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# Long term trend and variability of atmospheric $\mathrm{PM}_{10}$ 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 dataset of $\mathrm{PM}_{10}$ 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 deseasonalised monthly means, in annual quantiles and in monthly frequency distribution. A widespread significant decreasing trend has been observed at most sites, up to few percent per year, by Generalised Least Square 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 $\mathrm{PM}_{10}$ 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 gathering the metropolitan areas of Turin and Milan and their respective nearby sites and the other three clusters gathering north-east, north-west and central Po Valley sites respectively. Finally the observed trends in atmospheric $\mathrm{PM}_{10}$ 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. Significant basin-wide drop in emissions occurred for gaseous pollutants, contrarily to emissions of $\mathrm{PM}_{10}$ and $\mathrm{PM}_{2.5}$, whose drop resulted low and restricted to few provinces. It is not clear whether the decrease for only gaseous emissions is sufficient to explain the observed drop in atmospheric $\mathrm{PM}_{10}$, 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 or smaller than $10\,\mu\mathrm{m}$ 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 lead to a clear decrease for some atmospheric pollutants. Among these, $\mathrm{SO_2}$ showed a decrease at a continental scale (e.g. Vestreng et al., 2007), whereas reduction amount for $\mathrm{PM_{10}}$ resulted site-dependent (e.g. Anttila and Tuovinen, 2010; Barmpadimos et al., 2011). Most recent European Directive on air quality limits (2008/50/EC) provides limits both for $\mathrm{PM_{10}}$ and $\mathrm{PM_{2.5}}$ 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 $\mathrm{PM_{10}}$ 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 focussed on ambient air quality, particularly on particulate aerosols, and relied on medium to short term sampling campaigns. Main outcome of these studies is a detailed information on chemical and physical properties of particulate matter, highlighting a large presence of Secondary Inorganic Aerosols (SIA): in Bologna urban background Putaud et al. (2010) and Matta et al. (2003) found a concentration range of 40 – 44 % of ammonium, nitrate and sulphate in $\mathrm{PM_{2.5}}$ and $\mathrm{PM_{10}}$. Different composition has been observed by Carbone et al. (2010) at the Po Valley rural background site of San Pietro Capofiume, where $\sim 50\,\%$ of $\mathrm{PM_{10}}$ is represented by ammonium, nitrate and sulphate. Observations from Milan urban background (Carbone et al., 2010) showed how ammonium, nitrate and sulphate account for $\sim 30\,\%$ of $\mathrm{PM_{10}}$, consistently with a continental-wide decreasing trend of soluble ions percentage in $\mathrm{PM_{10}}$ from rural to kerbside sites (Putaud et al., 2004). Notwithstanding differences in aerosol composition and concentration across the Po Valley, throughout the region $\mathrm{PM_{10}}$ and $\mathrm{PM_{2.5}}$ 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 evidenced an increasing number of Po Valley sites respecting the annual average limits for $\mathrm{PM_{10}}$ over the last decade (e.g. ARPA Emilia-Romagna, 2012); although the high $\mathrm{PM_{2.5}}$ to $\mathrm{PM_{10}}$ 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 for the respect of $\mathrm{PM_{2.5}}$ limits.

To authors knowledge extremely few studies in the literature involved 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 $\mathrm{CO_2}$ concentration at mount Cimone over the period 1979 – 1985. Bigi et al. (2012) found a decreasing trend for many pollutants at a urban background site in Modena, Po Valley, over the period 1998 – 2010. Artuso et al. (2009) investigated $\mathrm{CO_2}$ concentration trend at Lampedusa from 1992 to 2008.

A large number of studies worldwide focussed on the climatology and trend in atmospheric pollutants: e.g. Anttila and Tuovinen (2010) used Generalised Least Squares method to estimate trends of various gaseous pollutants and $\mathrm{PM}_{10}$ in Finland; Tripathi et al. (2010) used a similar method to estimate Ozone trends in eight sites in Ireland. Lefohn et al. (2010) used 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 GAW sites. Some authors removed the influence of meteorology on pollutant concentration, prior the estimate of trends: Wise and Comrie (2005) estimated trend in Ozone and $\mathrm{PM}_{10}$ in south-western United States by using a Kolmogorov – Zurbenko filter; Flaum et al. (1996) used this same method to remove seasonality and influence of selected meteorological variables on tropospheric Ozone data. Mueller (2005) used Generalised Additive Models (GAM) to estimate trends in sulphate concentration in eastern United States without the influence of meteorology; GAM have been also used by Barmpadimos et al. (2011) to estimate meteorologically-adjusted trends for $\mathrm{PM}_{10}$ across Switzerland.

$\mathrm{PM}_{10}$ measurements in the Po Valley started in late 1997, early 1998; the monitoring network underwent few redesign through the last fifteen years. In order to provide a representative study of $\mathrm{PM}_{10}$ in the Po Valley, a dataset comprising 41 sites with different activation times and all active up to 1 January 2012 (Table 1) has been analysed. Monitoring sites, described in details in Sect. 2, are part of the network ran by the Regional Environmental Protection Agencies operating in the Po Valley. In Sects. 2.1 through 2.4 description of the methods used are presented, the results and their discussion are described in Sect. 3 and in Sect. 4 conclusions are found.

## 2 Data and methods

This study involved $\mathrm{PM}_{10}$ sampled at 41 air quality monitoring stations within the Regional Environmental Protection Agencies (ARPA) operating over the Po Valley: site listing is reported in Table 1 and mapped in Fig. 1. All data have been referred to actual sampling conditions, as required by 2008/50/EC. Different sampling instruments are used over the network: beta attenuator (Swam 5A RL by FAI, SM200 by Opsis, MP101M by Environnement S.A.), TEOM and TEOM-FDMS (by Thermo Environmental), 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 respective ARPA, i.e. the data are obtained by calibrated instruments, undergo a daily, seasonal and annual comparison with nearby sites as well as with previous data. Nevertheless, all data have been manually inspected by 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 $\mathrm{PM}_{10}$ and $\mathrm{PM}_{2.5}$ by road vehicle tyre and brake wear (SNAP 0707). The inventory do not include emissions from road surface wear (SNAP 0708) since considered not sufficiently reliable (Romano et al., 2012). An overall uncertainty analysis of the Italian inventory is not available, besides for a general assessment of uncertainty for GHG emissions (Romano et al., 2012). National emissions estimates (including those from SNAP 0707) for 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 for direct particulate emissions, $\mathrm{PM}_{10}$ and $\mathrm{PM}_{2.5}$, and main particle precursors, $\mathrm{SO}_2$, $\mathrm{NO}_\mathrm{x}$, Non-Methane Volatile Organic Carbon (NM-VOC), $\mathrm{CH}_4$, $\mathrm{NH}_3$ 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 on the valley part of the province, where most of activities and population are settled, instead of the mountain part. Also data on vehicular fleet composition and fleet age for each province have been used. These have been provided by the Italian Automobile Club (ACI). Data on fuel sales used in this study, still 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

18 sites out of 41 have been analysed for the presence of long term trend, having a record of at least ten 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 in trend, seasonal and remainder components by STL 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 common to air pollution data (Bencala and Seinfeld, 1976), therefore data has been log-transformed prior to decomposition in order to achieve normally distributed residuals, whose normality and independence have been tested by QQ-plot, Shapiro test and autocorrelation function. Finally analysis of monthly trend time series was performed on back-transformed logarithmic trend data.

In order to test trend component for a significant slope, Generalized Least Square (GLS) method

(Brockwell and Davis, 2002) has been applied: GLS is used to estimate the linear relation between an autocorrelated time-series and time allowing 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 square, 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 minimisation 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 on which the slope has been again 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 due primarily for comparison among sites, because all 18 sites have been simultaneously active only since 2002; moreover this would allow to estimate the presence of possible changes in slope over the investigated period for older sites.

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.

TS approach shares the same statistics (named $S$) of 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 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 $S$. 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 resulted 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 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 $p$ 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, also the long term trend for $\mathrm{PM}_{10}$ concentration within each month has been computed. In order to assess a seasonal long term trend, $\mathrm{PM}_{10}$ daily concentration for each month have been binned by $15\,\mu\mathrm{g\,m}^{-3}$ increments; 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 resulting graphs for Castelnovo Bariano and Parma sites are presented in Fig. 4.

## 2.2 Analysis of weekly cycles

Few different indexes and few different statistical tests can be used to verify the significance of a weekly cycle (see Daniel et al., 2012, for a critical review). In the present study the analysis of weekly cycles involved the complete dataset of 41 $\mathrm{PM}_{10}$ time series, investigating both the continuous time series and separately winter (January, February, March) and summer (June, July, August) seasons. The study of weekly cycle focussed on $\mathrm{PM}_{10}$ anomalies, derived as follows: the seasonal cycle has been filtered out by computing the deviation of daily data to a running mean of daily data, which has been calculated as the centred mean with a window of 31 days. The result is a new time series of deviations, where the interference of the seasonal cycle is negligible. Being the data highly non – normal, the analysis of deviations used non parametric statistical tests (Barmet et al., 2009): each of the newly created time series has been grouped by weekdays, and the mean and standard deviation of each group has been calculated, resulting in a weekly cycle of mean anomalies.

These latter have been analysed by 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). Kruskal – Wallis statistics follows a $\chi^2$ distribution. In order to double check the significance of weekly cycles, deviations have been group in 6 and 8 day weeks, and Kruskal – Wallis test for these anomalies have been performed.

The presence of a weekly periodicity has been furtherly verified by testing for a significant weekend effect magnitude at each site, i.e. the difference between the mean $\mathrm{PM}_{10}$ anomaly of Saturday through Monday and the mean $\mathrm{PM}_{10}$ anomaly between Wednesday through Friday (Daniel et al., 2012). Series of weekend effect magnitude has been tested by the non-parametric Wilcoxon test for zero median: results are presented in Table 4, while graphs of 7 day week mean anomaly for all sites are presented in Fig. S1 and Fig. S2 for full year and seasons respectively. An analysis of weekly periodicity has been performed also for $\mathrm{PM}_{2.5}$ at the sites within Table 1 where both $\mathrm{PM}_{10}$ and $\mathrm{PM}_{2.5}$ were sampled. Analysis of weekly periodicity on $\mathrm{PM}_{2.5}$ provided possible insights on its differences in composition with $\mathrm{PM}_{10}$ and on the possible cause of an eventually significant periodicity on both pollutants. Results for $\mathrm{PM}_{2.5}$ are presented in Table 5.

### 2.3 Cluster analysis

Cluster analysis on $\mathrm{PM}_{10}$ daily data has been performed on the whole Po Valley dataset in order to capture both differences and correlations in absolute concentration levels among monitoring sites. Febbio (ID 28 in Table 1 and Fig. 1) has been excluded from this analysis being a remote rural site at $1121\ \mathrm{m}$ a.m.s.l in the Apennines and therefore being an outlier and possibly fouling the classification (Kaufman and Rousseeuw, 1990). Cluster analysis has been performed by hierarchical agglomerative clustering using two different metrics for distance. In the former the dissimilarity matrix has been calculated using Euclidean distances (Fig. 5a) to highlight differences in absolute $\mathrm{PM}_{10}$ levels. In the latter the distance $d_{x,y}$ between two samples $x$ and $y$ has been computed using a metric based on Pearson's correlation coefficient $r$ according to the following $d_{x,y} = (1 - r_{x,y})/2$. This latter metrics allows to highlight linear correlation structures among sites (Fig. 5b). Cluster aggregation has been computed using the Ward's method. A simple sensitivity analysis has been performed by a “leave-one-out” test, consisting in 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 dataset. Finally results have been 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 in only 5 yearly data (1990, 1995, 2000, 2005, 2010); being the aim of this analysis the comparison of trends in emissions and concentration, data for year 1990 and 1995 were discarded since no $\mathrm{PM}_{10}$ data are available for that period. Slope by TS method has been estimated for each province and relative $p$ value as been obtained via bootstrap as described in Sect. 2.1. 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, then to the very few observations available (5 observations in $20\,\mathrm{yr}$) and finally due to the slope estimate method, being not suitable for non-monotonic trends (and therefore set as not-significant whenever non-monotonic trends occurred).

## 3 Results and discussion

Different type of trends have been computed in this study. The data pre-processing procedures used are aimed to minimise 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 also Theil-Sen slope estimate is robust to outliers. Uncommon weather conditions are more likely to influence trend analyses focussed on one month at the 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 minimise the bias due to meteorology. Finally, the use of resampling techniques reduces the possible influence of outliers on trend estimates.

Also the influence by long term trends in meteorological variables are expected to be negligible: Toreti et al. (2009) estimated a drop in $1.47\,\mathrm{mm\,yr^{-1}}$ in winter precipitation over Northern Italy for the period 1961 – 2006, when annual precipitation ranges between $750 - 1000\,\mathrm{mm}$. Trends for average, minimum and maximum atmospheric temperature in the Po valley ranged between $0.9$ and $1.1\,\mathrm{K}$ 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 $\sim 0.4$ and $\sim 0.1\,\mathrm{K}$ per decade, depending upon season and similar trends for minimum temperature have been found by these same authors. The trends observed in these studies for precipitation and temperature range around few mil per year and few hundredth of $\mathrm{K}$ per year respectively. Reasonably assuming these latter trends valid also over the period 1998 – 2011, we can consider their influence on $\mathrm{PM_{10}}$ concentration negligible compared to variability of emissions and meteorology.

### 3.1 Results from long term trend analysis

GLS estimate assumes trend to be linear, i.e. do not take into account possible non-linearities in the trend component. Nonetheless, due to the features of the monthly data investigated, inaccuracy in slope estimates due to non-linearity are assumed to be negligible, because of the efficient deseasonalisation 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 over the period 2002 – 2011 for all observations besides Modena, Reggio Emilia and Vimercate, contrarily for instance to the $\mathrm{PM_{10}}$ trends observed in the U.K. (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.

$\mathrm{PM_{10}}$ 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. Results from the analysis of monthly frequency distribution of daily $\mathrm{PM_{10}}$ is 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 indicates a shift from lower to higher concentration bins and a $\pm$ sign indicates a shift in lower and higher concentration bins towards median concentrations. Results of 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 eventually 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 $\mathrm{PM_{10}}$ decrease ranging between $-0.5$ to $-1.3\,\mathrm{\mu g\,m^{-3}}$ in five rural sites within the EMEP network over the period 1999 – 2010 and ascribed most of decrease to a change in $\mathrm{PM_{2.5}}$ concentrations. Significant decrease in $\mathrm{PM_{10}}$ found by Anttila and Tuovinen (2010) in Finland is lower in absolute value (ranging between $-0.5$ to $-0.1\,\mathrm{\mu g\,m^{-3}}$), but similar in relative drop; however, in this latter study, $\mathrm{PM_{10}}$ drop is significant almost exclusively at industrial or traffic sites, contrarily to the broad decrease in the Po Valley.

### 3.2 Results from weekly cycle analysis

This significant and widespread decrease in $\mathrm{PM_{10}}$ concentration across the Po Valley suggests its strong anthropogenic origin. This assumption has been furtherly investigated by testing time series for significant weekly pattern by two procedures: weekly cycle analysis and weekend effect magnitude in $\mathrm{PM_{10}}$ and $\mathrm{PM_{2.5}}$ deviations. Table 4 presents sites with $\mathrm{PM_{10}}$ daily data exhibiting a significant cycle and figures S1 and S2 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, and it is believed to be generated by an increase in emissions (e.g. wood-burning for domestic heating or traffic) during weekends: the village counts $\sim 170$ inhabitants, with private houses for holidays and a nearby ski area whose plants have been operating since $\sim$1950 until 2010.

Results from the two tests for weekly periodicity are highly similar. Considering the whole year, a significant weekly periodicity is present during 7 day week at all sites besides Febbio (accordingly to weekend effect magnitude only), Forlì and Sannazzaro (see Figure S1). As shown in Figure S2 and table 4, most of shorter time series show a weekly periodicity in summer and not in winter for the 7 day weeks, whereas many of longer ones still exhibits a weekly periodicity in both seasons. The lack of weekly periodicity in winter might be due to the large fraction of SIA in $\mathrm{PM_{10}}$ in this season (Larsen et al., 2012), uncoupling the weekly fluctuations of primary anthropogenic emissions (non-exhaust included) and $\mathrm{PM_{10}}$ concentration. This behaviour has been observed by Bernardoni et al. (2011) in Milan urban background conditions, where relative contribution of direct human-related particulate sources (e.g. re-suspension, traffic, industry) to summer $\mathrm{PM_{10}}$ is higher than in winter, consistently with a significant periodicity in summer weeks. Possibly this buffering effect by SIA is dimmed in longer time series by a higher $\mathrm{primary/SIA}$ ratio in the late 90s early 2000, leading more likely to significant weekly cycles in winter, although this hypothesis should be substantiated by further analyses. Test of weekly cycles for 6 and 8 day weeks resulted 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.

$\mathrm{PM_{2.5}}$ in the Po Valley has been shown to have a larger relative fraction of secondary aerosol than $\mathrm{PM_{10}}$, ranging between 27 – 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, contribution from re-suspended dust to $\mathrm{PM_{2.5}}$ is expected to be smaller than to $\mathrm{PM_{10}}$ (Amato et al., 2009). Consistently a significant weekly cycle in $\mathrm{PM_{2.5}}$ is observed only at few sites, maybe driven by a stronger contribution of anthropic primary particulate compared to other $\mathrm{PM_{2.5}}$ sites (table 5).

### 3.3 Results from cluster analysis

$\mathrm{PM_{10}}$ 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 $\mathrm{PM_{10}}$ concentration. Classifications showed in Fig. 5 exhibit five main clusters, confirmed by sensitivity analyses: a group based in the south-east side of the valley having similar patterns and lower concentration compared to other sites in the valley. Also two north-western 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). Two clusters identify quite nicely the two main metropolitan areas of the valley, Turin and Milan, having distinctive $\mathrm{PM}_{10}$ levels compared to the rest of the valley (see Fig. 5a). Finally, both the north-east and the centre of the Po Valley are grouped according to their $\mathrm{PM}_{10}$ levels and patterns leading to two different clusters. Sensitivity analysis and divisive hierarchical clustering showed a persistent structure featured by 4 main clusters representative of the metropolitan area of Turin and Milan and the ones of the south-east and north-east 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 result significant for gaseous pollutants and not significant for $\mathrm{PM}_{10}$ and $\mathrm{PM}_{2.5}$. Significant slope for each investigated gaseous compound results: $-3.5\,\%\,\mathrm{yr}^{-1}$ ($\mathrm{SO}_2$), $-2.5\,\%\,\mathrm{yr}^{-1}$ ($\mathrm{NO}_\mathrm{x}$), $-3.7\,\%\,\mathrm{yr}^{-1}$ (NM-VOC), $-1.9\,\%\,\mathrm{yr}^{-1}$ ($\mathrm{CH}_4$), $-6.7\,\%\,\mathrm{yr}^{-1}$ (CO) and $-1.2\,\%\,\mathrm{yr}^{-1}$ ($\mathrm{NH}_3$). At a province scale there is large variability in emission trend: thematic maps of significant trend in NM-VOC, $\mathrm{NO}_\mathrm{x}$ and $\mathrm{PM}_{10}$ emissions are presented in Fig. S3. No significant statistical correlation arose from the comparison of trends in background $\mathrm{PM}_{10}$ and emissions in each province, however, the outcomes of the analyses in Sects 3.1, 3.2, 3.3 strongly suggest that the drop observed in $\mathrm{PM}_{10}$ 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. S4). From 2000 to 2010 road transport almost zeroed its contribution to $\mathrm{SO}_2$ emissions, thanks to the directive 2003/17/EC and unleaded gasoline. Also relative contribution of road traffic to NM-VOC, CO, $\mathrm{PM}_{10}$ and $\mathrm{PM}_{2.5}$ has dropped, and only $\mathrm{NO}_\mathrm{x}$ kept road traffic as its main source over the 2000 – 2010 period (see Fig. S4). 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 (LDV). This increase occurred along with a dieselization of the fleet, with the rate of diesel vehicles (considering passenger cars, LDV and HDV) raising from $\sim$26 % to $\sim$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 of 41 % and the latter increased of 19 % over the period 2002 – 2011 considering the whole Po Valley. Fleet renewal has been forced by driving restrictions to older vehicles applied over the Po Valley since 2002. Initially restrictions focussed 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 FAP and two-stroke engines; afterwards, stricter restrictions have been applied. In 2002 32 % and 42 % of circulating cars and LDV were respectively built prior than 1993 (i.e. were older than 10 yr) and not EURO-1 compliant. In 2011 13 % of the cars and 22 % of LDV were built prior than 1995, i.e. possibly not EURO-1 compliant, leading to an increase in vehicles having more efficient engines and improved emission control systems. Nonetheless mean age of car and LDV fleets has slightly increased from 2002 to 2011, switching from $7.1\,\mathrm{yr}$ to $7.7\,\mathrm{yr}$ for cars and $8.1\,\mathrm{yr}$ and $8.7\,\mathrm{yr}$ for LDV.

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 emission inventory for year 2000. The former used the same inventory of this study and simulated the effect of a drop in the emission of $\mathrm{PM_{10}}$ and of its main precursors over the Po Valley: scenarios with drop in emissions between 30 % and 60 % produced a simulated drop in $\mathrm{PM_{10}}$ concentration ranging between 15 % and 30 %. de Meij et al. (2009) used the high resolution City Delta III emission inventory and focussed on simulation of $\mathrm{O_3}$ and $\mathrm{PM_{2.5}}$ for the Lombardia region only. Although the study by de Meij et al. (2009) deals on $\mathrm{PM_{2.5}}$, it can still be useful for a rough comparison with the observed $\mathrm{PM_{10}}$ trends. To ease this comparison the $\mathrm{PM_{2.5}}\backslash\mathrm{PM_{10}}$ 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 $\mathrm{PM_{2.5}}$ up to $2.7\,\mathrm{\mu g\,m^{-3}}$ from a 4 % reduction in $\mathrm{NO_x}$ and $\mathrm{PM_{2.5}}$ all from road transport (SNAP sector 7); simulated results suggested also a drop in $0.1\,\mathrm{\mu g\,m^{-3}}$ in $\mathrm{PM_{2.5}}$ from a drop in 7 % of $\mathrm{SO_2}$ 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 $\mathrm{PM_{10}}$ 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) (e.g. see Bukowiecki et al., 2010) and uncertainty in $\mathrm{PM_{10}}$ 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 $\mathrm{PM_{10}}$ in the Po Valley.

## 4 Conclusions

The analysis of long term trend, of weekly periodicity and of cluster analysis for $\mathrm{PM_{10}}$ concentration time series in the Po Valley has been performed. Long term trend has been estimated by Generalized Least Squares (GLS) on monthly deseasonalised time series, by Theil-Sen (TS) method on annual quantiles and by TS method on frequency of daily binned concentration for each month. Slope resulting from TS and GLS shows good agreement, besides few cases (e.g. Limito or Meda). A significant and widespread decrease in $\mathrm{PM_{10}}$ 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 $\mathrm{PM}_{10}$. Notwithstanding similar trends and patterns, a hierarchical cluster analysis of daily $\mathrm{PM}_{10}$ concentration showed some geographically-based differences among sites, with main metropolitan areas being clustered along with the surrounding sites regardless of the station type. A comparison between trends in atmospheric $\mathrm{PM}_{10}$ concentration and in provincial emissions of $\mathrm{PM}_{10}$ and of $\mathrm{PM}_{10}$ 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 stays unclear and further studies are planned to investigate it: a combined analysis of $\mathrm{PM}_{2.5}$, $\mathrm{PM}_{10}$ and of the coarse fraction ($\mathrm{PM}_{10}-\mathrm{PM}_{2.5}$) might reveal the role of SIA in the observed trends, due to the larger contribution of SIA to $\mathrm{PM}_{2.5}$ than to $\mathrm{PM}_{10}$, although a similar analysis would deal only for data later than 2006, when $\mathrm{PM}_{2.5}$ measurement started.

**Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/0/1/2014/acp-0-1-2014-supplement.pdf.**

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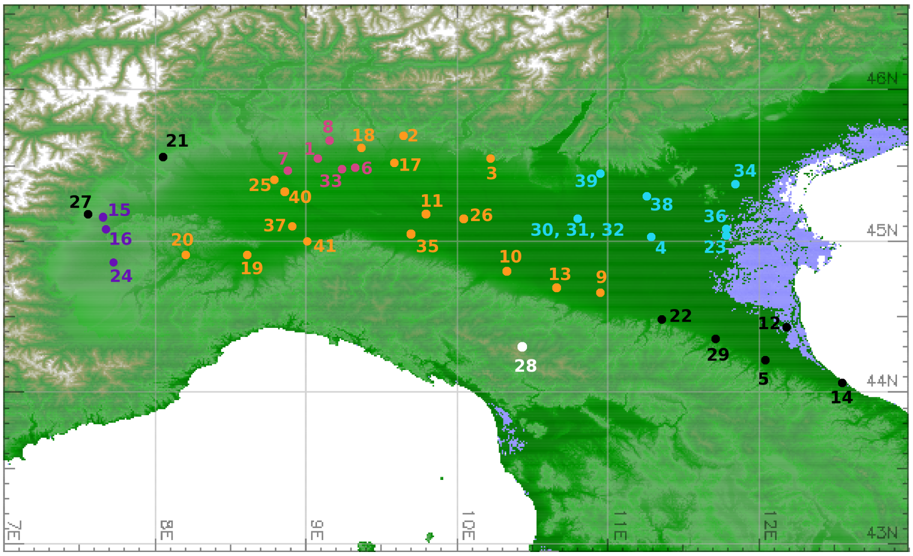

Fig. 1: Location of $\mathrm{PM}_{10}$ monitoring stations included in the analysis. Key for ID number is found in Table 1, colour code refers to result of cluster analysis using Euclidean distance (Fig. 5a).

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Table 1: Analysed $\mathrm{PM}_{10}$ 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. $^*$All are within the Po Valley besides Febbio, sited at $1121\,\mathrm{m}$ a.m.s.l.

| ID | Station name | Station type | Activation date |
|---|---|---|---|
| Long term trend dataset | | | |
| 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 dataset | | | |
| 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 |

Table 2: GLS trend (± standard error) for deseasonalised monthly mean time series of daily $\mathrm{PM}_{10}$ concentration. Boldfaced values indicate slope significantly different from zero at a 95 % confidence level.

| Station | Slope 2002–2011 $\mu\mathrm{g\,m^{-3}\,yr^{-1}}$ | Change 2002–2011 $\%\,\mathrm{yr^{-1}}$ | Slope since time series start $\mu\mathrm{g\,m^{-3}\,yr^{-1}}$ | Change since time series start $\%\,\mathrm{yr^{-1}}$ |
|---|---|---|---|---|
| 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** |

Table 3: Analysis of trend for annual quantiles and for monthly frequency of $\mathrm{PM}_{10}$. Slope for annual quantiles is computed by Theil-Sen method: boldfaced values indicate slope significantly different from zero at a 95 % confidence level.

| Station | 5th annual quantile | | 50th annual quantile | | 95th annual quantile | | Months with significant trend |
|---|---|---|---|---|---|---|---|
| | Slope | Change | Slope | Change | Slope | Change | |
| | $\mathrm{\mu g\,m^{-3}\,yr^{-1}}$ | $\mathrm{\%\,yr^{-1}}$ | $\mathrm{\mu g\,m^{-3}\,yr^{-1}}$ | $\mathrm{\%\,yr^{-1}}$ | $\mathrm{\mu g\,m^{-3}\,yr^{-1}}$ | $\mathrm{\%\,yr^{-1}}$ | |
| 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 (–) |

Table 4: Results of weekly cycle analysis on $\mathrm{PM}_{10}$: 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 $\mathrm{PM}_{2.5}$ at monitoring sites where both $\mathrm{PM}_{10}$ and $\mathrm{PM}_{2.5}$ 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. Last column indicates the mean $\mathrm{PM}_{2.5}/\mathrm{PM}_{10}$ ratio.

| Sites | W. E. magnitude | Weekly cycle | | | $\mathrm{PM}_{2.5}/\mathrm{PM}_{10}$ 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 |

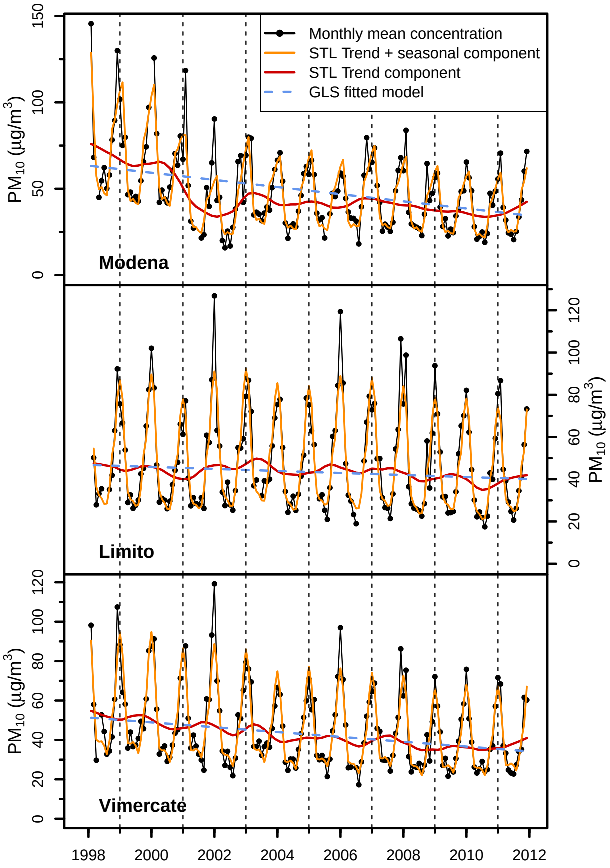


Fig. 2: STL decomposition for monthly mean $\mathrm{PM}_{10}$ along with GLS fitted slope for three selected sites.

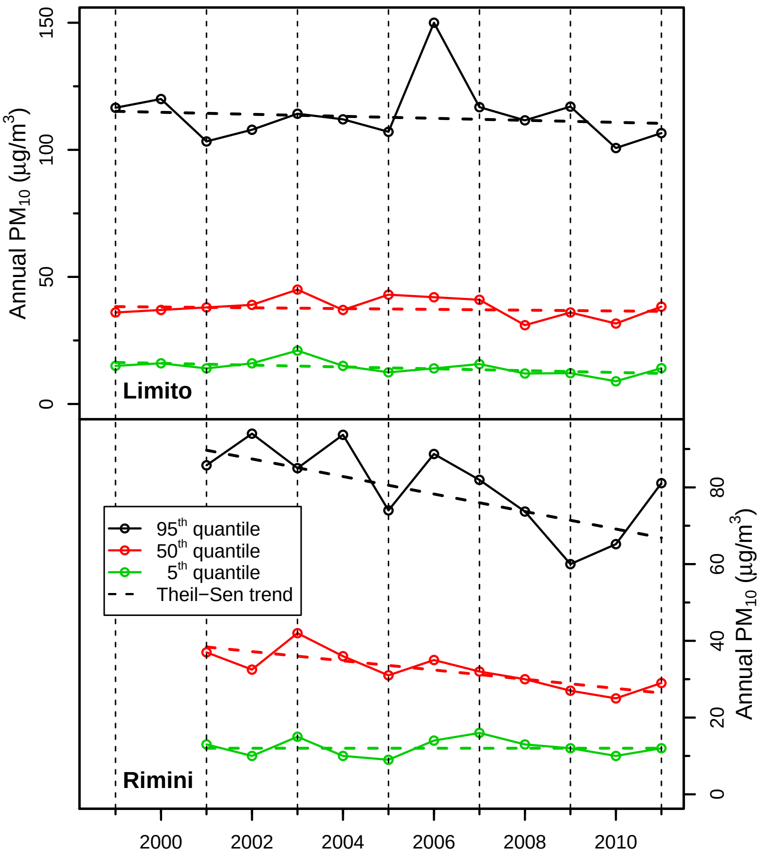
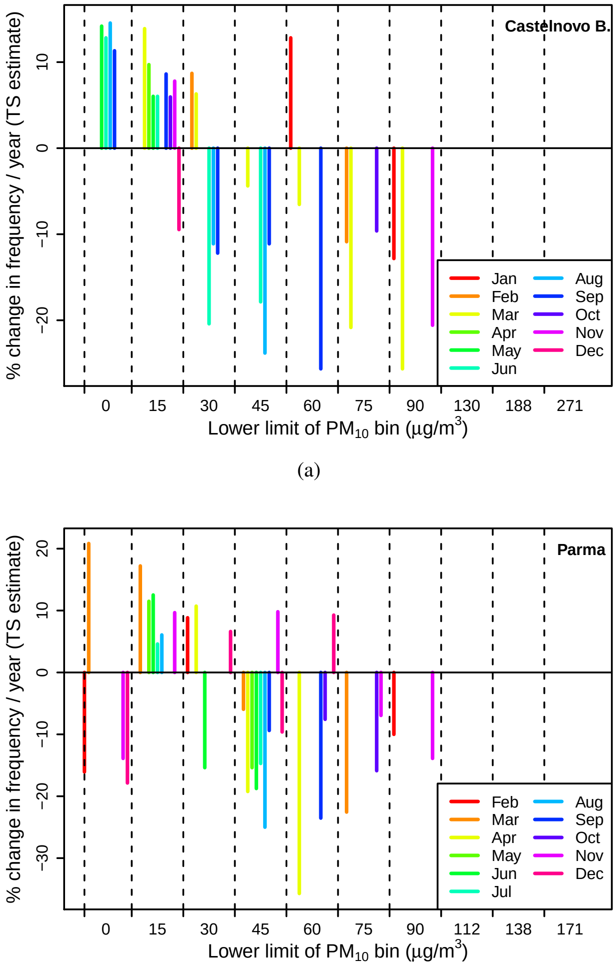


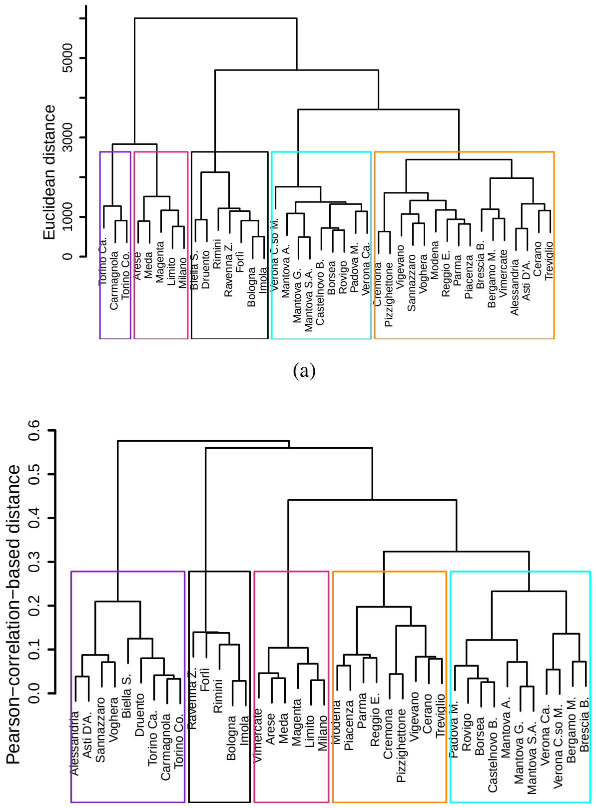
Fig. 3: Annual quantiles along with Sen slope for daily $\mathrm{PM}_{10}$ at Limito and Rimini.



(a)

(b)

Fig. 4: Significant changes in monthly frequency distribution of $\mathrm{PM}_{10}$ at Castelnovo Bariano **(a)** and Parma **(b)**.



(a)

(b)

Fig. 5: Results of cluster analysis on daily $\mathrm{PM}_{10}$ data using Euclidean distance **(a)** and Pearson-correlation-based distance **(b)**. Coloured boxes indicate clusters; monitoring sites position is found in Fig. 1.