Acknowledgement

S. Gao for helping OC/EC and carbon isotope measurements

L. Graham for Tail-pipe sample collections at ECT

H. Moosmüller, at DRI, US for biomass burning sample collections 2003

D. Ernst, S. Racki, A. Chivulescu for technical support and standards making

M. Ernst, D. Worthy for CO2 measurements

EC, OC & their $\delta^{13}C$ Measurements in Fine PM from Urban, to Rural, to Background Air Over Canada:

Tracking & Understanding Human Impacts on Atmospheric Compositions

L. Huang, W. Zhang, S. Sharma, J. Brook, T. Chan, R. Leaitch, F. Yang, A. M. Macdonald

Climate Chemistry Measurements & Research, Climate Research Division
& Air Quality Research Division
Atmospheric Science & Technology Directorate

Clean Air Regulatory Agenda (CARA) Emission Targets by 2015

by Government of Canada (Benchmark Year: **2006**)

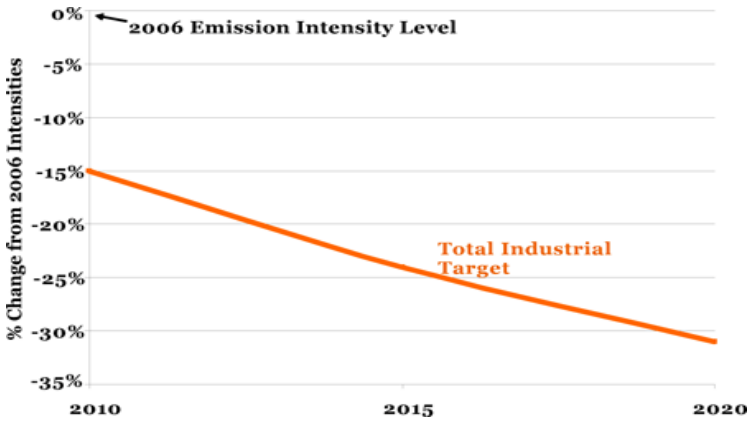
GHGs: - 25 %

PM: - 20 %

Current status (Based on UN data 2004)

Average daily human-induced CO_2 equivalent signal from Great -Toronto-Area (GTA):

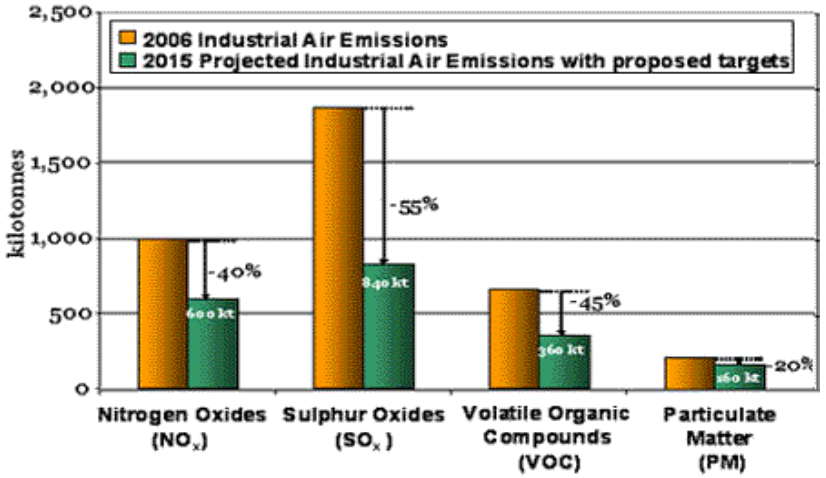
1 ~ 3 ppm



Current status (by direct measurements in 2006)

Average signal of EC or BC in fine PM from GTA:

0.3 ~ 0.7 μgC/m^3

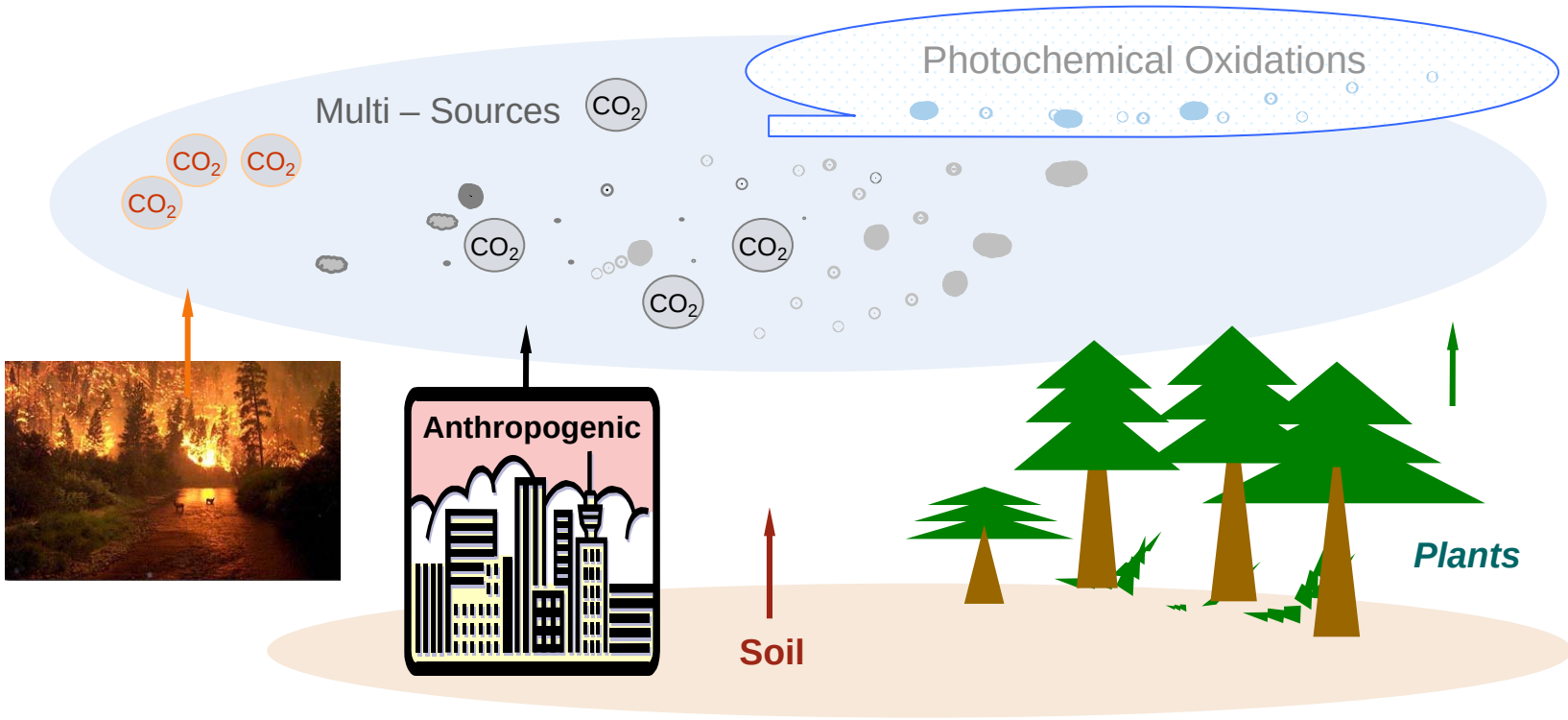


Environment Canada Environnement Canada

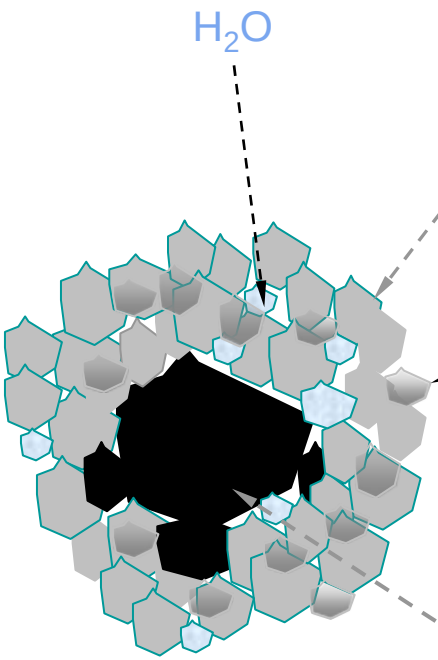
Why EC, OC in Carbonaceous aerosols ?

- **Regional Air Quality** (health, visibility & environment issues)
- **Global Climate Change** (direct and indirect effect)
- **Bridging air quality & carbon cycle research on regional scales**

- Distribution of emission sources (primary), dispersion & secondary formation processes are not well understood



Schematic of Carbon Components Measured by a Thermal Evolution Method (Total_900_EnCan) & Implications



Organic Carbon (OC)

- Condensed outside of the core as the coating;
- Could be primary or secondary aerosols;
- **Thermally released at relatively low temperature** (550°C);
- The isotopic composition ($\delta^{13}C_{OC}$) reflects mainly process information.

Pyrolysis Organic Carbon (POC)

- oxygenated organic carbon
- charred OC during analysis
- **Thermally released at high temperature** (870°C).

Carbonate Carbon (CC)

- Usually from soil dust /cement; or sea salt
- **Thermally decomposed at high temperature** (870°C).

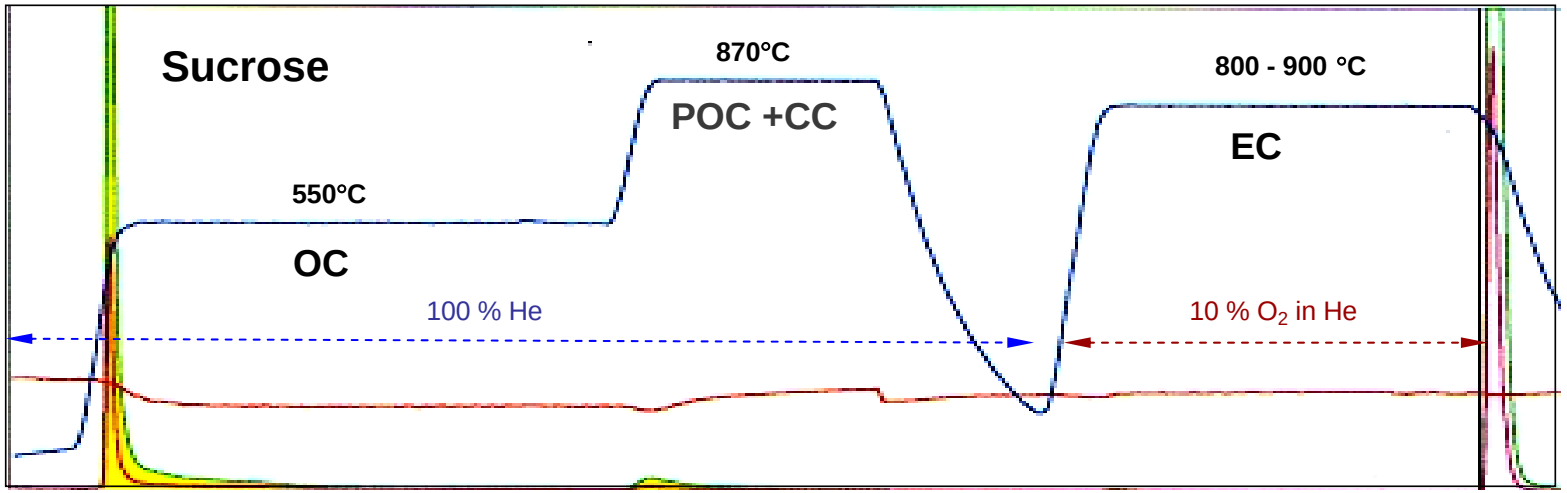
Black Carbon (BC) **or Elemental Carbon** (EC)

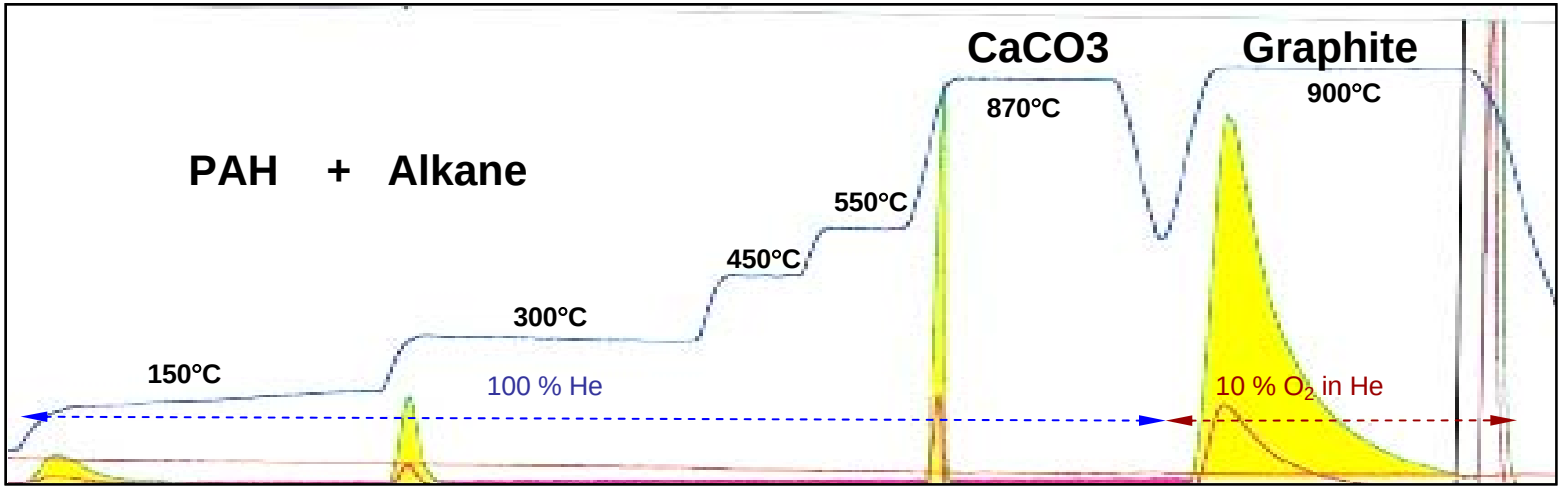
- Located at the core;
- as primary aerosols from fossil fuel combustions or biomass burning;
- **Oxidized at relatively high temperature** (900°C);
- The isotopic composition ($\delta^{13}C_{EC}$) reflects mainly source information.

OC/EC

POC/OC

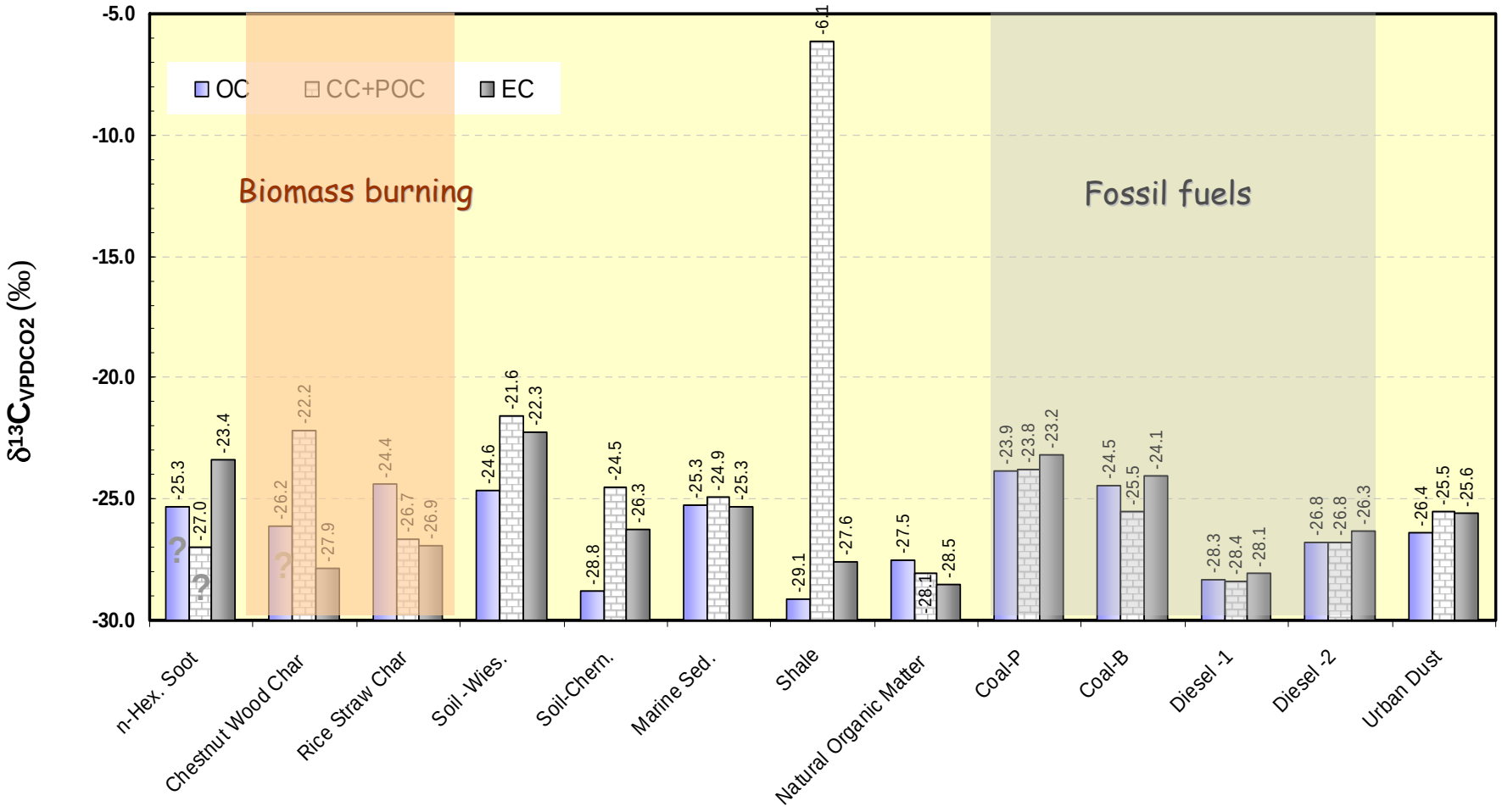
OCs, CC and EC Separations via Standards





Isotopic Profiles of EC & OC in BC Reference Materials

(Potential sources for carbonaceous PM)



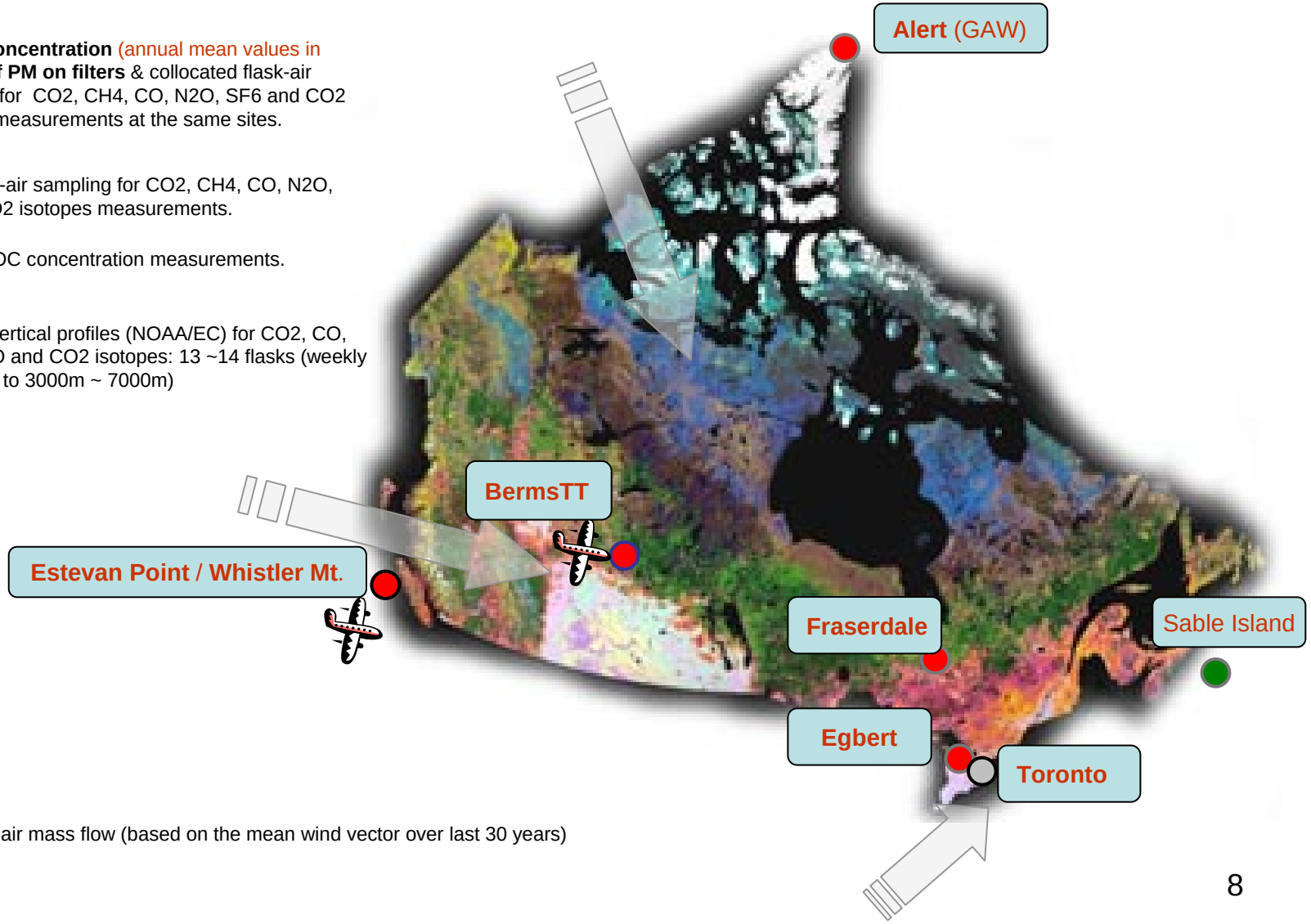
EnCan GHGs/Aerosol Observation Network

EC/OC concentration (annual mean values in μg/m^3) **of PM on filters** & collocated flask-air sampling for CO2, CH4, CO, N2O, SF6 and CO2 isotopes measurements at the same sites.

Only flask-air sampling for CO2, CH4, CO, N2O, SF6 & CO2 isotopes measurements.

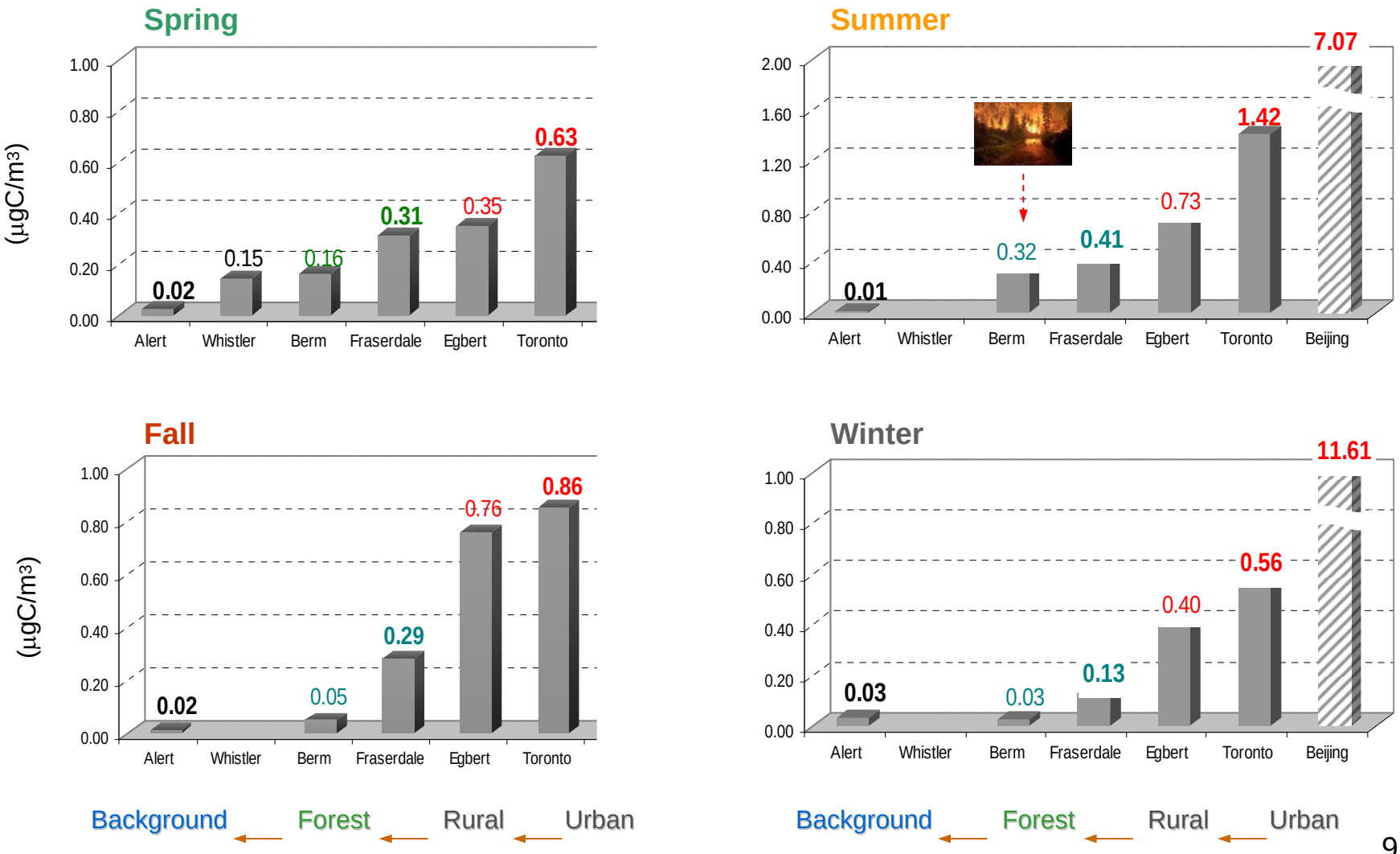
Only EC/OC concentration measurements.

Regular vertical profiles (NOAA/EC) for CO2, CO, CH4, N2O and CO2 isotopes: 13 ~14 flasks (weekly from 20m to 3000m ~ 7000m)

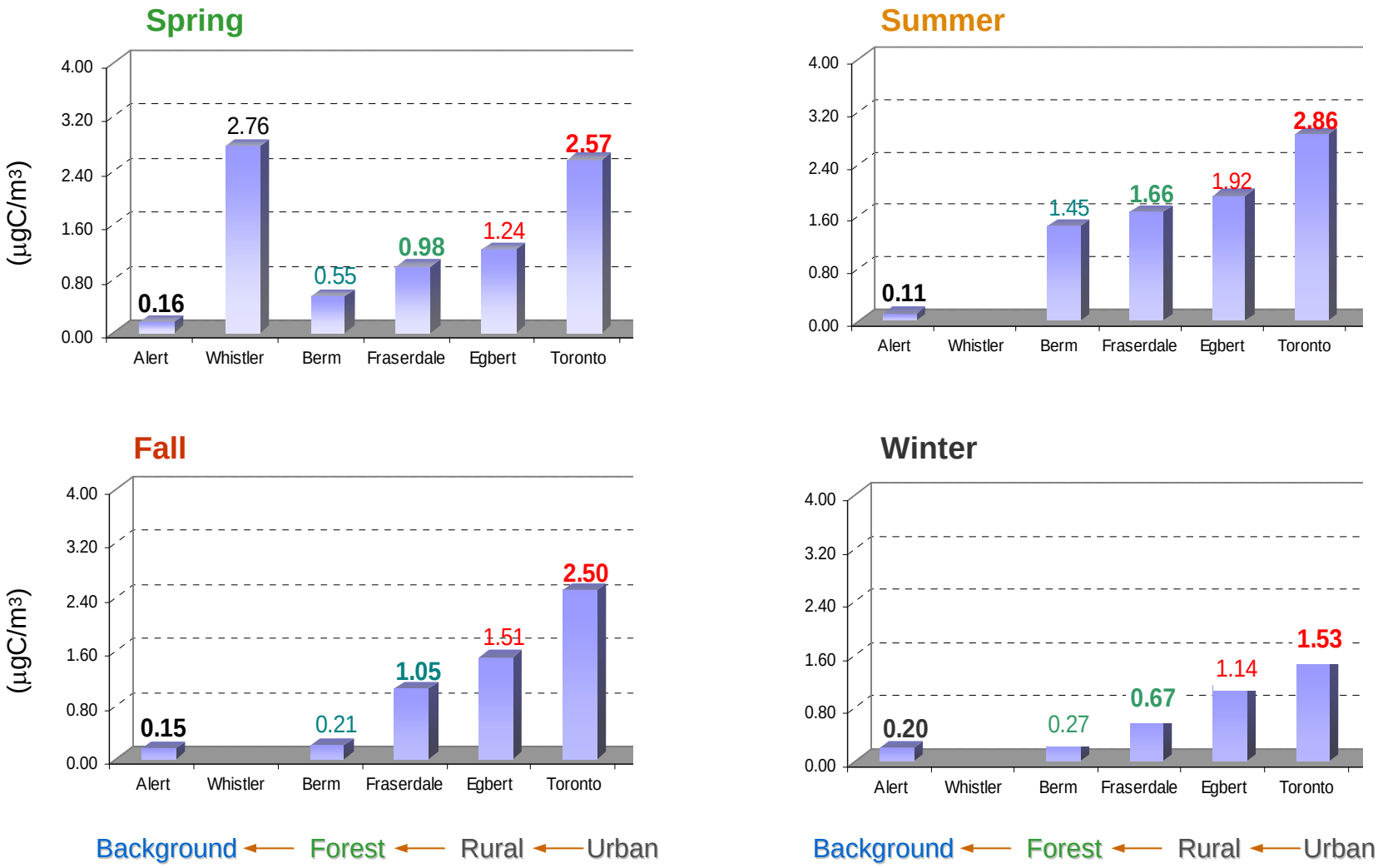


Major air mass flow (based on the mean wind vector over last 30 years)

Seasonal Variation in Spatial Gradients of EC Contents over Canada

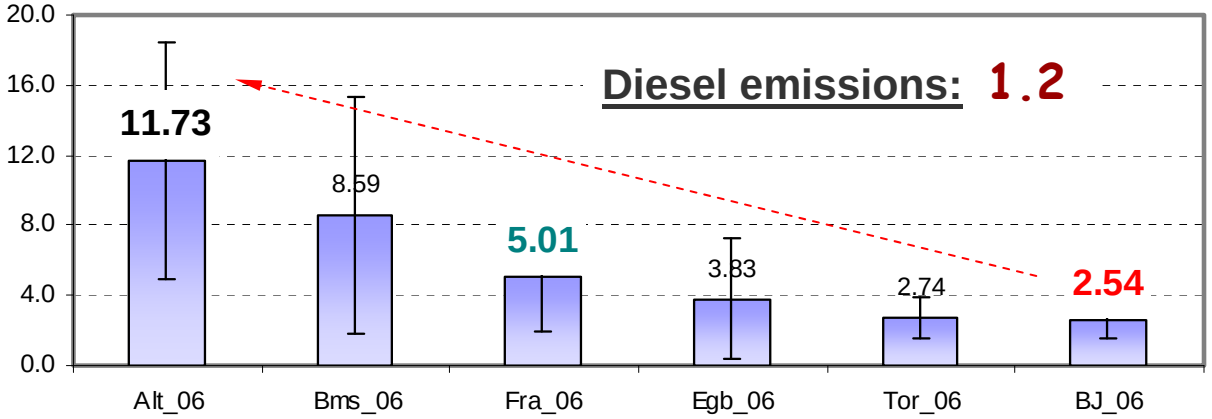


Seasonal Variation in Spatial Gradients of OC Contents over Canada
(2006-2007)

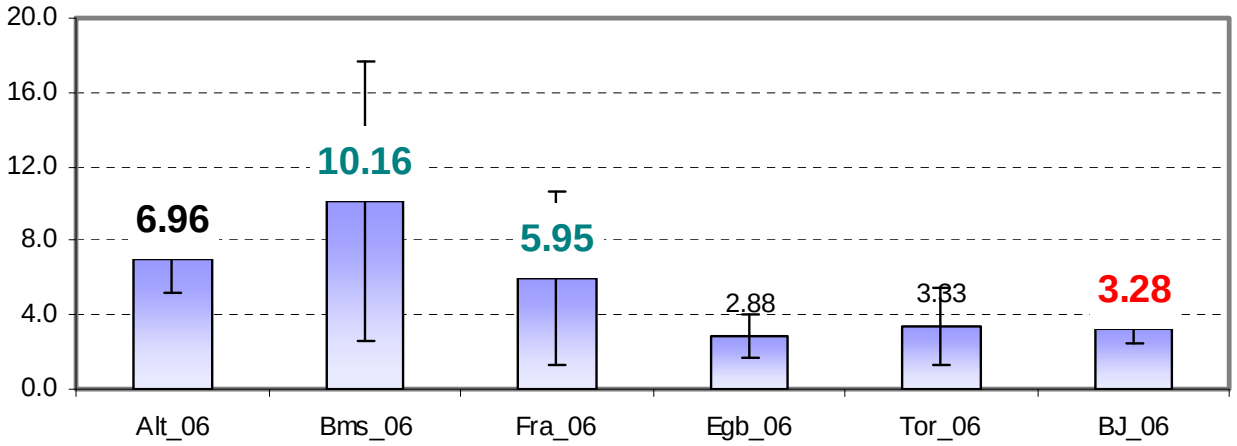


What Could These OC/EC Ratios Tell Us?

Spring-Summer

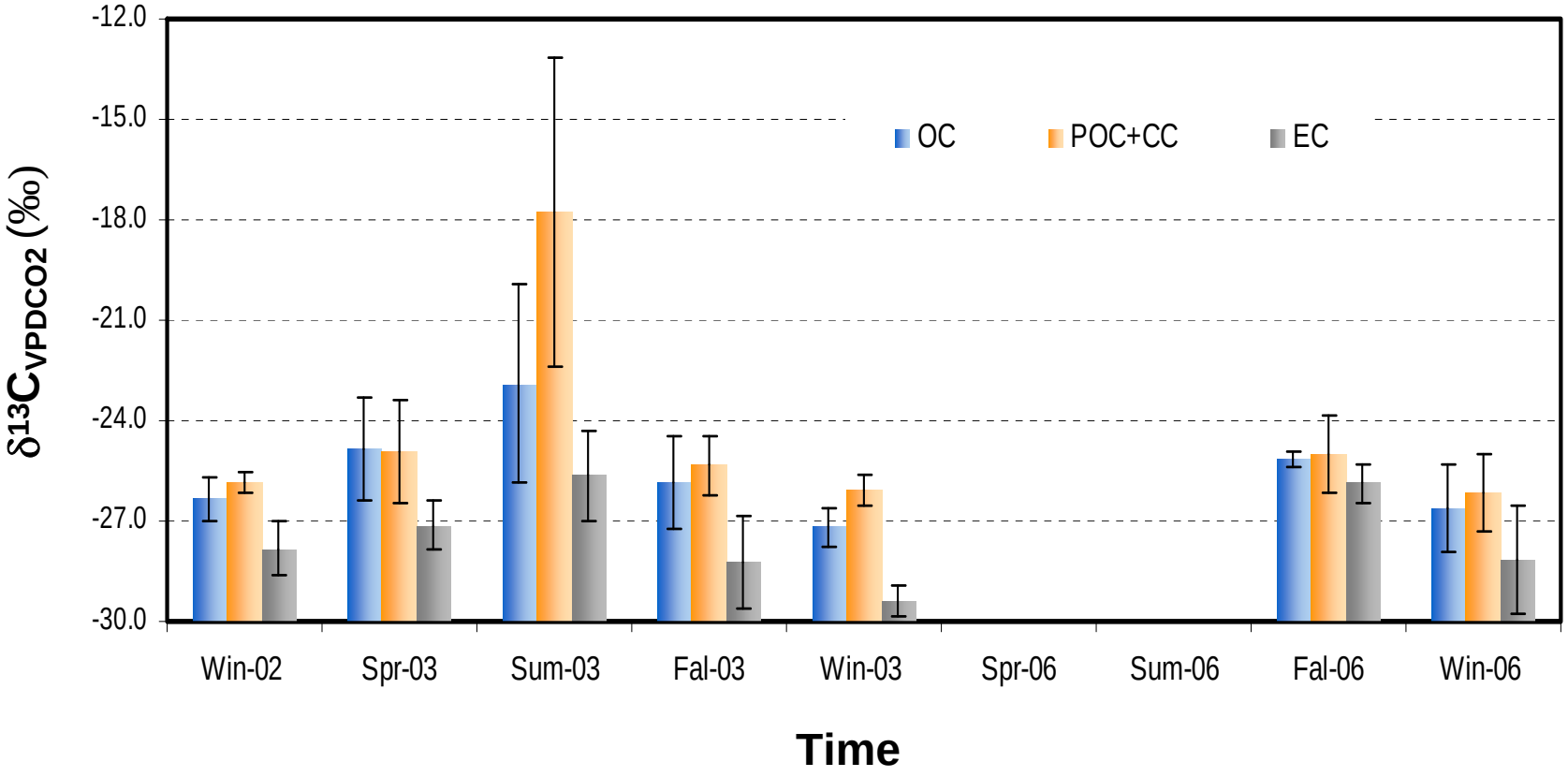


Fall - Winter



Background ← Forest ← Rural ← Urban

OC-EC Isotopic Compositions in fine PM at Alert
(2002-06)



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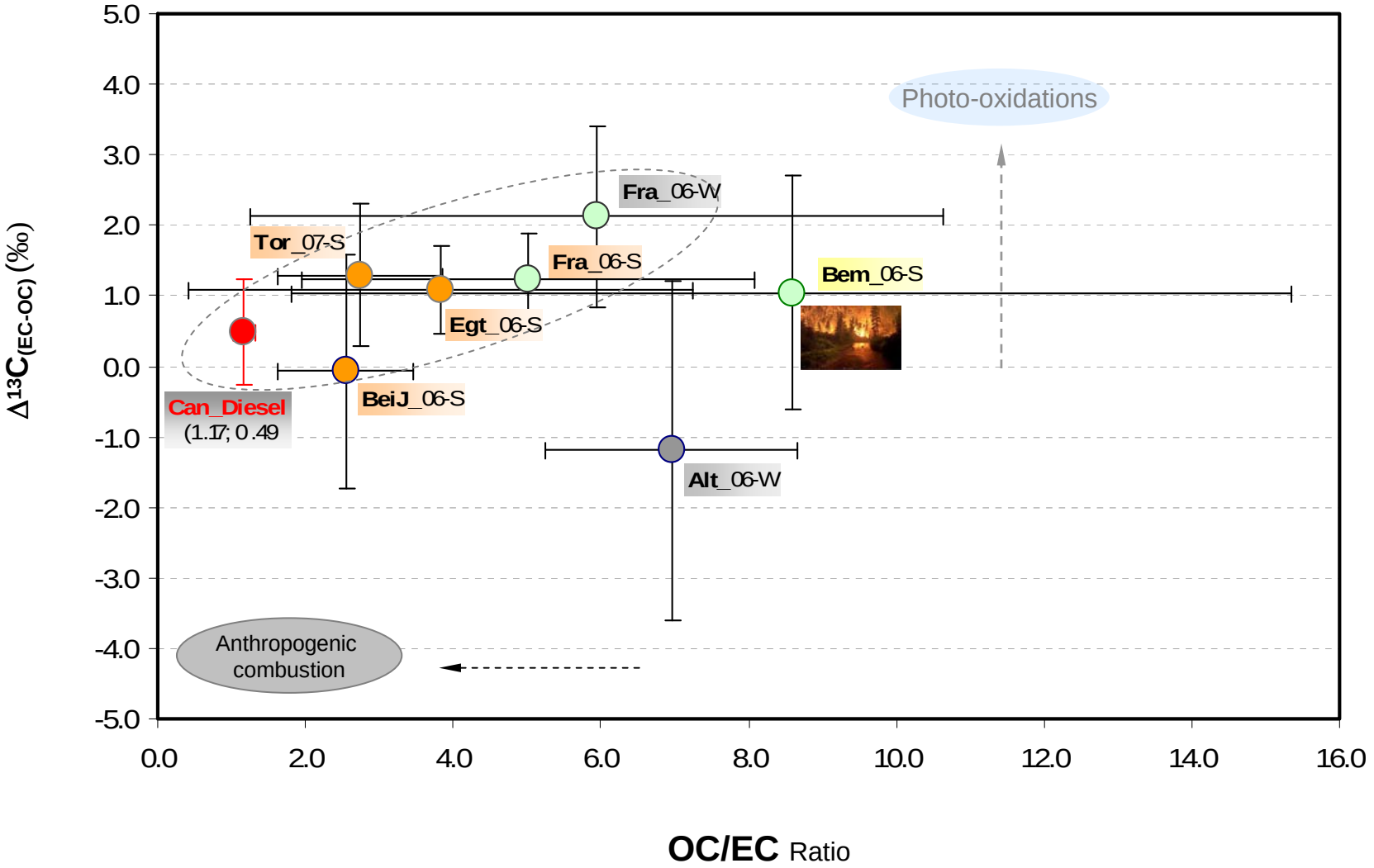
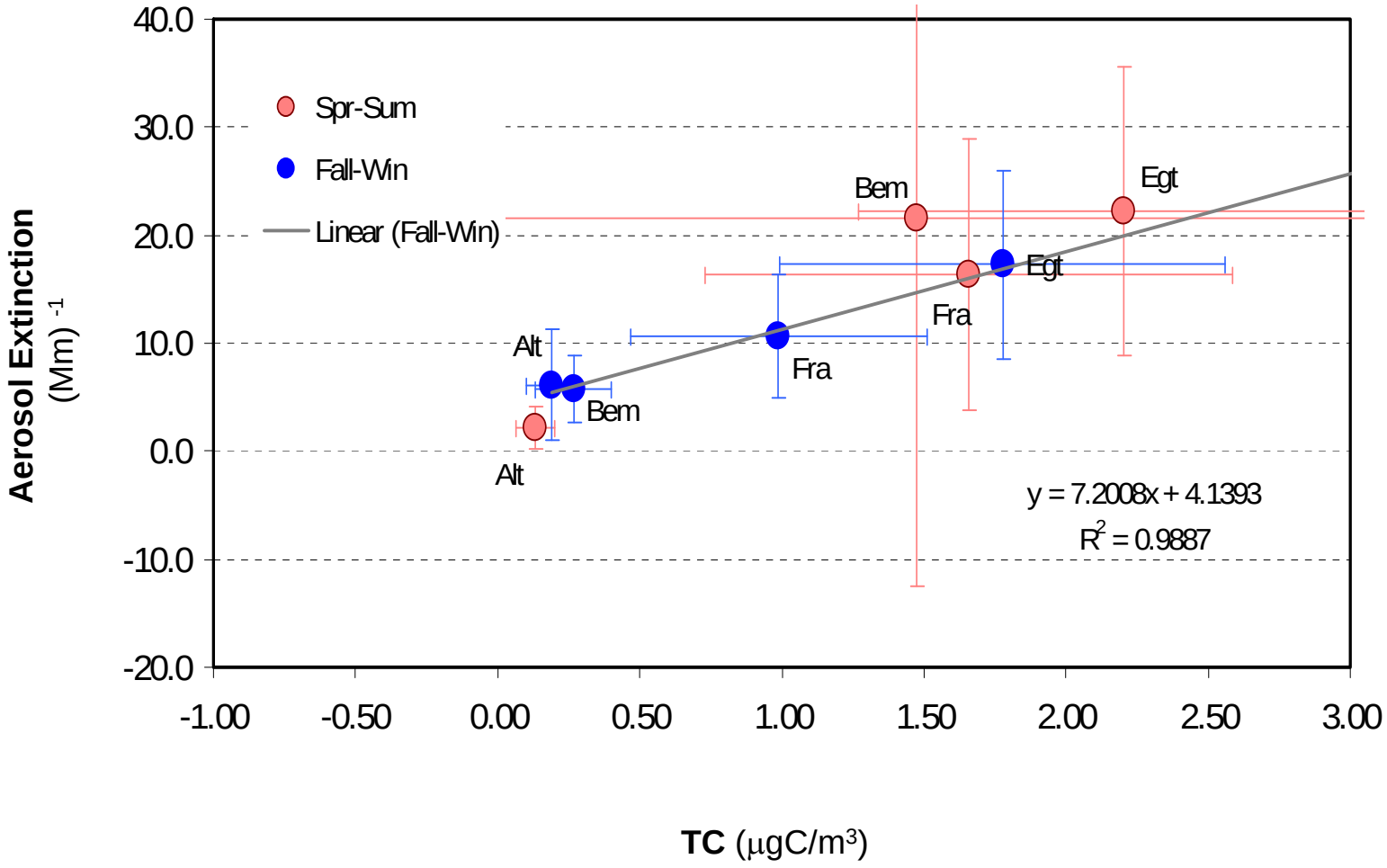
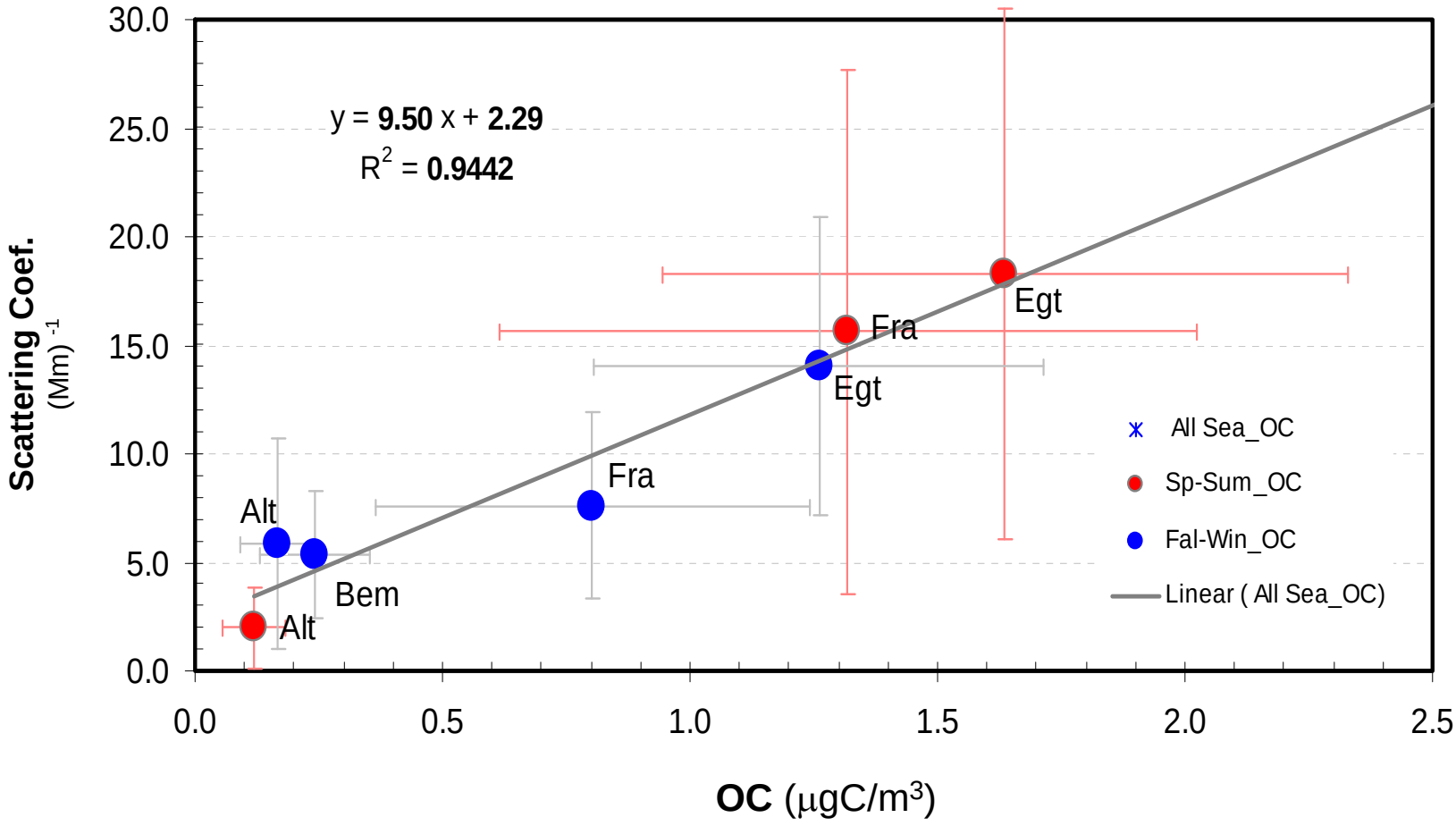
$\Delta^{13}C_{(EC-OC)}$ vs. OC/EC Ratios in fine PM from Urban, to Rural, to Background air: Anthropogenic/Photo-oxidations ?



Aerosol Extinction: Abs + Scat vs. Carbon Content in fine PM

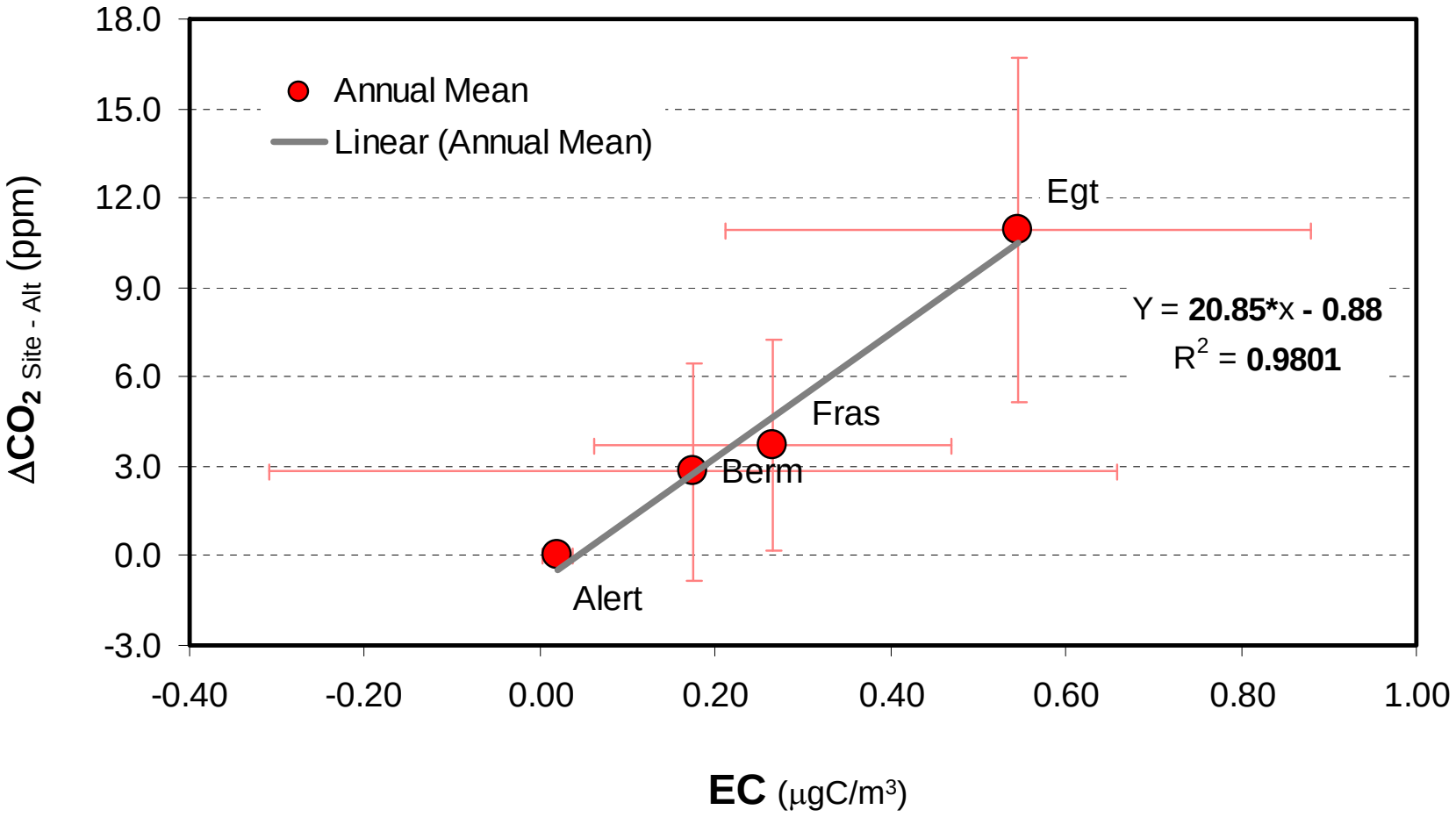


Aerosol Scattering & Organic Carbon Content in fine PM



Human Induced CO_2 ?

$\Delta CO_2 = CO_2$ (site) – CO_2 (Alert)



Conclusions ?

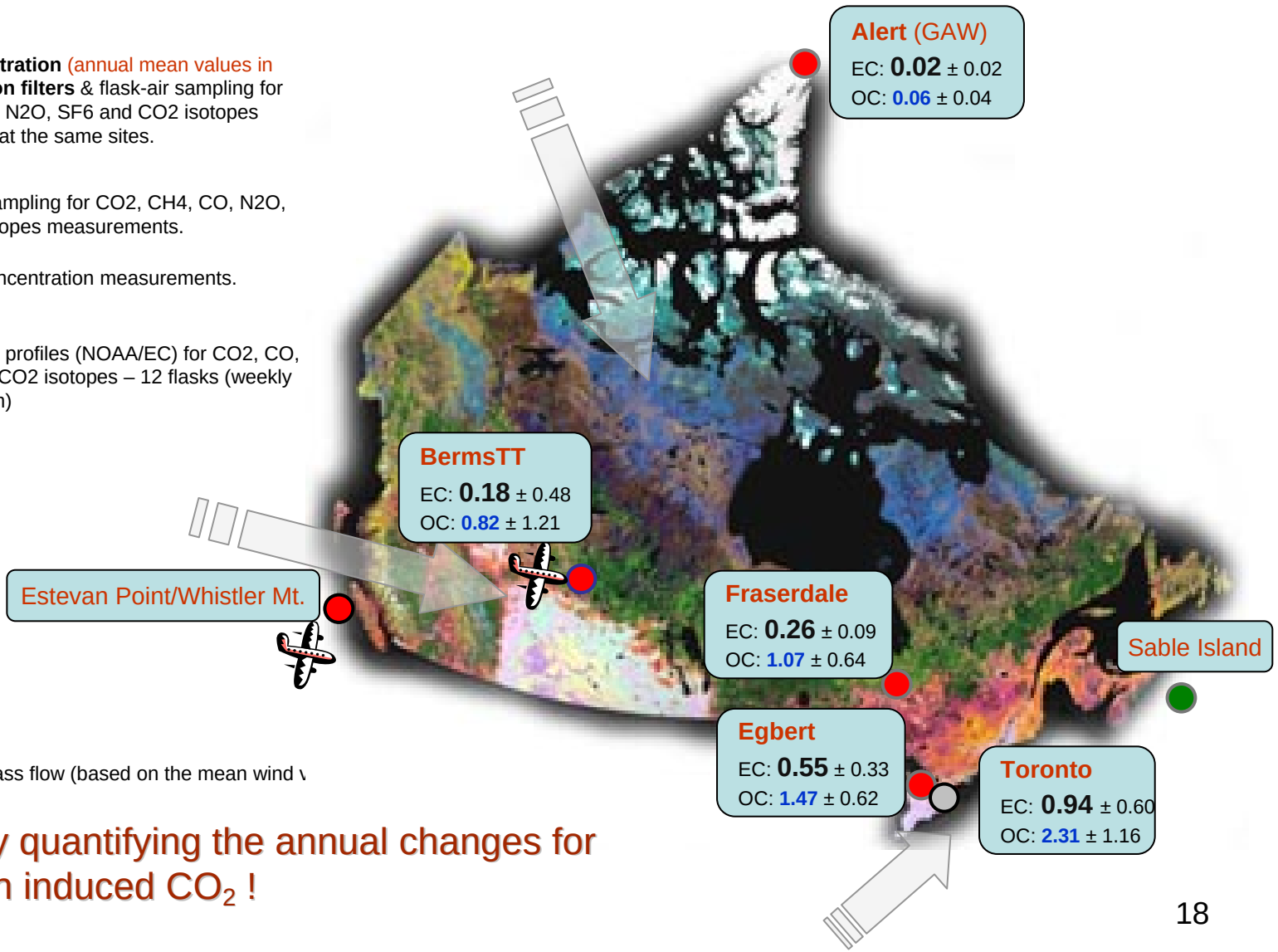
It is possible to track human Induced signals in atmospheric compositions via an Integrated Approach !

EC/OC concentration (annual mean values in μg/m^3) **of PM on filters** & flask-air sampling for CO2, CH4, CO, N2O, SF6 and CO2 isotopes measurements at the same sites.

Only flask-air sampling for CO2, CH4, CO, N2O, SF6 & CO2 isotopes measurements.

Only EC/OC concentration measurements.

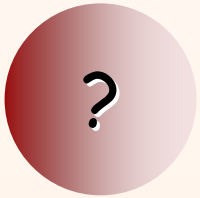
Regular vertical profiles (NOAA/EC) for CO2, CO, CH4, N2O and CO2 isotopes – 12 flasks (weekly from 0.5 to 7 km)



Major air mass flow (based on the mean wind v

Potentially quantifying the annual changes for the human induced CO_2 !

Thanks !

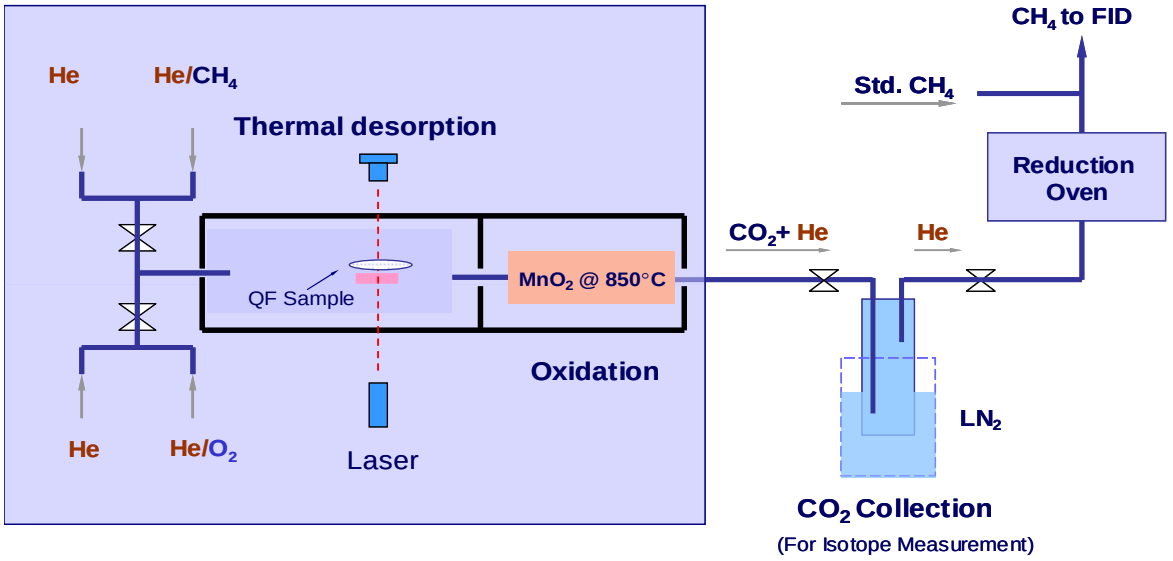


Schematic of EC, OC & their Carbon Isotope Measurements

OC, EC conc. Analysis

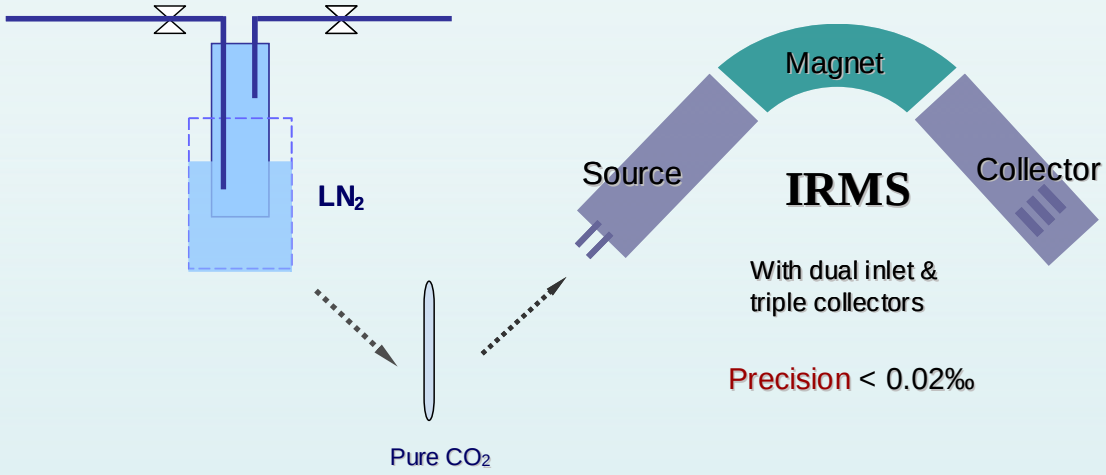
& CO_2 collection

via a TOT analyzer by Sunset Lab



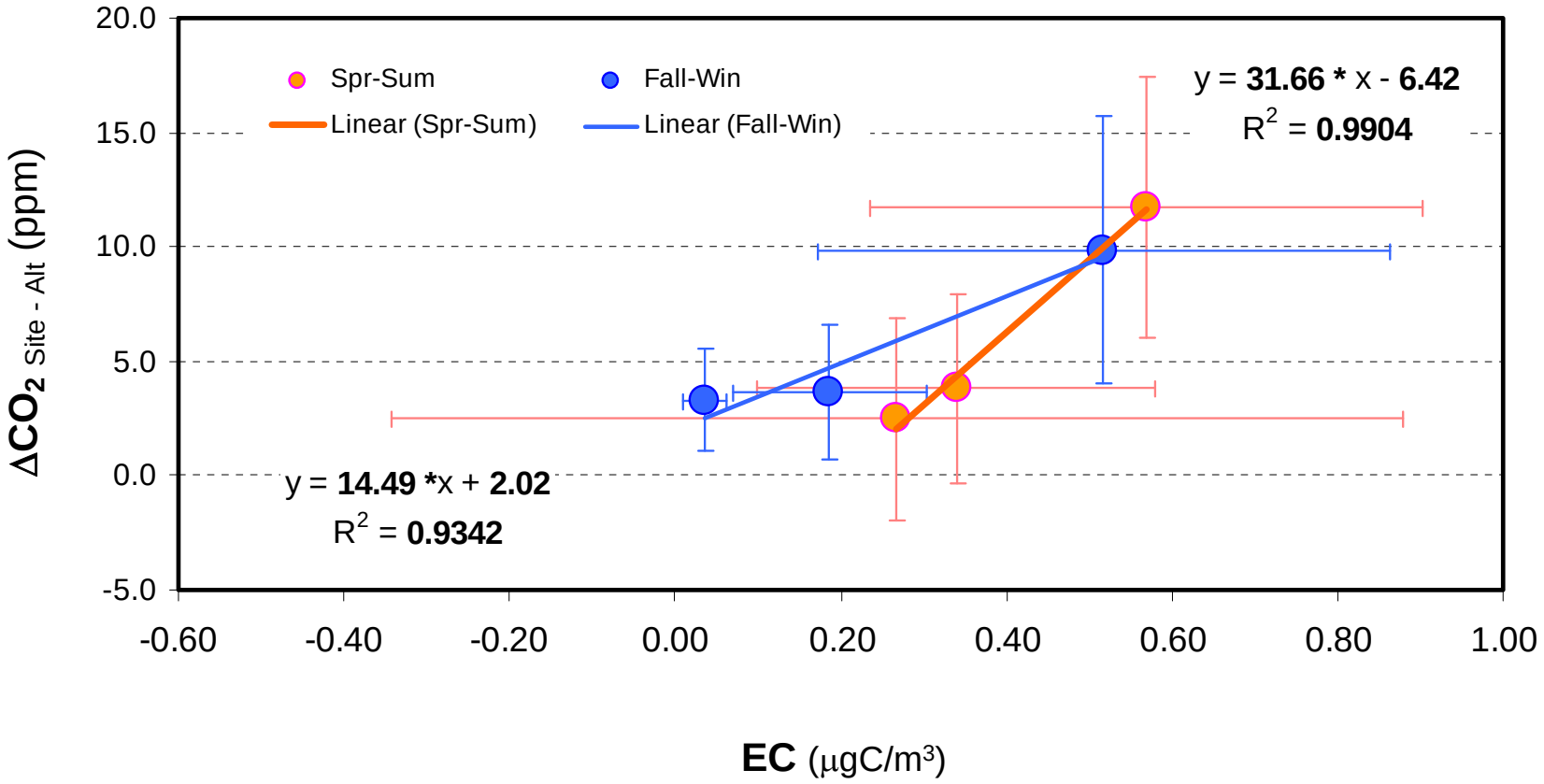
$\delta^{13}C$ analysis
using cold finger mode

Of an IRMS (IsoPrime)



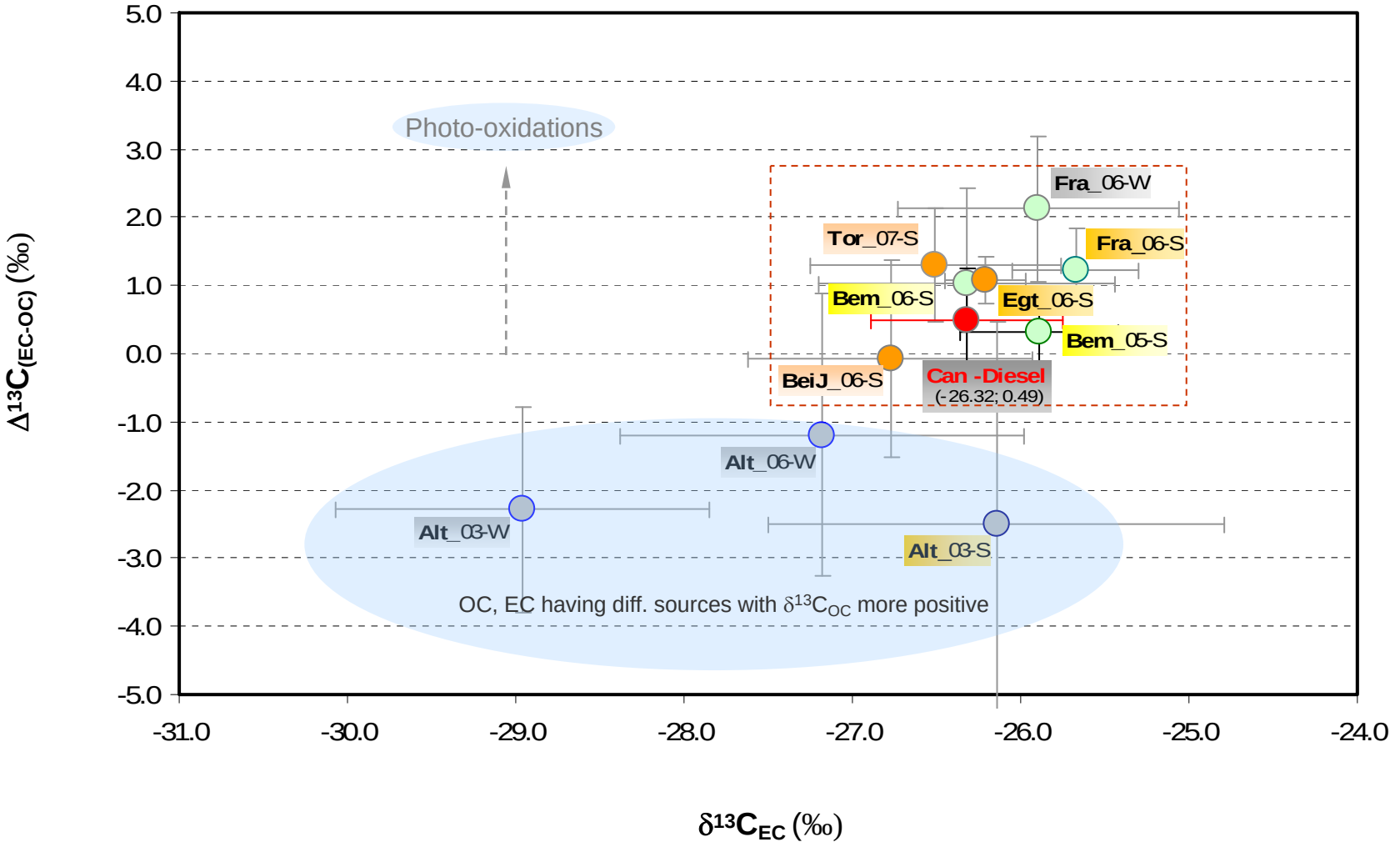
Overall accuracy and precision of the method: **0.3** permil

Seasonal Variations of Human Induced CO_2 ?



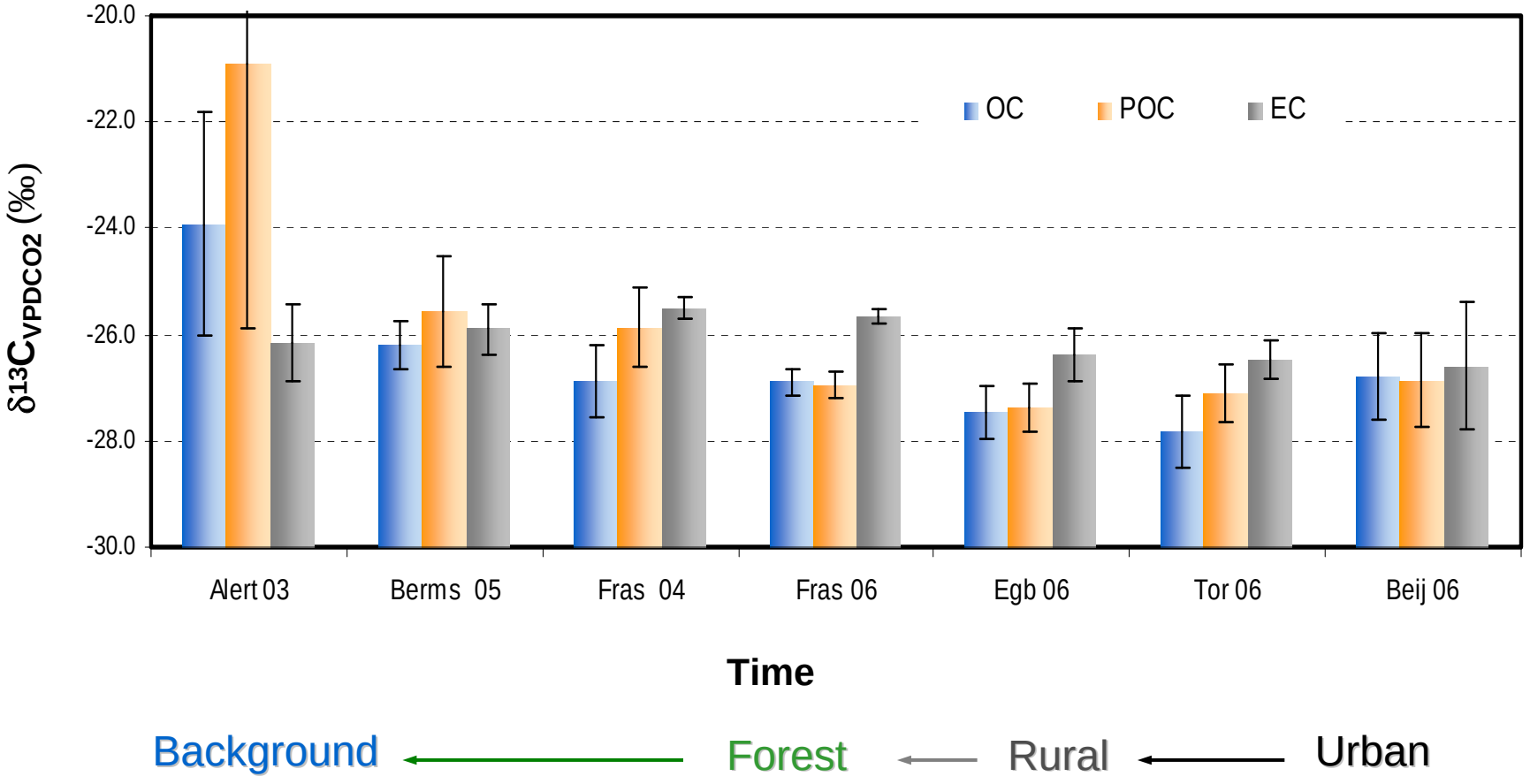
Carbon Isotopic Compositions of EC/OC in fine PM

from Urban, to Rural, to Background air



OC-EC Isotopic Compositions in fine PM over Canada

All sites (Apr – Oct)

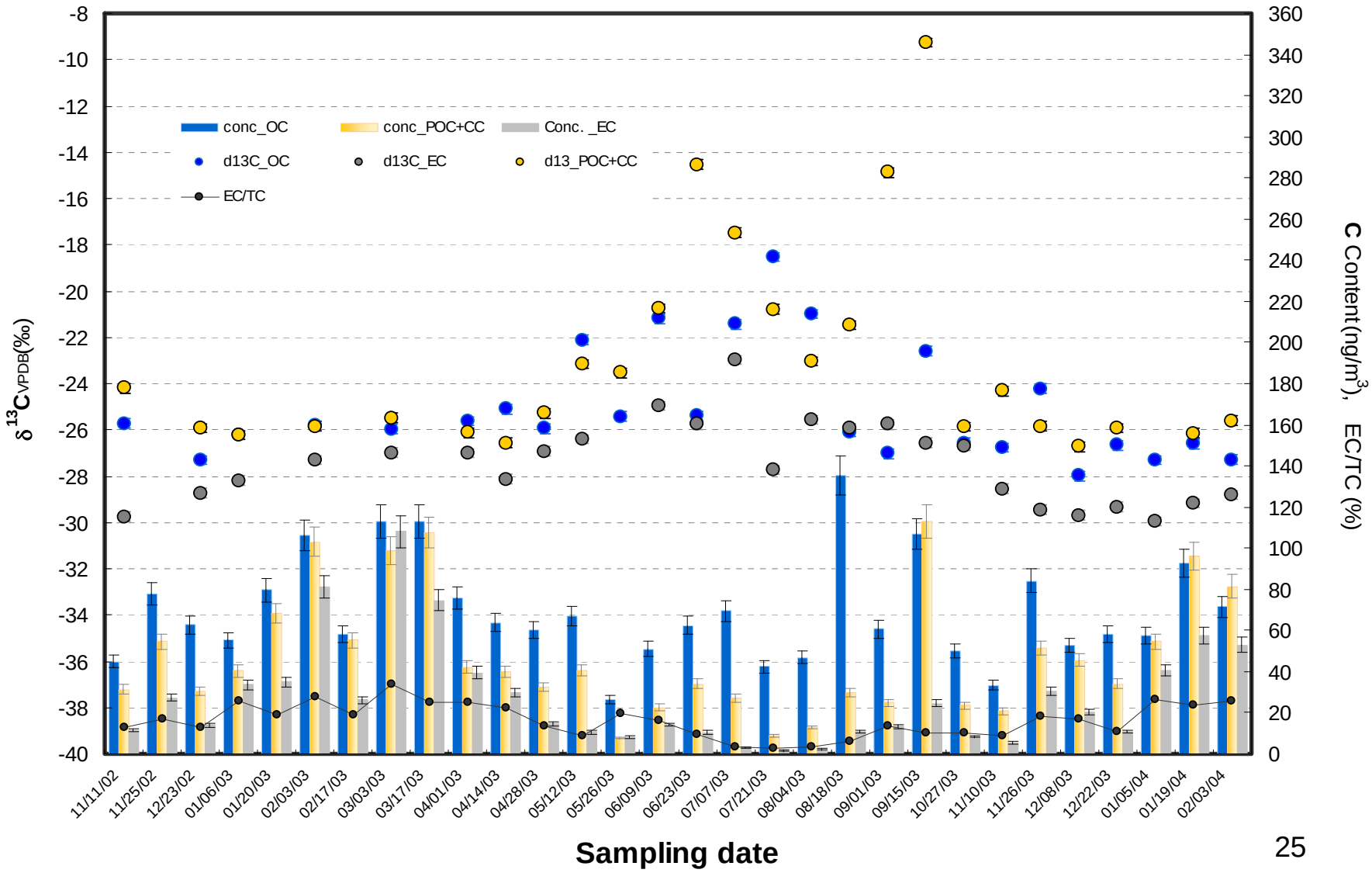


Outline

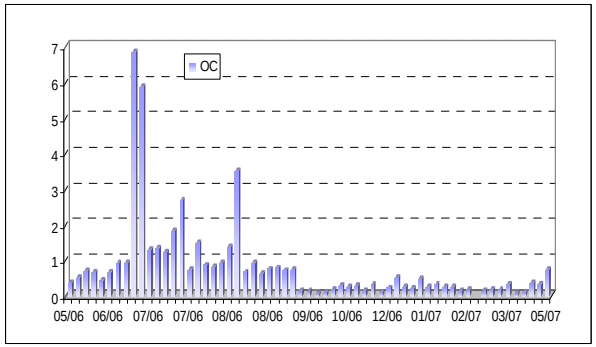
- **Why** (background information)?
- **How** did we conduct the research ?
- **What** have been found and what do the results mean ?

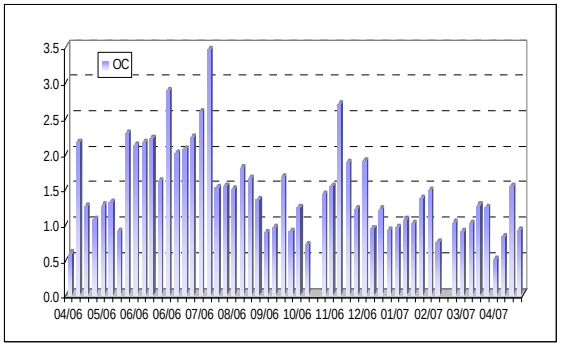
EC/OC & Their Carbon Isotopic Compositions in fine PM

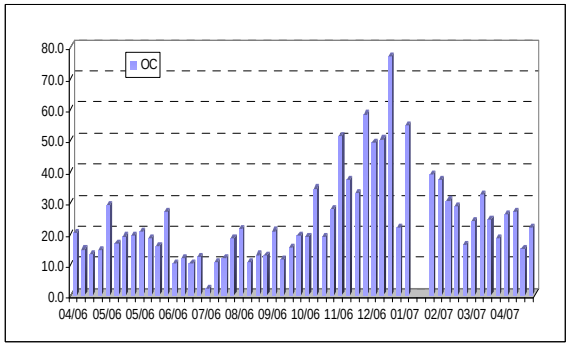
Alert (Nov. 2002-Feb. 2004)

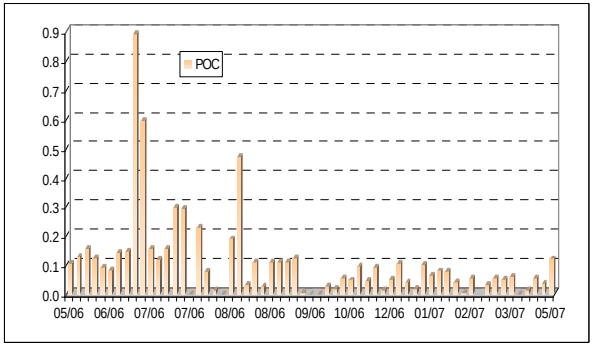


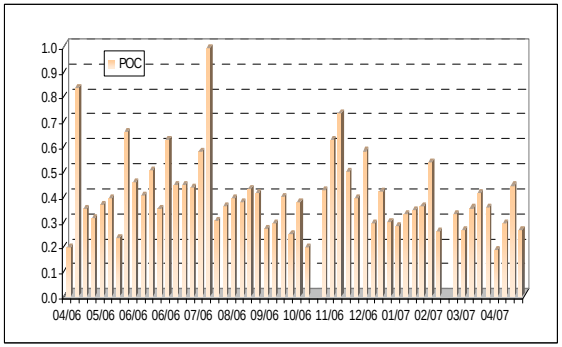
OC, EC Measurements in fine PM (May 2006- Apr 07)

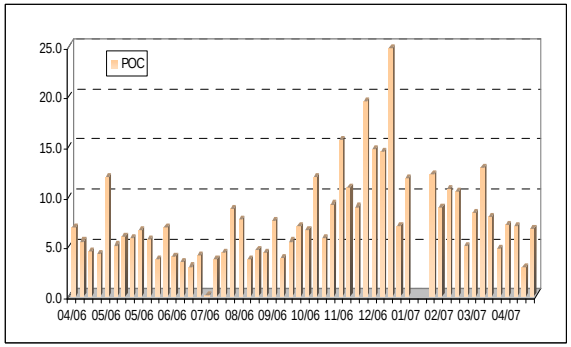


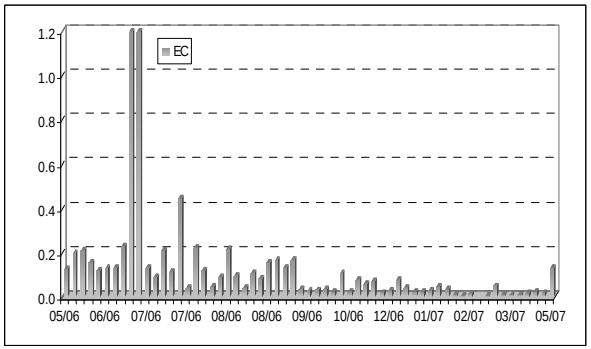


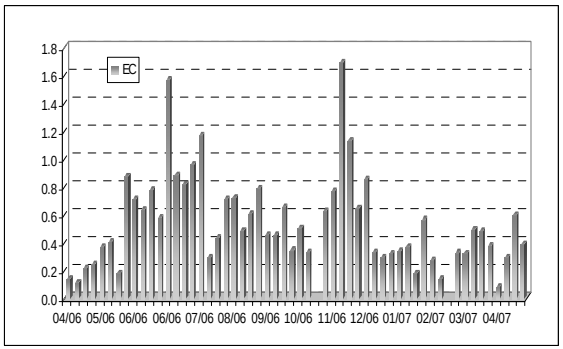


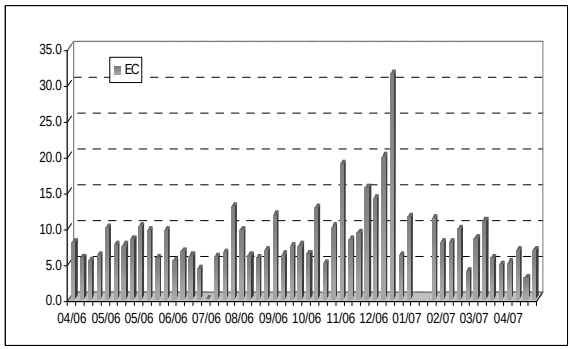










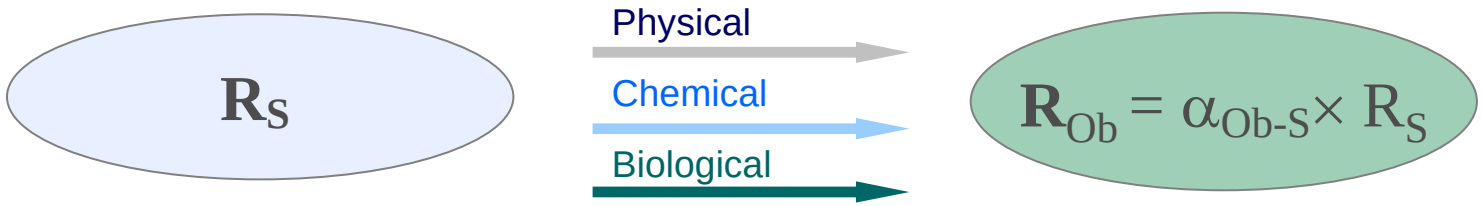


Berms

Egbert

Beijing

Tracing Source and Process via Stable Isotopes



Source **Processes** **Observations**

$$\alpha_{Ob-S} = R_{Ob}/R_S$$

Expression

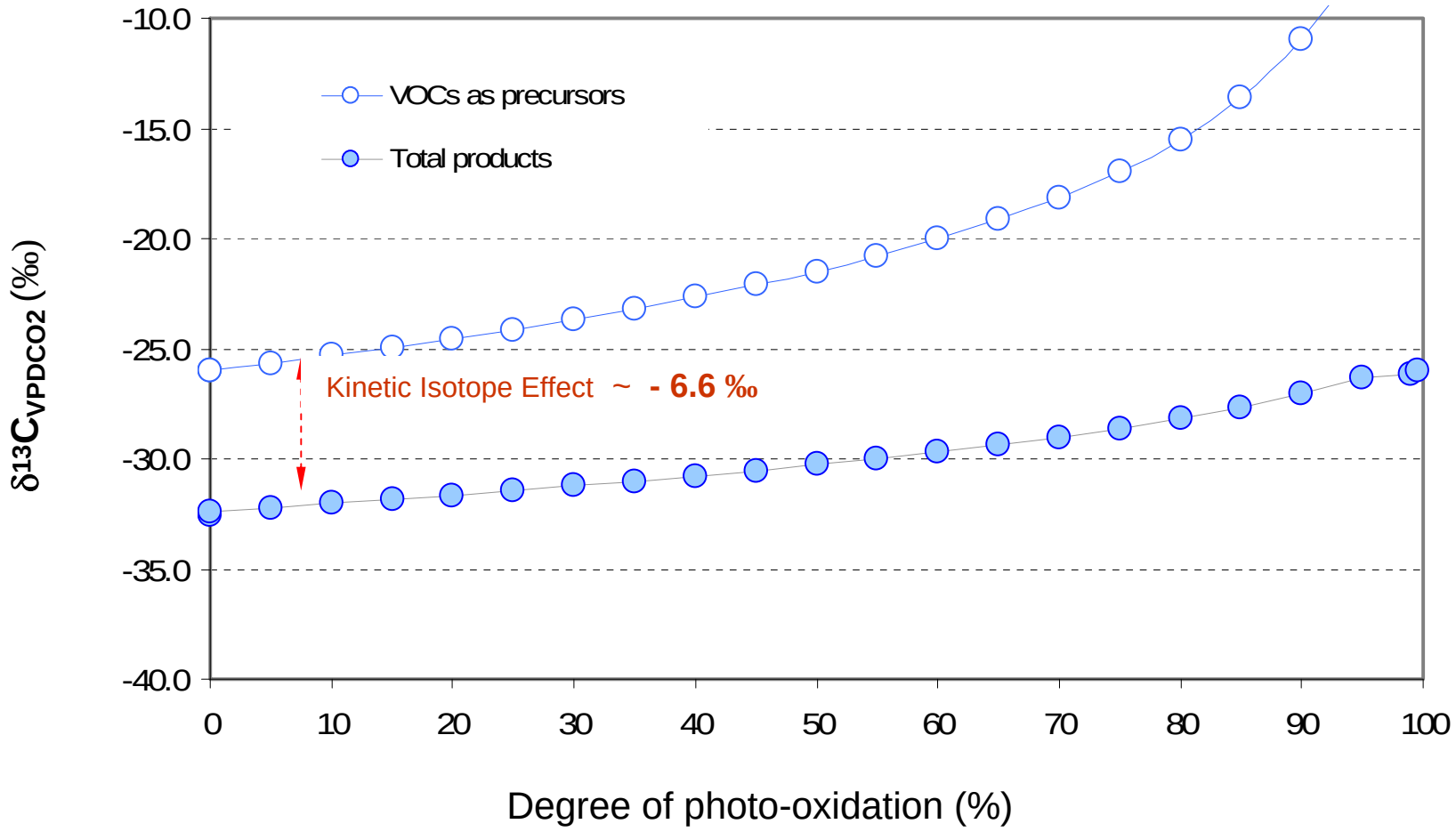
The Primary Scale: **VPDB**

$\delta^{13}C = [(R_{sam}/R_{Std}) - 1]*10^3$, **$R = {}^{13}C/{}^{12}C$**

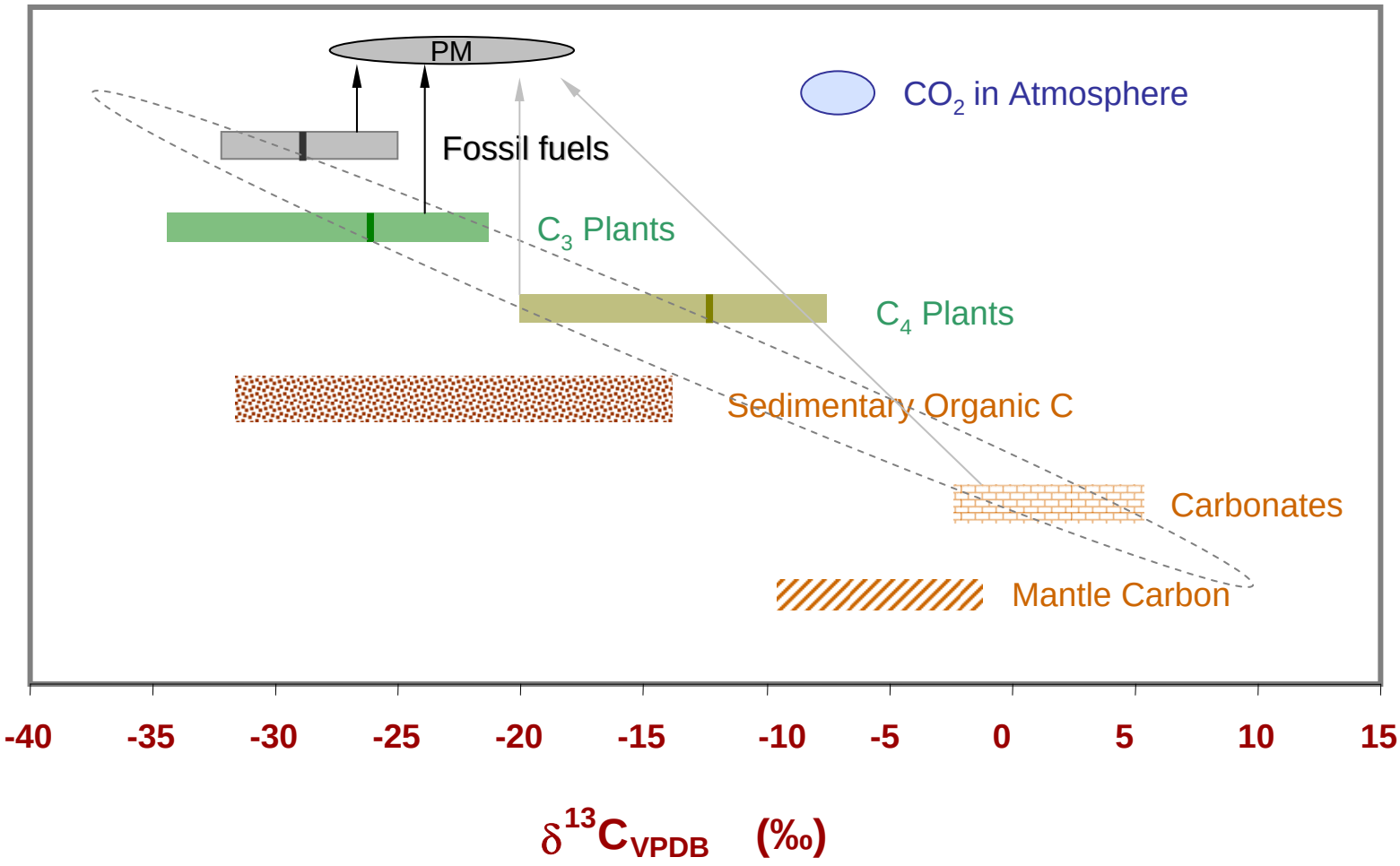
$R\ ({}^{13}C/{}^{12}C)$	$\delta^{13}C$	
0.0112934	**5**	***Carbonate***
0.0112372	**0**	***VPDB***
0.0111473	**- 8**	***ATMCO2***
0.0110799	**- 12**	***C4***
0.0109226	**- 28**	***C3***

Example of Carbon Isotopic Fractionations

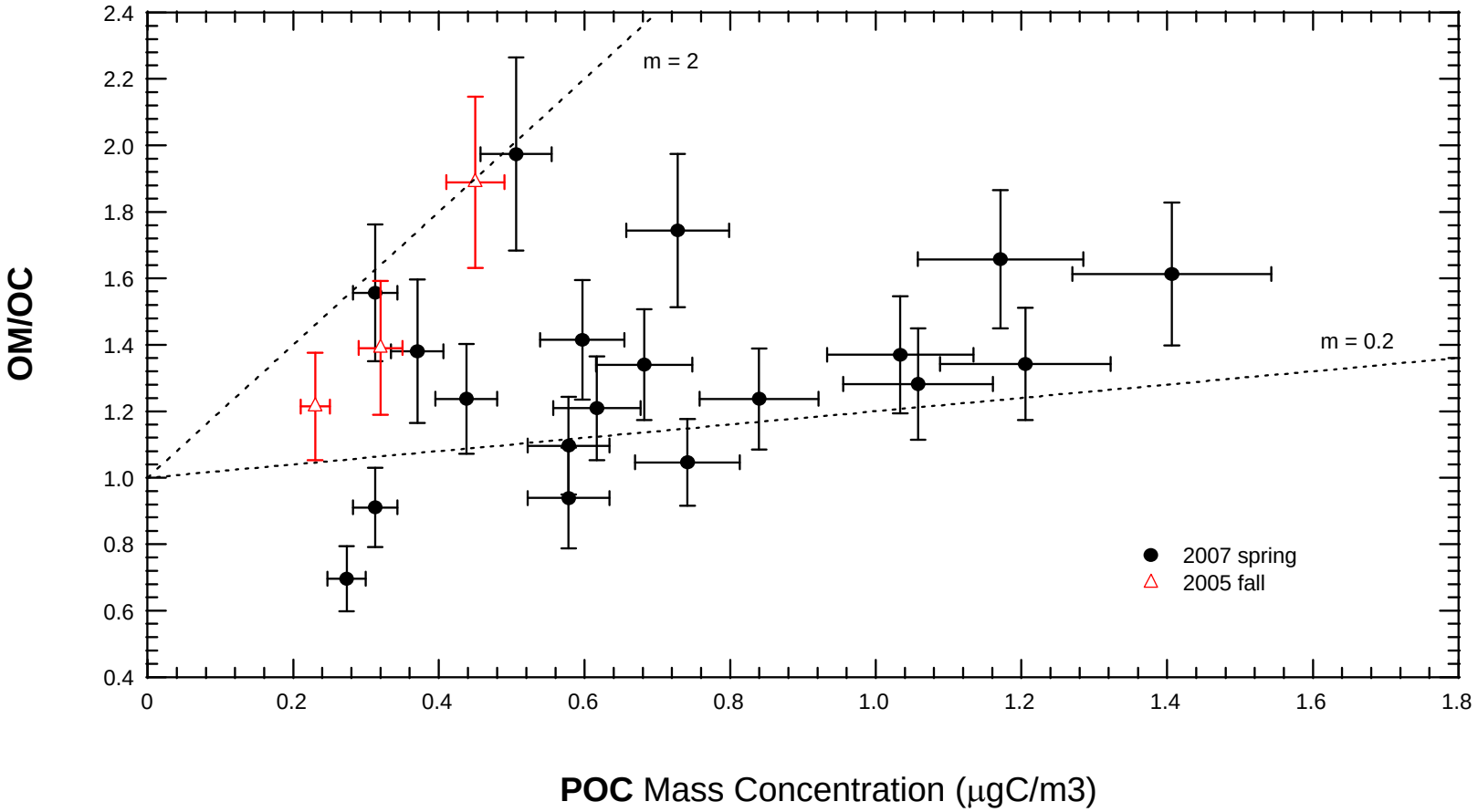
During VOC Reactions with OH^-



$\delta^{13}C$ values of Important Reservoirs/Sources in the Earth



Comparison Between OM/OC and POC from two intensive study at Rural site (Egbert, Ontario)

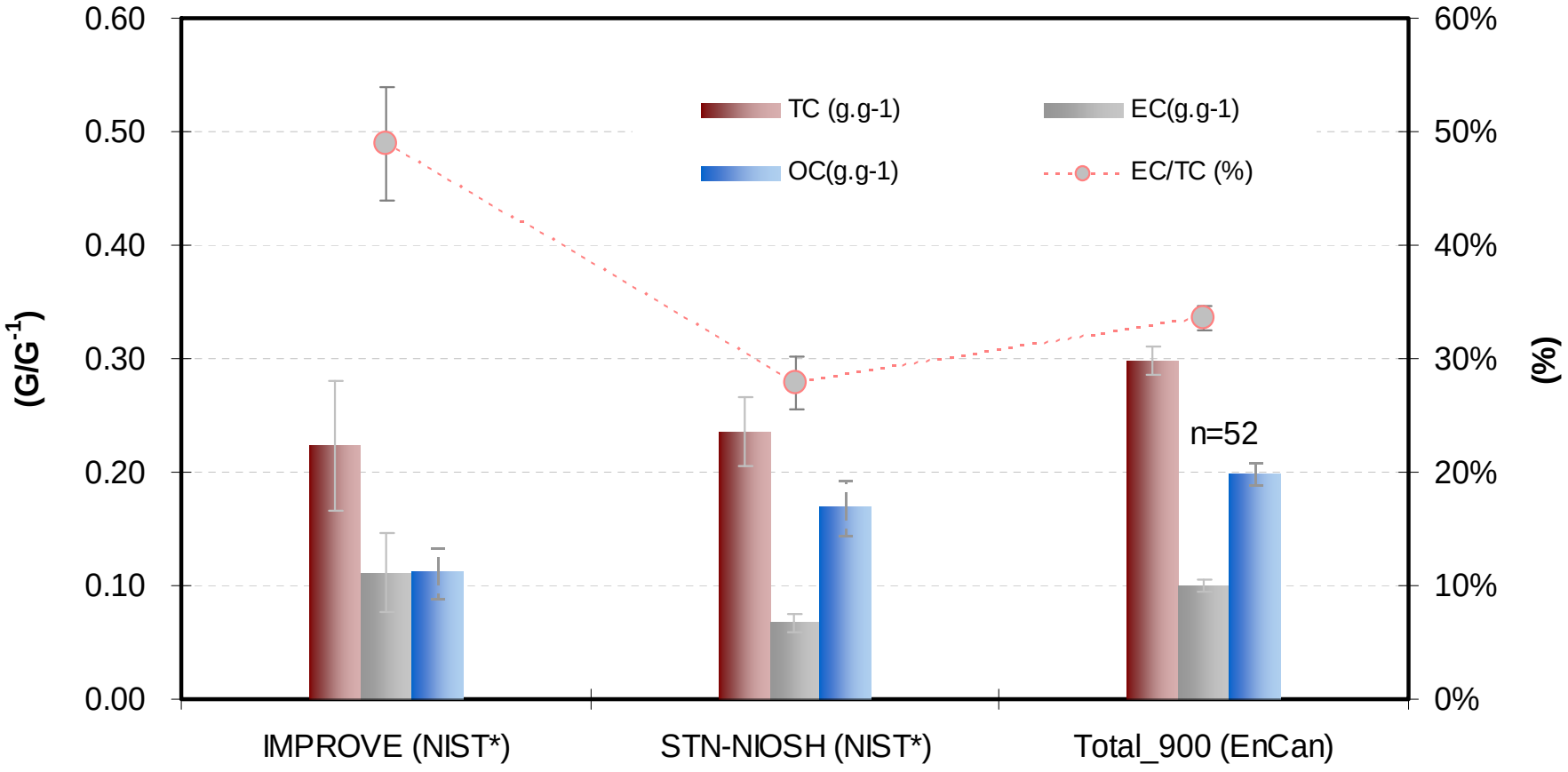


*POC is proportional to **oxygenated** organic carbon !*

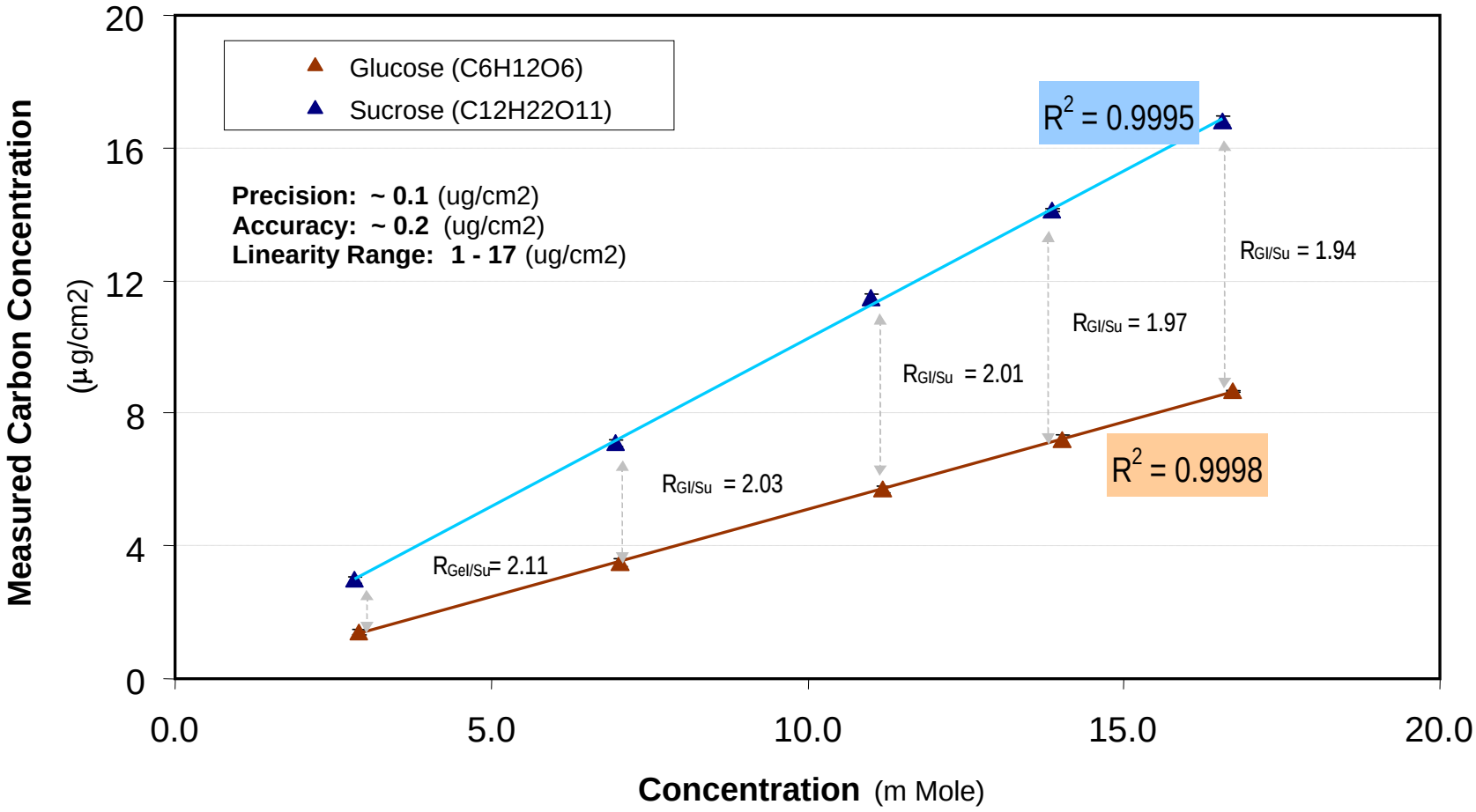
* OM measured by Aerosol Mass Spectrometer, OC, POC measured by thermal method

OC/EC Measurements of NIST Standard

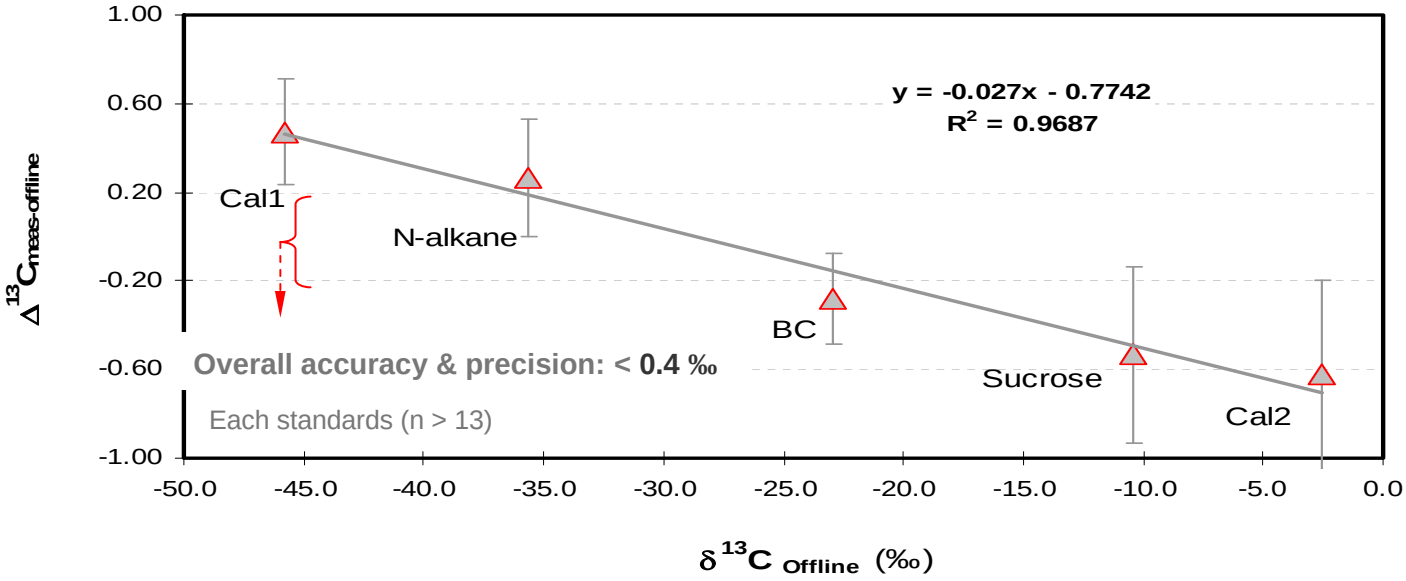
(SRM8785: urban dust)

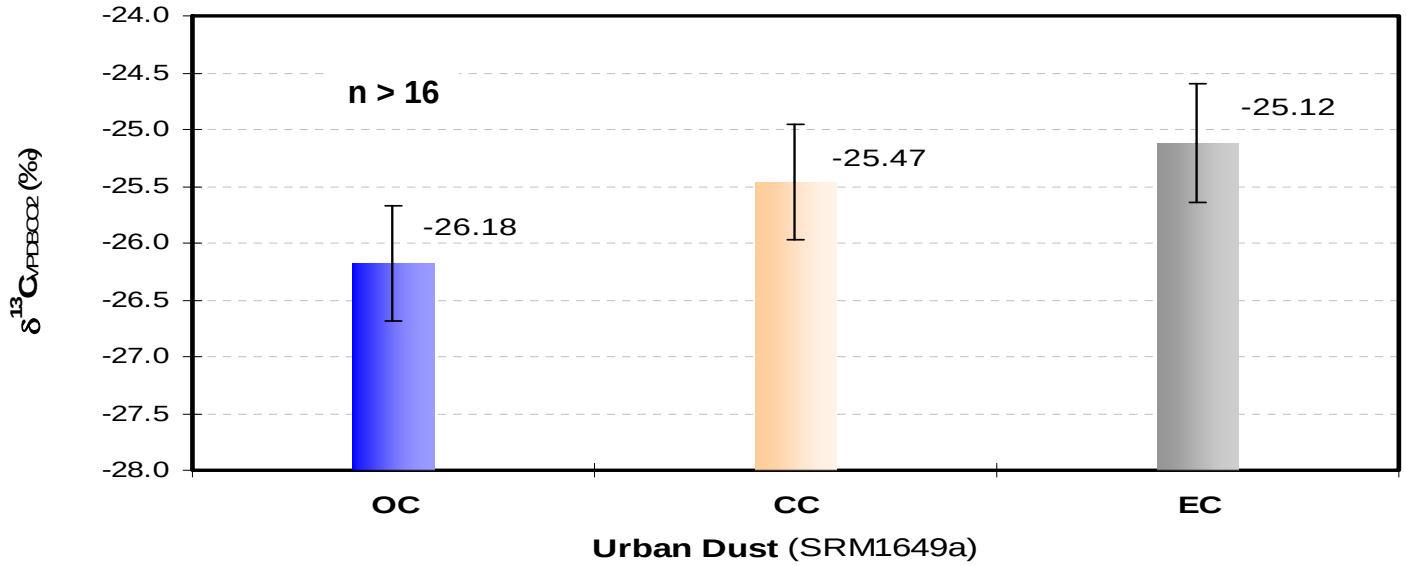


Precision, Accuracy and Linearity Range of OC/EC Analyzer



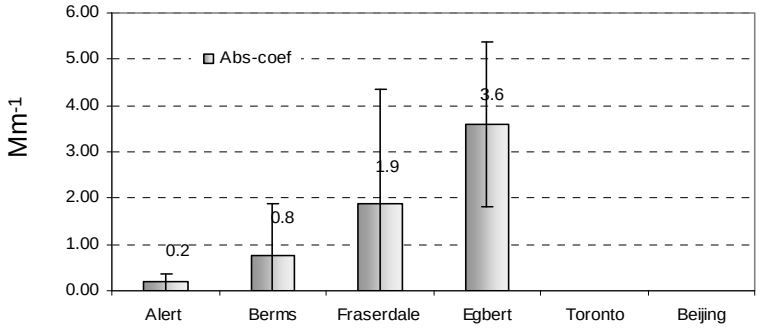
Accuracy & Precision of Isotope Measurements

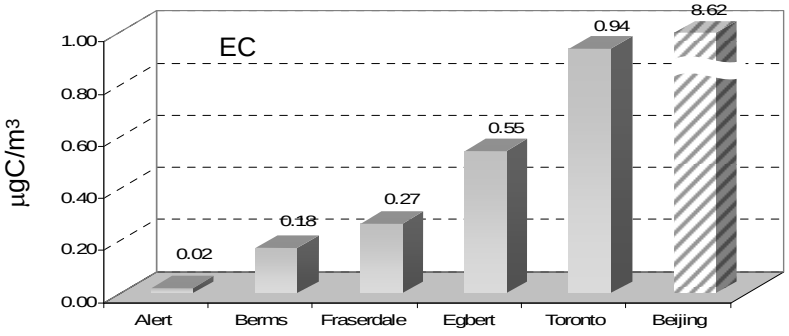


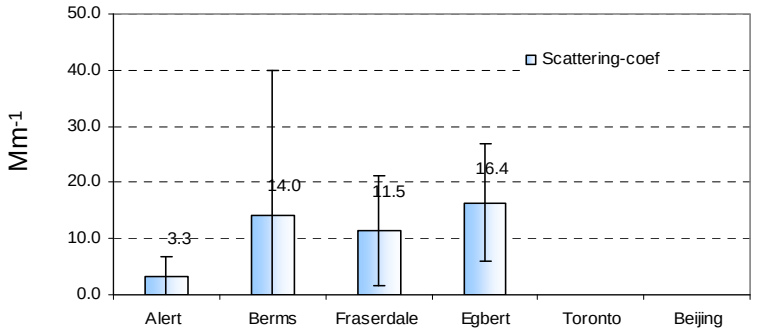


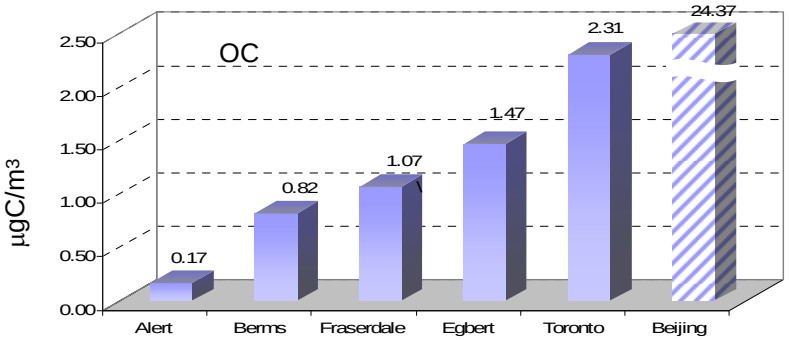
Annual Variations of EC & OC in PM over Canada

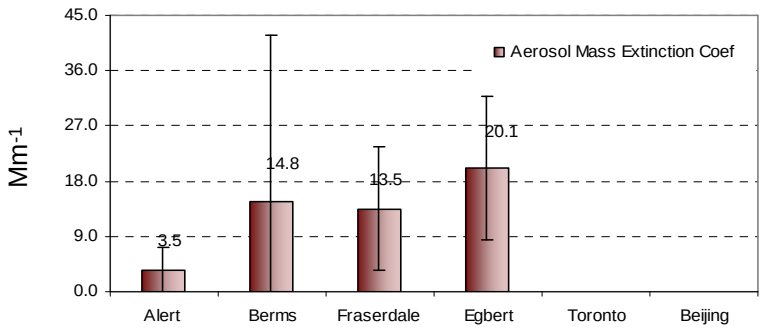
In Comparison with corresponding Absorption & Scattering values (2006-2007)

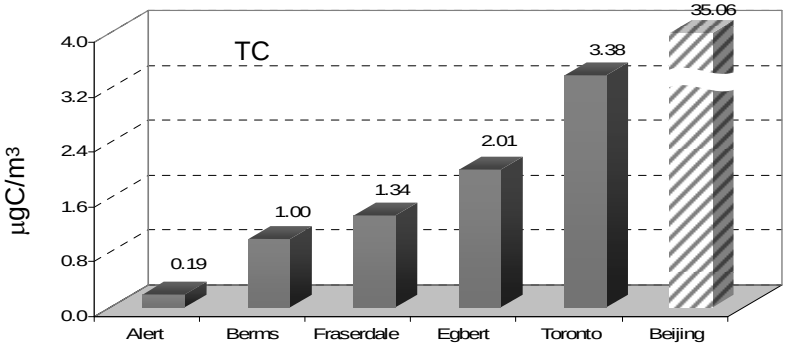








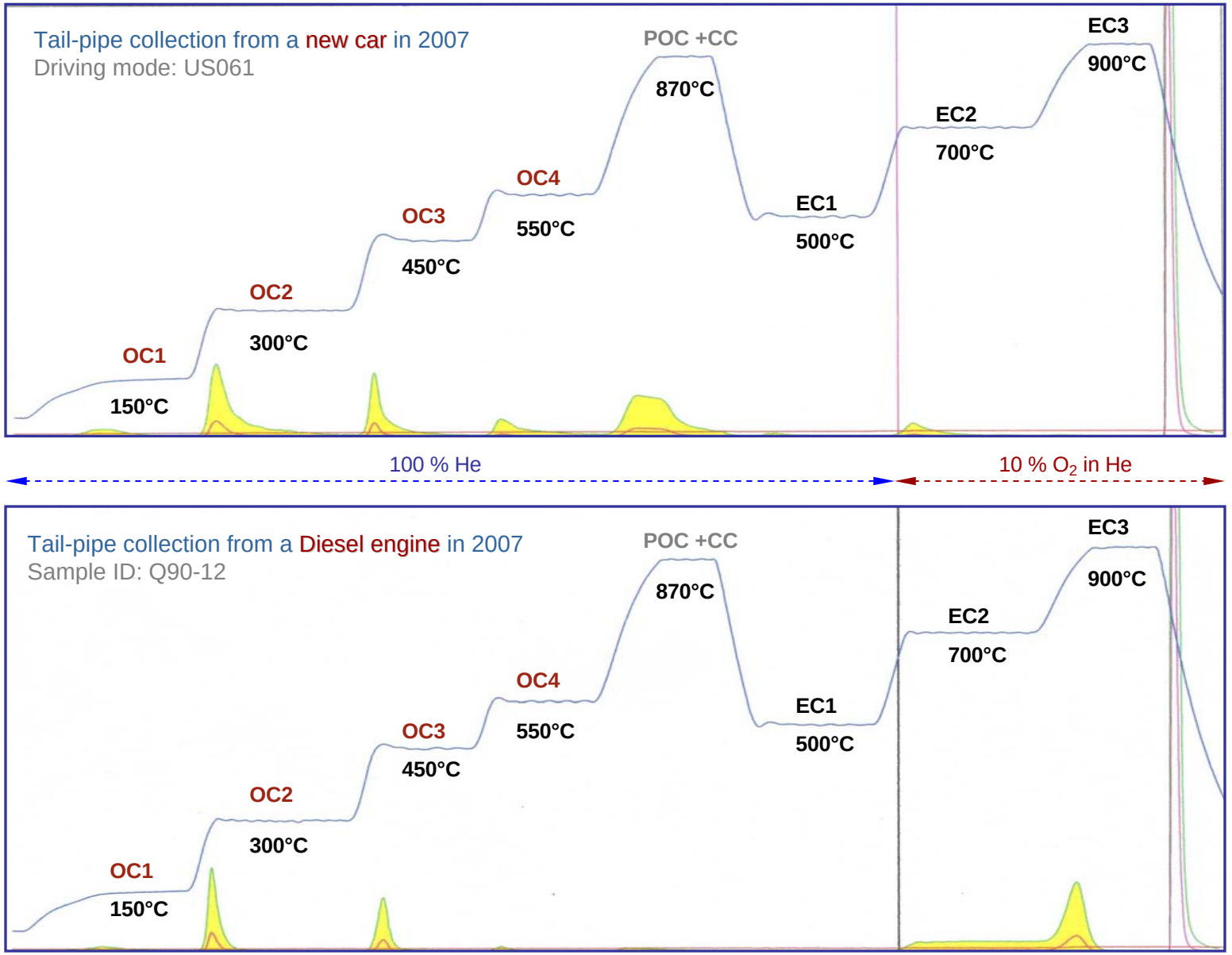




Background ← **Urban**

Background ← **Urban**

Thermogram of OC/EC in PM from Transportation Emissions



Measurements in carbonaceous PM, Indicators & Implications

Elemental carbon (EC or **BC):** absorbing light, positive climate forcing

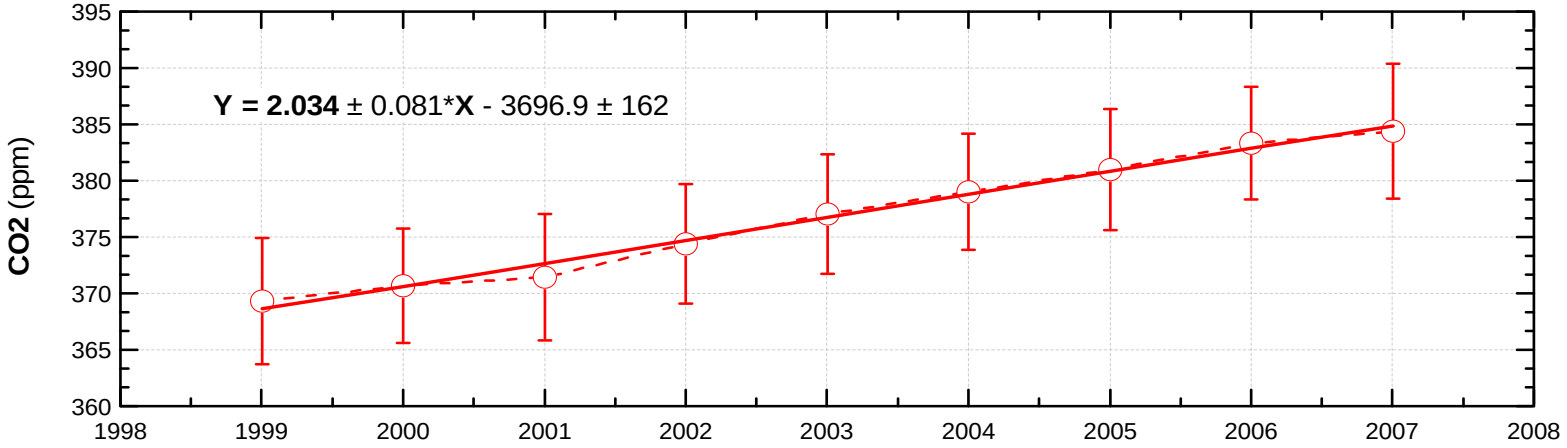
Organic Carbon (OC): health issues, visibility, scattering light, negative climate forcing

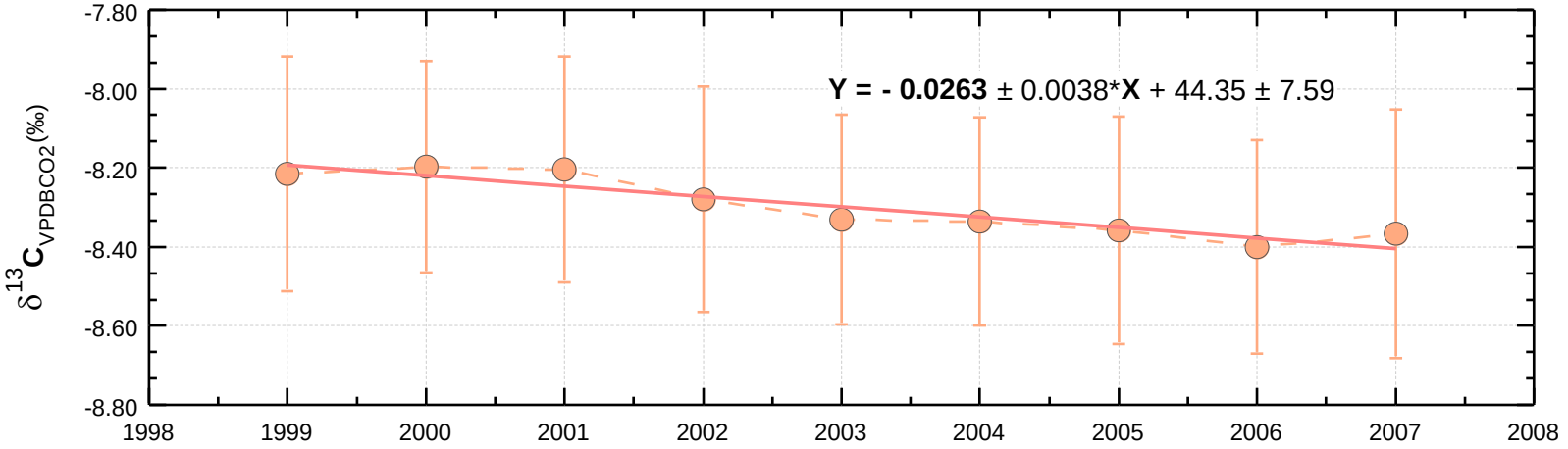
Pyrolysis OC (POC): oxygenated OC, health issues, visibility, scattering light, negative climate forcing

Indicator/tracers	Implications
OC/EC:	Fossil fuel combustion, biomass burning, photo-oxidations
POC/OC:	Photo-oxidations?
POC/EC:	Net climate forcing?
$\delta^{13}C$ (OC):	Emission sources, photo-oxidation
$\delta^{13}C$ (EC):	Emission sources
$\Delta^{13}C$ (EC-OC):	Emission sources, photo-oxidation

Trend in CO_2 & Carbon Isotopic Composition at Alert

(Annual Means, 1999 - 2007)

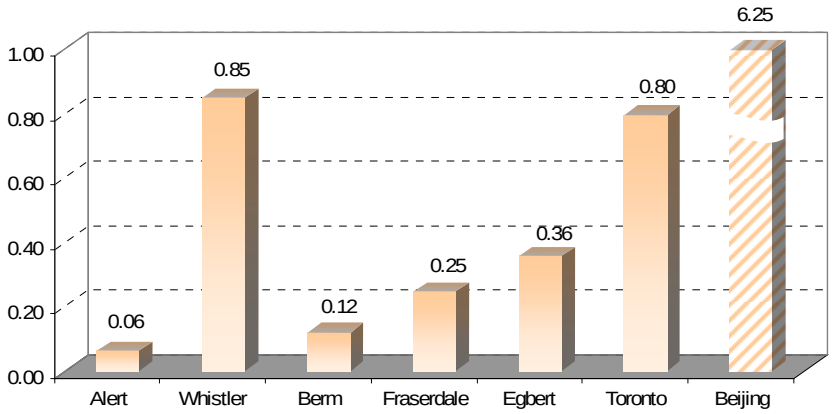




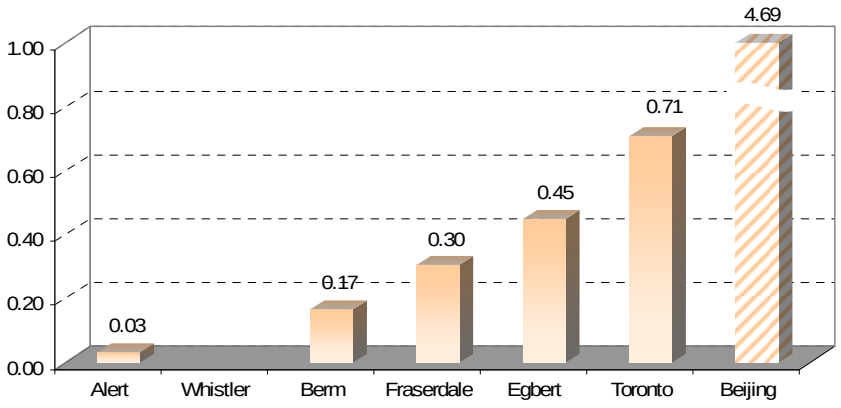
Environment Canada Environnement Canada

Seasonal Variation in Spatial Gradients of POC Contents over Canada

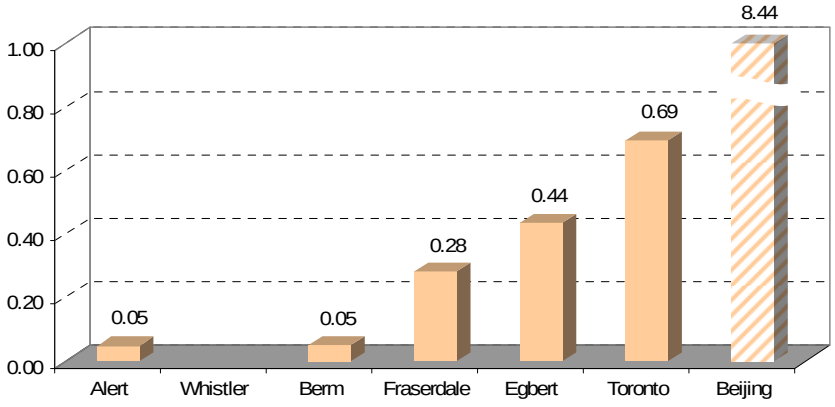
Spring



Summer

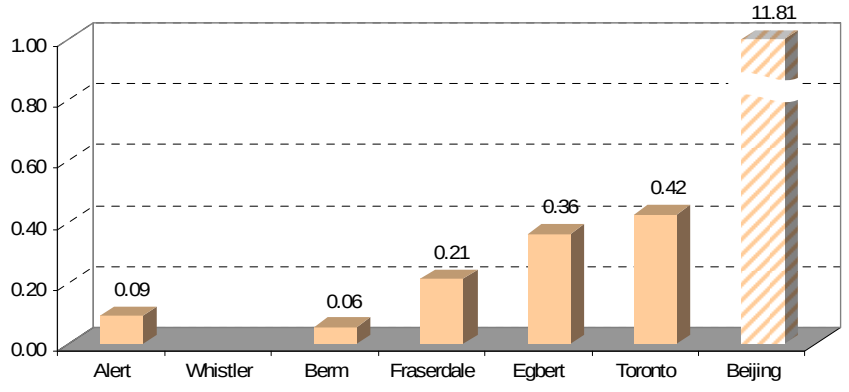


Fall



Background ← Urban

Winter



Background ← Urban

Thermogram of OC/EC in Biomass Burning PM

(Fire Science Lab, US Forest Service, Missoula, MT)