Convention on Long–Range Transboundary Air Pollution

emep

Co–operative programme for monitoring and evaluation of the long–range transmissions of air pollutants in Europe

ASSESSMENT REPORT

NATIONAL CONTRIBUTION OF ITALY

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1. The monitoring stations

Italy has been participating actively to the EMEP program since the beginning. Over these years, data quality has improved due to both improvements in analytical methods and laboratory activity. Five monitoring stations have been created in order to analyze and evaluate air quality in the EMEP framework, but only two of them are currently active on the Italian territory:

- Montelibretti station (IT01), situated in central Italy (42°06'N, 12°38'E) at an altitude of 48 m;
- Ispra station (IT04), of the EU - Joint Research Centre, situated in northern Italy (45°49'N, 8°38'E) at an altitude of 209 m.

The measurement program at these stations is reported in Table 1.

Table 1: Parameters regularly measured at EMEP stations in Italy during the 1983-2001 period. Other parameters were measured occasionally.

Matrix	Montelibretti (IT01)	Ispra (IT04)
Air	SO_2, HNO_3, NH_3 (annular denuders) NO_2, O_3 (continuous monitors)	SO_2, NO, NO_2, O_3, CO (continuous monitors)
Aerosol	NO_3^-, SO_4^{2-}, and NH_4^+ (filter packs downstream of annular denuders)	TSP (PM_{10} since Nov 2000), SO_4^{2-}, NH_4^+, HNO_3+NO_3^- (cellulose acetate filters)
Precipitation	Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+} (IC), conductivity, pH	Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+} (IC), conductivity, pH
Meteorology	Precipitation	Wind speed and direction Temperature Relative Humidity Pressure Precipitation Irradiation

At Montelibretti, SO_2 and $SO_4^=$ have been measured from 1984 to 1988 by using filter packs, while since 1994 they are measured, as well as HNO_3, NO_3^-, NH_3, NH_4^+, by using diffusion lines comprised of 5 annular denuders, a cyclone and a triple filter pack (teflon, nylon, acid-impregnated). Diffusion lines proved to be a robust and reliable method for the separate determination of gases and particulate species without mutual inter-conversion, and the only method suitable for determining ammonium salts and related species in countries, such as Italy, where the thermodynamic conditions strongly favour the evolution of nitrate salts.
NO/NOx and O_3 are monitored since 1996 by chemiluminescence analyzers with molybdenum converters and by UV photometric analyzers, respectively.
Precipitation is collected since 1983 with a wet-only collector.
Ionic compounds are all measured by ion chromatography.

At Ispra, SO_2, and NO/NOx have been monitored since 1986 with UV fluorescence analyzers and chemiluminescence analyzers with molybdenum converters, respectively. O_3 has been measured since 1990 with UV photometric analyzers.
Aerosols have been sampled until 2000 on acetate cellulose filters. Laboratory and field experiments showed that these filters efficiently trap NH_4NO_3, but also HNO_3. In contrast, they do not trap NH_3.
Precipitations were collected with a wet-only collector.
Ionic species in aerosols and precipitations were measured by ion chromatography.

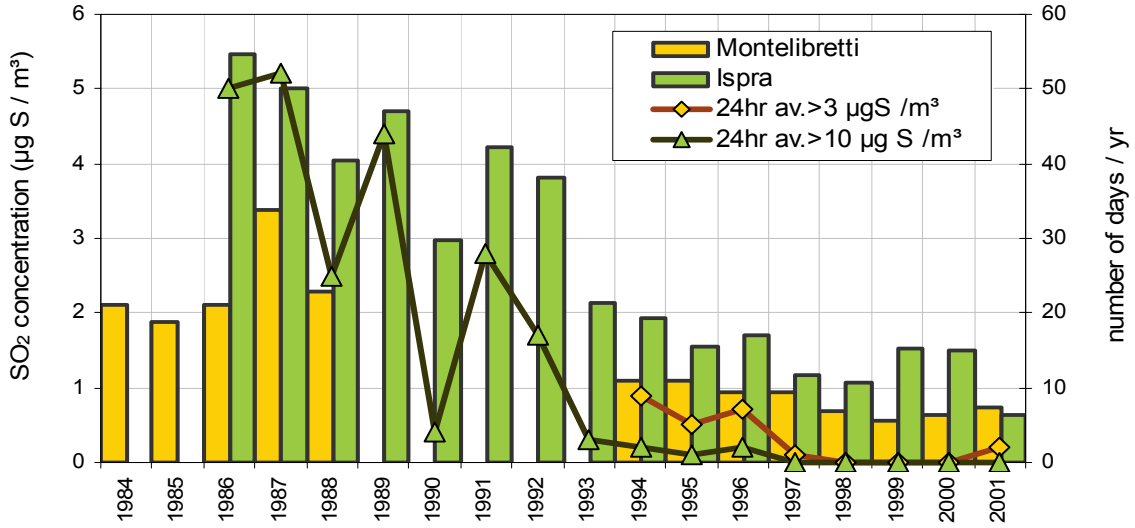

Fig. 1: Annual mean SO_2 concentrations and number of days on which given values were exceeded

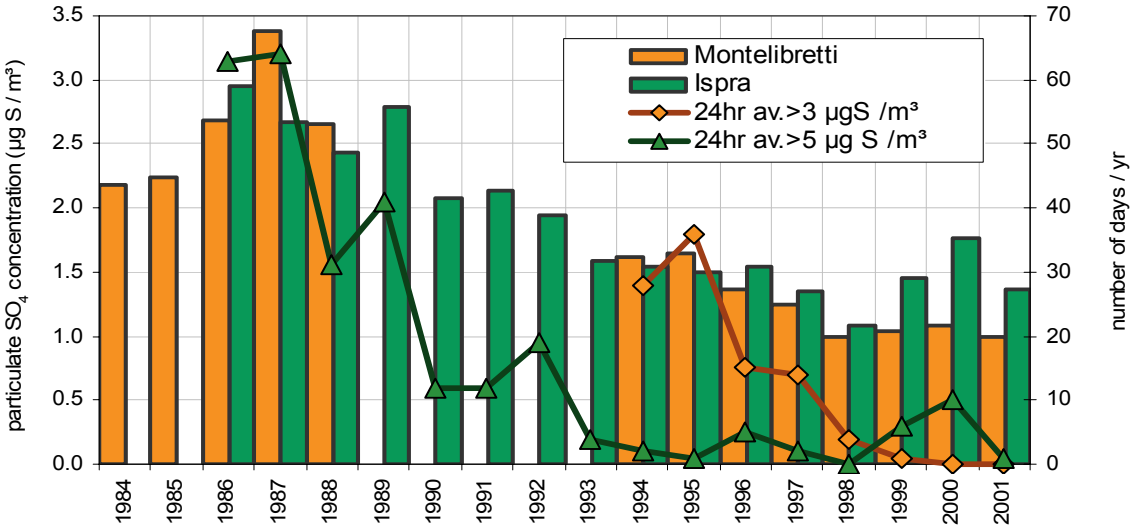

Fig. 2: Annual mean SO_4 concentrations and number of days on which given values were exceeded

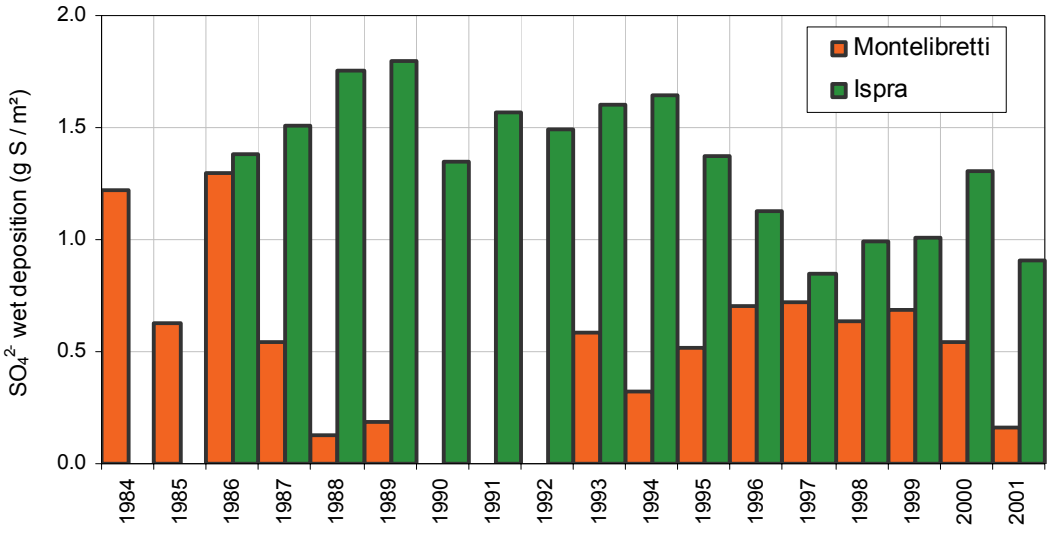

Fig. 3: SO_4^{2-} annual wet deposition fluxes

2. Assessment of time series and trends in Italy

2.a. Concentrations, deposition and emissions of sulfur

- SO_2 concentrations

SO_2 concentrations are consistently larger in Ispra than in Montelibretti (Fig. 1). The annual (and winter) EU limit value of 10 µgS/m³ was never exceeded during the past 15-20 years, for which data are available. The 24-hr EU limit value (62.5 µgS/m³) was reached twice in Ispra in February 1987 and never again since then. The highest SO_2 concentrations are observed in Ispra when local wind blows from a broad south sector (yr 2000 data).
Over the last 15-20 years, annual mean SO_2 concentrations decreased at a rate of 0.1 and 0.3 µg m^{-3} yr^{-1} at Montelibretti and Ispra, respectively. Also the number of days with high SO_2 concentrations (SO_2 > 3 and >10 µgS/m³ at Montelibretti and Ispra, respectively) dropped over the period. The large decrease (> factor of 2) in SO_2 at Ispra over 1986-1996 is not reproduced by the EMEP model.

- Particulate SO_4^{2-} concentrations

Particulate SO_4^{2-} concentrations are quite similar at the two stations (Fig.2). This is consistent with the fact that sub - µm particles, in which most non sea-salt sulfate sits, have a quite long lifetime (days). Over the 15-20 last years, particulate SO_4^{2-} concentrations decreased at a rate of 0.1 µg m^{-3} yr^{-1} at both stations. However, this decreasing trend is no more observed during 1998-2001. Also the number of days with high SO_4 concentrations (SO_4 > 3 and >5 µgS/m³ at Montelibretti and Ispra, respectively) dropped over the studied period, except for 1998-2000 in Ispra. The SO_4^{2-} trend observed in Ispra is very well reproduced by the EMEP model, at least over the 1989-1996 period.

- Comparison between SO_2 and SO_4^{2-} trends.

Trends in SO_2 and SO_4^{2-} are very similar at Montelibretti. At Ispra, in contrast, SO_2 decreased much more than SO_4^{2-} over the 15 last years. Rather than a change in the SO_2 oxidizing capacity of the atmosphere, this might reflect the fact that local sources of SO_2 have been reduced more than regional sources leading to the formation of long-range transported sulfate.

- Sulfur wet deposition

Annual sulfur wet deposition is much more variable in Montelibretti than in Ispra, mainly due to the quite variable annual amount of precipitation recorded at that site. At Ispra, a decreasing trend in SO_4^{2-} wet deposition (ca. – 5% / yr) is observed, in line with the aerosol SO_4^{2-} concentration trend. Sulfur wet deposition is generally well reproduced by the model, with a couple of exceptions mainly due to a bad estimation of the precipitation amount.

- SO_2 emissions

National SO_2 emissions decreased from 3440 kton in 1980 to 700 kton in 2001, with a total reduction of 80% (Fig. 4). The main emission sources are the combustion in energy and transformation industries, which represent 61% of the total emissions. The reductions in these sectors since 1988 are due to the introduction of several normative instruments (D.M 12 July 1990, and the Large Combustion Plant Directive), which brought to a shift in energy consumptions from heavy fuel oils to low sulphur oils or to natural gas, reducing sulphur emissions.

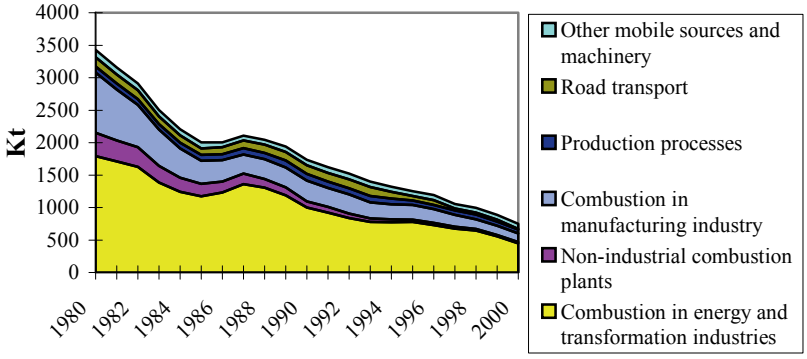

Fig. 4: SO_2 emissions in Italy by sector

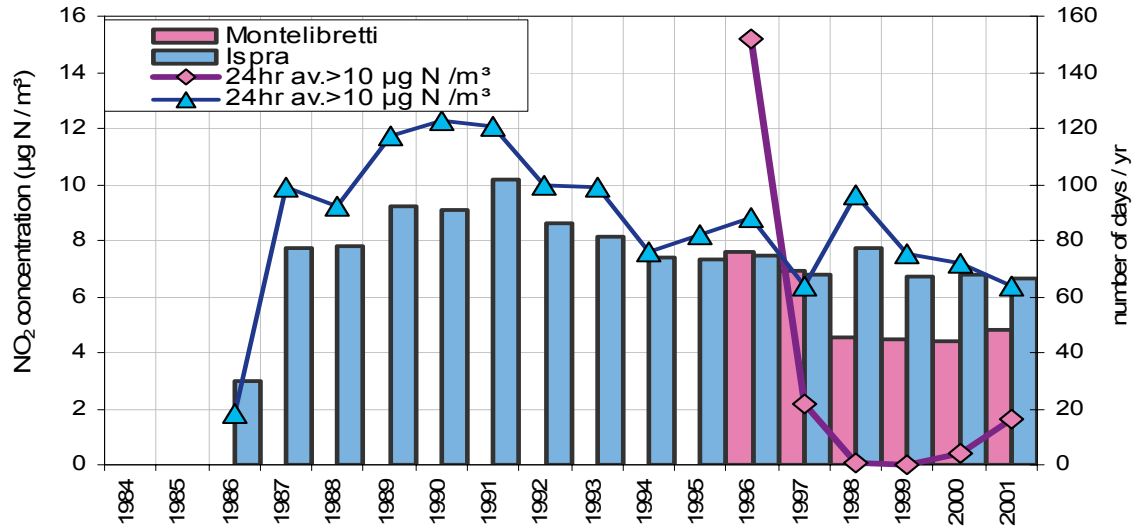

Fig. 5: NO_2 annual mean concentrations and number of days on which given values were exceeded

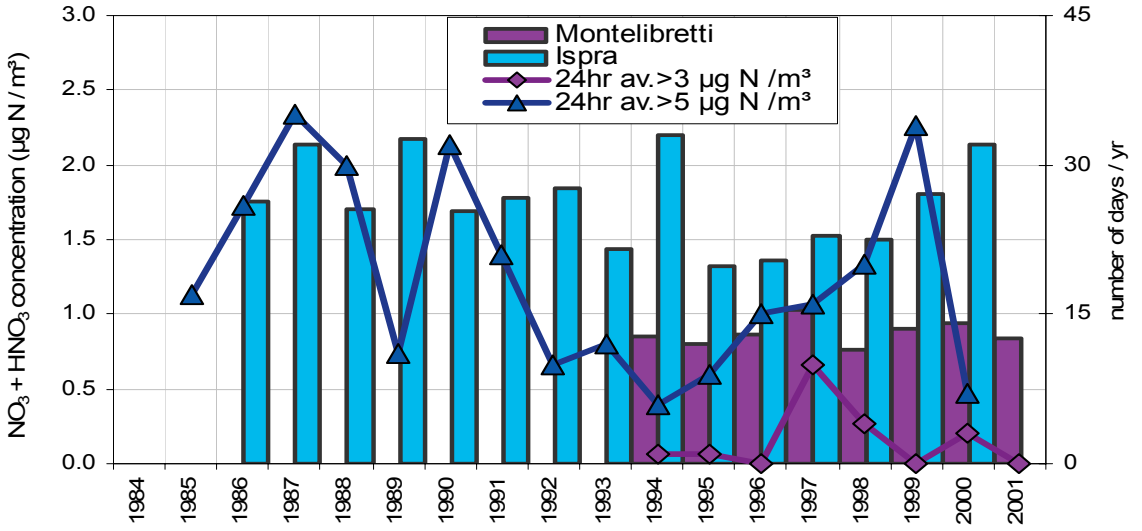

Fig. 6: NO_3^- + HNO_3 annual mean concentrations and number of days on which given values were exceeded

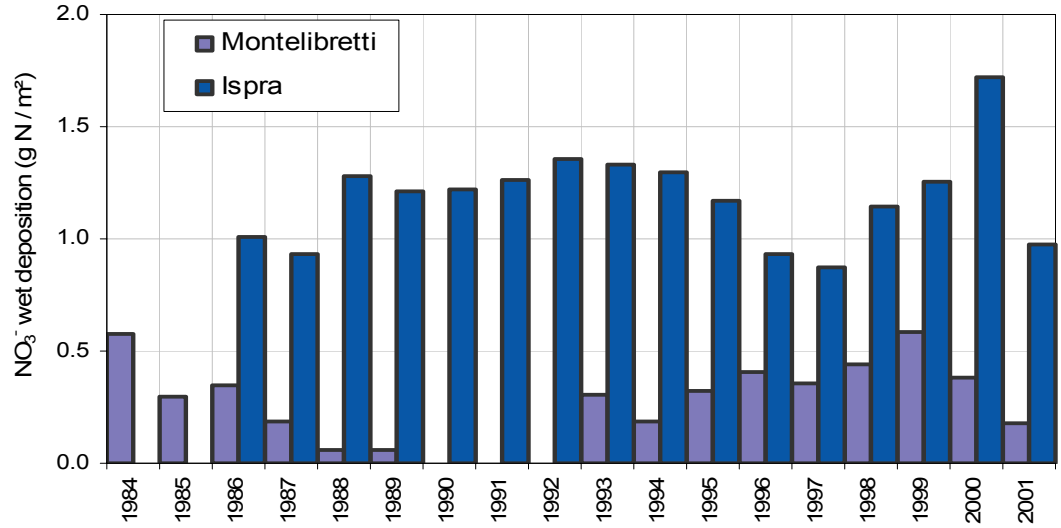

Fig. 7: NO_3^- annual wet deposition fluxes

2.b. Concentrations, deposition and emissions of oxidized nitrogen

- NO_2 concentrations.

The EU limit value for protection of human health (40 µg/m³ NO_2, i.e. 12 µg N/m³) has never been reached at any of the two stations during the period of measurements. Since 1998, NO_2 concentrations in Montelibretti are quite constant and significantly smaller than in Ispra. The maximum NO_2 annual mean concentration was observed in Ispra in 1991. Since then, NO_2 decreased by ca. 5% yr^{-1} till 1994. No further decrease was observed since 1997. The number of days with high NO_2 concentrations (NO_2 > 10 µg N/m³) decreased by a factor of 2 in Ispra between 1990 and 2001. It dropped sharply between 1996 and 1997 at Montelibretti, but increased again to reach significant values since then (Fig. 5). The NO_2 concentrations observed in Ispra are 4-5 times as large as calculated by the EMEP model, which does not predict any trend over the 1986-1996 period. The wind rose for 2000 shows that the highest NO_2 concentrations in Ispra are observed when local wind blows from the SE sector, i.e. from the Milan conurbation direction.

- NO_3^- + HNO_3 concentrations.

As cellulose acetate filters (which were proved to trap efficiently NO_3^- but also HNO_3) were used in Ispra to collect aerosol from 1986, we used this variable assess the long-term trends at the 2 sites located in Italy. NO_3^- + HNO_3 concentrations remained quite constant at Montelibretti since 1994. They were more variable in Ispra, without any clear trend, except for the 1995-2000 period, during which it increased by ca. 3% yr^{-1}. The number of days with high NO_3^- + HNO_3 concentrations (> 3 and >5 µg N/m³ at Montelibretti and Ispra, respectively) reached a minimum in Ispra in 1992-1995. At Montelibretti the number of exceedances follows the concentration trend, with the highest value in 1997 (Fig. 6). The particulate NO_3^- concentrations predicted by the EMEP model for Ispra are much larger that the NO_3^- + HNO_3 concentrations observed at the station. Model predictions for Montelibretti in 1996 are also quite larger (> 2 times) than nitrate experimental observations.
At Montelibretti the denuder technique allowed the discrimination between HNO_3 and NO_3^- and showed a HNO_3/NO_3^- ratio between 1:6 and 1:4, with an annual average concentration ranging between 0.13 and 0.19 and between 0.62 and 0.80 µg N/m³ for HNO_3 and NO_3^- respectively.

- NO_3^- wet deposition

NO_3^- wet deposition has always been larger at Ispra than at Montelibretti over the period for which simultaneous measurements are available (Fig. 7). After reaching a minimum in 1997 (partially due to low precipitation amounts), NO_3^- wet deposition in Ispra reached in 2000-2001 values comparable to the early 90's maximum.

- NO_x emissions

Transport is the main responsible for NOx emissions in Italy: the road transport accounts for more than 50% of total emissions, while the other mobile sources give a contribution of around 17%. The emissions from this sector increased from 649 kton in 1980 to 701 kton in 2001 with a peak in 1992, which can be explained by the growth of the car park during the first decade and the following introduction of measures and normative instruments to reduce emissions. Combustion in energy and transformation industries also showed a significant reduction since 1988, following, as for SO_2 emissions, the introduction of several normative instruments, and in particular of the D.M 12 July 1990 (emission limits at stacks).

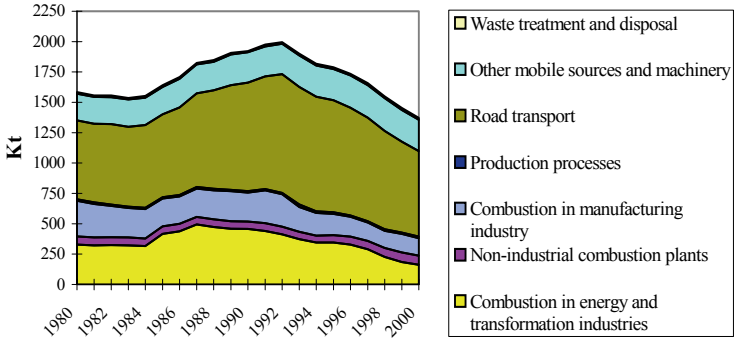

Fig. 8: NOx emissions in Italy by sector

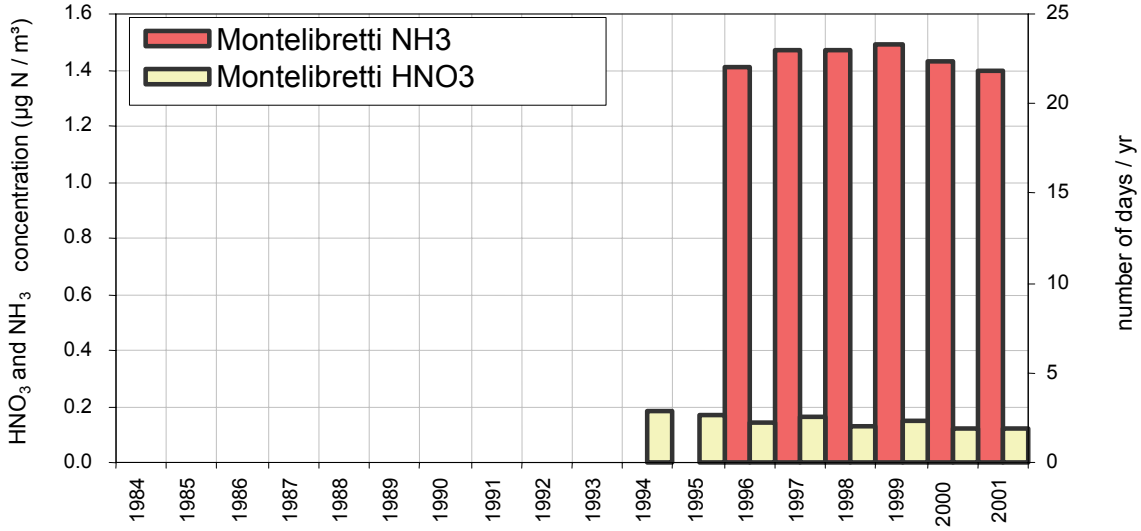

Fig. 9: Gas phase HNO_3 and NH_3 at Montelibretti and number of days on which the given value was exceeded

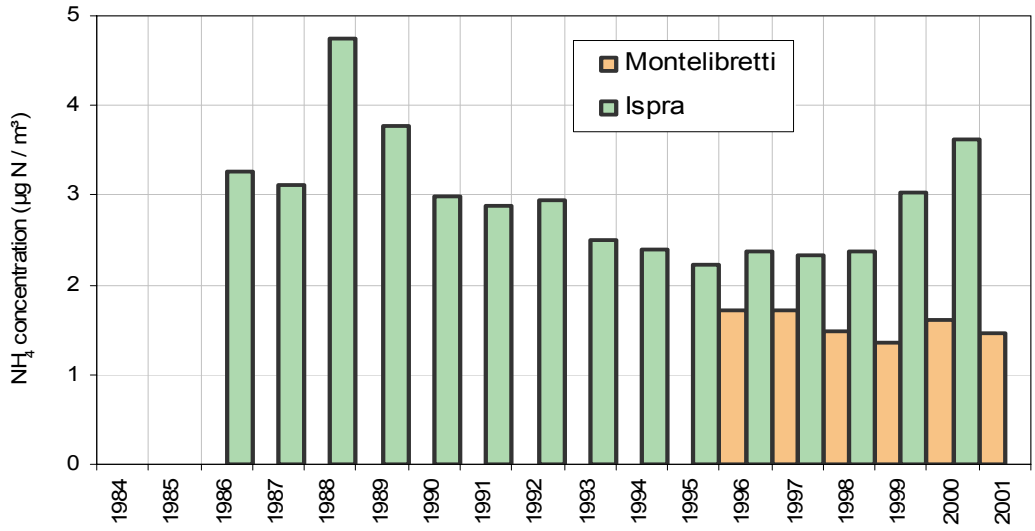

Fig.10: Annual mean NH_4 concentrations in aerosol

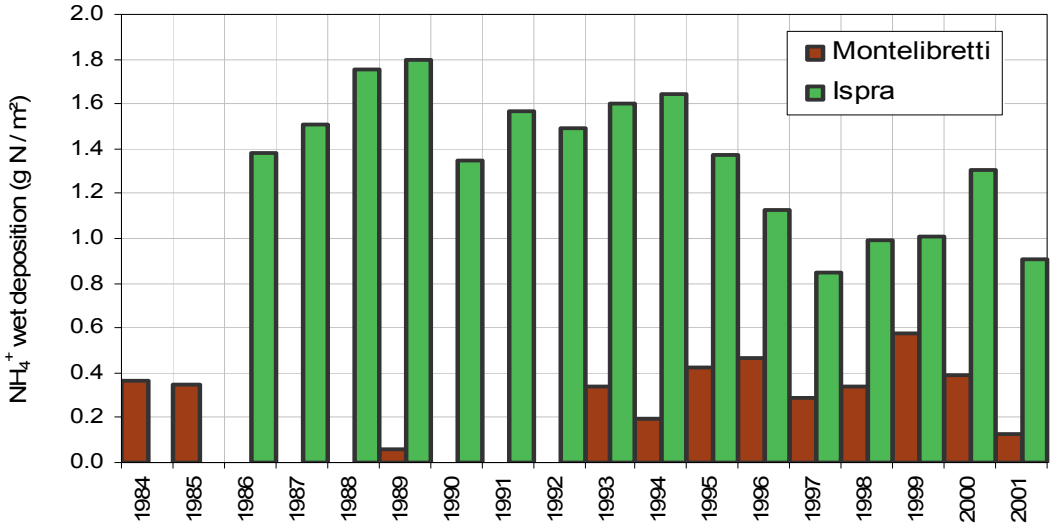

Fig.11: NH_4^+ annual wet deposition fluxes

2.c. Concentrations, deposition and emissions of reduced nitrogen

- NH_3 concentrations

NH_3 was measured continuously in Montelibretti only since 1996. NH_3 concentrations have been very constant over the 1996-2001 period and almost one order of magnitude higher than nitric acid concentration level (Fig. 9); the value calculated by the EMEP model for ammonia in 1996 was about 30% lower than the experimental values.

- NH_4^+ concentrations

Variations in NH_4^+ concentrations reflect variations in SO_4^{2-} and NO_3^-. Indeed, over the 1996-2000 period, NH_4^+ and ($2 \times SO_4^{2-} + NO_3^-$) in µmol m^{-3} are very well correlated, with slopes of 1.20 and 1.07 at Montelibretti and Ispra, respectively, which indicate that the inorganic aerosol acidity is almost completely neutralized by ammonia.

At Montelibretti, NH_4^+ concentration was quite constant over the 1996-2001 period, as SO_4^{2-} and NO_3^- concentrations. In Ispra the NH_4^+ concentration decreased from 1988 to 1995, following the SO_4^{2-} trend, and increased again from 1995 to 2000, following the increase in NO_3^- (Fig. 10).

The NH_4^+ variations in Ispra over the 1986 – 1996 periods are relatively well captured by the EMEP model.

- NH_4^+ wet deposition

As for SO_4^{2-} and NO_3^-, NH_4^+ wet deposition are much larger in Ispra than in Montelibretti (Fig. 11). NH_4^+ wet deposition flux is also correlated with ($2 \times SO_4^{2-} + NO_3^-$) flux, but NH_4^+ is able to neutralize only about 2/3 of the acidity brought by SO_4^{2-} and NO_3^-, which shows the importance of the other base cations for buffering the rain water acidity in Italy.

There is a somewhat decreasing trend in NH_4^+ wet deposition at Ispra over the 10-15 last years and no defined trend at Montelibretti.

The EMEP model generally underestimates the NH_4^+ wet deposition flux at Ispra by a factor of 2.

- NH_3 emissions

Total ammonia emissions in Italy were quite constant over the last two decades, with a total value of 442 kton in 2001 (Fig. 12). The agriculture sector, that includes both the livestock and the use of nitrogenous fertilizers, is responsible for 92% of the total emissions, while the transport sector gives a contribution of around 4%.

The contribution of the transport sector increased remarkably since 1995 – 1996, following the introduction of vehicles equipped with catalytic converters, which are known to emit ammonia.

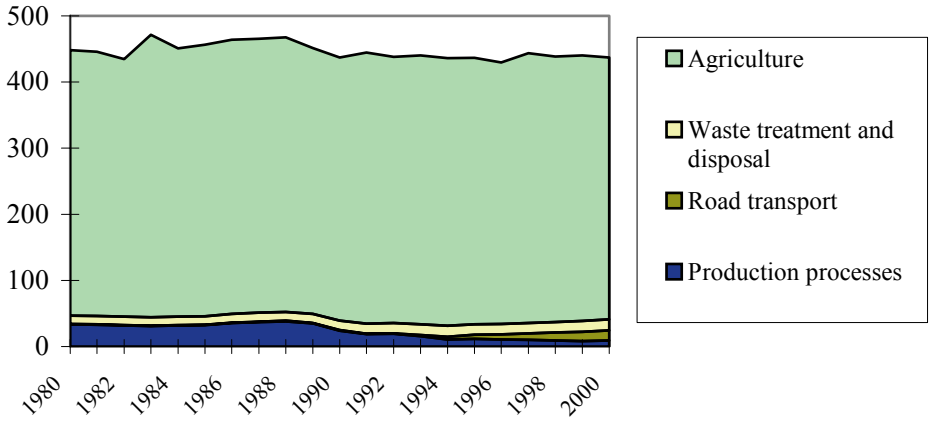

Fig. 12: NH_3 emissions in Italy by sector

2.d Acidity wet deposition

A clear decreasing trend in acidity wet deposition in Ispra can be observed since 1987. Acidity wet deposition, which used to be much smaller in Montelibretti than in Ispra in the 80's, increased sharply at Montelibretti from 1993 to 1998, and then decreased then to reach values close (but still higher) than in the early 80's (Fig. 13).

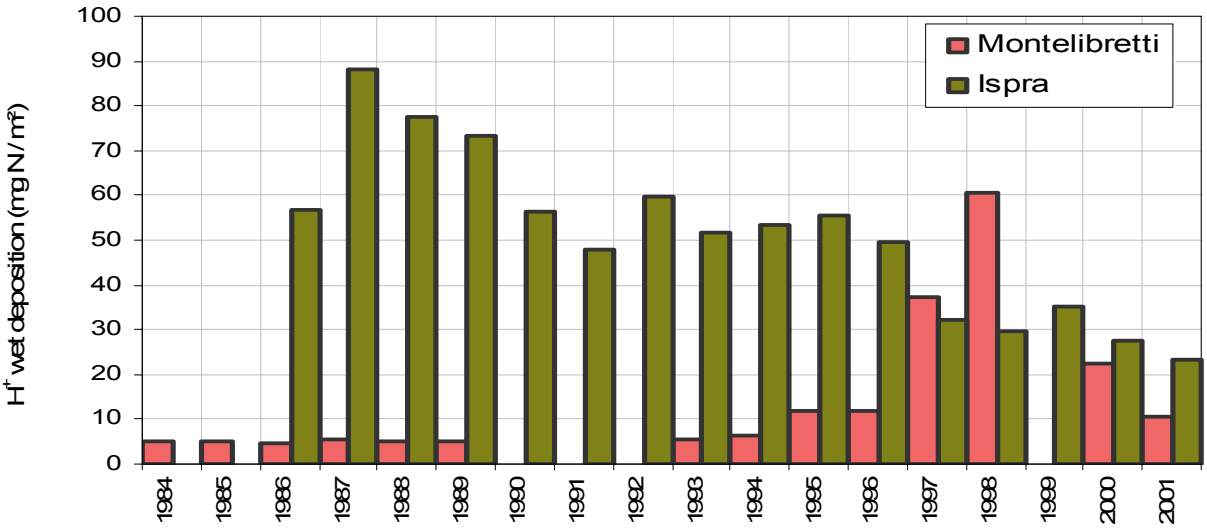

Fig. 13: Annual acidity wet deposition fluxes

2.e Changes in ozone concentrations

- O_3 yearly and monthly concentrations

The O_3 concentrations are quite similar at Montelibretti and Ispra (Fig. 14). No decreasing trend can be observed at Ispra over the 1990-2001 period. On the contrary, annual mean O_3 concentrations seem to slightly increase since 1996 at both stations.
O_3 monthly mean concentrations (Fig. 15) show large seasonal variations (close to a factor of 3).
On average, minimum and maximum monthly mean concentrations are observed at both stations in January and July, respectively (Fig. 16). Over the 1996-2001 period, O_3 was higher at Ispra than at Montelibretti in April, May, and June and equal or lower during the other months. O_3 has been increasing both during winter and summer months since 1996.

- O_3 hourly mean concentrations

Ozone diurnal variations are shown for winter and summer for both stations (Fig. 17). It can be observed that O_3 maximum occurs later in Ispra (15:00-16:00) than in Montelibretti (13:00-14:00). This may be due to the transport of O_3 and/or O_3 precursors from more polluted areas to Ispra when mountain breeze develops in the afternoon. In Montelibretti, ozone is transported from the urban area of Roma, about 20 km SW of the EMEP site, following the sea breeze which develops in the very early afternoon, mostly during the spring and summer.
In winter, O_3 maximums are observed at the same time at both stations. However, in the early morning (6:00-10:00) O_3 is significantly higher at Montelibretti. Wind roses (Fig. 18) show that maximum O_3 concentrations are observed at both sites when winds are blowing from SW sectors, i.e. from the most polluted areas.

- O_3 exceedances

The number of days on which the 24 hr average limit of 65 µg/m³ O_3 was exceeded (EU limit for vegetation protection) has not been decreasing since 1990 in Ispra. On the contrary, it seems to increase since 1996 at both Ispra and Montelibretti (Fig. 19).
The number of days on which the 1 hr average limit of 180 µg/m³ O_3 was exceeded (EU limit for population information) quite clearly decreased at Ispra from 1991 to 1997, but this trend is no more observed, as for Montelibretti, since 1997 (Fig. 20).
The AOT40 values (ppbh), representing the exposure of vegetation to O_3 concentrations > 40 ppb (80 µg/m³) also decreased in Ispra over the 1991-1996 period (Fig. 21). It is quite constant (or perhaps slightly increasing) at both Montelibretti and Ispra since 1996.

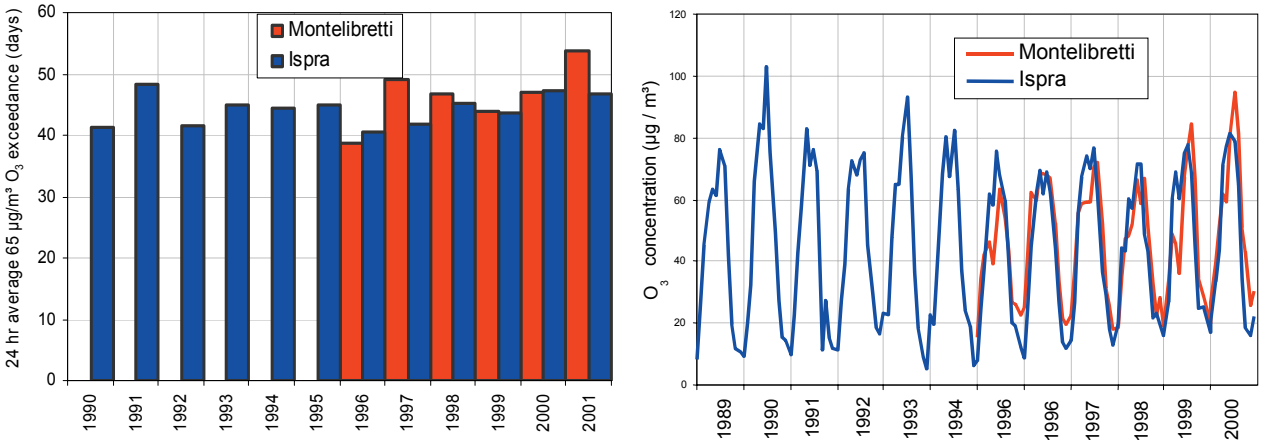

Fig. 14 and 15: Annual and monthly mean ozone concentrations

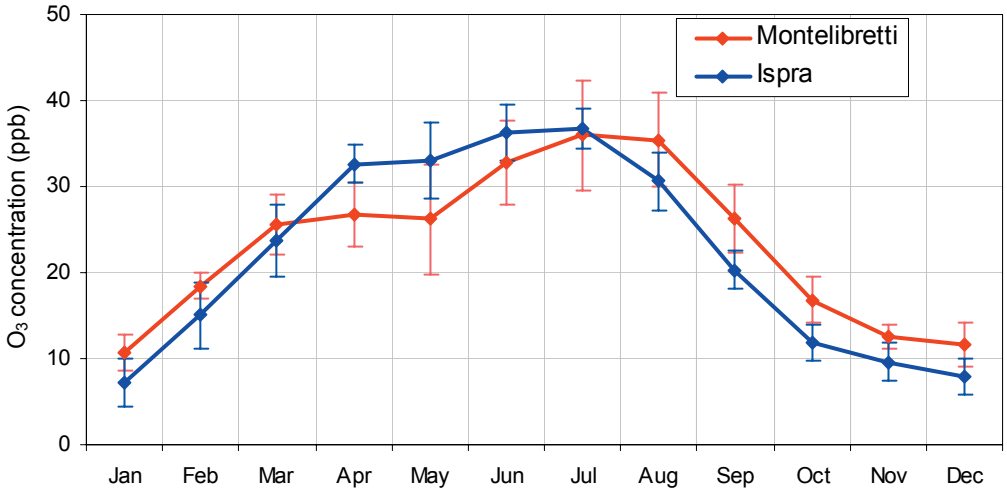

Fig.16: Mean ozone seasonal trend over the 1996-2001 period

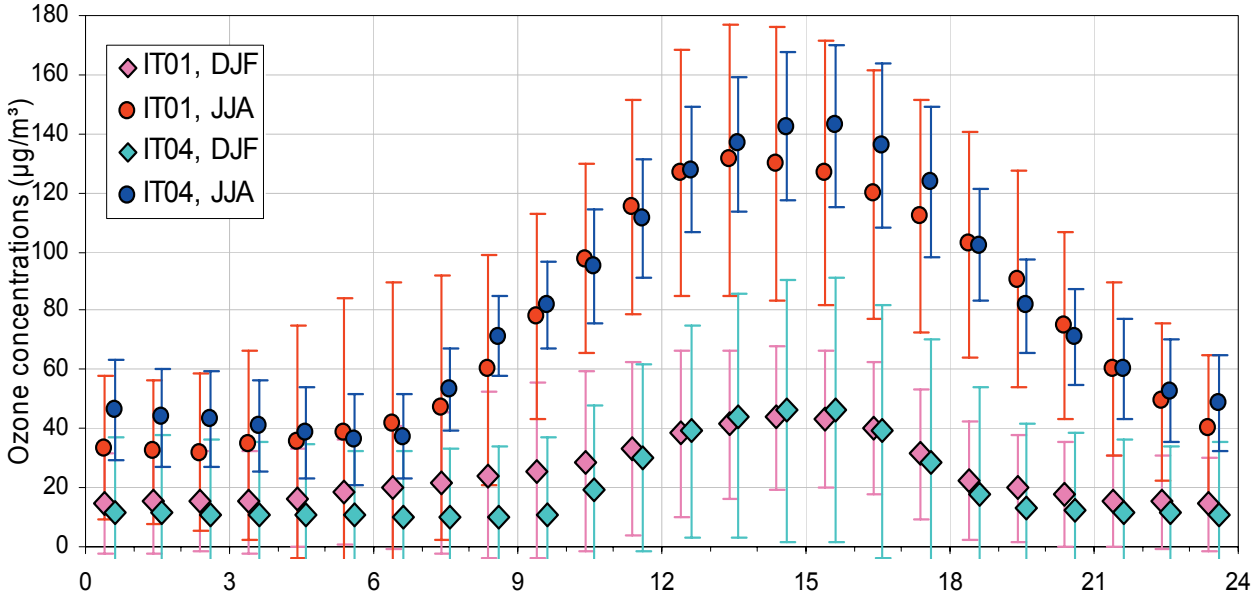

Fig.17: Hourly mean O_3 (µg/m³) at Montelibretti (IT01) and Ispra (IT04) during winter (DJF) and summer (JJA) 2000

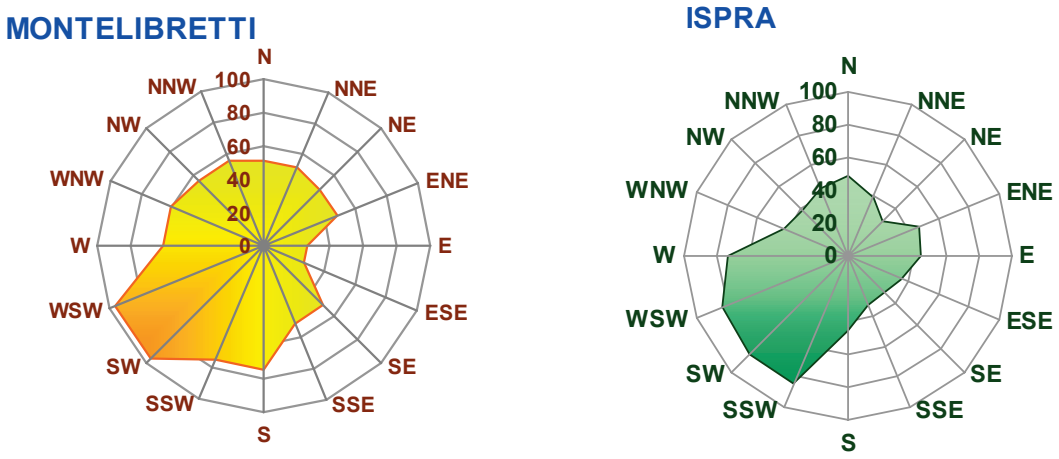

Fig. 18: O_3 concentration (µg/m³) as a function of wind direction (1-hr average) at Montelibretti and Ispra in 2000

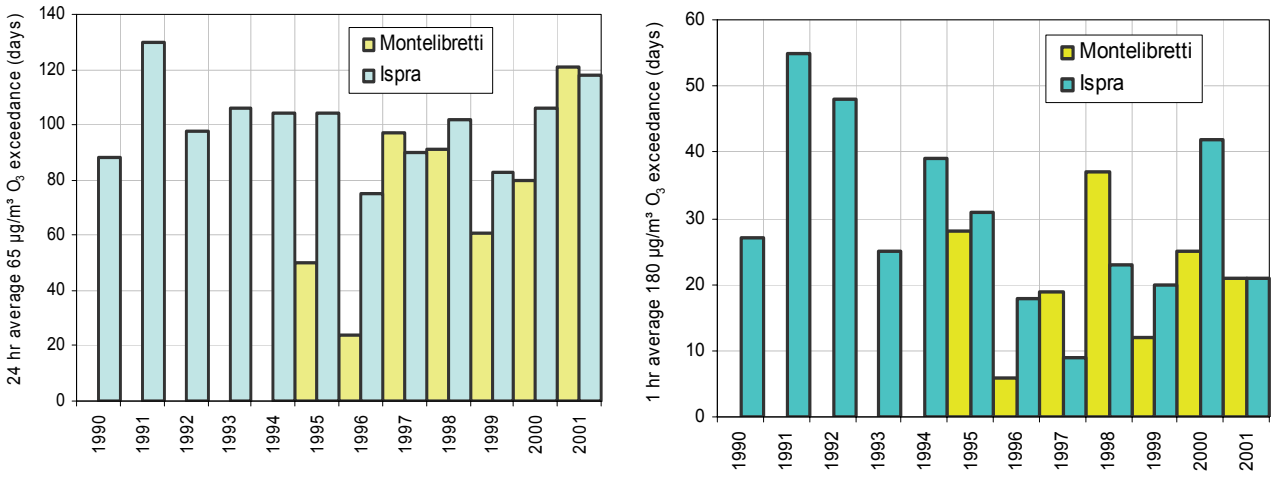

Fig.19 and 20: Exceedances (days) of 65 µg/m³ over 24 hr limit value and of 180 µg/m³ over 1 hr limit value

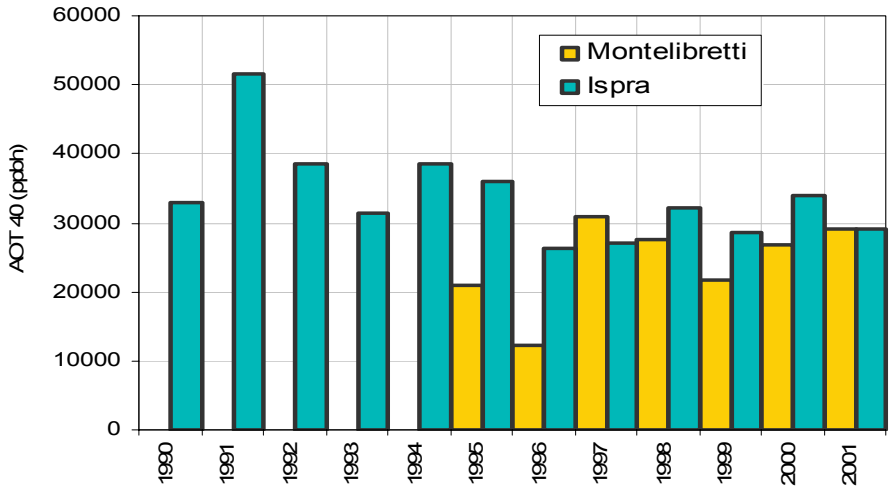

Fig.21: Exposure to above the ozone 40 ppb threshold (ppb hr)

3. Mixing properties of the lower atmosphere

A driving force for the 24-h concentration of atmospheric pollutants, that in Italy is not clearly linked to a specific transport direction, is constituted by the mixing properties of the lower boundary layer. This parameter, which can be well estimated on the basis of natural radioactivity

measurements, permits a satisfactory interpretation of the time trend of both primary and secondary pollutants. The correlation between atmospheric stability and the concentration time trend of particulate nitrate during the winter and of nitric acid during the summer of the year 2000 is shown in Fig. 22 and 23. This parameter constitutes a precious tool for the interpretation of both short- and long-term temporal pattern of pollutant concentrations, particularly in the areas, such as Italy, where the strongest contribution to pollution episodes is given by an insufficient mixing of the lower atmospheric layers.

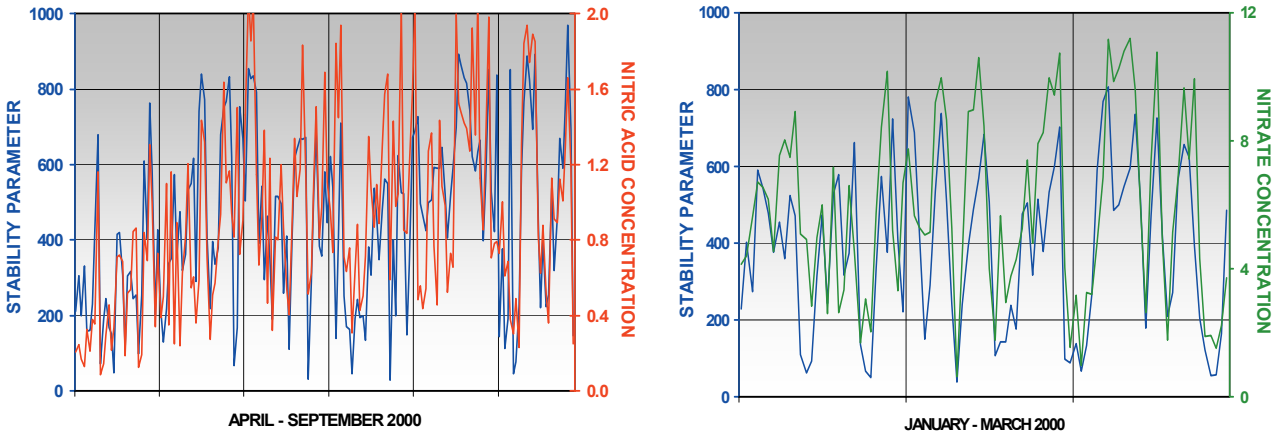

Fig.22 and 23: Interpretation of the temporal pattern of nitric acid (summer) and of particulate nitrate (winter) in the light of the mixing properties of the lower atmosphere.

4. **Major conclusions**

The large decrease in SO_2 emissions between 1980 and 2000 (from 3440 to 700 kt/yr) has resulted in a net decrease in both the air concentration and the wet deposition of sulfur compounds in Italy. Air concentration values for SO_2 are largely below the limits set by EU for the protection of the ecosystem.

A less satisfactory situation is observed for nitrogen compounds. NOx emissions peaked in 1992, with a decreasing trend from 1992 to 2000. NO_2 concentration showed a somewhat decreasing trend during the last decade and is well below the EU limits, but nitric acid and particulate nitrate air level are substantially stable or even increasing (Ispra station) during the last five years. Ammonia emissions were quite constant over the last two decades, with an increase in emissions from the transport sector. Reduced nitrogen concentration in the atmosphere was stable, with an increase for ammonium at the Ispra station during the last five years.

Ozone pollution in Italy showed no downward trend during the last decade, and the EU limit for the protection of vegetation is often exceeded during the summer at both the north and the central station (AOT40 of the order of 30.000 ppb/h). Monthly average ozone values exceeding 60 $\mu g/m^3$ (northern Italy) and even 80 $\mu g/m^3$ (central Italy) are common during the summer period.

The study of the pollutant concentrations as a function of wind direction shows that at Ispra the highest concentrations occur when the prevailing wind direction is from the south, where the urban and the industrial areas are located.

At the Montelibretti station, instead, no prevailing wind direction leading to high pollutant concentrations was identified. The area of Rome, which generates pollution, is sited at SW with respect to the EMEP station, and the transport of the air masses from this direction generally occurs during the sea-breeze, that is only during early afternoon hours. Hence, the time duration of this process is not long enough to influence 24-hours average concentrations. As far as ozone is concerned, instead, the sector distribution analysis carried out over 1-h average values showed a net increase in ozone concentration when the wind blows from the urban area of Rome.

More than the horizontal wind direction, a driving force for the 24-h average concentration of pollutants in Italy is the mixing of the lower atmosphere.