

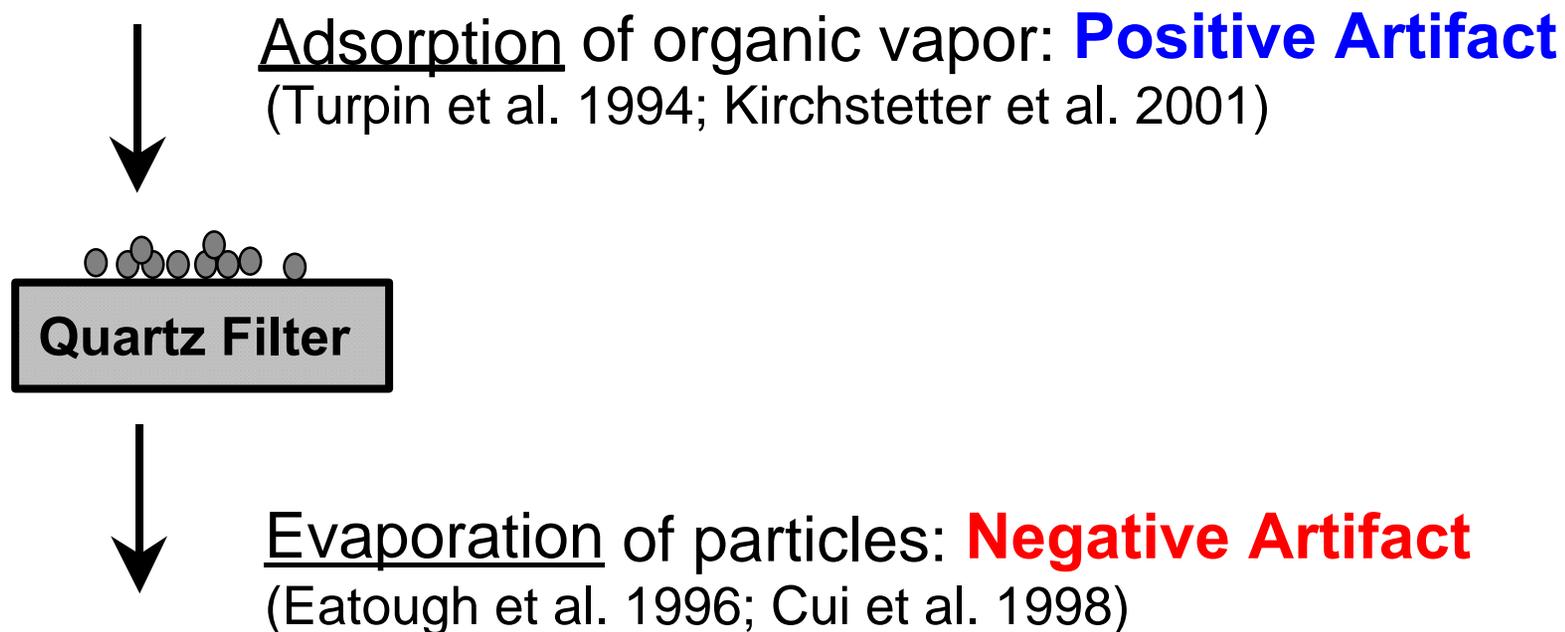
**Sampling Artifact:
Significance in Organic Aerosol
Carbon Determination**

Tom Kirchstetter and T. Novakov
Lawrence Berkeley National Laboratory

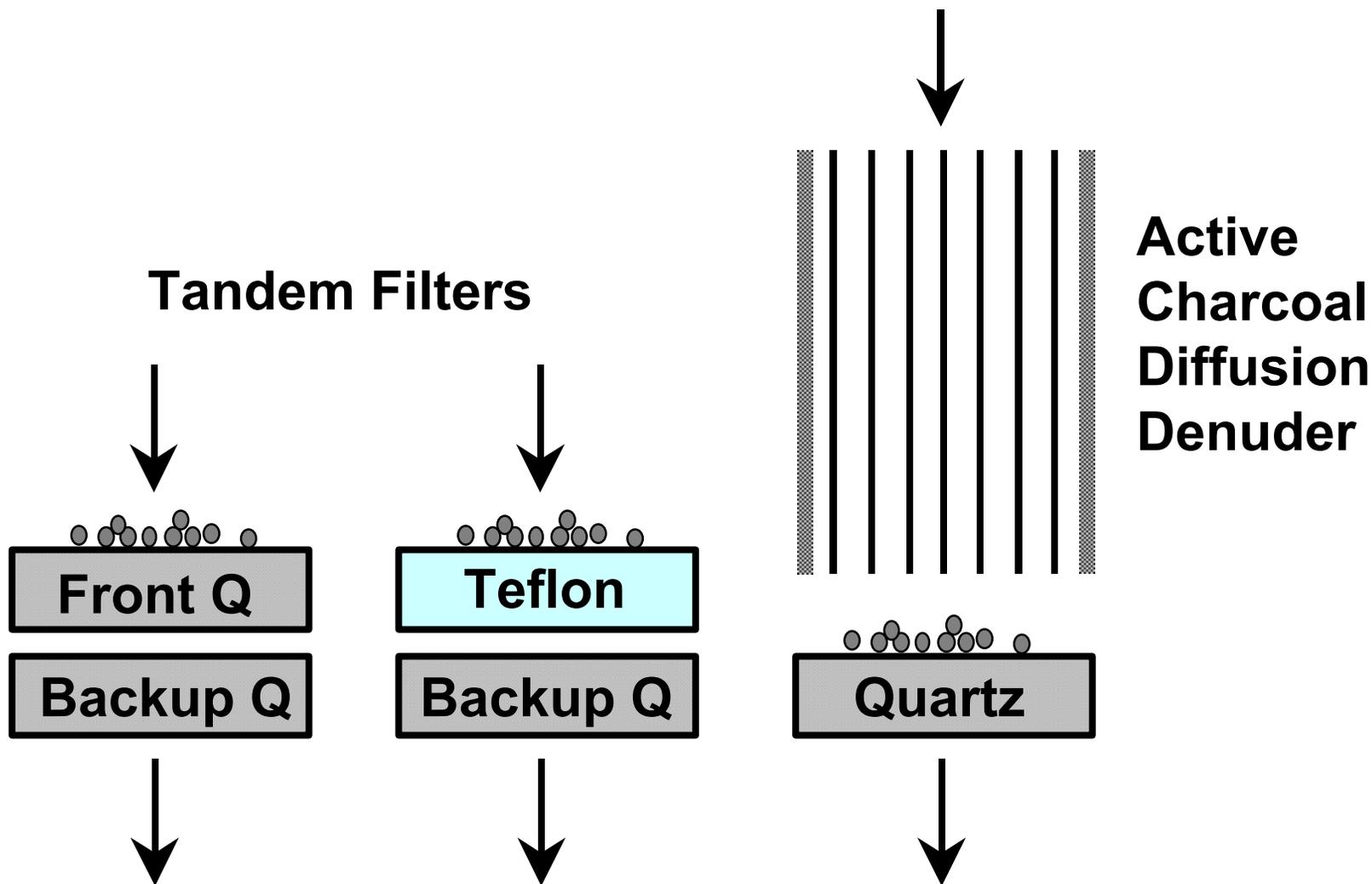
Carbonaceous Aerosol

- Comprises a major portion of aerosol mass
- Impacts radiation transfer directly
 - Organic carbon (OC) scatters light
 - Black carbon (BC) absorbs light
- No standard method exists for measurement of carbonaceous particles
- Sampling artifact for OC is significant and poorly understood
- LBNL analytical method is well-suited to study OC sampling artifact

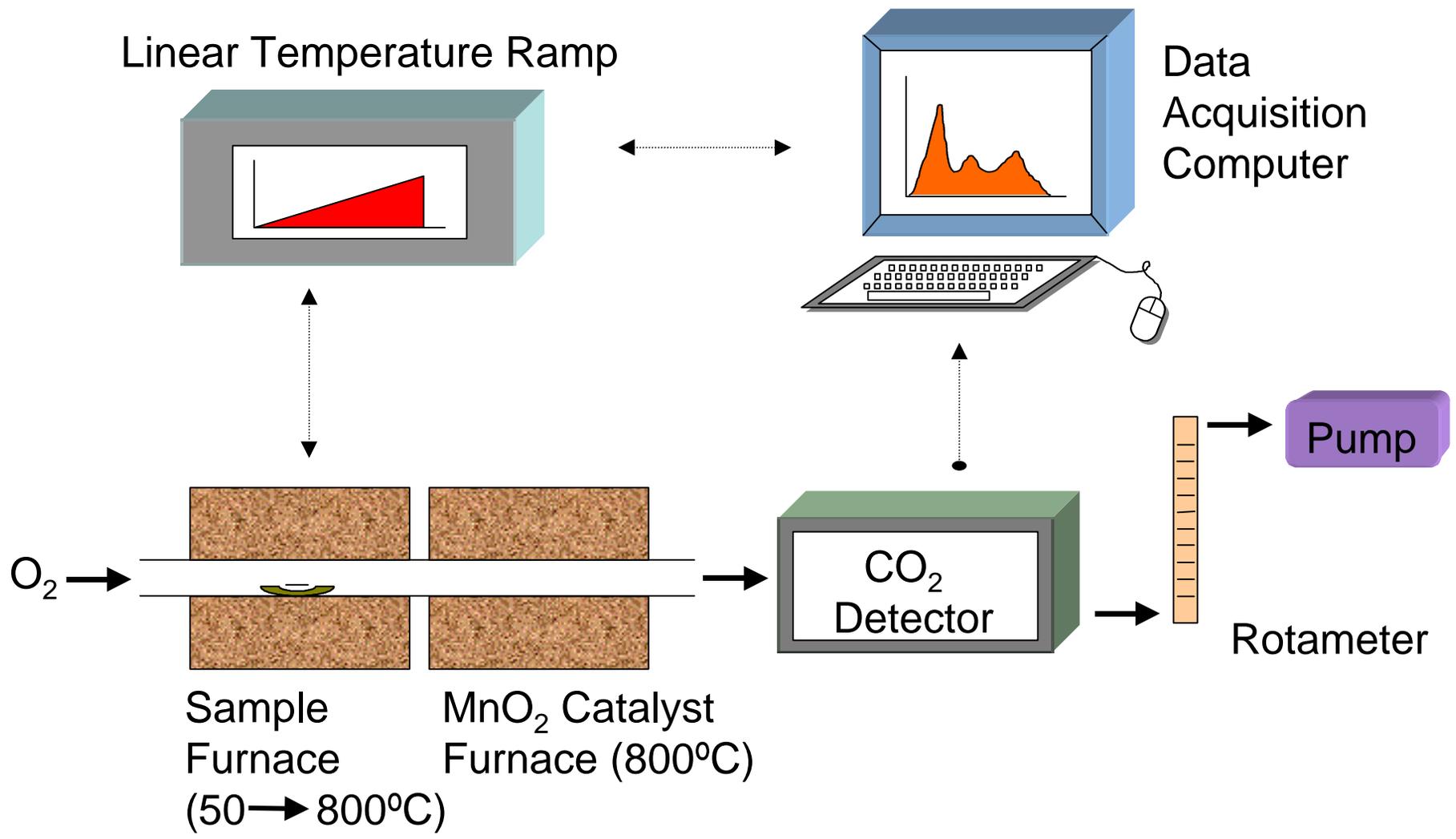
Quartz Filter Sampling Artifacts



Sampling Methods to Correct for Adsorption Artifact



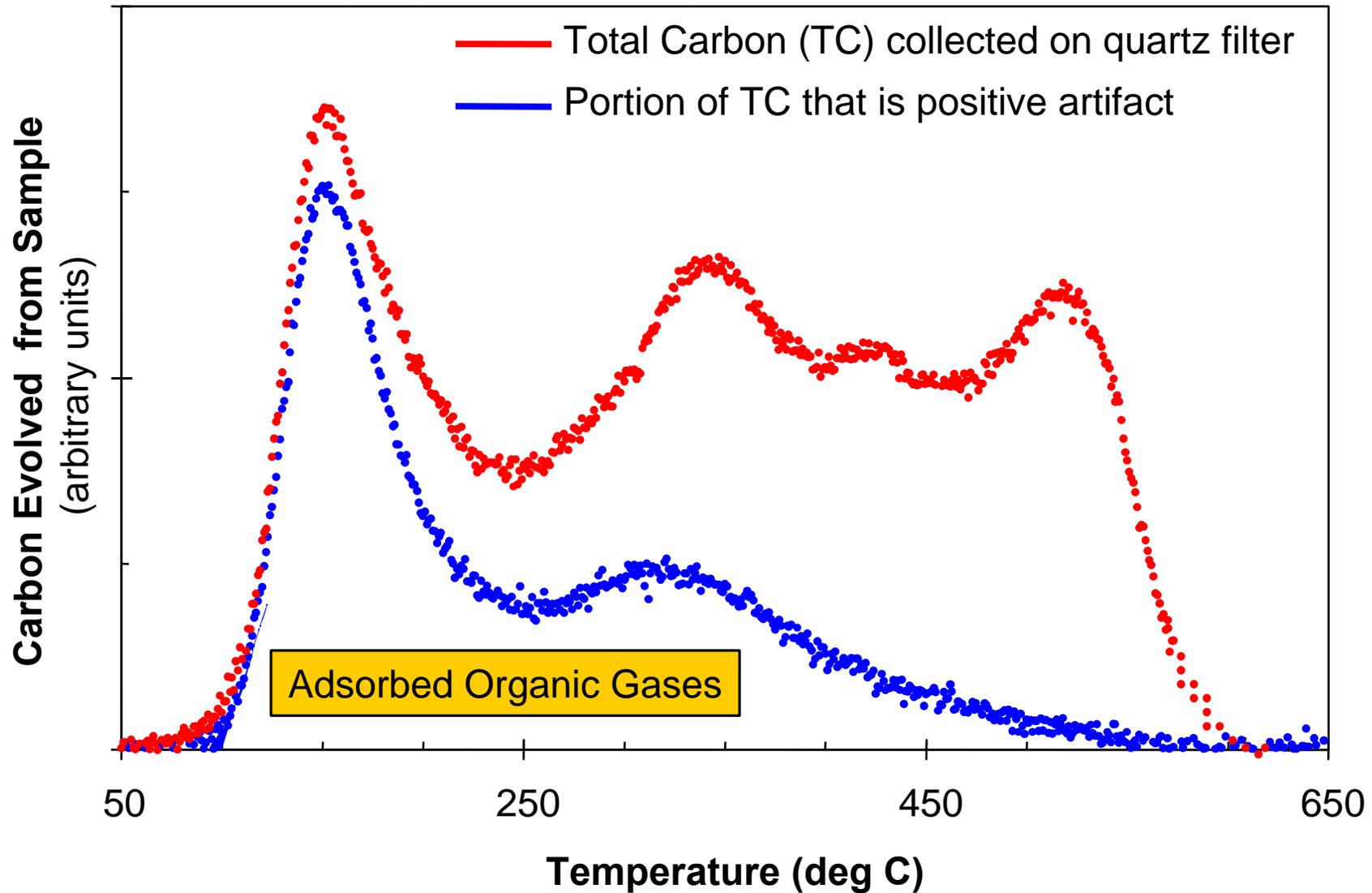
LBNL Evolved Gas Analysis (EGA)



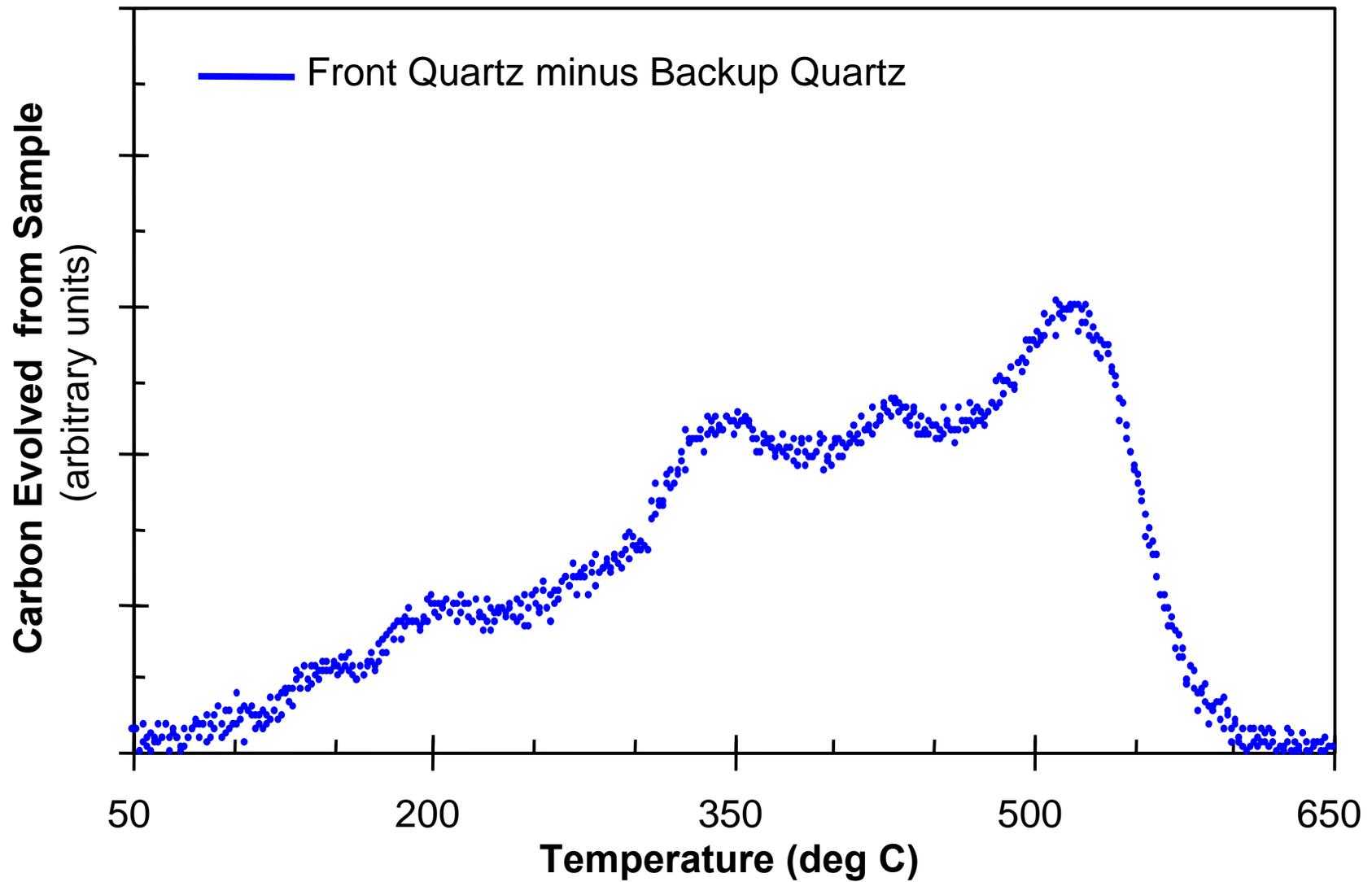
EGA Thermograms Illustrate Positive Artifact



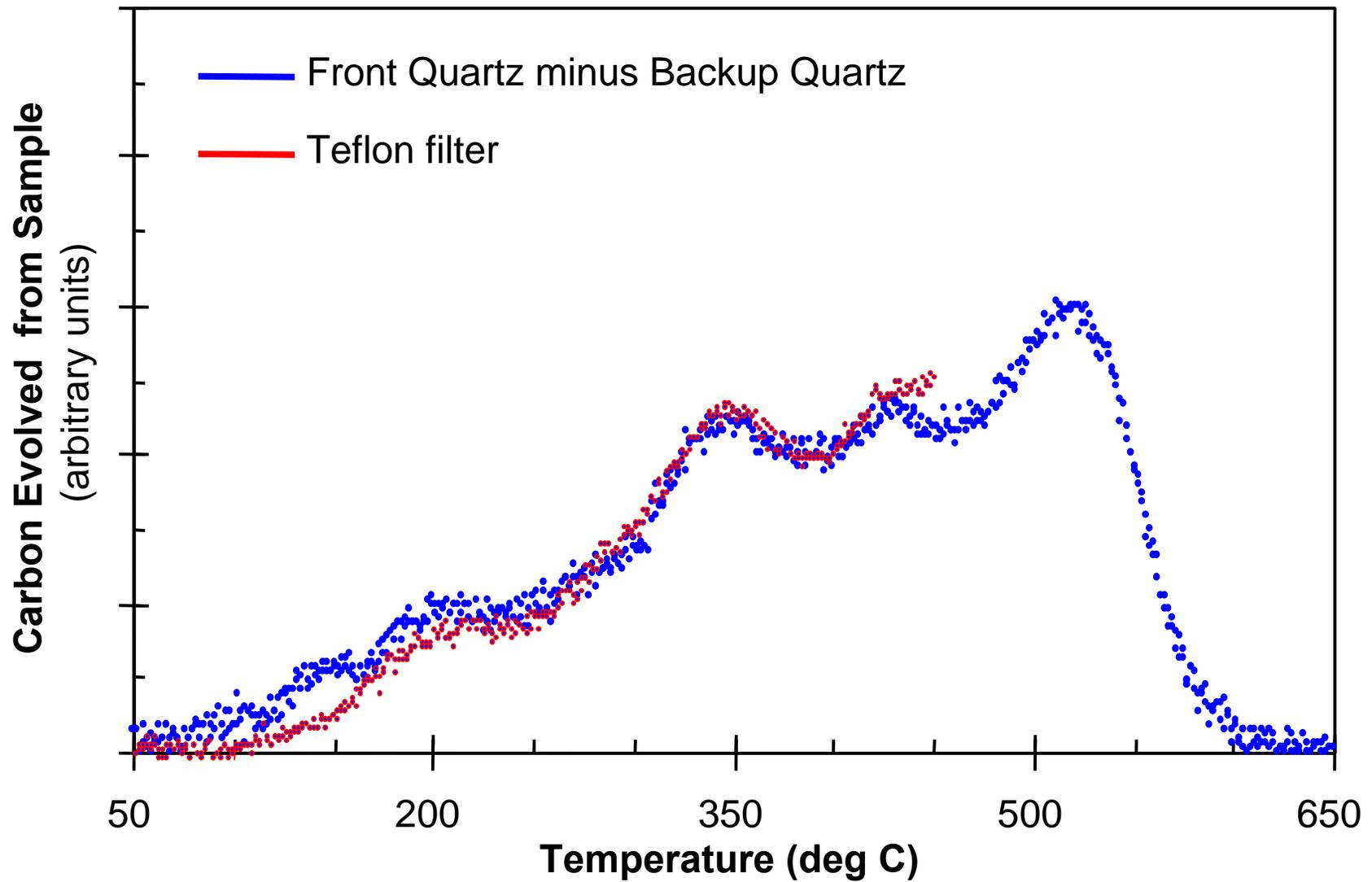
Urban Sample (Well-behaved)



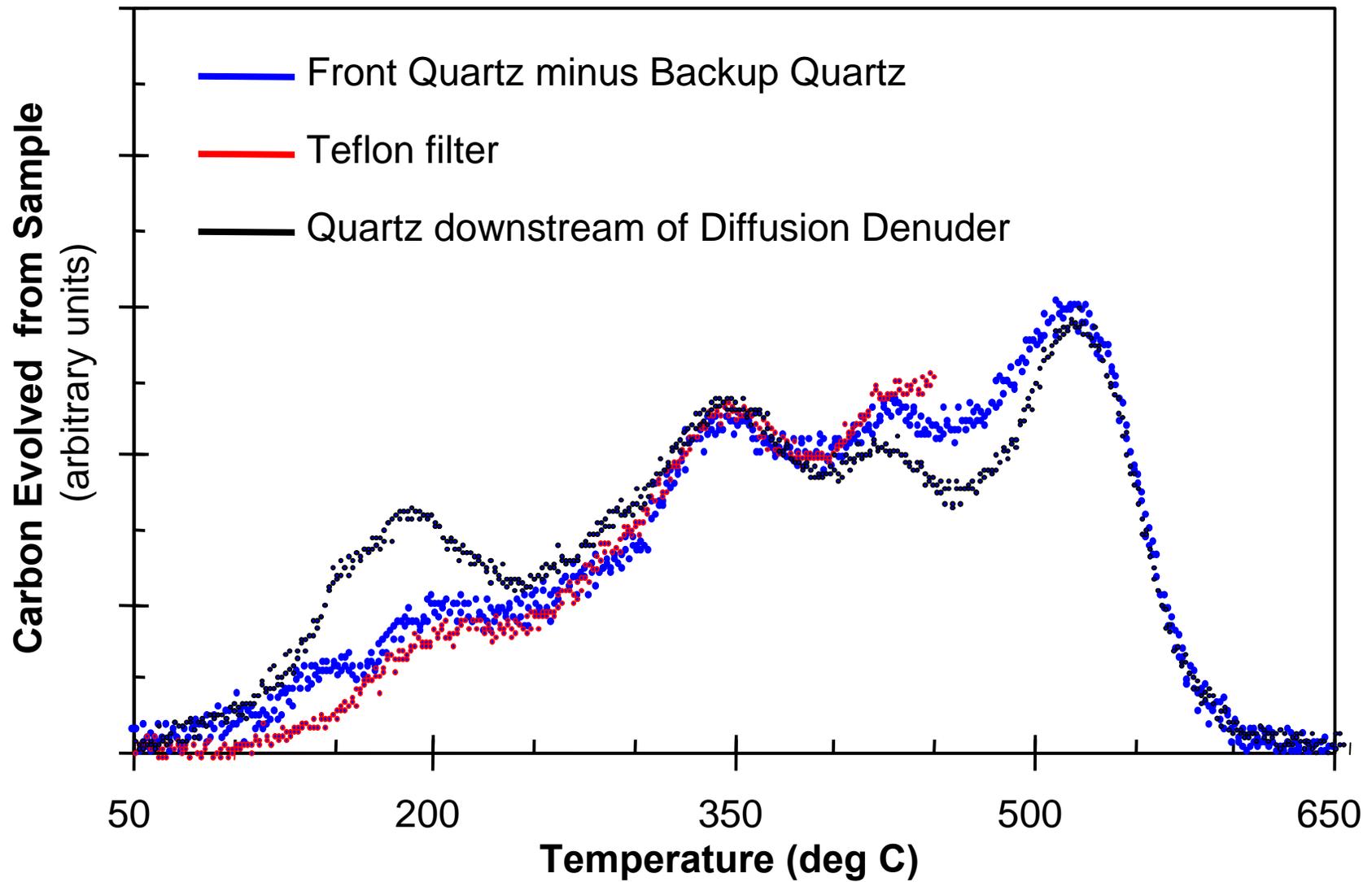
Ways to Correct for Positive Artifact



Ways to Correct for Positive Artifact



Ways to Correct for Positive Artifact



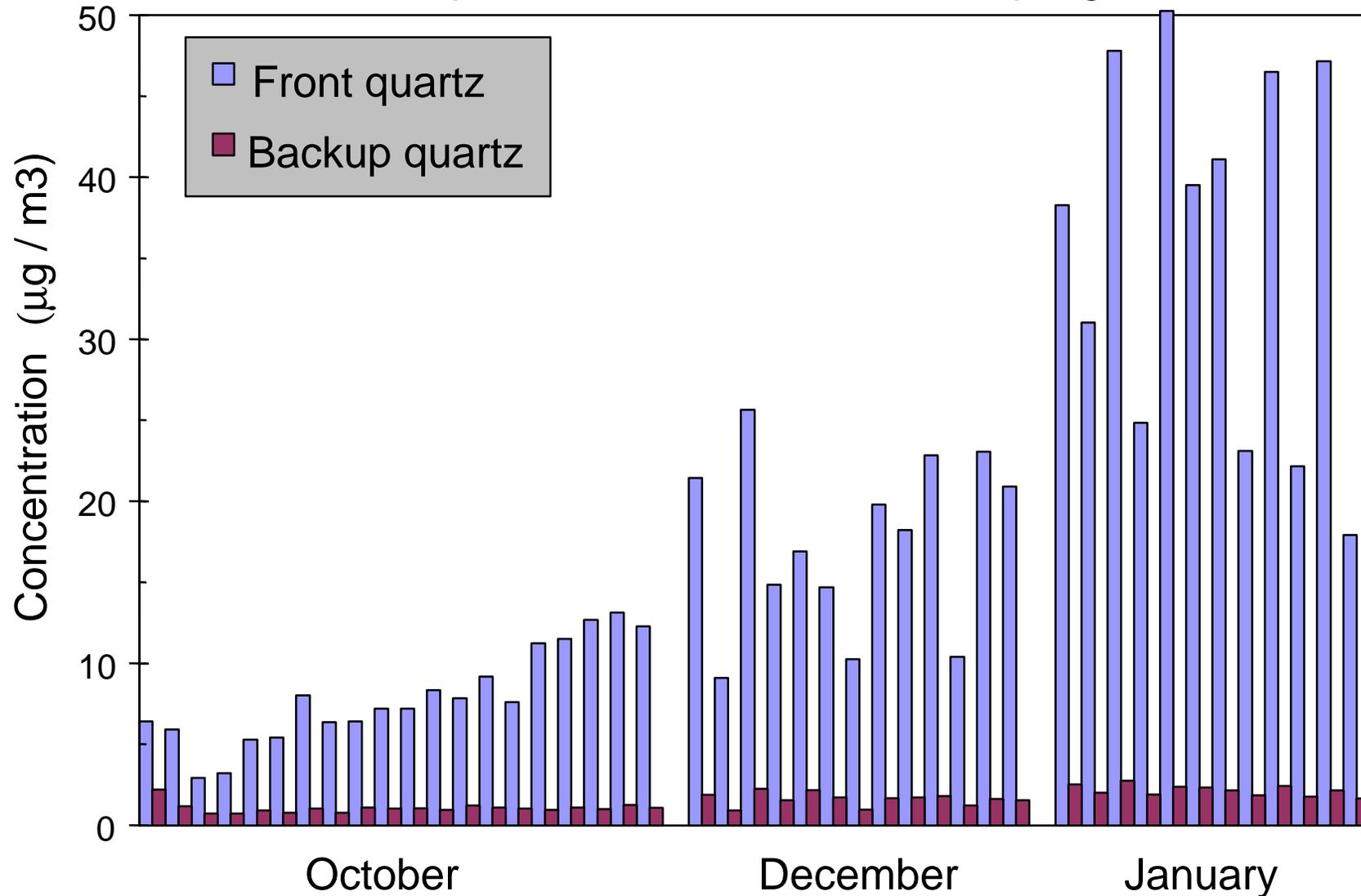
How large is Positive Artifact?

<u>Field Experiment</u>	<u>Back Quartz TC ÷ Front Quartz TC (%)</u>
• CALSPAN (Smog chamber)	90 ± 34 (n = 34)
• CLAMS (UW CV-580)	77 ± 09 (n = 19)
• TARFOX (UW CV-580)	66 ± 07 (n = 28)
• SAFARI (UW CV-580)	54 ± 19 (n = 54)
• PRIDE (Tropical Trade Winds)	45 ± 16 (n = 04)
• ACE-2 (RV Vodyanitskiy)	30 ± 10 (n = 12)
• Berkeley, CA (LBNL)	30 ± 06 (n = 12)
• Fresno, CA (EPA Supersite, Oct 2000)	15 ± 06 (n = 20)

Positive Artifact is Less Important in High Pollution



Fresno Supersite Total Carbon vs. Sampling Period



Consequences of Positive Artifact



Overestimation of TC and OC concentrations in excess of 100%

- ❖ Chemical budget of light scattering (TARFOX, Hegg et al., 1997)
⇒ $\sigma_{sp}(500 \text{ nm}) = 4.0 \text{ m}^2 \text{ g}^{-1} [\text{carbon g/m}^3] + 2.7 \text{ m}^2 \text{ g}^{-1} [\text{sulfate g/m}^3]$
- ❖ Contribution of absorption to extinction (SAFARI, Kirchstetter et al., 2003)
⇒ carbon aerosol has 60% larger co-albedo if OC is corrected for artifact
- ❖ Source apportionment using pollutant ratios (INDOEX, Novakov et al., 2000)
⇒ $\text{BC/TC} = 0.45 \pm 0.16$ (corrected) vs. 0.24 ± 0.10 (uncorrected)

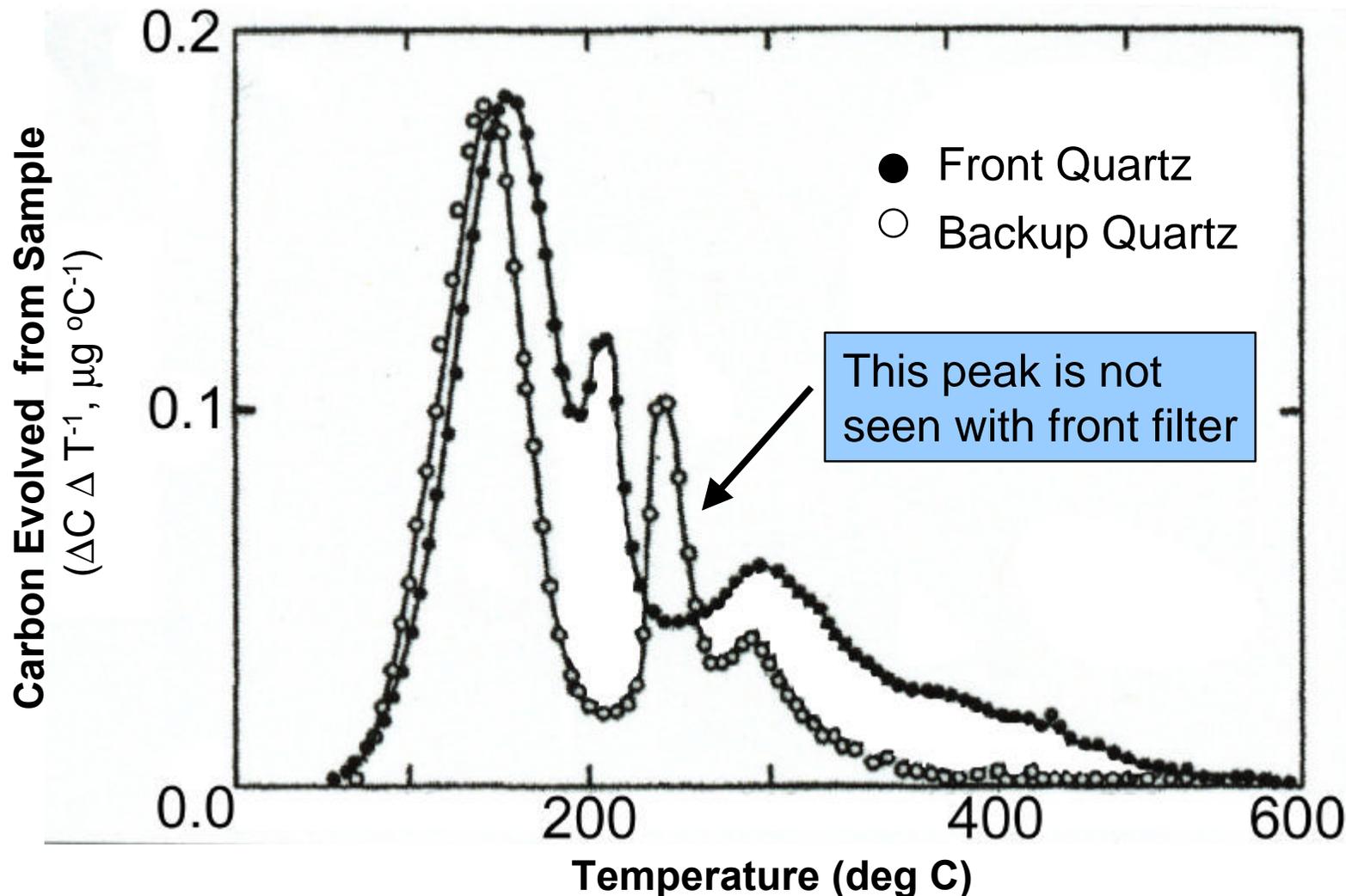
Caveats of Tandem (front minus backup) Correction Method

- Backup filter underestimates artifact if sample volume is small
- Quartz filters can have variable adsorption capacity
- ❖ **This correction may not work away from the polluted urban location**
for example...
 - TARFOX
 - CLAMS
 - Brazil Biomass Burning

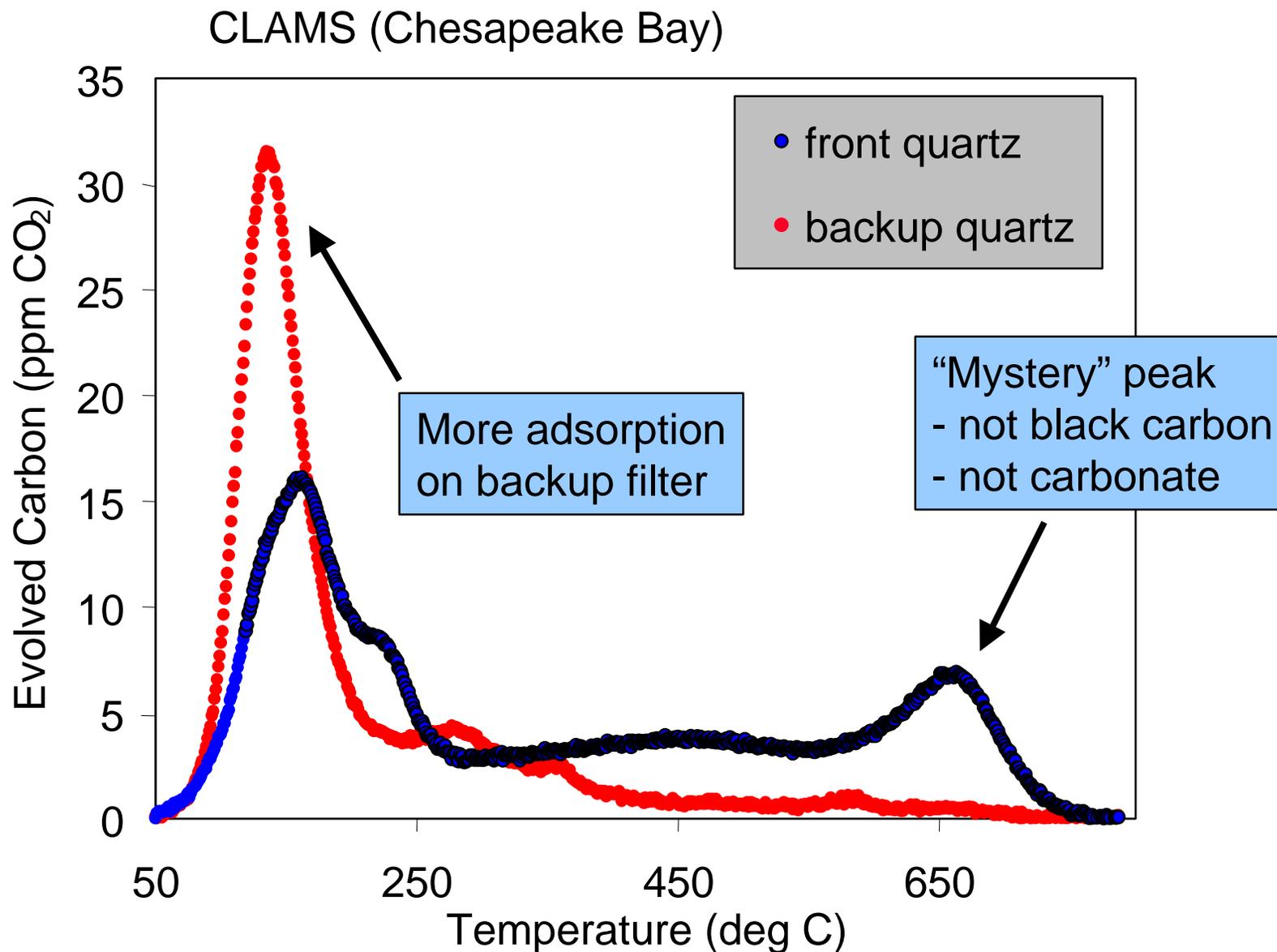
Carbon on backup filter but not on front filter?



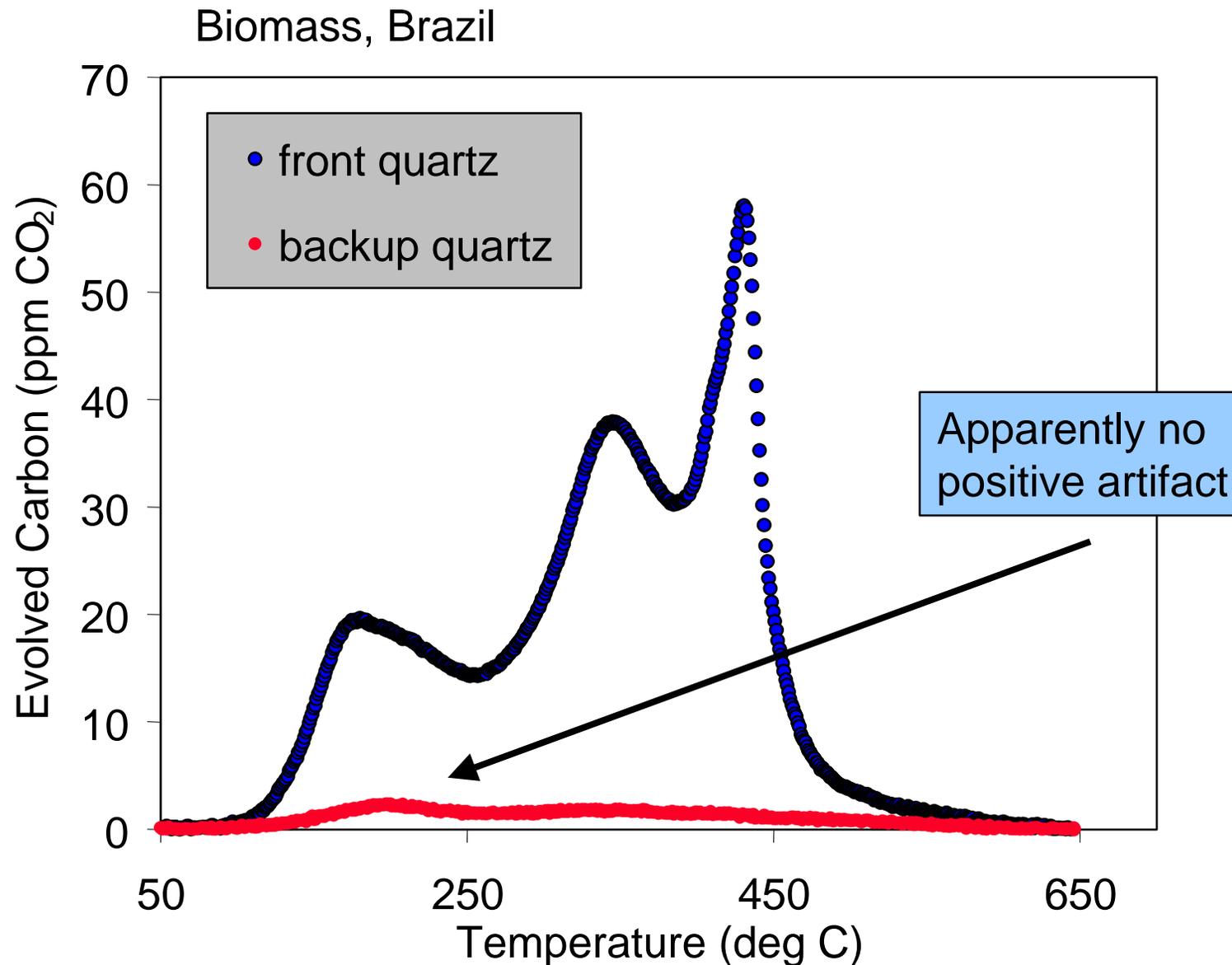
TARFOX - Novakov et al, 1997



Adsorption of organic gas greater on backup filter?



Backup filter indicates negligible artifact?



Final Remarks



- Given the magnitude of the positive artifact, question the accuracy of uncorrected TC and OC data
- Further study is needed to understand positive artifact
- Most thermal methods are not well-suited to study artifact
 - 2-step method = 2 data points
 - TOR method = 7 data points
- EGA method = 700 data points
- Eatough et al. claim the negative artifact is significant
- Comparison of analytical methods indicate consistency for TC
- Sampling artifacts lead to large uncertainty in TC and OC data