

# TOWARDS AN OZONE CLIMATOLOGY OVER THE MEDITERRANEAN BASIN: ENVIRONMENTAL ASPECTS

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Ozone ( $O_3$ ) is an allotrope of oxygen that occurs at significant levels in the planetary boundary layer. As it is a strong oxidant and a highly reactive gas, its recurrence deserves special attention, particularly due to its harmful effects on biological systems. High  $O_3$  levels not only play a role in the damage to materials (especially elastomers, dyes and paints) and plant species, but also lead to the irritation of mucous membranes and therefore adversely affect human health and welfare. Paradoxically,  $O_3$  in the stratosphere performs the critical task of absorbing some of the sun's ultraviolet radiation which is harmful to living organisms. The chemistry of tropospheric  $O_3$  is quite complex and its budget is subjected to dynamic changes: its concentration at any given location is the combined result of  $O_3$  originating from a number of different sources and of depletion mechanisms. The sources include: (i) «background» troposphere; (ii) photochemical generation from local anthropogenic emissions (precursors), especially in the urban plumes; (iii) long-range transport and accumulation in high-pressure weather systems; (iv) injection from the stratosphere into the troposphere and subsequent transport to the surface.  $O_3$  is quickly depleted by chemical scavengers (such as nitrogen monoxide) and physical quenching (dry deposition).

Nowadays, a great and growing concern is associated with photochemical, «anthropogenic»  $O_3$ . This is a classical «secondary pollutant», which is formed — together with other oxidants — by chemical reactions which occur within the atmosphere, between precursors such as volatile non-methane hydrocarbons and nitrogen oxides, and oxygen. The whole phenomenon takes the name of «photochemical smog» and has been elucidated in great detail. Vehicle exhaust emissions and other combustion processes are the main sources of these pollutants.

Meteorological conditions play an essential role: high temperatures, intense solar radiation and air stability are all factors conducive to the formation and build-up of elevated levels of  $O_3$ , with sunlight acting as the driving force. Due to these reasons,  $O_3$  pollution presents some peculiarities: (i) its geographical distribution, linked to the meteorological conditions necessary for its

## Abstract

Photochemically-produced ozone is a widely distributed air pollutant. Its formation depends on the availability of precursors such as nitrogen oxides and volatile hydrocarbons. As sunshine and high temperature are essential requirements for the chain of reactions which results in ozone, the Mediterranean regions have for a long time been recognized as areas at a high risk of ozone pollution. In spite of this, the topic has so far received little attention. The data concerning ground ozone concentrations in some countries are reviewed and commented upon: there is a shortage of information due to the scarcity of monitoring sites, but the data available confirm the recurrence of relevant mixing ratios. During the summertime ozone levels systematically go far beyond the thresholds of biological effects. The use of biomonitors (tobacco Bel-W3 plants) has demonstrated the wide geographical distribution of phytotoxic ozone and filtration experiments in ozone-polluted environments have led to significant yield increases of agricultural plants. The biological implications of the present state of pollution are described and the need for future studies is stressed.

## Résumé

L'ozone troposphérique d'origine photochimique est un polluant atmosphérique très diffus, dont la formation dépend de la disponibilité des précurseurs comme les oxydes d'azote et les hydrocarbures volatils. Comme la radiation solaire et la température sont les qualités requises pour les réactions en chaîne qui portent à la formation de l'ozone, ce sont les régions méditerranéennes que l'on considère depuis longtemps comme étant des aires avec un risque élevé de pollution d'ozone. Malgré tout, le problème n'a pas en jusqu'ici beaucoup d'attention. Les données relatives aux concentrations d'ozone dans certains Pays sont résumées et commentées: l'analyse met en évidence la carence d'informations, en conséquence de l'insuffisance des sites de monitoring, mais — en même temps — les données disponibles indiquent la haute fréquence des niveaux d'ozone intéressants. Pendant l'été les valeurs dépassent toujours les seuils pour les effets biologiques. L'emploi de bioindicateurs (plantes de tabac Bel-W3) a montré la large distribution géographique de l'ozone phytotoxique. En outre, les expériences de filtrage de l'air dans les régions polluées par l'ozone ont comporté des accroissements importants de rendement de plusieurs plantes agricoles. Les implications biologiques de la situation actuelle de pollution sont décrites et la nécessité d'ultérieures recherches est soulignée.

formation; (ii) its temporal variations, with a well-defined circadian cycle on a night-and-day basis (very low levels at night, due to the absence of solar radiation and to the short life time of  $O_3$ ) and strong seasonal differences and (iii) the possibility of specific episodes, with the warmest periods being more favorable to pollution. Therefore, the «classical» numerical parameters which describe the behaviour of other pollutants, such as the the daily and/or the monthly average concentrations are of relatively scarce significance for  $O_3$ .

Multi-hour indicators, such as «the highest daily 7-consecutive-hours average» are regarded as the best indicators for discovering biological effects. In the same way, extrapolating results from one monitoring site to a regional scale is not easy. Two sites may well experience a similar regional scale  $O_3$  average but because of different diurnal cycles,  $O_3$  dosage could be markedly different.

Another point must be stressed: even if the precursor pollutants are typically produced in urban and metropolitan areas, relevant  $O_3$  levels are frequent in rural (and remote) regions, due to the medium/long range transport of precursors and of  $O_3$  itself. The problem may be verified in downwind

remote areas, up to 1000 km from large sources of precursors (Derwent and Kay, 1987).

Natural background  $O_3$  mixing ratios in surface air are around 10 ppb (parts per  $10^{-3}$ , in vol.; 1 ppb =  $1.96 \mu\text{g m}^{-3}$  at standard temperature and pressure); this  $O_3$  plays an important role in tropospheric chemistry. Severe episodes may experience levels of the magnitude of 200 ppb and over for many hours.

Over the last few decades there has been a sharp increase in the interest shown in this air pollutant, starting from the late 1940's, when its environmental implications began to be realized.

These include deleterious effects on human health and on vegetation, firstly detected in the Los Angeles area, where meteorological conditions and vehicle exhaust emissions created a situation particularly favorable to the formation of secondary pollutants. Whereas, interest in ambient  $O_3$  measurements was for a long time lacking in Europe, as it was thought that photochemical pollution was concentrated mainly in some urban areas in the U.S.A.

The Mediterranean climate presents hot, dry summers, and mild winters; global solar radiation is rather strong, with average daily

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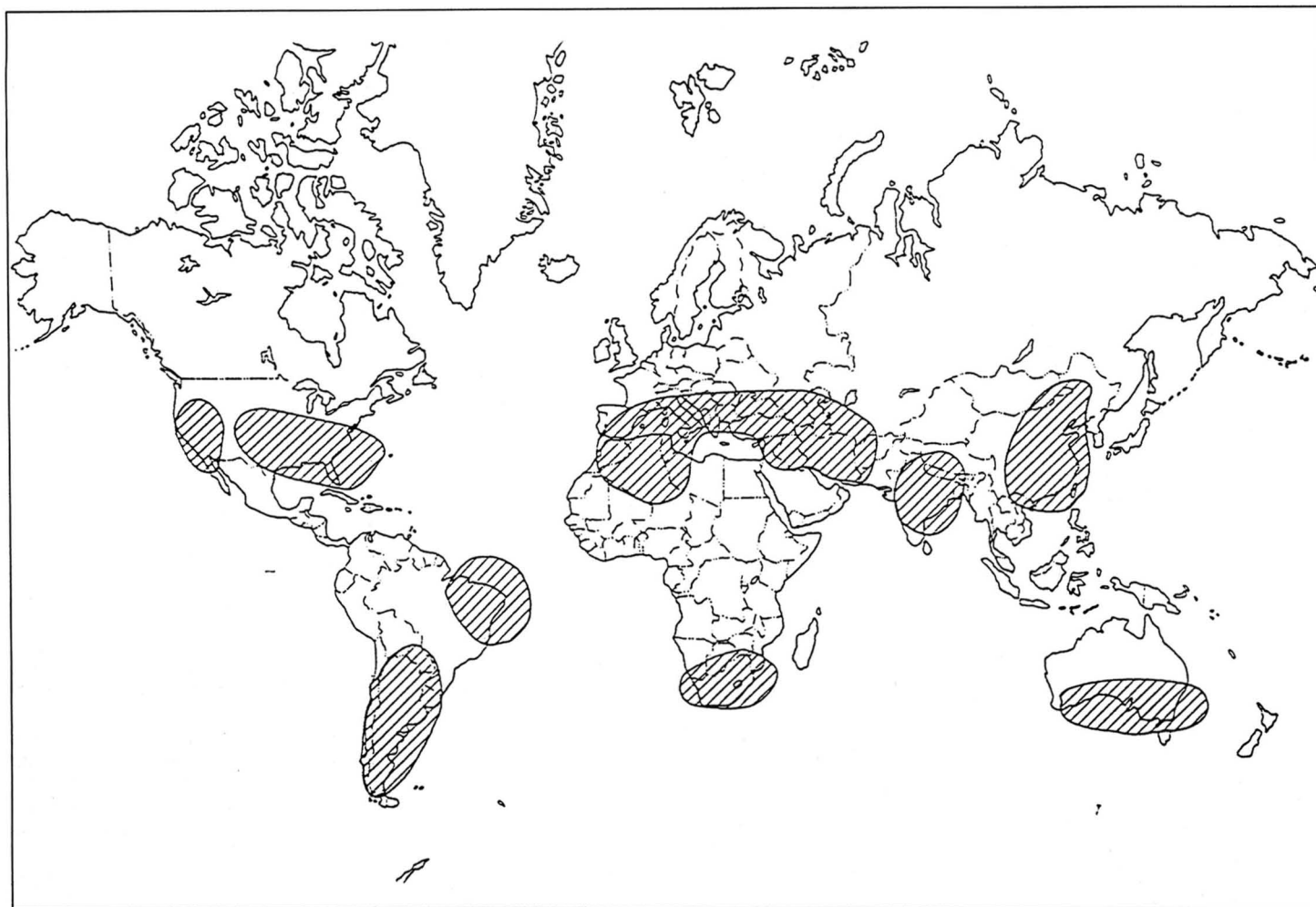


Figure 1 - Regions of high susceptibility to photochemical smog (after Hidy and Mueller, 1986).

values around  $20 \text{ MJm}^{-2}$  or above in the summer (with peaks above  $1000 \text{ Wm}^{-2}$ ) and  $8 \text{ MJm}^{-2}$  in the winter. Therefore, the Mediterranean basin for a long time has been recognized as a region of high susceptibility to photochemical smog, while Middle Europe is not (Hidy and Mueller, 1986) (figure 1).

This is mainly due to North-South gradients in isotherms and solar radiation (figure 2). In spite of this, the subject has received only minimal attention in Mediterranean Europe, while it has attracted substantial interest in other countries, where the climate seems to be less conducive to  $\text{O}_3$  formation (Derwent and Kay, 1988). The situation in the Southern regions of our continent is not taken into account by European surveys (e.g. Grennfelt et al., 1987).

The aim of this paper is to summarize the available knowledge on  $\text{O}_3$  distribution in some countries of the Mediterranean basin, with special reference to its environmental implications.

The information which will be given here comes from a review of the available literature and from personal contacts with several colleagues involved in  $\text{O}_3$  monitoring; it must not be considered exhaustive.

## Ozone distribution in various countries

### Spain

Only a dozen monitoring stations are known to be working, none of them in remote sites; until a couple of years ago, no organic publication was edited (Bouscaren, 1989).

The same source reports that in Barcelona in summer it is not rare to exceed 50 ppb 15-20% of the time. Martin et al. (1991) report significant levels of  $\text{O}_3$  from the coastal site of Castellon.

### France

$\text{O}_3$  measurements in France started in the late '70s (Bénarie et al., 1979); surprisingly, information seems to be very poor, even if more than 40 monitors are active (Delandre, 1991). An Agency for Air Quality will in the future collect data from local associations. According to Bouscaren (1989), the most dense network covers the area of Marseille-Fos; the « $\text{O}_3$  concentration in the town of Marseille seems to be low». Some remote stations are monitoring on a regular basis; in one of them (Plan d'Aups)

the value of 50 ppb has been exceeded 25% of the time.

### Italy

Measurements of ground level  $\text{O}_3$  started in Northern Italy in the 1860's. A series of historical data, obtained by a version of the Schoenbein method, at Moncalieri, near Turin, has been analyzed and the data have been converted into a form comparable to present day  $\text{O}_3$  concentrations. Results show that one century ago,  $\text{O}_3$  levels in the Po valley were more than two times lower than today's values, not only on the surface, but also in the free troposphere (Anfossi et al., 1991). In comparison to recent  $\text{O}_3$  levels these historical data also indicate that no trend in time was observed in those years (in contrast with the positive trend of ca. 2% per year of today).

Nowadays, air quality in the major Italian urban sites is not good, and during high-pressure situations harmful levels of pollutants such as nitrogen oxide and carbon monoxide are frequently experienced, eliciting stringent restrictions in vehicular traffic. The first exploratory measurements of surface  $\text{O}_3$  in Italy were made in 1974

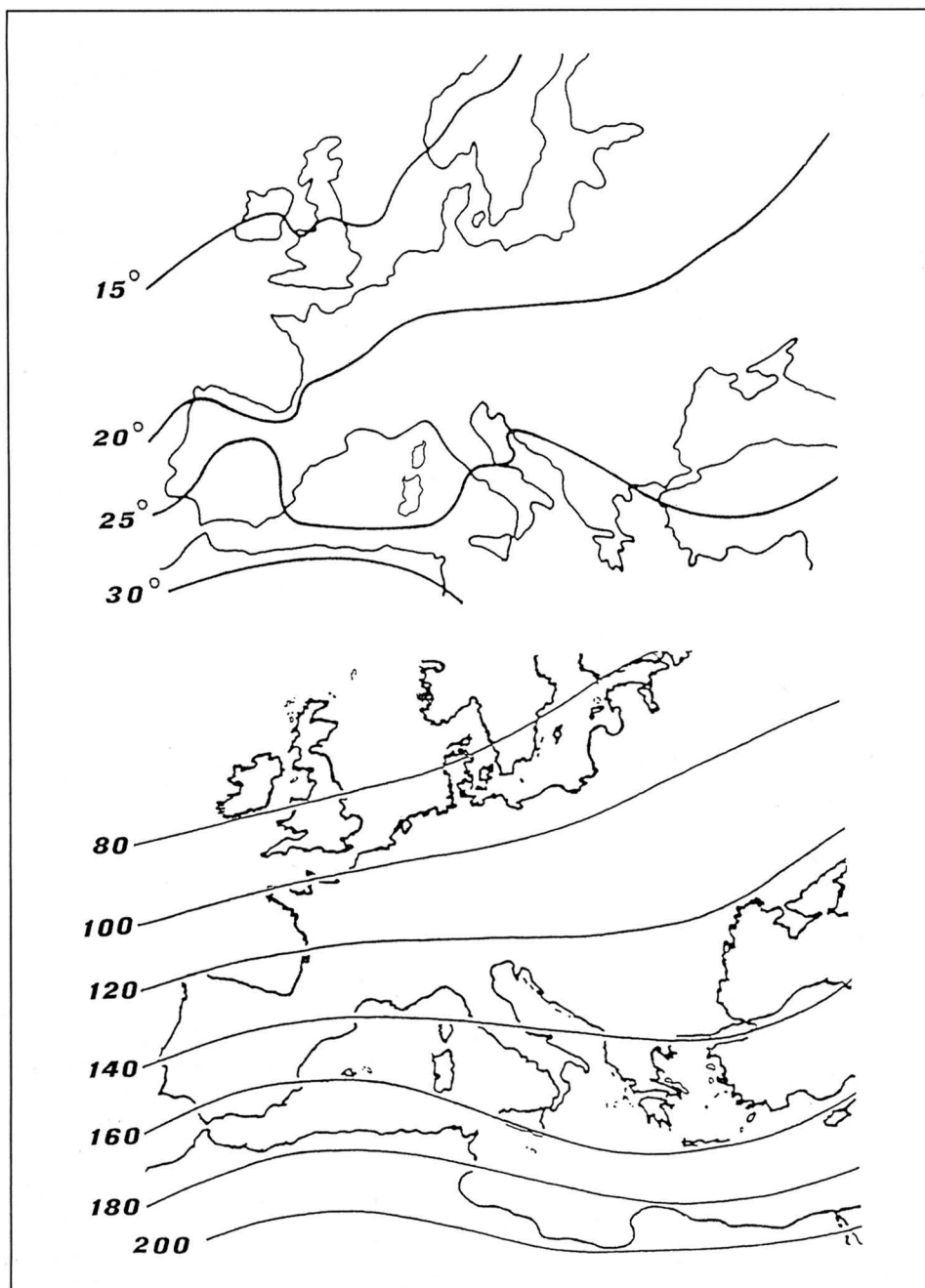


Figure 2 - Climatic characteristics of Europe, pointing to North-South gradients in photochemical ozone. Above: the July sea level isotherms in degrees Celsius; below: global solar radiation, in  $10^3 \text{ cal cm}^{-2} \text{ year}^{-1}$  (1 cal = 4.1868 J).

with a galvanometric instrument in a suburban part of Rome. The maximum hourly mean in that year amounted to 140 ppb  $\text{O}_3$  (see Becker et al., 1985).

Concern has grown only in the last two decades, with the diffusion of automatic monitoring instruments, most of them operating on the principle of UV absorption. At present there are some 30 operational  $\text{O}_3$  monitoring facilities, whose geographical coverage is irregular. The pattern of spatial distribution shows a concentration of sites in Lombardy and in the Po plain; there is some coverage in Central Italy, but information on the Southern regions is absolutely deficient (see Lorenzini, 1991). Only a handful of the stations have long term records — and these are restricted to a few geographical areas. Rural and forest areas are almost uncovered, with a few exceptions. A complete review of the published data on air quality in Italy has not been produced so far. This could be due to the fragmentation of the services involved and the absence of a central (national) authority in charge of co-ordinating all the efforts. **tables 1 and 2** show a synopsis of some selected available data.

A synthesis of the results produced at the University of Pisa is reported in figure 3. In the period 1896-1991, 102 days with a daily hourly peak above 80 ppb were been observed. Maximum hourly average concentration resulted to be 128 ppb. No temporal trend has been identified, but year-to-year fluctuations are evident (Lorenzini et al., 1992). A strong seasonal fluctuation with maxima values during the summertime and a winter minimum has been observed (figure 4). This is a marker of photochemical  $\text{O}_3$  production, as studies at sites remote from anthropogenic sources show that the summer peak is absent (Singh et al., 1978). At the same time, the diurnal cycle is clear, with a marked minimum early in the morning, 0600-0900 h, and a broad maximum between 1400-1700 h. Again, the atmospheric photochemistry of  $\text{O}_3$  is capable of producing strong diurnal variations. The role of anemological conditions is determinant on  $\text{O}_3$  build up, as during extremely windy days the diurnal profile was almost flat, without relevant differences between night and daytime (Lorenzini et al., 1988). One of the most detailed studies is that car-

**Table 1** Maximum 1-h ozone average (ppb) from selected monitoring stations located in urban and suburban Italian sites (after Lorenzini, 1991).

Station-typology	Period covered	Max 1-h average
Milano-urban	10.80-03.90	160
Ravenna-urban	10.79-10.83	235
Pisa-suburban	12.85-11.86	128
Livorno-urban	06.90-09.90	217
Roma-suburban	06-08.76-80	200
Roma-urban	10.87-09.88	112

**Table 2** Maximum hourly concentration (M1) and maximum monthly average concentration (MMA) of ozone (both in ppb) during January 1987 through June 1991, with indication of the corresponding day and the month, in three remote Italian alpine stations: Sestriere (Turin, 2555 m a.s.l.), Mottarone (Novara, 920 m a.s.l.), Brennero (Bolzano, 1900 m a.s.l.). Some original series were incomplete (elaborated after the semestral reports produced by ENEL-National Electricity Generating Board).

Year	Sestriere		Mottarone		Brennero	
	M1	MMA	M1	MMA	M1	MMA
1987	79 (24.04)	55 (07)	109 (29.07)	58 (07)	62 (10.05)	37 (05)
1988	57 (25.05)	40 (05)	125 (22.07)	67 (07)	70 (28.07)	46 (06)
1989	70 (06.09)	46 (09)	103 (20.07)	54 (07)	70 (05.08)	46 (08)
1990	77 (01.04)	55 (05)	133 (03.08)	67 (07)	91 (11.05)	57 (05)
1991	—	—	154 (25.06)	53 (05)	—	—

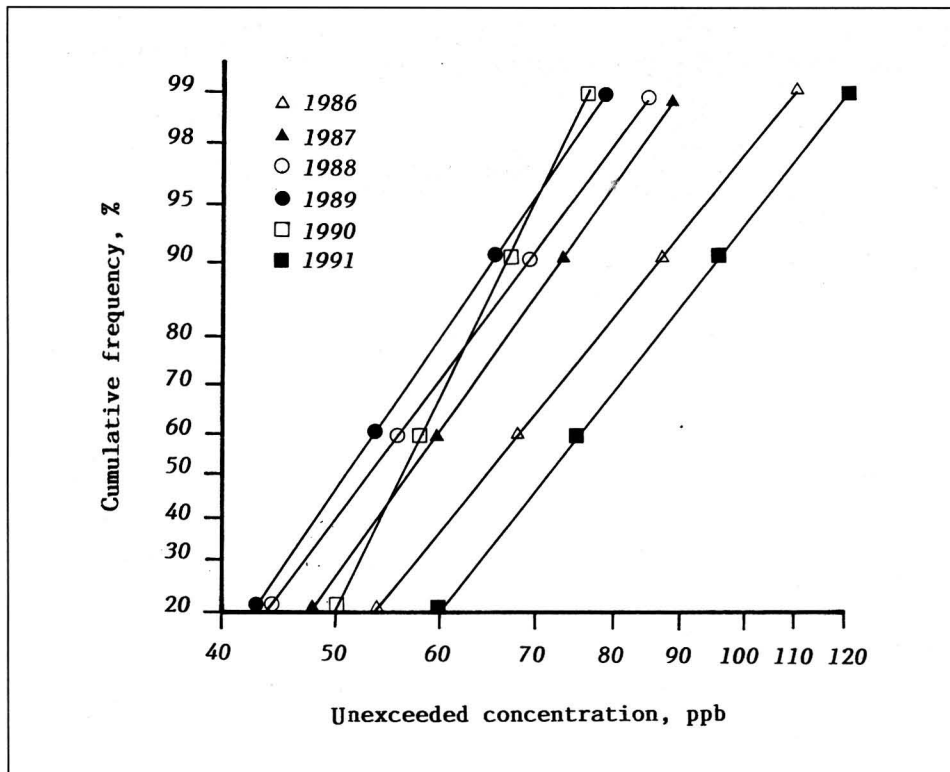


Figure 3 - Cumulative frequency distribution of maximum daily ozone concentration at San Piero a Grado, near Pisa, May to September, 1986-1991. Data for 1990 relative only to August and September.

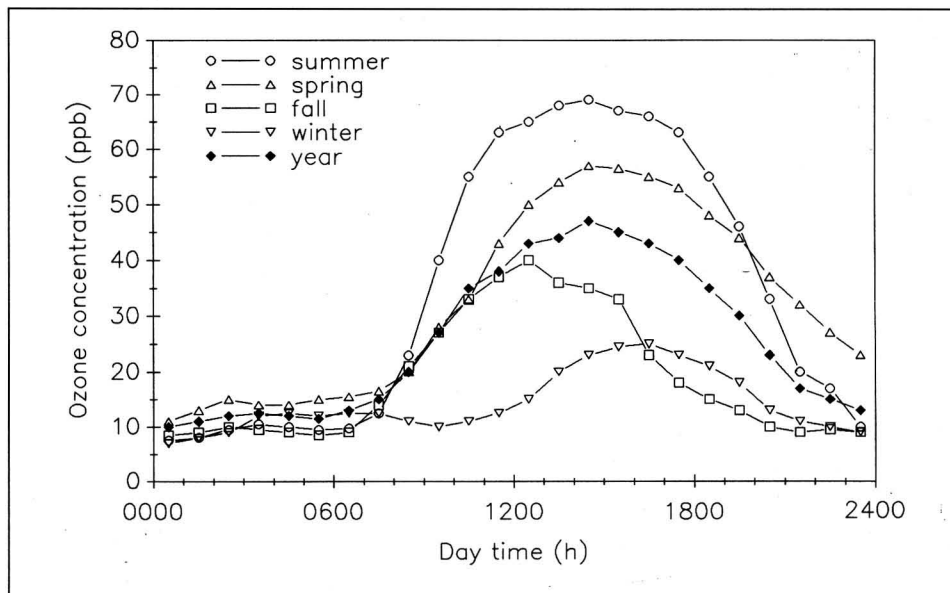


Figure 4 - Diurnal concentration profiles as seasonal mean of ozone at San Piero a Grado, near Pisa, Italy.

ried out near Ravenna, a heavily industrialized Adriatic coastal area, by a joint research group from CNR-FISBAT and the local health authorities (Giovanelli *et al.*, 1982; Fortezza and Strocchi, 1986). Here, the measurements recorded since 1978 revealed pronounced photochemical  $O_3$  formation in the entire area. The concentration-time profiles of  $O_3$  depend quite distinctly on the prevalent wind direction. High  $O_3$  inland during the night was connected to a

land-sea-breeze effect, as confirmed by  $O_3$  measurements offshore, where the threshold of 100 ppb has been exceeded. A serious photochemical oxidant problem exists in the Rome metropolitan area, even though the highest hourly average oxidants seldom exceed 150 ppb and the value of 100 ppb is exceeded about 30% of the time in the summer (Cecinato *et al.*, 1979; Pos-sanzini, 1981; Cerquiglini Monteriolo *et al.*, 1982); PAN has also been investigated (Cic-

coli *et al.*, 1989).

The Italian situation needs improvement as far as co-ordination of different groups is concerned: a national authority should be operating with the aim of collecting and elaborating environmental data.

#### Ex-Yugoslavia, Croatia and Slovenia

Oxidant concentrations were determined in the atmosphere of Belgrade during the warm periods of 1981 and 1982, founding significant levels (Vukmirovic *et al.*, 1987).  $O_3$  concentrations in ambient air were measured in Zagreb, on the island of Krk and Split during the five warm months in the mid '70s; about 5% of the measured hourly averages exceeded the threshold of 80 ppb, with peak values above 120 ppb (Cvitas *et al.*, 1979; Butkovic *et al.*, 1983; Butkovic *et al.*, 1990). In Zagreb an old record (1889-1900) of data collected by means of Schoenbein's method has been analyzed. Conclusions show an increase of concentrations from 36 to 67 ppb for daytime and from 30 to 56 ppb for night-time, compared to recent times.

Results from the monitoring network operating in Slovenia (Hrecek, 1991, 1992) do not put in evidence harmful levels of  $O_3$ , even though peak 1-h concentrations above 100 ppb are recorded in Ljubljana and on Mt Krvavec.

#### Greece

Photochemical pollution is under study in Greece with a high level of seriousness, also within international co-operative efforts. «Greater» Athens is considered one of the most polluted cities in the world and acknowledgement of air pollution dates back to 1975 (Sabatakakis, 1991). This city of nearly 4 million inhabitants is located in a small basin bordered by fairly high (> 1000 m) mountains on three sides and is open on one side to the sea. Here about 40% of Greek industry and almost one million vehicles (50% of all those registered in the country) are concentrated. The «nepfos» (meaning a cloud or plume), as it is known locally, has inspired public health fears and increasingly stringent controls on emissions. An historic series of  $O_3$  measurements carried out with colorimetric papers from 1901 to 1940 has been re-evaluated with comparative criteria: daily  $O_3$  values vary around 20 ppb, with maxima during the periods April-June (Varotsos and Cartalis, 1991). Since the early '80s high values of  $O_3$  up to nearly 300 ppb have been detected (Cvitas *et al.*, 1985); they are among the highest values reported in Europe and confirm that photochemical air pollution is the main environmental problem in Athens. Significant levels of PAN in Athens have also been observed (Tsalkan, 1988; Tsani-Bazaca *et al.*, 1988). Road traffic is generally considered to be the main source of the high levels of oxidants.

Athenian photosmog has been accurately

characterized and mathematical models developed (Moussioulos *et al.*, *in press*). Strong insolation is the cause of sea breeze flows which develop during more than 30% of the days in the spring and summer months. Because of the peculiar topography of the Athens basin, as a consequence of the sea breeze circulation, precursors are transported from the city over Saronikos Bay in the morning by the land breeze, then the sea breeze that starts around noon brings the air back over the centre, increasing the  $O_3$  concentration by a factor of 3-5 times; pollutant levels often remain high throughout the night (Guesten *et al.*, 1988). It is known that polluted air masses over the sea find favourable conditions to generate and retain high  $O_3$  concentrations, due to the lack of catalytic surfaces, smaller vertical transport coefficients, and no fast-acting sinks (Aldiz, 1969).  $O_3$  levels in the suburban periphery of Athens often exceed those in the city centre (Moussioulos *et al.*, *in press*).

#### Israel

Systematic  $O_3$  monitoring began in 1985, but biomonitoring started earlier. Some ten analyzers are active. The maximum  $O_3$  1/2 hour average recorded is 360 ppb, and the threshold of 100 ppb is regularly surpassed every year in the monitoring sites located in the major cities such as Jerusalem and Tel Aviv; a trend of increase in  $O_3$  concentrations seems preliminarily evident (Graber, 1990). The recurrence of significant levels of  $O_3$  at a rural site, 25 km from Jerusalem, has been described (Lifshitz *et al.*, 1988).

#### Egypt

Oxidant concentrations above 100 ppb have been found on 74% of the monitored days over one year in the «Greater» Cairo (Nasralla and Shakour, 1981).

#### Algeria

A preliminary campaign carried out in the Algiers region in winter-spring (Aoudia, 1991) gave evidence of a photochemical pollution problem, even if maxima  $O_3$  values in May did not exceed 60 ppb.

### Biomonitoring of ozone

Since 1962, the super-sensitive tobacco (*Nicotiana tabacum* L.) cultivar Bel-W3 has been used in many countries all over the world as an indicator of the presence of phytotoxic concentrations of  $O_3$  (Heggestad, 1991) (figure 5). The main advantages of biomonitoring are related to the possibility of carrying out extensive, capillary, and reliable investigations over large geographical areas with low costs.

A series of pioneering surveys of phytotoxic  $O_3$  were carried out in Israel in the «70s (Naveb *et al.*, 1978). Regionwide ex-

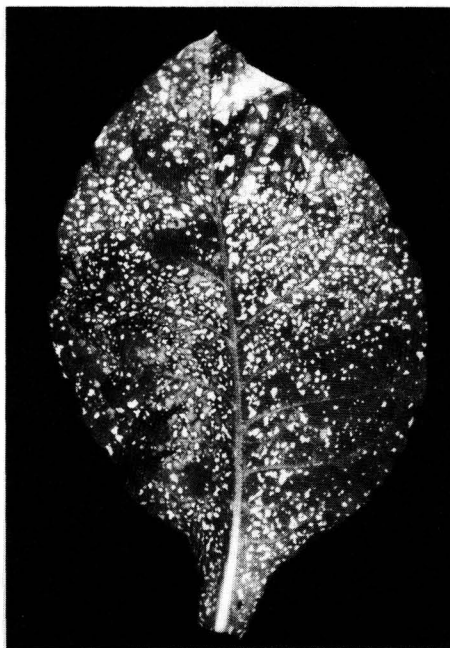


Figure 5 - Typical foliar symptoms («flecking») induced by ambient ozone on the indicator plant tobacco Bel-W3.

perimental surveys have been conducted in Italy, in Tuscany and in the Po plain. A standardized methodology (Ashmore *et al.*, 1978) was followed for growing and exposing plants to ambient air and recording the amount of leaf visible injury at weekly intervals. Results have already been given (Lorenzini and Panattoni, 1986a and b; Lorenzini *et al.*, 1988; Mignanego *et al.*, 1992; Schenone and Mignanego, 1988). Other spot investigations have been performed in the metropolitan areas of Rome (F. Manes, *pers. comm.*, 1990) and Bologna (N. Bagni, *pers. comm.*, 1990). Other minor and local studies have been carried out. In all the trials substantial leaf injury was found in urban as well in rural regions, also distant from any major source area. This implies that the threshold for manifest phytotoxicity (40-50 ppb for exposures of some 4 hours) has been frequently and abundantly passed. Weekly variation in the amount of leaf injury was constantly reported and generally resulted to be associated with meteorological parameters.

In both Tuscany and the Po plain there was a satisfactory correlation between data collected from biomonitors and the actual level of  $O_3$  as detected by physico-chemical analyzers. In Tuscany (Lorenzini *et al.*, 1988) the amount of visible injury on the indicator plants was negatively correlated with the presence of lead in leaf tissues of ryegrass (accumulator plant for heavy metals). The reason for this is that most ambient lead comes from vehicle exhausts, which also contain a mass of other pollutants, which easily react with  $O_3$  molecules and deplete them. A linear multiple correlation model computed for plants exposed in Milan has shown that leaf damage on indicator plants was influenced positively by

temperature and negatively by vapor pressure deficit (Biondi *et al.*, 1992). In Northern Italy (Mignanego *et al.*, 1992) the chronological analysis of variations in leaf necrosis showed a high correlation between all the sites in the Po plain, even for stations hundreds of kilometers apart. This can be explained by the existence of synchronous patterns of  $O_3$  pollution on a wide geographical scale.

In Greece, phytotoxic concentrations of  $O_3$  have been demonstrated to occur during the summer throughout Attica, in a 75 km radius of Athens (Velissariou *et al.*, 1992). The same methodology has been positively followed in the Vosges region, France (Garrec and Rose, 1988).

The spread of  $O_3$  over large areas means that the potential quantity of biological effects it can cause is much greater than in the case of many other pollutants, which only occur in relevant concentrations close to their source of emission.

### Effects on cultivated and forest plants

On a global scale,  $O_3$  is suspected to cause more damage to vegetation than all other pollutants combined. However, under natural conditions it is not easy to perform correct diagnoses which link foliar symptoms to the phytotoxic activity of atmospheric oxidants. This is mainly due to the relatively low specificity of visible markings that «normal» concentrations of pollution can elicit on plants. Most growers do not know they have a problem because they cannot see the disease; even for «experts» the symptoms of  $O_3$  are difficult to recognize. In most cases  $O_3$  injury simply mimics symptoms of normal senescence or diseases or disorders caused by other factors. In addition,  $O_3$  may hinder qualitative and quantitative plant performances without concomitant visible injury. As a consequence, we must admit that the present picture is underestimating reality.

Apart from an early isolated report of symptoms on vegetable crops resembling the typical ones induced by the Los Angeles-type smog at Pavia (Ciferri, 1955), evidence of  $O_3$ -induced visible phytotoxic markings was first reported in Tuscany in the early 1980's (Lorenzini *et al.*, 1984), but the unquestionable proof of the detrimental effects of regional air pollution on plant productivity under field conditions was only obtained a few years ago. The settlement by ENEL-CRTN of two air filtration experiments in Northern Italy, based on the open-top exposure technique (Schenone and Lorenzini, 1992) evidenced the relevant beneficial effect of filtering ambient air on productive performances of different crops (table 3). In bean (Panattoni *et al.*, 1990) the appearance of typical interveinal brown stipple associated with mesophyll histopathological alterations — which were reproduced under experimental conditions

**Table 3 Effects of air filtration on yield parameters of different crops grown in open-top chambers at two sites in the Po Plain, Northern Italy. The figures refer to the per cent differences between unfiltered and filtered air (after Schenone and Lorenzini, 1992).**

Species	Year	Site	Parameter	Observed variation (%)	
Wheat «Gemini»	1980	Urban	Kernel dry wt.	-27.4**	
		Rural		-17.9 ns <sup>1</sup>	
	1989	Urban		-21.7**	
		Rural		-21.2*	
	1990	Urban		-20.0**	
		Rural		-22.8**	
Barley «Barberousse»	1988	Urban	Kern dry wt.	-3.8 ns	
		Rural		-11.2 ns	
	1989	Urban		-20.1**	
		Rural		-15.5*	
	1988	Urban		Seed dry wt.	-31.5**
		Rural			-24.3*
1989	Urban	-18.3*			
	Rural	-31.0**			
1988	Urban	Hypocotil fresh wt.	-28.7**		
	Rural		-16.8 ns		
1988	Urban		Fruit dry wt.	-30.8**	
	Rural			-19.1**	
1990	Rural			-6.0 ns	
1990	Urban			-10.0	

\* \*\* Significant at 0.05 and 0.01 levels, respectively.

<sup>1</sup> Non-significant at  $P=0.05$ .

by fumigating healthy plants with realistic doses of  $O_3$  — was positively attributed to  $O_3$  toxicity. There are other cases under investigation in Italy, and among them a severe foliar white flecking of vegetable marrow, which only appears in ambient air chambers and not in filtered-air plots (*G. Schenone, pers. comm., 1990*). A similar symptomatology has been reported for watermelon from the Ebro Delta (Spain) and  $O_3$  is heavily suspected to be the culprit (*Reinert et al., in press*).

*Velissariou et al.* (1992) report a Greek farm where tobacco cultivation was stopped partly because of what were later identified as  $O_3$  lesions. The same authors found visible foliar lesions identical to those of  $O_3$  injury on Aleppo pine (*Pinus halepensis*) around Athens.

But the major problems are probably not connected to obvious visible injury: research in the last decades has increased our knowledge of the effects of  $O_3$  on plants and we have learned that foliar symptoms and effects on growth and yield are not closely associated. In other words, there is no proven relationship between foliar injury and crop yield (*Heagle, 1989*). So, sub-symptomatic long-term exposures to  $O_3$  under experimental conditions bring about a significantly greater rate of senescence and several metabolic disturbances (*Jacobson, 1982*). Strong productive effects (both quantitative and qualitative) on vegetation are expected for the growing season, with averaged  $O_3$  concentrations of 50 ppb or above. So, estimated percentage yield losses per seasonal 7-h per day mean  $O_3$  concentrations of 60 ppb may reach astonishing values of 21% (for cotton), 20% (for

peanut), 18% (for tomato), 15% (for kidney bean), and so on (*Heagle, 1989*).

### The necessity for national/international networks and other future needs

Formation of  $O_3$  in the planetary boundary layer during photochemical pollution episodes is likely to be the most important regional air pollution problem involving the Mediterranean basin, and there has been growing evidence of an increase in the concentration of  $O_3$  over the past decades. This means that «clean air» today differs from that present a few decades ago, and this could be very important for consequences on ecosystems.  $O_3$  concentrations in most agricultural areas of Southern Europe are now estimably two or three times higher than they would be without human influence. In spite of this, the knowledge about atmospheric pollution by oxidants does not appear particularly favorable. In no Mediterranean country does there appear to be in activity a national service for the collection, systematic processing and spreading of data concerning air quality and the subject is yet scarcely investigated, even if there are several situations which should be managed with seriousness. A notable exception is Athens, where photochemical pollution is regularly assessed. Important regions which are probably suffering from photochemical pollution have no  $O_3$  monitors or only a few (South coast of Spain, South Italy, North-African large cities). Generally speaking, the number of  $O_3$  devices is far

too low. Many monitoring stations are located inside the most polluted places of towns and often present not very high concentrations of  $O_3$ ; these low levels are mainly due to the destructive action towards  $O_3$  of nitrogen monoxide emitted load traffic and combustions.

The on-ground  $O_3$  distribution in Southern Europe is a relatively young field of research, less than 15 years old; great efforts are required in order to acquire a reliable overview of the actual status. An  $O_3$  climatology for Europe and the Mediterranean basin is needed. A better coordinated effort is required to collect data from the monitoring stations and administrate them, possibly at a few centers and in the public domain. A watch should be kept on trends; this applies especially for rising trends which can provide early warning of increasing seriousness of effects. Nation-wide monitoring networks which give a complete coverage of the countries should be organized, by implementing the present availability of analyzers. A group of task-forces should be put in charge of supervising all the aspects of the problem, including meteorological and biological ones, following the example offered by the *United Kingdom Photochemical Oxidants Review Group* (*Derwent, 1987*). An inter-calibration activity is advisable. The effort for publication of photochemical data should be increased, for instance editing a bulletin or technical letters. Periodic meetings and workshops should be organized on this topic.

The use of indicator plants has been proven to give satisfactory information, which have incomparable value from the didactic and educational points of view: the vision of the severe macroscopic injury which ambient air causes to sensitive organisms may stimulate in the citizen a deeper involvement in environmental issues. A standardization of methodologies, even at an international level (e.g. EEC, OECD) is strongly felt to be needed, in order to attain official acknowledgement of biomonitoring procedures. The use of species less sensitive than Bel-W3 tobacco could be advised, due to the very extreme response that this indicator gives in the Mediterranean pollution situations (see *Schenone and Lorenzini, 1990*). The recorded  $O_3$  concentrations in both rural and urban areas in some countries often approach and exceed air quality criteria levels which have been established (in Italy, for instance,  $200 \mu\text{g m}^{-3}$  [100 ppb] as an hourly mean not to be reached more than once a month). Another point of concern is that high  $O_3$  levels are regularly associated with the presence of raised concentrations of other dangerous pollutants in the photochemical smog (i.e. nitrogen dioxide, peroxyacetyl nitrate, volatile organic compounds), even if experimental data in this field are scarce. From this point of view,  $O_3$  should be regarded as a marker of a complex and potentially dangerous state of air pollution.

An assessment of yield losses caused by

regional air pollution should improve the global knowledge of environmental contamination also in economic terms and encourage authorities and decision-makers to put into action proper measures to improve the quality of our atmospheric environment. Comparison of the observed O<sub>3</sub> concentrations with the United States crop damage criteria suggests that in normal summers the yield of many crops will be significantly reduced (Adams et al., 1984; Lorenzini, 1987). Filtering ambient air in the presence of prevailing O<sub>3</sub> concentrations results in significant increases in productivity. There is not as yet a sufficient data base on which to develop dose-response relationships and provide a quantitative estimate of the impact of O<sub>3</sub> on vegetation in the Mediterranean basin. A provisional assessment based on theoretical dose-response modeling has indicated an annual economic loss, due to O<sub>3</sub> in the sole Province of Piacenza (Italy) and for 13 herbaceous and fruit crops, of 2.2-4.7 10<sup>9</sup> Italian lire (1-2.1 10<sup>6</sup> UK£) (Bocola et al., 1988).

Other biological effects of O<sub>3</sub> deserve special attention, mainly those which involve forest plants, in connection with the decline of forest health in Central Europe (Ashmore et al., 1985). An overall evaluation of the global impact of O<sub>3</sub> pollution should also include harmful effects to human health, surface warming due to the absorption of infrared radiation, decline in visibility, not to mention damages to materials and manufactured products. Global emissions have to be stabilized to avoid a further increase in ground level O<sub>3</sub> concentrations.

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