



Tropospheric ozone in a mountain forest area: spatial distribution and its relation with meteorology and emission sources

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Abstract

Biological injuries to forest ecosystems in two lateral valleys of Valtellina (Italy) have been studied. The selected areas are characterized by different forest novel decline symptoms and ozone concentration levels. Analyses of meteorological and air quality data collected by fixed and mobile stations located in the two valleys are presented. Ozone concentration has been measured both by passive samplers and continuous analyzers and the ozone vertical gradient in one valley has been determined. In order to investigate the relation between emission sources, ambient ozone levels and plant biological injuries, a modeling research project has been started. As preliminary results the wind field obtained by the application of two diagnostic meteorological models, MINERVE and CALMET, and the computation of the biogenic emissions are presented. Some examples of spatial distribution and temporal trend of the most important pollutants emitted by plants are discussed.

1 Introduction

In many European countries there is a large concern on ozone, photo-oxidants and their effects on human health and on agricultural and forest ecosystems.

Ozone levels are often very high in areas far away from emission sources, but data measured in mountain sites are in many cases insufficient. In this framework, the Lombardy Foundation for the Environment (FLA) had carried on a three year campaign of air quality monitoring in two mountain sites (from 1994 to 1996), giving particular emphasis on tropospheric ozone

concentrations. The same monitoring campaign went on during the summer season of the current year.

The two sites are ten kilometers apart and are located in two lateral valleys, *Val Gerola* and *Val Masino*, of the same main valley, Valtellina, in the Alpine region of northern Italy. These areas have been chosen for their different biological damages [1] on the main plant species according an health monitoring survey based on the IPC-Forest Programme. One possible cause of novel decline symptoms, observed especially in *Val Gerola*, could be the oxidative power of ozone, even if it is very difficult to isolate ozone effects from other stress factors.

To deep the causes of the vegetation health decline, for each site a series of meteorological parameters as well as the main inorganic gaseous pollutants have been analyzed. Data have been collected by fixed and mobile stations located in the two selected sites. Ozone concentrations have been measured also using groups of passive samplers located in different sites, along an altitudinal gradient. The two sites showed marked differences in ozone concentrations with *Val Gerola* site well above the mean toxicity level for sensitive plant species.

Some hypotheses have been suggested to explain the difference in ambient ozone levels in the areas under investigation: wind transport of precursors from the metropolitan area of Milan and local biogenic emissions are some of the possible causes. For this reason, a modeling study is currently in progress aimed at the estimation of the ozone field over the region of interest, after computation of anthropogenic and biogenic emissions and reproduction of wind fields.

2 Selection of the sample sites

The two valleys under investigation, have a N-S orientation contrarily to the main valley which is atypically located from West to East. They are characterized by the same plant species (mainly Norway spruce, silver fir, larch and beech), but with a different spatial distribution, and by the same type of wind circulation (mountain-valley breeze). *Val Gerola* has a fluvial morphology, with sharp slopes, but the highest peak reaches 2550 meters. *Val Masino*, instead, has a typically glacial morphology, with steep granite walls which are in contrast with the flat valley bottom; its highest peak is about 3500 meters. Therefore, the two valleys have been selected, besides the differences showed in novel decline symptoms, for their particular morphology which offers a different protection degree to air mass fluxes coming from the plane south of Valtellina.

The location of Valtellina in Italy is showed in Figure 1. Figure 2 shows the 3-D reproduction of the topography of the area of study used in the modeling research, described in paragraph 5. In the graph are showed the sites of measure; in particular, B. Masino is located in *Val Masino* and *Alpe Culino* and *Larice* in *Val Gerola*, the most damaged site.



Figure 1: Location of Valtellina in Italy

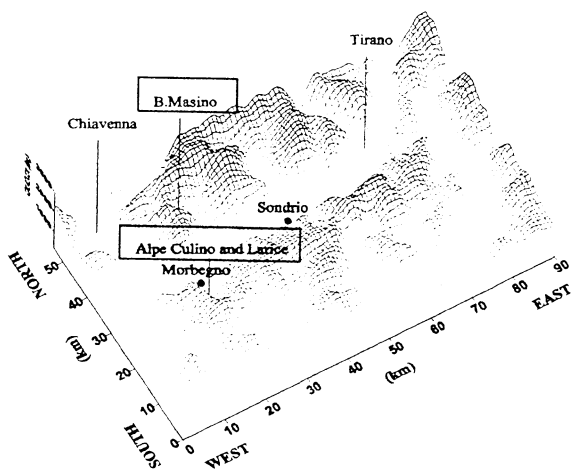


Figure 2: Topography of the modeling study area.

3 Meteorological characterization

Meteorological measurements in the valleys have been taken from two permanent stations located at *Alpe Culino* (1500 m a.s.l.) in *Val Gerola* and at *Bagni di Masino* (1200 m a.s.l.) which provide hourly measurements of wind speed and direction, pressure, temperature, solar radiation, relative humidity and precipitation. Data have been collected from May 1 to September 30 1996. Two other mobile stations have been available at *Larice* (1200 m a.s.l.) in *Val Gerola* and at *Bagni di Masino* (1200 m a.s.l.) whose hourly meteorological and chemical data have been partially used. Figures 3 shows frequency distribution of wind direction in the two valleys.

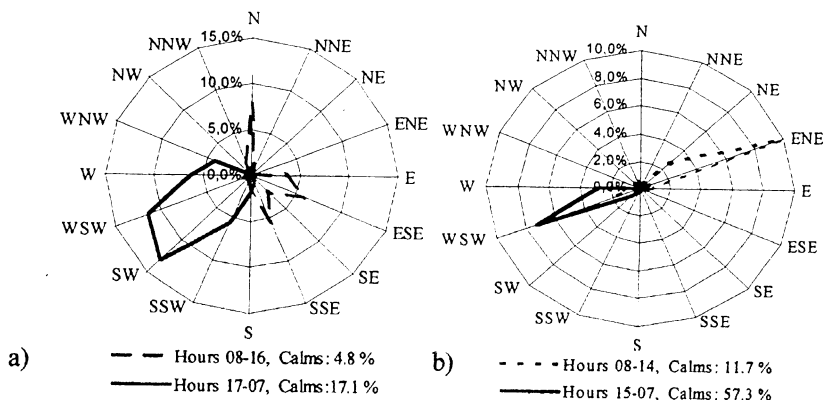


Figure 3: Wind direction distribution at a) *Alpe Culino (Val Gerola)* and b) *B. di Masino (Val Masino)*

Figures 4 and 5 show frequency distribution of wind speed and a typical daily wind speed profile.

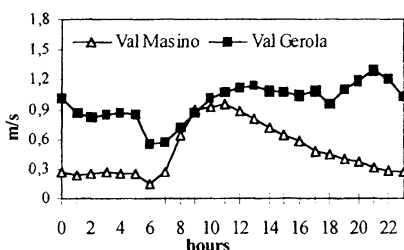


Figure 4: Wind speed distribution

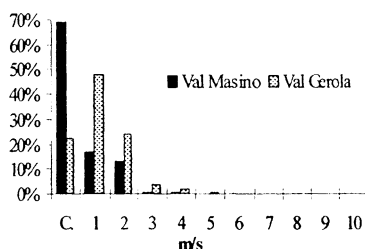


Figure 5: Wind speed mean day

In *Val Masino* breeze circulation is prevailing; wind blows along WSW - ENE direction, with a clear inversion within day and night. Speed is very low and there are about 70 % of wind calms (indicated with C in Figure 5). This is probably due to the presence of high mountains surrounding the valley bottom (more than 2.000 m between peaks and station altitude).

Also in *Val Gerola* there is breeze circulation, but wind speed is little higher than *Val Masino* particularly during night-time. Wind blows from several directions, but mainly from Valtellina during day-time and from mountains limiting the valley during night-time. *Val Gerola*, therefore, seems to be more exposed to air coming from the outside of the valley than *Val Masino*.

Figures 6 and 7 show typical daily temperature and radiation profiles. Temperature in *Val Masino* is higher than in *Val Gerola*, but this is probably due to the different altitude of the two sites. Radiation, on the other hand, results higher in *Val Gerola* and this may be due to a difference in cloud covering between the two valleys.

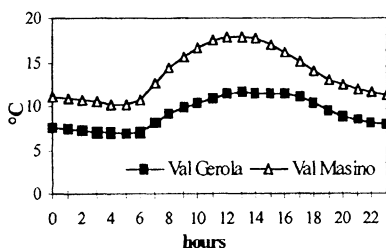


Figure 6: Temperature mean day

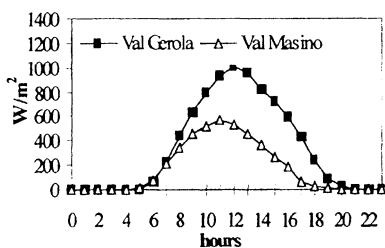


Figure 7: Total solar radiation mean day

Meteorological analysis seems to agree with air quality data and plant damage observations; in fact *Val Gerola*, the most damaged valley, is more exposed to solar radiation, which is, as known, very important in photochemical

smog. Moreover, this valley is more subjected to air transport coming from more polluted areas.

4 Air quality data

Stations providing air quality data were placed at *Larice* in *Val Gerola* and at *Bagni di Masino* in *Val Masino* and collect hourly measurements of O_3 , NO , NO_2 , CO , SO_2 and, only in *Val Masino*, NMHC. Measurements have been available from June 1 to July 31 1996 in *Val Gerola* and from June 4 to July 15 1996 in *Val Masino*. Besides, ozone concentrations from passive samplers [2] (expressed as weekly mean) have been recorded from the beginning of June to the end of September 1996. Some samplers were placed near the stations in order to compare their data with continuous analyzers measurements. Data show that (see Figure 8) *Val Gerola* is more polluted than *Val Masino*. Ozone daily mean concentration in *Val Gerola* is always higher than in *Val Masino* (with a difference up to $100 \mu g/m^3$) and it is always above the conventional phytotoxicity threshold (AOT40). Passive samplers are in good agreement with continuous analysers, as shown in Figure 9, confirming the presence of different pollution patterns in the valleys [3].

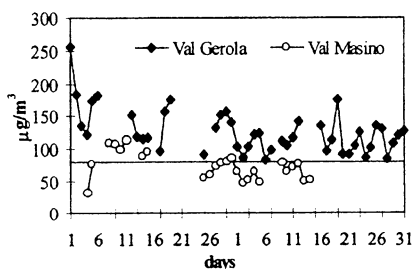


Figure 8: Ozone daily mean concentrations (June and July 1996)

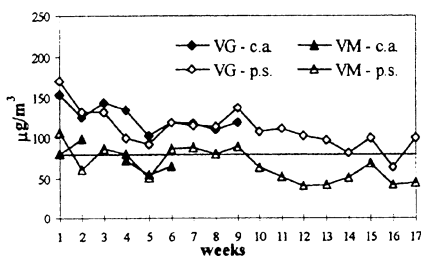


Figure 9: Ozone weekly mean concentrations (June-September 1996): continuous analyzers (c.a.) and passive samplers (p.s.)

Ozone mean day (Figure 10) show a typical mountain situation with quite constant concentrations. In particular in *Val Gerola* highest concentrations occur during night-time, probably due to polluted air coming from outside the valley. In *Val Masino*, where concentration is often below phytotoxicity threshold, highest concentrations occur during daytime, but with little difference with night-time values suggesting a reduced photochemical activity.

In 1995 passive samplers had been placed in 4 sites at different altitude in *Val Gerola* in order to study ozone gradient (Figure 11).

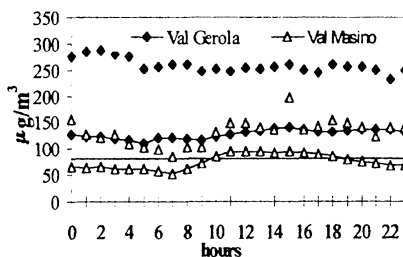


Figure 10: Ozone mean day and maximum hourly concentration

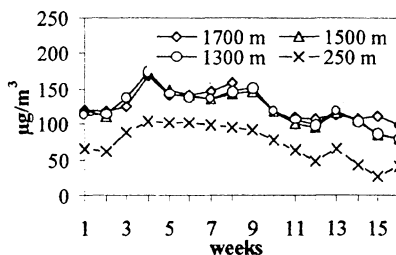


Figure 11: Ozone gradient with altitude

Ozone data in the two valleys had been available for three years (summer '94, '95 and '96). Figures 12 and 13 show no significant trends in either valleys.

NO and NO₂ concentrations were not very meaningful (always $\leq 10 \mu\text{g}/\text{m}^3$), as it was expected in mountain regions (data not shown).

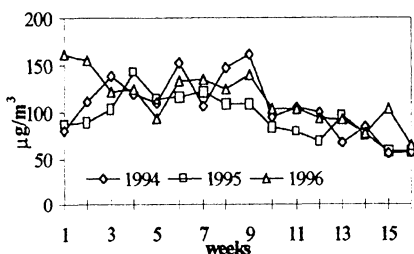


Figure 12: Ozone concentrations in Val Gerola

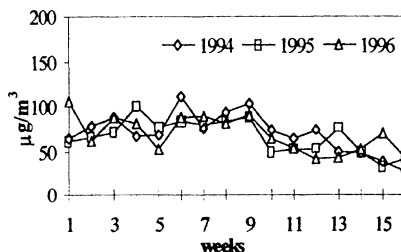


Figure 13: Ozone concentrations in Val Masino

5 Photochemical model application: preliminary results

A new development of the present research is being aimed at the investigation of possible causes of the observed asymmetry in ozone concentrations in the two selected sites and the possible relation between ozone dry deposition and novel decline symptoms exhibited by plant species.

The selected region of this new study covers an area of (90x54) km² (see Figure 2) on which a computational grid has been built, with an horizontal grid step of 2 km. We intend to use the 3-D eulerian photochemical grid model CALGRID [4], able to treat the main chemical and physical processes to which pollutants are subjected in atmosphere. The model requires, among others, emission data, geophysical and meteorological data.

Fields of meteorological parameters have been built by the application of two diagnostic models, MINERVE [5] and CALMET [6], and biogenic emissions

have been computed by Tingey algorithms [7]. The methodology used and the preliminary results are shown in the following paragraphs.

5.1 Wind fields

Photochemical model CALGRID needs 3-D fields of wind and temperature and 2-D fields of parameters describing turbulence. Available data are based on ground measurements of wind, pressure, temperature, cloud cover, ceiling height and on profile measurements of wind and temperature. MINERVE model has been used to build up synoptic flow, then CALMET model has been applied to obtain wind and temperature fields and turbulence parameters. Figure 14 shows an example of wind field (at ground level) obtained applying MINERVE and CALMET models.

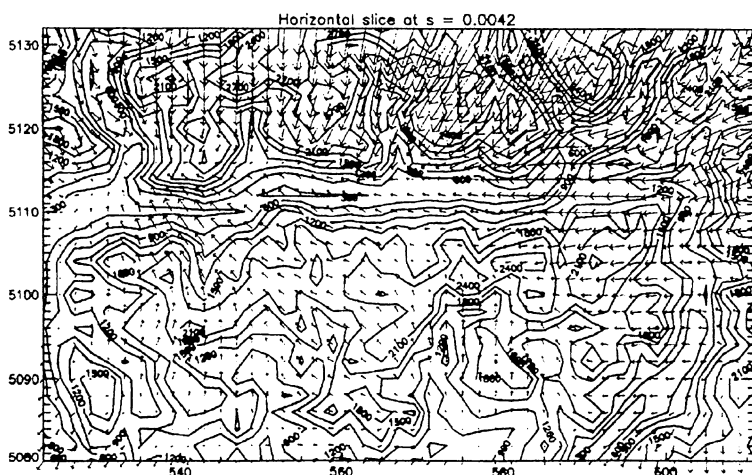


Figure 14: Wind field computed on June 9, 1996 - hour 4.00 a.m.

5.2 Biogenic emissions

Tingey algorithms allow to estimate, on the basis of temperature and solar radiation data, pollutants emitted from plant species whose emission and biomass factors are known (isoprene, α -pinene, monoterpenes and unknown VOC). Moreover, the area covered by each selected species over the domain cells has to be known.

The selected vegetation classes include: deciduous high isoprene emitters (*Quercus*, *Platanus*, *Populus*, *Salix*), deciduous non-isoprene emitters (all the other deciduous), coniferous (*Pinus*, *Abies*, *Picea*, *Larix*), crops (corn, wheat) and grassland-pastures. Trees biomass and emission factors (estimated at 30°C)

have been taken from the CORINAIR [8] emission inventory and crops and grassland-pasture from Lamb [7].

The spatial distribution over the study area for each vegetation class has been achieved using a Lombardy Region land-use map, which represents 17 land-use classes, lumped in the five groups of vegetation here adopted.

5.2.1 Emissions spatial distribution

In order to estimate biogenic emissions, an appropriate program has been developed. The program utilizes hourly temperature and solar radiation values measured by all monitoring stations located in the area of study. The solar radiation is calculated as the average of all the available values. The temperature, on the other hand, depends on the height assigned to the particular grid cell under computation.

A summer period has been chosen for the simulation, from June 4 to June 11 1996, because of the very high ozone levels recorded in that period. As an example of the obtained results, Figure 15 shows the α -pinene emission map on June 7 1996. As it can be seen from the map, emissions are much higher in the most damaged valley (*Val Gerola*) than in the other one. This result depends both on different temperatures recorded in the two sites, and on the different spatial distribution of the most emitters plant species.

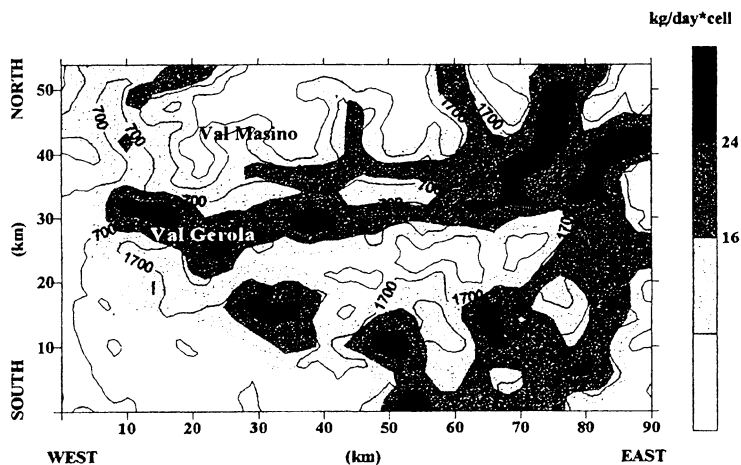


Figure 15: α -Pinene hourly emissions in kg/day*cell coming from all vegetation classes.

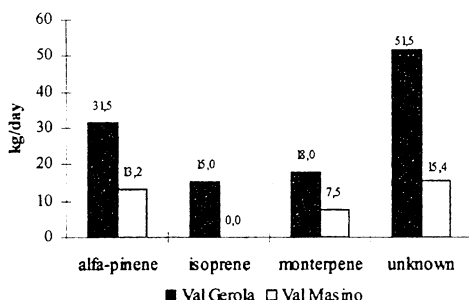


Figure 16: Total daily emissions coming from selected vegetation classes in the two valleys under investigation ((2x2) km² cells).

Figure 16 shows the total daily emissions of isoprene, α -pinene, monoterpenes and unknown VOC coming from all the selected vegetation classes (June 7, 1996).

Total daily emissions are higher in *Val Gerola* than in *Val Masino*; in particular unknown VOC values are three times higher than those coming from the less damaged site.

Zero isoprene emission in *Val Masino* is caused by the

absence, in the particular grid cell, of the isoprene emitters plant species.

Conclusions

Ozone concentrations are related to the differences of the observed biological injuries and calculated emission levels of the two valleys under investigation.

The comparison between data measured by automatic analyzers and passive samplers showed a negligible difference in the two measure methods, pointing out the reliability of the passive samplers. Results presented in this paper are still preliminary regarding the modeling research project that is currently under way.

Further investigations will be necessary in the future in order to understand quantitative relations among emission sources (and consequently precursors concentrations), adsorbed dose and novel decline symptoms exhibited by the main plant species of the study area.

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References

- [1] Ballarin Denti A., Rabotti G., Tagliaferri A., Rapella A. (1995) Novel decline symptoms in an alpine forest system and biochemical indicators of air pollution stress, *Life Chemistry Reports* **13**, pp. 111-119.
- [2] Hangartner M. (1990) Einsatz von Passivsammelern für verschiedene Schadstoffe in der Aussenluft. *VDI Berichte* N° **838**, pp. 515-526.
- [3] Ballarin Denti A., Brambilla E., Dell'Era R. (1997) Ozone and air particulate measurements in mountain forest sites, *Chemosphere* in press.
- [4] Scire J.S., Yamartino R.J., Carmichael G.R., Chang Y.S. (1989) *CALGRID: A Mesoscale Photochemical Grid Model*. Vol. I: Model Formulation Document and Vol. II: User's Guide, Final report on contract A6-215-74 for the CARB, Sacramento, CA.
- [5] Geai P. (1987) *Methode d'interpolation et de reconstitution tridimensionnelle d'un champ de vent: le code d'analyse objective MINERVE*. Rep. ARD-AID: E34-E11, EDF, Chatou, France.
- [6] Scire J.S., Insley E.M., Yamartino R.J. (1990) *Model Formulation and User's Guide for the CALMET Meteorological Model*. California Air Resources Board, Report n°A025-1.
- [7] Lamb B., Gay D., Westberg H. (1993) A Biogenic Hydrocarbon Emission Inventory for the U.S.A. using a Simple Forest Canopy Model, *Atmospheric Environment* Vol. **27A**, n° 11, pp. 1673-1690.
- [8] CORINAIR, Veldt C. (1990) Technical Annexes, Default emission factors from nature, pp. 101-128.
- [9] Morselli M.G., Calori G., Finardi S., Mazzola C. (1997) *A 3-D wind and temperature pre-processor for ATD Models*. Int. J. Environment and Pollution, Vol. 8, Nos. 3-6, in press.



Section 4:

Data Analysis and

Observation