Biomass Burning Impacts on Air Quality in the Upper Midwest

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Outline

- Background
- Overview of Detection Method for Levoglucosan
- Details about Sites and Measurements
  - 6 weeks of Hi-Volume Quartz filters from 5 sites
  - 1 year of FRM Teflon filters from 2 sites
- Results from both studies
  - Investigate Various Species Measured both Spatially and Temporally
  - Determination of Contribution of Biomass Burning
  - Fraction of Contemporary vs. Fossil Carbon
- Summary

Background

- Biomass burning one of major sources of organic aerosols
  - Urban Organics Study in 2004-2005 found 15-25% of organic carbon from biomass burning in 5 Midwest cities
- Common approach to quantifying fire contribution to organic carbon is use of smoke markers
  - Levoglucosan, sugar anhydride produced during combustion of cellulose, generally used

Measurement of Levoglucosan

- Traditionally performed using gas chromatography/mass spectroscopy (GC-MS)

- Major disadvantage of GC-MS:
  - Requires chemical derivatization

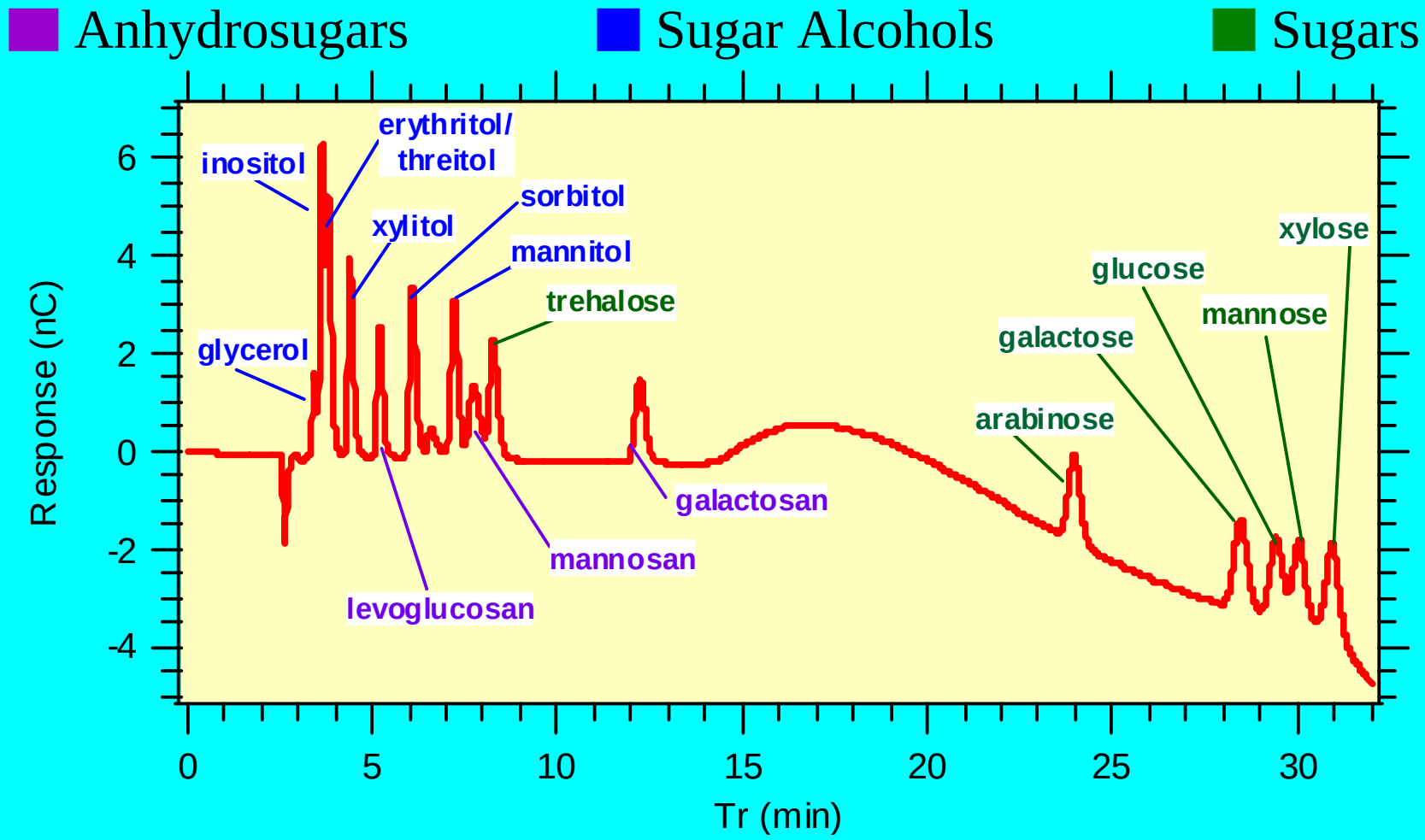
- Alternative Method:
  - Simpler filter extraction procedure
  - Ability to analyze extract directly

High-Performance Anion Exchange Chromatography – Pulsed Amperometric Detection (HPAEC-PAD)

- Analytes electroanalytically oxidized on surface of gold working electrode by application of positive potential
- To prevent “poisoning” of electrode surface continuously cleaned via a different potential being applied followed by regeneration step
- Pulsed amperometric detection based on repeated application of these potentials

- CarboPac PA1 column (4 x 250 mm)
- Eluents: deionized water and 200 mM sodium hydroxide
- Run time is 59 min
  - Includes isocratic elution for anhydrosugars and sugar alcohols, linear gradient for sugars, column cleaning, and re-equilibration
- Limit of Detection < ~1 ng/m^3

Calibration Chromatogram

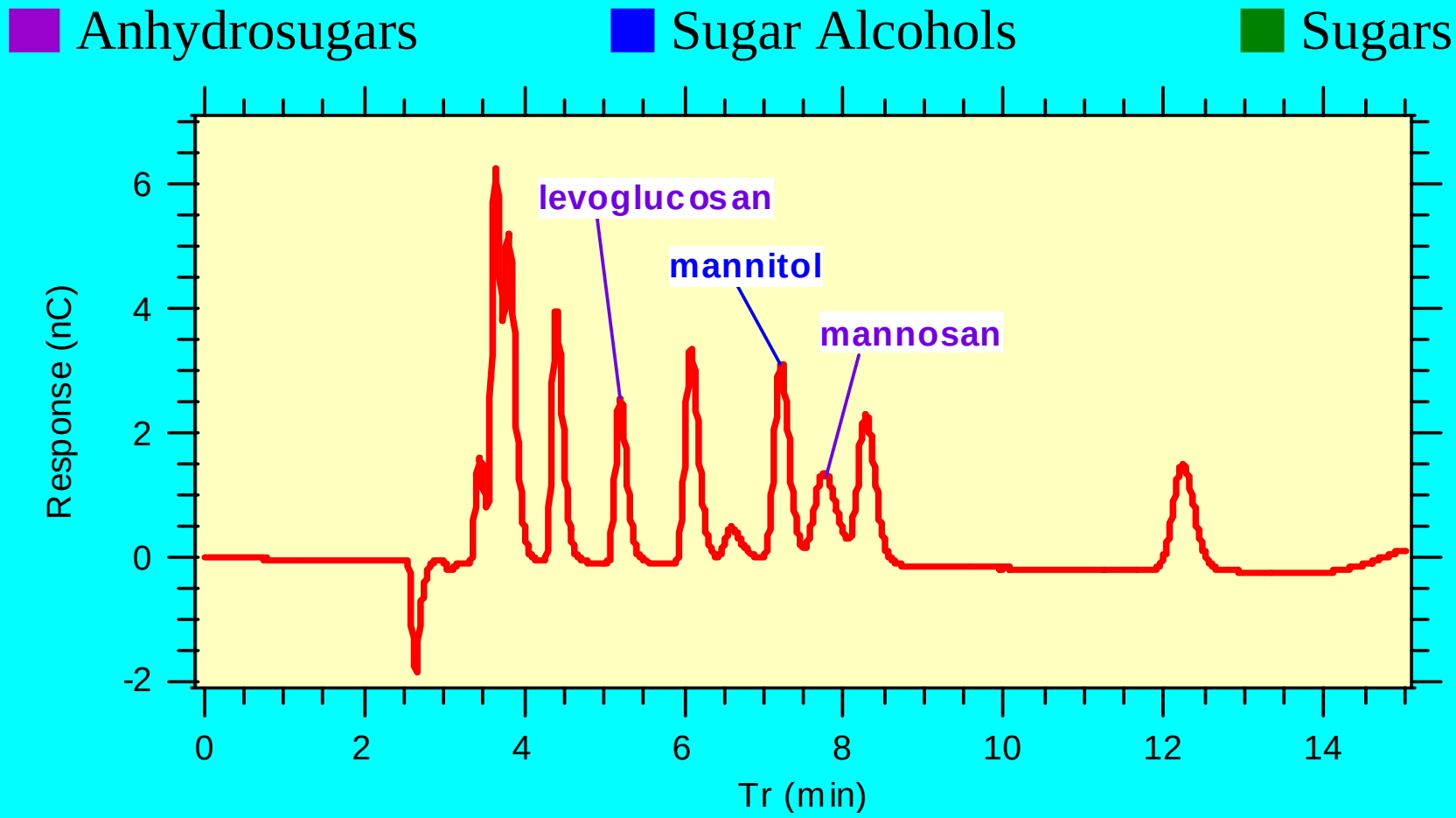


-Anhydrosugars and sugar alcohols in first 15 min

-Sugars after 20 min

-Good agreement with GC-MS

Calibration Chromatogram



-Separation of mannitol from mannosan allows arabitol, which can overlap with levoglucosan, to be determined

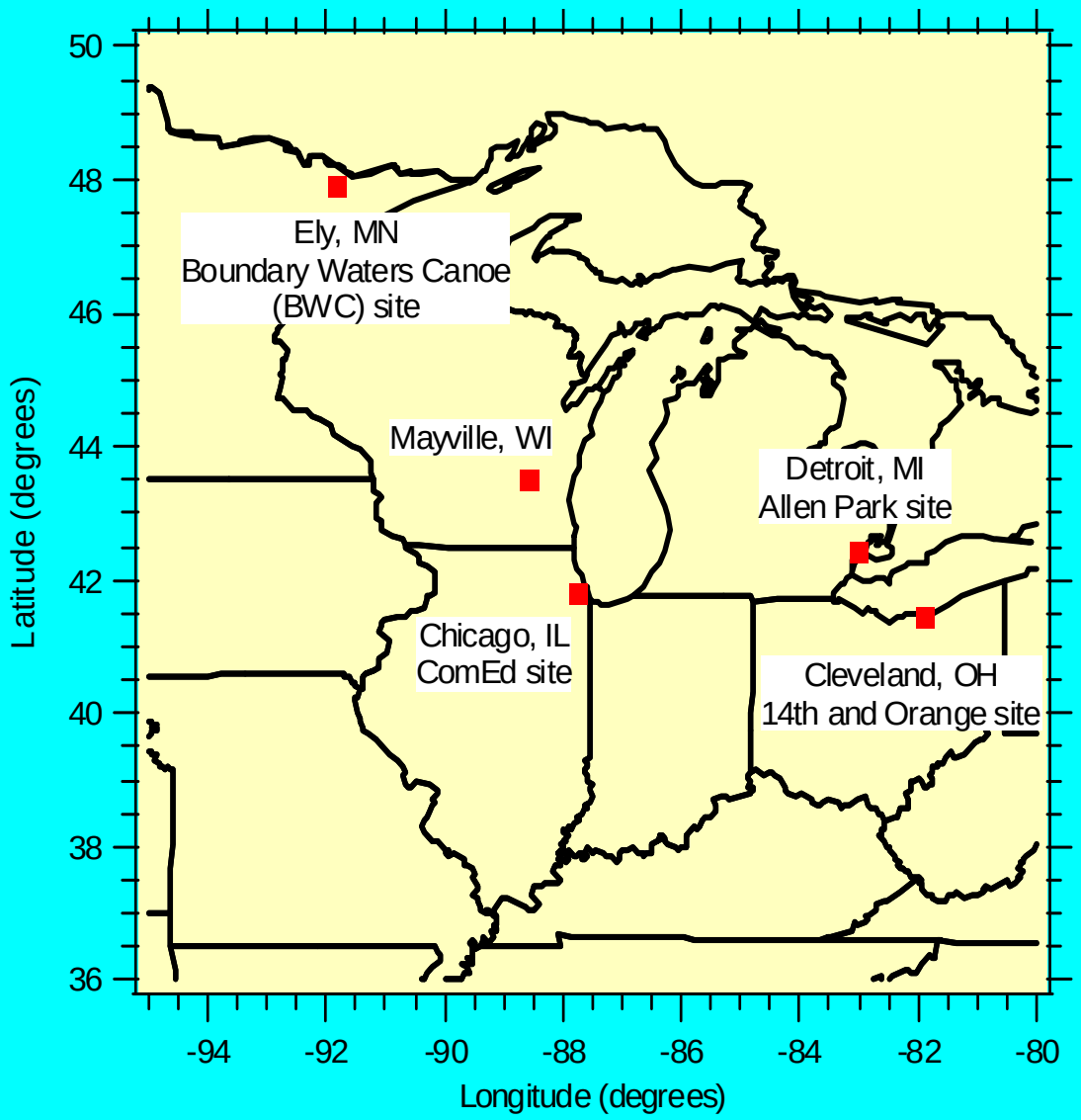
-[mannitol] = 1.5 x [arabitol]

-Mannitol and arabitol found during summer originating from spores

Sources of the Carbohydrates

- Anhydrosugars are primary thermal degradation products from burning biomass
- Sugar alcohols from fungi, lichens, and bacteria
- Sugars released into atmosphere by micro-organisms, plants, and animals

Hi-Volume Sample Study Details



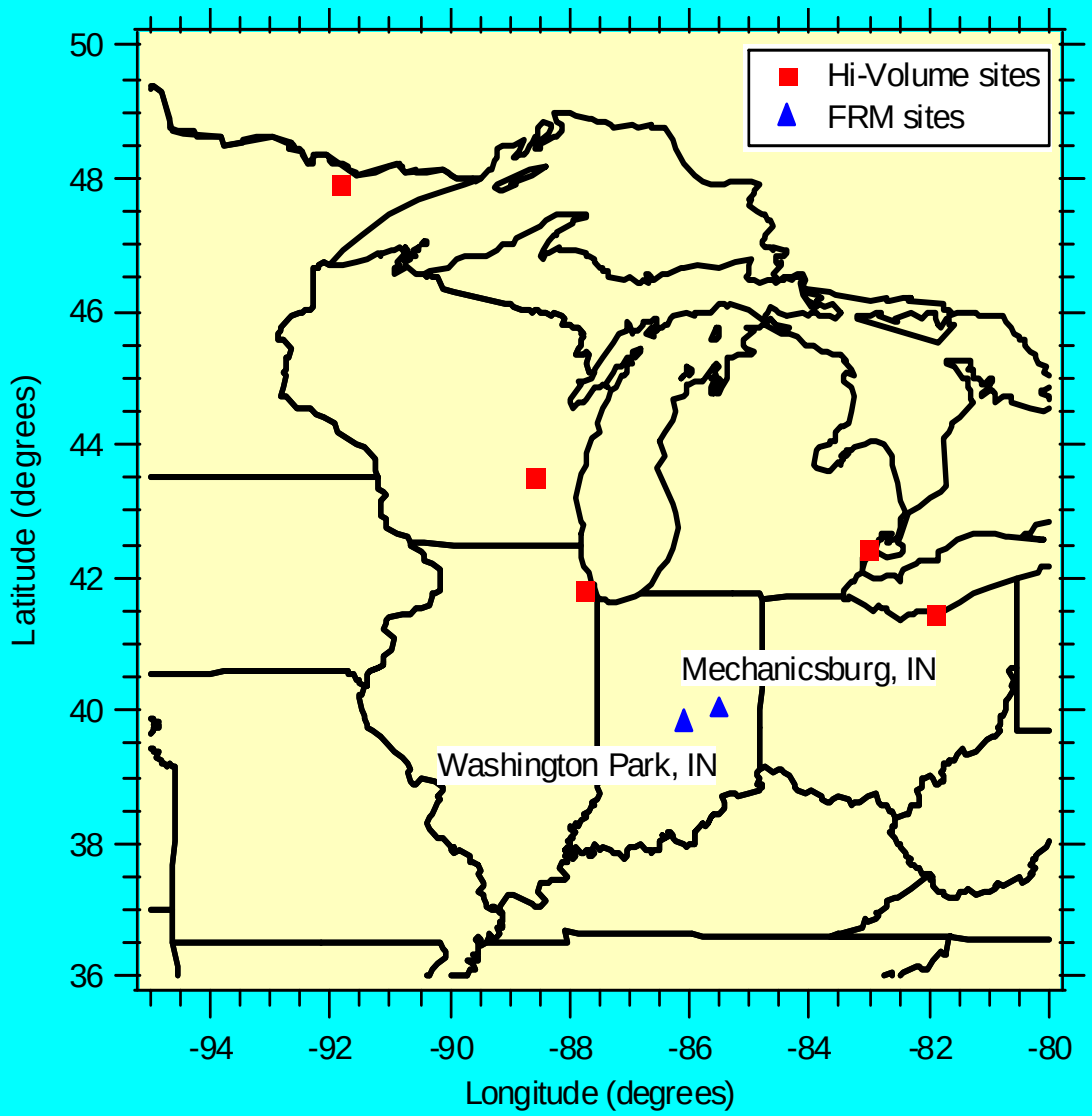
-Collected 7 day integrated quartz filter samples at BWC, 3 day integrated quartz filter samples at other sites

-6 weeks in summer (July-Aug. 2007) and winter (Jan.-Feb. 2008)

-Summer = prescribed burning and wildfires

-Winter = residential burning

FRM Sample Study Details



-Archived 47 mm Teflon filters used for network's $PM_{2.5}$ mass measurement

-1-in-6 day samples for 1 year from March 2004 to February 2005

-Additional sites to be analyzed, including others involved in Urban Organics Study 2004-2005

Aerosol Composition Measurements

	Hi-Volume Samples	FRM Samples
Amount of Filter Extracted	10 punches	whole filter
Extraction Volume	20 ml	15 ml

- Analyzed liquid extract for:
  1. Levoglucosan and other carbohydrates by high-performance anion exchange chromatography – pulsed amperometric detection
  2. Potassium by cation exchange chromatography
  3. Water-soluble organic carbon (WSOC) using Sievers Total Organic Carbon (TOC) analyzer

- Additional Measurements for Hi-Volume Samples:
  - Sunset Labs OCEC Analyzer used to determine organic carbon (OC) and elemental carbon (EC)
    - Average of 2 punches
  - Radiocarbon (^{14}C) Analysis performed on a subset of the samples to determine fraction of contemporary and fossil carbon
    - Fossil carbon has no ^{14}C, lost by radioactive decay
    - Analysis performed at Lawrence Livermore National Laboratory using an AMS (Accelerator Mass Spectrometer)

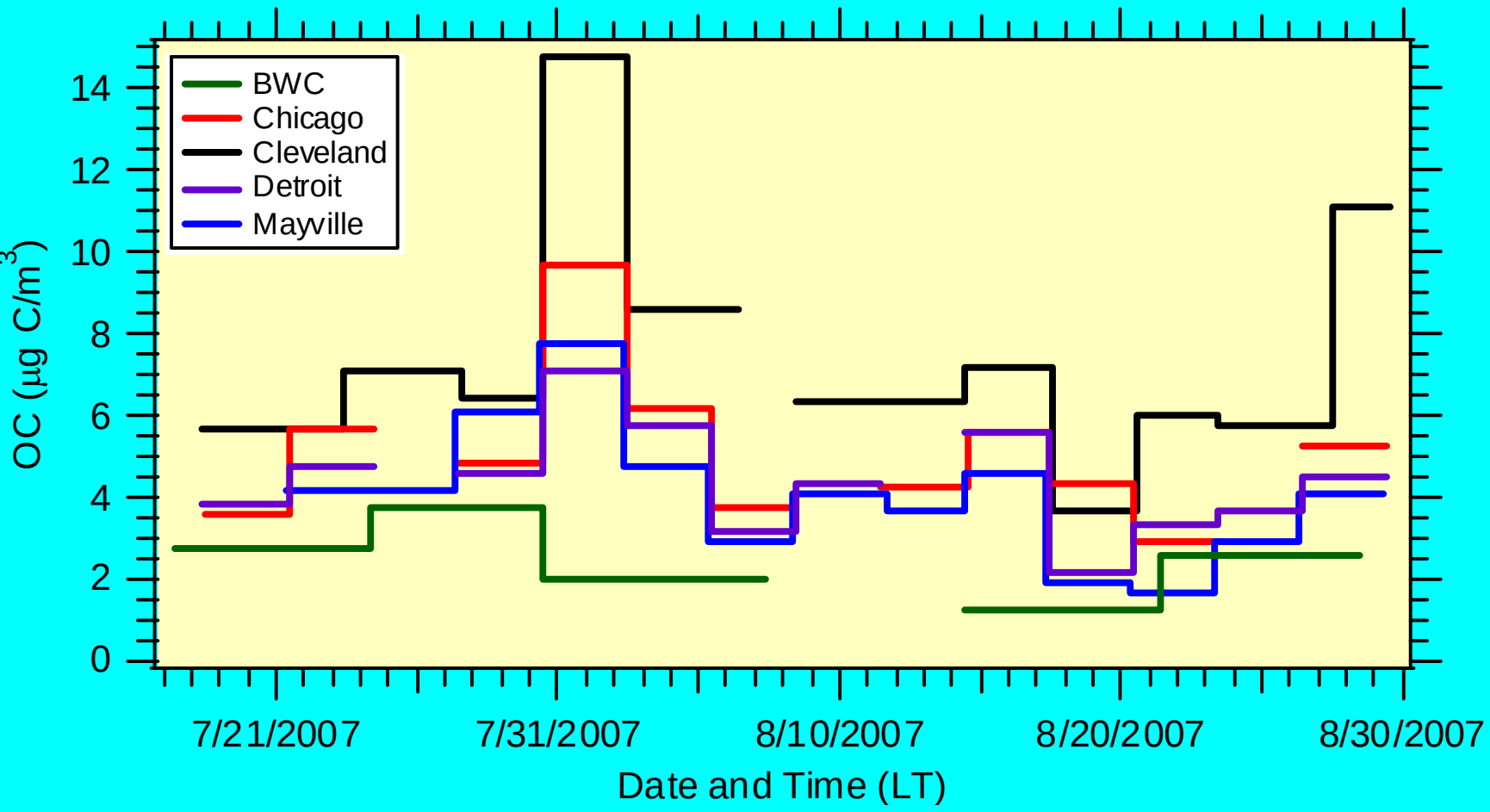
Radiocarbon (^{14}C) Analysis

- AMS determines fraction of carbon that modern (F_M) based on comparison of $^{14}C/^{12}C$ in sample to a modern carbon standard reference material

- F_M corrected for variability in past atmospheric ^{14}C concentrations to provide fraction of contemporary carbon (F_C)
  - $F_C = F_M/1.05$
  - Correction of 1.05 derived from average $^{14}C/^{12}C$ ratio of contemporary material from 2003 to 2008

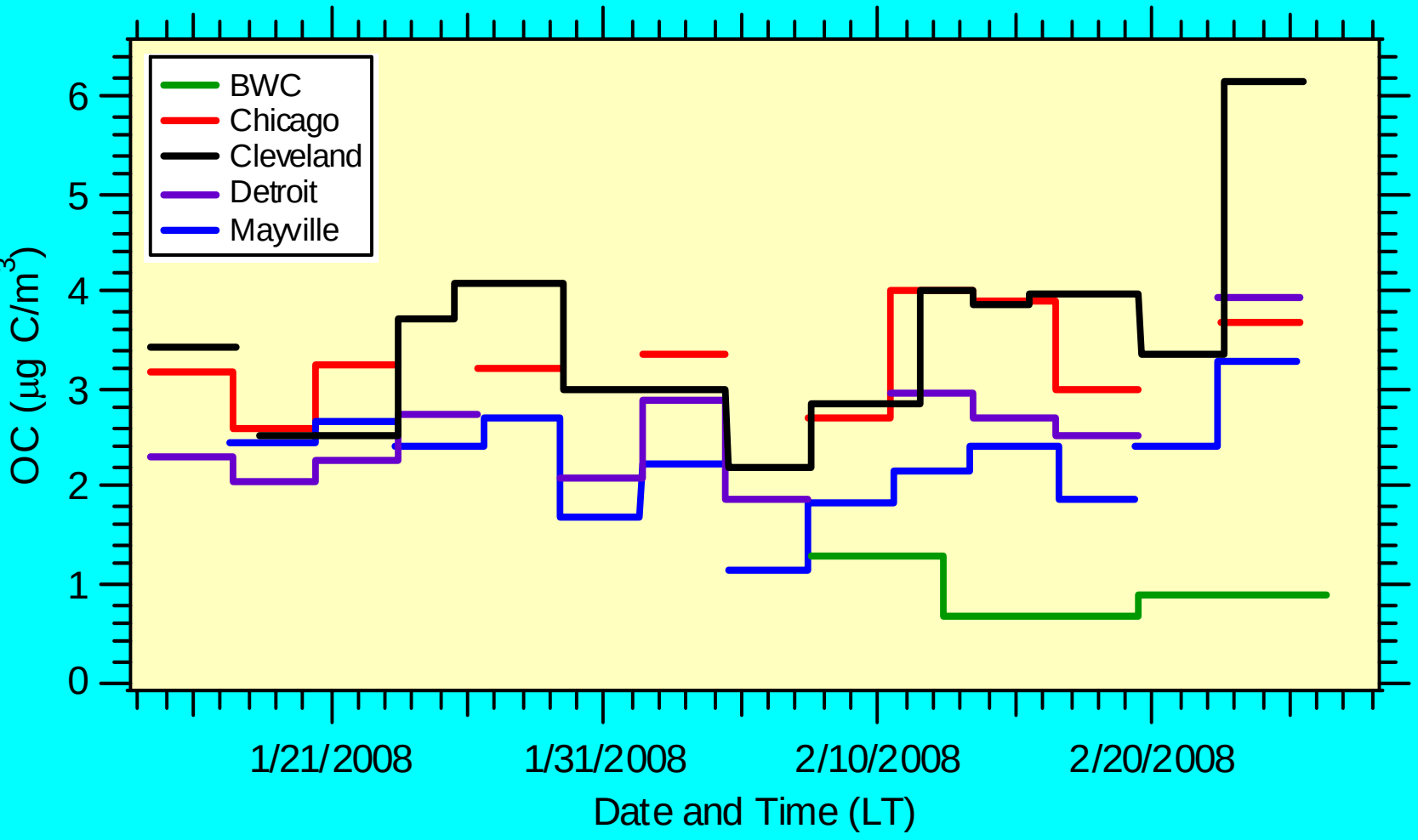
- Assume two component model to determine fraction of fossil carbon (F_F)
  - $F_F = 1 - F_C = 1 - (F_M/1.05)$

Hi-Volume Summer: Time Series of Organic Carbon



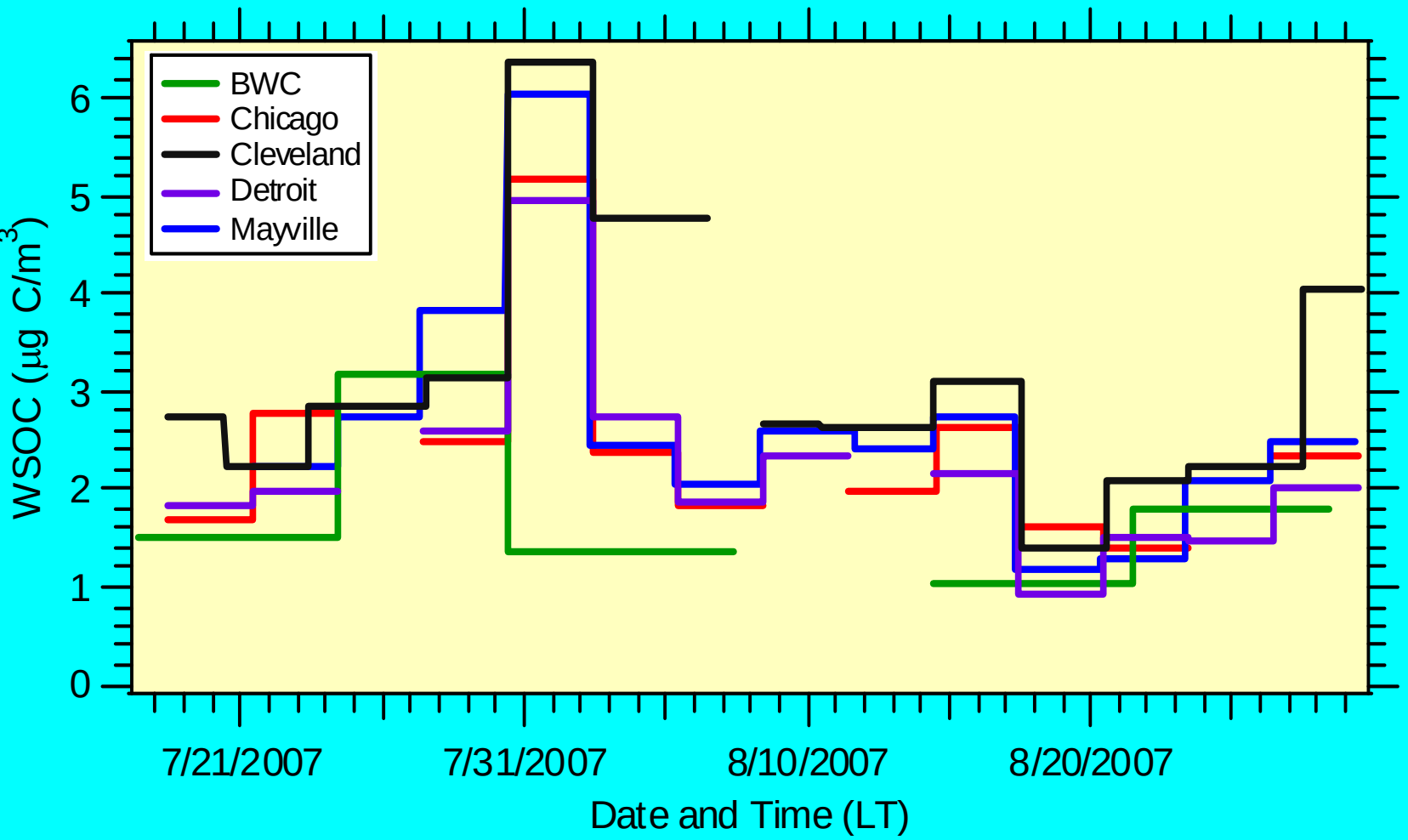
-OC concentration appears to have large regional component, Mayville concentrations fairly similar to urban sites

Hi-Volume Winter: Time Series of Organic Carbon



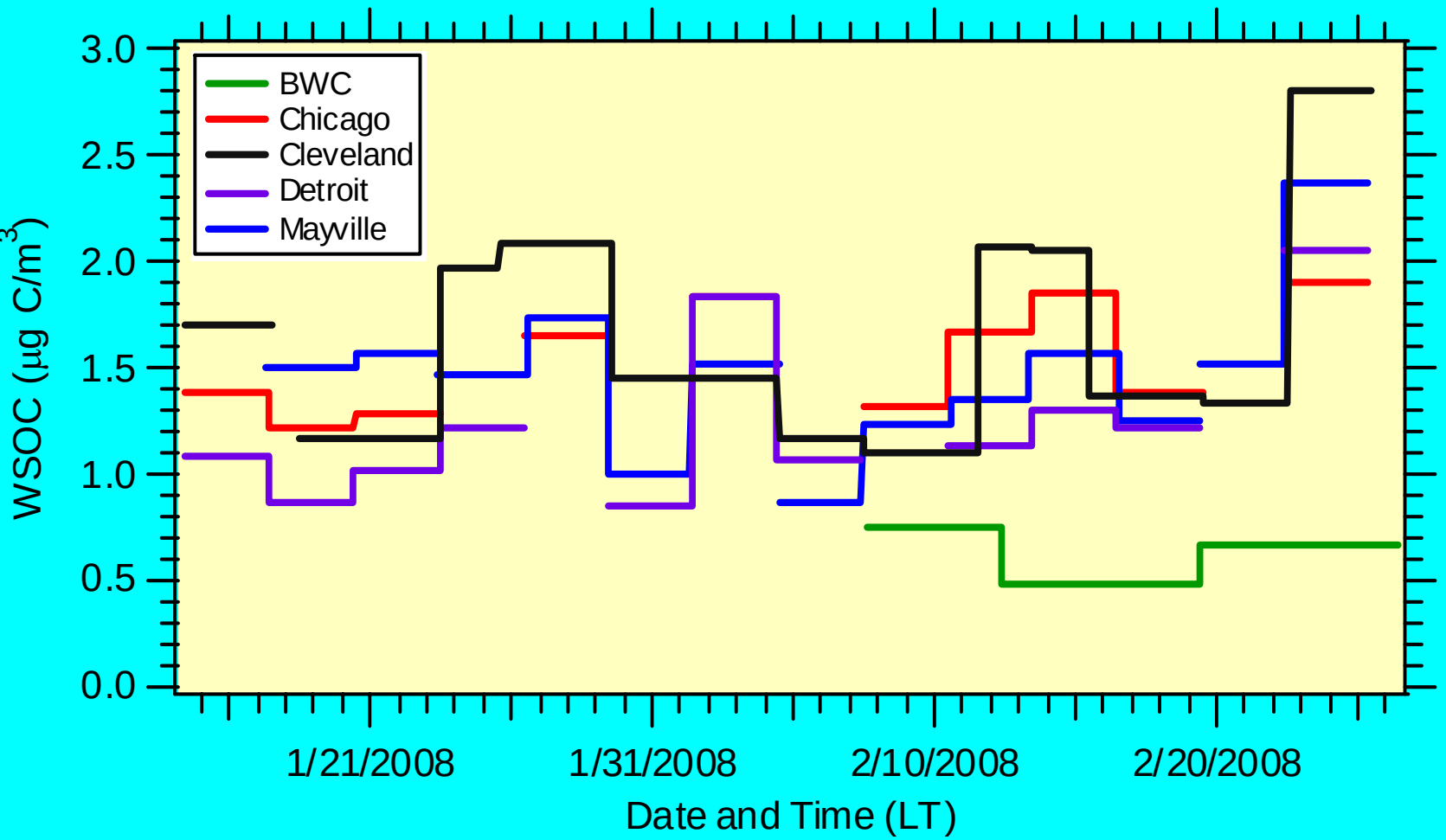
-With exception of BWC results similar to summer

Hi-Volume Summer: Time Series of WSOC



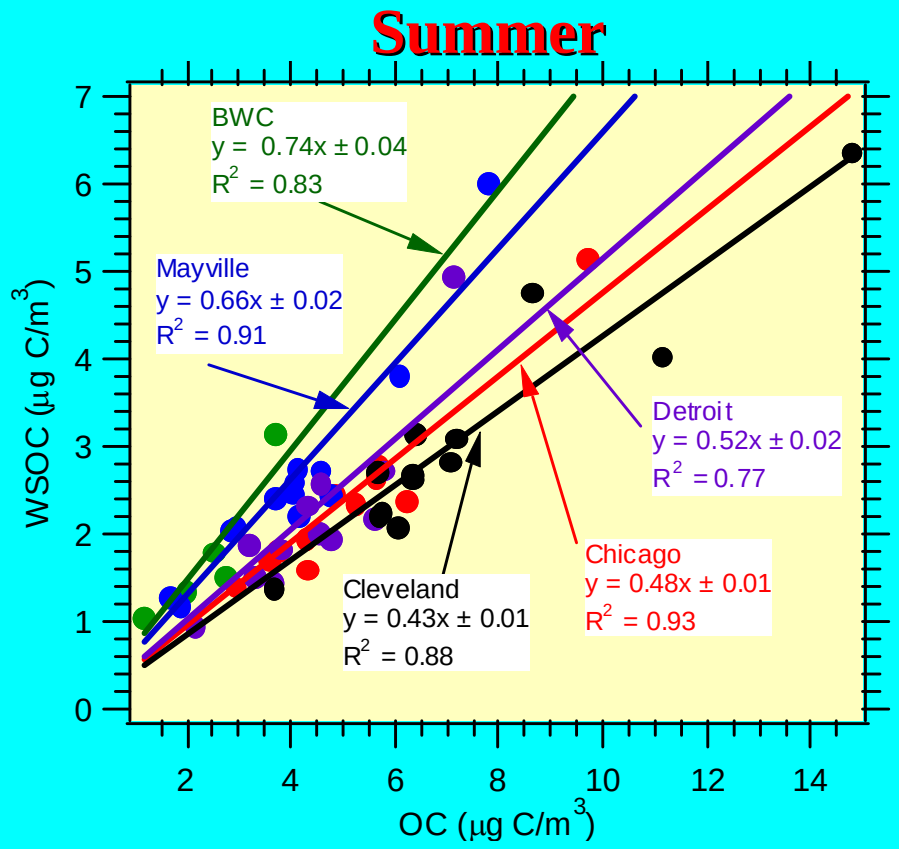
-Concentration similar at all sites

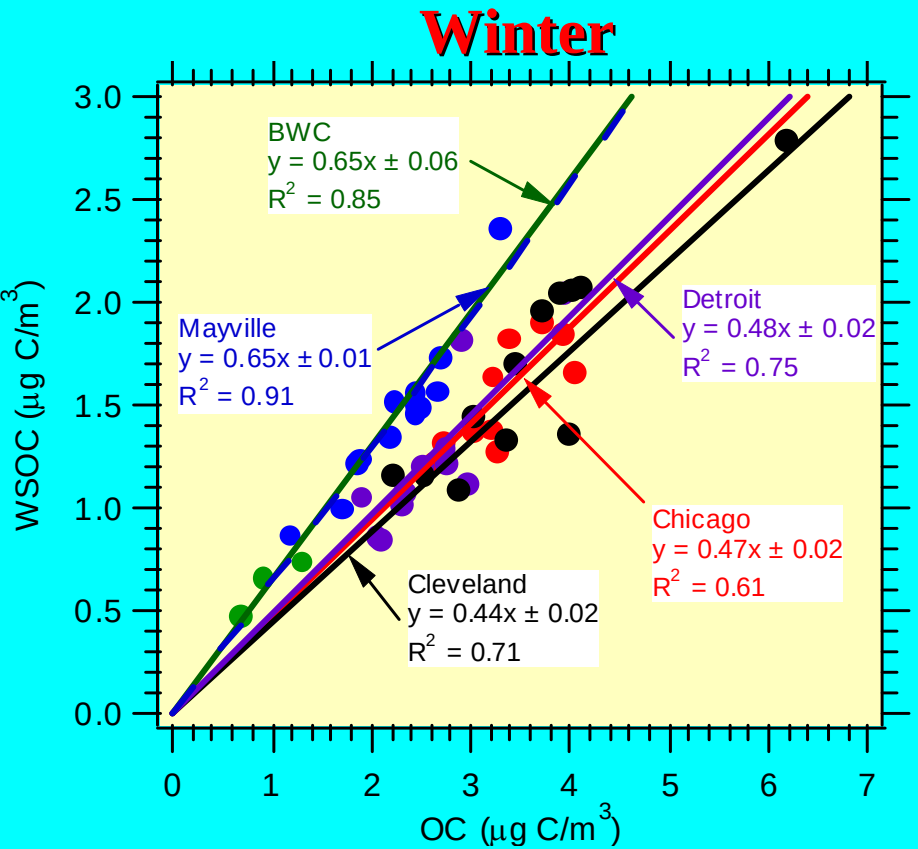
Hi-Volume Winter: Time Series of WSOC



-With exception of BWC similar pattern to summer

Hi-Volume: WSOC vs. OC



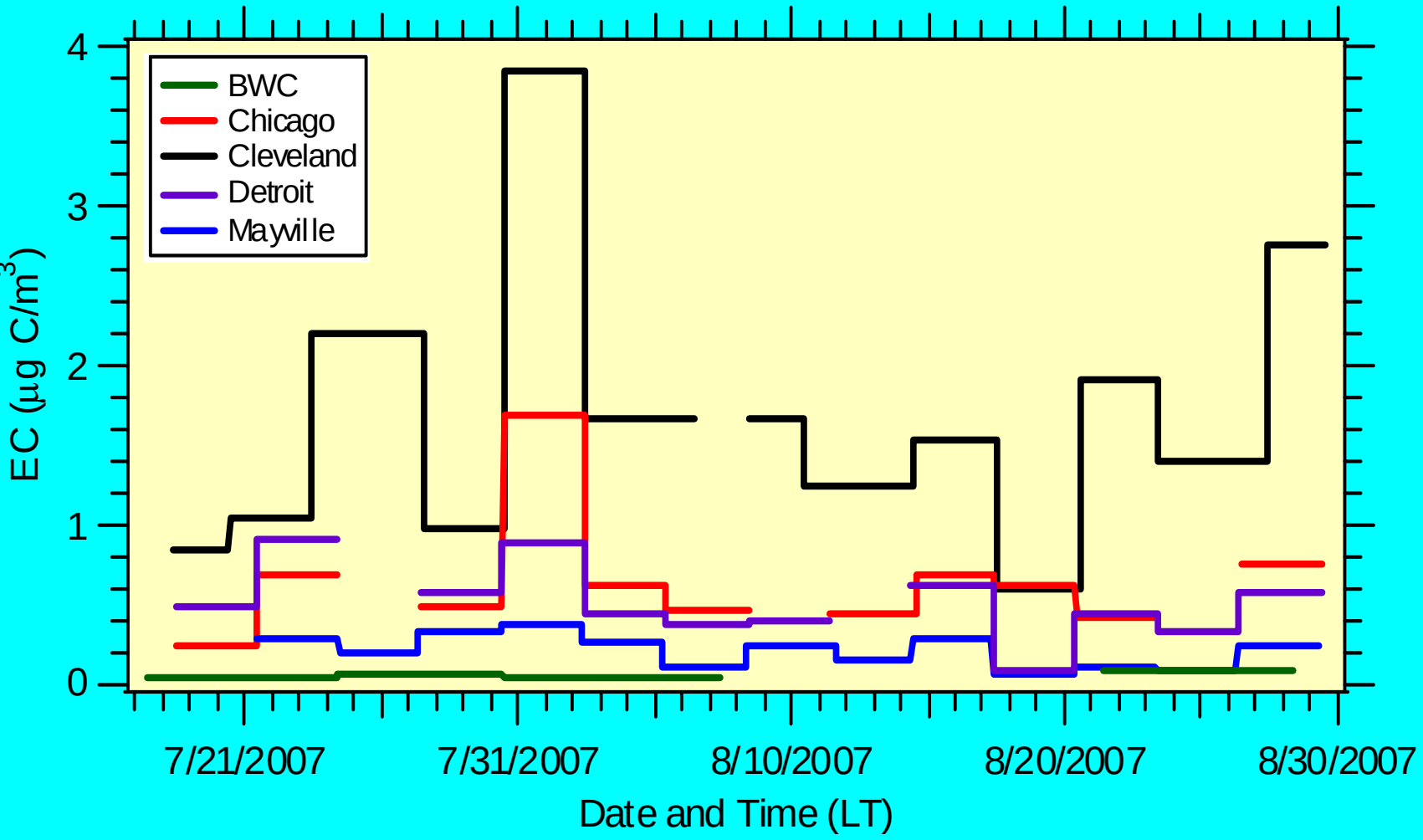


-WSOC and OC highly correlated for almost all sites

-WSOC and OC highly correlated only for rural sites

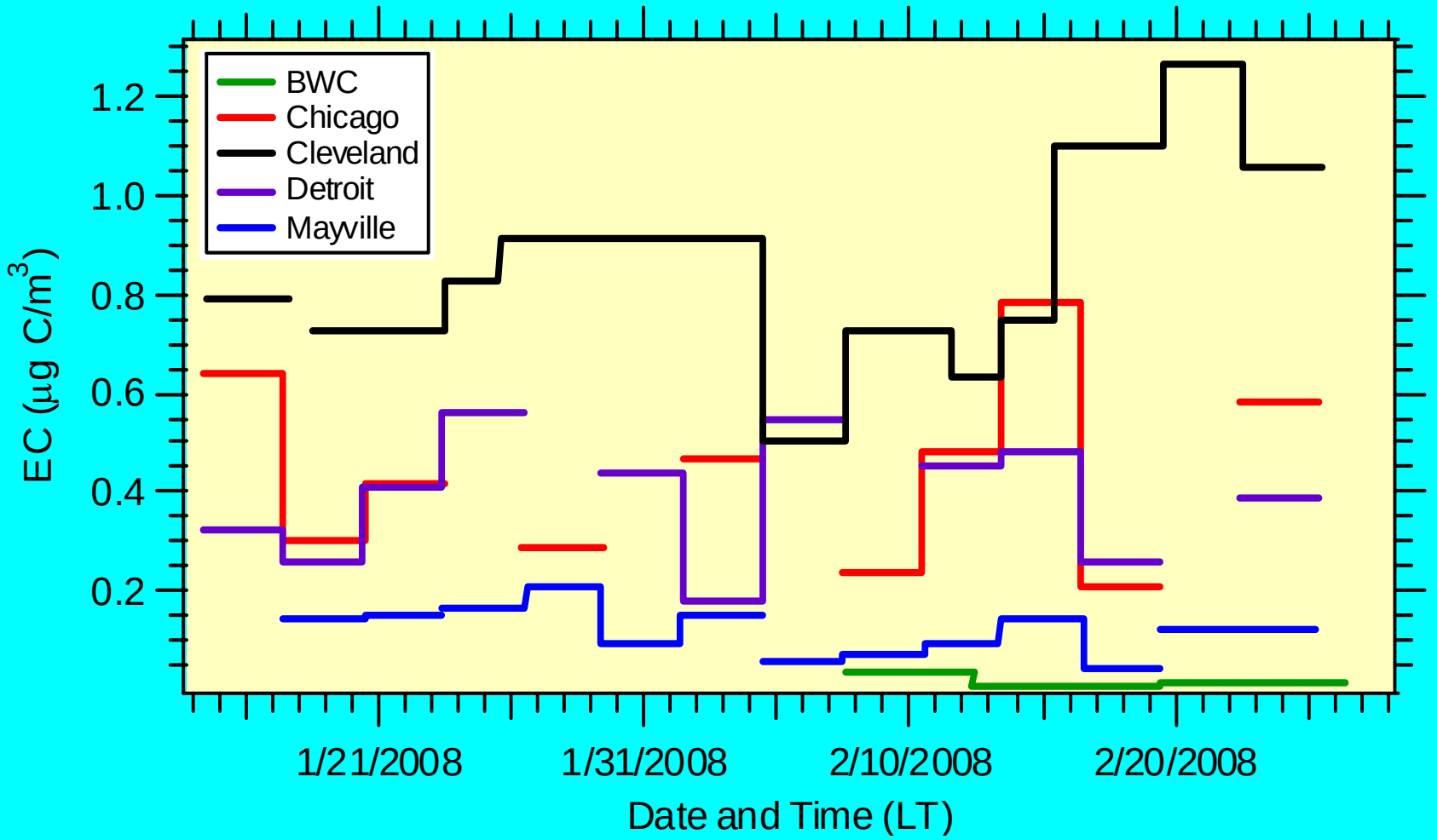
-WSOC/OC ratio at particular site similar in both summer and winter

Hi-Volume Summer: Time Series of Elemental Carbon



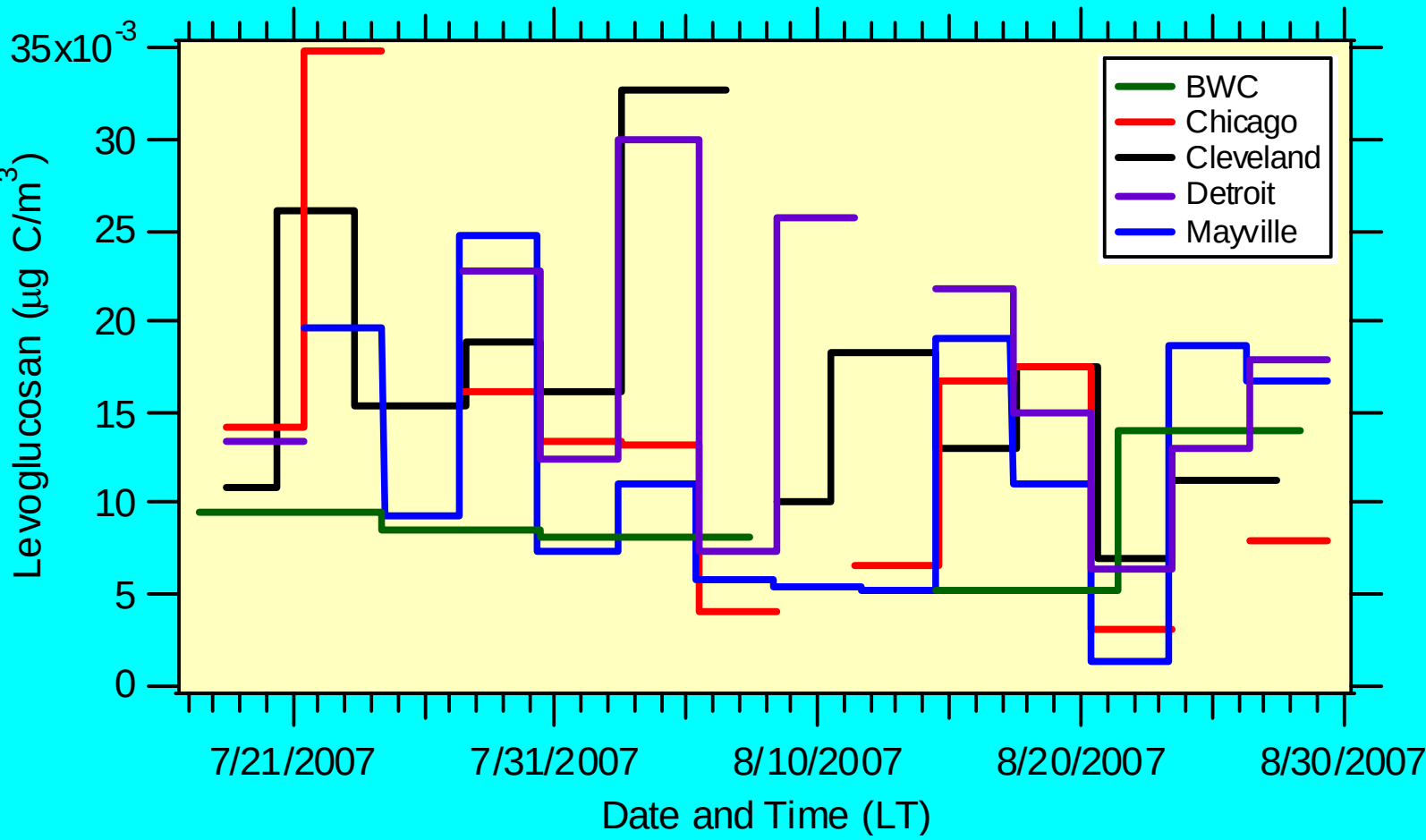
-EC concentrations higher for urban sites than rural sites

Hi-Volume Winter: Time Series of Elemental Carbon



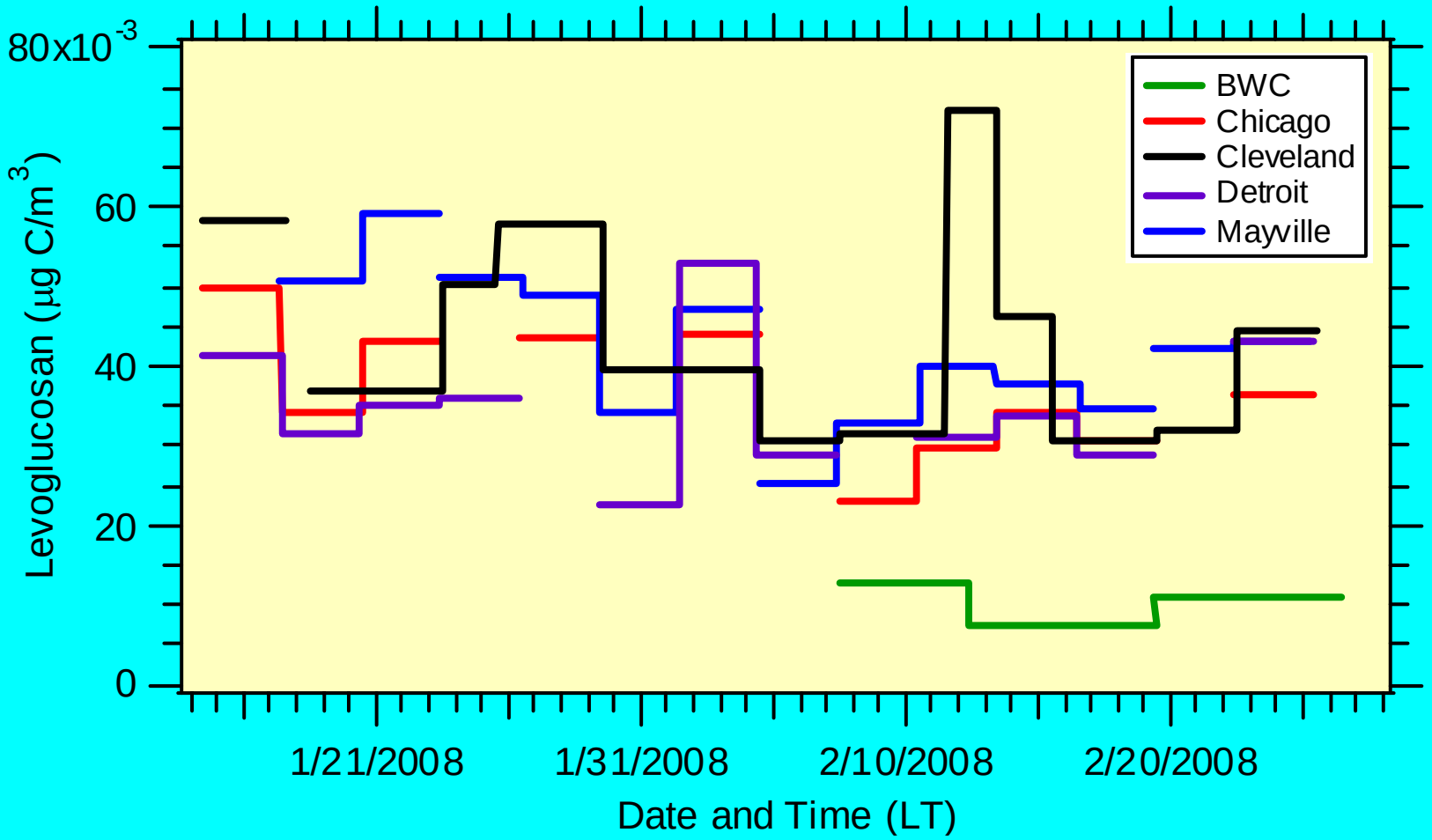
-Similar pattern to summer

Hi-Volume Summer:
Time Series of Levoglucosan
(On Carbon Mass Basis and Corrected for Arabitol)



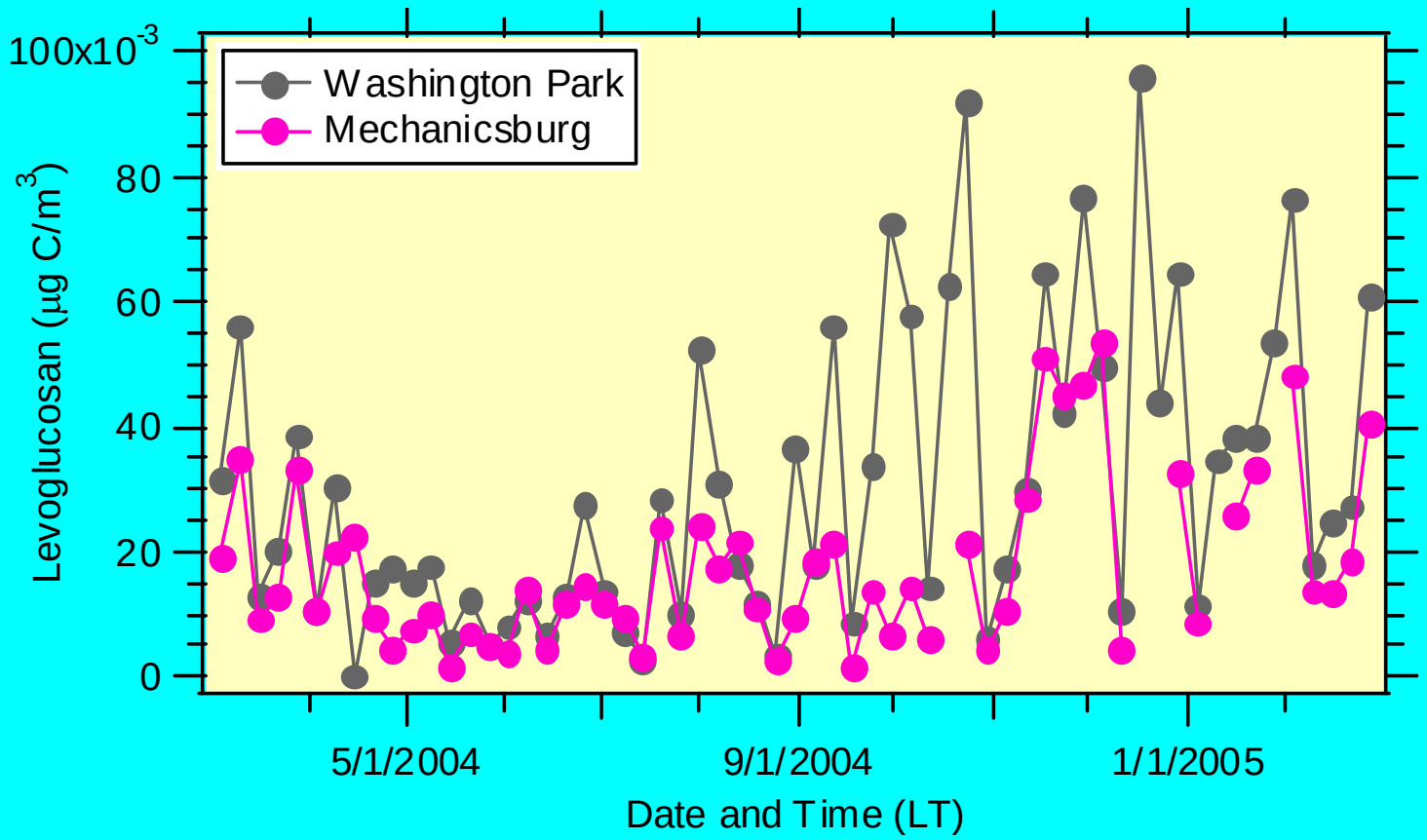
-Levoglucosan concentration appears to be regional

Hi-Volume Winter: Time Series of Levoglucosan (On Carbon Mass Basis)



-Average concentration fairly similar at each site except BWC

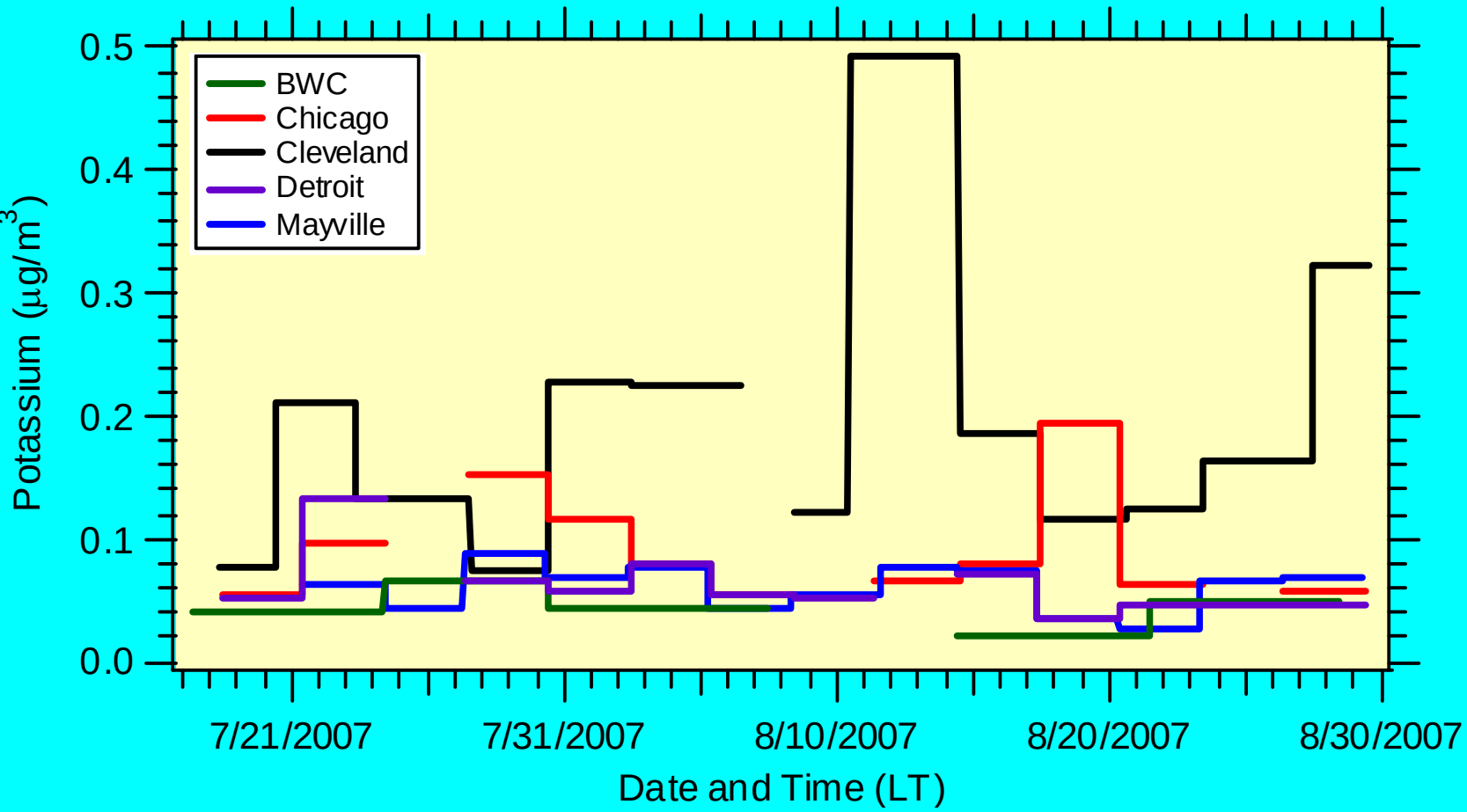
FRM:
Times Series of Levoglucosan
(On Carbon Mass Basis)



-Concentration increases in winter

-Mostly regional, but more local differences in winter

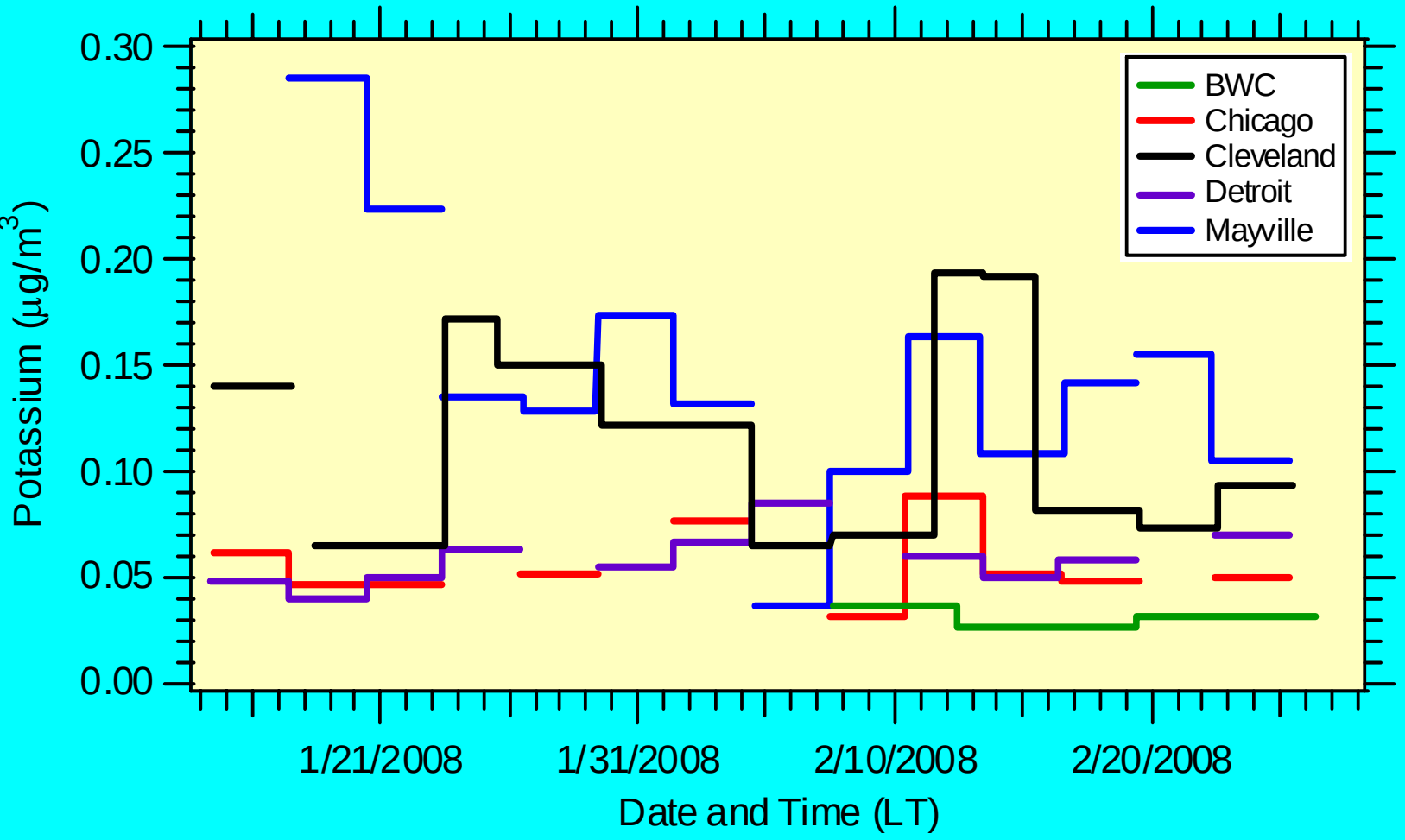
Hi-Volume Summer: Time Series of Potassium



-Potassium no real pattern

-Fairly similar concentrations except at Cleveland, differences due to local influences

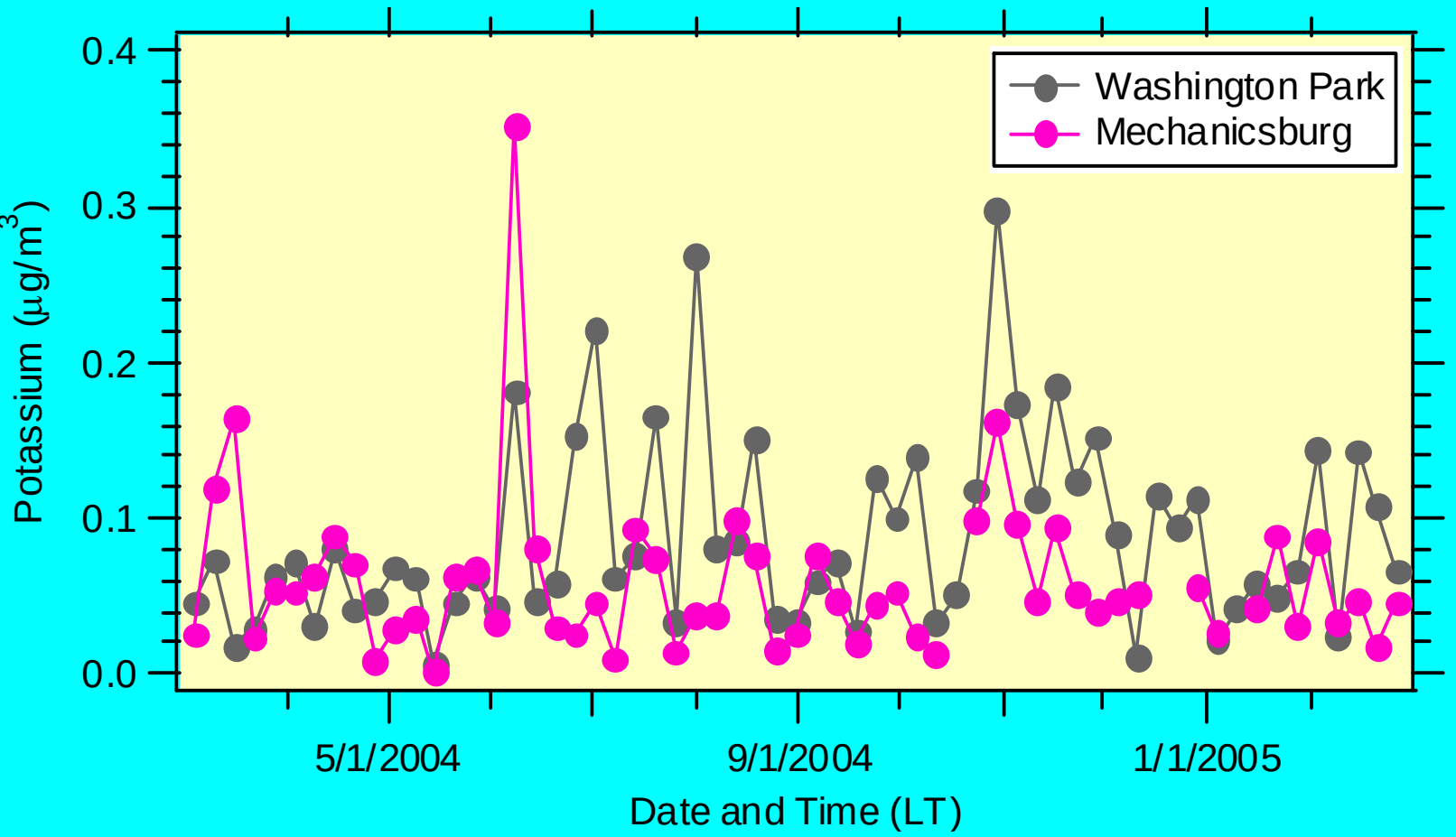
Hi-Volume Winter: Time Series of Potassium



-Like summer, no real pattern

-Although Mayville additionally has elevated concentrations

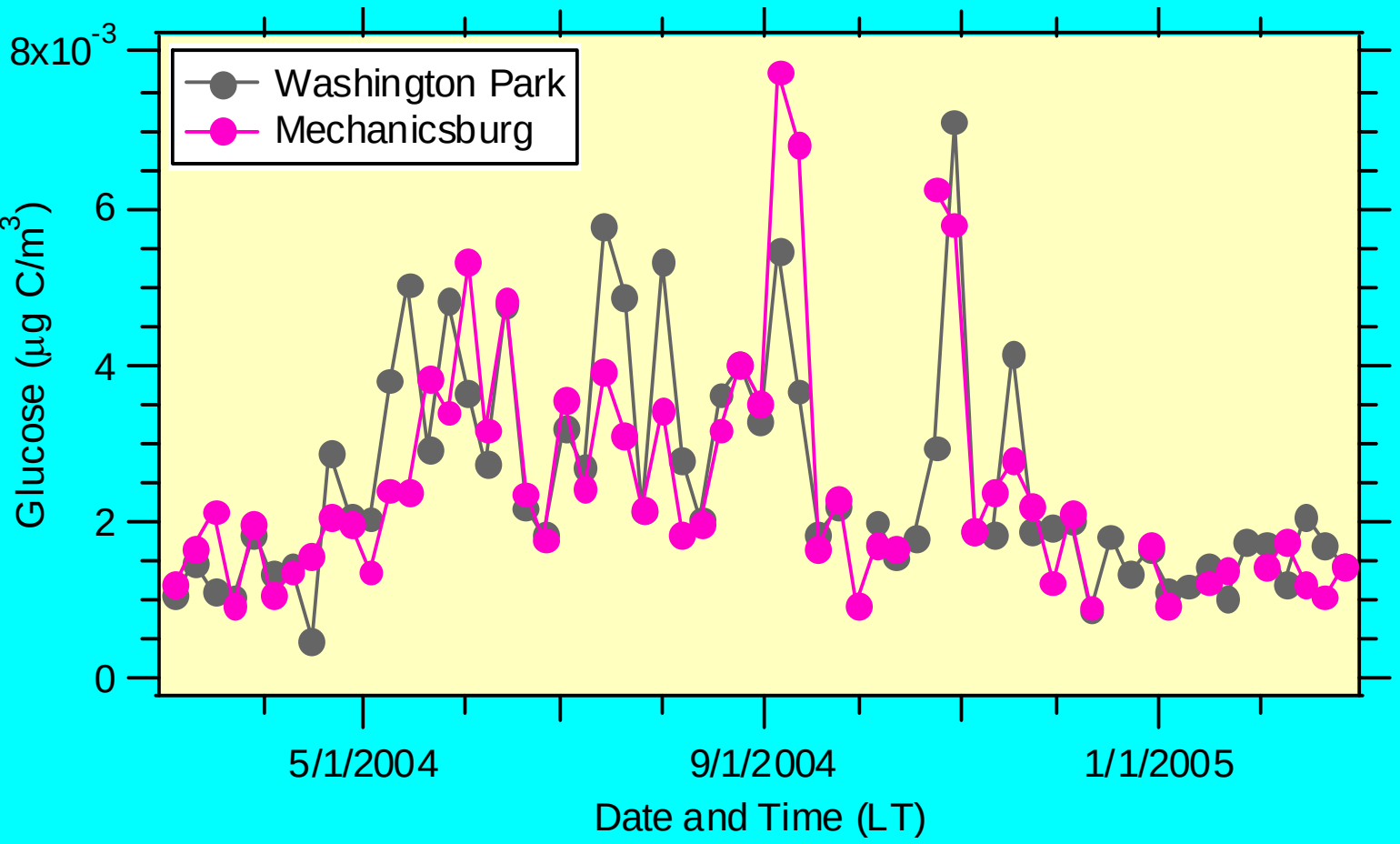
FRM:
Time Series of Potassium



-Slightly elevated concentration for Washington Park

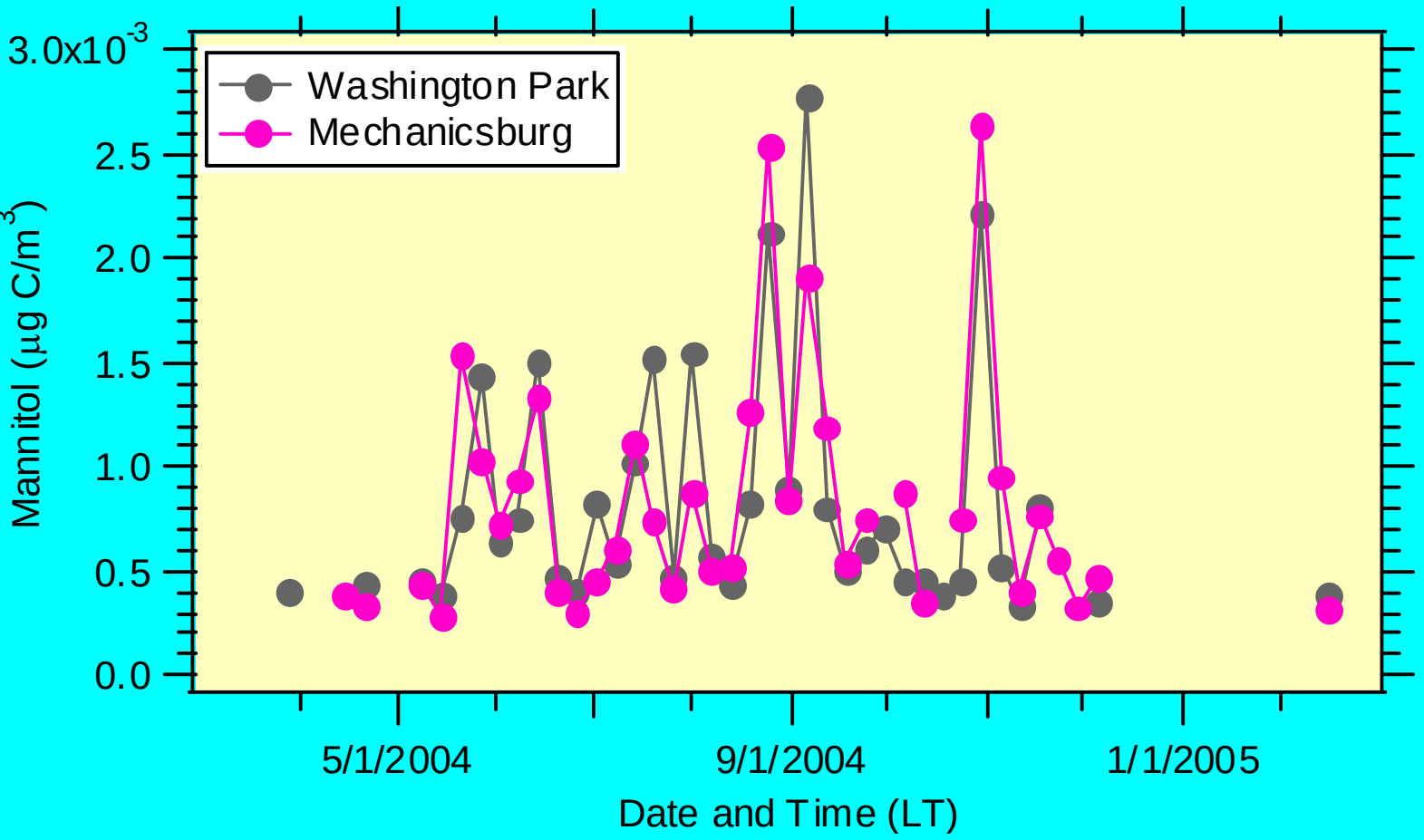
-Local influences in winter and summer observed

FRM:
Time Series of Glucose
(On Carbon Mass Basis)



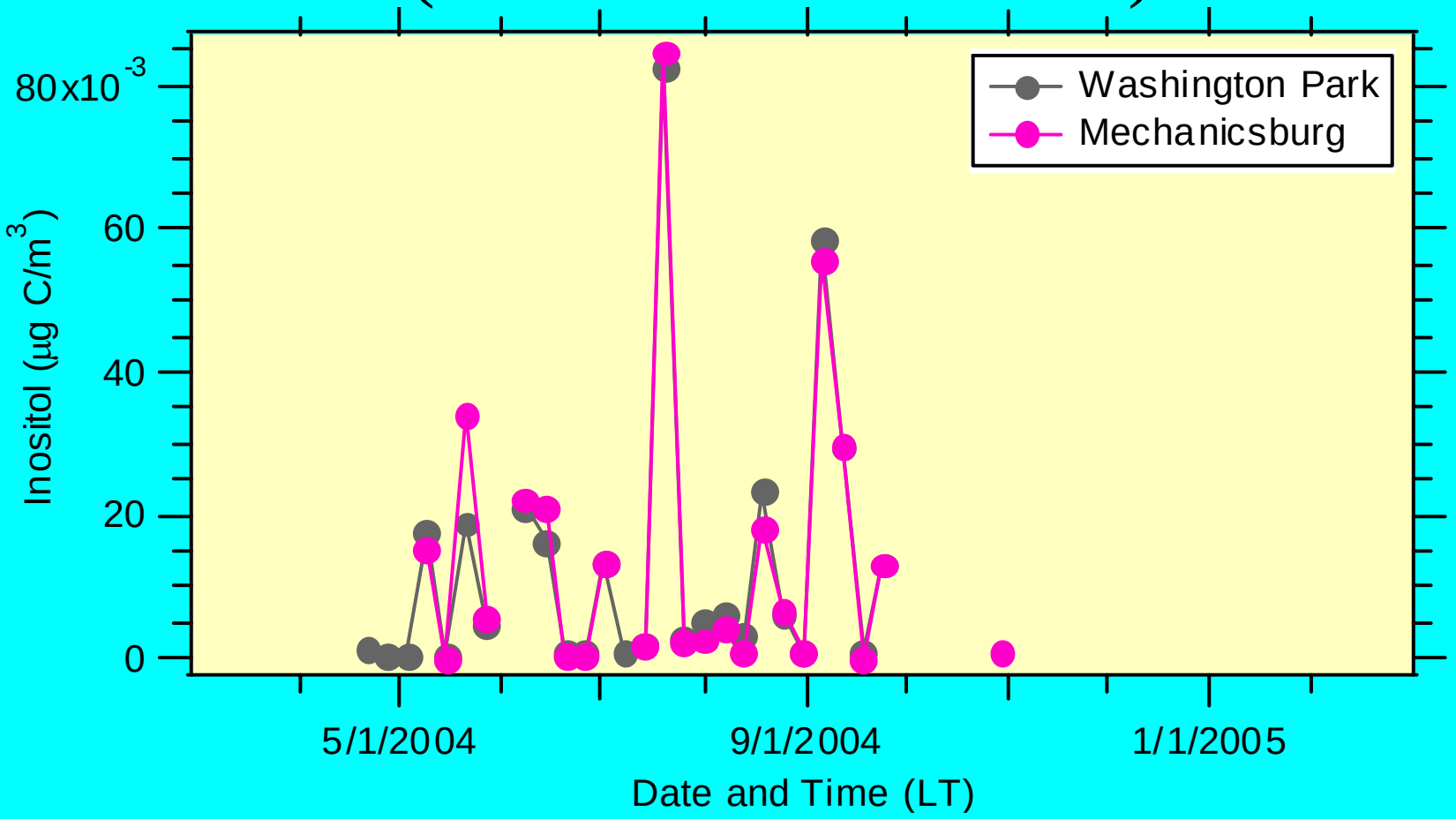
-Similar concentration at both sites and higher in summer

FRM:
Time Series of Mannitol
(On Carbon Mass Basis)



-Similar concentration at both sites, not present year round

FRM:
Time Series of Inositol
(On Carbon Mass Basis)

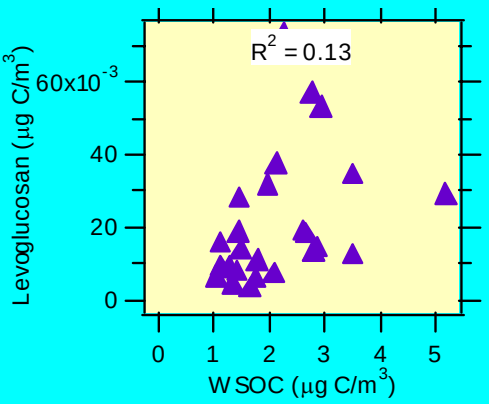


-Also similar concentrations at both sites

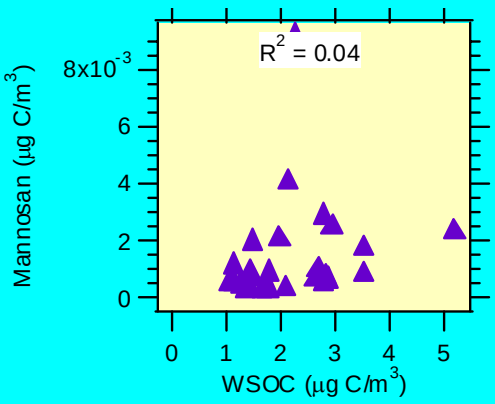
-Also not detected year round, but not over same time as mannitol

Carbohydrates vs. WSOC
Summer

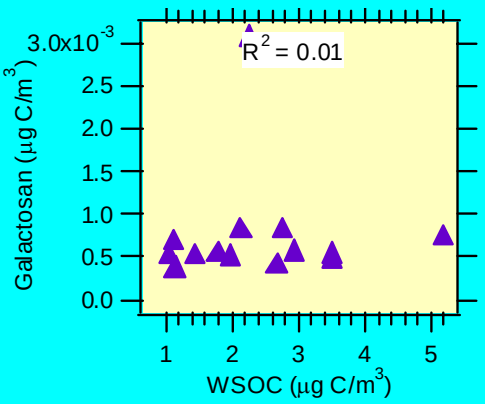
Levoglucosan



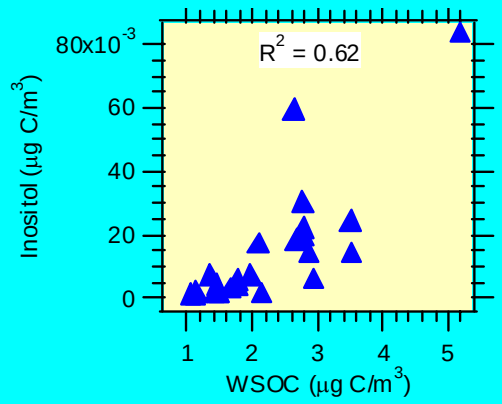
Mannosan



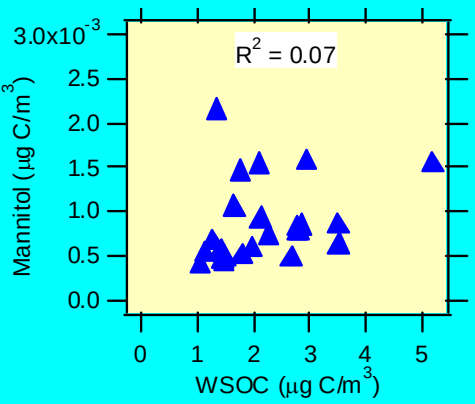
Galactosan



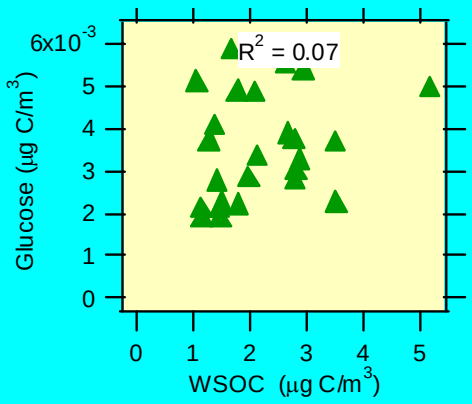
Inositol



Mannitol

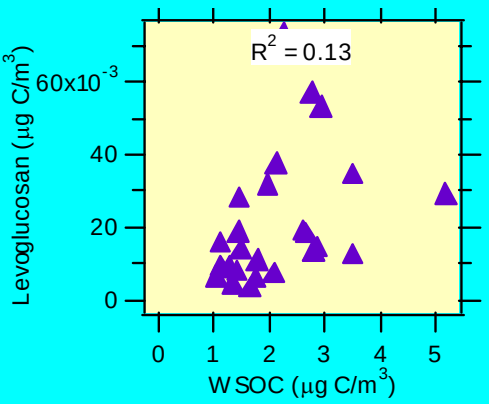


Glucose

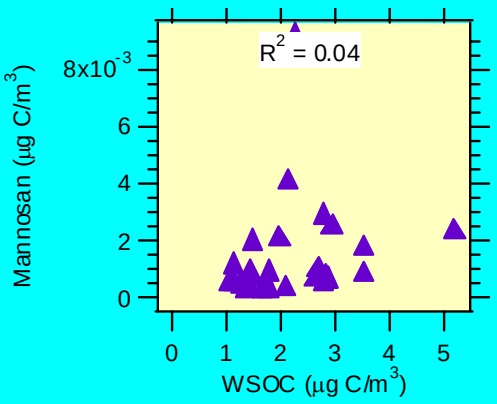


Carbohydrates vs. WSOC
Summer

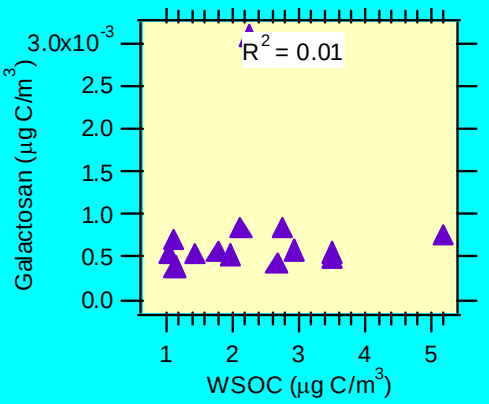
Levoglucosan



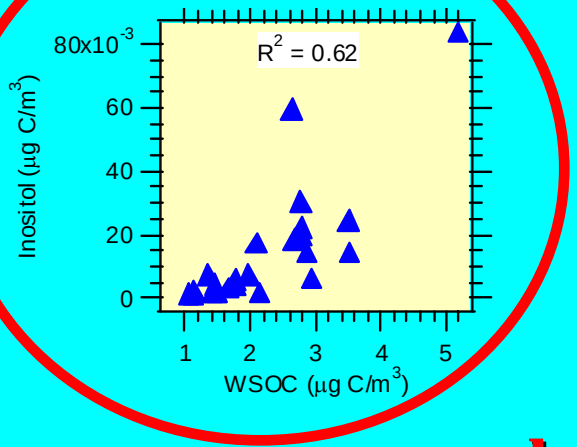
Mannosan



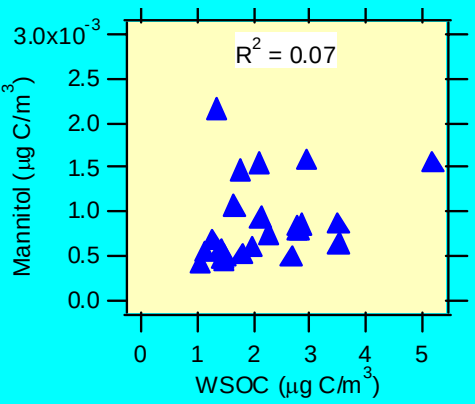
Galactosan



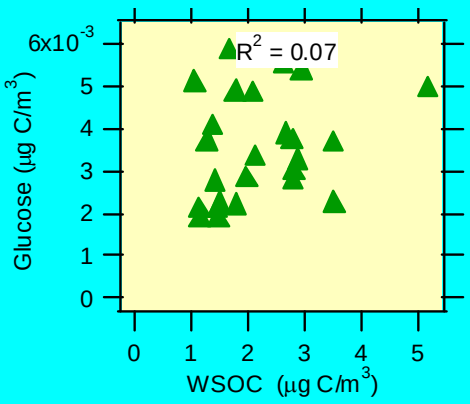
Inositol



Mannitol



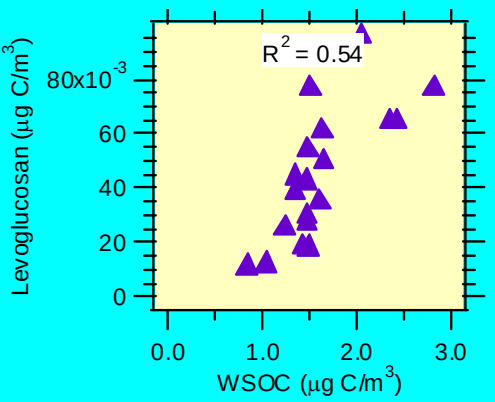
Glucose



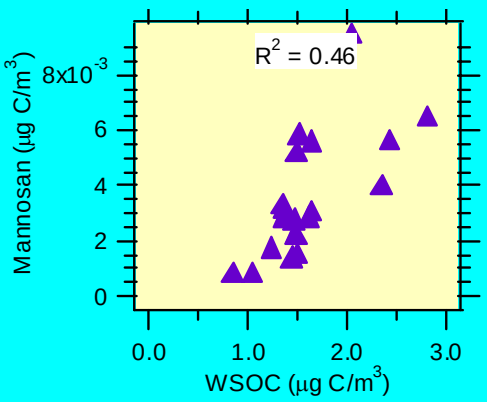
-only inositol is correlated with WSOC

Carbohydrates vs. WSOC
Winter

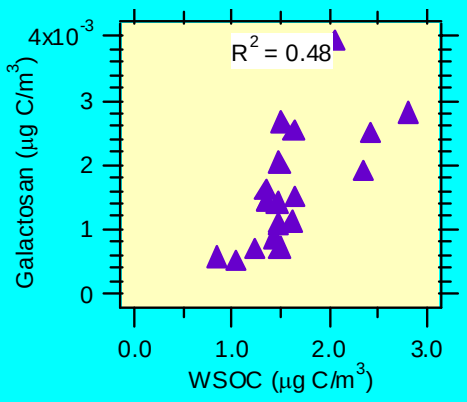
Levoglucosan



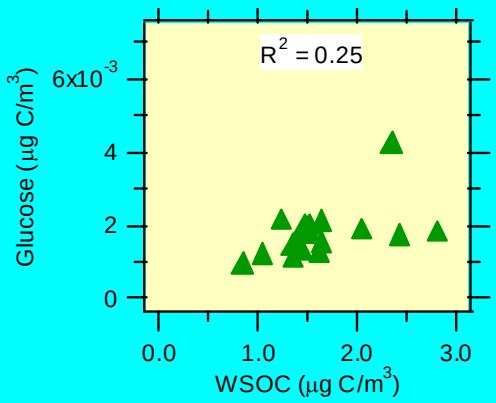
Mannosan



Galactosan

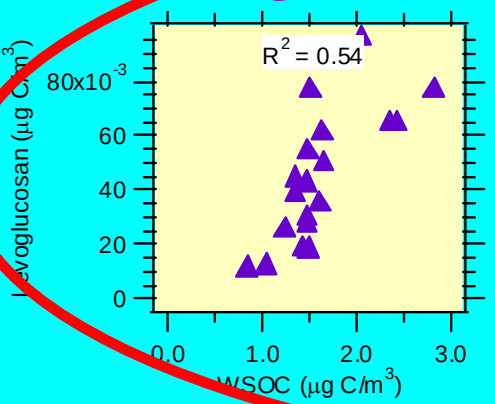


Glucose

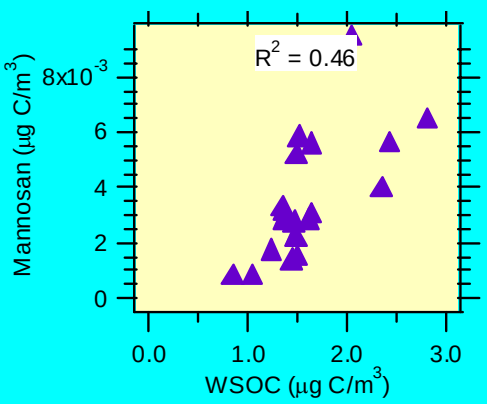


Carbohydrates vs. WSOC
Winter

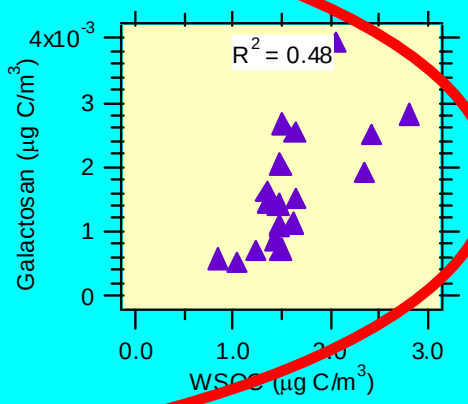
Levoglucosan



Mannosan

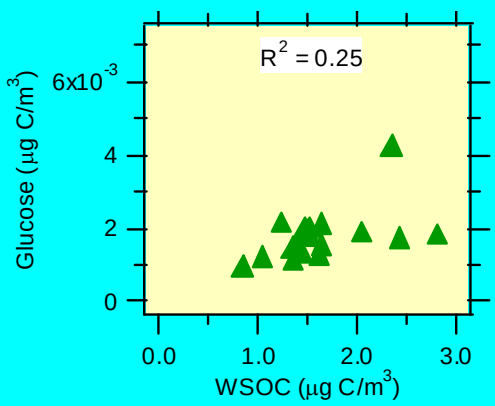


Galactosan



-During winter anhydrosugars somewhat correlated with WSOC

Glucose



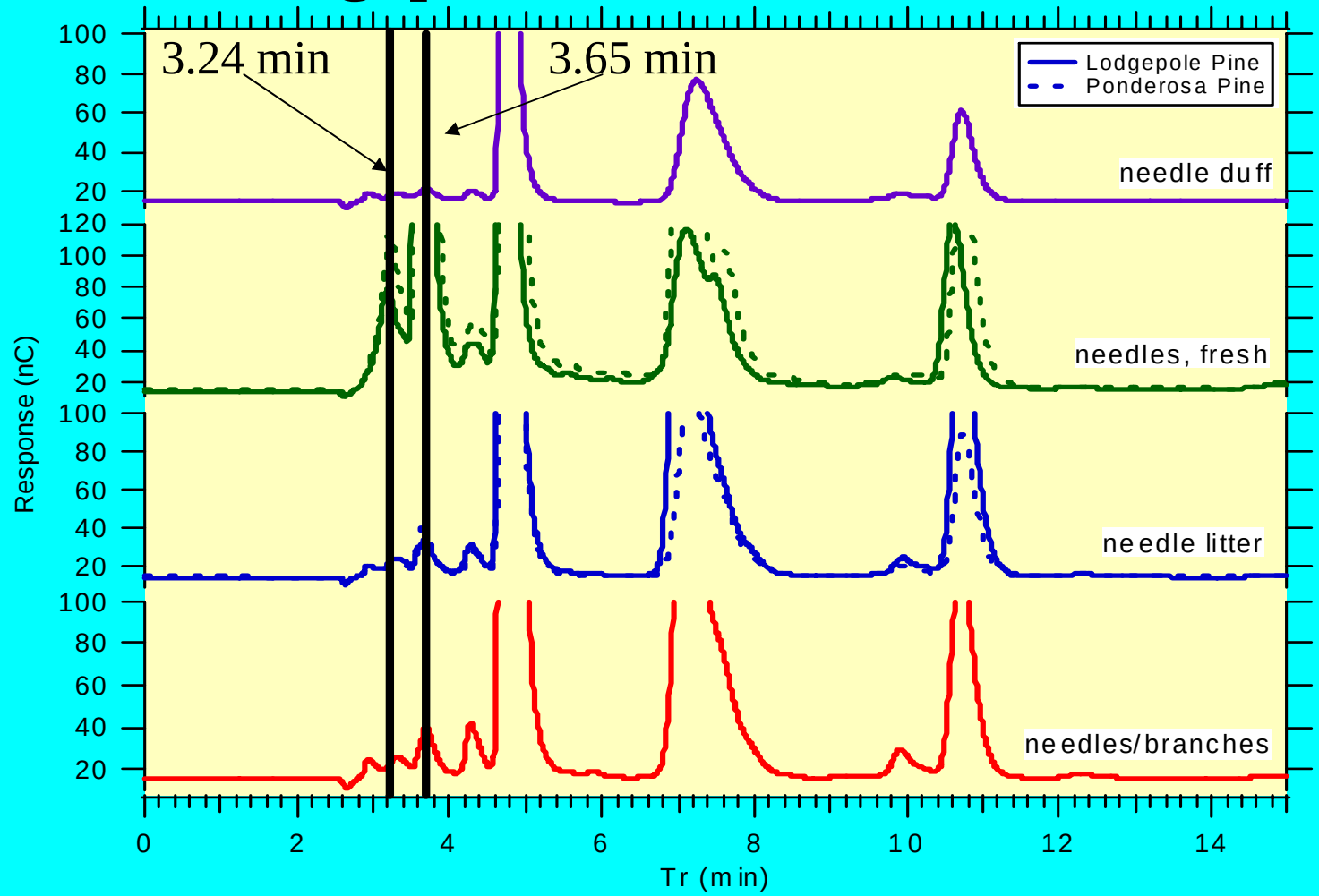
Determination of Contribution of OC from Biomass Burning

- Calculated by dividing levoglucosan/OC ratio of sample by levoglucosan/OC ratio from source profile

- For summer: source profiles used from Sullivan et al., *J. Geophys. Res.*, 2008
  - Studied emissions of fuels known to burn in wild and prescribed fires
  - Use combination of peak ratios in carbohydrate chromatogram and back trajectory analysis to pick most appropriate source profile for each sample

- For winter: source profiles used from Fine et al., *Environ. Eng. Sci.*, 2004
  - Studied emissions from fireplace combustion for 10 different woods from Midwestern and Western U.S.
  - Average levoglucosan/OC = 0.071 µg C/µg C

Chromatogram Comparison for Burning of Lodgepole and Ponderosa Pine

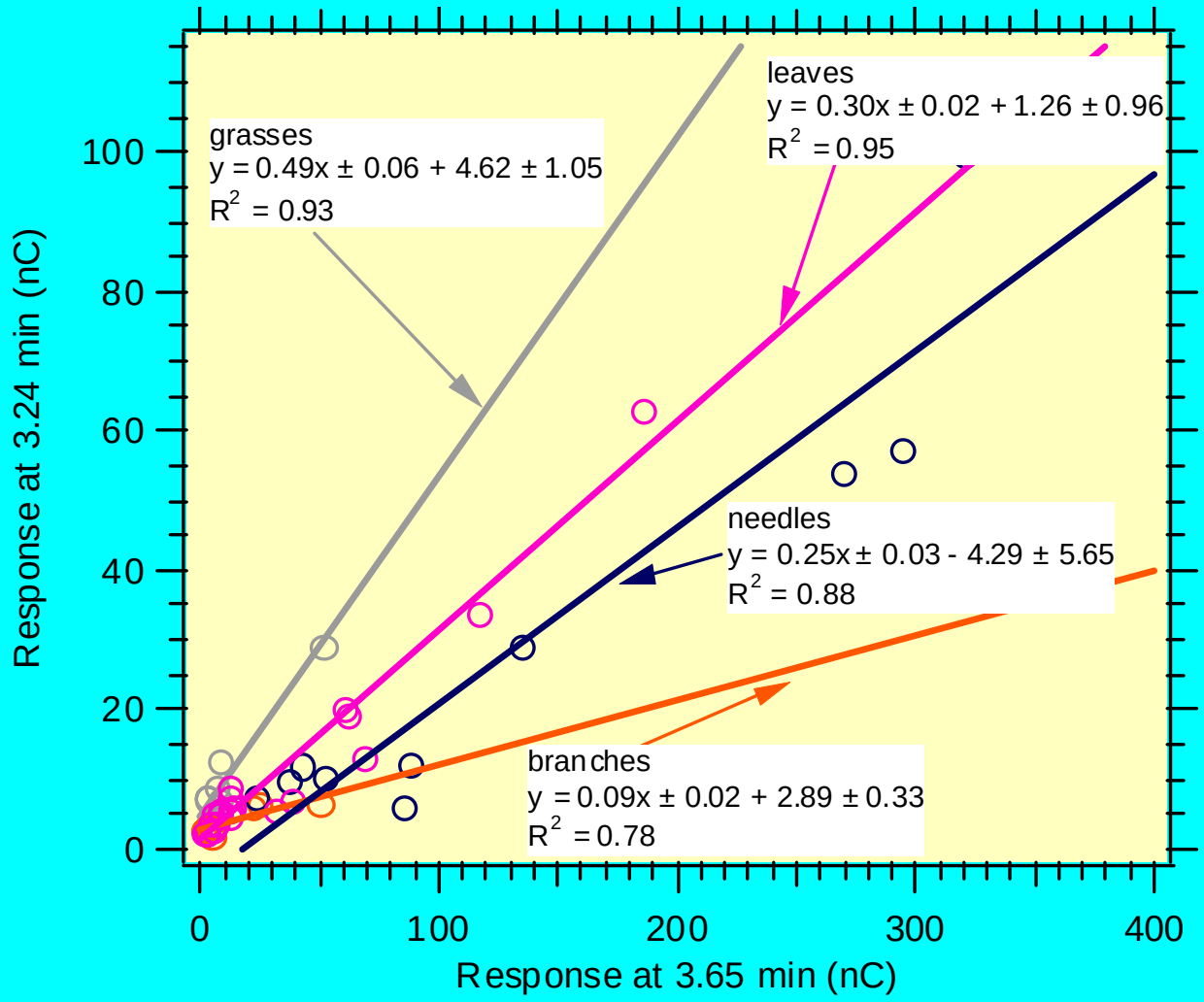


-Exact same pattern in chromatograms for two different fuels

-Found correlation between response at 3.24 and 3.65 min based on fuel component burned

Peak Response at 3.24 min vs. 3.65 min

- branches
- needles
- leaves
- grasses

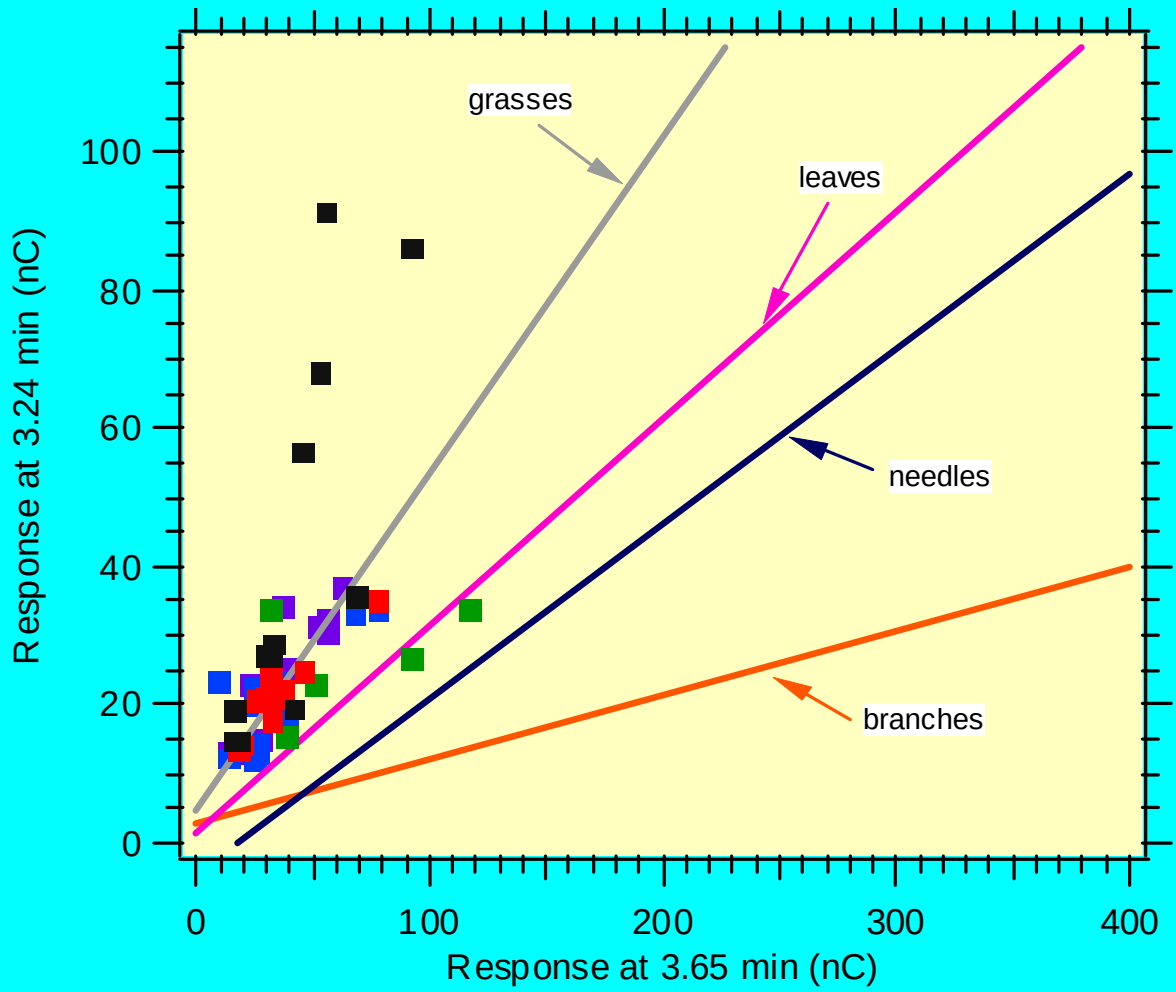


-Creates bounds for determining fuel component

-Suggests could help in constraining choice of source profile

Peak Response at 3.24 min vs. 3.65 min for Ambient Hi-Volume Summer Data

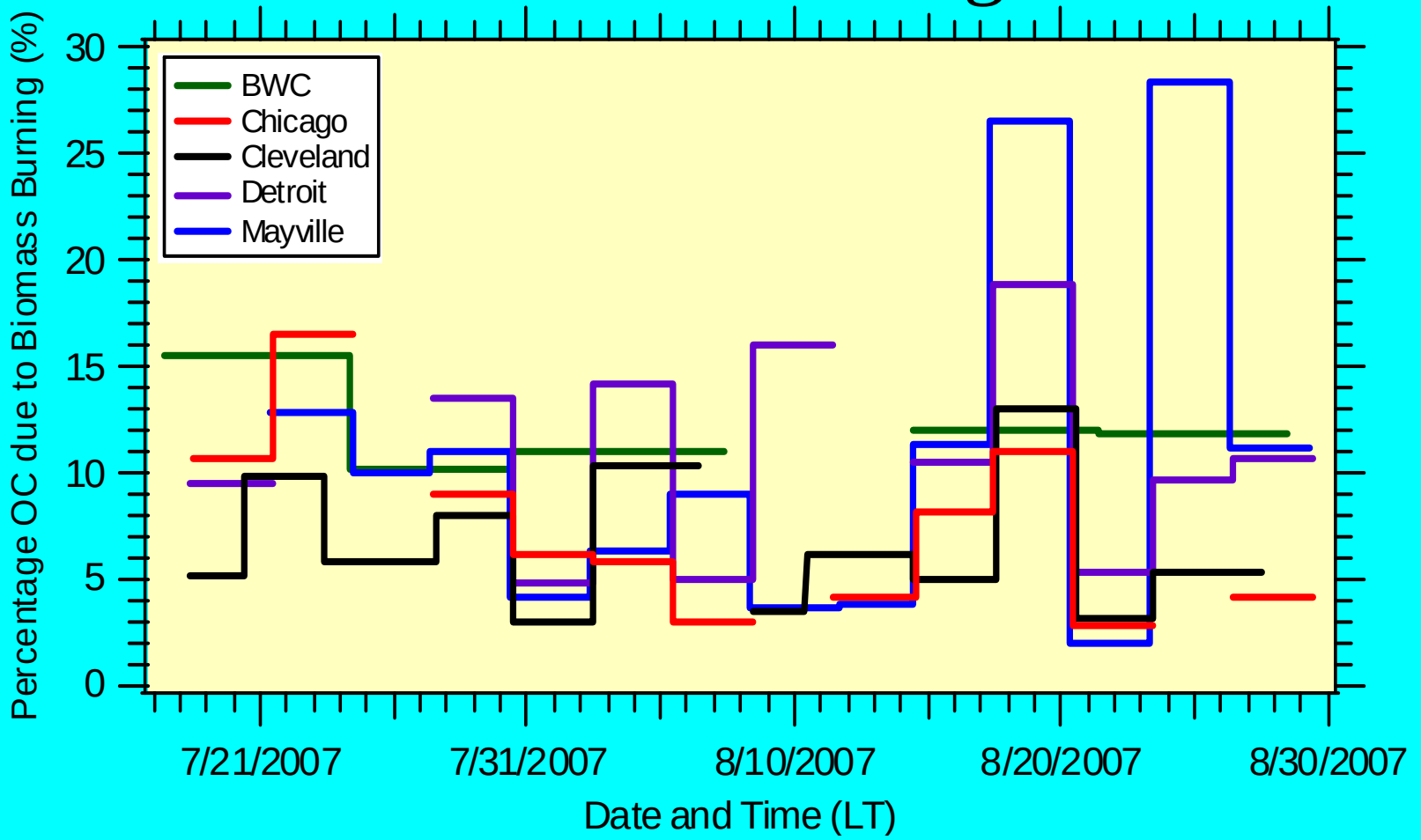
branches
needles
leaves
grasses
BWC
Chicago
Cleveland
Detroit
Mayville



-Ambient data falls within lines

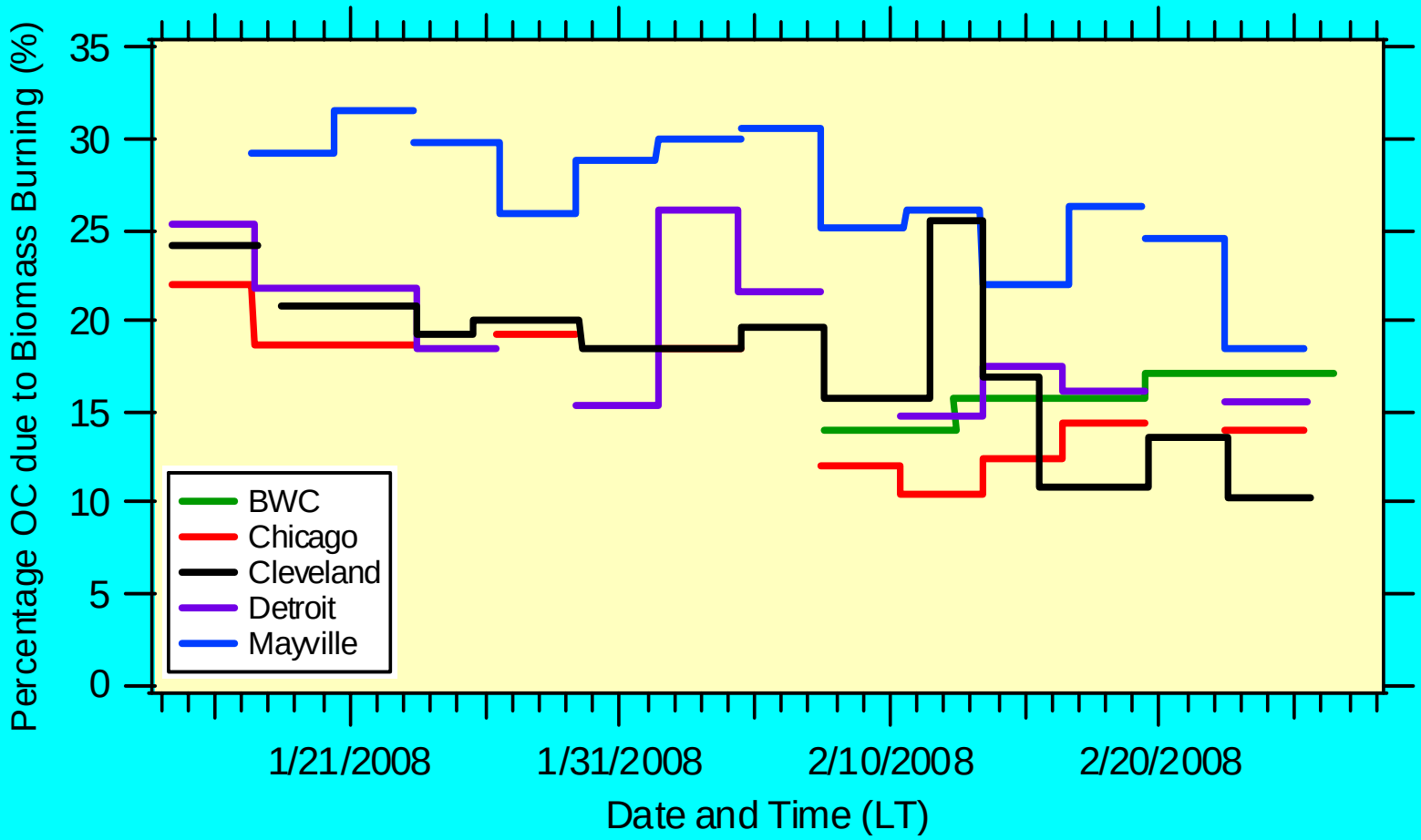
-Average levoglucosan/OC ratio ~0.036 µg C/µg C

Hi-Volume Summer: Time Series for Percentage of OC due to Biomass Burning



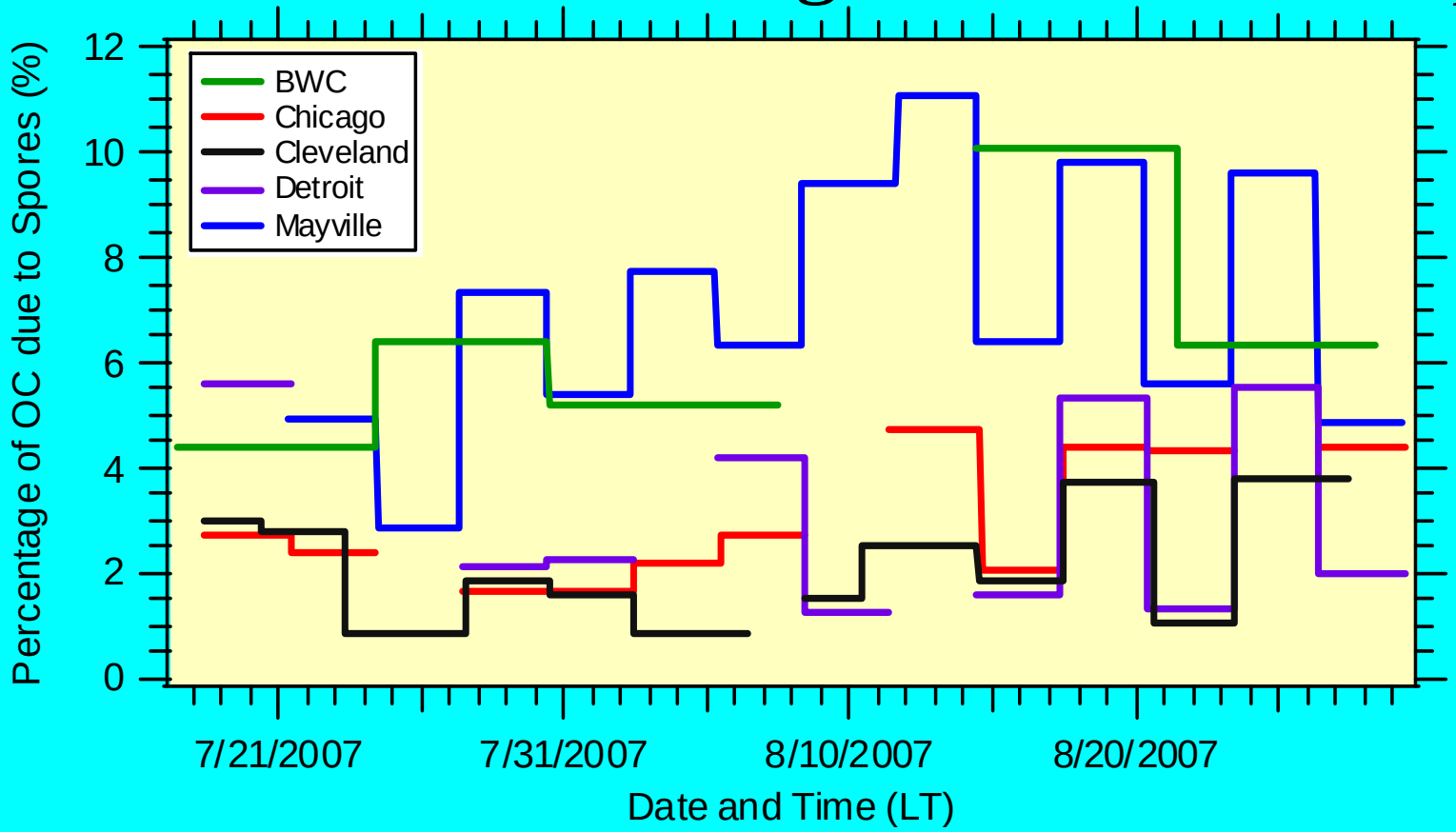
-Contribution only slightly higher at the rural sites, on average ~10%

Hi-Volume Winter: Time Series for Percentage of OC due to Biomass Burning



-Contribution higher than in summer, on average ~20%

Hi-Volume Summer:
Time Series for Percentage of OC due to Spores



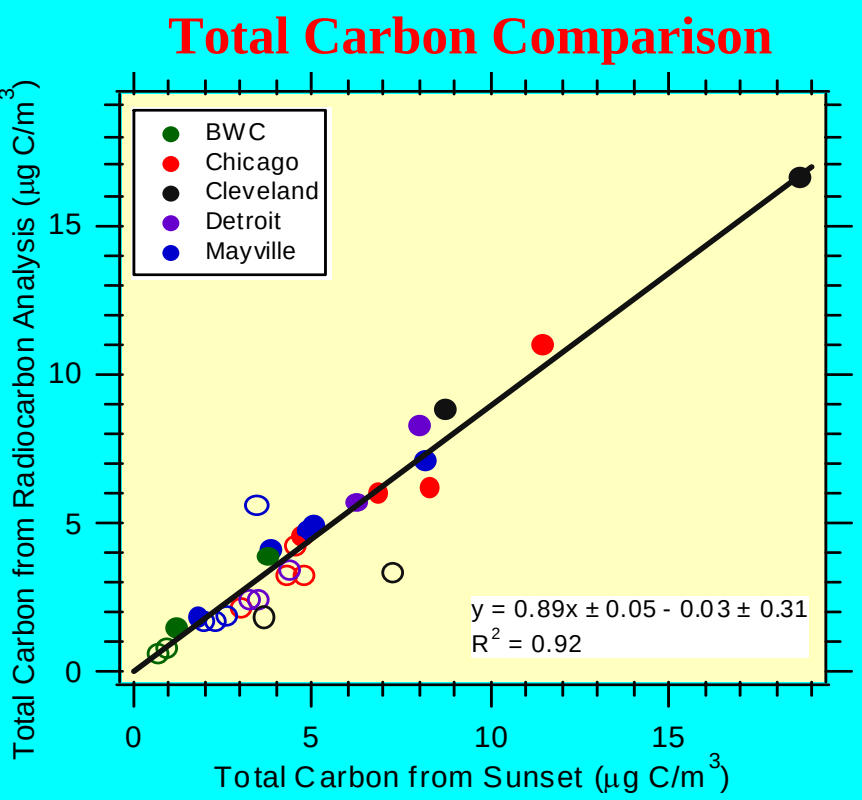
-Determined from concentration of mannitol

-Bauer et al., *Atmos. Environ.*, 2008 found relationship of 1.7 pg mannitol/spore and 13 pg OC/spore

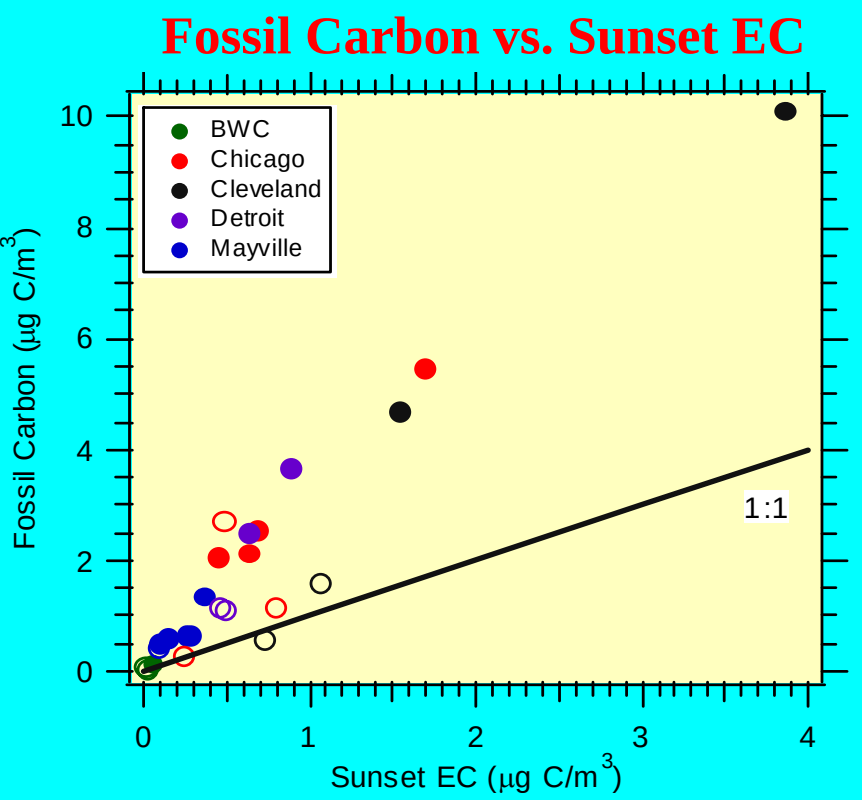
-Contribution ~6% at rural sites and ~3% at urban sites

Comparison of Total Carbon and Fossil Carbon vs. EC for the Radiocarbon and Sunset OCEC Data

Winter Summer

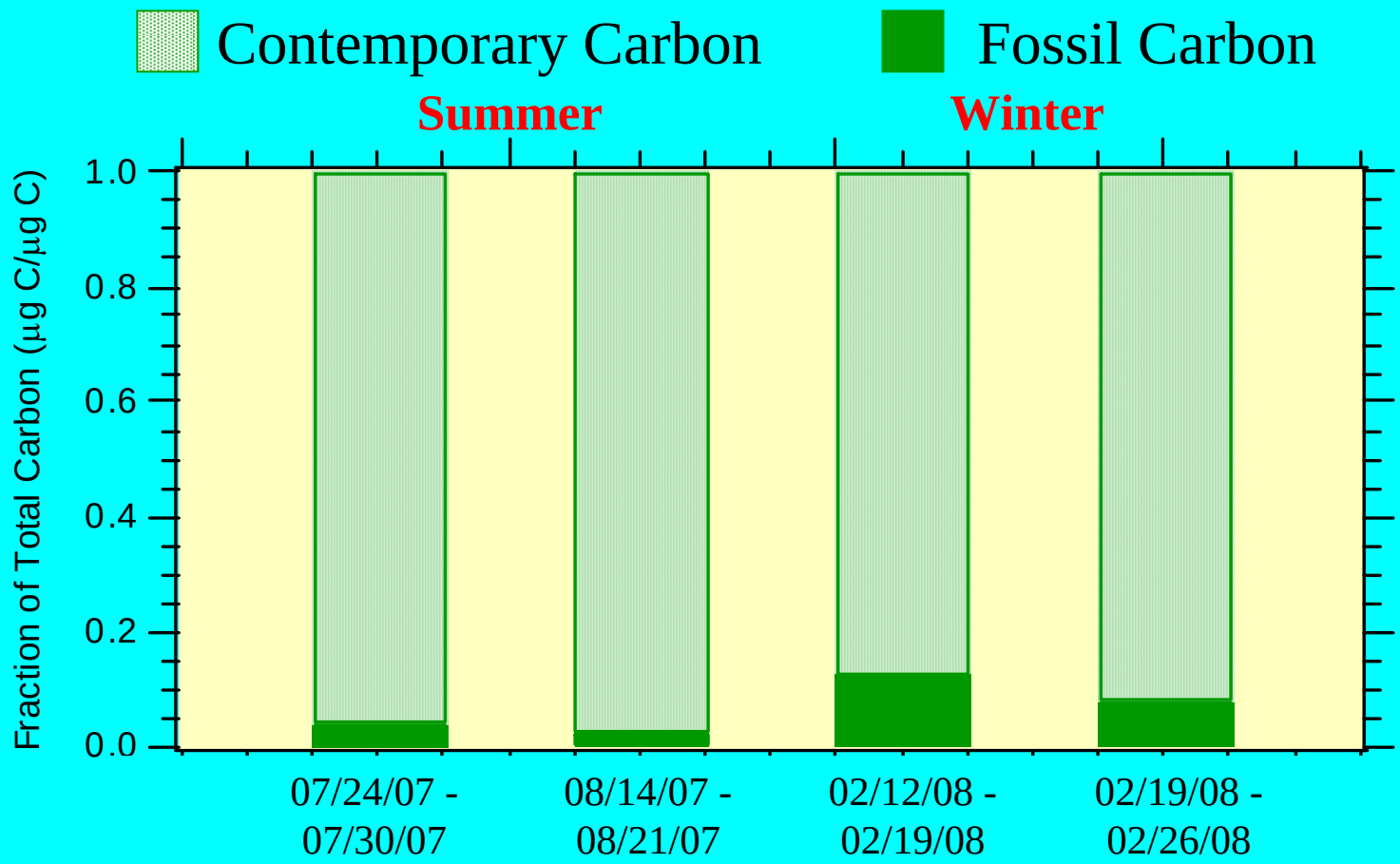


-Good agreement between both total carbon measurements



-Fossil carbon higher than EC, especially in summer

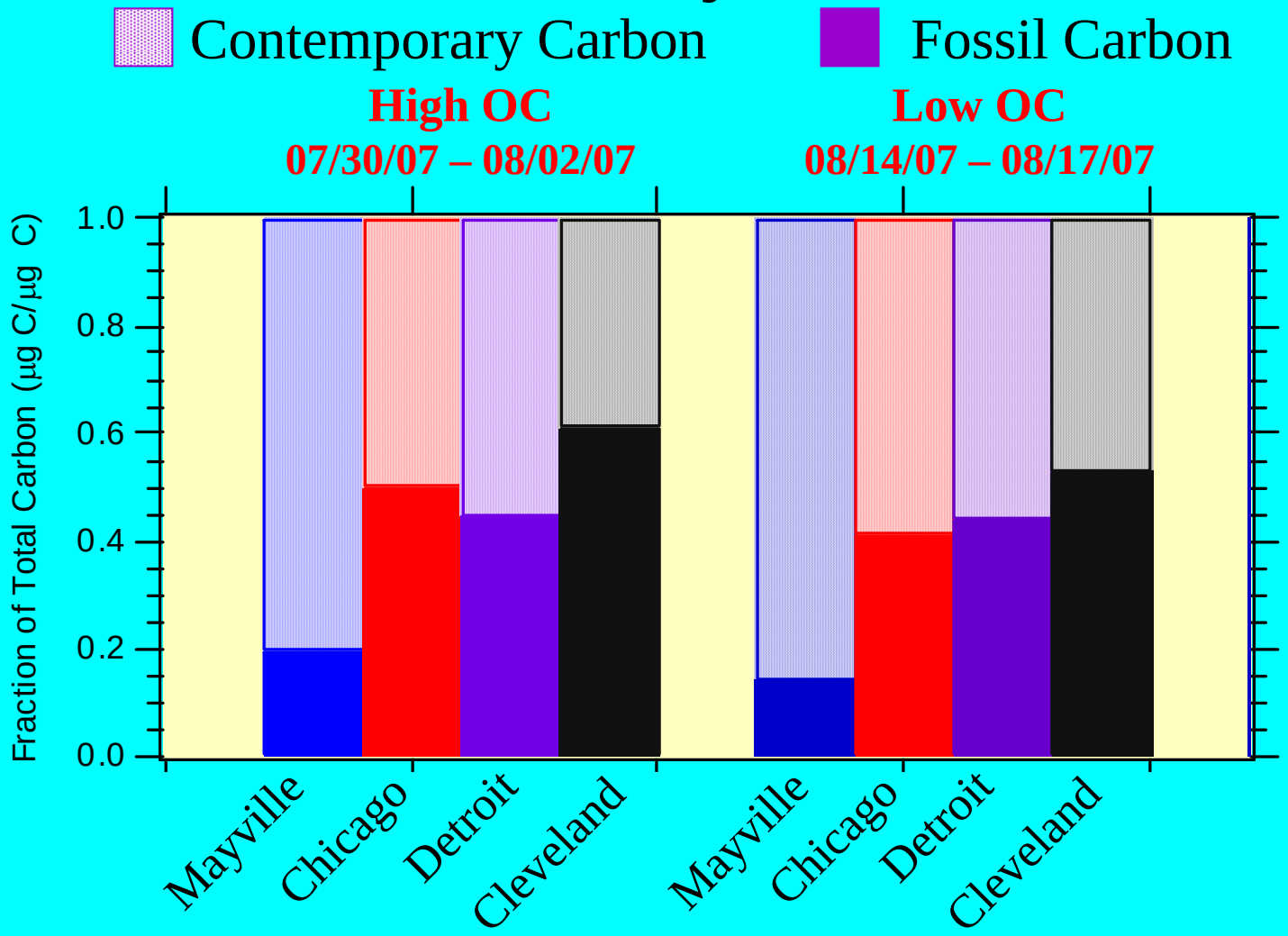
Fraction of Contemporary and Fossil Carbon to the Total Carbon for Boundary Waters Canoe



-Carbon almost entirely contemporary carbon

-Fraction of contemporary carbon slightly higher in summer

Fraction of Contemporary and Fossil Carbon to the Total Carbon by Site in Summer



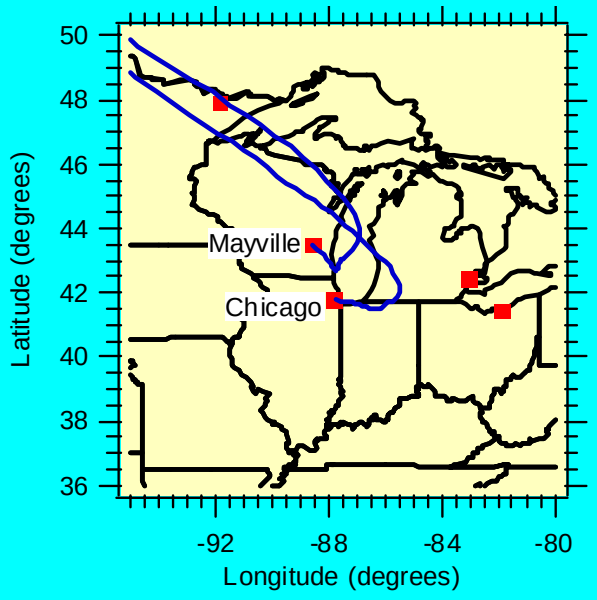
-Contemporary fraction highest at rural site

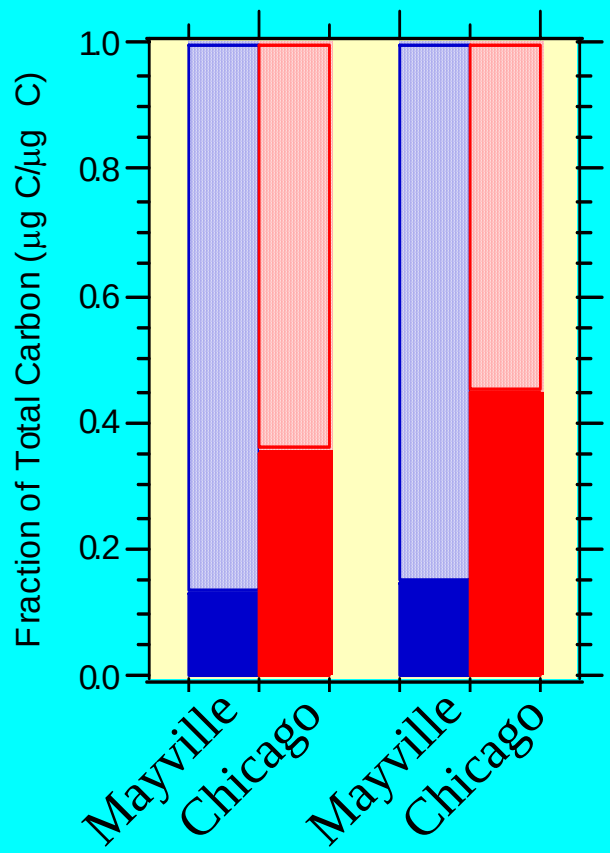
-Fractions about the same whether high or low OC concentration

Fraction of Contemporary and Fossil Carbon to the Total Carbon for Summer Transport Events

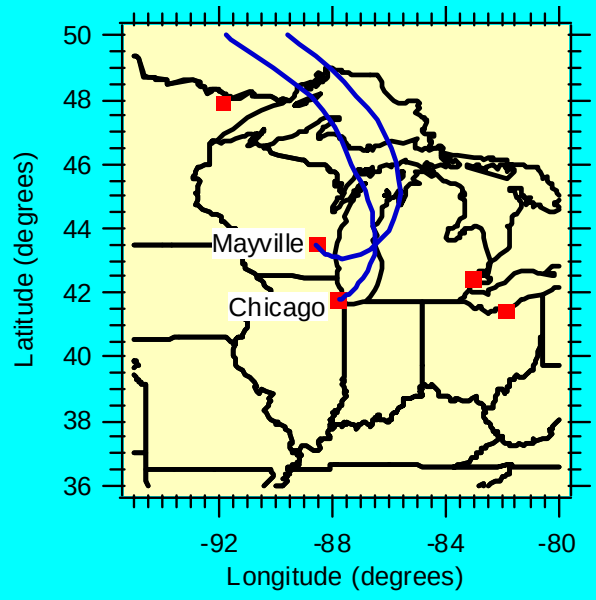
Contemporary Carbon Fossil Carbon

08/02/07 – 08/05/07



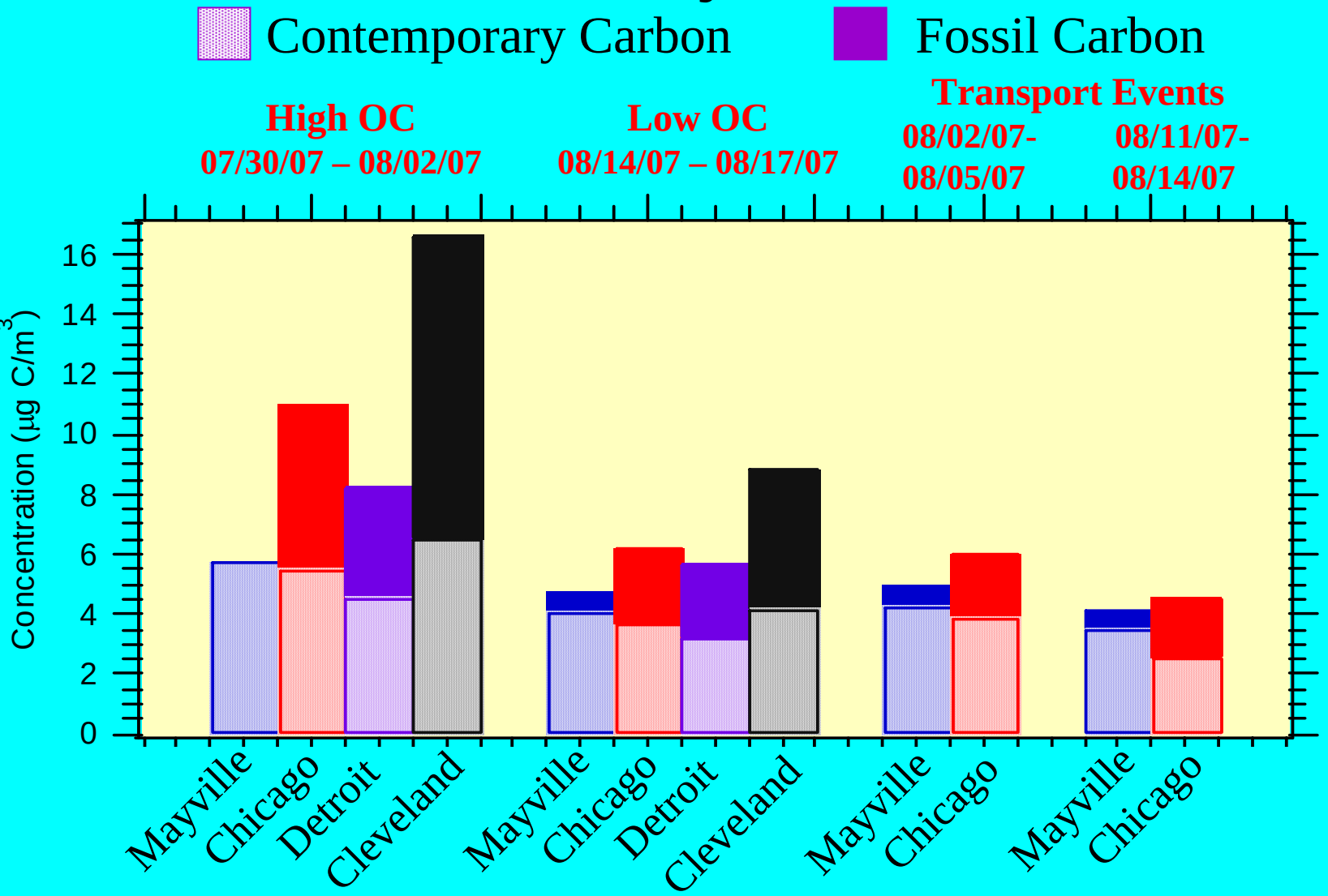


08/11/07 – 08/14/07



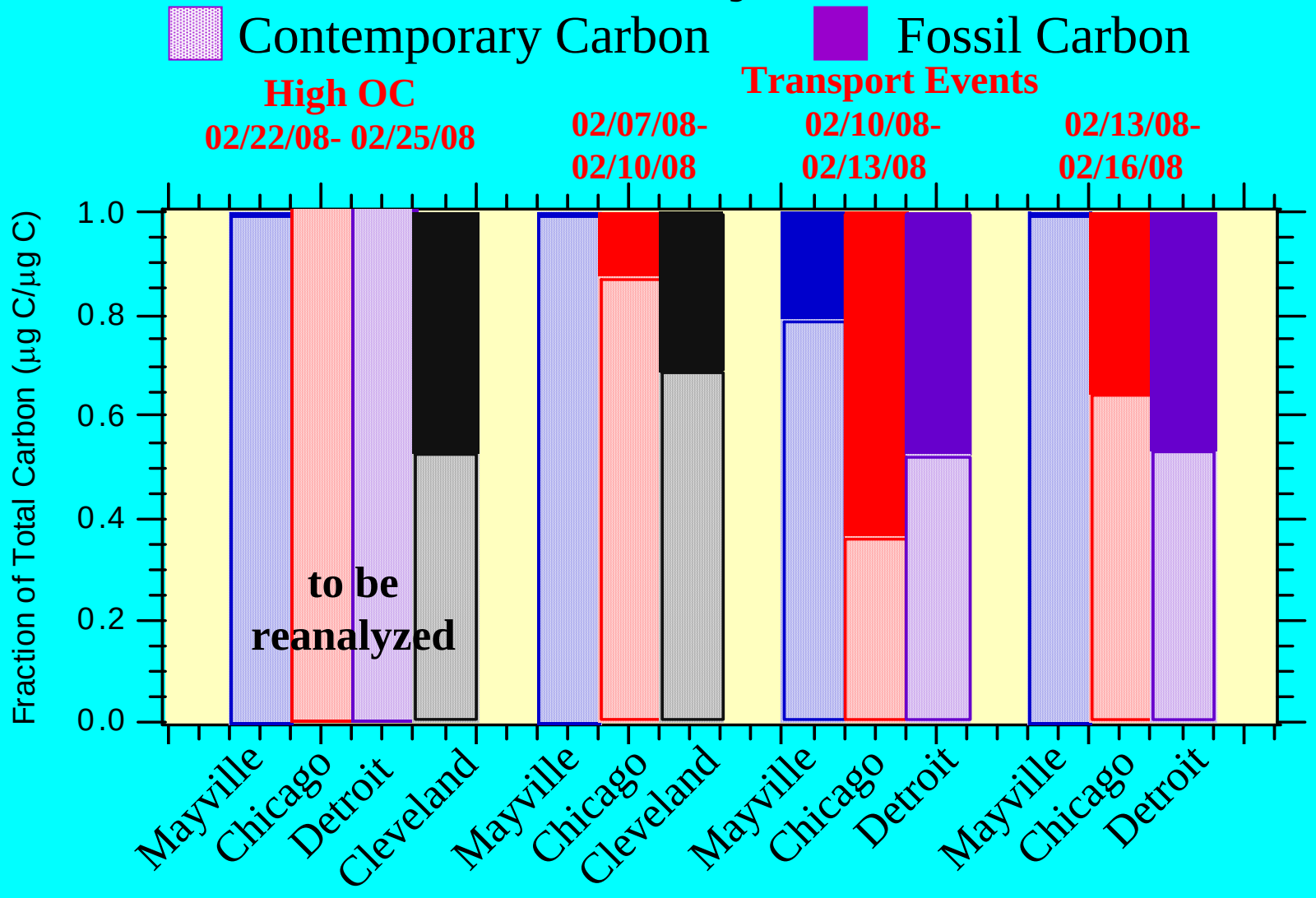
-Pattern for fractions also similar for different transport events

Contemporary and Fossil Carbon Concentrations by Site in Summer



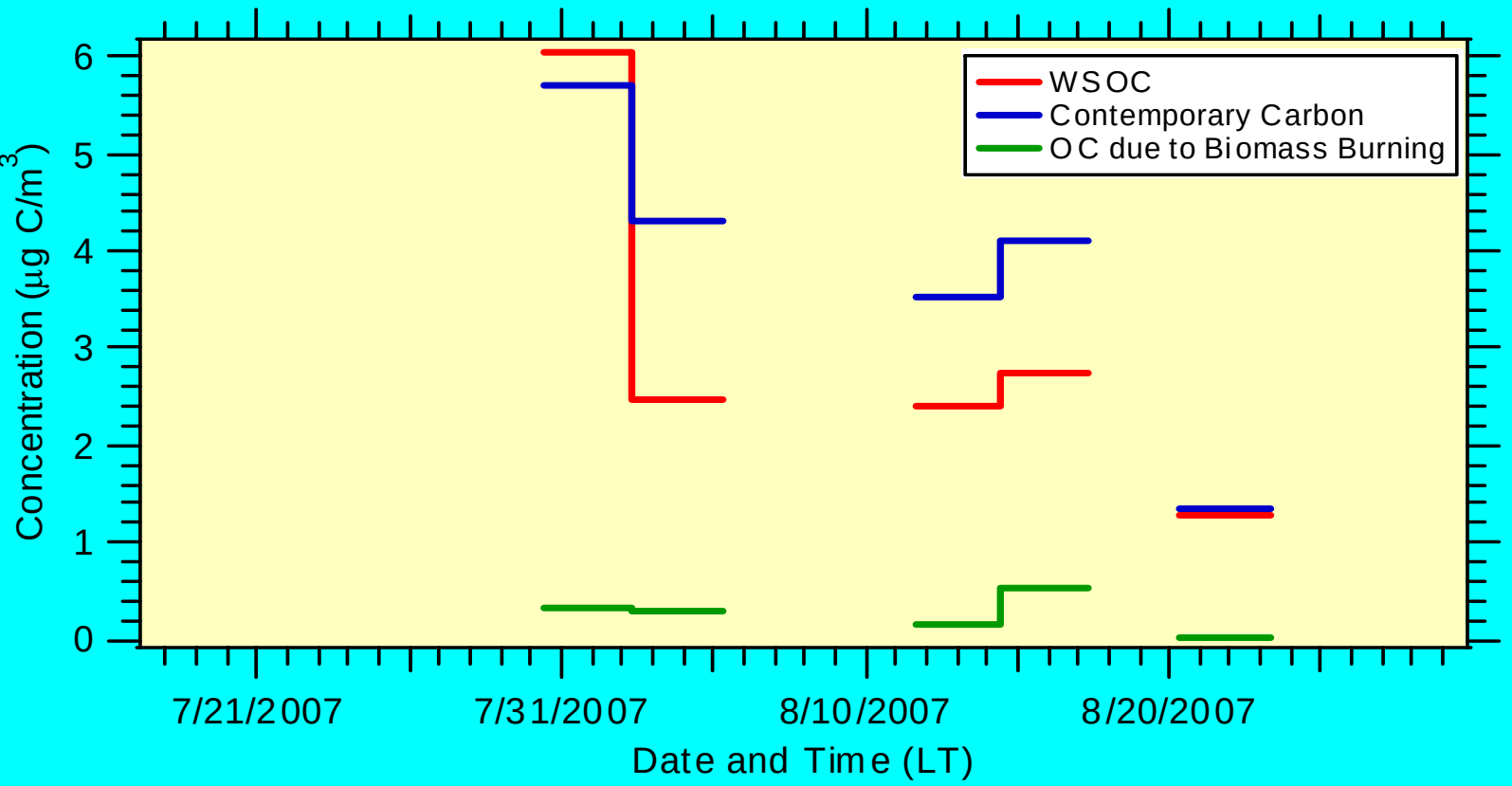
-Contemporary carbon concentration fairly similar at each site

Fraction of Contemporary and Fossil Carbon to the Total Carbon by Site in Winter



-Generally have larger contemporary fraction compared to summer

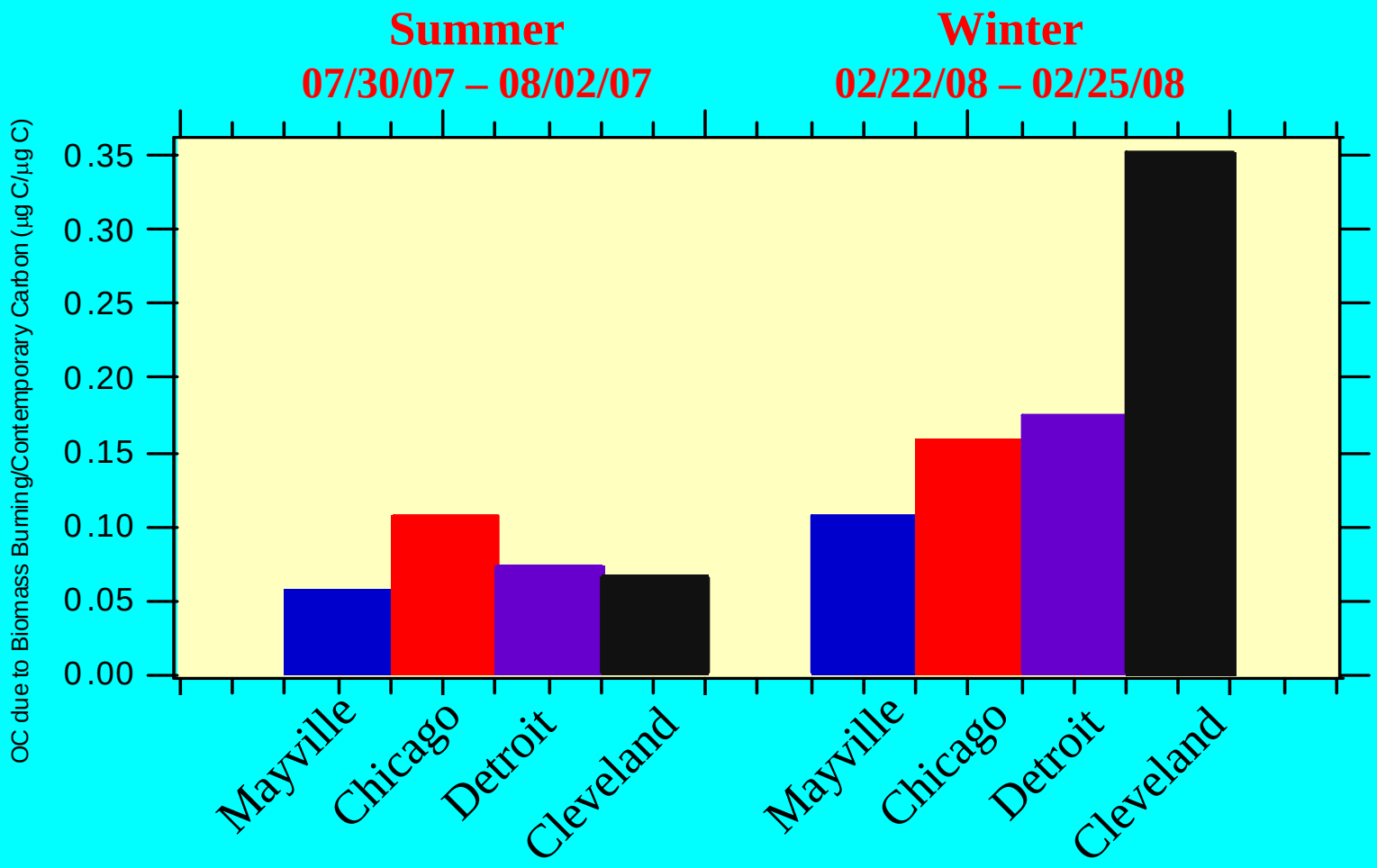
Time Series for Contemporary Carbon, WSOC, and OC due to Biomass Burning for Mayville Summer



-Generally contemporary carbon is larger than WSOC

-OC due to biomass burning small fraction of contemporary carbon

Fraction of Contemporary Carbon due to Biomass Burning for high OC day in Summer and Winter



-Fraction slightly higher in winter

Summary

- Direct alternative method for detection of levoglucosan
  - Summer concentration ranged from 3 to 78 ng/m^3 and winter from 17 to 163 ng/m^3
- Time series:
  - OC generally appears to be regional
  - EC higher in urban areas
  - Levoglucosan generally regional in summer
    - Some local influences observed in winter
  - No real pattern in potassium
    - Occasionally observed more locally influenced potassium

- From contribution of OC due to biomass burning found:
  - Range from ~2 to 28% in the summer and ~10 to 30% in the winter

	Average Summer	Average Winter
BWC	12%	16%
Chicago	7%	16%
Cleveland	6%	18%
Detroit	11%	19%
Mayville	11%	27%

- Radiocarbon data showed fraction of contemporary carbon generally > 50%, being largest at rural sites
  - Contemporary carbon regional and generally larger than WSOC with OC due to biomass burning comprising very small fraction

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