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Climatology 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 yr or longer record have been analysed for long term trend in de-seasonalized 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 Torino and Milano 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.

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1 Introduction

Airborne particulate matter with aerodynamic diameter equal or smaller than 10 µm have been proved to have detrimental effects on air quality and on human health (for a review see World Health Organization, 2006, and references therein). European regulations on ambient air quality and on atmospheric emissions have 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 renown 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: Putaud et al. (2010) showed how the contribution of Ammonium, Nitrate and Sulphate represents 40 % and and 44 % of PM_{10} and $PM_{2.5}$ respectively in Bologna urban background. Similar results have been found by Matta et al. (2003), who observed that Ammonium, Nitrate and Sulphate account for 40 % of PM_{10} in Bologna urban background conditions. Different composition has been observed by Carbone et al. (2010) at the Po Valley rural background site of San Pietro Capofiume, where ~ 50 % of PM_{10} is represented by Ammonium, Nitrate and Sulphate. Observations from Milano urban background (Carbone et al., 2010) showed how Ammonium, Nitrate and Sulphate account for ~ 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

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in aerosol composition and concentration across the Po Valley, throughout the region PM_{10} and $PM_{2.5}$ exhibited a distinctive seasonality and 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, Milano in Putaud et al. (2010) and Marcazzan et al., 2003) represents a challenge for the respect of $PM_{2.5}$ limits.

Few studies in the literature involved long term trend of atmospheric pollutant 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 in a urban background site in Modena, Po Valley. 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 pollutants: 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 (e.g. peaks from festival bonfires).

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Concentration data have been compared to emission estimates provided by the National Environmental Protection Agency (ISPRA). Total national emissions are estimated according to the EMEP-CORINAIR protocol and classified accordingly to SNAP (Selected Nomenclature for Air Pollution). National emissions estimates for years 1990, 1995, 2000, 2005 and 2010 have been attributed to each Italian province through a top-down procedure (Liburdi et al., 2004). In this study we considered provincial emissions estimates for direct particulate emissions, PM_{10} and $PM_{2.5}$, and main particle precursors, SO_2, NO_x, Non-Methane Volatile Organic Carbon (NM-VOC), CH_4, NH_3 and finally CO, as a tracer for gasoline combustion. Only provinces having a significant part of their land within the Po Valley have been considered, assuming that most of the emissions occur 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 nor-

mality 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 indipendent 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

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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

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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 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 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 is presented in Fig. S1. An analysis of weekly periodicity 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 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 PM_{10}

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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

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 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).

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3 Results and discussion

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 de-seasonalization 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 to observations in other regions in Europe (e.g. 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 ± 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. 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.

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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 ascribing 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.

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, figure S1 presents 7 day week anomaly for all sites. All sites besides Febbio showed the same pattern for mean anomaly, although with differences in concentration range, 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 ascribed to an increase in emissions (e.g. wood-burning for domestic heating or traffic) during weekends: the village counts ∼ 170 inhabitants, with private houses for holidays and a nearby ski area whose plants have been operating since ∼1950 until 2010.

A significant weekly cycle and weekend effect magnitude is present during winter 7 day week for all stations besides two: Forlì and Sannazzaro. Most of shorter time series show a weekly periodicity in winter and not in summer for the 7 day weeks, whereas many of longer ones still exhibits a weekly periodicity both in winter and summer. This might be due to the large fraction of secondary inorganic aerosol in PM_{10} in winter (Larsen et al., 2012), uncoupling the weekly fluctuations of primary emissions or re-suspension and PM_{10} concentration. Similar behaviour has been observed by Bernardoni et al. (2011) in Milano 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

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summer weeks. 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.

$PM_{2.5}$ 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.

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). Two clusters identify quite nicely the two main metropolitan areas of the valley, Torino and Milano, having 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 Torino and Milano 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.

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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-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 NO_x, CO and PM_{10} emissions are presented in Fig. S2. No significant statistical correlation arose from the comparison of trends in background PM_{10} and emissions in each province, however, the drop observed in PM_{10} concentration most likely derives from an overall decrease in emissions, primarily 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. S3). 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, 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. S3). 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 has been associated to a renewal of the vehicle fleet, along with an increase in diesel fuelled vehicles and a decrease in gasoline fuelled ones. 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 in the 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 %

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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 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 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 %. The latter study used the high resolution City Delta III emission inventory and focussed on simulation of $PM_{2.5}$ and O_3 for the Lombardia region only. 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 results 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

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of the role of primary 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 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 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 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. Uncertainties remain in the role of primary particulate emissions in the observed atmospheric trends.

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References

Amato, F., Pandolfi, M., Escrig, A., Querol, X., Alastuey, A., Pey, J., Perez, N., and Hopke, P.: Quantifying road dust resuspension in urban environment by multilinear engine: a comparison with PMF2, Atmos. Environ., 43, 2770–2780, doi:10.1016/j.atmosenv.2009.02.039, 2009. 150

Anttila, P. and Tuovinen, J.: Trends of primary and secondary pollutant concentrations in Finland in 1994–2007, Atmos. Environ., 44, 30–41, doi:10.1016/j.atmosenv.2009.09.041, 2010. 139, 140, 144, 149

ARPA Emilia-Romagna: Air quality in Emilia-Romagna. 2012 Edition, Original title: La qualità dell'aria in Emilia Romagna, Edizione 2012, ARPA Emilia-Romagna, available at: http://www.arpa.emr.it/cms3/documenti/_cerca_doc/aria/report_aria2012.pdf (last access: 21 December 2013), 2012. 140

Artuso, F., Chamard, P., Piacentino, S., Sferlazzo, D., De Silvestri, L., di Sarra, A., Meloni, D., and Monteleone, F.: Influence of transport and trends in atmospheric CO_2 at Lampedusa, Atmos. Environ., 43, 3044–3051, doi:10.1016/j.atmosenv.2009.03.027, 2009. 140

Asmi, A., Collaud Coen, M., Ogren, J. A., Andrews, E., Sheridan, P., Jefferson, A., Weingartner, E., Baltensperger, U., Bukowiecki, N., Lihavainen, H., Kivekäs, N., Asmi, E., Aalto, P. P., Kulmala, M., Wiedensohler, A., Birmili, W., Hamed, A., O'Dowd, C., G Jennings, S., Weller, R., Flentje, H., Fjaeraa, A. M., Fiebig, M., Myhre, C. L., Hallar, A. G., Swietlicki, E., Kristensson, A., and Laj, P.: Aerosol decadal trends – Part 2: In-situ aerosol particle number concentrations at GAW and ACTRIS stations, Atmos. Chem. Phys., 13, 895–916, doi:10.5194/acp-13-895-2013, 2013. 140

Barmet, P., Kuster, T., Muhlbauer, A., and Lohmann, U.: Weekly cycle in particulate matter versus weekly cycle in precipitation over Switzerland, J. Geophys. Res., 114, D05206, doi:10.1029/2008JD011192, 2009. 145

Barmpadimos, I., Hueglin, C., Keller, J., Henne, S., and Prévôt, A. S. H.: Influence of meteorology on PM_{10} trends and variability in Switzerland from 1991 to 2008, Atmos. Chem. Phys., 11, 1813–1835, doi:10.5194/acp-11-1813-2011, 2011. 139, 141

Barmpadimos, I., Keller, J., Oderbolz, D., Hueglin, C., and Prévôt, A. S. H.: One decade of parallel fine ($PM_{2.5}$) and coarse (PM_{10}–$PM_{2.5}$) particulate matter measurements in Europe: trends and variability, Atmos. Chem. Phys., 12, 3189–3203, doi:10.5194/acp-12-3189-2012, 2012. 149

Bell, M., Dominici, F., Ebisu, K., Zeger, S., and Samet, J.: Spatial and temporal variation in $PM_{2.5}$ chemical composition in the United States for health effects studies, Environ. Health Persp., 115, 989–995, 2007. 139

Bencala, K. E. and Seinfeld, J. H.: On frequency distributions of air pollutant concentrations, Atmos. Environ., 10, 941–950, 1976. 142

Bernardoni, V., Vecchi, R., Valli, G., Piazzalunga, A., and Fermo, P.: PM_{10} source apportionment in Milan (Italy) using time-resolved data, Sci. Total Environ., 409, 4788–4795, doi:10.1016/j.scitotenv.2011.07.048, 2011. 149

Bigi, A., Ghermandi, G., and Harrison, R. M.: Analysis of the air pollution climate at a background site in the Po Valley, J. Environ. Monitor., 14, 552–563, doi:10.1039/C1EM10728C, 2012. 139, 140

Brockwell, P. J. and Davis, R. A.: Introduction to Time Series and Forecasting, 2nd edn., Springer-Verlag, New York, USA, 2002. 143

Bukowiecki, N., Lienemann, P., Hill, M., Furger, M., Richard, A., Amato, F., Prévôt, A., Baltensperger, U., Buchmann, B., and Gehrig, R.: PM_{10} emission factors for non-exhaust particles generated by road traffic in an urban street canyon and along a freeway in Switzerland, Atmos. Environ., 44, 2330–2340, doi:10.1016/j.atmosenv.2010.03.039, 2010. 152

Carbone, C., Decesari, S., Mircea, M., Giulianelli, L., Finessi, E., Rinaldi, M., Fuzzi, S., Marinoni, A., Duchi, R., Perrino, C., Sargolini, T., Vard, M., Sprovieri, F., Gobbi, G., Angelini, F., and Facchini, M.: Size-resolved aerosol chemical composition over the Italian Peninsula during typical summer and winter conditions, Atmos. Environ., 44, 5269–5278, doi:10.1016/j.atmosenv.2010.08.008, 2010. 139

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Ciattaglia, L., Cundari, V., and Colombo, T.: Further measurements of atmospheric carbon dioxide at Mt. Cimone, Italy: 1979–1985, Tellus B, 39, 13–20, doi:10.1111/j.1600-0889.1987.tb00266.x, 1987. 140

Cleveland, R. B., Cleveland, W. S., McRae, J., and Terpenning, I.: STL: a seasonal-trend decomposition procedure based on Loess, Journal of Official Statistics, 6, 3–33, 1990. 142

Collaud Coen, M., Andrews, E., Asmi, A., Baltensperger, U., Bukowiecki, N., Day, D., Fiebig, M., Fjaeraa, A. M., Flentje, H., Hyvärinen, A., Jefferson, A., Jennings, S. G., Kouvarakis, G., Lihavainen, H., Lund Myhre, C., Malm, W. C., Mihapopoulos, N., Molenar, J. V., O'Dowd, C., Ogren, J. A., Schichtel, B. A., Sheridan, P., Virkkula, A., Weingartner, E., Weller, R., and Laj, P.: Aerosol decadal trends – Part 1: In-situ optical measurements at GAW and IMPROVE stations, Atmos. Chem. Phys., 13, 869–894, doi:10.5194/acp-13-869-2013, 2013. 140

Colombi, C., Gianelle, V., Lazzarini, M., Chiesa, M., Cigolini, G., Cosenza, R., Ferrari, R., Gentile, N., Ledda, F., and Raddrizzani, F.: Report on air quality in the provinces of Milano and Monza–Brianza – Year 2010 (in Italian), Original title: Rapporto sulla qualità dell'aria delle province di Milano e di Monza–Brianza – Anno 2010, ARPA Lombardia, Milan, Italy, 2011. 141

Daniel, J. S., Portmann, R. W., Solomon, S., and Murphy, D. M.: Identifying weekly cycles in meteorological variables: the importance of an appropriate statistical analysis, J. Geophys. Res., 117, D13203, doi:10.1029/2012JD017574, 2012. 145, 146

Davison, A. and Hinkley, D.: Bootstrap Methods and Their Application, Cambridge University Press, Cambridge, UK, 1997. 143

de Meij, A., Thunis, P., Bessagnet, B., and Cuvelier, C.: The sensitivity of the CHIMERE model to emissions reduction scenarios on air quality in Northern Italy, Atmos. Environ., 43, 1897–1907, doi:10.1016/j.atmosenv.2008.12.036, 2009. 152

Deserti, M., Bande, S., Angelino, E., Pession, G., Dalan, F., Minguzzi, E., Stortini, M., Bonafè, G., Maria, R. D., Fossati, G., Peroni, E., Costa, M. P., Liguori, F., and Pillon, S.: Technical report on the application of simulation models on the Adriatic-Po basin (in Italian), Original title: Rapporto tecnico sulla applicazione di modellistica al bacino padano adriatico, APAT (National Agency for Environmental Protection and Technical Services), available at: http://www.arpa.emr.it/cms3/documenti/_cerca_doc/meteo/ambiente/rapporto_modellistica_finale_pdf.pdf (last access: 21 December 2013), 2006. 152

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14, 137–170, 2014

Climatology of atmospheric PM_{10} concentration in the Po Valley

A. Bigi and G. Ghermandi

Flaum, J. B., Rao, S. T., and Zurbenko, I. G.: Moderating the influence of meteorological conditions on ambient ozone concentrations, J. Air Waste Manage., 46, 35–46, doi:10.1080/10473289.1996.10467439, 1996. 140

Giugliano, M., Lonati, G., Butelli, P., Romele, L., Tardivo, R., and Grosso, M.: Fine particulate ($PM_{2.5}$–PM_1) at urban sites with different traffic exposure, Atmos. Environ., 39, 2421–2431, doi:10.1016/j.atmosenv.2004.06.050, 2005. 150

Hamed, K. H.: Enhancing the effectiveness of prewhitening in trend analysis of hydrologic data, J. Hydrol., 368, 143–155, doi:10.1016/j.jhydrol.2009.01.040, 2009. 144

Hamed, K. and Ramachandrarao, A.: A modified Mann-Kendall trend test for autocorrelated data, J. Hydrol., 204, 182–196, doi:10.1016/S0022-1694(97)00125-X, 1998. 144

Harrison, R. M., Stedman, J., and Derwent, D.: New directions: why are PM_{10} concentrations in Europe not falling?, Atmos. Environ., 42, 603–606, doi:10.1016/j.atmosenv.2007.11.023, 2008. 148

Hipel, K. W. and Mcleod, A. I.: Time Series Modelling of Water Resources and Environmental Systems, Elsevier, Amsterdam, available at: http://www.stats.uwo.ca/faculty/aim/1994Book/ (last access: 21 December 2013), 1994. 144

Hirsch, R. M. and Slack, J. R.: A nonparametric trend test for seasonal data with serial dependence, Water Resour. Res., 20, 727–732, doi:10.1029/WR020i006p00727, 1984. 144

Kaufman, L. and Rousseeuw, P.: Finding Groups in Data: an Introduction to Cluster Analysis, Wiley Series in Probability and Mathematical Statistics: Applied Probability and Statistics, Wiley, Hoboken, NJ, USA, 1990. 146

Larsen, B., Gilardoni, S., Stenström, K., Niedzialek, J., Jimenez, J., and Belis, C.: Sources for PM air pollution in the Po Plain, Italy: II. Probabilistic uncertainty characterization and sensitivity analysis of secondary and primary sources, Atmos. Environ., 50, 203–213, doi:10.1016/j.atmosenv.2011.12.038, 2012. 149

Lefohn, A. S., Shadwick, D., and Oltmans, S. J.: Characterizing changes in surface ozone levels in metropolitan and rural areas in the United States for 1980–2008 and 1994–2008, Atmos. Environ., 44, 5199–5210, doi:10.1016/j.atmosenv.2010.08.049, 2010. 140, 144

Liburdi, R., De Lauretis, R., Corrado, C., Di Cristofaro, E., Gonella, B., Romano, D., Napoletani, G., Fossati, G., Angelino, E., and Peroni, E.: The disaggregation of the national emission inventory to a province level (in Italian), Tech. rep., National Environmental Protection Agency, Rome, Italy, 2004. 142

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14, 137–170, 2014

Climatology of atmospheric PM_{10} concentration in the Po Valley

A. Bigi and G. Ghermandi

Lonati, G., Pirovano, G., Sghirlanzoni, G., and Zanoni, A.: Speciated fine particulate matter in Northern Italy: a whole year chemical and transport modelling reconstruction, Atmos. Res., 95, 496–514, doi:10.1016/j.atmosres.2009.11.012, 2010. 150

Marcazzan, G., Ceriani, M., Valli, G., and Vecchi, R.: Source apportionment of PM_{10} and $PM_{2.5}$ in Milan (Italy) using receptor modelling, Sci. Total. Environ., 317, 137–147, doi:10.1016/S0048-9697(03)00368-1, 2003. 140

Matta, E., Facchini, M. C., Decesari, S., Mircea, M., Cavalli, F., Fuzzi, S., Putaud, J.-P., and Dell'Acqua, A.: Mass closure on the chemical species in size-segregated atmospheric aerosol collected in an urban area of the Po Valley, Italy, Atmos. Chem. Phys., 3, 623–637, doi:10.5194/acp-3-623-2003, 2003. 139, 150

Mueller, S. F.: Ambient sulfate trends and the influence of meteorology, J. Appl. Meteorol., 44, 1745–1760, doi:10.1175/JAM2307.1, 2005. 140

Oltmans, S., Lefohn, A., Harris, J., Galbally, I., Scheel, H., Bodeker, G., Brunke, E., Claude, H., Tarasick, D., Johnson, B., Simmonds, P., Shadwick, D., Anlauf, K., Hayden, K., Schmidlin, F., Fujimoto, T., Akagi, K., Meyer, C., Nichol, S., Davies, J., Redondas, A., and Cuevas, E.: Long-term changes in tropospheric ozone, Atmos. Environ., 40, 3156–3173, doi:10.1016/j.atmosenv.2006.01.029, 2006. 145

Putaud, J.-P., Raes, F., Van Dingenen, R., Bruggemann, E., Facchini, M. C., Decesari, S., Fuzzi, S., Gehrig, R., Huglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Muller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., Brink, H. T., Torseth, K., and Wiedensohler, A.: A European aerosol phenomenology – 2: Chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, Atmos. Environ., 38, 2579–2595, 2004. 139, 140

Putaud, J.-P., Dingenen, R. V., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H., Harrison, R., Herrmann, H., Hitzenberger, R., Hüglin, C., Jones, A., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T., Löschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten Brink, H., Tursic, J., Viana, M., Wiedensohler, A., and Raes, F.: A European aerosol phenomenology – 3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe, Atmos. Environ., 44, 1308–1320, doi:10.1016/j.atmosenv.2009.12.011, 2010. 139, 140

ACPD
14, 137–170, 2014

R Development Core Team: R: A Language and Environment for Statistical Computing, R Foundation for Statistical Computing, Vienna, Austria, available at: http://www.R-project.org (last access: 21 December 2013), ISBN 3-900051-07-0, 2011. 142
Rodríguez, S., Van Dingenen, R., Putaud, J.-P., Dell'Acqua, A., Pey, J., Querol, X., Alastuey, A., Chenery, S., Ho, K.-F., Harrison, R., Tardivo, R., Scarnato, B., and Gemelli, V.: A study on the relationship between mass concentrations, chemistry and number size distribution of urban fine aerosols in Milan, Barcelona and London, Atmos. Chem. Phys., 7, 2217–2232, doi:10.5194/acp-7-2217-2007, 2007. 140, 150
Roemer, W., Hoek, G., Brunekreef, B., Clench-Aas, J., Forsberg, B., Pekkanen, J., and Schutz, A.: PM_{10} elemental composition and acute respiratory health effects in European children (PEACE project), Eur. Respir. J., 15, 553–559, 2000. 139
Sen, P.: Estimates of the regression coefficient based on Kendall's tau, J. Am. Stat. Assoc., 63, 1379–1389, 1968. 140
Tripathi, O. P., Jennings, S. G., O'Dowd, C. D., Coleman, L., Leinert, S., O'Leary, B., Moran, E., O'Doherty, S. J., and Spain, T. G.: Statistical analysis of eight surface ozone measurement series for various sites in Ireland, J. Geophys. Res., 115, D19302, doi:10.1029/2010JD014040, 2010. 140
Vautard, R., Builtjes, P., Thunis, P., Cuvelier, C., Bedogni, M., Bessagnet, B., Honoré, C., Moussiopoulos, N., Pirovano, G., Schaap, M., Stern, R., Tarrason, L., and Wind, P.: Evaluation and intercomparison of Ozone and PM_{10} simulations by several chemistry transport models over four European cities within the CityDelta project, Atmos. Environ., 41, 173–188, doi:10.1016/j.atmosenv.2006.07.039, 2007. 152
Vestreng, V., Myhre, G., Fagerli, H., Reis, S., and Tarrasón, L.: Twenty-five years of continuous sulphur dioxide emission reduction in Europe, Atmos. Chem. Phys., 7, 3663–3681, doi:10.5194/acp-7-3663-2007, 2007. 139
Wise, E. K. and Comrie, A. C.: Meteorologically adjusted urban air quality trends in the Southwestern United States, Atmos. Environ., 39, 2969–2980, doi:10.1016/j.atmosenv.2005.01.024, 2005. 140
World Health Organization: Air quality guidelines, global update 2005, particulate matter, ozone, nitrogen dioxide and sulfur dioxide, World Health Organization, Regional office for Europe, Copenhagen, Denmark, 2006. 139

ACPD
14, 137–170, 2014

Yue, S. and Pilon, P.: A comparison of the power of the *t* test, Mann–Kendall and bootstrap tests for trend detection, Hydrolog. Sci. J., 49, 21–37, doi:10.1623/hysj.49.1.21.53996, 2004. 145

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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 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	Milano	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

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Table 2. GLS trend (± 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**

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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 Slope µg m^{-3} yr^{-1}	5th annual quantile Change % yr^{-1}	50th annual quantile Slope µg m^{-3} yr^{-1}	50th annual quantile Change % yr^{-1}	95th annual quantile Slope µg m^{-3} yr^{-1}	95th annual quantile Change % yr^{-1}	Months with significant trend
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 (–)

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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.	•	•		•
Milano	•	•		•
Padova M.	•	•		•
Piacenza	•	•		•
Rovigo	•	•		•
Sannazzaro				
Verona Ca.	•	•		•
Verona C.so M.	•	•	•	•
Vigevano	•	•		•
Voghera	•	•		

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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.

Sites	W. E. magnitude	Weekly cycle		
	Complete series	Complete series	Winter	Summer
Asti D'A.				
Bergamo	•	•		•
Bologna				
Cerano				
Cremona				
Forlì				•
Mantova S.A.	•	•		•
Milano	•			•
Parma				
Reggio E.				
Rimini				
Torino Ca.				
Verona Ca.	•	•		•

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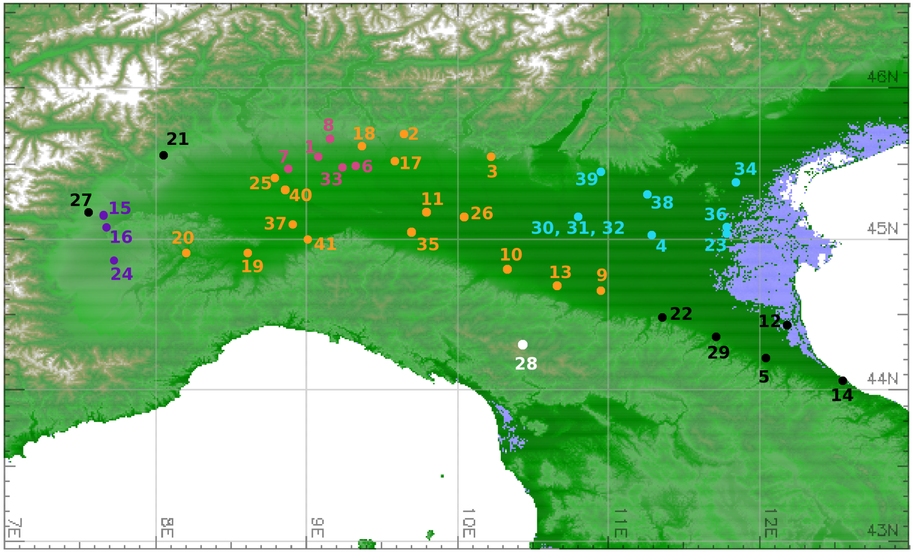

Fig. 1. Location of PM_{10} monitoring stations included in the analysis. Key for ID number is found in Table 1, colour code refers to result of cluster analysis using Euclidean distance (Fig. 5a).

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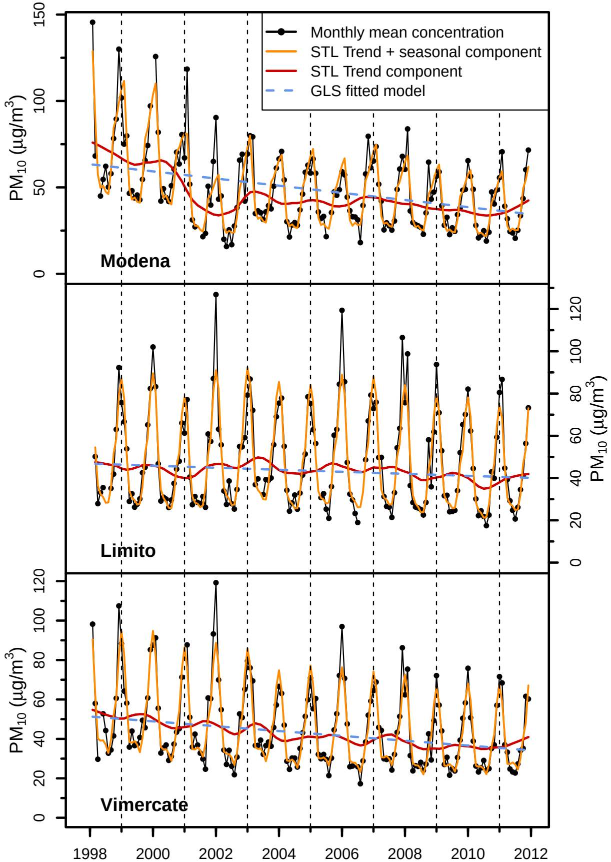

Fig. 2. STL decomposition for monthly mean PM_{10} along with GLS fitted slope for three selected sites.

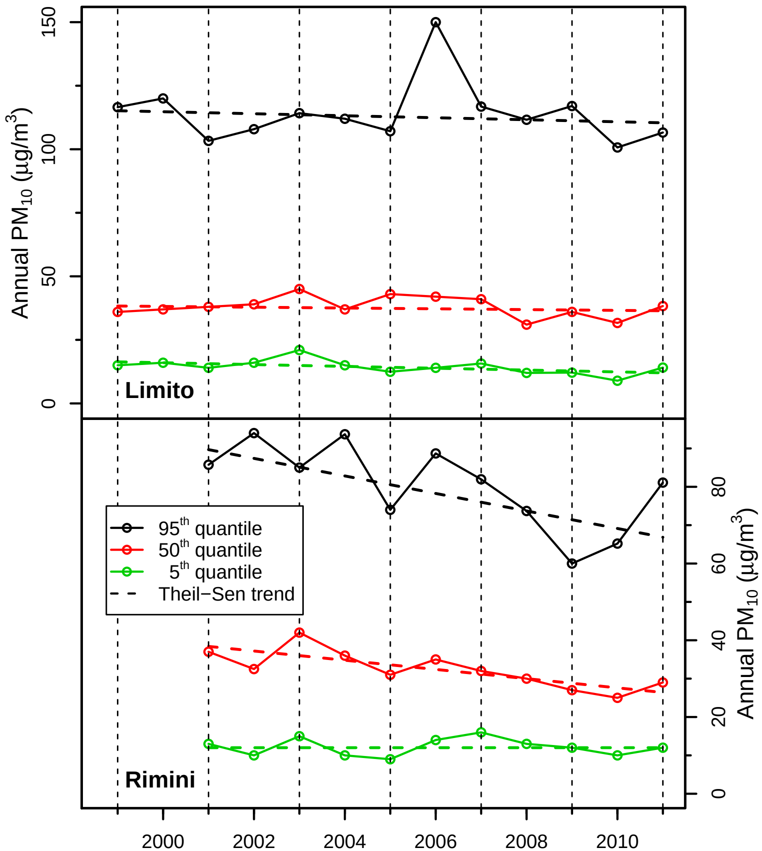

Fig. 3. Annual quantiles along with Sen slope for daily PM_{10} at Limito and Rimini.

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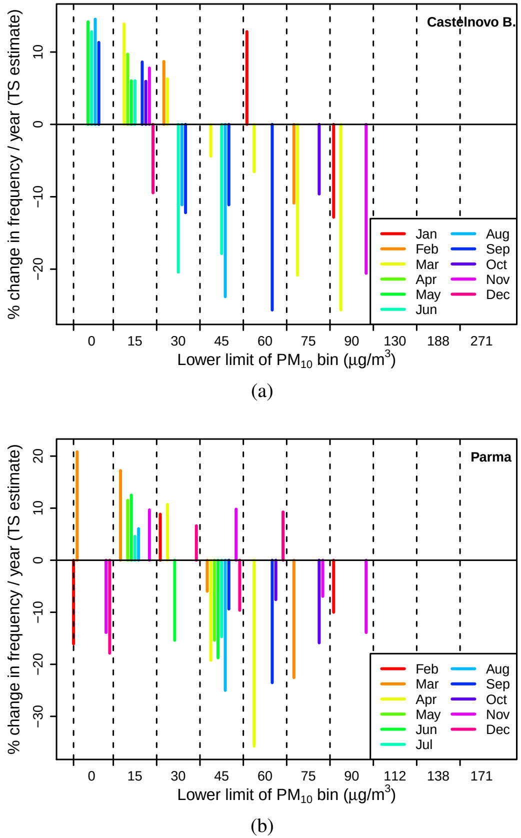

Fig. 4. Significant changes in monthly frequency distribution of PM_{10} at Castelnovo Bariano **(a)** and Parma **(b)**.

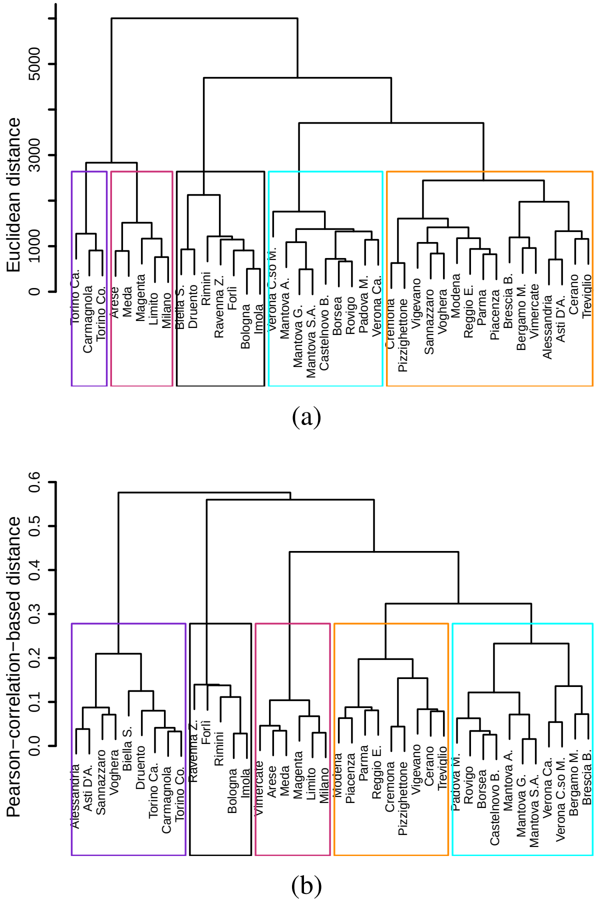

Fig. 5. Results of cluster analysis on daily PM_{10} data using Euclidean distance **(a)** and Pearson-correlation-based distance **(b)**. Coloured boxes indicate clusters; monitoring sites position is found in Fig. 1.

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