IL NUOVO CIMENTO Vol. 26 C, N. 12 Novembre-Dicembre 2003
DOI 10.1393/ncc/i2004-10002-6

Ozone in Lombardy: Years 1998-1999

L. Sesana([1])(*), S. Begnini([1]), D. Toscani([1]), U. Facchini([1]), A. Balasso([2]) and P. Borelli([2])

([1]) *Istituto di Fisica Generale Applicata, Università di Milano - via Celoria, 16 20133 Milano, Italy*
([2]) *Direzione Generale Tutela Ambientale - Regione Lombardia, Italy*

(ricevuto il 27 Gennaio 2004; approvato il 3 Marzo 2004)

Summary. — Photochemical pollutants, especially ozone, have reached very high levels in Lombardy in recent years, with peaks of up to 150 ppb in late spring and summer. Lombardy, lying on the Po Plain, supports a large number of cities and industries and these, along with heavy traffic, produce copious amounts of primary pollutants such as nitrogen oxides and numerous volatile organic compounds. Furthermore, the peculiar orography of this region fosters the stagnation of air masses on a basin-scale and the presence of diurnal breezes towards northern areas, along with the evolution of the Mixing Layer, spread the polluted air masses over a large territory. Numerous stations in Lombardy give the concentrations of ozone and of nitrogen oxides. In this paper, ozone measurements carried out at the plain area around Milan and at pre-alpine sites in the spring and summer 1998 and 1999 will be shown and discussed, focusing on the months of May and July. The study of temporal and spatial behaviour of ozone goes hand in hand with the analysis of the Boundary Layer's evolution. A number of radon stations were operating in Milan and in other sites in Lombardy. Measurements of atmospheric concentrations of radon yield an index of atmospheric stability, of the formation of thermal inversion, of convective turbulence, and of the movement of air masses, and hence they are very relevant to the understanding of the conditions of atmospheric pollutants.

PACS 92.60.Hp – Chemical composition and chemical interactions.
PACS 92.60.Sz – Air quality and air pollution.

1. – Introduction

Photochemical pollution is one of the main sources of noxious gases present in the air of metropolitan and surrounding areas. Ozone is a major photochemical pollutant.

(*) E-mail: lucia.sesana@unimi.it

TABLE I. – *Indicators as defined by Sillman* [4].

Indicator	NO_x sensitive	VOC sensitive
NO_y	< 20 ppb	> 20 ppb
O_3 / (NO_y- NO_x)	> 7	< 7
(O_3-40/ (NO_y- NO_x)	> 5	< 4
HCHO/NO_y	> 0.28	< 0.28
H_2O_2 / HNO_3	> 0.4	< 0.4

In Lombardy, a large number of cities with heavy traffic and industrial plants produce copious amounts of pollutants such as nitrogen oxides and numerous volatile organic compounds, namely the precursors of ozone.

Kleinman [1,2] described two regimes in ozone formation processes, one in which VOC concentrations dominate and another in which NO_x concentrations dominate:

– where NO_x concentrations are low, ozone production is strongly influenced by NO_x concentrations, and weakly influenced by VOC concentrations;

– where NO_x concentrations are higher, ozone production basically depends on VOC concentrations.

In a wide investigation, Sillman [3, 4] analysed the NO_x–VOC–O_3 system and developed a set of parameters useful for establishing whether ozone concentration was more dependent on VOCs or NO_x (table I).

In a study conducted by Maffeis *et al.* [5] and by De Martini *et al.* [6], the urban area of Milan was found to be the major source of these pollutants.

The presence of diurnal breezes towards northern areas, along with the evolution of the Mixing Layer, spread the polluted air masses over the plain and toward the lakes area and the Prealps.

The Environment Department of the "Regione Lombardia" and the Provincial Administrations contribute hourly NO_x and ozone measurements as well as meteorological data by the Regional Station Network. In the present analysis the data were gathered within an area including the city of Milan and extending around and north of it to the foot of the Prealps.

The Applied Physics Institute of the University of Milan conducted ozone measurements both in the Prealps [7] and in Milan, at the Torre di Brera [8].

A key parameter to understand air pollution, together with the intensity of pollution itself, is the rate of dispersion into the atmosphere (wind and vertical diffusion). In fact, besides the usual meteorological data, a number of radon stations were operating in Milan and in other sites in Lombardy [9-11]. Continuous measurements of radon near the ground give a valuable method for monitoring the conditions of stability or turbulence of the atmosphere on a local scale.

The paper reports the results and the analysis of ozone presence in the area around Milan in spring and summer of 1998 and 1999.

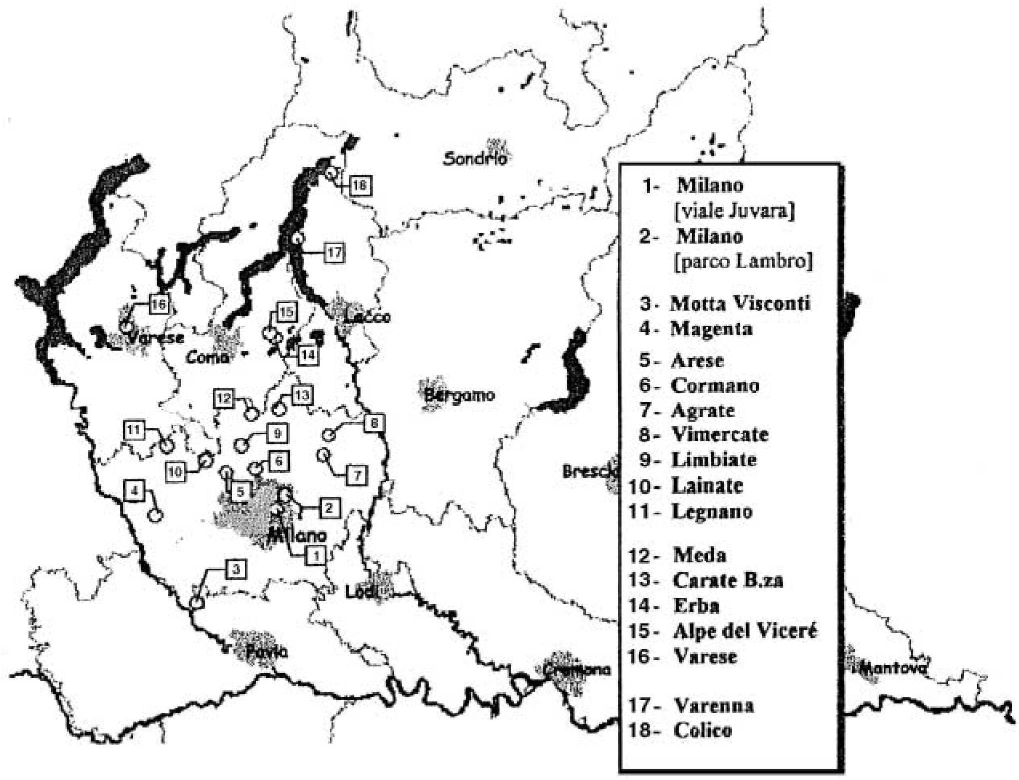


Fig. 1. – The area investigated and the stations considered in the analysis.

2. – Materials and methods

a) *The regional network stations*

The area studied is shown in fig. 1.

The data taken into consideration are those from stations where both NO_x and ozone were measured, in remote locations or those situated in areas not directly affected by traffic emissions, *i.e.*

– in the city of Milan: Juvara and Parco Lambro;

– in the plain around Milan: Magenta, Motta Visconti, Cormano, Arese, Legnano; Lainate station for nitrogen oxides only;

– in the hilly area to the north of Milan: Agrate, Vimercate, Carate, Limbiate and Meda;

– in the pre-Alpine area to the north of Milan: Erba, Varese and the high altitude station of Alpe del Viceré;

– on the east coast of Lake Como: Varenna and Colico.

b) *The stations of the Physics Institute*

– The ozone stations. The station Torre di Brera is located 30 m height over the city level, in the center of the town. Ozone measurements at Torre di Brera [8] permitted to gain data for the city center which would not be directly affected by local emissions. Not being directly exposed to vehicle traffic, the station yielded excellent measurements of photochemical pollution levels. Other ozone stations operated in the Prealps at Alpe del Viceré, Monte Barro, Monte Bisbino [7].

– The radon stations. Two radon stations operated in the garden of Physics Institute in the east area of Milan. Another two radon measurements stations were positioned at Erba and Alpe del Viceré. The models used for analysis of radon data are described in recent papers [12].

3. – The town and the plain

3˙1. NO_x. – The concentration of nitrogen oxides is generally dependent on the location of the station and on motor traffic in the area around the station. Let us discuss the data of Juvara station in May 1998; this station is situated in a road with little traffic in the east of Milan.

The maximum concentrations of NO are observed in the morning and in the late evening hours. The morning peaks, usually reached between 7:00-8:00, vary widely, generally being lower than 80 ppb, with a few days in which values of up and even beyond 100 ppb are reached. At this time of the day, nitrogen monoxide is due to intense motor traffic. The peak is of very short duration: NO is very reactive and oxidizes rapidly into NO_2 (fig. 2a and b).

The peaks of the late evening hours are observed both for NO and NO_2 around 22:00 and 23:00 and are at their highest on nights when there is a ground-based thermal inversion and thus the Stable Nocturnal Layer forms.

The nocturnal peaks of NO_2 are followed by a rapid decrease in concentrations. NO_2 concentrations begin to increase again with the start of urban traffic the following day. In the early hours of the day, two processes cause concentrations to fall again after a brief peak, generally between 7:00 and 9:00, has been reached. These are:

– the photochemical dissociation of NO_2 and the consequent formation of ozone;

– the establishment of vertical thermal turbulence which carries pollutants upwards and reduce the concentrations at ground level.

NO and NO_2 concentrations measured in stations located in the plain area to the north and west of the city were very high but lower on the whole than those observed in Milan. Very low concentrations were measured at Motta Visconti station to the south of Milan, an agricultural area with very limited traffic.

3˙2. *Ozone*. – Figure 3 shows the comparison between ozone concentrations measured at Juvara station and Brera Tower from 23 May to 2 June 1999. It is interesting to observe that the measurements at height 30 meters, Brera station, give a concentration of ozone greater than the one observed at ground, at Juvara station. In fact, the NO production at the ground shall reduce local ozone formation due to titration reaction.

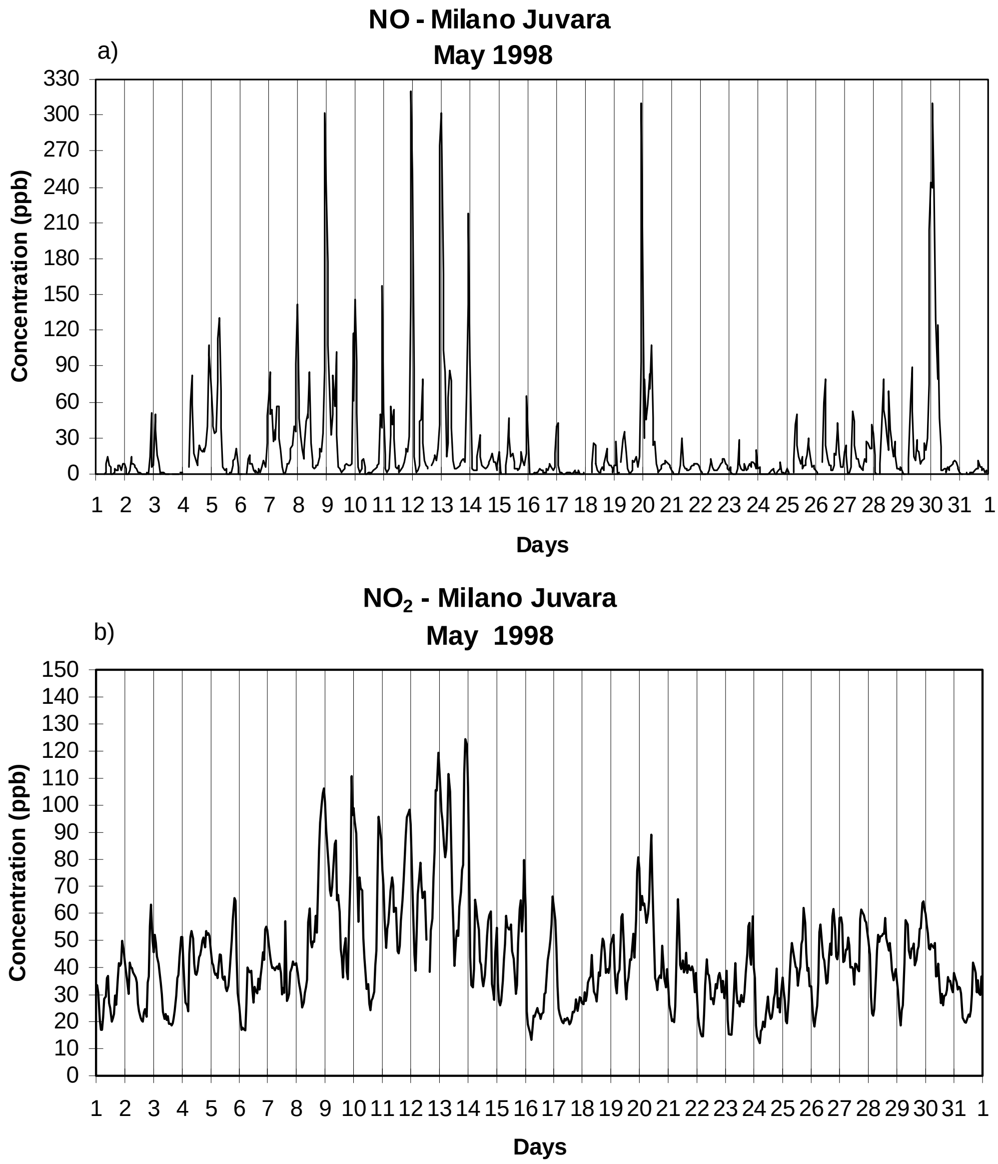


Fig. 2. – a) Nitrogen monoxide concentration at Juvara station in May 1998. b) Nitrogen dioxide concentration at Juvara station in May 1998.

In figs. 4a, b and c we represent the ozone data for May 1998 in three stations sited in the plain around Milan: in the plain area to the North, Cormano; to the West, Magenta, and to the South, Motta Visconti.

When examinating ozone data for the plain it can be seen clearly that in the measurement periods there are some series of days characterized by very high ozone concentrations.

In the days of intense ozone the meteorological conditions are particularly favourable

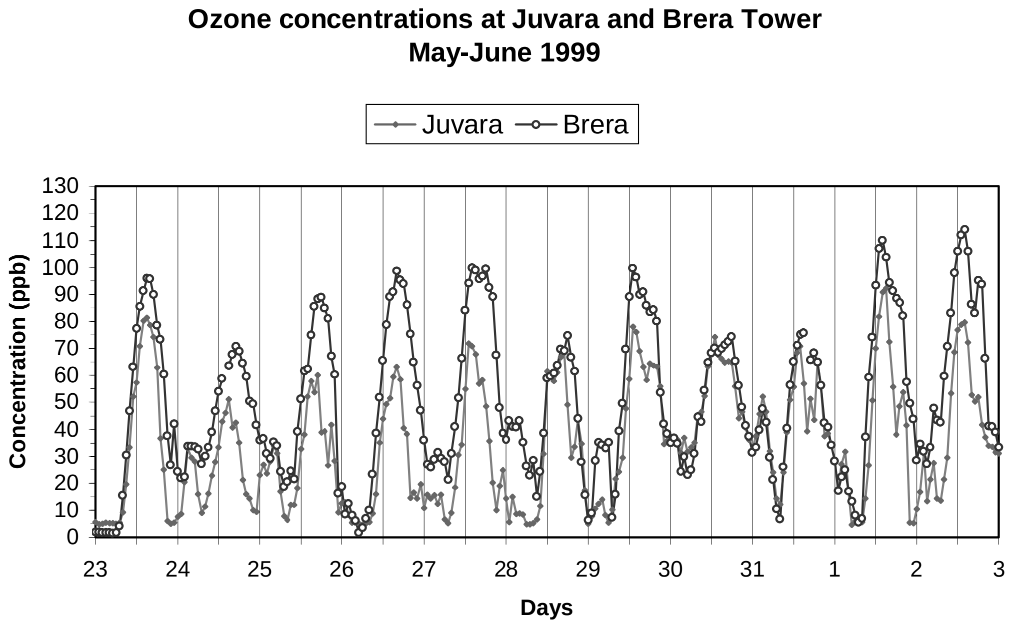


Fig. 3. – Ozone concentrations at Juvara and at Brera Tower, from 23 May to 2 June 1999.

for the ozone production. As an example, we quote the data of days 9-13 May 1998, 19-24 July 1998. In these days of strong sunshine, high temperature and high pressure, there is an interesting similarity in daytime ozone concentration patterns for all the different stations sited in the plain area, with ozone levels increasing from those at 08:00 to peak levels generally of around 90–100 ppb at about 15:00. This is followed by a decrease in ozone levels until the lowest concentrations are reached at around 23:00–24:00.

Generally speaking, night time concentrations remained low at the stations in the plain area; Legnano station, sited in the plain to the north-west of Milan, measured a daytime concentration pattern similar to that for the stations in the plain area, but presented a peak of 20–40 ppb at around 04:00 almost every night.

What appears very interesting is that the Brera data give similar or only slightly higher peak ozone concentrations than the whole plain. Figures 5a and b show the comparison between these concentration trends for two different periods: 9-13 May 1998 and 23 May-2 June 1999. Brera Tower well represents the behaviour of ozone in the whole plain around Milan.

3˙3. *Radon measurements and the sequences of high ozone concentration.* – After a day of strong sunshine, a temperature inversion based at ground level forms in the evening hours. This is followed by the formation of a Stable Nocturnal Layer [13]. In conditions of high stability, this layer extends over the whole plain as far as the Prealps. The Planetary Boundary Layer (PBL) is divided into two regions:

– the Stable Nocturnal Layer, which extends vertically toward the height of the inversion;

– above this, the Residual Layer.

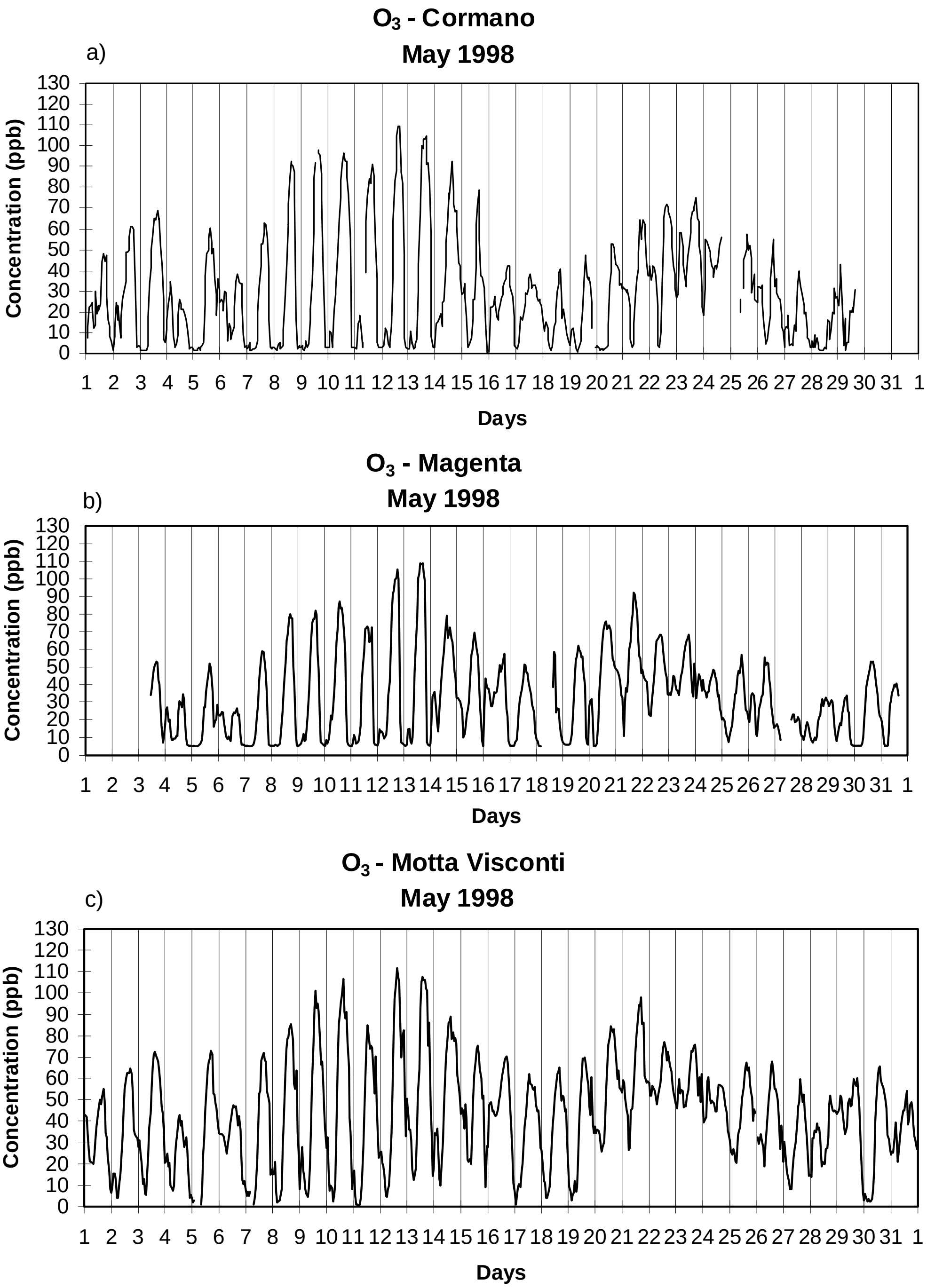


Fig. 4. – Ozone concentration in the plain area to the north of Milan, Cormano station, in May 1998 (a), to the west of Milan, Magenta station, in May 1998 (b) and to the south of Milan, Motta Visconti station, in May 1998 (c).

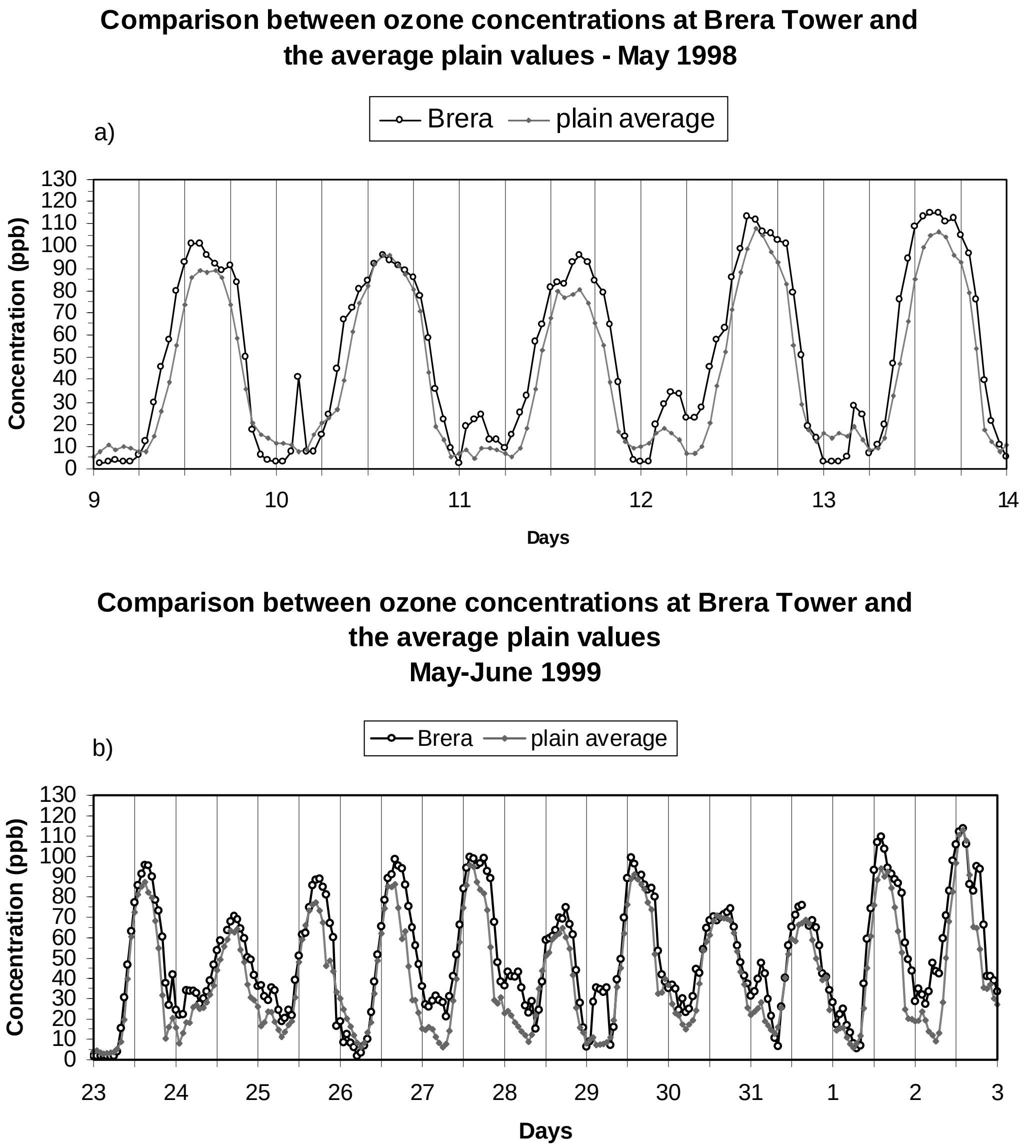


Fig. 5. – Comparison between ozone concentrations at Brera and the average values for the plain from 9 to 13 May 1998 (a) and from 23 May to 2 June 1999 (b).

The inversion is destroyed when the sun rises, and the height of the Mixing Layer increases hourly to reach a maximum height in the afternoon.

A hour-by-hour indication of the conditions of stability or turbulence in the low troposphere can be obtained directly by measuring radon concentration. Radon 222 is a natural radioactive tracer emitted by the ground in a nearly homogenous way over large areas and time spans. It has a half-life of 3.8 days, long enough to permit analysis and since it is a noble gas, does not participate in chemical reactions.

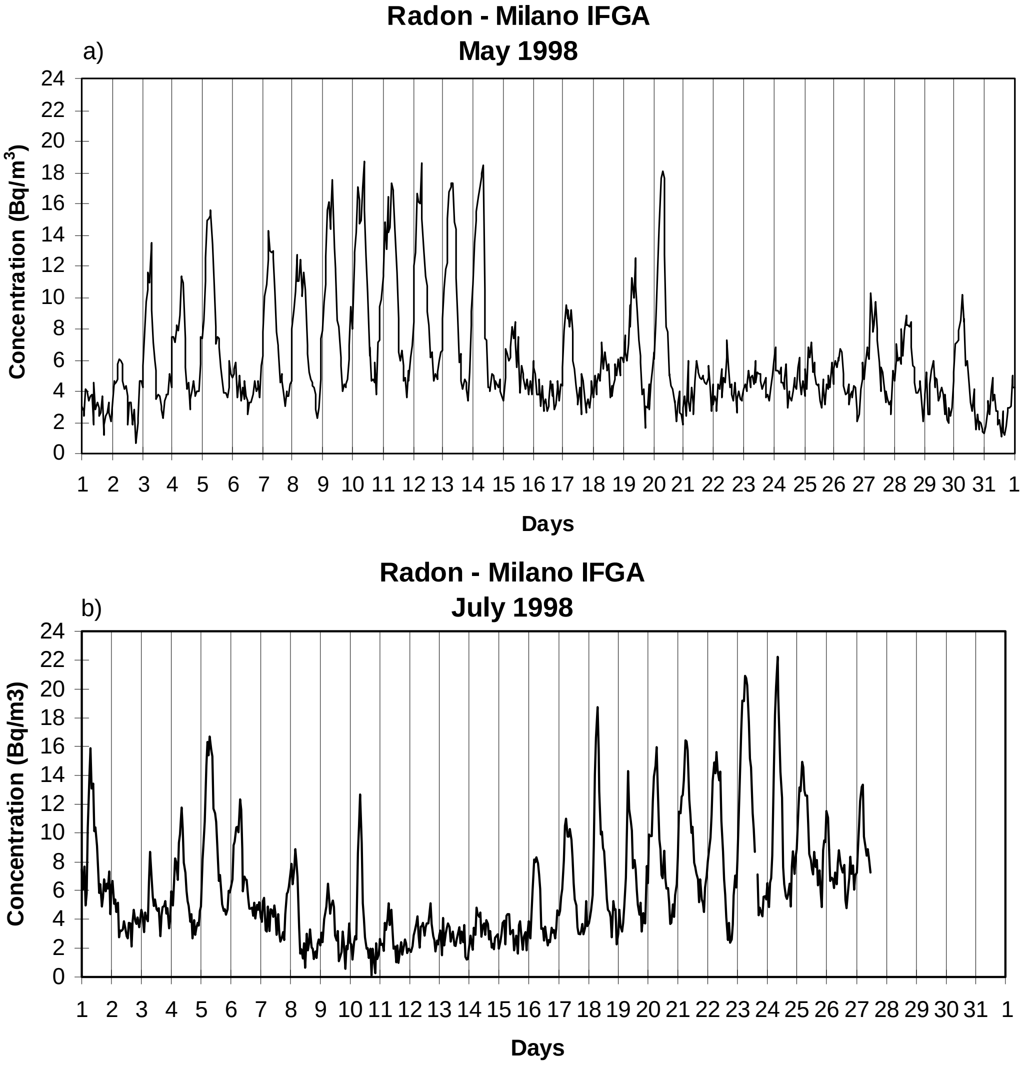


Fig. 6. – Radon concentration in Milan (Applied Physics Institute, IFGA) in May 1998 (a) and in July 1998 (b).

Figures 6a and b show the radon measurements conducted in May and July 1998 in the garden of the Physics Institute, not far from Juvara station. Wide variations in radon levels over single days and over sequences of days can be seen.

Radon accumulation is a direct index of the particular nocturnal conditions when the Stable Layer forms. As can be seen, some nights in Milan the radon concentration reaches values as high as 15–20 Bq/m^3. These are clear, windless nights following days of intense sunshine. Radon exhaled from the ground at nights accumulates in the Stable Nocturnal Layer. Particularly substantial accumulation was observed during the nights of 9-13 May and 18-24 July '98.

Nocturnal radon accumulation can be described by means of a box model, which allows the determination of the equivalent mixing height, a quantitative parameter of the intensity of the vertical diffusion through the Stable Nocturnal Layer [12].

From the analysis of the radon data it results that the equivalent height is of the order of 50–70 meters in May, 50 meters in July, with values of about 30 meters for 23 and 24 July.

The Stable Nocturnal Layer forms around 21:00-22:00 and dissolves in the early morning at around 7:00, with the sun rising. Mixing extends upwards hour by hour to reach a maximum value for the height of the Mixing Layer in the afternoon. The descent of radon concentration toward minimum values in the late afternoon corresponds to this process of vertical atmospheric turbulence.

In these meteorological conditions, several distinct phases can be distinguished in the daily evolution of ozone concentrations.

- At ground level in the early morning, the cloud of NO_x and VOC precursors is still concentrated.
- Ozone-producing reactions begin. It is possible that the compounds trapped during the night in the Stable Nocturnal Layer contribute to the morning increase in ozone levels, *e.g.*, the photolysis of nitrous acid produces OH radicals.
- In the morning the continuous emission of precursors leads to the formation of ozone, whose concentration increases until it peaks in the early hours of the afternoon.
- Vertical and horizontal mixing in the subsequent hours distributes the ozone over vast areas; ozone mixes with ozone present at height.

3˙4. *Ozone and NO_x in the late evening and at night.* – Evening and night time levels of ozone and nitrogen oxides show particularly interesting behaviour.

a) First consider nights with a ground-based temperature inversion and thus with a Stable Nocturnal Layer. The presence of the Stable Layer, as said, is indicated by radon accumulation. Pollutants emitted by the evening traffic accumulate in the Stable Nocturnal Layer. NO reacts with the ozone present, resulting in a decrease to a few ppb of the ozone concentration. As ozone concentrations decrease, NO_2 concentrations increase, NO_2 being one of the products of the titration reaction. The presence of NO_2 indicates that the drop in ozone levels observed in the town is mainly due to its reaction with NO, rather than to deposition on the ground.

Figures 7a and b show ozone and NO_2 concentrations for the Milan (Juvara) and Motta Visconti stations on the 11 and 12 May 1998, when the Stable Nocturnal Layer forms.

The correlation between decrease in ozone concentration and increase in NO_2 concentration was not observed at the Motta Visconti station, located in an isolated site. Decrease in ozone concentration here is thus mainly attributable to deposition on the ground, which depletes ozone in the Stable Nocturnal Layer.

b) On days when there is scarce solar insulation or when there is rain there is no significant variation in vertical diffusion processes for day and night; if there is strong wind the mixing up extends over a large area and upwards both during the day and at night. Radon does not accumulate in the night, ozone in fact at the late hours of the night presents an intrusion of 40-50 ppb, measured at all stations. Figures 8a and b show

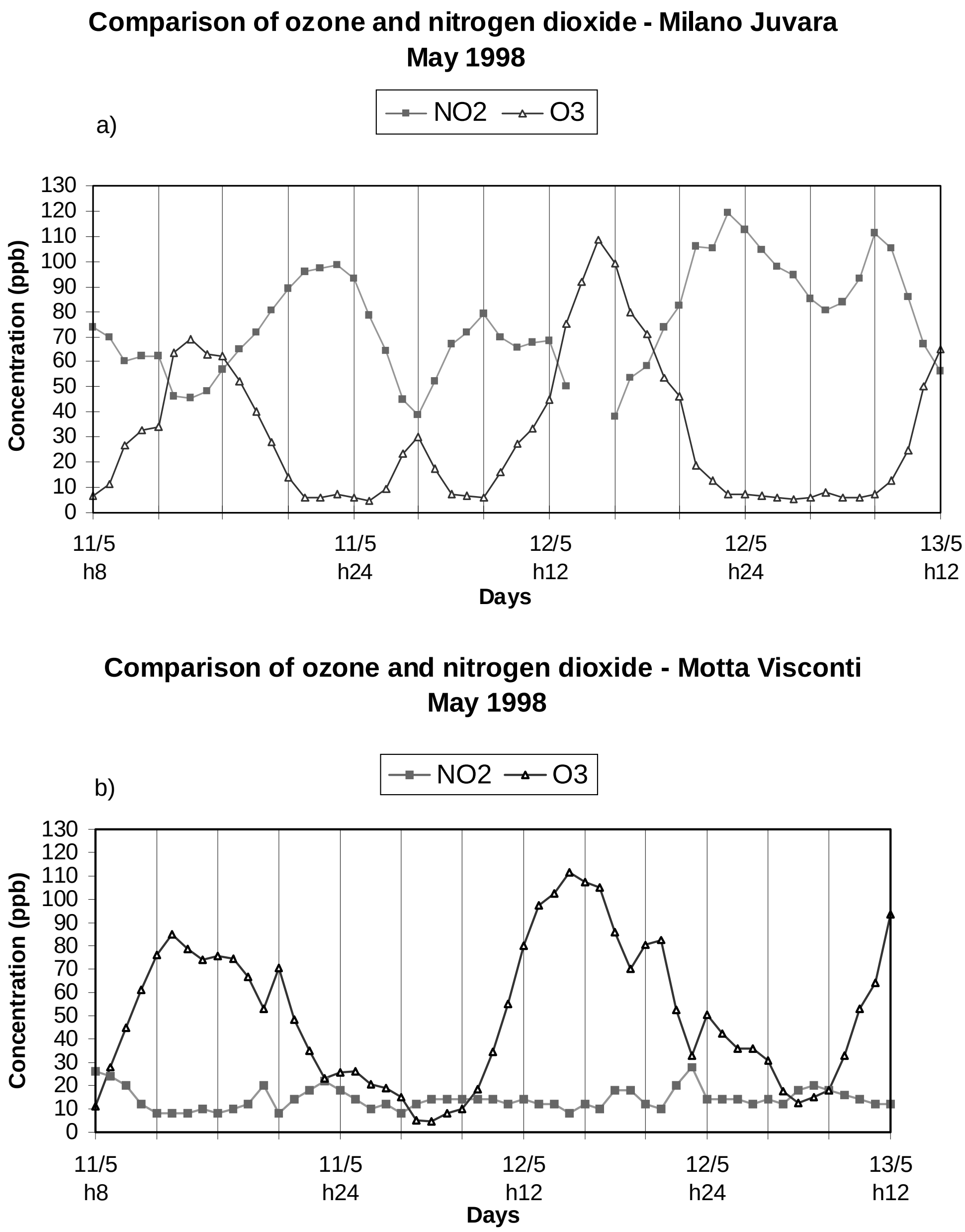
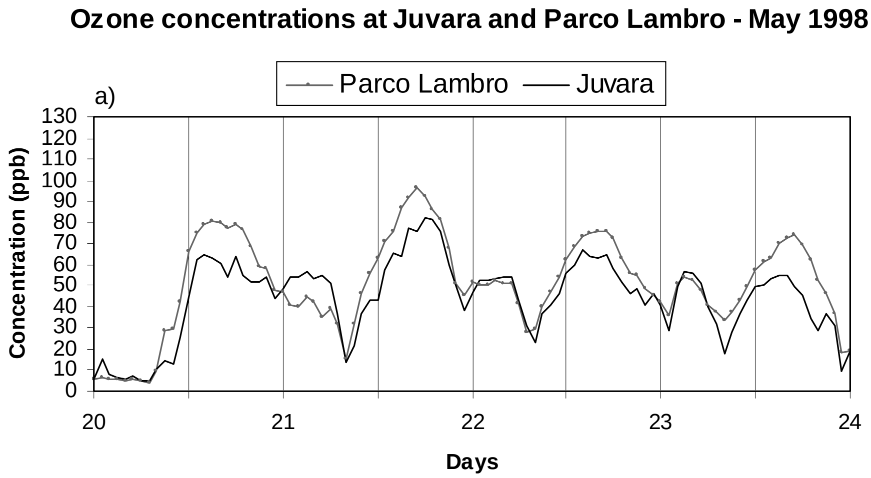


Fig. 7. – Ozone and nitrogen dioxide concentrations at Juvara (11-12 May, 1998) (a) and at Motta Visconti (11-12 May, 1998) (b).



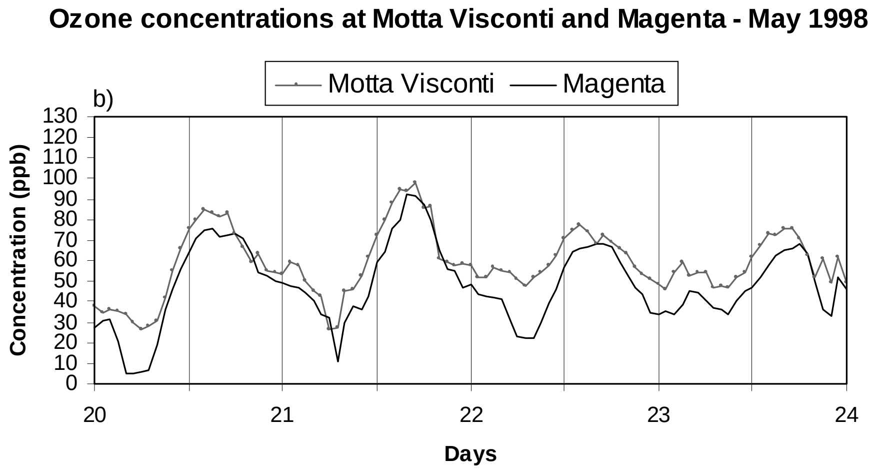


Fig. 8. – a) Ozone concentrations at Juvara and Parco Lambro stations from 20 to 23 May 1998, days in which the Stable Nocturnal Layer does not form. b) Ozone concentrations at Motta Visconti and Magenta stations from 20 to 23 May 1998, days in which the Stable Nocturnal Layer does not form.

the 20-23 May '98 ozone concentrations in four stations of the analysis area surrounding Milan. The nocturnal ozone is due to the mixing with high-altitude ozone reservoirs.

3˙5. *A possible mode for ozone concentrations enhancement.* – Nitrous acid, HONO, forms in the night and remains in the atmosphere until the following morning, when the first sunlight splits the acid to form NO and radical OH.

The process of formation of HONO is not known precisely, it forms from reactions between NO_2 and H_2O as liquid water or water vapour. So, to estimate the HONO nocturnal levels, we have to consider the NO_2 concentrations.

As we said, the nocturnal formation of NO_2 in the urban atmosphere is essentially due to the evening and nocturnal traffic, namely the NO emissions; these interact with ozone.

Nocturnal NO_2 concentrations are particularly high in the nights where there is the Stable Nocturnal Layer, when the pollutants accumulate at low levels.

In some measurements conducted at the station Torre di Brera [14] the presence of HONO was observed, with levels of 10 ppb, by the DOAS technics.

Recent interesting researches conducted by the Heidelberg school [15, 16] studied in detail the formation of HONO in a peripherical area of the city of Milan and , in particular, the presence of the radical OH in the early morning; according to these researches, during the first 4 to 6 hours after sunrise HONO photolysis is by far the most important OH source in the low troposphere. The presence of nocturnal HONO sensibly increases the ozone production.

4. – Brianza and Prealps. Ozone toward northern areas

4·1. *Brianza area*

NO_x

NO concentrations measured at stations located in the hill area to the north of Milan were lower in general than those observed in the plain area surrounding Milan.

NO_2 concentrations were, on the whole, only slightly lower than those for the plain area.

Ozone

In days of intense ozone the daytime ozone concentration pattern in Brianza area was similar to that for the plain area, with similar or slightly higher daytime peak values in the early afternoon. Given the similarity in concentration patterns observed in the Brianza hill area, we present the values averaged over all the stations in it. Figures 9a and b compare the average concentration pattern for the Brianza area with that for the Magenta, Motta Visconti, Cormano and Arese stations, situated in the plain in 9-13 May '98 and 19-24 July '98.

We note that during daytime hours the wind moves from south to north, while the nocturnal wind blows southerly.

Quite interesting are the nocturnal ozone peaks observed in Brianza stations. Nocturnal peaks in ozone concentration, usually within the 30–40 ppb range, were observed in all the stations situated to the north of Milan, closer to the Prealps. These peaks can be attributed to the transport of ozone from prealpine heights.

In the Prealps, for instance at Alpe del Viceré, at 1000 meters height, the ozone levels persist high overnight (see further). The mountain breezes in the night are directed toward the plain. The nocturnal ozone reaches values of 30–40 ppb in Brianza, but quite lower values in the plain.

It is interesting to note that the ozone coming from Prealps area moves under the Stable Nocturnal Layer.

In nights where the Stable Nocturnal Layer is not formed the nocturnal peaks of ozone are comparable in the whole area, the plain and the Brianza.

In figs. 10a, b, c, d are shown the Kriging analysis (a technique for interpolation of data) of ozone concentrations [17] for the whole studied area at respectively 10:00, 12:00, 14:00, 16:00 hours of 12 May'98. We can see the ozone lake overhanging at this time the plain and the hilly area around Milan.

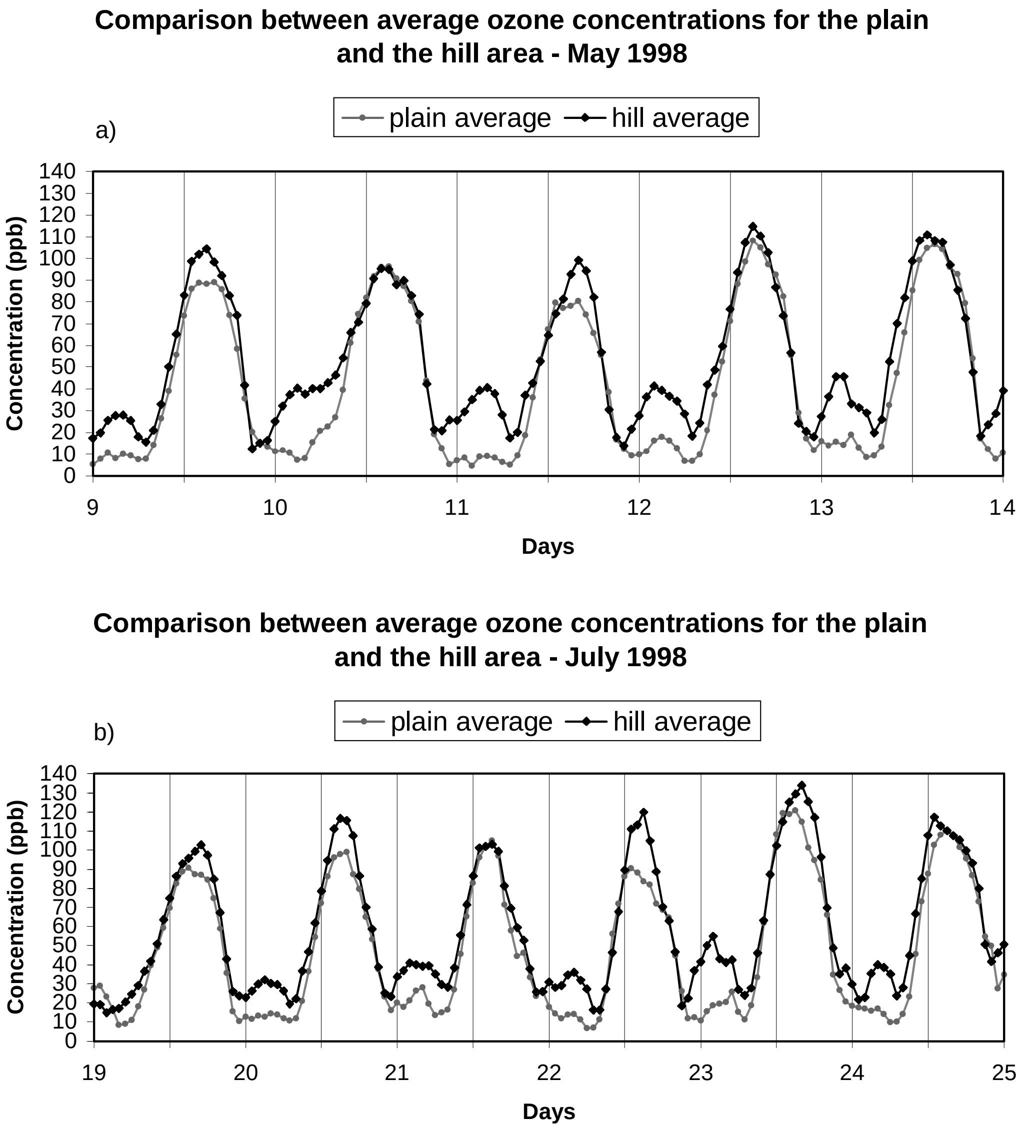


Fig. 9. – Comparison between average ozone concentrations for the plain area (stations of Motta Visconti, Magenta, Cormano and Arese) and the hill Brianza area (stations of Agrate, Vimercate, Carate, Meda and Limbiate) from 9 to 13 May 1998 (a) and from 19 to 24 July 1998 (b).

4·2. *The Prelpine area*

NO_x

Far lower concentrations of nitrogen oxides were measured at the foot of the Prealps and at the lakes than in Milan area. Peaks in NO concentrations were generally in the 10–40 ppb range, while peaks measured in NO_2 concentrations were in the range of 30–50 ppb.

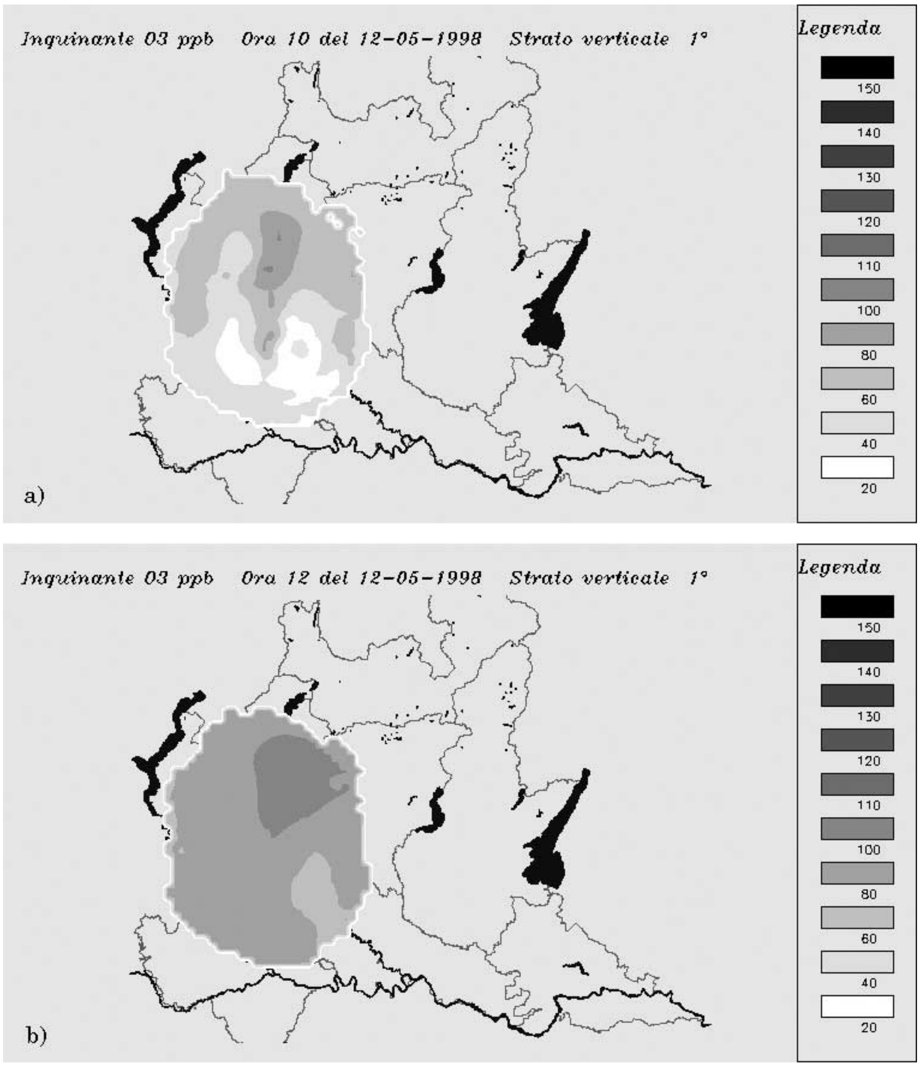


Fig. 10. – Kriging analysis for ozone concentrations on 12 May 1998.

NO levels were almost zero and NO_2 levels were normally below 20 ppb at the high-altitude station at Alpe del Viceré.

4˙2.1. Stations at the foot of the Prealps: Erba and Varese

Ozone

In sunlight hours, the breeze blowing from South to North carries ozone precursors from the plain towards the Prealps, accounting for the high ozone concentrations measured in the Prealpine areas. Maximum ozone concentration values for Erba during the intense ozone production days (9-13 May'98 and 19-24 July '98) are generally higher than those for the Brianza hill area (fig. 11) in particular on 13 May, a day characterized

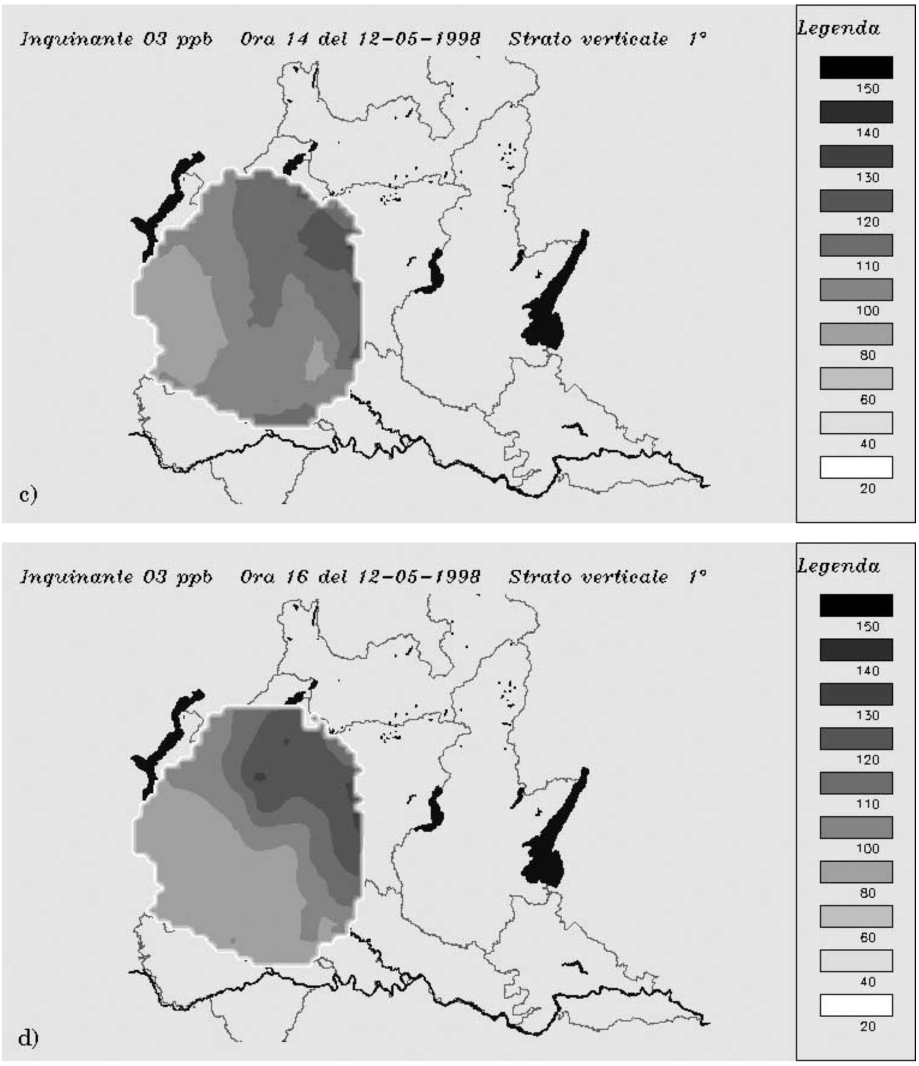


Fig. 10. – Continued.

by an episode of high ozone concentration.

Levels measured at Varese were on the whole comparable or slightly lower (in general around 10-15 ppb) than those found at Erba; on 13 May the difference between the daytime peaks is of about 40 ppb.

High nocturnal ozone concentrations were measured at Erba; the values measured at Varese in the night, between 40 and 70 ppb, are comparable or only slightly lower than those observed at Erba. These nocturnal values can be attributed both to scarce NO concentrations and to the downward transport of ozone from the Prealps by the night-time mountain breeze. Further evidence for the role of the wind at night comes from radon measurements conducted at Erba (see further).

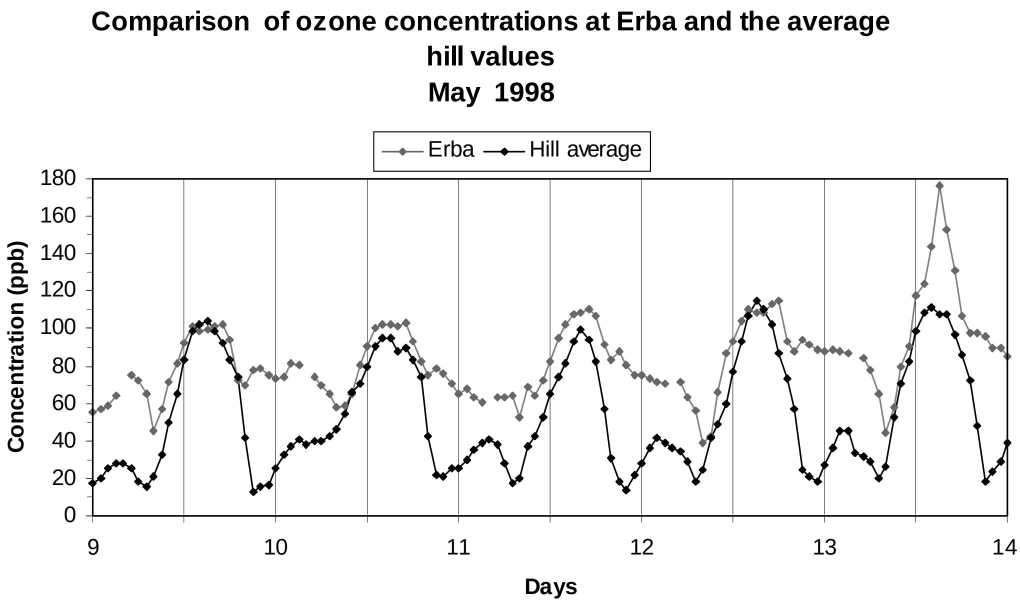


Fig. 11. – Comparison of ozone concentrations at Erba and the average values for the hill Brianza area from 9 to 13 May 1998.

4·2.2. The high-altitude station of Alpe del Viceré

Ozone

Ozone measurements were conducted from 13 May to 31 July 1998 by a mobile station belonging to Como Provincial Administration. Maximum concentrations are generally higher than those for the Brianza hill area on the days analysed. Substantial peaks in the order of 140–150 ppb were observed in days of intense ozone production, with a peak of 165 ppb being measured on 13 May (fig. 12a and b). Daytime peaks occurred at more or less the same time as at Erba.

With respect to nocturnal patterns, in days with high ozone concentrations ozone persists at values as high as 80–90 ppb (fig. 12b). The presence of ozone at night is due on the one hand to very low concentrations of NO and, on the other, to the absence of the Stable Nocturnal Layer.

Radon

The pattern of nocturnal accumulation and daylight diluition of radon was observed in Erba almost every day of the study period (fig. 13a).

In some days a modest decrease in radon concentrations lasting only a few hours often took place in the night during the radon accumulation. The concentration peaks up again in the early hours of the morning (up to 20 Bq/m^3). This is attributable to the influence of mountain breezes carrying radon-poor air down from the Prealps.

The average radon concentration at Alpe del Viceré (fig. 13b) was at 4–8 Bq/m^3 and almost constant from day to night. Nocturnal accumulation did not take place. The peaks observed around 10-11:00 were due to the slope winds carrying radon-rich air up from the Erba basin.

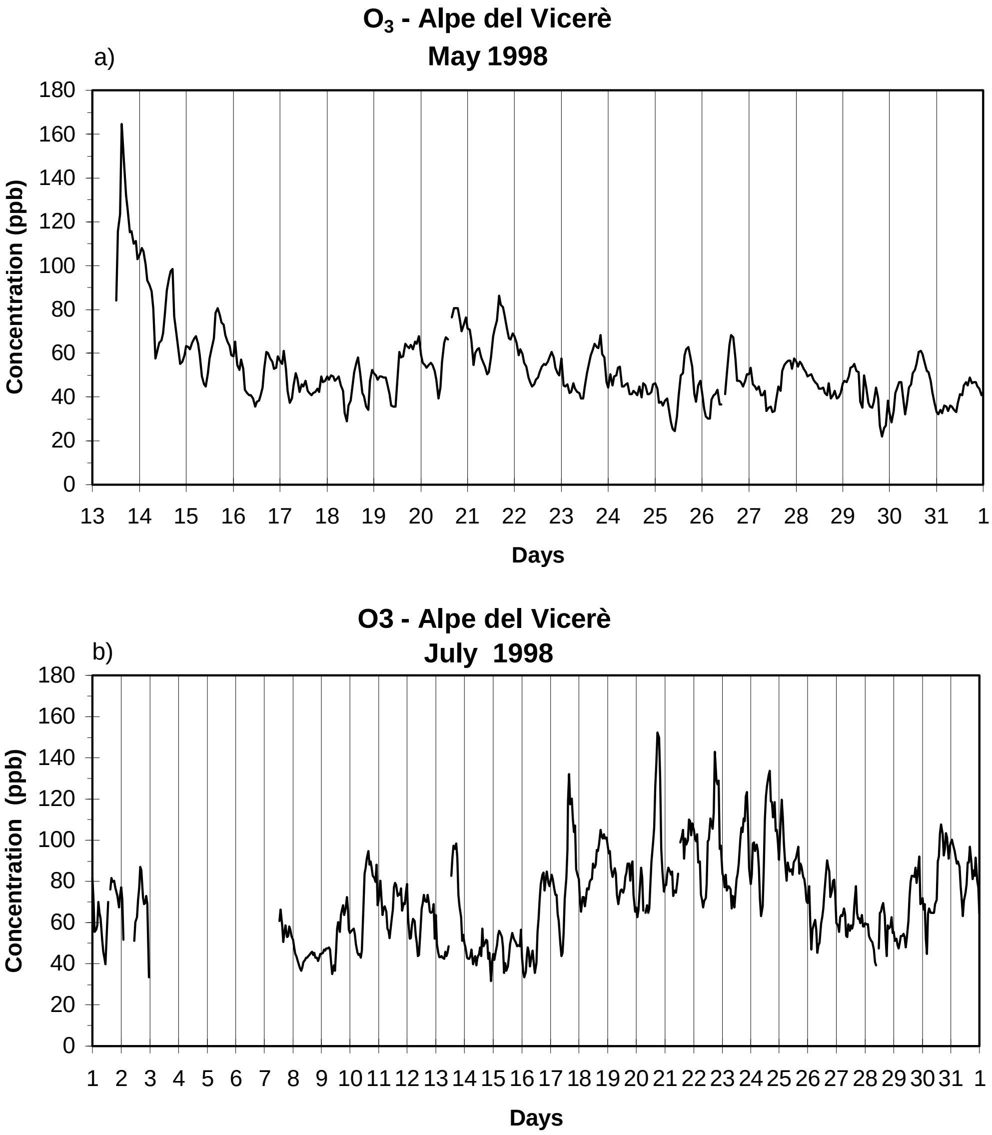


Fig. 12. – Ozone concentration at Alpe del Viceré in May 1998 (a) and in July 1998 (b).

4.2.3. Stations on the east coast of Lake Como: Varenna and Colico

Ozone

In May '98 these two stations showed interesting ozone concentration patterns. In days of intense ozone production values measured at Varenna were always higher than those for the Brianza area, with peak concentration values normally being higher by about 15–30 ppb in Varenna than in Brianza. Early morning values were also always higher. Afternoon peak values measured at Colico for the same month are comparable with or slightly higher than those for the Brianza area. The delay in onset of the afternoon peak

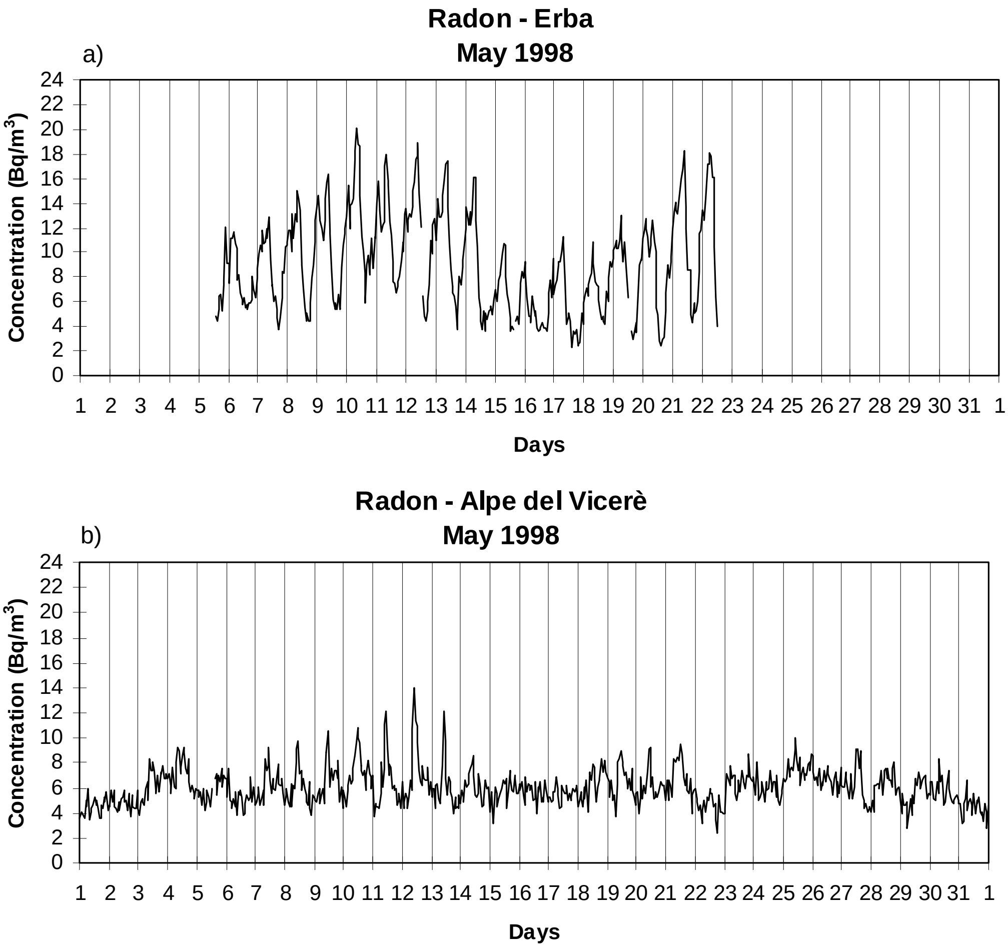


Fig. 13. – Radon concentration at Erba in May 1998 (a) and at Alpe del Vicerè in May 1998 (b).

is due to the transport of ozone and its precursors from the plain areas. This delay is of about 1–2 hours in Varenna and about 2–3 hours at Colico. The 13 May episode of very high concentrations was measured at both stations.

4·3. *Episodes of very high ozone concentrations*. – On some days in the late spring and early summer, ozone peaks of up to and over 150 ppb were recorded in the Prealpine area as well as in the Canton Ticino area [18, 19]. They have generally been attributed to the northwards transport of a cloud of ozone precursors and ozone in high concentrations. In year 1998, episodes of this intensity took place on 13 May, 5 and 19-21 June and 23 and 24 July.

The 13 May episode, illustrated and discussed by Neftel *et al.* [20] and by Lanzani *et al.* [17] has also been subject to a detailed model analysis by the Joint Research Centre in Ispra [21]. With respect to our analysis, peak ozone concentration values were recorded at Alpe del Viceré (fig. 12a) and at Erba (fig. 14a) at 15:00 on 13 May 1998 and,

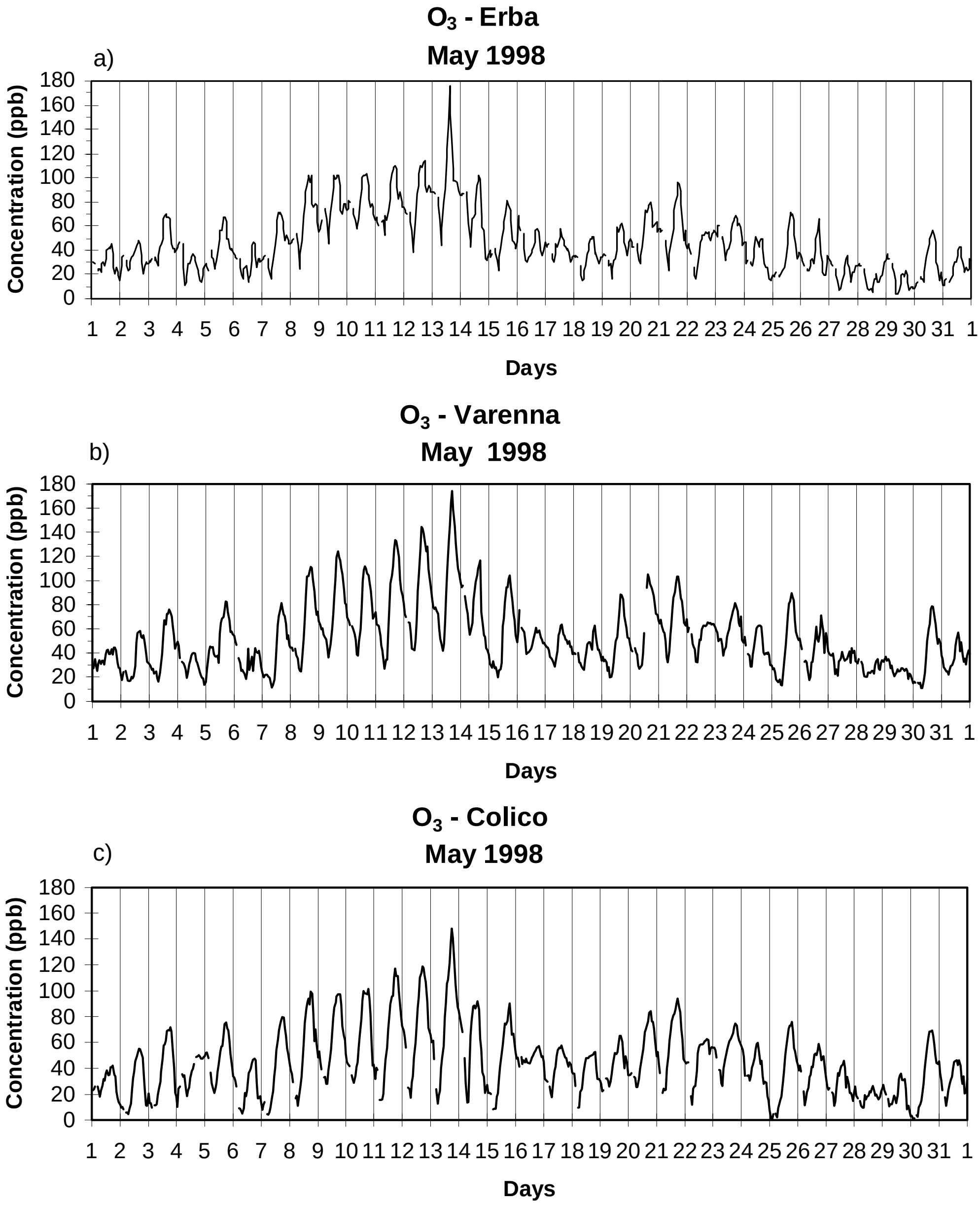


Fig. 14. – Ozone concentration at Erba in May 1998 (a), at Varenna in May 1998 (b) and at Colico in May 1998 (c).

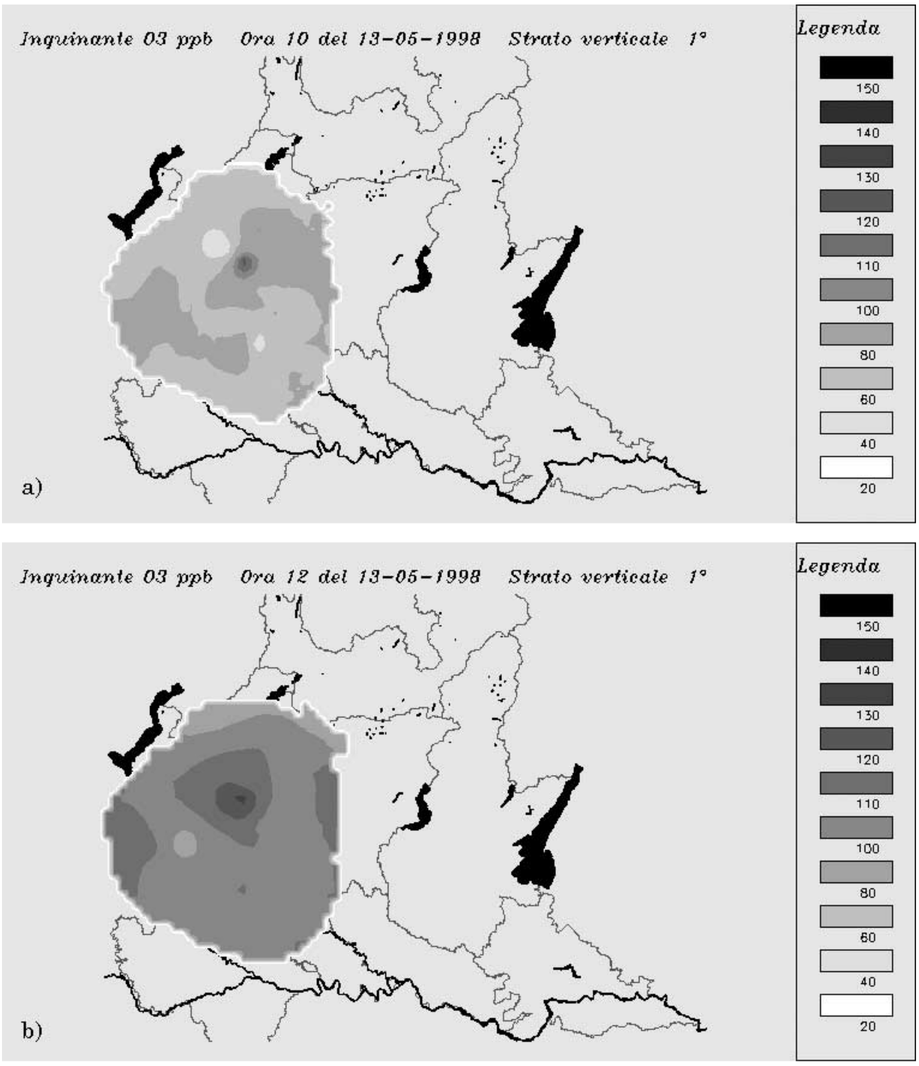


Fig. 15. – Kriging analysis for ozone concentrations on 13 May 1998.

after a lapse of few hours, at Varenna and Colico (figs. 14b and c), with the intensity diminishing only further north in the Valle Chiavenna. Figures 15a, b, c, d, show the Kriging analysis at, respectively, 10:00, 12:00, 14:00, 16:00 hours of 13 May '98. The plume motion towards northern areas of Lombardy is shown.

The episode of 24 July was recorded at the station of Varese where a peak of ozone concentration, around 170 ppb, was reached at 15:00 (fig. 16).

Both the episodes have been ascribed to the northward transport of a cloud of photochemical pollutants from the Milan area, taking into consideration the presence of the breeze blowing from South to North in the daytime hours.

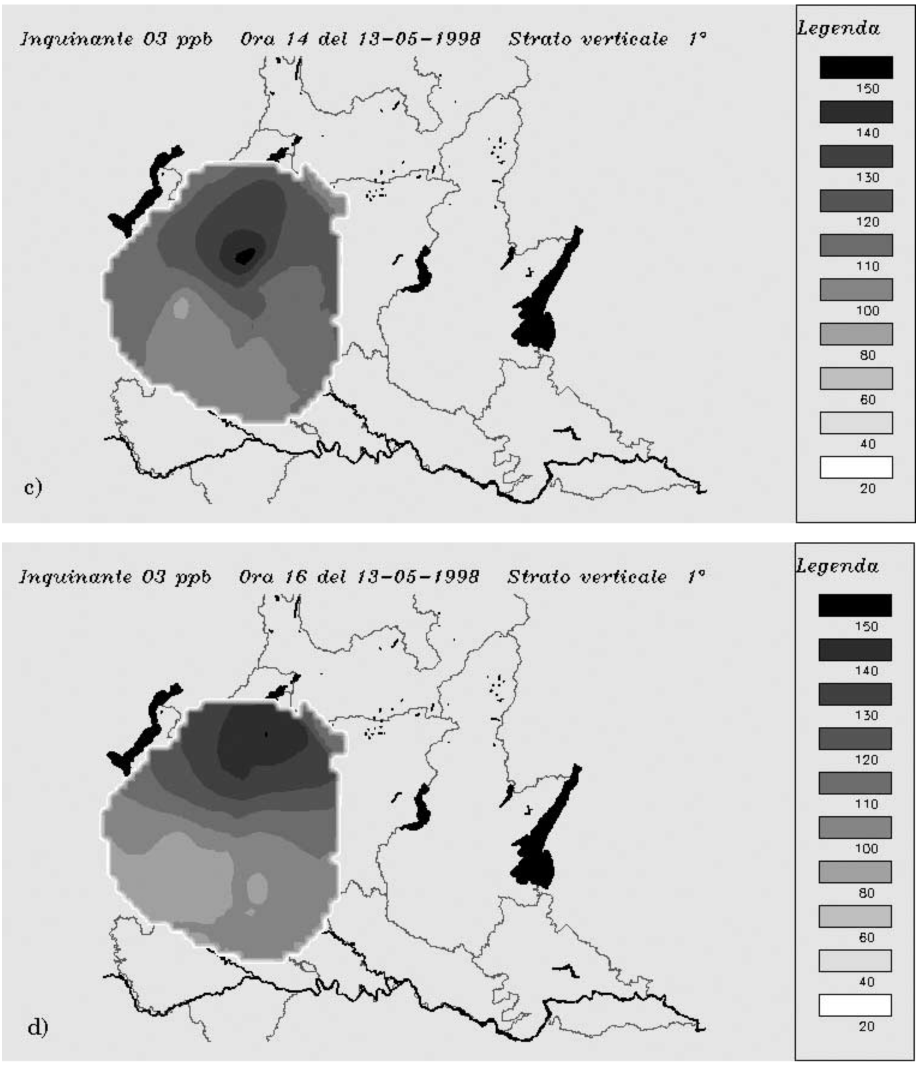


Fig. 15. – Continued.

5. – Discussion and conclusions

Days when high ozone concentrations are recorded are characterized by specific meteorological conditions: strong sunshine; high temperature; high pressure; and the formation of a ground-based thermal inversion and a Stable Nocturnal Layer at night. In the plain and in the hill areas, the atmosphere was divided into two separate regions during these nights: the Stable Nocturnal Layer and the Residual Layer above it. This division between the two layers of the PBL persists until the early hours of the morning when the thermal inversion is destroyed and the air trapped in the Stable Nocturnal Layer is released and disperses upwards as the ground heats up.

Early afternoon ozone concentrations up to and beyond 100 ppb were recorded on the

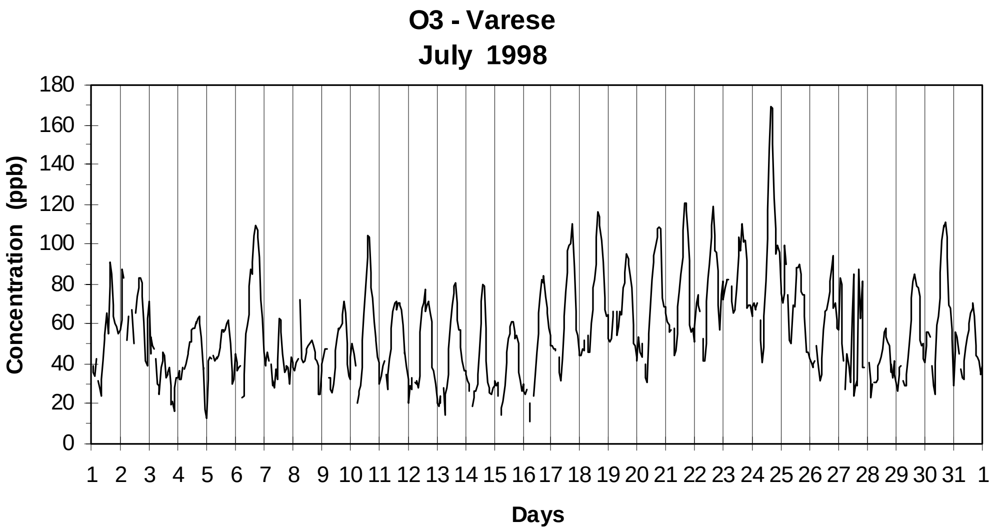


Fig. 16. – Ozone concentration at Varese in July 1998.

days studied over a vast area covering Milan and the plain area surrounding it; north of Milan an area around the Lombard lakes and the Prealps. Measurements conducted at Alpe del Viceré show that ozone concentrations of up to 100 ppb are also present at altitudes of 1000 m.

Ozone originating in the plain area, where ozone precursors are emitted in large quantities, is transported northwards in the afternoon by the south-north wind that blows during the daytime. This conclusion is supported by the increasing time lapses recorded between the peak concentration in Milan and those recorded in the areas increasingly distant from Milan.

With regard to nocturnal patterns, it can be seen that concentrations at the high-altitude station of Alpe del Viceré are high at night. The downwards transport of ozone to areas at the foot of the Prealps is shown by the nocturnal concentrations recorded at Erba and further south the nocturnal peaks (30–40 ppb) in the Brianza hill area. Ozone is transported on the north-south night breeze that blows down the slopes and through the valleys of the mountains.

For the things said and for the data relative to the whole studied area, we can see how the presence of ozone is not simply linked to a site but is a process involving the analysis area and the high-altitude ozone rate.

The question of whether ozone production is dependent on NO_x or VOCs might have a general answer in accordance with Sillman's parameters: on the ground in the town and nearly in the whole area where NO_x concentrations exceed 20 ppb, ozone production results to be VOC dependent.

REFERENCES

[1] Kleinman L. I., *J. Geophys. Res.*, **91** (1986) 10889.
[2] Kleinman L. I., *J. Geophys. Res.*, **96** (1991) 20721.
[3] Sillman S., Logan J. A. and Wofsy S. C., *J. Geophys. Res.*, **95** (1990) 1837.

[4] Sillman S., *J. Geophys. Res.*, **100** (1995) 14175.

[5] Maffeis G., Longoni M. G., De Martini A. and Tamponi M., *Stime delle emissioni dei precursori dell'ozono durante la Campagna PIPAPO*, in *Photochemical Oxidants and Aerosols in Lombardy Region. The Contribution of European Projects, Proceedings, Milan, 21-22 June 1999*, pp. 185-192.

[6] De Martini A., Zabot S., Longoni M. G., Maffeis G., Toscani D., Cattaneo R. and Tamponi M., *Il contributo della modellazione*, in *Photochemical Oxidants and Aerosols in Lombardy Region. The Contribution of European Projects, Proceedings, Milan, 21-22 June 1999*, pp. 193-203.

[7] Vecchi R., Valli G. and Lanzani G., *Observations of summertime ozone in the Prealpine area at different altitudes*, in *Photochemical Oxidants and Aerosols in Lombardy Region. The Contribution of European Projects, Proceedings, Milan, 21-22 June 1999*, pp. 81-88.

[8] Sesana L. and Barbieri L., *Ingegneria Ambientale*, **28** (1999) 465.

[9] Facchini U., Sesana L. and Milesi M., The PIPAPO Project: Radon 222 Measurements, in LOOP- EUROTRAC-2, Annual Report, 1998.

[10] Facchini U., Sesana L., Milesi M., De Saeger E. and Ottobrini B., *A Year's radon measurements in Milan and at EMEP station in Ispra (Lake Maggiore, Italy)*, in *Air Pollution VII, S.Francisco, 1999*, pp. 609-616.

[11] Sesana L., Barbieri L., Facchini U. and Marcazzan G., *Radiat. Prot. Dosim.*, **78** (1998) 65.

[12] Sesana L., Caprioli E. and Marcazzan G. M., *J. Environ. Radioactivity*, **65** (2003) 147.

[13] Stull R. B., *An Introduction to Boundary Layer Meteorology*, Department of Meteorology, University of Wisconsin, Atmospheric Sciences Library (1988).

[14] Pasqualotto C., *Misure a Distanza di Inquinanti Atmosferici*, Thesis in Physics, University of Milan (1991).

[15] Platt U., Alicke B. and Stutz J., *J. Geophys. Res.*, **107** (2002) LOP 9/1.

[16] Stutz J., Alicke B. and Neftel A., *J. Geophys. Res.*, **107** (2002) LOP 5/1.

[17] Lanzani G., Cadenazzi M., Cattaneo R., Gottardi R. and Valore M., *Analisi della distribuzione spaziale e temporale dell'ozono nella Regione Lombardia durante la Campagna PIPAPO*, in *Photochemical Oxidants and Aerosols in Lombardy Region. The Contribution of European Projects, Proceedings, Milan, 21-22 June 1999*, pp. 109-120.

[18] Prévot A., Staehelin J., Kok G. L., Schillawski R. D., Neininger B., Staffelbach T., Neftel A., Wernli H. and Dommen J., *J. Geophys. Res.*, **102** (D19) (1997) 23375.

[19] Staffelbach T., Neftel A., Blatter A., Gut A., Fahrni M., Staehelin J., Prévot A., Hering A., Lehning M., Neininger B., Bäumle M., Kok G. L., Dommen J., Hutterli M. and Anklin M., *J. Geophys. Res.*, **102** (D19) (1997) 23345; Staffelbach T., Neftel A. and Horowitz W., *J. Geophys. Res.*, **102** (D19) (1997) 23363.

[20] Neftel A., Spirig C. and Favaro G., *The LOOP Project: results and future aims*, in *Photochemical Oxidants and Aerosols in Lombardy Region. The Contribution of European Projects, Proceedings, Milan, 21-22 June 1999*, pp. 29-35.

[21] Dosio A., Galmarini S. and Graziani G., *J. Geophys. Res.*, **107** (2002) LOP 2/1.