Measurements of black and brown carbon in atmospheric aerosols with the integrating sphere method

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Background

- Light absorbing carbonaceous material (Black carbon, BC) causes most of light absorption by atmospheric aerosols in visible range of spectrum
- Influence on global radiative balance
- Enhanced positive radiative forcing
- Health effects
- No standard measurement method available
- Thermally refractory organic carbon

Definition

- **Black carbon (BC)** → optical methods

  measured parameter: absorption coefficient σ_a; conversion to BC mass

- **Elemental carbon (EC)** → thermal methods

  measured parameter: CO_2 or CH_4

  separation of EC and organic carbon (OC)

- Graphitic carbon
- Thermally refractory carbon
- „**Brown carbon**“

Objectives:

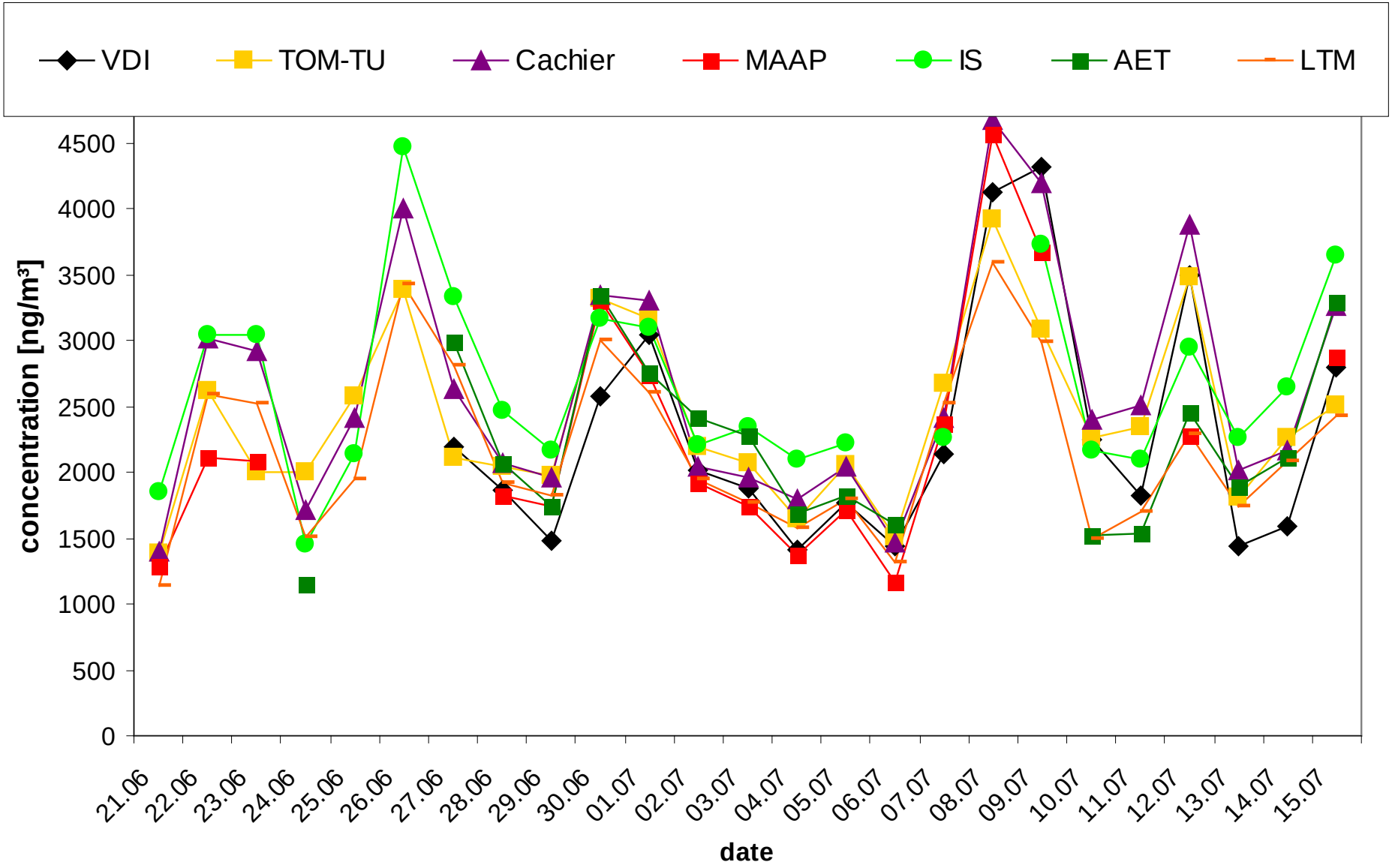
- Correction of optical Integrating Sphere (IS) technique for the influence of brown carbon
- Estimation of influence of „brown“ carbon
- Test under conditions of known large biomass source contribution
- Application in method intercomparison study

HULIS / Brown carbon

- Weakly light absorbing
- Strong spectral dependence of absorption
  - Interference with optical methods

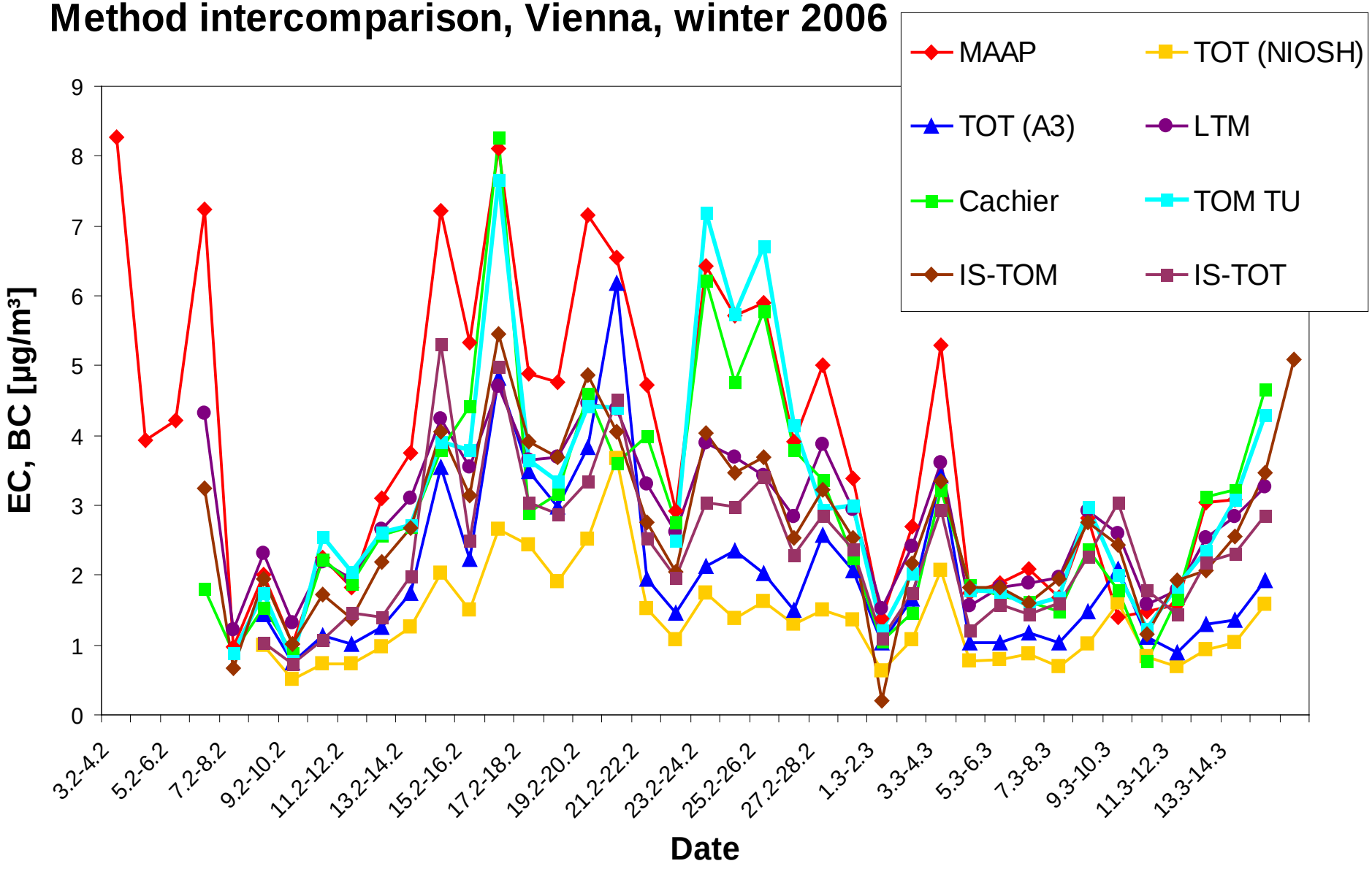
- Thermally refractory
- Chars easily
  - Na, K (in biomass smoke)
  - Interference with thermal methods

Method intercomparison, Vienna, summer 2004



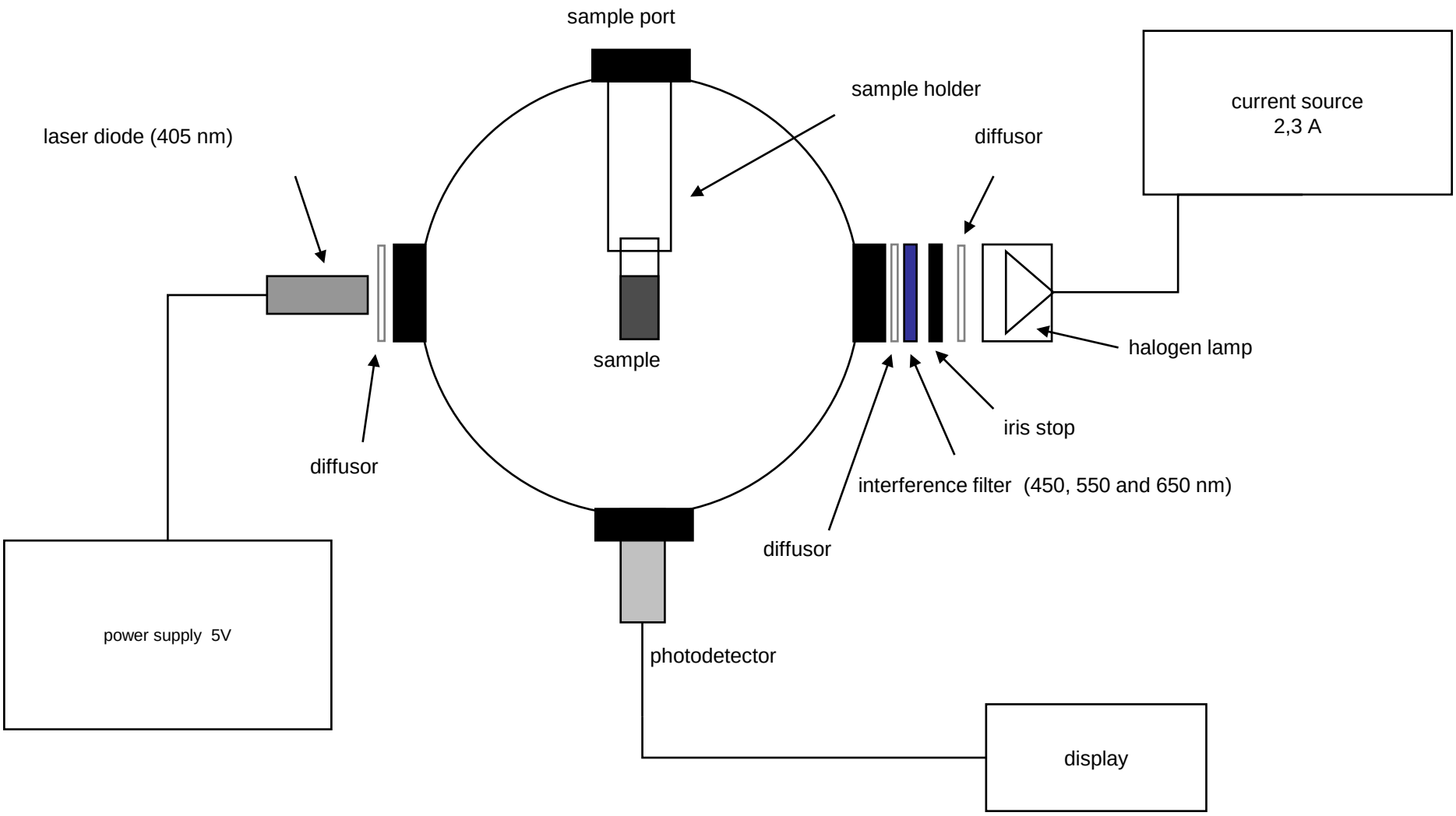
Hitzenberger et al. (2006) ES&T 40, 6377-6383

Method intercomparison, Vienna, winter 2006



Reisinger et al.(2008) ES&T 42, 884–889

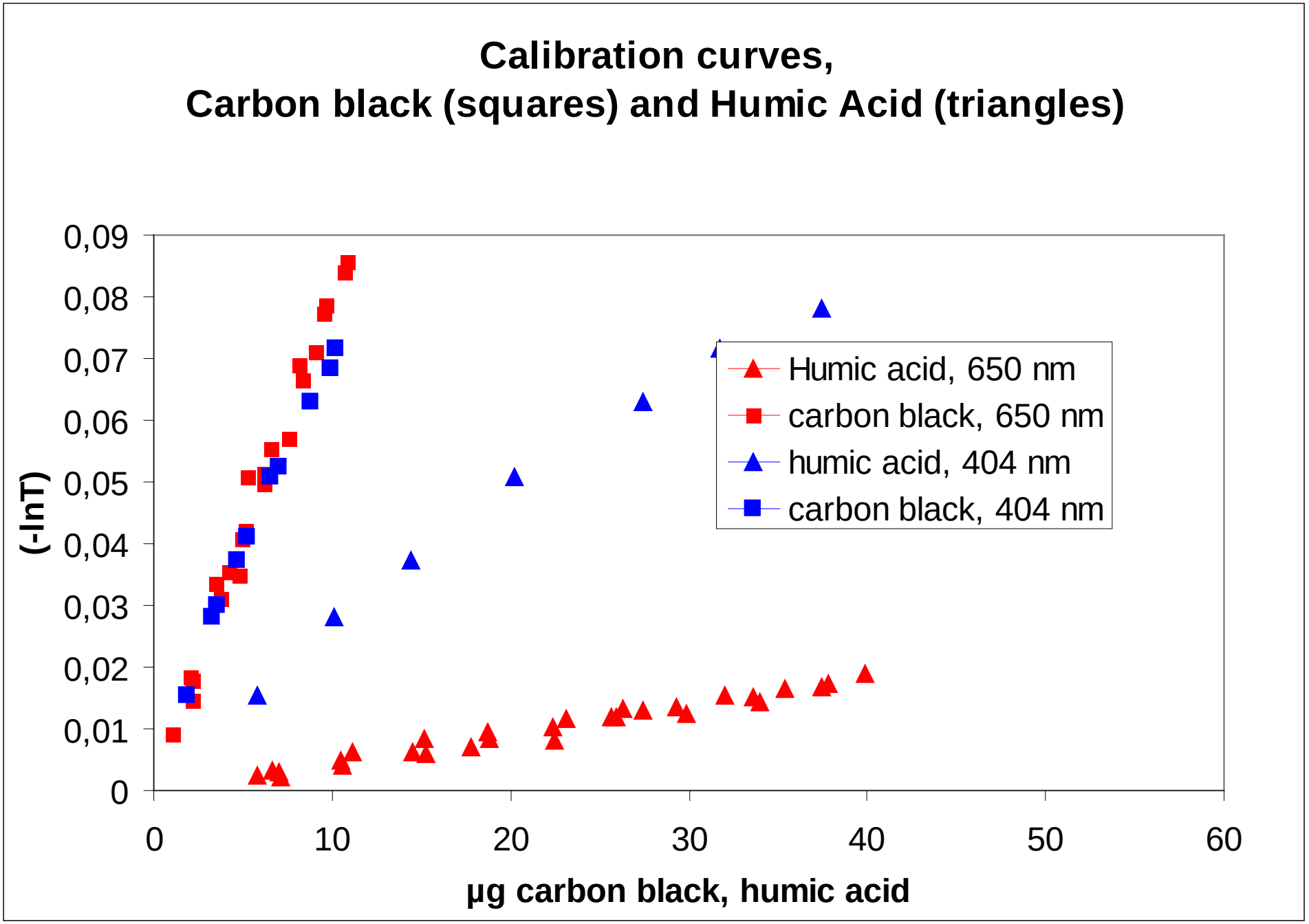
Integrating Sphere Technique

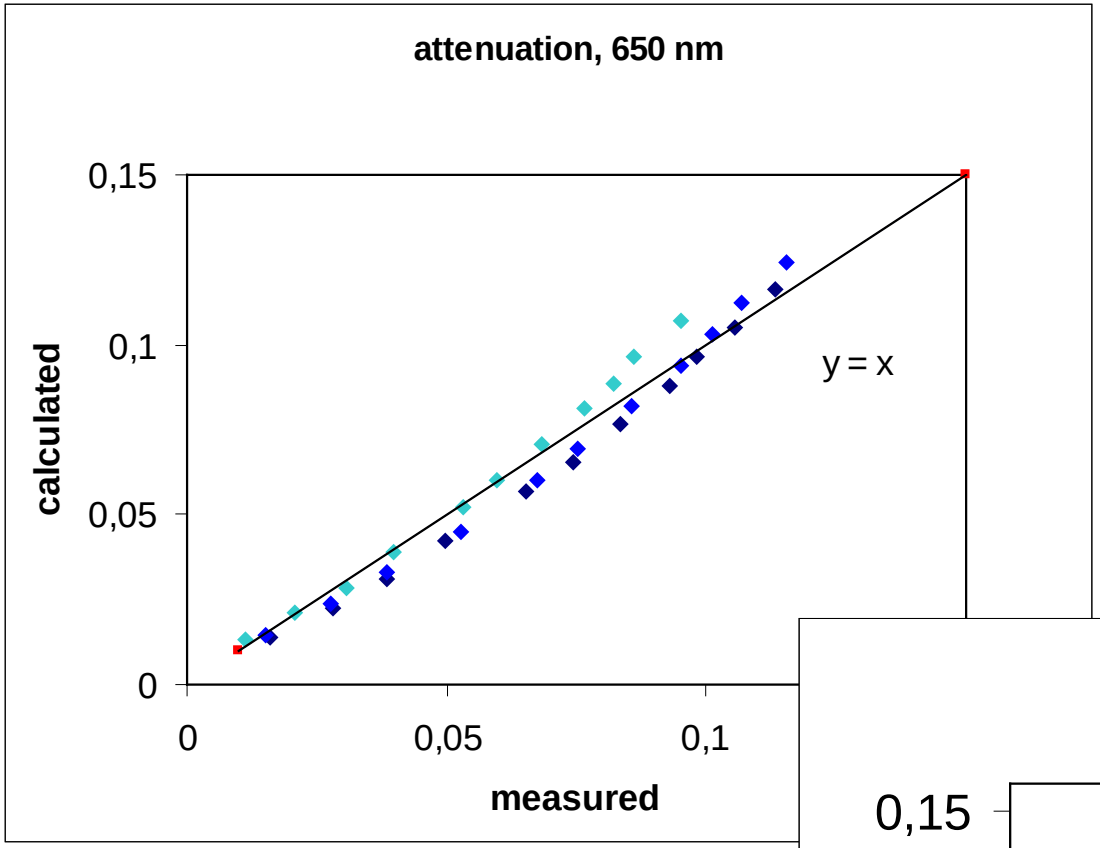


Calibration / Assumptions

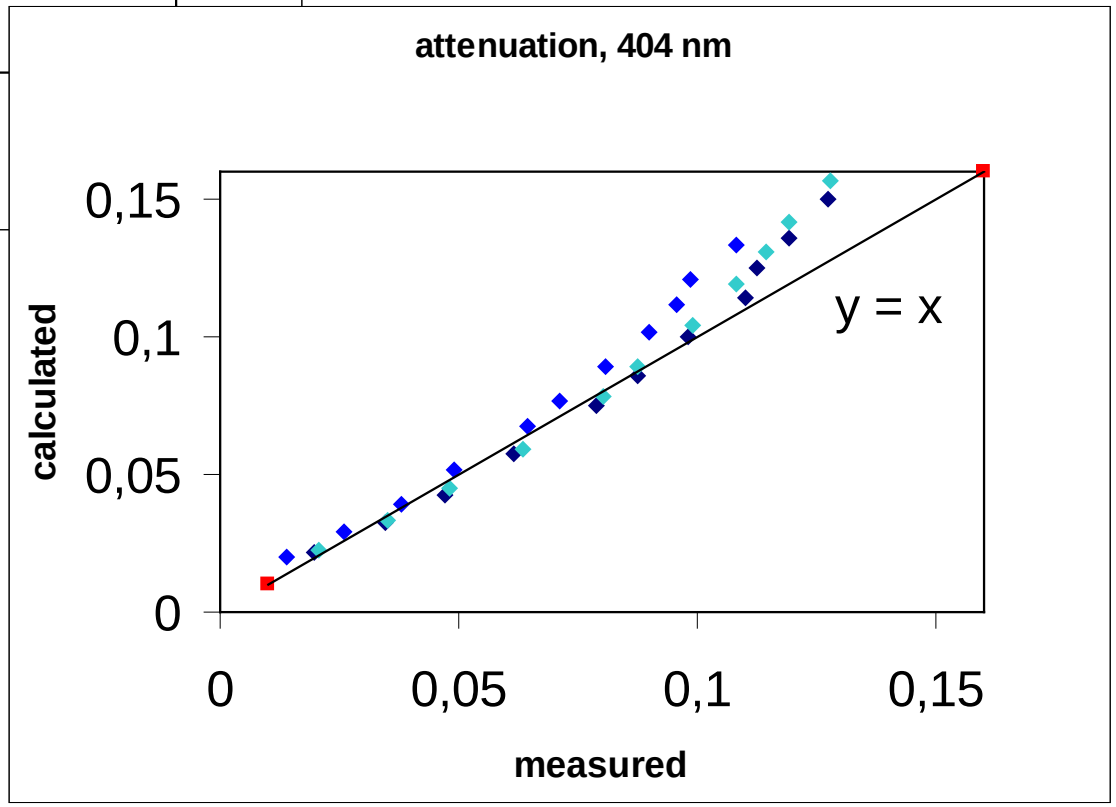
- Proxy substances
  - Elftex 124 (Cabot Corp.)
  - Humic Acid Sodium Salt (Acros Organics)
- BC behaves like Elftex 124
- BrC behaves like Humic Acid Sodium salt

- → BC concentration
- → BrC concentration


Calibration curves,
Carbon black (squares) and Humic Acid (triangles)
0,09
0,08
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
(-lnT)
0
10
20
30
40
50
60
µg carbon black, humic acid
Humic acid, 650 nm
carbon black, 650 nm
humic acid, 404 nm
carbon black, 404 nm



Mixtures of test substances

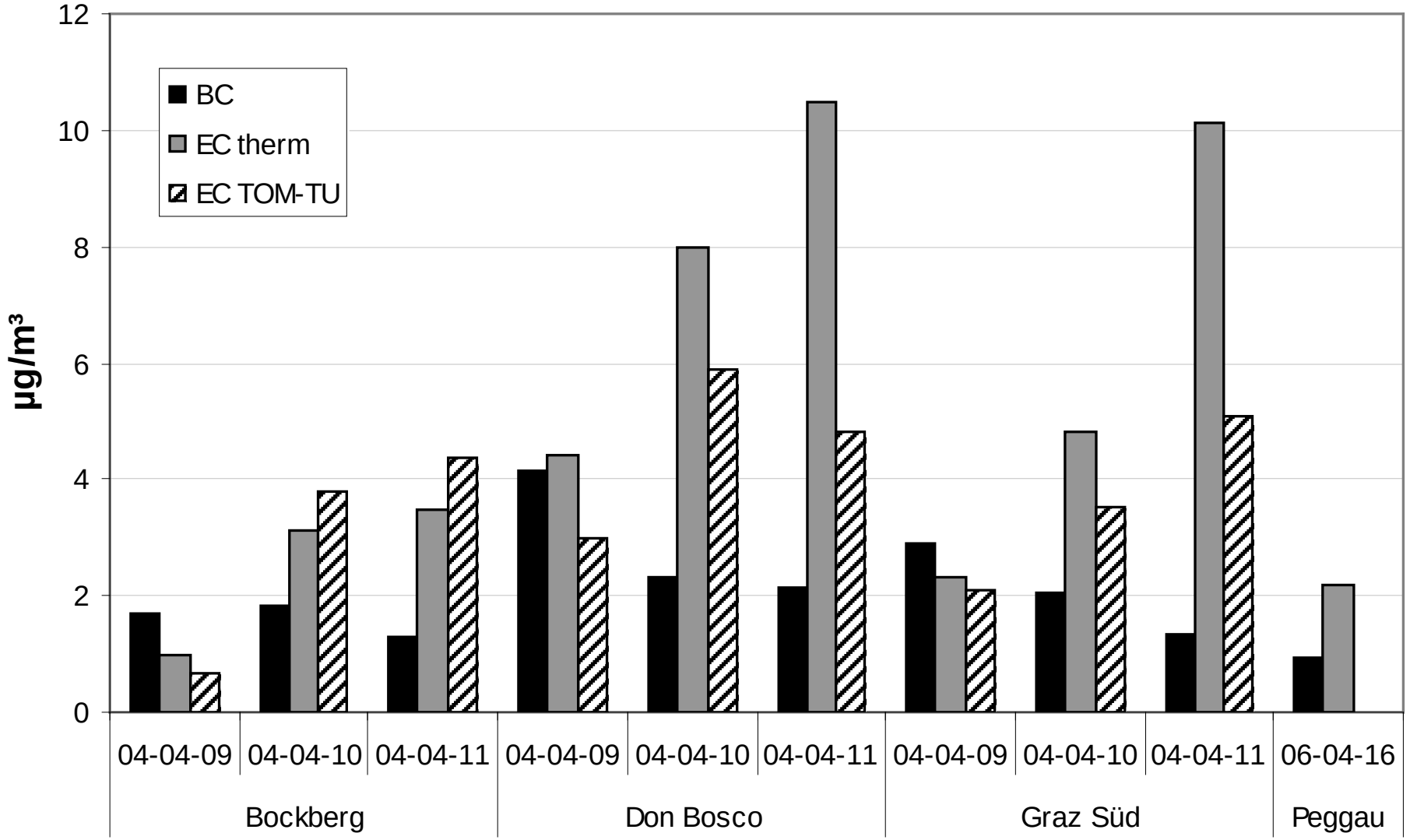


Biomass smoke episodes

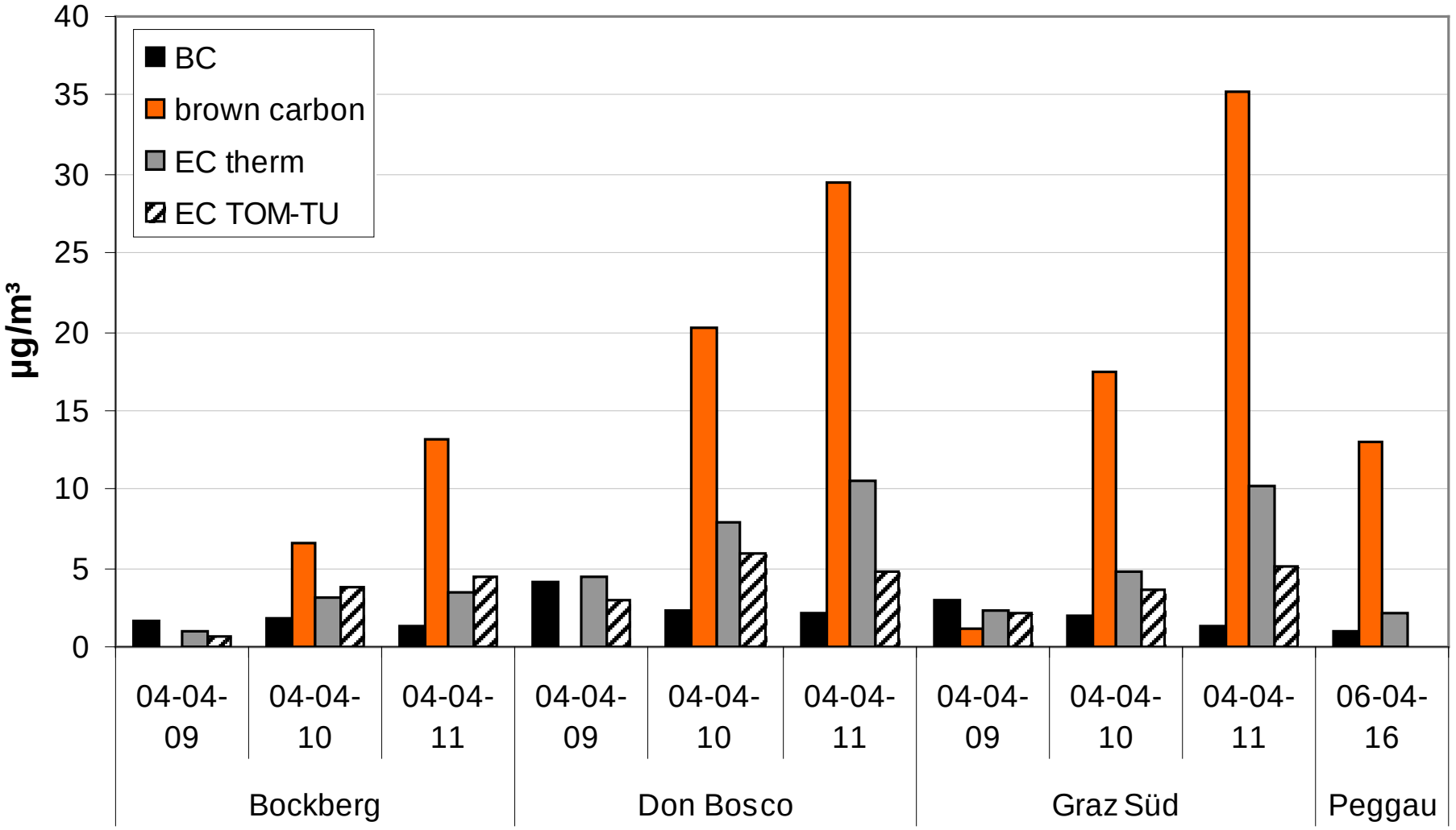
- AQUELLA samples April 2004
  - 24 hr PM10 filters
  - Kerbside → Don Bosco, PM10 mo. av. 38 µg/m³
  - Urban background → Graz Süd
  - Rural → Bockberg, PM10 mo. av. 20 µg/m3

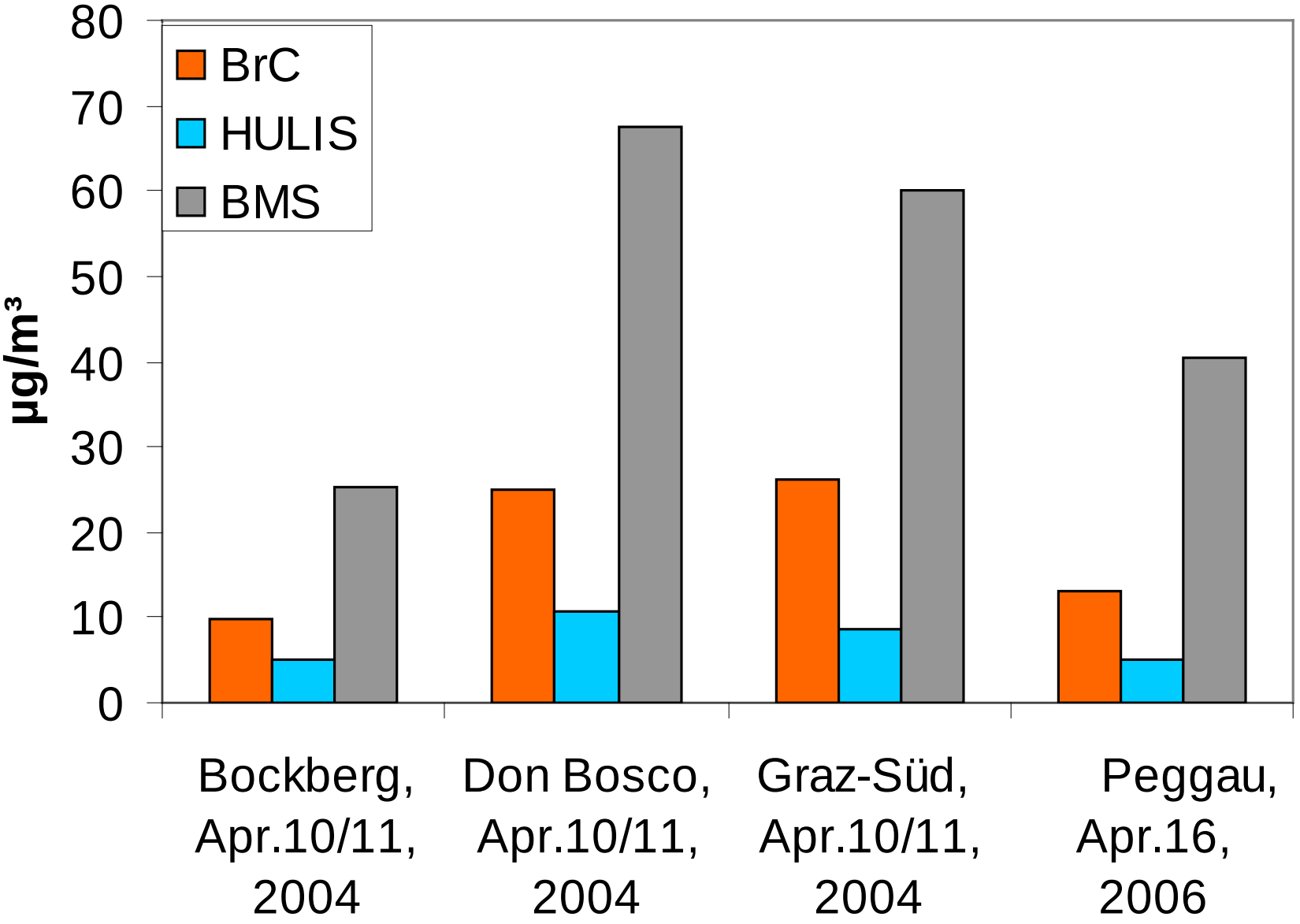
- Easter bonfires
  - PM10 > 100 µg/m³

Concentrations Easter 2004 and 2006

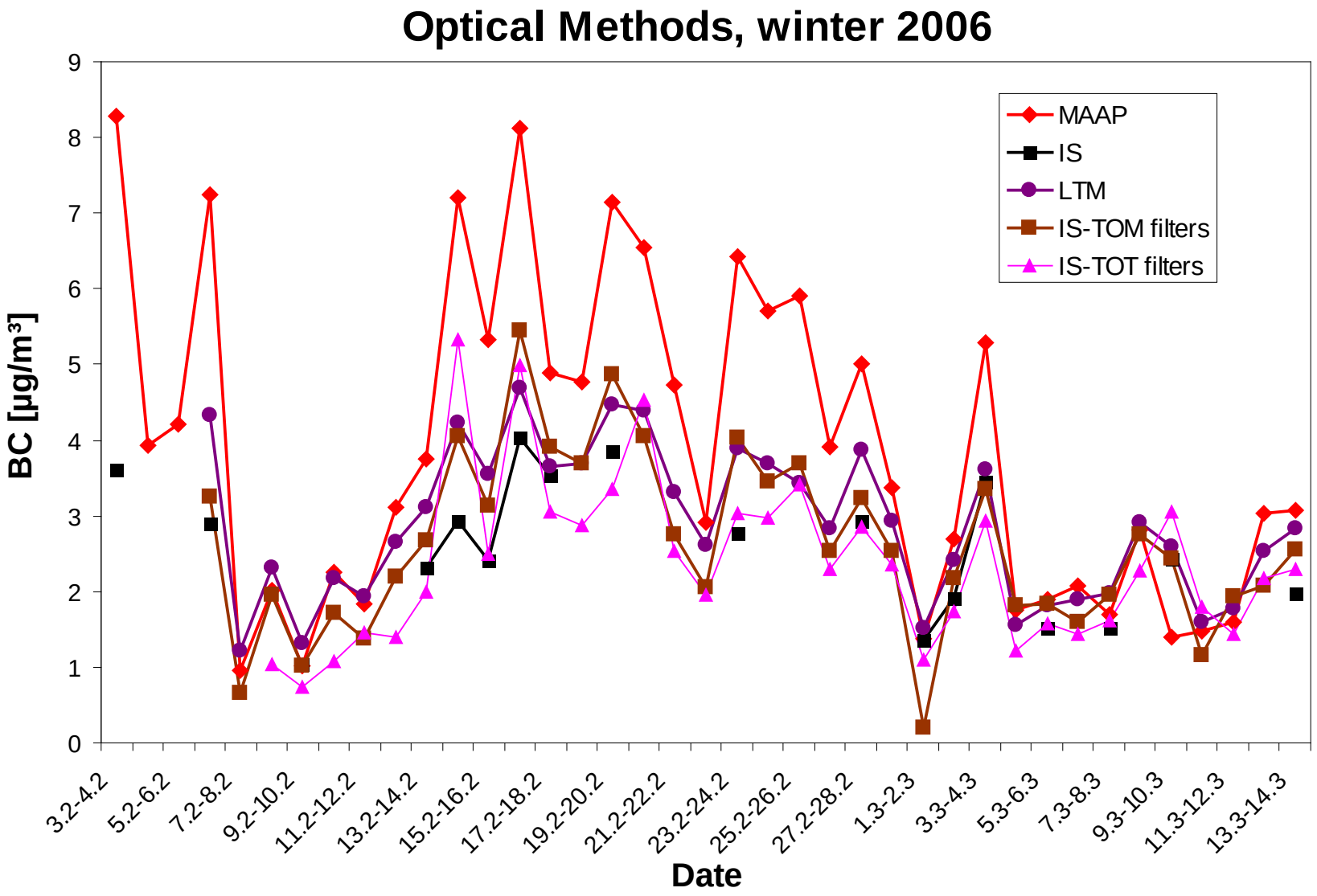


Concentrations Easter 2004 and 2006

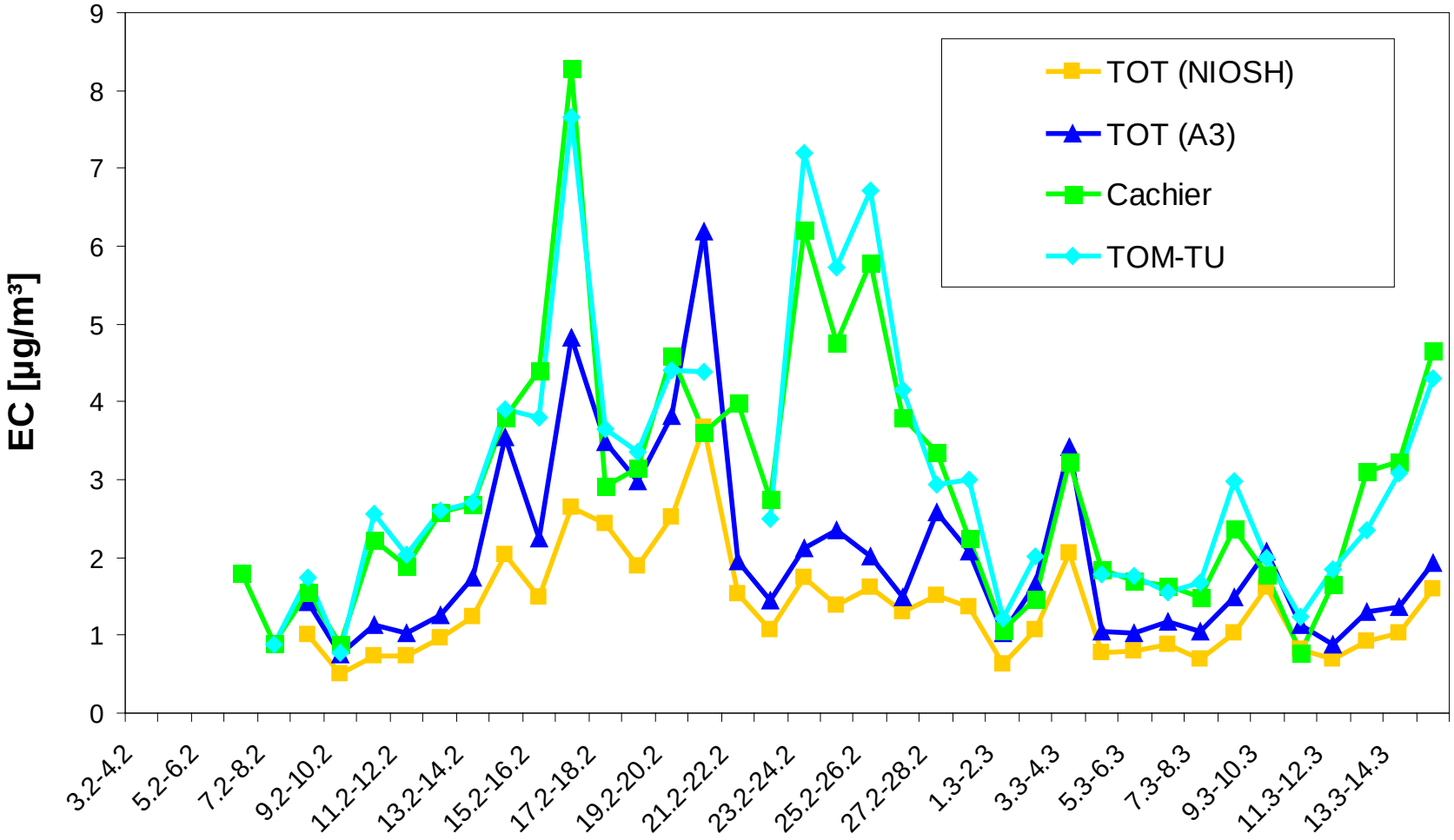


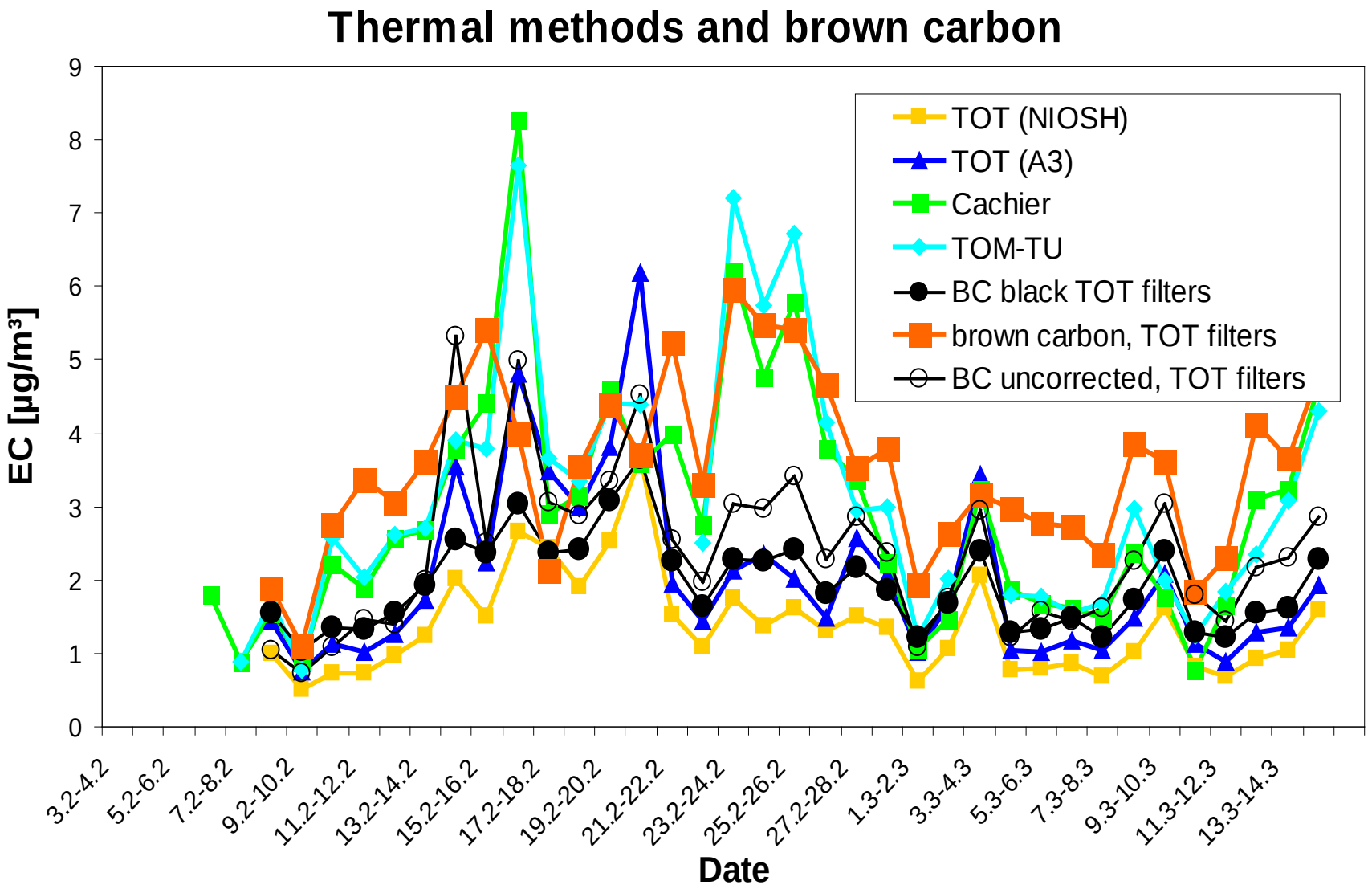

80
70
60
50
40
30
20
10
0
µg/m³
BrC
HULIS
BMS
Bockberg, Apr.10/11, 2004
Don Bosco, Apr.10/11, 2004
Graz-Süd, Apr.10/11, 2004
Peggau, Apr.16, 2006

All data from winter 2006: Reisinger et al.(2008) ES&T 42, 884–889



Thermal methods, winter campaign




Thermal methods and brown carbon
EC [µg/m³]
0
1
2
3
4
5
6
7
8
9
3.2-4.2
5.2-6.2
7.2-8.2
9.2-10.2
11.2-12.2
13.2-14.2
15.2-16.2
17.2-18.2
19.2-20.2
21.2-22.2
23.2-24.2
25.2-26.2
27.2-28.2
1.3-2.3
3.3-4.3
5.3-6.3
7.3-8.3
9.3-10.3
11.3-12.3
13.3-14.3
Date
TOT (NIOSH)
TOT (A3)
Cachier
TOM-TU
BC black TOT filters
brown carbon, TOT filters
BC uncorrected, TOT filters

Conclusions

- BC from IS method corrected for influence of BrC
- Estimation of BrC concentration
- Effect of biomass smoke on EC or BC methods

- But: depends on proxy substances

Acknowledgements

- AQUELLA - Steiermark
- Hochschuljubiläumstiftung der Stadt Wien

EC methods used in AQUELLA

- Cachier method „EC therm“
  - Cachier et al., 1989, Tellus 41B, 379-390
    - Two-step, 2 hrs. 340°C, then 1000°C, O_2
    - Here: no treatment with HCl, CC from soluble Ca
- Thermal-optical method „TOM-TU“
  - 20°C /min, T_{max} = 800°C, O_2
  - Laser transmission for charring correction
  - Jankowski et al., 2008, AE in press

Comparison with other parameters

- HULIS
  - Limbeck et al. 2005, Anal. Chem. 77, 7288-7293
  - HULIS mass = HULIS C * 2
- Biomass smoke mass
  - OC = TC – BC (corrected for BrC)
  - Traffic OC = OC * 0.5
  - Secondary OC: 10 - 20% of OC
  - BSM = (OC – traffic OC) * 1.6 (Schmidl et al., 2008, AE, in press)