



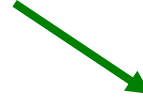
UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO DI FISICA

Review of the methodologies for the
quantification of wood and biomass
burning contributions to PM

Roberta Vecchi
roberta.vecchi@unimi.it

Context

- Biomass/wood combustion has increased and is still increasing in many countries of Europe (especially after the "Biomass Action Plan" launched by the European Commission in 2005)



Pragmatic motivation:

increasing price of fossil fuels

Strategic motivation:

to reduce human carbon footprint
(i.e. GHGs emission)

- At many European locations (also in large urban areas) during wintertime wood burning for residential heating is a relevant PM source impacting on both local and regional air quality -> **an accurate quantification of this source is mandatory**

Open problem: high uncertainties in emission factors, which are highly variable depending upon the type of combustion appliances used, wood type, and the burning conditions



Examples of tracers for Wood Smoke

-Inorganic tracers: stable but very often not specific due to additional sources

(e.g. soil dust, sea spray, meat cooking, incinerators emissions, industrial emissions,...)

- Fine particle water-soluble K (K⁺)
- Zn, Rb, S, halogens (Cl, Br, I)
- BC

- Organic tracers: atmospheric stability sometimes debatable

- Anhydrosugars, i.e. Levoglucosan, Mannosan, Galactosan (cellulose, hemicellulose combustion)
- Methoxyphenols (lignin comb.), diterpenoids (conifers, angiosperm comb.), PAHs, and many others...

e.g. about 50 listed in the review

by Simoneit (2002)

B.R.T. Simoneit / Applied Geochemistry 17 (2002) 129–162

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Table 1
Major biomarker tracers in smoke from biomass burning

Compound	Structure	Composition	MS key ions ^a	Indicator for source
Anisic acid (p-methoxy-benzoic acid)	V	C ₈ H ₈ O ₃	224, 209, RT ^b	Gramineae lignin
Vanillic acid	II	C ₈ H ₈ O ₄	73, 267, 297, 312 ^b	Lignin
Syringic acid	IV	C ₉ H ₁₀ O ₅	73, 312, 327, 342 ^b	Angiosperm lignin
Matairesinol	VII, R = O	C ₂₀ H ₂₂ O ₆	73, 179, 209, 502 ^b	Conifer lignin ^c
Shonanin	VII, R = H ₂	C ₂₀ H ₂₄ O ₅	73, 179, 209, 488 ^b	Conifer lignin ^c
Divanillyl	VIII	C ₁₆ H ₁₈ O ₄	73, 209, 267, 403, 418 ^b	Lignin dimer
Divanillylmethane	IX	C ₁₇ H ₂₀ O ₄	73, 209, 417, 432 ^b	Lignin dimer
Divanillylethane	X	C ₁₈ H ₂₂ O ₄	73, 209, 446 ^b	Lignin dimer
Vanillylsyringyl	XI	C ₁₇ H ₂₀ O ₅	73, 209, 239, 448 ^b	Angiosperm lignin dimer
Disyringyl	XII	C ₁₈ H ₂₂ O ₆	73, 209, 239, 478 ^b	Angiosperm lignin dimer
Dianisyl	XIII	C ₁₆ H ₁₈ O ₂	121, 242	Gramineae lignin dimer
Levo glucosan	XIV	C ₆ H ₁₀ O ₅	73, 204, 217, 333, 378 ^b	Cellulose
Mannosan	–	C ₆ H ₁₀ O ₅	73, 204, 217, 333, 378 ^b	Hemicellulose
Galactosan	–	C ₆ H ₁₀ O ₅	73, 204, 217, 363, 378 ^b	Hemicellulose
1,4:3,6-Dianhydro-β-D-glucopyranose	–	C ₆ H ₈ O ₄	69, 98, 144	Cellulose



About the Levoglucosan stability

In recent years, some authors have risen concerns about levoglucosan atmospheric stability because of:

- degradation at high OH concentrations (*e.g. Hennigan et al. 2010*)
- degradation in high relative humidity conditions (*e.g. Hoffmann et al. 2010*)
- degradation during air masses ageing (*e.g. Lai et al. 2014*)

➔ atmospheric lifetime of levoglucosan typically estimated to be **10.6 days** (*Kessler et al. 2010*) but a recent assessment reports **1.2-3.9 days** under different conditions (*Lai et al. 2014*).

Therefore, levoglucosan can be considered a good tracer if the **receptor site is close to the source** and the above-mentioned conditions are of little relevance.

It is noteworthy that very recent experiments (*Lai et al., 2014*) show that compounds like $(\text{NH}_4)_2\text{SO}_4$ or NaCl internally mixed with levoglucosan prominently inhibits the degradation of levoglucosan.



The macro-tracer approach

Introduced for wood burning during the AQUELLA project in Austria (*Schmidl et al. 2008*).

It uses a numerical factor for each specific compound in each source of interest to estimate the contributions of individual sources.

$$\text{wood smoke OC} = \text{Levoglucosan} \times 6.1$$

Softwood vs hardwood

$$\text{wood smoke OM} = \text{Levoglucosan} \times 9.1$$

$$\% \text{spruce} = (14.8 - R_{\text{levo/manno}}) / 0.112$$

$$\text{wood smoke PM} = \underbrace{\text{Levoglucosan}}_{\text{tracer}} \times \underbrace{10.7}_{ER_{\text{wb}}}$$

(*Caseiro et al. 2009*)

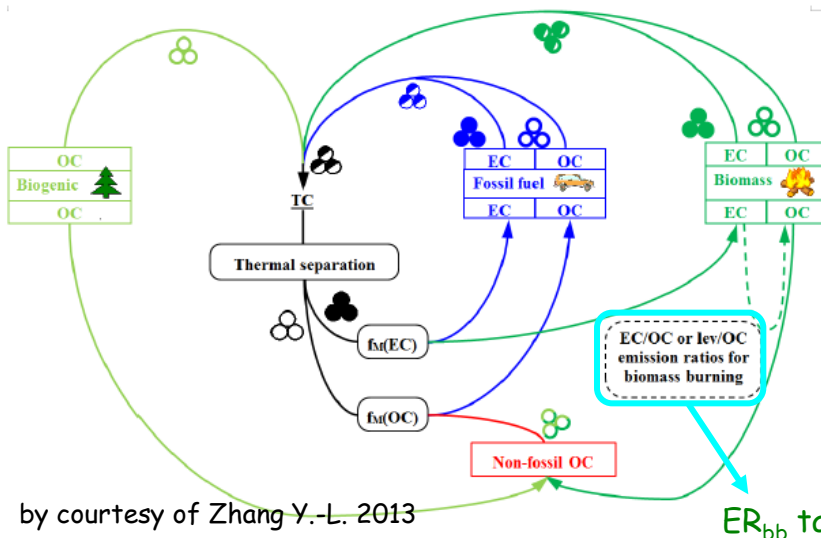
ER_{wb} : emission ratio experimentally determined on wood species burned in Austria

Example for Austria
with levoglucosan
(*Schmidl et al. 2008*)

Example for Switzerland with radiocarbon:

based on the assumption that biomass burning is the only non-fossil source of EC

-> effectiveness of size-resolved source apportionment of carbonaceous components based on ^{14}C determined in OC, EC, WSOC, WINSOC fractions (*Szidat et al. 2006*)

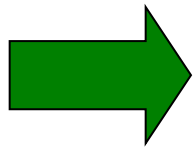


ER_{bb} taken as average value from the literature



Major requirements for the macro-tracer approach:

1. The tracer is ideally emitted by only 1 source
2. Knowledge of emission ratios from wood burning in the study area
 - > information on emission ratios (ER) not always available
 - > ad-hoc and/or ambient measurements of ER challenging
 - > high variability in ER in relation to wood type, burning appliances and combustion conditions



the "improved" macro-tracer approach

using "tailored" emission factors *(Piazzalunga et al. 2011)*

- a) an average emission factor was calculated from literature data (using only those data reporting the tree species of interest) and **weighed by the percentage of wood types felled in the investigated area** (i.e. Lombardy, Italy)
- b) "real world" emission factors were derived **from the PMF chemical profile** resolved for the wood burning source at the investigated site



Results from tailored emission factors

	Levo/PM ($\mu\text{g}/\mu\text{g}$)	Levo-C/OC ($\mu\text{g}/\mu\text{g}$)	Levo/Manno ($\mu\text{g}/\mu\text{g}$)	OC/EC ($\mu\text{g}/\mu\text{g}$)
Emission factors taken from the literature				
<i>n. data</i>	62	74	68	62
<i>average</i>	0.113 \pm 0.070	0.100 \pm 0.067	13.7 \pm 15.0	14.0 \pm 19.0
Weighed emission factors				
<i>n. data</i>	9	9	9	9
<i>weighed average</i>	0.096 \pm 0.005	0.075 \pm 0.004	8.1 \pm 0.5	6.5 \pm 0.4
PMF-derived emission ratios				
<i>wood burning source</i>	0.059 \pm 0.012	0.082 \pm 0.016	10.2 \pm 2.0	5.5 \pm 1.1

table adapted from Piazzalunga et al. (2011)

with EF taken from literature - although weighed for specific wood species - the entire PM_{wb} mass seems to be accounted for by OM ($\text{PM}/\text{OC} \approx 2$).

Major finding: PM_{wb} could be largely underestimated when using literature wood smoke emission factors, which do not consider correctly the water uptake and the ageing of wood burning aerosol.

The ambient mono-tracer approach

Very recently introduced (Herich et al. 2014), it uses published results on EC_{wb} , OC_{wb} , and PM_{wb} obtained by different SA approaches (e.g. macro-tracer method, multivariate RM, CMB, Aethal.-method) to estimate representative relationships between them and wood burning tracers measured at a location (i.e. levoglucosan and mannosan).



Using CMB for WB source apportionment: the role of profiles

1. Due to differences in EC-OC concentrations using different thermal protocols, it is mandatory to use profiles which were obtained using the same experimental methods applied to the receptor samples.

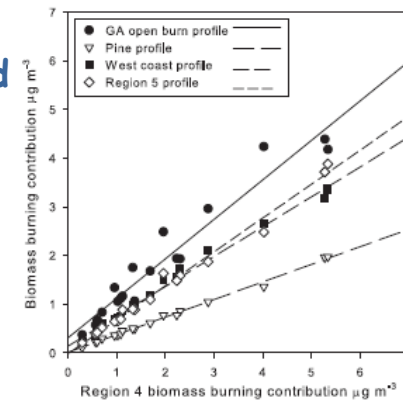
E.g. in *Favez et al. (2010)* the most representative profile for the alpine area under investigation was discarded because of large EC overestimation due to different experimental methodologies used for EC-OC determination.

2. Source profiles sensitivity tests in CMB modelling by *Sheesley et al. (2007)* showed that

a) 5 different biomass burning profiles (*Fine et al., 2001, 2002, 2004; Schauer et al., 2001; Lee et al. 2005*) resulted in different biomass contributions with a **standard deviation of the annual averages just a little over 30%**

b) Choosing **geographically relevant profiles** is more important than the burning method for the CMB modelling

c) The choice of biomass burning profile **impacted the model output for traffic sources** due to the influence of PAHs and EC



CMB for WB source apportionment: the role of profiles with organic markers

Table 3. Fitting species^a used in CMB modeling for Fresno winter intensive samples.

Traditional species	Organic species
NO ₃ ⁻	Indeno[123-cd]pyrene (INCDPY)
SO ₄ ²⁻	Benzo(ghi)perylene (BGHIPE)
NH ₄ ⁺	Coronene (CORONE)
Na ⁺	17a(H),21b(H)-29-Hopane (HOP17)
K ⁺ (soluble K)	Levoglucosan (LEVUG)
OC3	Syringaldehyde (SYRALD)
OC4	Palmitoleic acid (PALOL)
OC	Oleic acid (OLAC)
EC2	Cholesterol (CHOL)
EC3	Norfarnesane (NORFAR)
EC	Farnesane (FARNES)
Al	Norpristane (NORPRI)
Si	Pristane (PRIST)
Cl	Phytane (PHYTAN)
K (total K)	
Fe	
Se	
Br	
Pb	

Results of tests undertaken by *Chow et al. (2007)* with and without the inclusion of organic markers in the profiles used for source apportionment show that organics were not relevant for obtaining the best solution

Table 4. Source contribution estimates from the CMB trial runs for average Fresno winter intensive samples during the early morning (00:00–05:00 PST) period, with and without organics for various source mixes.

Case	PVRD	GAS	DIES	Source contributions ($\mu\text{g}/\text{m}^3$)								
				BURN-H	BURN-S	COOK	MARINE	AMSUL	AMNIT	PCMASS	R.SQR	CHI.SQR
1 ^a	0	1.9±1.3	6.6±2.2	16±3	5.8±6.2	20±5	0	1.1±0.4	18±2	92	0.96	0.6
2 ^b	0	0	7.1±2.3	15±3	7.0±6.4	23±6	0	1.3±0.3	18±2	94	0.98	0.7
3 ^a	0	2.2±1.4	7.6±2.2	18±2	–	21±6	0	1.1±0.4	18±2	89	0.96	0.6
4 ^b	0.04±0.3	0	8.5±2.2	17±2	–	25±6	0	1.3±0.4	18±2	91	0.97	0.7
5 ^a	0	1.0±0.9	3.0±1.6	–	37±3	23±5	0.49±0.12	1.3±0.3	18±2	110	0.88	3.0
6 ^b	0	0	3.2±1.6	–	36±3	24±6	0.49±0.12	1.4±0.3	18±2	109	0.91	4.1
7 ^a	0	2.4±1.4	8.2±2.4	19±3	10±6	–	0	1.0±0.4	18±2	77	0.92	1.2
8 ^b	0	30±7	0	18±2	0	–	0.05±0.20	0	17±2	85	0.97	0.4

a With organics.
b Without organics.

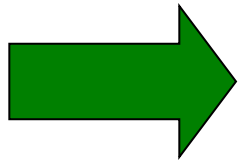
Indeed, organics were NOT required to estimate hardwood contributions and did not increase the precision of softwood burning contribution.

Water soluble K⁺ resulted to be the most suitable WB tracer but did not allow the distinction between hard- and soft-wood contributions.



Multivariate analysis for WB source apportionment: the role of levoglucosan

Opposite to CMB, in PMF studies the use of K^+ (or K) as tracer for WB was not always effective to unambiguously resolve the wood burning source (especially in PM₁₀) as it is emitted also by other sources (e.g. soil dust resuspension, sea spray, meat cooking, refuse incinerators,...).



attempts to estimate the fraction of potassium from biomass

burning; e.g. using relationships between K and other elements

(e.g. Miranda et al. 1994; Pio et al., 2008; Pachon et al. 2013).

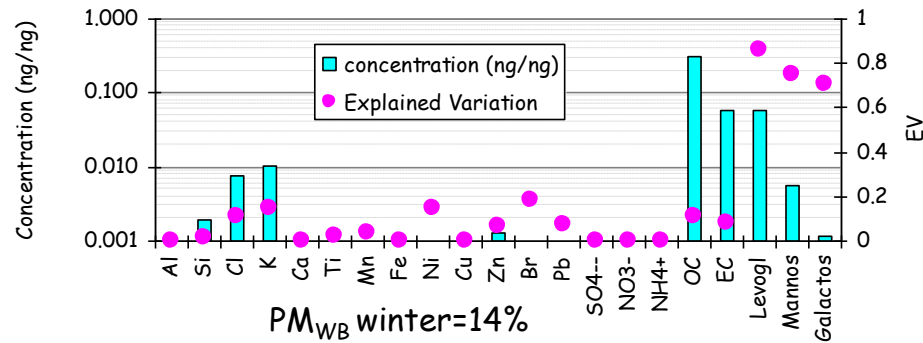
In most cases, when levoglucosan is introduced as input variable in multivariate analysis the WB source is more clearly resolved and the source apportionment is improved.



1) The case of Milan

In many cases levoglucosan effectively resolved the wood burning source and PMF gave levoglucosan-to-OC ratios in very good agreement with literature ones.

Wood Burning - PM10
Milan 2006



$$\langle \text{Levoglucosan} \rangle_{\text{winter}} = 940 \pm 560 \text{ ng/m}^3$$

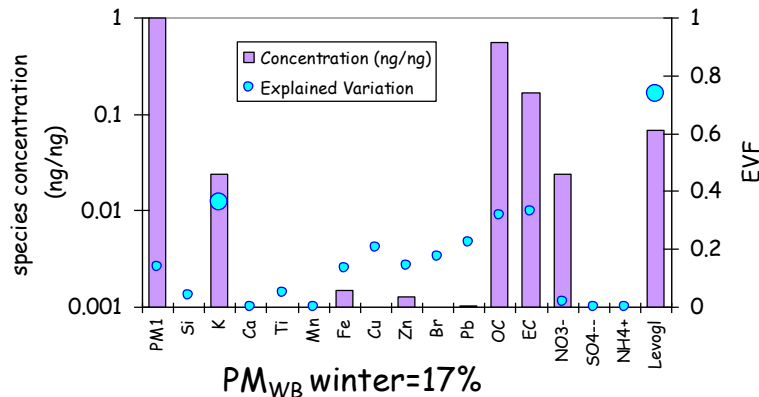
$$\text{from PMF profiles: Levo/OC} = 0.19 \pm 0.02$$

(Bernardoni et al. 2011)

Noteworthy that before including levoglucosan the wb source was not clearly identified

(Vecchi et al. 2008)

Wood burning - PM1
Milan, winter 2012



$$\langle \text{Levoglucosan} \rangle_{\text{winter}} = 520 \pm 400 \text{ ng/m}^3$$

$$\text{from ME-2 profiles: Levo/OC} = 0.13 \pm 0.03$$

(Vecchi et al., paper in preparation)

Noteworthy higher EV for K in PM1

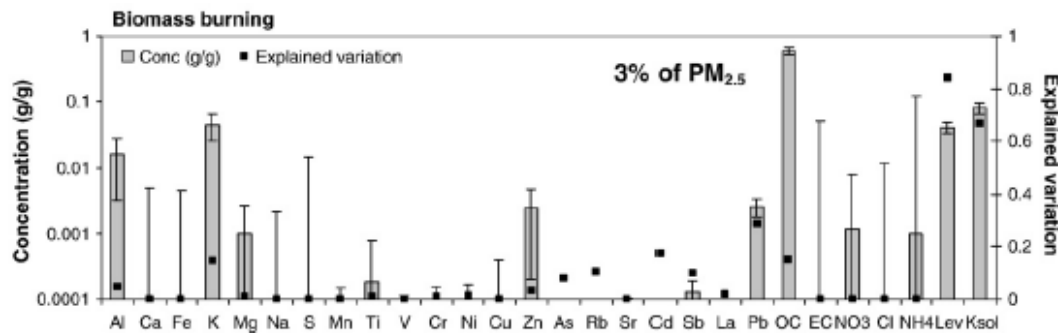
(indeed $K^+/K=0.92$ $R^2=0.96$)



2) The case of Barcelona

Constrained ME-2 was applied by *Reche et al. (2012)* to PM1, PM2.5, PM10 datasets but without levoglucosan and K⁺ the biomass burning source was not identified.

It is noteworthy that the biomass burning source identification was possible only after imposing the levoglucosan/OC target ratio (0.16 ± 0.01) and upper/lower limits for NH₄⁺, K⁺ and OC



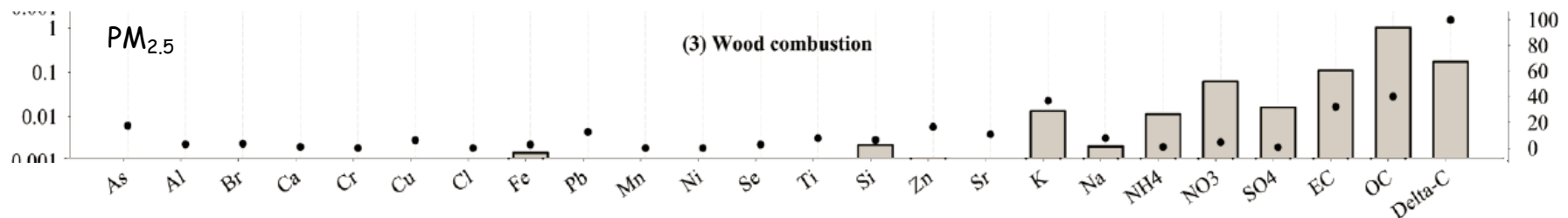
$$\langle \text{Levo} \rangle_{\text{winter}} = 60 \pm 40 \text{ ng/m}^3$$

In this case, levoglucosan was not very useful as input variable but it was helpful for imposing a constraint in ME-2 to resolve the bb source

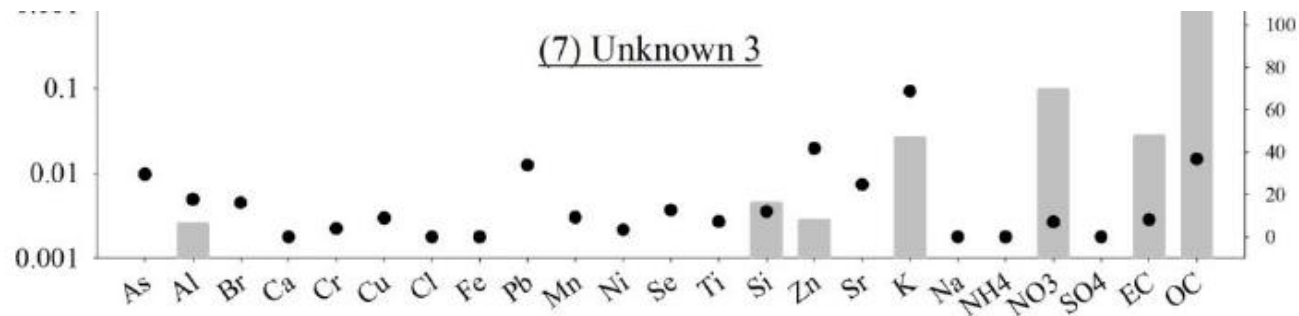


PMF incorporating Delta-C as a variable

In PMF the so-called $\Delta C = UVBC_{370nm} - BC_{880nm}$ signal (from the 2-wavelength Aethalometer) has been suggested to serve as an indicator of wood burning particles. Noteworthy that it is NOT a direct quantitative measurement of mass concentration (e.g. Wang et al. 2011).

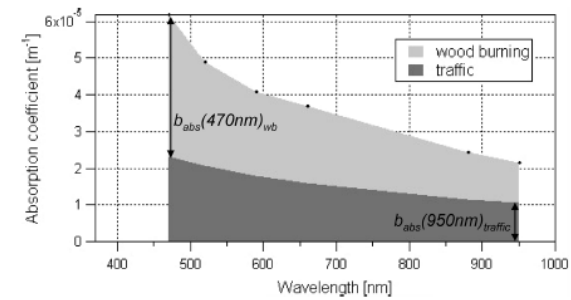


PMF could not effectively resolve wood combustion when removing Delta-C from the input dataset (Wang et al. 2013).



The Aethalometer-model

Originally based on the difference in light-absorption of wood burning and traffic emitted particles (*Sandradewi et al. 2008*).



This methodology provides carbonaceous matter apportionment between fossil fuels and wood combustion with known Ångström exponents (e.g. $\alpha_{ff} \approx 1$ $\alpha_{wb} \approx 2$) and measurements of the absorption coeff. $b_{abs,\lambda}$ at 2 wavelengths by an Aethalometer.

Source Apportionment : cf. *Sandradewi et al., ACPD, 2008*

Favez et al., ACP, 2010

$$CM_{total} = BC + OM$$

$$b_{abs, \lambda} = b_{abs, ff, \lambda} + b_{abs, wb, \lambda}$$

$$\frac{b_{abs, ff, 470 \text{ nm}}}{b_{abs, ff, 950 \text{ nm}}} = \left(\frac{470}{950}\right)^{-\alpha_{ff}}$$

$$\frac{b_{abs, wb, 470 \text{ nm}}}{b_{abs, wb, 950 \text{ nm}}} = \left(\frac{470}{950}\right)^{-\alpha_{wb}}$$

$$BC_{Aethalo.} + OM_{AMS} = \frac{C_1 \times b_{abs, 950nm, ff}}{\{BC+OM\}_{fossil \ fuel}} + \frac{C_2 \times b_{abs, 470nm, wb}}{\{BC+OM\}_{wood \ burning}} + \frac{C_3}{\{OM\}_{other}}$$

Assumptions: - $\alpha_{fossil \ fuel} = 1$, $\alpha_{wood \ burning} = 2$ et $C_1 = 260000$

- No light absorption by dust aerosols

- $BC_{fossil \ fuel} \approx BC_{total} \times (b_{abs, 950nm, ff} / b_{abs, 950nm, total})$

→ $BC_{ff}, BC_{wb}, OM_{ff}, OM_{wb}, OM_{other}$ taken from *Favez et al., SA workshop, JRC 2010*

Recently, this approach has been extended to apportion wood burning at locations where only **daily filters** are collected as far as they are properly analysed for light-absorption at multiple wavelengths in the lab (*Massabò et al., 2013*).



...about the Aethalometer-model and the use of Delta-C...

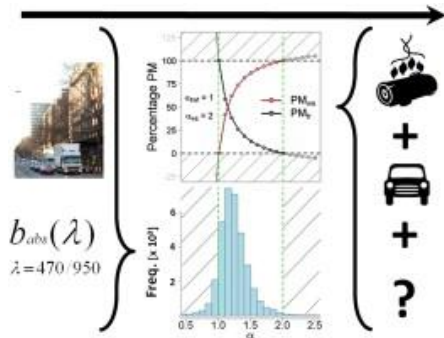
Recently, some issues have been raised about the reliability of the "optical approaches" for PM apportionment (e.g. Harrison et al., 2013):

a. Delta-C is not a chemical material and its seasonal variation is more similar to BC than to other wb tracers;

b. The 2-components hypothesis it's an oversimplification;

c. The detection of UV-specific absorption cannot be directly related to a specific wood burning component as for example PAHs, HULIS, and coal absorb in the UV range at different extent;

d. Results are very sensitive to the choice of α -value



Harrison et al. (2013)

Table 2
Summary of the effect of changing α_{road} & α_{wb} on PM_{road} and PM_{wb} ($\mu\text{g m}^{-3}$).

Harrison et al. (2013)

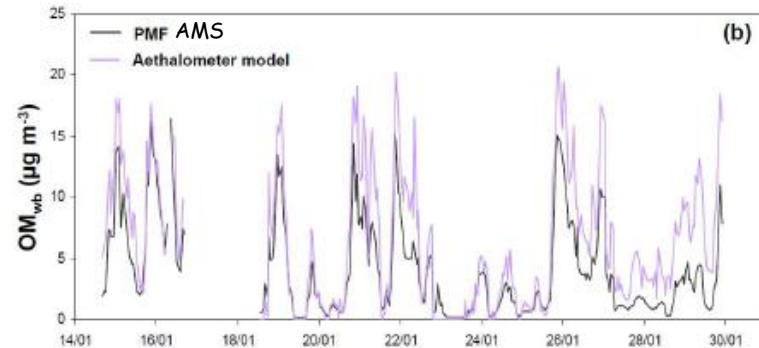
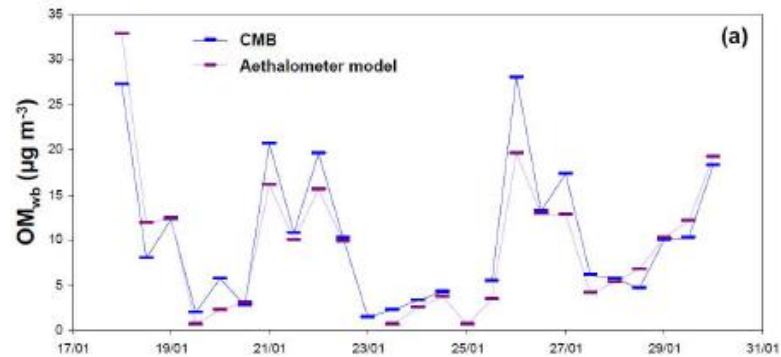
α_{road}	α_{wb}	C_1	Budbrooke		EROS		NK2010		NK2011	
			CM _{traffic}	CM _{woodsmoke}	CM _{traffic}	CM _{woodsmoke}	CM _{traffic}	CM _{woodsmoke}	CM _{traffic}	CM _{woodsmoke}
1.07	2.0	1.49	2.13	1.83	1.85	0.61	3.63	0.26	4.03	1.68
1.10	1.8	1.50	2.35	1.62	2.11	0.35	4.21	-0.33	4.56	1.13
1.00	1.8	1.53	1.33	2.63	1.19	1.26	2.37	1.49	2.58	3.10
1.00	2.0	1.52	1.42	2.54	1.24	1.22	2.43	1.45	2.69	3.00
1.00	2.2	1.51	1.49	2.47	1.27	1.19	2.47	1.40	2.78	2.92
0.9	2.0	1.53	0.60	3.37	0.52	1.95	1.02	2.86	1.13	4.58
1.1	2.0	1.50	2.45	1.50	2.14	0.33	4.18	-0.30	4.65	1.05
0.8	2.2	1.54	-0.08	4.03	-0.07	2.53	-0.13	4.01	-0.15	5.84

Note: CM is carbonaceous matter (equivalent to PM) as in Equations (3) and (4).

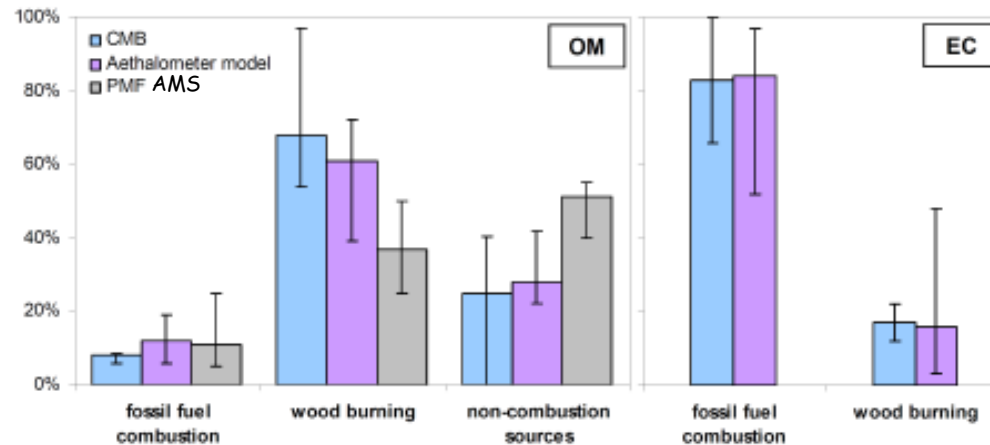


...nevertheless...from *Favez et al. (2010)*

Inter-comparison results from different methodologies gave a fair agreement in OM_{wb} temporal variations



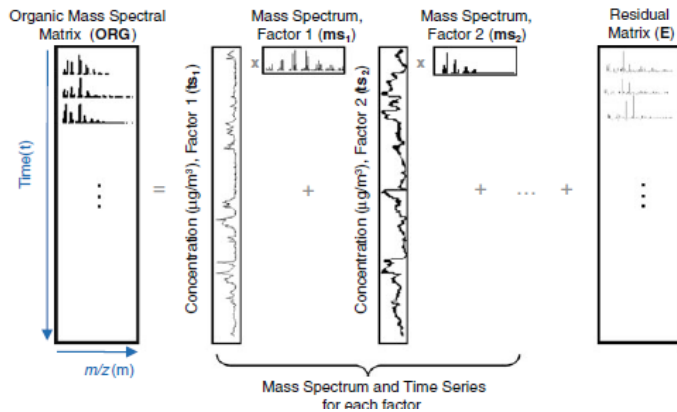
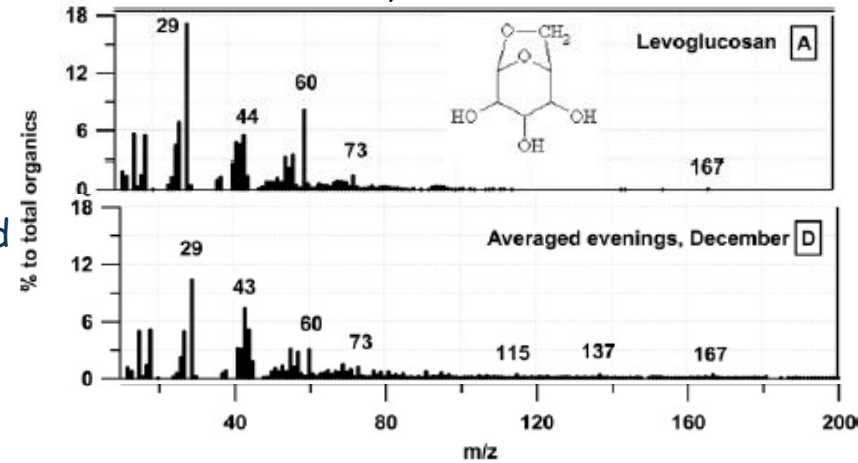
...although OM_{wb} contributions show discrepancies...



The AMS-approach

Mass spectral signature of ambient organic aerosol from wood burning mainly related to m/z 60 (but also m/z 29 and 73 used as can be ascribed to anhydrosugars fragmentation)

(adapted from Alfarrar et al. 2007)



PMF very often used for apportioning the measured organic mass spectra (e.g. Zhang et al. 2011).

PMF not always effective in resolving multiple sources because of large co-variance of the sources due to the meteorology and to the little variation in relative source contributions (e.g. at rural and remote sites but also at urban locations, Lanz et al. 2008)

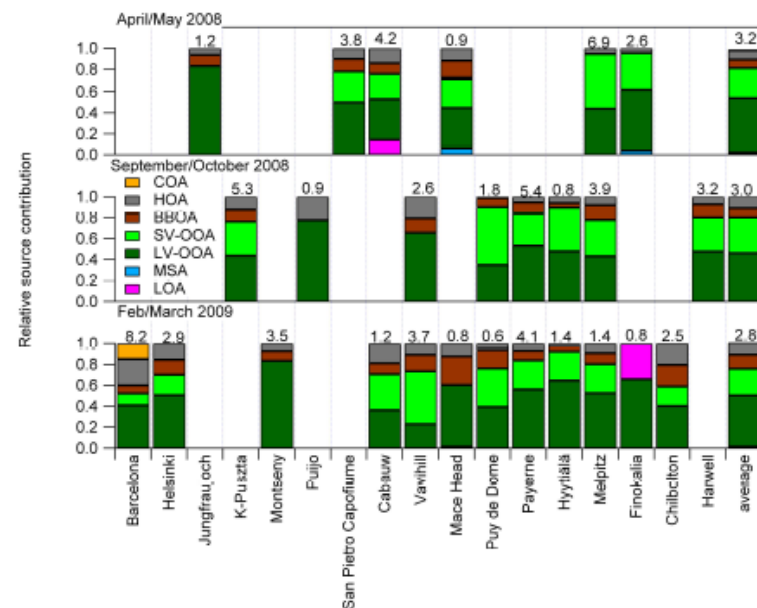


The improved AMS-approach

Constrained ME-2 providing a priori factor profiles for some or all of the expected factors was successfully implemented (e.g. SoFi tool at PSI, *Canonaco et al. 2013*).

A standardised ME-2 source apportionment strategy has been introduced by *Crippa et al. (2013)* and applied to 25 AMS datasets across Europe (EUCAARI-EMEP data) overcoming limitations previously shown by unconstrained PMF

The BBOA reference mass spectrum was the one introduced by *Ng et al. (2011)* as considered representative of average ambient biomass burning conditions.



...in summary...

1. Wood burning emission profiles are still an issue in source apportionment methods; literature works suggest that:
 - “real world” profiles could be a better choice but they are still challenging
 - choosing geographically relevant profiles is important in CMB modelling
2. The choice of wood burning tracers depend also on the modelling approach; e.g.
 - K^+ in PM_{fine} it's ok in CMB not always effective in PMF
 - organics not relevant for CMB but often very useful in multivariate analysis
3. Constrained factor analysis can be effective in resolving the wood burning source in cases where PMF has limitations (e.g. Barcelona case, AMS datasets at rural sites)



Thank
You!



roberta.vecchi@unimi.it



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