



ID	Station name	Station type	Activation date	ID	Station name	Station type	Activation date
Long term trend dataset				Extended analysis dataset			
1	Anno	UB	Jan 2002	19	Alessandria Lame	UB	Feb 2007
2	Bergamo Mucchi	UB	Jul 2000	20	Asolo d'Acquino	UB	Dec 2002
3	Brescia Bolzano	UT	Oct 2000	21	Belluno Sarnon	UB	Jan 2003
4	Castelnuovo Bariano	Sub	Jan 2002	22	Bologna	UB	Nov 2007
5	Forlì	UB	Jan 2001	23	Brescia	UB	Jan 2003
6	Imola	UB	Mar 1998	24	Carruggioli	Sub	Jan 2006
7	Magenta	UB	Mar 1998	25	Caserta	UB	Mar 1998
8	Modena	UT	Feb 1998	26	Cerignola	UB	Apr 2006
9	Modena	UB	Apr 2002	27	Cesena	UB	Mar 2002
10	Parma	UB	Feb 1998	28	Forlì	UB	Nov 2004
11	Pesiglionone	UB	Oct 1999	29	Imola	UB	Jan 2003
12	Ravenna Zalamella	UB	Jan 2001	30	Manzoni Antonio	UB	Jan 2003
13	Reggio Emilia	UB	Jan 2001	31	Manzoni Antonio	UB	Jan 2003
14	Rimini	UB	Jan 2001	32	Manzoni S. Agnese	UB	Jan 2003
15	Torino Caduti	Sub	Jan 2002	33	Milano	UB	May 2007
16	Torino Consolata	UT	Jul 1999	34	Padova Mandria	UB	Jan 2005
17	Treviso	UB	Feb 2000	35	Pavia	UB	Jan 2005
18	Vercelli	UB	Feb 1998	36	Samazzaro De' Bergandi	UB	Jan 2005
				37	Vercelli	UB	Jan 2004
				38	Vercelli	UB	Jan 2004
				39	Vercelli	UB	Jan 2004
				40	Vercelli	UB	Jan 2004
				41	Vercelli	UB	Jan 2004

Dataset:

- gravimetric equivalent PM_{10} downloaded from respective ARPA websites (or provided by ARPA)
- PM_{10} data manually inspected: annual, monthly, weekly and daily patterns examined and spurious values removed
- Provincial emissions estimates (inventory version 13, 05 2013) for PM_{10} , $PM_{2.5}$, SO_2 , NO_x , NM-VOC, CH_4 , NH_3 , CO by ISPRA

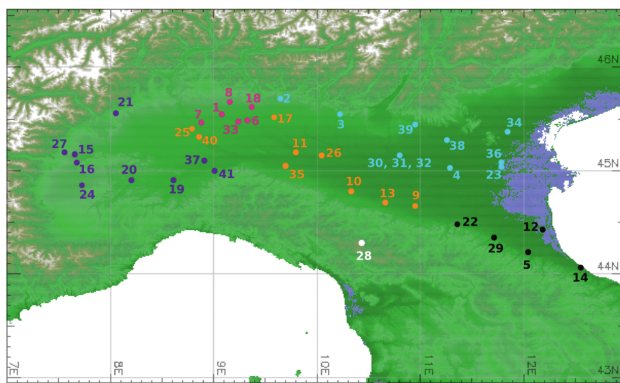


Figure: Location of PM_{10} monitoring stations included in the analysis. Key for ID number is found in Table, colour code refers to result of cluster analysis using Euclidean distance.

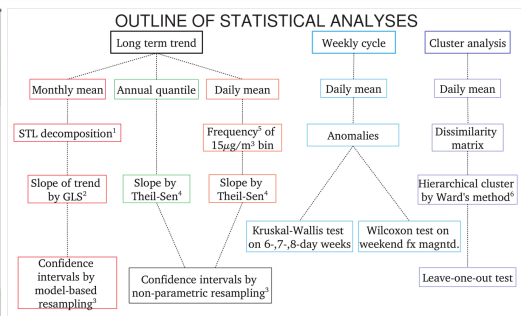


Table: Analysed PM_{10} sampling sites for long term trend and for extended statistical analysis.

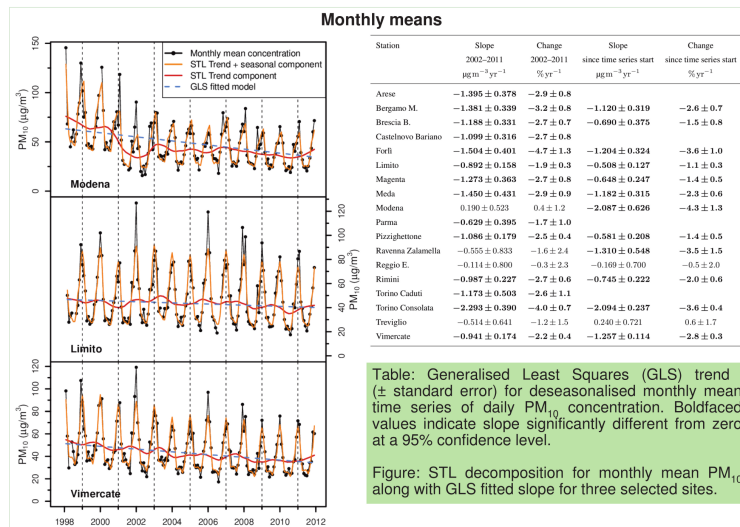
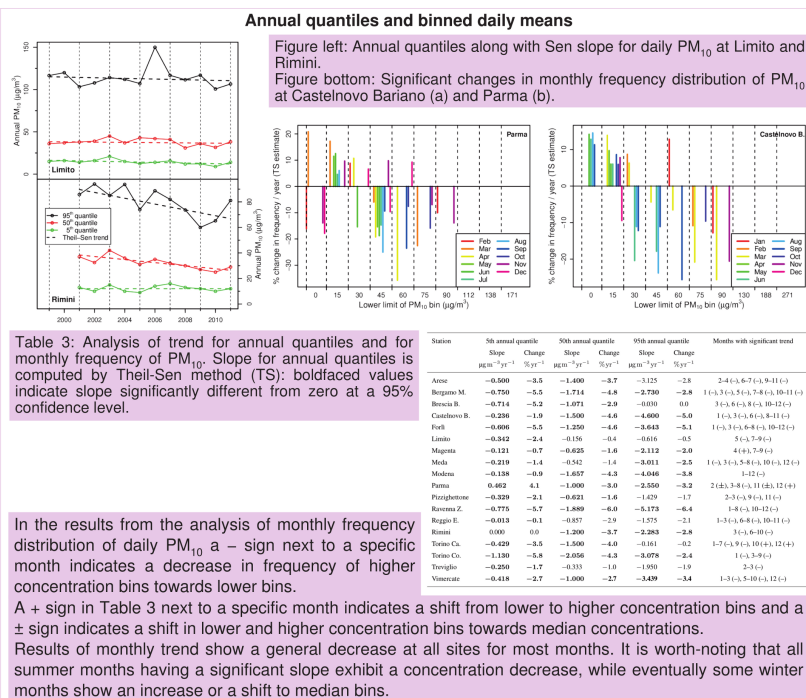


Table: Generalised Least Squares (GLS) trend (± standard error) for deseasonalised monthly mean time series of daily PM_{10} concentration. Boldfaced values indicate slope significantly different from zero at a 95% confidence level.

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

The trend for monthly means is significantly decreasing for almost all sites; the slope is generally steeper over the period 2002 – 2011 for almost all observations. Annual trends are partially consistent with GLS estimates. 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.



In the results from the analysis of monthly frequency distribution of daily PM_{10} 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.

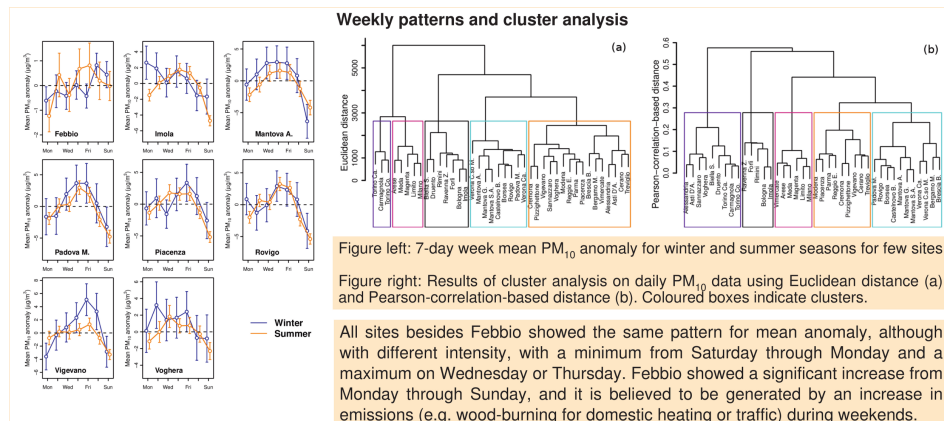


Figure left: 7-day week mean PM_{10} anomaly for winter and summer seasons for few sites

Figure right: Results of cluster analysis on daily PM_{10} data using Euclidean distance (a) and Pearson-correlation-based distance (b). Coloured boxes indicate clusters.

All sites besides Febbio showed the same pattern for mean anomaly, although with different intensity, with a minimum from Saturday through Monday and a maximum on Wednesday or Thursday. Febbio showed a significant increase from Monday through Sunday, and it is believed to be generated by an increase in emissions (e.g. wood-burning for domestic heating or traffic) during weekends.

Considering the whole year, a significant weekly periodicity is present during 7 day week at all sites besides Febbio, Forlì and Sannazzaro. Most of shorter time series show a weekly periodicity in summer and not in winter, whereas many of longer ones still exhibit a weekly periodicity in both seasons. The lack of weekly periodicity in winter might be due to the large fraction of SIA in PM_{10} in this season, uncoupling the weekly fluctuations of primary anthropogenic emissions (non-exhaust included) and PM_{10} concentration. Possibly this buffering effect by SIA is dimmed in longer time series by a higher primary/SIA ratio in the late 90s early 2000. $PM_{2.5}$ in the Po Valley has been shown to have a larger relative fraction of secondary aerosol than PM_{10} , and a lower contribution from re-suspension. Consistently a significant weekly cycle in $PM_{2.5}$ is observed only at very few sites. Cluster analysis identifies five main clusters, confirmed by sensitivity analyses: a group based SE having similar patterns and lower concentration including also two NW background sites (Biella and Druento) having relatively low concentration. Two clusters identify the two main metropolitan areas of the valley, Turin and Milan. Finally, both NE and 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 generally sites at cluster boundaries, occasionally assigned to the geographically adjacent cluster.

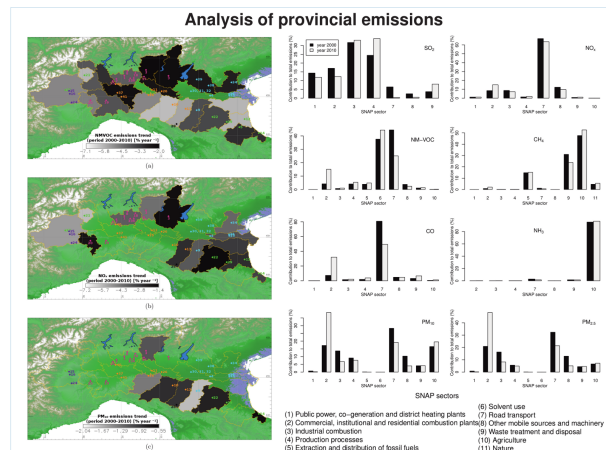


Figure left: Significant annual trend in total emissions of NM-VOC (a), NO_x (b) and PM_{10} (c)

Figure right: Change in percent contribution by each SNAP sector to the emission of 8 atmospheric pollutants in the Po valley (period 2000-2010).

No significant statistical correlation arose from the comparison of trends in background PM_{10} and emissions in each province, although the results from analyses above strongly suggest that the drop observed in PM_{10} concentration derives primarily from a decrease in local emissions. Simulation studies by De Meij et al. (2009) and Deserti et al. (2006) showed that, in order to have a decrease in PM_{10} similar to the one observed in this study, a large reduction in both primary and secondary PM_{10} sources is required. On the contrary, a minor and restricted decrease in PM_{10} emissions is observed from inventory data.

Conclusions

- Significant downward trend at most sites for different time scales (monthly, annual, seasonal) and for different pollution regimes (5th, 50th and 95th quantile)
- Weekly cycle (i.e. anthropogenic) for PM_{10} at most sites, particularly in summer (increase in the percentage of secondary fraction through years)
- Spatial-based differences in PM_{10} with impact of large urban areas on the surroundings
- Large decrease in emissions for some species (mostly SO_2 , NO_x , NMVOC) and small decrease in PM_{10} and $PM_{2.5}$ emissions (uncertainties both in chemical-transport models and inventories)