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PAPER

Analysis of the air pollution climate at a background site in the Po valley†

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The Po valley in northern Italy is renowned for its high air pollutant concentrations. Measurements of air pollutants from a background site in Modena, a town of 200 thousand inhabitants within the Po valley, are analysed. These comprise hourly data for CO, NO, NO_2, NO_x, and O_3, and daily gravimetric equivalent data for PM_{10} from 1998–2010. The data are analysed in terms of long-term trends, annual, weekly and diurnal cycles, and auto-correlation and cross-correlation functions. CO, NO and NO_2 exhibit a strongly traffic-related pattern, with daily peaks at morning and evening rush hour and lower concentrations over the weekend. Ozone shows an annual cycle with a peak in July due to local production; notwithstanding the diurnal cycle dominated by titration by nitrogen oxide, the decreasing long term trend in NO concentration did not affect the long term trend in O_3, whose mean concentration remained steady over the sampling period. PM_{10} shows a strong seasonality with higher concentration in winter and lower concentration in summer and spring. Both PM_{10} and ozone show a marked weekly cycle in summer and winter respectively. Regressions of PM_{10} upon NO_x show a consistently greater intercept in winter, representing higher secondary PM_{10} in the cooler months of the year. There is a seasonal pattern in primary PM_{10} to NO_x ratios, with lower values in winter and higher values in summer, but the reasons are unclear.

Introduction

In order to assess correctly population exposure to air pollutants, concentration patterns are a key factor since the seasonal, weekly and diurnal variability can be substantial. Additionally, understanding the temporal variability in urban air quality is a key element informing pollution control policies designed to minimize population exposure. The observed temporal pattern of air pollutants is due to the combined effect of many factors, each one with its own seasonality: atmospheric and hydrological processes, human activities, long-range transport, natural emissions and extreme events. Numerous studies have sought to describe and interpret long and short-term trends, seasonality and sub-annual patterns for air pollutants worldwide. A detailed analysis of multiple air pollutant patterns in Northern Spain has been carried out by Moreno *et al.*,[1] who found strong weekly and diurnal patterns forced by anthropogenic sources, along with the impact of the industrial district on urban air quality, as well as of that of occasional Saharan dust transport events. So *et al.*[2] showed seasonality in $PM_{2.5}$ at three different sites in Hong Kong during 2001 and 2005 and found increasing concentrations of secondary aerosols at all sites and decreasing concentrations for carbonaceous aerosols at the traffic site. Wise and Comrie[3] investigated the effect of emission sources on PM_{10} and ozone long term concentration in the south-western United States by

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Environmental impact

The Po valley experiences a strong anthropic pressure due to wide urban areas (*e.g.* Milano), intensive breeding and agriculture and wide manufacturing districts, along with topographic and meteorological conditions unfavourable to pollutant dispersion. This study focussed on a decadal time series of concentration of atmospheric pollutants in an urban background site of Modena, representative of southern-central Po valley. The analysis showed a distinct anthropic periodicity for many pollutants both at hourly and weekly time scales, and a strong dependence on atmospheric conditions. A significant downward trend has been detected for all atmospheric pollutants besides ozone, which resulted steady. A comparison of PM_{10} weekly pattern between Modena and a pool of other European sites confirmed the peculiarity of the Po valley.

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removing the influence of meteorology and found a non-steady trend for PM across the whole region.

Previous studies assessing concentration patterns from long term (*e.g.* longer than 10 years) measurements in Italy are very few. Both Artuso *et al.*[4] and Gratani and Varone[5] investigated CO_2 concentration trends. Although studies from Italy on long term air concentration time series are few, several studies have involved diurnal and seasonal patterns of atmospheric pollutants over a shorter time period in the Po valley. Bigi and Ghermandi[6] studied the concurrent seasonal variation of 10–700 nm particles, $PM_{2.5}$ and meteorological variables in Modena describing the strong influence of dispersion condition for all particle ranges. Vecchi *et al.*[7] investigated PM_{10} composition (ions, metals and OC/EC) at an urban background site in Milan, during summer and winter with a 4 h resolution sampling campaign, finding a strong seasonal and diurnal pattern in secondary aerosols and a weekly pattern in secondary organic carbon; Matta *et al.*[8] studied the seasonal pattern of ions, OC/BC and water soluble organic carbon in size-segregated atmospheric aerosol in Bologna showing a seasonal pattern similar to the ones of Vecchi *et al.*[7] both for secondary and carbonaceous aerosols.

In the present study a 13-year time series (1998–2010) from an urban background site in Modena, a Po valley town with 200 000 inhabitants, is analysed in detail: yearly, seasonal, weekly and diurnal patterns have been investigated and presented as a synthesised description of a pollution climate regime for a typical urban site in the South-Central Po valley. Data have been tested for the presence of a long-term trend and of a significant weekly cycle; data have been also correlated with key meteorological variables. The outcomes of this study give insights into pollutant sources at the site, influences upon concentrations and key interrelationships in pollutant behaviour.

Experimental

The air quality data analysed in this study have been measured at the Nonantolana urban background monitoring site (ID: MO01), Modena, Italy (44° 39′ 25″ N, 10° 56′ 58″ E, 30 m asl.; Fig. 1): the instrumentation at the site has experienced few changes over many years and a summary table with data available and measurement techniques is presented in Table 1. All sampling equipment follows a quality management system which is certified to ISO 9001:2008. The analysis investigated in detail all available data from January 1998 to December 2010; data are collected at hourly and at daily time resolution for gaseous and particulate pollutants respectively. Daily statistics of hourly data have been computed according to the European Commission Decision 2001/752/CE, *i.e.* with at least 13 one-hour values available and not more than six successive one-hour values missing. Monthly and annual statistics have been computed over daily data if at least 75% of the daily data were available for a specific month or year. Representative meteorological data have been collected at the Environmental Agency weather station (~2.5 km from the monitoring site), consisting of hourly air temperature, atmospheric pressure, solar and terrestrial radiation in the infrared and visible wavelength range, precipitation, relative humidity, wind direction and wind speed. The weather station started hourly measurements in 2004 for all variables besides atmospheric pressure, which started in 2006; therefore hourly atmospheric pressure data used in the present study have been measured at the Piazza Roma weather station (~1.8 km from the monitoring site) of the Geophysical Observatory (University of the Modena and Reggio Emilia). At the latter station, atmospheric pressure data are available since 1998 and correlate perfectly (Pearson's coefficient of correlation $r = 0.998$; a linear model with atmospheric pressure at the Geophysical Observatory and at the Environmental Agency station being the dependent and independent variable respectively, results: slope 1.01 hPa hPa^{-1}, $R^2 = 0.997$) over the concurrent measurement period at the Environmental Agency weather station.

Data analyses have been performed with the statistical software package R, version 2.12.[9] Summer was taken as June to August, and winter December to February.

Results and discussion

Long-term trend and seasonal patterns

Monthly average concentrations have been calculated from daily data for all the species over their respective sampling period. In order to analyse separately trend and seasonal components in monthly time series, they have been decomposed through the STL technique[10] (see Appendix A for details). Each time series which showed a non-normal distribution was transformed prior to decomposition in order to achieve normally distributed residuals from STL decomposition: all pollutants underwent a log-transformation, except ozone, which was square-rooted. A qualitative and quantitative analysis of monthly trend time series was performed on back-transformed logarithmic trend data. Monthly mean time series along with estimated deseasonalized and seasonal components are presented in Fig. 2. The extracted seasonal component for benzene, toluene, and *m*-xylene (BTX) shows a peak in January, a minimum in August, and a steadily decreasing trend during the whole sampling period. The annual mean BTX concentration decreased from 4.1 μg m^{-3} in 2002 to 1.8 μg m^{-3} in 2008, showing a significant decreasing trend, estimated by Sen's method,[11] of −0.44 μg m^{-3} $year^{-1}$: this decreasing rate is slightly steeper than Sen's trend for annual mean benzene concentration at UK urban background sites presented by Dollard *et al.*,[12] where a trend of −0.33 μg m^{-3} $year^{-1}$ was found over the period 1993–2004. The seasonal components for carbon monoxide, nitric oxide and nitrogen dioxide are fairly similar, all showing a wide range in monthly concentration, while the trend component shows a fairly steady downward rate for CO and NO. An anomalous concentration drop occurred in winter 2001 for almost all pollutants and may be attributable to significantly milder than normal temperatures in January 2001,[13] probably enhancing atmospheric dispersion. Annual NO_2 means remain well above the EU limit value of 40 μg m^{-3}. The seasonal pattern for ozone shows a minimum in December and a maximum in July, whereas its long-term trend is steady, notwithstanding the drop in NO and NO_2. Finally, STL decomposition of the PM_{10} monthly mean series resulted in a seasonal component peaking in February with a minimum in August, and in a deseasonalized trend with a net long term decrease, showing a drop in summer 2001 and 2002. The change between 2001 and 2007 was very small, in common with many Western European sites.[14]

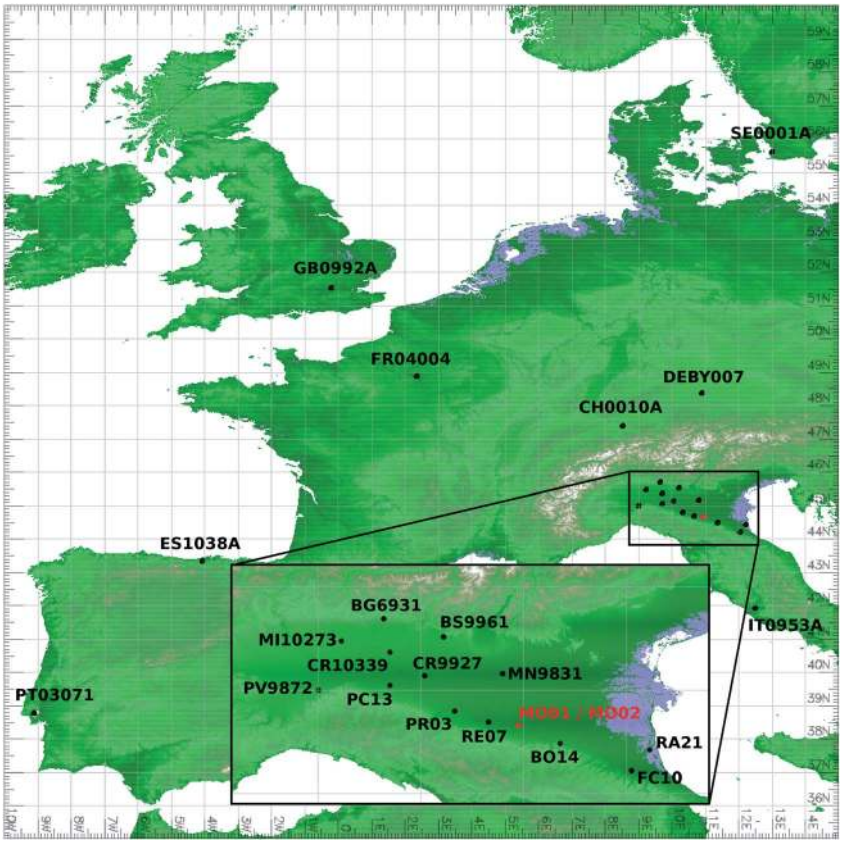

Fig. 1 Location of the Nonantolana monitoring site in Modena (named MO01) and other urban background PM_{10} monitoring sites used as comparison in this study (see Table 3 for the listing). Sites in two major Po valley urban areas are MI10273 in Milano and BO14 in Bologna (digital elevation model data from Jarvis *et al.*[34]).

Table 1 Summary of available data and sampling instruments

Pollutant	Monitoring period	Sampling instrument
BTX	Jan 2002–Dec 2008	GC/PID
CO	Jan 1998–Feb 2008	IR absorption
NO	Jan 1998	Chemiluminescence
NO_2	Jan 1998	Chemiluminescence
NO_x	Jan 2002	Chemiluminescence
O_3	Jan 1998–Jan 2007	UV absorption
PM_{10}	Feb 1998	Beta attenuation

In order to estimate the average long-term trend over the deseasonalized monthly means time series a generalised least squares regression model (GLS) has been applied to the data. Contrary to ordinary least squares (*i.e.* a linear regression model), GLS regression allows correct estimation of model variance since it concurrently estimates both the parameters of the linear model and the parameters of the ARMA model of the residuals: GLS is necessary, since the residuals of a linear regression of time series of monthly data are not independent. The time series of the resultant residuals satisfactorily fitted by an ARMA (2,2) model for all variables. Standard errors for GLS parameters have been estimated *via* bootstrap by a model-based re-sampling technique.[15] Results of GLS analysis are shown in Table 2. All pollutants show a significant downward trend, except ozone.

Ozone seasonality at the Nonantolana site has been compared to observations at the Mount Cimone GAW station (44°11′N, 10°42′E; 2165 m asl) which represents background conditions for the Po valley: data collected at this site by Cristofanelli *et al.*[16] and Bonasoni *et al.*[17] showed a peak in spring, as common to background sites in the Northern Hemisphere, and a peak in August, due to very high mixing heights over the Po valley in summer.

Further insights can be gained by viewing better time-resolved average cycles, shown in Fig. 3 and 4. The average year computed from daily mean concentrations for each Julian day of all the years available exhibits some clear seasonal patterns with minimum and maximum values (Fig. 3). There are at least two recurrent events in the annual pattern: on August 15th, one of the most popular Italian holidays, nitrogen dioxide has a minimum, leading to a peak in ozone concentration. Another event occurs on Christmas day, when CO, NO, NO_2 and PM_{10} show a minimum. Notably, on Christmas day the drop in NO is not associated with a peak in O_3, contrary to summer conditions in Modena, to Christmas day in London,[18] or mean winter conditions (see paragraph on lagged correlations), but with an equivalent rise in NO_2. PM_{10} shows a peak also on New Year's Day due to fireworks, and a corresponding minimum in vehicular traffic emission of CO and NO is seen on this day. This PM_{10} peak is followed by a drop in concentration due to reduced emissions on January 2nd and 3rd.

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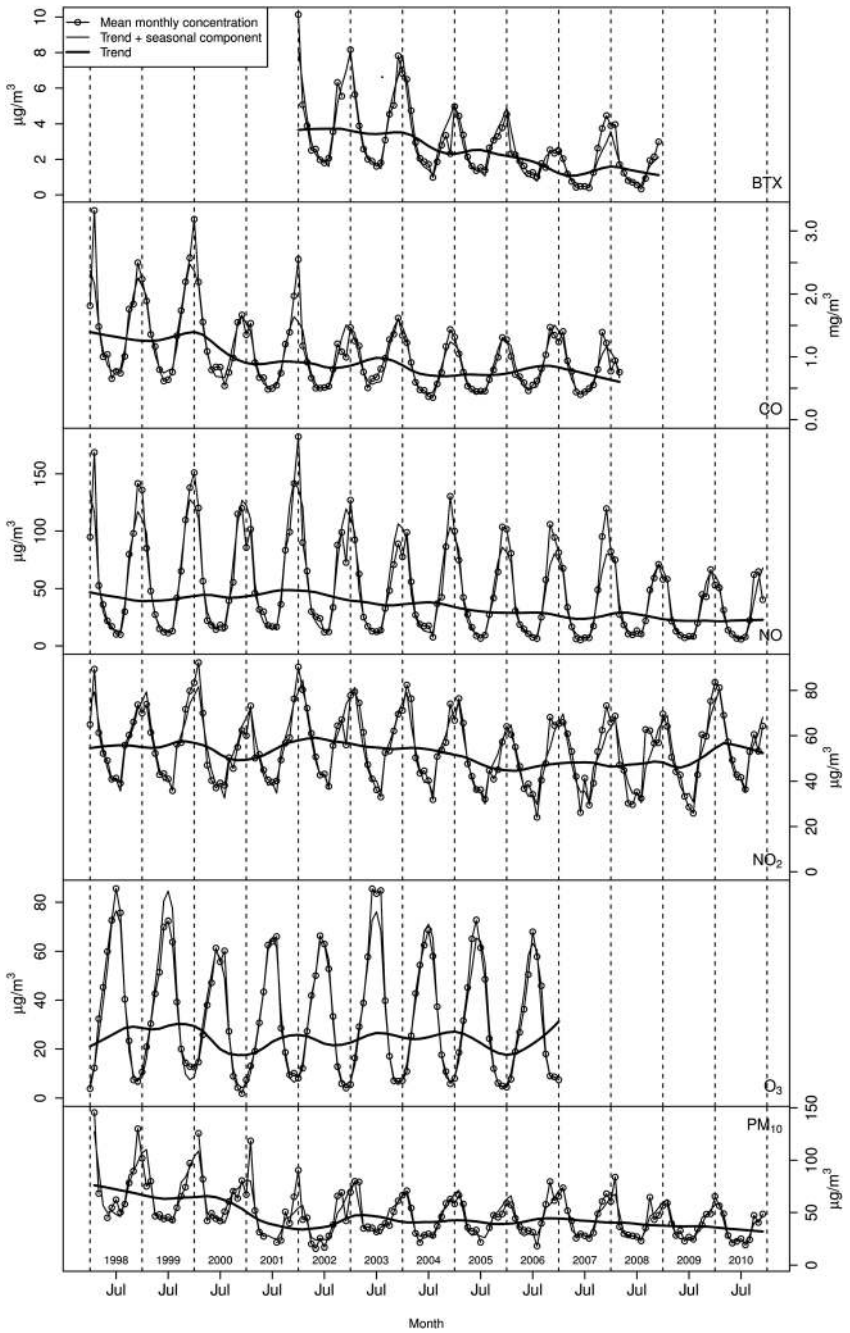

Fig. 2 Time series of monthly average concentrations of air pollutants showing deseasonalized and seasonal components.

The seasonal variation in PM_{10} seen in Fig. 3 is strongly at variance with the behaviour of PM_{10} at the North Kensington site in London (*cf.* Fig. 6b, site ID: GB0992A), a city with relatively similar mean annual temperatures to Modena (the annual mean hourly temperature in London at the London Weather Centre was 12.3 °C (1996–2009), while the annual mean hourly temperature in Modena was 14.7 °C (2004–2010)), but a far smaller seasonal variation in temperature. Wind speeds in the Po valley are light throughout the year, and vertical mixing determined largely by ground surface heating and cooling is the main determinant of dispersion of primary emissions. In Modena, the mixing height shows a wider seasonal variation compared to London. SODAR measurement of mixing height in central London by Spanton and Williams[19] demonstrated a median mixing height equal to or higher than 1000 m at 1400 GMT throughout the year, and recent Doppler LIDAR measurements[20] indicated a mean of daily maximum mixing height of 800–850 m in autumn. From CALMET simulation, the daily maximum mixing height in Modena has a median of ~850 m in November and February and of ~450 m in December and January. Over the period 2004–2010 the hourly scalar wind speed in Modena showed a median of 2.0 m s^{-1} and a 75th percentile of 2.8 m s^{-1}, while at London (Heathrow meteorological station) the wind had a median speed of 3.6 m s^{-1} and a 75th percentile of 5.1 m s^{-1}.

Table 2 Average concentration and temporal trend from GLS analysis; standard errors are shown in parentheses; only the ozone trend slope is null at a 95% confidence level

	Intercept (std. error)/μg m^{-3}	Slope (std. error)/ μg m^{-3} year^{-1}	% Change/% year
BTX	3.885 (0.107)	−0.429 (0.027)	−6.608 (0.412)
CO[a]	1.314 (0.043)	−0.073 (0.007)	−7.034 (0.826)
NO	48.404 (2.666)	−2.153 (0.368)	−4.277 (0.554)
NO_2	55.325 (1.688)	−0.5132 (0.221)	−1.259 (0.445)
O_3	29.848 (0.978)	−0.120 (0.191)	−0.239 (0.708)
PM_{10}	65.466 (4.525)	−2.879 (0.594)	−5.834 (1.544)

[a] Concentration units are in mg m^{-3}.

Because of its climatic conditions, in the Po valley concentrations of water-soluble carbonaceous material, deriving largely from road traffic emissions, are much elevated in winter relative to summer, and nighttime relative to daytime in Milan.[21] Concentrations of ammonium nitrate are also highly temperature sensitive[22] and these are also much greater in winter than summer.[21] These factors account for the seasonal variation in PM_{10} in Modena. In London, seasonal variations in temperature, and hence the changes in nitrate concentrations are less, and winter weather is often typified by high winds which tend to reduce primary pollutant concentrations.

Sub-monthly patterns

Diurnal patterns. During winter weekdays, diurnal patterns of BTX and traffic-related gaseous pollutants (*i.e.* NO, NO_2 and CO) show a pattern typical for urban areas (Fig. 4): the double peaked pattern observed in winter is due to traffic emissions during the rush hour periods, with the evening peak extended longer than the morning peak by nighttime atmospheric stability. The two peaks are divided by a minimum resulting from smaller traffic volumes and enhanced dispersion. The diurnal pattern on Sundays shows a single peak in the evening, with the same timing of weekdays, probably generated by a small increase in traffic and mostly poor dispersion conditions; morning concentrations are very different between weekdays and Sundays with BTX, CO and NO morning peak concentration up to 300% higher on weekdays than on Sundays. The ozone diurnal pattern in winter is similar between weekdays and Sundays, with the latter showing a higher peak probably due to the lower NO_x concentration on Sundays—the so-called weekend effect.[23] This kind of diurnal behaviour is similar to that reported for London.[18]

The summer diurnal pattern is highly influenced by the enhanced dispersion induced by the warm summer weather of the Po valley: combustion emission pollutants exhibit a main peak in the morning rush hour, earlier than in wintertime, and a secondary minor peak at night, mostly due to reduced dispersion. This differs from the pattern seen at more northerly latitudes in Europe. Ozone exhibits one single peak at 1600 due to photochemical pollution. All gaseous pollutants besides ozone show a lower concentration on summer Sundays than on summer weekdays; on summer Sundays there is no evidence of a higher ozone peak due to the reduced NO_x concentrations, differently from winter Sundays, although the ozone minimum in summer is higher than in winter, falling on Saturday night. This pattern and the fairly elevated concentrations are clearly indicative of a contribution of local primary pollutants to ozone formation, not so evident in London.[18]

Weekly patterns. The weekly pattern for mean daily PM_{10} concentrations at the Nonantolana (Modena) site (Fig. 5) shows a minor decrease on both winter and summer Sundays; winter PM_{10} concentrations exhibit also a wide standard deviation, which, contrary to mean concentration, does not show a weekly pattern. The small change between weekdays and weekend (*cf.* BTX, CO and NO in Fig. 4) reflects a pollutant with both primary and secondary sources.

The presence of weekly cycles has been tested for ozone and PM_{10} at the Nonantolana site: the former compound has been tested in order to statistically assess the presence of a weekend effect, the latter to estimate its relation to anthropogenic primary sources. Following Barmet *et al.*[24] and Bäumer and Vogel[25] the analysis of the weekly cycle involved the study of pollutant concentration anomalies. First, a time series of deviations from a running mean with a period of 31 days has been computed, in order to remove seasonality; this time series of deviations has been grouped by weekdays and for each group both mean and standard deviation have been calculated, resulting in a weekly cycle of anomalies. Finally the presence of a weekly cycle in the time series of anomalies has been checked with a Kruskal–Wallis (KW) test, which is robust against non-normally distributed data; KW is a nonparametric test with the null hypothesis that the median of the distribution of observation is the same in each day of the week. Results from the KW test show that only summer daily PM_{10} concentration and winter O_3 hourly concentration have a non-null weekly cycle, with p values of 10^{-5} and 0.07 respectively.

A comparison of the PM_{10} weekly pattern between the Nonantolana site and several urban background sites in the Po valley and in other European countries[26] has been performed (Fig. 6). The European sites have been chosen either because of their representativeness of densely inhabited cities with varying climates (*e.g.* Lisboa, London, Paris, Roma, Zürich), or because the sites have been involved in other detailed studies (*e.g.* London,[18] Torrelavega[1]), or to have data from towns with a population size similar to Modena, but under different climatic conditions (*e.g.* Augsburg and Malmö).

Site locations are presented in Fig. 1 and are listed in Table 3. For Po valley sites, the comparison has been performed over the period 2007–2009, in order to achieve the maximum homogeneity among measurement techniques. For European sites, the comparison involved the period 2002–2009. At all sites PM_{10} concentration is reported under the sampling conditions. Data from TEOM instruments at Po valley sites are provided as follows: the EPA equivalent TEOM output (*i.e.* with both 1.03 multiplicative and 3.0 μg m^{-3} built-in factors) is corrected with a further multiplicative monthly coefficient ranging from 1.35, in January, to 1.00, in July.[27]

All Po valley sites exhibit a strong seasonality, and a wide range in concentrations between sites. In order to capture also some of the variability within the Modena urban area, PM_{10} daily data from another urban background site in Modena have been included in the comparison (ID: MO02). This latter

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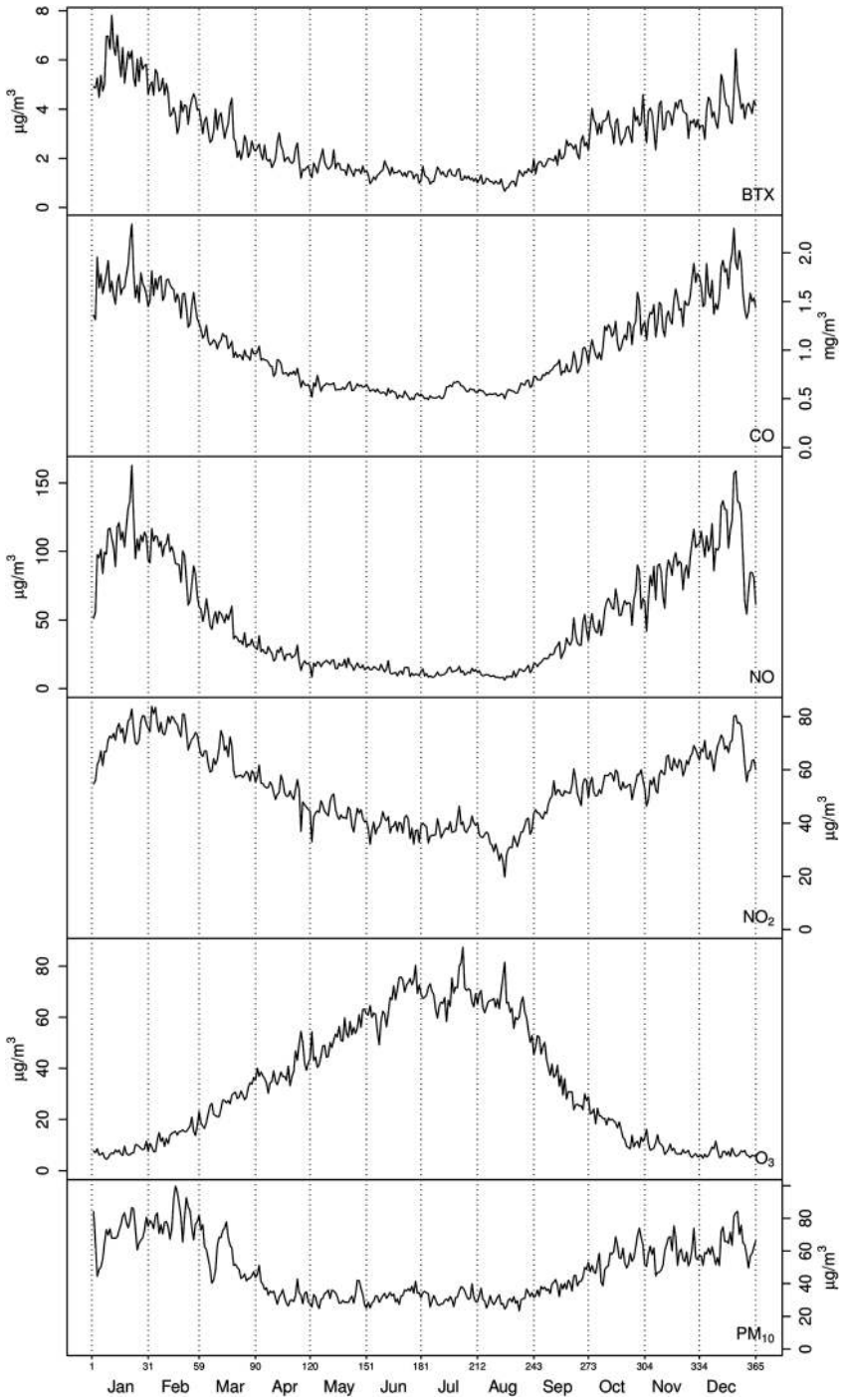

Fig. 3 Average daily time series of concentration for the air pollutants.

sampling station was activated in 2006, within the largest municipal park, and exhibits concentrations lower than the Nonantolana site. Differences between mean concentration among Po valley sites are highest in winter, whereas in summer mean concentrations are similar (Fig. 6). In winter-time, sites with a mean concentration higher than 50 µg m^{-3} show a weekly pattern exhibiting lower concentrations over the weekend, indicating an influence from anthropogenic sources.

If compared to other European urban background sites, MO01 and MO02 exhibit the highest seasonality and the highest winter concentration, similar to other Po valley sites in European comparison studies.[28–31] MO01 and MO02 show the greatest day-of-the-week variation among all sites during winter, although also CH0010A (Zürich) and PT03071 (Lisboa) show some weekly periodicity in winter. Similar to the analysis for the MO01 site, a KW test for a constant median over the week in the time series of the anomalies has been performed. For the pool of

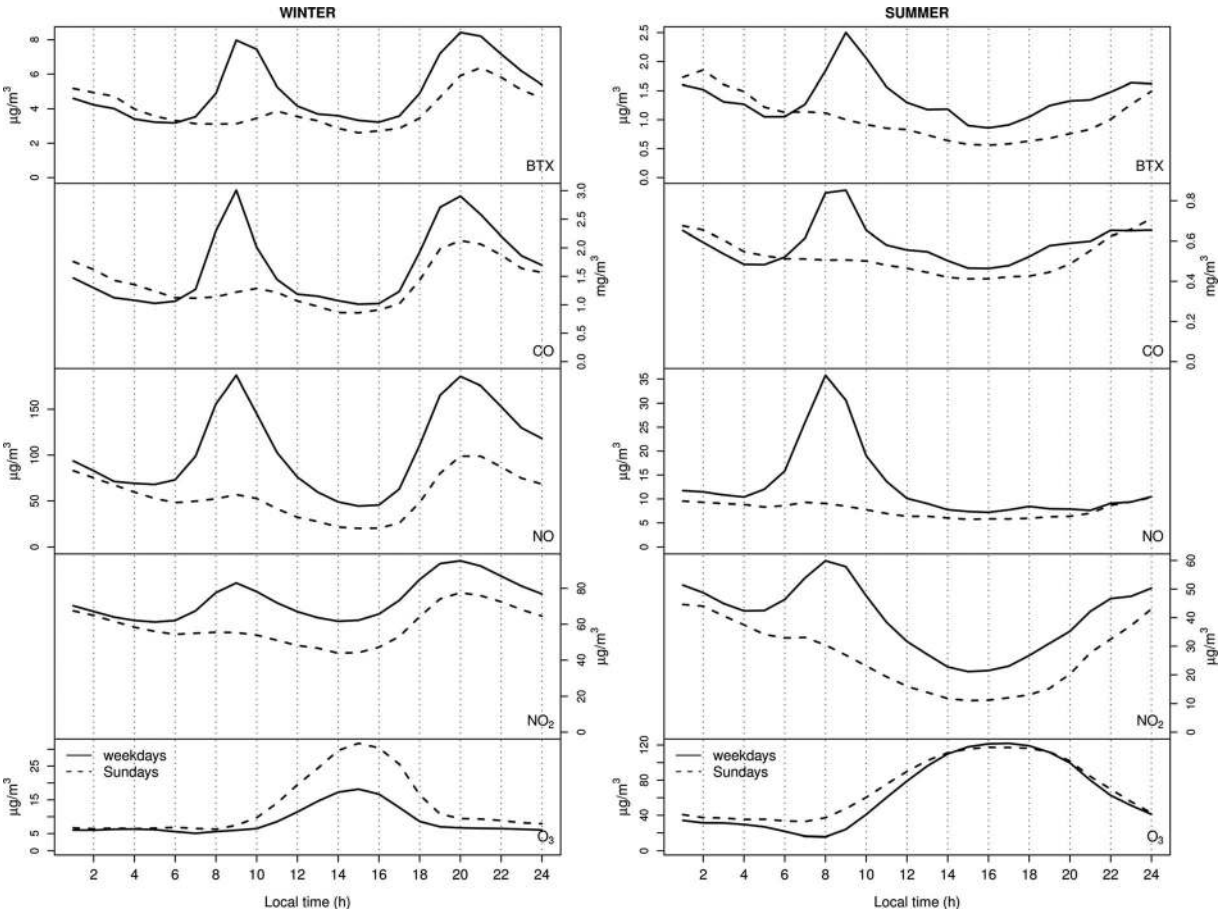

Fig. 4 Average diurnal pattern of mean hourly concentration.

European sites the KW test showed a significant difference in daily median concentrations in summer at almost all European sites associated with PM_{10} variation during the warmer season; in winter, the median was found to be constant at DEBY007, ES1038A, FR04004 and GB0992A sites. This is explicable by the greater relative contribution of primary anthropogenic sources in summer, whereas in winter secondary particles play a more major role: in winter atmospheric dispersion is generally reduced, particularly in the Po valley, and the relative contribution of secondary particulate matter to daily PM_{10} is higher than in summer (secondary particles may represent up to 30–50% of urban PM_{10} in the Po valley[8,21]), therefore weekly patterned variations in anthropogenic primary emissions are less likely to affect the PM_{10} median in wintertime.

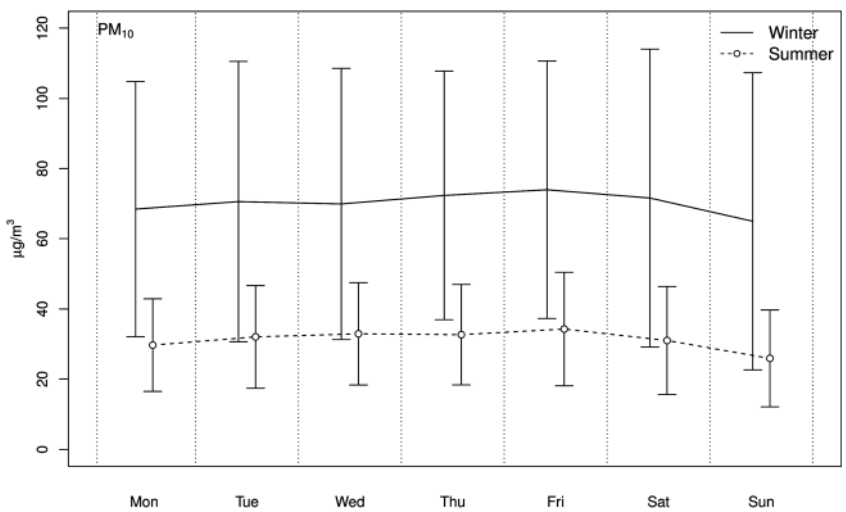

Fig. 5 Weekly pattern of mean daily concentration (PM_{10}) along with standard deviation.

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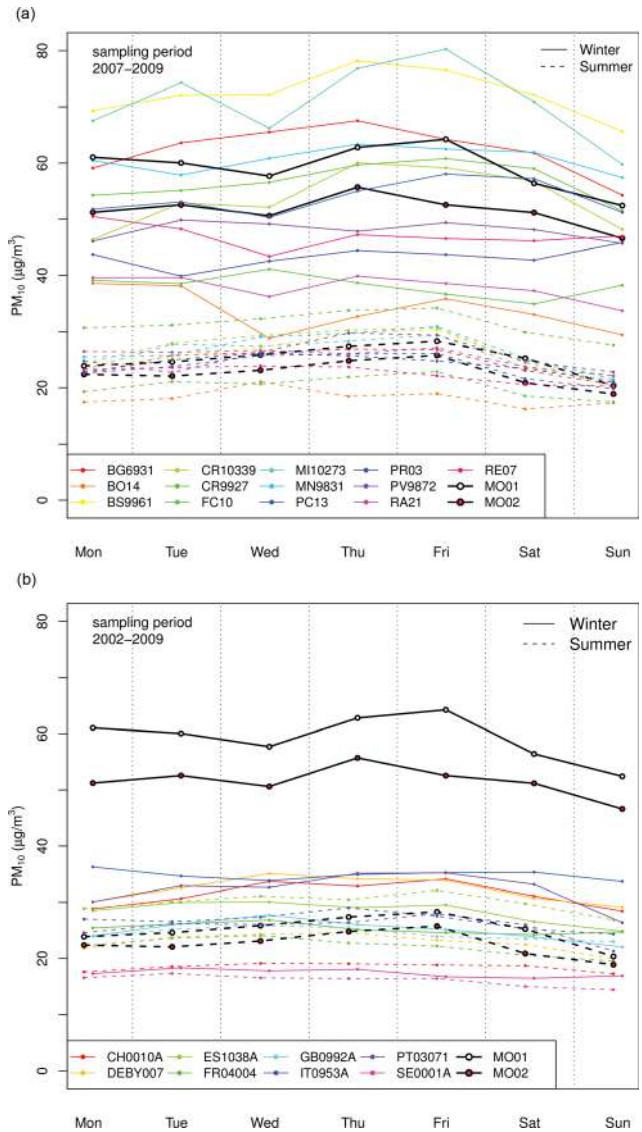

Fig. 6 Weekly pattern of mean daily concentration (PM_{10}) at urban background sites in the Po valley (a) and Europe (b) (a listing of the sites is presented in Table 3).

Table 3 Listing of the urban background sites and instrument type used in the comparison in Fig. 6

ID	Station name	Instrument type
Po valley		
BG6931	Bergamo	Beta gauge
BO14	Bologna	Beta gauge
BS9961	Brescia	Beta gauge
CR10339	Crema	TEOM
CR9927	Cremona	TEOM
FC10	Forlì	Beta gauge
MI10273	Milano	Beta gauge
MO01	Modena	Beta gauge
MO02	Modena	Beta gauge
MN9831	Mantova	Beta gauge
PC13	Piacenza	Beta gauge
PR03	Parma	Beta gauge
PV9872	Pavia	Beta gauge
RA21	Ravenna	Beta gauge
RE07	Reggio Emilia	Beta gauge
Europe		
CH0010A	Zürich (CH)	Gravimetric
DEBY007	Augsburg (D)	Beta gauge
ES1038A	Torrelavega (E)	Beta gauge
FR04004	Paris (F)	TEOM
IT0953A	Roma (I)	—
PT03071	Lisboa (P)	Beta gauge
SE0001A	Malmö (S)	TEOM
GB0992A	London (UK)	TEOM

Lagged correlations

Hourly data have been tested for autocorrelation (ACF) to check pollutant persistence both in winter and summer. In both seasons all species show positive correlation at 24 h lags, although in summer ACF decays quickly for photochemically active gases (O_3, NO, and NO_2) with null and negative correlation at 12 h lags for nitrogen oxides and ozone respectively. More stable species such as BTX and CO show a very slow decay in summer (Fig. S1†), consistent with their low concentration and their small peak-to-baseline ratio (1.3–1.4). The lower ACF for BTX and CO in summer than winter is due to less diurnal variation in summer as seen in Fig. 4. Since the magnitude of the traffic source varies little with season (although its temporal pattern may vary), this is likely to be mainly the result of differing meteorology. In the case of NO, the presence of strong morning and evening traffic-related peaks leads to an elevated ACF at both 12 and 24 hours in winter, while the better evening dispersion in summer or more extended traffic pattern leaves only the morning rush hour peak (Fig. 4) and hence a null ACF at 12 hours. Ozone shows a different diurnal pattern with an afternoon peak which is much stronger in summer than winter due to enhanced photochemistry. This leads to the strongly negative ACF seen at 12 hours for ozone in summer, but not winter (Fig. S1†). The wintertime diurnal profile of NO and O_3 is largely driven by an excess of NO causing suppression of O_3 for most of the 24 hours, while in summer, concentrations of NO_x are much reduced due to better dispersion and daytime ozone formation dominates the profile.

In order to test cross-variability of pollutants, the cross-correlation function (CCF) has been calculated for hourly concentration data of pollutant pairs, both in winter and summer (see Fig. 7). In winter BTX, CO, NO and NO_2 are positively cross-correlated at backward and forward 12 h interval lags (*i.e.* 12 h, 24 h, 36 h,…), with higher CCF values at ±24 h lags, particularly for the major primary traffic gaseous emissions, BTX, CO and NO (Fig. 7). Winter concentrations of nitric oxide and ozone are slightly anti-correlated at ±24 h and ±48 h lags; winter NO_2 and O_3 are anti-correlated at lag 0 (Fig. 7), and moderately correlated at negative lags and positive lags (−41 h, +30 h), indicating a similar diurnal cycle with a reciprocal delay of 6–7 hours. During summertime, BTX, CO, NO and NO_2 show a persistent positive cross-correlation, with peaks at 24 h interval lags, both backward and forward, due to their similar source and diurnal cycle (Fig. 7). Consistently, these latter pollutants show a similar cross-correlation pattern with O_3, with positive correlation at ±12 h and ±36 h lags and negative correlation at ±24 h and ±48 h lags (*i.e.* they have a similar diurnal cycle with a shift of 12 h, see Fig. 4).

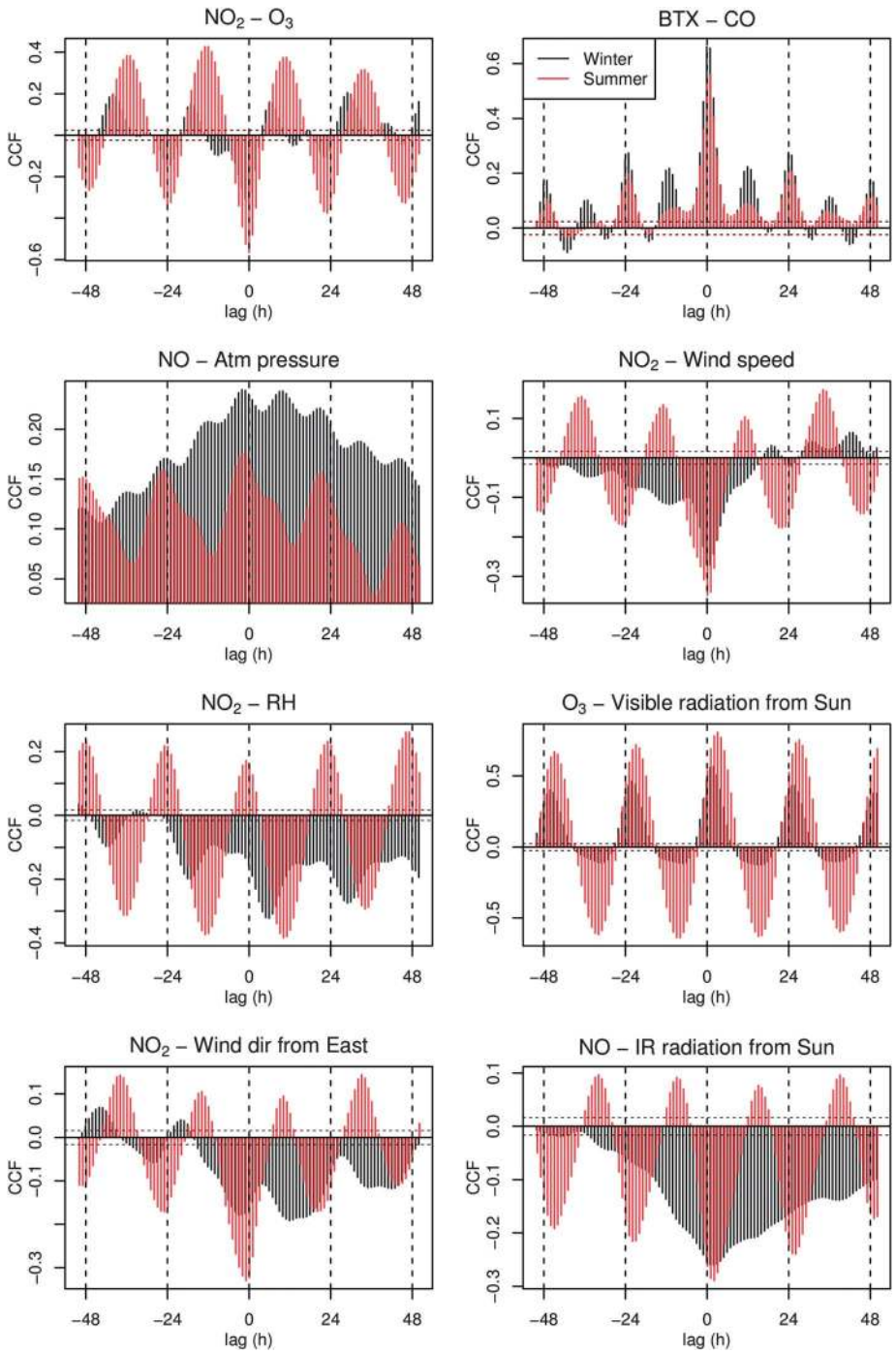

Fig. 7 Lagged correlation for mean hourly concentration and meteorological variables (black = winter, red = summer).

Finally cross-correlations of pollutant concentration and meteorological data give some insights into the meteorological influences upon pollutant removal and accumulation: highest positive or negative correlations are found with atmospheric pressure, radiation terms (both in the infrared and visible wavelength range), relative humidity, wind speed and wind direction. Atmospheric pressure shows a moderate positive correlation at all lags, both in summer and winter, with all pollutants besides CO and O_3 (Fig. 7). Taking atmospheric pressure as an index of regional atmospheric stability, this outcome indicates a moderate influence of atmospheric stability on air quality, confirmed by other studies in Modena[6,32] and elsewhere in Italy.[21] Consistently, infrared solar radiation, a good indicator of atmospheric dispersion, shows a moderate negative correlation with pollutant concentration in winter. Infrared and visible radiation in summer both from Sun and Earth, as well as infrared radiation from Earth in wintertime, have a strong diurnal cycle, therefore they negatively correlate with pollutant concentration at lag 0, ±24 and ±48 (Fig. S2†). Relative humidity is moderately anti-correlated with BTX, NO and NO_2

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Table 4 Estimated coefficients for orthogonal and linear regression models of daily mean PM_{10} (y-variable) upon daily mean NO_x concentration (x-variable) in Modena

	Orthogonal regression		Linear regression (±95% conf. int)	
Season	Intercept/μg m^{-3}	Slope/μg m^{-3} per μg m^{-3}	Intercept/μg m^{-3}	Slope/μg m^{-3} per μg m^{-3}
Spring	2.09	0.79	11.96 ± 2.62	0.58 ± 0.05
Summer	−4.05	1.23	17.67 ± 2.36	0.39 ± 0.08
Autumn	9.77	0.56	16.84 ± 3.06	0.45 ± 0.04
Winter	20.45	0.40	26.62 ± 3.90	0.34 ± 0.03

in winter, particularly at forward lags, *i.e.* the past level of relative humidity anti-correlates with successive pollutant concentration; this correlation pattern is driven by the diurnal pattern of atmospheric relative humidity, featuring a rise at night and a drop at midday, when mixing height is maximum. Wind speed shows a strong anti-correlation with all pollutants during winter, but mostly at lag 0 and at small negative lag numbers, indicating that the effect of pollutant removal by high winds stops few hours after wind ceases (Fig. 7). Similarly, during wintertime, easterly winds are negatively correlated with BTX, CO, NO and NO_2 at small negative lags, suggesting an efficient removal of pollutants by easterly winds at the monitoring site, where otherwise concentrations are dominated by traffic emission of nearby streets. Finally, in winter ozone shows a correlation pattern opposite to nitrogen oxides, *i.e.* a moderately positive correlation with wind speed, a quite low correlation with atmospheric pressure at positive lags and a positive correlation with easterly winds, suggesting that low NO_x conditions, *i.e.* strong winds eventually becoming easterly, lead to an increase in ozone (Fig. S2†); note that in the town of Modena winds blow almost exclusively along the East–West axis of the Po valley.

Relationship between PM_{10} and NO_x

The regression of PM_{10} on NO_x was suggested by Deacon *et al.*[33] as a means of distinguishing primary combustion-generated PM_{10} (associated with NO_x) from non-primary PM_{10} (represented by the intercept). Table 4 shows regressions estimated using both ordinary least squares and orthogonal regression. The latter should be less influenced by outlying points. The consistently higher intercept in winter than summer (Table 4) is reflective of a greater contribution of secondary particles, especially ammonium nitrate. The slope is not expected to vary appreciably with season, as seen in the linear regression, but surprisingly not the orthogonal regression data. The higher slope seen in the summer data analysed by orthogonal regression may reflect a correlation of secondary nitrate with precursor nitrogen dioxide, which is very probable in the highly reactive summer atmosphere of the Po valley.

Conclusions

The data from Modena show some strong similarities to other European sites, but also some appreciable contrasts with other locations such as London, North Kensington, analysed in an earlier paper,[18] and with other sites in Europe and the Po valley. Major similarities with London are seen in the general downward trend in primary, largely traffic-generated pollutants such as BTX, CO and the nitrogen oxides. In common with many other western European sites, concentrations of PM_{10} have shown only a very modest downward trend since 2000.[14]

The different features in the data relative to London, North Kensington, and other sites in Europe, arise from both meteorological and chemical factors. The different seasonal pattern of PM_{10} is striking and attributable to a greater difference in the dispersive capabilities of the atmosphere between winter and summer in Modena, and the Po valley in general, than London, and greater seasonality in ammonium nitrate concentrations attributable to the greater seasonal fluctuation in temperatures in Modena. The diurnal pattern in primary pollutants is similar in the two cities in the winter, but markedly different in summer due to far better dispersion of the afternoon rush hour emissions in summer in Modena, and possibly a different pattern of traffic. The third important difference lies in the behaviour of ozone. In London this appears to be dominated by the behaviour of nitrogen oxides; an increase in NO_x concentrations leads to a decrease in ozone and *vice versa*. The same behaviour appears to prevail in Modena in winter, but not in summer when local primary emissions contribute to ozone formation.

Appendix A: STL: a seasonal-trend decomposition procedure based on loess

"STL technique is a filtering procedure for decomposing a time-series into a trend, a seasonal and a remainder components",[10] respectively T_i, S_i and R_i, with $i = 1$ to N, according to the additive model:

$$Y_i = T_i + S_i + R_i \quad \text{(A1)}$$

STL performs multiple smoothing procedures *via* locally weighted regression (loess), a smoothing technique by Cleveland and Devlin,[35] through two nested loops: an "inner" loop and an "outer" loop. Given the periodicity of the time-series $n_{(p)}$ (*e.g.* $n_{(p)} = 12$ for monthly average observations), the STL algorithm performs $n_{(i)}$ passes through the inner loop, where each pass consists in a seasonal smoothing to update the seasonal component followed by a trend smoothing to update the trend component. Once completed the $n_{(i)}$ iteration of the inner loop, the outer loop is performed: in each pass of the outer loop N weights are computed from the residual series R_i then the inner loop is repeated with loess smoother using the previously computed weights. The outer loop consists of $n_{(o)}$ iterations. STL shows a few distinctive features, most notably: flexibility in specifying the variation in trend and seasonal components through the loess trend and seasonal smoothing window, the

ability of handling missing values in the series and robust trend and seasonal components that are not influenced by outliers. Cleveland *et al.*[10] provided a recommended value for most STL parameters according to the periodicity of the series $n_{(p)}$ and the smoothing parameter for the seasonal component $n_{(s)}$, which is one of the most critical parameter of the model. In this study $n_{(s)}$ has been set so that seasonal components are exactly periodical, *i.e.* are constant throughout the time series; in this study this seemed to be a reasonable approach given the length of the time series, and being the STL analysis used as a tool to estimate the trend component.

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