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 dataset 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 $10\,\mathrm{yr}$ 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 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 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 PM$_{10}$ and 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 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 $10\,\mu m$ 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, SO_2 showed a decrease at a continental scale (e.g. Vestreng et al., 2007), whereas reduction amount for 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 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 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 $PM_{2.5}$ and 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 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 PM_{10}, consistently with a continental-wide decreasing trend of soluble ions 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 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 for the respect of $PM_{2.5}$ 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 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 CO_2 concentration trend at Lampedusa from 1992 to 2008.

A large number of studies worldwide focussed on the climatology and trend in atmospheric pol-

lutants: e.g. Anttila and Tuovinen (2010) used Generalised Least Squares 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 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 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 PM_{10} across Switzerland.

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 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 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

95 (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).

100 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 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.,

105 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 (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

110 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

115 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

120 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

125 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.

130 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

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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 PM_{10} concentration within each month has been computed. In order to assess a seasonal long term trend, PM_{10} daily concentration for each month have been binned by $15\,\mu g\,m^{-3}$ 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 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 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 χ^2 distribution. In order to double check the sig-
nificance 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 week-
end 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). 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. S2 and Fig. S3 for full year and seasons respectively. An analysis of weekly pe-
riodicity has been 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 possible insights on its differences
in composition with PM_{10} and on the possible cause of an eventually significant periodicity on both
pollutants. Results for $PM_{2.5}$ are presented in Table 5.

2.3   Cluster analysis

Cluster analysis on 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 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 agglomer-
ative clustering using two different metrics for distance. In the former the dissimilarity matrix has
been calculated using Euclidean distances (Fig. 1 and Fig. 5a) to highlight differences in absolute
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 and Fig. S1).
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 ag-
gregation 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 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

240 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 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).

245 ## 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

250 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 meteorol-

255 ogy. 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

260 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 ~ 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 tem-

265 perature range around few mil per year and few hundredth of K per year respectively. Reasonably assuming these latter trends valid also over the period $1998-2011$, we can consider their influence on 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

270 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.

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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 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.

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 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 PM_{10} decrease ranging between -0.5 to $-1.3\,\mu g\,m^{-3}$ in five rural sites within the EMEP network over the period $1999-2010$ and ascribed most of decrease to a change in $PM_{2.5}$ concentrations. Significant decrease in PM_{10} found by Anttila and Tuovinen (2010) in Finland is lower in absolute value (ranging between -0.5 to $-0.1\,\mu g\,m^{-3}$), but similar in relative drop; however, in this latter study, 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 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 PM_{10} and $PM_{2.5}$ deviations. Table 4 presents sites with PM_{10} daily data exhibiting a significant cycle and figures 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, and it is believed to be generated by an increase in emissions (e.g. wood-burning for domestic heating or

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traffic) during weekends: the village counts ~ 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 S2). As shown in Figure S3 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 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 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 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 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.

$PM_{2.5}$ in the Po Valley has been shown to have a larger relative fraction of secondary aerosol than PM_{10}, ranging between $27 - 52\%$ 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 $PM_{2.5}$ is expected to be smaller than to PM_{10} (Amato et al., 2009). Consistently a significant weekly cycle in $PM_{2.5}$ is observed only at few sites, maybe 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. 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 and Fig. S1). Two clusters identify quite nicely the two main metropolitan areas of the valley, Turin and Milan, having

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345 distinctive 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 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

350 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 PM_{10} and $PM_{2.5}$. Significant slope for each investigated gaseous compound results: $-3.5\,\%\,yr^{-1}$ (SO_2), $-2.5\,\%\,yr^{-1}$ (NO_x), $-3.7\,\%\,yr^{-1}$ (NM-

355 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 trend in NM-VOC, NO_x and PM_{10} emissions are presented in 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, 3.3 strongly suggest that the drop observed in PM_{10} concentration

360 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). From 2000 to 2010 road transport almost zeroed its contribution to SO_2 emissions, thanks to the directive 2003/17/EC and unleaded gasoline. Also relative contribution of road traffic to NM-VOC, CO,

365 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 Fig. S5). 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 (con-

370 sidering 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

375 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.

380 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 yr to 7.7 yr for cars and 8.1 yr and 8.7 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 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 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 O_3 and $PM_{2.5}$ for the Lombardia region only. Although the study by de Meij et al. (2009) deals on $PM_{2.5}$, it can still be useful for a rough comparison with the observed PM_{10} trends. To ease this comparison the $PM_{2.5}\backslash PM_{10}$ 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 $PM_{2.5}$ 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 suggested also 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) (e.g. see 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 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 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

420   PM_{10}. Notwithstanding similar trends and patterns, a hierarchical cluster analysis of daily 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 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 vehic-

425   ular 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 $PM_{2.5}$, PM_{10} and of the coarse fraction ($PM_{10}-PM_{2.5}$) might reveal the role of SIA in

430   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 for data later than 2006, when $PM_{2.5}$ 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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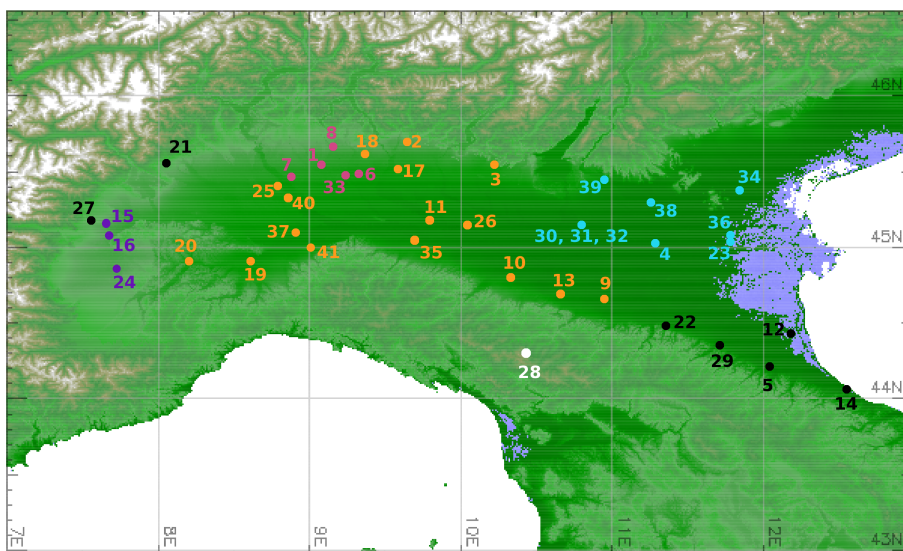Vautard, R., Builtjes, P., Thunis, P., Cuvelier, C., Bedogni, M., Bessagnet, B., Honoré, C., Moussiopoulos, N.,

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Fig. 1: Location of 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 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 ($\pm$ standard error) for deseasonalised 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**

Table 3: Analysis of trend for annual quantiles and for monthly frequency of 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	
	$\mu g\,m^{-3}\,yr^{-1}$	$\%\,yr^{-1}$	$\mu g\,m^{-3}\,yr^{-1}$	$\%\,yr^{-1}$	$\mu g\,m^{-3}\,yr^{-1}$	$\%\,yr^{-1}$	
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 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. 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
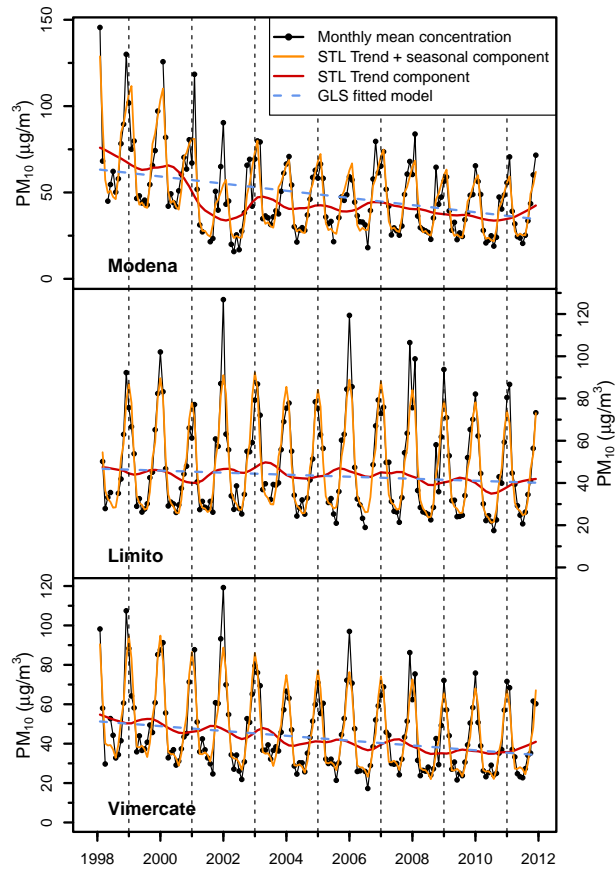
Fig. 2: STL decomposition for monthly mean PM_{10} along with GLS fitted slope for three selected sites.
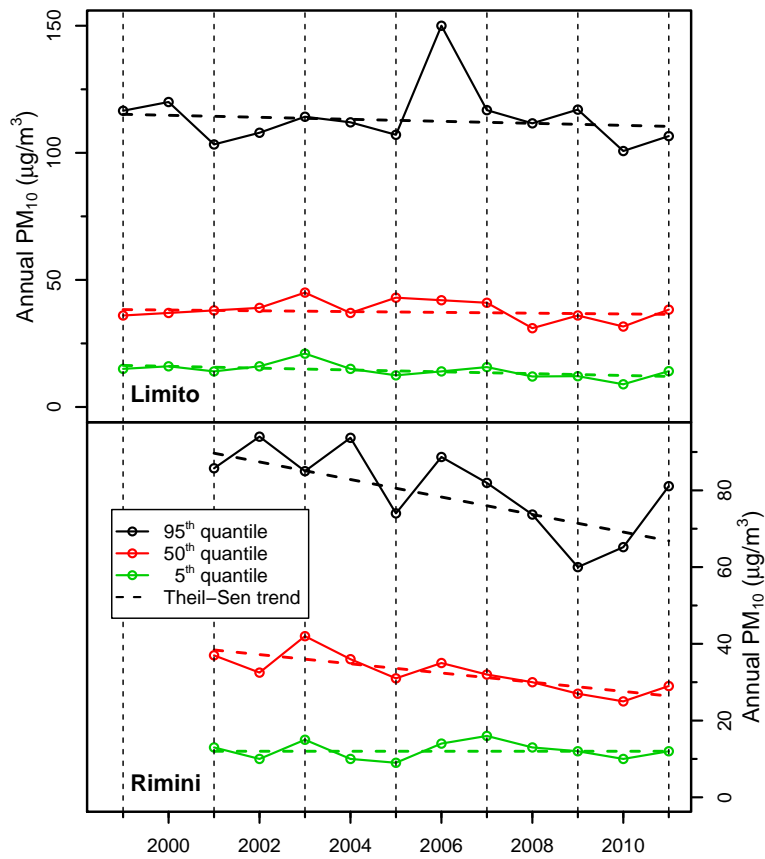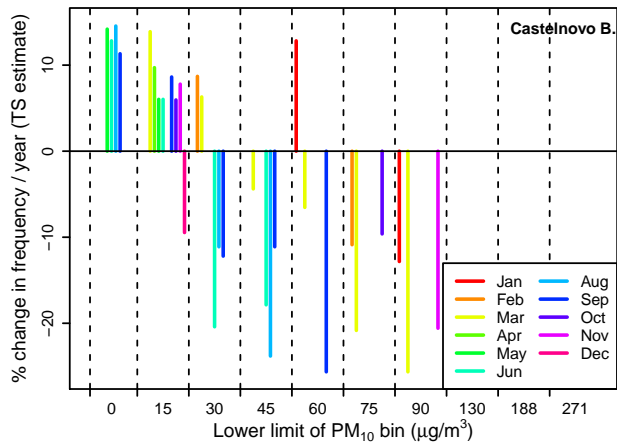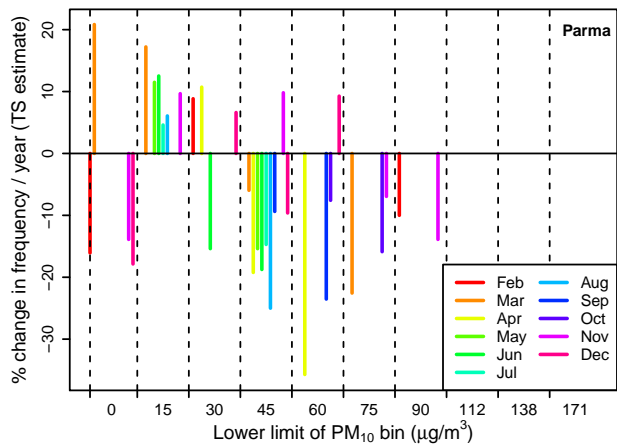
Fig. 3: Annual quantiles along with Sen slope for daily PM_{10} at Limito and Rimini.
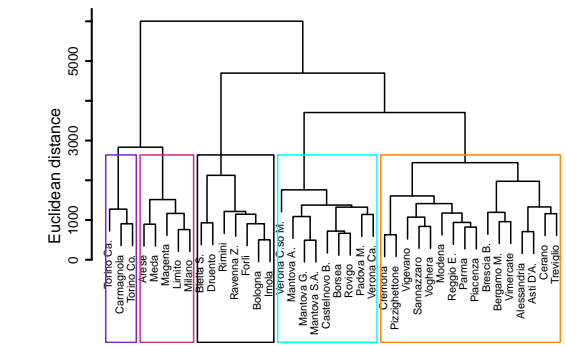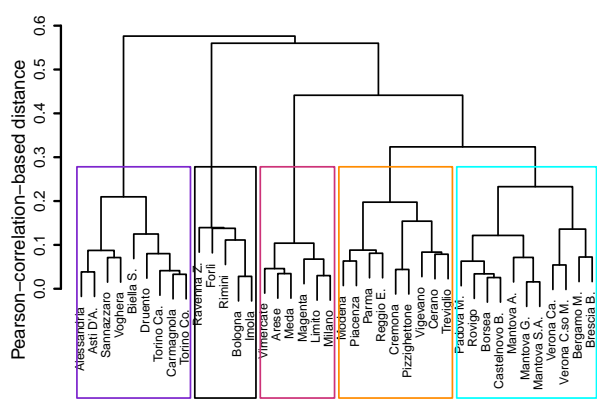
Fig. 4: Significant changes in monthly frequency distribution of PM_{10} at Castelnovo Bariano **(a)** and Parma **(b)**.

Fig. 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 position is found in Fig. 1.