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Long-term trend and variability of atmospheric PM_{10} concentration in the Po Valley

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Abstract. The limits to atmospheric pollutant concentration set by the European Commission provide a challenging target for the municipalities in the Po Valley, because of the characteristic climatic conditions and high population density of this region. In order to assess climatology and trends in the concentration of atmospheric particles in the Po Valley, a data set of PM_{10} data from 41 sites across the Po Valley have been analysed, including both traffic and background sites (either urban, suburban or rural). Of these 41 sites, 18 with 10 yr or longer record have been analysed for long-term trend in deseasonalized monthly means, in annual quantiles and in monthly frequency distribution. A widespread significant decreasing trend has been observed at most sites, up to a few percent per year, by a generalized least squares and Theil–Sen method. All 41 sites have been tested for significant weekly periodicity by Kruskal–Wallis test for mean anomalies and by Wilcoxon test for weekend effect magnitude. A significant weekly periodicity has been observed for most PM_{10} series, particularly in summer and ascribed mainly to anthropic particulate emissions. A cluster analysis has been applied in order to highlight stations sharing similar pollution conditions over the reference period. Five clusters have been found, two encompassing the metropolitan areas of Turin and Milan and their respective nearby sites and the other three clusters gathering northeast, northwest and central Po Valley sites respectively. Finally, the observed trends in atmospheric PM_{10} have been compared to trends in provincial emissions of particulates and PM precursors, and analysed along with data on vehicular fleet age, composition and fuel sales. A significant basin-wide drop in emissions occurred for gaseous pollutants, contrarily to emissions of PM_{10} and $PM_{2.5}$, whose drop was low and restricted to a few provinces. It is not clear whether the decrease for only gaseous emissions is sufficient to explain the observed drop in atmospheric PM_{10}, or if the low drop in particulate emissions is indeed due to the uncertainty in the emission inventory data for this species.

1 Introduction

Airborne particulate matter with aerodynamic diameter equal to or smaller than 10 µm have been proved to have detrimental effects on air quality and on human health (for a review see World Health Organization, 2006, and references therein). European regulations on ambient air quality and on atmospheric emissions have led to a clear decrease for some atmospheric pollutants. Among these, SO_2 showed a decrease at a continental scale (e.g. Vestreng et al., 2007), whereas the reduction amount for PM_{10} was site dependent (e.g. Anttila and Tuovinen, 2010; Barmpadimos et al., 2011). The most recent European Directive on air quality limits (2008/50/EC) provides limits both for PM_{10} and $PM_{2.5}$ and recognizes also the importance of their chemical composition, concordantly with the scientific literature (e.g. Bell et al., 2007; Roemer et al., 2000).

This study focuses on the climatology of PM_{10} in the Po Valley, a European region well known for its remarkably high concentration levels of air pollutants, compared to most of the rest of Europe (Bigi et al., 2012; Putaud et al., 2010). In this region several previous studies focused on ambient air quality, particularly on particulate aerosols, and relied on medium- to short-term sampling campaigns. The main outcome of these studies is a set of detailed information on the chemical and physical properties of particulate matter, highlighting a large presence of secondary inorganic aerosols

(SIAs): in Bologna urban background Putaud et al. (2010) and Matta et al. (2003) found a concentration range of 40–44 % of ammonium, nitrate and sulfate in $PM_{2.5}$ and PM_{10}. A different composition was observed by Carbone et al. (2010) at the Po Valley rural background site of San Pietro Capofiume, where ~ 50 % of PM_{10} is represented by ammonium, nitrate and sulfate. Observations from the Milan urban background (Carbone et al., 2010) showed ammonium, nitrate and sulfate to account for ~ 30 % of PM_{10}, consistently with a continental-wide decreasing trend of soluble ion percentage in PM_{10} from rural to kerbside sites (Putaud et al., 2004). Notwithstanding differences in aerosol composition and concentration across the Po Valley, throughout the region PM_{10} and $PM_{2.5}$ exhibited a distinctive seasonality and large concentration amounts if compared to most of Europe (e.g. Rodríguez et al., 2007; Putaud et al., 2004). Nonetheless, local environmental agencies have evidenced an increasing number of Po Valley sites respecting the annual average limits for PM_{10} over the last decade (e.g. ARPA Emilia-Romagna, 2012); although the high $PM_{2.5}$ to PM_{10} ratios (up to 0.9) at many sites (e.g. Ispra, Bologna, Milan in Putaud et al. (2010) and Marcazzan et al., 2003) represents a challenge with respect to the $PM_{2.5}$ limits.

To the authors' knowledge, there are extremely few studies in the literature concerning the long-term trend of atmospheric compound concentration in the Po Valley and in Italy in general: Ciattaglia et al. (1987) found an increasing trend in CO_2 concentration at Monte Cimone over the period 1979–1985; Bigi et al. (2012) found a decreasing trend for many pollutants at an urban background site in Modena, Po Valley, over the period 1998–2010; Artuso et al. (2009) investigated CO_2 concentration trend at Lampedusa from 1992 to 2008.

A large number of studies worldwide have focused on the climatology and trend in atmospheric pollutants: e.g. Anttila and Tuovinen (2010) used a generalized least squares (GLS) method to estimate trends of various gaseous pollutants and PM_{10} in Finland; Tripathi et al. (2010) used a similar method to estimate ozone trends at eight sites in Ireland. Lefohn et al. (2010) used the Theil–Sen slope (Sen, 1968) to show the trend in three different exposure metrics of tropospheric ozone in the United States over the period 1980–2008. More recently Collaud Coen et al. (2013) and Asmi et al. (2013) used several techniques to detect long-term trends of optical properties and number concentration of aerosols at Global Atmosphere Watch sites. Some authors removed the influence of meteorology on pollutant concentration prior to the estimate of trends: Wise and Comrie (2005) estimated the trends in ozone and PM_{10} in the southwestern United States by using a Kolmogorov–Zurbenko filter; Flaum et al. (1996) used this same method to remove seasonality and the influence of selected meteorological variables on tropospheric ozone data. Mueller (2005) used generalized additive models (GAMs) to estimate trends in sulfate concentration in the eastern United States without the influence of meteorology; GAMs were also used by Barmpadimos et al. (2011) to estimate meteorologically adjusted trends for PM_{10} across Switzerland.

PM_{10} measurements in the Po Valley started in late 1997; the monitoring network has seen little redesign in the last 15 years. In order to provide a representative study of PM_{10} in the Po Valley, a data set comprising 41 sites with different activation times and all active up to 1 January 2012 (Table 1) has been analysed. The monitoring sites, described in detail in Sect. 2, are part of the network run by the Regional Environmental Protection Agencies operating in the Po Valley. In Sects. 2.1–2.4 descriptions of the methods used are presented. The results and their discussion are described in Sect. 3 and conclusions are found in Sect. 4.

2 Data and methods

This study involved PM_{10} sampled at 41 air quality monitoring stations of the Regional Environmental Protection Agencies (ARPA) operating in the Po Valley: site listing is reported in Table 1 and mapped in Fig. 1. All data refer to actual sampling conditions, as required by 2008/50/EC. Different sampling instruments are used over the network: the beta attenuator (Swam 5A RL by FAI, SM200 by Opsis, MP101M by Environnement S.A.), TEOM and TEOM-FDMS (by Thermo Environmental), and low-volume samplers (TCR by TECORA). TEOM data are corrected by a multiplicative factor, whose value is derived by ARPA-Lombardia and changes on a monthly basis, ranging from 1 (July) to 1.35 (January) (Colombi et al., 2011). 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, i.e. the data are obtained by calibrated instruments, and undergo daily, seasonal and annual comparison with nearby sites as well as with previous data. Nevertheless, all data have been manually inspected by the authors: annual, monthly, weekly and daily patterns have been examined for all sites and spurious values have been removed (e.g. peaks from festival bonfires).

Concentration data have been compared to emission estimates provided by the National Institute for Environmental Protection and Research (ISPRA). Total national emissions are estimated according to the EMEP-CORINAIR guidebook, the IPCC guidelines and the Good Practice Guidance and classified accordingly to SNAP (Selected Nomenclature for Air Pollution) (Romano et al., 2012). Total national emissions from road transport (SNAP sector 7) derive from COPERT 4 v9.0 and include non-exhaust emissions of PM_{10} and $PM_{2.5}$ by road vehicle tyre and brake wear (SNAP 0707). The inventory does not include emissions from road surface wear (SNAP 0708) since this is not considered sufficiently reliable (Romano et al., 2012). An overall uncertainty analysis of the Italian inventory is not available, aside from a general

Table 1. Analysed PM_{10} sampling sites for long-term trend and for extended statistical analysis. All sites have been active up to January 2012. Station type lookup: UB – urban background, UT – urban traffic, SuB – suburban background, SuT – suburban traffic, RB – rural background, RR – rural remote.

ID	Station name	Station type	Activation date
	Long-term trend data set		
1	Arese	UB	Jan 2002
2	Bergamo Meucci	UB	Jul 2000
3	Brescia Broletto	UT	Oct 2000
4	Castelnovo Bariano	SuB	Jan 2002
5	Forlì	UB	Jan 2001
6	Limito	UB	Mar 1998
7	Magenta	UB	Mar 1998
8	Meda	UT	Feb 1998
9	Modena	UB	Feb 1998
10	Parma	UB	Apr 2002
11	Pizzighettone	UB	Feb 2000
12	Ravenna Zalamella	UT	Oct 1999
13	Reggio Emilia	UB	Jun 2001
14	Rimini	UB	Jan 2001
15	Torino Caduti	SuB	Jan 2002
16	Torino Consolata	UT	Jul 1999
17	Treviglio	UT	Feb 2000
18	Vimercate	UB	Feb 1998
	Extended analysis data set		
19	Alessandria Lanza	UB	Feb 2007
20	Asti D'Acquisto	UB	Dec 2002
21	Biella Sturzo	UB	Feb 2003
22	Bologna	UB	Nov 2007
23	Borsea	UB	Jan 2003
24	Carmagnola	SuT	Jan 2006
25	Cerano	SuB	Jan 2005
26	Cremona	UB	Apr 2006
27	Druento	RB	Nov 2002
28	Febbio*	RR	Nov 2004
29	Imola	UT	Nov 2003
30	Mantova Ariosto	UB	Jan 2003
31	Mantova Gramsci	UT	Aug 2005
32	Mantova S.Agnese	UB	Jan 2005
33	Milan	UB	May 2007
34	Padova Mandria	UB	Jan 2004
35	Piacenza	UB	Jan 2005
36	Rovigo	UT	Jan 2004
37	Sannazzaro De' Burgondi	UB	Jan 2007
38	Verona Cason	RB	Jan 2004
39	Verona C.so Milano	UT	Jan 2003
40	Vigevano Petrarca	UT	Sep 2004
41	Voghera Pozzoni	UB	Nov 2005

* All are within the Po Valley besides Febbio, sited at 1121 m a.m.s.l.

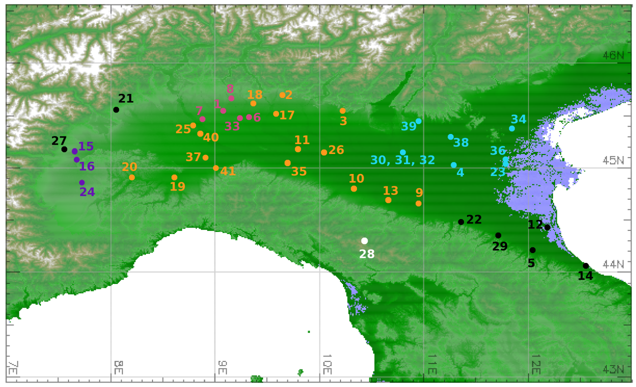

Figure 1. Location of PM_{10} monitoring stations included in the analysis. The key for ID number is found in Table 1, the colour coding refers to the result of cluster analysis using Euclidean distance (Fig. 5a).

assessment of uncertainty for greenhouse gas emissions (Romano et al., 2012). National emissions estimates (including those from SNAP 0707) for the years 1990, 1995, 2000, 2005 and 2010 have been attributed to each Italian province through a top-down procedure (De Lauretis et al., 2009; Bernetti et al., 2010). In this study we considered provincial emissions estimates (inventory version 13_05_2013) for direct particulate emissions (i.e. PM_{10} and $PM_{2.5}$) and main particle precursors, SO_2, NO_x, non-methane volatile organic carbon (NM-VOC), CH_4, NH_3 and finally CO, as a tracer for gasoline combustion. Only provinces having a significant part of their land within the Po Valley have been considered, assuming that most of the emissions occur in the valley part of the province, where most of the activities and population are located, instead of the mountainous parts. Also data on vehicular fleet composition and fleet age for each province have been 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 have been performed by the software environment R 2.14.1 (R Development Core Team, 2011).

2.1 Analysis of long-term trends

Eighteen sites out of 41 have been analysed for the presence of long-term trend, having a record of at least 10 years and being spread across the whole valley. Trends have been studied on monthly and annual data, where monthly and annual statistics of daily data have been computed if at least 75 % of the daily data were available for the respective month or year. Monthly average concentrations have been decomposed into trend, seasonal and remainder components by STL (Seasonal-Trend decomposition by Loess) technique (Cleveland et al., 1990), assuming a steady periodicity and amplitude in the seasonal component throughout the sampling period. All time series showed a lognormal distribution, as is common for air pollution data (Bencala and Seinfeld, 1976), therefore data have been log-transformed prior to decomposition in order to achieve normally distributed residuals, whose normality and independence have been tested by Q–Q plot, Shapiro test and autocorrelation function. Finally, the analysis of monthly trend time series was performed on back-transformed logarithmic trend data.

In order to test the trend component for a significant slope, the GLS method (Brockwell and Davis, 2002) has been applied: GLS is used to estimate the linear relation between an autocorrelated time series and time so as to obtain independent residuals and a correct estimate of the variance of the regression coefficients. GLS consists of a combined application of two models: a linear model to the data and an ARMA(p, q) model to the residuals of the linear model. GLS has been used instead of standard ordinary least squares, since the application of the latter on autocorrelated time series would lead to an incorrect estimate of the variance of the model coefficients, therefore fouling their significance test. In the present study the ARMA model parameters have been selected via minimization of the Bayesian information criterion (BIC) (Brockwell and Davis, 2002). In this study, residuals exhibited an ARMA(2,2) correlation structure for all time series. Finally, 95 % confidence bands of GLS slope have been estimated via bootstrap by model-based resampling (Davison and Hinkley, 1997): the residuals from the fitted GLS model have been centred and equiprobably resampled with replacement to provide innovations to an ARMA process whose parameters are the ones initially estimated on the original time series. This simulated ARMA process has been added to the fitted GLS model to obtain a bootstrapped time series for which the slope has again been calculated by GLS method. With this technique $N = 1999$ bootstrapped time series have been generated. Results are found in Table 2 and graphs for Modena, Limito and Vimercate in Fig. 2. Long-term trend has been estimated both for the whole time series length and over the period 2002–2011. This latter interval is primarily for comparison among sites, because all 18 sites have been simultaneously active only since 2002; moreover, this allows us to estimate the presence of possible changes in slope over the investigated period for older sites.

The parametric estimate of trend slope by GLS has been compared to a fully non-parametric trend estimate. This latter has been computed on annual statistics of daily data. The 5th, 50th and 95th annual quantiles have been calculated for each year from the daily data for all years with at least 75 % data capture of daily data per year: this limiting data capture percentage is lower than the 95 % required by the 2008/50/EC for computing annual statistics, but it has been considered a good compromise between representativeness and the need for continuous quantile time series (see also Lefohn et al., 2010; Anttila and Tuovinen, 2010). In order to test for the occurrence of a non-null slope in the data the non-parametric Theil–Sen slope estimate (hereafter TS) has been calculated.

The TS approach shares the same statistics (named S) as the Mann–Kendall test (MK) for trend (Hipel and Mcleod, 1994): the latter estimates the significance of the trend, TS provides an estimate for the slope of the trend. The null

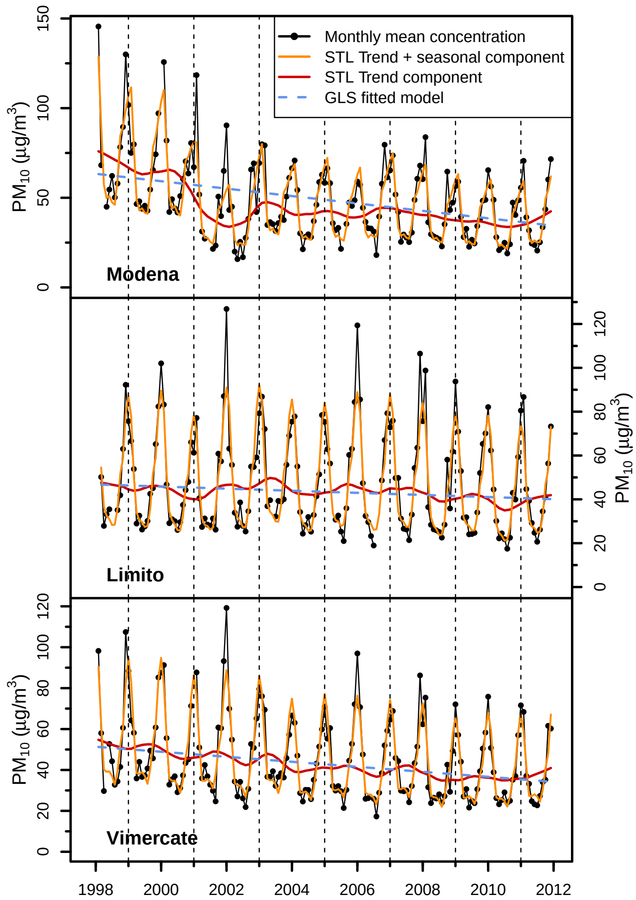

Figure 2. STL decomposition for monthly mean PM_{10} along with GLS fitted slope for three selected sites.

hypothesis for MK (and TS) requires the data to be independent and randomly ordered, which rarely occurs in time series of natural phenomena. Dependence in the time series invalidates the test, leading to an inflated estimate of the variance of S. A corrected estimate of the variance of S for seasonal and slightly autocorrelated data and for non-seasonal autocorrelated data has been provided respectively by Hirsch and Slack (1984) and Hamed and Ramachandrarao (1998). Prewhitening (i.e. estimating and removing the autocorrelation in the data) has been considered an effective pre-processing of the data, allowing a correct application of the MK test to the prewhitened data; however, this procedure is still debated in the scientific community (for a discussion see Hamed, 2009). Another solution to dependency issues is the use of annual data, since these are generally non-autocorrelated. For the annual quantiles of daily data within this study, autocorrelation was negligible, therefore no prewhitening procedure has been applied. The distribution of the S statistics approaches the Normal distribution for large numbers of observations, allowing reliable estimates of the p value for the null hypothesis; due to the few annual data available, asymptotic approximations

Table 2. GLS trend (± standard error) for deseasonalized monthly mean time series of daily PM_{10} concentration. Boldfaced values indicate slope significantly different from zero at a 95 % confidence level.

Station	Slope 2002–2011 $\mu g\, m^{-3}\, yr^{-1}$	Change 2002–2011 $\%\, yr^{-1}$	Slope since time series start $\mu g\, m^{-3}\, yr^{-1}$	Change since time series start $\%\, yr^{-1}$
Arese	**−1.395 ± 0.378**	**−2.9 ± 0.8**		
Bergamo M.	**−1.381 ± 0.339**	**−3.2 ± 0.8**	**−1.120 ± 0.319**	**−2.6 ± 0.7**
Brescia B.	**−1.188 ± 0.331**	**−2.7 ± 0.7**	**−0.690 ± 0.375**	**−1.5 ± 0.8**
Castelnovo Bariano	**−1.099 ± 0.316**	**−2.7 ± 0.8**		
Forlì	**−1.504 ± 0.401**	**−4.7 ± 1.3**	**−1.204 ± 0.324**	**−3.6 ± 1.0**
Limito	**−0.892 ± 0.158**	**−1.9 ± 0.3**	**−0.508 ± 0.127**	**−1.1 ± 0.3**
Magenta	**−1.273 ± 0.363**	**−2.7 ± 0.8**	**−0.648 ± 0.247**	**−1.4 ± 0.5**
Meda	**−1.450 ± 0.431**	**−2.9 ± 0.9**	**−1.182 ± 0.315**	**−2.3 ± 0.6**
Modena	0.190 ± 0.523	0.4 ± 1.2	**−2.087 ± 0.626**	**−4.3 ± 1.3**
Parma	**−0.629 ± 0.395**	**−1.7 ± 1.0**		
Pizzighettone	**−1.086 ± 0.179**	**−2.5 ± 0.4**	**−0.581 ± 0.208**	**−1.4 ± 0.5**
Ravenna Zalamella	−0.555 ± 0.833	−1.6 ± 2.4	**−1.310 ± 0.548**	**−3.5 ± 1.5**
Reggio E.	−0.114 ± 0.800	−0.3 ± 2.3	−0.169 ± 0.700	−0.5 ± 2.0
Rimini	**−0.987 ± 0.227**	**−2.7 ± 0.6**	**−0.745 ± 0.222**	**−2.0 ± 0.6**
Torino Caduti	**−1.173 ± 0.503**	**−2.6 ± 1.1**		
Torino Consolata	**−2.293 ± 0.390**	**−4.0 ± 0.7**	**−2.094 ± 0.237**	**−3.6 ± 0.4**
Treviglio	−0.514 ± 0.641	−1.2 ± 1.5	0.240 ± 0.721	0.6 ± 1.7
Vimercate	**−0.941 ± 0.174**	**−2.2 ± 0.4**	**−1.257 ± 0.114**	**−2.8 ± 0.3**

are hardly reliable, therefore bootstrap techniques have been applied to estimate the p value of the TS slope b_0 as in Yue and Pilon (2004). An empirical cumulative distribution function of the null distribution of b_0 with null hypothesis H_0: $b_0 = 0$ has been produced by taking $N = 1999$ bootstrap samples, and the p value under H_0 has been estimated. Results from TS analysis on annual quantiles are presented in Table 3 and sample graphs for Rimini and Limito time series are presented in Fig. 3.

Due to the strong seasonality of pollutant concentration in the Po Valley, the long-term trend for PM_{10} concentration within each month has also been computed. In order to assess a seasonal long-term trend, PM_{10} daily concentration for each month has been binned in 15 $\mu g\, m^{-3}$ increments, and the frequency of each bin in each month for each year over the sampling period has been computed. The long-term trend in these frequencies for each month have been estimated by TS method and significance has been tested by non-parametric bootstrap, similarly to annual quantiles. As shown in Oltmans et al. (2006), this kind of analysis highlights changes in frequency distribution of concentration data in a specific month. Months with significant trends at each site are listed in the rightmost column of Table 3 and the resulting graphs for Castelnovo Bariano and Parma sites are presented in Fig. 4.

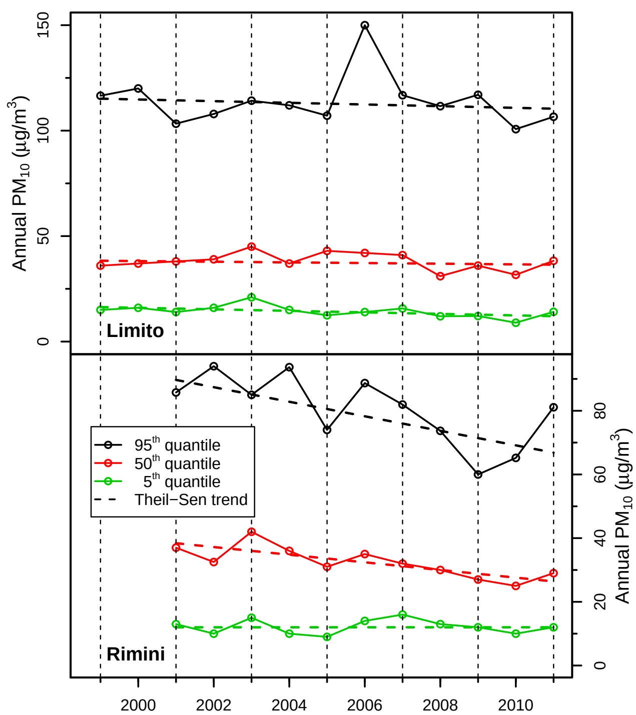

Figure 3. Annual quantiles along with Sen slope for daily PM_{10} at Limito and Rimini.

2.2 Analysis of weekly cycles

A few different indices and few different statistical tests can be used to verify the significance of a weekly cycle (see

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

Station	5th annual quantile		50th annual quantile		95th annual quantile		Months with significant trend
	Slope $\mu g\,m^{-3}\,yr^{-1}$	Change $\%\,yr^{-1}$	Slope $\mu g\,m^{-3}\,yr^{-1}$	Change $\%\,yr^{-1}$	Slope $\mu g\,m^{-3}\,yr^{-1}$	Change $\%\,yr^{-1}$	
Arese	**−0.500**	**−3.5**	**−1.400**	**−3.7**	−3.125	−2.8	2–4 (–), 6–7 (–), 9–11 (–)
Bergamo M.	**−0.750**	**−5.5**	**−1.714**	**−4.8**	**−2.730**	**−2.8**	1 (–), 3 (–), 5 (–), 7–8 (–), 10–11 (–)
Brescia B.	**−0.714**	**−5.2**	**−1.071**	**−2.9**	−0.030	0.0	3 (–), 6 (–), 8 (–), 10–12 (–)
Castelnovo B.	**−0.236**	**−1.9**	**−1.500**	**−4.6**	**−4.600**	**−5.0**	1 (–), 3 (–), 6 (–), 8–11 (–)
Forlì	**−0.606**	**−5.5**	**−1.250**	**−4.6**	**−3.643**	**−5.1**	1 (–), 3 (–), 6–8 (–), 10–12 (–)
Limito	**−0.342**	**−2.4**	−0.156	−0.4	−0.616	−0.5	5 (–), 7–9 (–)
Magenta	**−0.121**	**−0.7**	**−0.625**	**−1.6**	**−2.112**	**−2.0**	4 (+), 7–9 (–)
Meda	**−0.219**	**−1.4**	−0.542	−1.4	**−3.011**	**−2.5**	1 (–), 3 (–), 5–8 (–), 10 (–), 12 (–)
Modena	**−0.138**	**−0.9**	**−1.657**	**−4.3**	**−4.046**	**−3.8**	1–12 (–)
Parma	**0.462**	**4.1**	**−1.000**	**−3.0**	**−2.550**	**−3.2**	2 (±), 3–8 (–), 11 (±), 12 (+)
Pizzighettone	**−0.329**	**−2.1**	**−0.621**	**−1.6**	−1.429	−1.7	2–3 (–), 9 (–), 11 (–)
Ravenna Z.	**−0.775**	**−5.7**	**−1.889**	**−6.0**	**−5.173**	**−6.4**	1–8 (–), 10–12 (–)
Reggio E.	**−0.013**	**−0.1**	−0.857	−2.9	−1.575	−2.1	1–3 (–), 6–8 (–), 10–11 (–)
Rimini	0.000	0.0	**−1.200**	**−3.7**	**−2.283**	**−2.8**	3 (–), 6–10 (–)
Torino Ca.	**−0.429**	**−3.5**	**−1.500**	**−4.0**	−0.161	−0.2	1–7 (–), 9 (–), 10 (+), 12 (+)
Torino Co.	**−1.130**	**−5.8**	**−2.056**	**−4.3**	**−3.078**	**−2.4**	1 (–), 3–9 (–)
Treviglio	**−0.250**	**−1.7**	−0.333	−1.0	−1.950	−1.9	2–3 (–)
Vimercate	**−0.418**	**−2.7**	**−1.000**	**−2.7**	**−3.439**	**−3.4**	1–3 (–), 5–10 (–), 12 (–)

Daniel et al., 2012, for a critical review). In the present study the analysis of weekly cycles involved the complete data set of 41 PM_{10} time series, and investigating both the continuous time series separately for winter (January, February, March) and summer (June, July, August) seasons. The study of the weekly cycle focused on PM_{10} anomalies, and proceeded as follows: the seasonal cycle was filtered out by computing the deviation of daily data to a running mean of daily data, which was calculated as the centred mean with a window of 31 days. The result is a new time series of deviations, in which the interference of the seasonal cycle is negligible. As the data are highly non-normal, the analysis of deviations used non-parametric statistical tests (Barmet et al., 2009): each of the newly created time series was grouped by weekdays, and the mean and standard deviation of each group were calculated, resulting in a weekly cycle of mean anomalies.

These latter were analysed by the Kruskal–Wallis test, a non-parametric test with the null hypothesis that the location parameters of the distribution of observations are the same in each group (i.e. weekday). The Kruskal–Wallis statistic follows a χ^2 distribution. In order to double check the significance of weekly cycles, deviations were grouped into 6- and 8-day weeks, and the Kruskal–Wallis test for these anomalies was performed.

The presence of a weekly periodicity was further verified by testing for a significant weekend effect magnitude at each site, i.e. the difference between the mean PM_{10} anomaly of Saturday through Monday and the mean PM_{10} anomaly between Wednesday through Friday (Daniel et al., 2012). The series of weekend effect magnitude was tested by the non-parametric Wilcoxon test for zero median: the results are presented in Table 4, while graphs of the 7-day week mean anomaly for all sites are presented in Supplement Figs. S2 and S3 for full year and seasons respectively. An analysis of weekly periodicity was performed also for $PM_{2.5}$ at the sites within Table 1 where both PM_{10} and $PM_{2.5}$ were sampled. Analysis of weekly periodicity on $PM_{2.5}$ provided insight into the differences in composition with PM_{10} and into the possible cause of an eventually significant periodicity for both pollutants. The results for $PM_{2.5}$ are presented in Table 5.

2.3 Cluster analysis

Cluster analysis on PM_{10} daily data was performed on the whole Po Valley data set in order to capture both differences and correlations in absolute concentration levels among monitoring sites. Febbio (ID 28 in Table 1 and Fig. 1) was excluded from this analysis being a remote rural site at 1121 m a.m.s.l in the Apennines and therefore being an outlier and possibly fouling the classification (Kaufman and Rousseeuw, 1990). The cluster analysis was performed by hierarchical agglomerative clustering using two different metrics for distance. In the former the dissimilarity matrix was calculated using Euclidean distances (Figs. 1 and 5a) to highlight differences in absolute PM_{10} levels. In the latter the distance $d_{x,y}$ between two samples x and y was computed using a metric based on Pearson's correlation coefficient r according to

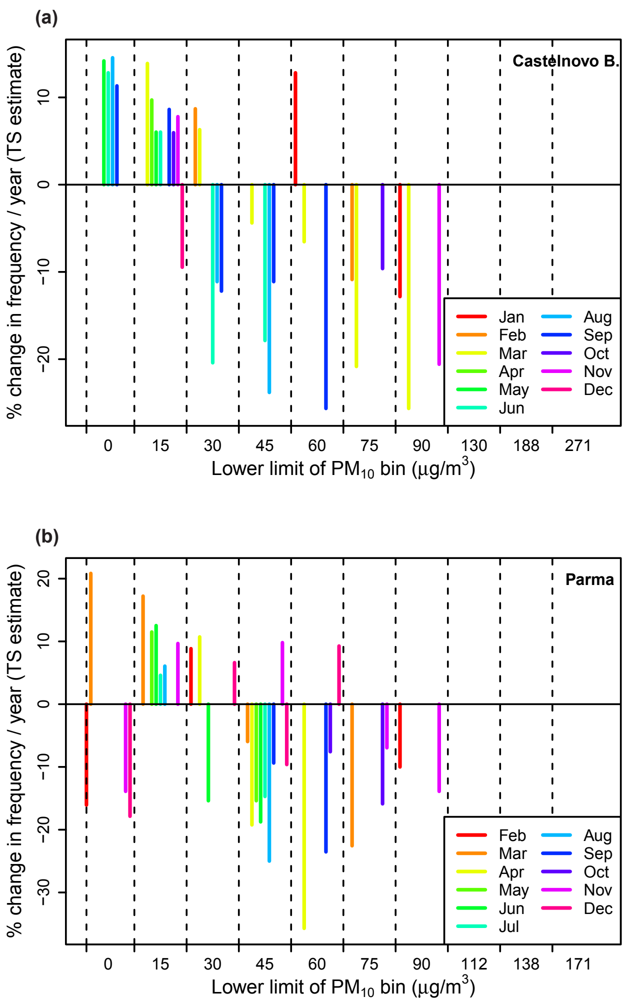

Figure 4. Significant changes in monthly frequency distribution of PM_{10} at Castelnovo Bariano **(a)** and Parma **(b)**.

$d_{x,y} = (1-r_{x,y})/2$. This latter metrics enables us to highlight linear correlation structures among sites (Fig. 5b and Supplement Fig. S1). Cluster aggregation was computed using Ward's method. A simple sensitivity analysis was performed by a "leave-one-out" test, consisting of the production of multiple hierarchical clusters using the same parameters of the original analysis (e.g. Euclidean distance and Ward's aggregation method), but with the removal of one site at the time from the data set. Finally, results were compared with hierarchical divisive clustering computed using the same metrics as above.

2.4 Analysis of long-term trend for inventory emissions

Emission time series for each province consisted of only 5-yearly data (1990, 1995, 2000, 2005, 2010); the aim of this analysis being the comparison of trends in emissions and concentration, data for year 1990 and 1995 were discarded since no PM_{10} data are available for that period. Slope by the TS method was estimated for each province and the relative p value was obtained via bootstrap as described in Sect. 2.1. The rationale of this analysis is to have a quantitative estimate of the drop rate in emissions, notwithstanding the several sources of uncertainty affecting the estimate of long-term trend in emissions. Uncertainties are firstly due to the intrinsic uncertainty in the national inventory emission data (particularly for particulate emissions), secondly to the top-down disaggregation process, thirdly to the very few observations available (five observations in 20 yr) and finally due to the slope estimate method not being suitable for non-monotonic trends (and therefore set as not-significant whenever non-monotonic trends occurred).

Table 4. Results of weekly cycle analysis on PM_{10}: black dots indicate a significant weekly cycle or weekend effect (W. E.) magnitude, at a 95 % confidence level. Results shown are from test application on full year, winter and summer by grouping data in 7-day weeks.

Sites	W. E. magnitude	Weekly cycle		
	Complete series	Complete series	Winter	Summer
Arese	•	•	•	•
Bergamo M.	•	•	•	•
Brescia B.	•	•	•	•
Castelnovo B.	•	•		•
Forlì				
Limito	•	•	•	•
Magenta	•	•	•	•
Meda	•	•	•	•
Modena	•	•		•
Parma	•	•		•
Pizzighettone	•	•	•	•
Ravenna Z.	•	•		•
Reggio E.	•	•	•	•
Rimini	•	•		•
Torino Ca.	•	•	•	•
Torino Co.	•	•	•	•
Treviglio	•	•	•	•
Vimercate	•	•	•	•
Alessandria	•	•		
Asti D'A.	•	•		•
Biella S.	•	•		•
Bologna	•	•		•
Borsea	•	•		•
Carmagnola	•	•		•
Cerano	•	•		
Cremona	•	•		•
Druento	•	•		•
Febbio		•	•	
Imola	•	•		•
Mantova A.	•	•		•
Mantova G.	•	•		•
Mantova S.A.	•	•		•
Milan	•	•		•
Padova M.	•	•		•
Piacenza	•	•		•
Rovigo	•	•		•
Sannazzaro				
Verona Ca.	•	•		•
Verona C.so M.	•	•	•	•
Vigevano	•	•		•
Voghera	•	•		

Table 5. Results of weekly cycle analysis on $PM_{2.5}$ at monitoring sites where both PM_{10} and $PM_{2.5}$ are sampled: black dots indicate a significant weekly cycle or weekend effect (W. E.) magnitude, at a 95 % confidence level. Results shown are from test application on full year, winter and summer by grouping data in 7-day weeks. The last column indicates the mean $PM_{2.5}$ / PM_{10} ratio.

Sites	W. E. magnitude	Weekly cycle			$PM_{2.5}$ / PM_{10} ratio
	Complete series	Complete series	Winter	Summer	
Asti D'A.					0.77
Bergamo	•	•		•	0.79
Bologna					0.69
Cerano					0.94
Cremona					0.70
Forlì				•	0.67
Mantova S.A.	•	•		•	0.76
Milan	•			•	0.65
Parma					0.61
Reggio E.					0.66
Rimini					0.58
Torino Ca.					0.75
Verona Ca.	•	•		•	0.72

3 Results and discussion

Different type of trends have been computed in this study. The data pre-processing procedures used are aimed to minimize the influence of meteorology on the slope estimate. STL is extremely efficient in extracting an almost meteorology-free trend component by the removal of both the seasonal component and the possible outliers (e.g. data influenced by uncommon weather conditions). Similarly quantiles, used for annual statistics, are more robust to outliers than mean values, and therefore less influenced by uncommon weather conditions; moreover, the Theil–Sen slope estimate is also robust to outliers. Uncommon weather conditions are more likely to influence trend analyses focused on one month at a time (e.g. see Barmpadimos et al., 2011); in this study, the use of frequency of binned concentration and Theil–Sen slope estimates are again aimed to minimize the bias due to meteorology. Finally, the use of resampling techniques reduces the possible influence of outliers on trend estimates.

The influence of long-term trends in meteorological variables are also expected to be negligible: Toreti et al. (2009) estimated a drop in 1.47 mm yr^{-1} in winter precipitation over northern Italy for the period 1961–2006, when annual precipitation ranged between 750 and 1000 mm. Trends for average, minimum and maximum atmospheric temperature in the Po Valley ranged between 0.9 and 1.1 K per century (period 1865–2003) according to Brunetti et al. (2006). Simolo et al. (2010) found a significant increase in maximum atmospheric temperature in northern Italy ranging between ~ 0.4 and ~ 0.1 K per decade, depending upon season, and similar trends for minimum temperature have been found by the same authors. The trends observed in these studies for precipitation and temperature range around a few mil per year and a few hundredth of K per year respectively. It is not unreasonable to assume that these latter trends are also valid for the period 1998–2011, and we can consider their influence on PM_{10} concentration as negligible compared to the variability of emissions and meteorology.

3.1 Results from long-term trend analysis

A GLS estimate assumes the trend to be linear, i.e. it does not take into account possible nonlinearities in the trend component. Nonetheless, due to the features of the monthly data investigated, inaccuracy in slope estimates due to nonlinearity are assumed to be negligible, because of the efficient deseasonalization by STL and the steady trend observed for nearly all time series.

Slopes resulting from GLS analysis are presented in Table 2. The trend is significantly decreasing for almost all sites investigated; the slope is generally steeper for the period 2002–2011 for all observations besides Modena, Reggio Emilia and Vimercate, contrarily for instance to the PM_{10} trends observed in the UK (Harrison et al., 2008). Results from TS trend analysis are partially consistent with GLS estimates, as in the case of Arese, Magenta, Pizzighettone, Rimini or Ravenna, whose trend for monthly means is fairly close to the trend for annual medians. Treviglio, exhibiting a null slope for monthly mean over both analysed intervals, has a null TS slope for all quantiles. As expected, significant slopes occur more frequently for 50th and 95th quantiles than for lower concentration, indicating a more widespread decrease in peak concentration.

PM_{10} in the Po Valley exhibits a distinctive seasonality, and the steeper drop in annual higher concentrations (occurring in winter) is coupled with a significant drop in daily concentration also for summer months. The results of the analysis of monthly frequency distribution of daily PM_{10} are presented in Table 3, where a − sign next to a specific month indicates a decrease in frequency of higher concentration bins towards lower bins, a + sign in Table 3 next to a specific month indicating a shift from lower to higher concentration bins and a ± sign indicating a shift in lower and higher concentration bins towards median concentrations. The results for monthly trend show a general decrease at all sites for most months, indicating that these trends are negligibly influenced by meteorology. It is worth noting that all summer months having a significant slope exhibit a concentration decrease, while some winter months show an increase or a shift to median bins.

Trend slopes are similar to other sites in Europe: Barmpadimos et al. (2012) found a PM_{10} decrease ranging between -0.5 and $-1.3\,\mu g\,m^{-3}$ in five rural sites within the EMEP network over the period 1999–2010 and ascribed most of the decrease to a change in $PM_{2.5}$ concentrations. The significant decrease in PM_{10} found by Anttila and Tuovinen (2010) in Finland is lower in absolute value (ranging between -0.5 and $-0.1\,\mu g\,m^{-3}$), but similar in relative drop; however, in that study, PM_{10} drop was significant almost exclusively at industrial or traffic sites, contrarily to the broad decrease in the Po Valley.

3.2 Results from weekly cycle analysis

The significant and widespread decrease in PM_{10} concentration across the Po Valley suggests its strong anthropogenic origin. This assumption has been further investigated by testing time series for significant weekly pattern by two procedures: weekly cycle analysis and weekend effect magnitude in PM_{10} and $PM_{2.5}$ deviations. Table 4 presents sites with PM_{10} daily data exhibiting a significant cycle and Supplement Figs. S2 and S3 show the 7-day week anomaly for the whole year and for the winter and summer seasons. All sites besides Febbio showed the same pattern for mean anomaly, although with different intensity, with a minimum from Saturday through Monday and a maximum on Wednesday or Thursday. Febbio showed a significant increase from Monday through Sunday, which is believed to be due to an increase in emissions (e.g. wood-burning for domestic heating or traffic) during weekends: the village counts ~ 170 inhabitants, with private houses for holidays and a nearby ski area whose plants have been operating since ~ 1950 (until 2010).

Results from the two tests for weekly periodicity are very similar. Considering the whole year, a significant weekly periodicity is present during the 7-day week at all sites besides Febbio (according to weekend effect magnitude only), Forlì and Sannazzaro (see Fig. S2 in the Supplement). As shown in Supplement Fig. S3 and Table 4, most of the shorter time series show a weekly periodicity in summer and not in winter for the 7-day weeks, whereas many of the longer ones still exhibit a weekly periodicity in both seasons. The lack of weekly periodicity in winter might be due to the large fraction of SIA in PM_{10} in this season (Larsen et al., 2012), uncoupling the weekly fluctuations of primary anthropogenic emissions (non-exhaust included) and PM_{10} concentration. This behaviour was observed by Bernardoni et al. (2011) in Milan urban background conditions, where the relative contribution of direct human-related particulate sources (e.g. resuspension, traffic, industry) to summer PM_{10} is higher than in winter, consistently with a significant periodicity in summer weeks. Possibly this buffering effect by SIA is dimmed in the longer time series by a higher primary / SIA ratio in the late 1990s early 2000s, leading more likely to significant weekly cycles in winter, although this hypothesis should be substantiated by further analyses. The test of weekly cycles for 6- and 8-day weeks was non-significant for all sites besides Magenta in winter 6-day week and Voghera in the complete series 8-day week, supporting the significance of tests on 7-day weeks.

$PM_{2.5}$ in the Po Valley has been shown to have a larger relative fraction of secondary aerosol than PM_{10}, ranging between 27 and 52 % in Milan from observations by Giugliano et al. (2005), Rodríguez et al. (2007) and Lonati et al. (2010) or between 32 and 47 % in Bologna (Matta et al., 2003). Moreover, the contribution from re-suspended dust to $PM_{2.5}$ is expected to be smaller than to PM_{10} (Amato et al., 2009). Consistently a significant weekly cycle in $PM_{2.5}$ is observed at only a few sites, perhaps driven by a stronger contribution of anthropic primary particulate compared to other $PM_{2.5}$ sites (Table 5).

3.3 Results from cluster analysis

PM_{10} showed persistent features across the Po Valley: strong seasonality, decrease in annual and monthly statistics and change in monthly frequency distribution. Results from hierarchical cluster analysis showed some differences among the investigated sites, mostly due to their geographical location instead of their classification according to the air-quality network, suggesting a not so uniform spatial distribution of PM_{10} concentration. The classifications in Fig. 5 shows five main clusters, confirmed by sensitivity analyses. There is a group based in the southeast side of the valley having similar patterns and lower concentration compared to other sites in the valley. Also two northwestern background sites (Biella and Druento) having relatively low concentration are included in the SE cluster (Fig. 5a), although their pattern is similar to the surrounding sites (Fig. 5b and Supplement Fig. S1). Two clusters identify quite nicely the two main metropolitan areas of the valley, Turin and Milan, having distinctive PM_{10} levels compared to the rest of the valley (see Fig. 5a). Finally, both the northeast and the centre of the Po Valley are grouped according to their PM_{10} levels and patterns leading to two different clusters. Sensitivity analysis and divisive hierarchical clustering showed a persistent structure featured by the four main clusters representative of the metropolitan areas of Turin and Milan and the ones of the southeast and northeast of the valley, with the sites in the central Po Valley, and generally sites at cluster boundaries, occasionally assigned to the geographically adjacent cluster.

3.4 Results from emission trend analysis and discussion

Estimated emission trends for the whole Po Valley over the period 2000–2010 were significant for gaseous pollutants and not significant for PM_{10} and $PM_{2.5}$. The significant slope for each investigated gaseous compound was as follows: $-3.5\,\%\,yr^{-1}$ (SO_2), $-2.5\,\%\,yr^{-1}$ (NO_x), $-3.7\,\%\,yr^{-1}$ (NM-VOC), $-1.9\,\%\,yr^{-1}$ (CH_4), $-6.7\,\%\,yr^{-1}$ (CO) and $-1.2\,\%\,yr^{-1}$ (NH_3). At a province scale there is large variability in emission trend: thematic maps of significant trends in NM-VOC, NO_x and PM_{10} emissions are presented in Supplement Fig. S4. No significant statistical correlation arose from the comparison of trends in background PM_{10} and emissions in each province. However, the outcomes of the analyses in Sects. 3.1, 3.2 and 3.3 strongly suggest that the drop observed in PM_{10} concentration derives primarily from an overall decrease in emissions in the Po Valley.

The SNAP sectors responsible for the investigated emissions are few, with road transport (SNAP sector 7) being the main source for several of the pollutants listed above (see Fig. S5 in the Supplement). From 2000 to 2010 road transport almost zeroed its contribution to SO_2 emissions, thanks to directive 2003/17/EC and unleaded gasoline. Also relative contribution of road traffic to NM-VOC, CO, PM_{10} and $PM_{2.5}$ has dropped, and only NO_x kept road traffic as its main source over the 2000–2010 period (see Supplement Fig. S5). The drop in both absolute and percentage emissions from road transport occurred notwithstanding an increase of 15 % in total number of vehicles in the Po Valley (period 2002–2011), with an increase of 10 % in passenger cars and of 22 % in light duty vehicles (LDVs). This increase occurred along with a dieselization of the fleet, with the rate of diesel vehicles (considering passenger cars, LDVs and HDVs) rising from ~26 % to ~42 % over the period 2002–2011, along with a renewal of the fleet. Changes in vehicular fleet composition and estimated emissions are consistent with the observed trend in unleaded gasoline and diesel sales: the former decreased by 41 % and the latter increased by 19 % over the period 2002–2011 considering the whole Po Valley. Fleet renewal has been forced by driving restrictions applied to older vehicles in the Po Valley since 2002. Initially restrictions focused only on gasoline vehicles non-EURO-1 compliant (i.e. 91/441/EC and 93/59/EC), diesel vehicles non-EURO-2 compliant and/or without DPF (Diesel Particulate Filter) and two-stroke engines; later, stricter restrictions were applied. In 2002, 32 and 42 % of circulating cars and LDVs respectively were built prior to 1993 (i.e. were older than 10 yr) and were not EURO-1 compliant. In 2011 13 % of the cars and 22 % of LDVs were built prior to 1995, i.e. possibly not EURO-1 compliant, thus showing an increase in vehicles having more efficient engines and improved emission control systems. Nonetheless, mean age of car and LDV fleets slightly increased from 2002 to 2011, from 7.1 to 7.7 yr for cars and 8.1 and 8.7 yr for LDVs.

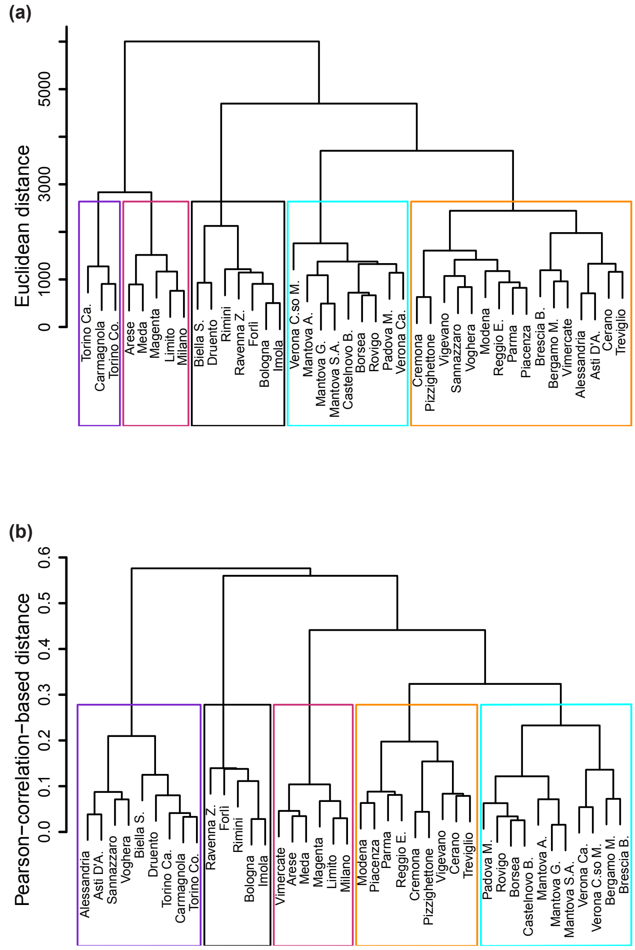

Figure 5. Results of cluster analysis on daily PM_{10} data using Euclidean distance **(a)** and Pearson-correlation-based distance **(b)**. Coloured boxes indicate clusters; monitoring sites' positions can be found in Fig. 1.

These results have been compared with the outcome of the only two simulation studies investigating the effects of emission reduction scenarios on air quality in the Po Valley by Deserti et al. (2006) and de Meij et al. (2009), who both used the emission inventory for the year 2000. The former used the same inventory as this study and simulated the effect of a drop in the emission of PM_{10} and of its main precursors over the Po Valley: scenarios with a drop in emissions of between 30 and 60 % produced a simulated drop in PM_{10} concentration ranging between 15 and 30 %. de Meij et al. (2009) used the high-resolution City Delta III emission inventory and focused on simulation of O_3 and $PM_{2.5}$ for the Lombardia region only. Although the study by de Meij et al. (2009) deals with $PM_{2.5}$, it can still be useful for a rough comparison with the observed PM_{10} trends. To ease this comparison the $PM_{2.5}$ / PM_{10} ratio for the sites where both pollutants are sampled is presented in Table 5; this ratio ranges from 0.61 (Parma) to 0.94 (Cerano). Simulations by de Meij et al. (2009) foresaw a drop in $PM_{2.5}$ of up to 2.7 $\mu g\,m^{-3}$ from a 4 % reduction in NO_x and $PM_{2.5}$, all from road transport (SNAP sector 7); simulated results also suggested a drop in 0.1 $\mu g\,m^{-3}$ in $PM_{2.5}$ from a drop in 7 % of SO_2 and of VOCs, all from SNAP sector 2. The variability within the results from this present study and within the outcome of simulations by Deserti et al. (2006) and de Meij et al. (2009) leads to a hard quantitative comparison. However, drop in concentration and emissions have a similar order of magnitude among simulations and observations. It is noteworthy how almost all scenarios in the cited simulations assumed a large and significant drop in emissions of particulates, which rarely occurred according to the emission inventory; nonetheless, a widespread drop in PM_{10} atmospheric concentration has been shown in this study. The difference among trends in observed atmospheric concentration, in emissions and in simulated concentrations is likely due to several causes, including wide uncertainty in particulates emission estimate (e.g. the handling of non-exhaust particle emissions from road transport) (see e.g. Bukowiecki et al., 2010) and uncertainty in PM_{10} simulation in chemical transport models (Vautard et al., 2007). These uncertainties lead to a challenging assessment of the role of primary (both exhaust and non-exhaust) emissions on the observed decrease in atmospheric PM_{10} in the Po Valley.

4 Conclusions

The analysis of long-term trend, of weekly periodicity and of cluster analysis for PM_{10} concentration time series in the Po Valley has been performed. Long-term trend has been estimated by GLS on monthly deseasonalized time series, by Theil–Sen (TS) method on annual quantiles and by TS method on frequency of daily binned concentration for each month. The slope resulting from TS and GLS shows good agreement, apart from a few cases (e.g. Limito or Meda). A significant and widespread decrease in PM_{10} occurred at the investigated monitoring sites, both for lower and higher concentration quantiles, both during colder and warmer months. At least one significant weekly cycle (i.e. possibly forced by anthropic emissions) has been found for all stations besides two, Forlì and Sannazzaro. Weekly periodicity occurs more likely in summer probably because of the lower contribution of secondary particulates and larger impact of primary sources on PM_{10}. Notwithstanding similar trends and patterns, a hierarchical cluster analysis of daily PM_{10} concentration showed some geographically based differences among sites, with the main metropolitan areas being clustered along with the surrounding sites regardless of the station type. A comparison between trends in atmospheric PM_{10} concentration and in provincial emissions of PM_{10} and of PM_{10} precursors did not show significant correlation. Nonetheless, the occurred renewal of vehicular fleet over the Po Valley during the last decade, i.e. the introduction of vehicles having more efficient engines and improved emission control systems, appears to be responsible for part of the observed drop in atmospheric concentration. The role of primary particulate emissions in the observed atmospheric trends remains unclear and further studies are planned to investigate it: a combined analysis of $PM_{2.5}$, PM_{10} and of the coarse fraction (PM_{10} – $PM_{2.5}$) might reveal the role of SIA in the observed trends, due to the larger contribution of SIA to $PM_{2.5}$ than to PM_{10}, although a similar analysis would deal only with data for later than 2006, when $PM_{2.5}$ measurement started.

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