Status and trend of ground-level ozone at the CONECOFOR plots, 1996 - 2005

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Abstract – Ozone measurements are performed since 1996 at the Permanent Monitoring Plots (PMPs) of the National Integrated Programme for Forest Ecosystem Monitoring (CONECOFOR). Weekly ozone concentrations are determined by passive samplers during spring and summer months, over a time period of 10 yrs. We analyzed data collected over a time period of ten years. Ozone shows potentially phytotoxic concentrations especially at the plots located in the central and Southern regions. Although monitoring periods at the different plots are not homogeneous, statistically significant differences between yearly concentrations of subsequent years were observed, highlighting a considerable temporal variability of ozone pollution levels. Trend analysis performed on ten years data series points out an increase of ozone concentrations over the considered time period at seven plots, all located in central and Southern Italy. The same analysis performed on data collected during the vegetative period (April - September) at the different PMPs from 2001 to 2005 shows significant positive trends at 5 plots, three of them located in the Alpine region, and 2 in Southern Italy.

Key words: *Ozone, passive sampler, long-term monitoring, temporal trends.*

Riassunto – Stato e tendenza dell'ozono troposferico nelle aree CONECOFOR nel periodo 1996 - 2005. Dal 1996 vengono effettuate misurazioni di ozono presso le aree permanenti del programma nazionale integrato di monitoraggio delle foreste (CONECOFOR). Le concentrazioni medie settimanali sono misurate mediante dosimetri passivi durante i mesi primaverili ed estivi. L'ozono mostra concentrazioni potenzialmente fitotossiche, specialmente nelle aree del centro e sud Italia. Sebbene i periodi di misura siano diversi tra le aree, ci sono differenze statisticamente significative tra i diversi anni che evidenziano notevoli variazioni temporali. Le tendenze temporali su 10 anni hanno mostrato un aumento delle concentrazioni medie da Giugno a Settembre in sette aree al centro e sud Italia. Nel periodo 2000-2005, un'aumento significativo è stato evidenziato in cinque aree, di cui tre localizzate nella Regione alpina e due nel sud Italia.

Parole chiave: *ozono, campionatori passivi, monitoraggio a lungo termine, tendenze temporali.*

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Introduction

Ozone (O_3) in the lower troposphere forms through a photochemical reaction between different compounds generally divided into two groups, namely nitrogen oxides (NO_x=NO+NO_2), mostly emitted by human activities, and volatile organic components (VOC) of human and biogenic origin. High O_3 concentrations during the vegetative period can cause negative impacts on vegetation, resulting in yield losses in agriculture and damage to forest species (Fuhrer *et al.* 1997).

Tropospheric O_3 was first measured in ambient air in the second half of the XIXth century. At Moncalieri, Italy, O_3 levels were measured on a daily basis by the Schönbein technique (a colorimetric method) for twenty years showing an average concentration of 10 ppb (Anfossi *et al.* 1991). Similar studies were carried out in Paris, France, from 1876 to 1910 with comparable results (Volz and Kley 1988). Between 1899 and 1900 measurements were performed in Zagreb (Croatia) during day and night time and in this area higher mean concentrations (30 ppb) than in France are reported by Lisac and Grubisic (1991). Measurements at high elevation (Pic du Midi, France, 3000 m a.s.l.) showed, at the end of the last century, mean concentrations of about 10 ppb (Marenco *et al.* 1994). Although there are some uncertainties about the Schönbein technique and on possible interferences (Pavelin *et al.* 1999), the reported figures highlight a relevant increase of O_3 concentrations in the past century. Analysis of historical O_3 records indicated

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that tropospheric O_3 levels, in both hemispheres, have increased by a factor of 3-4 during that time (Sandroni *et al.* 1992; Sandroni and Anfossi 1994).

More recently tropospheric O_3 was found to increase in the northern hemisphere. Mean O_3 concentrations raised, for example, by a factor of two between the end of the 50's and 1990 at the Swiss site Arosa (Staehelin *et al.* 1998). Although reliable surface O_3 measurements are available since the late 1980's at a number of sites, studies on O_3 trends are complex due to large inter-annual variations in O_3 levels related to the influence of meteorological conditions, making it difficult to identify significant trends (Jonson *et al.* 2005).

Roemer (2001) reports that the average O_3 concentrations in Finland over the period 1989 – 2001 are stable or slightly increasing. In UK gradual increase in background O_3 values are reported, even if the pollutant's precursors emissions (NO_x and VOC) have been reduced successfully over the past 10 years (Monks *et al.* 2003). Also Coyle *et al.* (2000) showed an overall picture of an increasing background concentration in the UK and decreasing concentrations during photochemical episodes, although only a few of the considered sites had statistically significant temporal trends. According to the UK National Expert Group on Transboundary Air Pollution (NEGTAP, 2001), there is an evidence that the mean ground-level concentration over the UK is increasing and is expected to continue over the coming decades, despite the peak concentrations decreased by about 30% since the 1980's. Some rural Belgium and German EMEP sites showed a concentrations increase over the period 1990-2002, whereas measurements at the same network sites in the Netherlands displayed opposite trends (Derwent 2006). Results from more than 300 German O_3 sites between 1990 and 2000 including urban locations, showed a pronounced downward trend of the higher percentiles while upward trend was indicated for low and medium percentiles (Beilke and Wallasch 2000). Sicard *et al.* (2006) investigated O_3 background concentrations in France from 1995 to 2003, reporting increasing trends for annual, winter and autumn concentrations. Other overviews of reported trends are given in Derwent *et al.* (2003) and TOR-2 (2003).

Since the late 1980's the emissions of O_3 precursors, NO_x, CO and VOC, were substantially reduced in most parts of Europe (Vestreng *et al.* 2004) as a result of international agreements (*e.g.* CLRTAP Convention) and of a stricter EU legislation about national measures. The emission reduction resulted in a corresponding decrease of the O_3 precursor species concentrations (Derwent *et al.* 2003). The expected effects are that O3 levels in the summer months would consequently reduced and O_3 thresholds, for the human health and environment protection, would be less frequently violated. At many monitoring sites, however, O_3 ambient concentrations increased during all seasons, but particularly in winter and spring. At mountain tops (1000–3000 m) in Europe this pollutant levels continuously raised since the first measurements were made in 1870 and are still increasing (Marenco *et al.* 1994; Jonson *et al.* 2005; Scheel *et al.* 2002). A comprehensive evaluation of long-term measurements over Europe is provided by the European Environmental Agency (Beck *et al.* 1998).

Scarce information is available for South European countries. Actually, trend analysis of O_3 measurements are mainly restricted to Northern and Western parts of Europe where routine measurement of O_3 first started, yielding time series long enough for this kind of analysis. In Italy a limited number of background and rural monitoring stations are available, few of them in Central and Southern regions. Additional information is provided for forest areas by the Italian Intensive Forest Monitoring Programme (CONECOFOR) co-ordinated by the Italian National Forest Service (Petriccione and Pompei 2002).

The CONECOFOR Programme covers at the moment (2006) 31 Permanent Monitoring Plots (PMP) located at forest sites. At each plot O_3 concentrations are measured from April to September by passive samplers. These devices are particular suited for measurements at remote sites as they can be easily handled, transported and are not dependent from electric supply. The low time resolution of data, however, greatly limits their use to analyse O_3 trends.

Data recording began in 1996 and 5 to 10 years data series are available for most of the plots. This paper gives a general description of the research activities carried out in this time period to assess O_3 concentration levels, and reports the calculated trend of O_3 concentrations over the same period.

Materials and methods

Measurement devices

Weekly O_3 concentrations were measured at the

Permanent Monitoring Plots (PMPs) of the Italian intensive forest monitoring programme (CONECOFOR) by means of passive (diffusion) samplers. From 1996 to 2000 passive samplers, developed by the Institute for Bioclimatology and Environmental Research of the University of Munich, were used to measure O_3 concentrations (Method 1). The sampling founds on the principle of gas molecules passive diffusion to an absorbing medium, in this case indigo blue dye. Cellulose filters coated with indigo blue were placed in 70 cm tubes which represent the diffusion path. The indigo molecule contains 1 carbon double bond (C = C) that reacts with O_3 and results in nearly colourless reaction products. The determinations were done by spectrophotometry, at 250 and 600 nm. A detailed description of these samplers and the related analytical procedure are reported in Werner (1991 and 1992), and Werner *et al.* (1999).

Since 2001 passive samplers were provided by the Swiss company Passam AG (Method 2). As recommended, the exposition period was set to 7 days. The tubes were protected from sunlight, rain and wind disturbances by an opaque cylindrical shelter. The passive samplers consist of 4.9 cm long calibrated tubes with an inside diameter of 0.9 cm, inside which air diffuses by molecular diffusion. The chemical compound, which reacts with O_3 is 1,2-di (4-pyridyl) ethylene (DPE) solution, deposited in the sampler on a fibreglass filter supported by a grid. The other end is left open to permit air diffusion. Addition of MBTH reactant produces a coloured complex, which is measured in a spectrophotometer at 442 nm. The reaction is specific to O_3, although interferences due to the presence of other oxidants may occur. The diffusion coefficient for O_3 is unknown and the reaction of O_3 with DPE is not stoichiometric. The samplers were therefore calibrated by the manufacturer on the basis of long term parallel measurements with co-located O_3 automatic analyser.

The two methods were subjected to parallel measurements in previous studies (Hangartner *et al.* 1996; Werner *et al.* 1999). The samplers adopted since 2001 were tested for precision and accuracy (Bernard *et al.* 1999). Recent tests (Gerboles *et al.* 2006) have shown that these samplers (Method 2) are in good agreement with the reference methods of the European Directive (EEC, 2002) and fulfil the 30% accuracy requirement for O_3 monitoring. Accuracy was checked also during this study by comparing passive samplers measurements with co-located O_3 continuous analyser (Buffoni and Tita 2003). Regression analysis and two samples comparison tests were applied to the different datasets. Results of additional parallel measurements carried out at the EMEP monitoring stations located at the JRC (Ispra Italy) in 2004 and 2005 show a good agreement but display a rather constant overestimate (Table 1), although within the mentioned accuracy requirements.

Table 1 - Results of the regression analysis performed on passive sampler data and a co-located continuous analyser (JRC, Ispra).
Risultati dell'analisi di regressione svolta sui dati del campionatore passivo e di un analizzatore automatico situati nel medesimo sito (JRC, Ispra).

	n	R^2	Slope	Intercept (ppb)
2004	24	0.74	0.85	8.44
2005	25	0.75	0.92	10.18

Measurement periods and location

O_3 measurements started as an experimental activity which covered only a part the vegetative period (June-September) until 2000. Since 2001 O_3 monitoring became a more regular activity, parallel to the mandatory studies requested by the EU Regulation 1091/94. Thus, from 2001 to 2005 sampling activity has a duration of 26 weeks, from the beginning of April until the end of September, each year.

The geographical location of PMPs and a detailed description of their characteristics are given in Allavena *et al.* (2000). O_3 measurements were first performed at 20 PMPs (1996 - 2000). Following the establishment of new PMPs the number of O_3 measurement sites grew consequently to 31 in 2005 (Table 2). O_3 measurements were performed generally close to the forest plots at 2-3 m from the ground and within a maximum distance of 1.5 km from PMPs. A number of requirements, fulfilled by most of the PMPs, were set for O_3 measurements (Buffoni and Tita 2003). Air pollutant measurements have to be carried out at sites with free circulating air and without relevant obstacles which may influence ambient air characteristics. Measurement devices are generally placed in clearings near the forest plots (PMPs). A location close to the PMPs is preferred to perform investigations about ecosystem-atmosphere interactions but this is not always possible, especially for wide and closed forest stands without suitable clearings. Dif-

Table 2 - Periods covered by O3 measurements at the CONECOFORPMPs over the years 1996 – 2005.
Periodi coperti dalle misurazioni di O3 alle PMP di CONECOFOR dal 1996 al 2005.

Year	n. of PMPs	Begin	End	Weeks n.
1996	19	15/6	1/10	15
1997	20	17/6	7/10	16
1998	20	16/6	6/10	16
1999	20	18/5	5/10	20
2000	21	4/5	3/10	22
2001	25	3/4	2/10	26
2002	25	9/4	1/10	26
2003	26	1/4	30/9	26
2004	26	30/3	5/10	26
2005	31	5/4	4/10	26

ferences in exposition and elevation (positive and negative) between O_3 monitoring sites and the related PMPs are generally small. At few sites measurements are carried out above the tree canopies (LAZ2, TOS2, SIC1; TOS1 since 2005)

Morever, long-term studies should be performed at the same site avoiding changes in location or measurement height during the monitoring period. Unfortunately, for different reasons, some monitoring sites initially located close to the CONECOFOR plots have been moved during the 10 years considered. The main displacement took place at the PMP ABR1, where O_3 measurements were initially carried out close to the plot. Since 2001 instruments were moved to another more open and elevated location. In addition, the new measurement site presents stronger winds which may overpass the indicated threshold to avoid disturbances to the passive diffusion process, on which the O_3 measurements are based. Consequently, the two 5-year periods (1996-2000 and 2001-2005) are considered separately and the corresponding measurement sites are indicated as ABR1a and ABR1b. At the PMP CAL1 and CAM1 measurement sites moved from a non ideal position for O_3 monitoring to a new one. Finally, the samplers exposed at the PMP TOS1, previously placed at ground level at short distance from the plot, were lifted in 2005 above the canopies by means of an aluminium tower. At present, the effects of the mentioned changes cannot be fully evaluated.

Data quality

Several measures were taken to provide high quality data. Passive samplers were monthly sent to the local operators to keep the time period between the preparation and the analysis to a minimum. As O_3 diffusion tubes (Method 2) are known to degrade over time they were kept refrigerated before and after exposure and care was taken during transport from and to the laboratory (blanks were used to check the possible transport influence). Manuals with detailed instructions were provided to local operators.

While the 7-days exposition period, set in 1996, was maintained over time, the number of replications varied from 5 (1996) to 1 (1998-2000). Since 2001 two samplers were exposed in parallel every week according to the suggestions of UN-ECE/ICP Forests regarding monitoring of air quality (UN-ECE 2000).

Statistical methods

Comparison between years

As the majority of the annual data series present a non-normal distribution, they were log (base 10) transformed. The distance from the normal distribution of the transformed data were analysed, year by year and plot by plot, by means of the skewness and kurtosis tests. According to data distribution, the parametric *T* test (Welch 1947) or the non-parametric *U* test (Mann and Whitney 1947) have been adopted.

The arithmetic means (x) and the variance (σ^2) have been calculated for each year and plot, to determine if the differences between subsequent years, for each PMP, are significantly different from 0. As the pooled variances for the different data groups are different, the *T* test, a variant of the *t* test, was applied:

$$T = \frac{\left|\bar{x}_1 - \bar{x}_2\right|}{\sqrt{\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}}} \qquad \text{[eq. 1]}$$

where n_n are the data available for each year and plot. This ratio does not follow the t distribution, but can be approximated to it, by means of freedom degrees calculation.

For non-normal distribution of data, significance of the differences between means has been verified by the *U* test. All the observations were arranged into a single ranked series and the number of precedences were summed. U_{x_n} is the smallest number of precedences:

$$U = \sum_{x=n}^{x=1} U_{x_1}, U_{x_2} \ldots U_{x_n} \qquad \text{[eq. 2]}$$

U was than transformed to *Z*, because of high repetitions number:

$$Z = \frac{U - \frac{n_1 \cdot n_2}{2}}{\sqrt{\frac{n_1 \cdot n_2 \cdot (n_1 + n_2 + 1)}{12}}} \quad \text{[eq. 3]}$$

Z can be thus compared with the tabulated values of the normal distribution, to verify the difference significance.

Trend analysis

Considering the prevailing non-normal distribution of the data, two statistical analyses were performed: the first, the Mann-Kendall test, analyses the presence of a monotonic increasing or decreasing trend, the second, the non-parametric Sen's method (Sen 1968), estimates the magnitude of the trend. The two approaches are proposed within the procedure "MAKESENS" (Salmi *et al.* 2002), which has been developed by the Finnish Meteorological Institute within an EMEP project (the European Environmental Monitoring Programme of the United Nations), to easily detect and estimate the temporal trends in air pollution time series. The model has been implemented using the O_3 annual median levels (in ppb) measured at the PMPs with a data capture greater than 75%, with a minimum of four yearly medians. The Mann-Kendall test is suitable for time series which may be assumed to be monotonic; the Sen's method deals with the estimate of the slope of the observed trend (Gilbert 1987).

The Mann-Kendall test is applicable to time series which fit the linear model:

$$x_1 = f(t) + \varepsilon_1 \quad \text{[eq. 4]}$$

where $f(t)$ is a continuous monotonic increasing or decreasing function of time. This test is based on two statistics, the so called S and the normal approximation (Z statistics).

The Mann-Kendall statistic S is calculated according to:

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^{n} \mathrm{sgn}(x_i - x_k) \quad \text{[eq. 5]}$$

where x_j and x_k are the annual values in years j and k, with $j > k$.

If the data available are nine or less, the absolute value of S is compared directly to the theoretical distribution of S, derived from Mann and Kendall (Gilbert 1987), using the two-tailed test for two significance levels (0.05 and 0.01). If the absolute value of S equals or exceeds the tabulated value at certain probability, means that the presence of a monotonic upward or downward trend, according to the S sign, is respectively probable or very probable.

The variance of S is computed as follows:

$$VAR(S) = \frac{1}{18}\left[n(n-1)(2n+5) - \sum_{p=1}^{q} t_p (t_p - 1)(2t_p + 5)\right]$$

Where q is the number of tied groups and t_p is the number of data values in the p^{th} group. The tested significance levels α are 0.05 and 0.01.

If the data available are equal ten or more the value of the normal approximation Z is used, to assess the presence of a statistically significant trend. However, if there are several tied values (*i.e.* equal values) in the time series, it may reduce the validity of the normal approximation when the number of data values is close to 10.

The values of S and VAR(S) are exploited to calculate Z:

$$Z = \begin{cases} \dfrac{S-1}{\sqrt{VAR(S)}} \ldots if \ldots S > 0 \\ 0 \ldots\ldots\ldots\ldots if \ldots S = 0 \\ \dfrac{S+1}{\sqrt{VAR(S)}} \ldots if \ldots S < 0 \end{cases} \quad \text{[eq. 7]}$$

A positive (negative) value of Z indicates an upward (downward) trend. To test for either an upward or downward monotone trend (*i.e.* a two-tailed test) at α level of significance, the Z value is compared with tabulate values obtained from the standard normal cumulative distribution tables. The tested significance levels α, as for S, are 0.05 and 0.01.

To assess the true slope of an existing tendency (as change per year) the Sen's non-parametric method could be used. This method can be utilized when the trend can be assumed as linear. This means that $f(t)$ in equation 4 equate to:

$$f(t) = Qt + B \quad \text{[eq. 8]}$$

where Q is the slope and B is the intercept. A 100 (1-α) two-sides confidence interval about the slope estimate is obtained by non-parametric technique based on the normal distribution. The method is valid for n as small as 10 unless there are many ties. The procedure in MAKESENS computes the confidence interval at two

different confidence levels (0.01 and 0.05), resulting in two different confidence intervals. To get the slope estimate Q in equation 8 the slopes of all data pairs were first computed:

$$Q_i = \frac{x_i - x_k}{j - k} \qquad \text{[eq. 9]}$$

The Sen's estimator of the slope is the median of the n values of Q_i. To obtain an estimate of the intercept B in equation 8 the n values of differences $x_i - Q_{ti}$ are calculated. The median of these values gives the estimate of B (Sirois 1998). The estimates for the lines constant B at 99 and 95% confidence intervals are calculated by a similar procedure of the slope one.

Results and discussion

More than 10,000 measurements were carried out from 1996 to 2005. Descriptive parameters of the data collected are given in Table 3 (1996-2000) and Table 4 (2001-2005). Data capture is generally high. For plots with data capture lower than 75%, measurements of

Plot	1996 D.c.	1996 Median	1996 C.V.	1996 Max	1996 Min	1997 D.c.	1997 Median	1997 C.V.	1997 Max	1997 Min	1998 D.c.	1998 Median	1998 C.V.	1998 Max	1998 Min
	%	ppb	%	ppb	ppb	%	ppb	%	ppb	ppb	%	ppb	%	ppb	ppb
ABR1a	100	35.6	22	48.5	22.6	100	43.9	7	49.7	40.0	100	41.8	11	54.3	34.5
BAS1	94	34.1	16	41.7	21.5	75	53.6	13	65.8	42.8	81	35.8	15	42.7	21.8
CAL1	94	27.7	22	40.9	20.4	100	43.6	11	52.1	35.8	100	33.0	15	44.1	27.4
CAM1	94	38.1	25	49.7	12.5	38	55.5	25	83.6	46.4	81	36.9	9	44.6	33.8
EMI1	100	33.6	20	41.6	18.1	100	48.7	15	57.0	30.8	100	39.6	14	46.8	27.3
EMI2	100	36.3	17	42.9	19.8	81	55.1	25	92.2	34.8	94	40.7	31	66.1	0.0
FRI1	94	29.4	18	40.3	17.6	100	37.9	14	42.6	25.8	100	39.0	16	47.8	30.0
FRI2	88	28.8	28	44.3	12.0	100	39.4	16	62.9	37.2	13	33.4	1	33.7	33.1
LAZ1	100	35.7	13	44.6	25.2	100	50.5	7	56.7	43.4	100	43.2	8	50.0	37.1
LOM1						100	36.7	16	49.8	27.1	100	34.5	10	40.7	27.7
MAR1	82	38.2	17	46.8	25.2	100	53.5	11	63.6	42.9	100	39.4	10	45.3	32.0
PIE1	94	34.4	17	44.7	20.1	100	44.4	11	49.4	33.2	69	34.6	5	37.4	31.2
PUG1	94	36.2	26	45.4	14.9	94	56.4	14	73.1	43.0	100	45.6	13	57.2	36.1
SIC1	100	43.6	15	52.4	33.2	100	59.6	20	87.1	38.7	100	43.8	18	66.7	37.6
SAR1	94	36.9	14	43.9	25.3	100	42.9	10	50.4	36.0	100	36.2	11	39.5	27.2
TOS1	100	32.6	14	40.2	23.5	100	40.5	12	48.2	31.4	100	37.5	10	43.5	29.2
TRE1	100	34.1	18	43.8	20.1	100	49.1	10	58.2	41.3	100	41.2	11	48.2	34.5
UMB1	100	32.2	17	44.1	21.4	100	45.0	13	55.8	39.2	100	34.0	7	38.3	27.1
VAL1	100	33.6	15	44.0	24.3	100	42.6	18	59.6	35.6	100	39.6	19	62.2	32.2
VEN1	94	32.9	12	42.3	25.6	100	39.1	9	46.0	31.0	94	34.4	16	51.7	30.4
LIG1															

Plot	1999 D.c.	1999 Median	1999 C.V.	1999 Max	1999 Min	2000 D.c.	2000 Median	2000 C.V.	2000 Max	2000 Min
	%	ppb	%	ppb	ppb	%	ppb	%	ppb	ppb
ABR1a	91	43.4	13.18	60.0	35.0	91	44.7	14	59.2	37.5
BAS1	95	42.6	6.64	48.2	37.7	95	53.1	17	73.8	39.0
CAL1	100	40.5	10.61	48.6	27.1	100	45.7	8	54.6	38.0
CAM1	100	47.5	12.93	70.8	41.8	100	47.7	20	69.3	34.2
EMI1	95	41.2	12.17	48.7	29.3	95	47.9	17	64.0	35.7
EMI2	77	46.1	12.36	57.5	39.1	95	42.8	12	51.1	34.0
FRI1	100	44.4	12.21	58.7	38.0	100	40.5	11	48.7	31.3
FRI2	100	43.7	11.24	55.6	38.4	100	40.6	12	51.2	32.5
LAZ1	100	46.1	8.31	51.9	38.9	91	44.5	15	62.4	31.9
LOM1	100	37.4	9.09	44.5	32.0	100	38.0	12	44.3	26.6
MAR1	100	51.9	9.80	64.4	43.0	100	50.9	9	57.4	40.2
PIE1	100	47.9	12.43	56.2	37.3	95	42.9	12	50.6	30.4
PUG1	100	47.4	10.32	60.5	42.8	100	48.5	13	59.7	37.9
SIC1	100	50.1	23.11	71.7	32.3	100	61.2	28	89.4	27.1
SAR1	100	47.3	9.44	58.6	42.8	100	46.4	15	68.5	35.2
TOS1	100	46.0	9.96	55.0	36.3	100	43.3	13	53.1	31.9
TRE1	100	45.7	10.36	56.8	38.5	100	43.7	13	51.7	23.6
UMB1	100	47.4	10.39	57.0	36.9	95	43.5	11	55.8	37.7
VAL1	91	43.7	18.47	67.6	38.0	91	40.5	9	47.2	33.6
VEN1	100	42.7	10.34	52.0	36.5	100	43.3	4	47.1	39.8
LIG1						95	53.4	13	68.6	44.2

Table 3 - Data capture (D.c.), median monthly concentrations (median) over the monitoring period, coefficient of variation (C.V.), maximum and minimum monthly concentrations (Max, Min) at the CONECOFOR PMPs data over the years 1996–2000.
Completezza dati (D.c.), mediana mensile delle concentrazioni (median) nel periodo di monitoraggio, coefficiente di variazione (C.V.), concentrazioni massime e minime (Max, Min) nelle aree CONECOFOR dal 1996 al 2000.

the corresponding year were excluded from further statistical analysis.

Median concentrations, weekly maximum and minimum recorded over the monitoring periods, vary substantially from year to year. The lowest weekly medians were recorded in 1996, the maxima, depending from the plot, between 2003 and 2005.

As measurement locations are located in a wide range of latitudes and elevations, PMPs display different climatic conditions and meteorological trend

	2001					2002					2003				
Plot	D.c. %	Median ppb	C.V. %	Max ppb	Min ppb	D.c. %	Median ppb	C.V. %	Max ppb	Min ppb	D.c. %	Median ppb	C.V. %	Max ppb	Min ppb
ABR1b	96	70.0	20	96.9	45.4	85	68.2	15	89.0	47.3	77	81.6	16	94.4	46.1
BAS1	88	56.8	26	105.6	35.4	88	60.7	16	76.6	40.0	96	57.8	17	77.6	41.2
CAL1	100	51.7	13	67.7	40.6	96	53.2	15	67.8	39.5	100	58.5	16	68.4	33.3
CAM1	100	61.8	13	80.8	48.6	96	60.8	12	72.9	42.5	92	66.9	15	91.7	56.2
EMI1	96	46.7	14	62.3	36.0	88	46.8	11	56.4	31.9	100	44.5	32	84.3	27.3
EMI2	35	37.0	20	47.8	29.1	92	50.8	12	61.0	35.0	100	54.7	16	73.2	40.4
FRI1	96	39.6	18	49.5	27.0	96	39.4	17	55.5	26.5	100	41.0	19	54.5	27.7
FRI2	92	41.4	14	52.0	26.5	92	45.8	15	55.8	34.3	100	45.6	24	82.5	28.1
LAZ1	96	50.7	12	66.1	35.4	96	55.6	12	72.3	46.1	96	49.6	24	65.9	19.5
LOM1	100	37.2	20	49.5	16.9	96	40.1	19	50.6	26.9	100	40.4	20	59.1	29.8
MAR1	96	51.4	15	68.9	37.4	96	52.6	11	61.2	40.1	96	54.5	22	83.5	34.0
PIE1	100	51.3	14	61.7	35.5	92	52.2	13	69.2	43.2	100	68.8	13	84.0	53.5
PUG1	96	51.1	10	60.1	38.7	85	51.4	8	57.3	41.9	100	50.2	18	68.9	31.4
SIC1	92	60.2	30	86.9	18.8	96	52.9	20	77.2	32.9					
SAR1	100	56.7	20	87.7	41.1	100	53.2	12	66.7	40.3	88	54.8	19	76.7	26.4
TOS1	96	38.1	19	54.5	25.0	100	37.6	16	54.7	30.2	92	47.3	14	69.2	36.1
TRE1	96	50.5	24	94.2	32.5	92	55.0	14	69.0	43.6	96	61.9	14	77.0	42.8
UMB1	96	45.5	13	61.5	25.6	96	49.4	9	58.7	42.0	100	53.7	16	69.3	37.0
VAL1	96	45.6	13	56.0	30.2	100	47.8	21	71.7	29.5	73	64.5	14	81.4	47.7
VEN1	96	38.1	20	52.6	19.5	96	45.7	12	54.8	30.8	92	50.1	21	89.0	32.9
LIG1	100	43.0	18	56.7	27.8	100	46.1	16	58.2	30.3					
ABR2											65	49.3	18	62.5	36.6
LOM2	100	54.8	28	85.5	36.0	100	46.1	18	68.6	32.3	100	50.3	21	74.7	31.0
LOM3	100	52.0	27	92.8	40.3	96	69.7	16	88.0	36.9	100	74.8	18	100.6	50.6
TOS2	100	49.7	23	83.9	38.4	92	52.0	12	60.4	39.9	100	46.6	26	68.1	25.5
TOS3	96	48.0	18	64.9	30.5	77	52.8	10	61.9	43.6	100	58.6	16	72.4	37.8
BOL1	88	50.0	15	63.3	32.2	100	60.0	14	77.9	44.2	88	66.1	15	80.0	48.2
LIG1	100	43.0	18	56.7	27.8	100	46.1	16	58.2	30.3					

	2004					2005				
Plot	D.c. %	Median ppb	C.V. %	Max ppb	Min ppb	D.c. %	Median Ppb	C.V. %	Max ppb	Min ppb
ABR1b	96	82.5	11	95.0	62.8	92	97.3	35	141.5	69.3
BAS1	96	61.0	9	71.7	48.6	96	66.3	23	81.1	47.0
CAL1	85	60.1	11	79.0	52.2	62	60.6	39	70.7	33.8
CAM1	93	79.9	21	122.7	51.4	92	87.7	35	127.5	49.1
EMI1	89	46.0	13	59.4	38.3	96	50.5	26	63.4	34.7
EMI2	100	57.3	11	68.0	46.3	96	58.2	34	69.2	29.5
FRI1	85	40.4	18	53.8	28.9	100	46.8	45	60.3	22.9
FRI2	96	45.1	15	52.0	28.0	100	46.2	51	70.2	19.3
LAZ1	100	54.3	13	72.7	40.5	85	61.6	33	83.5	40.4
LOM1	96	42.4	20	60.1	20.0	100	49.3	40	64.7	27.0
MAR1	96	57.1	10	68.2	46.9	100	61.5	28	76.9	36.2
PIE1	93	60.5	14	78.1	45.7	100	62.7	34	86.5	46.0
PUG1	96	53.3	12	65.5	37.6	100	59.1	22	68.9	37.2
SIC1										
SAR1	93	53.8	15	71.8	35.9	88	59.8	34	86.2	44.7
TOS1	85	46.0	14	55.9	32.8	100	56.5	25	73.2	39.9
TRE1	96	63.1	16	86.4	42.2	100	63.9	40	91.6	42.2
UMB1	100	53.1	10	68.0	45.0	100	57.0	23	70.6	44.1
VAL1	74	49.7	15	71.8	38.7	77	62.0	45	90.1	21.0
VEN1	78	45.3	18	56.3	26.3	100	52.4	42	73.2	24.0
LIG1						92	69.0	25	78.9	48.6
ABR2	96	53.7	13	75.0	42.6	100	60.0	30	73.8	38.1
LOM2	93	47.9	23	66.0	28.9	92	51.7	50	76.5	14.9
LOM3	100	77.7	44	125.7	48.4					
TOS2	67	60.0	8	69.9	52.3	92	72.5	26	89.6	50.1
TOS3	93	60.8	11	75.7	48.1	100	61.3	18	72.7	48.2
BOL1	85	56.0	16	75.0	42.8	81	61.5	48	104.3	39.6
LIG1						92	69.0	25	78.9	48.6
PIE2	59	32.7	16	38.2	17.9	100	56.6	36	68.3	33.1
PIE3	70	52.5	17	62.8	31.5	77	44.3	70	72.2	16.7
LAZ2						77	70.0	26	87.7	57.8
VEN2						96	39.6	35	50.2	23.2

Table 4 - Data capture (D.c.), median monthly concentrations (median) over the morning period, coefficient of variation (C.V.), maximum and minimum monthly concentrations (Max, Min) at the CONECOFOR PMPs over the years 2001 – 2005.
Completezza dati (D.c.), mediana mensile delle concentrazioni (median) nel periodo di monitoraggio, coefficiente di variazione (C.V.), concentrazioni massime e minime (Max, Min) nelle aree CONECOFOR dal 2000 al 2005.

Table 5 - Differences (expressed as percentages: [ppb year (x) – ppb year (x+1)]/ ppb year (x)) between means of the monitoring periods of consecutive years. Significance level *: p<0.05, **: p < 0.001.
*Differenze (espresse come percentuali: [ppb year (x) – ppb year (x+1)]/ ppb year (x)) tra le medie di periodi di monitoraggio di anni consecutivi. Significatività: *: p<0.05, **: p < 0.001.*

Plot	97'-96'	98'-97'	99'-98'	00'-99'	01'-00'	02'-01'	03'-02'	04'-03'	05'-04'
ABR1a	30 **	-6	8						
ABR1b						-16 *	7	17 *	22 **
BAS1	71 **	-36**	22 **	29 **	14	-16 *	1	15 **	3
CAL 1	46 **	-24**	20 **	17 **	15 **	-10 *	9	15 *	
CAM1			28 **	3	25 **	-8 *	15 *	38 **	-12 *
EMI1	52 **	-19**	2	32 **	-6	-6	-13 *	15 *	2
EMI2	61 **	-24**	8 *	-6			9	3	-7
FRI1	23 **	5	14 *	-11 **	4	-9	4	6	4
FRI2	42 **			-9	-1	8	-4	0	0
LAZ1	45 **	-15**	4	-1	17 **	8	-29 **	38 **	2
LOM1		-7	11 *	-1	-10	9	12	-1	6
MAR 1	49 **	-27 **	36 **	-7	7	-5	-4	24 **	-2
PIE1	30 **			-3	19 *	1	37 **	-23 **	14 *
PUG1	64 **	-17 **	6	3	8	-8 **	-5	9 *	6
SAR1	20 **	-20 **	37 **	-3	24 *	-12	0	1	-4
SIC 1	45 **	-24 **	21 **	7	-11	1			
TOS1	26 **	-6	23 **	-11 *	-7	-8	35 **	-7	17 *
TRE1	51 **	-17 **	15 **	-7	23 *	1	13	2	1
UMB1	47 **	-27 **	41 **	-7	2	9 *	2	0	10
VAL1	33 **	-9	14 *	-14 *	5	11			
VEN1	20 **	-9 *	18 **	-3	-14	16 *	16 *	-19 *	9
ABR2									7
LOM2						-26 **	21 *	-6	-6
LOM3						9	10	8	1
TOS2						-6	-15 *		
TOS3						1	3	17 *	-5
BOL1						22 **	16 *	-17 **	7
PIE2									
PIE3									
LIG1					-17 **	-1			
LAZ2									
VEN2									

for each years. Meteorological conditions greatly influence O_3 concentrations, especially during the warm season (Amoriello *et al.* 2003). In this respect, variations in climatic conditions can exert sufficiently large impact on O_3 concentrations to mask any trends, that could be traced to variations in precursor emissions. The meteorological adjustment of tropospheric O_3 can be achieved by statistical modelling of the association between ozone concentrations and meteorological variables, capable to detect disguised O_3 trends by meteorological variations (Vingarzan and Taylor 2003). The O_3 concentrations, measured during these sampling campaigns, were not meteorologically adjusted as they should reflect the actual level of the pollutant that may impact on the vegetation health, growth and dynamics.

To investigate the amplitude and significance of year-to-year variations and O_3 trend over time, differences between consecutive years were determined and statistically tested. Due to the differences in duration of the monitoring periods between years, the time interval from 15/06 to 30/09 was analysed.

Results of the tests performed are given in Table 5. Comparing data of the first two years of measurements (1996-1997) a relevant increase can be observed. The differences reported for all the PMPs are highly significant indicating a sudden and relevant increase of O_3 pollution. This is due to the 1996 character which can be considered as an O_3-poor year over Italy as over large parts of Europe (EEA 2006). Actually, the O_3 levels of this year are the lowest recorded during considered 10-years period.

The comparisons of the subsequent pairs of years show a decreasing number of significant and highly significant differences. The yearly mean concentrations in 1997 and in 1999 were generally higher than in 1998. This figure is confirmed by the O_3 records collected by the EEA (2006).

From 2000 to 2005 the concentrations generally increase over years and, in general, the significance level of differences decreases. Since 2001 differences between consequent years, expressed as percentages, relevantly decreased from 24% to 6%. In particular, the last comparison (2004-2005) shows highly significant or significant differences only at the PMPs ABR1a, CAM1, PIE1 and TOS1. As mentioned before, it should be noticed that measurements were performed at the PMP TOS1 above the canopies in 2005 while in the previous years the measurement site was located in a near clearing, at the ground level. As observed in other studies O_3 concentrations at ground level may display substantially lower O_3 levels compared to measurements performed above the canopies (Gerosa *et al.* 2001).

O_3 monthly median concentration data are reported in Figure 1. The data reported highlight the frequent occurrence of high temporal and spatial variability. In general, this high variability can be attributed, to a relevant extent, to the inter-annual meteorological variations.

The expected "bell-shaped" O_3 seasonal trend can be recognized at several sites when the sampling period extends from April to September (*e.g*, LOM2, BOL1, PIE1); at a number of locations, however, the seasonal profile may be substantially different. Actually, monthly maxima are recorded in some years in April (ABR1b and EMI2 in 2003) or even in September (EMI2 in 1997 and 2004, MAR1 and UMB1 in 2003, SIC1

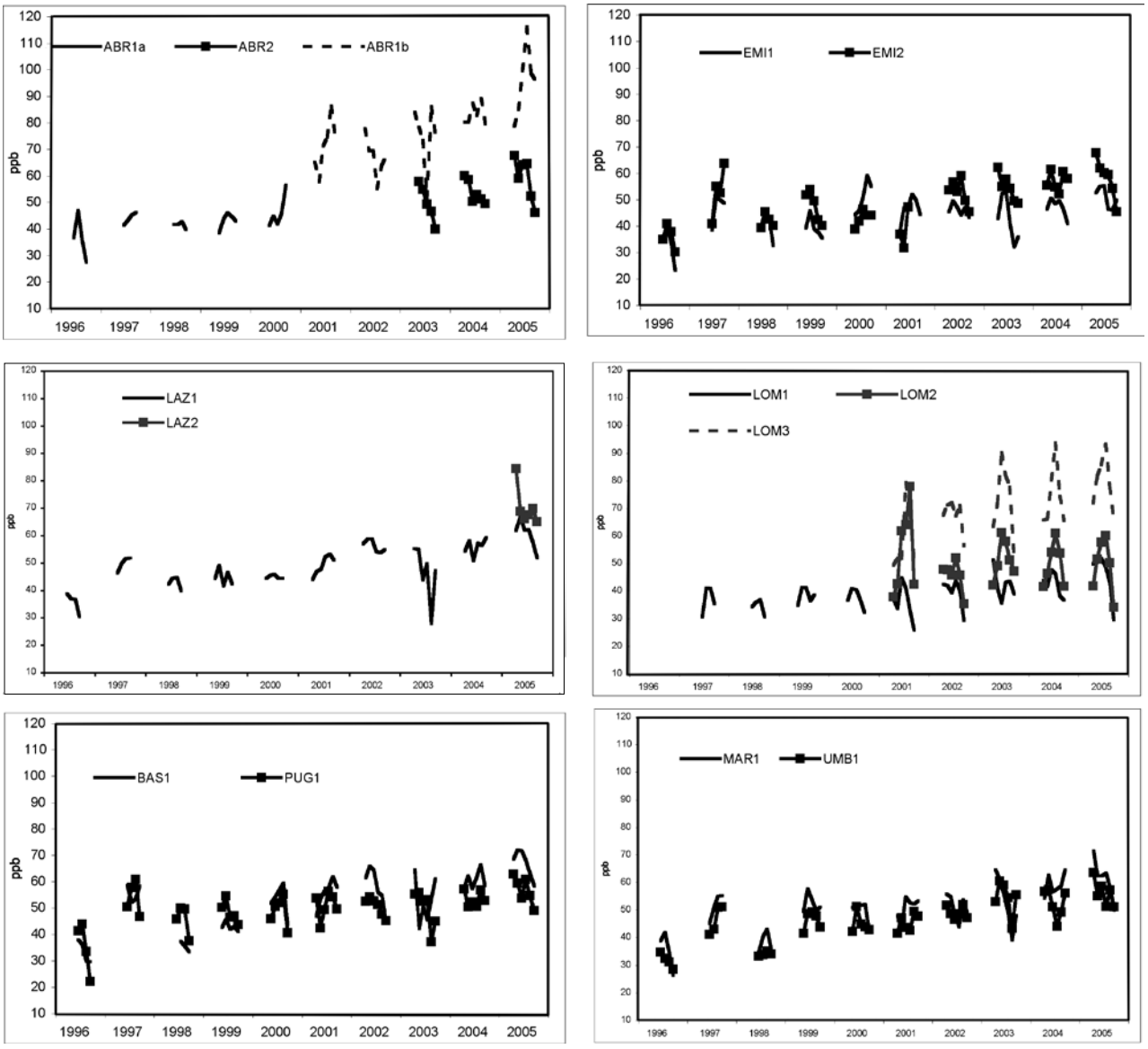
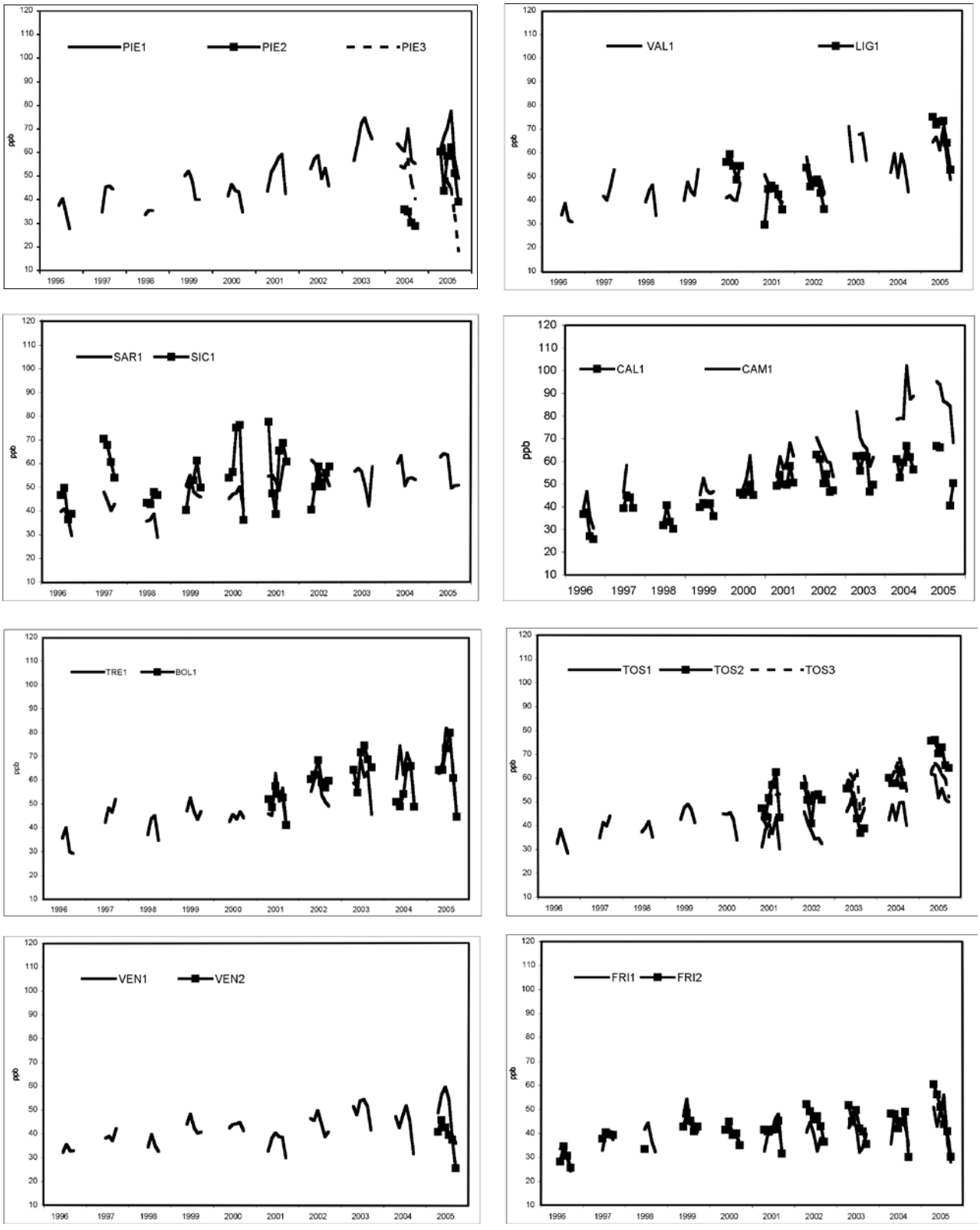


Figure 1 - Monthly median concentrations recorded at the PMPs of the CONECOFORnetwork from 1996 to 2005.
Concentrazioni mediane mensili alle aree delle rete CONECOFOR dal 1996 al 2005.

in 2002). Similar temporal concentrations tendencies are reported, as example, from the Carpathian area by Kellerova and Janik (2006). Monthly mean concentration data display the maximum value at ABR1b in July 2005 and the lowest in June 1997 at ABR1a. The sites ABR1a and ABR1b refer, as reported previously, to the same PMP ABR1. The relevant difference between the two 5-year periods can be reasonably attributed to the above mentioned location change, occurred in 2001, when instruments were moved to another probably more exposed site.

Moreover, the PMPs LOM1 and LOM3, both located in Lombardy, Northern Italy, display very different figures although the site are separated by approximately 35 km. The first is placed in a small valley protected by air mass transport from the densely populated and industrialized Po plain, the second, on the other hand, faces this area. Median concentration levels are very different but data distribution over time is similar. Both in North and South Italy parallel temporal trends between different locations can be observed, probably showing the broad climatic influence on O_3 levels. In these cases the differences in O_3 concentrations medians could be attributed to the microclimatic scenarios and local transport phenomena. In some sampling locations situated in Central Italy (Toscana, Marche

figure 1 (continued)



and Umbria) both tendencies and medians O_3 values are analogous.

Trend analysis performed on seasonal data is based on the evaluation of the possible approximation to the linearity. Data were not corrected for the different lengths of the monitoring periods. Referring to the collected O_3 data and their temporal distribution, an increasing trend can be hypothesized for several plots. Data from PMPs located in Southern Italy (ABR1b, PUG1, CAL1 and CAM1) display a rather clear upward tendency, while plots situated in Central Italy (EMI1, EMI2, TOS1, MAR1, UMB1 and LAZ1) show a positive but less evident trend. The PMPs in the Alpine region show generally a slight increasing tendency, with the exception of LOM3, PIE1 and TRE1 (Figure 2).

The results obtained from trend analysis are reported in Table 6. The first analysis was performed on 1996-2005 annual medians, computed on non-modified data derived from measurements carried out from middle of June to the end of September. A large part of the PMPs show positive slopes which means an increasing trend of the considered pollutant in the examined areas. In particular, 12 PMPs out of 27, display a significant or highly significant monotonic and upward trend. Their slopes (Q) exhibit higher values in case of substantial increments of O_3. This can be observed, for example, at the PMPs CAL1 and CAM1, both located in Southern Italy. The lowest values among the significant trends are shown at PMPs of the Alpine regions, as LOM1 and VEN1.

For 11 PMPs ten annual (seasonal) medians are available, consequently the slope and intercept significance has been tested. Results, given in Table 6, show that 7 PMPs present slopes significantly different from 0, therefore data fit a linear model.

Finally the analysis has been conducted on annual (seasonal) medians from 2001 and 2005, calculated on data collected during the complete vegetative period

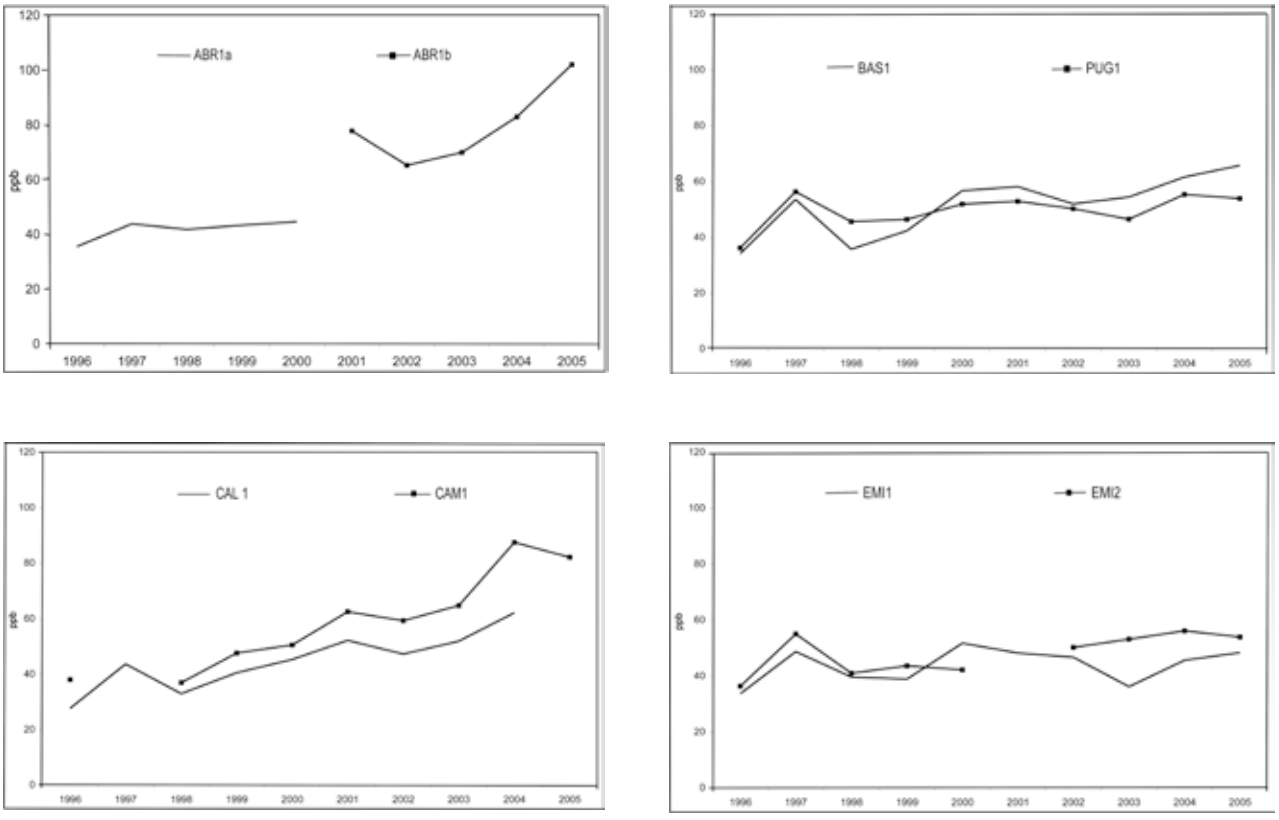
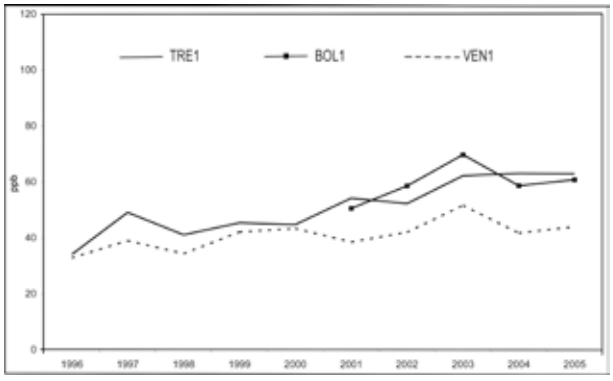
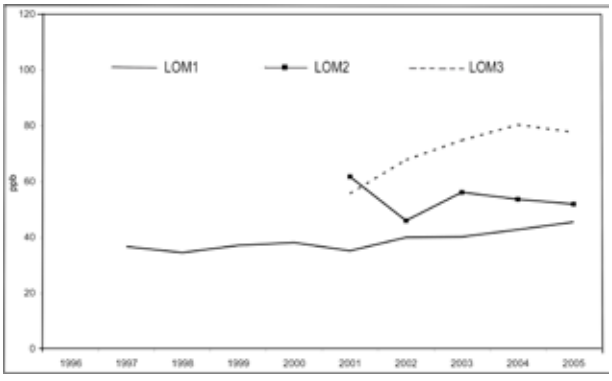
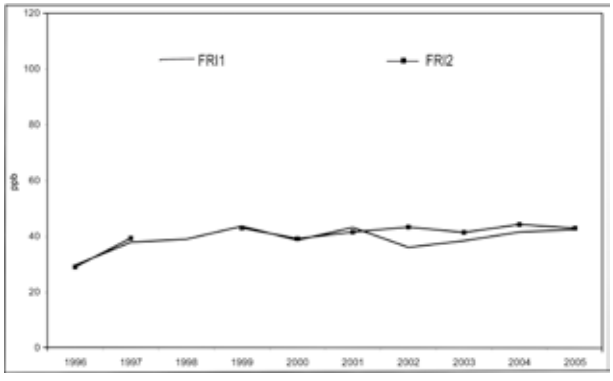


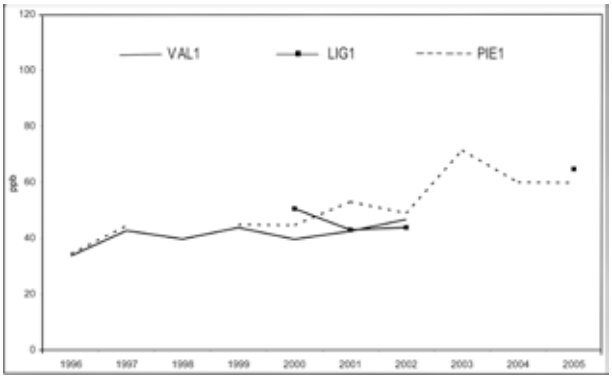
Figure 2 - Median seasonal concentrations over the measurement periods recorded at the PMPs of the CONECOFORnetwork from 1996 to 2005. Monitoring periods are of different length; measurement start and end of each year are reported in Table 1.
Concentrazioni mediane stagionali per I vari anni alle aree della rete CONECOFOR dal 1996 al 2005. I periodi sono di diversa lunghezza; inizio e fine delle misurazioni sono riprotati per ciascun anno in Tabella 1.

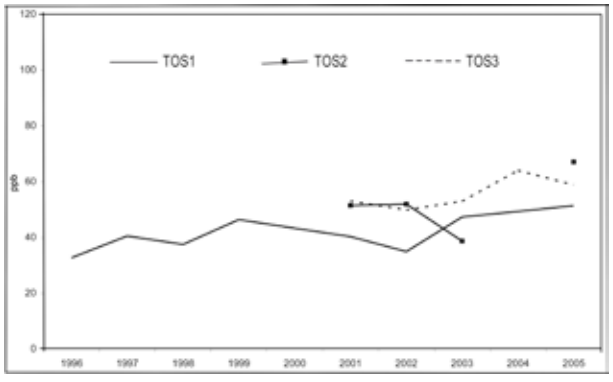
figure 2 (continued)

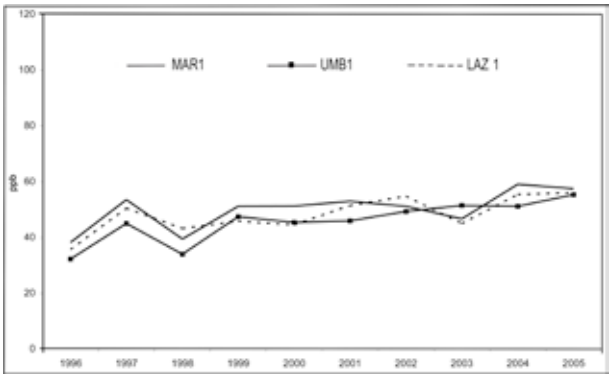


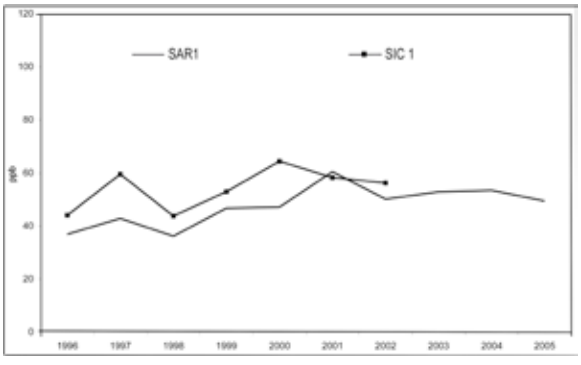












(April - September), (Table 7). The significance of the linearity has only a geometric meaning because of the small number of data. Only 5 PMPs out of 23 with at least 4 yearly medians display a significant monotonic upward trend, highlighting that the concentrations recorded in April and May can noticeably influence the tendency of this pollutant, reducing the monotonic character of the trend. In cases of non significance, the data are randomly ordered in the considered period.

The influence of individual years, both with high or

Table 6 - Results of the S and Z tests performed on data series with more than 4 and 10 annual (seasonal) data, respectively. Significance level *: p<0.05, **: p < 0.001.
*Risultati dei test S e Z effettuati su serie di dati con più di 4 e 10 annualità, rispettivamente. Significatività: *: p<0.05, **: p < 0.001.*

PMP	First year	Last Year	n.	Test S	Test Z	Slope	Intercept
ABR1a	1996	2000	5	8			
ABR1b	2001	2005	5	6			
BAS1	1996	2005	10		2.68**	3.03*	
CAL1	1996	2005	9	28**			
CAM1	1996	2005	9	30**			
EMI1	1996	2005	10		0.36		
EMI2	1996	2005	9	20*			
FRI1	1996	2005	10		1.07		
FRI2	1996	2005	9	18			
LAZ1	1996	2005	10		2.50*	1.83*	23.47*
LOM1	1997	2005	9	28**			
MAR1	1996	2005	10		1.61		
PIE1	1996	2005	9	26**			
PUG1	1996	2005	10		1.43		
SIC1	1996	2002	7	5			
SAR1	1996	2005	10		2.33*	1.57*	26.72*
TOS1	1996	2005	10		2.15*	1.62*	21.56*
TRE1	1996	2005	10		2.86**	3.20*	
UMB1	1996	2005	10		3.22**	2.00*	19.27*
VAL1	1996	2005	8	16			
VEN1	1996	2005	10		1.97*	1.24*	22.64*
LOM2	2001	2005	5	-4			
LOM3	2001	2005	5	8			
TOS2	2001	2005	4	2			
TOS3	2001	2005	5	4			
BOL1	2001	2005	5	6			
LIG1	2000	2005	4	2			

low mean O_3 levels, occurring at the beginning or the end of time series, is important. For example, 1996 has been a O_3-poor year, as mentioned before. If the corresponding data are neglected in the trend analysis the amount of PMPs with a significant trend drops from 12 to 9 PMPs. As well similar figures could be observed, depending on the PMP considered, if O3-rich years as 2003, 2004 or 2005 are neglected.

Conclusions

With 19 PMPs displaying O_3 time series of 7 to 10 years, the CONECOFOR network represents a valuable information source regarding O_3 pollution at Italian forest sites in term of concentrations and their trends through time. The data show, for a large extent, relevant mean concentrations during spring and summer months. PMPs with the highest O_3 concentration levels are located in Central and Southern Italy although some PMPs in the Alpine region highlight similarly high values. As most of PMPs are situated at remote sites, transport phenomena play a relevant role.

The influence of the recent hot and O_3-rich years play a relevant role in determining the observed trend. As there is a strong link between increasing temperatures and tropospheric O_3, a warmer and dryer climate is very likely to lead to increased O_3 concentrations. Increasing temperature are expected to influence transport phenomena, and O_3 precursor release from plants could become more active in a warmer environment. Moreover, the study highlights the importance of long-term investigations in Italy and underlines the need to develop a O_3 permanent monitoring network in remote areas.

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Table 7 - Results of the S test performed on data series referring to the years 2001 - 2005. Significance level *: p < 0.05, **: p < 0.001.
*Risultati dei test S e Z effettuati su serie di dati con più di 4 e 10 annualità, rispettivamente Significatività: *: p<0.05, **: p < 0.001.*

PMP	First year	Last Year	Valid data	Test S	Significance	Slope	Intercept
ABR1b	2001	2005	5	8		7.01	-30.52
BAS1	2001	2005	5	8		2.12	27.18
CAL1	2001	2005	4	6		3.12	7.55
CAM1	2001	2005	5	8		7.16	-41.82
EMI1	2001	2005	5	2		0.52	39.06
EMI2	2001	2005	4	6		2.53	13.54
FRI1	2001	2005	5	6		1.16	22.50
FRI2	2001	2005	5	4		0.67	34.16
LAZ1	2001	2005	5	4		2.36	17.76
LOM1	2001	2005	5	10	*	2.49	2.35
MAR1	2001	2005	5	10	*	2.38	16.88
PIE1	2001	2005	5	6		2.97	9.69
PUG1	2001	2005	5	6		1.48	29.15
SAR1	2001	2005	5	2		0.53	46.28
TOS1	2001	2005	5	6		4.60	-26.28
TRE1	2001	2005	5	10	*	3.72	-0.76
UMB1	2001	2005	5	8		2.70	8.42
VEN1	2001	2005	5	6		2.98	-1.27
LOM2	2001	2005	5	0		-0.02	50.65
LOM3	2001	2005	5	10	*	4.14	5.69
TOS2	2001	2005	4	2		3.99	-7.00
TOS3	2001	2005	5	10	*	3.65	-1.98
BOL1	2001	2005	5	4		2.44	17.49

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