (Hawley and Mazurek, 2008b).

The percent relative standard deviations (RSD) were calculated for the peak area and retention time for each level for each compound. The RSDs for each level were averaged for each compound as shown in Table 3-7. The data points ranged between 50 and 70 per compound and are listed as N in Table 3-7. The peak areas had RSDs between 0.62 and 3.07. The retention times had percent RSDs between 0.08 and 0.36. The consistent peak area and retention time data indicated method reproducibility (Hawley and Mazurek, 2008b). Appendix A presents the individual RSD values for the peak areas and retention times at each level corresponding to each compound.

Table 3-7 Carbonyl statistical data (adapted from Hawley and Mazurek, 2008b)

Carbonyl	N	R^2 value	% RSD Peak area	% RSD Retention time
Formaldehyde-DNPH	70	0.999	0.99	0.36
Acetaldehyde-DNPH	70	0.999	1.01	0.32
Acrolein-DNPH	70	0.999	1.19	0.23
Acetone-DNPH	60	0.999	0.72	0.24
Propionaldehyde-DNPH	60	0.999	1.00	0.22
Crotonaldehyde-DNPH	60	0.999	0.89	0.18
Methacrolein-DNPH	60	0.999	1.27	0.17
2-Butanone-DNPH	60	0.999	0.62	0.15
Butyraldehyde-DNPH	60	0.999	0.90	0.15
Benzaldehyde-DNPH	50	0.994	1.76	0.12
Valeraldehyde-DNPH	50	0.981	1.76	0.11
m-Tolualdehyde-DNPH	50	0.993	3.07	0.10
Hexaldehyde-DNPH	50	0.988	2.71	0.08

A comparison was made to other published methods for the analysis to ensure the new method based on the monolithic column separated the compounds as well as the other methods. First, the analysis time was shorter than with traditional packed columns. Sigma-Aldrich developed a method for the standard carbonyls with the mobile phase containing tetrahydrofuran as well. The mass injected onto the packed column was 30 ng, which is considerably higher than used by this study. The column was a C-18 with

the dimensions of 15 cm by 46 mm and 5 μm packing. This method took over 20 minutes to elute out the same chemicals separated in under ten minutes using the method developed in this study (Doughty et al., 1995).

The EPA has a standard method for the analysis of carbonyl containing compounds which is Method 8315a procedure 2 for ambient samples collected on an adsorbent cartridge (where hexanal is the same as hexanaldehyde). The sample injection volume was 25 μL, the flow rate was 1.0 mL/min and two C18 columns were used in series each having the dimensions 4.6 mm by 250 mm ID. The initial concentrations were approximately 1 or 0.5 ng/μL resulting in injected masses between 25 and 12.5 ng. The mobile phases were acetonitrile:water in the following proportions 60:40 for 0 minutes; 60:40 to 75:25 over 30 minutes; 75:25 to 100% acetonitrile in 20 minutes; hold 100% acetonitrile for 5 minutes; 100% to 60:40 over 1 minute; and finally hold 60:40 for 15 minutes. This method resulted in a much longer run time, with the hexanaldehyde eluted around 34 minutes (EPA, 1996).

California Air Resources Board Standard Operating Procedure (SOP) MLD 104 is another published government method used to analyze airborne carbonyl compounds. This method consisted of acetonitrile as mobile phase A and water with 10% methanol as mobile phase B. Similar to the EPA method, the California Air Resources Board method used two packed columns in series. The packed columns were C18 with dimensions 4.6 X 250 mm and 5 μm packing with a C18 5 μm guard cartridge. The flow rate was 1.2 mL/min. The initial conditions were 50% A with a gradient of 1% A per minute until 60% of the mobile phase was A. The gradient was then slowed to 0.5 % A per minute until 65% of the mobile phase A then the gradient was increased to 3.5 % A per minute

until the mobile phase was 100% A. The method run time was 32 minutes (California Air Resource Board, 2006).

As shown in the preceding discussions the monolithic column not only demonstrated statistical precision, it also was faster than the three existing packed column methods. A faster method reduces analysis time which in turn costs less in solvents and produces less hazardous waste from the solvents (Hawley and Mazurek, 2008b). This column evaluation and optimization study demonstrates new monolithic silica column technology is effective for the separation of polar organic compounds present in environmental samples and, therefore, was used in this study.

3.3.2. Aromatic and Oxoacids with DNPH Derivatives on HPLC with Monolithic Column

HPLC, unfortunately, did not work as well for the atmospheric polar organic marker compounds of interest. Aromatic compounds, which are visible under an UV-Vis lamp, created clear peaks in the chromatograph when individually run through the instrument. Once all four aromatic compounds (vanillic acid, syringic acid, anisic acid and catechol) were run at the same time, however, peak coelution became a problem. As a mixture, the compounds partitioned similarly between the monolithic silica column and the mobile phase solvents thus eluting at the same time. However, when ran individually each acid had a different retention time. The compounds could not be differentiated further with the LC because there was no MS configured in the HPLC system. Changing the gradient rate and organic percent composition did not aid in the full separation of these acids.

The secondary organic aerosol markers, the oxoacids, did not form chromophors, and were not detected by the UV/Vis. DNPH derivatives were attempted to convert the C=O in the oxoacids to form a compound that could be visible with the existing detector. The DNPH portion contributes the chromophore to the carbonyl-DNPH by-product. The DNPH derivatives were not successful for the oxoacids since the compounds were weak chromophores and, therefore, difficult to detect. Additionally, the same coelution problem appeared again. The compounds altered the relative retention time based on what other compounds were in the standard mixture. The complex mixture and coelution posed difficult problems if the method was expected to perform consitently when evaluating ambient PM with complex chemical compositions (Hawley and Mazurek, 2008). As a result, GCMS analysis with prior chemical derivatization was then considered as an alternative quantitation method for polar organic atmospheric molecular markers.

This HPLC experiment resulted in an unexpected finding: the oxoacids formed DNPH derivatives and eluted at similar times to the aldehydes and ketones found in the CARB standard. The oxoacids were detectable at the same wavelength, 365 nm, used to quantify carbonyls as DNPH derivatives. Therefore, the oxoacids might interfere with the carbonyl analyses if UV/Vis detection alone and compound retention times are used without MS confirmation of the peaks (Hawley and Mazurek, 2008).

3.3.3. GCMS with BSTFA-TMS Derivatives

Polar organic compounds have been studied in atmospheric particulate matter as derivatives with GCMS analysis (Simoneit, 2002; Medeiros et al., 2006). We adapted and improved the BSTFA method in this study. The following figures are samples of

chromatograms from the GCMS as the total ion current (TIC) (Figure 3-3) which is abundance versus retention time. The selected ion monitoring (SIM) mode spectra for a particular compound is the TIC extracted for a specific ion. It is the SIM mode of the chromatogram which is used to quantify the peaks for translation into a concentration or a mass. In order to quantify a peak as the compound of interest, several factors need to match the original standard. The first is the retention time. The second is the characteristic ion (m/z) that is used as the quantification ion followed by evaluating four additional ions that are the confirming ions as shown in Figure 3-4. Finally, the compound is evaluated for its match to the NIST or Wiley mass spectral standard libraries, if applicable. Results for the compound specific information used for quantitation can be seen in Appendix B. Most marker compounds in this reseach were compared routinely to the GCMS libraries and had similarities typically over 90%. Additionally, other studies identified a number of the same markers and found similar spectra and quantification ions (Simoneit, 2002; Medeiros et al., 2006). The saccharides have m/z values of 73, 147, 191, 204, 217; the disaccharides have an additional m/z of 361; and the reduced anhydrides have m/z values of 205, 217, 307 and 319. As the same groups of sugars have the same m/z values it is essential the GC retention time also be used to confirm the presence of a compound (Simoneit et al., 2004). It is important to note that not of all of the compounds evaluated for this research can be found in MS libraries.

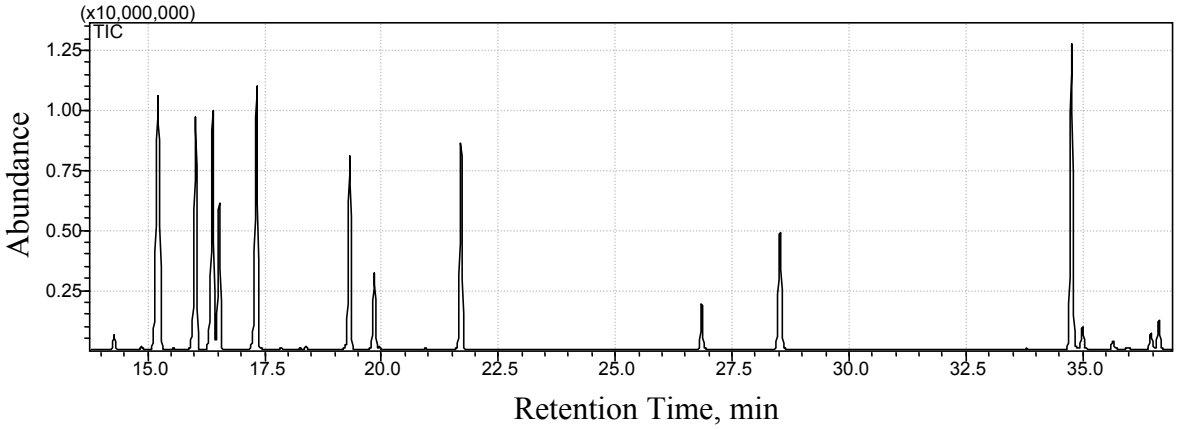


Figure 3-3 TIC of nine sugars, three with α and β isomers, and the internal standard at an injected mass of 10 ng (this study)

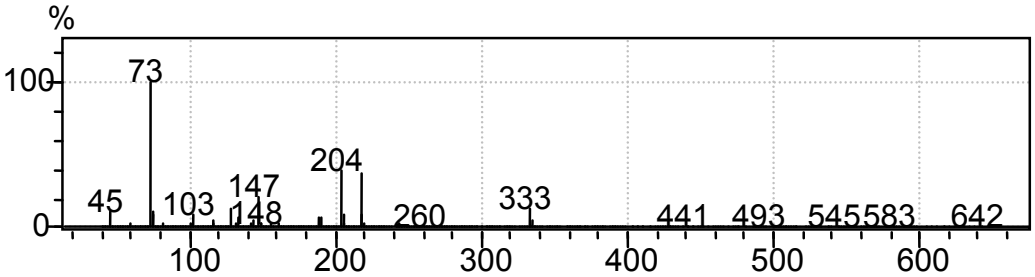


Figure 3-4 Mass spectral data of levoglucosan extracted from the above chromatogram (this study)

3.3.4. Optimal Method

The GCMS with BSTFA derivitization was chosen as the method to quantify the polar organic compounds of interest in the ambient samples. This method was selected because it is a one-step synthesis, is applicable to a wide range of compounds, is rapid, and yields stable trimethyl silyl (TMS) ether or ester derivatives. Also, this GCMS method has the capability of using multiple verifications to ensure the compounds detected in the samples are those of interest. The retention time can be used as the first verification followed by the mass spectral data which provides key ions and a library of compounds that can be matched. The HPLC method only provides a retention time and UV/Vis absorption profile. Additionally, the GC FID detects a larger array of chemical

species within the same analysis. The BSTFA derivative was successful for the entire list of target polar organic compounds (Table 3-4) whereas the HPLC with or without derivatization was unable to detect the full list. As ambient samples are complex mixtures, it is desirable to have a single method to quantify a large array of organic species.

As can be seen from the earlier analytical tests, not all of the compounds of interest were evaluated with both GCMS and HPLC. This was because some compounds, such as the monosaccharides, are not seen with a UV-Vis detector. Compounds containing an aromatic ring can typically form a chromophor which is detectable with a UV-Vis lamp, thus the four aromatic compounds were chosen for that test. Organic compounds containing a carbonyl functional group form derivatives with DNPH, as can be seen with the CARB standard mixture. However, not all chemicals will fully form the derivative and, therefore, emit a weak signal measured by the UV/Vis detector. The oxoacids analyzed in this study fell into the latter category. Although these organic acids have a C=O bond, the absorption in the UV/Vis range was weak when compared to the CARB standard compounds. Newer research has shown HPLC analysis with a mass spectrometer (LCMS) detects compounds without chromophors otherwise undetectable with a standard HPLC UV/Vis instrument, for example glucose. However, LCMS analysis has analytical difficulties due to the mobile phase and adducts and artifacts formed in the MS source. Depending on the mobile phase chemical composition and the complex mixture of the sample, a target compound may be present in several forms, all with different m/z. Thus, confirming the compound identity with LCMS is not straightforward or consistent. Finally, the LC currently does not have a detector as

versatile as the GC FID thus limiting the range of compounds that can be detected with such equipment (Miller, 2005).

Calibration curves for all compounds were created using the optimized GCMS BSTFA method. The calibration curves were made at five levels ranging from 0.2 ng/µL to 40 ng/µL for each compound. The calibration curves were created using the method of response factors to relate the peak area of the compound of interest to the peak area of the internal standard (Equation 3). The internal standard was perdeuturated n-tetracosane, $C_{24}D_{50}$, and was added to each standard at the same concentration, 10 ng/µL. The ratio of the concentration of the standard divided by the concentration of the internal standard was plotted versus the ratio of the response of the compound (area counts) to the response of the internal standard (area counts). A linear regression line was added and the slope was the relative response factor (RRF) (Mazurek et al., 1987; Li et al., 2005). The calibration curves and raw data are shown in Appendix C. The relative response factor can be described from the following equation (Mazurek et al., 1987). Li et al. (2005) studied the variation in the RRF for organic compounds and found the RRFs' were consistent over the three-month study period.

$$RRF = \frac{Response_{Compound}}{Response_{Internal\ Standard}} * \frac{Concentration_{Internal\ Standard}}{Concentration_{Compound}}$$

Equation 3

The internal standard was fully deuterated and prepared commercially to distinguish from the hydrogen-containing analog which is produced from biogenic, anthropogenic and geogenic sources. A known amount of internal standard was added to the sample before the sample extraction step to monitor the recovery of the compounds of

interest throughout each analysis step (i.e. extraction, derivatization) (Mazurek et al., 1987; Mazurek et al., 1989).

The ambient detection limits were determined using "clean" background samples. In this case the samples chosen were spring, Chester, NJ and the June, 2006 Pinnacle State Park, NY sample for the 2002-2003 study and the 2005-2007 study, respectively. The samples were evaluated for the smallest peak that corrresponded to the m/z quantitation ion of the organic compound of interest. The responses for the internal standard and the standard compound were used to calculate the target marker ambient concentration (Equation 3). The ambient detection limits can be found in Appendix D. Significant figures are reported to a maximum of two decimal places (except the ambient detection limits which are reported to three decimal places if the first two decimals were zero). Two decimal places were chosen because it corresponds to the ambient detection limit for the majority of compounds quantified. Concentrations obtained from other studies for comparison purposes were reported to three significant figures.

3.4. *Application to Ambient Samples*

Fine PM samples were collected from the sampling network, *Speciation of Organics for Apportionment of* $PM_{2.5}$ (SOAP) program. The SOAP program monitored four sites in the Northeast U.S. between May 2002 and April 2003. The first field experiment is designated "SOAP 2002-2003". Queens, New York was the urban site with high traffic; Chester, New Jersey was the "clean" background site (upwind of NYC); Elizabeth, New Jersey was the traffic-dominated site, and Westport, Connecticut was a residential site generally downwind on NYC and near Interstate 95 (Figure 3-5). The sites operated 24 hours a day, from midnight to midnight. Ambient filters were collected

once every three days according to the U.S. EPA Species Trend Network (STN) schedule. The filter samples were collected with high volume Tisch TE-1020 or TE-1040, 2 or 4 channel samplers respectively, onto 102 mm quartz fiber filters. Prior to sample collection, the quartz fiber filters were baked at 550 °C for at least 8 hours to remove organic contamination and were wrapped individually in pre-baked out pieces of aluminum foil throughout the cleaning process until loaded into the filter holder cassette (Li et al., 2005). The Tisch samplers were fitted with Teflon gaskets to reduce organic contamination and operated at a constant flow rate of 113 L/minute. The SOAP 2002-2003 study collected about 700 filters, however not all filters were examined. The filters were composited into seasonal samples with the requirement all four sites had a successful filter collected on the same day. The successful filters were composited to ensure enough mass of the marker compound was likely to be detected and measured reliably for an "average" daily concentration. The one exception was the first summer composite which had fine PM composites generated for Chester, NJ, Elizabeth, NJ and Queens, NY. Problems with the sampler at the Westport, CT site were corrected by mid-summer. Field blanks, trip blanks and dynamic blanks also were collected as part of the SOAP 2002-2003 study. Field blanks were collected in the Tisch samplers without air flow; trip blanks were transported and stored identical to the ambient samples but were unopened; and dynamic blanks were collected in the Tisch samplers but for only ten minutes (McDow et al., 2007; Kurian, 2007). The composite schemes describing the filter collection dates is given in Appendix E.

A second sampling program was conducted with two different sites: Pinnacle State Park, NY and in Bronx, NY (Figure 3-5). Pinnacle State Park was a clean

background site and Bronx was a heavily populated urban site near two high-volume highways. The second field experiment is referred to as "SOAP-NY." The sites operated from October, 2005 to March, 2007; samples were collected in the same manner as the previous samples running 24 hours a day however the filter collection was once every six days. The site in Pinnacle State Park, NY had two Tisch samplers (one 4-channel and one 2-channel) running to increase the fine PM mass on the combined filters. Based on the SOAP 2002-2003 Chester, NJ background site, the ambient masses of the target molecular markers were near the detection limits of the GCMS instrument, therefore, the Pinnacle State Park, NY composites had about double the number of filters. The filters were composited monthly instead of seasonally in order to more easily compare the temporal results with other studies. The composite schemes with the filter collection dates are presented in Appendix E.

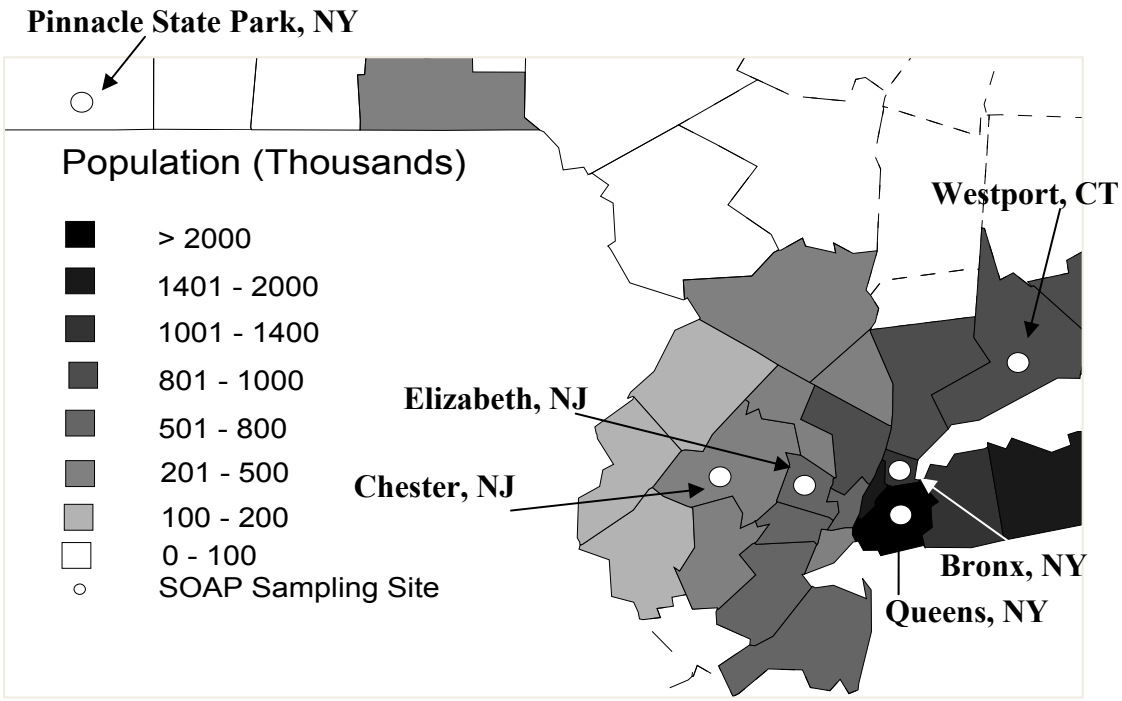


Figure 3-5 SOAP 2002-2007 sampling locations

All filters were mailed by overnight mail to Rutgers University in coolers with ice packs to keep the temperature cold (about 4 °C). The intact filter cassette was shipped in each direction to minimize handling steps, adsorption of semi-volatile organic carbon compounds, and possible filter contamination. Once the cassettes arrived at Rutgers University, the filters were removed from the cassette and inventoried. The filters were placed in annealed borosilicate amber jars wrapped in aluminum foil and stored in a freezer set to 4 °C to ensure preservation. The filters were removed from the freezer to remove a subsample for EC/OC analysis. The filter subsample was taken using a 1 cm by 1.5 cm rectangular punch that was cleaned with several solvents prior to and after each use. The filter subsample was placed in a small annealed aluminum foil envelope, labeled, placed in a plastic zipper bag and put in to the freezer. When ready, the EC/OC filter aliquots were sent to Sunset Laboratories (Tigard, Oregon) for EC and OC analysis (for more information on the Sunset Laboratory analysis process see Kurian, 2007). The remaining filter was placed back in the jar, wrapped in aluminum foil and stored in the freezer for filter preservation. The EC and OC data was provided as the C mass in μg for the 1.5 cm^2 punch. The data was converted to ambient concentration using the flow rate and the area of the exposed filter (56 cm^2). The following equation is an example of the conversion to ambient OC or EC.

$$OC\,\frac{\mu g}{m^3} = OC\,\frac{\mu g}{cm^2} * Exposed\ Area,\ cm^2 * \frac{1}{Air\ Volume,\ m^3}$$

Equation 4

The filters were extracted as composites with a soxhlet extraction system. The solvent was a mixture of 250 mL dichloromethane and 250 mL acetone and the extractor refluxed for approximately four hours. For the 2002-2003 study, half of each filter was

used for the composite; the remaining half was used for the EC/OC punch and archived. The 2005-2007 study filters were portioned as described in Appendix E. The filter composites were spiked with 10 μg of the internal standard, perdeuterated-$C_{24}D_{50}$, prior to extraction. The composites were evaporated to about 5 mL with a Kuderna-Danish apparatus (Li et al., 2005). The first set of filters collected from 2002 to 2003 were condensed further to 100 μL for each sample and separated into two aliquots: neutral and fatty acids. After the neutral fraction was analyzed by GCMS the samples were derivitized with BSTFA for the analysis of polar organic compounds. The extracts from the second set of filters collected from 2005 to 2007 were condensed to approximately 150 μL and separated into three aliquots: one to be used for neutral compounds, one to be derivitized with diazomethane for fatty acid analysis and one for the polar organics to be derivitized by BSTFA. The first two aliquots were used for other research and are not evaluated in this work. Equation 5 describes the conversion of the target compound to a mass equivalent from the compound area (response):

$$C_{compound} = \left(\frac{Area_{compound}}{Area_{IS}}\right) * \left(\frac{C_{IS}}{RRF}\right) \quad \text{(units = ng/m}^3\text{)}$$

Equation 5

where IS is the internal standard and Area is the response as peak area counts. The following equation is how the C_{IS} is calculated and accounts for the air volume sampled.

$$C_{IS} = \frac{Mass\ of\ IS}{\left(Flow\ rate, \frac{L}{\min}\right) * (Number\ of\ filters) * \left(\frac{60\ \min}{1\ hour}\right) * \left(\frac{24\ hours}{1\ filter}\right) * \left(\frac{1\ m^3}{1000\ L}\right)}$$

Equation 6

All statistical analyses of the data were completed with Microsoft Office Excel. Simple descriptive statistics first were compiled for each molecular marker at each site for the entire sampling period. The interquartile range was used for the outlier test. The interquartile range (IQR) is $Q_3 - Q_1$, or the middle 50% of the data as shown in Appendix H. The equations for the low and high outlier tests are presented in Equation 7 (Burns et al., 2005). ANOVA (analysis of variance) tables were completed for selected molecular markers to determine whether seasonal and temporal variations existed (see Appendix I). If a sample had a non-detected level for a specific compound, a zero was used as the concentration value in place of the not detected entry (ND). Figure 3-6 illustrates the input for the the ANOVA analysis in Microsoft Office Excel. An alpha value, 0.05, is selected prior to analysis. The values are input and the software calculates the ANOVA table and displays the results (Figure 3-7). A null hypothesis (no difference) is rejected when the p-value is less than or equal to the α-value, 0.05 or 5% (Hicks and Turner, 1999).

$$Low\,outlier = Q_1 - (1.5 * IQR)$$
$$High\,outlier = Q_3 + (1.5 * IQR)$$

Equation 7

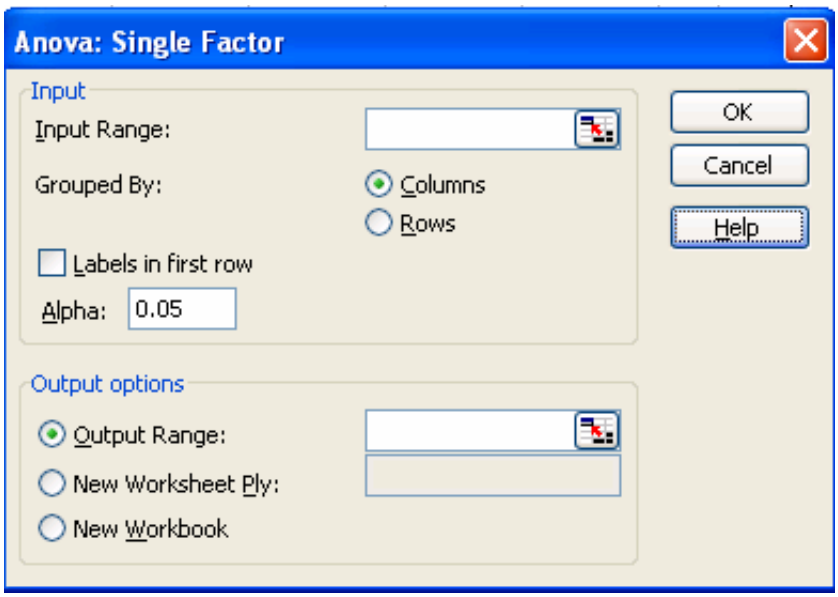


Figure 3-6 Example input for ANOVA analysis

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	11.00	662.17	60.20	787.70		
Column 2	6.00	107.34	17.89	281.74		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6948.82	1.00	6948.82	11.22	0.00	4.54
Within Groups	9285.75	15.00	619.05			
Total	16234.56	16.00				

Figure 3-7 Example output of ANOVA analysis (levoglucosan in Bronx, NY SOAP NY)

The molecular marker ambient mass concentrations were normalized to the OC and EC ambient mass concentrations. This conversion allows for improved analysis of temporal and spatial trends. VOC's can form new SOAs and reactive OC components can degrade in the atmosphere into SOAs, therefore the OC unstable fraction is not a conservative atmospheric tracer. EC does not degrade in the atmosphere and it is not formed photochemically in the atmosphere. These characteristics make EC a

conservative atmospheric tracer that is useful for "adjusting" the molecular marker ambient mass concentrations for seasonal atmospheric conditions. Normalizing molecular markers to EC removes seasonal dilution effects caused by the height of the mixed layer. This lowest layer in the atmosphere is the air column containing gaseous and particulate pollutants. It typically is lower in the winter and late fall, causing smaller volumes and, therefore, higher ambient concentrations of organic molecular markers, EC and OC constituents (Li et al., 2006; Kurian, 2007). For more information on OC and EC SOAP 2002-2003 results, see Kurian (2007).

The federal Specitation Trends Network (STN) data was used to create chemical mass balances for the SOAP 2002-2007 fine particles samples. The total $PM_{2.5}$ mass concentration was determined directly in the field at each site with federally approved continuous $PM_{2.5}$ mass instruments. The inorganic species ambient mass concentrations were determined by contract laboratories at Research Triangle Park, NC and reported to the U.S. EPA for review and distribution to the state monitoring agencies. The fine particle concentrations of nitrate, sulfate, ammonium and inorganic species obtained from NY, NJ and CT air monitoring agencies from the STN network were composited into the same dates as the collected filters. Several instruments measured the fine PM mass at the six SOAP sites; however, the $PM_{2.5}$ mass from the STN database was used for consistency in the mass balance calculations. The OC and EC ambient mass concentration data used for the chemical mass balance calculations were the values obtained from the SOAP 2002-2007 (Rutgers) filters and analyzed by Sunset Laboratory (Tigard, OR). The SOAP filters were carefully prepared, shipped, handled, stored and analyzed to reduce OC artifacts. The SOAP EC and OC results typically were lower than

the concentrations reported for the STN network. A slightly faster face velocity and greaseless sampling equipment (SOAP Tisch collectors) were two major differences between the EC and OC sampling protocols for STN and SOAP. For more information on OC and EC data see Kurian (2007).

Selected molecular markers were normalized to the ambient $PM_{2.5}$ mass concentrations. The fine particle mass for the SOAP 2002-2003 sites was obtained as part of the STN as described in more detail in Kurian (2007). The STN data was received as average daily mass concentrations in $\mu g/m^3$. Fine particle mass information for the SOAP filters were compiled and grouped according to the same filter collection dates within each composite. The fine particle ambient mass concentration for a sample composite was calculated as the average of the combined sampling days in the composite. The $PM_{2.5}$ data for 2005, 2006 and 2007 for the NY sampling locations were the STN values, but were obtained from new federally approved fine particle collectors which had reduced sampling bias. The newer sampler is the current instrument recommended by the EPA for federal monitoring and compliance of $PM_{2.5}$ mass concentrations at monitoring sites throughout each state. The $PM_{2.5}$ mass concentration data was processed in the same manner as the earlier SOAP 2002-2003 EC and OC data.

4. Results

This chapter reports the results from the GCMS quantification of polar organic compounds in atmospheric fine PM in the NJ, NY and CT area for the SOAP 2002-2003 and the SOAP NY field studies. This chapter is separated into sections based on the molecular markers for emission sources. The wood smoke markers are described first, followed by the biogenic sources. Meat charbroiling results are presented followed by biogenic oxidation byproduct and finally the low molecular weight highly oxidized acids. The ambient mass concentration data was compiled in Microsoft Office Excel worksheets and can be found in Appendix F. The laboratory, travel, and dynamic filter blank data are given in Appendix G. Statistical analysis of all compounds can be found in Appendix H. Statistical ANOVA tests can be found in Appendix I. Mass balances of the $PM_{2.5}$ mass concentrations are presented in this chapter and in Appendix J.

4.1. *Wood smoke Markers*

Levoglucosan was the dominant sugar found in the ambient samples and was found in all seasons in the SOAP 2002-2003 experiment at all sites as illustrated in Figures 4-1 through 4-4. Levoglucosan had the highest concentration at every site during late fall (November to early December 2002). Urban sites had higher concentrations of levoglucosan than the rural sites by factors of less than 1.5. This unexpected concentration gradient is counter to the hypothesis that levoglucosan was transported into metropolitan NYC from the rural locations. Chester, NJ (upwind NYC) showed the highest ambient yearly concentrations through the cold months (80.15 ng/m^3 in late fall) with lows in the warmer months (2.73 ng/m^3 in spring), as did Westport, CT (downwind

NYC) (3.36 ng/m^3 in summer and 189.47 ng/m^3 in late fall). This seasonal difference could be due to increased use of fireplaces, woodstoves and residential outdoor woodfired boilers for home heating during the winter months. Elizabeth, NJ and Queens, NY had the highest levels in the colder months (138.11 ng/m^3 in the late fall and 146.92 ng/m^3 in the late fall, respectively), however the two sites also had high amounts in the summer (55.28 ng/m^3 in summer and 78.98 in early summer ng/m^3, respectively). This was an unexpected seasonal concentration for both highly urbanized sites since emissions inventories indicate low levels of wood burning activities in summer (NJDEP, 2006). Statistical analysis showed Westport, CT and Queens, NY had no outliers (Appendix H). Elizabeth, NJ and Chester, NJ both had outliers in the late fall. Chester, NJ had an additional outlier in the winter season. All the levoglucosan values are shown in the plot regardless because it is difficult to disregard the late fall and winter concentrations when it was expected the levoglucosan concentrations would be highest. The seasonal patterns for levoglucosan at the SOAP 2002-2003 sites indicate wood burning is a year-round activity for the NY-NJ-CT metropolitan area. The 20-80 ng/m^3 levoglucosan summer concentrations present in Elizabeth, NJ and Queens, NY equaled or exceeded that for rural Chester, NJ. These distributions suggest a significant urban source of wood burning or cellulosic material combustion. Cardboard and paper combustion is a possible activity in this urban area that also would emit the levoglucosan marker in the fine PM fraction.

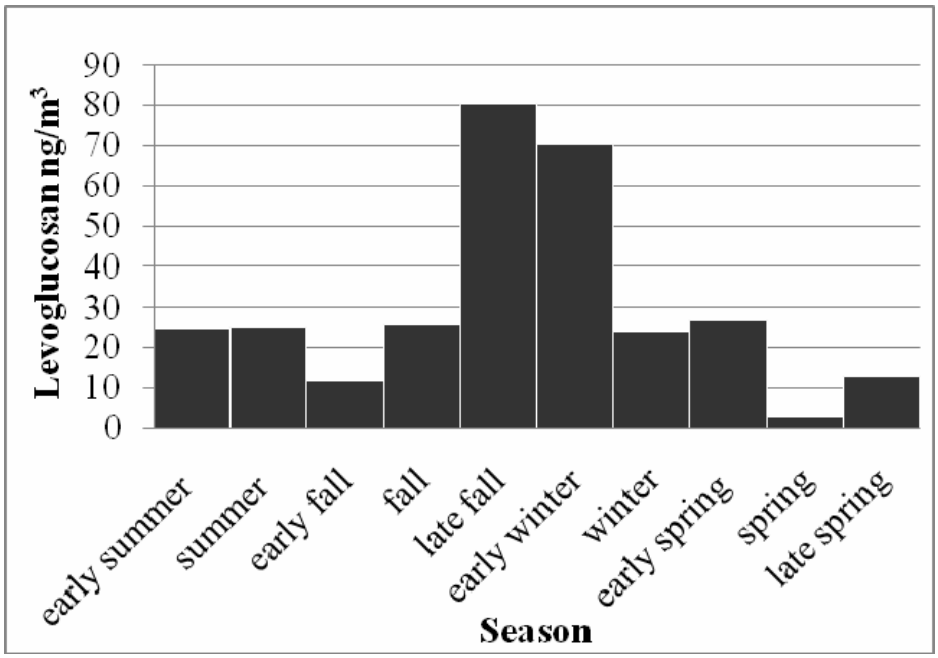


Figure 4-1 Levoglucosan at Chester, NJ (SOAP 2002-2003)

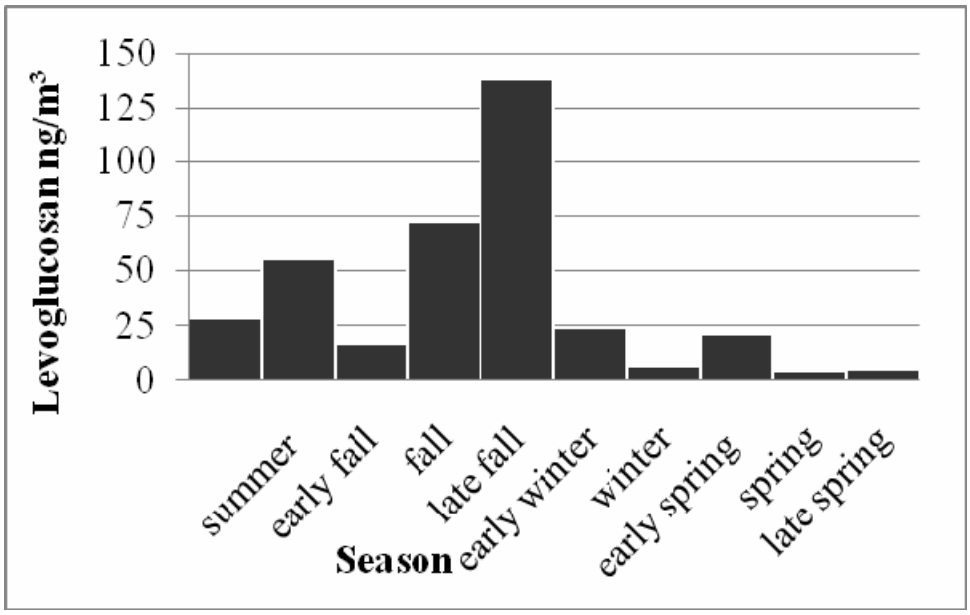


Figure 4-2 Levoglucosan in Elizabeth, NJ (SOAP 2002-2003)

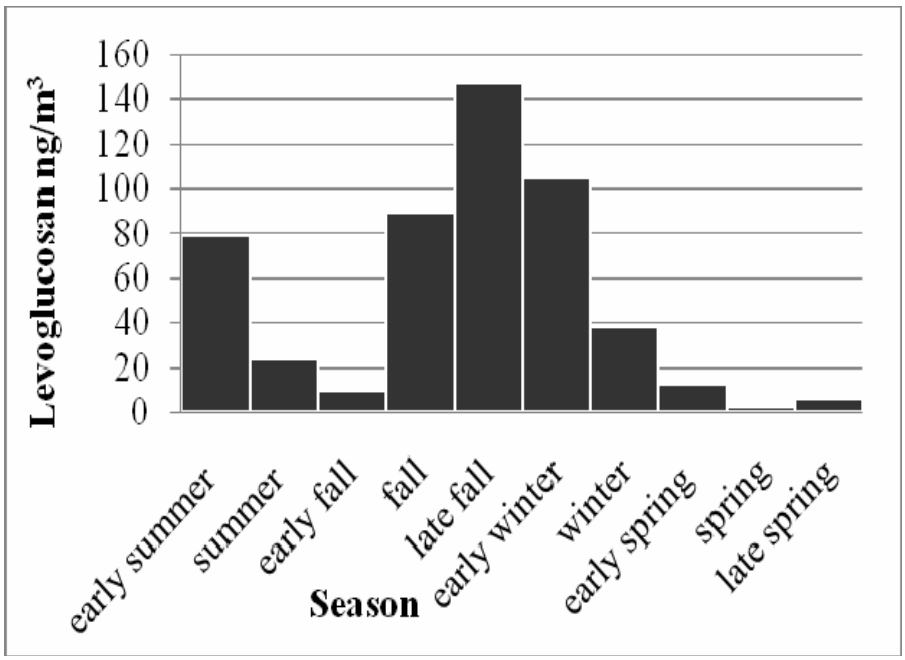


Figure 4-3 Levoglucosan in Queens, NY (SOAP 2002-2003)

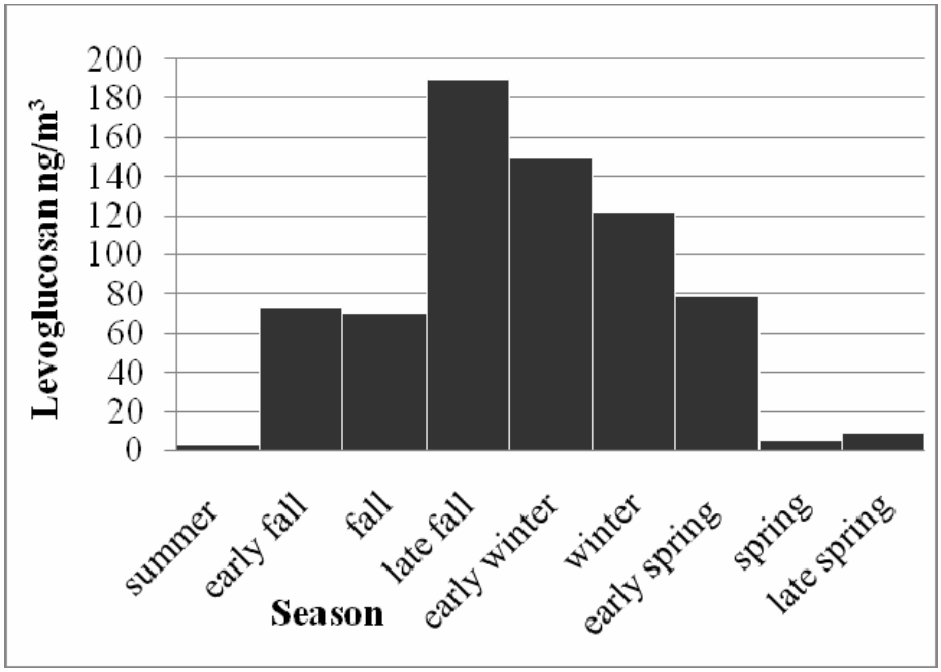


Figure 4-4 Levoglucosan in Westport, CT (SOAP 2002-2003)

The results from the SOAP 2002-2003 study indicate that there is seasonal variability in levoglucosan concentrations in the NJ, NY and CT airshed. The statistical tests confirm the high variation with few to no outlier concentrations at the SOAP 2002-

2003 sites as seen in Table 4-1. ANOVA tables (Appendix I) were created to compare the early fall-winter samples with the early spring-summer at each location. Only Westport, CT showed significant differences between the winter and summer seasons at the 95% significant level (p-value = 0.02). The other three sites did not show statistically significant differences between the two seasons for levoglucosan (p-values ranged from 0.31 to 0.10).

Table 4-1 Statistical summary of levoglucosan in ng/m^3 for SOAP 2002-2003 and SOAP NY

Site	Queens, NY	Elizabeth, NJ	Chester, NJ	Westport, CT	Bronx, NY	Pinnacle State Park, NY
Annual Mean	51.04	37.32	30.43	77.63	45.27	46.37
Standard Deviation	50.36	41.77	24.97	66.27	31.85	37.05
Range	2.36-146.92	4.34-138.11	2.73-80.15	3.36-189.47	7.21-98.77	1.80-118.78
IQR	76.00	39.42	10.91	111.83	44.82	47.91
Winter Mean	70.99	15.39	47.16	135.24	75.09	73.91
Spring Mean	6.81	10.42	14.15	30.97	27.94	38.36
Summer Mean	51.11	41.89	25.03	3.36	7.84	8.83
Fall Mean	81.92	75.80	39.15	110.63	42.32	40.66

In the SOAP-NY field experiment, the Bronx, NY and Pinnacle State Park, NY sites followed more expected trends as shown in Figure 4-5 and Figure 4-6. From October, 2005 to February, 2007, levoglucosan concentrations were highest in the winter (95.99 ng/m^3 in December 2005 in Bronx, NY; 118.78 ng/m^3 in December, 2005 in Pinnacle State Park, NY), lowest in the summer (7.21 ng/m^3 in August 2006 in Bronx, NY; 1.80 ng/m^3 in June 2006 at Pinnacle State Park, NY), showed a gradual decline in the spring and a gradual incline in the fall. These patterns indicate a heating pattern

where people are burning wood for heating sources in the colder weather. Both sites showed the highest concentrations in the winter of 2006 and lower concentrations in the winter of 2007, comparatively. The winter concentrations of levoglucosan were roughly similar at the two sites, however, in summer, the concentration of levoglucosan was approximately three times higher in Bronx, NY than at Pinnacle State Park, NY. This gradient suggests more sources of wood, cellulose, or biomass burning are expected in the metropolitan area based on the seasonal state emission inventories. Interannual variation in levoglucosan concentrations also were found. In Bronx, NY the concentrations were higher in 2006 (98.77 ng/m^3, February) compared to 2007 (48.90 ng/m^3, February). At Pinnacle State Park, NY the interannual trend was the same; the winter of 2007 (34.01 ng/m^3, February) had concentrations roughly half of what they were the preceding year (95.78 ng/m^3, February). The SOAP-NY results for levoglucosan also indicate seasonal as well as interannual variations for the urban NYC and upwind sites. Climate, meteorology, heating fuel cost and availability, and human activity factor into the SOAP 2002-2007 levoglucosan spatial and seasonal patterns.

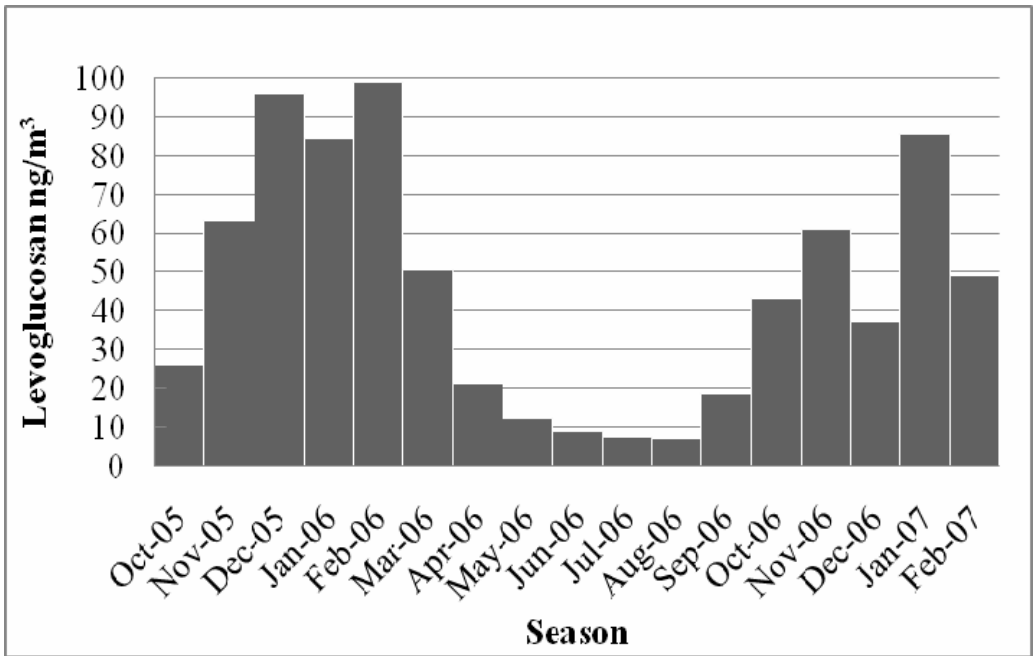


Figure 4-5 Levoglucosan in Bronx, NY (SOAP NY)

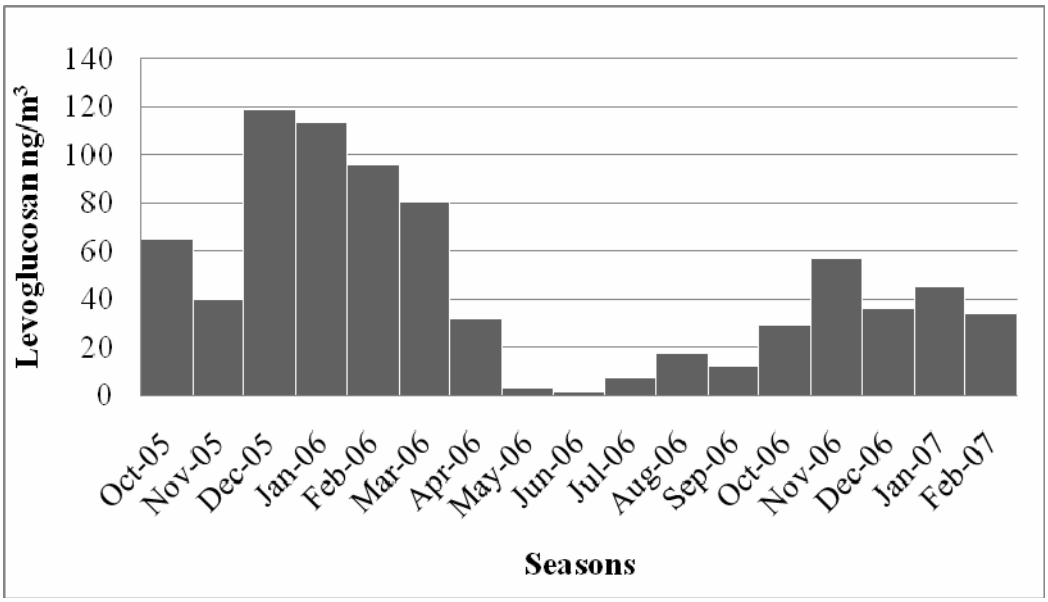


Figure 4-6 Levoglucosan in Pinnacle State Park, NY (SOAP NY)

The statistical analysis of levoglucosan at Bronx, NY and Pinnacle State Park, NY indicated no outliers for the sampling period (Appendix H, Table 4-1). ANOVA tables were completed at the 95% confidence level (one-sided, normal probability distribution). There was no difference between the summer-spring and winter-fall seasons for

levoglucosan, i.e. wood smoke, at Pinnacle State Park, NY (p-value = 0.058). At Bronx, NY the p-value obtained comparing spring-summer and winter-fall levoglucosan concentrations also was found to be significantly different at the 95% confidence level (p-value = 0.004). These results indicate a seasonal variation of levoglucosan. This finding is similar to the SOAP 2002-2003 levoglucosan ANOVA results regarding seasonal variations as only Westport, CT, the downwind site, showed seasonal variations and not the rural background site.

Additional ANOVA tables were generated to determine the statistical significance of levoglucosan at urban (Queens, NY, Elizabeth, NJ, Westport, CT and Bronx, NY) versus rural (Chester, NJ and Pinnacle State Park, NY) locations for the entire year and each season. No difference was found between urban and rural sites for the entire year or any of the four seasons at the 95% confidence level (p-values ranged from 0.30 to 0.70). Table 4-2 summarized the ANOVA results for SOAP 2002-2007.

Table 4-2 Summary of ANOVA results for SOAP 2002-2007

	Chester, NJ	Queens, NY	Elizabeth, NJ	Westport, CT	Bronx, NY	Pinnacle State Park, NY	Urban versus rural
Levoglucosan	No	No	No	Yes	Yes	No	No
Total n-alkanols	No	No	No	No	No	No	No
Cholesterol	No	No	No	No	Yes	No	Yes
cis-Pinonic acid	No	No	No	No	No	No	Yes
Levulinic acid	No	No	No	No	Yes	Yes	No

The remaining sugar molecular markers consisted of two anhydro-saccharides (mannopyranose and galactopyranose), three mono-saccharides (glucose, xylose and mannose), and three disaccharides (sucrose, maltose and trehalose). For the SOAP 2002-

2003 field experiment, the seasonal concentration of sugars, without levoglucosan, did not show definitive profiles by season at any of the six locations over the five-year time period (Figures 4-7 through 4-12). The highest sugar concentrations generally were present at all sites during summer, with the exception of Westport, CT, which had a fall maximum. Typically, the anhydrosaccharides were more prevalent than the mono- or disaccharides. Glucose was the most common monosaccharide found in the samples. Trehalose was not found in the samples indicating soil dust was not a significant source of $PM_{2.5}$. This is understandable as trehalose tends to be found in the coarse fraction.

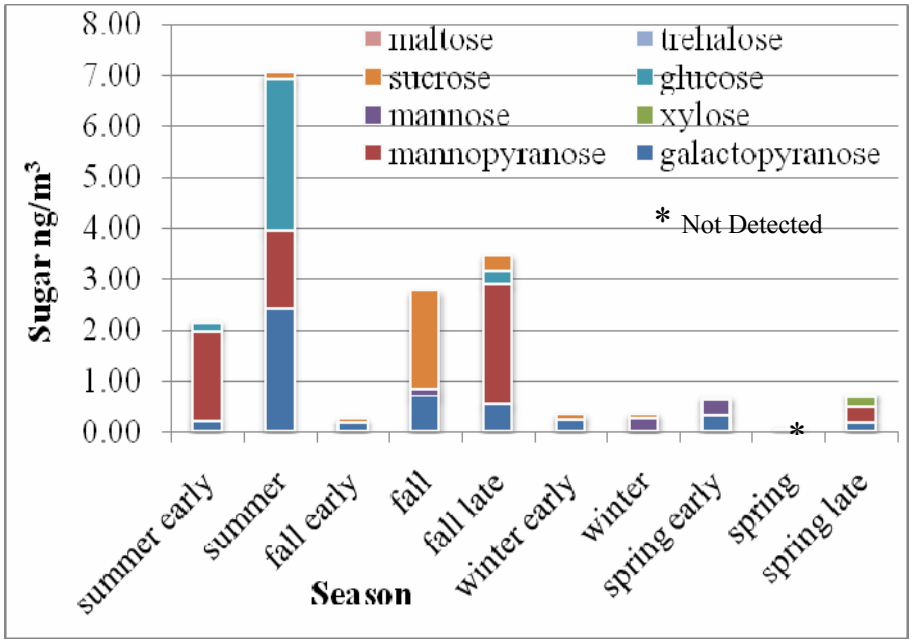


Figure 4-7 Sugar profiles in Chester, NJ (SOAP 2002-2003)

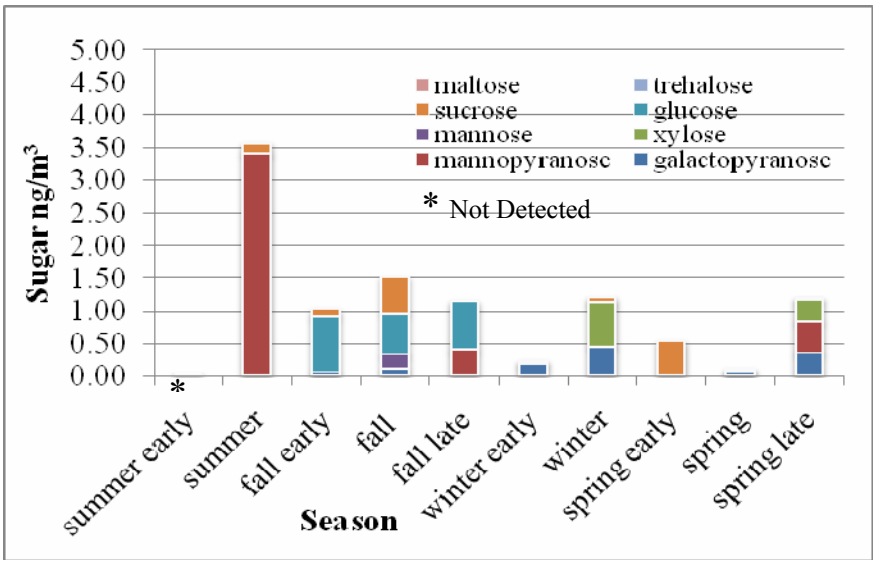


Figure 4-8 Sugar Profiles in Elizabeth, NJ (SOAP 2002-2003)

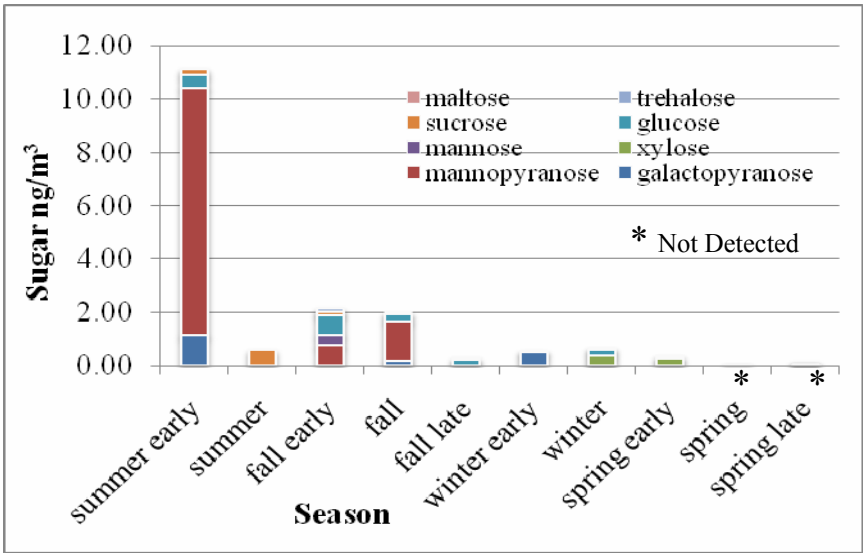


Figure 4-9 Sugar Profiles in Queens, NY (SOAP 2002-2003)

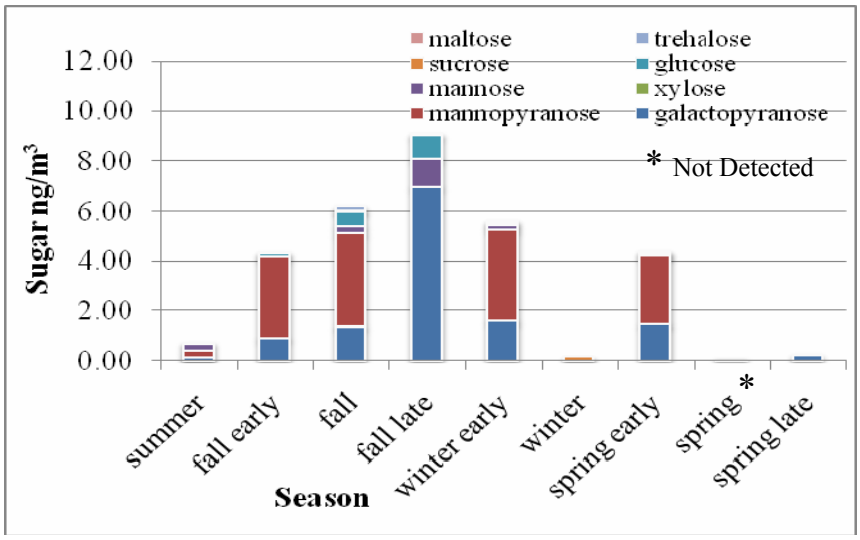


Figure 4-10 Sugar Profiles in Westport, CT (SOAP 2002-2003)

The total concentration of the sugars, without the levoglucosan, for the SOAP NY field experiment was higher in the rural, background site of Pinnacle State Park, NY than in the Bronx, NY for the same time period as shown in Figure 4-11 and Figure 4-12. The sugars were 25.34 ng/m^3 in October, 2005 for Pinnacle State Park, NY; the maximum value for the Bronx, NY was 16.85 ng/m^3 in February, 2006. Both levels were higher than the sugar concentrations found in the 2002-2003 samples.

Outlier tests were conducted on all of the sugar concentrations for the 2002-2007 ambient samples as described previously (Appendix H). The four sites monitored from 2002-2003 had positive outliers throughout the sampling period, however there was no consistency as to which season or sugar was the outlier. In general, any measured xylose, mannose or trehalose sugar markers was judged as an outlier according to Equation 7 because of the dominance of days with concentrations near the detection level. The outliers were not removed in the seasonal profile plots. Bronx, NY had positive outliers for both glucose and sucrose (September, 2006) and for mannopyranose (February, 2006). All detectable levels of mannose were positive outliers since the remaining

concentrations were near the detection limit. Pinnacle State Park, NY exhibited once a positive outlier for almost every sugar, usually in the late fall or winter months. Appendix H shows the results from the outlier tests. Table 4-3 shows statistical information on the total sugars (without levoglucosan). The standard deviations were larger than the annual averages for several sugars indicating the high variability in sugar concentrations.

Table 4-3 Statistical information on total sugars, ng/m^3, for SOAP 2002-2003 and SOAP NY

Site	Queens, NY	Elizabeth, NJ	Chester, NJ	Westport, CT	Bronx, NY	Pinnacle State Park, NY
Annual Mean	1.77	1.06	1.79	3.41	6.30	6.00
Standard Deviation	3.37	1.03	2.20	3.28	4.48	6.24
Range	0.05-11.12	0.04-3.57	0.06-7.05	0.05-9.10	1.31-16.85	0.00-25.32
IQR	1.37	0.90	2.27	5.38	5.33	6.10
Winter Mean	0.58	0.72	0.35	2.88	8.59	7.25
Spring Mean	0.16	0.61	0.48	1.55	2.41	3.08
Summer Mean	5.84	1.81	4.61	0.71	4.08	3.03
Fall Mean	1.45	1.24	2.17	6.54	7.22	8.02

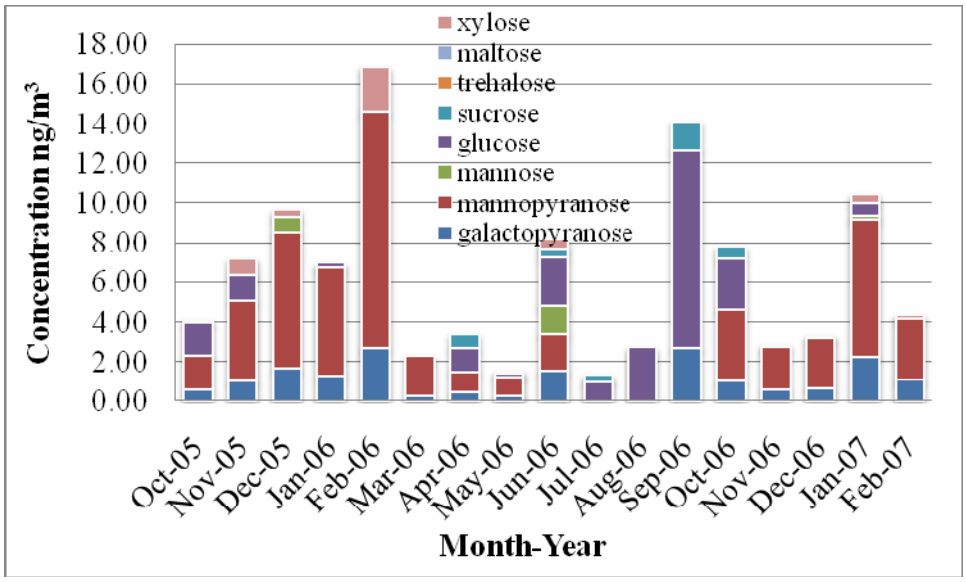


Figure 4-11 Sugar profiles in Bronx, NY (SOAP NY)

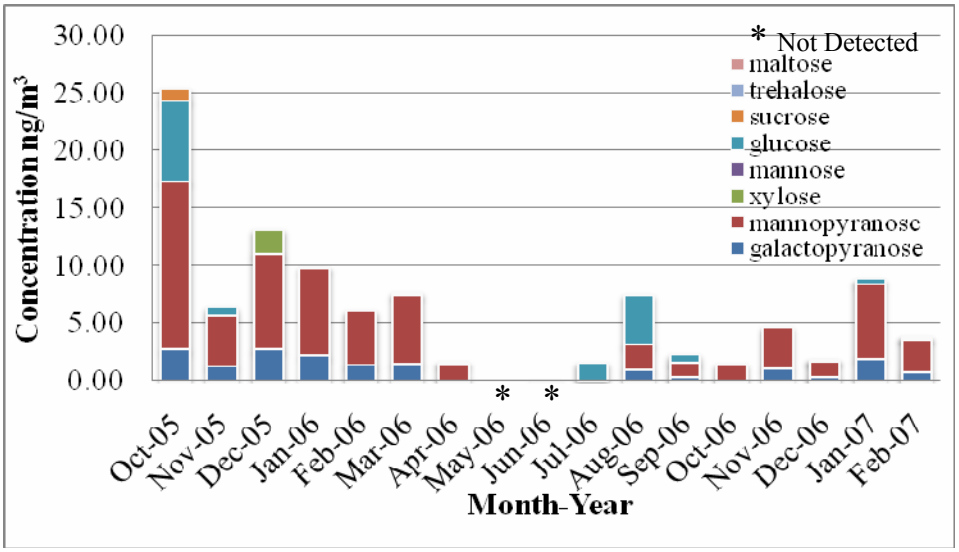


Figure 4-12 Sugar Profiles in Pinnacle State Park, NY (SOAP NY)

Dehydroabietic acid was found in all the SOAP 2002-2003 samples as was levoglucosan, indicating combustion of coniferous fuels. The seasonal abundance varied from site to site as indicated by the standard deviations shown in Table 4-4. Elizabeth, NJ had distinct higher concentrations in the early spring (98.97 ng/m^3) and the summer (89.30 ng/m^3) indicating a preferential burning of soft woods as shown in Figure 4-14.

Queens, NY had concentrations in similar ranges as Elizabeth, NJ, however the highest levels were present in early summer (84.98 ng/m^3), see Figure 4-15. Westport, CT (Figure 4-16) showed similar concentration ranges to Chester, NJ. The highest concentration was in early spring (61.07 ng/m^3). Chester, NJ had higher levels throughout the year compared to Westport, CT, as shown in Figure 4-13. Outlier tests indicated positive outliers for dehydroabietic acid only in the warm months. Early summer had one outlier (Queens, NY 84.98 ng/m^3) and summer had one outlier (Elizabeth, NJ 89.30 ng/m^3). Two positive outliers were present in the early spring (Elizabeth, NJ 98.97 ng/m^3 and Westport, CT 61.07 ng/m^3).

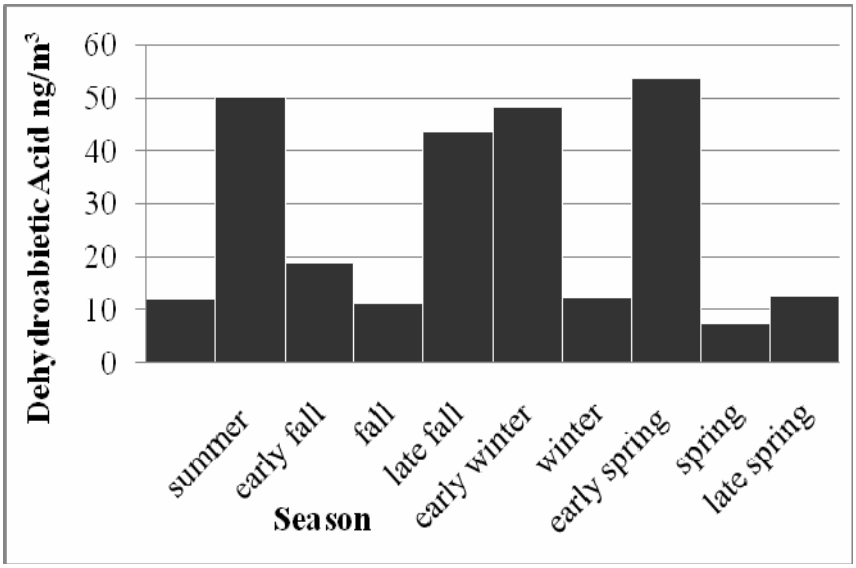


Figure 4-13 Dehydroabietic acid in Chester, NJ (SOAP 2002-2003)

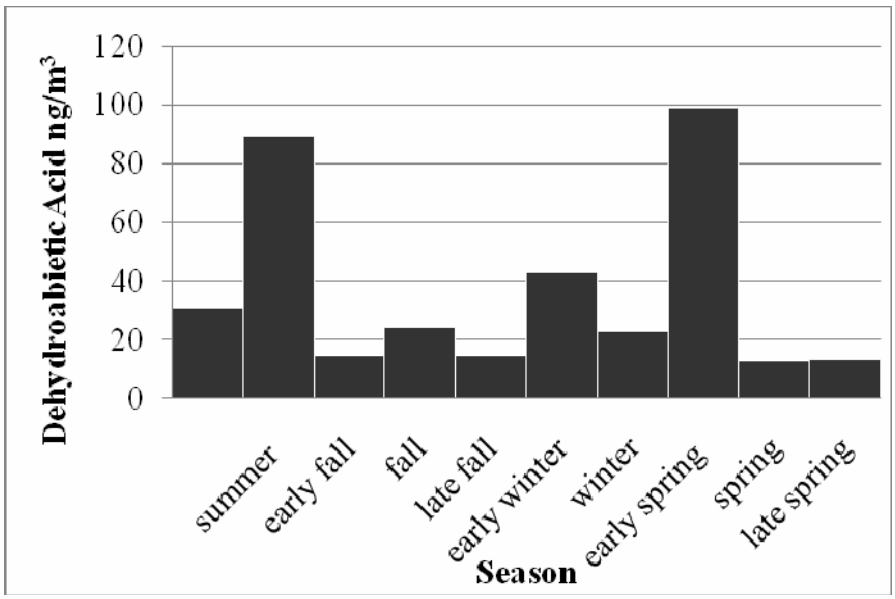


Figure 4-14 Dehydroabietic acid in Elizabeth, NJ (SOAP 2002-2003)

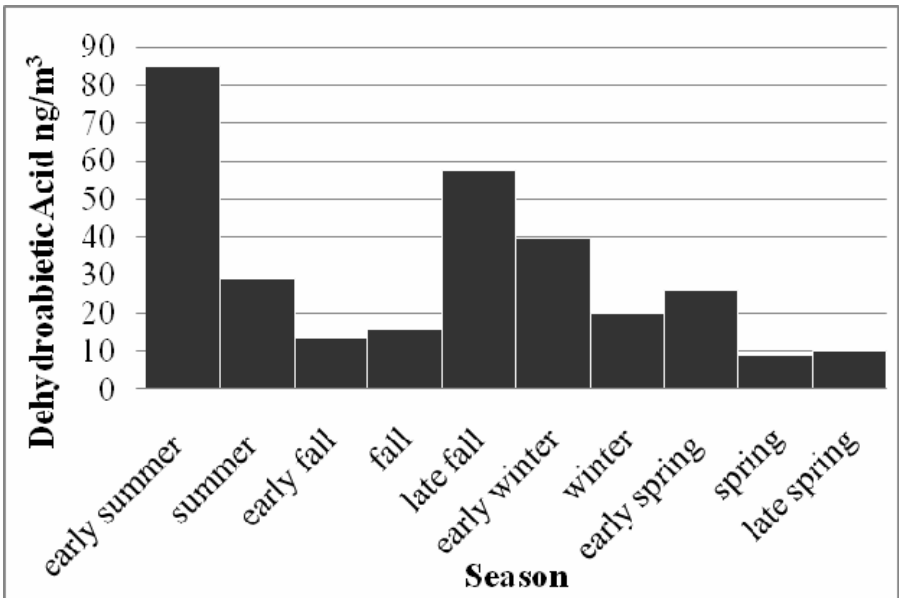


Figure 4-15 Dehydroabietic acid in Queens, NY (SOAP 2002-2003)

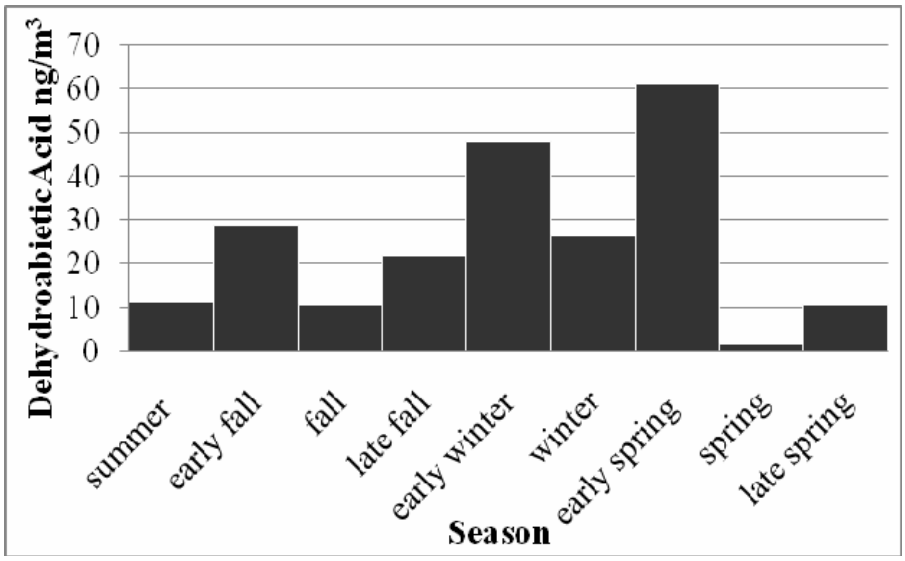


Figure 4-16 Dehydroabietic acid in Westport, CT (SOAP 2002-2003)

Table 4-4 Statistical information for dehydroabietic acid, ng/m^3, for SOAP 2002-2007

Site	Queens, NY	Elizabeth, NJ	Chester, NJ	Westport, CT	Bronx, NY	Pinnacle State Park, NY
Annual Mean	30.48	36.32	27.09	24.38	9.42	12.59
Standard Deviation	24.30	31.97	19.21	19.36	6.90	25.79
Range	9.13-84.98	12.52-98.97	7.50-53.91	1.61-61.07	2.23-27.26	1.79-111.19
IQR	23.13	25.29	34.83	18.13	6.49	3.23
Winter Mean	29.77	32.70	30.39	36.99	16.35	7.68
Spring Mean	15.12	41.48	24.71	24.39	5.80	9.45
Summer Mean	56.87	60.07	31.19	11.16	3.28	2.94
Fall Mean	28.72	17.75	24.54	20.38	6.98	26.17

In Bronx, NY and Pinnacle State Park, NY (SOAP-NY sites) the dehydroabietic acid followed a seasonal profile similar to levoglucosan (Figure 4-17). Pinnacle State Park, NY had a maximum concentration (111.19 ng/m^3) in October, 2005 where the

concentration was almost six times higher than the next highest month (18.99 ng/m^3 in January, 2006) in the 1.5 year continuous study. Other than October 2005, the two sites matched each other in seasonal trend. Though the two sites were similar in concentration for dehydroabietic acid, Bronx, NY, the urban site, generally had higher concentrations. Statistical analysis on the Pinnacle State park, NY dehydroabietic acid data identified the October, 2005 sample as a positive outlier. Bronx, NY had two high outliers both in the same season (December, 2006, 27.26 ng/m^3, and February, 2006, 21.19 ng/m^3). The dehydroabietic acid seasonal distributions did not follow exactly the levoglucosan patterns, which could be due to the different types of wood fuels. Levoglucosan is a tracer for combustion of wood and cellulosic material, whereas dehydroabietic acid is a marker for soft wood combustion (pine). Therefore, different combinations of soft and hard wood combustion would generate different emissions, and thus profiles of dehydroabietic acid.

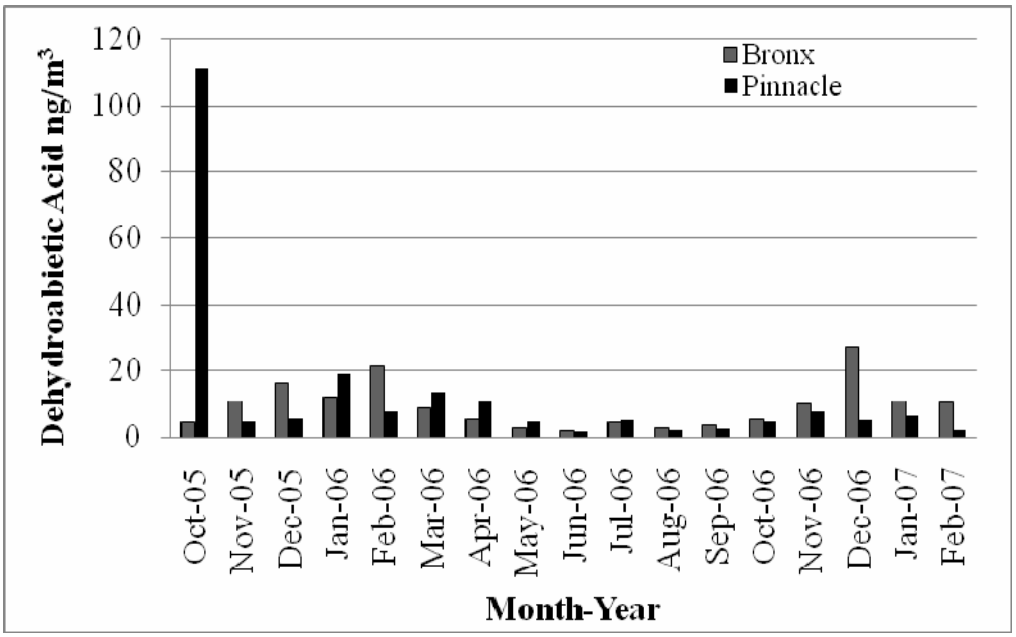


Figure 4-17 Dehydroabietic acid in NY (SOAP NY)

Four polar aromatic compounds were evaluated for their presence in SOAP 2002-2007 fine particle samples. Catechol and ansic acid never were found in the samples at the six locations. The catechol detection limits were 0.021 ng/m^3 for SOAP 2002-2003 and 0.009 ng/m^3 for SOAP NY. The detection limits for anisic acid were 0.013 ng/m^3 for SOAP 2002-2003 and 0.006 ng/m^3 for SOAP NY. Vanillic acid was not detected in the 2002-2003 samples (detection limit = 0.003 ng/m^3 for both SOAP 2002-2003 and SOAP NY). Syringic acid (detection limit = 0.02 ng/m^3 for SOAP 2002-2003 and 0.009 ng/m^3 for SOAP NY) was found once near the detection limit (early winter) in Westport, CT over the SOAP 2002-2003 13-month sampling period. Syringic acid concentrations corresponded with increased levels of levoglucosan, dehydroabietic acid and total sugars (Figure 4-4 and Figure 4-10). An outlier test for the 2002-2003 sampling campaign found one positive outlier, the syringic acid measured in Westport, CT in early winter (0.15 ng/m^3).

Vanillic acid was present in Bronx, NY for three months in the SOAP-NY (1.5 year continuous sampling). This period occurred in the colder months, corresponding to increased use of wood fuels for residential home heating (November, 2005, February, 2006 and December, 2006). At Pinnacle State Park, NY, vanillic acid was present in five months (winter and early spring months) and syringic acid in three months (winter and early spring months). The syringic acid was found only when vanillic acid also was present. In every case, the vanillic acid was dominant over syringic acid. Three months were in colder weather; however two months were March and April, indicating possible continued use of wood fuels for residential heating. In addition, variation in the height of the atmospheric mixed layer also influences the concentration or dilution of a marker

compound at a receptor site. Because vanillic acid was a marker of soft wood combustion such as pine, the presence of this marker in the NYC metropolitan region indicates possible widespread use of this fuel. Work by Simoneit (2002) and Simoneit et al. (1993) found vanillic acid was the dominant aromatic organic compound in PM sampled from soft wood combustion. An outlier test on the Bronx, NY samples determined all the samples containing vanillic acid were high outliers, indicating possibly less soft wood combustion emissions impacting this highly populated urban site. The same statistical result was found for syringic acid in Pinnacle State Park, NY. The seasonal distributions of markers at both sites indicate variable concentrations influenced by types of wood fuels burned, meteorological and climate factors. Local wood smoke emissions rather than regional and long-range transport of wood smoke appear to be the most dominant influences seen at the SOAP sites. Multiyear sampling design is necessary in order to adequately identify average concentrations of wood smoke PM for the NY-NJ-CT background and urban monitoring sites.

In late June and early July 2002, a wildfire had broken out in Canada and the resulting pollution was carried into the United States and towards the New York City area (Medeiros et al., 2006). On July 2, 2002 a 24-hr $PM_{2.5}$ filter was collected at Chester, NJ, Elizabeth, NJ and Queens, NY. The filters were not used in the composited samples because the filters were impacted by the regional smoke plume produced by the Canadian wildfires. Consequently, the mass loading was atypical and the filters were not representative of air quality for the region. The three filters were extracted as three separate samples based on site for analysis of polar organic compounds. Only ¾ of each

filter was extracted; the remaining quarter was used for an EC/OC punch and was analyzed by Sunset Laboratory as described previously.

The levoglucosan values for July 2, 2002 at each site were about ten times higher than the largest value found throughout the entire SOAP 2002-2003 sampling period (13-months). At Queens, NY the value was 1359.66 ng/m^3 compared to the summer sample with 23.24 ng/m^3 and the highest value of the year in the late fall was 146.92 ng/m^3. In Elizabeth, NJ the levoglucosan was 912.43 ng/m^3 during the wildfire compared to the summer value of 55.28 ng/m^3 and year high in late fall of 138.11 ng/m^3. The background site of Chester, NJ had a value of 1423.21 ng/m^3 while the summer was 25.15 ng/m^3 and the year long high in the late fall was 80.15 ng/m^3. Medeiros et al. (2006) collected PM_{10} samples in Maine during the same wildfire and also found a ten-fold increase in levoglucosan levels. The concentrations of the other sugar anhydrides also increased tenfold (Appendix F). Dehydroabietic acid levels increased by a factor of over 2 times the three SOAP sites and had values ranging from 215 to 253 ng/m^3. Vanillic acid and syringic acid also were detected at all three sites. Vanillic acid was 19.31 ng/m^3 in Queens, NY, 17.35 ng/m^3 in Elizabeth, NJ, and 22.04 ng/m^3 in Chester, NJ. Syringic acid was 1.43 ng/m^3 in Queens, NY, 0.89 ng/m^3 in Elizabeth, NJ, and 1.65 ng/m^3 in Chester, NJ.

Results from the July 2002 Canadian wildfire event demonstrate the significant impact of large-scale burning, either episodic or chronic, on air quality in regions hundreds to thousands of kilometers downwind. For the July 2002 Canadian wildfire, the levoglucosan was an order of magnitude higher than the rest of the SOAP 2002-2003 samples. The aromatic compounds increased to measurable concentrations during the

wildfire and were higher than the ambient concentrations measured throughout the 2002-2003 sampling period at the same sites. A complete list of all the compounds quantified in the wildfire samples can be found in Appendix F and the blank results as shown in Appendix G.

4.2. *Biogenic Sources*

The SOAP 2002-2003 samples had n-alkanols in almost every sample (Appendix F). Generally, more than one n-alkanol was found with tetracosanol and hexacosanol the most common. Elizabeth, NJ had the highest concentration in the early summer of 2002 with a concentration of total n-alkanols over 15 ng/m^3 (Figure 4-19). The seasonal pattern, as indicated by the difference in seasonal means shown in Table 4-5, had the highest value (14.60 ng/m^3) in the early summer with a decrease through the fall (1.76 ng/m^3), the lowest values in the early spring (0.37 ng/m^3) and a rise the following spring of 2003 (3.92 ng/m^3). Queens, NY also showed a seasonal pattern for n-alkanols, but with a slightly different distribution. The highest concentration was found in the early summer with a concentration over 12 ng/m^3, slightly less than in Elizabeth, NJ (Figure 4-20). The n-alkanol concentrations decreased through the summer (0.82 ng/m^3), with a sharp rise in the early fall when the concentration reached 9.91 ng/m^3, and then decreased through the winter (3.10 ng/m^3) but rose again the following spring 2003 (6.91 ng/m^3).

Table 4-5 Statistical summary of total n-alkanols, ng/m^3, in SOAP 2002-2003 and SOAP NY

Site	Queens, NY	Elizabeth, NJ	Chester, NJ	Westport, CT	Bronx, NY	Pinnacle State Park, NY
Annual Mean	4.86	3.61	2.61	1.96	1.17	1.62
Standard Deviation	3.90	4.04	1.85	1.28	0.83	0.82
Range	0.82-12.92	0.37-14.60	0.46-5.93	0.54-4.79	BDL-2.65	0.50-3.44
IQR	4.08	2.03	2.06	1.20	1.15	0.76
Winter Mean	3.08	1.63	2.07	3.11	1.38	1.30
Spring Mean	4.32	2.17	3.75	1.19	0.80	1.81
Summer Mean	6.87	9.42	3.20	0.91	1.26	1.15
Fall Mean	5.25	2.49	1.44	2.30	1.10	2.16

Chester, NJ showed a seasonal trend with a peak in the early summer of 2002 reaching 5.93 ng/m^3, a decrease in the summer (0.46 ng/m^3), an increase in the early fall (2.66 ng/m^3), a decrease in the winter (2.30 ng/m^3), and an increase in spring 2003 (Figure 4-18). The down-wind residential site of Westport, CT had the highest concentration of total n-alkanols in the early winter of 2002 with a concentration of 4.79 ng/m^3. Here, the seasonal trend increased in early fall (2.89 ng/m^3), decreased in fall (1.62 ng/m^3), rose sharply in early winter, decreased through winter, and increase slightly in early spring 2003 (1.84 ng/m^3) (Figure 4-21). The concentrations of the n-alkanols showed unexpected spatial patterns for the six SOAP sites (Table 4-5). The SOAP 2002-2003 Queens, NY and Elizabeth, NJ summer concentrations were 2 to 6 times greater than the rural Chester, NJ and Pinnacle State Park, NY levels. The winter n-alkanol concentrations at Queens, NY and Elizabeth, NJ were 0.8 to 1.3 times the levels at Chester, NJ and Pinnacle State Park, NY. Bronx, NY n-alkanol concentrations were

either lower (summer) or the same as the two rural sites. The results for the n-alkanol spatial comparisons suggest localized input.

ANOVA tests were conducted on the total n-alkanols concentrations to determine if a statistical difference was present between early spring-summer and the early fall-winter within each SOAP 2002-2003 site (Appendix I). No statistical difference was found comparing the hot and cold months for the total n-alkanols at any of the four sites (the p-values ranged from 0.08 to 0.72). This result was expected because each category contained one season with a higher level (fall, spring) of total n-alkanols and one season with lower levels of total n-alkanols. Therefore, the seasons were averaged and found to be similar to one another. Outlier tests were conducted on the total n-alkanols for all sites and for all seasons. Two high outliers were found in the early summer, both in urban areas (Elizabeth, NJ, 14.60 ng/m^3 and Queens, NY, 12.92 ng/m^3) and one high outlier was found in the early winter (Westport, CT, 4.79 ng/m^3).

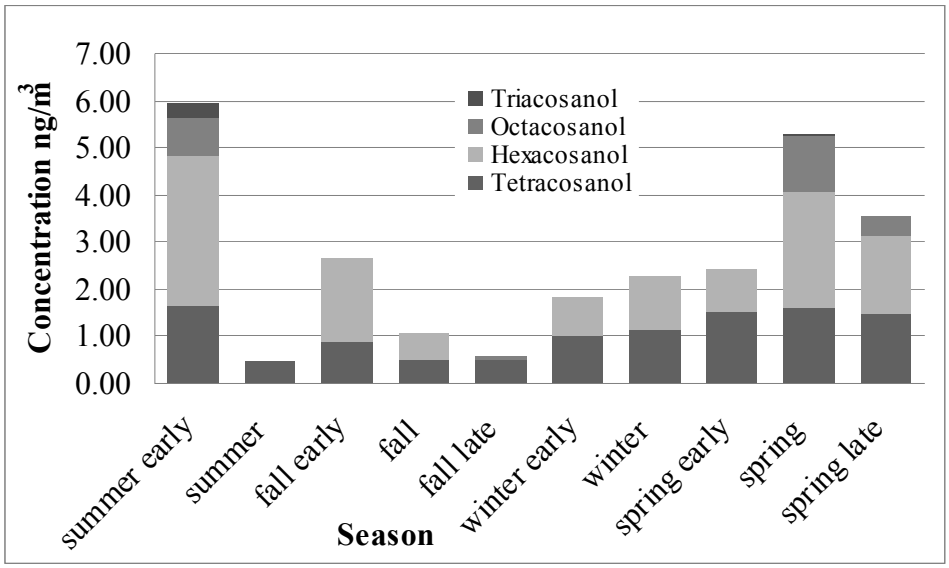


Figure 4-18 Total n-alkanols in Chester, NJ (SOAP 2002-2003)

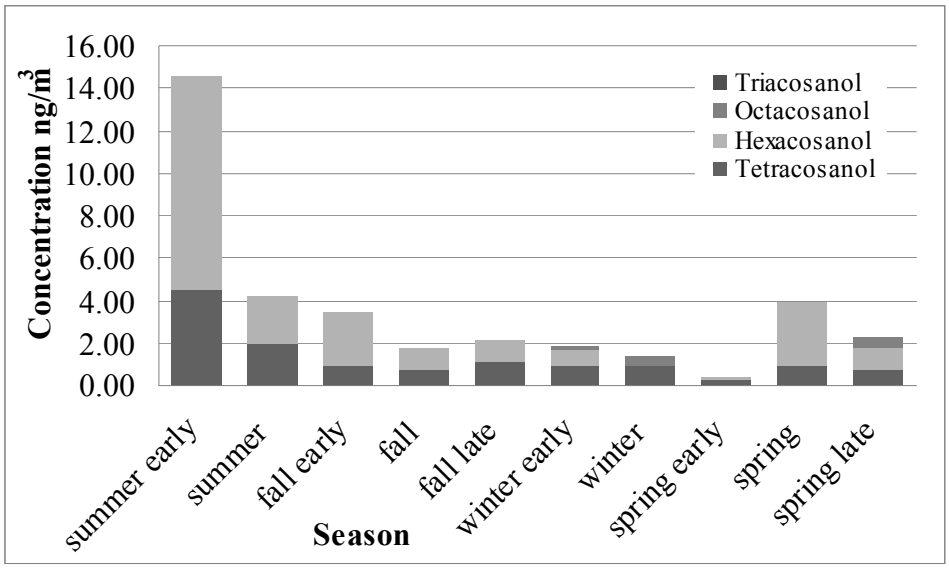


Figure 4-19 Total n-alkanols in Elizabeth, NJ (SOAP 2002-2003)

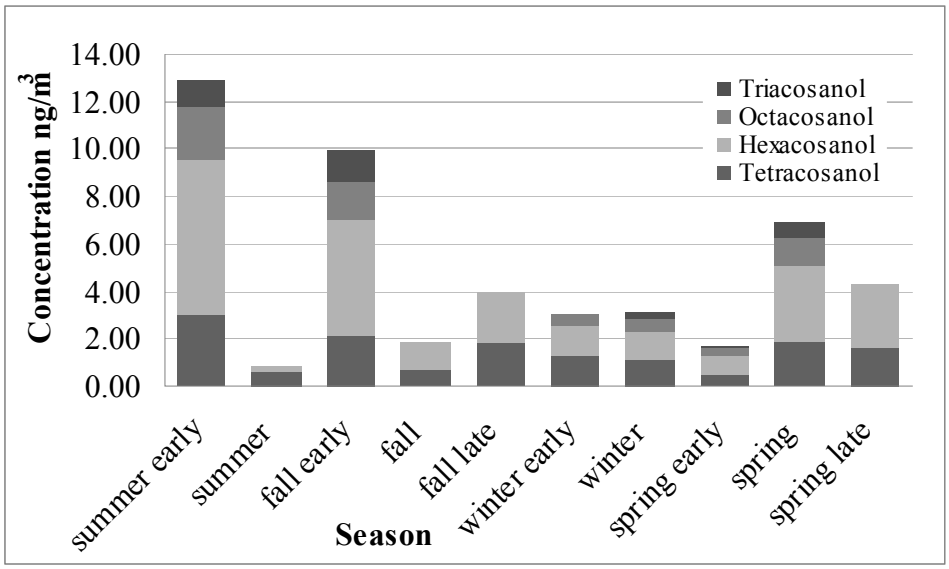


Figure 4-20 Total n-alkanols in Queens, NY (SOAP 2002-2003)

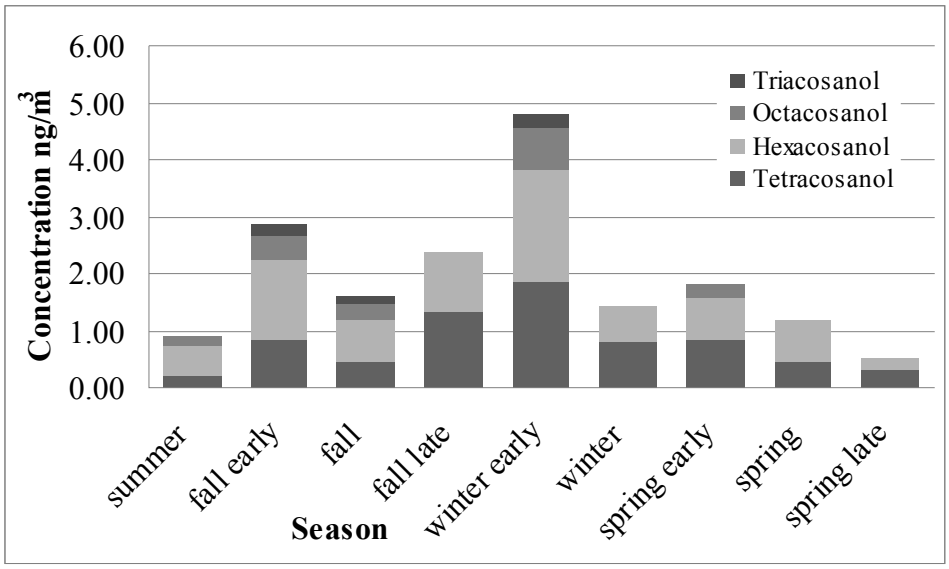


Figure 4-21 Total n-alkanols in Westport, CT (SOAP 2002-2003)

For the SOAP-NY field experiment, the n-alkanols were present every month in Pinnacle State Park, NY with the highest values in October and November of 2005 (3.44 ng/m^3 and 3.19 ng/m^3, respectively), May, 2006 (2.54 ng/m^3), and October and November of 2006 (1.89 ng/m^3 and 1.78 ng/m^3, respectively) (Figure 4-22). This pattern is consistent with leaf growth and die off where the highest concentrations occur during leaf senescence when surface waxes become brittle and are more readily abraded in the fall months. Bronx, NY, on the other hand, showed no seasonal pattern with n-alkanols being present randomly. The highest concentrations were found in December 2005 and June 2006 (2.65 ng/m^3 and 2.54 ng/m^3 respectively) (Figure 4-23).

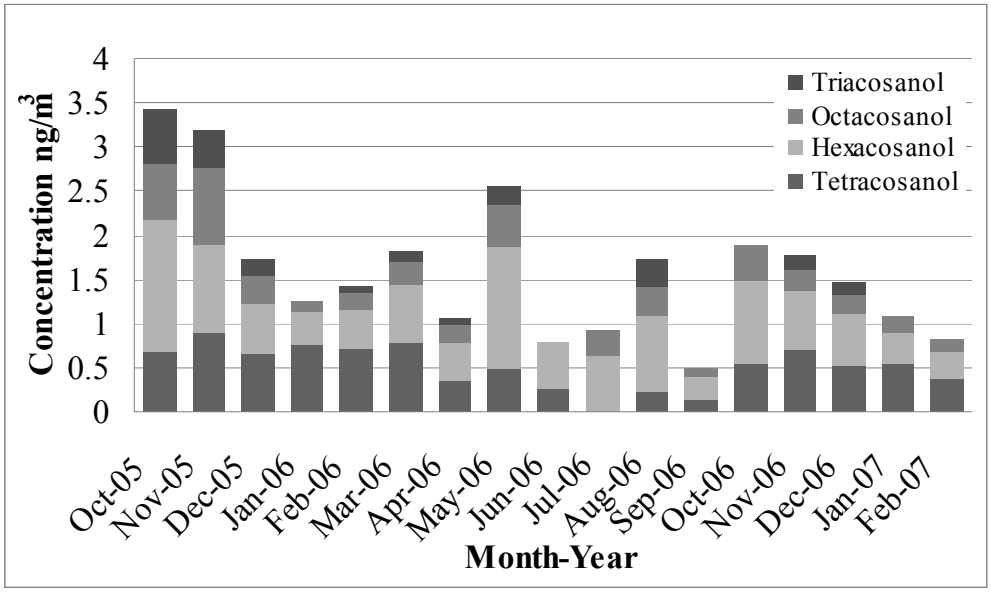


Figure 4-22 Total n-alkanols in Pinnacle State Park, NY (SOAP NY)

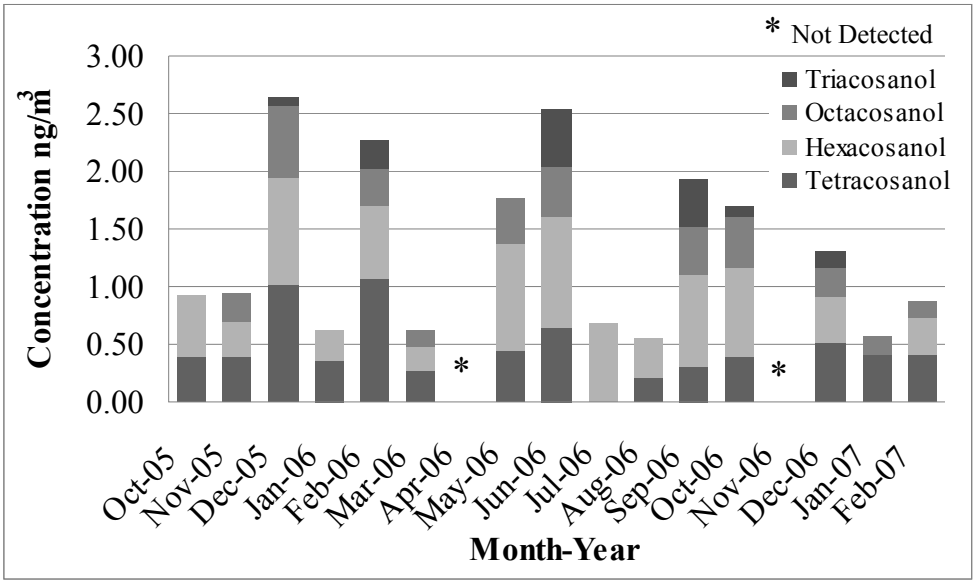


Figure 4-23 Total n-alkanols in Bronx, NY (SOAP NY)

A two-sided ANOVA test was performed with the SOAP-NY total n-alkanols concentration data to compare within each site the warm periods (March through August) and cool months (September through February). No statistical difference was found between the warm and cool periods for the total n-alkanols at either of the sites based on

the p-value (0.61 in Bronx, NY and 0.63 in Pinnacle State Park, NY). This result is the same found for the 2002-2003 sampling campaign. Again, because each category contained one season with a higher level (fall, spring) of total n-alkanols and one season with lower levels of total n-alkanols, the seasons were averaged and then were found to be similar to one another. Outlier tests on the total n-alkanol concentrations indicated two high outliers for Pinnacle State Park, NY: October, 2005 (3.44 ng/m^3) and November, 2005 (3.19 ng/m^3). Bronx, NY had no outliers. The annual average seasonal concentrations of n-alkanols appear to be uniform across the urban and rural NY sites due to the wide range in seasonal concentrations observed at each of the six SOAP study sites.

Additional ANOVA statistical tests were conducted to determine the significance of the total n-alkanols concentrations at urban sites (Queens, NY, Elizabeth, NJ, Westport, CT and Bronx, NY) versus rural sites (Chester, NJ and Pinnacle State Park, NY) for the 2002-2007 fine particle field measurement campaigns (Appendix I). No difference between urban and rural sites was found for the entire year or any of the four seasons at the 95% confidence level (p-values ranged from 0.28 to 0.48). This finding supports the within site comparisons discussed above.

The phytosterols were not detected in every sample during the SOAP 2002-2003 field campaign. β–sitosterol always was the dominant phytosterol when phytosterols were found. The detection limit for this marker was 0.023 ng/m^3. The total phytosterols were variable as indicated by the high standard deviation shown in Table 4-6.

Table 4-6 Statistical summary of total phytosterols, ng/m^3, in SOAP 2002-2007

Site	Queens, NY	Elizabeth, NJ	Chester, NJ	Westport, CT	Bronx, NY	Pinnacle State Park, NY
Annual Mean	8.38	1.75	0.09	0.38	0.37	0.09
Standard Deviation	25.49	4.62	0.16	0.47	0.39	0.08
Range	BDL-80.92	BDL-14.88	BDL-0.41	BDL-1.41	BDL-1.13	BDL-0.26
IQR	0.58	0.52	0.16	0.59	0.42	0.13
Winter Mean	40.77	0.00	0.20	0.71	0.79	0.11
Spring Mean	0.28	0.29	0.18	0.41	0.16	0.14
Summer Mean	0.28	0.36	BDL	BDL	0.03	BDL
Fall Mean	0.29	5.30	BDL	0.26	0.19	0.09

Chester, NJ had detectable levels of phytosterols in three samples: early winter (0.41 ng/m^3), spring (0.31 ng/m^3) and the late spring (0.22 ng/m^3) for 2003 (Figure 4-24). Elizabeth, NJ had the highest concentration in fall with the total phytosterol concentration reaching over 14 ng/m^3. Phytosterols were detected throughout the summer, with a slight increase in the early fall reaching a maximum in fall (14.88 ng/m^3) followed by a decrease in late fall to non-detectable levels through winter, and an increase through spring 2003 (Figure 4-25). Queens, NY had detectable levels of the phytosterols from the late fall through the spring (Figure 4-26). Westport, CT had the maximum total phytosterol concentration in early winter (Figure 4-27); the preceding late fall and the following early spring, spring and late spring also contained phytosterols. The phytosterols in Westport, CT had a similar distribution to the n-alkanols fluctuating at the same sampling periods. In general, the phytosterols were found in the spring to fall when deciduous trees have leaves.

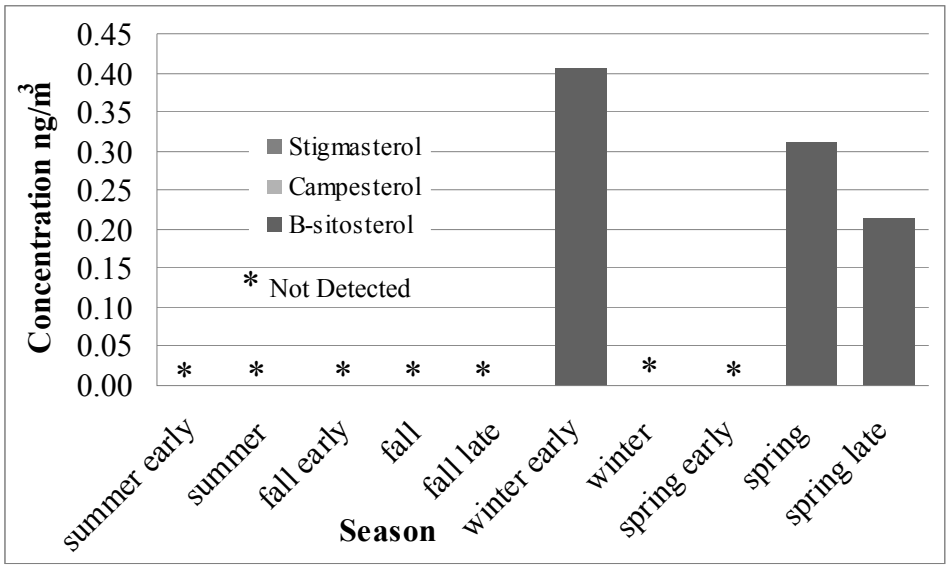


Figure 4-24 Phytosterols in Chester, NJ (SOAP 2002-2003)

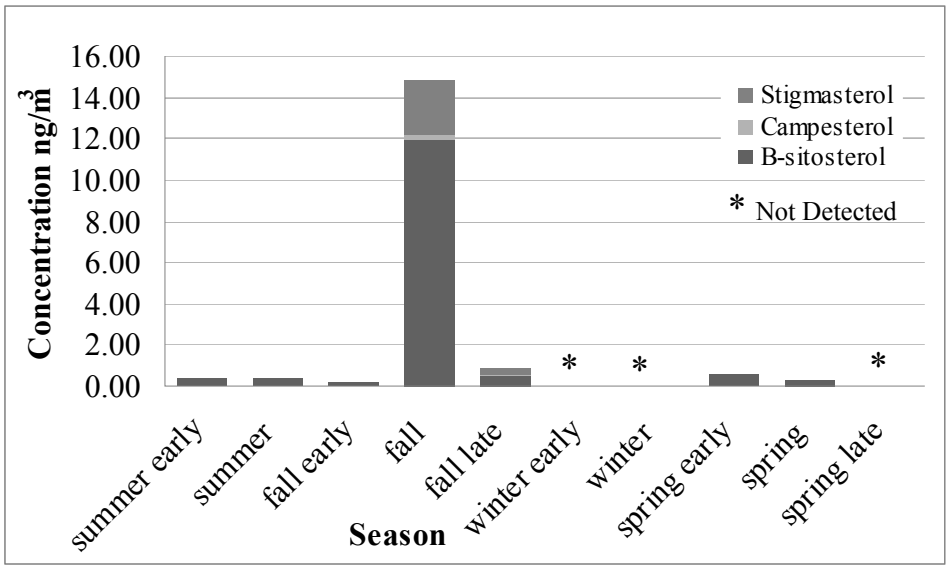


Figure 4-25 Phytosterols in Elizabeth, NJ (SOAP 2002-2003)

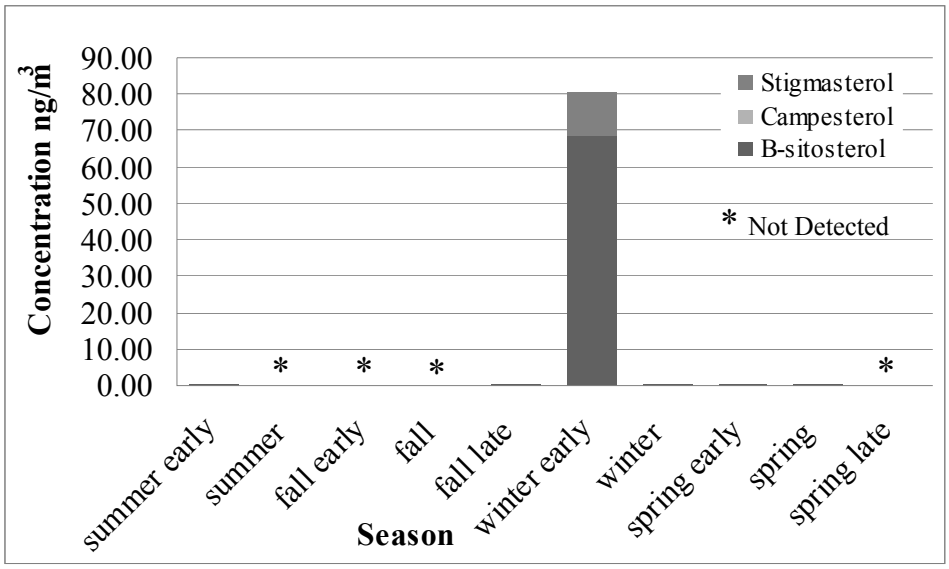


Figure 4-26 Phytosterols in Queens, NY (SOAP 2002-2003)

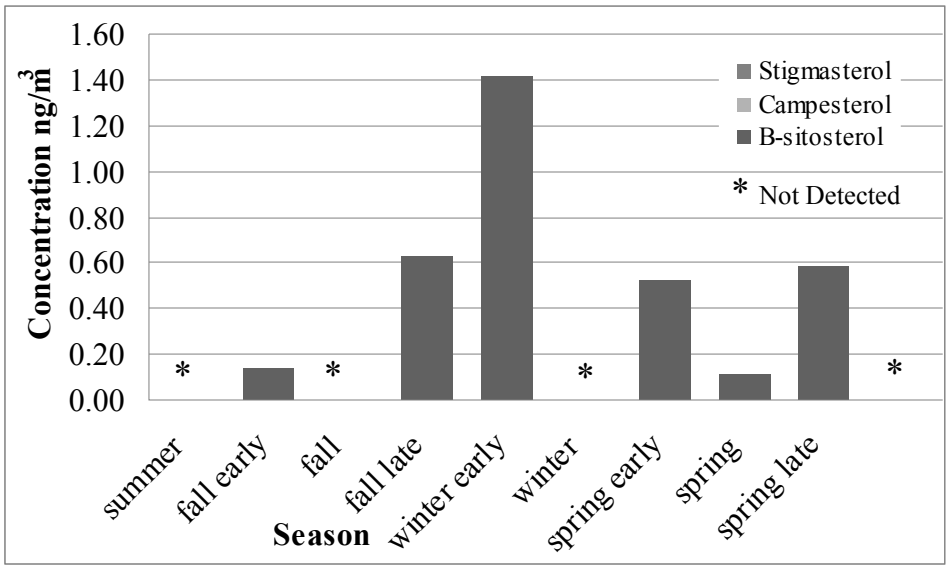


Figure 4-27 Phytosterols in Westport, CT (SOAP 2002-2003)

Phytosterols were found at Pinnacle State Park, NY for all months except summer (June to September 2006), with a maximum in March, 2006 (Figure 4-28). The phytosterols were present in the Bronx, NY, during the winter months and then randomly through the spring and summer with a small increase into the following fall and winter (Figure 4-29). An unexpected result was seen. Phytosterols concentrations were higher

in Bronx, NY (1.13 ng/m^3, February, 2006) than in the rural area of Pinnacle State Park, NY (0.26 ng/m^3, March, 2006). ANOVA tests for biogenic sources were conducted on the total n-alkanols only because the total n-alkanols were found more frequently than the phytosterols. The phytosterols were found sporadically especially in the 2002-2003 samples, making ANOVA tests not applicable.

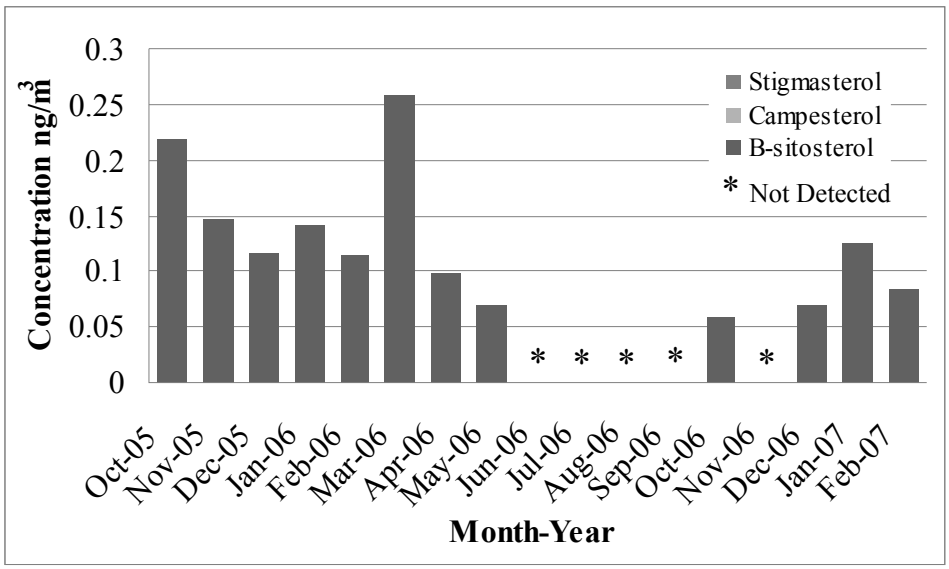


Figure 4-28 Phytosterols in Pinnacle State Park, NY (SOAP NY)

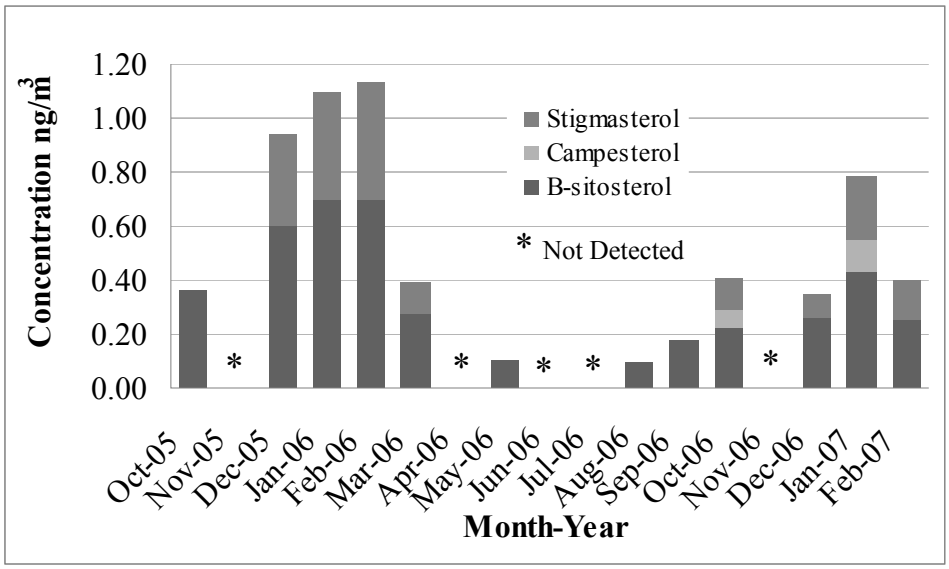


Figure 4-29 Phytosterols in Bronx, NY (SOAP NY)

4.3. *Meat Charbroiling*

Cholesterol was not found in every sample for SOAP 2002-2003 or SOAP NY. The detection level for cholesterol was 0.021 ng/m^3 for SOAP 2002-2003 and 0.011 ng/m^3 for SOAP NY. The high population sites, Elizabeth, NJ and Queens, NY, had greater cholesterol concentrations than the suburban (Westport, CT) and rural NJ (Chester, NJ) sites by approximately ten times. Chester, NJ had detectable levels in three samples: a maximum value in the winter (0.66 ng/m^3), the spring (0.04 ng/m^3) and the late spring (0.03 ng/m^3) (Figure 4-30). Elizabeth, NJ had a maximum cholesterol value in early summer (0.63 ng/m^3), followed closely by fall (0.49 ng/m^3), late fall (0.27 ng/m^3), late spring (0.42 ng/m^3), and lowest level in winter (0.23 ng/m^3) (Figure 4-31). In Queens, NY cholesterol first was detected in early fall (0.07 ng/m^3). The concentration continued to increase until it peaked in early winter (0.78 ng/m^3) then tapered off through spring (Figure 4-32). Cholesterol was detected only in two samples from Westport, CT: winter (0.07 ng/m^3) and spring (0.07 ng/m^3) (Figure 4-33).

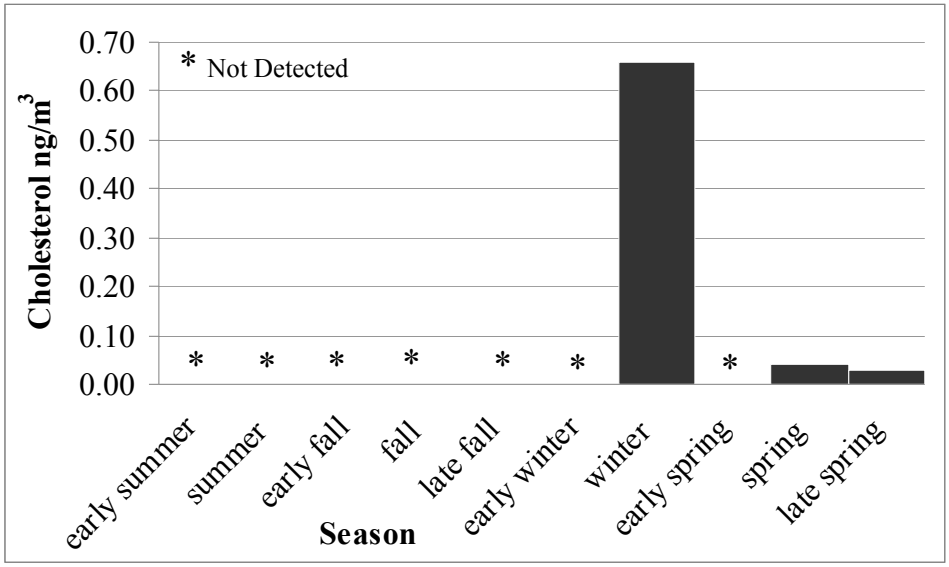


Figure 4-30 Cholesterol in Chester, NJ (SOAP 2002-2003)

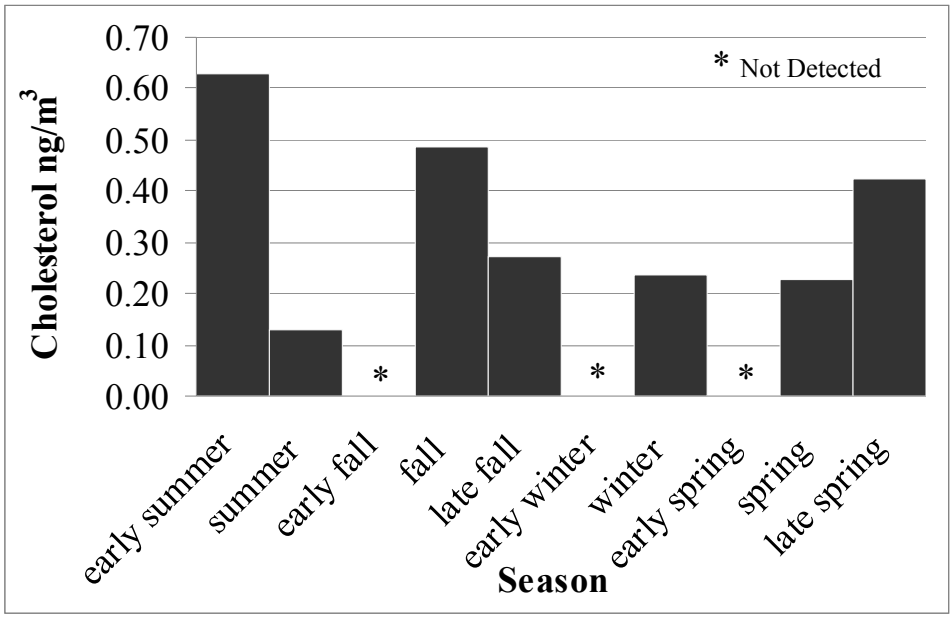


Figure 4-31 Cholesterol in Elizabeth, NJ (SOAP 2002-2003)

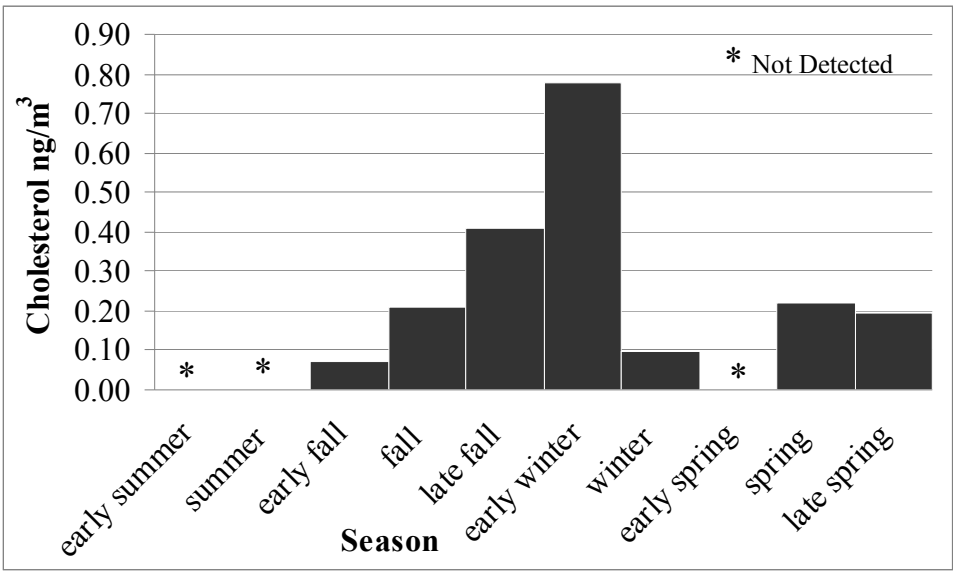


Figure 4-32 Cholesterol in Queens, NY (SOAP 2002-2003)

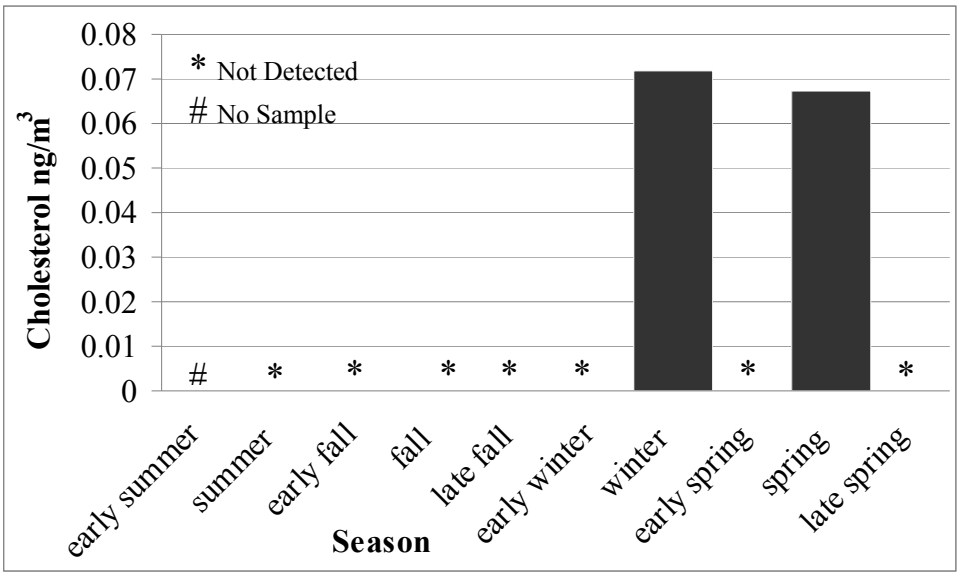


Figure 4-33 Cholesterol in Westport, CT (SOAP 2002-2003)

Single factor ANOVA tests were performed with the SOAP 2002-2003 cholesterol concentrations to determine if a statistical difference existed between ambient concentrations of the marker in early spring-summer (n=5) and early fall-winter samples (n=5) within each site. No statistical difference was found between the warm and cool months for cholesterol at any of the four sites (p-values ranged from 0.14 to 0.92). Outlier tests indicated the two Westport, CT seasons (winter and spring) were high outliers. Other high outliers were found in Queens, NY (early winter, 0.78 ng/m^3) and in Chester, NJ (winter, 0.66 ng/m^3). The results indicate cholesterol did not have seasonal variation and suggest meat cooking was a consistent emission source of fine PM in the SOAP 2002-2003 study.

Table 4-7 Statistical summary of cholesterol, ng/m^3, in SOAP 2002-2007

Site	Queens, NY	Elizabeth, NJ	Chester, NJ	Westport, CT	Bronx, NY	Pinnacle State Park, NY
Annual Mean	0.20	0.24	0.07	0.02	0.19	0.01
Standard Deviation	0.24	0.22	0.21	0.03	0.13	0.020409
Range	0.00-0.78	0.00-0.63	0.00-0.66	0.00-0.07	0.00-0.44	0.00-0.07
IQR	0.20	0.35	0.02	0.00	0.20	0.00
Winter Mean	0.44	0.12	0.33	0.04	0.28	0.01
Spring Mean	0.14	0.22	0.02	0.02	0.11	0.00
Summer Mean	0.00	0.38	0.00	0.00	0.05	0.00
Fall Mean	0.23	0.25	0.00	0.00	0.20	0.02

For SOAP NY, the rural site, Pinnacle State Park, NY, had detectable levels of cholesterol in three months, October, 2005, November, 2005 and January, 2007 (Figure 4-34). The low levels indicate meat charbroiling was not a significant contributor to the fine particle concentrations at Pinnacle State Park, NY. Cholesterol levels were fairly constant in Bronx, NY from 2005 to 2007 (Figure 4-35 and Table 4-7). The Bronx, NY samples ranged in concentration from BDL (0.01 ng/m^3) to 0.44 ng/m^3. Although there was a temporal variation in the data, the concentration range was not as broad as with wood smoke markers indicating a more constant input into the atmosphere from commercial and residential cooking. Statistical analysis also revealed no outliers at the Bronx, NY site. Unlike the Bronx, NY, the three months at Pinnacle State Park, NY where cholesterol was detected were positive outliers since the remaining months were BDL. The large difference in concentrations between the rural and urban NY sites suggests cholesterol as a good marker for urban pollution plumes.

Cholesterol was found only in the fall and winter months in the rural site of Pinnacle State Park, NY which could be due to two factors. First, Nolte et al. (2001) found cholesterol in wood smoke emission tests. Therefore, cholesterol could be emitted from fireplaces or from leaf burning in the fall. Another potential explanation is the lower height of the atmospheric mixing layer in winter, which creates a smaller volume of air to dilute the cholesterol emissions, resulting in increased concentrations.

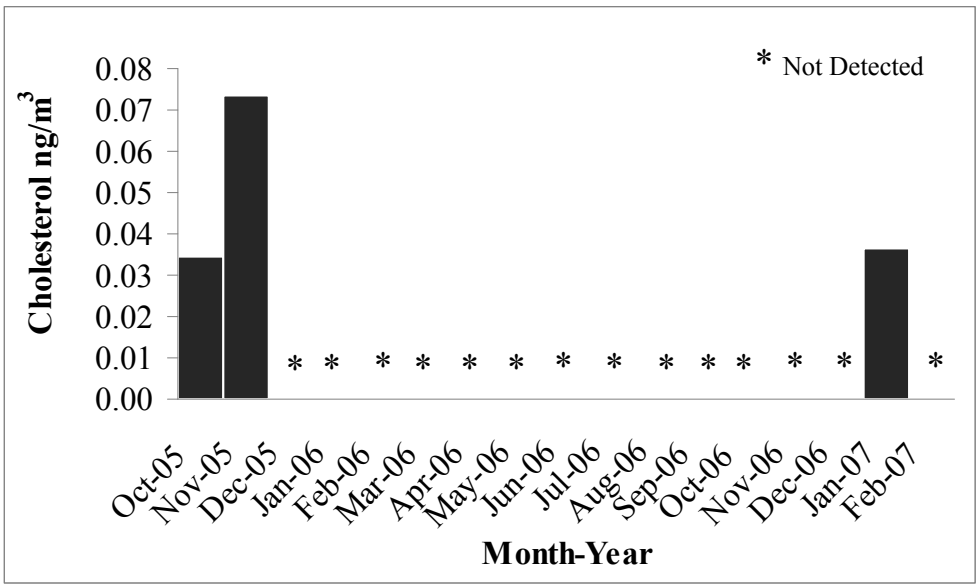


Figure 4-34 Cholesterol in Pinnacle State Park, NY (SOAP NY)

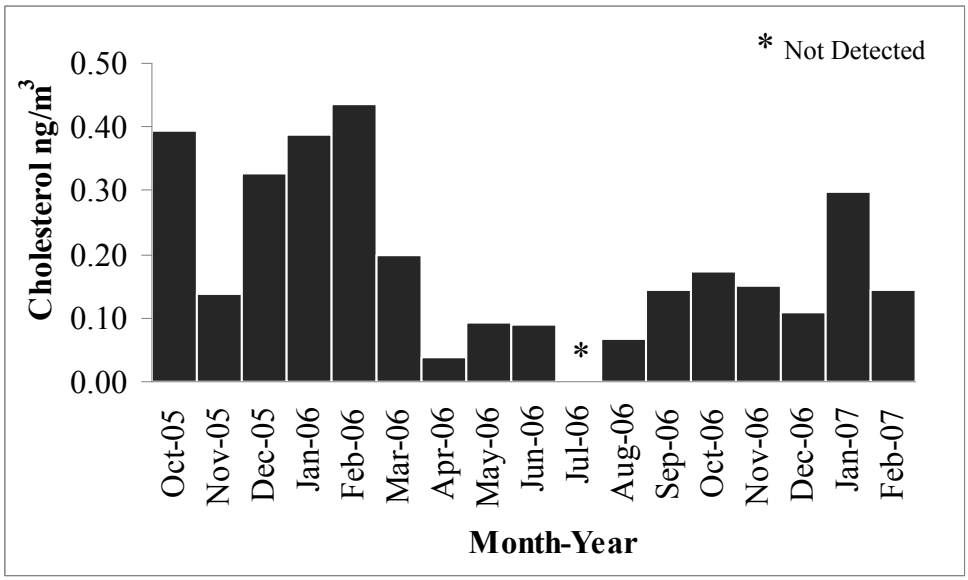


Figure 4-35 Cholesterol in Bronx, NY (SOAP NY)

ANOVA (single factor) tests were performed to determine if a statistical difference existed for cholesterol concentrations comparing the March through August samples and the September through February samples (cool months) at the SOAP NY sites. No statistical difference was found between the warm and cool periods for the cholesterol marker at Pinnacle State Park, NY (p-value = 0.22). The Bronx, NY samples had a statistically significant difference between the March through August samples and the September through February samples (p-value = 0.01). This outcome could be due to the lower mixing layer in the winter resulting in higher concentrations and to increased partitioning of cholesterol into the particle phase during cooler periods. A significant result of the outlier tests between the Bronx and Pinnacle State Park fine PM samples indicates large differences in cholesterol concentrations between urban and rural sites since all detectable concentrations at Pinnacle State Park were high outliers and were close to the detection limit. These results indicate that urban population centers upwind of Pinnacle State Park do not contribute significant $PM_{2.5}$ mass concentrations if

cholesterol is used as the diagnostic tracer. High cholesterol levels at the Bronx indicate the influence of local commercial and residential cooking operations occurring throughout the SOAP NY study period.

Additional ANOVA tests were performed on the entire suite of SOAP 2002-2007 fine PM samples to determine the statistical significance of cholesterol concentrations between the urban (Queens, NY, Elizabeth, NJ, Westport, CT and Bronx, NY) and rural (Chester, NJ and Pinnacle State Park, NY) sites for the entire year and each season. A statistical difference was found between the urban and rural sites for the entire sampling period (p-value = 0.001 and null hypothesis was there is no difference between urban and rural sites). No statistical difference was found between urban and rural sites for three (winter, spring, summer) of the four seasons at the 95% confidence level (p-values ranged from 0.06 to 0.16). Only the fall season showed a statistically significant difference between the urban and rural sites (p-value = 0.012). These results indicate consistent seasonal emissions of cholesterol from sources at the upwind background (Chester, NJ, Pinnacle State Park, NY) and urban (Elizabeth, NJ, Queens, NY, Bronx, NY, Westport, CT) over the 2002-2007 period.

4.4. *Biogenic Oxidation Product*

cis-Pinonic acid was the molecular marker used to trace secondary organic aerosols resulting from the photochemical degradation of volatile biogenic emissions, specifically from alpha-pinene. For SOAP 2002-2003, the seasonal samples from Chester, NJ had the highest levels of cis-pinonic acid in the early summer and the springtime (7.91 ng/m^3 and 5.84 ng/m^3, respectively). The concentrations were lower in the fall (5.52 ng/m^3). Non-detectable concentrations of cis-pinonic acid (detection limit =

0.04 ng/m^3) were present in summer and early fall, and early winter had a cis-pinonic acid at a concentration just below 2 ng/m^3 (Figure 4-36). Samples taken in Elizabeth, NJ had the highest concentration of cis-pinonic acid in the early summer, about 5 ng/m^3. The marker was found throughout each season, however there was a general trend of the compound decreasing from early summer through the winter, then increasing again in the spring (Figure 4-37). Queens, NY had the highest concentrations in the early summer, early fall and the spring (3.17 ng/m^3, 3.40 ng/m^3 and 3.33 ng/m^3, respectively). At this urban site, cis-pinonic acid increased in summer, decreased through the fall to non-detectable levels in winter, and then increased again in spring (Figure 4-38). Seasonal samples for Westport, CT also showed a trend that started with the highest level of cis-pinonic acid in the summer and gradually decreased through the fall into the winter, then increased in the following spring (Figure 4-39). Table 4-8 shows the variability in seasonal means. The seasonal results for the SOAP 2002-2003 fine PM samples were expected for two reasons. First, emissions of biogenic volatile organic compounds (VOCs) such as alpha-pinene are greatest during the growing season (spring through summer). Second, higher photochemical conversion rates of VOCs occur during summer due to longer days and to higher intensity of incoming solar radiation.

Table 4-8 Statistical summary of cis-pinonic acid, ng/m^3, in SOAP 2002-2007

Site	Queens, NY	Elizabeth, NJ	Chester, NJ	Westport, CT	Bronx, NY	Pinnacle State Park, NY
Annual Mean	1.53	1.61	2.78	2.55	2.82	3.65
Standard Deviation	1.46	1.95	2.77	1.80	1.33	2.50
Range	0.00-3.40	0.00-5.32	0.00-7.91	0.00-5.20	0.00-4.80	0.00-9.88
IQR	2.84	2.39	4.02	1.50	1.531002	2.709118
Winter Mean	0.29	0.88	0.07	0.88	2.21	3.04
Spring Mean	2.09	2.23	4.56	1.88	2.72	5.10
Summer Mean	2.54	2.66	3.96	5.20	3.85	1.53
Fall Mean	1.13	0.78	2.01	3.46	2.99	4.78

An ANOVA test was conducted for the four SOAP 2002-2003 sites to compare the summer-spring season versus the winter-fall samples within each site. None of the four sites showed statistically significant differences between the cool and warm seasons (p-values ranged from 0.07 to 0.83). This finding indicates biogenic oxidation products are produced year round in the northeast. The regional background level at the Chester, NJ site was lower than in the NYC metropolitan area. Therefore, the urban concentrations of cis-pinonic acid are not significantly influenced by rural background concentrations. It may be the case that higher ozone and NOx concentrations in the urban areas convert local biogenic emissions of alpha-pinene to cis-pinonic acid, hence the greater urban concentrations of this biogenic photochemical marker. Additionally in the summer and early fall Chester, NJ and Elizabeth, NJ were both BDL whereas Queens, NY, the urban site, had 1.92 ng/m^3 to 3.40 ng/m^3 cis-pinonic acid. Westport, CT, the suburban site down-wind of NYC had concentrations of 5.20 ng/m^3 and 4.70 ng/m^3 cis-pinonic acid for summer and early fall sampling periods. The emissions from urban

vegetation influenced air quality year-round as this secondary biogenic product was found in fall and winter seasons in the three urban and suburban locations. No outliers were found at any of the four sites, indicating variable seasonal concentrations consistent with vegetation growing cycles.

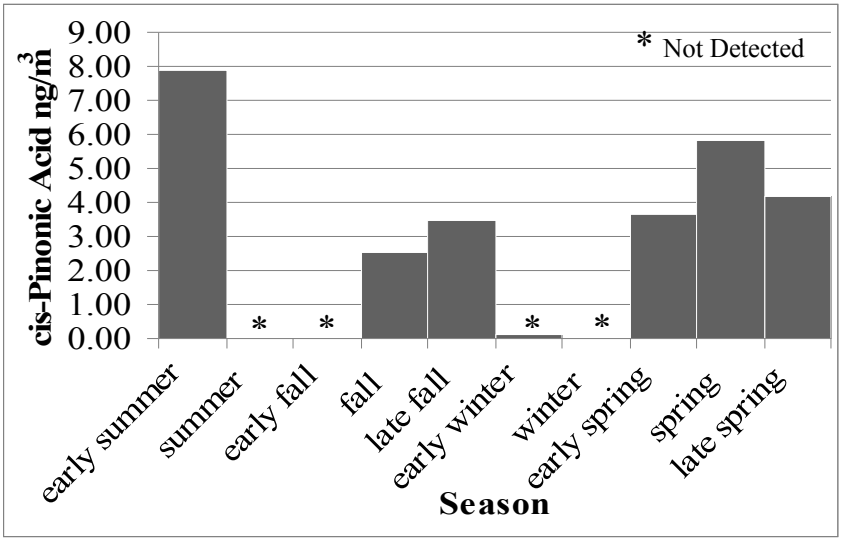


Figure 4-36 cis-Pinonic acid in Chester, NJ (SOAP 2002-2003)

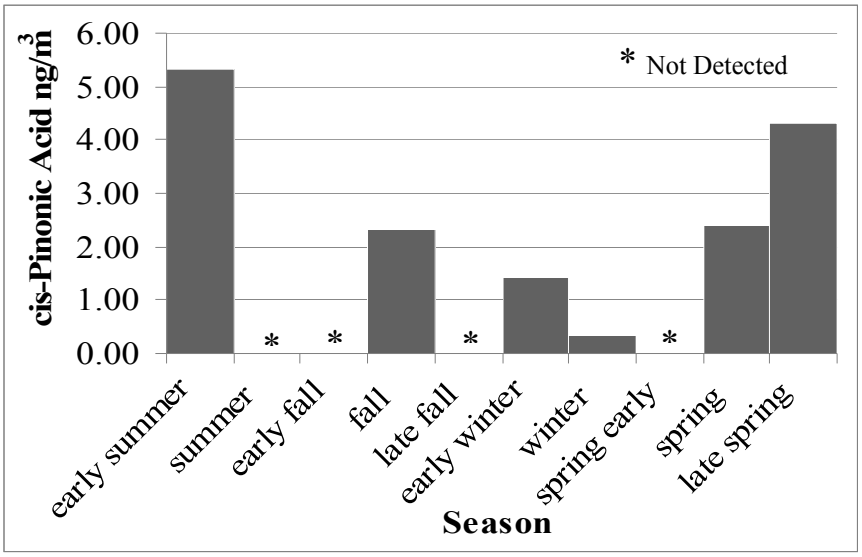


Figure 4-37 cis-Pinonic acid in Elizabeth, NJ (SOAP 2002-2003)

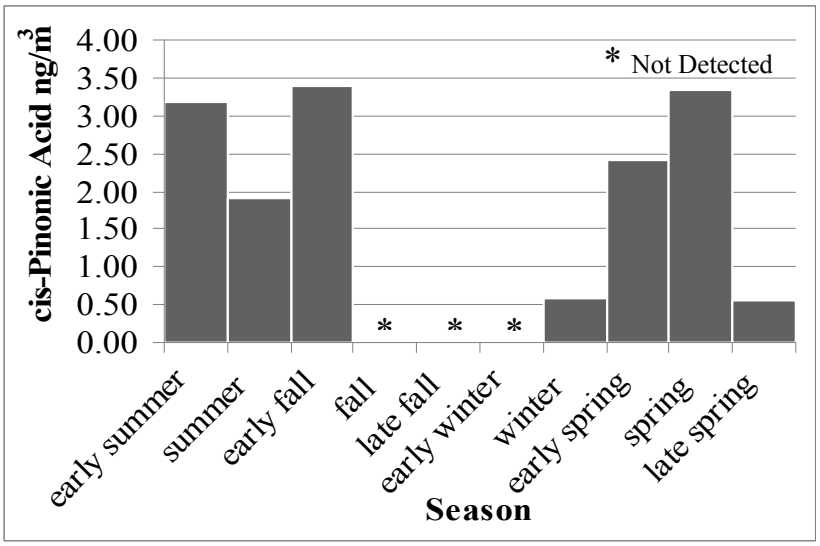


Figure 4-38 cis-Pinonic acid in Queens, NY (SOAP 2002-2003)

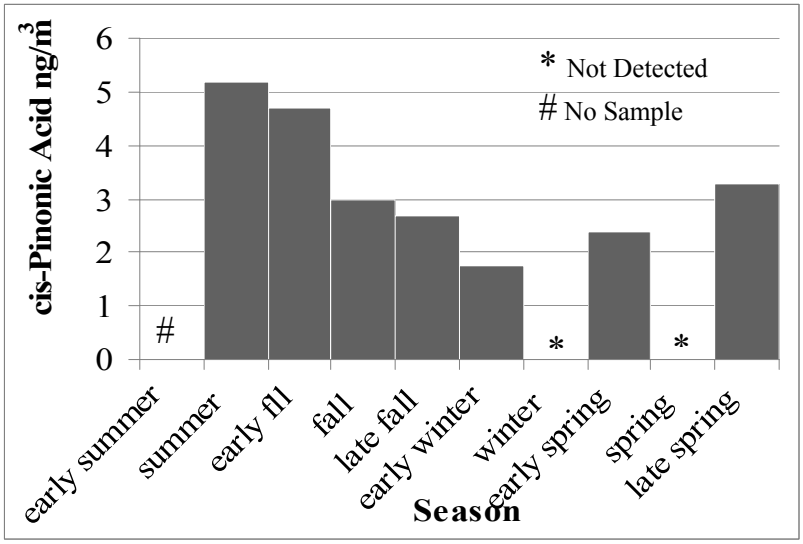


Figure 4-39 cis-Pinonic acid in Westport, CT (SOAP 2002-2003)

For the SOAP-NY field experiment, fine PM from Pinnacle State Park, NY contained variable levels of cis-pinonic acid (Figure 4-40). The trend shows a decrease through the winter with an increase in the spring. In the summer, however, cis-pinonic acid was below the detection level (0.04 ng/m^3). The absence of cis-pinonic acid is unusual in such a rural location and could be due to meteorological conditions resulting

in deep atmospheric mixed layers and low particle concentrations. In fall the marker was present and decreased through the winter (Figure 4-40). Bronx, NY samples show a seasonal trend that increased in spring (4.16 ng/m^3 in May, 2006), was steady through the summer (3.73 ng/m^3 in July, 2006), and then decreased in the fall and winter (1.16 ng/m^3 in February, 2007). The concentration of cis-pinonic acid was highest at Pinnacle State Park, NY (9.88 ng/m^3, November, 2006) when comparing all six SOAP 2002-2007 sites. The lowest cis-pinonic acid concentrations were found in Bronx, NY and Queens, NY with levels of approximately 4 ng/m^3. The combination of regional background concentrations of cis-pinonic acid with advection into the urban sites and native and cultivated vegetation within the urban centers could account for the consistent presence of the cis-pinonic acid marker at the NY City SOAP monitoring sites.

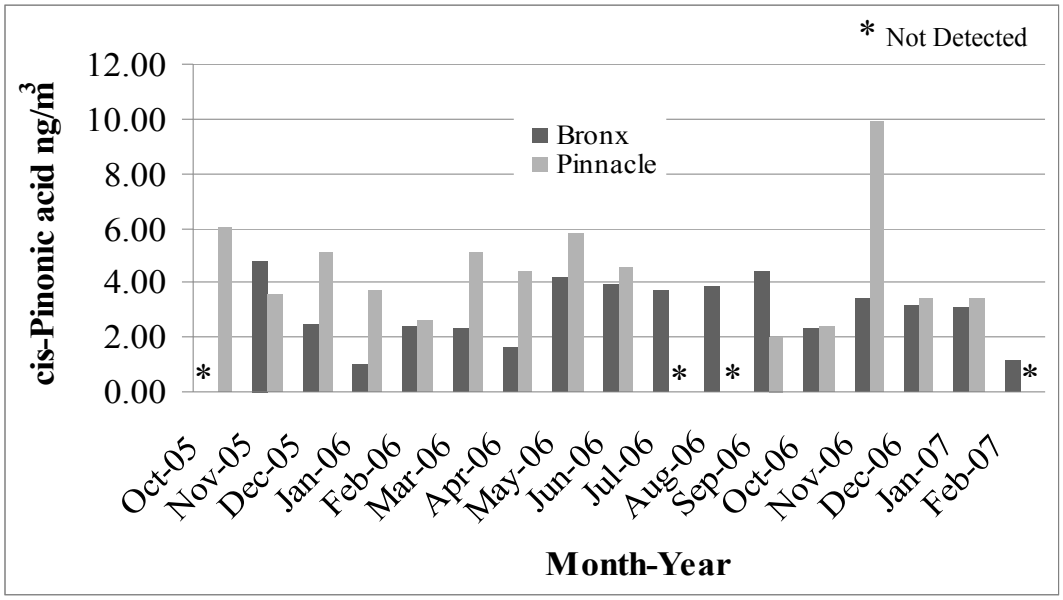


Figure 4-40 cis-Pinonic acid in NY (SOAP NY)

An ANOVA test was conducted for the two SOAP NY sites to compare the summer-spring months versus the winter-fall months within each site. No statistical difference was seen at the 95% confidence level between the cold and warm months for

either site (p-value = 0.30 in Bronx, NY and p-value = 0.70 in Pinnacle State Park, NY). These results were the same as those for the four SOAP 2002-2003 sites, indicating this marker was present year round. An outlier test showed the November 2006 for Pinnacle State Park, NY was a high outlier.

Additional ANOVA tests (one parameter) were performed to determine the statistical significance of cis-pinonic acid concentrations at the SOAP 2002-2007 urban sites (Queens, NY, Elizabeth, NJ, Westport, CT and Bronx, NY) versus the upwind rural sites (Chester, NJ and Pinnacle State Park, NY) for the entire year and for each season. Statistical differences resulted between urban and rural sites for the entire year (p-value = 0.03) and for the spring season (p-value = 0.001). No statistical difference was found between the urban and rural sites for the remaining three seasons (summer, p-value = 0.56; fall, p-value = 0.16; winter, p-value = 0.24) at the 95% confidence level.

4.5. *Low Molecular Weight Highly Oxidized Acids*

In the SOAP 2002-2003 and in the SOAP NY field campaigns levulinic acid was the dominant oxoacid found in the ambient samples followed by 4-acetylbutyric acid (Appendix F). The two compounds are markers for photochemically oxidized volatile organic compounds referred to as “secondary organic aerosols” (SOA). The detection limits for the SOAP 2002-2003 campaign were levulinic acid = 0.068 ng/m^3, 4-acetylbutyric acid = 0.032 ng/m^3, oxalacetic acid = 6.81 ng/m^3, pyruvic acid = 4.65 ng/m^3 and glyoxylic acid = 13.94 ng/m^3. The compounds were present in four seasons in Chester, NJ: early summer, late fall, spring and late spring. Although the five organic acids were not detected in the majority of the Chester, NJ samples, the plot indicates a general trend of maximum concentrations in the early summer (21.00 ng/m^3, levulinic

acid), decreasing through the fall and winter and then increasing in the spring (Figure 4-41). Levulinic acid and 4-acetylbutyric acid were found in Queens, NY in the winter and spring seasons, but not in the fall or the summer (Figure 4-43). The peak concentrations occurred in early winter and in the early spring when concentrations reached 10 ng/m^3. This is not the expected result for a compound produced by in-situ photo-oxidation unless the higher levels of oxidants present in summer and early fall converted these markers to other compounds. The Westport, CT site had non-detectable levels for all the SOA markers in the summer (Figure 4-44). Pyruvic acid was detected only once (summer, Queens, NY) and oxalacetic acid was detected only once (early fall, Queens, NY). Both of these incidences were determined to be outliers. It should be noted that pyruvic and glyoxylic acids are highly polar compounds which may not be fully soluble in the methylene chloride:acetone (1:1) extraction solvent. Filter aliquots would need to be extracted in methanol and evaluated by GCMS to determine the remaining mass fractions on the sample collection filters. This is future work, if funded.

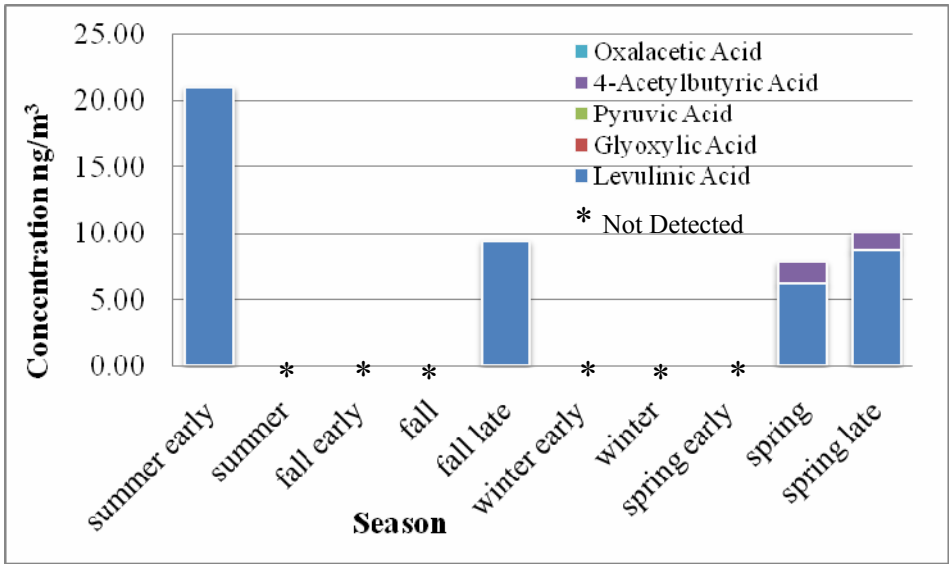


Figure 4-41 Oxoacids in Chester, NJ (SOAP 2002-2003)

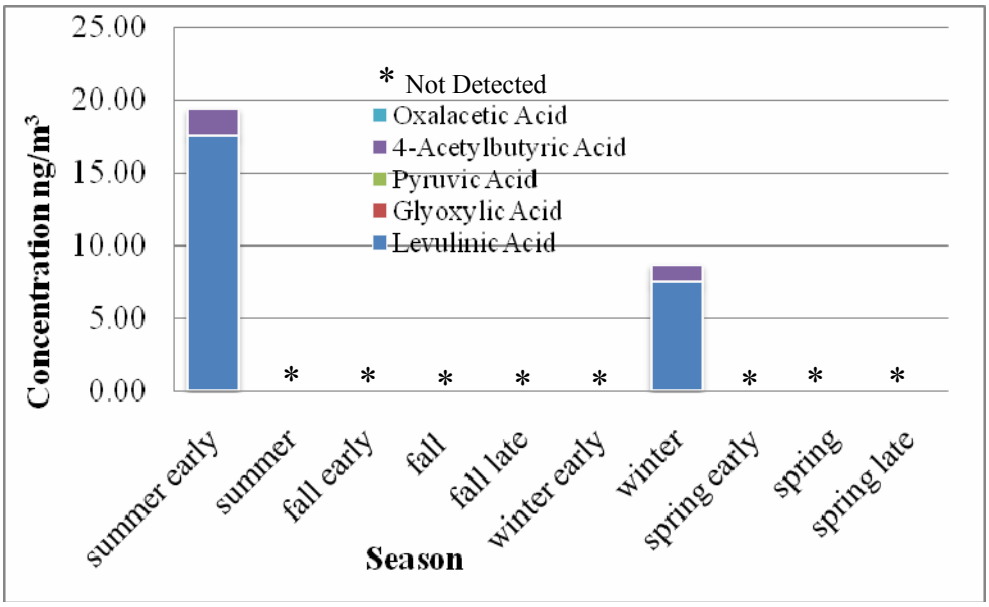


Figure 4-42 Oxoacids in Elizabeth, NJ (SOAP 2002-2003)

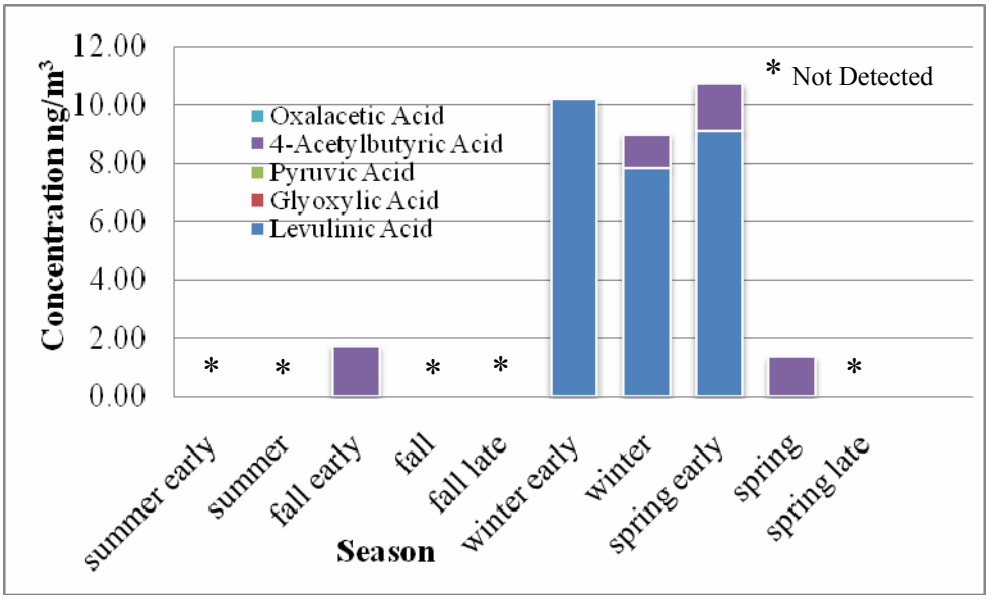


Figure 4-43 Oxoacids in Queens, NY (SOAP 2002-2003)

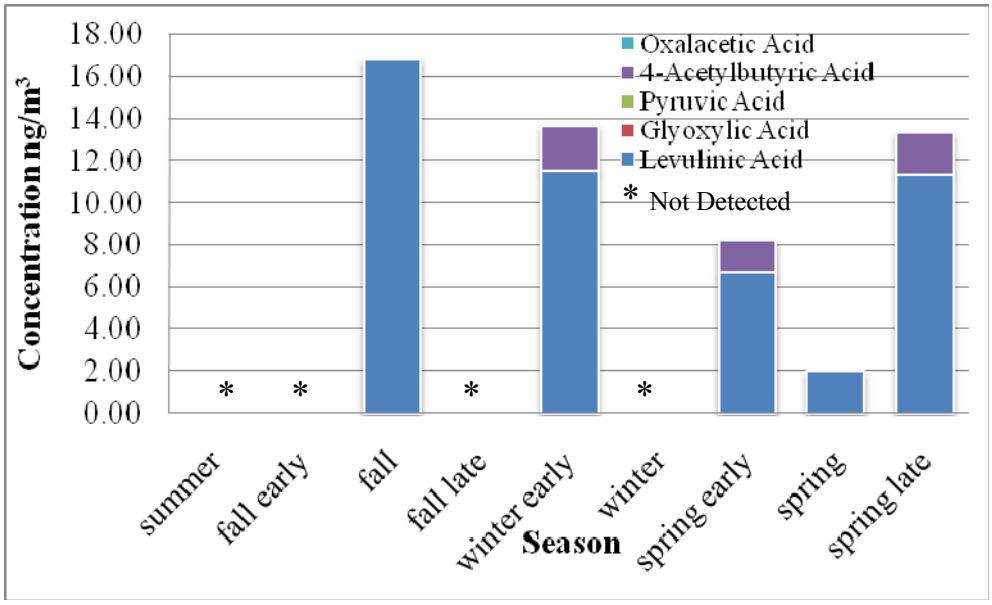


Figure 4-44 Oxoacids in Westport, CT (SOAP 2002-2003)

ANOVA tests (single factor) were conducted on the levulinic acid concentrations to determine if a statistical difference was present between early spring-summer and the early fall-winter within each site. Levulinic acid was chosen for this analysis because it was the only oxoacid with detectable levels. The average concentration was higher in the cooler months than in the warmer months. This could be due to the mixing layer height, but also indicates a year round input of levulinic acid into the atmosphere. There was no statistical difference between the warm and cool months for levulinic acid at any of the four SOAP 2002-2003 sites (p=values ranged from 0.25 to 0.89). Outlier tests were conducted on levulinic acid. Two seasons in Elizabeth, NJ had quantifiable levels of levulinic acid (early summer and winter). Both were outliers compared to the BDL levels for the remainder of the SOAP 2002-2003 sampling period. A high outlier was found in Chester, NJ in the early summer (21.00 ng/m^3).

In the Bronx, NY SOAP 2005-2007 samples, seasonal concentrations of levulinic acid consistently were higher than in Pinnacle State Park, NY (Figure 4-45 and Figure

4-46). Levulinic acid was the dominant acid at both sites along with lower concentrations of 4-acetylbutyric acid. Levulinic acid was found without 4-acetylbutyric acid present; however, 4-acetylbutyric acid was not observed without levulinic acid present in the sample. There were only two months, January and February of 2006, when levulinic acid was not detected in the Bronx, NY. Levulinic acid was present in January and February 2007. The general trend indicated by plotting the concentration versus month is a decrease in winter, increase during spring to a peak in the summer followed by a decrease in the fall and winter. Pinnacle State Park, NY samples contained levulinic acid in every month from October, 2005 to February, 2007. The concentrations generally were constant through the fall and winter (5.34 ng/m^3 in January, 2006), increased in the spring to a high in May, 2006 (13.22 ng/m^3), decreased through the summer until October, 2006 (4.40 ng/m^3), and then increaseed again in the late fall and winter (5.16 ng/m^3 in January, 2007). This seasonal pattern is consistent with photochemical production and destruction during the spring and summer months with fairly stable concentrations in the fall and winter months when insolation is weakest.

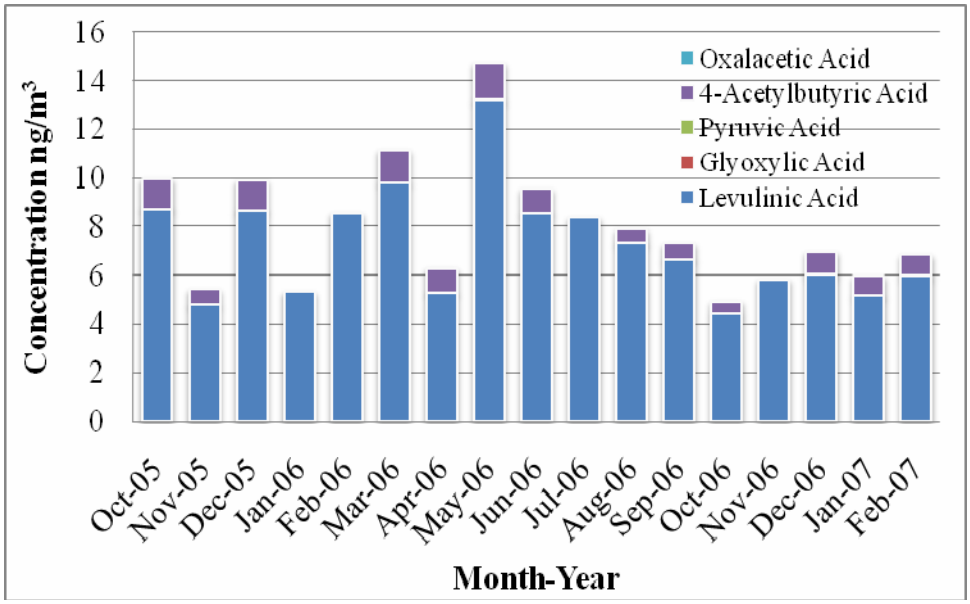


Figure 4-45 Oxoacids in Pinnacle State Park, NY (SOAP NY)

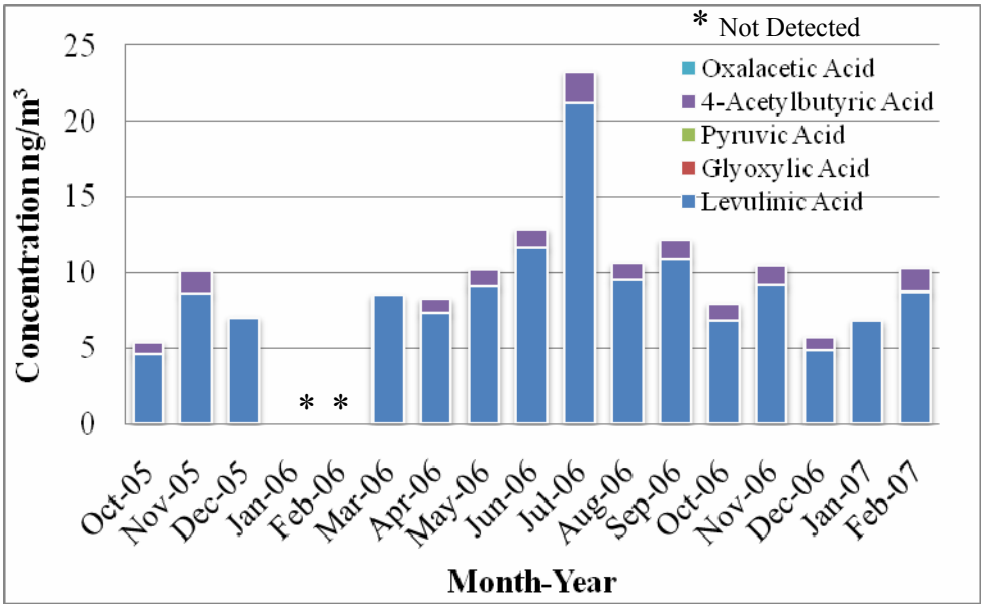


Figure 4-46 Oxoacids in Bronx, NY (SOAP NY)

ANOVA tests (single factor, alpha = 0.05) were conducted on the levulinic acid concentrations to determine if a statistical difference existed between March through August (2006) samples and September through February (2005, 2006 and 2007) at Pinnacle State Park, NY and Bronx, NY at the 95% confidence level. A statistical

difference was found between the warm and cool months for levulinic acid at both sites (p-value = 0.03 at Bronx, NY and p-value = 0.03 at Pinnacle State Park, NY). The two sites had higher average concentrations of levulinic acid in the warmer months indicating a seasonal difference (Table 4-9). An outlier test indicated a high outlier for the Bronx, NY July, 2006 sample.

Table 4-9 Statistical summary of levulinic acid, ng/m^3, in SOAP 2002-2007

Site	Queens, NY	Elizabeth, NJ	Chester, NJ	Westport, CT	Bronx, NY	Pinnacle State Park, NY
Annual Mean	2.71	2.50	4.54	5.35	7.95	7.23
Standard Deviation	4.40	5.78	6.98	6.44	4.72	2.27
Range	0.00-10.19	0.00-17.54	0.00-21.00	0.00-16.82	0.00-21.23	4.40-13.22
IQR	5.88	0.00	8.12	11.31	2.35	3.23
Winter Mean	9.01	3.71	0.00	5.72	4.57	6.63
Spring Mean	3.03	0.00	4.99	6.63	8.33	9.45
Summer Mean	0.00	8.77	10.50	0.00	14.15	8.10
Fall Mean	0.00	0.00	3.14	5.61	8.05	6.09

Additional ANOVA tests were performed for the SOAP 2002-2007 combined field studies to determine the statistical significance for levulinic acid $PM_{2.5}$ mass concentrations at urban (Queens, NY, Elizabeth, NJ, Westport, CT and Bronx, NY) versus rural (Chester, NJ and Pinnacle State Park, NY) sites for the entire year and each season. No difference was found between urban and rural sites for the entire year or any of the four seasons at the 95% confidence level (p-values ranged from 0.25 to 0.83 as shown in Appendix I), unlike cis-pinonic acid, the molecular marker for biogenic

oxidation products. These results imply that levulinic acid may originate from primary and secondary sources of atmospheric fine PM that may be biogenic or anthropogenic.

4.6. *$PM_{2.5}$ Mass Balance*

The material mass balances for the SOAP 2002-2003 and the SOAP NY fine particle samples were calculated using the analytical data reported by the Speciation Trends Network which operated in parallel with the two SOAP field programs. STN $PM_{2.5}$ mass, ammonium, nitrate, sulfate and inorganics ambient mass concentrations were summed and then added to the ambient mass concentrations for OC and EC measured on the SOAP filters (Appendix J). The OC and EC values used in the mass balance were derived from the EC and OC from the SOAP filters rather than the STN OC and EC mass concentration because of the known low to nondetectable OC background levels associated with the SOAP (Rutgers) carbonaceous PM sampling and analysis procedures The mass balance was the $PM_{2.5}$ mass concentration comprised of the inorganic constituents, EC and OC, and the remainder was characterized as “other” (bound water and cumulative analytical errors) (Figure 4-47 and Figure 4-48).

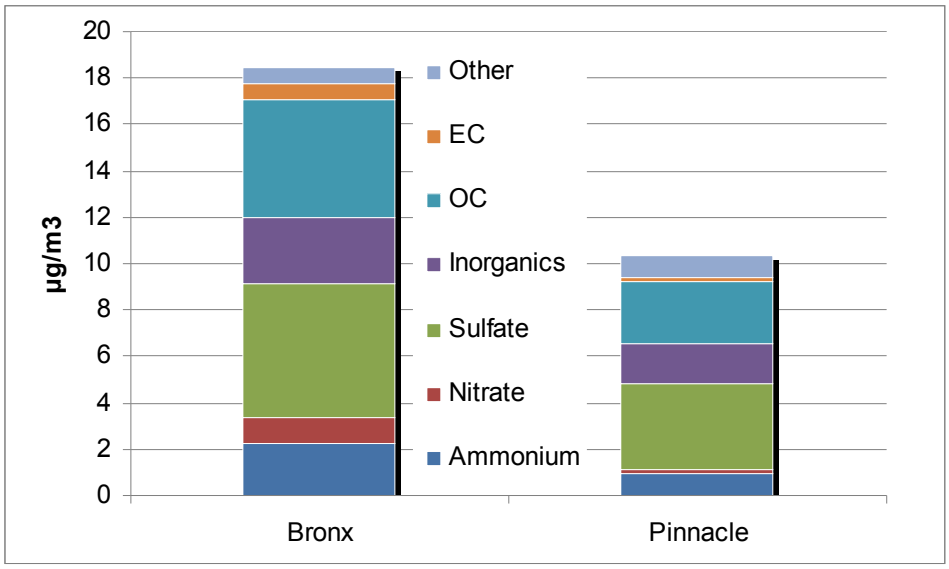


Figure 4-47 Summer $PM_{2.5}$ Mass Balance for SOAP NY

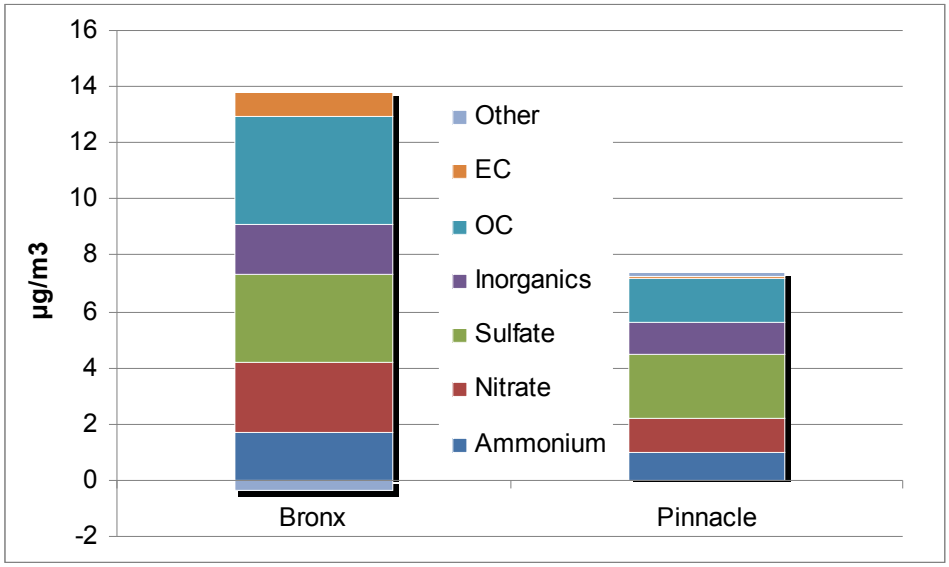


Figure 4-48 Winter $PM_{2.5}$ Mass Balance for SOAP NY

The OC mass is multiplied typically by a factor of 1.4 to account for the higher mass of heteroatoms, such as O and N, in the molecule. The estimated error is the "other" divided by the $PM_{2.5}$ mass and multiplied by 100%. The estimated percent error had to be less than 20% compared to the measured $PM_{2.5}$, an independent measure in order to be an acceptable materials mass balance. Standard cumulative measurement

errors < 20% are accepted practice in environmental applications. The total bulk species masses plus associated water mass should equal the measured total $PM_{2.5}$ mass.

The material mass balance analysis was conducted with four OC mass conversion factors: no factor (i.e. 1.0), 1.4, 1.8 and 2.0. The values for each $PM_{2.5}$ composite were averaged into one yearly composite for every site. The OC conversion factor was 1.4 for the urban locations (Elizabeth, NJ, Queens, NY, Westport, CT and Bronx, NY). The percent error for the 1.4 conversion factor for the urban sites ranged from 5.56% in Bronx, NY to 15.05% in Queens, NY. The conversion factor for Pinnacle State Park, NY ranged from 1.4 to 1.8 with corresponding percent errors of 6.03 % to 16.53%, respectively. The yearly mass balance in Chester, NJ proved difficult. The mass balance ended with a residual "other" category of -1.2 $\mu g/m^3$ which indicated that 113% of the measured $PM_{2.5}$ mass was accounted for by the separate organic and inorganic chemical analyses. The +13% extra mass is an indication of the cumulative analytical errors contributed by the multiple chemical measurements. Rogge et al. (1993b) also conducted mass balances in the same manner. The "other"category was near 20% of the $PM_{2.5}$ mass for the year 1982 in West Los Angeles, CA and Rubidoux, CA; however, inorganics were not included in the mass balance. Inorganics were included in the $PM_{2.5}$ mass balances for this study which may account for the differences in relative percent of "other" to $PM_{2.5}$ mass. The relatively lower "other" category in this study shows perhaps improved analytical chemical methods now applied compared to the 1982 mass balance methods used by Rogge et al. (1993b).

The mass balances also were determined for seasonal composites for all six SOAP sites. The seasonal composites were: summer (June, July, August); fall (September,

October, November): winter (December, January, and February); and spring (March, April, May). The seasonal averages did not show any trends. The OC seasonal and yearly average conversion factors were the same and did not appear to be influenced by the presence of SOAs. SOAs tend to have more oxygen and therefore, would require a higher mass conversion factor (1.8 or greater) to account for the additional oxygen atoms present in an "oxidized" organic compound. That was not found in this study. A $PM_{2.5}$ mass balance also was conducted on each 24-hour (daily) sample, with similar results to the summarized yearly and seasonal averages. Appendix J contains the supplemental material for these $PM_{2.5}$ material mass balance analyses.

5. Discussion

This chapter is a discussion of the results from the analysis of fine PM in the NYC metropolitan area and upwind rural sites. It is separated into several sections. Each present a different analysis on the data presented in the preceding sections. The first section is a comparison to other studies which used the same molecular markers and similar sample collection and chemical analysis methods to evaluate urban and biogenic emission sources of airborne particles (either $PM_{2.5}$ or PM_{10}). The focus is on U.S. studies, however if U.S. studies were not available than international studies were used. Emission estimates are then presented based on source emission test data. Selected ambient data were normalized and correlated to EC and OC (Appendix K and Appendix L). The same marker compounds then were normalized and correlated to $PM_{2.5}$ (Appendix M).

5.1. *Comparison to Other Studies*

5.1.1. Wood smoke

In the SOAP 2002-2007 field campaigns, levoglucosan showed maximum ambient concentrations in the late fall to early winter, or November into December and lower values in the warmer months. During the cooler periods in the northeastern United States, wood burning fireplaces and stoves are used for residential heating (NESCAUM, 2008).

In the U.S., Medeiros et al. (2006) studied bulk aerosols over the Howland Experimental Forest, Maine over the summer months (2002) and found levoglucosan at concentrations of 4.0 to 6.8 ng/m^3 except when a Canadian wildfire plume passed over

the site. PM_{10} measurements include resuspended soil particles which have been shown to contain markers for soil and fungal groups whereas $PM_{2.5}$ measurements exclude these groups (Herckes et al., 2006). Levoglucosan was shown to partition into the fine fraction (Herckes et al., 2006), so the Medeiros et al. (2006) study and the SOAP results are not directly comparable, however the studies do show the influence wood smoke can have on an air shed from sources hundreds of miles upwind.

Nolte et al. (2001) collected $PM_{2.5}$ samples in three locations in California during winter 12/5/1995 to 1/6/1996. The ambient concentrations of levoglucosan for the San Joaquin Valley, Bakersfield and Fresno were 106, 2390 and 2980 ng/m^3, respectively. Gorin et al. (2006) collected a $PM_{2.5}$ sample from Fresno, CA between 12/25/2003 and 1/15/2004, which had a concentration of 600 ng/m^3. These winter concentrations of levoglucosan were ten times higher compared to the SOAP samples collected in the NYC metropolitan area. The California studies did not provide yearlong trends as discussed in the SOAP studies and there is no data for the late fall (November) time frame when the NYC area showed its highest levels of levoglucosan. Reasons for the higher levoglucosan levels in CA studies could be due to differences in wood smoke emissions from residential sources in rural communities, agricultural practices in the Central Valley of CA, and to meteorological factors in winter (shallow mixed layers due to ground inversions). Also, both CA studies were not continuous and did not provide information on the seasonal emissions from wood combustion. Fine et al. (2004) collected fine PM samples from central Los Angeles, CA in January, 2003. The urban winter values from this study were comparable to the NYC study and both samples were collected in the same time frame (January, 2003).

In the southeastern U.S. the average levoglucosan concentration was 433.4 ng/m^3 from January 2 to 31, 2002 in Atlanta, GA (Zheng et al., 2007). This also was higher by a factor of at least two compared to those measured in NYC area in either the SOAP 2002-2003 or the SOAP NY projects. Sheesley et al. (2007) studied four sites in NC in 2003 and 2004. The winter values were a factor of two higher compared to the NYC area. The NC samples were composited differently than the NYC samples and this may account for some of the variation between NC and NYC.

The summer levoglucosan concentrations found in SOAP NY were similar to those found in Los Angeles, CA (Fine et al., 2004) and Pittsburgh, PA (Robinson et al., 2006) (Table 5-1 and Table 5-2). The summer SOAP 2002-2003 levoglucosan concentrations were similar to the Atlanta, GA samples (Zheng et al., 2007) and four of the six NC samples (Sheesley et al., 2007).

Table 5-1 U.S. winter time levoglucosan concentrations

Reference	Study Period	Levoglucosan, ng/m^3
Fine et al. (2004)	Los Angeles, CA (1/13-1/17/2003)	44
Robinson et al. (2006)	Pittsburgh, PA (12/2001-1/2002)	26
Sheesley et al. (2007)	Charlotte, NC (Mid-October – December, 2003)	196
Sheesley et al. (2007)	Charlotte, NC (Mid-October – December, 2004)	519
Sheesley et al. (2007)	Hickory, NC (Mid-October – December, 2003)	329
Sheesley et al. (2007)	Hickory, NC (Mid-October – December, 2004)	198
Sheesley et al. (2007)	Winston-Salem, NC (Mid-October – December, 2003)	240
Sheesley et al. (2007)	Lexington, NC (Mid-October – December, 2004)	504
Nolte et al. 2001	San Joaquin Valley, CA (12/5/1995-1/6/1996)	106
Nolte et al. 2001	Bakersfield, CA (12/5/1995-1/6/1996)	2390
Nolte et al. 2001	Fresno, CA (12/5/1995-1/6/1996)	2980
Gorin et al. 2006	Fresno, CA (12/25/03-1/15/04)	600
Zheng et al. (2007)	Atlanta, GA (1/2/2002-1/31/2001)	433.41
This Study	Queens, NY (winter)	37.66
This Study	Elizabeth, NJ (winter)	6.66
This Study	Chester, NJ (winter)	24.18
This Study	Westport, CT (winter)	120.89
This Study	Bronx, NY (January, 2006)	84.27
This Study	Pinnacle State Park, NY (January, 2006)	113.04
This Study	Bronx, NY (January, 2007)	85.58
This Study	Pinnacle State Park, NY (January, 2007)	45.53

Table 5-2 U.S. summer levoglucosan concentrations

Reference	Study Period	Levoglucosan, ng/m^3
Fine et al. (2004)	Los Angeles, CA (8/12-8/16/2002)	7
Fine et al. (2004)	Riverside, CA (8/26-8/30-2002)	7
Robinson et al. (2006)	Pittsburgh, PA (7/2001)	10
Sheesley et al. (2007)	Charlotte, NC (June –mid-October, 2003)	28.3
Sheesley et al. (2007)	Charlotte, NC (June –mid-October, 2004)	79.5
Sheesley et al. (2007)	Hickory, NC (June –mid-October, 2003)	55.5
Sheesley et al. (2007)	Hickory, NC (June –mid-October, 2004)	202
Sheesley et al. (2007)	Winston-Salem, NC (June –mid-October, 2003)	53.2
Sheesley et al. (2007)	Lexington, NC (June –mid-October, 2004)	117
Zheng et al. (2007)	Atlanta, GA (7/3/2001-8/4/2001)	45.60
Brown et al. (2002)	Big Bend National Park, TX (7/12/1999-10/19/1999	0.09
Engling et al. (2006)	Yosemite National Park, CA (7/14/2002-9/5/ 2002)	nd[1] to 50
This Study	Queens, NY (summer)	23.24
This Study	Elizabeth, NJ (summer)	55.28
This Study	Chester, NJ (summer)	25.15
This Study	Westport, CT (summer)	3.36
This Study	Bronx, NY (July, 2006)	7.31
This Study	Pinnacle State Park, NY (July, 2006)	7.36

[1]nd – not detected

The presence of levoglucosan in the rural and urban locations measured in the U.S. during the winter periods indicates residential heating is a significant source of fine PM to these airsheds. However, the SOAP 2002-2007 and the summer field studies in NC (Sheesley et al., 2007) indicate that combustion of wood and other cellulosic materials contribute to fine PM mass year-round in these metropolitan areas. Sources such as open refuse and yard waste burning and trash combustion may also be likely activities. In addition, urban summertime levels of levoglucosan might also have some

input from charcoal barbecue grills. Charcoal is produced from the carbonization, or pyrolysis, of biomass in a kiln at temperatures near 650 and 750 K (Antal et al., 1990; Demirbas, 2000). The biomass used can consist of hardwoods or softwoods, which are composed of cellulose, hemicellulose and lignins. Typical charcoal briquettes are from crushed charcoal combined with a binder, usually a starch (Antal et al., 1990; Demirbas, 2000). Starch is a polysaccharide consisting of D-glucose units and therefore, would release levoglucosan when burned (Lehninger, 1975). As a wood product derivative, charcoal used for cooking also is a possible source of levoglucosan emissions. Structural fires also contribute wood smoke fine PM in urban areas. This is a separate source emission category in State Implementation Plans (SIPs) for the control of fine particles, although the source strengths are weak estimates in most state emission inventories (NJ DEP, 2006; NARSTO, 2003). All of the above fugitive sources contribute episodic and uncertain levels of levoglucosan to urban airsheds. The emissions also may be highly localized. In the summer of 2006 there was not a significant increase in levoglucosan ambient mass concentrations in Bronx, NY compared to the summer 2002 concentrations in Queens, NY and Elizabeth, NJ. However, unexpected high concentrations occurred in summer 2002 in Queens, NY which was some mix of apparently localized emissions such as combustion of wood, refuse, and structures, and charcoal grilling.

5.1.2. Plant Waxes

Surface waxes from vegetation consisting of n-alkanols and phytosterols have been measured worldwide in atmospheric particulate matter for over two decades (Simoneit and Mazurek, 1982; Simoneit et al., 1981; Rogge et al., 1993). In urban atmospheres these marker compounds are an indication of primary particulate matter

emissions from biogenic sources. Biogenic contributions to the atmosphere depend on location such desert, urban or forest, which are described in detail in Chapter 2 (Simoneit and Mazurek, 1982; Simoneit et al., 1981; Rogge et al., 1993). Therefore, comparisons to studies outside of the northeast are difficult due to differences in vegetation. Atmospheric aerosol studies in the northeast, however, do not report biogenic markers such n-alkanols and phytosterols. Li et al. (2006) studied PM_{10} in Philadelphia, PA but did not measure n-alkanols or phytosterols. Instead n-alkanes were measured and the carbon preference index was reported as an estimate of plant wax particulate matter.

Table 5-3 compares winter concentrations of n-alkanols and phytosterols quantified in the SOAP 2002-2007 field studies with the n-alkanols and phytosterols quantified in Nolte et al. (2001). Nolte et al. (2001) is shown here because it also compared urban and rural locations in the U.S. Nolte et al. (2001) evaluated samples at three sites (urban and rural) in southern California for biogenic emissions and found that the urban locations had higher concentrations of n-alkanols and of phytosterols than the rural location. The Elizabeth, NJ site had a high concentration in the fall of 11.9 ng/m^3 of β-sitosterol which was similar to the winter concentrations in the urban locations (23 ng/m^3 and 20 ng/m^3) of the Nolte et al. (2001) study. The remaining three sites, Queens, NY, Chester, NJ and Westport, CT, had (0.62 ng/m^3, 0.41 ng/m^3, 1.41 ng/m^3, respectively) similar to the rural locations in the Nolte et al. (2001) study (0.5 ng/m^3). The β-sitosterol concentrations found in Bronx, NY and Pinnacle State Park, NY were less than 1 ng/m^3, therefore corresponding well with the rural CA site in the Nolte et al. (2001) study (0.5 ng/m^3).

Table 5-3 Winter comparison of n-alkanol and sterol biogenic molecular markers

Reference	Nolte et al. (2001) collected 12/5/1995 to 1/6/1996			This Study December, 2006	
Compound ng/m^3	San Joaquin Valley, CA	Bakersfield, CA	Fresno, CA	Bronx, NY	Pinnacle State Park, NY
Tetracosanol	1.6	11.9	18	0.51	0.52
Hexacosanol	8.9	44	61	0.41	0.59
Octacosanol	1.2	8.6	11	0.23	0.23
Triacontanol	1.2	2.4	2.3	0.16	0.13
Campesterol	nd	nd	0.8	nd	nd
Stigmasterol	nd	2.0	nd	0.09	nd
β-sitosterol	0.5	23	20	0.26	0.07

There are several explanations as to why the n-alkanols and phytosterols did not always agree with other studies or expected seasonal and spatial trends. First, the regional ecosytems are different which influences the types of native and cultivated biomass present. Consequently, the emissions of plant waxes and sterol biomarkers are not expected to be similar. Also, Nolte et al. (2001) found the same n-alkanols measured in NYC in source emissions tests present in wood smoke PM. Therefore, wood smoke also could be influencing the n-alkanols concentration in the ambient atmosphere. This would explain the increase in n-alkanols in the December, 2005 and February, 2006 in the Bronx, NY samples because there also was an increase in levoglucosan, the wood smoke marker. Additionally the SOAP 2002-2003 samples taken during the Canadian wildfire on July 2, 2002 showed an increase in the levels of the n-alkanols biomarkers. During the Canadian wildfire event the total n-alkanols concentration at all three SOAP 2002-2003 sites was over 100 ng/m^3, which is higher than the typical seasonal concentrations. The other SOAP 2002-2003 samples never reached total n-alkanol concentrations 20 ng/m^3 or higher. The Canadian smoke plume and source tests from wood combustion indicate that biomass burning, wood burning, or cellulose combustion,

can have an effect on the n-alkanol concentration and that the biomass burning may be a contributor to n-alkanols.

Phytosterols also were found in wood smoke emission source tests (Nolte et al., 2001; Fine et al., 2001; Fine et al., 2002; Rogge et al., 1998). β–sitosterol was the most commonly found phytosterol in the emission tests. The samples taken during the Canadian wildfire in July, 2002 had non-detectable levels for all three phytosterols indicating that woodsmoke does not contribute to phytosterol levels. The phytosterol pattern for the Bronx, NY site was a decrease in the spring and fall months when the vegetation is in less active growth periods compared to summer. The rural site of Pinnacle State Park, NY, for the same timeframe, showed increases in phytosterols in the spring months, but not in the fall months. There were increases in the winter that could be the contribution of surface waxes from evergreen vegetation and not wood burning.

Other sources of n-alkanols and phytosterols also may contribute to the ambient concentrations in urban atmospheres. Coal is composed of fossil organic carbon from terrigenous biomass (Oros and Simoneit, 2000; Simoneit et al., 2007). Chen et al. (2006) showed that different coal maturities emit varying amounts of OC and EC; the study did not report individual organic chemicals. Particulate matter sampled from coal combustion using controlled fires indicated the presence of n-alkanols, but in the opposite order where the higher carbon numbers were in higher concentrations than the lower carbon number n-alkanols (Oros and Simoneit, 2000). No data has been found on phytosterols in coal. Coal combustion would not be expected to be a major emission source in the SOAP study area.

Cigarette smoke can emit similar compounds as leaves because cigarettes originate from plant material, i.e. tobacco leaves. Rogge et al. (1994) conducted fine particle emission tests on cigarettes and determined that tetracosanol was emitted at a rate of 36.7 μg/cigarette and hexacosanol was emitted at a rate of 12.7 μg/cigarette. Octacosanol (C28) and triacosanol (C30) were not measured in the study. Plant sterols also were found in cigarette smoke and were emitted at higher rates than the quantified n-alkanols. Campesterol was emitted at a rate of 92.8 μg/cigarette, β-sitosterol was emitted at a rate of 100.4 μg/cigarette and the dominant phytosterol found was stigmasterol emitted at a rate of 252.2 μg/cigarette (Rogge et al., 1994). Tobacco smoke contributed a small but measureable level of fine PM in the 1982 metropolitan Los Angeles study (Rogge et al., 1993b). Identification of iso-and anteiso n-alkanes in addition to the phytosterol molecular markers would have aided in determining the contribution of cigarette smoke to the NYC area (Schauer et al., 1996).

Phytosterols also are common components in vegetable oils used in cooking processes (Schauer et al., 2002). Frying vegetable oils can release the n-alkanols and phytosterols in to the air (Schauer et al., 2002). Schauer et al. (2002) conducted source tests on several frying oils, however n-alkanols and phytosterols were not measured. Other studies measured n-alkanols and phtyosterols in vegetable oils before and after cooking to determine losses (Beveridge et al., 2002; Schwartz et al., 2008; Winkler et al., 2007).

Ginseng seed oil contained all three of the phytosterols measured in this study and found β-sitosterol to be the dominant sterol (Beveridge et al., 2002). Additionally it was found when the seeds were dried in the oven instead of by air the amount of phytosterols

within the seeds decreased. The lost phytosterols might have been emitted into the air. β-sitosterol decreased from 126 mg per gram of oil to 117 mg per gram of oil. Campesterol decreased from 9.10 mg per gram of oil to 8.51 mg per gram of oil. And stigmasterol decreased from 112 mg per gram of oil to 103 mg per gram of oil. The seed oil contained 153 mg of β-sitosterol per gram of oil, 9.96 mg campesterol per gram of oil and 113 mg stigmasterol per gram of oil. It was reported that corn oil, canola oil and sesame oil have similar phytosterol concentrations to ginseng oil (Beveridge et al., 2002).

Another study found all three of the phytosterols in rapeseed oil, olive oil, sunflower oil, corn oil, coconut oil, sesame oil, linseed oil, camelina oil, wheat germ oil, and walnut oil (Schwartz et al., 2008). The β-sitosterol was found as the dominant phytosterol and ranged in concentration from 45 mg per 100 gram of oil to 515 mg per 100 gram of oil, with a high value of 2510 mg per 100 gram of oil in wheat germ oil. Campesterol was found to be dominant over stigmasterol. Campesterol values ranged from 5.6 mg per 100 gram of oil to 315 mg per 100 gram of oil with a comparatively high value of 969 mg per 100 gram of oil again in the wheat germ sample. Stigmasterol ranged from 1.5 mg per 100 gram of oil to 48 mg per 100 gram of oil. The phytosterols were also found in margarine, rolling fat and frying fat (Schwartz et al., 2008).

Heating oils containing phytosterols reduced the relative content of these markers upon heating. Winkler et al. (2007) found continuously frying of potatoes in oil decreased the phytosterol concentrations by 4 to 6 % for sunflower oil, corn oil, expeller pressed soybean oil and expeller pressed low-linolenic acid soybean oil. When the oils were subjected to intermittent frying, all of the oils tests showed losses that appeared to be greater than continuous frying, with the phytosterol content dropping 14.8% for corn

oil after 35 hours of intermittent frying. High temperature heating of oils, such as deep-fat frying, may result in the alteration of phytosterols to form oxidized phytosterols (Winkler et al., 2007).

He et al. (2004) sampled fine PM emissions from two restaurants in China. The smoke was withdrawn with an overhead exhaust hood and the samplers were located at the exit of the duct from the exhaust hood. One restaurant was Hunan style (spicy and sour) and the other was Cantonese (fried, stewed or broiled food). Hunan style cooking emitted 1406 $\mu g/m^3$ $PM_{2.5}$, 1148 $\mu g/m^3$ of organic matter, 525 ng cholesterol/mg of particle emitted, 337 ng stigmasterol/mg of particles emitted and 1352 ng β-sitosterol/mg of particles emitted. Cantonese style cooking emitted 672 $\mu g/m^3$ $PM_{2.5}$, 354 $\mu g/m^3$ organic matter, 369 ng cholesterol/mg of particles emitted, 145 ng stigmasterol/mg of particles emitted and 2604 ng β-sitosterol/mg of particles emitted. Chinese cooking is one in which vegetables and vegetable oils are dominant over meat (He et al., 2004). The vegetable oils may be emitting phytosterols into the air which could explain their presence in urban environments where restaurants are abundant.

5.1.3. Meat Charbroiling

Cholesterol was found as a molecular marker in emission tests on meat charbroiling operations as described in detail in Chapter 2 (Schauer et al., 1999; Rogge et al., 1991; Hildemann et al., 1991). Table 5-4 summarizes early winter ambient cholesterol levels reported by other studies and compares these levels with the SOAP sites. Table 5-5 provides a comparison for the summer time period.

Nolte et al. (2001) collected fine aerosols in the winter from 12/5/1995 to 1/6/1996 in two urban and one rural site in California. The values found in California in

1982 (Rogge et al., 1991) and in 1995-1996 (Nolte et al., 2001) were higher (about ten times) than those found in this study during the same season. The winter 1982 Los Angeles study had 20 to 200 times the cholesterol concentrations compared to the winter urban SOAP levels. A second southern California study (winter 1995/1996) reported cholesterol levels about half of the 1982 level and with the urban sites about twice the rural site. Winter cholesterol concentrations were similiar in Atlanta, GA (Zheng et al., 2007), Los Angeles, CA and Riverside, CA (Fine et al., 2004) to NYC.

Table 5-4 Winter time fine PM cholesterol comparison

Reference Sampling period	Site	Cholesterol ng/m^3
Rogge et al. (1991) October, 1982	Los Angeles, CA (urban)	14.6
Nolte et al. (2001) Winter, 12/5/1995- 1/6/1996	San Joaquin Valley, CA (rural)	3.5
	Bakersfield, CA (urban)	9.9
	Fresno, CA (urban)	7.0
This study Winter 2002-2003	Queens, NY (urban)	0.10
	Elizabeth, NJ (urban)	0.23
	Chester, NJ (background)	0.66
	Westport, CT (downwind)	0.07
This study December, 2005	Bronx, NY (urban)	0.33
	Pinnacle State Park, NY (rural)	ND (0.01)
This study December, 2006	Bronx, NY (urban)	0.11
	Pinnacle State Park, NY (rural)	ND (0.01)
Zheng et al. (2007) January, 2002	Atlanta, GA (urban)	0.89
Fine et al. (2004) (1/13-1/17/2003)	Los Angeles, CA (urban)	0.75
Fine et al. (2004) (1/27-1/31/2003)	Riverside, CA (rural)	0.3

The summer cholesterol concentrations were on the same order of magnitude in all of the U.S. studies. The urban locations in GA and CA are similar to NYC.

Table 5-5 Summer time cholesterol concentrations

Reference Sampling period	Site	Cholesterol ng/m^3
This study Summer 2002	Queens, NY (urban)	ND (0.02)
	Elizabeth, NJ (urban)	0.13
	Chester, NJ (background)	ND (0.02)
	Westport, CT (downwind)	ND (0.02)
This study August, 2006	Bronx, NY (urban)	0.11
	Pinnacle State Park, NY (rural)	ND (0.01)
Zheng et al. (2007) 7/3/2001-8/4/2001	Atlanta, GA (urban)	0.71
Fine et al. (2004) (8/12-8/16/2002)	Los Angeles, CA (urban)	1
Fine et al. (2004) (8/26-8/30/2002)	Riverside, CA (rural)	0.25

Cholesterol in the NYC area is from meat charbroiling sources. However, the meat cooking emissions tests published in the early 1990's did not test emissions from deep fat frying operations. In 1982, McDonald's fast food restaurants were using 7% cotton seed oil and 93% beef lard for frying French fries (Schlosser, 2001). In the early 1990's pressure from citizens and government groups influenced this and other restaurant chains to use seed oils for frying. After the mid-1990's the principle oil for commercial deep fat frying is cotton seed oil with smaller proportions of lard (< 10%). Consequently, cholesterol is a molecular marker for commercial food preparation (meat cooking and deep-fat frying) and is a characteristic, stable marker of urban air pollution.

5.1.4. Biogenic Oxidation Products

Comparisons of the SOAP 2002-2007 ambient concentrations of cis-pinonic acid to the values found in other U.S. and Canada rural and urban studies indicate similar levels. Table 5-6 shows the average summertime concentrations of cis-pinonic acid found in these studies.

The urban areas of Bronx, NY and Queens, NY were on the same order of magnitude as the urban areas in Cheng et al. (2004) which ranged from 1.1 ng/m^3 to 9.7 ng/m^3. The higher concentrations quantified in the rural area Pinnacle State Park, NY, though the samples were in the fall, were on the same order of magnitude as other rural areas studied in Cheng et al. (2007) and Sheesley et al. (2004).

Table 5-6 Average summertime concentrations of cis-pinonic acid

Reference	Location	Sampling Period	cis-Pinonic Acid, ng/m^3
Cheng et al. (2004)	Lower Fraser Valley Vancouver, Canada forest (rural)	8/6-8/10/2001	11.1
Cheng et al. (2004)	Lower Fraser Valley traffic tunnel (urban)	8/9-8/14/2001	1.1
Cheng et al. (2004)	Lower Fraser Valley urban park	8/15-8/20& 8/24-30/2001	5.9
Cheng et al. (2004)	Lower Fraser Valley forest/urban mixed	8/15-8/20& 8/24-30/2001	9.7
Cheng et al. (2004)	Lower Fraser Valley rural	8/15-8/20& 8/24-30/2001	7.3
This study	Bronx, NY (urban)	August, 2006	3.84
This study	Pinnacle State Park, NY (rural)	August, 2006	ND
Sheesley et al. (2004)	Seney National Wildlife Refuge, Michigan (rural)	July, 2002	14
This study	Elizabeth, NJ (traffic, urban)	Early summer, 2002	5.32
This study	Queens, NY (urban)	Early summer, 2002	3.17
This study	Chester, NJ (rural)	Early summer, 2002	7.91

The ambient data for Pinnacle State Park, NY showed the highest concentration of cis-pinonic acid in November, 2006 when it reached 9.88 ng/m^3, and was not detected in the August summer composite. However, the rural Chester, NJ early summer sample had the same order of magnitude concentration of cis-pinonic acid as the Sheesley et al. (2004) high value found in the rural background Michigan site. All urban SOAP sites

had between 3-8 ng/m^3 cis-pinonic acid during the summer period. This pattern suggests that urban vegetation and higher oxidant levels may be contributing to local urban concentrations of this biogenic photochemical marker, rather than transport from upwind rural source regions alone. Reducing urban concentrations of ozone and NO_x would likely reduce ambient concentrations of biogenic oxidation products in metropolitan NYC.

5.1.5. Low Molecular Weight Highly Oxidized Acids

U.S. studies were not available for comparisons therefore the Pacific aerosol studies were used. Kawamura et al. (1996), Ortiz et al. (2006), and Wang et al. (2006) quantified pyruvic acid and glyoxylic acid in fine PM Pacific marine aerosols. These two acids, however, were not found in the NYC area. The most commonly found oxoacid in this study was levulinic acid followed by 4-acetylbutyric acid. Kawamura et al. (1996) quantified levulinic acid in fine PM over Alert, Canada (rural, near the Arctic) at a yearly average concentration of 0.02 ng/m^3. This cannot be compared directly to the SOAP 2002-2007 study due to differences in location.

The three earlier studies used more polar solvents for filter extraction than used in the SOAP 2002-2007 studies. The less polar extraction solvent could explain the absence of pyruvic acid and glyoxylic acid in the SOAP fine PM samples. To confirm this theory a laboratory experiment was conducted in which six low molecular weight acids (levulinic acid, 4-acetylbutyric acid, oxalacetic acid, pyruvic acid, glyoxylic acid and oxalic acid) were dissolved separately into the SOAP extraction solvent mixture according to the method for standard preparation described in Chapter 3. Levulinic acid and 4-acetylbutyric acid were soluble in the 50/50 by volume dichloromethane/acetone

extraction solvent mixture. The remaining three acids, oxalacetic acid, pyruvic acid and glyoxylic acid, were soluble in the extraction solvent mixture after rapid mixing. Oxalic acid (a highly oxidized acid not quantified in this study) did not dissolve into the dichloromethane/acetone extraction mixture. These solubility results indicated that dichloromethane and acetone extraction mixture was not the appropriate solvent for highly polar organic compounds. The three smallest acids in this study are questionable as far as quantification is concerned since they probably did not elute into the extraction solvents. Consequently, highly polar acids may be more abundant in the SOAP 2002-2007 fine PM samples, but additional extraction of the remaining filter aliquots and GCMS analysis would be necessary to confirm the presence of these polar markers in the NY area.

Edney et al. (2003) collected fine aerosol samples in summer 2000 from Research Triangle Park, NC, USA, a semi-rural area with biogenic and anthropogenic sources. One ambient sample filter was tested for polarity of the sorbed organic compounds by using four different solvents: hexane, acetone, ethanol and water. The procedure was to soak the filter in hexane for 30 minutes, the hexane was removed and this was repeated two times. The procedure was performed separately for acetone, then ethanol and water. Each fraction was analyzed for OC mass. The hexane contained about 11% of the organic mass, acetone contained 67%, ethanol contained 12% and water contained 10% (Edney et al., 2003). This suggests that acetone was a good solvent because it collected the majority of the organic mass; however there were highly polar compounds that did not dissolve and a more polar solvent was required. The study did not discuss what

individual organic compounds were in each fraction but relied on the bulk OC content to approximate the extractable complex organic mixture.

There are several additional explanations why levulinic acid was ubiquitous in urban and rural locations: oxoacids, in particular levulinic acid, has many sources. Although levulinic acid is known to be produced photochemically in the atmosphere, it also has primary emission sources. Levulinic acid is used in the manufacturing industry as a textile dye, coating material, solvent, food flavoring agent and in pharmaceuticals. Levulinic acid can be produced by heating hexose, or a carbohydrate containing hexose such as biomass, glucose and sucrose, with a dilute mineral acid (Cha and Hanna, 2002; Chang et al., 2007). Higher yields from carbohydrates were found when sulfuric acid was used as opposed to hydrochloric acid (Cha and Hanna, 2002). A recent study examined the feasibility of making levulinic acid from wheat straw. The researchers found it was possible to produce levulinic acid between temperatures of 190 and 210 °C, with 1 to 3 % acid by heating for 15 to 45 minutes (Chang et al., 2007). Levulinic acid also can be made from starch (Cha and Hanna, 2002). Starch is a polysaccharide consisting of D-glucose units and therefore, would release levoglucosan when burned (Lehninger, 1975). Levulinic acid has been produced since about 1870, however it was not until the 1940's that research began to evaluate cost effective methods to produce it. Research continues to be conducted to determine uses and manufacturing procedures for levulinic acid (Cha and Hanna, 2002; Wiley et al., 1955; Ragauskas et al., 2006). Levulinic acid was found in glucose thermodegration and in wood combustion smoke (Fagerson, 1969; Fiddler et al., 1970).

Levulinic acid also has primary emission sources similar to biogenic sources discussed in Chapter 5. Levulinic acid is present in acid hydrolyzed vegetable and soy protein. Soy sauce made by acid hydrolysis, as opposed to the naturally brewed soy sauce, contains levulinic acid (Sano et al., 2007). Levulinic acid was found in the plant metabolic fluxes in soybeans (Sriram et al., 2007), indicating that the oxoacid is found in natural plant material. Levulinic acid also is used as a cigarette additive. Concentrations have been reported as 29-56 μg levulinic acid/cigarette for mainstream smoke and 25-49 μg levulinic acid/cigarette for side stream smoke (Keithly et al., 2005). The maximum level of levulinic acid added to a cigarette is 2% or 20 μg in a typical 1.0 g cigarette (Keithly et al., 2005). Johnstone and Plimmer (1959) found levulinic acid, pyruvic acid and glyxoylic acid in tobacco smoke. All of these sources could be adding oxoacids, particularly levulinic acid, as direct emissions to the atmosphere.

An additional source of oxoacids is transport from other media. Human urine, of both males and females, contain glyoxylic acid, pyruvic acid, levulinic acid, and oxalacetic acid (4-acetylbutyric acid was not looked for in the study) (Lee et al., 1998). Therefore, wastewater processing operations could be injecting these oxoacids into the atmosphere. Pyruvic acid was found in natural waters and in soil in Sweden. Bylund et al. (2007) collected a soil sample and a stream sample in a coniferous forest in Bispgarden in central Sweden. The concentration of pyruvic acid was 0.33 μM in the stream and 0.22 μM in the soil (Bylund et al., 2007). Reactions between natural organic matter and ozone used to disinfect water was shown to produce ketoacids, in particular pyruvic acid and glyoxylic acid (Melin and Odegaard, 2000; Karnik et al., 2005). Therefore ketoacids could be emitted into the air by being released from other media.

5.2. *Emission Estimates*

An emission rate is deterimed directly from source tests and is defined as the mass of a molecular marker emitted per unit of OC or $PM_{2.5}$. The ambient $PM_{2.5}$ mass balance is critical because the sources are totaled to equal 100% of the OC or $PM_{2.5}$ mass. In order to run source apportionment models on airborne particles, ambient data and sources of emissions are necessary. Computer models also account for meteorology, dispersion parameters and deposition rates (Gray and Cass, 1998). Organic carbon is difficult to model because it can react in the atmosphere and this rate of degredation or accumulation is unknown.

The U.S. EPA publishes the Chemical Mass Balance (CMB8.2) source apportionment model which uses source testing information and ambient measurements to determine the contribution of a source to the OC for each sample (Robinson et al., 2006). SOAP 2002-2003 and SOAP NY samples coupled with the CMB8.2 is part of an ongoing collaboration with the U.S. EPA at Research Triangle Park, NC. Comparing published emission rates to estimate source contributions using basic mathametical models, as conducted in this study, is acceptable because it uses similar emission rate factors as the CMB 8.2. This calculation also is necessary to verify model output and understand source contributions to ambient air quality. Currently the CMB8.2 model relies on source profiles, and differences in source profiles were shown to change the source contribution estimates by a factor 2. This variability in source contribution highlights a disadvantage when applying the CMB model (Robinson et al., 2006).

Emission estimates were conducted for levoglucosan and cholesterol using results of mass emission rates from earlier published studies (Fine et al., 2001; Fine et al., 2002;

Schauer et al., 1999; Rogge et al., 1991; Hildemann et al., 1991). These two compounds were the only polar organic markers with published source emission rates that could be used to estimate the ambient mass concentrations of OC. Emission tests for plant waxes were conducted to determine which chemicals were emitted from the leaves (Rogge et al., 1993; Simoneit and Mazurek, 1982), however mass emission rates of the n-alkanols and sterols were not reported relative to EC, OC and $PM_{2.5}$ masses. Without the ratio of the marker mass to these other masses it is not possible to estimate the biogenic source contribution to the fine particle mass. Oxidation products do not have emission estimates because currently, there are no data on the formation rates from OC or $PM_{2.5}$ measurements due to the complex nature of atmospheric oxidation processes.

5.2.1. Wood Smoke

Levoglucosan is the dominant compound emitted from wood burning, based on information from emission tests (Fine et al., 2001; Fine et al., 2002), so it was chosen for the ambient mass concentration estimate. The data from Fine et al. (2001; 2002) was averaged to determine an approximate emission rate of 100 mg levoglucosan per gram of OC emitted from wood combustion. Equation 8 shows the method of using the ambient mass concentration of levoglucosan and the average mass ratio of this marker to OC in wood smoke fine PM emissions to estimate the percent of OC contributed from wood smoke combustion. Levoglucosan was the only woodsmoke marker chosen for this analysis because it was present year round and was the dominant marker. The other sugar compounds were not always present at every location and for every season. The aromatic acids and catechol were found sporadically, and thus did not show spatial or

seasonal trends. Dehydroabietic acid is a molecular marker primarily for soft wood combustion and also was not used in the wood smoke ambient source estimation.

$$\% OC = \frac{ng\ levoglu\cos an}{m^3} * \frac{m^3}{\mu g\ OC} * \frac{\mu g\ OC}{100\ ng\ levoglu\cos an} * 100\%$$

Equation 8

The results indicated the percentage of OC from wood smoke was not constant and changes occurred with seasonal and temporal variations (Figure 5-1 and Figure 5-2). The highest percentage of wood smoke emissions to the fine particle OC concentrations was present in Westport, CT in the late fall with 69% of the OC contributed from wood burning. The lowest wood smoke source contribution was 0.73% OC found in Queens, NY in spring. The estimated percent OC from wood smoke in Bronx, NY ranged from 1% in July 2006 to 20.8% in December of 2005. The estimated percent OC from woodsmoke in Pinnacle State Park, NY ranged from less than 1% in June of 2006 to a high of 45% in December of 2005. The rural (Pinnacle State Park, NY) and suburban (Westport, CT) sites had higher mass contributions of wood smoke emissions than their urban counterparts (Bronx, NY and Queens, NY, respectively). The general trend was an increase in winter with the lower levels occurring in the summer. This is an expected trend indicating that increased levoglucosan concentrations were consistent with increased wood burning particularly for heating purposes during the colder winter months.

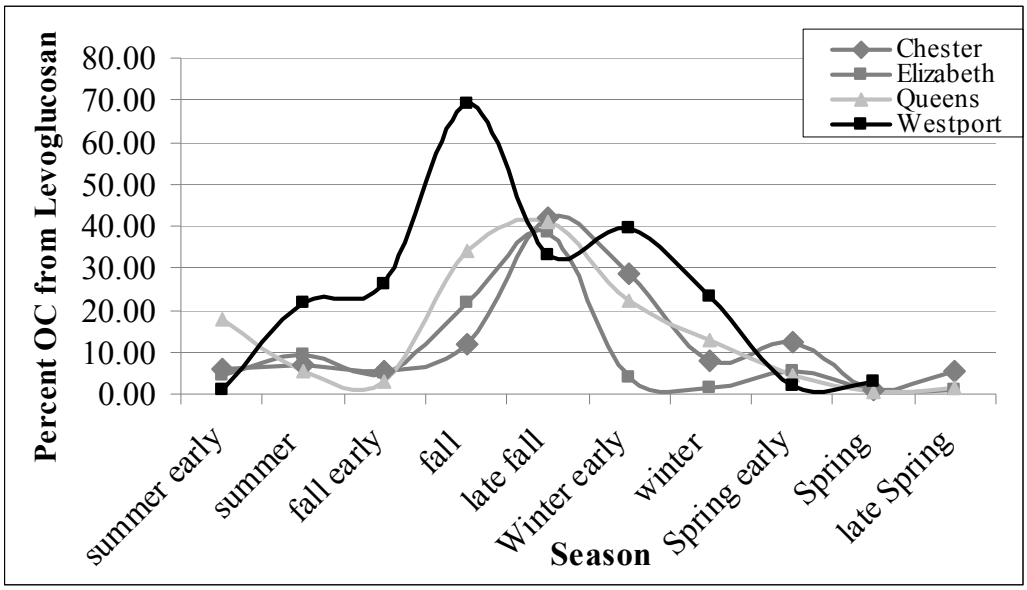


Figure 5-1 Estimated percent of OC from wood smoke in NYC area (SOAP 2002-2003)

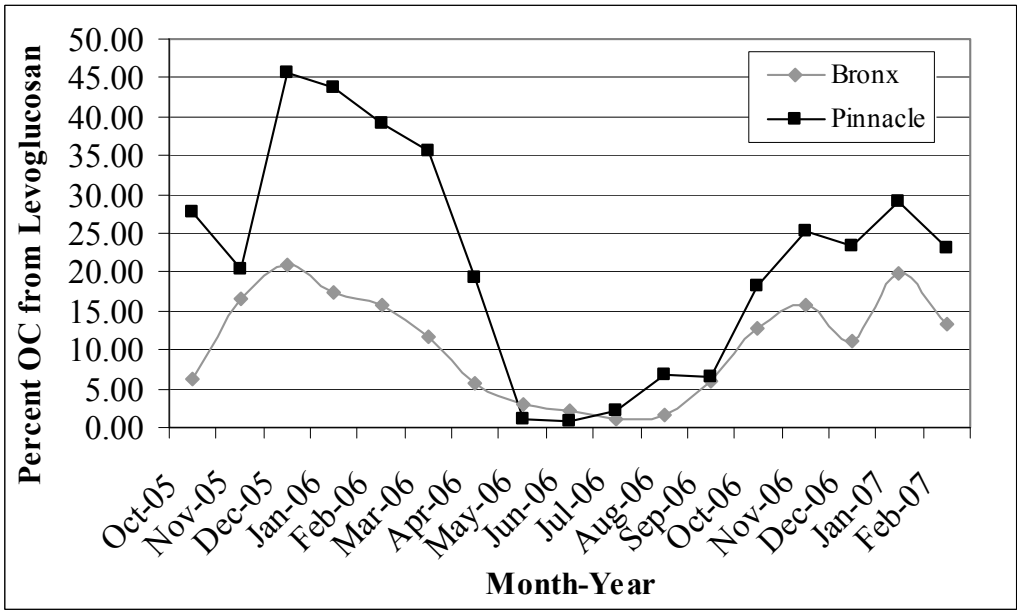


Figure 5-2 Estimated percent OC from wood smoke in NY (SOAP NY)

The data from the published studies discussed in Section 2, i.e. the ambient levoglucosan and OC concentrations, also were converted by Equation 8 to estimate the percent of OC mass contributed by woodsmoke. The percents of OC from wood combustion for winter sampling periods are shown in Table 5-7. The SOAP 2002-2007

winter values for this study given in Table 5-7 do not represent the highest yearly percentages of wood smoke emissions. However, the SOAP winter concentrations were the same season (winter) sampled by these previous studies (January). The urban locations from the SOAP 2002-2007 study had lower contributions of wood smoke relative to Fresno, CA and Atlanta, GA. The SOAP winter values along with the earlier field studies also indicate rural locations had higher percentages of OC mass contributed from wood combustion. In January 2006, the influence of wood smoke was over twice as high in Pinnacle State Park, NY than in Bronx, NY. In the winter of 2003, the Westport, CT level was over twice as high as Queens, NY or Elizabeth, NJ. Gorin et al. (2006) also used emission factors to estimate contributions in the California Central Valley (however, the equation used was not listed). It was found that 41% of the OC was from wood combustion, which was similar to the estimate here of 44% of OC from wood combustion using Equation 8. Engling et al. (2006) estimated that the contribution of wood smoke to fine particle OC mass was 20.6% in the summer at Yosemite National Park, CA, which was higher than the summer percentages determined for Chester, NJ (6.87% in summer 2002) and Pinnacle State Park (6.76% in August, 2006).

Table 5-7 Estimated influence of wood smoke on OC

Reference	Location (sample dates)	% OC from wood smoke
Gorin et al. (2006)	Fresno, CA (12/25/2003-/15/2004)	44
Zheng et al. (2007)	Atlanta, GA (1/2-1/31/2002)	79
He et al. (2006)	Beijing, China (1/3-1/10/2003)	2
This Study	Queens, NY (1/9-2/26, 2003)	13
This Study	Elizabeth, NJ (1/9-2/26, 2003)	1
This Study	Chester, NJ (1/9-2/26, 2003)	8
This Study	Westport, CT (1/9-2/26, 2003)	40
This Study	Bronx, NY (January, 2006)	17
This Study	Bronx, NY (January, 2007)	20
This Study	Pinnacle State Park, NY (January, 2006)	44
This Study	Pinnacle State Park, NY (January, 2007)	29

5.2.2. Meat Charbroiling

Source emission tests on meat charbroiling and frying (Schauer et al., 1999; Rogge et al., 1991; Hildemann et al., 1991) reported the emissions in gram of cholesterol per kg of meat. The value of interest is the mass of cholesterol per mass of OC, which was obtained using the following equation for the experiments presented in the aforementioned studies.

$$\frac{mass\,Cholesterol}{mass\,OC} = \frac{mass\,cholesterol}{mass\,meat} * \left(\frac{mass\,meat}{fine\,aerosol\,mass} * \frac{fine\,aerosol\,mass}{fraction\,of\,OC} \right)$$

Equation 9

An example of this equation with the Schauer et al. (1999) data is:

$$\frac{\mu g\,cholesterol}{g\,OC} = \frac{3970\,\mu g\,cholesterol}{Kg-meat} * \left(\frac{Kg-meat}{18.8\,g\,PM_{2.5}} * \frac{1\,g\,PM_{2.5}}{0.338\,g\,OC} \right) = 625\,\frac{\mu g\,cholesterol}{g\,OC}$$

$$\Rightarrow 625\,\frac{\mu g\,cholesterol}{g\,OC} * \frac{1000\,ng}{1\,\mu g} * \frac{1\,g}{10^6\,\mu g} = 0.625\,\frac{ng\,cholesterol}{\mu g\,OC}$$

Equation 10

The values of the four emission tests from meat charbroiling were 0.625, 2.58, 5.37 and 10.07 ng cholesterol per µg OC, with an average emission rate of 4.6 ng cholesterol per µg OC. The average mass emission rate was used to estimate the percent of OC contributed by meat charbroiling shown in Equation 11.

$$\%\,OC = \frac{ng\,cholesterol}{m^3} * \frac{m^3}{\mu g\,OC} * \frac{\mu g\,OC}{4.46\,ng\,cholesterol} * 100\%$$

Equation 11

The percent of OC from cholesterol generally was higher at the urban sites compared to the background and upwind sites in the 2002-2003 field sampling campaign. Chester, NJ had OC contributions from meat charbroiling near 0% OC due to meat

charbroiling because cholesterol was not detected in the samples. Westport, CT showed an increase in the spring when 0.5% of the OC was estimated to be from meat charbroiling. Elizabeth, NJ had seasonal variations in the percent of OC mass due to charbroiling. The highest percent was in the fall with over 3%. Queens, NY, the urban site, typically had the highest percent OC from meat cooking operations (Figure 5-3). This is due to the higher concentration of restaurants in urban areas.

The SOAP NY study showed the estimated percent OC mass from meat cooking operations in Bronx, NY was higher than in Pinnacle State Park, NY for each season. The percent OC mass from meat cooking at Bronx, NY in July, 2006 sample was the lowest with the estimated %OC at below the detection limits (0.011 ng/m^3). Organic carbon at Bronx, NY was determined to come from meat cooking in each of the other months tested with a high of 2% of OC from cholesterol in October of 2005. Pinnacle State Park, NY had detectable levels of cholesterol only for three months in the late fall and winter. At Pinnacle State Park the percent of OC from meat cooking always was less than 1% as illustrated in Figure 5-4. A reason for this result could be the low density of commercial restaurants in this rural area.

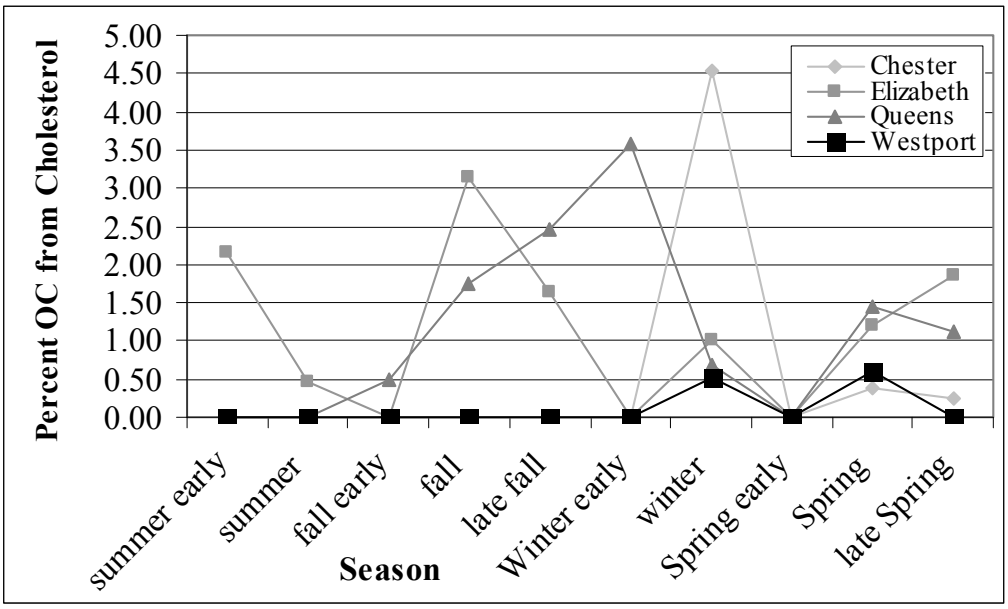


Figure 5-3 Estimated Percent of OC from meat charbroiling in NYC area (SOAP 2002-2003)

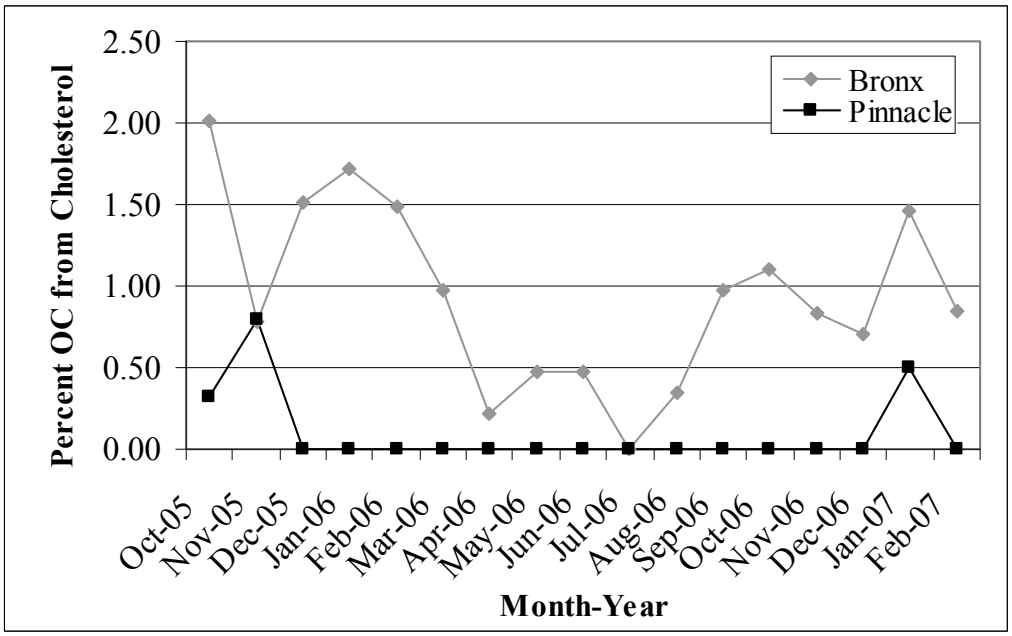


Figure 5-4 Estimated percent OC from meat charbroiling in NY (SOAP NY)

5.3. *Comparison to EC and OC*

Select molecular markers were normalized to OC and EC mass concentrations (Appendix K). These values were used to assess temporal trends. OC is comprised of

primary and secondary organic carbon compounds. EC, on the other hand, only originates from primary sources and is a conservative tracer in the atmosphere. The concentration of EC is influenced by meteorological conditions (i.e., depth of mixed layer) and by the sum of primary sources of fine particulate matter. Additionally, normalizing the molecular markers to EC provides a better understanding of the temporal concentration trends because the EC takes into account the height of the atmospheric mixing layer. The mixed layer depth decreases in the winter due to decreased insolation and cooler surface termperatures. This phenomenon causes the EC, OC and marker concentrations in mass per volume to increase due to the smaller volume of mixed surface air. ANOVA tables were created to determine seasonal and spatial trends for the EC normalized data (Appendix L).

5.3.1. Wood smoke

Levoglucosan ambient mass concentrations (ng/m^3) were normalized to OC and EC mass concentrations (μg/m^3) (Figure 5-5 and Figure 5-6). The normalized data for SOAP 2002-2003 also showed variations along with seasonal and spatial trends. The ratios generally followed the same trend as the molecular marker ambient mass concentration in all sites except for Westport, CT. At this site ratios were lowered in fall and rose in the winter, which was opposite to the other three sites. All SOAP 2002-2003 sites peaked in the late fall. The normalized levoglucosan:EC and levoglucosan:OC values were lowest in the spring with a slight increase in the summer in all four sites. The levoglucosan data from this study did not provide direct ratios to either OC or EC. Consequently, it was not possible to estimate levoglucosan, or cellulose combustion inputs, from the more easily measured OC and EC concentrations in the NYC area. In

general the background site (Chester, NJ) and suburban (Westport, CT) site had higher normalized levoglucosan:EC and levoglucosan:OC ratios than the urban sites (Elizabeth, NJ and Queens, NY) (Figure 5-5 and Figure 5-6). Westport, CT had significant wood smoke combustion emissions, which is supported by the high ratio of levoglucosan:EC.

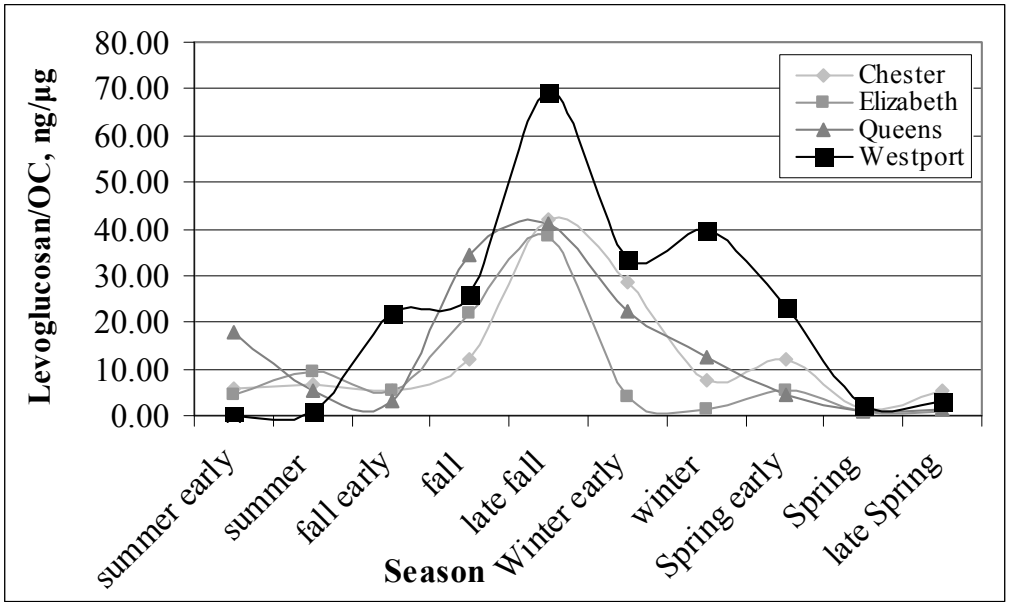


Figure 5-5 Levoglucosan normalized to OC for the NYC area (SOAP 2002-2003)

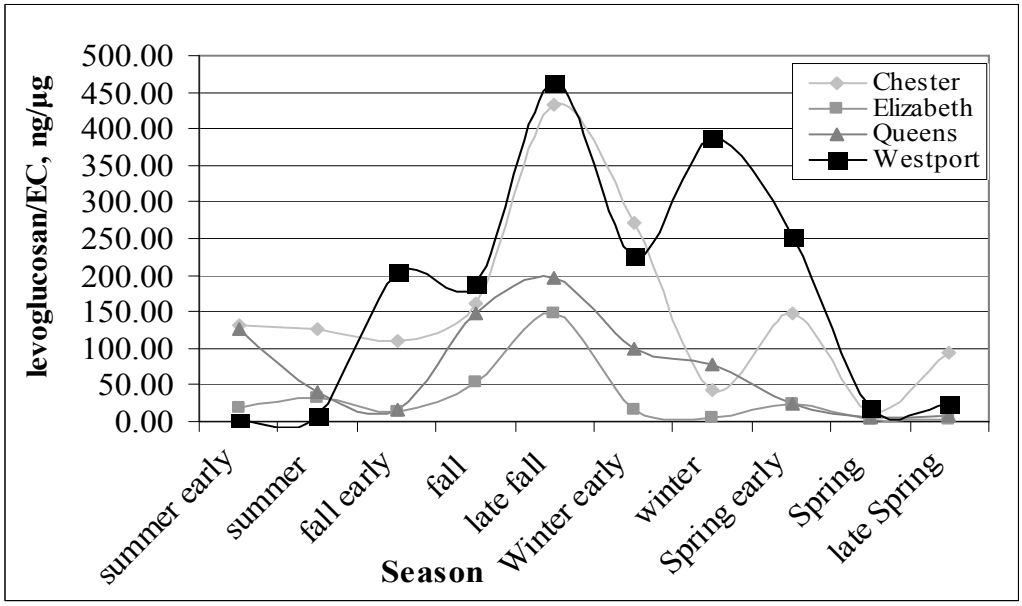


Figure 5-6 Levoglucosan normalized EC in the NYC area (SOAP 2002-2003)

Levoglucosan for the 2005 to 2007 SOAP NY project also was normalized to OC and EC ambient mass concentrations. The seasonal patterns were similar to those for the SOAP 2002-2003. The highest ratios of levoglucosan to OC and EC both peaked in December and January at both sites (Figure 5-7 and Figure 5-8). The lowest values were found in the summer from May to July for the SOAP NY sites. The levoglucosan data does not show a direct ratio to any of the EC or OC, so currently no ratio can be determined to estimate cellulose combustion from the more easily measured OC or EC concentrations. The highest ratio of levoglucosan to EC was found in the rural site, Pinnacle State Park, NY. Two factors relate to this difference between the rural and urban sites. First, there are fewer urban-type emissions sources in the vicinity of Pinnacle State Park, NY. Second, the low population density in the area results in fewer motor vehicle miles (principally diesel vehicles), which is the other dominant source of fine particle EC. Consequently, the relative importance of wood smoke and biomass combustion emissions in the Pinnacle State Park, NY airshed results in the higher levoglucosan:EC ratios compared to values for Bronx, NY. Controlling emissions from wood combustion and biomass burning would reduce fine particle concentrations in rural areas in the NY/NJ/CT study area.

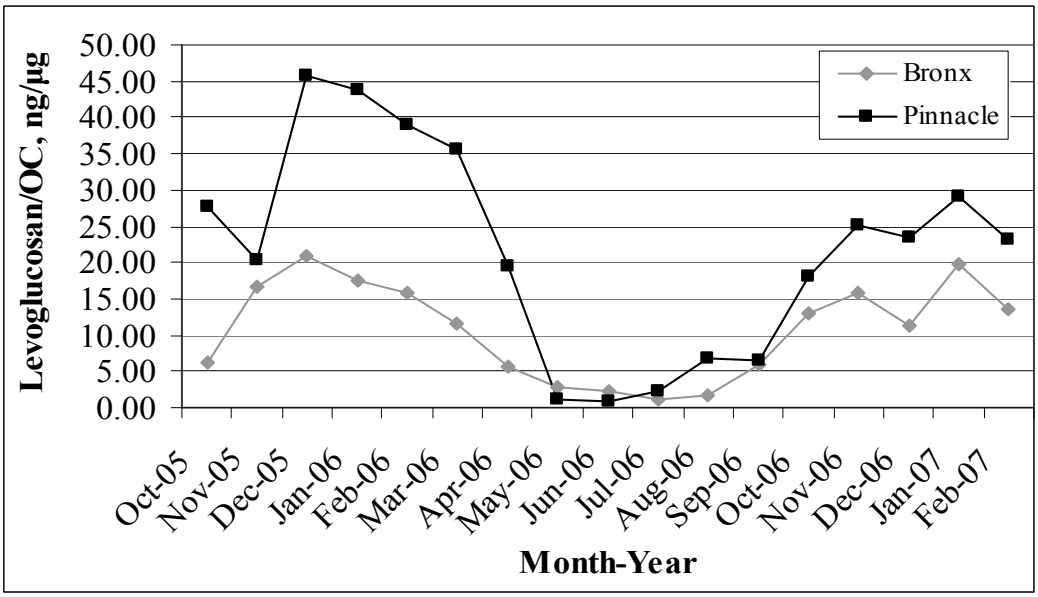


Figure 5-7 Levoglucosan normalized to OC in NY (SOAP NY)

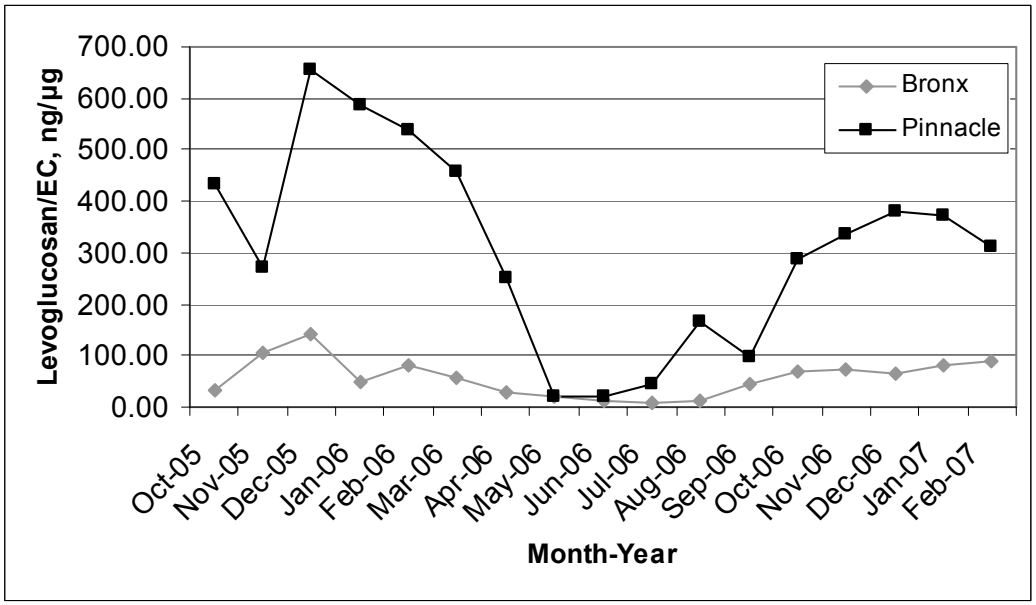


Figure 5-8 Levoglucosan normalized to EC in NY (SOAP NY)

The winter urban levoglucosan ambient concentrations found in other field studies of $PM_{2.5}$ were normalized to the OC ambient mass concentrations (Table 5-8). The Beijing, PRC study reported OC levels higher than in the U.S. sites, lowering the ratio of levoglucosan to OC. In NYC the ratio was more than 2 times higher in the Central

Valley, CA and Atlanta, GA. The lowest ratio of levoglucosan:OC was present in the winter 2003 Beijing study. Here, the relative input of fine OC from wood combustion and biomass combustion compared to other PM sources was significantly smaller. The urban NY sites, sampled in different years, were similar to one another, indicating fairly consistent emissions from wood, biomass and refuse combustion and structural fires in the metropolitan NYC area. Engineering controls for residential fireplaces, wood stoves, outdoor residential boilers would reduce emissions from these widespread sources in the NYC area.

Table 5-8 Comparison of OC normalized levoglucosan

Reference	Location (sampling dates)	OC $\mu g/m^3$	Levoglucosan/ OC, ng/µg
Gorin et al. (2006)	Fresno, CA (12/25/2003-/15/2004)	13.5	44
Zheng et al. (2007)	Atlanta, GA (1/2-1/31/2002)	5.50	79
He et al. (2006)	Beijing, PRC (1/3-1/10/2003)	39.27	2
This Study	Queens, NY (1/9-2/26, 2003)	2.98	13
This Study	Bronx, NY (January, 2006)	4.83	17
This Study	Bronx, NY (January, 2007)	4.34	20

Levoglucosan was plotted against the EC and OC concentrations for SOAP 2002-2003 sites using scatter plots to determine if there was a linear correlation between the two values. The plots were created so that only two sites are on a single plot; otherwise the plots were difficult to interpret as shown in Figures 5-9 through 5-12. The levoglucosan concentrations for Queens, NY, Westport, CT, Elizabeth, NJ and Chester, NJ showed no correlation to OC or EC ambient concentrations. The R^2 values for levoglucosan versus OC ranged from 0.0428 in Chester, NJ to 0.1166 in Westport, CT. The R^2 values for levoglucosan versus EC ranged from 0.0072 in Chester, NJ to 0.3616 in Queens, NY. The low to no correlation of levoglucosan ambient mass concentrations

to EC and OC mass concentrations suggest wood, biomass and refuse combustion and structural fires are variable sources of EC and OC in airborne fine PM in NYC.

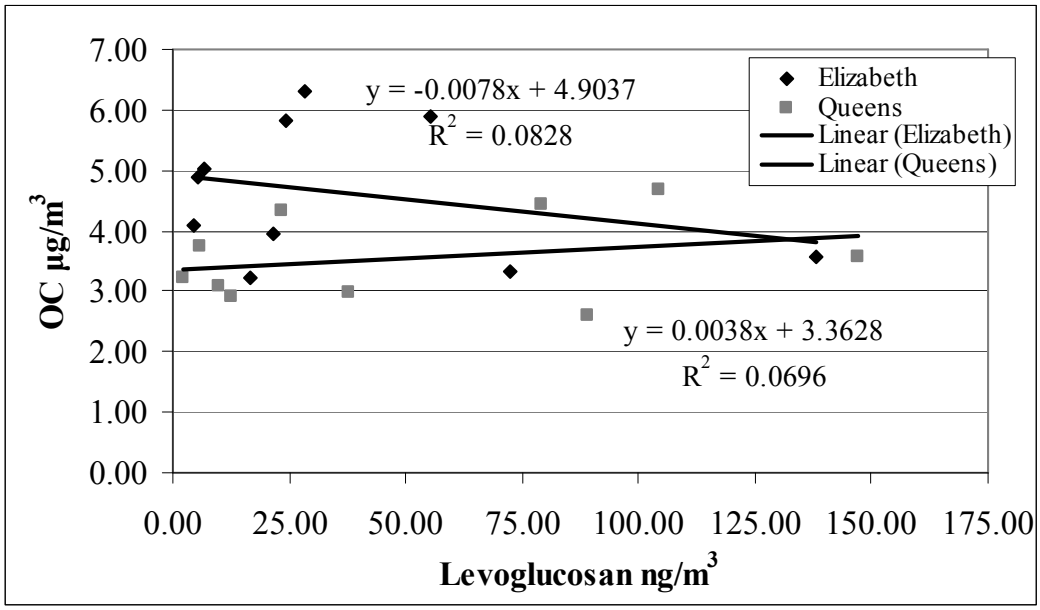


Figure 5-9 Levoglucosan versus OC in the urban NYC area (SOAP 2002-2003)

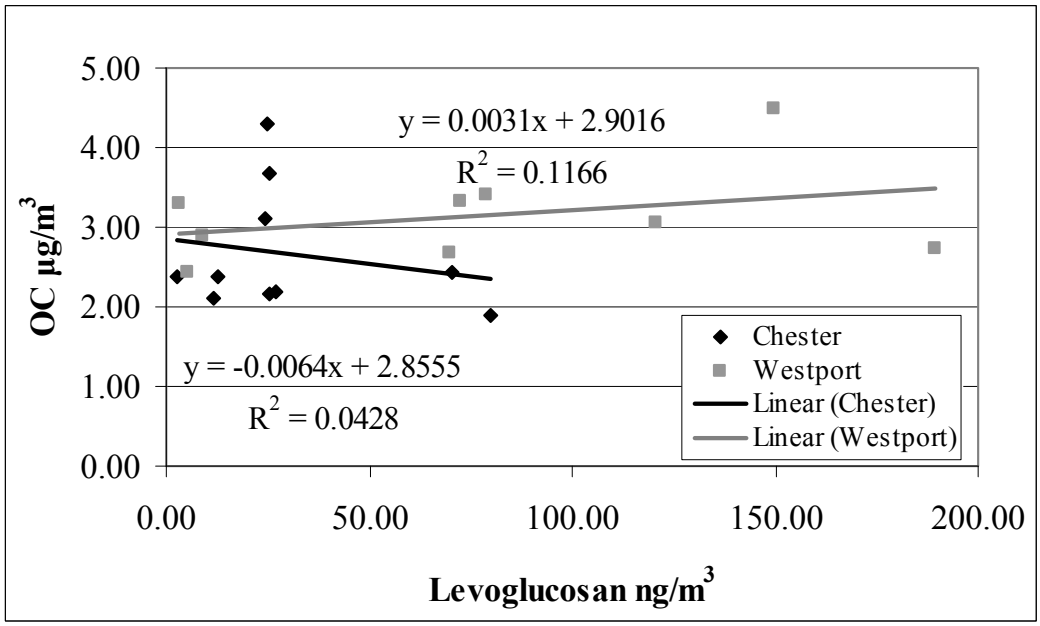


Figure 5-10 Levoglucosan versus OC in the NYC area (SOAP 2002-2003)

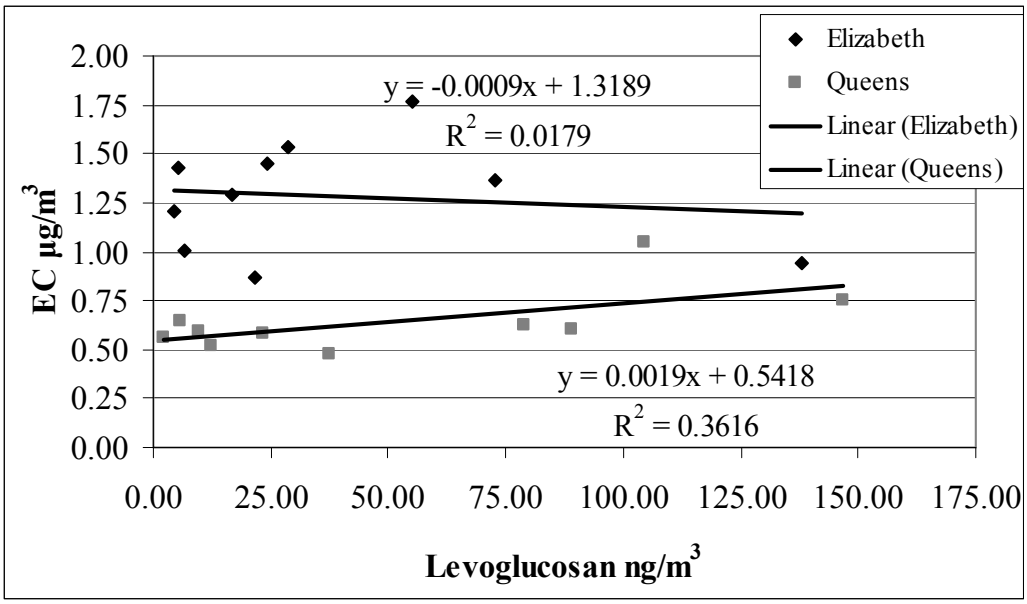


Figure 5-11 Levoglucosan versus EC in the urban NYC area (SOAP 2002-2003)

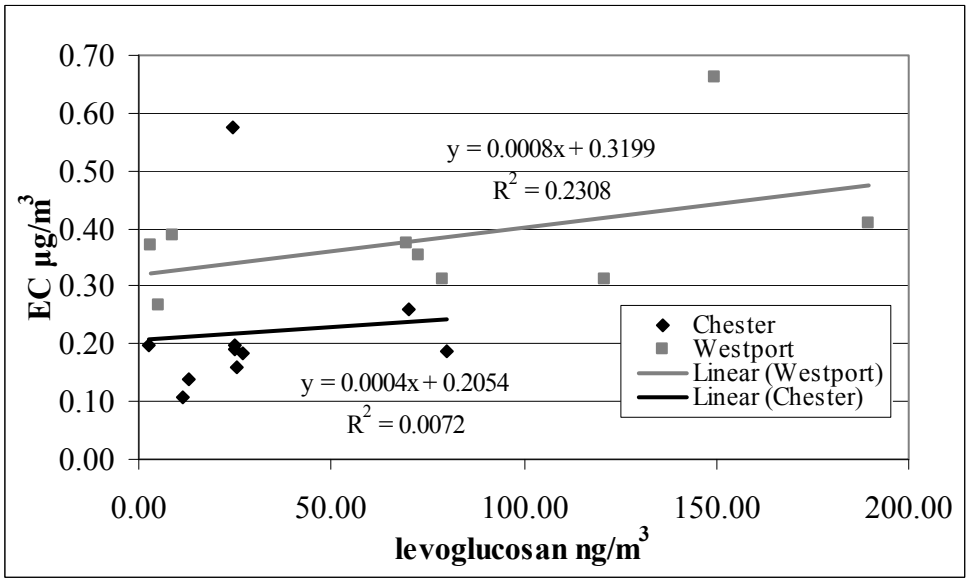


Figure 5-12 Levoglucosan versus EC for the NYC area (SOAP 2002-2003)

The Bronx, NY and Pinnacle State Park, NY also showed no correlation with EC or OC (Figure 5-13 and Figure 5-14). The R^2 values were typically below 0.1 except for levoglucosan versus EC in Bronx, NY where the R^2 value was 0.5. The conclusion from this analysis is the levoglucosan data cannot be interpolated from EC or OC. In order to

determine the concentration of levoglucosan, or the influence of wood, biomass and refuse combustion and structural fires to air quality, the levoglucosan itself must be measured.

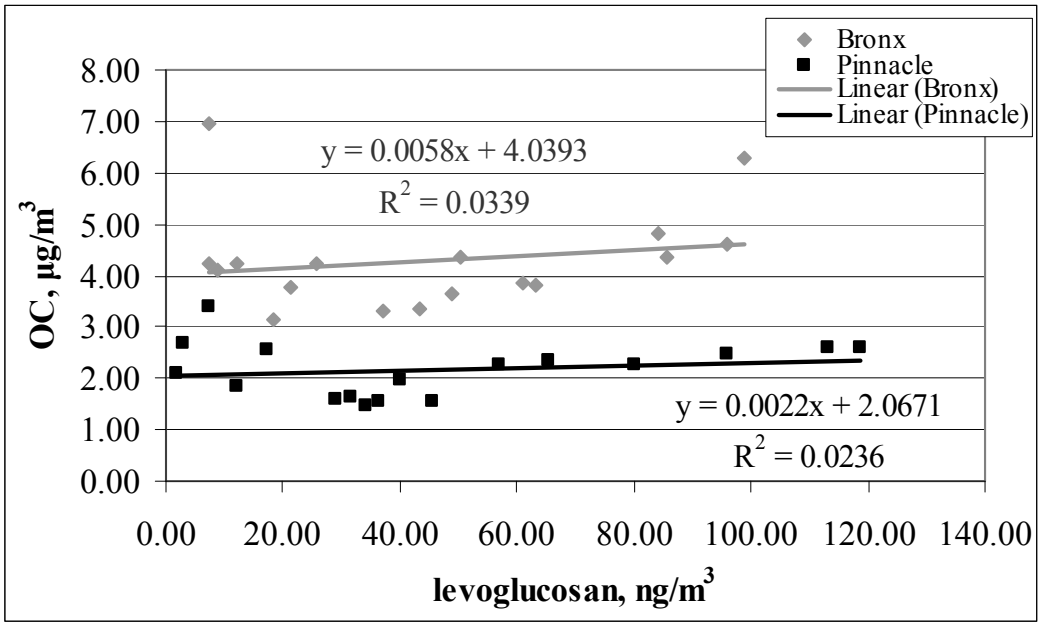


Figure 5-13 Levoglucosan versus OC in NY (SOAP NY)

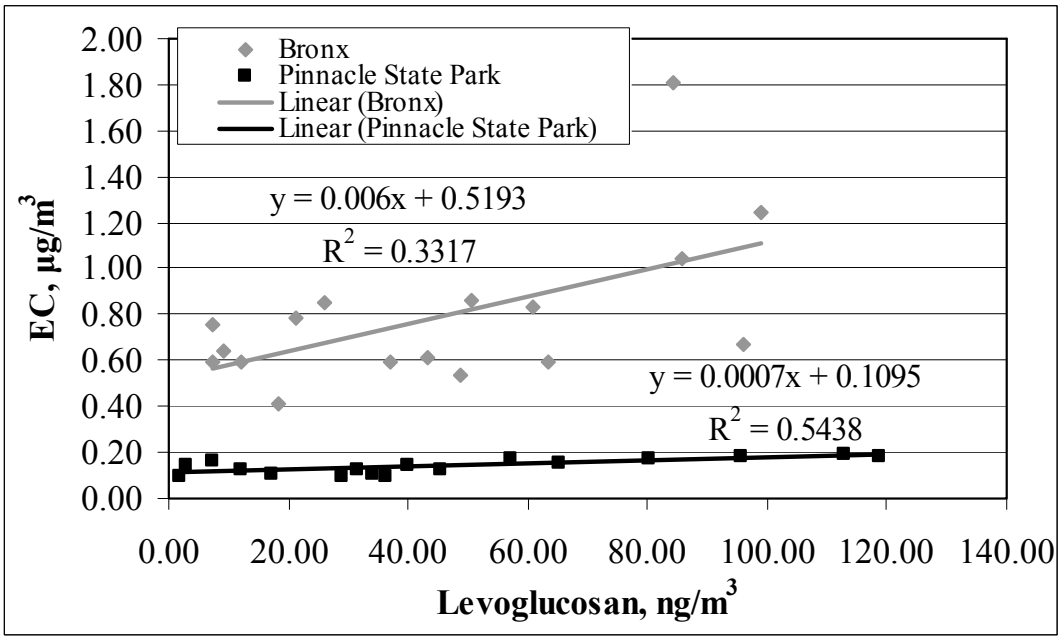


Figure 5-14 Levoglucosan versus EC in NY (SOAP NY)

The EC normalized levoglucosan data for the SOAP 2002-2007 experiments were separated into urban and rural sites and compared with ANOVA tables, as previously described. The data are given in Appendix L. A statistical difference was found for urban versus rural sites at the 95% confidence level for the entire year (p-value = 0.000003) and for all four seasons (p-value ranged from 0.0005 in winter to 0.04 in summer) as shown in Appendix L. The normalized levoglucosan:EC results are opposite to those from the ANOVA tables generated for the levoglucosan ambient concentrations which determined there was no statistical difference between urban and rural sites for the entire year. The EC normalized results suggest that meteorological conditions, such as depth of the mixing layer, have an effect on molecular marker concentration in ambient atmospheres. Therefore, atmospheric dilution effects must be considered in understanding seasonal and temporal variations in relation to sources of fine particles. The normalized levoglucosan:EC ratios also indicate differences in aggregate source emissions in rural and urban sites. Rural sites generally were more heavily influenced by wood and biomass combustion compared to the urban NYC sites.

5.3.2. Biogenic Sources

The quantified n-alkanols were summed and normalized to OC and EC ambient mass concentrations. The samples collected in 2002 to 2003 had the same general seasonal trends of the normalized total n-alkanols as with the total n-alkanols with increased ratios in the spring and fall. Chester, NJ typically had the highest ratio to EC and Queens has the highest ratio to OC (Figure 5-15 and Figure 5-16). This indicates that the air quality in Chester, NJ is more strongly influenced by biogenic sources compared to the urban locations.

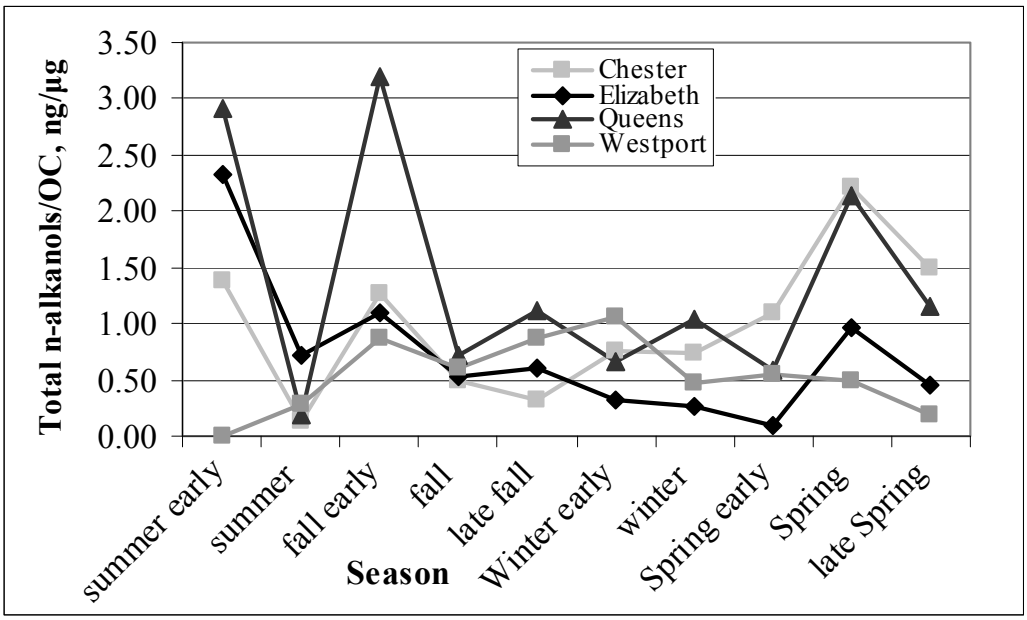


Figure 5-15 Total n-alkanols normalized to OC in the NYC area (SOAP 2002-2003)

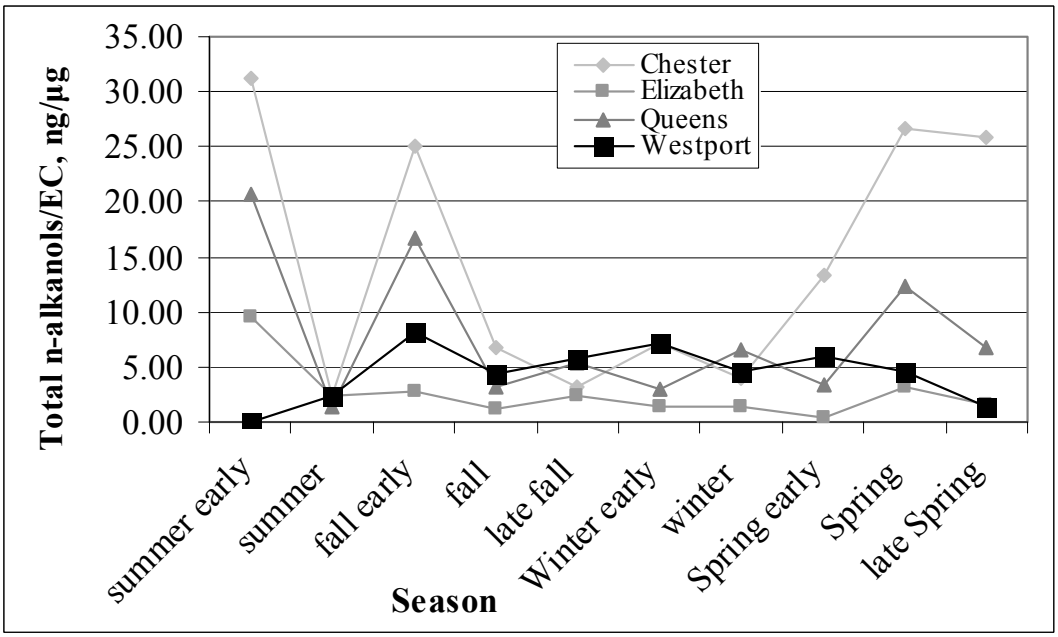


Figure 5-16 Total n-alkanols normalized to EC in the NYC area (SOAP 2002-2003)

The total n-alkanols ambient data were plotted versus EC and OC with scatter plots (Figure 5-17, Figure 5-18, Figure 5-19 and Figure 5-20) to determine the correlation between these molecular markers and the EC and OC ambient mass concentrations. The

2002 to 2003 sampling sites showed no correlation with EC or OC. The highest EC correlation was 0.62 found in Westport, CT. The other sites had lower values (0.0046 in Queens, NY, 0.0054 in Chester, NJ and 0.2247 in Elizabeth, NJ). The highest correlation with OC was 0.59 found in Westport, CT, with a range of 0.0357 to 0.2807 for the other sites. The correlations to OC and EC at Westport, CT were larger than at the other sites indicating that the source of n-alkanols is a constant input to the fine PM.

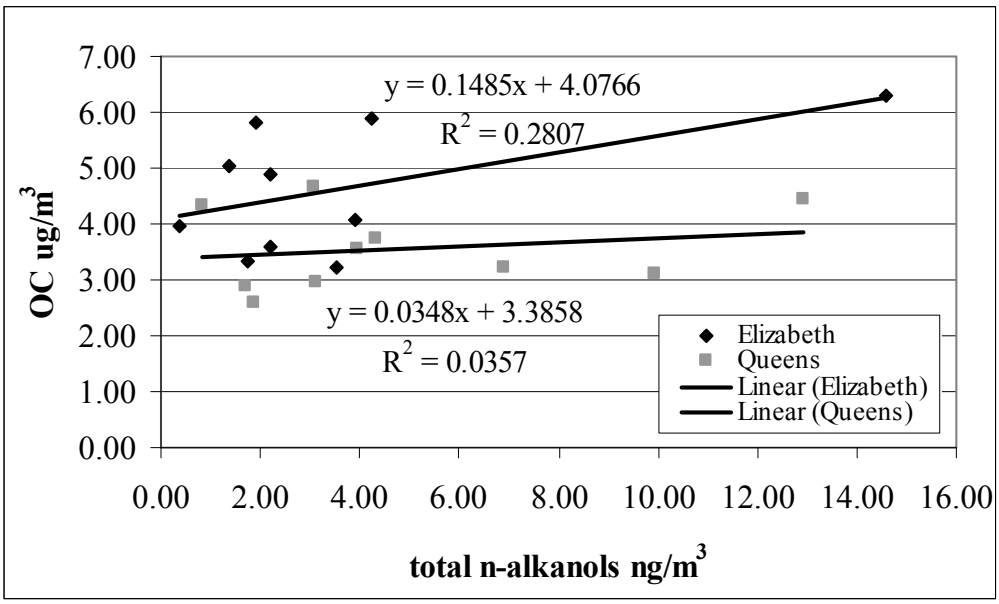


Figure 5-17 Total n-alkanols versus OC in the urban NYC area (SOAP 2002-2003)

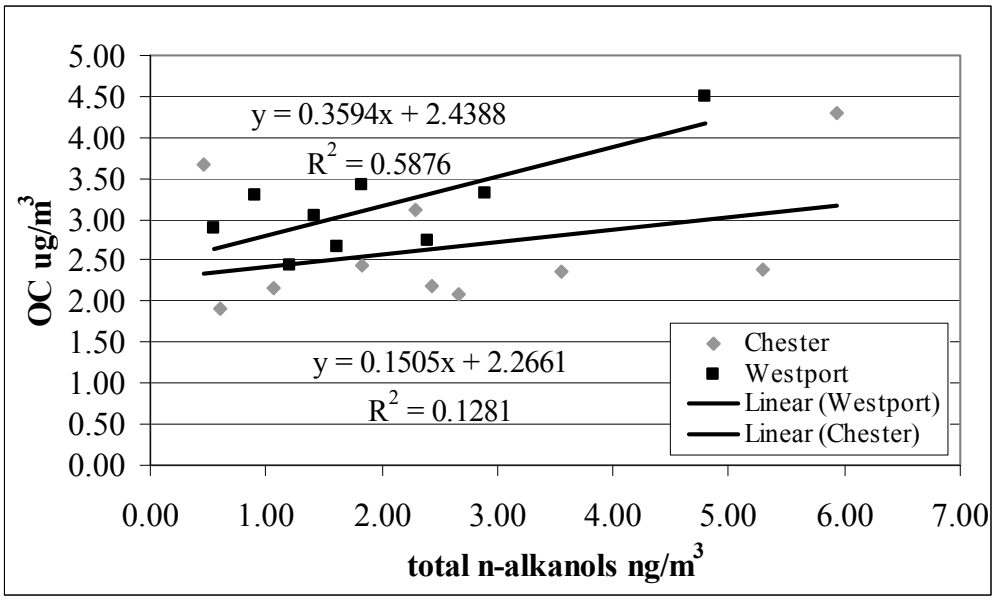


Figure 5-18 Total n-alkanols versus OC in the NYC area (SOAP 2002-2003)

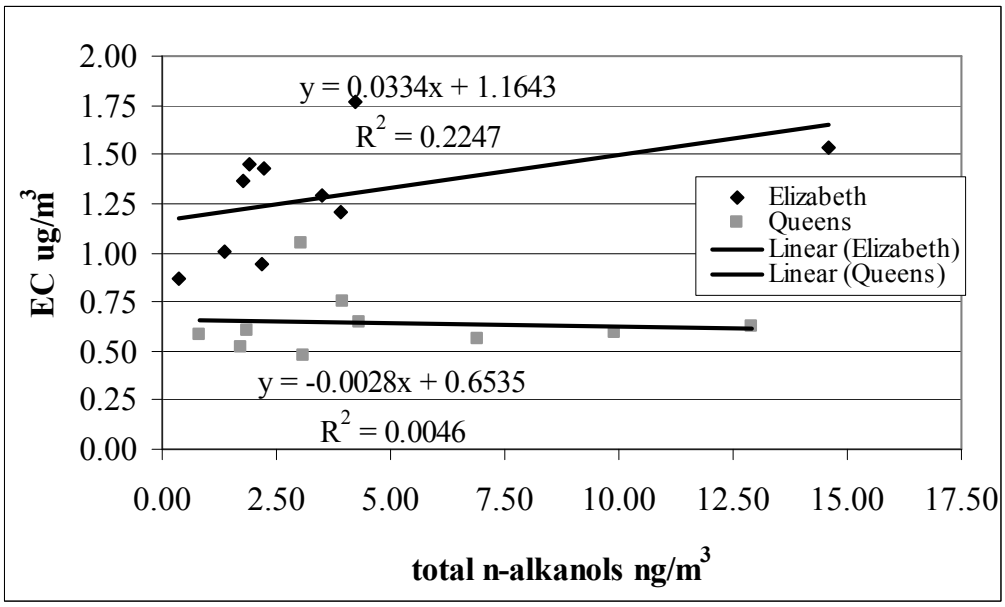


Figure 5-19 Total n-alkanols versus EC in the urban NYC area (SOAP 2002-2003)

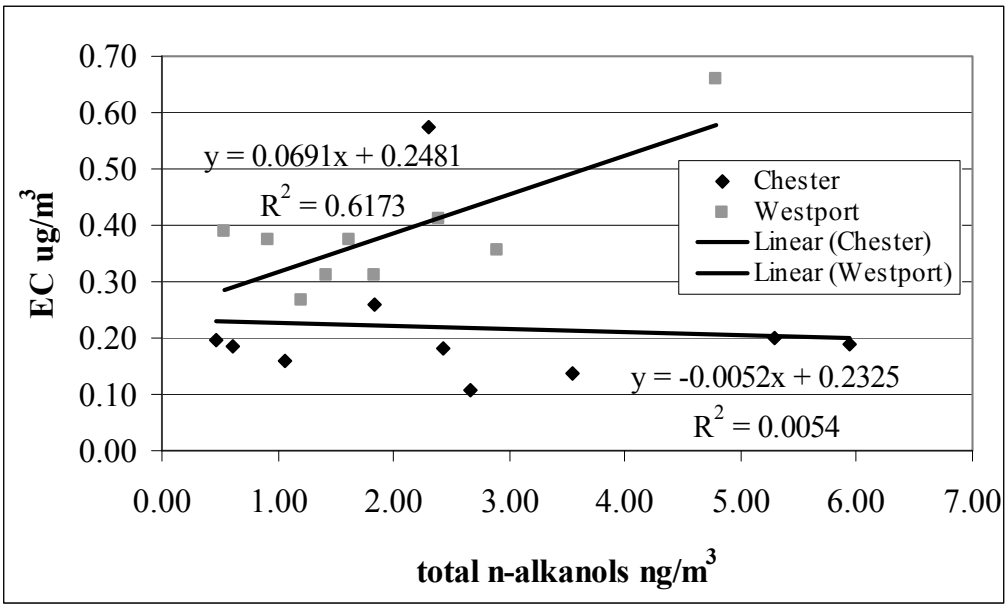


Figure 5-20 Total n-alkanols versus EC in the NYC area (SOAP 2002-2003)

The 2005 to 2007 SOAP sampling period showed similar results to the SOAP 2002-2003 total n-alkanol normalized data (Appendix K). The highest ratios were present in the fall and spring months for both sites. Pinnacle State Park, NY, the rural site, showed higher ratios to OC (0.27 ng/µg in July, 2006 and September, 2006 to 1.62 in ng/µg November, 2005) and EC (4.06 ng/µg in September, 2006 to 22.86 ng/µg in October, 2005) than Bronx, NY, (OC range = ND in April, 2006 and November, 2006 to 0.62 ng/µg in June, 2006; EC range = ND in April, 2006 and November, 2006 to 4.69 ng/µg in September, 2006) (Figure 5-21 and Figure 5-22). The correlation with OC concentrations had the maximum R^2 value of 0.02 (Figure 5-23). Similarly, the highest correlation with EC was an R^2 value of 0.05 (Figure 5-24). The conclusion from this analysis is the n-alkanols did not show a correlation with EC or OC at any of the six SOAP 2002-2007 sampling sites. The biogenic contribution to the NYC metropolitan area cannot be predicted using EC and OC concentrations but would need to be quantified separately according to this study.

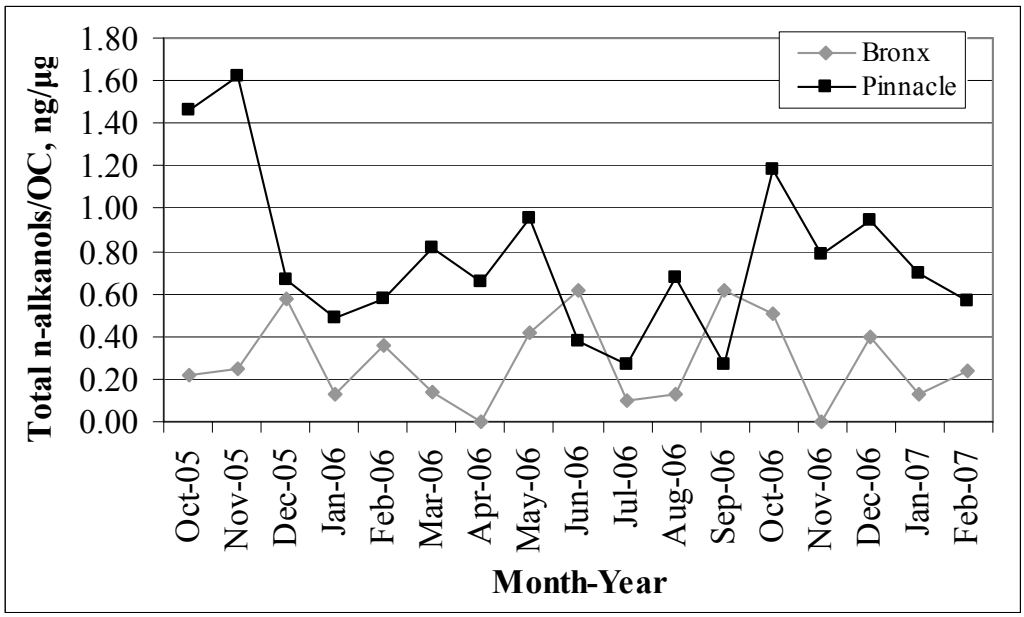


Figure 5-21 Total n-alkanols normalized to OC in NY (SOAP NY)

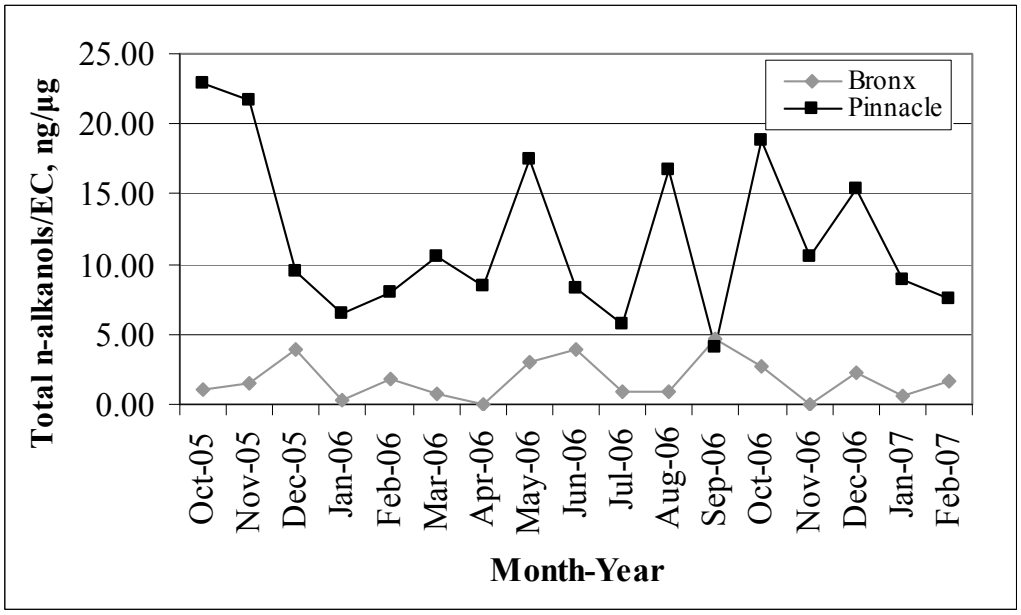


Figure 5-22 Total n-alkanols normalized to EC in NY (SOAP NY)

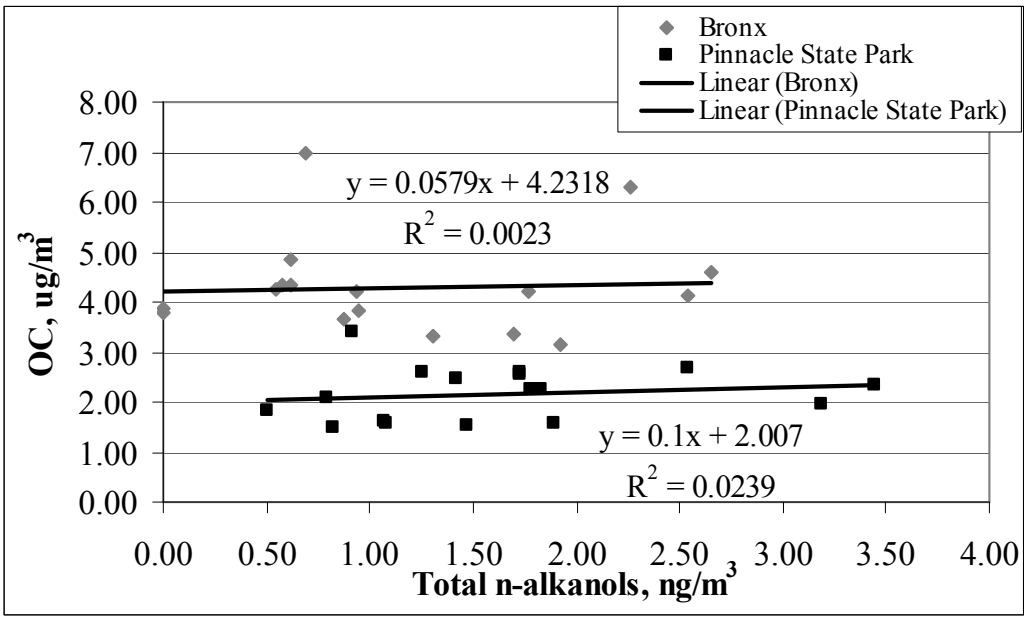


Figure 5-23 Total n-alkanols versus OC in NY (SOAP NY)

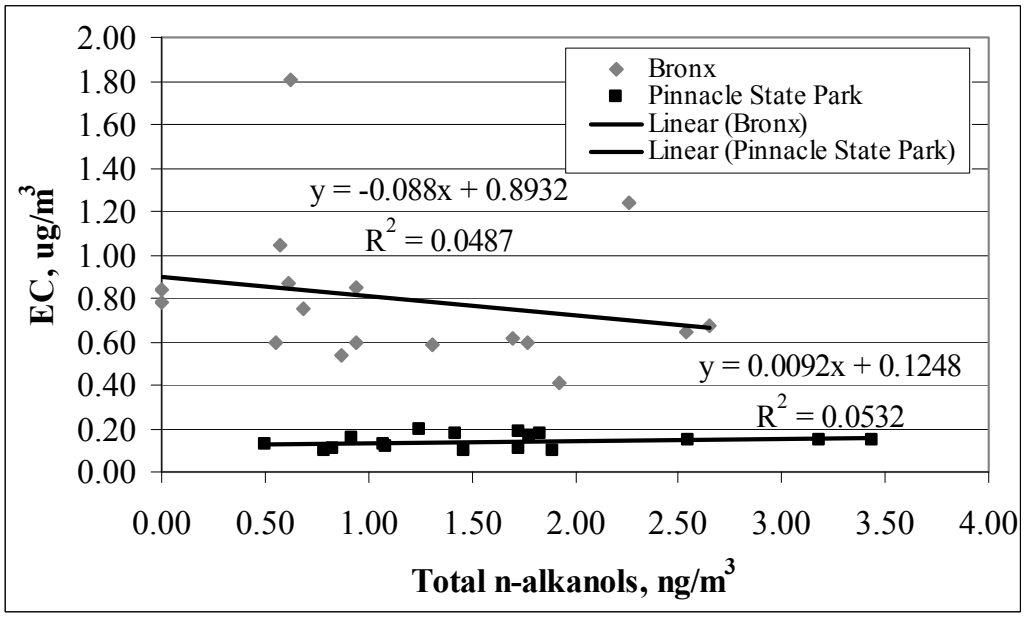


Figure 5-24 Total n-alkanols versus EC in NY (SOAP NY)

The EC normalized total n-alkanols data were separated into urban and rural sites and compared with ANOVA tables, as previously described. A statistical difference was found comparing the urban versus rural sites at the 95% confidence level for the entire

year (p-value = $3.8 * 10^{-8}$) and for all seasons except the summer (p-value = 0.16) (Appendix L). These results are opposite to the ANOVA tables generated for the ambient molecular marker concentrations, which found there was no statistical difference between urban and rural sites. These normalized results suggest that meteorological conditions, such as depth of the mixing layer, influence molecular marker concentrations in ambient atmospheres and are a preferred method to compare seasonal and spatial emissions at receptor sites. The normalization calculation also provides evidence that relative emissions of total n-alkanols in rural sites differ from urban sites indicating stronger biogenic input of fine PM.

5.3.3. Meat Charbroiling

The OC and EC normalized cholesterol data did not show constant ratios during the SOAP 2002-2003 sampling campaign for any of the four sites (Figure 5-25 and Figure 5-26). When the data was normalized to EC, the seasonal trends were not as apparent as with the OC normalized data. The ratio was highest in the colder weather at all sites. The high ratio found in Chester, NJ in the winter was for the sample that was deemed an outlier by statistical analysis. These results show year-round meat charbroiling emissions in urban areas; however the spatial and temporal variations of the cholesterol marker make it difficult to predict from OC or EC.

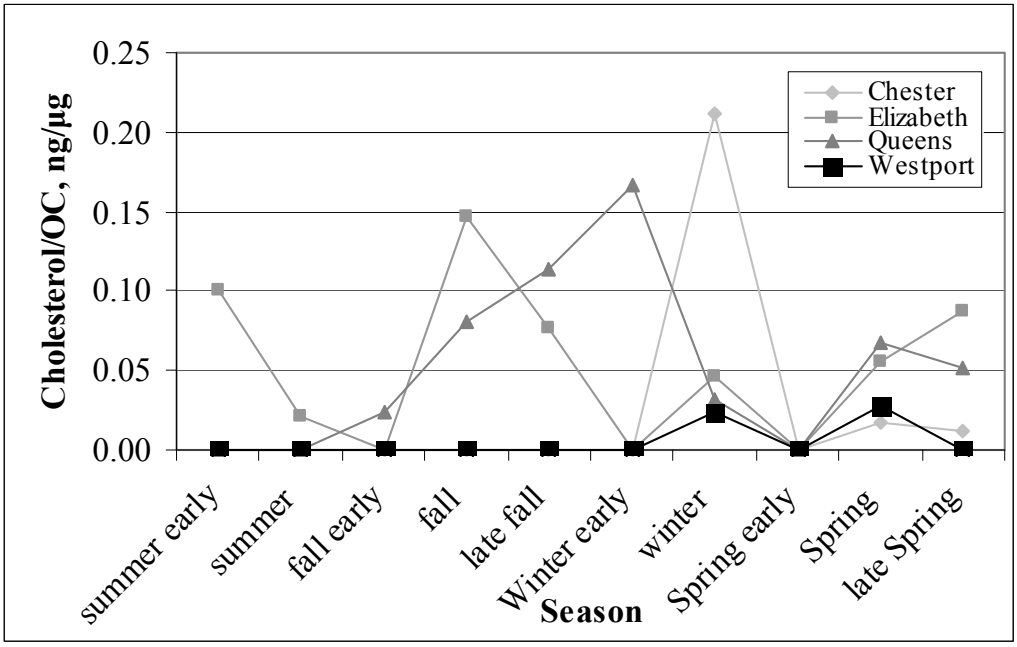


Figure 5-25 Cholesterol normalized to OC in the NYC area (SOAP 2002-2003)

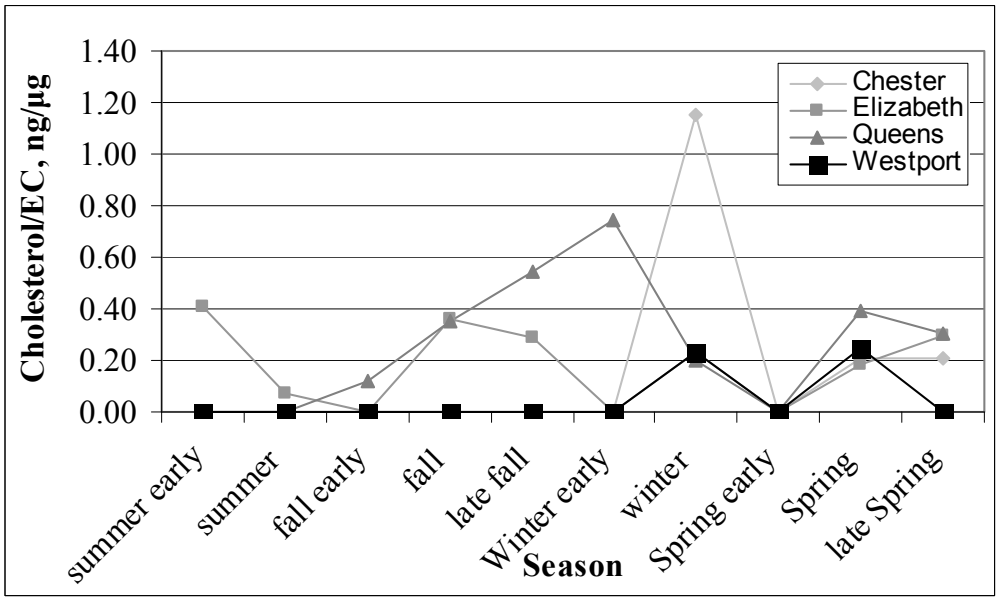


Figure 5-26 Cholesterol normalized to EC in the NYC area (SOAP 2002-2003)

The cholesterol data also was plotted against OC and EC with scatter plots. The correlations with OC were low for all sites and ranged from 0.0342 to 0.437 as shown in Figure 5-27 and Figure 5-28. Elizabeth, NJ, and Westport, CT, showed no correlation to

EC with R^2 values less than 0.2. Cholesterol versus EC in Chester, NJ had a correlation of 0.89, a value that suggests high statistical correlation (Figure 5-30). However, because most of the cholesterol concentrations cluster around zero, the least squares linear model shows there is not a definite correlation. Cholesterol rarely was found in samples from Chester, NJ, yet the linear correlation for EC suggests values could be predicted for cholesterol. However, this is not the case because most samples were non-detects or near the limit of detection with a single outlier which skewed the linear least squares model. Cholesterol versus EC in Queens, NY had an R^2 value of 0.82, indicating a strong linear correlation between cholesterol and EC (Figure 5-29). This is a valid result because cholesterol is present year round in Queens, NY. The SOAP 2002-2003 results suggest cholesterol and EC correlate better in urban sites than in the rural site. The higher density of restaurants in the NYC area collectively emit more cholesterol as a primary emission from meat charbroiling (and deep fat frying) compared to the Chester, NJ rural site.

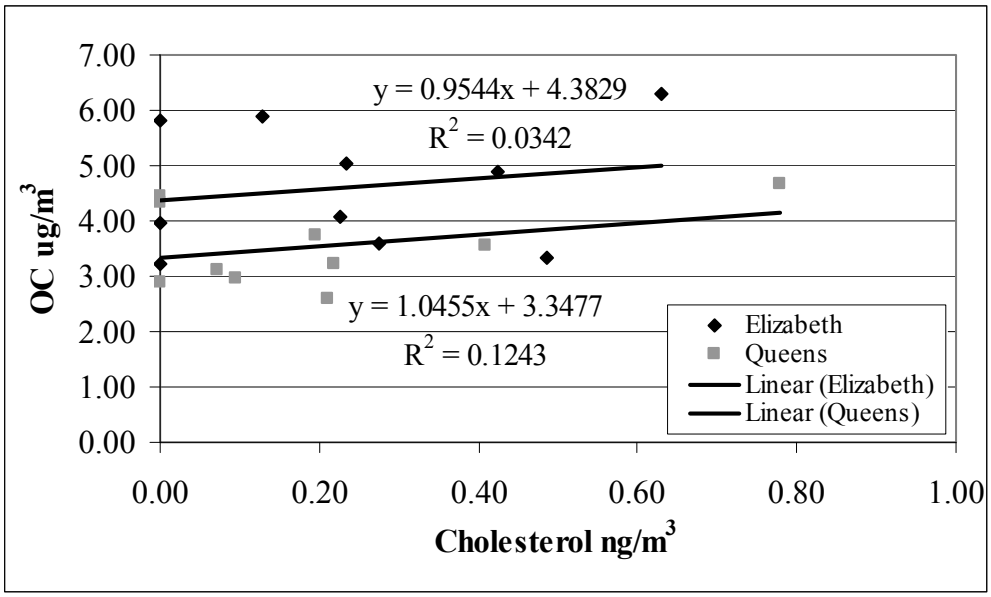


Figure 5-27 Cholesterol versus OC in the urban NYC area (SOAP 2002-2003)

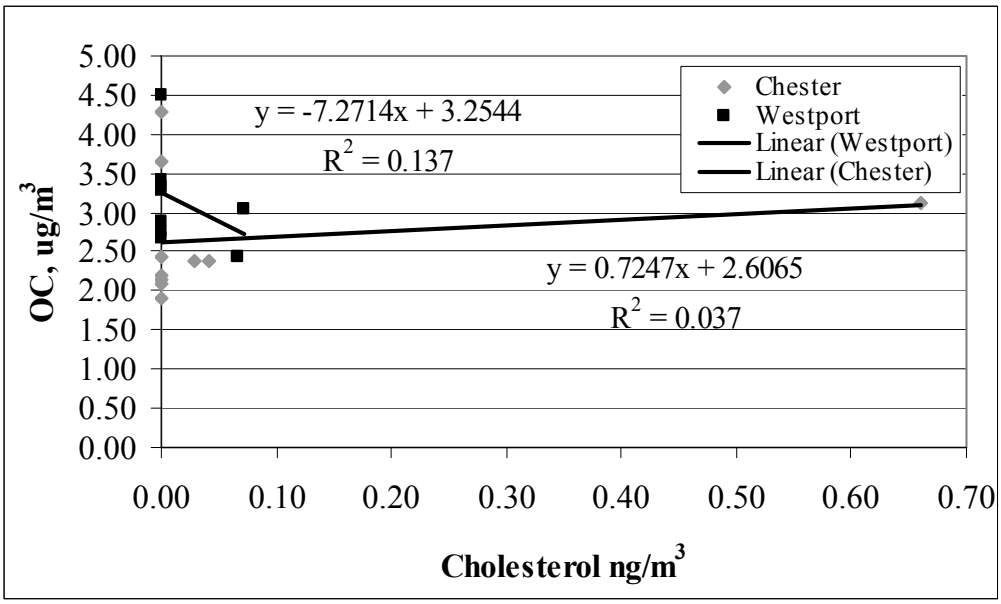


Figure 5-28 Cholesterol versus OC in the NYC area (SOAP 2002-2003)

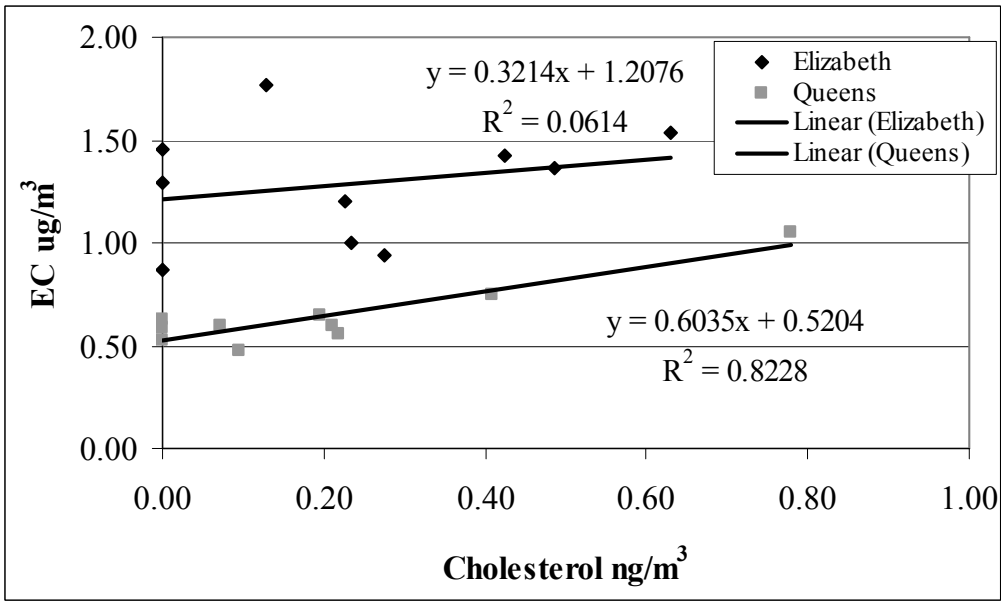


Figure 5-29 Cholesterol versus EC in the urban NYC area (SOAP 2002-2003)

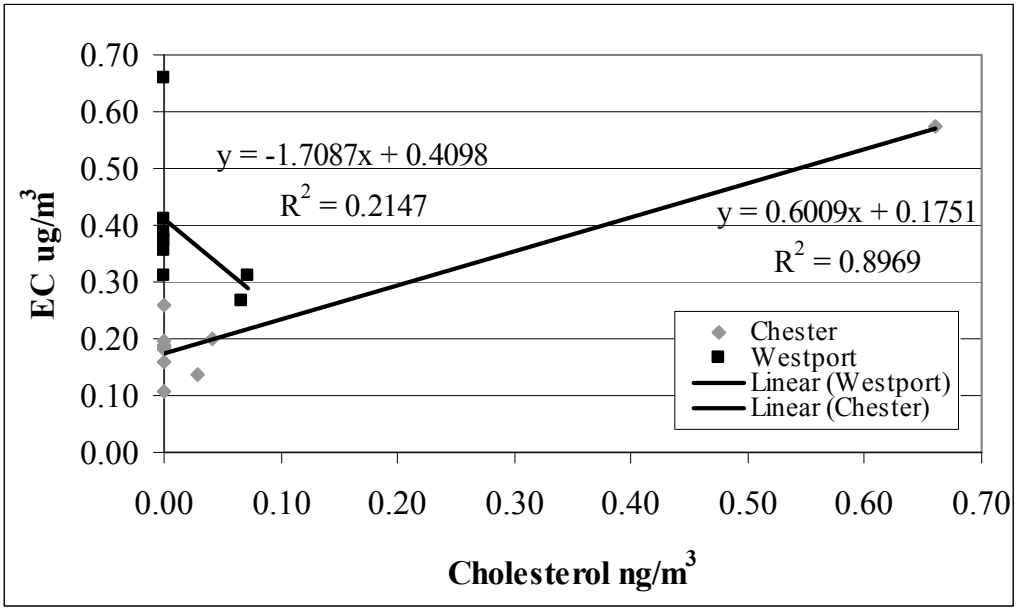


Figure 5-30 Cholesterol versus EC in the NYC area (SOAP 2002-2003)

The 2005-2007 cholesterol data was normalized to OC and EC. No trends were apparent for Pinnacle State Park, NY since the concentrations of the marker were slightly above the detection limit for only a few samples. The Bronx, NY site, however, showed seasonal trends when it was normalized to OC and EC ambient mass concentrations (Figure 5-31 and Figure 5-32). The normalized cholesterol peaked in the winter and decreased in the summer, but was consistently present in all samples. Cholesterol concentrations also were plotted versus the OC and EC concentrations with scatter plots. The correlation between OC and cholesterol was less than 0.14 indicating no linear correlation between these two variables (Figure 5-33). Cholesterol and EC had an R^2 = 0.4289 in Bronx, NY, indicating a weak correlation (Figure 5-34). Although meat charbroiling is a year round emission source of fine PM in Bronx, NY, it is not the dominant source of carbonaceous PM.

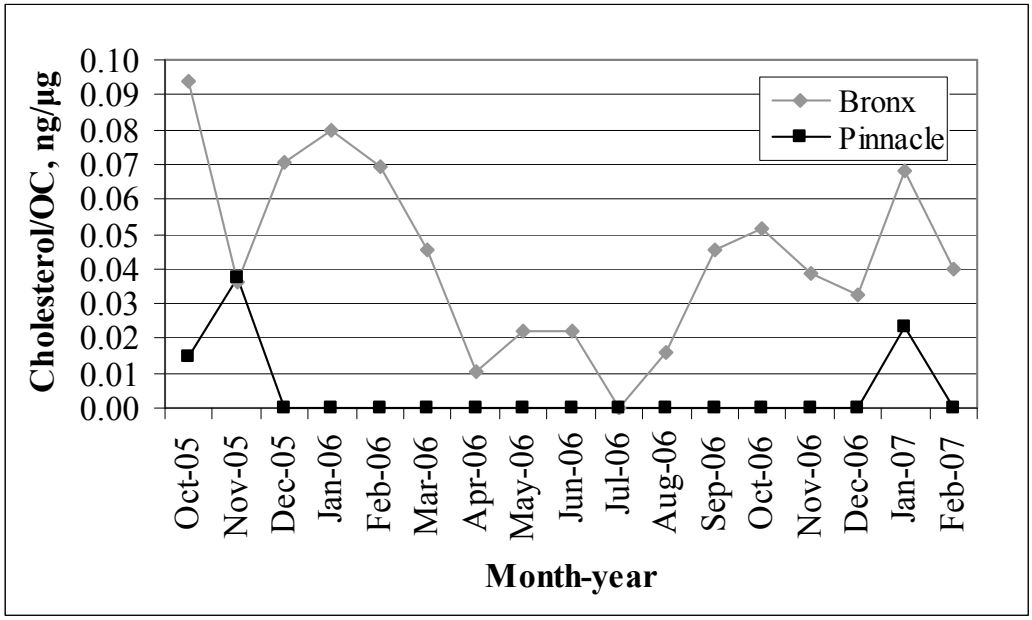


Figure 5-31 Cholesterol normalized to OC in NY (SOAP NY)

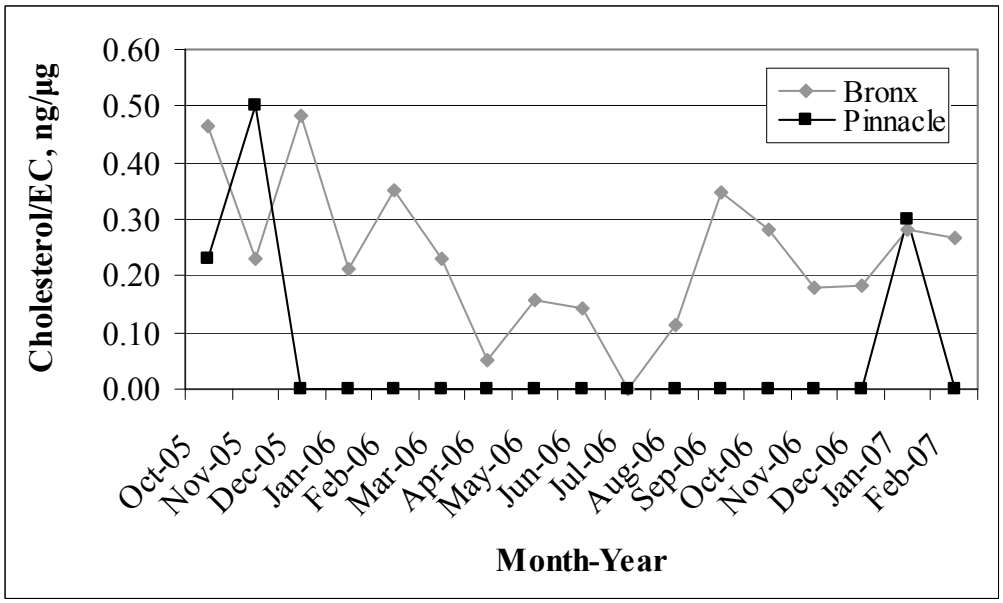


Figure 5-32 Cholesterol normalized to EC in NY (SOAP NY)

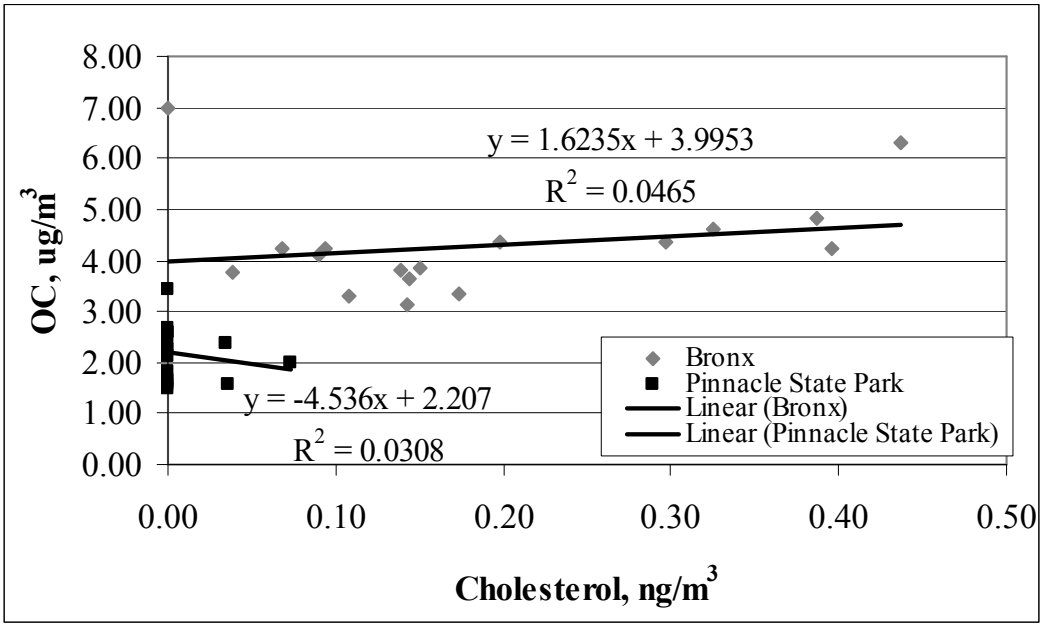


Figure 5-33 Cholesterol versus OC in NY (SOAP NY)

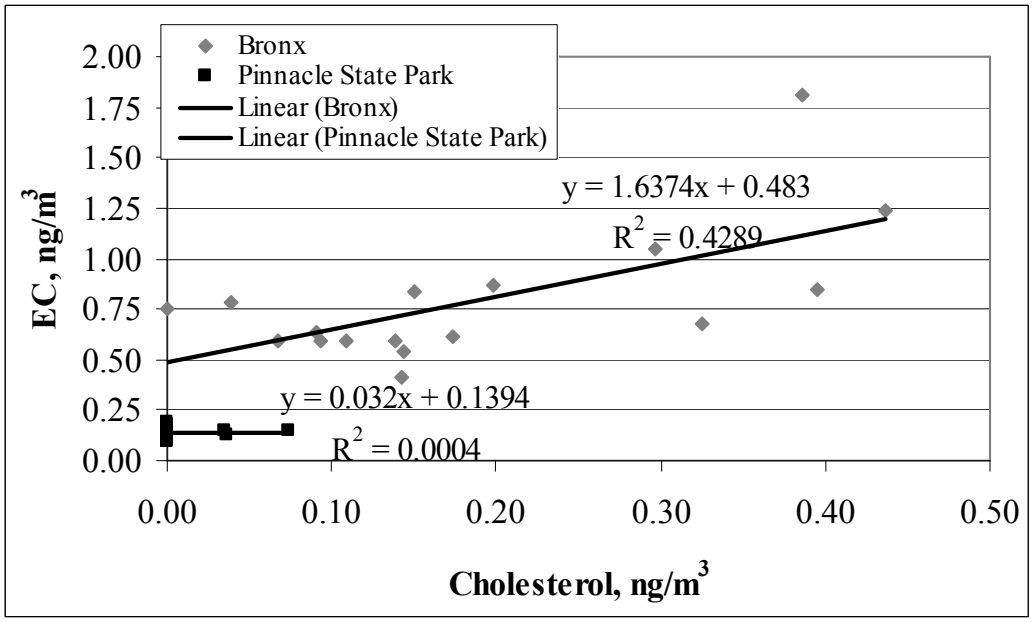


Figure 5-34 Cholesterol versus EC in NY (SOAP NY)

The EC normalized cholesterol data was separated into urban and rural sites for the SOAP 2002-2007 samples and were compared using ANOVA results, as previously described (Appendix L). A statistical difference was found between urban versus rural

sites at the 95% confidence level for the entire year (p-value = 0.049), but not for the individual seasons (p-values ranged from 0.11 to 0.54) (Appendix L). These results are similar to the results from the ANOVA evaluations on the molecular markers, which found a statistical difference between urban and rural sites for the full year SOAP 2002-2007.

5.3.4. Biogenic Oxidation Product

Ambient cis-pinonic acid mass concentrations were normalized to OC and EC concentrations. The data obtained from the 2002-2003 sampling campaign showed the highest ratio of cis-pinonic acid to OC in the rural location, Chester, NJ (Figure 5-35). The seasonal trend in Chester, NJ demonstrated an increase in the fall and spring and a minimum in the winter. The urban locations showed lower ratios with similar seasonal trends in summer and spring. The EC normalized cis-pinonic acid had similiar spatial and seasonal trends as the OC normalized cis-pinonic acid (Figure 5-36). The Westport, CT EC normalized cis-pinonic acid, however, showed less seasonal variation than the OC normalized cis-pinonic acid.

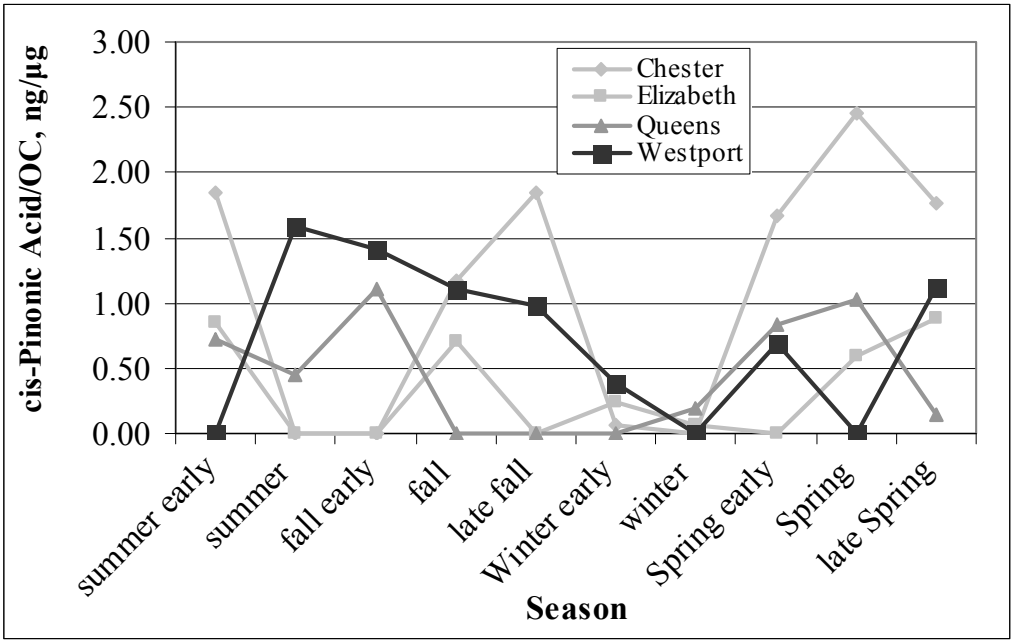


Figure 5-35 cis-Pinonic acid normalized to OC in the NYC area (SOAP 2002-2003)

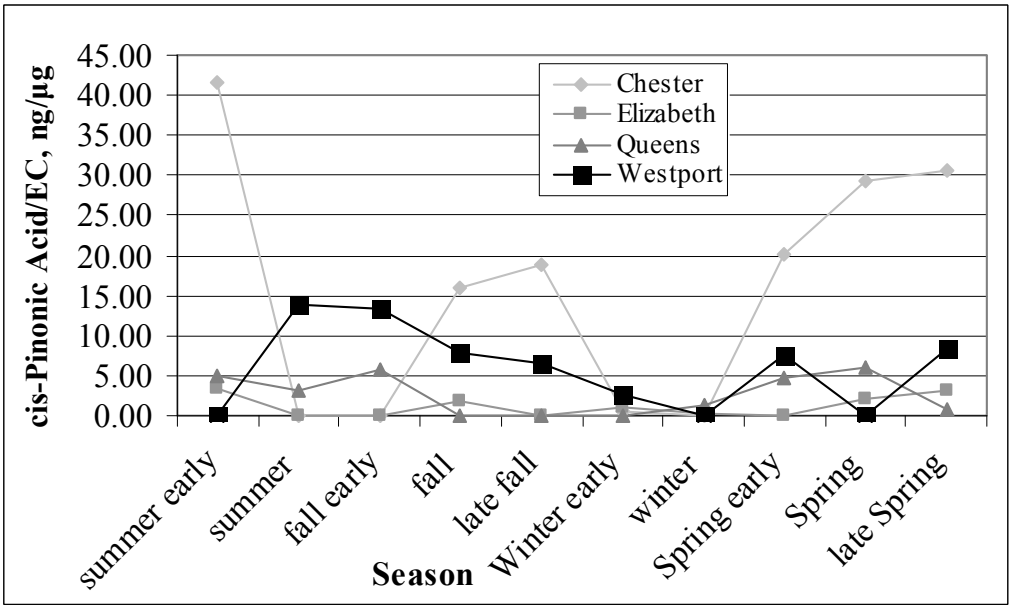


Figure 5-36 cis-Pinonic acid normalized to EC in the NYC area (SOAP 2002-2003)

Scatter plots of cis-pinonic acid versus OC and EC were prepared for each SOAP 2002-2003 sampling site (Figure 5-37, Figure 5-38, Figure 5-39 and Figure 5-40). No correlations were observed between cis-pinonic acid versus OC or EC. The highest

correlation found was an $R^2 = 0.2074$ at Queens, NY for cis-pinonic acid versus EC, indicating a very weak correspondence. These results indicate that cis-pinonic acid cannot be linearly determined from OC or EC.

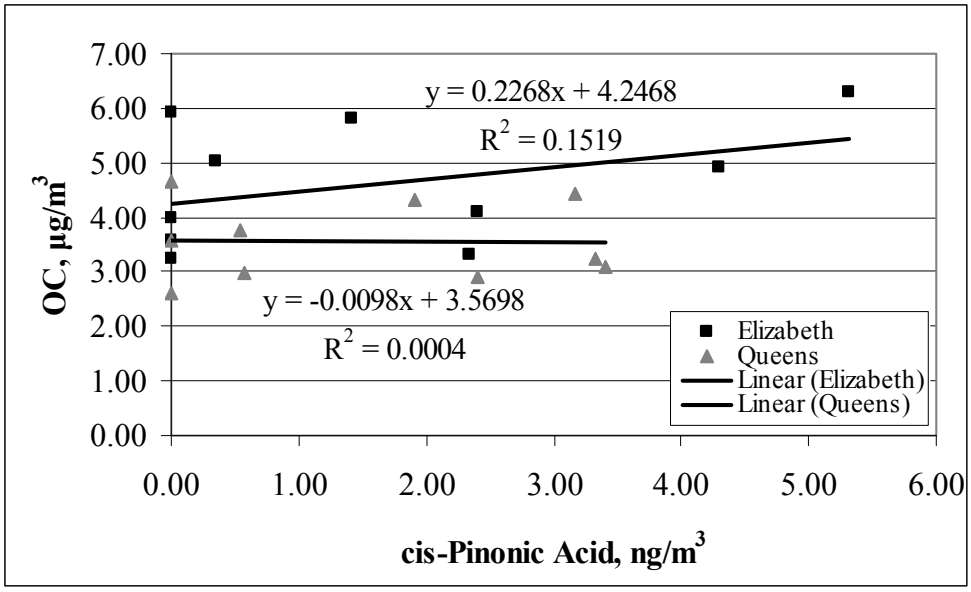


Figure 5-37 cis-Pinonic acid versus OC in the urban NYC area (SOAP 2002-2003)

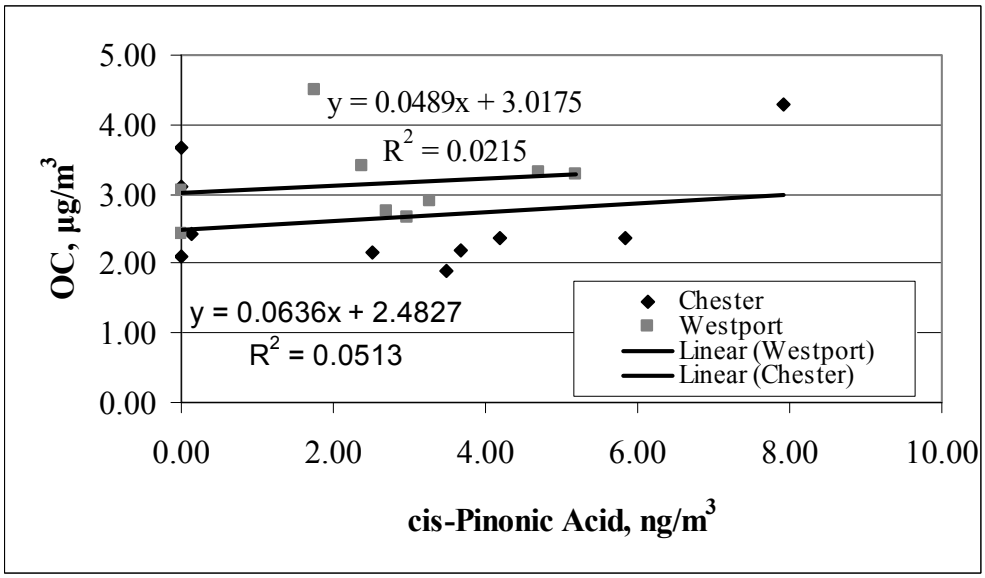


Figure 5-38 cis-Pinonic acid versus OC in the NYC area (SOAP 2002-2003)

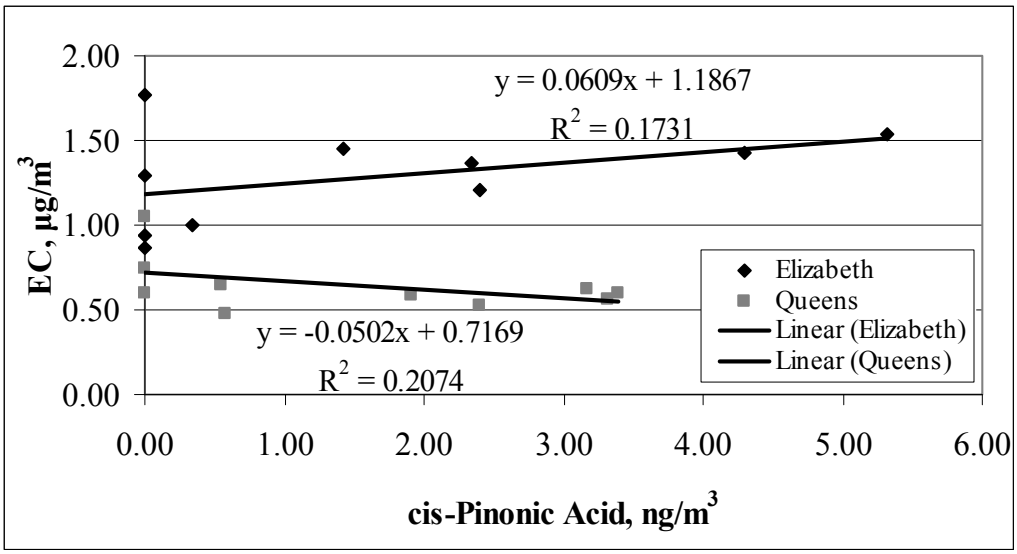


Figure 5-39 cis-Pinonic acid versus EC in the urban NYC area (SOAP 2002-2003)

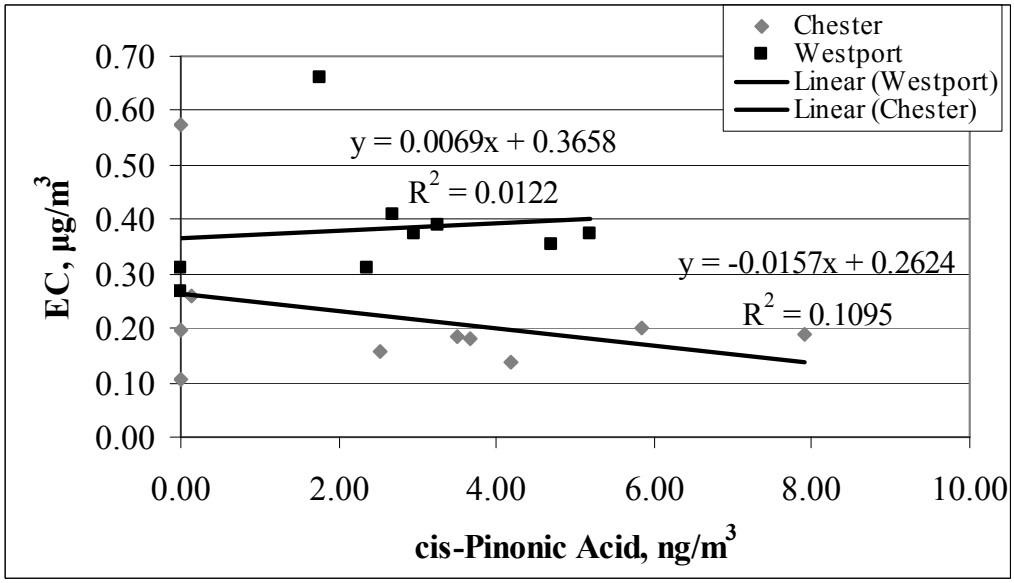


Figure 5-40 cis-Pinonic acid versus EC in the NYC area (SOAP 2002-2003)

The ratio of cis-pinonic acid to OC and to EC were found to be higher in Pinnacle State Park, NY than in Bronx, NY for all months except July and August when cis-pinonic acid was below the detection limit at Pinnacle State Park, NY (Figure 5-41 and Figure 5-42). The rural site tended to have higher ratios than the urban in both field sampling campaigns. This is expected because cis-pinonic acid is formed from the

oxidation of alpha-pinene which originates from higher plants. Land use patterns in rural areas have greater coverage of native vegetation and agricultural land compared to urban areas, resulting in higher concentrations of the monoterpene precursor. Again, the ratios were not constant but varied by season and location. The ratio was greatest at Pinnacle State Park, NY in November and December which indicates lower oxidant concentrations during winter, thus allowing cis-pinonic acid to persist.

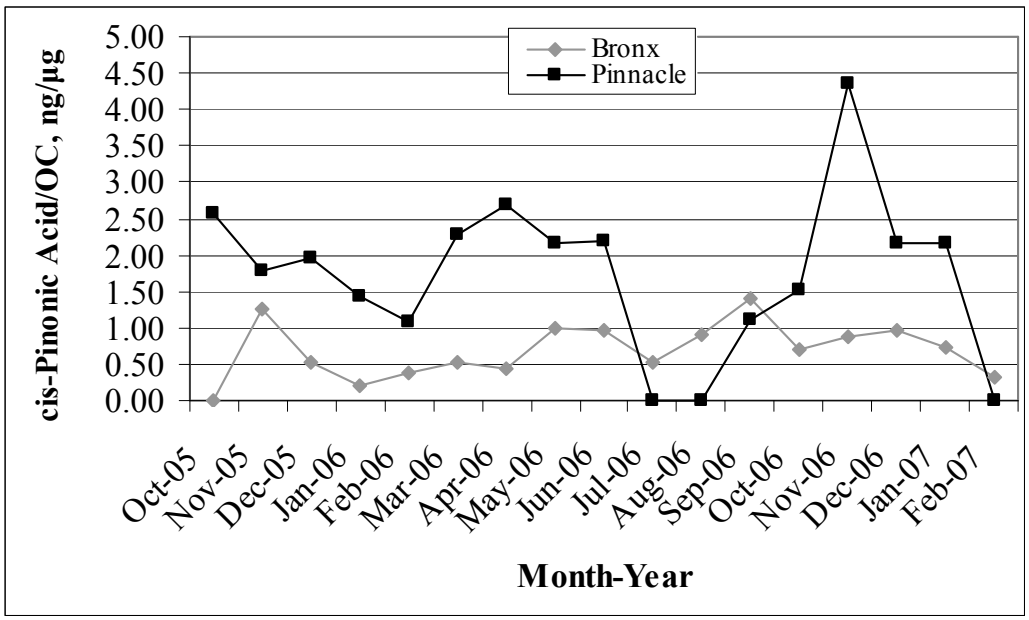


Figure 5-41 cis-Pinonic acid normalized to OC in NY (SOAP NY)

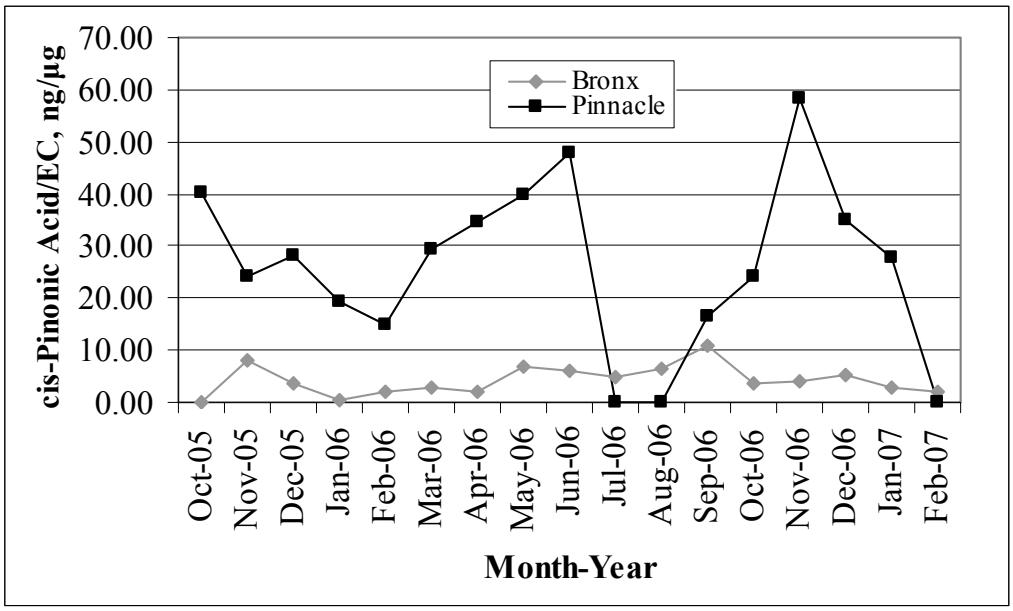


Figure 5-42 cis-Pinonic acid normalized to EC in NY (SOAP NY)

Scatter plots of cis-pinonic acid versus OC and EC ambient mass concentrations were prepared for the SOAP NY sites (Figure 5-43 and Figure 5-44). No correlation was found between cis-pinonic acid versus OC or EC. The highest correlation versus OC was an $R^2 = 0.0018$ at Bronx, NY. The highest correlation versus EC was an $R^2 = 0.2259$ at Bronx, NY. These results indicate that cis-pinonic acid cannot be interpolated from OC or EC in urban or rural locations.

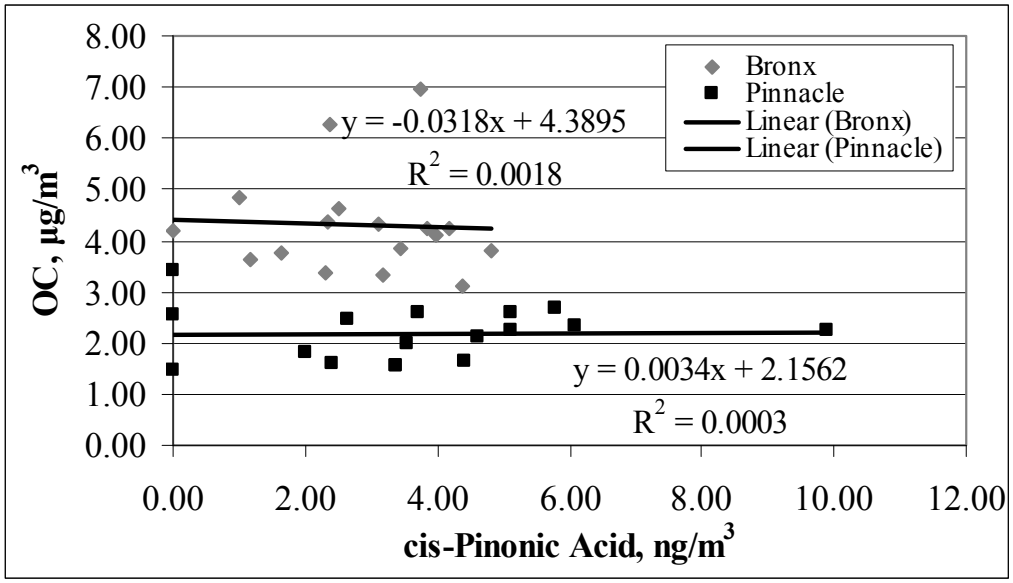


Figure 5-43 cis-Pinonic Acid versus OC in NY (SOAP NY)

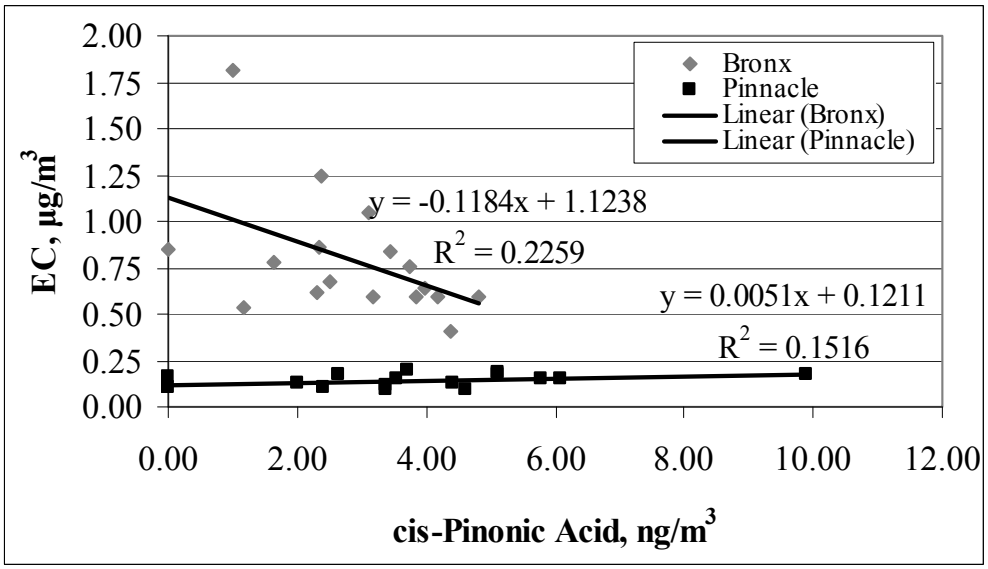


Figure 5-44 cis-Pinonic acid versus EC in NY (SOAP NY)

The EC normalized cis-pinonic acid data was separated into urban and rural sites for the SOAP 2002-2007 samples and were compared using ANOVA tables, as described previously. A statistical difference was found comparing urban versus rural sites at the 95% confidence level for the entire year (p-value = $3.55 * 10^{-10}$) and for winter (p-value =

0.003), spring (p-value = $1.66 * 10^{-9}$) and fall (p-value = 0.0005), but not for the summer (p-value = 0.18), as shown in Appendix L. These results are similar to the ANOVA test results for the molecular marker ambient concentrations. A statistical difference was determined comparing the SOAP 2002-2007 urban and rural sites for the entire year and for the spring, but not for the remaining three seasons. These results indicate levels of cis-pinonic acid in rural sites are different than urban sites. The higher normalized ratios of cis-pinonic acid to OC and EC at the rural sites suggest greater relative input of biogenic PM mass compared to urban sources.

5.3.5. Low Molecular Weight Highly Oxidized Acids

Ambient levulinic acid concentrations were normalized to OC and EC data. Levulinic acid was chosen for this analysis because it was the only oxoacid consistently found in the ambient samples. Additionally, as previously discussed, levulinic acid was soluble in the solvents used to extract filters. The data obtained from the 2002-2003 sampling campaign showed the highest ratio of levulinic acid to OC was found in Chester, NJ and Westport, CT (Figure 5-45). No seasonal trends were apparent for the OC normalized levulinic acid. The EC normalized levulinic acid had similiar spatial trends as the OC normalized levulinic acid (Figure 5-46). The highest values were found in Chester, NJ. Only the samples at Chester, NJ showed seasonal trends, with the highest values in the spring and early summer. The Westport, CT site demonstrated similar trends to Chester, NJ. The urban sites did not show a seasonal distribution. The ratios varied based on season and location. The highest levulinic acid to OC ratio was in Westport, CT in the fall and the highest levulinic acid to EC ratio was in Chester, NJ in the early summer.

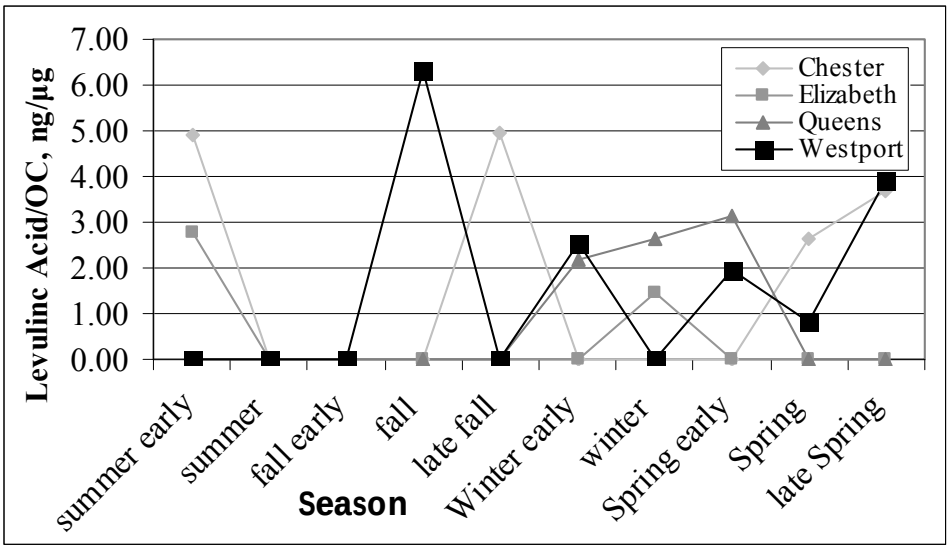


Figure 5-45 Levulinic acid normalized to OC in the NYC area (SOAP 2002-2003)

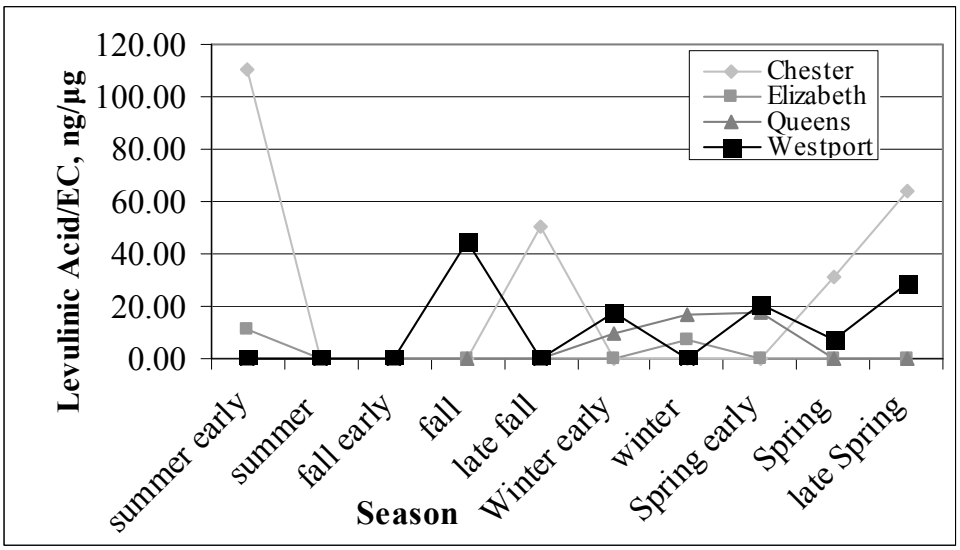


Figure 5-46 Levulinic acid normalized to EC in the NYC area (SOAP 2002-2003)

Scatter plots of levulinic acid versus OC and EC were constructed for each SOAP 2002-2003 sampling site. No correlation was found for levulinic acid versus OC or EC (Figure 5-47, Figure 5-48, Figure 5-49 and Figure 5-50). The highest correlation found was an $R^2 = 0.3076$ at Elizabeth, NJ for levulinic acid versus OC, indicating a very weak relationship.

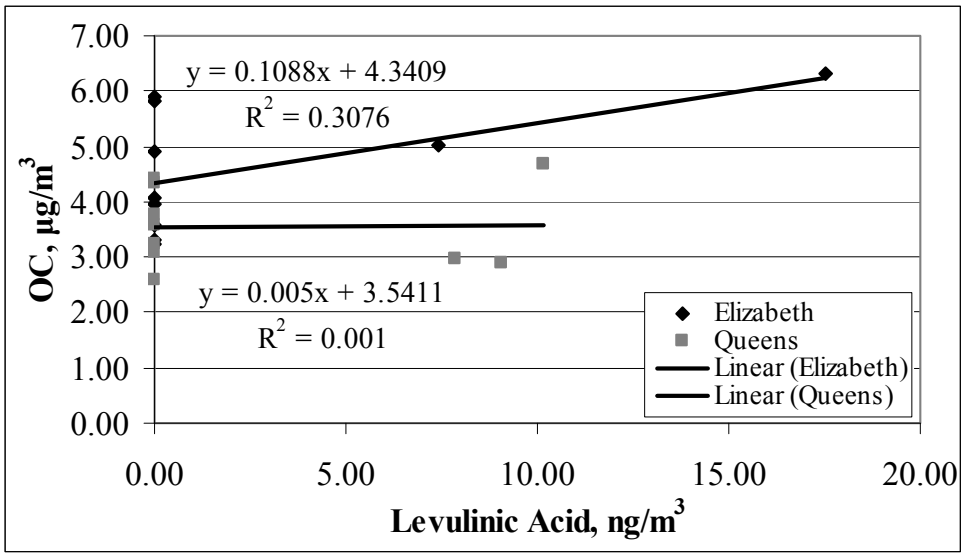


Figure 5-47 Levulinic acid versus OC in the urban NYC area (SOAP 2002-2003)

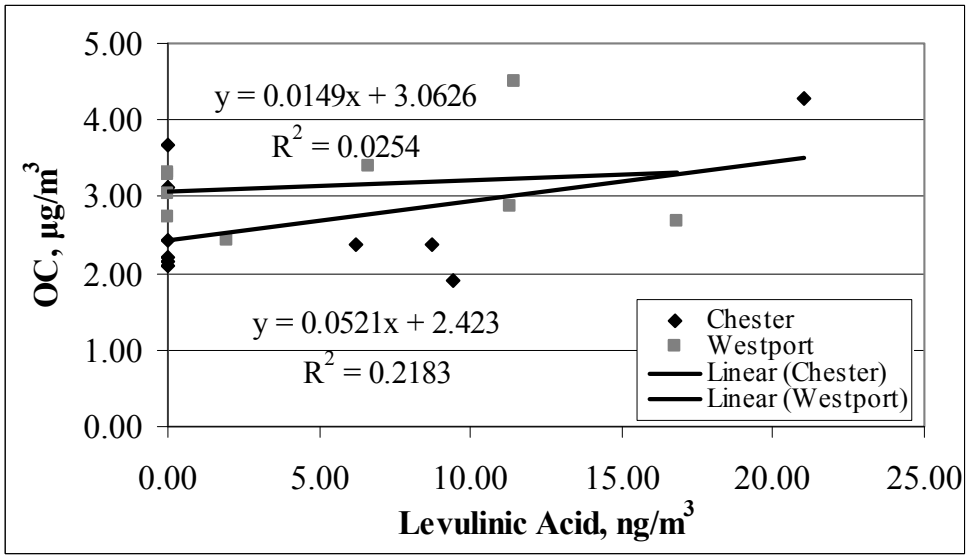


Figure 5-48 Levulinic acid versus OC in the NYC area (SOAP 2002-2003)

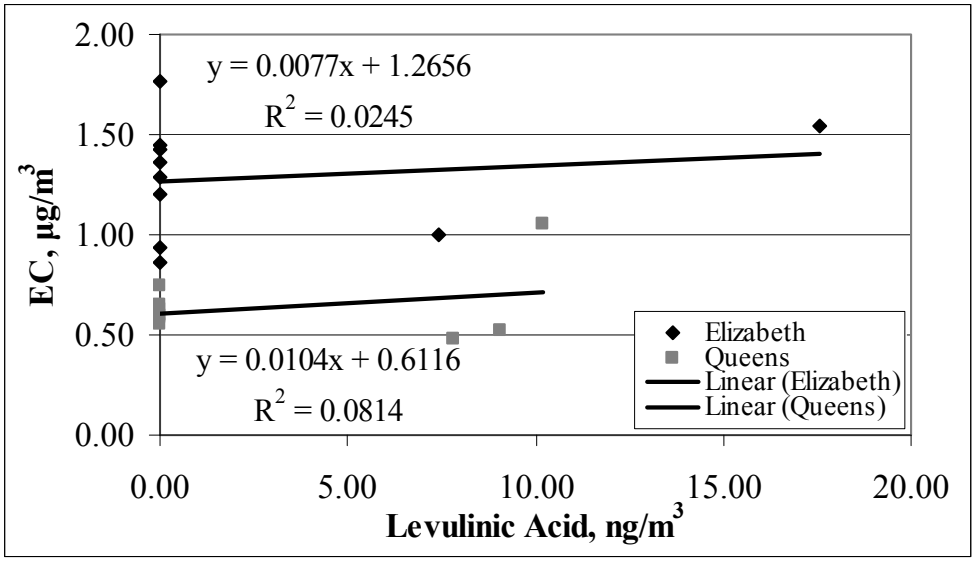


Figure 5-49 Levulinic acid versus EC in the urban NYC area (SOAP 2002-2003)

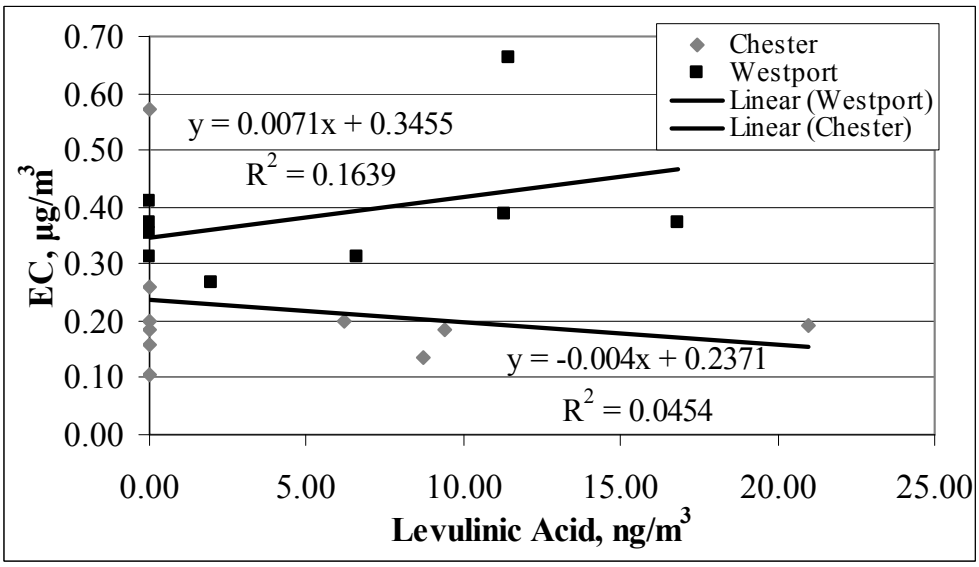


Figure 5-50 Levulinic acid versus EC in the NYC area (SOAP 2002-2003)

The ratios of levulinic acid to OC and to EC were higher in Pinnacle State Park, NY than in Bronx, NY for all months except July 2006 (Figure 5-51 and Figure 5-52). The highest ratio to OC was found in the spring months, May and June. The highest ratio to EC was found in the same two months, May and June. The rural sites tended to have

higher ratios than the urban in both field sampling campaigns, although there was no consistent seasonal maximum at either the rural or urban sites.

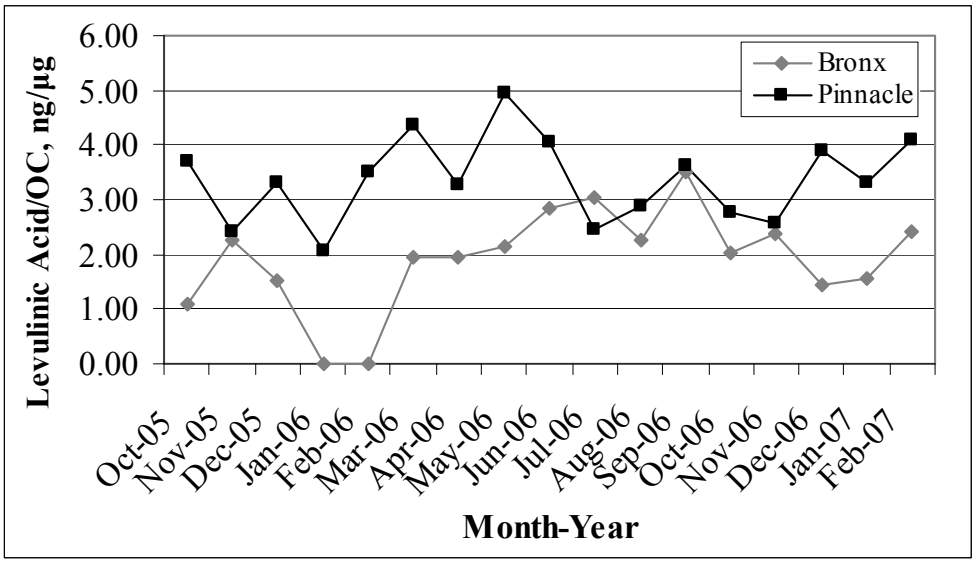


Figure 5-51 Levulinic acid normalized to OC in NY (SOAP NY)

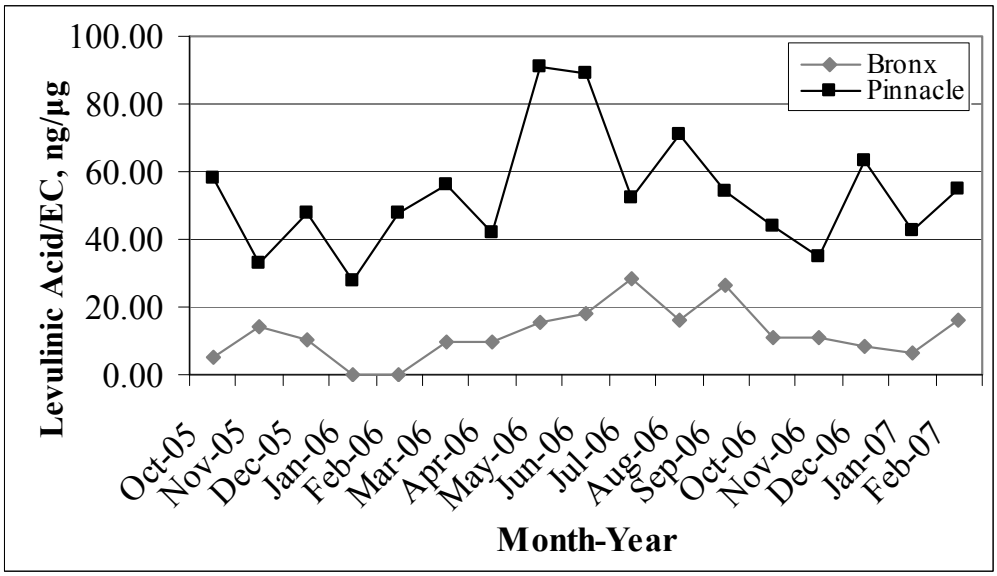


Figure 5-52 Levulinic Acid normalized to EC in NY (SOAP NY)

Scatter plots of levulinic acid versus OC and EC were generated for both SOAP NY sampling sites. No correlation was found comparing levulinic acid versus OC or EC ambient concentrations (Figure 5-53 and Figure 5-54). The highest correlation found was

an $R^2 = 0.3386$ and $R^2 = 0.3215$ at Pinnacle State Park, NY for levulinic acid versus OC and EC, respectively. Both values were higher than the highest correlation found in the SOAP 2002-2003 sampling campaign. These results indicate that levulinic acid can not be linearly determined from OC or EC at urban or rural locations.

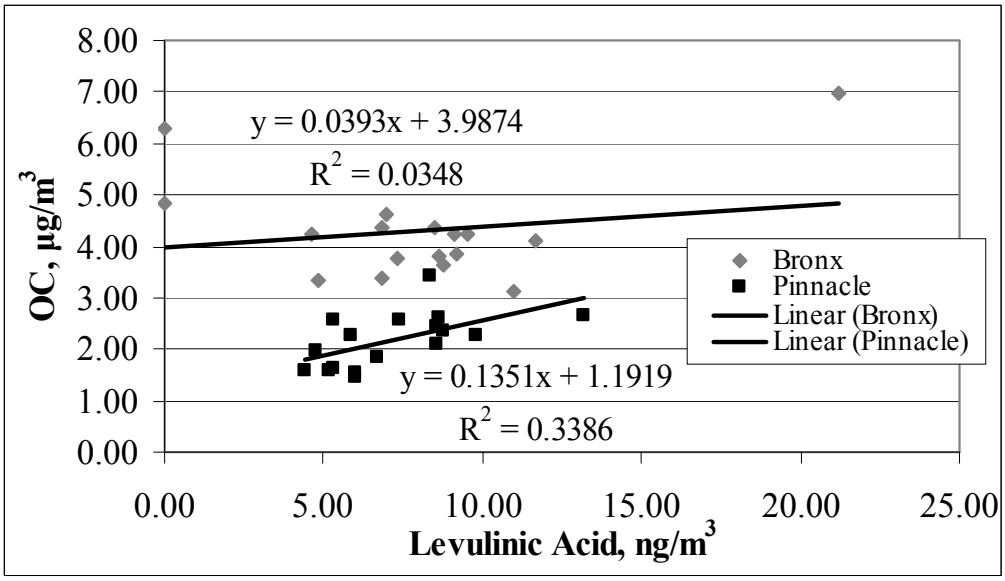


Figure 5-53 Levulinic acid versus OC in NY (SOAP NY)

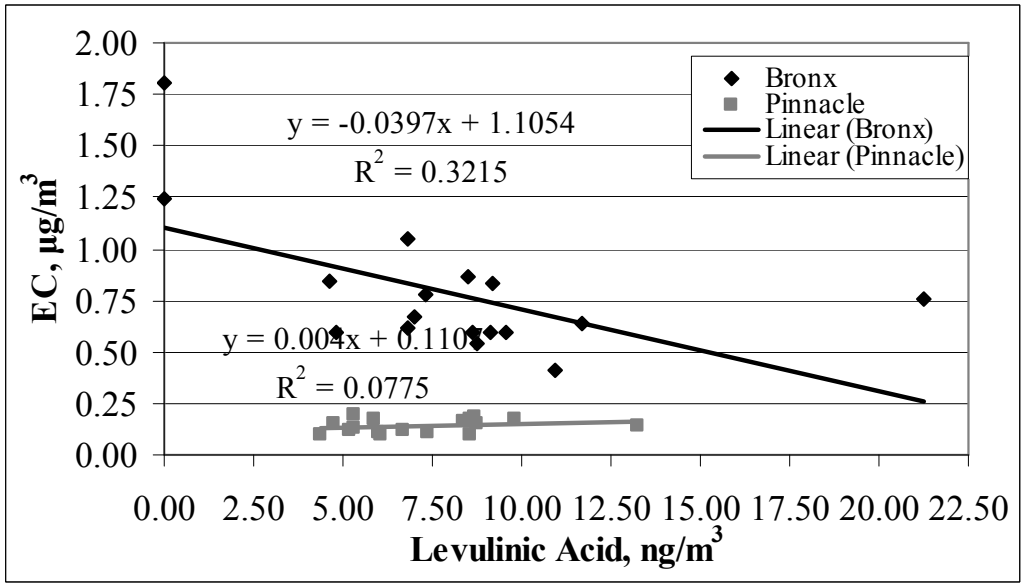


Figure 5-54 Levulinic acid versus EC in NY (SOAP NY)

The EC normalized levulinic acid data for SOAP 2002-2007 samples were separated into urban and rural sites and compared with ANOVA statistical analysis, as previously described. A statistical difference was found comparing the urban versus rural sites at the 95% confidence level for the entire year (p-value = $4.51 * 10^{-10}$) and for all four seasons (p-values ranged from 0.001 to 0.004) as shown in Appendix L. These results are contrary to the ANOVA results comparing the molecular marker ambient concentrations, which found no statistical difference between urban and rural sites for the entire year or for any of the four seasons. The EC normalized levulinic acid results indicate meteorological conditions, such as depth of the mixing layer, have an effect on molecular marker concentrations in ambient atmospheres. Therefore, the normalized concentrations are a better tool for assessing seasonal and spatial patterns of this marker compound. The normalized levulinic acid concentrations provide evidence for differing aggregate sources of the marker in urban and rural locations in the NY/NJ/CT area. Table 5-9 summarizes the results for the statistical significance at the 95% confidence level for molecular markers normalized to EC for the SOAP 2002-2007 projects.

Table 5-9 Summary of ANOVA results for normalized molecular markers for SOAP 2002-2007

EC normalized compound	Statistical difference between Urban versus rural
Levoglucosan/EC	Yes
Total n-alkanols/EC	Yes
Cholesterol/EC	Yes
Cis-Pinonic acid/EC	Yes
Levulinic acid/EC	Yes

5.4. *Comparison to $PM_{2.5}$*

5.4.1. Wood Smoke

Levoglucosan was normalized to $PM_{2.5}$ mass concentrations (Figure 5-55). These values were used to assess temporal trends. The data can be found in Appendix M. The normalized data again showed variations with seasonal and temporal differences. The ratios, however, tended to follow the same trend in all sites except for Westport, CT which showed increases in fall. All sites peaked in late fall (8.97 ng/µg in Elizabeth, NJ to 19.32 ng/µg in Westport, CT). The values were lowest in the spring (0.21 ng/µg in Queens, NY to 0.33 ng/µg in Elizabeth, NJ) with a slight increase in the summer in all four sites. The levoglucosan emissions data do not have a direct ratio to the $PM_{2.5}$ mass for any location; therefore, it is not possible to estimate levoglucosan, or cellulose combustion inputs, from the more easily measured $PM_{2.5}$.

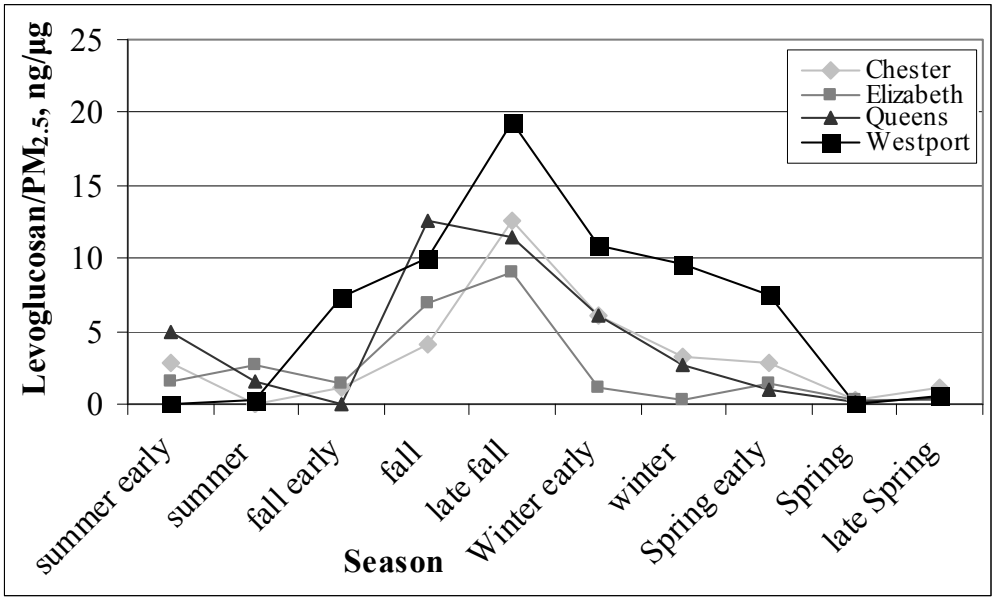


Figure 5-55 Levoglucosan normalized to $PM_{2.5}$ in the NYC area (SOAP 2002-2003)

Levoglucosan ambient mass concentrations were plotted against the $PM_{2.5}$ concentrations using a scatter plot to determine linear correlations. The levoglucosan concentrations for Queens, NY, Westport, CT, Elizabeth, NJ and Chester, NJ showed no correlation to $PM_{2.5}$ ambient concentrations (Figure 5-56 and Figure 5-57). The R^2 values generally were less than 0.1. Therefore, wood and biomass combustion were not a single dominant source of fine PM at these receptor sites.

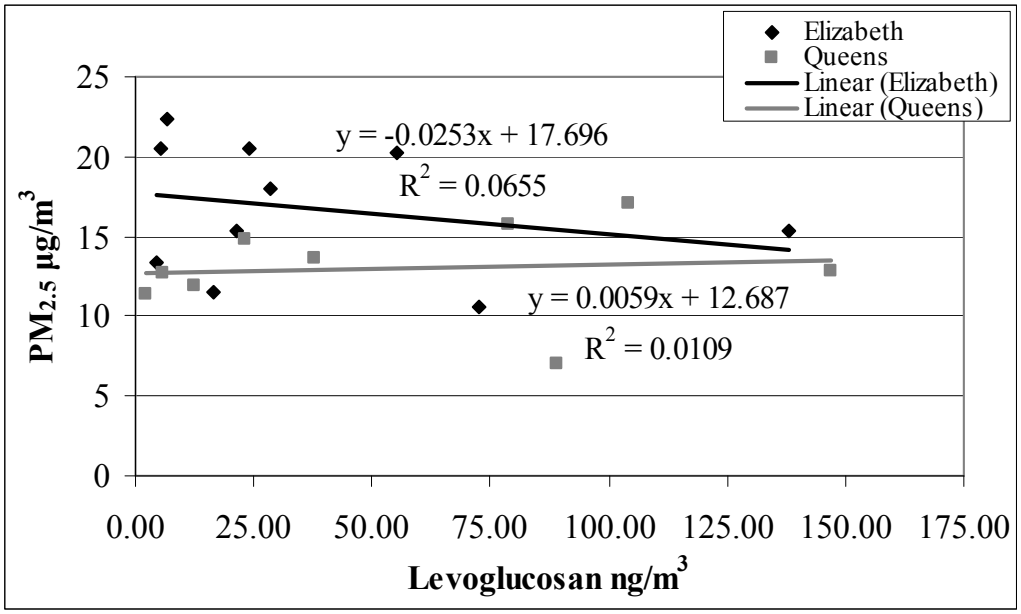


Figure 5-56 Levoglucosan versus $PM_{2.5}$ in the urban NYC area (SOAP 2002-2003)

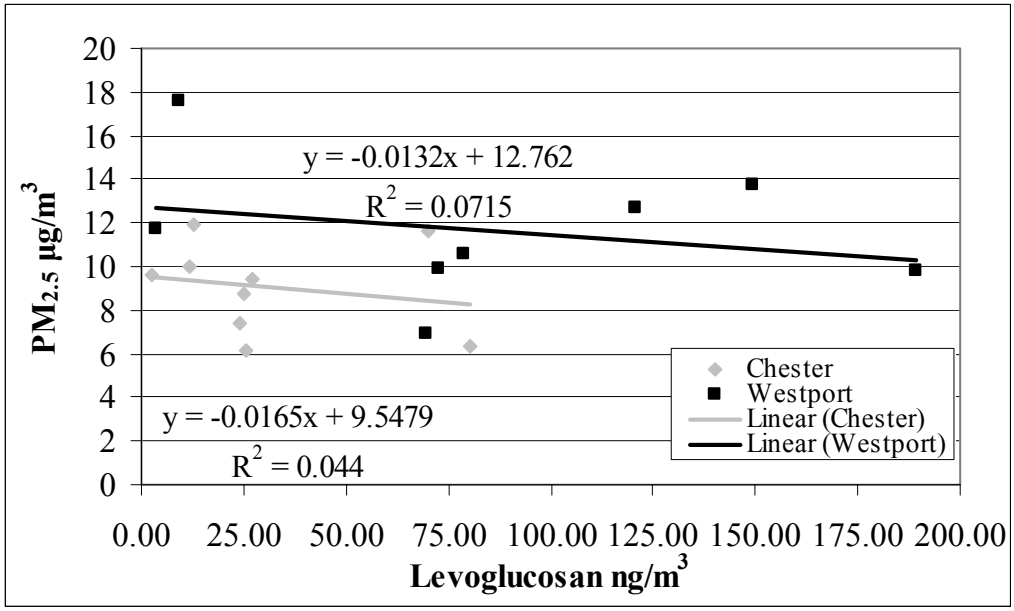


Figure 5-57 Levoglucosan versus $PM_{2.5}$ in the NYC area (SOAP 2002-2003)

Levoglucosan for the 2005 to 2007 SOAP NY project also was normalized to $PM_{2.5}$. The seasonal patterns were similar to those for the SOAP 2002-2003 project. The highest ratios of levoglucosan for $PM_{2.5}$ peaked in December and January at both sites (4.24 ng/µg in Bronx, NY to 12.96 ng/µg in Pinnacle State Park, NY) (Figure 5-58). The lowest values (0.24 ng/µg in Pinnacle State Park, NY to 0.87 ng/µg in Bronx, NY) were found in the summer from May to July. The levoglucosan emissions studies data do not provide a direct ratio to the $PM_{2.5}$ mass at either site, so currently no ratio can be determined to estimate cellulose combustion from the more easily measured $PM_{2.5}$ concentrations.

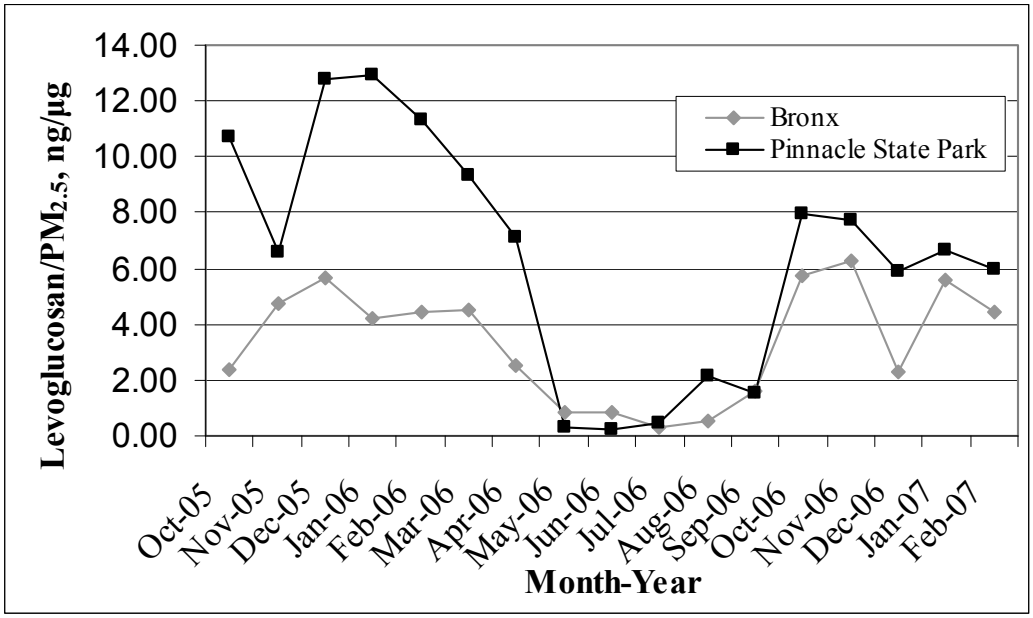


Figure 5-58 Levoglucosan normalized to $PM_{2.5}$ in NY (SOAP NY)

The Bronx, NY and Pinnacle State Park, NY showed no correlation with $PM_{2.5}$ (Figure 5-59). The R^2 values typically were below 0.1. The conclusion from this analysis is the levoglucosan data cannot be interpolated from $PM_{2.5}$. In order to determine the concentration of levoglucosan, or the influence of wood combustion to air quality, the levoglucosan itself must be measured.

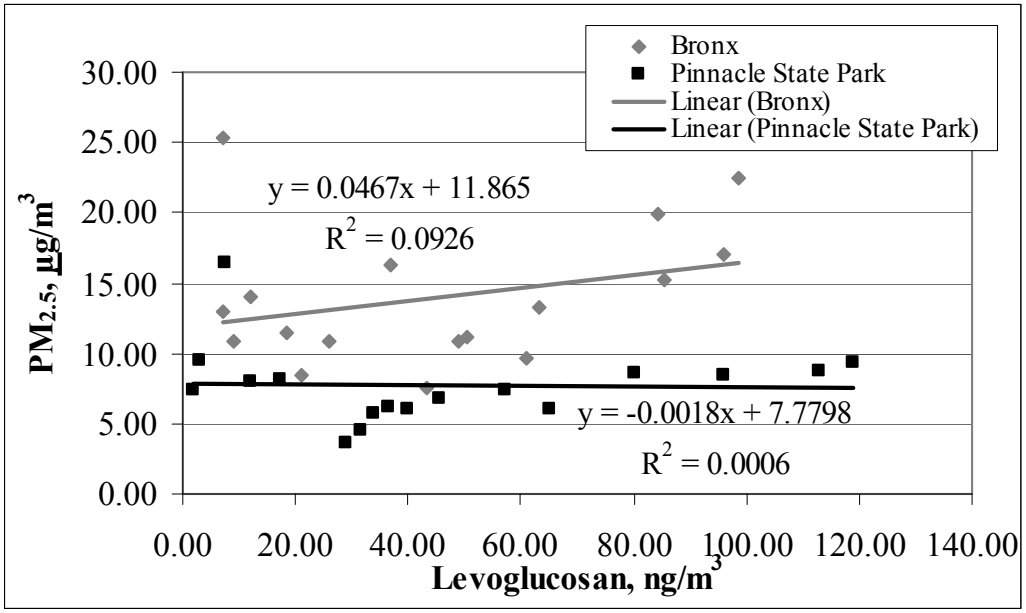


Figure 5-59 Levoglucosan versus $PM_{2.5}$ in NY (SOAP NY)

5.4.2. Biogenic Sources

The total n-alkanols were normalized to the $PM_{2.5}$ data for the 2002-2003 sampling campaign (Figure 5-60). The highest ratios (0.68 ng/µg to 0.81 ng/µg) for Queens, NY, Elizabeth, NJ and Chester, NJ were in early summer (no sample was collected for Westport, CT). The background site, Chester, NJ, generally had the lowest ratios in the late fall (0.09 ng/µg) whereas Westport, CT (0.35 ng/µg) and Queens, NY (0.23 ng/µg) both demonstrate the higher ratios in winter. The appearance of the n-alkanols in the urban areas in the winter indicates a primary emission, such as wood smoke or biomass combustion, of the n-alkanols (Nolte et al., 2001). The ratios were not constant within or between sites.

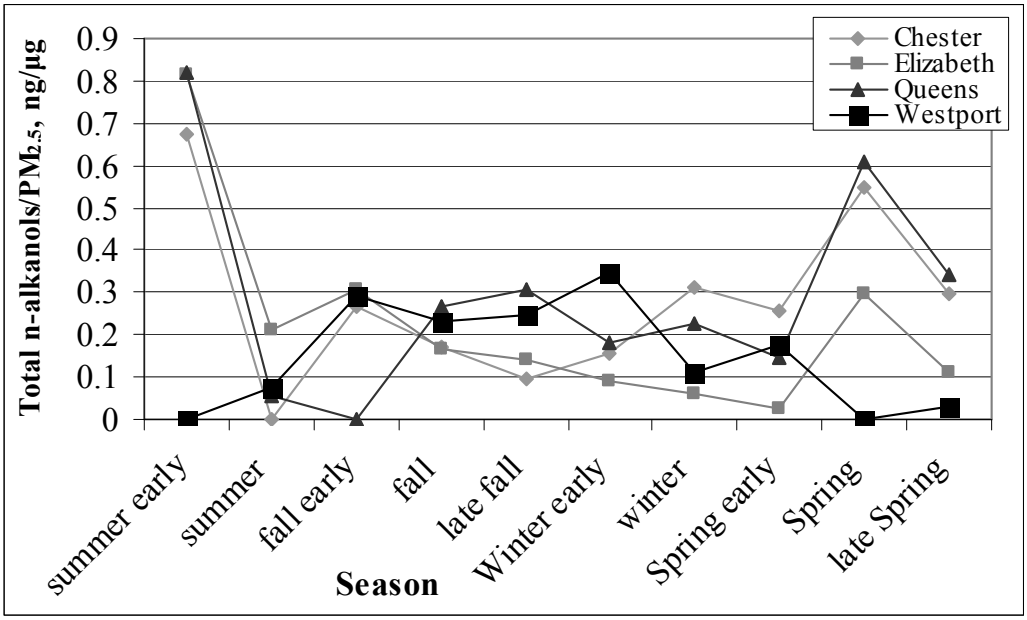


Figure 5-60 Total n-alkanols normalized to $PM_{2.5}$ in the NYC area (SOAP 2002-2003)

The total n-alkanols ambient data were plotted versus $PM_{2.5}$ with scatter plots as shown in Figure 5-61 and Figure 5-62. This was done to determine the correlation between these molecular markers and the fine PM mass which is easier to measure. The 2002 to 2003 sampling sites showed no correlation with $PM_{2.5}$ (0.0035 in Elizabeth, NJ to 0.1563 in Chester, NJ). The highest correlation with $PM_{2.5}$ was 0.16 at Chester, NJ. These results indicate the biogenic influences on air quality cannot be directly determined from $PM_{2.5}$ mass concentrations.

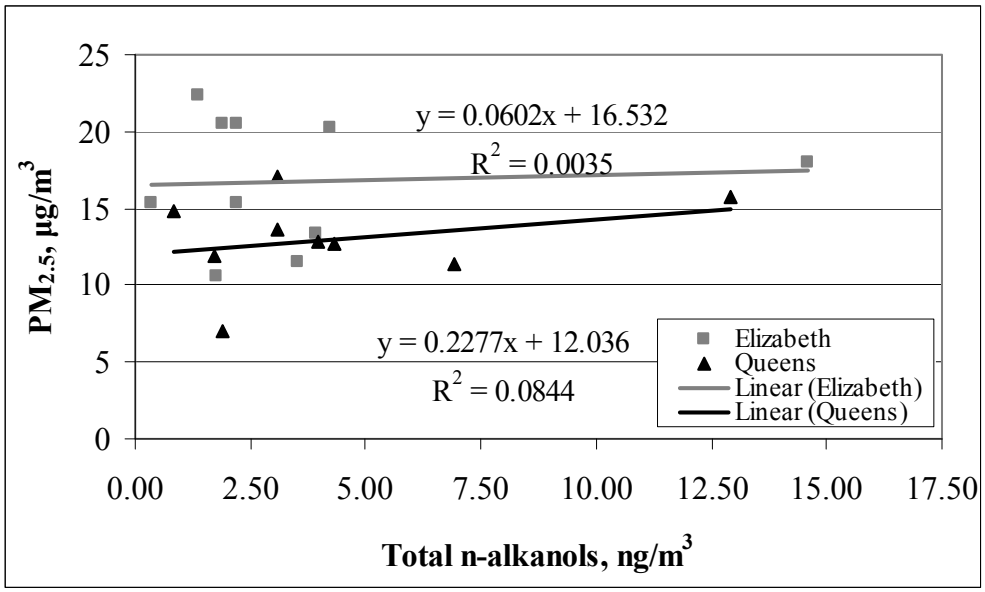


Figure 5-61 Total n-alkanols versus $PM_{2.5}$ in the urban NYC area (SOAP 2002-2003)

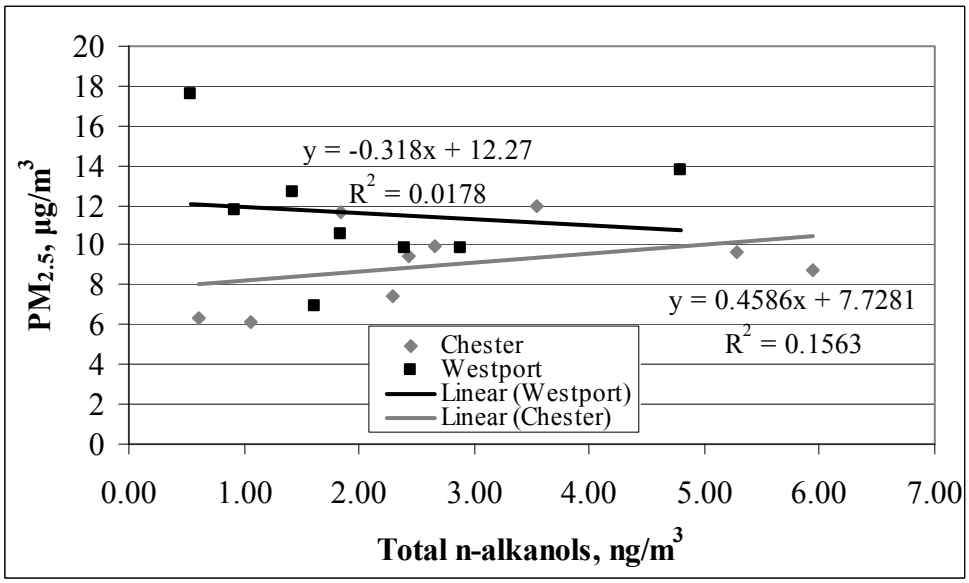


Figure 5-62 Total n-alkanols versus $PM_{2.5}$ in the NYC area (SOAP 2002-2003)

The 2005 to 2007 sampling period showed similar results to the SOAP 2002-2003 total n-alkanols normalized data. The ratios changed spatially and temporally. Pinnacle State Park, NY typically had higher ratios than Bronx, NY as shown in Figure 5-63. The highest ratios were found in the fall when leaves die and residential heating begins with

fireplaces and wood stoves. The lowest ratios appear to be in the summer (ND in Bronx, NY to 0.06 ng/µg in Pinnacle State Park, NY), the winter (0.03 ng/µg in Bronx, NY to 0.24 ng/µg in Pinnacle State Park, NY) also had lower ratios with an increase through the spring which is the beginning of the growing season.

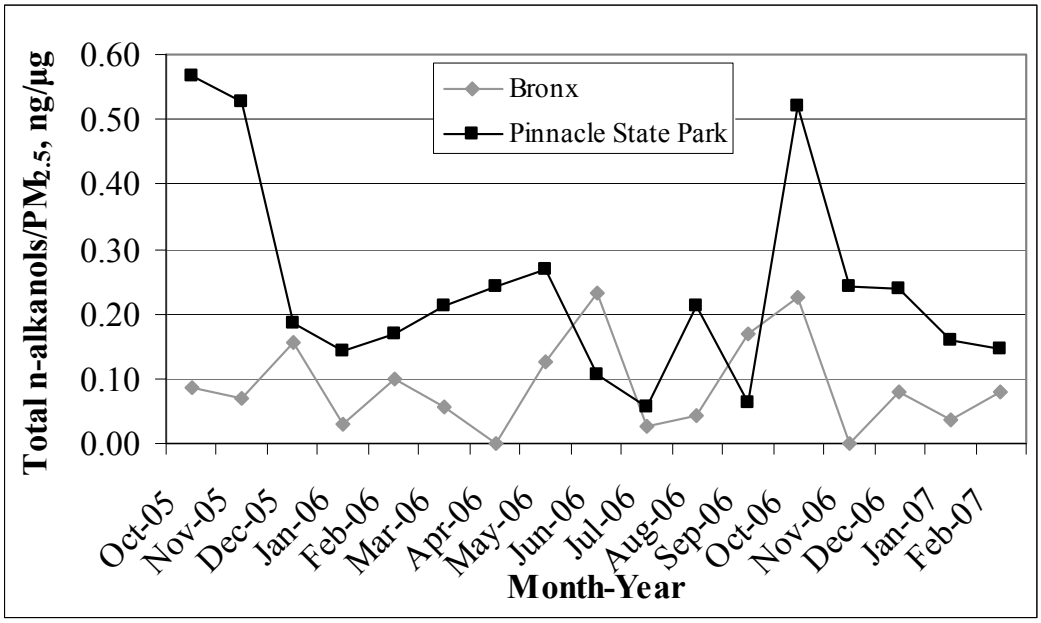


Figure 5-63 Total n-alkanols normalized to $PM_{2.5}$ in NY (SOAP NY)

The R^2 value comparing the n-alkanols and $PM_{2.5}$ ambient mass concentrations was less than 0.04 at both sites sampled from 2005 to 2007 (Figure 5-64). Therefore, the n-alkanols did not show a correlation with $PM_{2.5}$ at either of the SOAP NY sampling sites. The biogenic contribution to the NYC metropolitan area cannot be predicted using $PM_{2.5}$ concentrations but would need to be separately quantified according to this study.

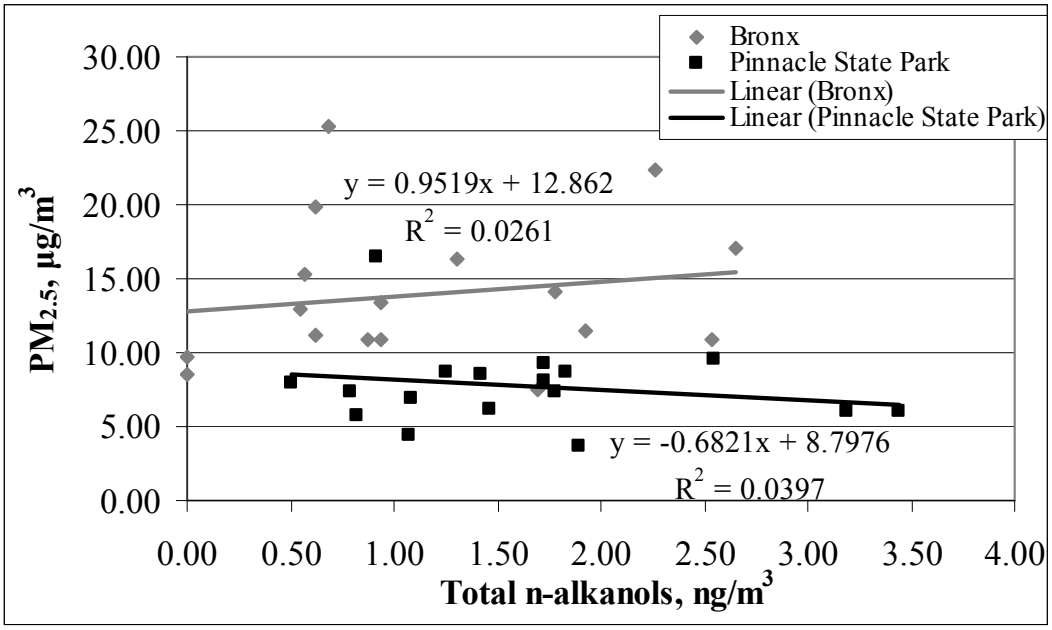


Figure 5-64 Total n-alkanols versus $PM_{2.5}$ in NY (SOAP NY)

5.4.3. Meat Charbroiling

Cholesterol was normalized to $PM_{2.5}$ for the 2002-2003 sampling campaign as shown in Figure 5-65. The background and down-wind sites, Chester, NJ and Westport, CT, showed no seasonal trends. In both cases cholesterol was not detected and the plot values were set to zero. Elizabeth, NJ normalized cholesterol concentrations peaked in the fall exhibited lower, variable trends the rest of the year. Queens, NY peaked in the early fall through winter with lower ratios the remainder of the year. The ratio was not constant either by season or by location. The cholesterol was plotted against $PM_{2.5}$ as shown in Figure 5-66 and Figure 5-67. Cholesterol had no correlation with $PM_{2.5}$ in any of the sites. The R^2 values were less than 0.1 for all sites. This analysis indicates meat charbroiling emissions were not major contributors to the ambient fine particle mass at the SOAP 2002-2003 locations.

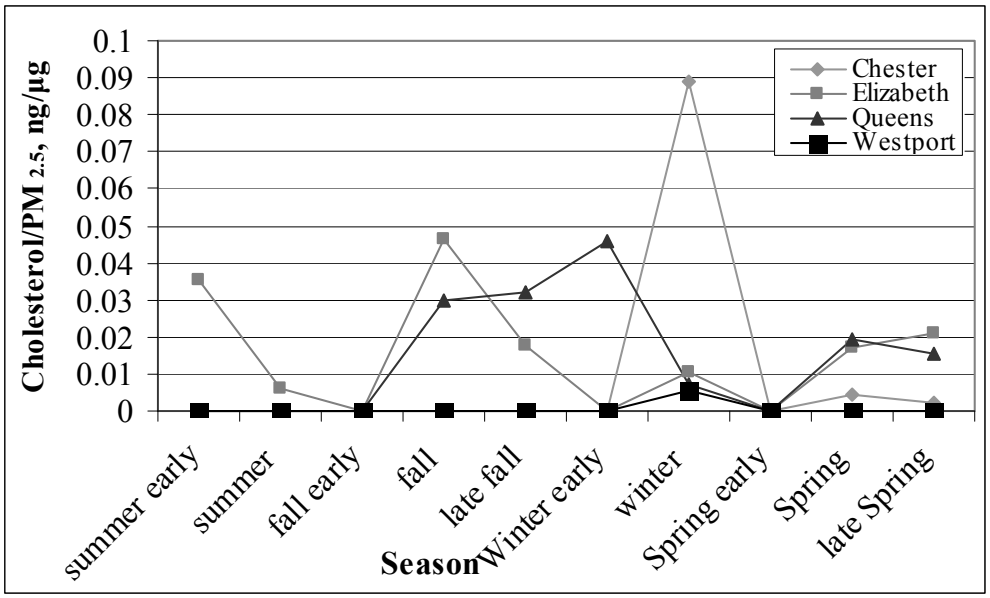


Figure 5-65 Cholesterol normalized to $PM_{2.5}$ for the NYC area (SOAP 2002-2003)

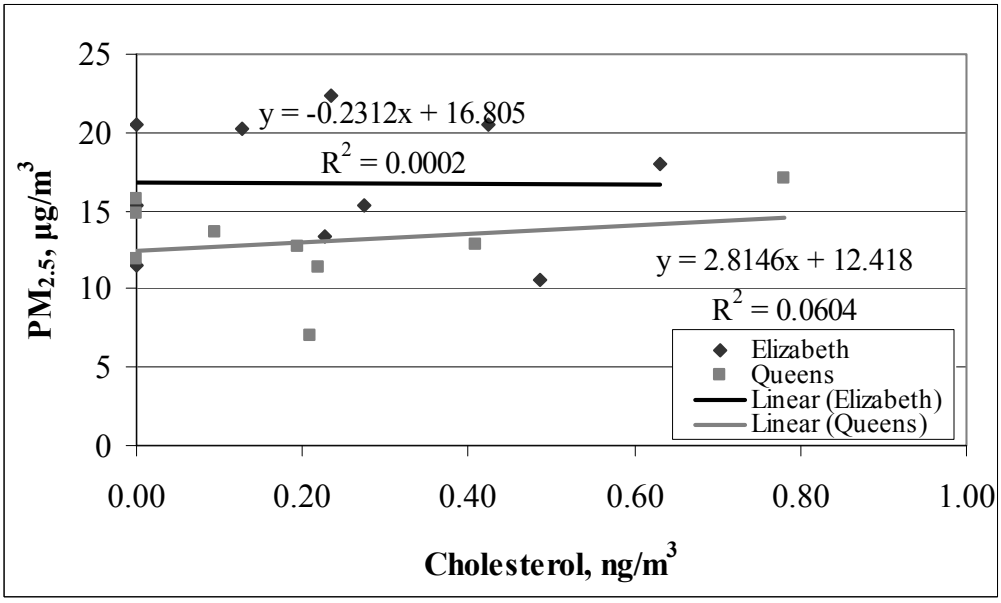


Figure 5-66 Cholesterol versus $PM_{2.5}$ in the urban NYC area (SOAP 2002-2003)

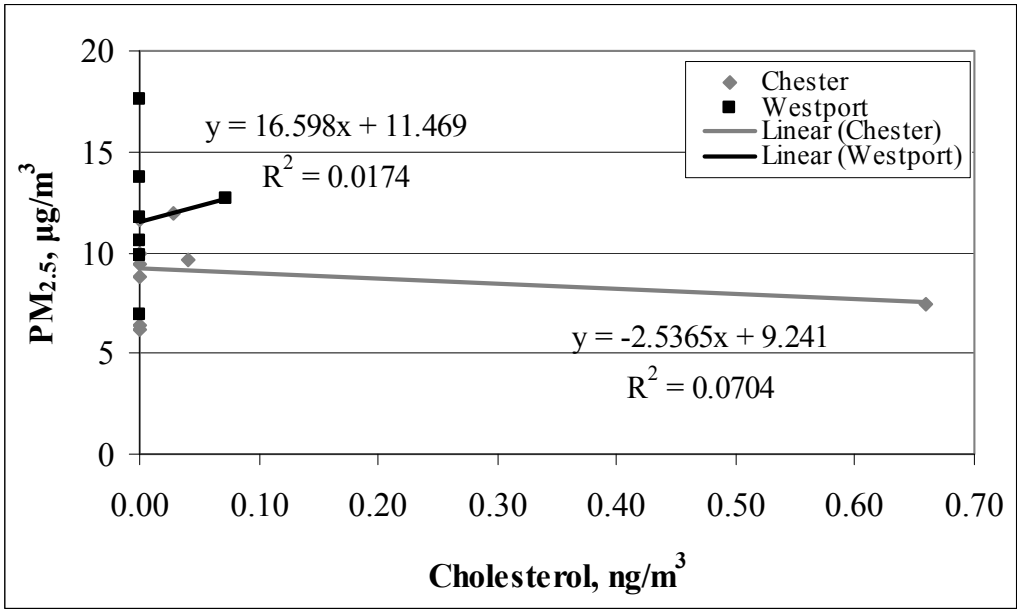


Figure 5-67 Cholesterol versus $PM_{2.5}$ in the NYC area (SOAP 2002-2003)

The Bronx, NY cholesterol $PM_{2.5}$ normalized data showed a low in the summer months (ND in Pinnacle State Park, NY to 0.01 ng/µg in Bronx, NY), was constant through the winter and fluctuated through the fall. Pinnacle State Park, NY samples were not above the detection limit; therefore the ratios were typically around zero and show no seasonal trends were present (Figure 5-68). These results indicate a consistent presence of cholesterol in $PM_{2.5}$ in urban locations, but not in rural locations. When the cholesterol data was plotted versus $PM_{2.5}$ in a scatter plot, no correlation was found at either site. The R^2 values were less than 0.1 (Figure 5-69). Therefore, a linear model cannot be used to estimate the cholesterol contribution without measuring cholesterol as an individual organic species.

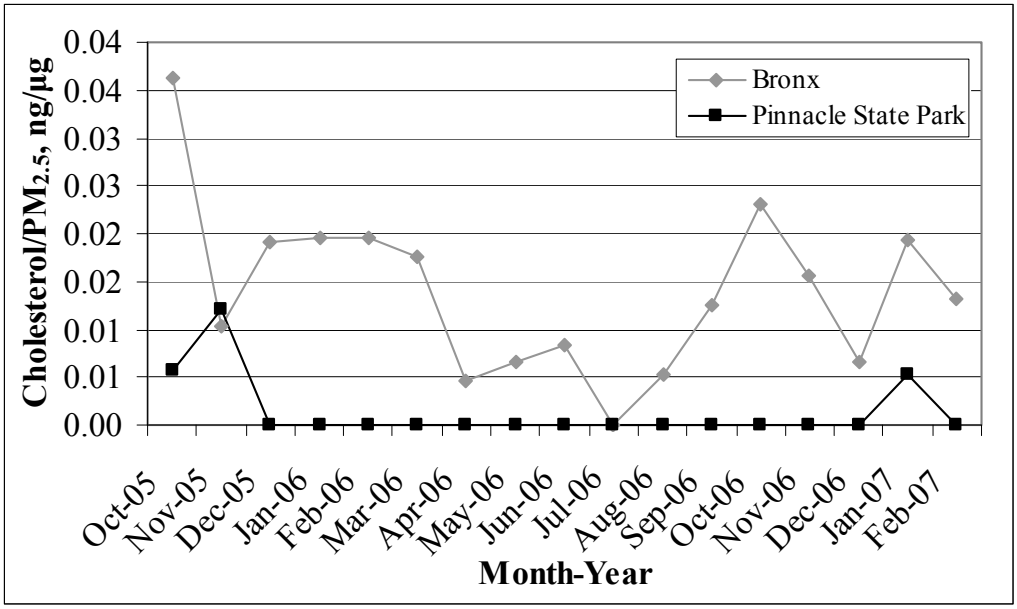


Figure 5-68 Cholesterol normalized to $PM_{2.5}$ in NY (SOAP NY)

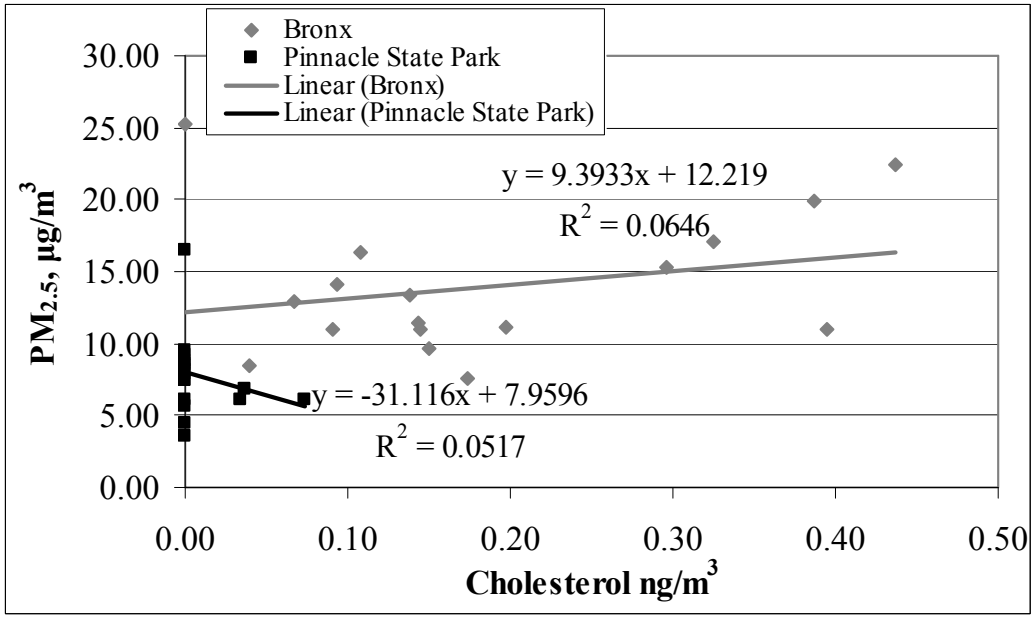


Figure 5-69 Cholesterol versus $PM_{2.5}$ in NY (SOAP NY)

5.4.4. Biogenic Oxidation Product

The ratio of cis-pinonic acid to $PM_{2.5}$ ambient mass concentrations for the 2002 to 2003 study showed the same trends as the OC normalized cis-pinonic acid. This could be

because the $PM_{2.5}$ contains the OC fraction therefore $PM_{2.5}$ is dependent on the OC fraction, whereas the EC fraction is independent of the OC fraction so the ratios could be different from each other. The ratios varied by season and by site. The ratios generally peaked in the fall and in the spring as shown in Figure 5-70. The ambient cis-pinonic acid concentrations were plotted versus $PM_{2.5}$ with scatter plots as shown in Figure 5-71 and Figure 5-72. None of the four sites showed a linear correlation between cis-pinonic acid and $PM_{2.5}$. The highest R^2 value was less than 0.0225 which was found between Westport, CT and $PM_{2.5}$.

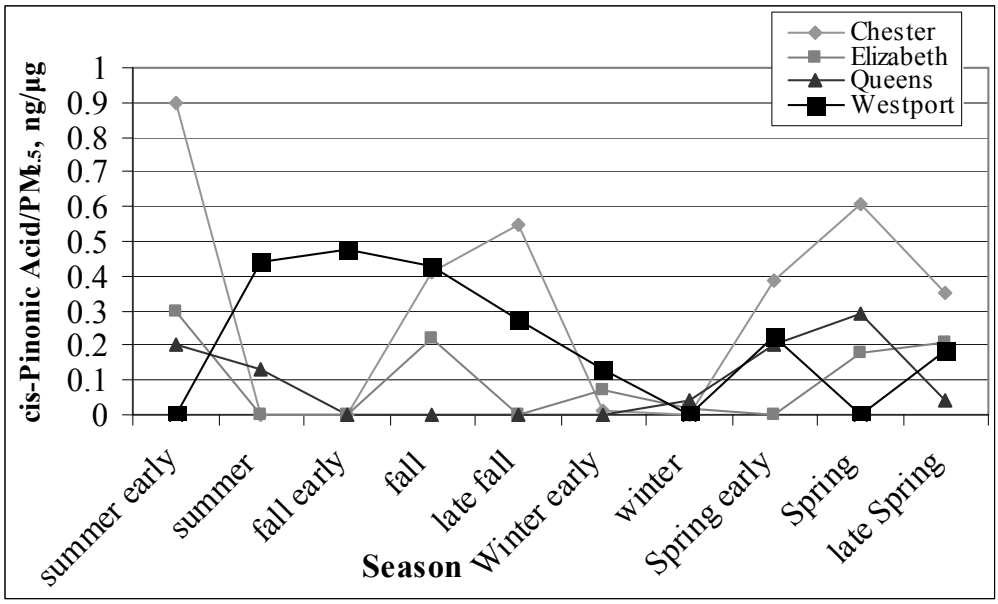


Figure 5-70 cis-Pinonic acid normalized to $PM_{2.5}$ in the NYC area (SOAP 2002-2003)

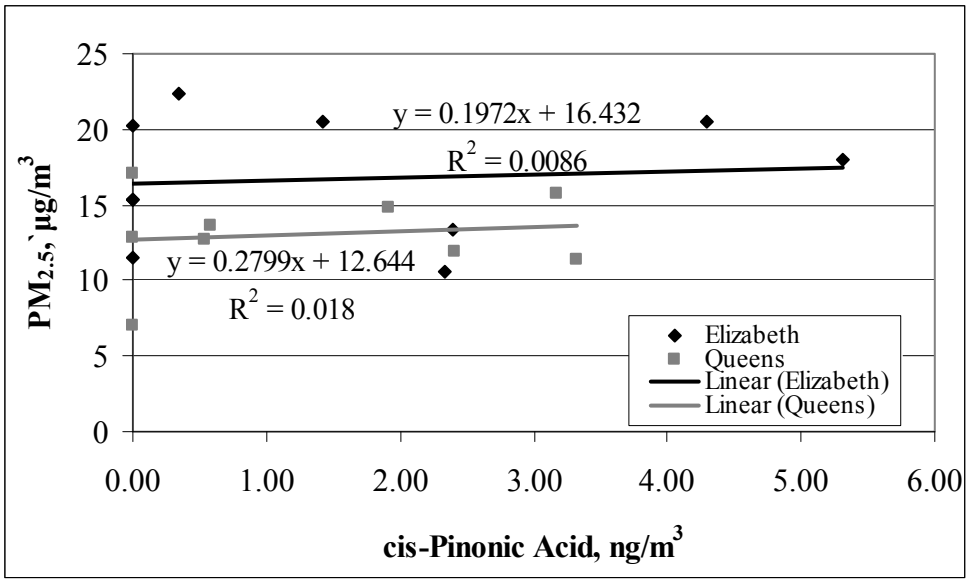


Figure 5-71 cis-Pinonic acid versus $PM_{2.5}$ in the urban NYC area (SOAP 2002-2003)

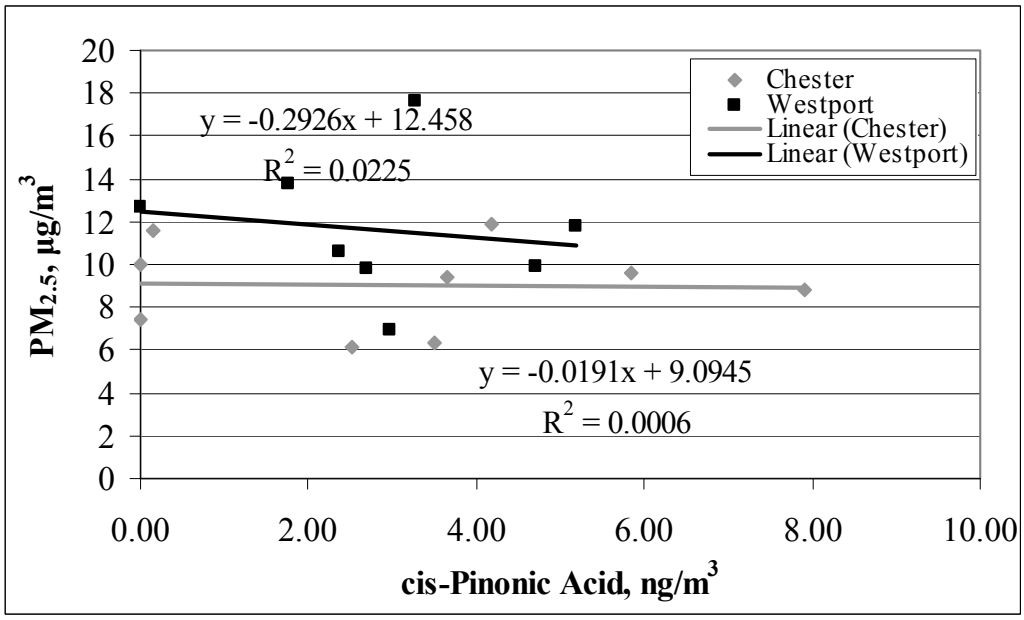


Figure 5-72 cis-Pinonic acid versus $PM_{2.5}$ in the NYC area (SOAP 2002-2003)

cis-Pinonic acid also was normalized to $PM_{2.5}$ for the 2005 to 2007 field sampling campaign. The seasonal pattern for Pinnacle State Park, NY, ratio consisted of an increase in the spring and in fall. The Bronx, NY ratio showed less dramatic seasonal trends than Pinnacle State Park, NY, however there was an increase in the ratio in the spring and fall. In general, the ratio of cis-pinonic acid to $PM_{2.5}$ was higher at the rural site, Pinnacle State Park, NY, compared to the urban site, Bronx, NY (Figure 5-73). The ambient cis-pinonic acid concentrations were plotted versus $PM_{2.5}$ with scatter plots as shown in Figure 5-74. Neither Bronx, NY nor Pinnacle State Park, NY demonstrated a linear correlation of cis-pinonic acid with $PM_{2.5}$. Therefore, cis-pinonic acid cannot be determined from a linear correlation with $PM_{2.5}$. The variation of cis-pinonic acid with $PM_{2.5}$ mass suggests aggregate sources of fine PM far exceed those for this marker compound.

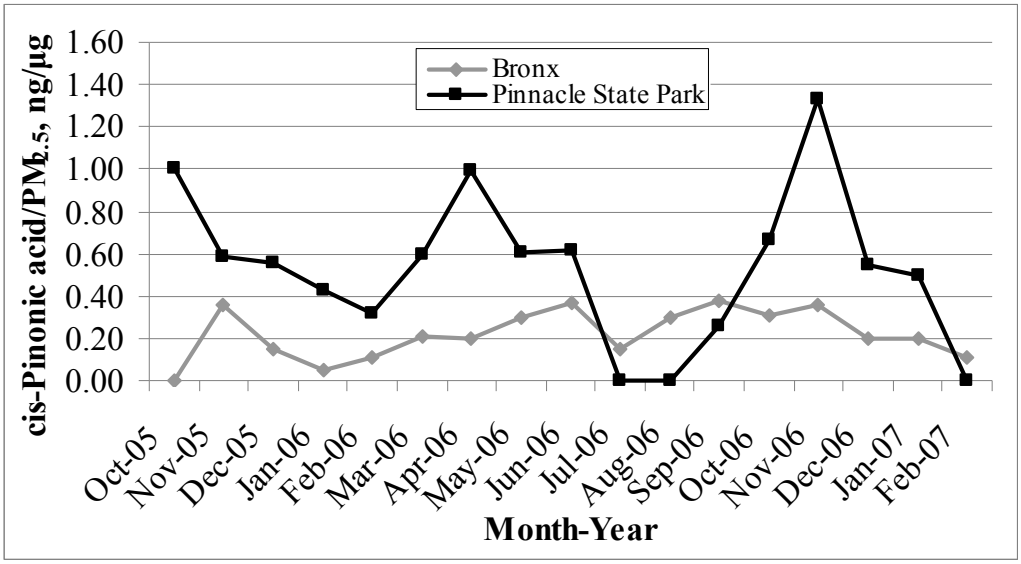


Figure 5-73 cis-Pinonic acid normalized to $PM_{2.5}$ in NY (SOAP NY)

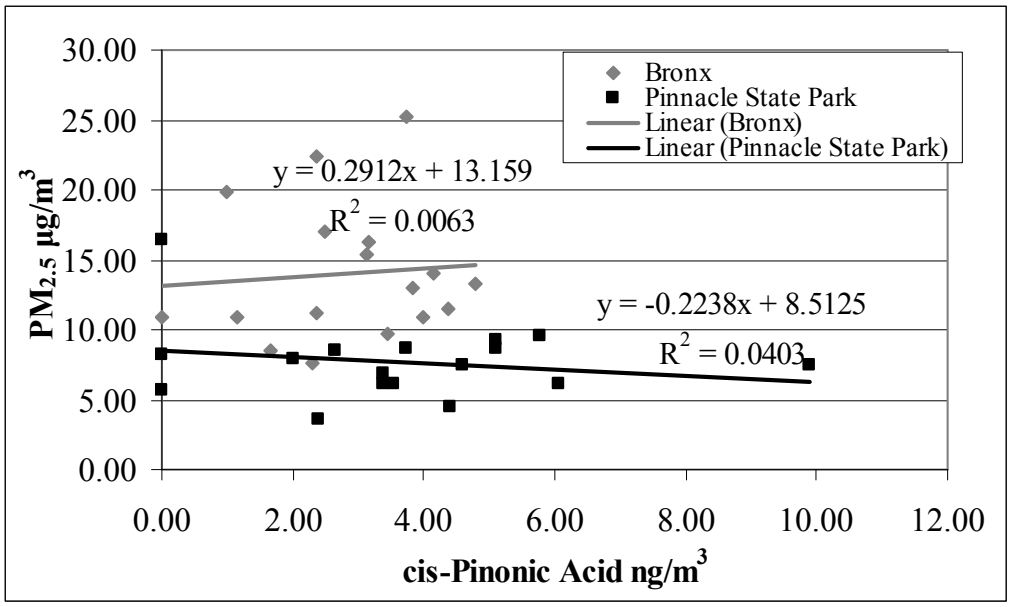


Figure 5-74 cis-Pinonic acid versus $PM_{2.5}$ in NY (SOAP NY)

5.4.5. Low Molecular Weight Highly Oxidized Acids

Levulinic acid ambient mass concentratons were normalized to those for $PM_{2.5}$ for the 2002 to 2003 field sampling campaign. The seasonal trends showed increases into the winter, indicating that the input of levulinic acid was contributed by other unknown sources in addition to photooxidation of reactive volatile organic compounds to form secondary fine PM. The ratios were not constant as shown in Figure 5-75. Chester, NJ showed the highest ratios in the spring and the fall (0.74 ng/µg to 1.48 ng/µg). The urban sites showed the highest ratios in the winter (0.83 ng/µg in Westport, CT to 0.33 ng/µg in Elizabeth, NJ), which is opposite to the background site. Levulinic acid also was plotted against $PM_{2.5}$ to determine correlations between the two constituents. No correlation was found at any of the four sites. The highest R^2 value was 0.1344 at Queens, NY (Figure 5-76 and Figure 5-77). Therefore, levulinic acid cannot be determined from a direct ratio to fine PM mass.

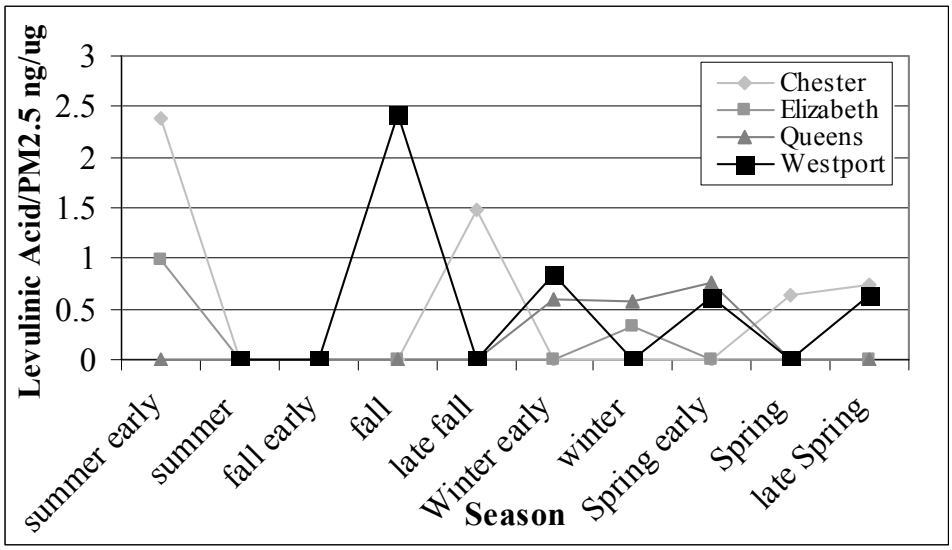


Figure 5-75 Levulinic acid normalized to $PM_{2.5}$ in the NYC area (SOAP 2002-2003)

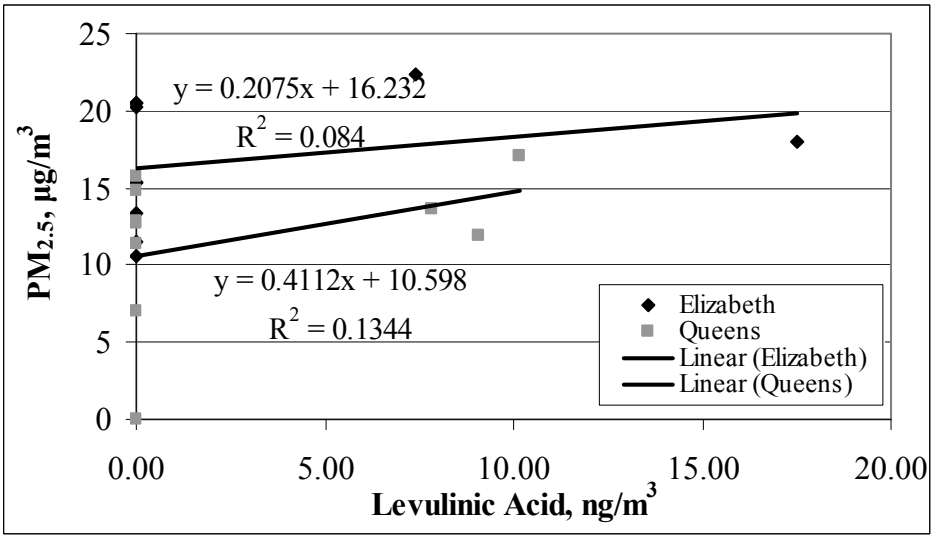


Figure 5-76 Levulinic acid versus $PM_{2.5}$ in the urban NYC area (SOAP 2002-2003)

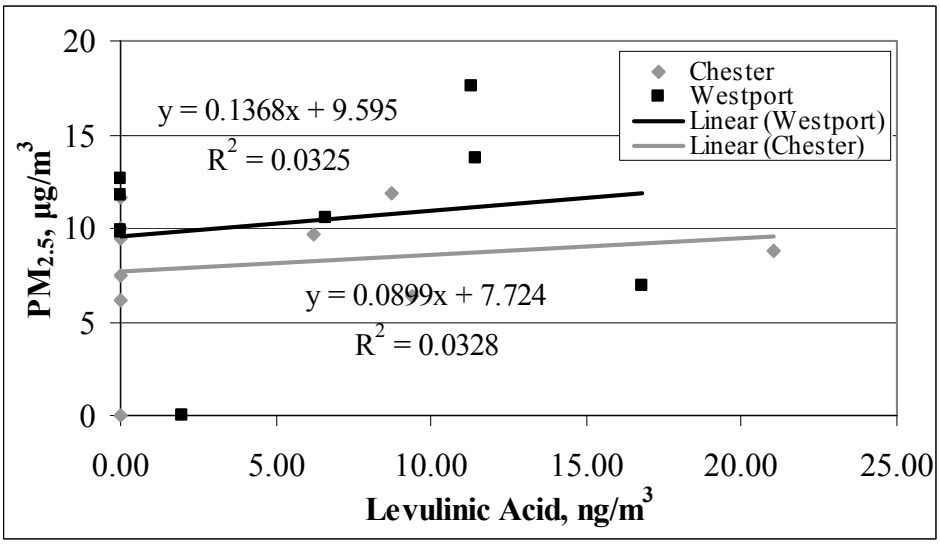


Figure 5-77 Levulinic acid versus $PM_{2.5}$ in the NYC area (SOAP 2002-2003)

Levulinic acid was normalized to $PM_{2.5}$ for the 2005 to 2007 field sampling campaign as shown in Figure 5-78. The trends indicate an increase in the spring and in fall in Pinnacle State Park, NY. The Bronx, NY ratio showed less pronounced seasonal trends than Pinnacle State Park, NY. In general, the ratio of levulinic acid to $PM_{2.5}$ was higher at the rural site, Pinnacle State Park, NY, compared to the urban site, Bronx, NY. The ambient levulinic acid concentrations were plotted versus $PM_{2.5}$ with scatter plots (Figure 5-79). Neither Bronx, NY nor Pinnacle State Park, NY had a linear correlation of levulinic acid with $PM_{2.5}$ (0.0016 in Bronx, NY and 0.2432 in Pinnacle State Park, NY). Therefore, levulinic acid cannot be determined with a linear correlation with $PM_{2.5}$ at any of the six locations. This could be because of the complex nature of the formation of secondary organic aerosols and the other possible primary sources of levulinic acid. There are variety sources of levulinic acid including wood smoke and biomass combustion (Fagerson, 1969; Fiddler et al., 1970), which might explain the presence of levulinic acid as discussed in Chapter 5.1.

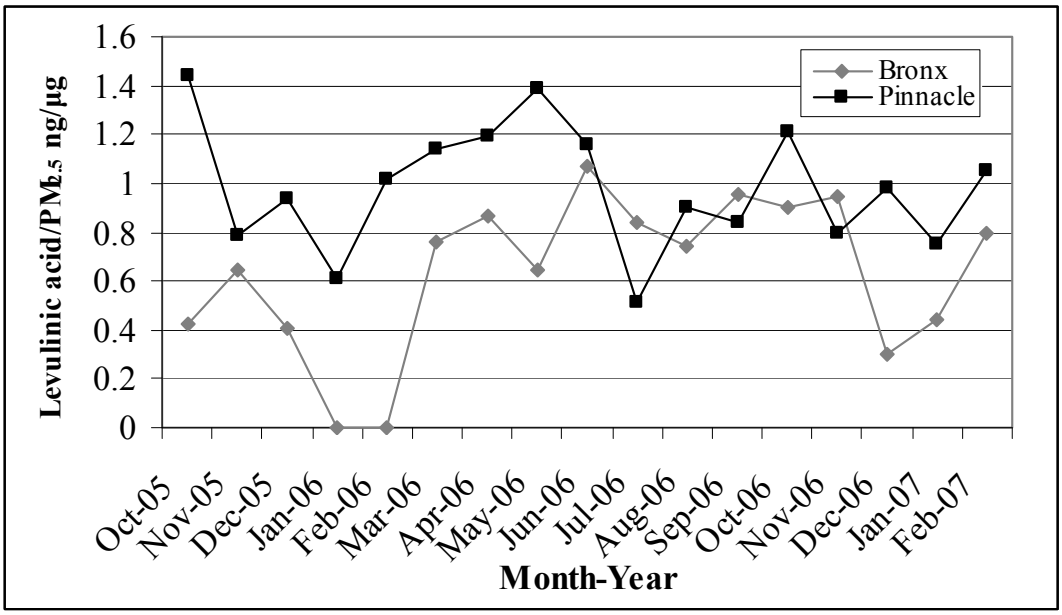


Figure 5-78 Levulinic acid normalized to $PM_{2.5}$ in NY (SOAP NY)

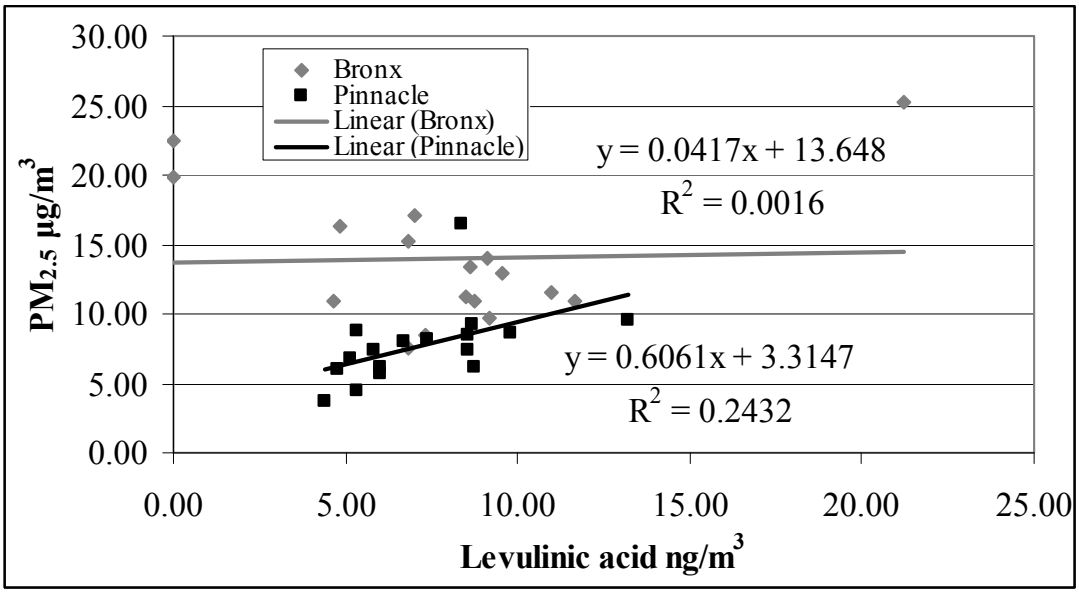


Figure 5-79 Levulinic acid versus $PM_{2.5}$ in NY (SOAP NY)

6. Context

This chapter discusses the SOAP molecular marker data and presents examples of how this information may be applied to improve air quality. First, a summary is presented of the results from ambient samples taken in the NYC area. A review of the key scientific questions is given in the following section. Engineering controls to reduce emissions are presented as a method to improve air quality in the NYC area. Finally, recommendations for future research are discussed in the final section of this chapter.

6.1. *Conclusion*

Polar organic compounds can influence the air quality in the New York City metropolitan area. Wood smoke emissions release fine PM which can contribute upwards of 50% of the fine PM in the atmosphere during the fall and winter months. Cooking operations, traced through meat sources, were quantified in urban areas where restaurants are abundant. These are both sources with direct, or point, emissions which could be controlled.

Polar organic compounds also originate from nonmanageable sources, such as vegetation and wildfires. Phytosterols and n-alkanols from biogenic sources were quantified in ambient samples from all six sites in the NYC metropolitan area. Oxidation products from monoterpenes originating from trees cannot be controlled, however evidence of this source was found in the northeastern area. It is important to understand background and uncontrollable sources of fine PM that cannot directly be regulated to reduce fine PM levels. However, reducing levels of primary oxidants such as NO_x and secondary oxidants such as ozone, could result in lower concentrations of SOAs from

biogenic precursors (VOCs and reactive PM). Low molecular weight highly oxidized oxoacids were found with both photochemical and primary sources. Levulinic acid was the dominant oxoacid found in fine PM samples, however its sources are not clear. Photooxidation reactions may be the cause of levulinic acid; reduction in precursors from primary emissions would be a necessary step to reduce SOAs. Further research on emission sources of polar PM in the NY-NJ-CT area, including extensive source tests, are needed to expand the current understanding of the sources and spatial and temporal concentrations of low molecular weight water-soluble organic compounds.

Analyses were conducted to determine if molecular marker concentrations can be interpolated from easier to measure constituents, such as EC, OC and fine PM mass concentrations. Select molecular markers were normalized to the constituents with no constant proportions determined for any of the constituents. However, there were seasonal trends of the normalized data which typically followed similar seasonal trends as the original molecular markers. The same selected molecular markers were plotted against the constituents with scatter plots to determine if a linear correlation existed between the two variables. No correlation was found for EC, OC or $PM_{2.5}$ mass with any of the molecular markers except for one. Cholesterol versus EC in Queens, NY had a correlation of $R^2 = 0.82$.

Statistical analyses in the form of ANOVA tables were completed for the same selected molecular markers at the 95% confidence level. The ANOVA tables, based on p-values, indicated whether or not molecular marker concentrations were statistically different for the fall and winter versus the spring and summer at each site (i.e. seasonal differences at one site, not a comparison between sites). Levoglucosan showed seasonal

differences in the Bronx, NY and Westport, CT but not in Pinnacle State Park, NY, Chester, NJ, Elizabeth, NJ or Queens, NY. It is important to note that at Pinnacle State Park, NY the p-value was 0.058 which is close to the confidence limit of 0.05. The total n-alkanols ambient data showed no seasonal variation at any of the six locations. Cholesterol showed seasonal differences in Bronx, NY but not at other sites. Cis-Pinonic acid showed no seasonal variation at any site. Levulinic acid showed no statistical difference between seasons in any of the four sites sampled in 2002-2003, but did show differences in both the sites sampled in 2005-2007.

Statistical analyses were also conducted for urban versus rural locations for the same selected molecular markers. The analyses were conducted for the selected molecular markers normalized to EC. Levoglucosan concentrations had no statistical difference between urban and rural sites, but the ratio of levoglucosan to EC had a statistical difference between urban and rural sites. The same result also was found for total n-alkanols and the ratio of total n-alkanols to EC. Cholesterol and the ratio of cholesterol to EC also had a statistical difference found between urban and rural sites at the 95% confidence level. The same was found for cis-pinonic acid and the ratio of cis-pinonic acid to EC. Levulinic acid did not have a statistical difference between urban and rural sites, however the ratio of levulinic acid to EC was found to have a statistical difference between urban and rural sites at the 95% confidence level. These results indicate the concentration of some molecular markers are influenced by the depth of the mixing layer to the extent that it changes the apparent influence of a source at the receptor site. These results also indicate urban areas may have different sources than

rural areas; therefore control strategies may need to be redefined for rural communities versus densely populated metropolitan regions to reduce fine PM concentrations.

6.2. *Key Scientific Questions*

Five key scientific questions guiding this research were presented in Chapter 1. They are given here with responses gained from this research.

How can polar organic compounds be measured in atmospheric fine particulate matter? Is there potential analytical equipment that could quantify the compounds without a derivatization technique?

Polar organic compounds can be measured using GCMS. It was determined a mass selective detector (MS) was crucial for quantifying organic compounds in complex mixtures such as atmospheric fine PM. A derivatization step was necessary for the quantification of polar organic compounds in fine PM extracts. The derivatization technique used in this study was BSTFA because it worked for all polar organic marker compounds of interest.

What is the contribution of wood smoke to the atmosphere in the New York City (NYC) area?

The wood smoke molecular marker levoglucosan was quantified year round in the NYC area. In the fall and winter levoglucosan values reached a high of 189.47 ng/m^3 in the late fall in Westport, CT making it one of the most abundant individual organic compounds quantified in fine PM. The estimated influence of wood smoke, based on emission factors, ranged from less than 1% OC from wood smoke to a high of 69 % OC

from wood smoke (fall season in Westport, CT). These results indicate seasonal fine PM concentrations could be reduced with the management of wood burning practices.

Is meat charbroiling a significant cause of fine aerosols in the NYC area?

Meat charbroiling was found to have a higher influence in urban areas than in rural areas. There was no seasonal distribution of cholesterol in the urban areas, therefore it appeared to be a constant source of fine PM to the urban sites. The estimated influence on fine aerosol OC was lower than 5%; this is the estimate of meat cooking only and does not include the influence of oils which may in turn increase the expected influence of cooking emissions on fine PM in this study area.

What is the contribution of vegetative detritus to this highly urbanized area?

Biogenic sources were quantified in the urban and rural areas of this study. The molecular markers did show seasonal trends, with the highest concentrations occurring in the spring and fall. The urban areas showed increases in the winter, which may be due to wood combustion for heating purposes. There are no emission factors so an estimated influence on fine PM was not attainable.

What secondary organic aerosol markers, found in smog chamber experiments, can be seen in urban and regional background sites in the northeastern United States? What is the estimated primary versus secondary contribution based on molecular markers?

cis-Pinonic acid was found in the samples from the NYC area indicating that biogenic oxidation products are present in the northeastern atmosphere. The oxoacids were difficult to interpret. Levulinic acid was found in many samples however it is unclear whether this compound is formed only in the atmosphere or if its presence is a combination of primary emissions and oxidation byproducts. The remaining oxoacids were not quantifiable in the samples because it was not established the extent to which the oxoacids were soluble in the extraction solvents used for this research. It is difficult to estimate primary and secondary emissions based on molecular markers at this point. The concentration of cis-pinonic acid, a known secondary oxidation product, and levulinic acid, a suspected secondary oxidation product, were both lower than levoglucosan. The proportion of primary versus secondary polar organic compounds in the SOAP 2002-2007 samples could not be determined.

6.3. *What can be done to lower emissions?*

Polar organic compounds can have an effect on concentrations of organic carbon emitted into the atmosphere. Engineering air quality controls can be designed to reduce atmospheric emissions. This could be particularly important for urban metropolitan areas with high populations that tend to exceed the National Ambient Air Quality Standards for fine PM. Fireplaces and other controlled wood burning devices and cooking sources can be retrofitted to reduce emissions (NESCAUM, 2008). There are unmanageable sources, however, that cannot be reduced through engineered controls. Among these emissions are wildfires, structural fires, illegal burning, and emission from vegetation and other biogenic sources. The oxidation by-products could be reduced if the primary emission

sources (e.g. VOCs) are controlled. Biogenic oxidation products cannot be controlled directly as the precursors are natural products emitted by biomass and biota.

6.3.1. Reduction Strategies for Woodsmoke Emissions

In 1988 the U.S. EPA established regulations requiring new woodstoves and fireplace inserts to have a maximum output of 7.5 grams of smoke per hour, however fireplaces and outdoor wood boilers were exempt (NESCAUM, 2008; Houck and Eagle, 2006). There are two basic ways to meet this regulation, catalytic or non-catalytic combustion (NESCAUM, 2008; Houck and Eagle, 2006). The non-catalytic woodstove is the more common of the two types. Wood pellet stoves also are becoming popular. Wood pellet stoves burn sawdust and other wood products pressed into pellets. These stoves produce lower emissions than traditional stoves (NESCAUM, 2008; Houck and Eagle, 2006). Another method to reduce emissions is the use of manufactured logs which emit lower amounts of particles. The average cost of an U.S. EPA-certified wood stove is $2,500 and lowers the emissions by about 50% (NESCAUM, 2008). Unfortunately, it does not appear that a wood stove can be retrofitted to reduce emissions (NESCAUM, 2008; Houck and Eagle, 2006). Traditional fireplaces can be retrofitted with pellet inserts, catalytic inserts and non-catalytic inserts to reduce emissions (Houck and Eagle, 2006).

Outdoor residential wood boilers are wood-fired furnaces that can provide hot water, heat and other household uses. These cost about $8,000 to $10,000 to purchase and install. This source of wood burning emits about 12 times more PM than an U.S. EPA certified wood stove. Since 1990, it is estimated that 13,182 wood-boilers have been sold in New York State, indicating their increase in popularity (NESCAUM, 2008).

A pellet furnace or gas furnace would reduce particulate emissions compared to wood boilers (Houck and Eagle, 2006). Given this information, it appears that outdoor wood-boilers may be a source of current pollution levels. Without emission controls their increase use could produce noticeable adverse effects on air quality in rural communities in the future. The idea of replacing the wood boilers with gas furnaces probably would not work as these hot water external heating systems are becoming popular due to the increase in gas prices and the relatively low cost of wood; however the use of pellet furnaces may be marketable.

Burning of household wastes is another potential source of pollution that could be emitting particulate matter, and in particular, levoglucosan. New Jersey and Connecticut have statewide bans on burning household wastes. New York does not have a statewide ban on this practice, though some counties prohibit burning household wastes (NESCAUM, 2008).

A controllable technology that could be retrofitted to improve air quality is fireplaces, which currently are an unregulated emission source. There are many sources that give off levoglucosan that could not be controlled such as wildfires and structural fires. Reducing just a portion of the emissions, however, could be enough to improve the air quality and lower the number of daily exceedances of fine particle mass.

6.3.2. How could charbroiling emissions be reduced?

Charbroilers could be equipped with control strategies to reduce particulate emissions. Chain-driven style charbroilers can be retrofitted with a catalytic oxidizer which could reduce emissions up to 90% (NESCAUM, 2008). The catalytic oxidizer is considered cost-effective for particulate matter reduction. The capital cost of the retrofit

would be $1,200 to $2,400 (NESCAUM, 2008). The South Coast Air Quality Management District (SCAQMD) in Southern California adopted a rule resulting in a large number of restaurants retrofitting their charbroilers. The SCAQMD estimated the cost of catalytic oxidizers was $1,680 to $2,800 per ton of PM and VOCs reduced (NESCAUM, 2008).

Underfired charbroilers, however, cannot be retrofitted as cost effectively. The SCAQMD evaluated two options, replacement with Smokeless™ broilers and add-on scrubbers, however neither where implemented due to cost (NESCAUM, 2008). The Smokeless™ broiler is not a retrofit but an actual replacement with a cost of about $5,550. Another option is the electrostatic precipitator which costs around $20,000 to $30,000 which is higher than the aforementioned option (NESCAUM, 2008). Implementation of the cost effective retrofits in restaurants in urban areas should help reduce fine particle emissions.

6.4. *Future Recommendations*

The oxoacids may not have been soluble in acetone and therefore not found in ambient samples in the NYC area. It is recommended to extract the remaining portions of the ambient filters in a more polar solvent, such as methanol, and quantify the low molecular weight, highly oxidized acids. This research showed that oxalic acid, a low molecular weight highly oxidized acid, was not soluble in the 50/50 dicholoromethane/acetone solvent mixture used to extract the filters for GCMS analysis. Edney et al. (2003) conducted solubility tests on ambient filters and found that hexane contained about 11% of the organic mass, acetone contained 67%, ethanol contained 12% and water contained 10%. This demonstrated that acetone did not collect all of the polar

organic compounds from the filters. Quantification of oxoacids may aid in the determination of primary versus secondary emissions in the NYC metropolitan area.

GCMS analysis of oxoacids with derivatization techniques other than BSTFA can be studied further to quantify oxoacids in the NYC area. Kleindienst et al. (2004) and Yu et al. (1999) treated samples with O-(2,3,4,5,6-pentafluorobenzyl)-hydroxyamine (PFBHA) to derivatize the carbonyl groups followed by BSTFA to derivatize the OH groups. Kleindienst et al. (1999) used only PFBHA to derivatize samples. Esterification of samples with boronitrifluoride (BF_3)/*n*-butanol was used to derivatize carboxyl and aldehyde groups in order to quantify oxoacids on GCMS in several studies (Kawamura et al., 1996; Kawamura et al., 2005; Sampere and Kawamura, 1996; Wang et al., 2006). These methods could be used if the BSTFA derivatization procedure is found inappropriate for oxoacids. BSTFA was chosen for this research because it is a versatile derivatizing agent which also was used to quantify molecular markers for wood smoke emissions, meat charbroiling operations, biogenic sources and biogenic oxidation products.

Further investigations into cooking emissions, including oils, may provide information necessary to determine the influence of cooking emissions, and not just meat charboiling, in the NYC area. Although retrofits for cooking operations do exist, they are currently high cost alternatives. New cost-effective engineering controls may be developed which specifically target cooking emissions from restaurants and commercial food preparation industries.

Levoglucosan was quantified in the summer of 2002 in the urban location Queens, NY. Several urban sources of this marker include wood and biomass

combustion, and charcoal barbeques for outdoor cooking. Source tests on charcoal briquettes should be conducted to determine the emission profile. The fine PM emissions should be tested for sources of levoglucosan and other wood smoke markers in the NY/NJ/CT region.

Further testing is necessary for biogenic sources to determine compounds, for example levulinic acid. Levulinic acid was discovered year round in quantifiable levels. Determining whether levulinic acid can be directly emitted into the atmosphere, as opposed to produced in the atmosphere, is an important distinction if the influence of SOAs on air quality is to be determined.

Source emission tests on domestic and industrial solid waste combustion could identify and confirm tracers from this category. Large wastewater and solid waste facilities in the NYC area could be adversely impacting air quality and releasing low molecular weight organic acids into the atmosphere. Determining molecular markers for this emission source, then reevaluating these samples for those markers would provide additional information that could be used to reduce air pollution.

7. References

Alves, Celia; Oliveira, Tiago; Pio, Casimiro; Silvestre, Armando J.D.; Fialho, Paulo; Barata, Filipe; Legrand, Michel. Characterization of Carbonaceous Aerosols from the Azorean Island of Terceira. *Atmos. Environ*. **2007**, 41, 1359-1373.

Anderson, Theodore L.; Charlson, Robert J.; Schwartz, Stephen E.; Knutti, Reto; Boucher, Olivier; Rodhe, Henning; Heintzenberg, Jost. Climate Forcing by Aerosols—a Hazy Picture. *Science*. **2003**, 300 (16), 1103-1104.

Antal, Michael Jerry Jr.; Mok, William S. L.; Varhegyi, Garbor; Szekely, Tamas. Review of Methods for Improving the Yield of Charcoal from Biomass. *Energy Fuels*. **1990**, 4 (3), 221-225.

Beveridge, Thomas H.J.; Li, Thomas S.C.; Drover, John C.G. Phytosterol Content in American Ginseng Seed Oil. *J. Agric. Food. Chem*. **2002**, 50 (4), 744-750.

Blanchard, Charles L. Spatial and Temporal Characterization of Particulate Matter. In *Particulate Matter Science for Policy Makers. A NARSTO Assessment Part I*. NARSTO. February, 2003. EPRI 1007735.

Bylund, Dan; Norstrom, Sara H.; Essen, Sofia A.; Lundstrom, Ulla S. Analysis of Low Molecular Mass Organic Acids in Natural Waters by Ion Exclusion Chromatography Tandem Mass Spectrometry. *J. Chromatogr. A*. **2007**, 1176, 89-93.

Breon, Francois-Marie. How Do Aerosols Affect Cloudiness and Climate? *Science* **2006**, 313 (4), 623-624.

Brown, Steven G.; Herckes, Pierre; Ashbaugh, Lowell; Hannigan, Michael P.; Kreidenweis, Sonia M.; Collett, Jeffrey, L. Jr. Characterization of Organic Aerosol in Big Bend National Park, Texas. *Atmos. Environ*. **2002**, 36, 5807-5818.

Burns, Malcolm J.; Nixon, Gavin J.; Foy, Carole A.; Harris, Neil. Standardisation of Data from Real-Time Quantitative PCR Methods—Evaluation of Outliers and Comparison of Calibration Curves. *BMC Biotechnol*. **2005**, 31, 1-13.

California Air Resource Board. SOP MLD 104: Standard Operating Procedure For the Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography. Revision 3.0. April 1, 2006.

Cha, J.Y.; Hanna, M.A. Levulinic Acid Production Based on Extrusion and Pressurized Batch Reaction. *Ind. Crops. Prod*. **2002**, 16, 109-118.

Chang, Chun; Cen, Peilin; Ma, XiaoJian. Levulinic Acid Production from Wheat Straw. *Bioresour. Technol*. **2007**, 98, 1448-1453.

Chen, Yingjun; Zhi, Guorui; Feng, Yanli; Fu, Jiamo; Feng, Jialiang; Sheng, Guoying; Simoneit, Bernd R.T. Measurements of Emission Factors for Primary Carbonaceous Particles from Residential Raw-Coal Combustion in China. *Geophys. Res. Lett*. **2006**, 33 (L20815), 1-4.

Cheng, Yu; Li, Shao-Meng; Leithead, Amy; Brickell, Peter C.; Leaitch, W. Richard. Characterization of cis-Pinonic Acid and n-Fatty Acids on Fine Aerosols in the Lower Fraser Valley During Pacific 2001 Air Quality Study. *Atmos. Environ*. **2004**, 38, 5789-5800.

Chowdhury, Zohir; Zheng, Mei; Schauer, James J.; Sheesley, Rebecca J.; Salmon, Lynn G.; Cass, Glen R.; Russell, Armistead G. Speciation of Ambient Fine Organic Carbon Particles and Source Apportionment of $PM_{2.5}$ in Indian Cities. *J. Geophys. Res. [Atmo*s] **2007**, 112 (D15303), 1-14.

Demirbas, Ayhan. Biomass to Charcoal, Liquid, and Gaseous Products Via Carbonization Process. *Energy Source*. **2001**, 23, 579-587.

Dockery, D. W. Epidemiologic evidence of cardiovascular effects of particulate air pollution, *Environ. Health Perspect*., **2001**, 109, 483-486.

Doughty, E.; DeGraff, I.; Henderson, D.; Nolan, L. Monitoring Aldehydes in Air, Using a New Adsorbent Cartridge and Reference Standard and HPLC. *The Reporter* **1995**, 14 (2), 8-9.

Edney, E.O.; Kleindienst, T.E.; Conver, T.S.; McIver, C.D.; Corse, E.W.; Weathers, W.S. Polar Organic Oxygenates in $PM_{2.5}$ at a Southeastern Site in the United States. *Atmos. Environ.*.[North America] **2003**, 37, 3947-3965.

Engling, Guenter; Herckes, Pierre; Kreidenweis, Sonia M.; Malm, William C.; Collett, Jeffrey L. Jr. Composition of the Fine Organic Aerosol in Yosemite National Park during the 2002 Yosemite Aerosol Characterization Study. *Atmos. Environ*. **2006**, 40 (15), 2959-2972.

Fagerson, Irving S. Thermal Degradation of Carbohydrates. *J. Agr. Food Chem*. **1969**, 17 (4), 747-750.

Fiddler, Walter; Doerr, Robert C.; Wasserman, Aaron E. Composition of an Ether-Soluble Fraction of a Liquid Smoke Solution. *J. Agr. Food Chem*. **1970**, 18 (2), 310-312.

Fine, Philip M.; Cass, Glen R.; Simoneit, Bernd, R. T. Chemical Characterization of Fine Particle Emissions from Fireplace Combustion of Woods Grown in the Northeastern United States. *Environ. Sci. Technol*. **2001**, 35 (13), 2665-2675.

Fine, Philip M.; Cass, Glen R.; Simoneit, Bernd, R. T. Chemical Characterization of Fine Particle Emissions from Fireplace Combustion of Woods Grown in the Southern United States. *Environ. Sci. Technol*. **2002**, 36 (7), 1442-1451.

Fine, Philip M.; Chakrabarti, Bhabesh; Krudysz, Meg; Schauer, James, J.; Sioutas, Constantos. Diurnal Variations of Individual Organic Compound Constituents of Ultrafine and Accumulation Mode of Particulate Matter in the Los Angeles Basin. *Environ. Sci. Technol*. **2004**, 38 (5), 1296-1304.

Ghan, Steven R.; Schwartz, Stephen E. Aerosol Properties and Processes: A Path from Field and Laboratory Measurements to Global Climate Models. *Bull. Am. Metero. Soc*. **2007**, 1059-1083.

Grey, H. Andrew; Cass, Glen R. Source Contributions to Atmospheric Fine Carbon Particle Concentrations. *Atmos. Environ*. **1998**, 32 (22), 3805-3825.

Gorin, Courtney A.; Collett, Jeffrey L. Jr.; Herckes, Pierre. Wood Smoke Contribution to Winter Aerosol in Fresno, CA. *J. Air Waste Manage. Assoc*. **2006**, 56, 1584-1590.

Hawley, Harmonie A; Mazurek, Monica A. Oxocarboxylic Acids as DNPH Derivatives with a Monolithic Silica Column and UV-Vis Detection. *Am. Lab. On-Line* In press, June, 2008.

Hawley, Harmonie A.; Mazurek, Monica A. Improved Measurement of Atmospheric Carbonyl Compounds as 2,4-DNPH-carbonyl Derivatives with HPLC UV/Vis Detection. In preparation. 2008b.

Hays, Michael D.; Fine, Philip M.; Geron, Christopher D.; Kleeman, Michael J.; Gullett, Brian K. Open Burning of Agricultural Biomass: Physical and Chemical Properties of Particle-Phase Emissions. *Atmos. Environ*. **2005**, 39, 6747-6764.

He, Ling-Yan; Hu, Min; Huang, Xiao-Feng; Zhang, Yuan-Hang; Tang, Xiao-Yan. Seasonal Pollution Characteristics of Organic Compounds in Atmospheric Fine Particles in Beijing. *Sci. Total Environ*. **2006**, 359, 167-176.

He, Ling-Yan; Hu, Min; Huang, Xiao-Feng; Yu, Ben-De; Zhang, Yuan-Hang; Liu, De-Quan. Measurement of Emissions of Fine Particulate Organic Matter From Chinese Cooking. *Atmos. Environ*. **2004**, 36, 6557-6564.

Herckes, Pierre; Engling, Guenter; Kreidenweis, Sonia M; Collett, Jeffrey L. Jr. Particle Size Distributions of Organic Aerosol Constituents during the 2002 Yosemite Aerosol Characterization Study. *Environ. Sci. Technol*. **2006**, 40 (15), 4554-4562.

Hicks, Charles R.; Turner, Kenneth V. Jr. Fundamental Concepts in the Design of Experiments. 5th Edition. Oxford University Press. 1999. Page 14.

Hildemann, Lynn M.; Markowski, Gregory R.; Cass, Glen R. Chemical Composition of Emissions from Urban Sources of Fine Organic Aerosol. *Environ. Sci. Technol*. **1991**, 25 (4), 744-759.

Houck, James E.; Eagle, Brian N. Task 6 Technical Memorandum 4 (Final Report): Control Analysis and Documentation for Residential Wood Combustion in the MANE-VU Region. Prepared for: Mid-Atlantic Regional Air Management Association, Inc. December 19, 2006.

Jacoby, Mitch. Monolithic Chromatography: Nontraditional Column Materials Improve Separations of Biomixtures. *Chem. Eng. News* **2006**, 84 (50), 14-19.

Johnstone, Robert A. W.; Plimmer, Jack R. The Chemical Constituents of Tobacco and Tobacco Smoke. *Chem. Rev*. **1959**, 59,885-905.

Jordan, Timothy B.; Seen, Andrew J.; Jacobsen, Geraldine E. Levoglucosan as an atmospheric tracer for woodsmoke. *Atmos. Environ*. **2006**, 40, 5316-5321.

Karl, Thomas R.; Trenberth, Kevin E. Modern Global Climate Change. *Science* **2003**, 302 (5), 1719-1723.

Karnik, Bhavana S.; Davies, Simon H.; Baumann, Melissa J.; Masten, Susan J. Fabrication of Catalytic Membranes for Treatment of Drinking Water Using Combined Ozonation and Ultrafiltration. *Environ. Sci. Technol*. **2005**, 39 (19), 7656-7661.

Kawamura, Kimitaka; Kasukabe, Hideki; Barrie, Leonard A. Source and Reaction Pathways of Dicarboxylic Acids, Ketoacids, and Dicarbonyls in Arctic Aerosols: One Year of Observations. *Atmos. Environ*. **1996**, 30 (10/11), 1709-1722.

Kawamura, Kimitaka; Imai, Yoshie; Barrie, Leonard A. Photochemical Production and Loss of Organic Acids in High Arctic Aerosols During Long-Range Transport and Polar Sunrise Ozone Depletion Events. *Atmos. Environ*. **2005**, 39, 599-614.

Keithly, Lois; Wayne, Geoffrey Francis; Cullen, Doris M.; Connolly, Gregory N. Industry Research on the Use and Effects of Levulinic Acid: A Case Study in Cigarette Additives. *Nicotine & Tobacco Res*. **2005**, 7 (5), 761-771.

Kleindienst, T.E.; Smith, D.F.; Li, W.; Edney, E.O.; Driscoll, D.J.; Speer, R.E.; Weathers, W.S. Secondary Organic Aerosol Formation From the Oxidation of Aromatic Hydrocarbons in the Presence of Dry Submicron Ammonium Sulfate Aerosol. *Atmos. Environ*. **1999**, 33, 3669-3681.

Kleindienst, T.E.; Conver, T.S.; McIver, C.D.; Edney, E.O. Determination of Secondary Organic Aerosol Products from the Photooxidation of Toluene and their Implications in Ambient $PM_{2.5}$. *J. Atmos. Chem*. **2004**, 47, 79-100.

Kurian, Steven. Spatial and Temporal Trends of Organic and Elemental Carbon as a Component of $PM_{2.5}$ within the New York Metropolitan Area. MS Thesis, Rutgers University, Piscataway, NJ, 2007, pp 98.

Lee, Seon Hwa; Kim, Soon Ok; Chung, Bong Chul. Gas Chromatographic—Mass Spectrometric Determination of Urinary Oxoacids Using O-(2,3,4,5,6-pentafluorobenzyl)Oxime-Trimethylsilyl Ester Derivatization and Cation-Exchange Chromatography. *J. Chromatogr. B* **1998**, 719, 1-7.

Lehninger, Albert L. Biochemistry. Worth Publishers, New York, NY, 1975.

Levart, A.; Veber, M. Determination of Aldehydes and Ketones in Air Samples Using Cryotrapping Sampling. *Chemosphere.* **2001**, 44, 701-708.

Li, Min; Mc Dow, Stephen R.; Tollerud, David; Mazurek, Monica A. Quantitation, Detection and Measurement Precision of Molecular Markers in Urban Particulate Matter from Philadelphia, PA, AWMA's 98th Annual Conference & Exhibition Proceedings, Minneapolis, Minnesota, 2005.

Li, Min; McDow, Stephen R.; Tollerud, David J.; Mazurek, Monica A. Seasonal Abundance of Organic Molecular Markers in Urban Particulate Matter from Philadelphia, PA. *Atmos. Environ*. **2006**, 40, 2260-2273.

Lough, G.C.; Schauer, J.J.; Lawson, D.R. Day-of-Week Trends in Carbonaceous Aerosol Composition in the Urban Atmosphere. *Atmos. Environ*. **2006**, 40 (22), 4137-4149.

Mazurek, Monica A.; Simoneit, Bernd R.T.; Cass, Glen R.; Gray, H. Andrew. Quantitative High-Resolution Gas Chromatography and High-Resolution Gas Chromatography/Mass Spectrometry Analysis of Carbonaceous Fine Aerosol Particles. *Int. J. Environ. Anal. Chem*. **1987**, 29, 119-139.

Mazurek, Monica A.; Cass, Glen R.; Simoneit, Bernd R.T. Interpretation of High-Resolution Gas Chromatography and High-Resolution Gas Chromatography/Mass Spectrometry Data Acquired from Atmospheric Organic Aerosol Samples. *Aerosol Sci. Technol*. **1989**, 10, 408-420.

Mazurek, Monica A. Molecular Identification of Organic Compounds in Atmospheric Complex Mixtures and Relationships to Atmospheric Chemistry and Sources. *Environ. Health Perspect*. **2002**, 110 (6), 995-1003.

MacCracken, Michael C. Prospects for Future Climate Change and the Reasons for Early Action. *J. Air & Waste Manag. Assoc*. **2008**, 59, 735-786.

McDonald, J. D.; Zielinska B.; Fujita E. M.; Sagebiel, J. C.; Chow, J. C.; Watson, J.G. Emissions from charbroiling and grilling of chicken and beef, *J. Air Waste Manage. Assoc*. **2003**, 53(2), 185-194.

McDow, Stephen R.; Mazurek, Monica A.; Li, Min; Alter, Lee; Graham, John; Felton, H. Dirk; McKenna, Thomas; Pietarinen, Charles; Leston, Alan; Bailey, Steve; Tong-Argao, Sania. Speciation and Atmospheric Abundance of Organic Compounds in PM2.5 from the New York City Area. I. Sampling Network, Sampler Evaluation, Molecular Level Blank Evaluation. *Aerosol Sci. Technol*. **2008**, 42 (1), 50-63.

Medeiros, Patricia M.; Conte, Maureen H.; Weber, John C.; Simoneit, Bernd R. T. Sugars as Source Indicators of Biogenic Organic Carbon in Aerosols Collected Above the Howland Experimental Forest, Maine. *Atmos. Environ.* **2006**, 40, 1694-1705.

Melin, Esa S.; Odegaard, Hallvard. The Effect of Biofilter Loading Rate on the Removal of Organic Ozonation By-Products. *Water Res*. **2000**, 34 (18), 4464-4476.

Miller, James M. *Chromatography: Concepts and Contrasts*, Second Edition; John Wiley & Sons, Inc.: Hoboken, NJ. 2005.

NARSTO. Particulate Matter Science for Policy Makers. A NARSTO Assessment Part I. February, 2003. EPRI 1007735.

Northeast States for Cooridanted Air Use Management and MJB Associates (NESCAUM). Assessment of Carbonaceous $PM_{2.5}$ for New York and the Region. NYSERDA 8641. March, 2008.

New Jersey Department of Environmental Protection (NJ DEP). Proposed State Implementation Plan (SIP) Revisions for the Attainment and Maintenance of the 8-Hour Ozone National Ambient Air Quality Standard, 1-Hour Ozone National Ambient Air Quality Standard, and Fine Particulate Matter National Ambient Air Quality Standard; and the 2002 Periodic Emission Inventory. February, 2006.

Nolte, Christopher G.; Schauer, James J.; Cass, Glen R.; Simoneit, Bernd R.T. Highly Polar Organic Compounds Present in Wood Smoke and in the Ambient Atmosphere. *Environ. Sci. Technol*. **2001**, 35 (10), 1912-1919.

Oros, D.R.; Simoneit, B.R.T. Identification and Emission Rates of Molecular Tracers in Coal Smoke Particulate Matter. *Fuel* **2000**, 79, 515-536.

Ortiz, Ricardo; Hagino, Hiroyuki; Sekiguchi, Kazuhiko; Wang, Qingyue; Sakamoto, Kazuhiko. Ambient Air Measurements of Six Bifunctional Carbonyls in a Suburban Area. *Atmos. Res*. **2006**, 82, 709-718.

Pandis, Spyros. Atmospheric Aerosol Processes. In *Particulate Matter Science for Policy Makers. A NARSTO Assessment Part I*. NARSTO. February, 2003. EPRI 1007735.

Pio, Casimiro; Alves, Celia; Duarte, Armando. Organic Components of Aerosols in a Forested Area of Central Greece. *Atmos. Environ*. **2001**, 35, 389-01.

Ragauskas, Arthur J.; Williams, Charlotte K.; Davison, Brian H.; Britovsek, George; Cairney, John; Eckert, Charles A.; Frederick, William J. Jr.; Hallett, Jason P.; Leak, David J.; Liotta, Charles L.; Mielenz, Jonathon R.; Murphy, Richard; Templer, Richard; Tschaplinski, Timothy. The Path Forward for Biofuels and Biomaterials. *Science*. **2006**, 311, 484-489.

Raloff, Janet. Cholesterol: Up in Smoke. *Science News*. **1991**, 140, 60-61.

Robinson, Allen L.; Subramanian, R.; Donahue, Neil M.; Bernado-Bricker, Anna; Rogge, Wolfgang R. Source Apportionment of Molecular Markers and Organic Aerosol. 2. Biomass Smoke. *Environ. Sci. Technol*. **2006**, 40 (24), 7811-7819.

Rogge, Wolfgang F.; Hildemann, Lynn M.; Mazurek, Monica A.; Cass, Glen R.; Simoneit, Bernd R. T. Sources of Fine Organic Aerosol. 1. Charbroilers and Meat Cooking Operations. *Environ. Sci. Technol*. **1991**, 25 (6), 1112-1125.

Rogge, Wolfgang F.; Hildemann, Lynn M.; Mazurek, Monica A.; Cass, Glen R.; Simoneit, Bernd R. T. Sources of Fine Organic Aerosol. 4. Particulate Abrasion Products from Leaf Surfaces of Urban Plants. *Environ. Sci. Technol*. **1993**, 27 (13), 2700-2711.

Rogge, Wolfgang F.; Mazurek, Monica A.; Hildemann, Lynn M.; Cass, Glen R.; Simoneit, Bernd R.T. Quantification of Urban Organic Aerosols at a Molecular Level: Identification, Abundance and Seasonal Variations. *Atmos. Environ*. **1993b**, 27A (8), 1309-1330.

Rogge, Wolfgang F.; Hildemann, Lynn M.; Mazurek, Monica A.; Cass, Glen R. Sources of Fine Organic Aerosol. 6. Cigarette Smoke in the Urban Atmosphere. *Environ. Sci. Technol*. **1994**, 28 (7), 1375-1388.

Rogge, W. F.; Hildemann, L. M.; Mazurek, M.A.; Cass, G. R.; Simoneit, B. R. T. Sources of fine organic aerosol .7. Hot asphalt roofing tar pot fumes. *Environ. Sci. & Technol* ,**1997**, 31 (10), 2726-2730.

Rogge, Wolfgang F.; Hildemann, Lynn M.; Mazurek, Monica A.; Cass, Glen R.; Simoneit, Bernd R. T. Sources of Fine Organic Aerosol. 9. Pine, Oak, and Synthetic Log Combustion in Residential Fireplaces. *Environ. Sci. Technol*. **1998**, 32 (1), 13-22.

Rushdi, Ahmed I.; Al-Zarban, Sheikha; Simoneit, Bernd R. T. Chemical Composition and Sources of Organic Matter in Fine Particles of Soils and Sands From the Vicinity of Kuwait City. *Environ. Monit.Assess*. **2006**, 120, 537-557.

Sampere, Richard; Kawamura, Kimitaka. Low Molecular Weight Dicarboxylic Acids and Related Polar Compounds in the Remote Marine Rain Samples Collected from Western Pacific. *Atmos. Environ*. **1996**, 30 (10/11), 1609-1619.

Sano, Atsushi; Satoh, Tsuneo; Oguma, Tetsuya; Nakatoh, Akinori; Satoh, Jun-ichi; Ohgawara, Toshifumi. Determination of Levulinic Acid in Soy Sauce by Liquid Chromatography with Mass Spectrometric Detection. *Food Chem*. **2007**, 105, 1242-1247.

Schauer, James J.; Rogge, Wolfgang F.; Hildemann, Lynn M.; Mazurek, Monica A.; Cass, Glen R.; Simoneit, Bernd R. T. Source Apportionment of Airborne Particulate Matter Using Organic Compounds as Tracers. *Atmos. Environ*. **1996**, 30 (22), 3837-3855.

Schauer, James J.; Kleeman, Michael J.; Cass, Glen R.; Simoneit, Bernd R. T. Measurement of Emissions from Air Pollution Sources: 1. C_1 Through C_{29} Organic Compounds from Meat Charbroiling. *Environ. Sci. Technol*. **1999**, 33 (10), 1566-1577.

Schauer, James J.; Kleeman, Michael J.; Cass, Glen R.; Simonet, Bernd R.T. Measurement of Emissions from Air Pollution Sources. 3. C_1-C_{29} Organic Compounds from Fireplace Combustion of Wood. *Environ. Sci. T*echnol. **2001**, 35 (9), 1716-1728.

Schauer, James J.; Kleeman, Michael J.; Cass, Glen R.; Simoneit, Bernd R. T. Measurement of Emissions from Air Pollution Sources. 4. C_1—C_{27} Organic Compounds from Cooking with Seed Oils. *Environ. Sci. Technol*. **2002**, 36 (4), 567-575.

Schwartz, Heidi; Ollilainen, Velimatti; Piironen, Vieno; Lampi, Anna-Maija. Tocopherol, Tocotrienol and Plant Sterol Contents of Vegetable Oils and Industrial Fats. *J. Food Compos. Anal*. **2008**, 21, 152-161.

Sheesley, Rebecca J.; Schauer, James J.; Bean, Erin; Kenski, Donna. Trends in Secondary Organic Aerosol at a Remote Site in Michigan's Upper Peninsula. *Environ. Sci. Technol*. **2004**, 38 (24), 6491-6500.

Sheesley, Rebecca J.; Schauer, James J.; Zheng, Mei; Wang, Bo. Sensitivity of Molecular-Marker Based CMB Models to Biomass Burning Source Profiles. *Atmos. Environ*. **2007**, 41, 9050-9063.

Shepherd, Marjorie. Perspective for Managing PM. In *Particulate Matter Science for Policy Makers. A NARSTO Assessment Part I.* NARSTO. February, 2003. EPRI 1007735.

Schlosser, Eric. Fast Food Nation. Houghton Mifflin. New York, NY, 2001.

Simoneit, B. R. T.; Mazurek, M. A.; Reed, W. E. Characterization of Organic Matter in Aerosols over Rural Sites: Phytosterols. *Adv. Org. Geochem*. **1981**, 355-361.

Simoneit, Bernd R. T.; Mazurek, Monica A. Organic Matter of the Troposphere—II. Natural Background of Biogenic Lipid Matter in Aerosols over the Rural Western United States. *Atmos. Environ.* **1982**, 19 (9), 2139-2159.

Simoneit, Bernd R. T.; Rogge, W. F.; Mazurek, M. A.; Standley, L. J.; Hildemann, L. M.; Cass, G. R. Lignin Pyrolysis Products, Lignans, and Resin Acids as Specific Tracers of Plant Classes in Emissions from Biomass Combustion. *Environ. Sci. Technol*. **1993**, 27 (12), 2533-2541.

Simoneit, Bernd R. T.; Schauer, J. J.; Nolte, C. G.; Elias, V. O.; Fraser, M. P.; Rogge, W. F.; Cass, G. R. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmos. Environ.* **1999**, *33*(2), 173-182.

Simoneit, Bernd R. T. Biomass Burning—A Review of Organic Tracers for Smoke from Incomplete Combustion. *Applied Geochem*. **2002**, 17, 129-162.

Simoneit, Bernd R. T.; Elias, Vladmir O.; Kobayashi, Minoru; Kawamura, Kimitaka; Rushdi, Ahmed I.; Medeiros, Patricia M.; Rogge, Wolfgang F.; Didyk, Borys M. Sugars—Dominant Water-Soluble Organic Compounds in Soils and Characterization as Tracers in Atmospheric Particulate Matter. *Environ. Sci. Technol*. **2004**, 38 (22), 5939-5949.

Simoneit, Bernd R. T.; Medeiros, Patricia M.; Didyk, Borys M. Combustion Products of Plastics as Indicators for Refuse Burning in the Atmosphere. *Environ. Sci. Technol*. **2005**, 34 (18), 6961-6970.

Simoneit, Bernd R. T.; Bi, Xinhui; Oros, Daniel R.; Medeiros, Patricia M.; Sheng, Guoying; Fu, Jiamo. Phenols and Hydroxy-PAHs (Arylphenols) as Tracers for Coal Smoke Particulate Matter: Source Tests and Ambient Aerosol Asessments. *Environ. Sci. Technol*. **2007**, 41 (21), 7294-7302.

Sriram, Ganesh; Iyer, Vidya V.; Fulton, D. Bruce; Shanks, Jacqueline V. Identification of Hexose Hydrolysis Products in Metabolic Flux Analytes: A Case Study of Levulinic Acid in Plant Protein Hydrolysate. *Metabolic Eng*. **2007**, 9, 442-451.

Svec, Frantisek. Huber, Christian G. Monolithic Materials: Promises, Challenges, Achievements. *Anal. Chem*. April 1, **2006**, 2100-2107.

U.S. Environmental Protection Agency. Method 8315A: Determination of Carbonyl Compounds by High Performance Liquid Chromatography (HPLC). Revision 1. December, 1996.

Vogel, Martin; Buldt, Andrea; Karst, Uwe. Hydrazine reagents as derivatizing agents in environmental analysis – a critical review. *Fresnius J. Anal. Chem*. **2000**, 366, 781-791.

Wang, Haobo; Kawamura, Kimitaka; Yamazaki, Koji. Water-Soluble Dicarboxylic Acids, Ketoacids and Dicarbonyls in the Atmospheric Aerosols over the Southern Ocean and Western Pacific Ocean. *J. Atmos. Chem*. **2006**, 53, 43-61.

Wiley, Averill J.; Harris, John F.; Saeman, Jerome F.; Locke, Edward G. Wood Industries as a Source of Carbohydrates. *Industrial & Eng. Chem*. **1955**, 47 (7), 1397-1405.

Winkler, Jill K.; Warner, K.; Glynn, Martin T. Effect of Deep-Fat Frying on Phytosterol Content in Oils With Differing Fatty Acid Composition. *J. Am. Oil Chem. Soc*. **2007**, 84, 1023-1030.

Yu, Jianzhen; Cocker, David R. III; Griffin, Robert J.; Flagan, Richard C.; Seinfeld, John H. Gas-Phase Ozone Oxidation of Monoterpenes: Gaseous and Particulate Products. *J. Atmos. Chem*. **1999**, 34, 207-258.

Zheng, Mei; Cass, Glen R.; Ke, Lin; Wang, Fu; Schauer, James, J.; Edgerton, Eric S.; Russell, Armistead G. Source Apportionment of Daily Fine Particulate Matter at Jefferson Street, Atlanta, GA, during Summer and Winter. *J. Air Waste Manage. Assoc*. **2007**, 57, 228-242.

Appendices

Appendix A: HPLC Monolithic Columns Calibration Curves

RT = Retention Time, minutes

$$\% RSD = \frac{s\tan dard\ deviation}{average} * 100$$

95% confidence intervals (alpha = 0.05, two tail) on the mass level data replicates for each compound. Then the value given is the t-critical to be read as average ± t-critical.

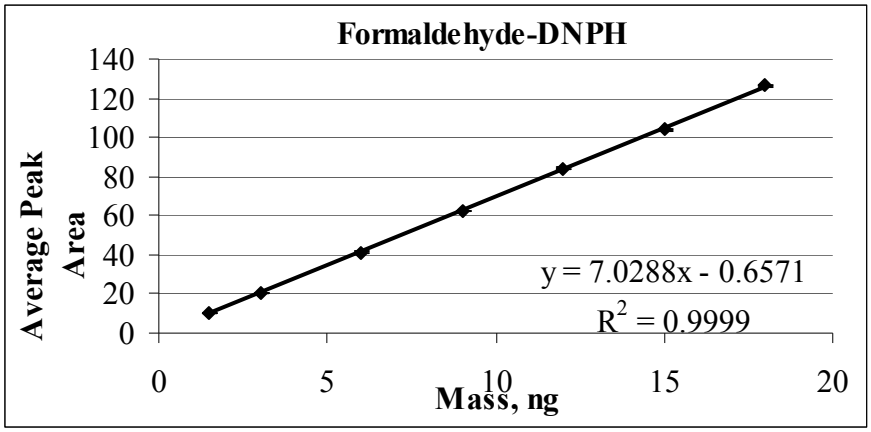
Peak 1 (Formaldehyde-2,4-DNPH)

Mass 1.5 ng			Mass 3 ng			Mass 6 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	10.2	3.450	1	19.8	3.452	1	41.1	3.441
2	9.9	3.439	2	20.4	3.440	2	41.4	3.435
3	10.1	3.446	3	20.1	3.438	3	41.1	3.433
4	10.3	3.441	4	20.4	3.442	4	41.1	3.437
5	10.4	3.436	5	20.6	3.436	5	41.3	3.431
6	10.2	3.433	6	20.1	3.417	6	41.3	3.409
7	10.1	3.415	7	20.4	3.398	7	41.5	3.416
8	10.9	3.427	8	20.5	3.415	8	41.7	3.416
9	10.7	3.400	9	20.6	3.416	9	41.1	3.415
10	10.5	3.415	10	20.1	3.420	10	41.5	3.416
Average	10.33	3.430	Average	20.3	3.427	Average	41.31	3.425
StdDev	0.30	0.016	StdDev	0.26	0.017	StdDev	0.21	0.012
% RSD	2.92	0.46	RSD	1.29	0.484	RSD	0.52	0.337
95% CI	0.19	0.01	95% CI	0.16	0.01	95% CI	0.13	0.01

Mass 9 ng			Mass 12 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT
1.00	62.00	3.44	1	83.2	3.443
2.00	62.20	3.44	2	83.4	3.425
3.00	62.00	3.44	3	83	3.428
4.00	62.20	3.43	4	84.6	3.433
5.00	62.40	3.44	5	84.1	3.429
6.00	62.40	3.40	6	84.4	3.459
7.00	63.00	3.42	7	84.3	3.430
8.00	62.20	3.42	8	84.5	3.433
9.00	62.00	3.41	9	84.7	3.444
10.00	62.00	3.42	10	84.7	3.445

Average	62.24	3.42	Average	84.09	3.437
StdDev	0.31	0.01	StdDev	0.65	0.011
RSD	0.50	0.38	RSD	0.77	0.307
95% CI	0.19	0.01	95% CI	0.40	0.01

Mass 15ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	103.4	3.433	1	12.5.5	3.429
2	103.9	3.429	2	125.9	3.425
3	104	3.428	3	125.7	3.424
4	104.2	3.417	4	126.2	3.426
5	103.5	3.433	5	125.6	3.431
6	104.9	3.406	6	126.8	3.433
7	104.7	3.408	7	126.9	3.427
8	104.1	3.410	8	127.2	3.441
9	103.8	3.408	9	126.4	3.444
10	104.4	3.409	10	126.9	3.438
Average	104.09	3.418	Average	126.4	3.432
StdDev	0.48	0.011	StdDev	0.58	0.007
RSD	0.46	0.332	RSD	0.46	0.205
95% CI	0.30	0.01	95% CI	0.36	0.00



Peak 2 (Acetaldehyde-2,4-DNPH)

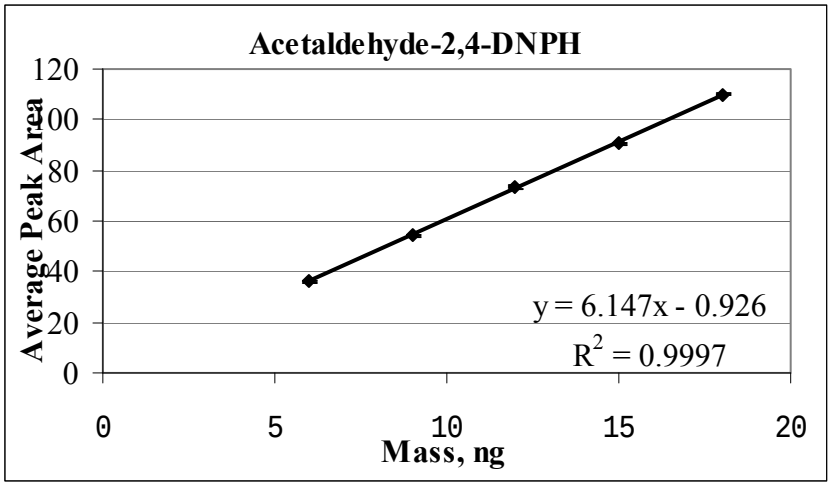
Mass 1.5 ng			Mass 3 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	8.9	4.232	1	17.2	4.231

2	8.5	4.219	2	17.9	4.219
3	8.5	4.226	3	17.6	4.218
4	8.6	4.222	4	17.8	4.224
5	8.9	4.216	5	17.9	4.218
6	8.7	4.208	6	17.7	4.195
7	8.6	4.190	7	17.8	4.174
8	9.4	4.202	8	17.8	4.191
9	9.2	4.188	9	18	4.193
10	8.9	4.192	10	17.6	4.194
Average	8.82	4.210	Average	17.73	4.206
StdDev	0.30	0.016	StdDev	0.23	0.019
RSD	3.41	0.378	RSD	1.28	0.440
95% CI	0.19	0.01	95% CI	0.14	0.01

Mass 6 ng			Mass 9 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	35.8	4.221	1	54	4.216
2	36.1	4.215	2	54.3	4.218
3	35.9	4.215	3	54.2	4.215
4	35.9	4.218	4	54.2	4.216
5	36	4.214	5	54.2	4.217
6	36	4.187	6	54.3	4.183
7	36.1	4.191	7	54.7	4.196
8	36.2	4.193	8	54	4.192
9	35.9	4.191	9	54	4.193
10	36.1	4.194	10	53.9	4.198
Average	36	4.204	Average	54.18	4.204
StdDev	0.12	0.014	StdDev	0.23	0.013
RSD	0.35	0.325	RSD	0.42	0.315
95% CI	0.08	0.01	95% CI	0.14	0.01

Mass 12 ng			Mass 15ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	73	4.221	1	90.1	4.213	1	109	4.203
2	72.8	4.204	2	90.5	4.208	2	109.5	4.204
3	72.8	4.208	3	90.6	4.209	3	109.8	4.205
4	73.4	4.215	4	90.6	4.197	4	109.4	4.202
5	73.4	4.210	5	90.5	2.411	5	109.9	4.211

6	74	4.241	6	91	4.184	6	110.7	4.218
7	73.5	4.217	7	91	4.184	7	110.3	4.211
8	73.9	4.222	8	90.5	4.186	8	111.2	4.221
9	73.9	4.226	9	90	4.180	9	110.3	4.222
10	74	4.235	10	90.1	4.187	10	110.4	4.217
Average	73.47	4.220	Average	90.49	4.194	Average	110.05	4.211
StdDev	0.48	0.012	StdDev	0.35	0.013	StdDev	0.66	0.008
RSD	0.65	0.278	RSD	0.38	0.304	RSD	0.60	0.183
95% CI	0.30	0.01	95% CI	0.22	0.01	95% CI	0.41	0.00



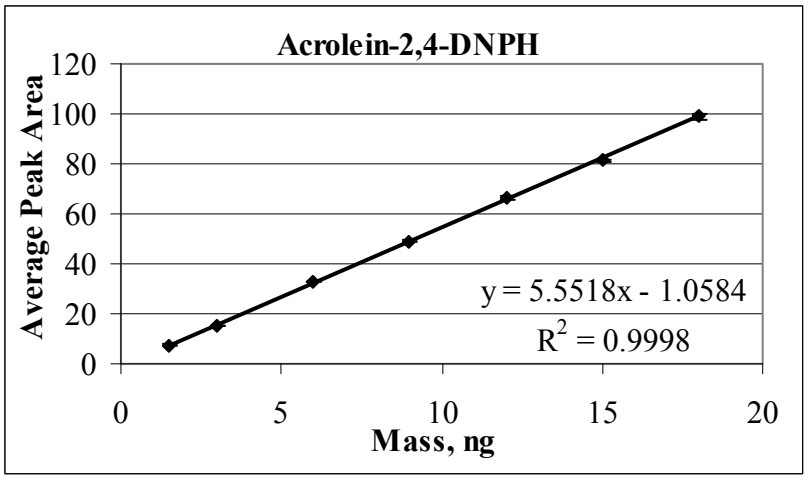
Peak 3 (Acrolein-2,4-DNPH)

Mass 1.5 ng			Mass 3 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	7.4	5.065	1	14.7	5.063
2	7.1	5.046	2	15.3	5.051
3	7.2	5.055	3	14.9	5.048
4	7.4	5.052	4	15.2	5.054
5	7.3	5.040	5	15.3	5.048
6	7.4	5.031	6	14.8	5.022
7	7.2	5.021	7	14.9	5.009
8	7.8	5.032	8	15	5.019
9	7.6	5.022	9	15.1	5.021
10	7.6	5.022	10	14.9	5.024
Average	7.4	5.039	Average	15.01	5.036
StdDev	0.22	0.016	StdDev	0.21	0.019
RSD	2.92	0.308	RSD	1.39	0.371

95% CI	0.13	0.01	95% CI	0.13	0.01

Mass 6 ng			Mass 9 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	32.7	5.054	1	48.8	5.049
2	32.6	5.045	2	49	5.047
3	32.5	5.043	3	49.1	5.046
4	32.6	5.049	4	48.3	5.044
5	32.9	5.040	5	49.1	5.048
6	32.3	5.022	6	48.7	5.012
7	32.6	5.017	7	49.6	5.026
8	32.7	5.026	8	48.8	5.028
9	32.5	5.025	9	48.8	5.026
10	32.8	5.025	10	49	5.028
Average	32.62	5.035	Average	48.92	5.035
StdDev	0.17	0.013	StdDev	0.34	0.013
RSD	0.52	0.258	RSD	0.69	0.256
95% CI	0.10	0.01	95% CI	0.21	0.01

Mass 12 ng			Mass 15ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	65.8	5.051	1	80.5	5.045	1	98.1	5.038
2	65.6	5.036	2	81.2	5.040	2	96.4	5.042
3	65.1	5.048	3	82	5.044	3	98.1	5.045
4	66.5	5.050	4	81.2	5.035	4	98.6	5.040
5	66.3	5.047	5	81.1	5.042	5	99.4	5.049
6	66.7	5.076	6	80.9	5.015	6	99.9	5.059
7	66.5	5.056	7	81.5	5.019	7	99.3	5.051
8	66.7	5.060	8	81.4	5.019	8	100.5	5.060
9	67	5.066	9	82	5.009	9	99.6	5.063
10	67	5.073	10	82.3	5.019	10	100.1	5.054
Average	66.32	5.056	Average	81.41	5.029	Average	99	5.050
StdDev	0.63	0.013	StdDev	0.55	0.014	StdDev	1.22	0.009
RSD	0.95	0.002	RSD	0.68	0.273	RSD	1.23	0.175
95% CI	0.39	0.01	95% CI	0.34	0.01	95% CI	0.76	0.01

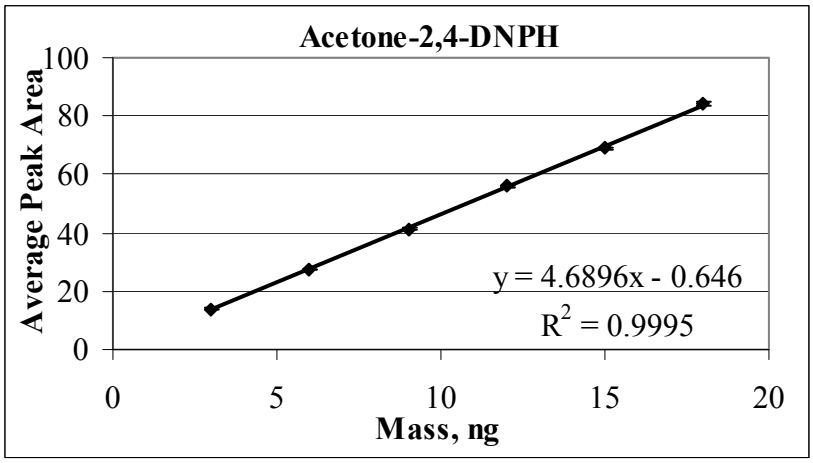


Peak 4 (Acetone-2,4-DNPH)

Mass 3 ng			Mass 6 ng			Mass 9 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	13.7	5.240	1	27.1	5.230	1	41	5.225
2	14.1	5.228	2	27.3	5.222	2	41.1	5.224
3	13.6	5.225	3	27.2	5.219	3	40.8	5.222
4	14.1	5.229	4	27.2	5.225	4	41.6	5.220
5	14	5.225	5	27.1	5.217	5	41.1	5.224
6	13.8	5.200	6	27.4	5.200	6	41.3	5.188
7	13.9	5.188	7	27.4	5.195	7	41.7	5.203
8	13.6	5.197	8	27.5	5.205	8	41.2	5.206
9	13.9	5.198	9	27.1	5.203	9	40.9	5.206
10	13.9	5.201	10	27.5	5.203	10	41.2	5.204
Average	13.86	5.213	Average	27.28	5.212	Average	41.19	5.212
StdDev	0.18	0.018	StdDev	0.16	0.011	StdDev	0.28	0.013
RSD	1.33	0.345	RSD	0.59	0.220	RSD	0.69	0.240
95% CI	0.11	0.01	95% CI	0.10	0.01	95% CI	0.18	0.01

Mass 12 ng			Mass 15ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	55.7	5.231	1	68.7	5.220	1	83.3	5.214
2	55.6	5.213	2	69.1	5.216	2	85.4	5.218
3	55.8	5.224	3	68.4	5.220	3	84.5	5.221
4	55.9	5.229	4	69	5.211	4	84.4	5.218
5	55.6	5.225	5	69.1	5.216	5	84.2	5.224
6	56.7	5.254	6	69.4	5.191	6	84.5	5.235

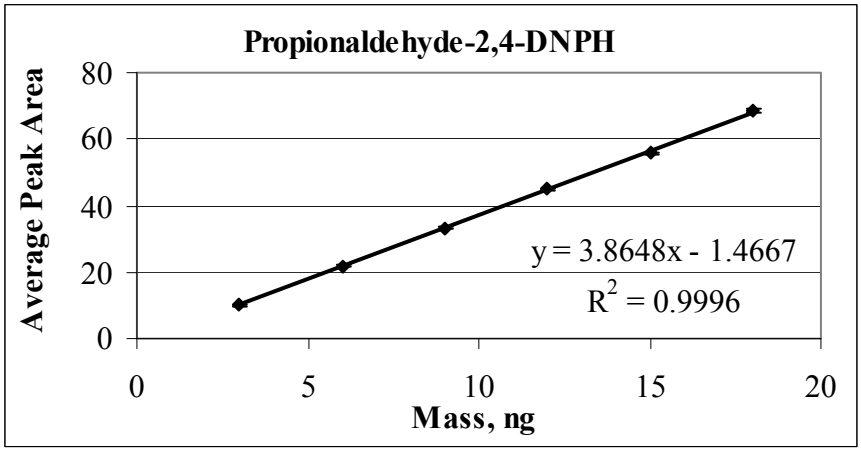
7	56	5.232	7	69.1	5.196	7	84.8	5.227
8	56.1	5.236	8	68.9	5.194	8	84.8	5.234
9	55.9	5.241	9	68.3	5.185	9	84.5	5.237
10	56	5.248	10	68.7	5.197	10	84	5.230
Average	55.93	5.233	Average	68.87	5.205	Average	84.44	5.226
StdDev	0.32	0.012	StdDev	0.34	0.013	StdDev	0.55	0.008
RSD	0.57	0.230	RSD	0.50	0.255	RSD	0.65	0.154
95% CI	0.20	0.01	95% CI	0.21	0.01	95% CI	0.34	0.00



Peak 5 (Propionaldehyde-2,2-DNPH)

Mass 3 ng			Mass 6 ng			Mass 9 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	10	5.561	1	21.8	5.551	1	33.2	5.546
2	10.1	5.548	2	22	5.541	2	33	5.543
3	10	5.544	3	21.8	5.540	3	32.9	5.542
4	9.9	5.547	4	22	5.543	4	33.8	5.541
5	10.5	5.543	5	21.8	5.536	5	33.1	5.544
6	9.7	5.520	6	22.3	5.521	6	33.7	5.511
7	9.8	5.512	7	22	5.516	7	33.6	5.524
8	10.1	5.518	8	22	5.525	8	33.2	5.527
9	10.1	5.519	9	21.8	5.524	9	33.1	5.529
10	10.3	5.518	10	22	5.523	10	33.3	5.525
Average	10.05	5.533	Average	21.95	5.532	Average	33.29	5.533
StdDev	0.23	0.017	StdDev	0.16	0.012	StdDev	0.31	0.012
RSD	2.31	0.312	RSD	0.72	0.210	RSD	0.92	0.210
95% CI	0.14	0.01	95% CI	0.10	0.01	95% CI	0.19	0.01

Mass 12 ng			Mass 15ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	45.2	5.555	1	55.7	5.541	1	68.3	5.537
2	44.6	5.537	2	55.9	5.537	2	69.3	5.540
3	45	5.543	3	55	5.524	3	68.5	5.544
4	45.1	5.553	4	55.9	5.535	4	68.6	5.543
5	45	5.546	5	55.7	5.536	5	68.8	5.547
6	45.8	5.574	6	56.5	5.513	6	68.4	5.558
7	44.9	5.554	7	56.1	5.516	7	68.8	5.552
8	45.2	5.559	8	55.8	5.515	8	68.9	5.556
9	45	5.563	9	55	5.505	9	68.1	5.559
10	45.2	5.571	10	55.2	5.520	10	68.4	5.555
Average	45.10	5.556	Average	55.68	5.524	Average	68.61	5.549
StdDev	0.31	0.012	StdDev	0.48	0.012	StdDev	0.35	0.008
RSD	0.68	0.212	RSD	0.87	0.223	RSD	0.51	0.143
95% CI	0.19	0.01	95% CI	0.30	0.01	95% CI	0.22	0.00

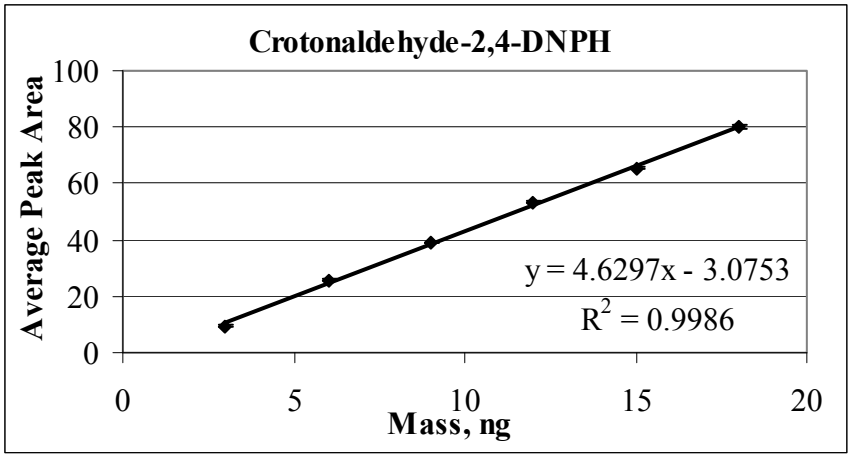


Peak 6 (Crotonaldehyde-2,4-DNPH)

Mass 3 ng			Mass 6 ng			Mass 9 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	9.4	6.264	1	25.8	6.251	1	39	6.248
2	9.5	6.253	2	26.1	6.244	2	38.9	6.247
3	8.9	6.248	3	25.9	6.242	3	38.9	6.248
4	9.4	6.250	4	25.8	6.250	4	39	6.246
5	9.7	6.241	5	26	6.240	5	39	6.243
6	9.5	6.226	6	25.8	6.225	6	39	6.218

7	9.2	1.300	7	25.7	6.224	7	39.6	6.233
8	9.5	6.224	8	25.9	6.232	8	39.2	6.234
9	9.5	6.229	9	25.7	6.230	9	39.1	6.239
10	9.6	6.224	10	26.1	6.228	10	39.3	6.228
Average	9.42	6.240	Average	25.88	6.237	Average	39.10	6.238
StdDev	0.23	0.015	StdDev	0.15	0.010	StdDev	0.22	0.010
RSD	2.39	0.236	RSD	0.57	0.162	RSD	0.55	0.161
95% CI	0.14	0.01	95% CI	0.09	0.01	95% CI	0.13	0.01

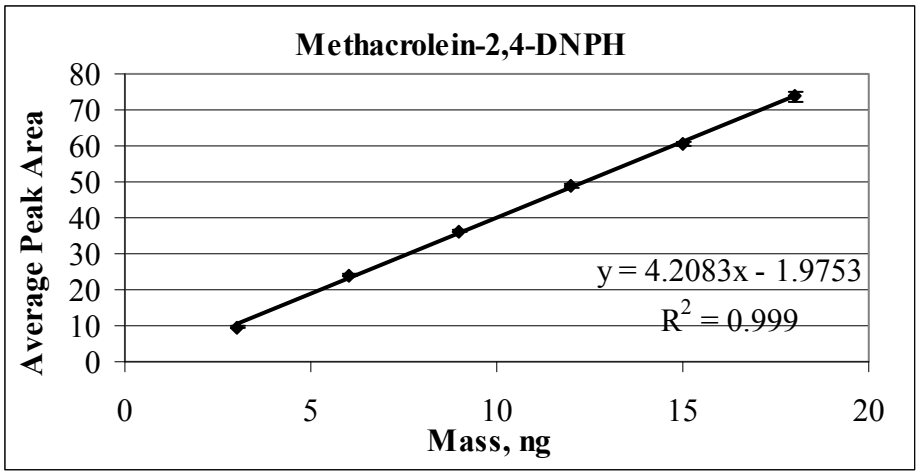
Mass 12 ng			Mass 15ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	53.1	6.265	1	65	6.247	1	79.3	6.243
2	52.6	6.248	2	65.5	6.243	2	79.4	6.252
3	52.7	6.246	3	65.7	6.247	3	79.5	6.257
4	53.4	6.260	4	65.6	6.240	4	79.7	6.249
5	53.3	6.260	5	65.4	6.239	5	79.7	6.256
6	53.7	6.280	6	65.5	6.219	6	80.4	6.268
7	53.1	6.261	7	65.6	6.224	7	80.3	6.263
8	53.5	6.264	8	65.5	6.219	8	81	6.267
9	53.3	6.273	9	65.9	6.213	9	80.3	6.267
10	53.8	6.278	10	66	6.228	10	80.4	6.264
Average	53.25	6.264	Average	65.57	6.232	Average	80.00	6.259
StdDev	0.39	0.011	StdDev	0.28	0.013	StdDev	0.56	0.009
RSD	0.73	0.181	RSD	0.42	0.205	RSD	0.69	0.137
95% CI	0.24	0.01	95% CI	0.17	0.01	95% CI	0.34	0.01



Peak 7 (Methacrolein-2,4-DNPH)

Mass 3 ng			Mass 6 ng			Mass 9 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	9.3	6.536	1	24.2	6.524	1	36.2	6.521
2	10	6.523	2	24	6.514	2	36.3	6.519
3	9.2	6.518	3	23.9	6.512	3	36.4	6.520
4	9.8	6.520	4	23.9	6.518	4	36.1	6.518
5	9.7	6.511	5	24.1	6.511	5	36.4	6.513
6	9.8	6.496	6	24	6.498	6	36.2	6.491
7	9.7	6.493	7	24.3	6.497	7	36.8	6.506
8	9.7	6.496	8	24	6.503	8	36.3	6.506
9	9.6	6.502	9	24.1	6.503	9	36.1	6.512
10	9.6	6.498	10	24.2	6.500	10	37	6.497
Average	9.64	6.509	Average	24.07	6.508	Average	36.38	6.510
StdDev	0.24	0.015	StdDev	0.13	0.009	StdDev	0.30	0.010
RSD	2.45	0.223	RSD	0.56	0.140	RSD	0.82	0.157
95% CI	0.15	0.01	95% CI	0.08	0.01	95% CI	0.18	0.01

Mass 12 ng			Mass 15ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	48.5	6.537	1	59.8	6.521	1	73.3	6.516
2	48.5	6.521	2	60.2	6.515	2	70.6	6.527
3	48.3	6.521	3	60.7	6.519	3	72.9	6.531
4	49	6.532	4	59.7	6.512	4	73.5	6.524
5	49	6.533	5	59.5	6.512	5	74.5	6.531
6	49.2	6.553	6	60.5	6.493	6	74.8	6.540
7	49.4	6.536	7	60.4	6.497	7	73.7	6.539
8	49.8	6.539	8	61.3	6.493	8	74.7	6.543
9	49.8	6.548	9	60.8	6.487	9	74.1	6.541
10	49.8	6.551	10	60.7	6.501	10	74.8	6.538
Average	49.13	6.537	Average	60.36	6.505	Average	73.69	6.533
StdDev	0.57	0.011	StdDev	0.56	0.012	StdDev	1.28	0.009
RSD	1.16	0.171	RSD	0.93	0.188	RSD	1.73	0.134
95% CI	0.35	0.01	95% CI	0.35	0.01	95% CI	0.79	0.01

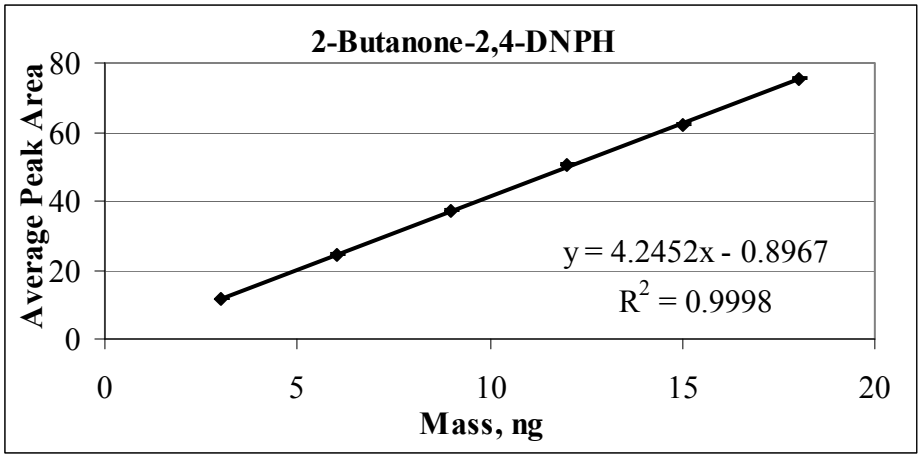


Peak 8 (2-Butanone-2,4-DNPH)

Mass 3 ng			Mass 6 ng			Mass 9 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	11.6	6.656	1	24.4	6.644	1	37.4	6.642
2	11.8	6.643	2	24.8	6.635	2	37.4	6.639
3	11.5	6.638	3	24.5	6.632	3	36.9	6.639
4	11.7	6.641	4	24.6	6.637	4	37.6	6.636
5	11.9	6.630	5	24.6	6.630	5	37.3	6.633
6	11.8	6.619	6	24.8	6.621	6	37.5	6.613
7	11.7	6.616	7	24.6	6.619	7	37.6	6.629
8	11.8	6.617	8	24.6	6.623	8	37.2	6.627
9	11.8	6.625	9	24.5	6.625	9	37.1	6.635
10	11.7	6.619	10	24.7	6.622	10	37.1	6.618
Average	11.73	6.630	Average	24.61	6.629	Average	37.31	6.631
StdDev	0.12	0.014	StdDev	0.13	0.008	StdDev	0.23	0.009
RSD	0.99	0.205	RSD	0.52	0.123	RSD	0.62	0.143
95% CI	0.07	0.01	95% CI	0.08	0.01	95% CI	0.14	0.01

Mass 12 ng			Mass 15ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	50.8	6.660	1	62.4	6.641	1	75.2	6.637
2	50.2	6.642	2	62.3	6.635	2	76.4	6.648
3	50.2	6.643	3	62	6.640	3	75.8	6.651
4	50.4	6.653	4	62.4	6.632	4	75.4	6.645
5	50.4	6.655	5	62.5	6.632	5	75.1	6.651

6	51.2	6.675	6	62.5	6.615	6	75.6	6.659
7	50.4	6.657	7	62.7	6.619	7	75.9	6.659
8	50.5	6.659	8	62.4	6.614	8	76	6.663
9	50.2	6.668	9	61.8	6.609	9	75.3	6.659
10	50.6	6.671	10	62	6.622	10	75.6	6.657
Average	50.49	6.658	Average	62.30	6.626	Average	75.63	6.653
StdDev	0.31	0.011	StdDev	0.28	0.012	StdDev	0.40	0.008
RSD	0.62	0.164	RSD	0.45	0.174	RSD	0.53	0.120
95% CI	0.19	0.01	95% CI	0.17	0.01	95% CI	0.25	0.00

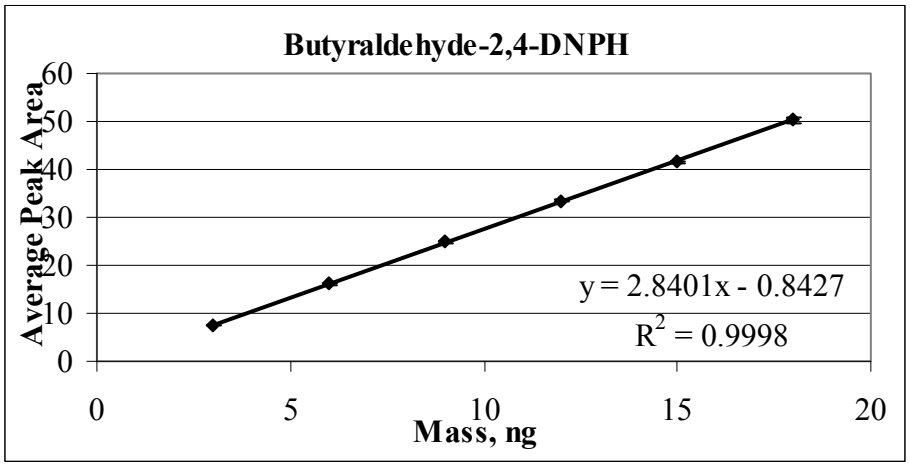


Peak 9 (Butyraldehyde-2,4-DNPH)

Mass 3 ng			Mass 6 ng			Mass 9 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	7.4	6.833	1	16	6.820	1	24.9	6.820
2	7.6	6.819	2	16.3	6.811	2	24.7	6.815
3	7.4	6.813	3	16.2	6.810	3	24.6	6.814
4	7.6	6.817	4	16.3	6.813	4	25.2	6.810
5	7.6	6.807	5	16.1	6.805	5	24.7	6.808
6	7.6	6.794	6	16.4	6.798	6	24.9	6.790
7	7.5	6.793	7	16.1	6.795	7	25.1	6.806
8	7.6	6.794	8	16.4	6.798	8	25	6.803
9	7.6	6.802	9	16	6.802	9	24.7	6.811
10	7.5	6.794	10	16.1	6.797	10	24.7	6.794
Average	7.54	6.807	Average	16.19	6.805	Average	24.85	6.807
StdDev	0.08	0.014	StdDev	0.15	0.008	StdDev	0.20	0.009
RSD	1.12	0.201	RSD	0.94	0.122	RSD	0.81	0.137

95% CI	0.05	0.01	95% CI	0.09	0.01	95% CI	0.12	0.01

Mass 12 ng			Mass 15ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	33.7	6.839	1	41.5	6.817	1	49.9	6.814
2	33.2	6.820	2	41.5	6.811	2	51.8	6.825
3	33.5	6.820	3	41.1	6.816	3	50.4	6.828
4	33.5	6.831	4	41.8	6.809	4	50.2	6.822
5	33.6	6.833	5	41.8	6.810	5	49.7	6.829
6	34	6.853	6	41.8	6.791	6	50.1	6.836
7	33.3	6.836	7	41.7	6.796	7	50.5	6.837
8	33.7	6.837	8	41.3	6.789	8	50.2	6.841
9	33.5	6.846	9	41.2	6.788	9	50.1	6.838
10	33.4	6.848	10	41.1	6.799	10	49.8	6.835
Average	33.54	6.836	Average	41.48	6.803	Average	50.27	6.831
StdDev	0.23	0.011	StdDev	0.29	0.011	StdDev	0.59	0.008
RSD	0.68	0.161	RSD	0.70	0.166	RSD	1.18	0.124
95% CI	0.14	0.01	95% CI	0.18	0.01	95% CI	0.37	0.01

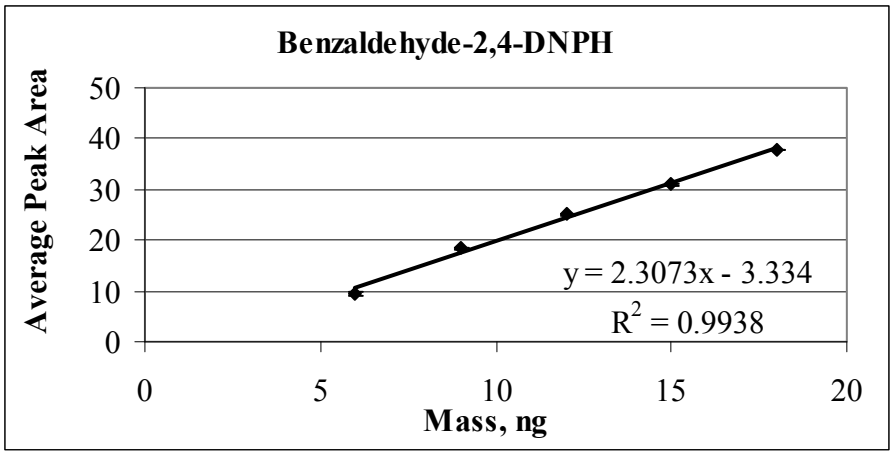


Peak 10 (Benzaldehyde-2,4-DNPH)

Mass 6 ng			Mass 9 ng			Mass 12 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	10.7	7.425	1	18.3	7.423	1	24.9	7.444
2	9.2	7.413	2	18.5	7.415	2	24.8	7.428
3	9.6	7.414	3	18.3	7.414	3	24.8	7.422

4	9.8	7.414	4	18.4	7.414	4	25	7.438
5	9.5	7.411	5	18.4	7.411	5	25	7.434
6	9.6	7.401	6	18.3	7.396	6	25.2	7.456
7	9	7.403	7	18.6	7.409	7	25	7.439
8	9	7.400	8	18.9	7.410	8	25.8	7.438
9	9	7.409	9	18.3	7.415	9	25.1	7.449
10	9.1	7.404	10	18.6	7.397	10	25.3	7.448
Average	9.45	7.409	Average	18.46	7.410	Average	25.09	7.440
StdDev	0.53	0.008	StdDev	0.20	0.008	StdDev	0.30	0.010
RSD	5.61	0.104	RSD	1.06	0.112	RSD	1.18	0.137
95% CI	0.33	0.00	95% CI	0.12	0.01	95% CI	0.18	0.01

Mass 15ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	30.6	7.419	1	37.5	7.421
2	30.9	7.416	2	37.7	7.432
3	30.9	7.415	3	37.8	7.436
4	31	7.414	4	37.8	7.429
5	30.9	7.409	5	37.7	7.438
6	31.1	7.395	6	38	7.443
7	31.2	7.396	7	37.9	7.442
8	31	7.390	8	38.1	7.443
9	30.9	7.390	9	37.8	7.441
10	31.1	7.406	10	37.8	7.442
Average	30.96	7.405	Average	37.81	7.437
StdDev	0.16	0.011	StdDev	0.17	0.007
RSD	0.53	0.152	RSD	0.44	0.099
95% CI	0.10	0.01	95% CI	0.10	0.00

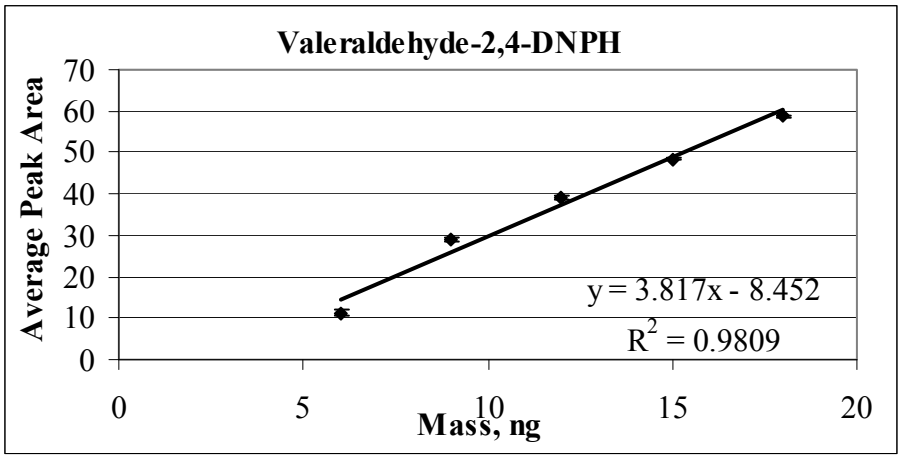


Peak 11 (Valeraldehyde-2,4-DNPH)

Mass 6 ng			Mass 9 ng			Mass 12 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	10.7	8.125	1	29.1	8.120	1	39.1	8.142
2	11.2	8.111	2	28.9	8.107	2	38.6	8.128
3	10.7	8.109	3	28.8	8.109	3	38.7	8.118
4	11	8.110	4	28.9	8.108	4	39.2	8.138
5	11.2	8.107	5	28.9	8.108	5	39	8.133
6	11.5	8.095	6	28.9	8.093	6	39.6	8.151
7	10.8	8.100	7	29.1	8.105	7	39.3	8.132
8	11.6	8.097	8	29.8	8.105	8	40.5	8.134
9	11.3	8.109	9	28.6	8.113	9	39.3	8.141
10	12.7	8.100	10	28.9	8.101	10	39.4	8.146
Average	11.27	8.106	Average	28.99	8.107	Average	39.27	8.136
StdDev	0.59	0.009	StdDev	0.32	0.007	StdDev	0.53	0.009
RSD	5.26	0.108	RSD	1.10	0.087	RSD	1.35	0.116
95% CI	0.37	0.01	95% CI	0.20	0.00	95% CI	0.33	0.01

Mass 15ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	48	8.119	1	58.6	8.119
2	48	8.114	2	58.5	8.129
3	48.6	8.110	3	58.6	8.136
4	48.3	8.110	4	58.4	8.125
5	48.2	8.102	5	58.7	8.133
6	48.5	8.091	6	59.1	8.143

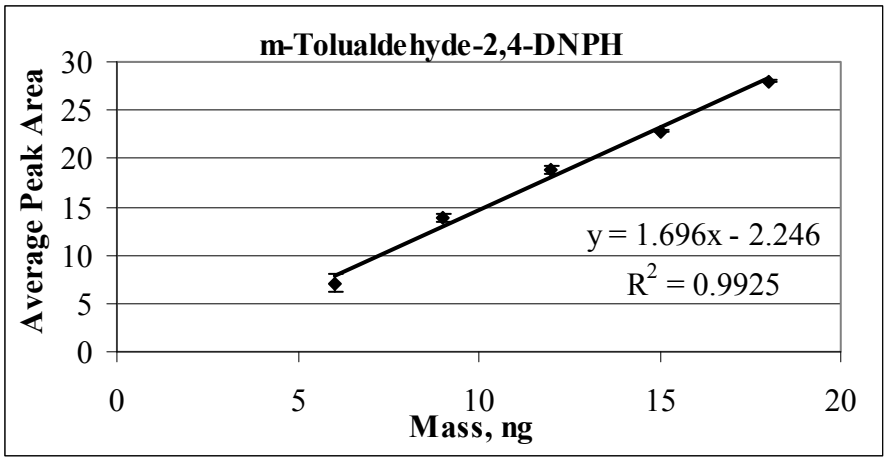
7	48.5	8.093	7	58.8	8.138
8	48.6	8.090	8	59.3	8.136
9	48.7	8.095	9	59.1	8.136
10	48.8	8.108	10	59	8.141
Average	48.42	8.103	Average	58.81	8.134
StdDev	0.28	0.010	StdDev	0.30	0.007
RSD	0.58	0.129	RSD	0.51	0.091
95% CI	0.17	0.01	95% CI	0.19	0.00



Peak 12 (m-Tolualdehyde-2,4-DNPH)

Mass 6 ng			Mass 9 ng			Mass 12 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	5.1	8.487	1	13.7	8.483	1	18.7	8.506
2	7.3	8.472	2	13.8	8.468	2	18.6	8.489
3	6.1	8.470	3	13.6	8.469	3	18.4	8.481
4	8	8.469	4	13.7	8.471	4	18.4	8.498
5	8.2	8.466	5	13.6	8.468	5	18.7	8.495
6	7.9	8.456	6	13.9	8.454	6	18.8	8.513
7	7.6	8.462	7	13.8	8.467	7	18.4	8.491
8	7.2	8.458	8	14.8	8.464	8	19.8	8.492
9	6.6	8.472	9	13.6	8.473	9	18.9	8.503
10	6.9	8.462	10	13.8	8.465	10	18.7	8.509
Average	7.4625	8.467	Average	13.83	8.468	Average	18.74	8.498
StdDev	0.69	0.009	StdDev	0.36	0.007	StdDev	0.41	0.010
RSD	9.29	0.105	RSD	2.57	0.086	RSD	2.20	0.118
95% CI	0.43	0.01	95% CI	0.22	0.00	95% CI	0.26	0.01

Mass 15ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	23	8.480	1	27.8	8.480
2	23	8.475	2	27.9	8.491
3	22.5	8.471	3	28.1	8.500
4	22.9	8.469	4	28.1	8.486
5	22.8	8.460	5	28.1	8.494
6	23	8.452	6	28	8.505
7	23.1	8.456	7	28.2	8.497
8	22.8	8.454	8	28.2	8.497
9	22.7	8.459	9	27.9	8.496
10	22.7	8.470	10	27.9	8.504
Average	22.85	8.465	Average	28.02	8.495
StdDev	0.18	0.010	StdDev	0.14	0.008
RSD	0.81	0.114	RSD	0.50	0.091
95% CI	0.11	0.01	95% CI	0.09	0.00

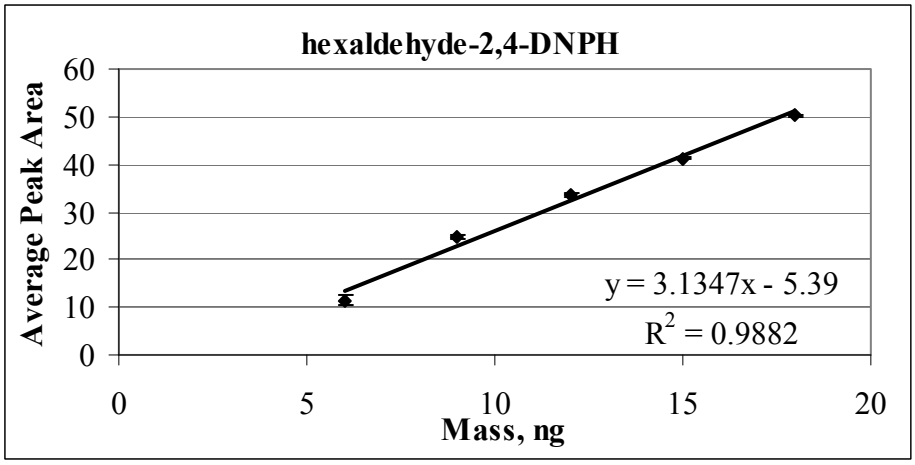


Peak 13 (Hexaldehyde-2,4-DNPH)

Mass 6 ng			Mass 9 ng			Mass 12 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	9.7	9.292	1	24.7	9.290	1	33.5	9.312
2	12.4	9.274	2	24.5	9.274	2	33	9.299
3	12.5	9.279	3	24.5	9.273	3	33.3	9.289
4	10.5	9.274	4	24.6	9.281	4	33.3	9.307
5	9.7	9.280	5	24.8	9.281	5	33.2	9.304

6	12	9.263	6	24.8	9.262	6	33.8	9.314
7	12.3	9.273	7	25	9.277	7	33.2	9.299
8	11.8	9.269	8	25.9	9.273	8	34.8	9.297
9	11.2	9.281	9	24.4	9.278	9	33.7	9.308
10	11.8	9.281	10	24.6	9.273	10	33.7	9.311
Average	11.39	9.277	Average	24.78	9.276	Average	33.55	9.304
StdDev	1.07	0.008	StdDev	0.43	0.007	StdDev	0.51	0.008
RSD	9.41	0.085	RSD	1.74	0.079	RSD	1.52	0.085
95% CI	0.66	0.00	95% CI	0.27	0.00	95% CI	0.32	0.00

Mass 15 ng			Mass 18 ng		
Replicate	Peak Area	RT	Replicate	Peak Area	RT
1	40.9	9.287	1	49.8	9.299
2	41	9.282	2	50	9.303
3	41	9.274	3	50.1	9.310
4	41.2	9.281	4	50.1	9.299
5	41.2	9.269	5	50.2	9.298
6	41.4	9.263	6	50.3	9.310
7	41.5	9.264	7	50.4	9.300
8	41.3	9.267	8	50.6	9.301
9	41.3	9.273	9	50.2	9.308
10	41.4	9.285	10	50.2	9.312
Average	41.22	9.275	Average	50.19	9.304
StdDev	0.20	0.009	StdDev	0.22	0.005
RSD	0.48	0.095	RSD	0.44	0.058
95% CI	0.12	0.01	95% CI	0.14	0.00



Appendix B: GCMS quantification ions

Compound	Molecular Weight g/mol	Quantification ion	Reference ion #1	Reference ion #2	Reference ion #3
levoglucosan	162.14	217	73	204	147
galactopyranose	162.14	217	73	204	147
mannopyranose	162.14	217	73	204	147
a-xylose	150.13	204	73	217	147
b-xylose	150.13	204	73	217	147
a-mannose	180.16	204	73	191	147
a-glucose	180.16	204	73	191	147
b-mannose	180.16	204	73	191	147
b-glucose	180.16	204	73	191	147
sucrose	342.30	361	73	362	217
trehalose	342.30	361	73	362	191
maltose	342.30	361	204	73	191
cis-Pinonic Acid	184.23	171	73	75	83
Dehydroabietic Acid	302.45	239	73	240	173
Tetracosanol	354.65	411	75	412	57
Hexacosanol	382.71	439	75	440	57
Octacosanol	410.76	467	75	468	57
Cholesterol	386.65	368	129	329	73
B-sitosterol	414.7	396	129	43	73
Campesterol	400.69	382	129	73	43
Stigmasterol	412.7	394	83	55	129
Triacosanol	438.81	495	75	57	43
Vanillic Acid	168.15	297	266	73	312
Anisic Acid	152.15				
Syringic Acid	198.17	327	73	312	342
Catechol	110.11	73	254	45	74
Pyruvic Acid	88.06	73	147	215	45
Glyoxalic Acid	74				
Levulinic Acid	116	75	73	145	173
4-Acetylbutyric Acid	130.14	145	75	73	43
Oxalacetic Acid	132.07	147	73	333	170

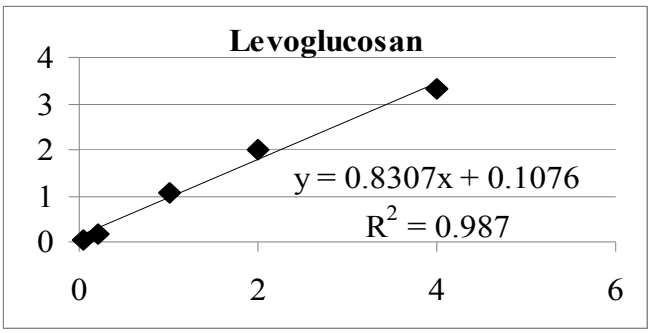
Appendix C: GCMS Calibration Curves

Conc = Concentration

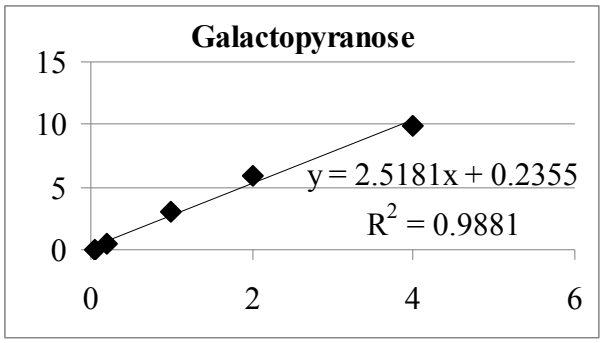
SOAP 2002-2003 calibration curves

$C_{24}D_{50}$	Concentration ng/uL	Peak Area
Run Level 1	10	2956835
Run Level 2	10	3465360
Run Level 3	10	3308511
Run Level 4	10	2828750
Run Level 5	10	3543488

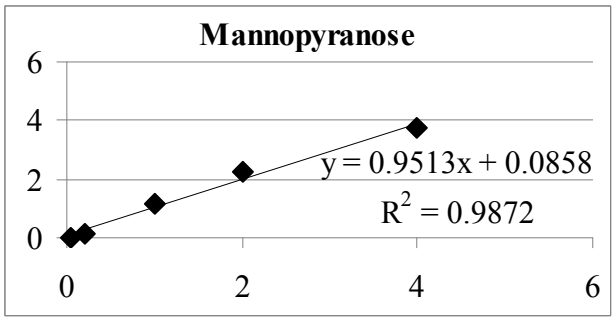
Levoglucosan	Conc, ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	121482	0.05	0.041085147
Run Level 2	2	637693	0.2	0.184019265
Run Level 3	10	3475166	1	1.050371602
Run Level 4	20	5614467	2	1.984787274
Run Level 5	40	11695386	4	3.300529309



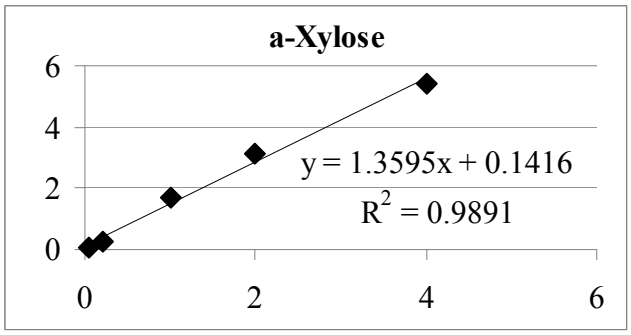
Galactopyranose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	215984	0.05	0.073045672
Run Level 2	2	1572828	0.2	0.453871459
Run Level 3	10	10171807	1	3.074436506
Run Level 4	20	16696040	2	5.902267786
Run Level 5	40	35188766	4	9.930544706



Mannopyranose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	91235	0.05	0.030855628
Run Level 2	2	588528	0.2	0.169831706
Run Level 3	10	3734361	1	1.128713491
Run Level 4	20	6380501	2	2.255590278
Run Level 5	40	13257251	4	3.741299815

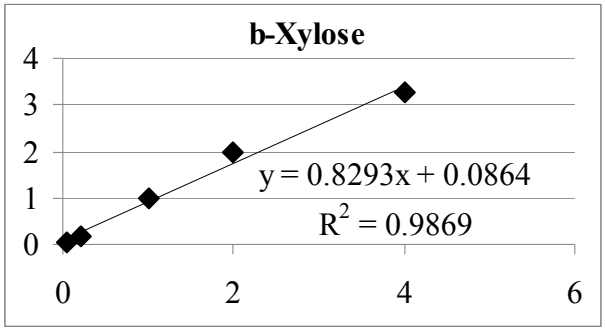


a-Xylose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	113804	0.05	0.038488451
Run Level 2	2	946735	0.2	0.27319961
Run Level 3	10	5650488	1	1.707864353
Run Level 4	20	8924697	2	3.15499673
Run Level 5	40	19099504	4	5.390029259

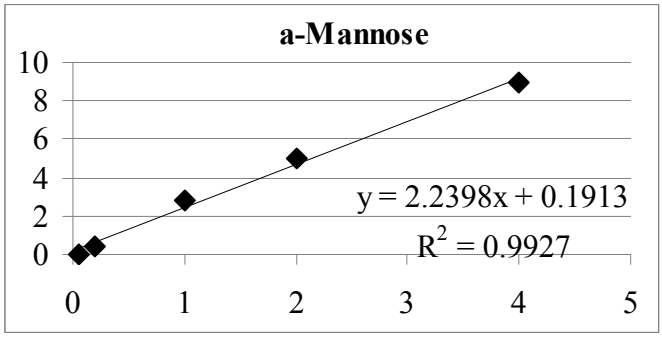


b-Xylose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	83599	0.05	0.028273137
Run Level 2	2	572622	0.2	0.165241706

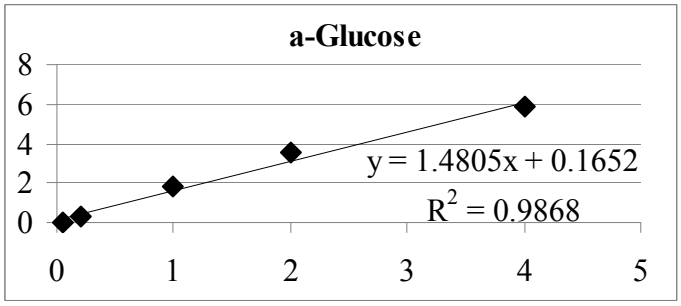
Run Level 3	10	3318378	1	1.002982308
Run Level 4	20	5589277	2	1.97588228
Run Level 5	40	11593539	4	3.27178729



a-Mannose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	144963	0.05	0.049026408
Run Level 2	2	1584246	0.2	0.457166355
Run Level 3	10	9167412	1	2.770857343
Run Level 4	20	14171491	2	5.009806805
Run Level 5	40	31567863	4	8.908697588

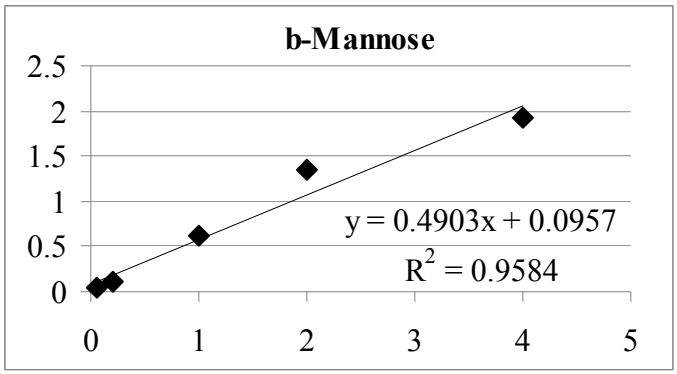


a-Glucose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	129153	0.05	0.043679475
Run Level 2	2	1073197	0.2	0.309692788
Run Level 3	10	6057118	1	1.830768584
Run Level 4	20	9966164	2	3.523168891
Run Level 5	40	20738785	4	5.852647166

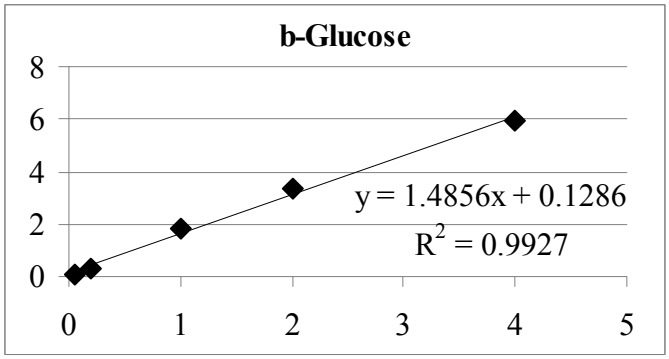


b-Mannose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	100593	0.05	0.034020498

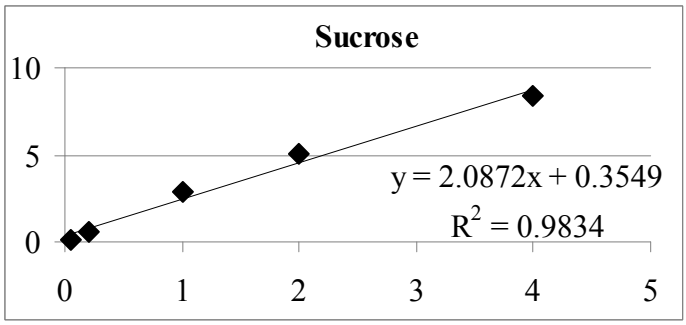
Run Level 2	2	373408	0.2	0.107754461
Run Level 3	10	2076922	1	0.627751275
Run Level 4	20	3811631	2	1.347461246
Run Level 5	40	6790728	4	1.9163965



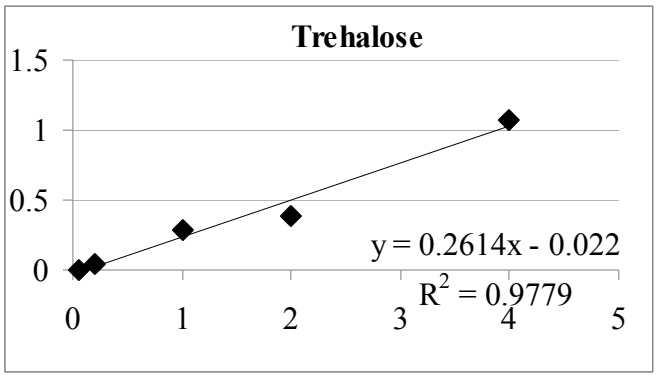
b-Glucose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	147369	0.05	0.049840116
Run Level 2	2	1001133	0.2	0.288897257
Run Level 3	10	6074443	1	1.836005079
Run Level 4	20	9416844	2	3.32897711
Run Level 5	40	20940405	4	5.909545905



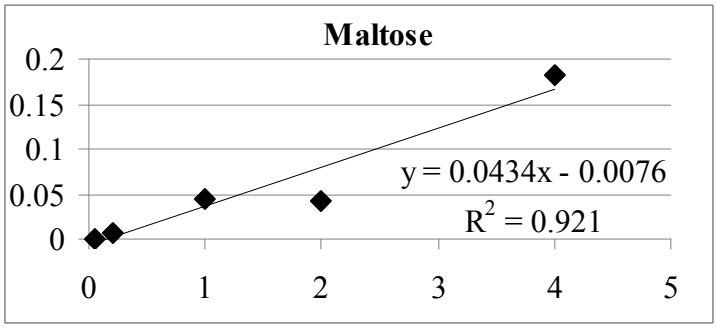
Sucrose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	273227	0.05	0.092405224
Run Level 2	2	1807257	0.2	0.521520708
Run Level 3	10	9687006	1	2.92790503
Run Level 4	20	14148009	2	5.001505612
Run Level 5	40	29635015	4	8.363232781



Trehalose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	14337	0.05	0.004848766
Run Level 2	2	138845	0.2	0.040066544
Run Level 3	10	934848	1	0.282558529
Run Level 4	20	1104197	2	0.390348034
Run Level 5	40	3783017	4	1.067596955



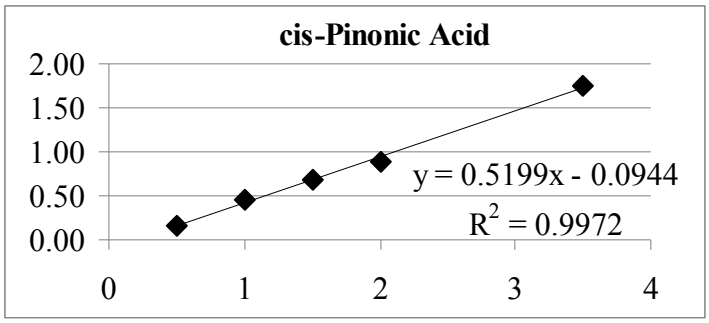
Maltose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	1715	0.05	0.000580012
Run Level 2	2	25813	0.2	0.007448865
Run Level 3	10	145127	1	0.043864748
Run Level 4	20	121576	2	0.042978701
Run Level 5	40	644107	4	0.181772028



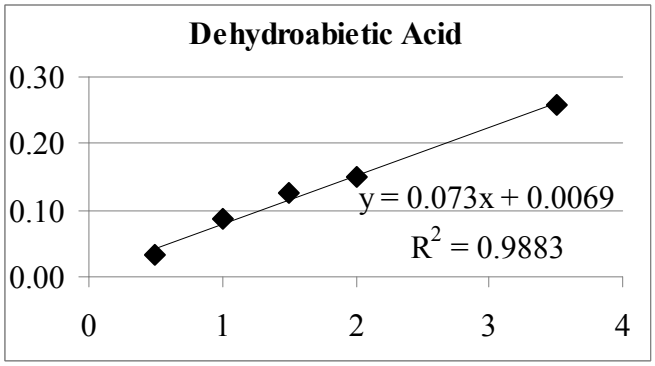
Second set of compounds

C24D50	Concentration ng/uL	Peak Area
Run Level 1	10	2418665
Run Level 2	10	2293039
Run Level 3	10	2098796
Run Level 4	10	2222977
Run Level 5	10	1583110

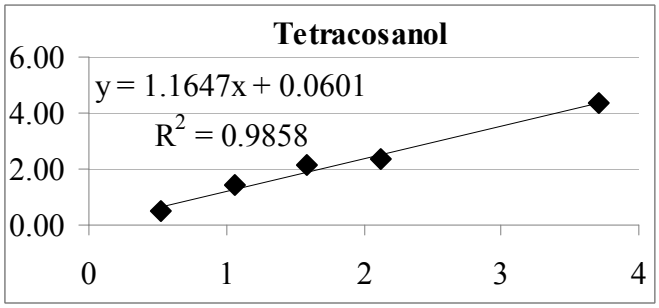
cis-pinonic acid	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	407852	0.5	0.17
Run Level 2	10	1050449	1	0.46
Run Level 3	15	1420626	1.5	0.68
Run Level 4	20	1992421	2	0.90
Run Level 5	35	2766127	3.5	1.75



Dehydroabietic acid	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	76789	0.5	0.03
Run Level 2	10	200340	1	0.09
Run Level 3	15	267302	1.5	0.13
Run Level 4	20	331584	2	0.15
Run Level 5	35	410690	3.5	0.26

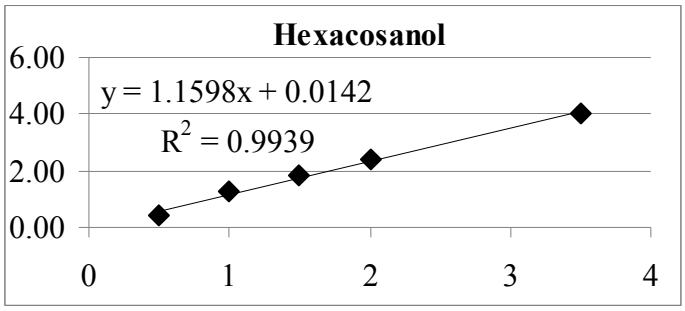


Tetracosanol	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5.3	1259917	0.53	0.52
Run Level 2	10.6	3221826	1.06	1.41
Run Level 3	15.9	4484137	1.59	2.14
Run Level 4	21.2	5243339	2.12	2.36
Run Level 5	37.1	6922911	3.71	4.37

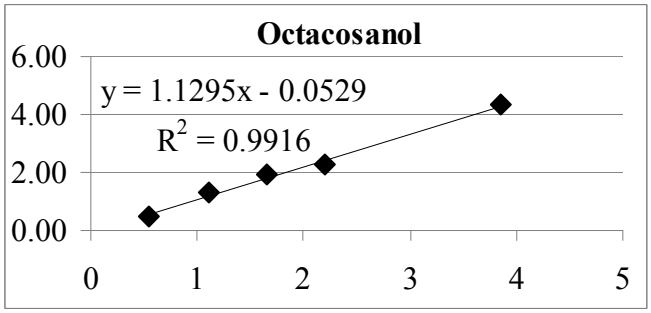


Hexacosanol	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	1069058	0.5	0.44
Run Level 2	10	2913093	1	1.27
Run Level 3	15	3857054	1.5	1.84

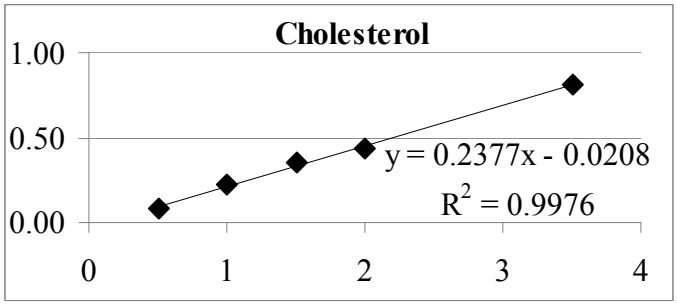
Run Level 4	20	5258060	2	2.37
Run Level 5	35	6353884	3.5	4.01



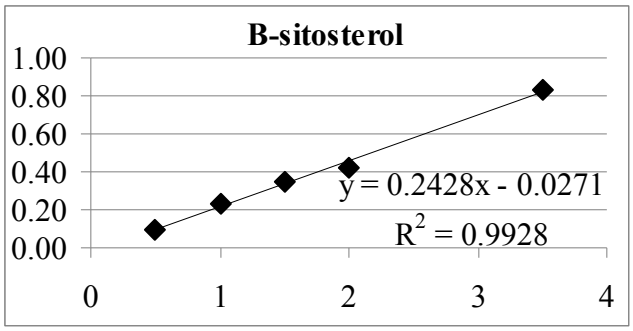
Octacosanol	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5.5	1152162	0.55	0.48
Run Level 2	11	3013192	1.1	1.31
Run Level 3	16.6	4068055	1.66	1.94
Run Level 4	22	5011124	2.2	2.25
Run Level 5	38.6	6864146	3.86	4.34



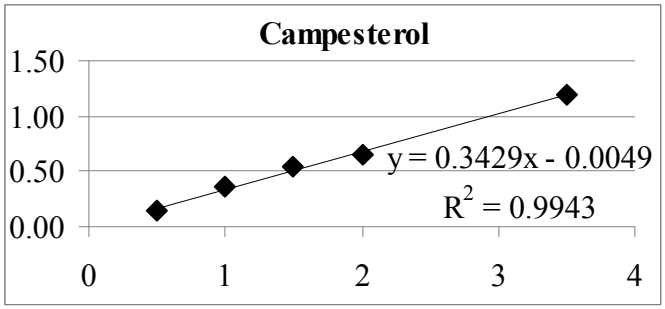
Cholesterol	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	212450	0.5	0.09
Run Level 2	10	522803	1	0.23
Run Level 3	15	734123	1.5	0.35
Run Level 4	20	973400	2	0.44
Run Level 5	35	1287172	3.5	0.81



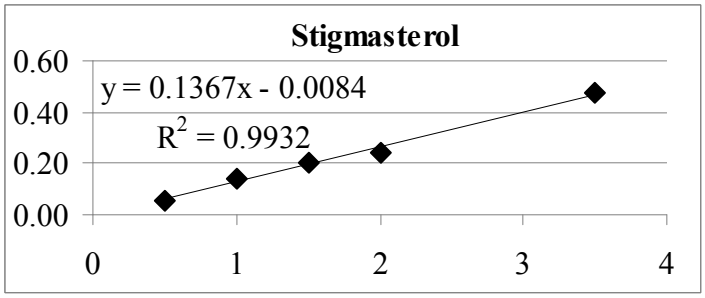
β-sitosterol	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	224114	0.5	0.09
Run Level 2	10	537206	1	0.23
Run Level 3	15	727199	1.5	0.35
Run Level 4	20	929578	2	0.42
Run Level 5	35	1324451	3.5	0.84



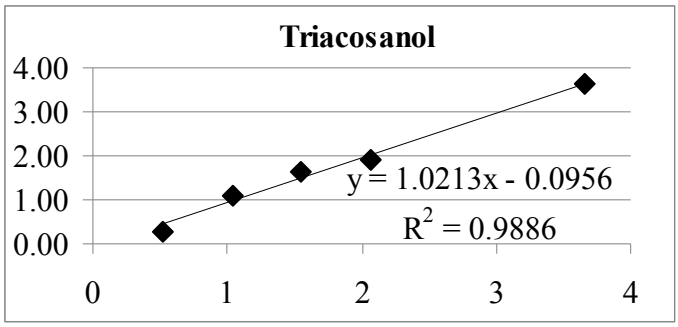
Campesterol	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	348956	0.5	0.14
Run Level 2	10	835080	1	0.36
Run Level 3	15	1131577	1.5	0.54
Run Level 4	20	1427311	2	0.64
Run Level 5	35	1900092	3.5	1.20



Stigmasterol	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	131789	0.5	0.05
Run Level 2	10	322460	1	0.14
Run Level 3	15	429377	1.5	0.20
Run Level 4	20	544149	2	0.24
Run Level 5	35	752588	3.5	0.48



Triacosanol	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5.2	681148	0.52	0.28
Run Level 2	10.4	2528601	1.04	1.10
Run Level 3	15.5	3401010	1.55	1.62
Run Level 4	20.7	4271295	2.07	1.92
Run Level 5	36.6	5737509	3.66	3.62

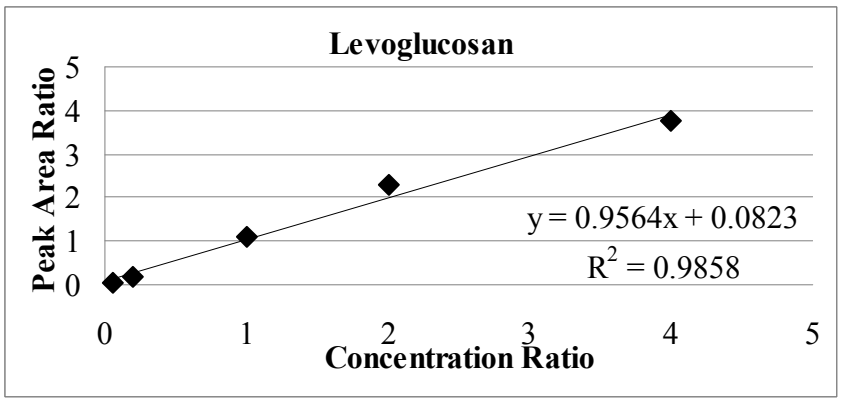


SOAP NY 2005-2007 Calibration Curves
(NOTE: the curves for the five oxoacids and the 4 aromatics are shown here but used for both sampling campaigns)

Aliquot one

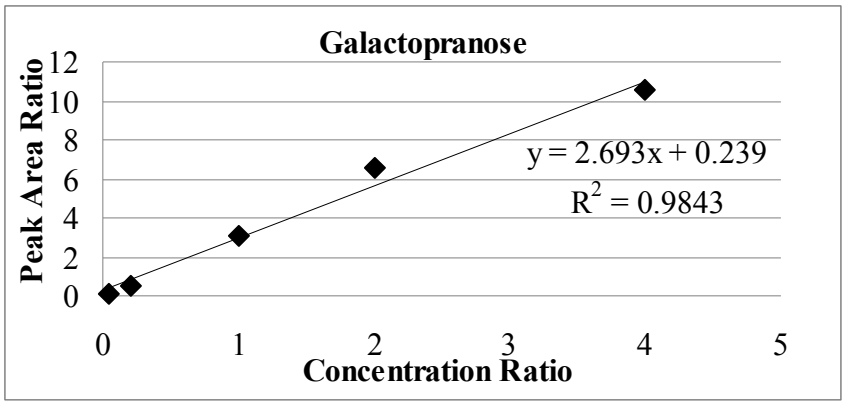
C24D50	Concentration ng/uL	Peak Area
Run Level 1	10	2393798
Run Level 2	10	2595528
Run Level 3	10	2495997
Run Level 4	10	1345879
Run Level 5	10	2080798

Levoglucosan	Conc, ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	78592	0.05	0.032831509
Run Level 2	2	449517	0.2	0.173189039
Run Level 3	10	2726262	1	1.092253717
Run Level 4	20	3092015	2	2.297394491
Run Level 5	40	7801992	4	3.749519175

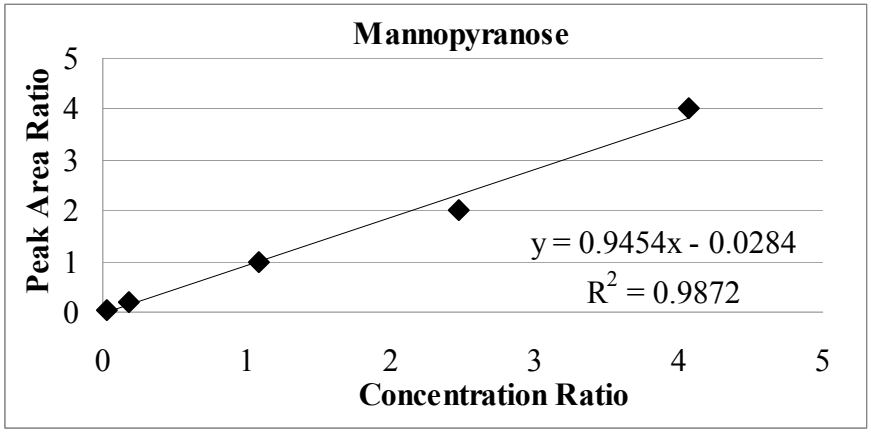


Galactopyranose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	159957	0.05	0.066821428
Run Level 2	2	1293832	0.2	0.498485087
Run Level 3	10	7718725	1	3.092441618

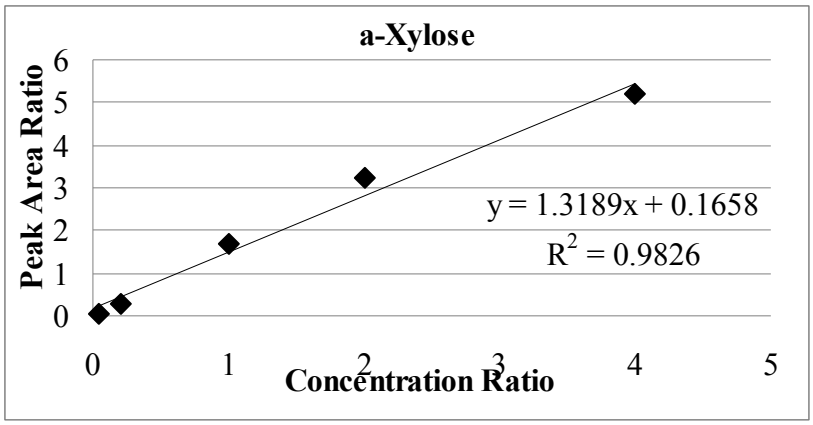
Run Level 4	20	8776023	2	6.520662704
Run Level 5	40	21933801	4	10.54105252



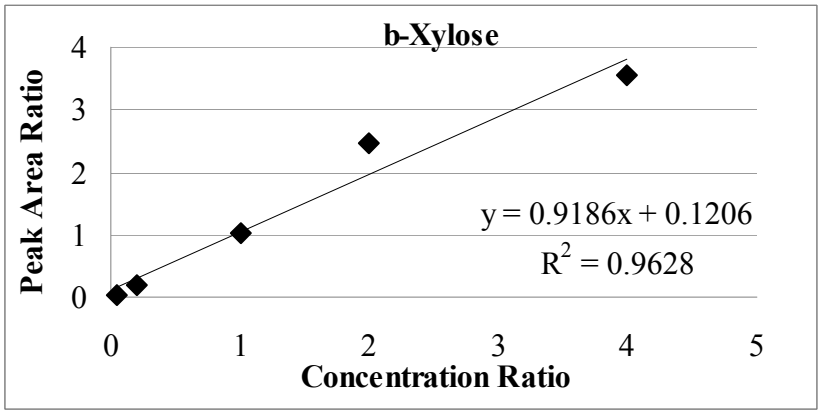
Mannopyranose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	53224	0.05	0.022234123
Run Level 2	2	456866	0.2	0.176020447
Run Level 3	10	2699373	1	1.081480867
Run Level 4	20	3325176	2	2.470635176
Run Level 5	40	8465871	4	4.068569366



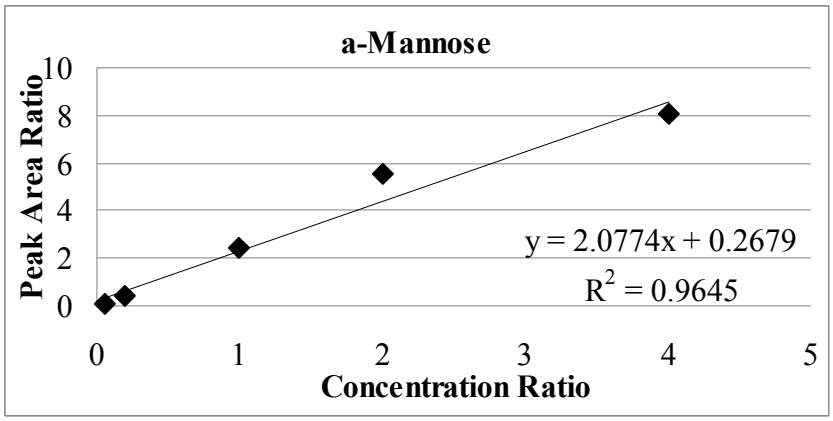
a-Xylose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	88979	0.05	0.037170638
Run Level 2	2	705607	0.2	0.271854898
Run Level 3	10	4154682	1	1.664538058
Run Level 4	20	4330901	2	3.217897746
Run Level 5	40	10819560	4	5.199716647



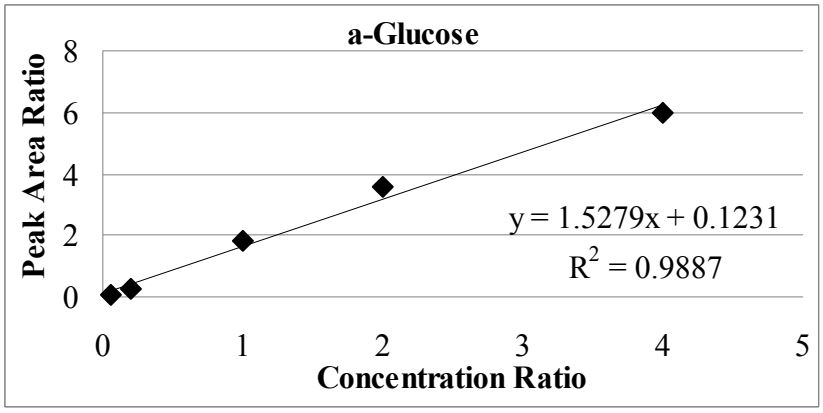
b-Xylose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	79566	0.05	0.033238394
Run Level 2	2	518483	0.2	0.199760126
Run Level 3	10	2518663	1	1.00908094
Run Level 4	20	3317054	2	2.464600458
Run Level 5	40	7398848	4	3.555774275



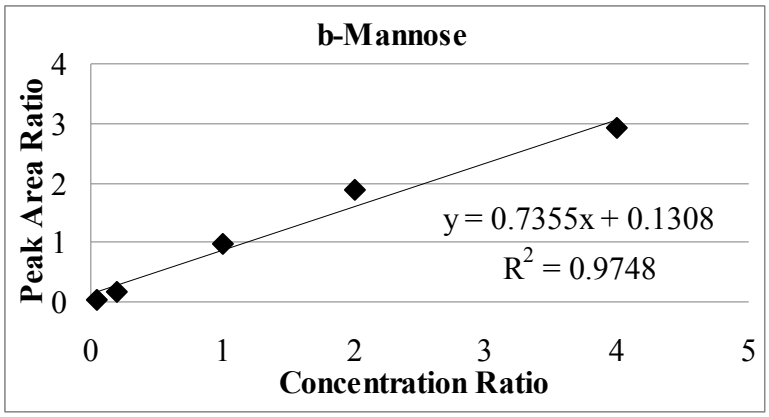
a-Mannose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	142888	0.05	0.059690918
Run Level 2	2	992203	0.2	0.38227405
Run Level 3	10	6019492	1	2.411658347
Run Level 4	20	7418151	2	5.511751799
Run Level 5	40	16719944	4	8.035351822



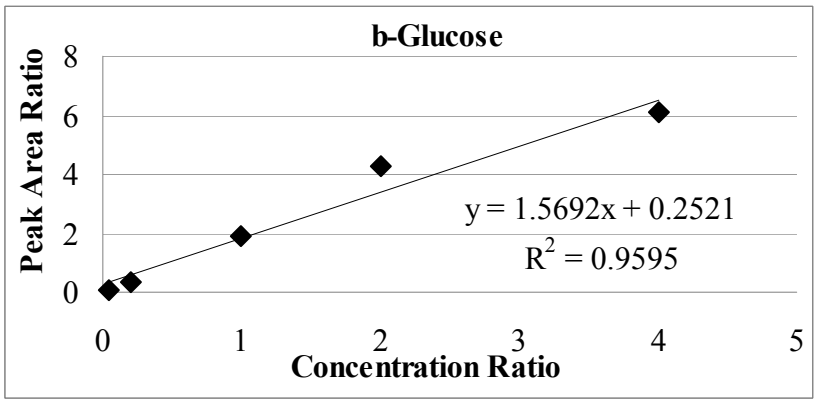
a-Glucose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	102746	0.05	0.04292175
Run Level 2	2	682635	0.2	0.26300429
Run Level 3	10	4504431	1	1.804662025
Run Level 4	20	4807955	2	3.572353087
Run Level 5	40	12505043	4	6.009734246



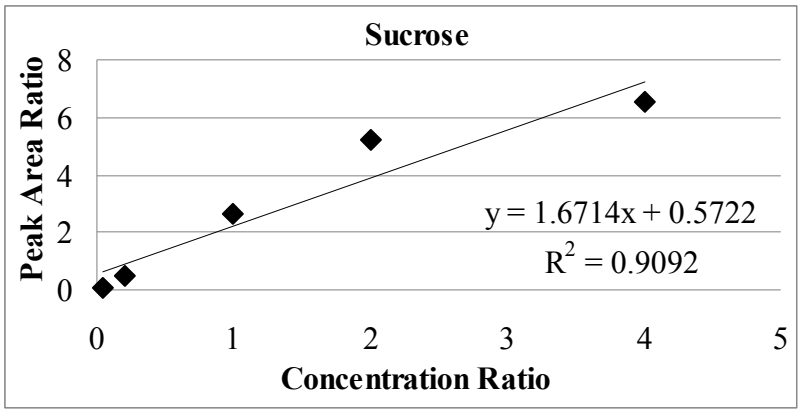
b-Mannose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	92815	0.05	0.038773113
Run Level 2	2	446559	0.2	0.172049386
Run Level 3	10	2451466	1	0.982159033
Run Level 4	20	2535415	2	1.883835768
Run Level 5	40	6055098	4	2.909988379



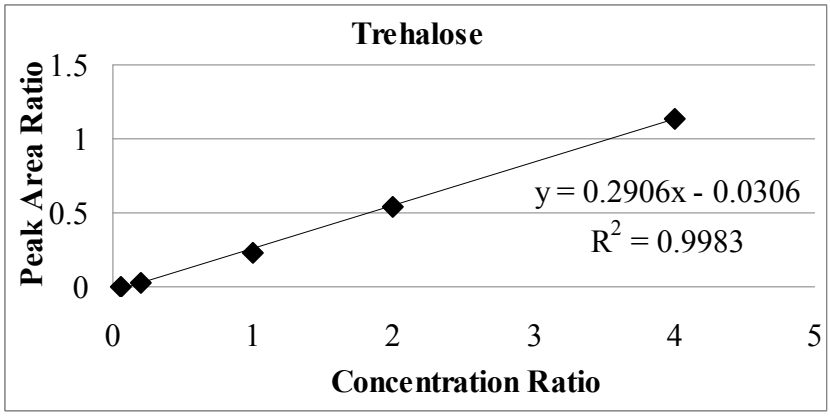
b-Glucose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	145368	0.05	0.060726929
Run Level 2	2	846401	0.2	0.326099738
Run Level 3	10	4736446	1	1.897616864
Run Level 4	20	5740077	2	4.264927976
Run Level 5	40	12668186	4	6.088138301



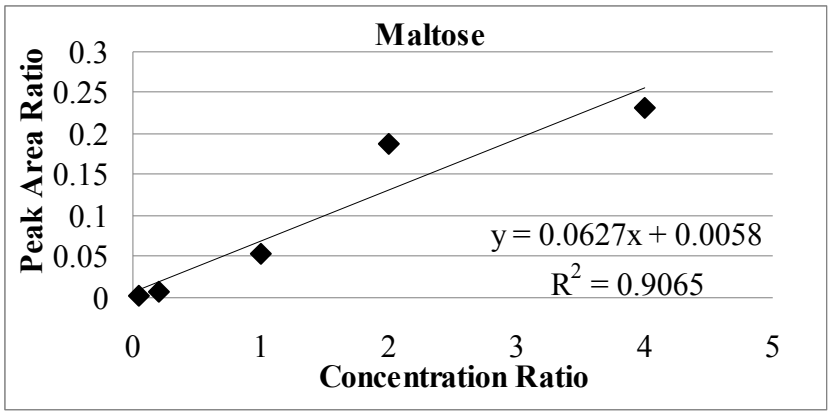
Sucrose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	202961	0.05	0.084786185
Run Level 2	2	1294031	0.2	0.498561757
Run Level 3	10	6557620	1	2.62725476
Run Level 4	20	7055869	2	5.242573069
Run Level 5	40	13578882	4	6.525805004



Trehalose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	15303	0.05	0.00639277
Run Level 2	2	79960	0.2	0.030806834
Run Level 3	10	575614	1	0.230614861
Run Level 4	20	732293	2	0.544100175
Run Level 5	40	2375806	4	1.141776376



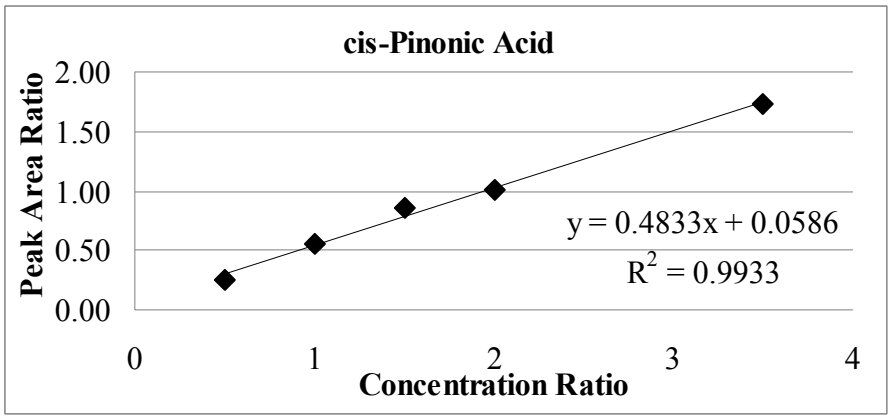
Maltose	Conc ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	3230	0.05	0.00134932
Run Level 2	2	20482	0.2	0.007891265
Run Level 3	10	133231	1	0.053377869
Run Level 4	20	253769	2	0.188552611
Run Level 5	40	483521	4	0.232372868



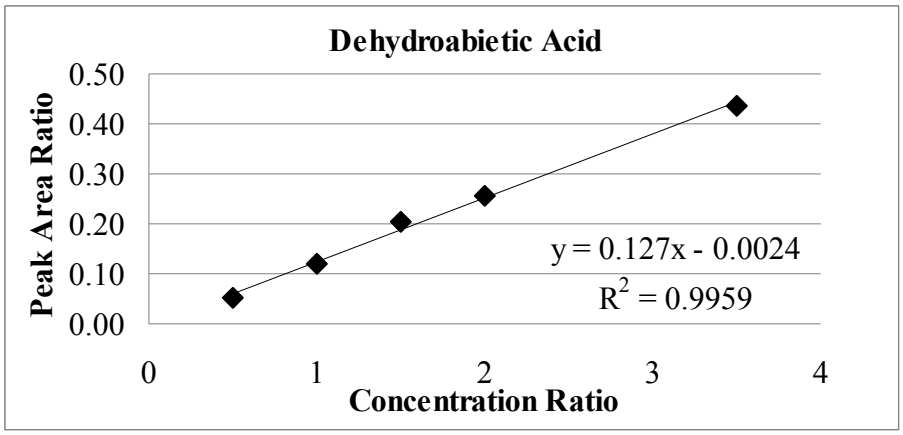
Aliquot 2

C24D50	Concentration ng/uL	Peak Area
Run Level 1	10	2821316
Run Level 2	10	1170607
Run Level 3	10	1762316
Run Level 4	10	4178049
Run Level 5	10	3181501

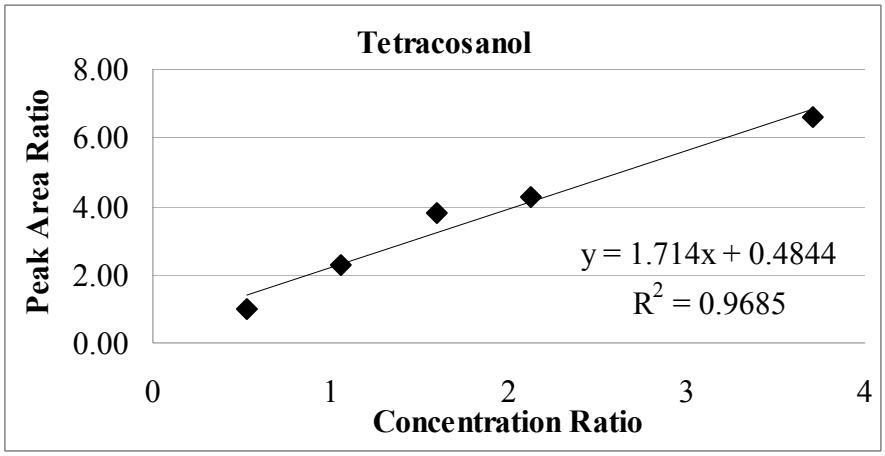
cis-pinonic acid	Concentration ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	699188	0.5	0.25
Run Level 2	10	653391	1	0.56
Run Level 3	15	1503208	1.5	0.85
Run Level 4	20	4220699	2	1.01
Run Level 5	35	5509400	3.5	1.73



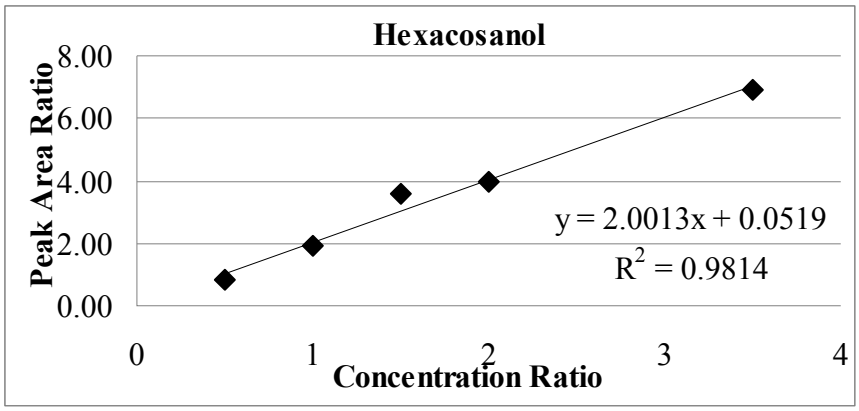
dehydroabietic acid	Concentration ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	151630	0.5	0.05
Run Level 2	10	139762	1	0.12
Run Level 3	15	357569	1.5	0.20
Run Level 4	20	1068119	2	0.26
Run Level 5	35	1387888	3.5	0.44



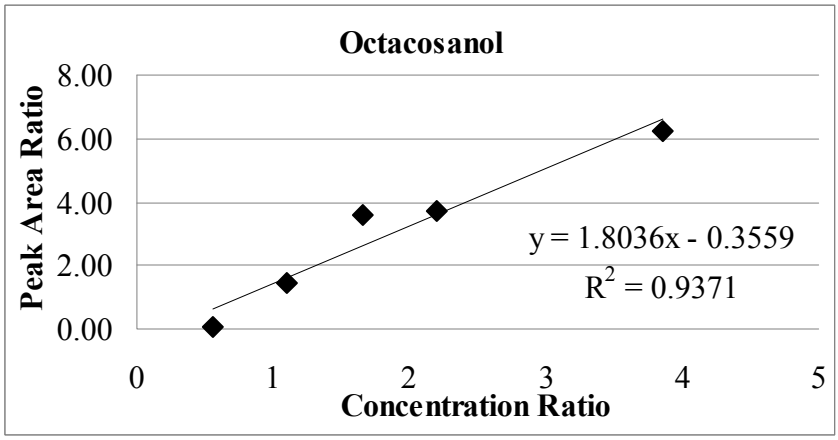
Tetracosanol	Concentration ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5.3	2776688	0.53	0.98
Run Level 2	10.6	2644598	1.06	2.26
Run Level 3	15.9	6654294	1.59	3.78
Run Level 4	21.2	17758601	2.12	4.25
Run Level 5	37.1	20982920	3.71	6.60



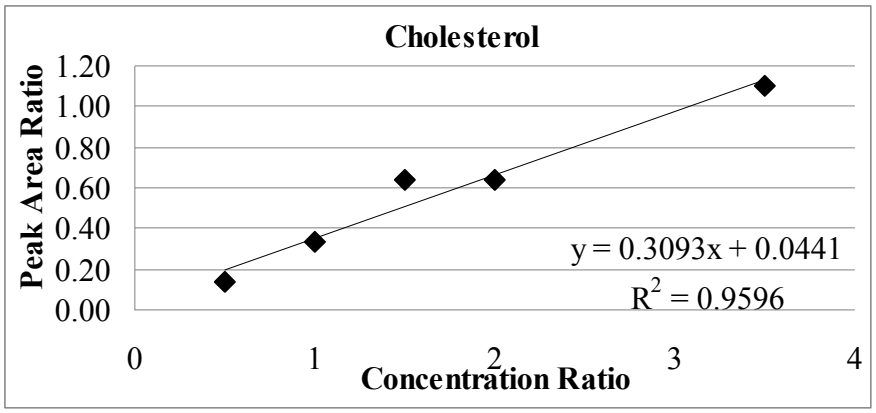
Hexacosanol	Concentration ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	2289209	0.5	0.81
Run Level 2	10	2275949	1	1.94
Run Level 3	15	6362664	1.5	3.61
Run Level 4	20	16614579	2	3.98
Run Level 5	35	22042187	3.5	6.93



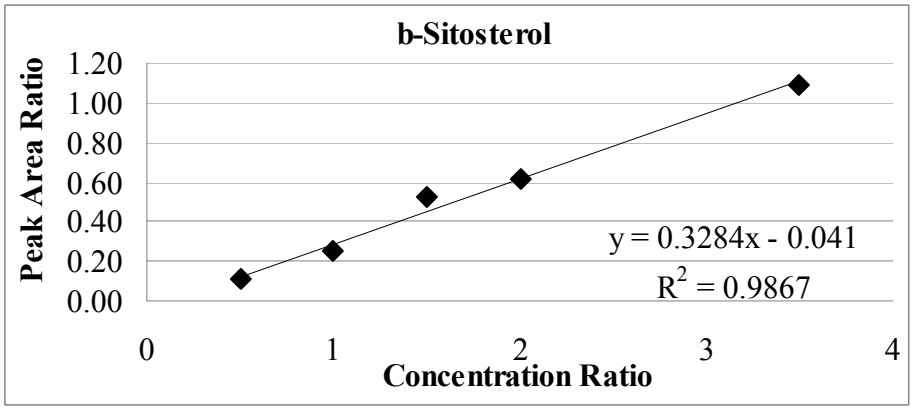
Octacosanol	Concentration ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5.5	227292	0.55	0.08
Run Level 2	11	1709592	1.1	1.46
Run Level 3	16.6	6356742	1.66	3.61
Run Level 4	22	15518460	2.2	3.71
Run Level 5	38.6	19909332	3.86	6.26



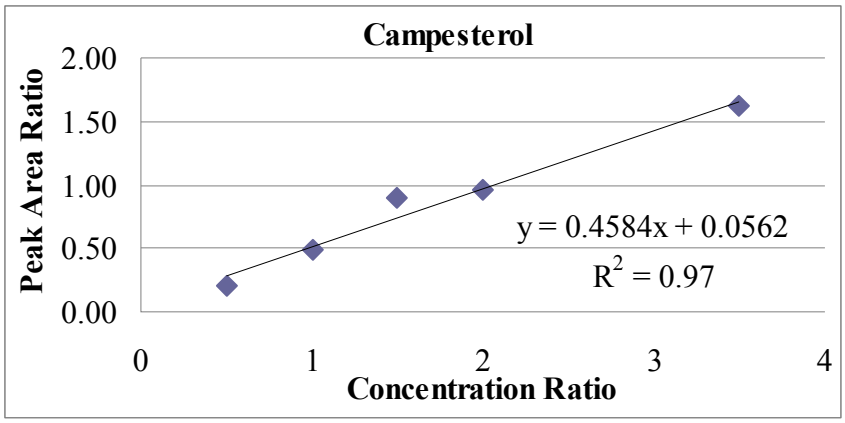
Cholesterol	Concentration ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	393303	0.5	0.14
Run Level 2	10	391320	1	0.33
Run Level 3	15	1119570	1.5	0.64
Run Level 4	20	2687986	2	0.64
Run Level 5	35	3490230	3.5	1.10



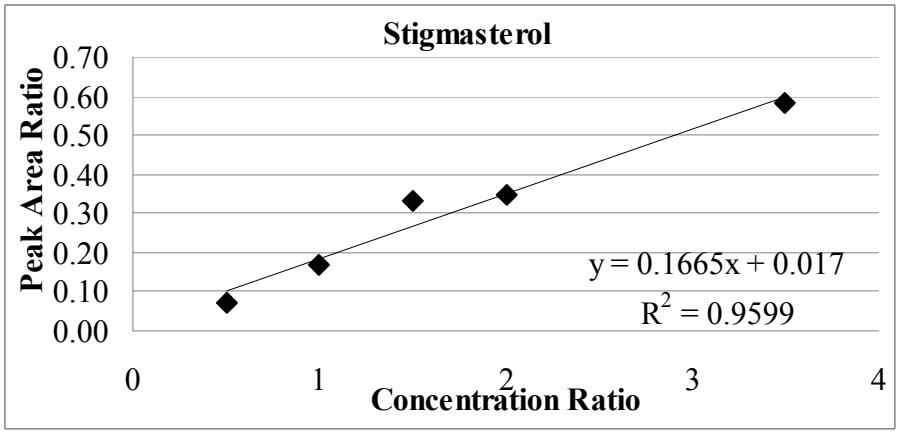
β-sitosterol	Concentration ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	299333	0.5	0.11
Run Level 2	10	291960	1	0.25
Run Level 3	15	928824	1.5	0.53
Run Level 4	20	2560146	2	0.61
Run Level 5	35	3471836	3.5	1.09



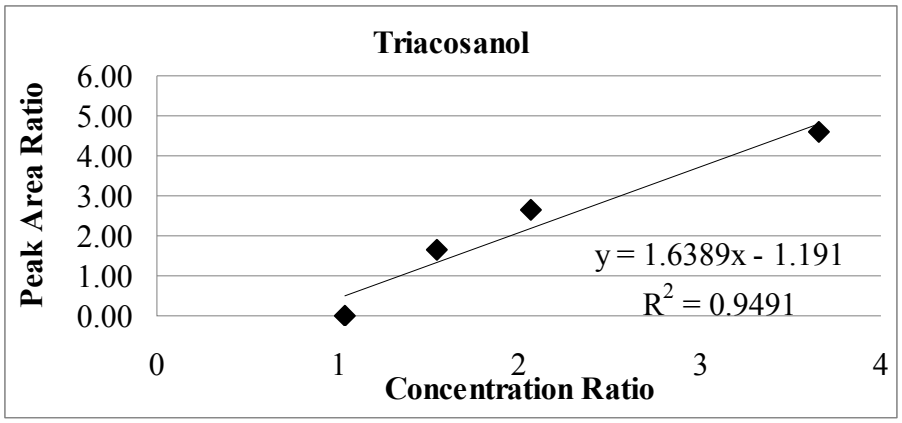
Campesterol	Concentration ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	570786	0.5	0.20
Run Level 2	10	578301	1	0.49
Run Level 3	15	1589603	1.5	0.90
Run Level 4	20	4020456	2	0.96
Run Level 5	35	5142724	3.5	1.62



Stigmasterol	Concentration ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5	197470	0.5	0.07
Run Level 2	10	195379	1	0.17
Run Level 3	15	589540	1.5	0.33
Run Level 4	20	1453721	2	0.35
Run Level 5	35	1848401	3.5	0.58



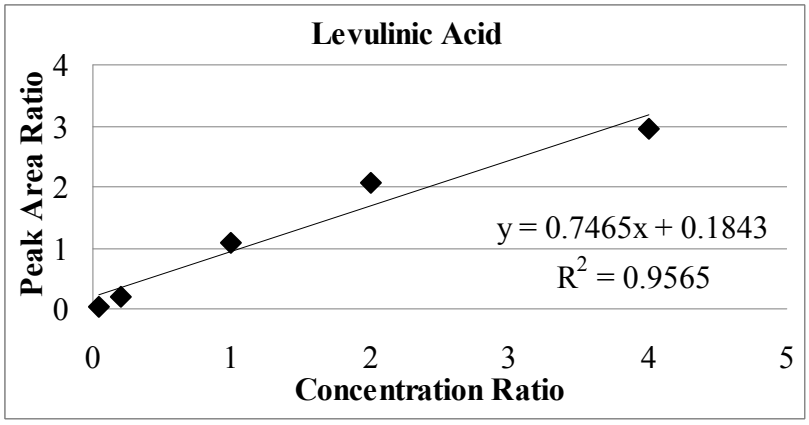
Triacosanol	Concentration ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	5.2	0	0.52	0.00
Run Level 2	10.4	25605	1.04	0.02
Run Level 3	15.5	2890982	1.55	1.64
Run Level 4	20.7	10968290	2.07	2.63
Run Level 5	36.6	14584482	3.66	4.58



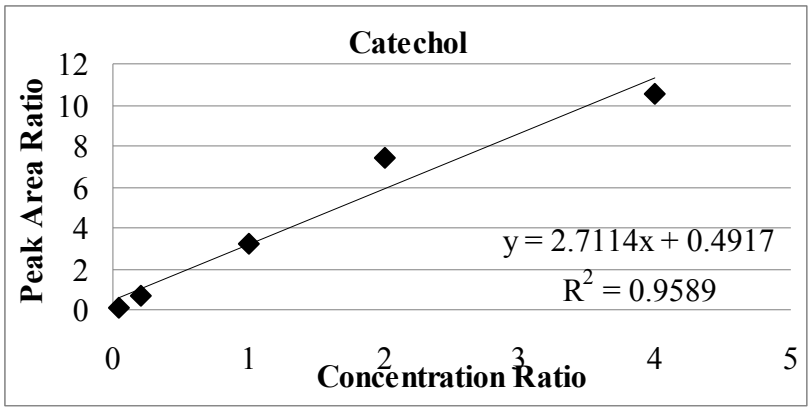
Aliquot 3

C24D50	Concentration ng/uL	Peak Area
Run Level 1	10	2863567
Run Level 2	10	2085107
Run Level 3	10	1856645
Run Level 4	10	2569411
Run Level 5	10	2427238

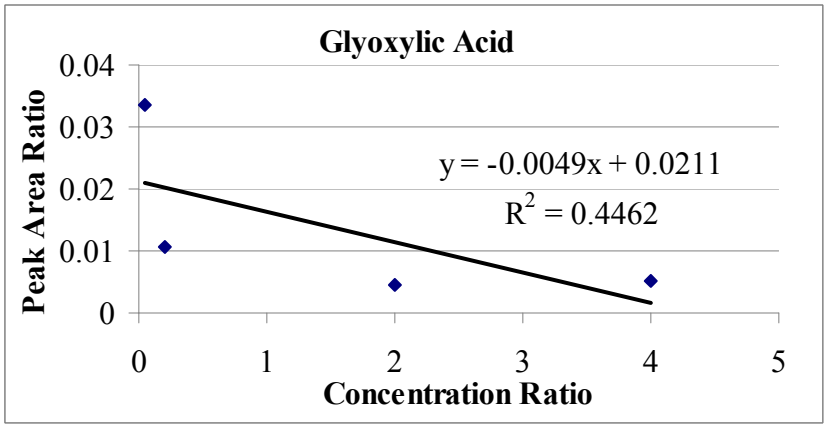
Levulinic Acid	Conc, ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	124677	0.05	0.043539055
Run Level 2	2	404146	0.2	0.193825065
Run Level 3	10	2026102	1	1.091270544
Run Level 4	20	5276764	2	2.053686234
Run Level 5	40	7163142	4	2.951149413



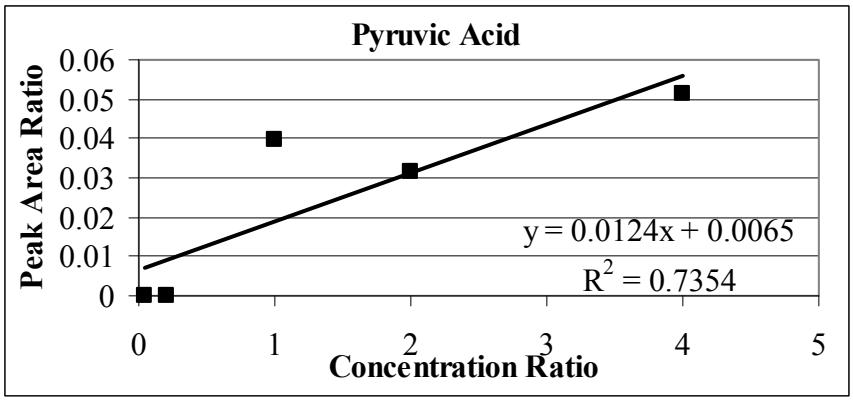
Catechol	Conc, ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	298672	0.05	0.104300685
Run Level 2	2	1500334	0.2	0.719547726
Run Level 3	10	6063975	1	3.266092872
Run Level 4	20	19142379	2	7.450103934
Run Level 5	40	25670577	4	10.57604446



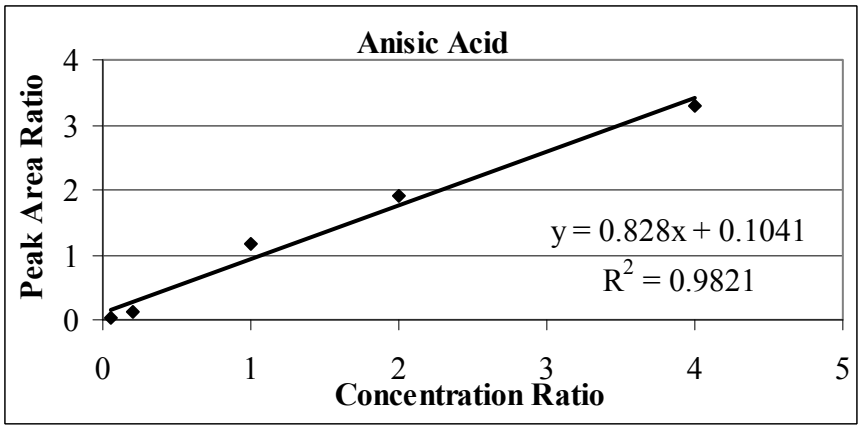
Glyoxylic Acid	Conc, ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	95771	0.05	0.033444651
Run Level 2	2	22145	0.2	0.010620558
Run Level 3	10	3282	1	0.012
Run Level 4	20	11997	2	0.004669163
Run Level 5	40	12598	4	0.005190262



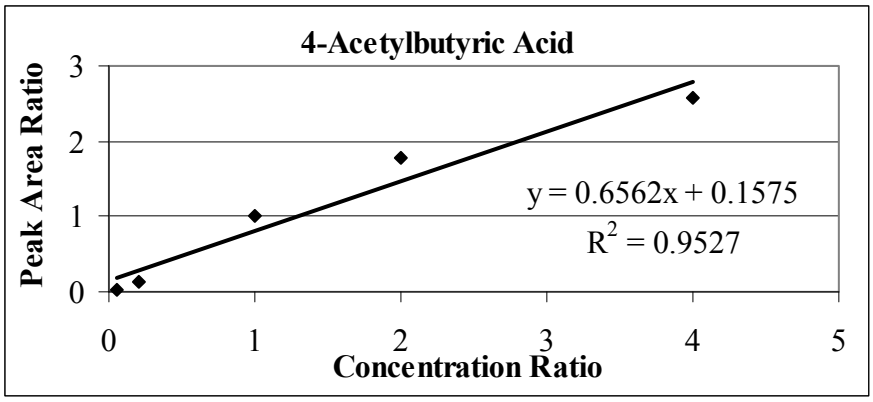
Pyruvic Acid	Conc, ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	0	0.05	0
Run Level 2	2	0	0.2	0
Run Level 3	10	73535	1	0.039606387
Run Level 4	20	80596	2	0.0313675
Run Level 5	40	124776	4	0.051406578



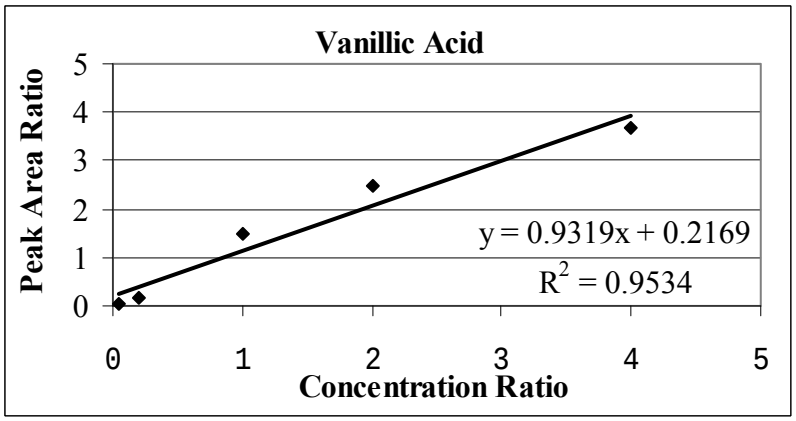
Anisic Acid	Conc, ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	73407	0.05	0.025634811
Run Level 2	2	262123	0.2	0.125712014
Run Level 3	10	2167154	1	1.167241988
Run Level 4	20	4926677	2	1.917434385
Run Level 5	40	7978755	4	3.287174558



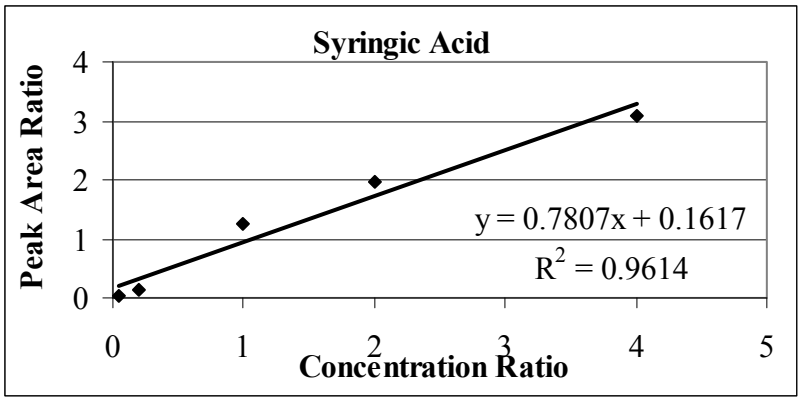
4-Acetylbutyric Acid	Conc, ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	77154	0.05	0.026943319
Run Level 2	2	294505	0.2	0.141242152
Run Level 3	10	1862089	1	1.002932171
Run Level 4	20	4596560	2	1.788954745
Run Level 5	40	6274268	4	2.584941403



Vanillic Acid	Conc, ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	105810	0.05	0.036950419
Run Level 2	2	337787	0.2	0.16199984
Run Level 3	10	2782815	1	1.498840651
Run Level 4	20	6324995	2	2.461651717
Run Level 5	40	8935433	4	3.681317201



Syringic Acid	Conc, ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	78752	0.05	0.027501365
Run Level 2	2	258326	0.2	0.123891004
Run Level 3	10	2339829	1	1.260245766
Run Level 4	20	5028382	2	1.957017386
Run Level 5	40	7523910	4	3.099782551

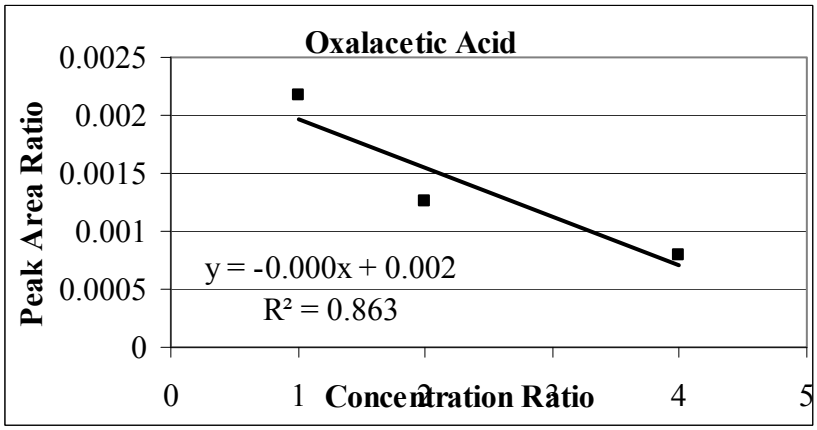


Aliquot 4

C24D50	Concentration ng/uL	Peak Area
Run Level 1	10	3905364
Run Level 2	10	5034228
Run Level 3	10	5034228
Run Level 4	10	11542768
Run Level 5	10	6048873

Oxalacetic Acid	Conc, ng/uL	Peak Area	Conc Ratio	Peak Area Ratio
Run Level 1	0.5	0	0.05	0
Run Level 2	2	0	0.2	0
Run Level 3	10	10896	1	0.0021644
Run Level 4	20	14504	2	0.0012565
Run Level 5	40	4838	4	0.0007998

Slope =	-0.00045



Appendix D: GCMS Ambient Detection Limits

SOAP 2002-2003

	Chester (CHS 56) Spring
Compound	Ambient Concentration ng/m^3
Levoglucosan	0.027
Galactopyranose	0.009
Mannopyranose	0.024
α-Xylose	0.010
β-Xylose	0.017
α-Mannose	0.006
α-Glucose	0.009
β-Mannose	0.028
β-Glucose	0.009
Sucrose	0.004
Trehalose	0.031
Maltose	0.188
cis-Pinonic Acid	0.040
Dehydroabietic Acid	0.151
Tetracosanol	0.007
Hexacosanol	0.007
Octacosanol	0.029
Cholesterol	0.021
β-sitosterol	0.023
Campesterol	0.010
Stigmasterol	0.026
Triacosanol	0.008
Levulinic Acid	0.068
Catechol	0.021
Glyoxylic Acid	13.942
Pyruvic Acid	4.647
Anisic Acid	0.013
4-Acetylbutyric Acid	0.032
Oxalacetic Acid	6.809
Vanillic Acid	0.003
Syringic Acid	0.020

SOAP 2005-2007

	Pinnacle (NYP09) June 2006
Compound	Ambient Concentration ng/m^3
Levoglucosan	0.038
Galactopyranose	0.014
Mannopyranose	0.039
α-Xylose	0.005
β-Xylose	0.007
α-Mannose	0.003
α-Glucose	0.005
β-Mannose	0.009
β-Glucose	0.004
Sucrose	0.004
Trehalose	0.020
Maltose	0.095
cis-Pinonic Acid	0.040
Dehydroabietic Acid	0.024
Tetracosanol	0.005
Hexacosanol	0.001
Octacosanol	0.002
Cholesterol	0.011
β-sitosterol	0.011
Campesterol	0.007
Stigmasterol	0.018
Triacosanol	0.003
Levulinic Acid	0.062
Catechol	0.009
Glyoxylic Acid	6.227
Pyruvic Acid	2.076
Anisic Acid	0.006
4-Acetylbutyric Acid	0.020
Oxalacetic Acid	1.966
Vanillic Acid	0.003
Syringic Acid	0.009

Appendix E: Filter Composite Scheme

Composite Scheme for SOAP 2002-2003 Project

Season, Sample names and filter collection dates. ½ of each filter was extracted.

Early Summer	Summer	Early Fall	Early Fall	Fall
ELZ21, QNS 22, CHS23	ELZ 24, QNS 25 WPT 26 CHS 27	ELZ 28 QNS 29 CHS 31	WPT 30	ELZ 32 QNS 33 WPT 34 CHS 35
5/26/2002	7/25/2002	9/2/2002	9/5/2002	9/26/2002
6/1/2002	7/28/2002	9/5/2002	9/8/2002	10/17/2002
6/4/2002	8/12/2002	9/8/2002	9/14/2002	10/20/2002
6/7/2002	8/15/2002	9/11/2002	9/29/2002	10/23/2002
6/10/2002	8/18/2002	9/20/2003	11/10/2002	10/26/2002
7/10/2002	8/21/2002	10/5/2002		10/29/2002
7/13/2002	8/24/2002			11/13/2002
7/16/2002	8/27/2002			
7/19/2002	7/25/2002			

Season, Sample names and filter collection dates (continued).

Late Fall	Early Winter	Early Winter	Winter	Early Spring	Spring
ELZ 36 QNS 37 WPT 38 CHS 39	ELZ 41 QNS 42 CHS 44	WPT 43	ELZ 45 QNS 46 WPT 47 CHS 48	ELZ 49 QNS 50 WPT 51 CHS 52	ELZ 53 QNS 54 WPT 55 CHS 56
11/1/2002	12/4/2002	12/4/2002	1/9/2003	3/1/2003	4/15/2003
11/4/2002	12/7/2002	12/7/2002	1/24/2003	3/4/2003	4/18/2003
11/16/2002	12/13/2002	12/10/2003	1/30/2003	3/10/2003	4/24/2003
11/19/2002	12/19/2002	12/13/2002	2/8/2003	3/16/2003	4/27/2003
11/22/2002	1/12/2003	12/19/2002	2/11/2003	3/19/2003	4/30/2003
11/28/2002	2/2/2003	1/3/2003	2/14/2003	3/22/2003	5/3/2003
12/1/2002		1/6/2003	2/17/2003	3/25/2003	5/6/2003
		2/5/2003	2/26/2003	4/6/2003	5/9/2003
		2/20/2003		4/9/2003	5/12/2003
				4/12/2003	5/15/2003

Late Spring	Late Spring
QNS 58 WPT 59 CHS 60	ELZ 57
3/28/2003	3/13/2003
3/31/2003	5/21/2003
4/3/2003	5/24/2003
5/18/2003	5/27/2003
5/21/2003	5/30/2003
5/24/2003	
5/30/2003	

Composite Scheme for SOAP 2005-2007 Project

Season, Sample names and filter collection dates for the Bronx, NY site.

Sampling Date	Saved for future analysis	Notes	Punches	Sample Name	Percent filter in each composite
OCT 05				1 NYB01 (4)	
10/1/05	1/4		2		1*(.75-.04)
10/7/05		not used - wet	0		
10/13/05		not used - wet	0		
10/19/05	1/4		1		3*(.75-.02)
10/25/05	1/4		1		
10/31/05	1/4		1		
NOV 05				2 NYB02 (5)	
11/6/05	1/4		1		4*(.75-.02)
11/12/05	1/4		2		1*(.75-.04)
11/18/05	1/4		1		
11/24/05	1/4		1		
11/30/05	1/4		1		
DEC 05				3 NYB03 (5)	
12/06/05	1/4		1		5*(.75-.02)
12/12/05	1/4		1		
12/18/05	1/4		1		
12/24/05	1/4		1		
12/30/05	1/4		1		
JAN 06				4 NYB04 (4)	
1/5/06		not used - wet & torn	1		
1/11/06	1/4		1		4*(.75-.02)
1/17/06	1/4		1		
1/23/06	1/4		1		
1/29/06	1/4		1		
FEB 06				5 NYB05 (5)	
2/4/06	1/4		1		5*(.75-.02)
2/10/06	1/4		1		
2/16/06	1/4		1		
2/22/06	1/4		1		
2/28/06	1/4		1		
MAR 06				6 NYB06 (5)	
3/6/06	1/4		1		5*(.75-.02)

3/12/06	1/4		1		
3/18/06	1/4		1		
3/24/06	1/4		1		
3/30/06	1/4		1		
APR 06				7 NYB07 (5)	
4/5/06	1/4		2		1*(.75-.04)
4/11/06	1/4		1		3*(.75-.02)
4/17/06	1/4		1		
4/23/06		Not Used moldy bad filter	0		
4/29/06	1/4		1		
MAY 06				8 NYB08 (5)	
5/5/06	1/4		1		4*(.75-.02)
5/11/06	1/4		1		
5/17/06	1/4		2		1*(.75-.04)
5/23/06	1/4		1		
5/29/06	1/4		1		
JUN 06				9 NYB09 (5)	
6/4/06	1/4		1		5*(.75-.02)
6/10/06	1/4		1		
6/16/06	1/4		1		
6/22/06	1/4		1		
6/28/06	1/4		1		
JUL 06				10 NYB010 (4)	
7/4/06	1/4		1		4*(.75-.02)
7/10/06	1/4		1		
7/16/06	1/4		1		
7/22/06	1/4		1		
7/28/06		Not used - torn	1		
AUG 06				11 NYB011 (5)	
8/3/06	1/4		1		4*(.75-.02)
8/9/06	1/4		1		
8/15/06	1/4		1		
8/21/06	1/4		2		1*(.75-.04)
8/27/06	1/4		1		

SEP 06				12 NYB012 (3)	
9/2/06	1/4		0		1*.75
9/8/06	1/4		1		2*(.75-.02)
9/14/06	1/4	Not used - wet	0		
9/20/06	1/4	Not used - wet	1		
9/26/06	1/4		1		
OCT 06				13 NYB013 (4)	
10/2/06	1/4		1		3*(.75-.02)
10/8/06	1/4		2		1*(.75-.04)
10/14/06	1/4		1		
10/20/06	1/4	Not used - wet	0		
10/26/06	1/4		1		
NOV 06				14 NYB014 (5)	
11/1/06	1/4		1		5*(.75-.02)
11/7/06	1/4		1		
11/13/06	1/4		1		
11/19/06	1/4		1		
11/25/06	1/4		1		
DEC 06				15 NYB015 (6)	
12/1/06	1/4		1		4*(.75-.02)
12/7/06	1/4		1		
12/13/06	1/4		1		**SAMPLE RAN FOR 4172 MIN 3 SECONDS!!!**
12/19/06	1/4		2		1*(.75-.04)
12/25/06	1/4		1		
12/31/06	1/4		1		
JAN 07				16 NYB016 (5)	
1/6/07	1/4		2		1*(.75-.04)
1/12/07	1/4		1		4*(.75-.02)
1/18/07	1/4		1		
1/24/07	1/4		1		

1/30/07	1/4		1		
FEB 07				17 NYB017 (4)	
2/5/07	1/4		1		4*(.75-.02)
2/11/07	1/4		1		
2/17/07	1/4		1		
2/23/07	1/4		1		
3/1/07	1/4	Not used - wet	2		

Season, Sample names and filter collection dates for the Pinnacle State Park, NY site.

Bar Code		Sampling Date	LCMS	Notes	Punches		Name	Percent filter in each composite
					2P	4P		
NYP01 (10)	OCT 05						18 NYP01 (10)	
2P	4P	10/1/05	4P - 1/2		1	1		5*(1-.02)
2P	4P	10/7/05	4P - 1/2	2P not used - wet	0	1		5*(.5-.02)
2P	4P	10/13/05	2P - 1/2	2P not used - filters torn	1	1		
2P	4P	10/19/05	2P - 1/2		1	1		
2P	4P	10/25/05	2P - 1/2		1	1		
2P	4P	10/31/05	4P - 1/2		1	1		
NYP02 (10)	NOV 05						19 NYP02 (10)	
2P	4P	11/6/05	2P - 1/2		1	1		4*(1-.02)
2P	4P	11/12/05	4P - 1/2	2P & 4P - 2 ECOC punches	2	2		4*(.5-.02)
2P	4P	11/18/05	2P - 1/2		1	1		1*(1-.04)
2P	4P	11/24/05	4P - 1/2		1	1		1*(.5-.04)
2P	4P	11/30/05	2P - 1/2		1	1		
NYP03 (6)	DEC 05						20 NYP03 (6)	
2P	4P	12/06/05	4P - 1/4	2P not used - torn	1	1		1*(.5-.02)
2P	4P	12/12/05	4P - 1/4	2P not used - wrong flow	1	1		4*(.75-.02)
2P	4P	12/18/05	4P - 1/4	2P not used - wrong flow	1	1		1*(1-.02)
2P	4P	12/24/05	2P - 1/2		1	1		
2P	4P	12/30/05	4P - 1/4	2P not used - wet	0	1		

NYP04 (10)	JAN 06						21 NYP04 (10)	
2P	4P	1/5/06	4P - 1/2		1	1		5*(.5-.02)
2P	4P	1/11/06	4P - 1/2		1	1		5*(1-.02)
2P	4P	1/17/06	4P - 1/2		1	1		
2P	4P	1/23/06	2P - 1/2		1	1		
2P	4P	1/29/06	2P - 1/2		1	1		
NYP05 (10)	FEB 06						22 NYP05 (10)	
2P	4P	2/4/06	2P - 1/2		1	1		5*(.5-.02)
2P	4P	2/10/06	2P - 1/2		1	1		5*(1-.02)
2P	4P	2/16/06	2P - 1/2		1	1		
2P	4P	2/22/06	4P - 1/2		1	1		
2P	4P	2/28/06	4P - 1/2		1	1		
NYP06 (10)	MAR 06						23 NYP06 (10)	
2P	4P	3/6/06	4P - 1/2		1	1		5*(.5-.02)
2P	4P	3/12/06	4P - 1/2		1	1		5*(1-.02)
2P	4P	3/18/06	2P - 1/2		1	1		
2P047FAS	4P	3/24/06	2P - 1/2		1	1		
2P	4P	3/30/06	2P - 1/2		1	1		
NYP07 (10)	APR 06						24 NYP07 (10)	
2P	4P	4/5/06	4P - 1/2		2	2		1*(1-.04)
2P	4P	4/11/06	4P - 1/2		1	1		1*(.5-.04)
2P	4P	4/17/06	4P - 1/2		1	1		4*(.5-.02)
2P	4P	4/23/06	2P - 1/2		1	1		4*(1-.02)
2P	4P	4/29/06	2P - 1/2		1	1		
NYP08 (9)	MAY 06						25 NYP08 (9)	
2P	4P	5/5/06	2P - 1/2		1	1		4*(.5-.02)
2P	4P	5/11/06	2P - 1/2	4P not used - wet & filters stuck	1	0		1*(1-.04)

				together				
2P	4P	5/17/06	2P - 1/2		2	2		1*(.5-.04)
2P	4P	5/23/06	4P - 1/2		1	1		3*(1-.02)
2P	4P	5/29/06	4P - 1/2		1	1		
NYP09 (10)	JUN 06						26 NYP09 (10)	
2P	4P	6/4/06	2P - 1/2		1	1		5*(.5-.02)
2P	4P	6/10/06	4P - 1/2		1	1		5*(1-.02)
2P	4P	6/16/06	4P - 1/2		1	1		
2P	4P	6/22/06	4P - 1/2		1	1		
2P	4P	6/28/06	2P - 1/2		1	1		
NYP10 10)	JUL 06						27 NYP10 (10)	
2P	4P	7/4/06	4P - 1/2		1	2		5*(1-.02)
2P	4P	7/10/06	4P - 1/2		1	1		1*(.5-.04)
2P	4P	7/16/06	4P - 1/2		1	1		4*(.5-.02)
2P	4P	7/22/06	2P - 1/2		1	1		
2P	4P	7/28/06	2P - 1/2		1	1		
NYP11 (10)	AUG 06						28 NYP11 (10)	
2P	4P0	8/3/06	4P - 1/2		1	1		5*(1-.02)
2P	4P	8/9/06	4P - 1/2		1	1		3*(.5-.02)
2P	4P	8/15/06	4P - 1/2	4P - 2 ECOC punches but only 1 used	1	1		2*(.5-.04)
2P	4P	8/21/06	2P - 1/2		1	1		
2P	4P	8/27/06	2P - 1/2		2	1		
NYP12 (08)	SEPT 06						29 NYP12 (8)	
2P	4P	9/2/06		2P & 4P both wet, not used	0	0		
2P	4P	9/8/06	4P - 1/2		1	2		4*(1-.02)
2P	4P0	9/14/06	2P - 1/2		1	1		3*(.5-.02)
2P	4P	9/20/06	4P - 1/2		1	1		1*(.5-.04)

2P	4P	9/26/06	2P - 1/2		1	1		
NYP13 (10)	OCT 06						30 NYP13 (10)	
2P	4P	10/2/06	2P - 1/2		1	1		5*(1-.02)
2P	4P	10/8/06	2P - 1/2		1	1		4*(.5-.02)
2P	4P	10/14/06	2P - 1/2		2	1		1*(.5-.04)
2P	4P	10/20/06	4P - 1/2		1	1		
2P	4P	10/26/06	4P - 1/2		1	1		
NYP14 (10)	NOV 06						31 NYP14 (10)	
2P	4P	11/1/06	4P - 1/2		1	1		5*(1-.02)
2P	4P	11/7/06	4P - 1/2		1	1		3*(.5-.02)
2P	4P	11/13/06	4P - 1/2	4P - 2 ECOC	1	2		2*(.5-.04)
2P	4P	11/19/06	2P - 1/2		1	1		
2P	4P	11/25/06	2P - 1/2	2P - 2 ECOC	2	1		
NYP15 (11)	DEC 06						32 NYP15 (11)	
2P	4P	12/1/06	2P - 1/2		1	1		5*(1-.02)
2P	4P	12/7/06	2P - 1/2		1	1		5*(.5-.02)
2P	4P	12/13/06	2P - 1/2		1	1		1*(.5-.04)
2P	4P	12/19/06	4P - 1/2		1	1		
2P	4P	12/25/06	4P - 1/2	2P not used - torn	0	1		
2P	4P	12/31/06	4P - 1/2		1	2		
NYP16 (10)	JAN 07						33 NYP16 (10)	
2P	4P	1/6/07	2P - 1/2		1	1		3*(1-.02)
2P	4P	1/12/07	4P - 1/2		1	1		5*(.5-.02)
2P	4P	1/18/07	2P - 1/2		1	1		2*(1-.04)
2P	4P	1/24/07	4P - 1/2		2	1		
2P	4P	1/30/07	2P - 1/2		1	2		
NYP17 (10)	FEB 07						34 NYP17 (10)	

2P	4P	2/5/07	4P - 1/2		1	1		5*(1-.02)
2P	4P	2/11/07	2P - 1/2		1	1		3*(.5-.02)
2P	4P	2/17/07	4P - 1/2		1	1		2*(.5-.04)
2P	4P	2/23/07	2P - 1/2		2	1		
2P	4P	3/1/07	4P - 1/2		1	2		

Appendix F: SOAP 2002-2007 Ambient Data

SOAP 2002-2003 Ambient Data in ng/m^3
Elz = Elizabeth, NJ
Qns = Queens, NY
Wpt = Westport, CT
Chs = Chester, NJ

Levoglucosan Data ng/m^3				
Season	Elz	Qns	Wpt	Chs
early summer	28.50	78.98		24.90
summer	55.28	23.24	3.36	25.15
early fall	16.65	9.86	72.67	11.67
fall	72.65	88.99	69.74	25.64
late fall	138.11	146.92	189.47	80.15
early winter	24.12	104.33	149.59	70.14
winter	6.66	37.66	120.89	24.18
early spring	21.52	12.38	78.79	26.89
spring	4.34	2.36	5.06	2.73
late spring	5.39	5.70	9.07	12.83

Dehydroabietic Acid ng/m^3				
Season	Elz	Qns	Wpt	Chs
early summer	30.84	84.98		12.18
summer	89.30	28.75	11.16	50.20
early fall	14.31	13.20	28.82	18.77
fall	24.36	15.43	10.69	11.22
late fall	14.57	57.52	21.62	43.63
early winter	42.61	39.60	47.83	48.25
winter	22.79	19.93	26.15	12.52
early spring	98.97	26.08	61.07	53.91
spring	12.52	9.13	1.61	7.50
late spring	12.95	10.15	10.48	12.71

Cholesterol ng/m^3				
Season	Elz	Qns	Wpt	Chs
early summer	0.63	0.00		0.00
summer	0.13	0.00	0.00	0.00
early fall	0.00	0.07	0.00	0.00
fall	0.49	0.21	0.00	0.00
late fall	0.27	0.41	0.00	0.00
early winter	0.00	0.78	0.00	0.00

winter	0.23	0.10	0.07	0.66
early spring	0.00	0.00	0.00	0.00
spring	0.23	0.22	0.07	0.04
late spring	0.42	0.20	0.00	0.03

Conc.(ng/m3)	summer early	summer	fall early	fall	fall late	winter early
Sugar	21Elz	24Elz	28Elz	32 Elz	36Elz	41Elz
levoglucosan	28.50	55.28	16.65	72.65	138.11	24.12
galactopyranose	0.00	0.00	0.07	0.11	0.00	0.19
mannopyranose	0.00	3.42	0.00	0.00	0.41	0.00
xylose	0.00	0.00	0.00	0.00	0.00	0.00
mannose	0.00	0.00	0.00	0.22	0.00	0.00
glucose	0.00	0.00	0.85	0.64	0.75	0.00
sucrose	0.04	0.16	0.12	0.55	0.00	0.04
trehalose	0.00	0.00	0.00	0.00	0.00	0.00
maltose	0.00	0.00	0.00	0.00	0.00	0.00

Conc.(ng/m3)	winter	spring early	spring	spring late
Sugar	45 Elz	49 Elz	53 Elz	57 Elz
levoglucosan	6.66	21.52	4.34	5.39
galactopyranose	0.46	0.00	0.06	0.36
mannopyranose	0.00	0.00	0.00	0.48
xylose	0.67	0.00	0.00	0.33
mannose	0.00	0.00	0.03	0.00
glucose	0.00	0.00	0.00	0.00
sucrose	0.08	0.54	0.02	0.02
trehalose	0.00	0.00	0.00	0.00
maltose	0.00	0.00	0.00	0.00

Conc.(ng/m3)	summer early	summer	fall early	fall	fall late	winter early
Sugar	22 Qns	25 Qns	29 Qns	33 Qns	37 Qns	42Qns
levoglucosan	78.98	23.24	9.86	88.99	146.92	104.33
galactopyranose	1.10	0.00	0.00	0.17	0.00	0.46
mannopyranose	9.29	0.00	0.73	1.49	0.00	0.00
xylose	0.00	0.00	0.00	0.00	0.00	0.00
mannose	0.00	0.00	0.37	0.00	0.00	0.00
glucose	0.49	0.00	0.78	0.25	0.21	0.00
sucrose	0.23	0.57	0.11	0.06	0.04	0.06
trehalose	0.00	0.00	0.15	0.00	0.00	0.00
maltose	0.00	0.00	0.00	0.00	0.00	0.00

Conc.(ng/m3)	winter	spring early	spring	spring late
Sugar	46 Qns	50 Qns	54 Qns	58 Qns
levoglucosan	37.66	12.38	2.36	5.70
galactopyranose	0.07	0.00	0.00	0.04
mannopyranose	0.00	0.00	0.00	0.00
xylose	0.30	0.25	0.00	0.00
mannose	0.00	0.00	0.00	0.03
glucose	0.21	0.00	0.00	0.00
sucrose	0.06	0.08	0.05	0.02
trehalose	0.00	0.00	0.00	0.00
maltose	0.00	0.00	0.00	0.00

Conc.(ng/m3)	summer early	summer	fall early	fall	fall late	winter early
Sugar	23 Chs	27 Chs	31 Chs	35 Chs	39 Chs	44 Chs
levoglucosan	24.90	25.15	11.67	25.64	80.15	70.14
galactopyranose	0.20	2.41	0.17	0.70	0.54	0.25
mannopyranose	1.76	1.54	0.00	0.00	2.36	0.00
xylose	0.00	0.00	0.00	0.00	0.00	0.00
mannose	0.00	0.00	0.00	0.13	0.00	0.00
glucose	0.16	2.96	0.00	0.00	0.27	0.00
sucrose	0.05	0.14	0.09	1.95	0.30	0.09
trehalose	0.00	0.00	0.00	0.00	0.00	0.00
maltose	0.00	0.00	0.00	0.00	0.00	0.00

Conc.(ng/m3)	winter	spring early	spring	spring late
Sugar	48 Chs	52 Chs	56 Chs	60 Chs
levoglucosan	24.18	26.89	2.73	12.83
galactopyranose	0.05	0.32	0.06	0.18
mannopyranose	0.00	0.00	0.00	0.31
xylose	0.00	0.00	0.00	0.19
mannose	0.22	0.30	0.00	0.00
glucose	0.00	0.00	0.00	0.02
sucrose	0.09	0.04	0.00	0.02
trehalose	0.00	0.00	0.00	0.00
maltose	0.00	0.00	0.00	0.00

Conc.(ng/m3)	summer	fall early	fall	fall late	winter early
Sugar	26 Wpt	30 Wpt	34 Wpt	38 Wpt	43 Wpt
levoglucosan	3.36	72.67	69.74	189.47	149.59
galactopyranose	0.11	0.90	1.37	6.94	1.58
mannopyranose	0.26	3.22	3.71	0.00	3.64

xylose	0.00	0.00	0.00	0.00	0.00
mannose	0.32	0.00	0.29	1.12	0.17
glucose	0.00	0.15	0.64	0.94	0.13
sucrose	0.02	0.06	0.03	0.10	0.08
trehalose	0.00	0.00	0.16	0.00	0.00
maltose	0.00	0.00	0.00	0.00	0.00

Conc.(ng/m3)	winter	spring early	spring	spring late
Sugar	47 Wpt	51 Wpt	55 Wpt	59 Wpt
levoglucosan	120.89	78.79	5.06	9.07
galactopyranose	0.05	1.44	0.03	0.22
mannopyranose	0.00	2.73	0.00	0.00
xylose	0.00	0.00	0.00	0.00
mannose	0.00	0.08	0.00	0.00
glucose	0.00	0.05	0.00	0.00
sucrose	0.09	0.05	0.03	0.00
trehalose	0.00	0.00	0.00	0.00
maltose	0.00	0.00	0.00	0.00

Conc.(ng/m3)	summer early	summer	fall early	fall	fall late	winter early
Compound	21Elz	24Elz	28Elz	32 Elz	36Elz	41Elz
Tetracosanol	4.53	1.95	0.99	0.74	1.11	0.97
Hexacosanol	10.07	2.29	2.53	1.01	1.08	0.76
Octacosanol	0.00	0.00	0.00	0.00	0.00	0.17
Triacosanol	0.00	0.00	0.00	0.00	0.00	0.00
B-sitosterol	0.35	0.38	0.17	11.91	0.46	0.00
Campesterol	0.00	0.00	0.00	0.29	0.12	0.00
Stigmasterol	0.00	0.00	0.00	2.68	0.25	0.00
Total n-alkanols	14.60	4.24	3.52	1.76	2.20	1.90

Conc.(ng/m3)	winter	spring early	spring	spring late
Compound	45 Elz	49 Elz	53 Elz	57 Elz
Tetracosanol	0.90	0.25	0.93	0.78
Hexacosanol	0.00	0.12	2.99	1.03
Octacosanol	0.47	0.00	0.00	0.41
Triacosanol	0.00	0.00	0.00	0.00
B-sitosterol	0.00	0.62	0.25	0.00
Campesterol	0.00	0.00	0.00	0.00
Stigmasterol	0.00	0.00	0.00	0.00
Total n-alkanols	1.37	0.37	3.92	2.22

Conc.(ng/m3)	summer early	summer	fall early	fall	fall late	winter early
Compound	22 Qns	25 Qns	29 Qns	33 Qns	37 Qns	42 Qns
Tetracosanol	3.01	0.56	2.15	0.68	1.83	1.23
Hexacosanol	6.56	0.26	4.81	1.21	2.13	1.31
Octacosanol	2.21	0.00	1.67	0.00	0.00	0.52
Triacosanol	1.14	0.00	1.29	0.00	0.00	0.00
B-sitosterol	0.56	0.00	0.12	0.00	0.66	68.72
Campesterol	0.00	0.00	0.00	0.00	0.10	0.00
Stigmasterol	0.00	0.00	0.00	0.00	0.00	12.19
Total n-alkanols	12.92	0.82	9.91	1.88	3.95	3.07

Conc.(ng/m3)	winter	spring early	spring	spring late
Compound	46 Qns	50 Qns	54 Qns	58 Qns
Tetracosanol	1.12	0.55	1.83	1.57
Hexacosanol	1.15	0.69	3.21	2.75
Octacosanol	0.60	0.35	1.20	0.00
Triacosanol	0.24	0.13	0.67	0.00
B-sitosterol	0.62	0.43	0.42	0.00
Campesterol	0.00	0.00	0.00	0.00
Stigmasterol	0.00	0.00	0.00	0.00
Total n-alkanols	3.10	1.72	6.91	4.32

Conc.(ng/m3)	summer early	summer	fall early	fall	fall late	winter early
Compound	23 Chs	27 Chs	31 Chs	35 Chs	39 Chs	44 Chs
Tetracosanol	1.66	0.46	0.88	0.50	0.51	1.00
Hexacosanol	3.18	0.00	1.78	0.56	0.00	0.84
Octacosanol	0.81	0.00	0.00	0.00	0.10	0.00
Triacosanol	0.29	0.00	0.00	0.00	0.00	0.00
B-sitosterol	0.00	0.00	0.00	0.00	0.00	0.41
Campesterol	0.00	0.00	0.00	0.00	0.00	0.00
Stigmasterol	0.00	0.00	0.00	0.00	0.00	0.00
Total n-alkanols	5.93	0.46	2.66	1.07	0.61	1.84

Conc.(ng/m3)	winter	spring early	spring	spring late
Compound	48 Chs	52 Chs	56 Chs	60 Chs
Tetracosanol	1.17	1.51	1.62	1.50
Hexacosanol	1.13	0.92	2.48	1.63
Octacosanol	0.00	0.00	1.17	0.42
Triacosanol	0.00	0.00	0.02	0.00
B-sitosterol	0.00	0.00	0.31	0.22
Campesterol	0.00	0.00	0.00	0.00

Stigmasterol	0.00	0.00	0.00	0.00
Total n-alkanols	2.30	2.43	5.29	3.54

Conc.(ng/m3)	summer	fall early	fall	fall late	winter early
Compound	26 Wpt	30 Wpt	34 Wpt	38 Wpt	43 Wpt
Tetracosanol	0.23	0.83	0.44	1.32	1.87
Hexacosanol	0.52	1.42	0.77	1.08	1.94
Octacosanol	0.17	0.42	0.26	0.00	0.74
Triacosanol	0.00	0.22	0.15	0.00	0.24
B-sitosterol	0.00	0.14	0.00	0.63	1.41
Campesterol	0.00	0.00	0.00	0.00	0.00
Stigmasterol	0.00	0.00	0.00	0.00	0.00
Total n-alkanols	0.91	2.89	1.62	2.40	4.79

Conc.(ng/m3)	winter	spring early	spring	spring late
Compound	47 Wpt	51 Wpt	55 Wpt	59 Wpt
Tetracosanol	0.82	0.85	0.44	0.31
Hexacosanol	0.60	0.72	0.76	0.24
Octacosanol	0.00	0.26	0.00	0.00
Triacosanol	0.00	0.00	0.00	0.00
B-sitosterol	0.00	0.52	0.11	0.59
Campesterol	0.00	0.00	0.00	0.00
Stigmasterol	0.00	0.00	0.00	0.00
Total n-alkanols	1.42	1.84	1.20	0.54

Conc.(ng/m3)	summer early	summer	fall early	fall	fall late	winter early
Compound	21Elz	24 Elz	28 Elz	32 Elz	36Elz	41 Elz
Levulinic Acid	17.54	0.00	0.00	0.00	0.00	0.00
Glyoxylic Acid	0.00	0.00	0.00	0.00	0.00	0.00
Pyruvic Acid	0.00	0.00	0.00	0.00	0.00	0.00
4-Acetylbutyric Acid	1.80	0.00	0.00	0.00	0.00	0.00
Oxalacetic Acid	0.00	0.00	0.00	0.00	0.00	0.00
Catechol	0.00	0.00	0.00	0.00	0.00	0.00
Anisic Acid	0.00	0.00	0.00	0.00	0.00	0.00
Vanillic Acid	0.00	0.00	0.00	0.00	0.00	0.00
Syringic Acid	0.00	0.00	0.00	0.00	0.00	0.00

Conc.(ng/m3)	winter	spring early	spring	spring late
Compound	45 Elz	49 Elz	53 Elz	57 Elz
Levulinic Acid	7.42	0.00	0.00	0.00
Glyoxylic Acid	0.00	0.00	0.00	0.00

Pyruvic Acid	0.00	0.00	0.00	0.00
4-Acetylbutyric Acid	1.20	0.00	0.00	0.00
Oxalacetic Acid	0.00	0.00	0.00	0.00
Catechol	0.00	0.00	0.00	0.00
Anisic Acid	0.00	0.00	0.00	0.00
Vanillic Acid	0.00	0.00	0.00	0.00
Syringic Acid	0.00	0.00	0.00	0.00

Conc.(ng/m3)	summer early	summer	fall early	fall	fall late	winter early
Compound	22 Qns	25 Qns	29 Qns	33 Qns	37 Qns	42Qns
Levulinic Acid	0.00	0.00	0.00	0.00	0.00	10.19
Glyoxylic Acid	0.00	0.00	0.00	0.00	0.00	0.00
Pyruvic Acid	0.00	1421.04	0.00	0.00	0.00	0.00
4-Acetylbutyric Acid	0.00	0.00	1.70	0.00	0.00	0.00
Oxalacetic Acid	0.00	0.00	25356.58	0.00	0.00	0.00
Catechol	0.00	0.00	0.00	0.00	0.00	0.00
Anisic Acid	0.00	0.00	0.00	0.00	0.00	0.00
Vanillic Acid	0.00	0.00	0.00	0.00	0.00	0.00
Syringic Acid	0.00	0.00	0.00	0.00	0.00	0.00

Conc.(ng/m3)	winter	spring early	spring	spring late
Compound	46 Qns	50 Qns	54 Qns	58 Qns
Levulinic Acid	7.84	9.09	0.00	0.00
Glyoxylic Acid	0.00	0.00	0.00	0.00
Pyruvic Acid	0.00	0.00	0.00	0.00
4-Acetylbutyric Acid	1.12	1.59	1.34	0.00
Oxalacetic Acid	0.00	0.00	0.00	0.00
Catechol	0.00	0.00	0.00	0.00
Anisic Acid	0.00	0.00	0.00	0.00
Vanillic Acid	0.00	0.00	0.00	0.00
Syringic Acid	0.00	0.00	0.00	0.00

Conc.(ng/m3)	summer early	summer	fall early	fall	fall late	winter early
Compound	23 Chs	27 Chs	31 Chs	35 Chs	39 Chs	44 Chs
Levulinic Acid	21.00	0.00	0.00	0.00	9.41	0.00
Glyoxylic Acid	0.00	0.00	0.00	0.00	0.00	0.00
Pyruvic Acid	0.00	0.00	0.00	0.00	0.00	0.00
4-Acetylbutyric Acid	0.00	0.00	0.00	0.00	0.00	0.00
Oxalacetic Acid	0.00	0.00	0.00	0.00	0.00	0.00
Catechol	0.00	0.00	0.00	0.00	0.00	0.00
Anisic Acid	0.00	0.00	0.00	0.00	0.00	0.00

Vanillic Acid	0.00	0.00	0.00	0.00	0.00	0.00
Syringic Acid	0.00	0.00	0.00	0.00	0.00	0.00

Conc.(ng/m3)	winter	spring early	spring	spring late
Compound	48 Chs	52 Chs	56 Chs	60 Chs
Levulinic Acid	0.00	0.00	6.23	8.75
Glyoxylic Acid	0.00	0.00	0.00	0.00
Pyruvic Acid	0.00	0.00	0.00	0.00
4-Acetylbutyric Acid	0.00	0.00	1.65	1.34
Oxalacetic Acid	0.00	0.00	0.00	0.00
Catechol	0.00	0.00	0.00	0.00
Anisic Acid	0.00	0.00	0.00	0.00
Vanillic Acid	0.00	0.00	0.00	0.00
Syringic Acid	0.00	0.00	0.00	0.00

Conc.(ng/m3)	summer	fall early	fall	fall late	winter early
Compound	26 Wpt	30 Wpt	34 Wpt	38 Wpt	43 Wpt
Levulinic Acid	0.00	0.00	16.82	0.00	11.45
Glyoxylic Acid	0.00	0.00	0.00	0.00	0.00
Pyruvic Acid	0.00	0.00	0.00	0.00	0.00
4-Acetylbutyric Acid	0.00	0.00	0.00	0.00	2.13
Oxalacetic Acid	0.00	0.00	0.00	0.00	0.00
Catechol	0.00	0.00	0.00	0.00	0.00
Anisic Acid	0.00	0.00	0.00	0.00	0.00
Vanillic Acid	0.00	0.00	0.00	0.00	0.00
Syringic Acid	0.00	0.00	0.00	0.00	0.15

Conc.(ng/m3)	winter	spring early	spring	spring late
Compound	47 Wpt	51 Wpt	55 Wpt	59 Wpt
Levulinic Acid	0.00	6.61	1.97	11.31
Glyoxylic Acid	0.00	0.00	0.00	0.00
Pyruvic Acid	0.00	0.00	0.00	0.00
4-Acetylbutyric Acid	0.00	1.57	0.00	1.97
Oxalacetic Acid	0.00	0.00	0.00	0.00
Catechol	0.00	0.00	0.00	0.00
Anisic Acid	0.00	0.00	0.00	0.00
Vanillic Acid	0.00	0.00	0.00	0.00
Syringic Acid	0.00	0.00	0.00	0.00

These are the results from the extracted filter that was collected during the 2002 Canadian wildfire.

	QNS	ELZ	CHS
Compound	Conc.(ng/m3)	Conc.(ng/m3)	Conc.(ng/m3)
levoglucosan	1359.66	912.43	1423.21
galactopyranose	149.63	66.75	144.43
mannopyranose	647.35	309.96	476.69
xylose	0.00	0.00	0.00
glucose	29.11	2.80	5.57
mannose	7.95	1.23	1.65
sucrose	0.45	0.25	0.18
trehalose	1.22	0.00	0.00
maltose	22.09	0.00	0.00
cis-Pinonic Acid	0.00	0.00	0.00
Dehydroabietic Acid	238.03	215.15	253.65
Tetracosanol	56.57	55.41	51.52
Hexacosanol	26.04	26.48	25.31
Octacosanol	32.98	42.25	33.29
Cholesterol	0.00	0.00	0.00
B-sitosterol	0.00	0.00	0.00
Campesterol	0.00	0.00	0.00
Stigmasterol	0.00	0.00	0.00
Triacosanol	15.73	19.44	14.40
Total n-alkanols	131.32	143.58	124.53
Levulinic Acid	31.10	0.00	0.00
Catechol	0.00	0.00	0.00
Glyoxylic Acid	0.00	0.00	0.00
Pyruvic Acid	0.00	0.00	0.00
Anisic Acid	0.00	0.00	0.00
4-Acetylbutyric Acid	0.00	0.00	0.00
Oxalacetic Acid	0.00	0.00	0.00
Vanillic Acid	19.31	17.35	22.04
Syringic Acid	1.43	0.89	1.65

SOAP 2005-2007, Concentration in ng/m^3

	Bronx	Pinnacle
Month-Year	Levoglucosan ng/m^3	Levoglucosan ng/m^3
Oct-05	25.86	65.25
Nov-05	63.26	39.96
Dec-05	95.99	118.78
Jan-06	84.27	113.04
Feb-06	98.77	95.78
Mar-06	50.46	80.27
Apr-06	21.17	31.69
May-06	12.20	3.11
Jun-06	9.00	1.80
Jul-06	7.31	7.36
Aug-06	7.21	17.34
Sep-06	18.43	12.02
Oct-06	43.24	28.99
Nov-06	60.83	57.06
Dec-06	37.05	36.33
Jan-07	85.58	45.53
Feb-07	48.90	34.01

	Bronx ng/m^3			
Month-Year	galactopyranose	mannopyranose	Xylose	Mannose
Oct-05	0.54	1.77	0.00	0.00
Nov-05	0.99	4.04	0.81	0.00
Dec-05	1.68	6.82	0.41	0.75
Jan-06	1.29	5.41	0.00	0.00
Feb-06	2.69	11.90	2.26	0.00
Mar-06	0.24	2.06	0.00	0.00
Apr-06	0.42	1.02	0.00	0.00
May-06	0.26	0.95	0.00	0.00
Jun-06	1.49	1.87	0.56	1.42
Jul-06	0.00	0.00	0.00	0.00
Aug-06	0.00	0.00	0.00	0.00
Sep-06	2.68	0.00	0.00	0.00
Oct-06	0.98	3.62	0.00	0.00
Nov-06	0.57	2.15	0.00	0.00
Dec-06	0.64	2.55	0.11	0.00
Jan-07	2.22	6.91	0.43	0.21
Feb-07	1.09	3.06	0.19	0.00

	Bronx ng/m^3			
Month-Year	Glucose	sucrose	trehalose	maltose
Oct-05	1.66	0.15	0.00	0.00

Nov-05	1.33	0.00	0.00	0.00
Dec-05	0.00	0.00	0.00	0.00
Jan-06	0.24	0.00	0.00	0.00
Feb-06	0.00	0.00	0.00	0.00
Mar-06	0.00	0.00	0.00	0.00
Apr-06	1.21	0.76	0.00	0.00
May-06	0.18	0.14	0.00	0.00
Jun-06	2.46	0.41	0.00	0.00
Jul-06	0.98	0.33	0.00	0.00
Aug-06	2.74	0.00	0.00	0.00
Sep-06	9.97	1.46	0.00	0.00
Oct-06	2.59	0.63	0.00	0.00
Nov-06	0.00	0.15	0.00	0.00
Dec-06	0.00	0.00	0.00	0.00
Jan-07	0.65	0.00	0.00	0.00
Feb-07	0.00	0.00	0.00	0.00

	Pinnacle ng/m^3			
Month-Year	galactopyranose	mannopyranose	Xylose	Mannose
Oct-05	2.68	14.65	0.00	0.00
Nov-05	1.29	4.38	0.00	0.00
Dec-05	2.68	8.30	2.15	0.00
Jan-06	2.17	7.55	0.00	0.00
Feb-06	1.32	4.74	0.00	0.00
Mar-06	1.48	5.94	0.00	0.00
Apr-06	0.22	1.34	0.00	0.00
May-06	0.00	0.00	0.00	0.00
Jun-06	0.03	0.00	0.00	0.00
Jul-06	0.00	0.00	0.00	0.00
Aug-06	0.98	2.16	0.00	0.00
Sep-06	0.36	1.18	0.00	0.00
Oct-06	0.23	1.24	0.00	0.00
Nov-06	1.08	3.56	0.00	0.00
Dec-06	0.26	1.44	0.00	0.06
Jan-07	1.93	6.50	0.00	0.00
Feb-07	0.75	2.88	0.00	0.07

	Pinnacle ng/m^3			
Month-Year	Glucose	sucrose	trehalose	maltose
Oct-05	7.00	1.01	0.00	0.00
Nov-05	0.70	0.00	0.00	0.00
Dec-05	0.00	0.00	0.00	0.00
Jan-06	0.11	0.00	0.00	0.00
Feb-06	0.00	0.00	0.00	0.00

Mar-06	0.25	0.00	0.00	0.00
Apr-06	0.01	0.00	0.00	0.00
May-06	0.00	0.00	0.00	0.00
Jun-06	0.00	0.00	0.00	0.00
Jul-06	1.57	0.00	0.00	0.00
Aug-06	4.36	0.00	0.00	0.00
Sep-06	0.73	0.00	0.00	0.00
Oct-06	0.00	0.00	0.00	0.00
Nov-06	0.00	0.00	0.00	0.00
Dec-06	0.03	0.00	0.00	0.00
Jan-07	0.44	0.00	0.00	0.00
Feb-07	0.14	0.00	0.00	0.00

	Bronx	Pinnacle	Bronx	Pinnacle
Month-Year	Dehydroabietic Acid ng/m^3	Dehydroabietic Acid ng/m^3	Cholesterol ng/m^3	Cholesterol ng/m^3
Oct-05	4.56	111.19	0.40	0.03
Nov-05	11.06	4.75	0.14	0.07
Dec-05	16.21	5.59	0.33	0.00
Jan-06	12.19	18.99	0.39	0.00
Feb-06	21.19	7.71	0.44	0.00
Mar-06	8.91	13.46	0.20	0.00
Apr-06	5.64	10.42	0.04	0.00
May-06	2.84	4.47	0.09	0.00
Jun-06	2.23	1.79	0.09	0.00
Jul-06	4.64	4.85	0.00	0.00
Aug-06	2.95	2.17	0.07	0.00
Sep-06	3.74	2.69	0.14	0.00
Oct-06	5.57	4.54	0.17	0.00
Nov-06	9.98	7.68	0.15	0.00
Dec-06	27.26	5.17	0.11	0.00
Jan-07	10.71	6.37	0.30	0.04
Feb-07	10.52	2.23	0.14	0.00

	Bronx	Pinnacle
Month-Year	cis-Pinonic Acid ng/m^3	cis-Pinonic Acid ng/m^3
Oct-05	0.00	6.07
Nov-05	4.80	3.53
Dec-05	2.49	5.12
Jan-06	0.99	3.72
Feb-06	2.36	2.66
Mar-06	2.35	5.11
Apr-06	1.65	4.40
May-06	4.16	5.79
Jun-06	3.98	4.60

Jul-06	3.73	0.00
Aug-06	3.84	0.00
Sep-06	4.38	2.02
Oct-06	2.31	2.41
Nov-06	3.43	9.88
Dec-06	3.17	3.37
Jan-07	3.11	3.37
Feb-07	1.16	0.00

	Bronx				
	Tetracosanol	Hexacosanol	Octacosanol	Triacosanol	Total n-alkanols
Oct-05	0.39	0.55	0.00	0.00	0.94
Nov-05	0.39	0.32	0.24	0.00	0.94
Dec-05	1.02	0.92	0.62	0.09	2.65
Jan-06	0.36	0.26	0.00	0.00	0.62
Feb-06	1.07	0.62	0.34	0.23	2.26
Mar-06	0.28	0.21	0.13	0.00	0.62
Apr-06	0.00	0.00	0.00	0.00	0.00
May-06	0.44	0.93	0.40	0.00	1.77
Jun-06	0.64	0.97	0.43	0.51	2.54
Jul-06	0.00	0.69	0.00	0.00	0.69
Aug-06	0.22	0.33	0.00	0.00	0.55
Sep-06	0.30	0.81	0.42	0.40	1.93
Oct-06	0.40	0.76	0.44	0.10	1.70
Nov-06	0.00	0.00	0.00	0.00	0.00
Dec-06	0.51	0.41	0.23	0.16	1.31
Jan-07	0.42	0.00	0.15	0.00	0.57
Feb-07	0.41	0.32	0.14	0.00	0.87

	Bronx		
	B-sitosterol	Campesterol	Stigmasterol
Oct-05	0.36	0.00	0.00
Nov-05	0.00	0.00	0.00
Dec-05	0.60	0.00	0.34
Jan-06	0.70	0.00	0.40
Feb-06	0.69	0.00	0.44
Mar-06	0.27	0.00	0.12
Apr-06	0.00	0.00	0.00
May-06	0.10	0.00	0.00
Jun-06	0.00	0.00	0.00

Jul-06	0.00	0.00	0.00
Aug-06	0.10	0.00	0.00
Sep-06	0.18	0.00	0.00
Oct-06	0.23	0.07	0.12
Nov-06	0.00	0.00	0.00
Dec-06	0.26	0.00	0.09
Jan-07	0.43	0.12	0.24
Feb-07	0.25	0.00	0.15

	Pinnacle				
	Tetracosanol	Hexacosanol	Octacosanol	Triacosanol	Total n-alkanols
Oct-05	0.68	1.49	0.64	0.63	3.44
Nov-05	0.90	0.99	0.89	0.41	3.19
Dec-05	0.66	0.56	0.32	0.19	1.73
Jan-06	0.76	0.38	0.12	0.00	1.25
Feb-06	0.70	0.45	0.19	0.07	1.42
Mar-06	0.79	0.65	0.27	0.12	1.83
Apr-06	0.37	0.42	0.22	0.07	1.07
May-06	0.49	1.39	0.47	0.20	2.54
Jun-06	0.27	0.52	0.00	0.00	0.79
Jul-06	0.00	0.64	0.28	0.00	0.92
Aug-06	0.24	0.85	0.33	0.31	1.73
Sep-06	0.14	0.27	0.09	0.00	0.50
Oct-06	0.55	0.94	0.40	0.00	1.89
Nov-06	0.70	0.67	0.24	0.16	1.78
Dec-06	0.52	0.59	0.23	0.13	1.47
Jan-07	0.55	0.36	0.17	0.00	1.08
Feb-07	0.39	0.31	0.13	0.00	0.83

	Pinnacle		
	B-sitosterol	Campesterol	Stigmasterol
Oct-05	0.22	0.00	0.00
Nov-05	0.15	0.00	0.00
Dec-05	0.12	0.00	0.00
Jan-06	0.14	0.00	0.00
Feb-06	0.11	0.00	0.00
Mar-06	0.26	0.00	0.00
Apr-06	0.10	0.00	0.00
May-06	0.07	0.00	0.00

Jun-06	0.00	0.00	0.00
Jul-06	0.00	0.00	0.00
Aug-06	0.00	0.00	0.00
Sep-06	0.00	0.00	0.00
Oct-06	0.06	0.00	0.00
Nov-06	0.00	0.00	0.00
Dec-06	0.07	0.00	0.00
Jan-07	0.13	0.00	0.00
Feb-07	0.08	0.00	0.00

	Bronx				
	Levulinic Acid	Glyoxylic Acid	Pyruvic Acid	4-Acetylbutyric Acid	Oxalacetic Acid
Oct-05	4.64	0.00	0.00	0.79	0.00
Nov-05	8.64	0.00	0.00	1.52	0.00
Dec-05	7.00	0.00	0.00	0.00	0.00
Jan-06	0.00	0.00	0.00	0.00	0.00
Feb-06	0.00	0.00	0.00	0.00	0.00
Mar-06	8.52	0.00	0.00	0.00	0.00
Apr-06	7.34	0.00	0.00	0.95	0.00
May-06	9.12	0.00	0.00	1.12	0.00
Jun-06	11.68	0.00	0.00	1.22	0.00
Jul-06	21.23	0.00	0.00	2.04	0.00
Aug-06	9.55	0.00	0.00	1.08	0.00
Sep-06	10.95	0.00	0.00	1.20	0.00
Oct-06	6.83	0.00	0.00	1.13	0.00
Nov-06	9.17	0.00	0.00	1.36	0.00
Dec-06	4.84	0.00	0.00	0.90	0.00
Jan-07	6.82	0.00	0.00	0.00	0.00
Feb-07	8.74	0.00	0.00	1.58	0.00

	Bronx			
	Vanillic Acid	Syringic Acid	Catechol	Anisic Acid
Oct-05	0.00	0.00	0.00	0.00
Nov-05	0.51	0.00	0.00	0.00
Dec-05	0.00	0.00	0.00	0.00
Jan-06	0.00	0.00	0.00	0.00
Feb-06	0.73	0.00	0.00	0.00
Mar-06	0.00	0.00	0.00	0.00
Apr-06	0.00	0.00	0.00	0.00

May-06	0.00	0.00	0.00	0.00
Jun-06	0.00	0.00	0.00	0.00
Jul-06	0.00	0.00	0.00	0.00
Aug-06	0.00	0.00	0.00	0.00
Sep-06	0.00	0.00	0.00	0.00
Oct-06	0.00	0.00	0.00	0.00
Nov-06	0.00	0.00	0.00	0.00
Dec-06	0.82	0.00	0.00	0.00
Jan-07	0.00	0.00	0.00	0.00
Feb-07	0.00	0.00	0.00	0.00

	Pinnacle				
	Levulinic Acid	Glyoxylic Acid	Pyruvic Acid	4-Acetylbutyric Acid	Oxalacetic Acid
Oct-05	8.74	0.00	0.00	1.24	0.00
Nov-05	4.78	0.00	0.00	0.66	0.00
Dec-05	8.66	0.00	0.00	1.25	0.00
Jan-06	5.34	0.00	0.00	0.00	0.00
Feb-06	8.57	0.00	0.00	0.00	0.00
Mar-06	9.83	0.00	0.00	1.36	0.00
Apr-06	5.31	0.00	0.00	0.98	0.00
May-06	13.22	0.00	0.00	1.54	0.00
Jun-06	8.56	0.00	0.00	1.01	0.00
Jul-06	8.39	0.00	0.00	0.00	0.00
Aug-06	7.36	0.00	0.00	0.55	0.00
Sep-06	6.67	0.00	0.00	0.66	0.00
Oct-06	4.40	0.00	0.00	0.53	0.00
Nov-06	5.85	0.00	0.00	0.00	0.00
Dec-06	6.04	0.00	0.00	0.93	0.00
Jan-07	5.16	0.00	0.00	0.82	0.00
Feb-07	5.99	0.00	0.00	0.86	0.00

	Pinnacle			
	Vanillic Acid	Syringic Acid	Catechol	Anisic Acid
Oct-05	0.00	0.00	0.00	0.00
Nov-05	0.00	0.00	0.00	0.00
Dec-05	0.00	0.00	0.00	0.00
Jan-06	0.65	0.23	0.00	0.00
Feb-06	0.39	0.00	0.00	0.00
Mar-06	0.40	0.00	0.00	0.00

Apr-06	0.31	0.15	0.00	0.00
May-06	0.00	0.00	0.00	0.00
Jun-06	0.00	0.00	0.00	0.00
Jul-06	0.00	0.00	0.00	0.00
Aug-06	0.00	0.00	0.00	0.00
Sep-06	0.00	0.00	0.00	0.00
Oct-06	0.00	0.00	0.00	0.00
Nov-06	0.34	0.11	0.00	0.00
Dec-06	0.00	0.00	0.00	0.00
Jan-07	0.00	0.00	0.00	0.00
Feb-07	0.00	0.00	0.00	0.00

Appendix G: Blank data

SOAP 2002-2003 Samples
Elz = Elizabeth, NJ
Qns = Queens, NY
Wpt = Westport, CT
Chs = Chester, NJ
nd = not detected

Internal standard was added to each blank composite prior to extraction.
Naming schematic is: site name, sample number (number of filters), derivative method

Blank	Elz 1 (1) BSTFA	ELZ 2 (2) BSTFA	ELZ 3 (4) BSTFA	ELZ 3 (4) Duplicate
Compound	Area			
C24 d50 IS	3205020	459435	774593	790105
levoglucosan	nd	nd	nd	nd
galactopyranose	nd	nd	nd	nd
mannopyranose	nd	nd	nd	nd
xylose	nd	nd	nd	nd
mannose	nd	nd	nd	nd
glucose	nd	nd	nd	nd
sucrose	nd	nd	nd	nd
trehalose	nd	nd	nd	nd
maltose	nd	nd	nd	nd
cis-Pinonic Acid	nd	nd	nd	nd
Dehydroabietic Acid	nd	nd	nd	nd
Tetracosanol	nd	nd	nd	nd
Hexacosanol	nd	nd	nd	nd
Octacosanol	nd	nd	nd	nd
Triacosanol	nd	nd	nd	nd
Cholesterol	nd	nd	nd	nd
B-sitosterol	nd	nd	nd	nd
Campesterol	nd	nd	nd	nd
Stigmasterol	nd	nd	nd	nd
Catechol	nd	nd	nd	nd
Anisic Acid	nd	nd	nd	nd
Vanillic Acid	nd	nd	nd	nd
Syringic Acid	nd	nd	nd	nd
Levulinic Acid	nd	nd	nd	nd

Glyoxylic Acid	nd	nd	nd	nd
Pyruvic Acid	nd	nd	nd	nd
4-Acetylbutyric Acid	nd	nd	nd	nd
Oxalacetic Acid	nd	nd	nd	nd

Blank	ELZ 4 (3) BSTFA	ELZ 5 (2) BSTFA	ELZ 5 (2) BSTFA Duplicate
Compound	Area		
C24 d50 IS	1819835	388318	372985
levoglucosan	nd	nd	nd
galactopyranose	nd	nd	nd
mannopyranose	nd	nd	nd
xylose	nd	nd	nd
mannose	nd	nd	nd
glucose	nd	nd	nd
sucrose	nd	nd	nd
trehalose	nd	nd	nd
maltose	nd	nd	nd
cis-Pinonic Acid	nd	nd	nd
Dehydroabietic Acid	nd	nd	nd
Tetracosanol	nd	nd	nd
Hexacosanol	nd	nd	nd
Octacosanol	nd	nd	nd
Triacosanol	nd	nd	nd
Cholesterol	nd	nd	nd
B-sitosterol	nd	nd	nd
Campesterol	nd	nd	nd
Stigmasterol	nd	nd	nd
Catechol	nd	nd	nd
Anisic Acid	nd	nd	nd
Vanillic Acid	nd	nd	nd
Syringic Acid	nd	nd	nd
Levulinic Acid	nd	nd	nd
Glyoxylic Acid	nd	nd	nd
Pyruvic Acid	nd	nd	nd
4-Acetylbutyric Acid	nd	nd	nd
Oxalacetic Acid	nd	nd	nd

Blank	QNS 6 (2) BSTFA	QNS 7 (2) BSTFA	QNS7 (2) BSTFA Duplicate	QNS 8 (4) BSTFA	QNS 9 (3) BSTFA	QNS 10 (3) BSTFA
Compound	Area					
C24 d50 IS	1930910	nd	nd	1719642	789083	1205659
levoglucosan	nd	nd	nd	nd	nd	nd
galactopyranose	nd	nd	nd	nd	nd	nd
mannopyranose	nd	nd	nd	nd	nd	nd
xylose	nd	nd	nd	nd	nd	nd
mannose	nd	nd	nd	nd	nd	nd
glucose	nd	nd	nd	nd	nd	nd
sucrose	nd	nd	nd	nd	nd	nd
trehalose	nd	nd	nd	nd	nd	nd
maltose	nd	nd	nd	nd	nd	nd
cis-Pinonic Acid	nd	nd	nd	nd	nd	nd
Dehydroabietic Acid	nd	nd	nd	nd	nd	nd
Tetracosanol	nd	nd	nd	nd	nd	nd
Hexacosanol	nd	nd	nd	nd	nd	nd
Octacosanol	nd	nd	nd	nd	nd	nd
Triacosanol	nd	nd	nd	nd	nd	nd
Cholesterol	nd	nd	nd	nd	nd	nd
B-sitosterol	nd	nd	nd	nd	nd	nd
Campesterol	nd	nd	nd	nd	nd	nd
Stigmasterol	nd	nd	nd	nd	nd	nd
Catechol	nd	nd	nd	nd	nd	nd
Anisic Acid	nd	nd	nd	nd	nd	nd
Vanillic Acid	nd	nd	nd	nd	nd	nd
Syringic Acid	nd	nd	nd	nd	nd	nd
Levulinic Acid	nd	nd	nd	nd	nd	nd
Glyoxylic Acid	nd	nd	nd	nd	nd	nd
Pyruvic Acid	nd	nd	nd	nd	nd	nd
4-Acetylbutyric Acid	nd	nd	nd	nd	nd	nd
Oxalacetic Acid	nd	nd	nd	nd	nd	nd

Blank	WPT 13 (2) BSTFA	WPT 14 (3) BSTFA	WPT 15 (2) BSTFA
Compound	Area		

C24 d50 IS	2048354	1172771	853016
levoglucosan	nd	nd	nd
galactopyranose	nd	nd	nd
mannopyranose	nd	nd	nd
xylose	nd	nd	nd
mannose	nd	nd	nd
glucose	nd	nd	nd
sucrose	nd	nd	nd
trehalose	nd	nd	nd
maltose	nd	nd	nd
cis-Pinonic Acid	nd	nd	nd
Dehydroabietic Acid	nd	nd	nd
Tetracosanol	nd	nd	nd
Hexacosanol	nd	nd	nd
Octacosanol	nd	nd	nd
Triacosanol	nd	nd	nd
Cholesterol	nd	nd	nd
B-sitosterol	nd	nd	nd
Campesterol	nd	nd	nd
Stigmasterol	nd	nd	nd
Catechol	nd	nd	nd
Anisic Acid	nd	nd	nd
Vanillic Acid	nd	nd	nd
Syringic Acid	nd	nd	nd
Levulinic Acid	nd	nd	nd
Glyoxylic Acid	nd	nd	nd
Pyruvic Acid	nd	nd	nd
4-Acetylbutyric Acid	nd	nd	nd
Oxalacetic Acid	nd	nd	nd

Blank	CHS 16 (1) BSTFA	CHS 17 (4) BSTFA	CHS 18 (3) BSTFA	CHS 19 (2) BSTFA	CHS 20 (2) BSTFA
Compound					
C24 d50 IS	5269	93227	142865	628656	1413245
levoglucosan	nd	nd	nd	nd	nd
galactopyranose	nd	nd	nd	nd	nd
mannopyranose	nd	nd	nd	nd	nd
xylose	nd	nd	nd	nd	nd
mannose	nd	nd	nd	nd	nd

glucose	nd	nd	nd	nd	nd
sucrose	nd	nd	nd	nd	nd
trehalose	nd	nd	nd	nd	nd
maltose	nd	nd	nd	nd	nd
cis-Pinonic Acid	nd	nd	nd	nd	nd
Dehydroabietic Acid	nd	nd	nd	nd	nd
Tetracosanol	nd	nd	nd	nd	nd
Hexacosanol	nd	nd	nd	nd	nd
Octacosanol	nd	nd	nd	nd	nd
Triacosanol	nd	nd	nd	nd	nd
Cholesterol	nd	nd	nd	nd	nd
B-sitosterol	nd	nd	nd	nd	nd
Campesterol	nd	nd	nd	nd	nd
Stigmasterol	nd	nd	nd	nd	nd
Catechol	nd	nd	nd	nd	nd
Anisic Acid	nd	nd	nd	nd	nd
Vanillic Acid	nd	nd	nd	nd	nd
Syringic Acid	nd	nd	nd	nd	nd
Levulinic Acid	nd	nd	nd	nd	nd
Glyoxylic Acid	nd	nd	nd	nd	nd
Pyruvic Acid	nd	nd	nd	nd	nd
4-Acetylbutyric Acid	nd	nd	nd	nd	nd
Oxalacetic Acid	nd	nd	nd	nd	nd

Blank data for SOAP 2005-2007 Samples

NYB = Bronx, NY
NYP = Pinnacle State Park, NY
TB = Trip Blank
FB = Field Blank
nd = not detected
Internal standard was added to each blank composite prior to extraction.
Naming schematic is: sample number, site name (number of filters), derivative method

Compound	35 NYBTB01 (8) BSTFA	36 NYBTB02 (9) BSTFA
C24 d50 IS	1818878	4054587
levoglucosan	nd	nd
galactopyranose	nd	nd
mannopyranose	nd	nd
xylose	nd	nd
mannose	nd	nd
glucose	nd	nd
sucrose	nd	nd
trehalose	nd	nd
maltose	nd	nd
cis-Pinonic Acid	nd	nd
Dehydroabietic Acid	nd	nd
Tetracosanol	nd	nd
Hexacosanol	nd	nd
Octacosanol	nd	nd
Cholesterol	nd	nd
B-sitosterol	nd	nd
Campesterol	nd	nd
Stigmasterol	nd	nd
Triacosanol	nd	nd
Levulinic Acid	nd	nd
Catechol	nd	nd
Glyoxylic Acid	nd	nd
Pyruvic Acid	nd	nd
Anisic Acid	nd	nd
4-Acetylbutyric Acid	nd	nd
Oxalacetic Acid	nd	nd
Vanillic Acid	nd	nd
Syringic Acid	nd	nd

Compound	37 NYBFB01 (7) BSTFA	38 NYBFB02 (5) BSTFA	39 NYBFB03 (6) BSTFA	40 NYBFB04 (6) BSTFA
C24 d50 IS	883559	700302	684269	156906
levoglucosan	nd	nd	nd	nd
galactopyranose	nd	nd	nd	nd
mannopyranose	nd	nd	nd	nd
xylose	nd	nd	nd	nd
mannose	nd	nd	nd	nd
glucose	nd	nd	nd	nd
sucrose	nd	nd	nd	nd
trehalose	nd	nd	nd	nd
maltose	nd	nd	nd	nd
cis-Pinonic Acid	nd	nd	nd	nd
Dehydroabietic Acid	nd	nd	nd	nd
Tetracosanol	nd	nd	nd	nd
Hexacosanol	nd	nd	nd	nd
Octacosanol	nd	nd	nd	nd
Cholesterol	nd	nd	nd	nd
B-sitosterol	nd	nd	nd	nd
Campesterol	nd	nd	nd	nd
Stigmasterol	nd	nd	nd	nd
Triacosanol	nd	nd	nd	nd
Levulinic Acid	nd	nd	nd	nd
Catechol	nd	nd	nd	nd
Glyoxylic Acid	nd	nd	nd	nd
Pyruvic Acid	nd	nd	nd	nd
Anisic Acid	nd	nd	nd	nd
4-Acetylbutyric Acid	nd	nd	nd	nd
Oxalacetic Acid	nd	nd	nd	nd
Vanillic Acid	nd	nd	nd	nd
Syringic Acid	nd	nd	nd	nd

Compound	41 NYPTB01 (18) BSTFA	42 NYPTB02 (18) BSTFA
C24 d50 IS	6125236	2486039
levoglucosan	nd	nd
galactopyranose	nd	nd
mannopyranose	nd	nd

xylose	nd	nd
mannose	nd	nd
glucose	nd	nd
sucrose	nd	nd
trehalose	nd	nd
maltose	nd	nd
cis-Pinonic Acid	nd	nd
Dehydroabietic Acid	nd	nd
Tetracosanol	nd	nd
Hexacosanol	nd	nd
Octacosanol	nd	nd
Cholesterol	nd	nd
B-sitosterol	nd	nd
Campesterol	nd	nd
Stigmasterol	nd	nd
Triacosanol	nd	nd
Levulinic Acid	nd	nd
Catechol	nd	nd
Glyoxylic Acid	nd	nd
Pyruvic Acid	nd	nd
Anisic Acid	nd	nd
4-Acetylbutyric Acid	nd	nd
Oxalacetic Acid	nd	nd
Vanillic Acid	nd	nd
Syringic Acid	nd	nd

Compound	43 NYPFB01 (18) BSTFA	44 NYPFB02 (10) BSTFA	45 NYPFB03 (12) BSTFA	46 NYPFB04 (12) BSTFA
C24 d50 IS	345494	172484	197906	284415
levoglucosan	nd	nd	nd	nd
galactopyranose	nd	nd	nd	nd
mannopyranose	nd	nd	nd	nd
xylose	nd	nd	nd	nd
mannose	nd	nd	nd	nd
glucose	nd	nd	nd	nd
sucrose	nd	nd	nd	nd
trehalose	nd	nd	nd	nd
maltose	nd	nd	nd	nd
cis-Pinonic Acid	nd	nd	nd	nd

Dehydroabietic Acid	nd	nd	nd	nd
Tetracosanol	nd	nd	nd	nd
Hexacosanol	nd	nd	nd	nd
Octacosanol	nd	nd	nd	nd
Cholesterol	nd	nd	nd	nd
B-sitosterol	nd	nd	nd	nd
Campesterol	nd	nd	nd	nd
Stigmasterol	nd	nd	nd	nd
Triacosanol	nd	nd	nd	nd
Levulinic Acid	nd	nd	nd	nd
Catechol	nd	nd	nd	nd
Glyoxylic Acid	nd	nd	nd	nd
Pyruvic Acid	nd	nd	nd	nd
Anisic Acid	nd	nd	nd	nd
4-Acetylbutyric Acid	nd	nd	nd	nd
Oxalacetic Acid	nd	nd	nd	nd
Vanillic Acid	nd	nd	nd	nd
Syringic Acid	nd	nd	nd	nd

Compound	SOAPNY Lab Blank BSTFA
C24 d50 IS	2461222
levoglucosan	nd
galactopyranose	nd
mannopyranose	nd
xylose	nd
mannose	nd
glucose	nd
sucrose	nd
trehalose	nd
maltose	nd
cis-Pinonic Acid	nd
Dehydroabietic Acid	nd
Tetracosanol	nd
Hexacosanol	nd
Octacosanol	nd
Cholesterol	nd
B-sitosterol	nd

Campesterol	nd
Stigmasterol	nd
Triacosanol	nd
Levulinic Acid	nd
Catechol	nd
Glyoxylic Acid	nd
Pyruvic Acid	nd
Anisic Acid	nd
4-Acetylbutyric Acid	nd
Oxalacetic Acid	nd
Vanillic Acid	nd
Syringic Acid	nd

Appendix H: Statistical Analyses (descriptive statistics and outlier tests)

SOAP 2002-2003

Elizabeth, NJ

	Levoglucosan	galactopyranose	mannopyranose
Average	37.32	0.12	0.43
Standard Deviation	41.77	0.16	1.07
Maximum	138.11	0.46	3.42
Minimum	4.34	0.00	0.00
Median	22.82	0.06	0.00
Q_0	4.34	0.00	0.00
Q_1	9.16	0.00	0.00
Q_2	22.82	0.06	0.00
Q_3	48.59	0.17	0.30
Q_4	138.11	0.46	3.42
IQR	39.42	0.17	0.30
Low Outlier	-49.98	-0.26	-0.46
High Outlier	107.72	0.43	0.76
Outlier	late fall	winter	summer

	xylose	mannose	glucose	sucrose	trehalose	maltose
Average	0.10	0.03	0.22	0.16	0.00	0.00
Standard Deviation	0.23	0.07	0.36	0.21	0.00	0.00
Maximum	0.67	0.22	0.85	0.55	0.00	0.00
Minimum	0.00	0.00	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.00	0.06	0.00	0.00
Q_0	0.00	0.00	0.00	0.00	0.00	0.00
Q_1	0.00	0.00	0.00	0.03	0.00	0.00
Q_2	0.00	0.00	0.00	0.06	0.00	0.00
Q_3	0.00	0.00	0.48	0.15	0.00	0.00
Q_4	0.67	0.22	0.85	0.55	0.00	0.00
IQR	0.00	0.00	0.48	0.12	0.00	0.00
Low Outlier	0.00	0.00	-0.72	-0.16	0.00	0.00
High Outlier	0.00	0.00	1.20	0.33	0.00	0.00
Outlier	all detected values	all detected values	none	fall	none	none

	Dehydroabietic Acid ng/m3	Cholesterol ng/m3	cis-Pinonic Acid
Average	36.32	0.24	1.61
Standard Deviation	31.97	0.22	1.95
Maximum	98.97	0.63	5.32
Minimum	12.52	0.00	0.00
Median	23.58	0.23	0.88
Q_0	12.52	0.00	0.00
Q_1	14.37	0.03	0.00
Q_2	23.58	0.23	0.88
Q_3	39.67	0.39	2.39
Q_4	98.97	0.63	5.32
IQR	25.29	0.35	2.39
Low Outlier	-23.57	-0.50	-3.58
High Outlier	77.61	0.92	5.96
Outlier	summer, early spring	none	none

	Tetracosanol	Hexacosanol	Octacosanol	Triacosanol	Total n-alkanols
Average	1.32	2.19	0.10	0.00	3.61
Standard Deviation	1.21	2.94	0.18	0.00	4.04
Maximum	4.53	10.07	0.47	0.00	14.60
Minimum	0.25	0.00	0.00	0.00	0.37
Median	0.95	1.05	0.00	0.00	2.21
Q_0	0.25	0.00	0.00	0.00	0.37
Q_1	0.81	0.83	0.00	0.00	1.79
Q_2	0.95	1.05	0.00	0.00	2.21
Q_3	1.08	2.47	0.13	0.00	3.82
Q_4	4.53	10.07	0.47	0.00	14.60
IQR	0.27	1.64	0.13	0.00	2.03
Low Outlier	0.40	-1.64	-0.19	0.00	-1.25
High Outlier	1.49	4.93	0.32	0.00	6.87
Outlier	early summer	early summer	winter	none	early summer

	B-sitosterol	Campesterol	Stigmasterol
Average	1.41	0.04	0.29
Standard Deviation	3.69	0.10	0.84
Maximum	11.91	0.29	2.68
Minimum	0.00	0.00	0.00
Median	0.30	0.00	0.00
Q_0	0.00	0.00	0.00
Q_1	0.04	0.00	0.00
Q_2	0.30	0.00	0.00
Q_3	0.44	0.00	0.00
Q_4	11.91	0.29	2.68
IQR	0.40	0.00	0.00
Low Outlier	-0.56	0.00	0.00
High Outlier	1.04	0.00	0.00
Outlier	fall	all detected values	all detected values

	Levulinic Acid	Glyoxylic Acid	Pyruvic Acid	4-Acetylbutyric Acid	Oxalacetic Acid
Average	2.50	0.00	0.00	0.30	0.00
Standard Deviation	5.78	0.00	0.00	0.65	0.00
Maximum	17.54	0.00	0.00	1.80	0.00
Minimum	0.00	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.00	0.00	0.00
Q_0	0.00	0.00	0.00	0.00	0.00
Q_1	0.00	0.00	0.00	0.00	0.00
Q_2	0.00	0.00	0.00	0.00	0.00
Q_3	0.00	0.00	0.00	0.00	0.00
Q_4	17.54	0.00	0.00	1.80	0.00
IQR	0.00	0.00	0.00	0.00	0.00
Low Outlier	0.00	0.00	0.00	0.00	0.00
High Outlier	0.00	0.00	0.00	0.00	0.00
Outlier	all detected values	none	none	all detected values	none

	Catechol	Anisic Acid	Vanillic Acid	Syringic Acid
Average	0.00	0.00	0.00	0.00
Standard Deviation	0.00	0.00	0.00	0.00
Maximum	0.00	0.00	0.00	0.00
Minimum	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.00	0.00
Q_0	0.00	0.00	0.00	0.00
Q_1	0.00	0.00	0.00	0.00
Q_2	0.00	0.00	0.00	0.00
Q_3	0.00	0.00	0.00	0.00
Q_4	0.00	0.00	0.00	0.00
IQR	0.00	0.00	0.00	0.00
Low Outlier	0.00	0.00	0.00	0.00
High Outlier	0.00	0.00	0.00	0.00
Outlier	none	none	none	none

Queens, NY

	Levoglucosan	galactopyranose	mannopyranose
Average	51.04	0.18	1.15
Standard Deviation	50.36	0.35	2.90
Maximum	146.92	1.10	9.29
Minimum	2.36	0.00	0.00
Median	30.45	0.02	0.00
Q_0	2.36	0.00	0.00
Q_1	10.49	0.00	0.00
Q_2	30.45	0.02	0.00
Q_3	86.49	0.14	0.55
Q_4	146.92	1.10	9.29
IQR	76.00	0.14	0.55
Low Outlier	-103.51	-0.21	-0.82
High Outlier	200.49	0.36	1.36
Outlier	none	early summer, early winter	early summer, fall

	xylose	mannose	glucose	sucrose	trehalose	maltose
Average	0.06	0.04	0.19	0.13	0.01	0.00
Standard Deviation	0.12	0.12	0.26	0.16	0.05	0.00
Maximum	0.30	0.37	0.78	0.57	0.15	0.00
Minimum	0.00	0.00	0.00	0.02	0.00	0.00
Median	0.00	0.00	0.10	0.06	0.00	0.00
Q_0	0.00	0.00	0.00	0.02	0.00	0.00
Q_1	0.00	0.00	0.00	0.05	0.00	0.00
Q_2	0.00	0.00	0.10	0.06	0.00	0.00
Q_3	0.00	0.00	0.24	0.10	0.00	0.00
Q_4	0.30	0.37	0.78	0.57	0.15	0.00
IQR	0.00	0.00	0.24	0.05	0.00	0.00
Low Outlier	0.00	0.00	-0.36	-0.03	0.00	0.00
High Outlier	0.00	0.00	0.60	0.18	0.00	0.00
Outlier	all detected values	all detected values	early fall	early summer, summer	all detected values	none

	dehydroabietic acid	Cholesterol	cis-Pinonic Acid
Average	30.48	0.20	1.53
Standard Deviation	24.30	0.24	1.46
Maximum	84.98	0.78	3.40
Minimum	9.13	0.00	0.00
Median	23.01	0.15	1.25
Q_0	9.13	0.00	0.00
Q_1	13.76	0.02	0.14
Q_2	23.01	0.15	1.25
Q_3	36.89	0.22	2.98
Q_4	84.98	0.78	3.40
IQR	23.13	0.20	2.84
Low Outlier	-20.93	-0.28	-4.12
High Outlier	71.58	0.51	7.23
Outlier	early summer	early winter	none

	Tetracosanol	Hexacosanol	Octacosanol	Triacosanol	Total n-alkanols
Average	1.45	2.41	0.66	0.35	4.86
Standard Deviation	0.79	1.99	0.79	0.50	3.90
Maximum	3.01	6.56	2.21	1.29	12.92
Minimum	0.55	0.26	0.00	0.00	0.82
Median	1.40	1.72	0.44	0.07	3.53
Q_0	0.55	0.26	0.00	0.00	0.82
Q_1	0.79	1.16	0.00	0.00	2.18
Q_2	1.40	1.72	0.44	0.07	3.53
Q_3	1.83	3.09	1.05	0.57	6.26
Q_4	3.01	6.56	2.21	1.29	12.92
IQR	1.04	1.93	1.05	0.57	4.08
Low Outlier	-0.77	-1.73	-1.57	-0.85	-3.94
High Outlier	3.39	5.99	2.62	1.41	12.39
Outlier	none	early summer	none	none	early summer

	B-sitosterol	Campesterol	Stigmasterol
Average	7.15	0.01	1.22
Standard Deviation	21.63	0.03	3.86
Maximum	68.72	0.10	12.19
Minimum	0.00	0.00	0.00
Median	0.43	0.00	0.00
Q_0	0.00	0.00	0.00
Q_1	0.03	0.00	0.00
Q_2	0.43	0.00	0.00
Q_3	0.60	0.00	0.00
Q_4	68.72	0.10	12.19
IQR	0.58	0.00	0.00
Low Outlier	-0.83	0.00	0.00
High Outlier	1.47	0.00	0.00
Outlier	early winter	all detected values	all detected values

	Levulinic Acid	Glyoxylic Acid	Pyruvic Acid	4-Acetylbutyric Acid	Oxalacetic Acid
Average	2.71	0.00	142.10	0.58	2535.66
Standard Deviation	4.40	0.00	449.37	0.76	8018.45
Maximum	10.19	0.00	1421.04	1.70	25356.58
Minimum	0.00	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.00	0.00	0.00
Q_0	0.00	0.00	0.00	0.00	0.00
Q_1	0.00	0.00	0.00	0.00	0.00
Q_2	0.00	0.00	0.00	0.00	0.00
Q_3	5.88	0.00	0.00	1.28	0.00
Q_4	10.19	0.00	1421.04	1.70	25356.58
IQR	5.88	0.00	0.00	1.28	0.00
Low Outlier	-8.82	0.00	0.00	-1.92	0.00
High Outlier	14.70	0.00	0.00	3.21	0.00
Outlier	none	none	summer	none	early fall

	Catechol	Anisic Acid	Vanillic Acid	Syringic Acid
Average	0.00	0.00	0.00	0.00
Standard Deviation	0.00	0.00	0.00	0.00
Maximum	0.00	0.00	0.00	0.00
Minimum	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.00	0.00
Q_0	0.00	0.00	0.00	0.00
Q_1	0.00	0.00	0.00	0.00
Q_2	0.00	0.00	0.00	0.00
Q_3	0.00	0.00	0.00	0.00
Q_4	0.00	0.00	0.00	0.00
IQR	0.00	0.00	0.00	0.00
Low Outlier	0.00	0.00	0.00	0.00
High Outlier	0.00	0.00	0.00	0.00
Outlier	none	none	none	none

Chester, NJ

	Levoglucosan	galactopyranose	mannopyranose
Average	30.43	0.49	0.60
Standard Deviation	24.97	0.71	0.92
Maximum	80.15	2.41	2.36
Minimum	2.73	0.05	0.00
Median	25.03	0.22	0.00
Q_0	2.73	0.05	0.00
Q_1	15.67	0.17	0.00
Q_2	25.03	0.22	0.00
Q_3	26.58	0.48	1.23
Q_4	80.15	2.41	2.36
IQR	10.91	0.31	1.23
Low Outlier	-0.70	-0.29	-1.84
High Outlier	42.94	0.95	3.07
Outlier	late fall, early winter	summer	none

	xylose	mannose	glucose	sucrose	trehalose	maltose
Average	0.02	0.06	0.34	0.28	0.00	0.00
Standard Deviation	0.06	0.11	0.92	0.59	0.00	0.00
Maximum	0.19	0.30	2.96	1.95	0.00	0.00
Minimum	0.00	0.00	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.00	0.09	0.00	0.00
Q_0	0.00	0.00	0.00	0.00	0.00	0.00
Q_1	0.00	0.00	0.00	0.04	0.00	0.00
Q_2	0.00	0.00	0.00	0.09	0.00	0.00
Q_3	0.00	0.09	0.13	0.13	0.00	0.00
Q_4	0.19	0.30	2.96	1.95	0.00	0.00
IQR	0.00	0.09	0.13	0.09	0.00	0.00
Low Outlier	0.00	-0.14	-0.19	-0.09	0.00	0.00
High Outlier	0.00	0.24	0.32	0.26	0.00	0.00
Outlier	all detected values	early spring	summer	fall, late fall	none	none

	dehydroabietic acid	cholesterol	cis-Pinonic Acid
Average	27.09	0.07	2.78
Standard Deviation	19.21	0.21	2.77
Maximum	53.91	0.66	7.91
Minimum	7.50	0.00	0.00
Median	15.74	0.00	3.01
Q_0	7.50	0.00	0.00
Q_1	12.27	0.00	0.04
Q_2	15.74	0.00	3.01
Q_3	47.10	0.02	4.06
Q_4	53.91	0.66	7.91
IQR	34.83	0.02	4.02
Low Outlier	-39.98	-0.03	-6.00
High Outlier	99.34	0.05	10.09
Outlier	none	winter	none

	Tetracosanol	Hexacosanol	Octacosanol	Triacosanol	Total n-alkanols
Average	1.08	1.25	0.25	0.03	2.61
Standard Deviation	0.48	1.03	0.42	0.09	1.85
Maximum	1.66	3.18	1.17	0.29	5.93
Minimum	0.46	0.00	0.00	0.00	0.46
Median	1.08	1.02	0.00	0.00	2.36
Q_0	0.46	0.00	0.00	0.00	0.46
Q_1	0.60	0.63	0.00	0.00	1.26
Q_2	1.08	1.02	0.00	0.00	2.36
Q_3	1.51	1.74	0.34	0.00	3.32
Q_4	1.66	3.18	1.17	0.29	5.93
IQR	0.90	1.11	0.34	0.00	2.06
Low Outlier	-0.75	-1.04	-0.51	0.00	-1.84
High Outlier	2.86	3.41	0.84	0.00	6.42
Outlier	none	none	spring	all detected values	none

	B-sitosterol	Campesterol	Stigmasterol
Average	0.09	0.00	0.00
Standard Deviation	0.16	0.00	0.00
Maximum	0.41	0.00	0.00
Minimum	0.00	0.00	0.00
Median	0.00	0.00	0.00
Q_0	0.00	0.00	0.00
Q_1	0.00	0.00	0.00
Q_2	0.00	0.00	0.00
Q_3	0.16	0.00	0.00
Q_4	0.41	0.00	0.00
IQR	0.16	0.00	0.00
Low Outlier	-0.24	0.00	0.00
High Outlier	0.40	0.00	0.00
Outlier	none	none	none

	Levulinic Acid	Glyoxylic Acid	Pyruvic Acid	4-Acetylbutyric Acid	Oxalacetic Acid
Average	4.54	0.00	0.00	0.30	0.00
Standard Deviation	6.98	0.00	0.00	0.64	0.00
Maximum	21.00	0.00	0.00	1.65	0.00
Minimum	0.00	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.00	0.00	0.00
Q_0	0.00	0.00	0.00	0.00	0.00
Q_1	0.00	0.00	0.00	0.00	0.00
Q_2	0.00	0.00	0.00	0.00	0.00
Q_3	8.12	0.00	0.00	0.00	0.00
Q_4	21.00	0.00	0.00	1.65	0.00
IQR	8.12	0.00	0.00	0.00	0.00
Low Outlier	-12.17	0.00	0.00	0.00	0.00
High Outlier	20.29	0.00	0.00	0.00	0.00
Outlier	early summer	none	none	all detected values	none

	Catechol	Anisic Acid	Vanillic Acid	Syringic Acid
Average	0.00	0.00	0.00	0.00
Standard Deviation	0.00	0.00	0.00	0.00
Maximum	0.00	0.00	0.00	0.00
Minimum	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.00	0.00
Q_0	0.00	0.00	0.00	0.00
Q_1	0.00	0.00	0.00	0.00
Q_2	0.00	0.00	0.00	0.00
Q_3	0.00	0.00	0.00	0.00
Q_4	0.00	0.00	0.00	0.00
IQR	0.00	0.00	0.00	0.00
Low Outlier	0.00	0.00	0.00	0.00
High Outlier	0.00	0.00	0.00	0.00
Outlier	none	none	none	none

Westport, CT

	Levoglucosan	galactopyranose	mannopyranose
Average	77.63	1.41	1.51
Standard Deviation	66.27	2.17	1.75
Maximum	189.47	6.94	3.71
Minimum	3.36	0.03	0.00
Median	72.67	0.90	0.26
Q_0	3.36	0.03	0.00
Q_1	9.07	0.11	0.00
Q_2	72.67	0.90	0.26
Q_3	120.89	1.44	3.22
Q_4	189.47	6.94	3.71
IQR	111.83	1.33	3.22
Low Outlier	-158.67	-1.89	-4.83
High Outlier	288.63	3.45	8.05
Outlier	none	late fall	none

	xylose	mannose	glucose	sucrose	trehalose	maltose
Average	0.00	0.22	0.21	0.05	0.02	0.00
Standard Deviation	0.00	0.36	0.34	0.03	0.05	0.00
Maximum	0.00	1.12	0.94	0.10	0.16	0.00
Minimum	0.00	0.00	0.00	0.00	0.00	0.00
Median	0.00	0.08	0.05	0.05	0.00	0.00
Q_0	0.00	0.00	0.00	0.00	0.00	0.00
Q_1	0.00	0.00	0.00	0.03	0.00	0.00
Q_2	0.00	0.08	0.05	0.05	0.00	0.00
Q_3	0.00	0.29	0.15	0.08	0.00	0.00
Q_4	0.00	1.12	0.94	0.10	0.16	0.00
IQR	0.00	0.29	0.15	0.05	0.00	0.00
Low Outlier	0.00	-0.43	-0.23	-0.05	0.00	0.00
High Outlier	0.00	0.72	0.38	0.16	0.00	0.00
Outlier	none	late fall	fall, late fall	none	all detected values	none

	dehydroabietic acid	cholesterol	cis-Pinonic Acid
Average	24.38	0.02	2.55
Standard Deviation	19.36	0.03	1.80
Maximum	61.07	0.07	5.20
Minimum	1.61	0.00	0.00
Median	21.62	0.00	2.70
Q_0	1.61	0.00	0.00
Q_1	10.69	0.00	1.76
Q_2	21.62	0.00	2.70
Q_3	28.82	0.00	3.26
Q_4	61.07	0.07	5.20
IQR	18.13	0.00	1.50
Low Outlier	-16.49	0.00	-0.49
High Outlier	56.01	0.00	5.51
Outlier	early spring	all detected values	none

	Tetracosanol	Hexacosanol	Octacosanol	Triacosanol	Total n-alkanols
Average	0.79	0.89	0.21	0.07	1.96
Standard Deviation	0.53	0.51	0.25	0.10	1.28
Maximum	1.87	1.94	0.74	0.24	4.79
Minimum	0.23	0.24	0.00	0.00	0.54
Median	0.82	0.76	0.17	0.00	1.62
Q_0	0.23	0.24	0.00	0.00	0.54
Q_1	0.44	0.60	0.00	0.00	1.20
Q_2	0.82	0.76	0.17	0.00	1.62
Q_3	0.85	1.08	0.26	0.15	2.40
Q_4	1.87	1.94	0.74	0.24	4.79
IQR	0.41	0.48	0.26	0.15	1.20
Low Outlier	-0.17	-0.12	-0.39	-0.23	-0.60
High Outlier	1.47	1.80	0.66	0.38	4.20
Outlier	early winter	early winter	early winter	none	early winter

	B-sitosterol	Campesterol	Stigmasterol
Average	0.38	0.00	0.00
Standard Deviation	0.47	0.00	0.00
Maximum	1.41	0.00	0.00
Minimum	0.00	0.00	0.00
Median	0.14	0.00	0.00
Q_0	0.00	0.00	0.00
Q_1	0.00	0.00	0.00
Q_2	0.14	0.00	0.00
Q_3	0.59	0.00	0.00
Q_4	1.41	0.00	0.00
IQR	0.59	0.00	0.00
Low Outlier	-0.88	0.00	0.00
High Outlier	1.47	0.00	0.00
Outlier	none	none	none

	Levulinic Acid	Glyoxylic Acid	Pyruvic Acid	4-Acetylbutyric Acid	Oxalacetic Acid
Average	5.35	0.00	0.00	0.63	0.00
Standard Deviation	6.44	0.00	0.00	0.96	0.00
Maximum	16.82	0.00	0.00	2.13	0.00
Minimum	0.00	0.00	0.00	0.00	0.00
Median	1.97	0.00	0.00	0.00	0.00
Q_0	0.00	0.00	0.00	0.00	0.00
Q_1	0.00	0.00	0.00	0.00	0.00
Q_2	1.97	0.00	0.00	0.00	0.00
Q_3	11.31	0.00	0.00	1.57	0.00
Q_4	16.82	0.00	0.00	2.13	0.00
IQR	11.31	0.00	0.00	1.57	0.00
Low Outlier	-16.96	0.00	0.00	-2.35	0.00
High Outlier	28.27	0.00	0.00	3.92	0.00
Outlier	none	none	none	none	none

	Catechol	Anisic Acid	Vanillic Acid	Syringic Acid
Average	0.00	0.00	0.00	0.02
Standard Deviation	0.00	0.00	0.00	0.05
Maximum	0.00	0.00	0.00	0.15
Minimum	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.00	0.00
Q_0	0.00	0.00	0.00	0.00
Q_1	0.00	0.00	0.00	0.00
Q_2	0.00	0.00	0.00	0.00
Q_3	0.00	0.00	0.00	0.00
Q_4	0.00	0.00	0.00	0.15
IQR	0.00	0.00	0.00	0.00
Low Outlier	0.00	0.00	0.00	0.00
High Outlier	0.00	0.00	0.00	0.00
Outlier	none	none	none	all detected values

SOAP NY 2005-2007

Bronx, NY

	Levoglucosan	galactopyranose	mannopyranose
Average	45.27	1.05	3.18
Standard Deviation	31.85373267	0.863041	3.117725
Maximum	98.77	2.69	11.90
Minimum	7.21	0.00	0.00
Median	43.24	0.98	2.15
Q_0	7.213858949	0	0
Q_1	18.43290624	0.42	1.02
Q_2	43.2358044	0.98	2.14861
Q_3	63.25786184	1.49	4.039152
Q_4	98.77140183	2.69	11.9
IQR	44.8249556	1.07	3.019152
Low Outlier	-48.8045272	-1.185	-3.50873
High Outlier	130.4952952	3.095	8.567879
Outlier	none	none	Feb-06

	Xylose	Mannose	Glucose	sucrose	trehalose	maltose
Average	0.28	0.14	1.41	0.24	0.00	0.00
Standard Deviation	0.566614	0.3773	2.412664	0.394737	0	0
Maximum	2.26	1.42	9.97	1.46	0.00	0.00
Minimum	0.00	0.00	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.65	0.00	0.00	0.00
Q_0	0	0	0	0	0	0
Q_1	0	0	0	0	0	0
Q_2	0	0	0.650484	0	0	0
Q_3	0.41	0	1.65693	0.333817	0	0
Q_4	2.258962	1.415259	9.965868	1.46	0	0
IQR	0.41	0	1.65693	0.333817	0	0
Low Outlier	-0.615	0	-2.4854	-0.50073	0	0
High Outlier	1.025	0	4.142326	0.834542	0	0
Outlier	none	all detected values	Sep-06	Sep-06	none	none

	Dehydroabietic Acid	cholesterol	cis-Pinonic Acid

Average	9.42	0.19	2.82
Standard Deviation	6.898074512	0.132271	1.327421
Maximum	27.26	0.44	4.80
Minimum	2.23	0.00	0.00
Median	8.91	0.14	3.11
Q_0	2.232768357	0	0
Q_1	4.560602056	0.093447	2.311244
Q_2	8.914582519	0.144354	3.112209
Q_3	11.05548784	0.296521	3.842246
Q_4	27.258474	0.436726	4.801414
IQR	6.494885788	0.203074	1.531002
Low Outlier	-5.181726626	-0.21117	0.014742
High Outlier	20.79781653	0.601133	6.138749
Outlier	Feb-06; Dec-06	none	none

	β-sitosterol	Campesterol	Stigmasterol
Average	0.25	0.01	0.11
Standard Deviation	0.240575	0.032765	0.152858
Maximum	0.70	0.12	0.44
Minimum	0.00	0.00	0.00
Median	0.23	0.00	0.00
Q_0	0	0	0
Q_1	0	0	0
Q_2	0.23	0	0
Q_3	0.36	0	0.15
Q_4	0.7	0.12	0.44
IQR	0.36	0	0.15
Low Outlier	-0.54	0	-0.225
High Outlier	0.9	0	0.375
Outlier	none	all detected values	Jan-06, Feb-06

	Tetracosanol	Hexacosanol	Octacosanol	Triacosanol	Total n-alkanols
Average	0.40	0.48	0.21	0.09	1.17
Standard Deviation	0.30037	0.333821	0.201129	0.155344	0.829405
Maximum	1.07	0.97	0.62	0.51	2.65
Minimum	0.00	0.00	0.00	0.00	0.00
Median	0.39	0.41	0.15	0.00	0.94

Q_0	0	0	0	0	0
Q_1	0.28	0.26	0	0	0.62
Q_2	0.39	0.41	0.15	0	0.94
Q_3	0.44	0.76	0.4	0.1	1.77
Q_4	1.07	0.97	0.62	0.51	2.65
IQR	0.16	0.5	0.4	0.1	1.15
Low Outlier	0.04	-0.49	-0.6	-0.15	-1.105
High Outlier	0.68	1.51	1	0.25	3.495
Outlier	high and low	none	none	two	none

	Levulinic Acid	Glyoxylic Acid	Pyruvic Acid	4-Acetylbutyric Acid	Oxalacetic Acid
Average	7.95	0.00	0.00	0.88	0.00
Standard Deviation	4.723296	0	0	0.648981	0
Maximum	21.23	0.00	0.00	2.04	0.00
Minimum	0.00	0.00	0.00	0.00	0.00
Median	8.52	0.00	0.00	1.08	0.00
Q_0	0	0	0	0	0
Q_1	6.82	0	0	0	0
Q_2	8.52	0	0	1.08	0
Q_3	9.17	0	0	1.22	0
Q_4	21.23	0	0	2.04	0
IQR	2.35	0	0	1.22	0
Low Outlier	3.295	0	0	-1.83	0
High Outlier	12.695	0	0	3.05	0
Outlier	Jul-06	none	none	none	none

	Vanillic Acid	Syringic Acid	Catechol	Anisic Acid
Average	0.12	0.00	0.00	0.00
Standard Deviation	0.275656	0	0	0
Maximum	0.82	0.00	0.00	0.00
Minimum	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.00	0.00
Q_0	0	0	0	0
Q_1	0	0	0	0

Q_2	0	0	0	0
Q_3	0	0	0	0
Q_4	0.82	0	0	0
IQR	0	0	0	0
Low Outlier	0	0	0	0
High Outlier	0	0	0	0
Outlier	all detectable	none	none	none

Pinnacle State Park, NY

	Levoglucosan	galactopyranose	mannopyranose
Average	46.37	1.03	3.87
Standard Deviation	37.05186	0.918445	3.848047
Maximum	118.78	2.68	14.65
Minimum	1.80	0.00	0.00
Median	36.33	0.98	2.88
Q_0	1.802803	0	0
Q_1	17.34359	0.233369	1.235167
Q_2	36.32864	0.977734	2.879093
Q_3	65.25235	1.480854	5.936778
Q_4	118.7847	2.684496	14.64766
IQR	47.90876	1.247484	4.701612
Low Outlier	-54.5196	-1.63786	-5.81725
High Outlier	137.1155	3.35208	12.9892
Outlier	none	none	Oct-05

	Xylose	Mannose	Glucose	sucrose	trehalose	maltose
Average	0.13	0.01	0.90	0.06	0.00	0.00
Standard Deviation	0.522146	0.021107	1.902181	0.244961	0	0
Maximum	2.15	0.07	7.00	1.01	0.00	0.00
Minimum	0.00	0.00	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.11	0.00	0.00	0.00
Q_0	0	0	0	0	0	0
Q_1	0	0	0	0	0	0
Q_2	0	0	0.107122	0	0	0
Q_3	0	0	0.700862	0	0	0
Q_4	2.152865	0.07	6.998208	1.01	0	0
IQR	0	0	0.700862	0	0	0
Low	0	0	-1.05129	0	0	0

Outlier						
High Outlier	0	0	1.752154	0	0	0
Outlier	Dec-05	Feb-07	10/2005; 8/2006	Oct-05	none	none

	Dehydroabietic Acid	cholesterol	cis-Pinonic Acid
Average	12.59	0.01	3.65
Standard Deviation	25.79062	0.020409	2.504857
Maximum	111.19	0.07	9.88
Minimum	1.79	0.00	0.00
Median	5.17	0.00	3.53
Q_0	1.785458	0	0
Q_1	4.47449	0	2.405626
Q_2	5.168237	0	3.527569
Q_3	7.706423	0	5.114744
Q_4	111.192	0.07332	9.879395
IQR	3.231933	0	2.709118
Low Outlier	-0.37341	0	-1.65805
High Outlier	12.55432	0	9.178422
Outlier	111.19, 18.99	all detected values	Nov-06

	Tetracosanol	Hexacosanol	Octacosanol	Triacosanol	Total n-alkanols
Average	0.51	0.68	0.29	0.13	1.62
Standard Deviation	0.247703	0.355407	0.215608	0.175966	0.815515
Maximum	0.90	1.49	0.89	0.63	3.44
Minimum	0.00	0.27	0.00	0.00	0.50
Median	0.55	0.59	0.24	0.07	1.47
Q_0	0	0.27	0	0	0.5
Q_1	0.37	0.42	0.17	0	1.07
Q_2	0.55	0.59	0.24	0.07	1.47
Q_3	0.7	0.85	0.33	0.19	1.83
Q_4	0.9	1.49	0.89	0.63	3.44
IQR	0.33	0.43	0.16	0.19	0.76
Low Outlier	-0.125	-0.225	-0.07	-0.285	-0.07
High Outlier	1.195	1.495	0.57	0.475	2.97
Outlier	none	none	Oct/2005; Nov/2005	Oct-05	Oct/2005; Nov/2005

	β-sitosterol	Campesterol	Stigmasterol
Average	0.09	0.00	0.00
Standard Deviation	0.077933	0	0
Maximum	0.26	0.00	0.00
Minimum	0.00	0.00	0.00
Median	0.08	0.00	0.00
Q_0	0	0	0
Q_1	0	0	0
Q_2	0.08	0	0
Q_3	0.13	0	0
Q_4	0.26	0	0
IQR	0.13	0	0
Low Outlier	-0.195	0	0
High Outlier	0.325	0	0
Outlier	none	none	none

	Levulinic Acid	Glyoxylic Acid	Pyruvic Acid	4-Acetylbutyric Acid	Oxalacetic Acid
Average	7.23	0.00	0.00	0.73	0.00
Standard Deviation	2.272368	0	0	0.500198	0
Maximum	13.22	0.00	0.00	1.54	0.00
Minimum	4.40	0.00	0.00	0.00	0.00
Median	6.67	0.00	0.00	0.82	0.00
Q_0	4.4	0	0	0	0
Q_1	5.34	0	0	0.53	0
Q_2	6.67	0	0	0.82	0
Q_3	8.57	0	0	1.01	0
Q_4	13.22	0	0	1.54	0
IQR	3.23	0	0	0.48	0
Low Outlier	0.495	0	0	-0.19	0
High Outlier	13.415	0	0	1.73	0
Outlier	none	none	none	none	none

	Vanillic Acid	Syringic Acid	Catechol	Anisic Acid
Average	0.12	0.03	0.00	0.00
Standard Deviation	0.207568	0.06772	0	0
Maximum	0.65	0.23	0.00	0.00
Minimum	0.00	0.00	0.00	0.00
Median	0.00	0.00	0.00	0.00
Q_0	0	0	0	0
Q_1	0	0	0	0
Q_2	0	0	0	0
Q_3	0.31	0	0	0
Q_4	0.65	0.23	0	0
IQR	0.31	0	0	0
Low Outlier	-0.465	0	0	0
High Outlier	0.775	0	0	0
Outlier	none	all detected values	none	none

Appendix I: Statistical Analyses (Anova tables)

SOAP 2002-2003 seasonal variations at each site. The alpha value was 0.05.
SS = sum of squares
df = degrees of freedom

Elizabeth, NJ						
Levoglucosan	Column 1	Column 2				
early summer	28.50	16.65	early fall			
summer	55.28	72.65	fall			
early spring	21.52	138.11	late fall			
spring	4.34	24.12	early winter			
late spring	5.39	6.66	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	115.03	23.01	433.16		
Column 2	5.00	258.20	51.64	2980.90		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2049.79	1.00	2049.79	1.20	0.31	5.32
Within Groups	13656.25	8.00	1707.03			
Total	15706.04	9.00				

Elizabeth, NJ						
cis-Pinonic Acid	Column 1	Column 2				
early summer	5.32	0.00	early fall			
summer	0.00	2.34	fall			
early spring	0.00	0.00	late fall			
spring	2.40	1.42	early winter			
late spring	4.29	0.35	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		

Column 1	5.00	12.01	2.40	5.91		
Column 2	5.00	4.11	0.82	1.06		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6.25	1.00	6.25	1.79	0.22	5.32
Within Groups	27.87	8.00	3.48			
Total	34.12	9.00				

Elizabeth, NJ						
Total n-alkanols	Column 1	Column 2				
summer early	14.60	3.52	fall early			
summer	4.24	1.76	fall			
spring early	0.37	2.20	fall late			
spring	3.92	1.90	winter early			
spring late	2.22	1.37	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	25.36	5.07	30.77		
Column 2	5.00	10.73	2.15	0.68		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	21.38	1.00	21.38	1.36	0.28	5.32
Within Groups	125.80	8.00	15.72			
Total	147.18	9.00				

Elizabeth, NJ						
Cholesterol ng/m3	Column 1	Column 2				
early summer	0.63	0.00	early fall			
summer	0.13	0.49	fall			
early spring	0.00	0.27	late fall			
spring	0.23	0.00	early winter			
late spring	0.42	0.23	winter			
Anova: Single Factor						
SUMMARY						

Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	1.41	0.28	0.06		
Column 2	5.00	1.00	0.20	0.04		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.02	1.00	0.02	0.33	0.58	5.32
Within Groups	0.42	8.00	0.05			
Total	0.43	9.00				

Elizabeth, NJ						
Levulinic Acid	Column 1	Column 2				
summer early	17.54	0.00	fall early			
summer	0.00	0.00	fall			
spring early	0.00	0.00	fall late			
spring	0.00	0.00	winter early			
spring late	0.00	7.42	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	17.54	3.51	61.50		
Column 2	5.00	7.42	1.48	11.00		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	10.24	1.00	10.24	0.28	0.61	5.32
Within Groups	290.00	8.00	36.25			
Total	300.24	9.00				

Queens, NY						
Levoglucosan	Column 1	Column 2				
early summer	78.98	9.86	early fall			
summer	23.24	88.99	fall			
early spring	12.38	146.92	late fall			
spring	2.36	104.33	early winter			
late spring	5.70	37.66	winter			
Anova: Single Factor						
SUMMARY						

Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	122.66	24.53	989.99		
Column 2	5.00	387.75	77.55	2958.55		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	7027.28	1.00	7027.28	3.56	0.10	5.32
Within Groups	15794.15	8.00	1974.27			
Total	22821.44	9.00				

Queens, NY						
cis-Pinonic Acid	Column 1	Column 2				
early summer	3.17	3.40	early fall			
summer	1.92	0.00	fall			
early spring	2.40	0.00	late fall			
spring	3.33	0.00	early winter			
late spring	0.55	0.58	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	11.36	2.27	1.26		
Column 2	5.00	3.98	0.80	2.18		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5.44	1.00	5.44	3.17	0.11	5.32
Within Groups	13.76	8.00	1.72			
Total	19.20	9.00				

Queens, NY						
Total n-alkanols	Column 1	Column 2				
summer early	12.92	9.91	fall early			
summer	0.82	1.88	fall			
spring early	1.72	3.95	fall late			
spring	6.91	3.07	winter early			
spring late	4.32	3.10	winter			
Anova: Single Factor						

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	26.69	5.34	23.61		
Column 2	5.00	21.92	4.38	10.09		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2.27	1.00	2.27	0.13	0.72	5.32
Within Groups	134.83	8.00	16.85			
Total	137.10	9.00				

Queens, NY						
Cholesterol ng/m3	Column 1	Column 2				
early summer	0.00	0.07	early fall			
summer	0.00	0.21	fall			
early spring	0.00	0.41	late fall			
spring	0.22	0.78	early winter			
late spring	0.20	0.10	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	0.41	0.08	0.01		
Column 2	5.00	1.57	0.31	0.09		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.13	1.00	0.13	2.69	0.14	5.32
Within Groups	0.39	8.00	0.05			
Total	0.53	9.00				

Queens, NY						
Levulinic Acid	Column 1	Column 2				
summer early	0.00	0.00	fall early			
summer	0.00	0.00	fall			
spring early	9.09	0.00	fall late			
spring	0.00	10.19	winter early			
spring late	0.00	7.84	winter			

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	9.09	1.82	16.53		
Column 2	5.00	18.03	3.61	25.06		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	7.98	1.00	7.98	0.38	0.55	5.32
Within Groups	166.36	8.00	20.80			
Total	174.34	9.00				

Chester, NJ						
Levoglucosan	Column 1	Column 2				
early summer	24.90	11.67	early fall			
summer	25.15	25.64	fall			
early spring	26.89	80.15	late fall			
spring	2.73	70.14	early winter			
late spring	12.83	24.18	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	92.50	18.50	109.15		
Column 2	5.00	211.79	42.36	938.13		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1422.96	1.00	1422.96	2.72	0.14	5.32
Within Groups	4189.14	8.00	523.64			
Total	5612.10	9.00				

Chester, NJ						
cis-Pinonic Acid	Column 1	Column 2				

early summer	7.91	0.00	early fall			
summer	0.00	2.52	fall			
early spring	3.66	3.49	late fall			
spring	5.84	0.14	early winter			
late spring	4.19	0.00	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	21.60	4.32	8.58		
Column 2	5.00	6.16	1.23	2.75		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	23.86	1.00	23.86	4.21	0.07	5.32
Within Groups	45.31	8.00	5.66			
Total	69.17	9.00				

Chester, NJ						
Total n-alkanols	Column 1	Column 2				
summer early	5.93	2.66	fall early			
summer	0.46	1.07	fall			
spring early	2.43	0.61	fall late			
spring	5.29	1.84	winter early			
spring late	3.54	2.30	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	17.66	3.53	4.87		
Column 2	5.00	8.46	1.69	0.72		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	8.45	1.00	8.45	3.02	0.12	5.32
Within Groups	22.37	8.00	2.80			
Total	30.82	9.00				

Chester, NJ						
Cholesterol	Column 1	Column 2				
early summer	0.00	0.00	early fall			
summer	0.00	0.00	fall			
early spring	0.00	0.00	late fall			
spring	0.04	0.00	early winter			
late spring	0.03	0.66	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	0.07	0.01	0.00		
Column 2	5.00	0.66	0.13	0.09		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.03	1.00	0.03	0.80	0.40	5.32
Within Groups	0.35	8.00	0.04			
Total	0.38	9.00				

Chester, NJ						
Levulinic Acid	Column 1	Column 2				
summer early	21.00	0.00	fall early			
summer	0.00	0.00	fall			
spring early	0.00	9.41	fall late			
spring	6.23	0.00	winter early			
spring late	8.75	0.00	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	5.00	35.98	7.20	74.38		
Column 2	5.00	9.41	1.88	17.72		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between	70.56	1.00	70.56	1.53	0.25	5.32

Groups						
Within Groups	368.39	8.00	46.05			
Total	438.95	9.00				

Westport, CT						
Levoglucosan	Column 1	Column 2				
summer	3.36	72.67	early fall			
early spring	78.79	69.74	fall			
spring	5.06	189.47	late fall			
late spring	9.07	149.59	early winter			
		120.89	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	4.00	96.28	24.07	1336.80		
Column 2	5.00	602.36	120.47	2617.07		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	20651.90	1.00	20651.90	9.98	0.02	5.59
Within Groups	14478.68	7.00	2068.38			
Total	35130.59	8.00				

Westport, CT						
cis-Pinonic Acid	Column 1	Column 2				
summer	5.20	4.70	early fall			
early spring	2.37	2.98	fall			
spring	0.00	2.70	late fall			
late spring	3.26	1.76	early winter			
		0.00	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	4.00	10.83	2.71	4.65		

Column 2	5.00	12.14	2.43	2.97		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.17	1.00	0.17	0.05	0.83	5.59
Within Groups	25.84	7.00	3.69			
Total	26.01	8.00				

Wesport, CT						
Total n-alkanols	Column 1	Column 2				
summer	0.91	2.89	fall early			
spring early	1.84	1.62	fall			
spring	1.20	2.40	fall late			
spring late	0.54	4.79	winter early			
		1.42	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	4.00	4.50	1.12	0.30		
Column 2	5.00	13.12	2.62	1.82		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5.00	1.00	5.00	4.28	0.08	5.59
Within Groups	8.17	7.00	1.17			
Total	13.18	8.00				

Westport, CT						
Cholesterol	Column 1	Column 2				
summer	0.00	0.00	early fall			
early spring	0.00	0.00	fall			
spring	0.07	0.00	late fall			
late spring	0.00	0.00	early winter			
		0.07	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		

Column 1	4.00	0.07	0.02	0.00		
Column 2	5.00	0.07	0.01	0.00		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.00	1.00	0.00	0.01	0.92	5.59
Within Groups	0.01	7.00	0.00			
Total	0.01	8.00				

Westport, CT						
Levulinic Acid	Column 1	Column 2				
summer	0.00	0.00	fall early			
spring early	6.61	16.82	fall			
spring	1.97	0.00	fall late			
spring late	11.31	11.45	winter early			
		0.00	winter			
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	4.00	19.89	4.97	25.51		
Column 2	5.00	28.27	5.65	63.54		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.03	1.00	1.03	0.02	0.89	5.59
Within Groups	330.67	7.00	47.24			
Total	331.70	8.00				

SOAP 2005-2007 Anova tables conducted to determine seasonal variations.

Bronx						
Levoglucosan	Column 1	Column 2				
Oct-05	25.86	50.46	Mar-06			
Nov-05	63.26	21.17	Apr-06			
Dec-05	95.99	12.20	May-06			
Jan-06	84.27	9.00	Jun-06			

Feb-06	98.77	7.31	Jul-06			
Sep-06	18.43	7.21	Aug-06			
Oct-06	43.24					
Nov-06	60.83					
Dec-06	37.05					
Jan-07	85.58					
Feb-07	48.90					
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	11.00	662.17	60.20	787.70		
Column 2	6.00	107.34	17.89	281.74		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6948.82	1.00	6948.82	11.22	0.00	4.54
Within Groups	9285.75	15.00	619.05			
Total	16234.56	16.00				

Pinnacle State Park						
Levoglucosan	Column 1	Column 2				
Oct-05	65.25	80.27	Mar-06			
Nov-05	39.96	31.69	Apr-06			
Dec-05	118.78	3.11	May-06			
Jan-06	113.04	1.80	Jun-06			
Feb-06	95.78	7.36	Jul-06			
Sep-06	12.02	17.34	Aug-06			
Oct-06	28.99					
Nov-06	57.06					
Dec-06	36.33					
Jan-07	45.53					
Feb-07	34.01					
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	11.00	646.76	58.80	1268.02		
Column 2	6.00	141.57	23.60	894.91		
ANOVA						
Source of	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*

Variation						
Between Groups	4810.72	1.00	4810.72	4.21	0.06	4.54
Within Groups	17154.73	15.00	1143.65			
Total	21965.45	16.00				

Bronx						
cis-Pinonic Acid	Column 1	Column 2				
Oct-05	0.00	2.35	Mar-06			
Nov-05	4.80	1.65	Apr-06			
Dec-05	2.49	4.16	May-06			
Jan-06	0.99	3.98	Jun-06			
Feb-06	2.36	3.73	Jul-06			
Sep-06	4.38	3.84	Aug-06			
Oct-06	2.31					
Nov-06	3.43					
Dec-06	3.17					
Jan-07	3.11					
Feb-07	1.16					
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	11.00	28.21	2.56	2.09		
Column 2	6.00	19.72	3.29	1.06		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2.02	1.00	2.02	1.16	0.30	4.54
Within Groups	26.17	15.00	1.74			
Total	28.19	16.00				

Pinnacle						
cis-Pinonic Acid	Column 1	Column 2				
Oct-05	6.07	5.11	Mar-06			
Nov-05	3.53	4.40	Apr-06			
Dec-05	5.12	5.79	May-06			
Jan-06	3.72	4.60	Jun-06			
Feb-06	2.66	0.00	Jul-06			

Sep-06	2.02	0.00	Aug-06			
Oct-06	2.41					
Nov-06	9.88					
Dec-06	3.37					
Jan-07	3.37					
Feb-07	0.00					
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	11.00	42.15	3.83	6.52		
Column 2	6.00	19.91	3.32	6.83		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.03	1.00	1.03	0.15	0.70	4.54
Within Groups	99.36	15.00	6.62			
Total	100.39	16.00				

Bronx						
Total n-alkanols	Column 1	Column 2				
Oct-05	0.94	0.62	Mar-06			
Nov-05	0.94	0	Apr-06			
Dec-05	2.65	1.77	May-06			
Jan-06	0.62	2.54	Jun-06			
Feb-06	2.26	0.69	Jul-06			
Sep-06	1.93	0.55	Aug-06			
Oct-06	1.7					
Nov-06	0					
Dec-06	1.31					
Jan-07	0.57					
Feb-07	0.87					
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	11.00	13.79	1.25	0.64		
Column 2	6.00	6.17	1.03	0.88		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*

Between Groups	0.20	1.00	0.20	0.27	0.61	4.54
Within Groups	10.81	15.00	0.72			
Total	11.01	16.00				

Pinnacle State Park, NY						
Total n-alkanols	Column 1	Column 2				
Oct-05	3.44	1.83	Mar-06			
Nov-05	3.19	1.07	Apr-06			
Dec-05	1.73	2.54	May-06			
Jan-06	1.25	0.79	Jun-06			
Feb-06	1.42	0.92	Jul-06			
Sep-06	0.5	1.73	Aug-06			
Oct-06	1.89					
Nov-06	1.78					
Dec-06	1.47					
Jan-07	1.08					
Feb-07	0.83					
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	11.00	18.58	1.69	0.82		
Column 2	6.00	8.88	1.48	0.45		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.17	1.00	0.17	0.24	0.63	4.54
Within Groups	10.47	15.00	0.70			
Total	10.64	16.00				

Bronx						
cholesterol	Column 1	Column 2				
Oct-05	0.40	0.20	Mar-06			
Nov-05	0.14	0.04	Apr-06			
Dec-05	0.33	0.09	May-06			
Jan-06	0.39	0.09	Jun-06			
Feb-06	0.44	0.00	Jul-06			
Sep-06	0.14	0.07	Aug-06			
Oct-06	0.17					
Nov-06	0.15					
Dec-06	0.11					

Jan-07	0.30					
Feb-07	0.14					
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	11.00	2.70	0.25	0.02		
Column 2	6.00	0.49	0.08	0.00		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.10	1.00	0.10	8.91	0.01	4.54
Within Groups	0.18	15.00	0.01			
Total	0.28	16.00				

Pinnacle						
cholesterol	Column 1	Column 2				
Oct-05	0.03	0.00	Mar-06			
Nov-05	0.07	0.00	Apr-06			
Dec-05	0.00	0.00	May-06			
Jan-06	0.00	0.00	Jun-06			
Feb-06	0.00	0.00	Jul-06			
Sep-06	0.00	0.00	Aug-06			
Oct-06	0.00					
Nov-06	0.00					
Dec-06	0.00					
Jan-07	0.04					
Feb-07	0.00					
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	11.00	0.14	0.01	0.00		
Column 2	6.00	0.00	0.00	0.00		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.00	1.00	0.00	1.67	0.22	4.54

Within Groups	0.01	15.00	0.00			
Total	0.01	16.00				

Bronx						
Levulinic Acid	Column 1	Column 2				
Oct-05	4.64	8.52	Mar-06			
Nov-05	8.64	7.34	Apr-06			
Dec-05	7	9.12	May-06			
Jan-06	0	11.68	Jun-06			
Feb-06	0	21.23	Jul-06			
Sep-06	10.95	9.55	Aug-06			
Oct-06	6.83					
Nov-06	9.17					
Dec-06	4.84					
Jan-07	6.82					
Feb-07	8.74					
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	11.00	67.63	6.15	12.63		
Column 2	6.00	67.44	11.24	25.99		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	100.66	1.00	100.66	5.89	0.03	4.54
Within Groups	256.30	15.00	17.09			
Total	356.95	16.00				

Pinnacle						
Levulinic Acid	Column 1	Column 2				
Oct-05	8.74	9.83	Mar-06			
Nov-05	4.78	5.31	Apr-06			
Dec-05	8.66	13.22	May-06			
Jan-06	5.34	8.56	Jun-06			
Feb-06	8.57	8.39	Jul-06			
Sep-06	6.67	7.36	Aug-06			
Oct-06	4.4					

Nov-06	5.85					
Dec-06	6.04					
Jan-07	5.16					
Feb-07	5.99					
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	11.00	70.20	6.38	2.52		
Column 2	6.00	52.67	8.78	7.01		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	22.30	1.00	22.30	5.54	0.03	4.54
Within Groups	60.32	15.00	4.02			
Total	82.62	16.00				

Appendix Statistical Analyses Urban versus rural sites

Alpha = 0.05 (95% confidence interval)

H_0 = there is no difference between urban and rural sites (i.e. $mean_{urban} = mean_{rural}$)
H_1 = there is a difference between urban and rural (i.e. $mean_{urban} \neq mean_{rural}$)

Levoglucosan Ambient Concentration ng/m^3

Ambient Levoglucosan Concentration, ng/m^3					
Season	Site	Urban	Rural	Site	Season
Oct-05	Bronx	25.86	65.25	Pinnacle	Oct-05
Nov-05		63.26	39.96		Nov-05
Dec-05		95.99	118.78		Dec-05
Jan-06		84.27	113.04		Jan-06
Feb-06		98.77	95.78		Feb-06
Mar-06		50.46	80.27		Mar-06
Apr-06		21.17	31.69		Apr-06
May-06		12.20	3.11		May-06
Jun-06		9.00	1.80		Jun-06
Jul-06		7.31	7.36		Jul-06
Aug-06		7.21	17.34		Aug-06
Sep-06		18.43	12.02		Sep-06

Oct-06		43.24	28.99		Oct-06
Nov-06		60.83	57.06		Nov-06
Dec-06		37.05	36.33		Dec-06
Jan-07		85.58	45.53		Jan-07
Feb-07		48.90	34.01		Feb-07
early summer	Queens	78.98	24.90	Chester	early summer
summer		23.24	25.15		summer
early fall		9.86	11.67		early fall
fall		88.99	25.64		fall
late fall		146.92	80.15		late fall
early winter		104.33	70.14		early winter
winter		37.66	24.18		winter
early spring		12.38	26.89		early spring
spring		2.36	2.73		spring
late spring		5.70	12.83		late spring
early summer	Elizabeth	28.50			
summer		55.28			
early fall		16.65			
fall		72.65			
late fall		138.11			
early winter		24.12			
winter		6.66			
early spring		21.52			
spring		4.34			
late spring		5.39			
summer	Westport	3.36			
early fall		72.67			
fall		69.74			
late fall		189.47			
early winter		149.59			
winter		120.89			
early spring		78.79			
spring		5.06			
late spring		9.07			
Statistical Analysis					
Q0 (Minimum)		2.363702	1.802803		
Q1 (25%)		10.44382	15.08653		
Q2 (Median)		37.35025	28.99332		
Q3 (75%)		78.93327	61.15653		
Q4 (Maximum)		189.4717	118.7847		
Inner quartile range		68.48945	46.07		
Low outlier		-92.2903	-54.0185		
High outlier		181.6674	130.2615		
skewness/kurtosis		0.531304	0.11636		

Urban Versus Rural All Seasons (2002-2007)

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	46	2351.793	51.12593402	2193.375011		
Column 2	27	1092.621	40.46745038	1122.236263		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1932.812	1	1932.811861	1.073112468	0.303759	3.97581
Within Groups	127880	71	1801.127019			
Total	129812.8	72				
The P value is greater than the significance level (0.05) we do not reject Ho,						
there is no difference between group means.						

Winter	
Ambient Levoglucosan concentrations, ng/m^3	
Urban	Rural
95.99	118.78
84.27	113.04
98.77	95.78
37.05	36.33
85.58	45.53
48.90	34.01
104.33	70.14
37.66	24.18
24.12	
6.66	
149.59	
120.89	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	893.7975	74.48312	1864.061	Urban	
Column 2	8	537.798	67.22475	1423.334	Rural	
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*

Between Groups	252.8828	1	252.8828	0.149399	0.703641	4.413873
Within Groups	30468	18	1692.667			
Total	30720.89	19				
The P-value is greater than 0.05, we do not reject H_0, there is no difference between winter urban and rural ambient means.						

Spring	
Ambient Levoglucosan concentrations, ng/m3	
Urban	Rural
50.46	80.27
21.17	31.69
12.20	3.11
2.36	26.89
5.70	2.73
28.50	12.83
21.52	
4.34	
5.39	
78.79	
5.06	
9.07	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	244.5592	20.37994	530.5777		
Column 2	6	157.5125	26.25208	843.3656		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	137.9285	1	137.9285	0.219518	0.645727	4.493998
Within Groups	10053.18	16	628.3239			
Total	10191.11	17				
The P value is greater than the significance level (0.05) we do not reject H_0,						
there is no difference between group means.						

Ambient Levoglucosan concentrations, ng/m^3	
Urban	Rural

9.00	1.80
7.31	7.36
7.21	17.34
78.98	24.90
23.24	25.15
28.50	
55.28	
3.36	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	8	212.8722	26.60902	739.9024		
Column 2	5	76.55904	15.31181	109.6795		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	392.6984	1	392.6984	0.768896	0.399304	4.844336
Within Groups	5618.035	11	510.7304			
Total	6010.733	12				
The P value is greater than the significance level (0.05) we do not reject H_0,						
there is no difference between group means.						

Fall	
Ambient Levoglucosan concentrations, ng/m^3	
Urban	Rural
25.86	65.25
63.26	39.96
18.43	12.02
43.24	28.99
60.83	57.06
9.86	11.67
88.99	25.64
146.92	80.15
16.65	
72.65	
138.11	
72.67	
69.74	

189.47	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	14	1016.682	72.62013	2848.103		
Column 2	8	320.7516	40.09395	636.2893		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5385.939	1	5385.939	2.596925	0.122741	4.351243
Within Groups	41479.37	20	2073.968			
Total	46865.31	21				
The P value is greater than the significance level (0.05) we do not reject Ho,						
there is no difference between group means.						

Ambient total n-alkanols Statistical Analysis

Ambient total n-alkanols ng/m^3				
Season		Urban	Rural	
Oct-05	Bronx	0.94	3.44	Pinnacle
Nov-05		0.94	3.19	
Dec-05		2.65	1.73	
Jan-06		0.62	1.25	
Feb-06		2.26	1.42	
Mar-06		0.62	1.83	
Apr-06		0.00	1.07	
May-06		1.77	2.54	
Jun-06		2.54	0.79	
Jul-06		0.69	0.92	
Aug-06		0.55	1.73	
Sep-06		1.93	0.50	
Oct-06		1.70	1.89	
Nov-06		0.00	1.78	
Dec-06		1.31	1.47	
Jan-07		0.57	1.08	
Feb-07		0.87	0.83	
early summer	Queens	12.92	5.93	Chester
summer		0.82	0.46	

early fall		9.91	2.66	
fall		1.88	1.07	
late fall		3.95	0.61	
early winter		3.07	1.84	
winter		3.10	2.30	
early spring		1.72	2.43	
spring		6.91	5.29	
late spring		4.32	3.54	
early summer	Elizabeth	14.60		
summer		4.24		
early fall		3.52		
fall		1.76		
late fall		2.20		
early winter		1.90		
winter		1.37		
early spring		0.37		
spring		3.92		
late spring		2.22		
summer	Westport	0.91		
early fall		2.89		
fall		1.62		
late fall		2.40		
early winter		4.79		
winter		1.42		
early spring		1.84		
spring		1.20		
late spring		0.54		
Statistical Analysis				
Q0 (Minimum)		0	0.463117	
Q1 (25%)		0.920127	1.069527	
Q2 (Median)		1.805983	1.729554	
Q3 (75%)		3.023951	2.486215	
Q4 (Maximum)		14.60237	5.931962	
Inner quartile range		2.103823	1.416688	
Low outlier		-2.23561	-1.05551	
High outlier		6.179686	4.611248	
skewness/kurtosis		7.566174	2.319754	

SOAP 2002-2007 all seasons

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	46	122.2667	2.657972	9.06419		
Column 2	27	53.58227	1.984529	1.835836		

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	7.716156	1	7.716156	1.20242	0.276544	3.97581
Within Groups	455.6203	71	6.417187			
Total	463.3364	72				
The p-value is greater than alpha do not reject H_0						

Total n-alkanols Winter	
Urban	Rural
2.65	1.73
0.62	1.25
2.26	1.42
1.31	1.47
0.57	1.08
0.87	0.83
3.07	1.84
3.10	2.30
1.90	
1.37	
4.79	
1.42	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	23.92909	1.994091	1.551712		
Column 2	8	11.91145	1.488931	0.213977		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.224896	1	1.224896	1.187511	0.290207	4.413873
Within Groups	18.56667	18	1.031482			
Total	19.79157	19				
The p-value is greater than alpha do not reject H_0						

Total n-alkanols Spring	
Urban	Rural
0.62	1.83
0.00	1.07
1.77	2.54
1.72	2.43
6.91	5.29
4.32	3.54
0.37	
3.92	
2.22	
1.84	
1.20	
0.54	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	25.43624	2.119687	4.051931		
Column 2	6	16.71347	2.785578	2.172911		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.773646	1	1.773646	0.511914	0.484623	4.493998
Within Groups	55.43579	16	3.464737			
Total	57.20944	17				
The p-value is greater than alpha do not reject H_0						

Total n-alkanols Summer	
Urban	Rural
2.54	0.79
0.69	0.92
0.55	1.73
12.92	5.93
0.82	0.46
14.60	
4.24	
0.91	

Anova: Single Factor					

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	8	37.26892	4.658615	33.31025		
Column 2	5	9.829055	1.965811	5.133154		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	22.31137	1	22.31137	0.967366	0.346477	4.844336
Within Groups	253.7044	11	23.06403			
Total	276.0158	12				
The p-value is greater than alpha do not reject H_0						

Total n-alkanols Fall	
Urban	Rural
0.94	3.44
0.94	3.19
1.93	0.50
1.70	1.89
0.00	1.78
9.91	2.66
1.88	1.07
3.95	0.61
3.52	
1.76	
2.20	
2.89	
1.62	
2.40	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	14	35.63246	2.545176	5.547088		
Column 2	8	15.1283	1.891038	1.278574		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2.178383	1	2.178383	0.53746	0.471994	4.351243

Within Groups	81.06216	20	4.053108			
Total	83.24055	21				
The p-value is greater than alpha do not reject H_0						

Ambient Cholesterol Statistical Analysis

Ambient Cholesterol ng/m^3				
Season		Urban	Rural	
Oct-05	Bronx	0.40	0.03	Pinnacle
Nov-05		0.14	0.07	
Dec-05		0.33	0.00	
Jan-06		0.39	0.00	
Feb-06		0.44	0.00	
Mar-06		0.20	0.00	
Apr-06		0.04	0.00	
May-06		0.09	0.00	
Jun-06		0.09	0.00	
Jul-06		0.00	0.00	
Aug-06		0.07	0.00	
Sep-06		0.14	0.00	
Oct-06		0.17	0.00	
Nov-06		0.15	0.00	
Dec-06		0.11	0.00	
Jan-07		0.30	0.04	
Feb-07		0.14	0.00	
early summer	Queens	0.00	0.00	Chester
summer		0.00	0.00	
early fall		0.07	0.00	
fall		0.21	0.00	
late fall		0.41	0.00	
early winter		0.78	0.00	
winter		0.10	0.66	
early spring		0.00	0.00	
spring		0.22	0.04	
late spring		0.20	0.03	
early summer	Elizabeth	0.63		
summer		0.13		
early fall		0.00		
fall		0.49		
late fall		0.27		
early winter		0.00		
winter		0.23		
early spring		0.00		
spring		0.23		
late spring		0.42		

summer	Westport	0.00		
early fall		0.00		
fall		0.00		
late fall		0.00		
early winter		0.00		
winter		0.07		
early spring		0.00		
spring		0.07		
late spring		0.00		
Statistical Analysis				
Q0 (Minimum)		0	0	
Q1 (25%)		0	0	
Q2 (Median)		0.117829	0	
Q3 (75%)		0.232811	0	
Q4 (Maximum)		0.779734	0.65958	
Inner quartile range		0.232811	0	
Low outlier		-0.34922	0	
High outlier		0.582028	0	
skewness/kurtosis		1.809163	25.75904	

Urban Versus Rural All Seasons (2002-2007)

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	46	7.711294	0.167637	0.033922		
Column 2	27	0.873266	0.032343	0.016046		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.311425	1	0.311425	11.37584	0.001208	3.97581
Within Groups	1.943697	71	0.027376			
Total	2.255122	72				
P-value is less than alpha, reject H_0, there is a difference between urban and rural areas.						

Ambient Cholesterol Winter	
Urban	Rural
0.33	0.00
0.39	0.00
0.44	0.00
0.11	0.00
0.30	0.04
0.14	0.00

0.78	0.00
0.10	0.66
0.00	
0.23	
0.00	
0.07	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	2.880067	0.240006	0.050263		
Column 2	8	0.695969	0.086996	0.053689		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.112377	1	0.112377	2.178037	0.157272	4.413873
Within Groups	0.928721	18	0.051596			
Total	1.041098	19				
P-value is greater than alpha, do not reject H_0.						

Ambient Cholesterol Spring	
Urban	Rural
0.20	0.00
0.04	0.00
0.09	0.00
0.00	0.00
0.22	0.04
0.20	0.03
0.00	
0.23	
0.42	
0.00	
0.07	
0.00	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	1.462994	0.121916	0.017558		

Column 2	6	0.06952	0.011587	0.000339		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.04869	1	0.04869	3.998536	0.062815	4.493998
Within Groups	0.194833	16	0.012177			
Total	0.243524	17				
P-value is greater than alpha, do not reject H_0.						

Ambient Cholesterol Summer	
Urban	Rural
0.09	0.00
0.00	0.00
0.07	0.00
0.00	0.00
0.00	0.00
0.63	
0.13	
0.00	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	8	0.915869	0.114484	0.045951		
Column 2	5	0	0	0		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.040328	1	0.040328	1.379113	0.26505	4.844336
Within Groups	0.321659	11	0.029242			
Total	0.361987	12				
P-value is greater than alpha, do not reject H_0.						

Ambient Cholesterol Fall	
Urban	Rural
0.40	0.03
0.14	0.07
0.14	0.00

0.17	0.00
0.15	0.00
0.07	0.00
0.21	0.00
0.41	0.00
0.00	
0.49	
0.27	
0.00	
0.00	
0.00	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	14	2.452364	0.175169	0.02673		
Column 2	8	0.107778	0.013472	0.00073		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.133106	1	0.133106	7.550054	0.012408	4.351243
Within Groups	0.352596	20	0.01763			
Total	0.485702	21				
P-value is less than alpha, reject H_0, there is a difference between urban and rural						
areas.						

Ambient cis-Pinonic Acid Statistical Analysis

Ambient cis-pinonic acid ng/m^3				
Season		Urban	Rural	
Oct-05	Bronx	0.00	6.07	Pinnacle
Nov-05		4.80	3.53	
Dec-05		2.49	5.12	
Jan-06		0.99	3.72	
Feb-06		2.36	2.66	
Mar-06		2.35	5.11	
Apr-06		1.65	4.40	
May-06		4.16	5.79	
Jun-06		3.98	4.60	
Jul-06		3.73	0.00	
Aug-06		3.84	0.00	

Sep-06		4.38	2.02	
Oct-06		2.31	2.41	
Nov-06		3.43	9.88	
Dec-06		3.17	3.37	
Jan-07		3.11	3.37	
Feb-07		1.16	0.00	
early summer	Queens	3.17	7.91	Chester
summer		1.92	0.00	
early fall		3.40	0.00	
fall		0.00	2.52	
late fall		0.00	3.49	
early winter		0.00	0.14	
winter		0.58	0.00	
early spring		2.40	3.66	
spring		3.33	5.84	
late spring		0.55	4.19	
early summer	Elizabeth	5.32		
summer		0.00		
early fall		0.00		
fall		2.34		
late fall		0.00		
early winter		1.42		
winter		0.35		
early spring		0.00		
spring		2.40		
late spring		4.29		
summer	Westport	5.20		
early fall		4.70		
fall		2.98		
late fall		2.70		
early winter		1.76		
winter		0.00		
early spring		2.37		
spring		0.00		
late spring		3.26		
Statistical Analysis				
Q0 (Minimum)		0	0	
Q1 (25%)		0.55448	1.07912	
Q2 (Median)		2.367984	3.493601	
Q3 (75%)		3.380541	4.856673	
Q4 (Maximum)		5.318402	9.879395	
Inner quartile range		2.826061	3.777553	
Low outlier		-3.68461	-4.58721	
High outlier		7.619631	10.523	
skewness/kurtosis		-1.12778	0.160634	

Urban Versus Rural All Seasons (2002-2007)

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	46	102.3635	2.225295	2.734081		
Column 2	27	89.81626	3.326528	6.706343		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	20.63278	1	20.63278	4.925805	0.029654	3.97581
Within Groups	297.3986	71	4.188712			
Total	318.0313	72				
The P-value is less than alpha, reject H_0, there is a difference.						

Ambient cis-Pinonic Acid Winter	
Urban	Rural
2.49	5.12
0.99	3.72
2.36	2.66
3.17	3.37
3.11	3.37
1.16	0.00
0.00	0.14
0.58	0.00
1.42	
0.35	
1.76	
0.00	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	17.39732	1.449777	1.291916		
Column 2	8	18.38738	2.298422	3.949598		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*

Between Groups	3.456956	1	3.456956	1.48657	0.238487	4.413873
Within Groups	41.85826	18	2.325459			
Total	45.31521	19				
The P-value is greater than alpha, do not reject H_0, there is no difference.						

Ambient cis-Pinonic Acid Spring	
Urban	Rural
2.35	5.11
1.65	4.40
4.16	5.79
2.40	3.66
3.33	5.84
0.55	4.19
0.00	
2.40	
4.29	
2.37	
0.00	
3.26	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	26.76661	2.230551	2.134035		
Column 2	6	29.00084	4.833473	0.794156		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	27.10082	1	27.10082	15.79925	0.001088	4.493998
Within Groups	27.44517	16	1.715323			
Total	54.54598	17				
The P-value is less than alpha, reject H_0, there is a difference.						

Ambient cis-Pinonic Acid Summer	
Urban	Rural
3.98	4.60
3.73	0.00
3.84	0.00

3.17	7.91
1.92	0.00
5.32	
0.00	
5.20	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	8	27.15094	3.393868	3.052331		
Column 2	5	12.5087	2.50174	13.10582		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2.4489	1	2.4489	0.365064	0.557963	4.844336
Within Groups	73.78959	11	6.708144			
Total	76.23849	12				
The P-value is greater than alpha, do not reject H_0, there is no difference.						

Ambient cis-Pinonic Acid Fall	
Urban	Rural
0.00	6.07
4.80	3.53
4.38	2.02
2.31	2.41
3.43	9.88
3.40	0.00
0.00	2.52
0.00	3.49
0.00	
2.34	
0.00	
4.70	
2.98	
2.70	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	14	31.04867	2.217762	3.526083		

Column 2	8	29.91935	3.739918	9.067696		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	11.79543	1	11.79543	2.158102	0.157374	4.351243
Within Groups	109.313	20	5.465648			
Total	121.1084	21				
The P-value is greater than alpha, do not reject H_0, there is no difference.						

Ambient Levulinic Acid Statistical Analysis

Ambient Levulinic acid ng/m^3				
Season		Urban	Rural	
Oct-05	Bronx	4.64	8.74	Pinnacle
Nov-05		8.64	4.78	
Dec-05		7.00	8.66	
Jan-06		0.00	5.34	
Feb-06		0.00	8.57	
Mar-06		8.52	9.83	
Apr-06		7.34	5.31	
May-06		9.12	13.22	
Jun-06		11.68	8.56	
Jul-06		21.23	8.39	
Aug-06		9.55	7.36	
Sep-06		10.95	6.67	
Oct-06		6.83	4.40	
Nov-06		9.17	5.85	
Dec-06		4.84	6.04	
Jan-07		6.82	5.16	
Feb-07		8.74	5.99	
early summer	Queens	0.00	21.00	Chester
summer		0.00	0.00	
early fall		0.00	0.00	
fall		0.00	0.00	
late fall		0.00	9.41	
early winter		10.19	0.00	
winter		7.84	0.00	
early spring		9.09	0.00	
spring		0.00	6.23	
late spring		0.00	8.75	
early summer	Elizabeth	17.54		
summer		0.00		

early fall		0.00		
fall		0.00		
late fall		0.00		
early winter		0.00		
winter		7.42		
early spring		0.00		
spring		0.00		
late spring		0.00		
summer	Westport	0.00		
early fall		0.00		
fall		16.82		
late fall		0.00		
early winter		11.45		
winter		0.00		
early spring		6.61		
spring		1.97		
late spring		11.31		
Statistical Analysis				
Q0 (Minimum)		0	0	
Q1 (25%)		0	4.59	
Q2 (Median)		4.74	6.04	
Q3 (75%)		9.003843	8.615	
Q4 (Maximum)		21.23	21.00244	
Inner quartile range		9.003843	4.025	
Low outlier		-13.5058	-1.4475	
High outlier		22.50961	14.6525	
skewness/kurtosis		0.151101	2.682996	

Urban Versus Rural All Seasons (2002-2007)

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	46	235.2972	5.115157	31.69562	Urban	
Column 2	27	168.2576	6.231763	21.81125	Rural	
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	21.21282	1	21.21282	0.75555	0.387654	3.97581
Within Groups	1993.395	71	28.07599			
Total	2014.608	72				

The P-value is greater than alpha, do not reject H_0, there is no difference.

Ambient Levulinic Acid Winter	
Urban	Rural
7.00	8.66
0.00	5.34
0.00	8.57
4.84	6.04
6.82	5.16
8.74	5.99
10.19	0.00
7.84	0.00
0.00	
7.42	
11.45	
0.00	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	64.28836	5.357363	18.37726		
Column 2	8	39.76	4.97	11.19089		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.720242	1	0.720242	0.046221	0.832192	4.413873
Within Groups	280.4861	18	15.58256			
Total	281.2063	19				
The P-value is greater than alpha, do not reject H_0, there is no difference.						

Ambient Levulinic Acid Spring	
Urban	Rural
8.52	9.83
7.34	5.31
9.12	13.22
9.09	0.00
0.00	6.23
0.00	8.75

0.00	
0.00	
0.00	
6.61	
1.97	
11.31	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	53.96272	4.496893	20.46083		
Column 2	6	43.33331	7.222219	20.37998		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	29.7096	1	29.7096	1.453818	0.245445	4.493998
Within Groups	326.969	16	20.43556			
Total	356.6786	17				
The P-value is greater than alpha, do not reject H_0, there is no difference.						

Ambient Levulinic Acid Summer	
Urban	Rural
11.68	8.56
21.23	8.39
9.55	7.36
0.00	21.00
0.00	0.00
17.54	
0.00	
0.00	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	8	59.99575	7.499469	76.55773		
Column 2	5	45.31244	9.062488	57.07357		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*

Between Groups	7.517005	1	7.517005	0.108201	0.748379	4.844336
Within Groups	764.1984	11	69.47258			
Total	771.7154	12				
The P-value is greater than alpha, do not reject H_0, there is no difference.						

Ambient Levulinic Acid Fall	
Urban	Rural
4.64	8.74
8.64	4.78
10.95	6.67
6.83	4.40
9.17	5.85
0.00	0.00
0.00	0.00
0.00	9.41
0.00	
0.00	
0.00	
0.00	
16.82	
0.00	

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	14	57.05038	4.075027	30.55869		
Column 2	8	39.85184	4.98148	12.48129		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4.182978	1	4.182978	0.172625	0.682213	4.351243
Within Groups	484.632	20	24.2316			
Total	488.8149	21				
The P-value is greater than alpha, do not reject H_0, there is no difference.						

Appendix J: $PM_{2.5}$ Mass Balances

Other = PM2.5 – (Nitrate+Sulfate+Ammonium+Inorganics+EC+OC)
EC and OC was obtained by filters analyzed by Sunset Labs
All other constituents from STN as explained in the Materials and Methods section

Chester, NJ SOAP 2002-2003

		µg/m^3				
CHS 23	$PM_{2.5}$	8.725				
Early Summer	Nitrate	0.73729				
	Sulfate	5.57286				
	Ammonium	1.79443	OM=OC*Factor			
	Inorganics	1.60518	Factor	1.4	1.8	2.0
	OC	4.29	OM	6.0077	7.724	8.582
	EC	0.19				
	Other	-5.47		-7.18	-8.90	-9.76
CHS 27		µg/m^3				
Summer	$PM_{2.5}$	NO DATA				
CHS 31		µg/m^3				
Early Fall	$PM_{2.5}$	9.96667				
	Nitrate	0.58478				
	Sulfate	3.71				
	Ammonium	1.113	OM=OC*Factor			
	Inorganics	2.20097	Factor	1.4	1.8	2.0
	OC	2.09	OM	2.9329	3.771	4.19
	EC	0.11				
	Other	0.16		-0.68	-1.52	-1.94
		µg/m^3				
CHS 35	$PM_{2.5}$	6.11429				
Fall	Nitrate	0.767				
	Sulfate	1.96571				
	Ammonium	0.70243	OM=OC*Factor			
	Inorganics	0.91803	Factor	1.4	1.8	2.0
	OC	2.15	OM	3.0103	3.87	4.3
	EC	0.16				
	Other	-0.55		-1.41	-2.27	-2.70

CHS 39		μg/m^3				
Late Fall	$PM_{2.5}$	6.3				
	Nitrate	1.28975				
	Sulfate	1.991				
	Ammonium	0.86225	OM=OC*Factor			
	Inorganics	0.98958	Factor	1.4	1.8	2.0
	OC	1.90	OM	2.6616	3.422	3.802
	EC	0.19				
	Other	-0.92		-1.68	-2.44	-2.82
CHS 44		μg/m^3				
Early Winter	$PM_{2.5}$	11.58				
	Nitrate	2.65583				
	Sulfate	3.28167				
	Ammonium	1.673	OM=OC*Factor			
	Inorganics	1.68227	Factor	1.4	1.8	2.0
	OC	2.44	OM	3.4102	4.385	4.872
	EC	0.26				
	Other	-0.41		-1.38	-2.36	-2.84
CHS 48		μg/m^3				
Winter	$PM_{2.5}$	7.4				
	Nitrate	2.87167				
	Sulfate	3.07167				
	Ammonium	1.655	OM=OC*Factor			
	Inorganics	1.42553	Factor	1.4	1.8	2.0
	OC	3.11	OM	4.3562	5.601	6.223
	EC	0.57				
	Other	-5.31		-6.55	-7.80	-8.42
CHS 52		μg/m^3				
Early Spring	$PM_{2.5}$	9.38571				
	Nitrate	1.19257				
	Sulfate	3.04629				
	Ammonium	1.10043	OM=OC*Factor			
	Inorganics	1.52287	Factor	1.4	1.8	2.0
	OC	2.20	OM	3.0761	3.955	4.394
	EC	0.18				
	Other	0.14		-0.74	-1.61	-2.05

CHS 56		μg/m^3				
Spring	$PM_{2.5}$	9.5				
	Nitrate	1.36738				
	Sulfate	2.54325				
	Ammonium	1.10675	OM=OC*Factor			
	Inorganics	1.23805	Factor	1.4	1.8	2.0
	OC	2.38	OM	3.3314	4.283	4.759
	EC	0.20				
	Other	0.67		-0.29	-1.24	-1.71
CHS 60		μg/m^3				
Late Spring	$PM_{2.5}$	11.4833				
	Nitrate	1.718				
	Sulfate	3.53667				
	Ammonium	1.3795	OM=OC*Factor			
	Inorganics	1.48969	Factor	1.4	1.8	2.0
	OC	2.37	OM	3.3166	4.264	4.738
	EC	0.14				
	Other	0.85		-0.09	-1.04	-1.52
2002-2003 Yearly Average		μg/m^3				
	$PM_{2.5}$	8.93944				
	Nitrate	1.46492				
	Sulfate	3.19101				
	Ammonium	1.2652	OM=OC*Factor			
	Inorganics	1.45246	Factor	1.4	1.8	2.0
	OC	2.54784	OM	3.567	4.586	5.096
	EC	0.22128				
	Other	-1.2033		-2.222	-3.24	-3.751
	% error	13.4602		24.861	36.26	41.96
Summer		μg/m^3				
	$PM_{2.5}$	8.725				
	Nitrate	0.73729				
	Sulfate	5.57286				
	Ammonium	1.79443	OM=OC*Factor			
	Inorganics	1.60518	Factor	1.4	1.8	2.0
	OC	4.29119	OM	6.0077	7.724	8.582

	EC	0.19022				
	Other	-5.4662		-7.183	-8.9	-9.757
	% error	62.6495		82.323	102	111.8
Fall		μg/m^3				
	$PM_{2.5}$	7.46032				
	Nitrate	0.88051				
	Sulfate	2.55557				
	Ammonium	0.89256	OM=OC*Factor			
	Inorganics	1.36953	Factor	1.4	1.8	2.0
	OC	2.04875	OM	2.8682	3.688	4.097
	EC	0.15002				
	Other	-0.4366		-1.256	-2.08	-2.485
	% error	5.85257		16.837	27.82	33.31
Winter		μg/m^3				
	$PM_{2.5}$	9.49				
	Nitrate	2.76375				
	Sulfate	3.17667				
	Ammonium	1.664	OM=OC*Factor			
	Inorganics	1.5539	Factor	1.4	1.8	2.0
	OC	2.77372	OM	3.8832	4.993	5.547
	EC	0.41619				
	Other	-2.8582		-3.968	-5.08	-5.632
	% error	30.1183		41.809	53.5	59.35
Spring		μg/m^3				
	$PM_{2.5}$	10.123				
	Nitrate	1.42598				
	Sulfate	3.04207				
	Ammonium	1.19556	OM=OC*Factor			
	Inorganics	1.41687	Factor	1.4	1.8	2.0
	OC	2.31524	OM	3.2413	4.167	4.63
	EC	0.17296				
	Other	0.55435		-0.372	-1.3	-1.761
	% error	5.47609		3.6723	12.82	17.39

Elizabeth, NJ SOAP 2002-2003

ELZ 21		μg/m^3				
Early Summer	$PM_{2.5}$	17.9				
	Nitrate	1.38975				
	Sulfate	5.01625				
	Ammonium	2.04675	OM=OC*Factor			
	Inorganics	2.66711	Factor	1.4	1.8	2.0
	OC	6.30	OM	8.8161	11.335	12.594
	EC	1.54				
	Other	-1.05		-3.57	-6.09	-7.35
ELZ 24		μg/m^3				
Summer	$PM_{2.5}$	20.1875				
	Nitrate	1.09575				
	Sulfate	5.88425				
	Ammonium	2.29113	OM=OC*Factor			
	Inorganics	2.94133	Factor	1.4	1.8	2.0
	OC	5.90	OM	8.2667	10.629	11.81
	EC	1.77				
	Other	0.30		-2.06	-4.42	-5.60
ELZ 28		μg/m^3				
Early Fall	$PM_{2.5}$	11.4333				
	Nitrate	0.97533				
	Sulfate	3.36117				
	Ammonium	1.20467	OM=OC*Factor			
	Inorganics	2.0468	Factor	1.4	1.8	2.0
	OC	3.23	OM	4.5153	5.8054	6.4505
	EC	1.29				
	Other	-0.67		-1.96	-3.25	-3.90
ELZ 32		μg/m^3				
Fall	$PM_{2.5}$	10.4714				
	Nitrate	1.40586				
	Sulfate	2.16714				
	Ammonium	1.095	OM=OC*Factor			
	Inorganics	1.21036	Factor	1.4	1.8	2.0
	OC	3.32	OM	4.6438	5.9706	6.634
	EC	1.36				

	Other	-0.09		-1.41	-2.74	-3.40
ELZ 36		μg/m^3				
Late Fall	$PM_{2.5}$	15.36				
	Nitrate	2.5				
	Sulfate	3.174				
	Ammonium	1.8086	OM=OC*Factor			
	Inorganics	1.98482	Factor	1.4	1.8	2.0
	OC	3.58	OM	5.0186	6.4525	7.1695
	EC	0.94				
	Other	1.37		-0.07	-1.50	-2.22
ELZ 41		μg/m^3				
Early Winter	$PM_{2.5}$	20.42				
	Nitrate	4.382				
	Sulfate	4.026				
	Ammonium	2.668	OM=OC*Factor			
	Inorganics	2.30951	Factor	1.4	1.8	2.0
	OC	5.81	OM	8.1357	10.46	11.622
	EC	1.45				
	Other	-0.23		-2.55	-4.88	-6.04
ELZ 45		μg/m^3				
Winter	$PM_{2.5}$	22.25				
	Nitrate	4.94333				
	Sulfate	3.92				
	Ammonium	2.96667	OM=OC*Factor			
	Inorganics	2.39727	Factor	1.4	1.8	2.0
	OC	5.03	OM	7.0474	9.061	10.068
	EC	1.00				
	Other	1.99		-0.03	-3.05	-3.05
ELZ 49		μg/m^3				
Early Spring	$PM_{2.5}$	14.1444				
	Nitrate	3.19133				
	Sulfate	3.34778				
	Ammonium	2.00111	OM=OC*Factor			
	Inorganics	1.89301	Factor	1.4	1.8	2.0
	OC	3.97	OM	5.5545	7.1415	7.935

	EC	0.87				
	Other	-1.12		-2.71	-4.30	-5.09
ELZ 53		μg/m^3				
Spring	$PM_{2.5}$	16.6857				
	Nitrate	2.79043				
	Sulfate	3.56143				
	Ammonium	1.764	OM=OC*Factor			
	Inorganics	2.17639	Factor	1.4	1.8	2.0
	OC	4.09	OM	5.7205	7.3549	8.1721
	EC	1.21				
	Other	1.10		-0.53	-2.17	-2.98
ELZ 57		μg/m^3				
Late Spring	$PM_{2.5}$	20.4				
	Nitrate	3.8275				
	Sulfate	5.095				
	Ammonium	2.7175	OM=OC*Factor			
	Inorganics	2.3072	Factor	1.4	1.8	2.0
	OC	4.90	OM	6.8553	8.814	9.7934
	EC	1.43				
	Other	0.13		20.4	-3.79	20.4
2002-2003 Yearly Average		μg/m^3				
	$PM_{2.5}$	16.9252				
	Nitrate	2.65013				
	Sulfate	3.9553				
	Ammonium	2.05634	OM=OC*Factor			
	Inorganics	2.19338	Factor	1.4	1.8	2.0
	OC	4.61243	OM	6.4574	8.3024	9.2249
	EC	1.28488				
	Other	0.17278		-1.672	-3.517	-4.44
	% error	1.02086		9.8799	20.781	26.231
Summer		μg/m^3				
	$PM_{2.5}$	19.0438				
	Nitrate	1.24275				
	Sulfate	5.45025				
	Ammonium	2.16894	OM=OC*Factor			

	Inorganics	2.80422	Factor	1.4	1.8	2.0
	OC	6.10101	OM	8.5414	10.982	12.202
	EC	1.65233				
	Other	-0.3758		-2.816	-5.257	-6.477
	% error	1.97309		14.788	27.603	34.01
Fall		μg/m^3				
	$PM_{2.5}$	12.4216				
	Nitrate	1.62706				
	Sulfate	2.90077				
	Ammonium	1.36942	OM=OC*Factor			
	Inorganics	1.74732	Factor	1.4	1.8	2.0
	OC	3.37567	OM	4.7259	6.0762	6.7513
	EC	1.19893				
	Other	0.20241		-1.148	-2.498	-3.173
	% error	1.6295		9.2408	20.111	25.546
Winter		μg/m^3				
	$PM_{2.5}$	21.335				
	Nitrate	4.66267				
	Sulfate	3.973				
	Ammonium	2.81733	OM=OC*Factor			
	Inorganics	2.35339	Factor	1.4	1.8	2.0
	OC	5.42253	OM	7.5915	9.7605	10.845
	EC	1.22517				
	Other	0.88092		-1.288	-3.457	-4.542
	% error	4.12897		6.0375	16.204	21.287
Spring		μg/m^3				
	$PM_{2.5}$	17.0767				
	Nitrate	3.26975				
	Sulfate	4.0014				
	Ammonium	2.16087	OM=OC*Factor			
	Inorganics	2.12553	Factor	1.4	1.8	2.0
	OC	4.31674	OM	6.0434	7.7701	8.6335
	EC	1.16566				
	Other	0.03676		-1.69	-3.417	-4.28
	% error	0.21525		9.8962	20.008	25.063

Queens, NY SOAP 2002-2003

QNS 22		μg/m^3				
Early Summer	$PM_{2.5}$	15.725				
	Nitrate	1.14038				
	Sulfate	4.67625				
	Ammonium	1.96288	OM=OC*Factor			
	Inorganics	2.33608	Factor	1.4	1.8	2.0
	OC	4.43	OM	6.2049	7.9777	8.8641
	EC	0.62				
	Other	0.55		-1.22	-2.99	15.73
QNS 25		μg/m^3				
Summer	$PM_{2.5}$	14.7375				
	Nitrate	1.23913				
	Sulfate	4.96				
	Ammonium	1.95488	OM=OC*Factor			
	Inorganics	2.39521	Factor	1.4	1.8	2.0
	OC	4.32	OM	6.0522	7.7815	8.6461
	EC	0.59				
	Other	-0.72		-2.45	-4.18	-5.04
QNS 29		μg/m^3				
Early Fall	$PM_{2.5}$	12.8				
	Nitrate	0.834				
	Sulfate	2.73				
	Ammonium	1.15	OM=OC*Factor			
	Inorganics	1.91752	Factor	1.4	1.8	2.0
	OC	3.09	OM	4.3298	5.5669	6.1855
	EC	0.59				
	Other	2.48		1.25	0.01	-0.61
QNS 33		μg/m^3				
Fall	$PM_{2.5}$	7.02				
	Nitrate	1.0726				
	Sulfate	2.016				
	Ammonium	0.8928	OM=OC*Factor			
	Inorganics	1.11715	Factor	1.4	1.8	2.0
	OC	2.60	OM	3.633	4.671	5.19
	EC	0.60				

	Other	-1.27		-2.31	-3.35	-3.87
QNS 37		μg/m^3				
Late Fall	$PM_{2.5}$	12.7429				
	Nitrate	2.64243				
	Sulfate	2.98429				
	Ammonium	1.73729	OM=OC*Factor			
	Inorganics	1.61608	Factor	1.4	1.8	2.0
	OC	3.57	OM	4.9962	6.4237	7.1374
	EC	0.75				
	Other	-0.55		-1.98	-3.41	-4.12
QNS 42		μg/m^3				
Early Winter	$PM_{2.5}$	17.4				
	Nitrate	4.47667				
	Sulfate	3.705				
	Ammonium	2.59333	OM=OC*Factor			
	Inorganics	2.11801	Factor	1.4	1.8	2.0
	OC	4.67	OM	6.5334	8.4001	9.3334
	EC	1.05				
	Other	-1.21		-3.08	-4.94	-5.88
QNS 46		μg/m^3				
Winter	$PM_{2.5}$	13.6375				
	Nitrate	3.18				
	Sulfate	3.145				
	Ammonium	1.97225	OM=OC*Factor			
	Inorganics	1.80079	Factor	1.4	1.8	2.0
	OC	2.98	OM	4.167	5.3576	5.9529
	EC	0.48				
	Other	0.09		-1.10	-2.29	-2.89
QNS 50		μg/m^3				
Early Spring	$PM_{2.5}$	11.89				
	Nitrate	2.7088				
	Sulfate	3.565				
	Ammonium	1.9005	OM=OC*Factor			
	Inorganics	1.72498	Factor	1.4	1.8	2.0
	OC	2.90	OM	4.0658	5.2274	5.8082

	EC	0.52				
	Other	-1.44		-2.60	-3.76	-4.34
QNS 54		μg/m^3				
Spring	$PM_{2.5}$	9.4875				
	Nitrate	1.78538				
	Sulfate	2.61375				
	Ammonium	1.2655	OM=OC*Factor			
	Inorganics	1.52293	Factor	1.4	1.8	2.0
	OC	3.23	OM	4.5216	5.8135	6.4595
	EC	0.56				
	Other	-1.49		-2.78	-4.07	-4.72
		μg/m^3				
QNS 58	$PM_{2.5}$	12.6286				
Late Spring	Nitrate	1.85986				
	Sulfate	4.18286				
	Ammonium	1.72886	OM=OC*Factor			
	Inorganics	1.94993	Factor	1.4	1.8	2.0
	OC	3.76	OM	5.2625	6.766	7.5178
	EC	0.65				
	Other	-1.50		-3.00	-4.51	-5.26
2002-2003 Yearly Average		μg/m^3				
	$PM_{2.5}$	12.8069				
	Nitrate	2.09392				
	Sulfate	3.45781				
	Ammonium	1.71583	OM=OC*Factor			
	Inorganics	1.84987	Factor	1.4	1.8	2.0
	OC	3.55475	OM	4.9767	6.3986	7.1095
	EC	0.63994				
	Other	-0.5052		-1.927	-3.349	-4.06
	% error	3.94497		15.048	26.15	31.702
Summer		μg/m^3				
	$PM_{2.5}$	15.2313				
	Nitrate	1.18975				
	Sulfate	4.81813				
	Ammonium	1.95888	OM=OC*Factor			

	Inorganics	2.36564	Factor	1.4	1.8	2.0
	OC	4.37755	OM	6.1286	7.8796	8.7551
	EC	0.60461				
	Other	-0.0833		-1.834	-3.585	-4.461
	% error	0.54687		12.043	23.539	29.287
Fall		μg/m^3				
	$PM_{2.5}$	10.8543				
	Nitrate	1.51634				
	Sulfate	2.57676				
	Ammonium	1.26003	OM=OC*Factor			
	Inorganics	1.55025	Factor	1.4	1.8	2.0
	OC	3.08549	OM	4.3197	5.5539	6.171
	EC	0.64611				
	Other	0.21929		-1.015	-2.249	-2.866
	% error	2.02035		9.3502	20.721	26.406
Winter		μg/m^3				
	$PM_{2.5}$	15.5188				
	Nitrate	3.82833				
	Sulfate	3.425				
	Ammonium	2.28279	OM=OC*Factor			
	Inorganics	1.9594	Factor	1.4	1.8	2.0
	OC	3.82159	OM	5.3502	6.8789	7.6432
	EC	0.76256				
	Other	-0.5609		-2.09	-3.618	-4.383
	% error	3.61448		13.465	23.315	28.24
Spring		μg/m^3				
	$PM_{2.5}$	11.3354				
	Nitrate	2.11801				
	Sulfate	3.45387				
	Ammonium	1.63162	OM=OC*Factor			
	Inorganics	1.73261	Factor	1.4	1.8	2.0
	OC	3.29759	OM	4.6166	5.9357	6.5952
	EC	0.57557				
	Other	-1.4739		-2.793	-4.112	-4.771
	% error	13.0028		24.639	36.276	42.094

Westport, CT SOAP 2002-2003

		μg/m^3				
WPT 26	$PM_{2.5}$	10.55				
Summer	Nitrate	0.4735				
	Sulfate	3.12683				
	Ammonium	0.86047	OM=OC*Factor			
	Inorganics	1.73927	Factor	1.4	1.8	2.0
	OC	3.29	OM	4.601	5.916	6.573
	EC	0.37				
	Other	0.69		-0.62	-1.94	-2.60
WPT 30		μg/m^3				
Early Fall	$PM_{2.5}$	9.55				
	Nitrate	0.79425				
	Sulfate	2.58525				
	Ammonium	0.8575	OM=OC*Factor			
	Inorganics	1.57975	Factor	1.4	1.8	2.0
	OC	3.32	OM	4.65	5.979	6.643
	EC	0.35				
	Other	0.06		-1.27	-2.60	-3.26
WPT 34		μg/m^3				
Fall	$PM_{2.5}$	6.87143				
	Nitrate	0.45314				
	Sulfate	1.71243				
	Ammonium	0.52371	OM=OC*Factor			
	Inorganics	0.99644	Factor	1.4	1.8	2.0
	OC	2.67	OM	3.738	4.807	5.341
	EC	0.37				
	Other	0.14		-0.93	-1.99	-2.53
WPT 38		μg/m^3				
Late Fall	$PM_{2.5}$	9.78				
	Nitrate	1.402				
	Sulfate	2.59				
	Ammonium	0.8674	OM=OC*Factor			
	Inorganics	1.57549	Factor	1.4	1.8	2.0
	OC	2.74	OM	3.837	4.934	5.482
	EC	0.41				

	Other	0.19		-0.90	-2.00	-2.55
WPT 43		μg/m^3				
Early Winter	$PM_{2.5}$	12.98				
	Nitrate	2.1944				
	Sulfate	3.256				
	Ammonium	1.6146	OM=OC*Factor			
	Inorganics	1.7959	Factor	1.4	1.8	2.0
	OC	4.49	OM	6.285	8.08	8.978
	EC	0.66				
	Other	-1.03		-2.83	-4.62	-5.52
		μg/m^3				
WPT 47	$PM_{2.5}$	12.0857				
Winter	Nitrate	2.22829				
	Sulfate	2.962				
	Ammonium	1.59271	OM=OC*Factor			
	Inorganics	1.52868	Factor	1.4	1.8	2.0
	OC	3.04	OM	4.258	5.475	6.083
	EC	0.31				
	Other	0.42		-0.80	-2.01	-2.62
WPT 51		μg/m^3				
Early Spring	$PM_{2.5}$	10.0625				
	Nitrate	1.10425				
	Sulfate	3.3125				
	Ammonium	1.16225	OM=OC*Factor			
	Inorganics	1.47768	Factor	1.4	1.8	2.0
	OC	3.41	OM	4.772	6.135	6.817
	EC	0.31				
	Other	-0.71		-2.08	-3.44	-4.12
WPT 55		μg/m^3				
Spring	$PM_{2.5}$	7.125				
	Nitrate	0.80613				
	Sulfate	2.07488				
	Ammonium	0.66138	OM=OC*Factor			
	Inorganics	1.073	Factor	1.4	1.8	2.0
	OC	2.44	OM	3.411	4.386	4.873

	EC	0.27				
	Other	-0.19		-1.17	-2.14	-2.63
WPT 59		μg/m^3				
Late Spring	$PM_{2.5}$	10.4				
	Nitrate	1.13325				
	Sulfate	3.5175				
	Ammonium	0.39625	OM=OC*Factor			
	Inorganics	2.19259	Factor	1.4	1.8	2.0
	OC	2.89	OM	4.04	5.194	5.771
	EC	0.39				
	Other	-0.11		-1.27	-2.42	-3.00
2002-2003 Yearly Average		μg/m^3				
	$PM_{2.5}$	9.93385				
	Nitrate	1.17658				
	Sulfate	2.79304				
	Ammonium	0.94847	OM=OC*Factor			
	Inorganics	1.55098	Factor	1.4	1.8	2.0
	OC	3.14229	OM	4.399	5.656	6.285
	EC	0.38349				
	Other	-0.06		-1.32	-2.57	-3.2
	% error	0.61		13.27	25.92	32.25
Summer		μg/m^3				
	$PM_{2.5}$	10.55				
	Nitrate	0.4735				
	Sulfate	3.12683				
	Ammonium	0.86047	OM=OC*Factor			
	Inorganics	1.73927	Factor	1.4	1.8	2.0
	OC	3.29	OM	4.601	5.916	6.573
	EC	0.37				
	Other	0.69		-0.62	-1.94	-2.60
	% error	6.55		5.91	18.37	24.61
Fall		μg/m^3				
	$PM_{2.5}$	8.73381				
	Nitrate	0.88313				
	Sulfate	2.29589				

	Ammonium	0.74954	OM=OC*Factor			
	Inorganics	1.38389	Factor	1.4	1.8	2.0
	OC	2.91094	OM	4.075	5.24	5.822
	EC	0.37888				
	Other	0.13154		-1.03	-2.2	-2.78
	% error	1.50608		11.83	25.16	31.82
Winter		μg/m^3				
	$PM_{2.5}$	12.5329				
	Nitrate	2.21134				
	Sulfate	3.109				
	Ammonium	1.60366	OM=OC*Factor			
	Inorganics	1.66229	Factor	1.4	1.8	2.0
	OC	3.76542	OM	5.272	6.778	7.531
	EC	0.48662				
	Other	-0.3055		-1.81	-3.32	-4.07
	% error	2.4374		14.46	26.47	32.48
Spring		μg/m^3				
	$PM_{2.5}$	9.19583				
	Nitrate	1.01454				
	Sulfate	2.96829				
	Ammonium	0.73996	OM=OC*Factor			
	Inorganics	1.58109	Factor	1.4	1.8	2.0
	OC	2.91009	OM	4.074	5.238	5.82
	EC	0.32303				
	Other	-0.3412		-1.51	-2.67	-3.25
	% error	3.71009		16.37	29.03	35.36

Pinnacle State Park, NY SOAP 2005-2007

		μg/m^3				
Pinn 01	$PM_{2.5}$	6.98119				
Oct-05	Ammonium	1.13364				
	Nitrate	0.3511				
	Sulfate	3.5724	OM=OC*Factor			
	Inorganics	1.1812	Factor	1.4	1.8	2.0
	OC	2.35	OM	3.292	4.2325	4.7028
	EC	0.15				
	Other	-1.76		-2.70	-3.64	-4.11
Pinn 02	$PM_{2.5}$	6.54461				
Nov-05	Ammonium	0.82596				
	Nitrate	0.69641				
	Sulfate	2.27594	OM=OC*Factor			
	Inorganics	1.07186	Factor	1.4	1.8	2.0
	OC	1.97	OM	2.759	3.5476	3.9417
	EC	0.15				
	Other	-0.44		-1.23	-2.02	6.5446
Pinn 03	$PM_{2.5}$	10.3328				
Dec-05	Ammonium	1.40804				
	Nitrate	1.74062				
	Sulfate	3.1049	OM=OC*Factor			
	Inorganics	1.58769	Factor	1.4	1.8	2.0
	OC	2.60	OM	3.644	4.6856	5.2062
	EC	0.18				
	Other	-0.29		-1.33	-2.38	-2.90
Pinn 04	$PM_{2.5}$	9.16179				
Jan-06	Ammonium	1.19708				
	Nitrate	1.43353				
	Sulfate	2.505	OM=OC*Factor			
	Inorganics	1.18953	Factor	1.4	1.8	2.0
	OC	2.59	OM	3.62	4.6545	5.1717
	EC	0.19				
	Other	0.06		-0.98	-2.01	-2.53
Pinn 05	$PM_{2.5}$	8.90891				

Feb-06	Ammonium	1.26				
	Nitrate	1.60819				
	Sulfate	2.79471	OM=OC*Factor			
	Inorganics	1.33067	Factor	1.4	1.8	2.0
	OC	2.45297	OM	3.434	4.4153	4.9059
	EC	0.17831				
	Other	-0.7159		-1.697	-2.678	-3.169
Pinn 06	$PM_{2.5}$	9.57072				
Mar-06	Ammonium	1.53484				
	Nitrate	1.78647				
	Sulfate	3.3933	OM=OC*Factor			
	Inorganics	1.53619	Factor	1.4	1.8	2.0
	OC	2.25	OM	3.155	4.057	4.5077
	EC	0.18				
	Other	-1.11		-2.01	-2.91	-3.36
Pinn 07	$PM_{2.5}$	4.79874				
Apr-06	Ammonium	0.56807				
	Nitrate	0.38928				
	Sulfate	1.56754	OM=OC*Factor			
	Inorganics	0.8202	Factor	1.4	1.8	2.0
	OC	1.63	OM	2.284	2.9366	3.2629
	EC	0.13				
	Other	-0.30		-0.96	-1.61	-1.94
May-06	$PM_{2.5}$	10.2653				
	Ammonium	1.2021				
	Nitrate	0.37042				
	Sulfate	4.03174	OM=OC*Factor			
	Inorganics	0.00555	Factor	1.4	1.8	2.0
	OC	2.67	OM	3.733	4.799	5.3322
	EC	0.15				
	Other	1.84		0.78	-0.29	-0.82
Pinn 09	$PM_{2.5}$	9.42447				
Jun-06	Ammonium	0.89876				
	Nitrate	0.14912				
	Sulfate	3.52764	OM=OC*Factor			

	Inorganics	1.45891	Factor	1.4	1.8	2.0
	OC	2.11	OM	2.949	3.7911	4.2123
	EC	0.10				
	Other	1.19		0.35	-0.50	-0.92
Pinn 10	$PM_{2.5}$	12.4442				
Jul-06	Ammonium	1.22611				
	Nitrate	0.24643				
	Sulfate	4.44487	OM=OC*Factor			
	Inorganics	2.26318	Factor	1.4	1.8	2.0
	OC	3.41	OM	4.774	6.1385	6.8205
	EC	0.16				
	Other	0.69		-0.67	-2.04	-2.72
Pinn 11	$PM_{2.5}$	9.24783				
Aug-06	Ammonium	0.76682				
	Nitrate	0.13863				
	Sulfate	3.09191	OM=OC*Factor			
	Inorganics	1.4255	Factor	1.4	1.8	2.0
	OC	2.57	OM	3.592	4.6185	5.1316
	EC	0.10				
	Other	1.16		0.13	-0.90	-1.41
Pinn 12	$PM_{2.5}$	10.4204				
Sep-06	Ammonium	0.69756				
	Nitrate	0.14152				
	Sulfate	3.33635	OM=OC*Factor			
	Inorganics	1.60324	Factor	1.4	1.8	2.0
	OC	1.83	OM	2.564	3.2961	3.6623
	EC	0.12				
	Other	2.69		1.95	1.22	0.86
Pinn 13	$PM_{2.5}$	3.62952				
Oct-06	Ammonium	0.36272				
	Nitrate	0.22614				
	Sulfate	1.10556	OM=OC*Factor			
	Inorganics	0.57759	Factor	1.4	1.8	2.0
	OC	1.59	OM	2.23	2.8666	3.1851
	EC	0.10				

	Other	-0.34		-0.97	-1.61	-1.93
Pinn 14	$PM_{2.5}$	8.45328				
Nov-06	Ammonium	1.14431				
	Nitrate	1.60159				
	Sulfate	2.19881	OM=OC*Factor			
	Inorganics	1.08552	Factor	1.4	1.8	2.0
	OC	2.26	OM	3.166	4.07	4.5222
	EC	0.17				
	Other	-0.01		-0.91	-1.82	-2.27
Pinn 15	$PM_{2.5}$	6.16492				
Dec-06	Ammonium	0.91066				
	Nitrate	0.85478				
	Sulfate	2.32807	OM=OC*Factor			
	Inorganics	0.99789	Factor	1.4	1.8	2.0
	OC	1.55	OM	2.172	2.7923	3.1025
	EC	0.10				
	Other	-0.57		-1.19	-1.81	-2.12
Pinn 16	$PM_{2.5}$	8.17618				
Jan-07	Ammonium	0.98207				
	Nitrate	1.32158				
	Sulfate	2.45548	OM=OC*Factor			
	Inorganics	1.16671	Factor	1.4	1.8	2.0
	OC	1.56	OM	2.188	2.8133	3.1259
	EC	0.12				
	Other	0.57		-0.06	-0.68	8.1762
Pinn 17	$PM_{2.5}$	7.85				
Feb-07	Ammonium	0.97				
	Nitrate	1.60				
	Sulfate	2.07	OM=OC*Factor			
	Inorganics	1.19141	Factor	1.4	1.8	2.0
	OC	1.47	OM	2.056	2.6433	2.937
	EC	0.11				
	Other	0.44		-0.15	7.8454	-1.03
2006 Yearly Average						

	$PM_{2.5}$	8.54084				
	Ammonium	0.98075				
	Nitrate	0.74551				
	Sulfate	2.86046	OM=OC*Factor			
	Inorganics	1.19117	Factor	1.4	1.8	2.0
	OC	2.24238	OM	3.139	4.0363	4.4848
	EC	0.13885				
	Other	0.38172		-0.515	-1.412	-1.861
	% error	4.46939		6.033	16.534	21.785
Summer						
	$PM_{2.5}$	10.3722				
	Ammonium	0.9639				
	Nitrate	0.17806				
	Sulfate	3.68814	OM=OC*Factor			
	Inorganics	1.71587	Factor	1.4	1.8	2.0
	OC	2.69408	OM	3.772	4.8493	5.3882
	EC	0.11996				
	Other	1.01214		-0.065	-1.143	-1.682
	% error	9.75829		0.631	11.021	16.216
Fall						
	$PM_{2.5}$	7.50106				
	Ammonium	0.73486				
	Nitrate	0.65642				
	Sulfate	2.21357	OM=OC*Factor			
	Inorganics	1.08878	Factor	1.4	1.8	2.0
	OC	1.89494	OM	2.653	3.4109	3.7899
	EC	0.13081				
	Other	0.78168		0.024	-0.734	-1.113
	% error	10.4209		0.316	9.7889	14.841
Winter						
	$PM_{2.5}$	7.40				
	Ammonium	0.95				
	Nitrate	1.26				
	Sulfate	2.28	OM=OC*Factor			
	Inorganics	1.12	Factor	1.4	1.8	2.0
	OC	1.53	OM	2.139	2.7496	3.0551

	EC	0.11				
	Other	0.14		-0.47	-1.08	-1.38
	% error	1.93		6.33	14.59	18.72
Spring	$PM_{2.5}$	8.2116				
	Ammonium	1.10167				
	Nitrate	0.84872				
	Sulfate	2.99753	OM=OC*Factor			
	Inorganics	0.78732	Factor	1.4	1.8	2.0
	OC	2.1838	OM	3.057	3.9308	4.3676
	EC	0.14919				
	Other	0.14338		-0.73	-1.604	-2.04
	% error	1.74601		8.892	19.529	24.848

Bronx, NY SOAP 2005-2007

		$\mu g/m^3$				
Bronx 01	$PM_{2.5}$	12.2974				
Oct-05	Ammonium	1.5814				
	Nitrate	1.7537				
	Sulfate	3.31945	OM=OC*Factor			
	Inorganics	2.06483	Factor	1.4	1.8	2.0
	OC	4.22	OM	5.902	7.59	8.43
	EC	0.85				
	Other	-1.49		-3.17	-4.86	-5.70
Bronx 02	$PM_{2.5}$	16.9522				
Nov-05	Ammonium	1.90165				
	Nitrate	2.49819				
	Sulfate	3.38827	OM=OC*Factor			
	Inorganics	2.18631	Factor	1.4	1.8	2.0
	OC	3.82	OM	5.35	6.88	7.64
	EC	0.60				
	Other	2.56		1.03	-0.50	-1.26
Bronx 03	$PM_{2.5}$	19.1931				
Dec-05	Ammonium	1.94215				
	Nitrate	2.91873				
	Sulfate	3.32606	OM=OC*Factor			
	Inorganics	2.0357	Factor	1.4	1.8	2.0

	OC	4.6066	OM	6.449	8.29	9.21
	EC	0.67451				
	Other	3.68933		1.847	0	-0.92
Bronx 04	$PM_{2.5}$	21.6246				
Jan-06	Ammonium	2.62194				
	Nitrate	3.35287				
	Sulfate	4.54981	OM=OC*Factor			
	Inorganics	2.58423	Factor	1.4	1.8	2.0
	OC	4.83	OM	6.763	8.7	9.66
	EC	1.81				
	Other	1.88		-0.06	-1.99	-2.96
Bronx 05	$PM_{2.5}$	26.2554				
Feb-06	Ammonium	3.26969				
	Nitrate	5.79628				
	Sulfate	5.43073	OM=OC*Factor			
	Inorganics	2.746	Factor	1.4	1.8	2.0
	OC	6.29	OM	8.806	11.3	12.6
	EC	1.24				
	Other	1.48		-1.03	-3.55	-4.81
Bronx 06	$PM_{2.5}$	18.4168				
Mar-06	Ammonium	2.27954				
	Nitrate	3.37509				
	Sulfate	3.75373	OM=OC*Factor			
	Inorganics	1.92228	Factor	1.4	1.8	2.0
	OC	4.36069	OM	6.105	7.85	8.72
	EC	0.86412				
	Other	1.86134		0.117	-1.63	-2.5
Bronx 07	$PM_{2.5}$	12.7226				
Apr-06	Ammonium	1.33403				
	Nitrate	1.91545				
	Sulfate	2.54955	OM=OC*Factor			
	Inorganics	1.40881	Factor	1.4	1.8	2.0
	OC	3.77	OM	5.273	6.78	7.53
	EC	0.78				
	Other	0.97		-0.54	-2.05	-2.80

Bronx 08	$PM_{2.5}$	17.0253				
May-06	Ammonium	2.6676				
	Nitrate	2.00134				
	Sulfate	5.91529	OM=OC*Factor			
	Inorganics	2.44729	Factor	1.4	1.8	2.0
	OC	4.22	OM	5.905	7.59	8.44
	EC	0.59				
	Other	-0.82		-2.50	-4.19	-5.03
Bronx 09	$PM_{2.5}$	12.8914				
Jun-06	Ammonium	1.55779				
	Nitrate	1.03738				
	Sulfate	3.55925	OM=OC*Factor			
	Inorganics	1.76985	Factor	1.4	1.8	2.0
	OC	4.11	OM	5.75	7.39	8.21
	EC	0.64				
	Other	0.22		-1.42	12.9	-3.89
Bronx 10	$PM_{2.5}$	27.3864				
Jul-06	Ammonium	3.64212				
	Nitrate	1.77305				
	Sulfate	9.07521	OM=OC*Factor			
	Inorganics	4.56165	Factor	1.4	1.8	2.0
	OC	6.97	OM	9.757	12.5	13.9
	EC	0.76				
	Other	0.61		-2.18	-4.97	-6.36
Bronx 11	$PM_{2.5}$	14.9747				
Aug-06	Ammonium	1.64609				
	Nitrate	0.46714				
	Sulfate	4.70365	OM=OC*Factor			
	Inorganics	2.17654	Factor	1.4	1.8	2.0
	OC	4.24	OM	5.941	7.64	8.49
	EC	0.59				
	Other	1.15		-0.55	-2.25	-3.10
Bronx 12	$PM_{2.5}$	11.9603				
Sep-06	Ammonium	1.31864				

	Nitrate	1.23323				
	Sulfate	3.17693	OM=OC*Factor			
	Inorganics	1.88433	Factor	1.4	1.8	2.0
	OC	3.13	OM	4.385	5.64	6.26
	EC	0.41				
	Other	0.81		-0.45	-1.70	-2.33
Bronx 13	$PM_{2.5}$	8.67482				
Oct-06	Ammonium	0.84533				
	Nitrate	0.95306				
	Sulfate	1.88903	OM=OC*Factor			
	Inorganics	1.06359	Factor	1.4	1.8	2.0
	OC	3.36	OM	4.707	6.05	6.72
	EC	0.61				
	Other	-0.05		-1.40	-1.40	-3.41
Bronx 14	$PM_{2.5}$	14.0593				
Nov-06	Ammonium	1.50649				
	Nitrate	2.14575				
	Sulfate	2.90079	OM=OC*Factor			
	Inorganics	1.74739	Factor	1.4	1.8	2.0
	OC	3.87	OM	5.417	6.96	7.74
	EC	0.84				
	Other	1.05		-0.49	-2.04	-2.82
Bronx 15	$PM_{2.5}$	11.9933				
Dec-06	Ammonium	1.25647				
	Nitrate	1.71694				
	Sulfate	2.58794	OM=OC*Factor			
	Inorganics	1.70069	Factor	1.4	1.8	2.0
	OC	3.31656	OM	4.643	5.97	6.63
	EC	0.58993				
	Other	0.82477		-0.5	-1.83	-2.49
Bronx 16	$PM_{2.5}$	16.3741				
Jan-07	Ammonium	2.31931				
	Nitrate	3.70098				
	Sulfate	3.72632	OM=OC*Factor			
	Inorganics	1.99325	Factor	1.4	1.8	2.0

	OC	4.34	OM	6.08	7.82	8.69
	EC	1.05				
	Other	-0.75		-2.49	-4.23	16.4
Bronx 17	$PM_{2.5}$	11.7778				
Feb-07	Ammonium	1.59962				
	Nitrate	2.77699				
	Sulfate	2.70284	OM=OC*Factor			
	Inorganics	1.52753	Factor	1.4	1.8	2.0
	OC	3.64	OM	5.099	6.56	7.28
	EC	0.54				
	Other	-1.01		-2.47	-3.92	-4.65
Yearly Average 2006						
	$PM_{2.5}$	16.4987				
	Ammonium	1.99548				
	Nitrate	2.1473				
	Sulfate	4.17433	OM=OC*Factor			
	Inorganics	2.16772	Factor	1.4	1.8	2.0
	OC	4.37	OM	6.121	7.87	8.74
	EC	0.81				
	Other	0.83		-0.92	-2.67	-3.54
	% error	5.04		5.56	16.16	21.46
Summer	$PM_{2.5}$	18.4175				
	Ammonium	2.282				
	Nitrate	1.09252				
	Sulfate	5.77937	OM=OC*Factor			
	Inorganics	2.83601	Factor	1.4	1.8	2.0
	OC	5.10686	OM	7.15	9.19	10.2
	EC	0.6624				
	Other	0.65832		-1.38	-3.43	-4.45
	% error	3.57441		7.517	18.6	24.2
Fall	$PM_{2.5}$	11.5648				
	Ammonium	1.22349				
	Nitrate	1.44401				
	Sulfate	2.65559	OM=OC*Factor			
	Inorganics	1.5651	Factor	1.4	1.8	2.0

	OC	3.45453	OM	4.836	6.22	6.91
	EC	0.6197				
	Other	0.6024		-0.78	-2.16	-2.85
	% error	5.20892		6.739	18.7	24.7
Winter	$PM_{2.5}$	13.3817				
	Ammonium	1.69409				
	Nitrate	2.52122				
	Sulfate	3.07168	OM=OC*Factor			
	Inorganics	1.81378	Factor	1.4	1.8	2.0
	OC	3.84301	OM	5.38	6.92	7.69
	EC	0.8239				
	Other	-0.386		-1.92	-3.46	-4.23
	% error	2.88425		14.37	25.9	31.6
Spring	$PM_{2.5}$	16.0549				
	Ammonium	2.09372				
	Nitrate	2.43063				
	Sulfate	4.07286	OM=OC*Factor			
	Inorganics	1.92613	Factor	1.4	1.8	2.0
	OC	4.11503	OM	5.761	7.41	8.23
	EC	0.74645				
	Other	0.67007		-0.98	-2.62	-3.44
	% error	4.17359		6.079	16.3	21.5

Appendix K: Ambient EC and OC Data Comparisons

Chs = Chester, NJ; Elz = Elizabeth, NJ; Qns = Queens, NY; Wpt = Westport, CT

Season	composite	composite OC ($\mu g/m^3$)	composite EC ($\mu g/m^3$)
summer early	Chs 23	4.29	0.19
summer	Chs 27	3.66	0.20
fall early	Chs 31	2.09	0.11
fall	Chs 35	2.15	0.16
late fall	Chs 39	1.90	0.19
Winter early	Chs 44	2.44	0.26
winter	Chs 48	3.11	0.57
Spring early	Chs 52	2.20	0.18
Spring	Chs 56	2.38	0.20
late Spring	Chs 60	2.37	0.14
Summer early	Elz 21	6.30	1.54
Summer	Elz 24	5.90	1.77
Fall early	Elz 28	3.23	1.29
Fall	Elz 32	3.32	1.36
late fall	Elz 36	3.58	0.94
Winter early	Elz 41	5.81	1.45
Winter	Elz 45	5.03	1.00
Spring early	Elz 49	3.97	0.87
Spring	Elz 53	4.09	1.21
late spring	Elz 57	4.90	1.43
Summer early	Qns 22	4.43	0.62
Summer	Qns 25	4.32	0.59
Fall early	Qns 29	3.09	0.59
Fall	Qns 33	2.60	0.60
late fall	Qns 37	3.57	0.75
Winter early	Qns 42	4.67	1.05
Winter	Qns 46	2.98	0.48
Spring Early	Qns 50	2.90	0.52
Spring	Qns 54	3.23	0.56
late Spring	Qns 58	3.76	0.65
Summer	Wpt 26	3.29	0.37
Fall Early	Wpt 30	3.32	0.35
Fall	Wpt 34	2.67	0.37
late fall	Wpt 38	2.74	0.41
Winter early	Wpt 43	4.49	0.66
Winter	Wpt 47	3.04	0.31
Spring early	Wpt 51	3.41	0.31
Spring	Wpt 55	2.44	0.27

late Spring	Wpt 59	2.89	0.39

Bronx = Bronx, NY; Pinn = Pinnacle State Park, NY

Month	composite	average OC ($\mu g/m^3$)	average EC ($\mu g/m^3$)
Oct-05	Bronx 01	4.22	0.85
Nov-05	Bronx 02	3.82	0.60
Dec-05	Bronx 03	4.61	0.67
Jan-06	Bronx 04	4.83	1.81
Feb-06	Bronx 05	6.29	1.24
Mar-06	Bronx 06	4.36	0.86
Apr-06	Bronx 07	3.77	0.78
May-06	Bronx 08	4.22	0.59
Jun-06	Bronx 09	4.11	0.64
Jul-06	Bronx 10	6.97	0.76
Aug-06	Bronx 11	4.24	0.59
Sep-06	Bronx 12	3.13	0.41
Oct-06	Bronx 13	3.36	0.61
Nov-06	Bronx 14	3.87	0.84
Dec-06	Bronx 15	3.32	0.59
Jan-07	Bronx 16	4.34	1.05
Feb-07	Bronx 17	3.64	0.54
Oct-05	Pinn 01	2.35	0.15
Nov-05	Pinn 02	1.97	0.15
Dec-05	Pinn 03	2.60	0.18
Jan-06	Pinn 04	2.59	0.19
Feb-06	Pinn 05	2.45	0.18
Mar-06	Pinn 06	2.25	0.18
Apr-06	Pinn 07	1.63	0.13
May-06	Pinn08	2.67	0.15
Jun-06	Pinn 09	2.11	0.10
Jul-06	Pinn 10	3.41	0.16
Aug-06	Pinn 11	2.57	0.10
Sep-06	Pinn 12	1.83	0.12
Oct-06	Pinn 13	1.59	0.10
Nov-06	Pinn 14	2.26	0.17
Dec-06	Pinn 15	1.55	0.10
Jan-07	Pinn 16	1.56	0.12
Feb-07	Pinn 17	1.47	0.11

Ambient SOAP 2002-2003 molecular markers normalized to EC and OC

Season	composite	Ratio Levoglucosan /OC, ng/ug	Ratio Levoglucosan /EC, ng/ug	Ratio Cholesterol /OC, ng/ug	Ratio Cholesterol /EC, ng/ug
summer early	Chs 23	5.80	130.90	0.00	0.00
summer	Chs 27	6.87	127.08	0.00	0.00
fall early	Chs 31	5.57	110.00	0.00	0.00
fall	Chs 35	11.92	161.90	0.00	0.00
late fall	Chs 39	42.16	431.84	0.00	0.00
Winter early	Chs 44	28.79	271.33	0.00	0.00
winter	Chs 48	7.77	42.13	0.21	1.15
Spring early	Chs 52	12.24	147.17	0.00	0.00
Spring	Chs 56	1.15	13.71	0.02	0.21
late Spring	Chs 60	5.42	93.58	0.01	0.21
Summer early	Elz 21	4.53	18.54	0.10	0.41
Summer	Elz 24	9.36	31.28	0.02	0.07
Fall early	Elz 28	5.16	12.88	0.00	0.00
Fall	Elz 32	21.90	53.27	0.15	0.36
late fall	Elz 36	38.53	146.81	0.08	0.29
Winter early	Elz 41	4.15	16.63	0.00	0.00
Winter	Elz 45	1.32	6.66	0.05	0.23
Spring early	Elz 49	5.42	24.85	0.00	0.00
Spring	Elz 53	1.06	3.60	0.06	0.19
late spring	Elz 57	1.10	3.78	0.09	0.30
Summer early	Qns 22	17.82	126.79	0.00	0.00
Summer	Qns 25	5.38	39.64	0.00	0.00
Fall early	Qns 29	3.19	16.63	0.02	0.12
Fall	Qns 33	34.29	148.59	0.08	0.35
late fall	Qns 37	41.17	196.77	0.11	0.55
Winter early	Qns 42	22.36	99.44	0.17	0.74
Winter	Qns 46	12.65	79.13	0.03	0.20
Spring Early	Qns 50	4.26	23.67	0.00	0.00
Spring	Qns 54	0.73	4.23	0.07	0.39
late Spring	Qns 58	1.52	8.82	0.05	0.30
Summer	Wpt 26	1.02	9.02	0.00	0.00
Fall Early	Wpt 30	21.88	205.15	0.00	0.00
Fall	Wpt 34	26.12	187.03	0.00	0.00
late fall	Wpt 38	69.13	462.67	0.00	0.00
Winter early	Wpt 43	33.32	226.43	0.00	0.00
Winter	Wpt 47	39.74	386.71	0.02	0.23
Spring early	Wpt 51	23.12	252.41	0.00	0.00
Spring	Wpt 55	2.08	18.87	0.03	0.25
late Spring	Wpt 59	3.14	23.33	0.00	0.00

Season	composite	Ratio n-alkanols/ OC, ng/µg	Ratio n-alknols/ EC, ng/µg	Ratio cis-pinonic acid/OC, ng/µg	Ratio cis-pinonic acid/EC, ng/µg
summer early	Chs 23	1.38	31.18	1.84	41.58
summer	Chs 27	0.13	2.34	0.00	0.00
fall early	Chs 31	1.27	25.05	0.00	0.00
fall	Chs 35	0.50	6.73	1.17	15.93
late fall	Chs 39	0.32	3.27	1.84	18.82
Winter early	Chs 44	0.75	7.11	0.06	0.55
winter	Chs 48	0.74	4.00	0.00	0.00
Spring early	Chs 52	1.10	13.29	1.67	20.06
Spring	Chs 56	2.22	26.57	2.45	29.34
late Spring	Chs 60	1.50	25.86	1.77	30.56
Summer early	Elz 21	2.32	9.50	0.84	3.46
Summer	Elz 24	0.72	2.40	0.00	0.00
Fall early	Elz 28	1.09	2.72	0.00	0.00
Fall	Elz 32	0.53	1.29	0.71	1.72
late fall	Elz 36	0.61	2.34	0.00	0.00
Winter early	Elz 41	0.33	1.31	0.25	0.98
Winter	Elz 45	0.27	1.36	0.07	0.35
Spring early	Elz 49	0.09	0.42	0.00	0.00
Spring	Elz 53	0.96	3.25	0.59	1.99
late spring	Elz 57	0.45	1.56	0.88	3.01
Summer early	Qns 22	2.91	20.74	0.71	5.08
Summer	Qns 25	0.19	1.40	0.44	3.27
Fall early	Qns 29	3.20	16.72	1.10	5.73
Fall	Qns 33	0.73	3.15	0.00	0.00
late fall	Qns 37	1.11	5.30	0.00	0.00
Winter early	Qns 42	0.66	2.92	0.00	0.00
Winter	Qns 46	1.04	6.51	0.19	1.22
Spring Early	Qns 50	0.59	3.29	0.83	4.59
Spring	Qns 54	2.14	12.40	1.03	5.96
late Spring	Qns 58	1.15	6.68	0.15	0.85
Summer	Wpt 26	0.28	2.46	1.58	13.95
Fall Early	Wpt 30	0.87	8.16	1.42	13.28
Fall	Wpt 34	0.61	4.34	1.11	7.98
late fall	Wpt 38	0.88	5.86	0.99	6.60
Winter early	Wpt 43	1.07	7.25	0.39	2.67
Winter	Wpt 47	0.47	4.55	0.00	0.00
Spring early	Wpt 51	0.54	5.89	0.70	7.60
Spring	Wpt 55	0.49	4.48	0.00	0.00
late Spring	Wpt 59	0.19	1.40	1.13	8.39

Season	composite	levulinic acid/OC ng/µg	levulinic acid/EC ng/µg
summer early	Chs 23	4.89	110.41
summer	Chs 27	0.00	0.00
fall early	Chs 31	0.00	0.00
fall	Chs 35	0.00	0.00
late fall	Chs 39	4.95	50.71
Winter early	Chs 44	0.00	0.00
winter	Chs 48	0.00	0.00
Spring early	Chs 52	0.00	0.00
Spring	Chs 56	2.62	31.29
late Spring	Chs 60	3.69	63.79
Summer early	Elz 21	2.78	11.41
Summer	Elz 24	0.00	0.00
Fall early	Elz 28	0.00	0.00
Fall	Elz 32	0.00	0.00
late fall	Elz 36	0.00	0.00
Winter early	Elz 41	0.00	0.00
Winter	Elz 45	1.47	7.41
Spring early	Elz 49	0.00	0.00
Spring	Elz 53	0.00	0.00
late spring	Elz 57	0.00	0.00
Summer early	Qns 22	0.00	0.00
Summer	Qns 25	0.00	0.00
Fall early	Qns 29	0.00	0.00
Fall	Qns 33	0.00	0.00
late fall	Qns 37	0.00	0.00
Winter early	Qns 42	2.18	9.71
Winter	Qns 46	2.63	16.47
Spring Early	Qns 50	3.13	17.38
Spring	Qns 54	0.00	0.00
late Spring	Qns 58	0.00	0.00
Summer	Wpt 26	0.00	0.00
Fall Early	Wpt 30	0.00	0.00
Fall	Wpt 34	6.30	45.11
late fall	Wpt 38	0.00	0.00
Winter early	Wpt 43	2.55	17.33
Winter	Wpt 47	0.00	0.00
Spring early	Wpt 51	1.94	21.18
Spring	Wpt 55	0.81	7.36
late Spring	Wpt 59	3.92	29.08

SOAP NY 2005-2007 Ratios

Month	Composite	Levoglucosan/ OC, ng/µg	Levoglucosan /EC, ng/µg	Cholesterol /OC, ng/ug	Cholesterol /EC, ng/ug
Oct-05	Bronx 01	6.13	30.50	0.09	0.47
Nov-05	Bronx 02	16.55	106.16	0.04	0.23
Dec-05	Bronx 03	20.84	142.31	0.07	0.48
Jan-06	Bronx 04	17.44	46.57	0.08	0.21
Feb-06	Bronx 05	15.70	79.65	0.07	0.35
Mar-06	Bronx 06	11.57	58.39	0.05	0.23
Apr-06	Bronx 07	5.62	27.05	0.01	0.05
May-06	Bronx 08	2.89	20.59	0.02	0.16
Jun-06	Bronx 09	2.19	14.07	0.02	0.14
Jul-06	Bronx 10	1.05	9.67	0.00	0.00
Aug-06	Bronx 11	1.70	12.18	0.02	0.11
Sep-06	Bronx 12	5.89	44.94	0.05	0.35
Oct-06	Bronx 13	12.86	70.52	0.05	0.28
Nov-06	Bronx 14	15.72	72.79	0.04	0.18
Dec-06	Bronx 15	11.17	62.80	0.03	0.18
Jan-07	Bronx 16	19.70	81.81	0.07	0.28
Feb-07	Bronx 17	13.43	90.62	0.04	0.27
Oct-05	Pinn 01	27.75	433.35	0.01	0.23
Nov-05	Pinn 02	20.28	272.90	0.04	0.50
Dec-05	Pinn 03	45.63	655.85	0.00	0.00
Jan-06	Pinn 04	43.72	588.34	0.00	0.00
Feb-06	Pinn 05	39.05	537.14	0.00	0.00
Mar-06	Pinn 06	35.61	458.59	0.00	0.00
Apr-06	Pinn 07	19.42	249.17	0.00	0.00
May-06	Pinn 08	1.17	21.41	0.00	0.00
Jun-06	Pinn 09	0.86	18.78	0.00	0.00
Jul-06	Pinn 10	2.16	45.82	0.00	0.00
Aug-06	Pinn 11	6.76	167.88	0.00	0.00
Sep-06	Pinn 12	6.56	97.61	0.00	0.00
Oct-06	Pinn 13	18.21	289.24	0.00	0.00
Nov-06	Pinn 14	25.24	337.55	0.00	0.00
Dec-06	Pinn 15	23.42	378.84	0.00	0.00
Jan-07	Pinn 16	29.13	374.06	0.02	0.30
Feb-07	Pinn 17	23.16	312.35	0.00	0.00

Month	Composite	Total n-alkanols/OC, ng/µg	Total n-alkanols/EC, ng/µg	Cis-pinonic acid/OC, ng/µg	Cis-pinonic acid/EC, ng/µg
Oct-05	Bronx 01	0.22	1.11	0.00	0.00
Nov-05	Bronx 02	0.25	1.58	1.26	8.06
Dec-05	Bronx 03	0.58	3.93	0.54	3.69
Jan-06	Bronx 04	0.13	0.34	0.20	0.55
Feb-06	Bronx 05	0.36	1.82	0.38	1.91
Mar-06	Bronx 06	0.14	0.71	0.54	2.72
Apr-06	Bronx 07	0.00	0.00	0.44	2.11
May-06	Bronx 08	0.42	2.99	0.99	7.03
Jun-06	Bronx 09	0.62	3.97	0.97	6.22
Jul-06	Bronx 10	0.10	0.91	0.54	4.94
Aug-06	Bronx 11	0.13	0.92	0.91	6.49
Sep-06	Bronx 12	0.61	4.69	1.40	10.68
Oct-06	Bronx 13	0.50	2.77	0.69	3.77
Nov-06	Bronx 14	0.00	0.00	0.89	4.11
Dec-06	Bronx 15	0.39	2.22	0.96	5.37
Jan-07	Bronx 16	0.13	0.55	0.72	2.98
Feb-07	Bronx 17	0.24	1.62	0.32	2.15
Oct-05	Pinn 01	1.46	22.86	2.58	40.34
Nov-05	Pinn 02	1.62	21.76	1.79	24.09
Dec-05	Pinn 03	0.66	9.55	1.97	28.28
Jan-06	Pinn 04	0.48	6.50	1.44	19.38
Feb-06	Pinn 05	0.58	7.98	1.08	14.90
Mar-06	Pinn 06	0.81	10.48	2.27	29.22
Apr-06	Pinn 07	0.66	8.44	2.70	34.62
May-06	Pinn 08	0.95	17.51	2.17	39.83
Jun-06	Pinn 09	0.37	8.21	2.18	47.90
Jul-06	Pinn 10	0.27	5.70	0.00	0.00
Aug-06	Pinn 11	0.67	16.74	0.00	0.00
Sep-06	Pinn 12	0.27	4.06	1.10	16.37
Oct-06	Pinn 13	1.19	18.87	1.51	24.00
Nov-06	Pinn 14	0.79	10.53	4.37	58.44
Dec-06	Pinn 15	0.95	15.31	2.17	35.15
Jan-07	Pinn 16	0.69	8.89	2.16	27.71
Feb-07	Pinn 17	0.56	7.58	0.00	0.00

Month	Composite	Levulinic Acid/OC ng/µg	Levulinic Acid/EC ng/µg
Oct-05	Bronx 01	1.10	5.47
Nov-05	Bronx 02	2.26	14.50
Dec-05	Bronx 03	1.52	10.38
Jan-06	Bronx 04	0.00	0.00
Feb-06	Bronx 05	0.00	0.00
Mar-06	Bronx 06	1.95	9.86
Apr-06	Bronx 07	1.95	9.38
May-06	Bronx 08	2.16	15.39
Jun-06	Bronx 09	2.84	18.27
Jul-06	Bronx 10	3.05	28.10
Aug-06	Bronx 11	2.25	16.12
Sep-06	Bronx 12	3.50	26.69
Oct-06	Bronx 13	2.03	11.14
Nov-06	Bronx 14	2.37	10.97
Dec-06	Bronx 15	1.46	8.20
Jan-07	Bronx 16	1.57	6.52
Feb-07	Bronx 17	2.40	16.20
Oct-05	Pinn 01	3.72	58.04
Nov-05	Pinn 02	2.43	32.64
Dec-05	Pinn 03	3.33	47.82
Jan-06	Pinn 04	2.07	27.79
Feb-06	Pinn05	3.49	48.06
Mar-06	Pinn 06	4.36	56.16
Apr-06	Pinn 07	3.25	41.75
May-06	Pinn 08	4.96	90.95
Jun-06	Pinn 09	4.06	89.15
Jul-06	Pinn 10	2.46	52.25
Aug-06	Pinn 11	2.87	71.24
Sep-06	Pinn 12	3.64	54.16
Oct-06	Pinn 13	2.76	43.90
Nov-06	Pinn 14	2.59	34.61
Dec-06	Pinn 15	3.89	62.99
Jan-07	Pinn 16	3.30	42.39
Feb-07	Pinn 17	4.08	55.02

Estimates for the percent of OC from wood smoke
SOAP 2002-2003 data

Season	composite	%OC from levoglucosan	%OC from cholesterol
summer early	Chs 23	5.80	0.00
summer	Chs 27	6.87	0.00
fall early	Chs 31	5.57	0.00
fall	Chs 35	11.93	0.00
late fall	Chs 39	42.16	0.00
Winter early	Chs 44	28.80	0.00
winter	Chs 48	7.77	4.55
Spring early	Chs 52	12.24	0.00
Spring	Chs 56	1.15	0.37
late Spring	Chs 60	5.42	0.26
Summer early	Elz 21	4.53	2.15
Summer	Elz 24	9.36	0.46
Fall early	Elz 28	5.16	0.00
Fall	Elz 32	21.90	3.15
late fall	Elz 36	38.53	1.64
Winter early	Elz 41	4.15	0.00
Winter	Elz 45	1.32	1.00
Spring early	Elz 49	5.42	0.00
Spring	Elz 53	1.06	1.19
late spring	Elz 57	1.10	1.86
Summer early	Qns 22	17.82	0.00
Summer	Qns 25	5.38	0.00
Fall early	Qns 29	3.19	0.50
Fall	Qns 33	34.29	1.74
late fall	Qns 37	41.17	2.45
Winter early	Qns 42	22.36	3.59
Winter	Qns 46	12.65	0.69
Spring Early	Qns 50	4.26	0.00
Spring	Qns 54	0.73	1.45
late Spring	Qns 58	1.52	1.12
Summer	Wpt 26	1.02	0.00
Fall Early	Wpt 30	21.88	0.00
Fall	Wpt 34	26.12	0.00
late fall	Wpt 38	69.13	0.00
Winter early	Wpt 43	33.32	0.00
Winter	Wpt 47	39.74	0.51
Spring early	Wpt 51	23.12	0.00
Spring	Wpt 55	2.08	0.59
late Spring	Wpt 59	3.14	0.00

SOAP NY 2005-2007 data

Month	Composite	%OC from levoglucosan	%OC from cholesterol
Oct-05	Bronx01	6.13	2.01
Nov-05	Bronx 02	16.55	0.78
Dec-05	Bronx03	20.84	1.52
Jan-06	Bronx 4	17.44	1.72
Feb-06	Bronx 05	15.70	1.49
Mar-06	Bronx 06	11.57	0.97
Apr-06	Bronx 07	5.62	0.22
May-06	Bronx 08	2.89	0.48
Jun-06	Bronx 09	2.19	0.47
Jul-06	Bronx 10	1.05	0.00
Aug-06	Bronx 11	1.70	0.34
Sep-06	Bronx 12	5.89	0.98
Oct-06	Bronx 13	12.86	1.11
Nov-06	Bronx 14	15.72	0.84
Dec-06	Bronx 15	11.17	0.70
Jan-07	Bronx 16	19.70	1.47
Feb-07	Bronx 17	13.43	0.85
Oct-05	Pinn 01	27.75	0.31
Nov-05	Pinn 02	20.28	0.80
Dec-05	Pinn 03	45.63	0.00
Jan-06	Pinn 04	43.72	0.00
Feb-06	Pinn05	39.05	0.00
Mar-06	Pinn 06	35.61	0.00
Apr-06	Pinn 07	19.42	0.00
May-06	Pinn08	1.17	0.00
Jun-06	Pinn 09	0.86	0.00
Jul-06	Pinn 10	2.16	0.00
Aug-06	Pinn 11	6.76	0.00
Sep-06	Pinn 12	6.56	0.00
Oct-06	Pinn 13	18.21	0.00
Nov-06	Pinn 14	25.24	0.00
Dec-06	Pinn 15	23.42	0.00
Jan-07	Pinn 16	29.13	0.50
Feb-07	Pinn 17	23.16	0.00

Appendix L: EC normalized ambient data anova tables

Summer = early summer + summer = June, July and August
Fall = early fall + late fall + fall = September, October and November
Winter = early winter + winter = December, January and February
Spring = early spring + spring + late spring = March, April and May
alpha = 0.05 H_0 = there is no difference between urban and rural sites H_1 = there is a difference between urban and rural sites

Levoglucosan/EC		Urban	Rural	
ng/µg		Bronx	Pinnacle	
	Oct-05	30.49959	433.3467	
	Nov-05	106.1553	272.9049	
	Dec-05	142.3142	655.8542	
	Jan-06	46.56604	588.3395	
	Feb-06	79.6451	537.1425	
	Mar-06	58.38885	458.5853	
	Apr-06	27.04706	249.1659	
	May-06	20.59315	21.41351	
	Jun-06	14.06903	18.77646	
	Jul-06	9.670913	45.82054	
	Aug-06	12.17906	167.8826	
	Sep-06	44.93659	97.60908	
	Oct-06	70.51515	289.2429	
	Nov-06	72.78625	337.5474	
	Dec-06	62.79582	378.8411	
	Jan-07	81.81405	374.0584	
	Feb-07	90.61566	312.35	
Queens	early summer	126.7925	130.90	Chester
	summer	39.63809	127.08	
	early fall	16.63397	110.00	
	fall	148.5879	161.90	
	late fall	196.7664	431.84	
	early winter	99.43847	271.33	
	winter	79.12896	42.13	
	early spring	23.67195	147.17	
	spring	4.233404	13.71	
	late spring	8.820128	93.58	
Elizabeth	early summer	18.54		
	summer	31.28		
	early fall	12.88		
	fall	53.27		
	late fall	146.81		

	early winter	16.63		
	winter	6.66		
	early spring	24.85		
	spring	3.60		
	late spring	3.78		
Westport	summer	9.02		
	early fall	205.15		
	fall	187.03		
	late fall	462.67		
	early winter	226.43		
	winter	386.71		
	early spring	252.41		
	spring	18.87		
	late spring	23.33		
Q0 (Minimum)		3.598809	13.71473	
Q1 (25%)		17.11007	103.8065	
Q2 (Median)		45.75132	249.1659	
Q3 (75%)		104.4761	376.4498	
Q4 (Maximum)		462.6666	655.8542	
Inner quartile range		87.366	272.6432	
Low outlier		-113.939	-305.158	
High outlier		235.5251	785.4146	
skewness/kurtosis		5.143782	-0.62599	

Entire year

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	46	3804.24	82.70086	9811.155	Urban	
Column 2	27	6768.533	250.6864	34076.4	Rural	
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	480112	1	480112	25.67853	3.08E-06	3.97581
Within Groups	1327488	71	18697.02			
Total	1807600	72				
The P-value is less then alpha, there is a difference between urban and rural.						

Winter

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	1318.757	109.8964	10906.96		
Column 2	8	3160.05	395.0063	38995.51		

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	390180.6	1	390180.6	17.87336	0.000506	4.413873
Within Groups	392945.1	18	21830.29			
Total	783125.7	19				
The P-value is less then alpha, there is a difference between urban and rural.						

Spring

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	469.599	39.13325	4736.417		
Column 2	6	983.6336	163.9389	28438.39		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	62305.83	1	62305.83	5.130889	0.037739	4.493998
Within Groups	194292.5	16	12143.28			
Total	256598.3	17				
The P-value is less then alpha, there is a difference between urban and rural.						

Summer

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	8	261.1903	32.64879	1566.187		
Column 2	5	490.4598	98.09195	3952.665		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	13177.87	1	13177.87	5.414085	0.040093	4.844336
Within Groups	26773.97	11	2433.997			
Total	39951.84	12				
The P-value is less then alpha, there is a difference between urban and rural.						

Fall

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	14	1754.693	125.3352	13947.64		
Column 2	8	2134.389	266.7987	17819.5		

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	101878.8	1	101878.8	6.657531	0.017875	4.351243
Within Groups	306055.9	20	15302.79			
Total	407934.7	21				
The P-value is less then alpha, there is a difference between urban and rural.						

Cholesterol/EC		Urban	Rural	
ng/µg		Bronx	Pinnacle	
	Oct-05	0.466257	0.228836	
	Nov-05	0.232187	0.500718	
	Dec-05	0.482645	0	
	Jan-06	0.213654	0	
	Feb-06	0.352158	0	
	Mar-06	0.229066	0	
	Apr-06	0.050019	0	
	May-06	0.157711	0	
	Jun-06	0.14136	0	
	Jul-06	0	0	
	Aug-06	0.114082	0	
	Sep-06	0.348597	0	
	Oct-06	0.282972	0	
	Nov-06	0.180246	0	
	Dec-06	0.183527	0	
	Jan-07	0.283484	0.298959	
	Feb-07	0.267518	0	
Queens	early summer	0	0.00	Chester
	summer	0	0.00	
	early fall	0.121098	0.00	
	fall	0.351389	0.00	
	late fall	0.546579	0.00	
	early winter	0.743176	0.00	
	winter	0.201038	1.15	
	early spring	0	0.00	
	spring	0.392316	0.21	
	late spring	0.302895	0.21	
Elizabeth	early summer	0.41		
	summer	0.07		
	early fall	0.00		
	fall	0.36		
	late fall	0.29		

	early winter	0.00		
	winter	0.23		
	early spring	0.00		
	spring	0.19		
	late spring	0.30		
Westport	summer	0.00		
	early fall	0.00		
	fall	0.00		
	late fall	0.00		
	early winter	0.00		
	winter	0.23		
	early spring	0.00		
	spring	0.25		
	late spring	0.00		
Q0 (Minimum)		0	0	
Q1 (25%)		0	0	
Q2 (Median)		0.194476	0	
Q3 (75%)		0.296142	0	
Q4 (Maximum)		0.743176	1.149342	
Inner quartile range		0.296142	0	
Low outlier		-0.44421	0	
High outlier		0.740354	0	
skewness/kurtosis		0.54447	13.82508	

Entire Year

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	46	8.974678	0.195102	0.031353	Urban	
Column 2	27	2.59128	0.095973	0.059624	Rural	
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.167184	1	0.167184	4.008692	0.049087	3.97581
Within Groups	2.961081	71	0.041705			
Total	3.128265	72				
The P-value is less than alpha, there is a difference.						

Winter

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	3.191452	0.265954	0.039995		

Column 2	8	1.448301	0.181038	0.164024		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.034612	1	0.034612	0.392301	0.538955	4.413873
Within Groups	1.588112	18	0.088228			
Total	1.622724	19				
The P-value is greater than alpha, there is no difference.						

Spring

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	1.867752	0.155646	0.020118		
Column 2	6	0.413425	0.068904	0.011395		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.030097	1	0.030097	1.730462	0.206892	4.493998
Within Groups	0.278275	16	0.017392			
Total	0.308372	17				
The P-value is greater than alpha, there is no difference.						

Summer

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	7	0.665537	0.095077	0.022983		
Column 2	5	0	0	0		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.026365	1	0.026365	1.911952	0.196842	4.964603
Within Groups	0.137898	10	0.01379			
Total	0.164264	11				
The P-value is greater than alpha, there is no difference.						

Fall

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		

Column 1	14	3.177849	0.226989	0.033338		
Column 2	8	0.729553	0.091194	0.033793		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.093878	1	0.093878	2.802537	0.109683	4.351243
Within Groups	0.669949	20	0.033497			
Total	0.763827	21				
The P-value is greater than alpha, there is no difference.						

cis-Pinonic Acid/EC		Urban	Rural	
ng/µg		Bronx	Pinnacle	
	Oct-05	0	40.34452	
	Nov-05	8.057423	24.09048	
	Dec-05	3.692602	28.27854	
	Jan-06	0.545749	19.38293	
	Feb-06	1.906795	14.89782	
	Mar-06	2.715296	29.22126	
	Apr-06	2.112461	34.62346	
	May-06	7.027508	39.8268	
	Jun-06	6.218759	47.89511	
	Jul-06	4.943884	0	
	Aug-06	6.486812	0	
	Sep-06	10.68344	16.36842	
	Oct-06	3.769509	23.99899	
	Nov-06	4.108728	58.4424	
	Dec-06	5.370184	35.14523	
	Jan-07	2.975378	27.70529	
	Feb-07	2.154653	0	
Queens	early summer	5.083539	41.58	Chester
	summer	3.267209	0.00	
	early fall	5.734144	0.00	
	fall	0	15.93	
	late fall	0	18.82	
	early winter	0	0.55	
	winter	1.217919	0.00	
	early spring	4.594553	20.06	
	spring	5.964791	29.34	
	late spring	0.845017	30.56	
Elizabeth	early summer	3.46		
	summer	0.00		

	early fall	0.00		
	fall	1.72		
	late fall	0.00		
	early winter	0.98		
	winter	0.35		
	early spring	0.00		
	spring	1.99		
	late spring	3.01		
Westport	summer	13.95		
	early fall	13.28		
	fall	7.98		
	late fall	6.60		
	early winter	2.67		
	winter	0.00		
	early spring	7.60		
	spring	0.00		
	late spring	8.39		
Q0 (Minimum)		0	0	
Q1 (25%)		0.620566	7.724534	
Q2 (Median)		2.994387	23.99899	
Q3 (75%)		5.907129	32.59123	
Q4 (Maximum)		13.95454	58.4424	
Inner quartile range		5.286563	24.86669	
Low outlier		-7.30928	-29.5755	
High outlier		13.83697	69.89127	
skewness/kurtosis		0.881728	-0.63681	

Entire Year

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	46	171.4473	3.727116	12.62789		
Column 2	27	597.0595	22.11331	274.293		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5751.52	1	5751.52	53.03436	3.55E-10	3.97581
Within Groups	7699.874	71	108.4489			
Total	13451.39	72				
The P-value is less than alpha, there is a difference.						

Winter

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	21.85839	1.821533	2.706442		
Column 2	8	125.961	15.74513	202.4456		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	930.5596	1	930.5596	11.5766	0.003174	4.413873
Within Groups	1446.89	18	80.38278			
Total	2377.45	19				
The P-value is less than alpha, there is a difference.						

Spring

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	44.25133	3.68761	8.782441		
Column 2	6	183.6248	30.60413	43.19628		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2897.997	1	2897.997	148.3355	1.66E-09	4.493998
Within Groups	312.5883	16	19.53677			
Total	3210.585	17				
The P-value is less than alpha, there is a difference.						

Summer

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	8	43.41392	5.42674	16.11569		
Column 2	5	89.47857	17.89571	605.4607		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	478.3856	1	478.3856	2.076119	0.177473	4.844336
Within Groups	2534.653	11	230.423			
Total	3013.038	12				
The P-Value is greater than alpha there is no difference.						

Fall

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	14	61.9237	4.423122	19.66017		
Column 2	8	197.9951	24.74938	310.7357		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2103.344	1	2103.344	17.30626	0.000484	4.351243
Within Groups	2430.732	20	121.5366			
Total	4534.076	21				
The P-value is less than alpha, there is a difference.						

total n-alkanols/EC		Urban	Rural	
ng/µg		Bronx	Pinnacle	
	Oct-05	1.105261	22.86087	
	Nov-05	1.580566	21.76073	
	Dec-05	3.930998	9.545201	
	Jan-06	0.343155	6.504071	
	Feb-06	1.821774	7.984007	
	Mar-06	0.714019	10.47759	
	Apr-06	0	8.442123	
	May-06	2.993465	17.50692	
	Jun-06	3.973658	8.21119	
	Jul-06	0.907598	5.704831	
	Aug-06	0.924423	16.74175	
	Sep-06	4.693924	4.063376	
	Oct-06	2.768499	18.86721	
	Nov-06	0	10.52586	
	Dec-06	2.218183	15.30614	
	Jan-07	0.546067	8.88875	
	Feb-07	1.619524	7.584169	
Queens	early summer	20.73599	31.18	Chester
	summer	1.398218	2.34	
	early fall	16.72132	25.05	
	fall	3.146545	6.73	
	late fall	5.295373	3.27	
	early winter	2.92429	7.11	
	winter	6.513342	4.00	
	early spring	3.287367	13.29	

	spring	12.39715	26.57	
	late spring	6.683284	25.86	
Elizabeth	early summer	9.50		
	summer	2.40		
	early fall	2.72		
	fall	1.29		
	late fall	2.34		
	early winter	1.31		
	winter	1.36		
	early spring	0.42		
	spring	3.25		
	late spring	1.56		
Westport	summer	2.46		
	early fall	8.16		
	fall	4.34		
	late fall	5.86		
	early winter	7.25		
	winter	4.55		
	early spring	5.89		
	spring	4.48		
	late spring	1.40		
Q0 (Minimum)		0	2.340089	
Q1 (25%)		1.373024	6.919096	
Q2 (Median)		2.744674	9.545201	
Q3 (75%)		4.65704	18.18707	
Q4 (Maximum)		20.73599	31.18438	
Inner quartile range		3.284016	11.26797	
Low outlier		-3.553	-9.98286	
High outlier		9.583065	35.08902	
skewness/kurtosis		6.621478	-0.59604	

Entire Year

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	46	179.7807	3.908277	17.26972		
Column 2	27	346.3612	12.82819	67.334		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1353.693	1	1353.693	38.02175	3.81E-08	3.97581
Within Groups	2527.822	71	35.60312			

Total	3881.515	72				
The P-value is less than alpha, there is a difference.						

Winter

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	34.38959	2.865799	5.089899		
Column 2	8	66.9235	8.365438	10.66965		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	145.1809	1	145.1809	19.99793	0.000295	4.413873
Within Groups	130.6764	18	7.2598			
Total	275.8573	19				
The P-value is less than alpha, there is a difference.						

Spring

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	43.07877	3.589897	12.17125		
Column 2	6	102.1389	17.02315	59.96248		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	721.809	1	721.809	26.62912	9.48E-05	4.493998
Within Groups	433.6961	16	27.10601			
Total	1155.505	17				
The P-value is less than alpha, there is a difference.						

Summer

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	8	42.29319	5.286649	46.83002		
Column 2	5	64.18224	12.83645	133.5811		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	175.383	1	175.383	2.237716	0.162808	4.844336

Within Groups	862.1347	11	78.37588			
Total	1037.518	12				
The P-value is greater than alpha, there is no difference.						

Fall

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	14	60.01919	4.287085	17.53762		
Column 2	8	113.1165	14.13957	80.45518		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	494.1817	1	494.1817	12.49234	0.002082	4.351243
Within Groups	791.1753	20	39.55876			
Total	1285.357	21				
The P-value is less than alpha, there is a difference.						

Levulinic Acid/EC		Urban	Rural	
ng/µg		Bronx	Pinnacle	
	Oct-05	5.472182	58.04312	
	Nov-05	14.49909	32.64358	
	Dec-05	10.37794	47.81506	
	Jan-06	0	27.79219	
	Feb-06	0	48.06102	
	Mar-06	9.859711	56.16019	
	Apr-06	9.377638	41.75371	
	May-06	15.39191	90.95158	
	Jun-06	18.26546	89.15367	
	Jul-06	28.103	52.25091	
	Aug-06	16.12314	71.24338	
	Sep-06	26.69441	54.16238	
	Oct-06	11.13934	43.89524	
	Nov-06	10.97195	34.60617	
	Dec-06	8.204339	62.98612	
	Jan-07	6.520153	42.39274	
	Feb-07	16.19703	55.01766	
Queens	early summer	0	110.41	Chester
	summer	0	0.00	
	early fall	0	0.00	
	fall	0	0.00	
	late fall	0	50.71	

	early winter	9.708576	0.00	
	winter	16.4726	0.00	
	early spring	17.38453	0.00	
	spring	0	31.29	
	late spring	0	63.79	
Elizabeth	early summer	11.41		
	summer	0.00		
	early fall	0.00		
	fall	0.00		
	late fall	0.00		
	early winter	0.00		
	winter	7.41		
	early spring	0.00		
	spring	0.00		
	late spring	0.00		
Westport	summer	0.00		
	early fall	0.00		
	fall	45.11		
	late fall	0.00		
	early winter	17.33		
	winter	0.00		
	early spring	21.18		
	spring	7.36		
	late spring	29.08		
Q0 (Minimum)		0	0	
Q1 (25%)		0	29.5396	
Q2 (Median)		6.940722	47.81506	
Q3 (75%)		15.16871	57.10166	
Q4 (Maximum)		45.10942	110.41	
Inner quartile range		15.16871	27.56206	
Low outlier		-22.7531	-11.8035	
High outlier		37.92176	98.44475	
skewness/kurtosis		2.360561	-0.18099	

Entire Year

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	46	389.6373	8.470376	104.8545	Urban	
Column 2	27	1165.126	43.15282	888.7545	Rural	
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*

Between Groups	20465.3	1	20465.3	52.21853	4.51E-10	3.97581
Within Groups	27826.07	71	391.9165			
Total	48291.37	72				
The P-value is less than alpha, there is a statistical difference.						

Winter

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	92.22055	7.685046	44.72039		
Column 2	8	284.0648	35.5081	581.8979		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3715.787	1	3715.787	14.65084	0.001233	4.413873
Within Groups	4565.21	18	253.6228			
Total	8280.996	19				
The P-value is less than alpha, there is a difference.						

Spring

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	12	109.6332	9.136102	97.36626		
Column 2	6	283.9432	47.32387	956.0742		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5833.222	1	5833.222	15.95029	0.001046	4.493998
Within Groups	5851.4	16	365.7125			
Total	11684.62	17				
The P-value is less than alpha, there is a difference.						

Summer

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	8	73.89712	9.23714	118.6927		
Column 2	5	323.058	64.6116	1767.809		
ANOVA						
Source of	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*

Variation						
Between Groups	9434.863	1	9434.863	13.13369	0.003998	4.844336
Within Groups	7902.083	11	718.3712			
Total	17336.95	12				
The P-value is less than alpha, there is a difference.						

Fall

SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Column 1	14	113.8864	8.134743	177.3579		
Column 2	8	274.0602	34.25753	525.0573		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3474.036	1	3474.036	11.6168	0.002787	4.351243
Within Groups	5981.053	20	299.0527			
Total	9455.089	21				
The P-value is less than alpha, there is a difference.						

Appendix M: $PM_{2.5}$ normalized molecular markers

SOAP 2002-2003
Chs = Chester, NJ
Elz = Elizabeth, NJ
Qns = Queens, NY
Wpt = Westport, Ct

$PM_{2.5}$ data was obtained through the STN network. All not detected samples were assumed zero for this analysis.

Season	Sample	$PM_{2.5}$ ug/m^3	Levoglucosan/PM2.5 ng/ug	Cholesterol/$PM_{2.5}$ ng/ug
summer early	Chs 23/(9)	8.78531	2.834332615	0
summer	Chs 27/(8)	no value	NA	NA
fall early	Chs 31/(6)	9.987051	1.168038555	0
fall	Chs 35/(7)	6.156244	4.165472076	0
late fall	Chs 39/(7)	6.352567	12.61764349	0
Winter early	Chs 44/(6)	11.62068	6.036158488	0
winter	Chs 48/(8)	7.418856	3.259166754	0.0889059
Spring early	Chs 52/(10)	9.443712	2.847294	0
Spring	Chs/56(10)	9.638814	0.282765239	0.0042798
late Spring	Chs/60(7)	11.9167	1.076595436	0.002372
Summer early	Elz/21(9)	17.95535	1.587395197	0.0351156
Summer	Elz/24(8)	20.23289	2.732151639	0.0062962
Fall early	Elz/28(6)	11.48635	1.44950296	0
Fall	Elz/32(7)	10.5254	6.902418014	0.0462773
late fall	Elz/36(7)	15.39737	8.969993305	0.0178004
Winter early	Elz/41(6)	20.46504	1.17870988	0
Winter	Elz/45(8)	22.30026	0.298849167	0.0105325
Spring early	Elz/49(10)	15.35885	1.400880954	0
Spring	Elz/53(10)	13.32543	0.32584303	0.0170062
late spring	Elz/57(5)	20.45114	0.26359722	0.0207484
Summer early	Qns/22(9)	15.77	5.006880981	0
Summer	Qns/25(8)	14.79	1.57096641	0
Fall early	Qns/29(6)	no value	NA	NA
Fall	Qns/33(7)	7.06	12.59826254	0.0297923
late fall	Qns/37(7)	12.80	11.4800789	0.0318891
Winter early	Qns/42(6)	17.04	6.123411029	0.0457658
Winter	Qns/46(8)	13.68	2.752417037	0.0069938
Spring Early	Qns/50(10)	11.94	1.037475805	0
Spring	Qns/54(10)	11.37	0.207864468	0.019233
late Spring	Qns/58(7)	12.68	0.449357269	0.0154408

Summer	Wpt/26(8)	11.77171	0.285011147	0
Fall Early	Wpt/30(5)	9.868	7.363772871	0
Fall	Wpt/34(7)	6.925115	10.07026927	0
late fall	Wpt/38(6)	9.80682	19.320405	0
Winter early	Wpt/43(9)	13.71878	10.90387788	0
Winter	Wpt/47(8)	12.65936	9.549623836	0.0056661
Spring early	Wpt/51(10)	10.55865	7.462574898	0
Spring	Wpt/55(10)	no value	NA	NA
late Spring	Wpt/59(7)	17.6325	0.514187225	0

Season	Sample	Total n-alkanols/$PM_{2.5}$, ng/ug	cis-pinonic acid/$PM_{2.5}$, ng/ug	Levulinicacid/$PM_{2.5}$ ng/µg
summer early	Chs 23/(9)	0.675213757	0.90037776	2.390631
summer	Chs 27/(8)	NA	NA	0
fall early	Chs 31/(6)	0.26604025	0	0
fall	Chs 35/(7)	0.173065446	0.40973488	0
late fall	Chs 39/(7)	0.095423223	0.54995111	1.481581
Winter early	Chs 44/(6)	0.158181108	0.01226256	0
winter	Chs 48/(8)	0.309443706	0	0
Spring early	Chs 52/(10)	0.257077254	0.38804847	0
Spring	Chs/56(10)	0.548690303	0.60586742	0.646124
late Spring	Chs/60(7)	0.297460629	0.35156634	0.733881
Summer early	Elz/21(9)	0.813259813	0.29620147	0.976631
Summer	Elz/24(8)	0.209636577	0	0
Fall early	Elz/28(6)	0.306128185	0	0
Fall	Elz/32(7)	0.166955388	0.22235126	0
late fall	Elz/36(7)	0.142681263	0	0
Winter early	Elz/41(6)	0.092755809	0.06957019	0
Winter	Elz/45(8)	0.061221033	0.01549983	0.332534
Spring early	Elz/49(10)	0.023927212	0	0
Spring	Elz/53(10)	0.294513989	0.18013163	0
late spring	Elz/57(5)	0.108618872	0.20999332	0
Summer early	Qns/22(9)	0.818844557	0.20074417	0
Summer	Qns/25(8)	0.055415478	0.12948904	0
Fall early	Qns/29(6)	NA	NA	0
Fall	Qns/33(7)	0.266777738	0	0
late fall	Qns/37(7)	0.308948466	0	0
Winter early	Qns/42(6)	0.180081891	0	0.597868
Winter	Qns/46(8)	0.226588219	0.04236934	0.573054
Spring Early	Qns/50(10)	0.144023051	0.20129227	0.761635
Spring	Qns/54(10)	0.60775951	0.29241864	0
late Spring	Qns/58(7)	0.340696208	0.04307674	0

Summer	Wpt/26(8)	0.077681459	#DIV/0!	
Fall Early	Wpt/30(5)	0.293005912	0.44145799	0
Fall	Wpt/34(7)	0.233473987	0.47666944	0
late fall	Wpt/38(6)	0.244894188	0.42964247	2.428896
Winter early	Wpt/43(9)	0.349223652	0.27545334	0
Winter	Wpt/47(8)	0.11226764	0.12846435	0.834387
Spring early	Wpt/51(10)	0.174101805	0	0
Spring	Wpt/55(10)	NA	0.22458035	0.626073
late Spring	Wpt/59(7)	0.030819653	#VALUE!	0
			0.18502895	0.641233

SOAP NY 2005-2007
BRONX = Bronx, NY
PINN = Pinnacle State Park, NY

The $PM_{2.5}$ data was obtained with URG samplers through the STN. All not detected samples were assumed to be zero for this analysis.

Season	Sample	SOAP Composite URG $PM_{2.5}$, ug/m^3	Levoglucosan /$PM_{2.5}$, ng/ug	Cholesterol /$PM_{2.5}$, ng/ug	n-alkanols/ $PM_{2.5}$, ng/ug
Oct-05	BRONX 01	10.92	2.37	0.04	0.09
Nov-05	BRONX 02	13.33	4.75	0.01	0.07
Dec-05	BRONX 03	17.04	5.63	0.02	0.16
Jan-06	BRONX 04	19.88	4.24	0.02	0.03
Feb-06	BRONX 05	22.40	4.41	0.02	0.10
Mar-06	BRONX 06	11.20	4.51	0.02	0.06
Apr-06	BRONX 07	8.49	2.49	0.00	0.00
May-06	BRONX 08	14.06	0.87	0.01	0.13
Jun-06	BRONX 09	10.92	0.82	0.01	0.23
Jul-06	BRONX 10	25.25	0.29	0.00	0.03
Aug-06	BRONX 11	12.93	0.56	0.01	0.04
Sep-06	BRONX 12	11.48	1.61	0.01	0.17
Oct-06	BRONX 13	7.55	5.73	0.02	0.22
Nov-06	BRONX 14	9.71	6.27	0.02	0.00
Dec-06	BRONX 15	16.27	2.28	0.01	0.08
Jan-07	BRONX 16	15.30	5.59	0.02	0.04
Feb-07	BRONX 17	10.93	4.47	0.01	0.08
Oct-05	PINN 01	6.08	10.74	0.01	0.57
Nov-05	PINN 02	6.05	6.60	0.01	0.53
Dec-05	PINN 03	9.28	12.80	0.00	0.19
Jan-06	PINN 04	8.73	12.96	0.00	0.14

Feb-06	PINN 05	8.46	11.32	0.00	0.17
Mar-06	PINN 06	8.63	9.31	0.00	0.21
Apr-06	PINN 07	4.45	7.12	0.00	0.24
May-06	PINN 08	9.50	0.33	0.00	0.27
Jun-06	PINN 09	7.41	0.24	0.00	0.11
Jul-06	PINN 10	16.45	0.45	0.00	0.06
Aug-06	PINN 11	8.14	2.13	0.00	0.21
Sep-06	PINN 12	7.94	1.51	0.00	0.06
Oct-06	PINN 13	3.63	7.99	0.00	0.52
Nov-06	PINN 14	7.39	7.72	0.00	0.24
Dec-06	PINN 15	6.15	5.90	0.00	0.24
Jan-07	PINN 16	6.84	6.65	0.01	0.16
Feb-07	PINN 17	5.71	5.96	0.00	0.14

Season	Sample	SOAP Composite URG $PM_{2.5}$, ug/m^3	cis-Pinonic acid/$PM_{2.5}$, ng/ug	Levulinic acid/$PM_{2.5}$, ng/µg
Oct-05	BRONX 01	10.92	0.00	0.425038
Nov-05	BRONX 02	13.33	0.36	0.648405
Dec-05	BRONX 03	17.04	0.15	0.410758
Jan-06	BRONX 04	19.88	0.05	0
Feb-06	BRONX 05	22.40	0.11	0
Mar-06	BRONX 06	11.20	0.21	0.760856
Apr-06	BRONX 07	8.49	0.19	0.864292
May-06	BRONX 08	14.06	0.30	0.64843
Jun-06	BRONX 09	10.92	0.36	1.069982
Jul-06	BRONX 10	25.25	0.15	0.84064
Aug-06	BRONX 11	12.93	0.30	0.73853
Sep-06	BRONX 12	11.48	0.38	0.953984
Oct-06	BRONX 13	7.55	0.31	0.904386
Nov-06	BRONX 14	9.71	0.35	0.944549
Dec-06	BRONX 15	16.27	0.19	0.297404
Jan-07	BRONX 16	15.30	0.20	0.445752
Feb-07	BRONX 17	10.93	0.11	0.799847
Oct-05	PINN 01	6.08	1.00	1.438048
Nov-05	PINN 02	6.05	0.58	0.789882
Dec-05	PINN 03	9.28	0.55	0.933413
Jan-06	PINN 04	8.73	0.43	0.612034
Feb-06	PINN 05	8.46	0.31	1.013177
Mar-06	PINN 06	8.63	0.59	1.13971
Apr-06	PINN 07	4.45	0.99	1.193258
May-06	PINN 08	9.50	0.61	1.391579

Jun-06	PINN 09	7.41	0.62	1.155456
Jul-06	PINN 10	16.45	0.00	0.509967
Aug-06	PINN 11	8.14	0.00	0.903992
Sep-06	PINN 12	7.94	0.25	0.840315
Oct-06	PINN 13	3.63	0.66	1.213022
Nov-06	PINN 14	7.39	1.34	0.791432
Dec-06	PINN 15	6.15	0.55	0.98167
Jan-07	PINN 16	6.84	0.49	0.754202
Feb-07	PINN 17	5.71	0.00	1.049343

Curriculum Vita

Harmonie A. Hawley, PhD, EIT

9/2005 – 10/2008	Rutgers, the State University of New Jersey, Civil & Environmental Engineering Department, PhD
5/2004-8/2005	Environmental Engineer, Prism Environmental Inc., Westborough, MA
5/2003-5/2004	Environmental Engineer, ENSR International Inc., Westford, MA
1/2002-5/2003	Worcester Polytechnic Institute, Civil & Environmental Engineering Department, MS
8/1997-5/2001	Worcester Polytechnic Institute, Civil & Environmental Engineering Department, BS