Supplementary materials

1. Time coverage of measurements

Table S1 lists the time coverage of data at the nine considered sites. Time resolution is defined as the time elapsed between two following measurements of EC mass concentration (m_{EC}), in days, and absorption coefficient (σ_{ap}), in hours, according to the specifications of the EBAS database. During the data analysis, absorption coefficient data were averaged to match the sampling time of EC mass concentration measurements. With "number of simultaneous measurements" we indicate the number of points when both m_{EC} and σ_{ap} were available.

Table S1
Data availability for the 9 sites presented in this work.

Site (Country)		Station code	Start time (month/year)	End time (month/year)	m_{EC} time resolution (days)	σ_{ap} time resolution (hours)	Number of simultaneous measurements
Aspvreten	(SE)	APT	01/2010	12/2011	3	1	223
Birkenes	(NO)	BIR	03/2010	12/2011	7	1	92
Finokalia	(GR)	FKL	02/2008	11/2010	2-4	1	168
Harwell	(GB)	HRL	01/2010	12/2010	1	1	200
Ispra	(IT)	IPR	09/2008	12/2011	1	1	1050
Melpitz	(DE)	MEL	01/2008	12/2011	1	1	874
Montseny	(ES)	MSY	01/2009	12/2011	1-4	1	228
Puy de Dôme	(FR)	PUY	01/2008	12/2010	4-7	1	95
Vavihill	(SE)	VAV	01/2010	12/2011	3	1	93

The study concerning the relation between mixing state and MAC, discussed in Section 3.4, is based on a shorter and less extended dataset composed by measurements acquired only in 2010 at 5 sites including Birkenes, Harwell, Ispra, Melpitz and Montseny. This was due to the limited availability of simultaneous measurements of the absorption coefficient and mass concentration of EC and NAM. A summary of the time coverage of this subset of all data is given in TableS2.

TableS2
Data availability for the 5 sites for which the relation between MAC and mixing state was assessed.

Site (Country)	Station code	Start time (month/year)	End time (month/year)	EC and NAM time resolution (days)	σ_{ap} time resolution (hours)	Number of simultaneous measurements
Birkenes (NO)	BIR	03/2010	12/2010	7	1	43
Harwell (GB)	HRL	01/2010	12/2010	1	1	200
Ispra (IT)	IPR	01/2010	12/2010	1	1	345
Melpitz (DE)	MEL	01/2010	12/2010	1	1	170
Montseny (ES)	MSY	01/2010	12/2010	4	1	62

2. Comparison of parallel EC mass measurements using the VDI-2465 and EUSAAR-2 protocols at Melpitz

Figure S1 shows the monthly statistics of the ratio between EC mass concentrations measured in parallel with the VDI-2465 (thermal) and EUSAAR-2 (thermal-optical) methods at the Melpitz site in 2012. This ratio varies in time because it depends on the composition of the aerosol (Cavalli et al., 2016), but it exhibits a clear seasonal pattern due to the typical seasonal characteristics of aerosol composition at Melpitz. Therefore, the monthly median ratios are shown in Figure S1, which are defined to be the correction factor CF_{VDI} as a function of “month of year”, form the basis to adjust VDI-2465 based EC mass measurements to EUSAAR-2 equivalent EC mass values, as detailed in Section 2.3.1 of the main manuscript.

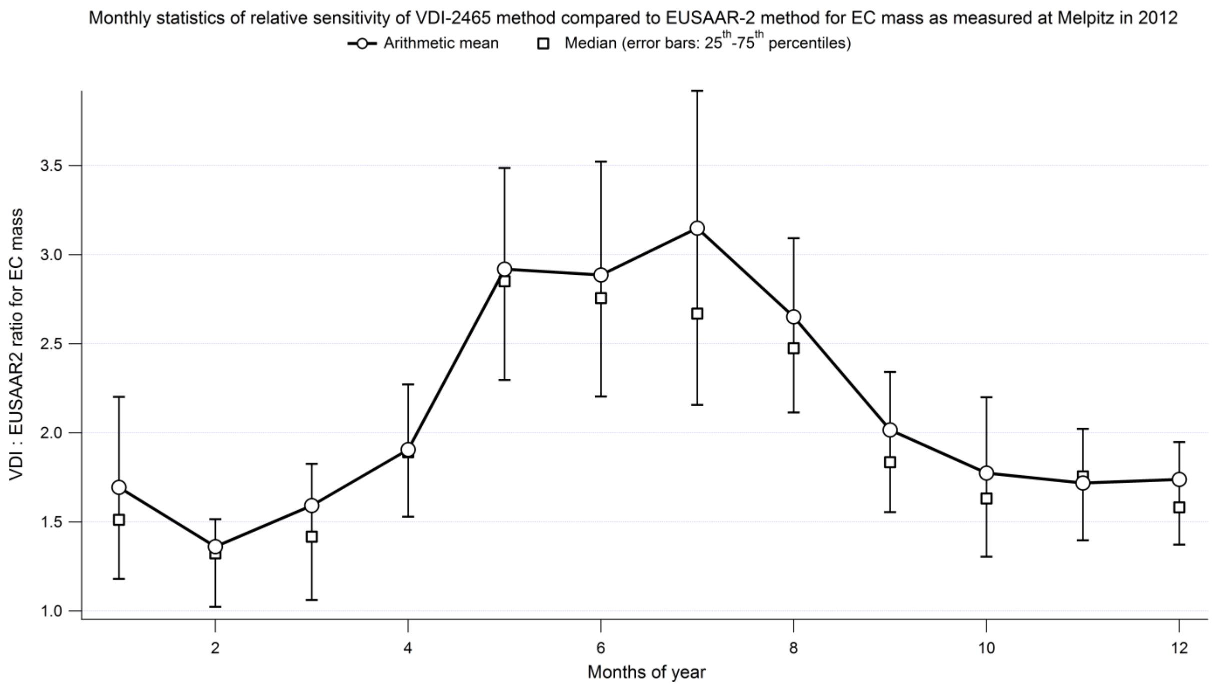

Figure S1. Seasonal pattern of the ratio between EC mass concentrations measured in parallel with the VDI-2465 (thermal) and EUSAAR-2 (thermal-optical) methods at the Melpitz site in 2012.

3. MAC versus NAM:EC - sensitivity analysis

The measured MAC was shown to depend on the measured NAM to EC ratio (NAM/EC) for most stations for which also the composition data were available (Figure 6b). However, the EC mass concentration appears as the denominator in the formulae to calculate both the MAC value and NAM/EC. Therefore, random noise in the EC mass measurement does change the dependence of MAC on NAM/EC to more positive (or less negative) gradients. Here we use Monte-Carlo simulations to assess whether this artefact caused by random measurement noise can potentially explain the observed dependence of the MAC value on NAM/EC by means of the example data set from Ispra in 2010. Figure S2 shows the observations from Ispra, which suggest a dependence of the MAC on NAM/EC (source data corresponding to the aggregated values shown in Figure 6b). In the following, we simulated three case studies in which we try to reproduce these observations with different assumptions on the true MAC values and random measurement noise.

The geometric standard deviation (gSD) of the random measurement noise of single EC measurements is expected to be ≤1.20 (Cavalli et al., 2016). Thus, we made the following primary assumption for the first Monte Carlo simulation (case 1):

- The random noise of the EC measurements has a gSD of 1.20.

- The “true MAC values” depend systematically on NAM/EC (linear trend with some random variability superimposed).

We optimized all free parameters under these boundary conditions until the observations were reproduced as well as possible (the free parameters are: geometric mean and gSD of the true EC, geom. mean and gSD of true NAM/EC, geom. mean and gSD of the true MAC, gradient of true MAC as a function of true NAM/EC, gSD of random measurement noise of NAM and of absorption coefficient). The synthetic data of the Monte Carlo simulation for case 1 are shown in Figure S3. This simulation reproduces the observations well (note: the variability of the simulated measurements is equal to that of the measurements; however, the graphical visualization makes it appear larger than it actually is because a total of 10^5 points are simulated). The key result is that the “measured” slope of MAC vs NAM/EC hardly differs from the prescribed “true” slope (Figure S3b) for an EC measurement noise at the upper limit of expectations. This indicates that the random measurement noise in EC is not an issue for the observations in Ispra, if it has a gSD≤1.20.

The second Monte Carlo simulation, case 2, aims at assessing how much artificial dependence of MAC on NAM/EC can be caused by the maximally expected random noise in the EC measurement if there was no such dependence in the actual aerosol properties. For this purpose we make the following primary assumptions for the Monte Carlo simulation:

- The “true MAC values” do not systematically depend on NAM/EC, while some random variability is possible.
- The random noise of the EC measurements has a gSD of 1.20.

All free parameters were again varied under these boundary conditions trying to achieve the best agreement between observation and simulation. It is possible to reproduce most observations well (e.g. Figure S4c) with reasonable assumptions on the true variability of the MAC value (Figure S4a) and the other parameters. However, the trend of the “measured MAC” versus “measured NAM/EC” in the case 2 simulation is much smaller than the observed trend (Figure S4b). This further supports the conclusion from the case 1 simulation that the maximally expected random noise in the measured EC is insufficient to artificially cause the observed dependence of MAC on NAM/EC if there was not any such trend in the actual aerosol properties.

The third Monte Carlo simulation, case 3, aims at assessing how much random noise in the EC measurement would be required to artificially cause the observed dependence of MAC on NAM/EC if there was no such dependence in the actual aerosol properties. For this purpose we make the following primary assumptions for the Monte Carlo simulation:

- The “true MAC values” do not systematically depend on NAM/EC, while some random variability is possible.

- The random noise of the EC measurements is increased as much as needed to artificially cause the observed dependence of MAC on NAM/EC.

The other free parameters are varied to reproduce the observations "as well as possible". It is possible to introduce an artificial dependence of MAC on NAM/EC that agrees with observed dependence by pushing the random measurement noise of EC up to a gSD of 1.40 (Figure S5b). However, such massive random measurement noise is unrealistic. Furthermore, the resulting variability of the "measured MAC" is substantially larger than variability of the observations, despite pushing the variability of the "true MAC" to "zero", which is also unrealistic (Figure S5a and Figure S5b), and also the correlation of absorption coefficient and EC cannot be reproduced (Figure S5c). Based on the results from all three simulations we can discard the hypothesis that the observed dependence of MAC on NAM/EC is, for the most part, an artefact caused by random noise in the EC measurement.

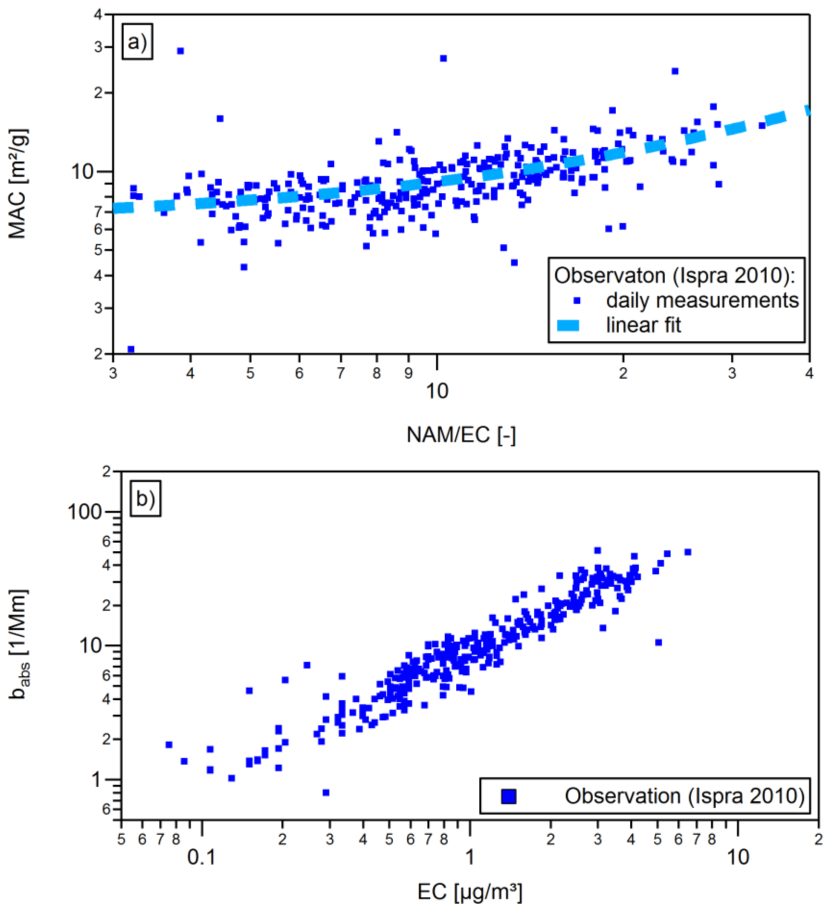

Figure S2. Observation at Ispra in 2010. (a) MAC as a function of NAM to EC ratio and (b) absorption coefficient as a function of EC mass concentration.

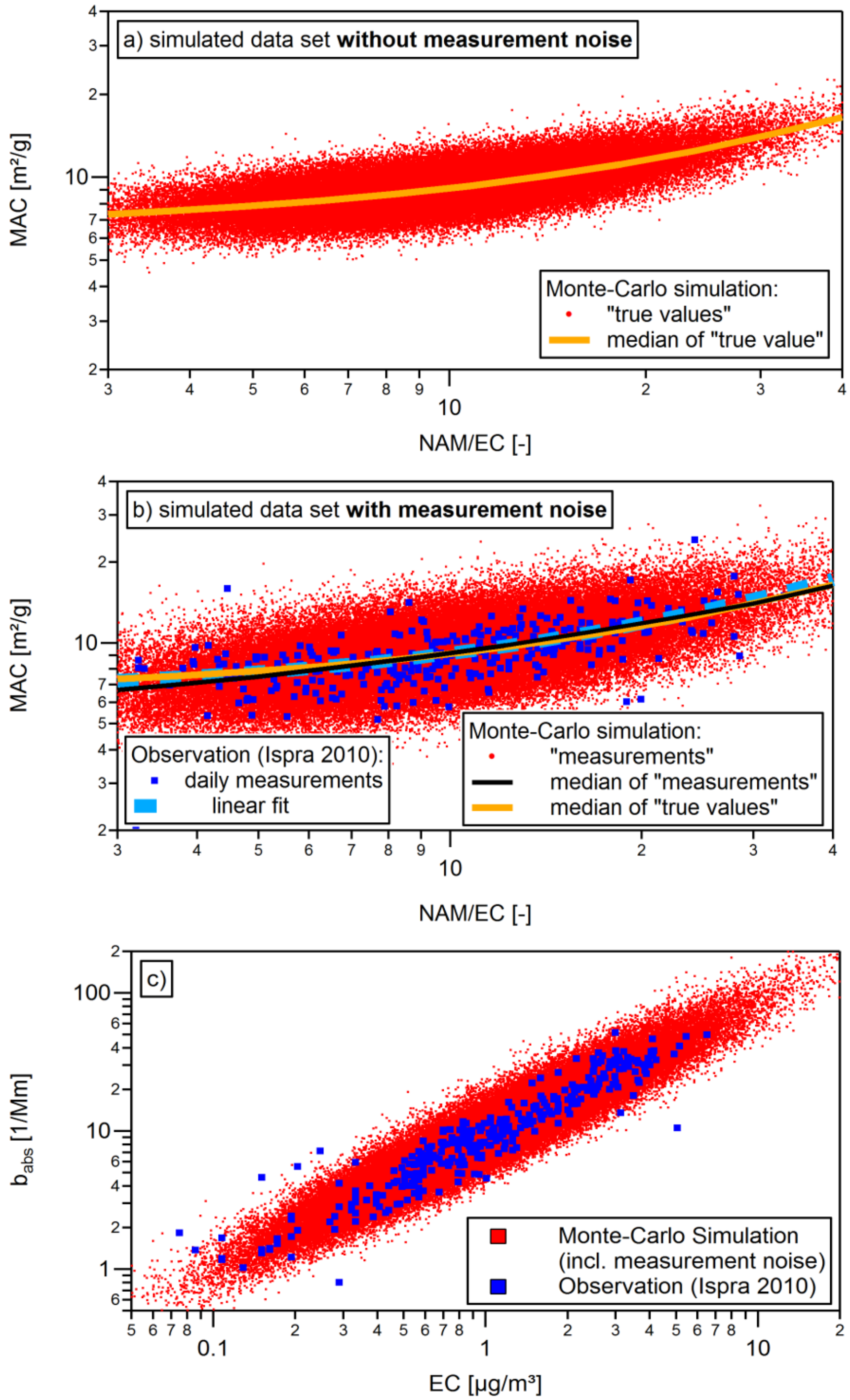

Figure S3. Monte-Carlo simulation of the effects of measurement noise for case 1. (a) MAC as a function of NAM to EC ratio for prescribed “true values” without random measurement noise and (b) simulated measurement with random noise and (c) absorption coefficient as a function of EC mass concentration.

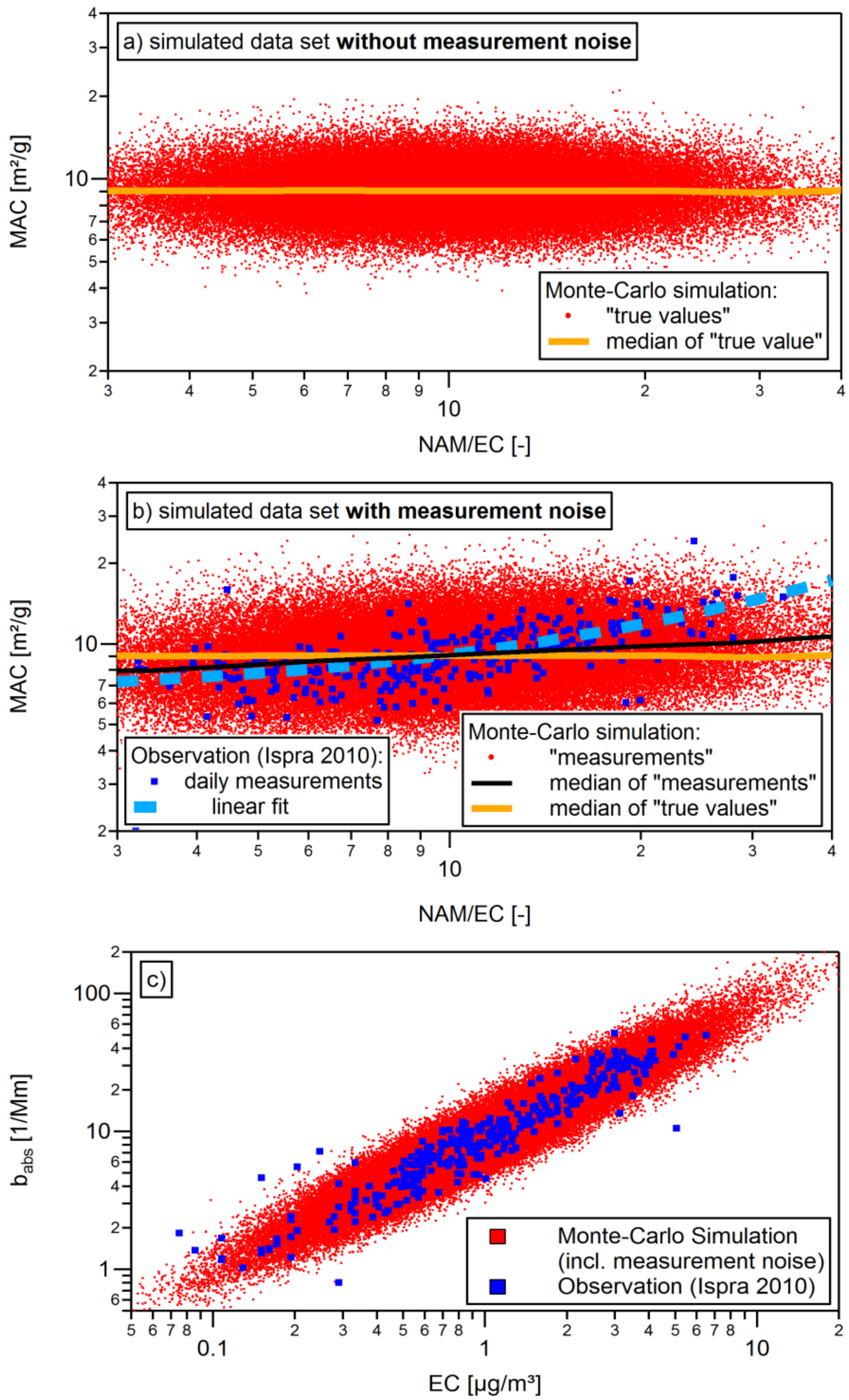

Figure S4. As Figure S2 but for case 2.

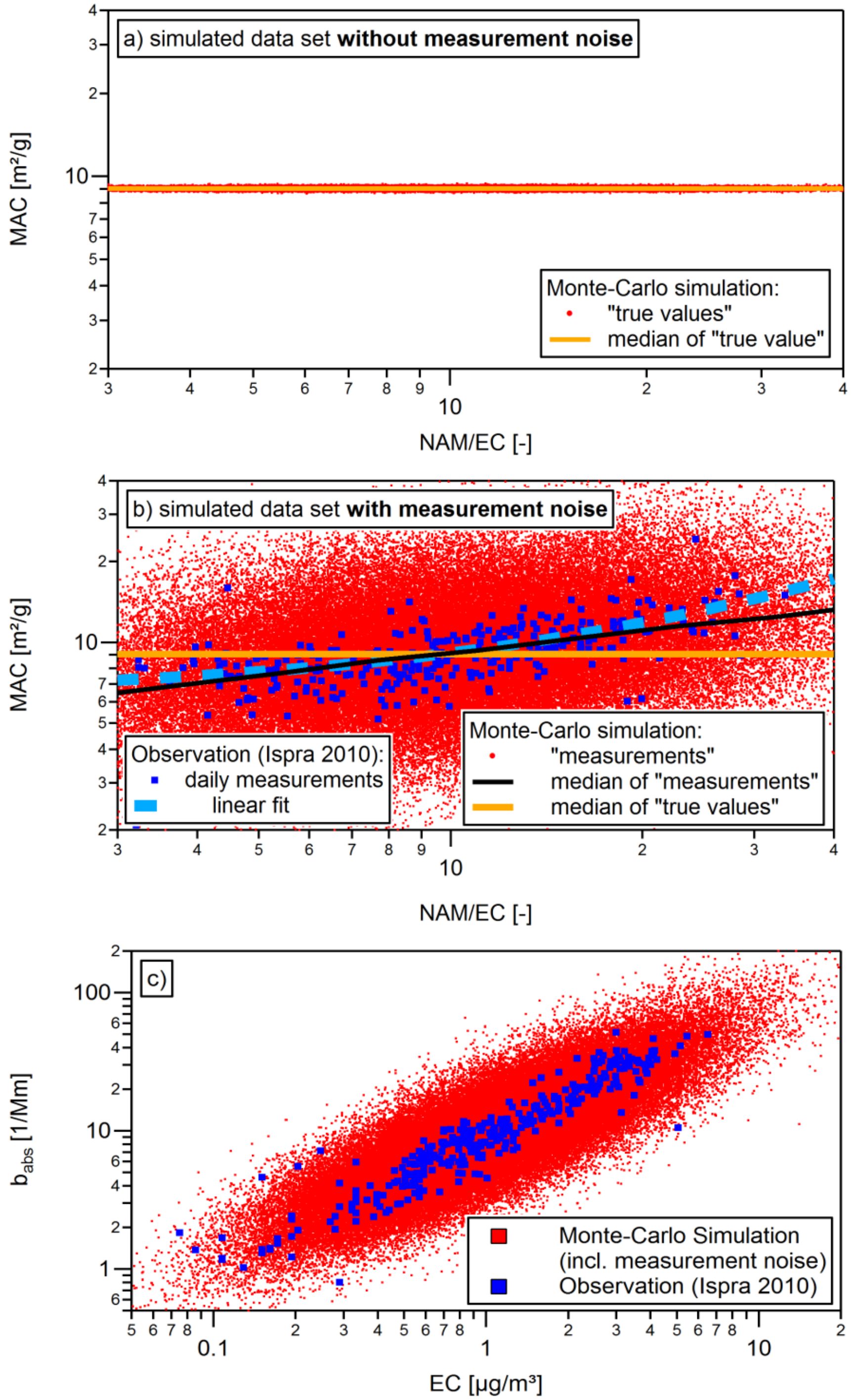

Figure S5. As Figure S2 but for case 3.

References

Cavalli, F., Alastuey, A., Areskoug, H., Cech, J., Ceburnis, D., Genberg, J., Harrison, R. M., Jaffrezo, J. L., Kiss, G., Mihalopoulos, N., Perez, N., Quincey, P., Schwarz, J., Sellegri, K., Spindler, G., Theodosi, C., Yttri, K. E., Aas, W. and Putaud, J. P.: A European aerosol phenomenology-4: harmonized concentrations of carbonaceous aerosol at 10 regional background sites across Europe, submitted to Atmos. Environ., 2016.