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Trends and variability of atmospheric $PM_{2.5}$ and $PM_{10–2.5}$ concentration in the Po Valley, Italy

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Abstract. The Po Valley is one of the largest European regions with a remarkably high concentration level of atmospheric pollutants, both for particulate and gaseous compounds. In the last decade stringent regulations on air quality standards and on anthropogenic emissions have been set by the European Commission, including also for $PM_{2.5}$ and its main components since 2008. These regulations have led to an overall improvement in air quality across Europe, including the Po Valley and specifically PM_{10}, as shown in a previous study by Bigi and Ghermandi (2014). In order to assess the trend and variability in $PM_{2.5}$ in the Po Valley and its role in the decrease in PM_{10}, we analysed daily gravimetric equivalent concentration of $PM_{2.5}$ and of $PM_{10–2.5}$ at 44 and 15 sites respectively across the Po Valley. The duration of the times series investigated in this work ranges from 7 to 10 years. For both PM sizes, the trend in deseasonalized monthly means, annual quantiles and in monthly frequency distribution was estimated: this showed a significant decreasing trend at several sites for both size fractions and mostly occurring in winter. All series were tested for a significant weekly periodicity (a proxy to estimate the impact of primary anthropogenic emissions), yielding positive results for summer $PM_{2.5}$ and for summer and winter $PM_{10–2.5}$. Hierarchical cluster analysis showed moderate variability in $PM_{2.5}$ across the valley, with two to three main clusters, dividing the area in western, eastern and southern/Apennines foothill sectors. The trend in atmospheric concentration was compared with the time series of local emissions, vehicular fleet details and fuel sales, suggesting that the decrease in $PM_{2.5}$ and in PM_{10} originates from a drop both in primary and in precursors of secondary inorganic aerosol emissions, largely ascribed to vehicular traffic. Potentially, the increase in biomass burning emissions in winter and the modest decrease in NH_3 weaken an otherwise even larger drop in atmospheric concentrations.

1 Introduction

Airborne particulate matter with aerodynamic diameter equal to or smaller than 2.5 µm has been regularly monitored in Europe for over a decade, with an increasing number of sampling sites following the requirements of 2008/50/EC. Notwithstanding that the occasional improper use of ambient $PM_{2.5}$ in epidemiological studies, leading to biased results, was acknowledged (Avery et al., 2010), several health-effects studies on bulk $PM_{2.5}$ assessed its harmfulness both in Europe (Boldo et al., 2006) and in the US (Franklin et al., 2006), with the latter study estimating $PM_{2.5}$ 3 times more dangerous than PM_{10}. Some studies included $PM_{2.5}$ composition to better infer its morbidity, highlighting the role of black carbon (Sørensen et al., 2003) and of sulfate (Strand et al., 2006), while recently also the International Agency for Research on Cancer (IARC) classified "particulate matter from outdoor air pollution as carcinogenic" (Loomis et al., 2013).

European regulatory limits on atmospheric concentration and atmospheric emissions for several pollutants led to a direct decrease for some species: for example, the SO_2 emission drop in Europe and in the US (Vestreng et al., 2007; Klimont et al., 2013) resulted in a continental-scale decrease in atmospheric SO_2 (for Europe see Denby et al., 2010) and in the content of sulfur in rainwater (for the US see Hicks et al., 2002). More spatial and seasonal variability was observed for the trends in atmospheric concentration of photochemically produced compounds, such as ozone

(Jonson et al., 2006; Simon et al., 2015; Wilson et al., 2012), and finally site-dependent trends were obtained for PM_{10} (Anttila and Tuovinen, 2010; Barmpadimos et al., 2011a). Cusack et al. (2012) found a decreasing trend in $PM_{2.5}$ at most EMEP sites across Europe, and observed that in the western Mediterranean the trend was due to a drop in secondary inorganic aerosol (SIA) and organic matter.

The $\sim 42\,000\,km^2$ of the Po Valley hosts wide urban areas, with an overall population of almost 15 million inhabitants, large industrial manufacturing districts (including oil refineries and large power plants) sensibly impacting local air quality (Bigi et al., 2017), and intensive agricultural and animal breeding activities. During colder months the Alps and Apennines surrounding the valley strongly limit maximum mixing layer height and prevent the development of moderate or strong winds, leading to recurrent thermal inversion both at daytime and at nighttime. These conditions cause the buildup and ageing of the intense atmospheric emissions of the valley and make air quality of this region one of the worst in Europe (EEA, 2010; Bigi et al., 2012).

In a companion study Bigi and Ghermandi (2014) performed a detailed analysis of the long-term trend and variability of PM_{10} across the Po Valley. The study found a large and valley-wide decline in PM_{10} atmospheric levels and partly ascribed it to the regulatory forced renewal of the vehicular fleet, leaving undetermined the role of SIA and of primary emissions. The main aim of the present study is to expand the previous analysis of PM_{10} trends over the Po Valley by analysing a dataset that includes 44 $PM_{2.5}$ and 15 $PM_{10-2.5}$ monitoring sites. $PM_{10-2.5}$ stands for the mass of coarse particles with aerodynamic diameters included between 2.5 and 10 µm. The present study allows a better understanding of the role of emissions in the previously observed PM_{10} trends and, together with the companion study, will provide an up-to-date and comprehensive representation of the trend and the variability of PM in the Po Valley. Most of the methods used in the present study follow the rationale of the companion study, to enhance the comparability between the two.

2 Materials and methods

The analysis involved daily $PM_{2.5}$ data obtained from 44 air quality monitoring stations within the Regional Environmental Protection Agency (ARPA) operating over the Po Valley. Data are derived from low-volume samplers (mainly EN-compliant SKYPOST, by TECORA, Fontenay-sous-Bois, France) and gravimetric equivalent beta attenuators (mostly SWAM, by FAI Instruments, Rome, Italy). The sites are listed in Table 1 and mapped in Fig. 1. All sampling equipment follows a quality management system which is certified to ISO 9001:2008. All analysed data have been automatically and manually validated by the respective ARPA. That is, the data are obtained by calibrated instruments, and they

Table 1. Analysed $PM_{2.5}$ sampling sites for trend and for extended statistical analysis. All sites were active until January 2015. At boldfaced stations also PM_{10} data were available. Station types: UT – urban traffic, UI – urban industrial, UB – urban background, SuB – suburban background, and RB – rural background.

ID	Station name	Station type	Activation date
	Trend analysis dataset		
1	Besenzone	RB	Jan 2008
2	**Borgofranco**	SuB	Dec 2006
3	**Brescia V. Sereno**	UB	Jun 2006
4	**Calusco d'Adda**	SuB	Jun 2006
5	**Casirate d'Adda**	RB	Nov 2005
6	Castano Primo	UB	Mar 2007
7	Chivasso	SuB	Jan 2005
8	Cornale	RB	Feb 2006
9	Leinì	SuB	Aug 2006
10	**Lodi**	UT	Jul 2006
11	**Mantua S. Agnese**	UB	Dec 2007
12	**Merate**	UT	Sep 2006
13	**Milan**	UB	Jun 2007
14	Modena[a]	UB	Oct 2007
15	Mortara	UI	Dec 2007
16	Padua Mandria[b]	UB	Jan 2005
17	**Parma**	UB	Jan 2008
18	**Ponti sul Mincio**	SuB	Jan 2007
19	**Reggio Emilia**	UB	Oct 2007
20	**Rimini**	UB	Jan 2006
21	**Saronno**	UB	Dec 2005
22	**Schivenoglia**	RB	Dec 2006
23	Seriate	UB	Nov 2005
24	**Turin Lingotto**	UB	Jul 2005
	Extended analysis dataset		
25	Alessandria Volta	UB	Feb 2011
26	Ballirana	RB	Jul 2008
27	Bergamo Meucci	UB	Dec 2008
28	Biella Sturzo	UB	Jun 2010
29	Bologna G.M.	UB	May 2008
30	Bologna P.S.F.	UT	Jan 2009
31	Faenza	UB	Apr 2009
32	Ferrara	UB	Nov 2008
33	Forlì	UB	May 2008
34	Gavello	RB	Jun 2008
35	Guastalla	RB	May 2008
36	Jolanda di Savoia	RB	Mar 2009
37	Langhirano	RB	Mar 2008
38	Novara	UB	Apr 2010
39	Piacenza	UB	Sep 2009
40	San Clemente	RB	May 2008
41	San Pietro C.	RB	Jan 2009
42	Turin Caduti	SuB	May 2010
43	Vercelli	SuB	May 2010
44	Vinchio	RB	Jan 2009

[a] This UB station is different from the UB station analysed in Bigi and Ghermandi (2014) for the same city. [b] This station was relocated in January 2014.

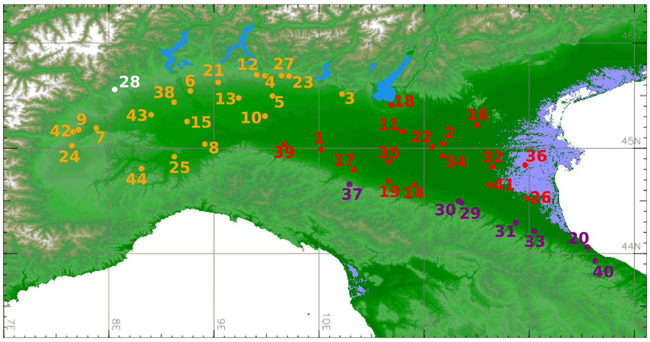

Figure 1. Location of $PM_{2.5}$ monitoring stations included in the analysis. The key for ID number is found in Table 1. Colour coding refers to the result of the cluster analysis performed using a divisive algorithm: sites within the same cluster have the same colour. Site 28 (Biella) resulted in an outlier and was not included in this classification. Results of the cluster analysis with partition around medoids algorithm are in Fig. S3. More details are in Sects. 2.3 and 3.3.

undergo a daily, seasonal and annual comparison with nearby sites as well as with previous data. The authors have double-checked the data by analysing annual, monthly, weekly and daily patterns for all sites and by removing any occasional biased value (e.g. peaks from festival bonfires). A total of 15 out of these 44 sites included daily gravimetric equivalent measurements of PM_{10}. At these 15 sites the mass concentration of coarse particles ($PM_{10-2.5}$) was computed and analysed equivalently to $PM_{2.5}$.

The variability in atmospheric particle concentration was compared to provincial emission estimates of PM_{10}, $PM_{2.5}$, CH_4, CO and other main particle precursors (SO_2, NO_x, non-methane volatile organic carbon (NMVOC) and NH_3). Emissions were provided by the National Institute for Environmental Protection and Research (ISPRA) for the years 1990, 1995, 2000, 2005 and 2010 (inventory version 22_05_2015). Provincial emissions are estimated by attribution of the national emissions to each Italian province by a top-down procedure. Further details on the inventory used can be found in the companion paper and references therein. Similarly to the companion study, only provinces with a significant part of their land within the Po Valley were considered, assuming that most of the emissions occur in the valley part of the province, where most of the activities occur and the population resides, instead of the mountainous parts. It is worth noting that there are some large differences between the inventory version used in this study and the one used in the companion paper, mostly related to emissions for SNAP sector 2 (i.e. commercial, institutional and residential combustion plants), where SNAP is the Standardized Nomenclature for Air Pollutants. In this study we also included the emission inventory for the Lombardy region: this is built with a bottom-up procedure, based on emission source databases at a municipality level, and it is available for the years 2005, 2007, 2008, 2010 and 2012. The building procedure for the latter inventory was improved through the years by changing emission factors for a few specific sources, e.g. biomass burning, biomass-fuelled power plants and air traffic. Nonetheless the homogeneity over time of both inventories was considered sufficient for the aim of the present study.

Also data on vehicular fleet composition and fleet age for each province were used. These were provided by the Italian Automobile Club (ACI). Data on fuel sales used in this study, also provided by ACI, were available at a regional scale and not at a provincial scale.

All statistical data analyses were performed within the software environment R 3.2 (R Core Team, 2015).

2.1 Trend estimate

The analysis for the presence of a trend involved a subset of 24 $PM_{2.5}$ series out of 44, i.e. the ones having a record between 7 and 10 years long, and all 15 $PM_{10-2.5}$ series, with a length ranging between 7 and 9 years. The limit of 7 years for the sampling duration for a trend analysis results from the compromise between the spatial and temporal representativeness of the valley by the analysed dataset. Similarly to the previous analysis for PM_{10}, slopes were estimated for monthly mean and annual quantiles of daily data, where these statistics were computed if at least 75 % of the daily data were available for the respective month or year.

Monthly average concentrations were decomposed in trend, seasonal and remainder components by the seasonal trend decomposition procedure based on LOESS (STL) (Cleveland et al., 1990). For a good performance, STL requires a clear seasonality in the analysed time series: this feature was shown by all $PM_{2.5}$ series and by only two $PM_{10-2.5}$ series (see Sect. 3.1). All time series were log-transformed prior to STL decomposition in order to achieve normally distributed residuals and to control heteroscedasticity, and the analysis of monthly trend time series was performed on back-transformed logarithmic trend data. Generalized least squares (GLS) (Brockwell and Davis, 2002) and model-based resampling (Davison and Hinkley, 1997) methods were used to estimate the presence of a significant slope in trend components. Details on these methods can be found in Bigi and Ghermandi (2014). All resulting slopes and two sample graphs are shown in Table 2 and in Fig. 2 respectively.

Similarly to in the companion study, the trends of monthly data were compared to non-parametric trends of annual quantiles: the slope of the 5th, 50th and 95th annual quantiles was estimated by the Theil–Sen (hereafter TS) method; significance test for slope on annual data was performed by non-parametric resampling as in Yue and Pilon (2004). Resulting slopes for annual quantiles are shown in Table 3. Finally each month was tested for the presence of a trend: $PM_{2.5}$ and $PM_{10-2.5}$ daily concentration for each month was binned in $10\,\mu g\,m^{-3}$ increments, and the frequency of each bin in each month over the sampling period was computed. The trend in

Table 2. Analysis of trend for monthly mean and for monthly frequency of $PM_{2.5}$ and $PM_{10–2.5}$. Slope (± standard error) for monthly mean is computed by generalized least squares (GLS) on deseasonalized monthly mean time series of daily $PM_{2.5}$ or $PM_{10–2.5}$ concentration. Boldfaced values indicate slope significantly different from zero at a 95 % confidence level. Variation in monthly frequency distribution was estimated by Theil–Sen method.

Station	Slope $\mu g\,m^{-3}\,yr^{-1}$	Change $\%\,yr^{-1}$	Months with significant trend
		$PM_{2.5}$	
Besenzone	−0.008 ± 0.121	0.0 % ± 0.5 %	5–6 (−), 12 (−)
Borgofranco	**−1.007 ± 0.139**	**−3.7 % ± 0.5 %**	1–2 (−), 4 (−), 10 (−)
Brescia	**−1.323 ± 0.249**	**−4.3 % ± 0.8 %**	1–2 (−), 3 (+), 5–6 (−), 12 (−)
Calusco d'Adda	**−1.428 ± 0.183**	**−5.4 % ± 0.7 %**	1–2 (−), 4–5 (−), 7 (−), 9 (−), 11–12 (−)
Casirate d'Adda	**−1.035 ± 0.395**	**−3.2 % ± 1.2 %**	1 (−), 11 (−)
Castano Primo	**−2.217 ± 0.177**	**−8.1 % ± 0.7 %**	1–2 (−), 4 (−), 10 (−), 12 (−)
Chivasso	**−0.411 ± 0.174**	**−1.3 % ± 0.6 %**	1–3 (−), 6 (±), 9–11 (−)
Cornale	**−0.953 ± 0.262**	**−4.5 % ± 1.3 %**	1–2 (−), 4 (−), 9–10 (−)
Leinì	−1.899 ± 0.969	−6.7 % ± 3.4 %	1–5 (−), 7 (−), 11–12 (−)
Lodi	**−1.605 ± 0.124**	**−6.4 % ± 0.5 %**	2–12 (−)
Mantua	**−1.090 ± 0.269**	**−3.7 % ± 0.9 %**	2 (−), 3 (±), 4–5 (−), 9–12 (−)
Merate	**−1.322 ± 0.427**	**−4.6 % ± 1.5 %**	1 (−), 4–5 (−), 9–10 (−)
Milan	−0.186 ± 0.154	−0.6 % ± 0.5 %	1–2 (−), 3–4 (+), 9 (−), 10 (±), 12 (−)
Modena	**−1.007 ± 0.402**	**−4.8 % ± 1.9 %**	1 (−), 5–6 (−), 8–11 (−)
Mortara	**−1.439 ± 0.214**	**−5.5 % ± 0.8 %**	1–2 (−), 4–5 (−), 8 (−), 10 (−)
Padua	**−1.271 ± 0.155**	**−3.9 % ± 0.5 %**	1 (−), 3 (−), 11 (−)
Parma	**−0.648 ± 0.176**	**−3.2 % ± 0.9 %**	1 (−), 3 (+), 5 (−), 12 (−)
Ponti sul Mincio	−0.103 ± 0.212	−0.4 % ± 0.8 %	2 (−), 3 (+), 4 (−), 9 (+), 10 (−), 12 (−)
Reggio Emilia	**−0.819 ± 0.153**	**−3.8 % ± 0.7 %**	1–2 (−), 3 (+), 5 (−), 12 (−)
Rimini	−0.486 ± 0.245	−2.2 % ± 1.1 %	2 (−), 3 (+)
Saronno	**−0.844 ± 0.156**	**−3.0 % ± 0.5 %**	1–2 (−), 5 (−), 12 (−)
Schivenoglia	**−0.496 ± 0.224**	**−1.9 % ± 0.8 %**	1–2 (−), 4 (−), 8 (+), 10–11 (−)
Seriate	**−0.935 ± 0.075**	**−3.5 % ± 0.3 %**	1 (−), 5 (−), 7 (−), 10 (−), 12 (−)
Turin Lingotto	**−1.717 ± 0.270**	**−5.2 % ± 0.8 %**	1–2 (−), 4–5 (−), 7 (−), 9–11 (−)
		$PM_{10–2.5}$	
Lodi	**−0.362 ± 0.248**	**−2.2 % ± 1.5 %**	1–2 (−), 4 (±), 10 (−)
Merate	**−0.806 ± 0.280**	**−6.3 % ± 2.2 %**	1–12 (−)

these frequencies for each month was estimated by the TS method, and its significance was tested by a non-parametric bootstrap, similarly as for the annual quantiles. For each site, months with a significant trend are listed in the rightmost column of Table 2 and two sample graphs are in Fig. 3. Contrarily to deseasonalized monthly means, these two latter trend estimates were performed on all 24 $PM_{2.5}$ + 15 $PM_{10–2.5}$ sites.

The TS method was used to estimate also trends in the emission inventory data, along with non-parametric resampling to asses the slope significance.

2.2 Weekly pattern

In order to investigate the presence of a weekly cycle in daily $PM_{2.5}$ and $PM_{10–2.5}$ (i.e. a significantly different concentration on a single weekday), three tests were used for all 44 + 15 series. Two tests involved both the complete and seasonal series (i.e. winter – January, February, March, and summer – June, July, August) and focussed on PM anomalies, similarly to Bigi and Ghermandi (2014): the Kruskal–Wallis test on weekly cycle of mean anomalies (WCY) and the Wilcoxon test on weekend effect magnitude (WEM). Their significance was double-checked by repeating WCY and WEM tests on anomalies grouped into 6- and 8-day weeks (Barmet et al., 2009).

The third test involved the analysis of the smoothed periodogram for each time series of anomalies and verified the presence of a significant signal with a 7-day periodicity above background noise. The periodogram estimates the spectral density of a continuous time series, showing the contribution by all frequency components (eventually associated to a specific process/source) to the variance of the series. The periodogram, in order to be estimated, needs a continuous series: in each time series, 1-day gaps were filled by linear interpolation of neighbouring data, and the periodogram

Table 3. Analysis of trend for annual quantiles of $PM_{2.5}$ and $PM_{10–2.5}$. Slope for annual quantiles is computed by the Theil–Sen method: boldface values indicate slope significantly different from zero at the 95 % confidence level.

Station	5th annual quantile		50th annual quantile		95th annual quantile	
	Slope µg m^{-3} yr^{-1}	Change % yr^{-1}	Slope µg m^{-3} yr^{-1}	Change % yr^{-1}	Slope µg m^{-3} yr^{-1}	Change % yr^{-1}
$PM_{2.5}$						
Besenzone	0.000	0.0	0.000	0.0	0.608	1.1
Borgofranco	−0.667	−8.3	**−1.000**	**−4.8**	−1.087	−1.8
Brescia	−0.250	−4.1	−0.367	−1.5	**−2.272**	**−3.0**
Calusco d'Adda	**−0.792**	**−13.1**	**−1.333**	**−7.0**	**−4.179**	**−6.1**
Casirate d'Adda	−0.225	−2.7	−0.225	−1.0	**−3.917**	**−4.9**
Castano Primo	−0.286	−4.9	−0.857	−4.6	−3.421	−5.4
Chivasso	0.200	3.7	**−0.817**	**−3.2**	−1.531	−2.0
Cornale	**−0.500**	**−8.5**	**−1.000**	**−6.5**	**−4.383**	**−9.4**
Leinì	−0.100	−2.4	−2.333	−13.2	−10.800	−17.9
Lodi	**−0.929**	**−12.2**	**−2.000**	**−10.3**	−1.875	−3.2
Mantua	−0.412	−6.4	−2.000	−8.1	−4.225	−6.0
Merate	−0.081	−1.0	−0.667	−3.0	−1.646	−2.3
Milan	0.000	0.0	0.200	0.9	−3.260	−4.3
Modena	−0.333	−5.4	−1.200	−7.7	−4.000	−7.6
Mortara	**−0.930**	**−12.9**	−1.000	−5.2	−2.988	−4.7
Padua	**−0.380**	**−4.4**	**−1.583**	**−6.6**	**−2.556**	**−3.0**
Parma	**−0.500**	**−10.0**	**−0.667**	**−4.5**	−1.000	−2.0
Ponti sul Mincio	0.071	1.3	0.000	0.0	−1.037	−1.7
Reggio Emilia	**−0.400**	**−6.7**	−0.500	−3.0	−1.850	−3.7
Rimini	−0.025	−0.5	0.000	0.0	−0.787	−1.4
Saronno	**−0.950**	**−23.8**	−0.414	−2.1	**−3.587**	**−4.7**
Schivenoglia	0.000	0.0	0.500	2.3	−1.450	−2.5
Seriate	−0.208	−3.7	−0.500	−2.5	**−2.875**	**−4.1**
Turin Lingotto	−0.134	−2.2	**−1.083**	**−4.8**	**−3.568**	**−4.1**
$PM_{10–2.5}$						
Borgofranco	**−0.500**	**−60.0**	0.000	0.0	1.060	5.4
Brescia	−0.025	−5.4	**−0.775**	**−8.2**	**−1.619**	**−6.7**
Calusco d'Adda	0.000	0.0	0.000	0.0	0.000	0.0
Casirate d'Adda	−0.250	−16.7	−0.375	−3.8	−1.900	−6.8
Lodi	−0.100	−2.7	−0.200	−1.6	−0.180	−0.5
Mantua	0.000	0.0	−0.550	−8.7	−1.667	−9.2
Merate	**−0.500**	**−12.1**	**−0.917**	**−8.4**	**−2.417**	**−9.2**
Milan	**−0.333**	**−23.3**	−0.750	−6.4	−1.167	−4.3
Parma	0.738	23.4	0.000	0.0	0.217	0.9
Ponti sul Mincio	**−0.667**	**−29.9**	**−1.400**	**−14.4**	**−2.310**	**−9.6**
Reggio Emilia	0.000	0.0	−0.333	−3.7	**−1.367**	**−6.6**
Rimini	**−0.500**	**−14.2**	**−0.750**	**−7.6**	−1.538	−7.9
Saronno	**−0.250**	**−25.0**	**−0.536**	**−5.8**	−1.434	−6.1
Schivenoglia	−0.492	−55.2	−0.292	−4.4	1.673	8.9
Turin Lingotto	0.000	0.0	−0.600	−6.5	−1.000	−4.3

was computed from the resulting longest continuous record within the series. Following Mann and Lees (1996), periodogram smoothing was achieved by the multiple-taper method (MTM), and background noise was estimated as an AR(1) red noise process, whose lag-1 autocorrelation coefficient proceeds from a robust estimate. The statistical significance of peaks in the periodogram was verified assuming a χ^2 distribution for spectral estimates. Therefore a peak in the smoothed periodogram at the frequency $1/7\,\mathrm{day}^{-1}$ is significant when exceeding the 95 % confidence bands for red noise at that same frequency (suggesting the presence of a periodic emission source inducing a similar periodicity in

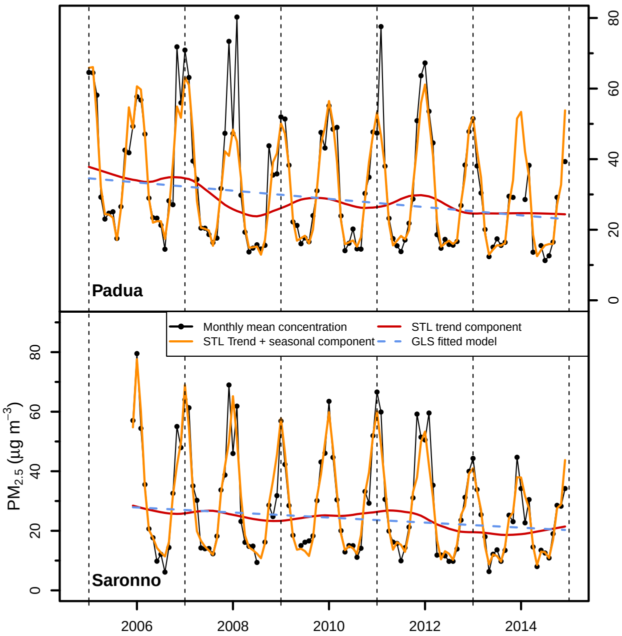

Figure 2. STL decomposition for monthly mean $PM_{2.5}$ along with generalized least squares (GLS) fitted slope for two selected sites.

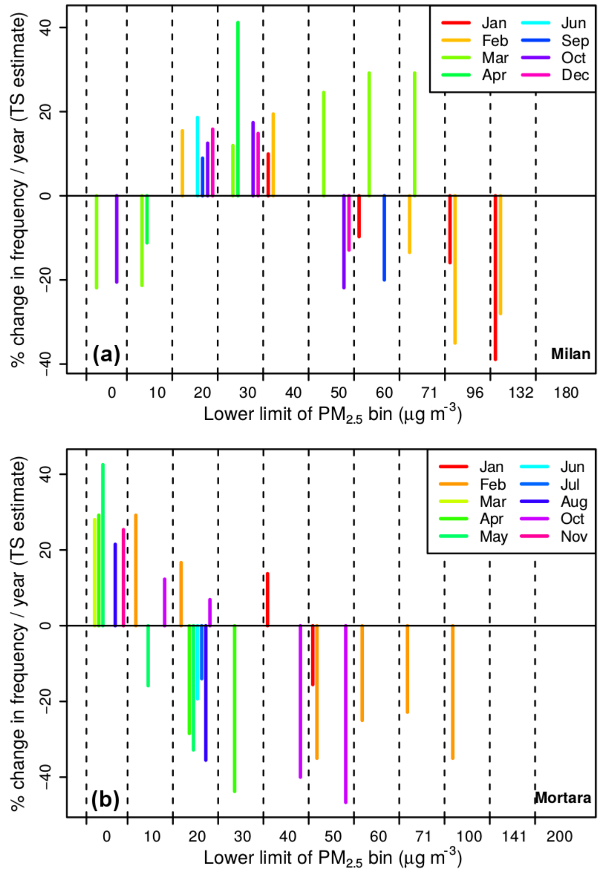

Figure 3. Significant changes in monthly frequency distribution of $PM_{2.5}$ at Milan **(a)** and Mortara **(b)**.

atmospheric pollutant concentration). The astrochron package in R (Meyers, 2012) was used to follow the approach by Mann and Lees (1996). Results for the weekly cycle analysis are presented in Table S1 in the Supplement and anomalies for $PM_{2.5}$ and $PM_{10-2.5}$ are shown in Fig. S1 and S2.

2.3 Cluster analysis

Cluster analysis was performed only on $PM_{2.5}$ daily data and included all 44 sites. Several distance metrics and clustering algorithms were tested. Best results were chosen depending on the cluster silhouette and the overall performance index, which led to two slightly different outcomes: one generated by divisive hierarchical clustering algorithm and one by partition around medoids (Kaufman and Rousseeuw, 1990). In the former an outlying site (Biella, ID 28) was removed from the dataset to prevent classification fouling (Kaufman and Rousseeuw, 1990). For both algorithms the dissimilarity matrix was based on a Pearson's correlation coefficient metric (see Bigi and Ghermandi, 2014), highlighting linear correlation structures among sites. Spatial representation of the two resulting set of clusters is found in Figs. 1 and S3.

3 Results and discussion

General comments on the pre-processing procedures and trends used in the companion paper apply to this study: we exploited the STL performance on extracting the trend component from the monthly data, featured by wide seasonality, and we took advantage of the robustness of both quantiles and resampling techniques, to minimize the influence of uncommon weather conditions on the estimated trends. Finally, the influence of a possible long-term trend in meteorological variables as temperature or precipitation was estimated to be negligible over the comparatively short length of these PM series.

A main assumption in the discussion of trends and patterns is that, notwithstanding the occasional influence of long-range transport on PM in the Po Valley (e.g. Masiol et al., 2015), we considered local emission sources to have the largest influence on particulates in the Po Valley: throughout the analysis we assumed trends in continental emissions to have a minor effect on the estimated PM trends. A reasonable assumption, particularly in winter when valley emissions are confined for long periods within the (often shallow) mixing layer.

3.1 Results from trend analysis

All estimated trends are assumed linear. This was mostly true for all trend components extracted by STL on monthly $PM_{2.5}$, while only in Lodi and Merate did monthly-mean $PM_{10-2.5}$ show a sufficiently wide seasonal pattern to allow a reliable extraction of a seasonal and a trend component by STL, with the latter being linear. Not surprisingly, these two sites are urban traffic stations and recorded the largest PM coarse concentration among all investigated sites (their overall mean is 16.2 and 12.7 $\mu g\,m^{-3}$ respectively).

The trend component for monthly $PM_{2.5}$ showed a significant decline at most sites, ranging from 0.5 to 2 $\mu g\,m^{-3}\,yr^{-1}$ (Table 2). $PM_{2.5}$ annual quantiles exhibited a decline at several sites (Table 3), indicating a decrease for large, median and low concentration levels. Significant decrease rate for annual median was highly similar to the GLS trend of monthly mean at the corresponding site (e.g. Borgofranco, Cornale, Parma); missing data or outliers in the annual series led the significance test for slope to fail at several sites, although the data showed a clear trend.

In order to detect months with a concentration change over the analysed period, TS trends in frequency of monthly bins were computed (see Fig. 3 for the results at two sites). In the rightmost column of Table 2, a $-$ sign next to a specific month indicates a decrease in frequency of higher concentration bins towards lower bins, a $+$ sign a shift from lower to higher concentration bins, and a $\pm$ sign a shift in lower and higher concentration bins towards median concentrations. The analysis of binned concentration levels indicates that at most sites higher concentrations decreased, mostly during winter months with January and February being the most frequent (see the rightmost column in Table 2). Occasional decrease of higher concentrations was observed also in summer months, while an increase in lower concentrations was found in spring at few sites. These results are partly consistent with slopes in fifth annual quantile, representative of spring–summer trends. As a matter of comparison, estimates of trends for $PM_{2.5}$ annual mean at several EMEP (European Monitoring and Evaluation Programme) sites, i.e. rural background, over 2002–2010 by Cusack et al. (2012) were between $\sim -3.8/-5.4\,\%\,yr^{-1}$, similar to significant trends occurring in the Po Valley for annual median at background sites (e.g. Borgofranco, Chivasso or Parma).

The trend component of monthly $PM_{10–2.5}$ at Lodi and Merate showed a drop of 2 and 6 $\%\,yr^{-1}$ respectively; in Lodi only winter months significantly contributed to this drop, whereas in Merate this drop occurred throughout the year. At Merate also annual quantiles exhibit a significant trend, while at Lodi the nonlinearity and a missing data lead to a non-significant slope. Both these are traffic sites and are directly affected by primary sources of coarse particles, i.e. motor exhausts and road, tire and break wear (either directly emitted or resuspended) (e.g. see Perrone et al., 2012, for a PM source apportionment in Milan). This outcome suggests that the previously observed decrease in PM_{10} (Bigi and Ghermandi, 2014) is partly due to a drop in exhaust traffic emission following the renewal of the vehicular fleet, at least at traffic sites. Indeed the trend in $PM_{10–2.5}$ annual quantiles shows some site dependency along with several cases of nonlinearity, suggesting occasional changes in active sources over time (e.g. construction works) and leading nonparametric bootstrap to negate slope significance, notwithstanding that a clear slope is present, as in the case of Rimini 95th quantile (see Fig. S4 for $PM_{10–2.5}$ annual trends).

Trends in $PM_{10–2.5}$ found by Barmpadimos et al. (2012) at five EMEP sites are largely smaller than the ones observed in this study, supporting the hypothesis of the influence by primary sources on Po Valley sites. Very few other studies investigated trends for $PM_{10–2.5}$ in Europe. Amato et al. (2014) found a trend of $-1.5/-2\,\mu g\,m^{-3}\,yr^{-1}$ in road dust in southern Spain (meteorologically very different from the Po Valley) and ascribed it to the decrease in construction works due to the severe financial crisis: from the data available for this study a similar explanation does not apply to the $PM_{10–2.5}$ trends observed in the Po Valley.

3.2 Results for weekly pattern

Three different tests were used to assess whether a significant weekly pattern was present. Results presented in Table S1 show how, to some extent, the tests confirm each other, with WCY and WEM outperforming MTM. Almost all $PM_{2.5}$ sites exhibit a significant weekly pattern in summer, however almost none in winter. A weekly periodicity is observed in $PM_{10–2.5}$ at almost all sites both in winter and in summer, as expected given the most common sources of coarse particles. For both PM fractions, significance in weekly periodicity was supported by the negative result of tests on 6- and 8-day weeks. This is consistent with the findings in Bigi and Ghermandi (2014), where a significant weekly pattern in PM_{10} was found in winter only at older sites (i.e. activated before 2002): this was ascribed to a larger contribution by the coarse fraction to PM_{10} in late 1990s early 2000s, as confirmed by the decrease in $PM_{10–2.5}$ reported here. Similar results are in the study by Barmpadimos et al. (2011b), where for seven different sites in Switzerland a significant weekly cycle was found, both in $PM_{2.5}$ and $PM_{10–2.5}$, including the rural background site of Payerne.

One of the most recent source apportionment studies of $PM_{2.5}$ in the Po Valley, by Perrone et al. (2012), based on samples over 2006–2009 in urban background Milan, estimates the contribution of SIA and biomass burning (BB) to be larger in $PM_{2.5}$ than in PM_{10}, and higher in winter than in summer (up to 53 % in winter $PM_{2.5}$). These results are consistent with the scientific literature (Finlayson-Pitts and Pitts, 2000) and are confirmed by the findings of other recent PM source apportionment studies in the Po Valley (e.g. Larsen et al., 2012), i.e. supporting the hypothesis of a buffering role by SIA+BB over sources having a weekly periodicity (e.g. traffic, industry, resuspension), whose relative contribution is estimated to be lowest in winter $PM_{2.5}$ and highest in summer $PM_{10–2.5}$. Interesting enough, for both PM fractions the significance in weekly periodicity is not dependent on station classification according to the air-quality network: this also supports the assumption on the minor influence of continental emission trends.

3.3 Results from cluster analysis

Similarly to Po Valley PM_{10}, also $PM_{2.5}$ exhibited a strong seasonality, a significant trend and changes in frequency distribution across the valley (note that the $PM_{2.5}$ / PM_{10} ratio in the Po Valley is approaching 1 over the years, particularly at urban sites and in winter). Similarly to the companion paper, cluster analysis allowed us to highlight the presence of groups having large internal correlation and showed how the spatial distribution of most similar sites derives mainly from their geographical position instead of their classification within the air-quality network. Nonetheless, some differences between the outcome of cluster analysis applied to PM_{10} and $PM_{2.5}$ exist: three or two clusters resulted for $PM_{2.5}$ depending on the algorithm used (Figs. 1 and S3), i.e. fewer than for PM_{10} (as expected spatial variability for finer particles is smaller). The influence of the metropolitan areas, evident for PM_{10}, is not shown by $PM_{2.5}$. Eastern and western part of the valley were split into fewer groups when analysed for $PM_{2.5}$, compared to PM_{10}. That is, a difference in $PM_{2.5}$ between eastern and western Po Valley exists. However, within each side of the valley $PM_{2.5}$ levels are more correlated than PM_{10} levels. Resulting clusters have to be understood as flexible, with sites on the "geographical boundary" between two groups having a weaker membership.

3.4 Results from emission trend analysis and discussion

$PM_{2.5}$ and $PM_{10-2.5}$ investigated in this study refer to the period 2005–2014, while valley-wide emission data are available every 5 years over the period 1990–2010, preventing any tentative comparison between the trends of the two datasets, only a qualitative assessment. Moreover, as shown by Finardi et al. (2014) with an Eulerian chemical transport model, change in emissions in the Po Valley leads to highly nonlinear change in atmospheric pollutants levels (e.g. O_3, $OH^{\cdot}$ and NO_3^-) and in PM in general: this would make trends in emissions and PM even harder to compare.

SNAP sector 1 (best represented by power plants) showed a large decrease in SO_2, NO_x and PM emissions, and its contribution to Po Valley emissions is minor, particularly since 2005 (see Fig. S5). A significant reduction occurred in NO_x, NMVOC and PM emissions by road transport SNAP 7, one of largest sources in the valley. The modest contribution of emissions by industrial combustion (SNAP 3) decreased further for SO_2, NO_x and PM, both by technological improvements and recent national economy slowdown. On the contrary, heating (SNAP 2) exhibits an increase in emission of several species (e.g. NO_x, NMVOC and $PM_{2.5}$), most likely due to an increase in the use of biomass, notwithstanding that this is a seasonal source. These trends were observed in both analysed inventories.

Over the period 2005–2014 the total number of passenger cars and light-duty vehicles (LDVs) in the Po Valley was almost constant (~ -0.02 %), with the mean age of gasoline and diesel passenger cars increasing to ~ 3 years. Note that diesel cars are on average 6 years younger than gasoline ones, consistent with the dieselization of the fleet observed in most of Europe (EEA, 2015a). Over the same period, fuel sales showed a significant linear trend for unleaded gasoline ($-6.2\,\%\,yr^{-1}$), a mild decline for diesel ($-0.8\,\%\,yr^{-1}$) and an increase for LPG ($6.9\,\%\,yr^{-1}$). This drop in fuel sales is ascribed to both the renewal of the fleet, i.e. the increased number of vehicles with a more efficient engine, and to a recent level-off (decrease) of the mean distance travelled by car according to EEA (2015b) (ACI, 2012).

The observed trends in atmospheric $PM_{2.5}$ occurred at several sites, including the rural background stations of Cornale and Schivenoglia; the drop occurred more often in winter, when no site exhibits a weekly cycle (i.e. a significant impact of primary anthropogenic emissions) and ranged from ~ -1 % to $\sim -8\,\%\,yr^{-1}$. Decrease was largest (in absolute and relative terms) at traffic urban sites and became lower from urban towards rural sites (see Fig. 4), although the small dataset did not allow us to robustly test for a significant difference in trends among station types. From an overview of some recent source apportionment and chemical composition studies of $PM_{2.5}$ in the Po Valley (Carbone et al., 2010; Khan et al., 2016; Larsen et al., 2012; Masiol et al., 2015; Matta et al., 2003; Perrino et al., 2013; Perrone et al., 2012; Pietrogrande et al., 2016) primary traffic emissions (including exhaust and non-exhaust) are highest at traffic sites in absolute and relative terms, decreasing towards rural background sites, suggesting that the decrease in $PM_{2.5}$ emissions by traffic had a significant role in the observed trends in atmospheric composition.

This possibility is supported by chemical transport model simulations of de Meij et al. (2009). The latter authors estimated that a single drop in total $PM_{2.5}$ emissions of only ~ 200 Mg for SNAP 7 across Lombardy would lead to a variation of $-2.3\,\mu g\,m^{-3}$ in primary $PM_{2.5}$ in the Milan metropolitan area. According to the Lombardy inventory, primary $PM_{2.5}$ emissions by SNAP 7 actually drop ~ 2000 Mg over 2005–2012, while the ISPRA provincial inventory estimated a drop of ~ 2500 Mg over 2005–2010. Over the same period, the observed mean absolute drop in monthly $PM_{2.5}$ for Lombardy resulted in $\sim 10\,\mu g\,m^{-3}$. Given the increase in PM emissions by heating in winter counterbalancing the drop in SNAP 7 (and in SNAP 3), the observed downward trend in atmospheric levels is potentially consistent with the outcome by de Meij et al. (2009) and partly generated by a drop in primary traffic emissions (potentially exhaust and non-exhaust).

A drop in atmospheric SIA is also expected due to the large decrease in NO_x emissions and the (relatively modest) drop in NH_3 ($\sim 17\,000$ Mg according to ISPRA provincial inventory); this would be consistent with the decrease of nitrate, ammonium and sulfate ion concentration in fog at the rural

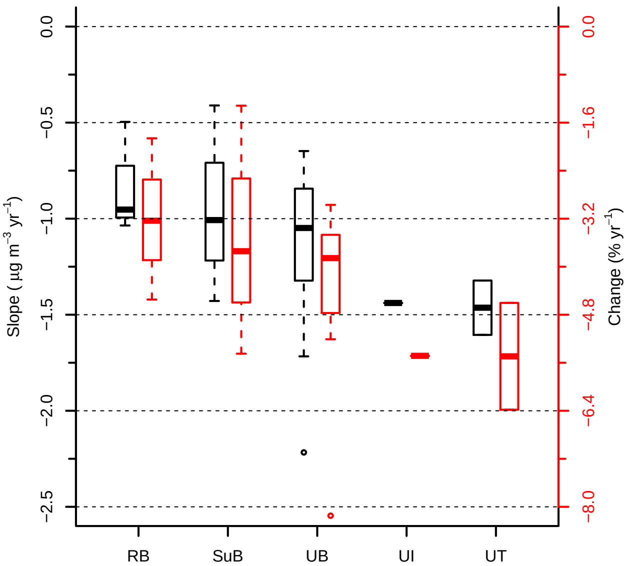

Figure 4. Boxplot of absolute and percentage significant slope of deseasonalized monthly mean $PM_{2.5}$ by station type.

background station San Pietro C. over the period 1990–2011 (Giulianelli et al., 2014). In agreement, simulation results by de Meij et al. (2009) showed a significant drop in SIA only with a concurrent decrease in NO_x and NH_3 emissions.

Available data do not allow the assessment of whether also a variation in secondary organic aerosol (SOA) occurred: NMVOC and NO_x, whose emissions drop over the investigated period, have a competing effect on SOA formation (Andreani-Aksoyoglu et al., 2004), and meanwhile biomass burning emissions increased. The latter is a large source of both primary and secondary OC (e.g. Piazzalunga et al., 2011; Gilardoni et al., 2011; Ozgen et al., 2014), contributing to the large levels of SOA found in winter PM in the Po Valley (e.g. Khan et al., 2016; Larsen et al., 2012; Perrino et al., 2013; Pietrogrande et al., 2016). Indeed Putaud et al. (2014) found a significant trend in $PM_{2.5}$ mass and optical properties at the Ispra EMEP site over 2004–2010. This trend was explained by an increment in brown carbon, i.e. in OC content, most likely originating from an increase in biomass burning emissions. The slower decrease in PM at rural sites compared to urban ones might be eventually due also to the wider use of biomass for heating in rural areas, consistent with the spatial results of the simulations by de Meij et al. (2009).

Finally, the results from the present study hint to a rationale to explain the decreasing trends previously found for PM_{10} in the Po Valley (Bigi and Ghermandi, 2014) over 1998–2012: these seem to originate from a drop in the fraction of both primary particles and SIA, with their respective role in the observed trends being site-dependent. This rationale is supported by the decrease in $PM_{10-2.5}$ at Lodi and Merate (traffic sites) and at several UB sites, partly because of the still ongoing technology renewal, a process that started around the year 2000. Rimini experienced a decrease in PM_{10} of $\sim 1\,\mu g\,m^{-3}\,yr^{-1}$, while $PM_{2.5}$ and $PM_{10-2.5}$ decreased by $\sim 0.5\,\mu g\,m^{-3}\,yr^{-1}$ each, suggesting that both primary and SIA significantly contributed to the change in PM_{10} atmospheric concentration. Similar changes occurred in Parma, where the trends were significant for both PM_{10} and $PM_{2.5}$; at the latter site it is worth noting that the increase observed in the fifth quantile of PM_{10} is present (although not significant) for this same quantile of $PM_{10-2.5}$. Finally, similar results apply to Reggio Emilia, i.e. to the other site included both in the present study and in the companion paper.

3.5 Analysis of valley-wide episodes

Two consecutive and worth noting $PM_{2.5}$ pollution episodes occurred in 2012: the first from 16 to 23 January 2012 and the second from 15 to 19 February 2012. These episodes are briefly presented as representative, although extreme, examples of valley-wide PM events.

The episode in January was generated by a persistent inversion layer confining surface emissions; 12:00 UTC radiosoundings at Milan Linate Airport showed thermal inversions up to 10 °C, at a height between ∼ 200 and ∼ 500 m throughout the event. $PM_{2.5}$ concentration was largest in the N–NW sector of the valley (i.e. at the foothill of the Alps) and decreased towards S–SE. The peak in daily $PM_{2.5}$ during this event represented the maximum record ever for several sites (e.g. Bergamo, Turin Caduti) and is equal to or above the respective 94th quantile for all other sites (see Fig. S6). The severity of the event was locally mitigated thanks to aerosol deposition by the several fog precipitation events which occurred across the valley, triggered by the high relative humidity (similarly to the process shown by Gilardoni et al., 2014, during the fog scavenging events of winter 2011).

The second episode occurred during the European cold wave in February 2012, when in most of the valley the coldest temperature over the last ∼ 60 years was observed. In the first days of February large snowfalls occurred over the valley (leading to a 100-year peak in snow height across the E sector), followed by several days of clear-sky conditions, i.e. when the episode occurred. This event featured extremely cold temperatures and thermal inversions at night, confining the intense emissions by heating, and warm–dry conditions at daytime, with a diurnal temperature variation up to 15 °C and with either a minor inversion or an isothermal profile at noon (by radiosounding profile at Milan). The episode was ended by precipitation which occurred on 20 February. This second $PM_{2.5}$ episode was more severe than the former, with $PM_{2.5}$ concentration peaking at $186\,\mu g\,m^{-3}$ (see Fig. S7).

For both events we computed 36 h long backtrajectories by HYSPLIT (Draxler and Rolph, 2013) using 0.5° GDAS meteorological data, and the results refute the possibility of a transboundary pollution episode.

4 Conclusions

Analysis of the trend, of the weekly periodicity, and of the similarity in $PM_{2.5}$ and $PM_{10-2.5}$ concentration time series in the Po Valley was performed. The trend was estimated by generalized least squares (GLS) on monthly deseasonalized time series, by the TS method on annual quantiles and by the TS method on frequency of daily binned concentration for each month. The slopes estimated by TS and GLS on the same time series show good agreement. A significant and widespread decrease in monthly $PM_{2.5}$ and $PM_{10-2.5}$ occurred at the investigated monitoring sites, most often during colder months for the finest particle fraction, with slope getting steeper from rural background towards urban traffic sites. Fewer cases of significant slopes occurred for annual quantiles due to non-linearities, missing data and limited length of annual series. A significant weekly cycle (i.e. possibly forced by anthropogenic emissions) was found for several $PM_{2.5}$ series. This periodicity occurred more often in summer, probably because of the lower contribution to PM by SIA and by biomass burning emission compounds during warmer months, along with an increase of the primary particle fraction. For all $PM_{10-2.5}$ series a significant weekly cycle was found throughout the year. Notwithstanding that the investigated sites show similar trends and patterns, a hierarchical cluster analysis of daily $PM_{2.5}$ concentration showed some differences between western, eastern and southern areas of the valley.

Finally, the trends in atmospheric $PM_{2.5}$ and $PM_{10-2.5}$ concentration, in emissions, in the vehicular fleet composition, and in fuel sales were compared: the results suggest that the observed drop in $PM_{2.5}$ was generated by the renewal in vehicular fleet over the Po Valley, i.e. the introduction of vehicles having more efficient engines and improved emission control systems, leading to a drop in the fraction of primary particles and of SIA (triggered by the reduced NO_x emissions). Regarding $PM_{10-2.5}$, results suggest that a significant decrease in primary coarse particulate emissions occurred until recently, again due to a technology renewal in the vehicular fleet: most likely the latter is partly responsible for the drop in atmospheric PM_{10} previously observed in the Po Valley in the companion paper.

Study outlooks include the assessment of the role of SOA and of emissions in neighbouring regions on the observed trends.

5 Data availability

The data used in this study are available at the Air Quality e-Reporting (AQ e-Reporting). Permalink to the current version is http://www.eea.europa.eu/ds_resolveuid/c0483fb2753342cabda8e7b4f4fea3f7 (EEA, 2016).

The Supplement related to this article is available online at doi:10.5194/acp-16-15777-2016-supplement.

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