SEASONAL BUDGETS OF OZONE AND OXIDANT PRECURSORS IN AN INDUSTRIAL COASTAL AREA OF NORTHERN ITALY

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ABSTRACT

The seasonal budgets and evolution of photochemical oxidants reported for greater Ravenna's urban-industrial area in the present study were calculated using the combined data from on-site systematic surveys (1978-1989) and from the monitoring network of the local environmental authorities. The notable differences in the concentrations of ozone and nitrogen oxides depended on season, and meteorological variables showed a marked correlation to the seasonal budget of trace constituents. The weak local circulation, the land-sea breeze system, and high solar radiation in summer, which may persist at length because of the anticylonic conditions, can produce episodes of intense photochemical reactions. In winter, by contrast, low solar radiation and the absence of the breeze system result in very different evolutions of both pollutant concentrations and their seasonal budget.

1. INTRODUCTION

Oxidant concentrations in the lower atmospheric levels close to industrial sites are the result of emissions, chemical reactions and transport mechanisms. Local concentration values and their diurnal variations are highly dependent on solar radiation and the emission of primary pollutants such as nitrogen oxides and hydrocarbons. In addition to the atmospheric chemical reactions that occur in the presence of specific emissions by industrial or power-plants, topographic discontinuities like coastlines can induce peculiar anemologic circulation systems in which pollutants are transported (Giovanelli *et al.*, 1985).

Geographically and climatically part of the Po valley, Greater Ravenna (Figure 1) is bordered on the east by the upper Adriatic Sea and features an extensive seaboard industrial belt (petrochemical and chemical plants, an electric power station and other industries). These plants produce large amounts of oxidant precursors whose concentrations levels show that the entire coastal area is affected by chemical pollution (Bonasoni *et al.*, 1991). The city proper, located a few kilometers inland, is characterized by congested viability and the resulting accumulation of motor vehicle pollutants.

Ozone concentration readings taken since 1978 by the air quality network show values of hourly concentration several-fold greater than those of Italy's national health standards (Fortezza *et al.*, 1986). The total emissions in the Ravenna area of certain pollutants from industrial, traffic and domestic production are reported in Table 1.

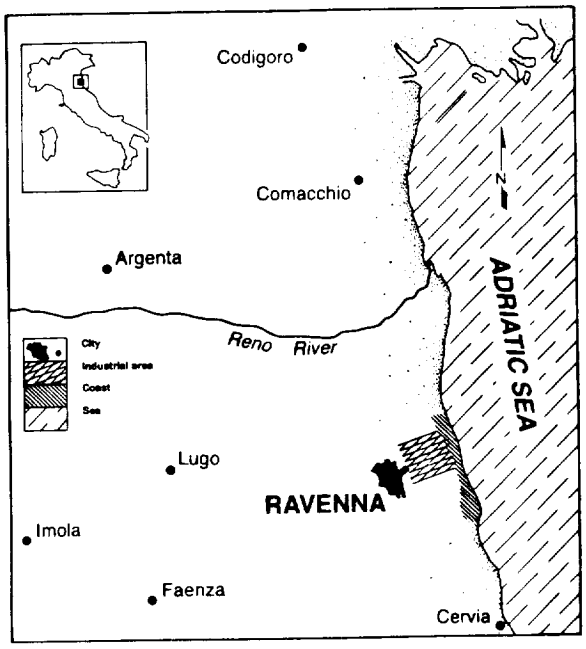

Fig. 1. Map of the Ravenna area.

2. DATA ANALYSIS AND DISCUSSION

Measurements were performed at an environmental protection network station equipped with the Philips analyzers PW9760 for NO_x (from 1986 monitored with an Environment AC30M) and PW9771 for O_3; meteorological sensors were placed at a representative site of the area under investigation. The solar radiation intensity was measured by a Kipp & Zonen AL4-MICROVA.

Figure 2 shows the average daily solar radiation for the period 1978-1989. Note the well-defined trend due to the sharp differentiation of the local climate at the change of seasons. Figure 3 has the average daily ozone concentration for the same period. Its seasonal variation is not so well defined throughout the period as that of solar radiation. The periods corresponding to zero value of O_3 concentrations are due to analyzer malfunction. Figure 4 shows the average diurnal NO_x concentration; the maxima correspond to the winter season.

Compound	Amount (T/Y)
SO_x	42,095
NO_x	13,053
CO	28,760
Particles	7,003
Hydrocarbons	3,026

Table 1. Yearly emissions from Ravenna area (industrial, civil and traffic)

The lengthy time span of this data set makes it possible to calculate the seasonal diurnal variation of O_3 and NO_x concentrations and of solar radiation with high statistical confidence. The seasonal trends were computed by averaging the half-hourly measurements collected in three-month periods. Figure 5 shows seasonal diurnal variations of solar radiation and figure 6 the seasonal diurnal variation trends of ozone concentration. A comparison of the summer and winter peaks reveals that the value of the former is three times higher than the latter. The spring and autumn concentration levels exhibit trends quite similar to each other over the day, noticeable differences appearing only in the tails of the trends corresponding to the late night and early morning hours. The relative maximum values are found about halfway between those of summer and winter.

Focusing on the position of the maximum it is possible to note during summer and spring high concentration values for many hours of the day and in the summer a secondary peak appears around 7:00 p.m..

This phenomena must be ascribed to transport mechanisms: in the warmer seasons the local prevailing circulation is driven by land-sea breeze system in which air masses rich in pollutants are transported out to sea in the morning, where they undergo photochemical reactions with subsequent ozone formation, and in the afternoon are transported back to the coast by the sea breeze, thereby causing persistent high concentration levels.

Figure 7 shows the seasonal diurnal variation trends of NO_x concentration. Note the strong decrease in values during the middle hours of the day due to photochemical reactions and turbulent diffusion in the increasing height of the mixing layer. The relative seasonal intensities are reversed compared to the ozone's, with high concentrations values recorded in winter rather than in summer.

During the coldest months the less dispersive condition of the atmosphere causes pollutant enrichment close to the emission sites, and the reduced incoming solar radiation prevents marked photochemical reactions and consequent NO_x depletion.

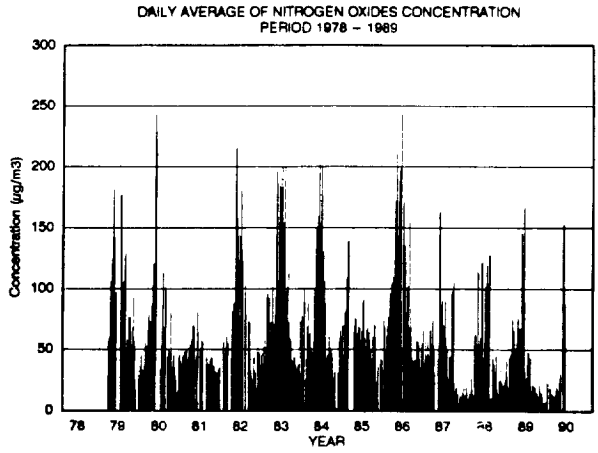

Fig. 2. Daily averages of solar radiation (1978-1989)

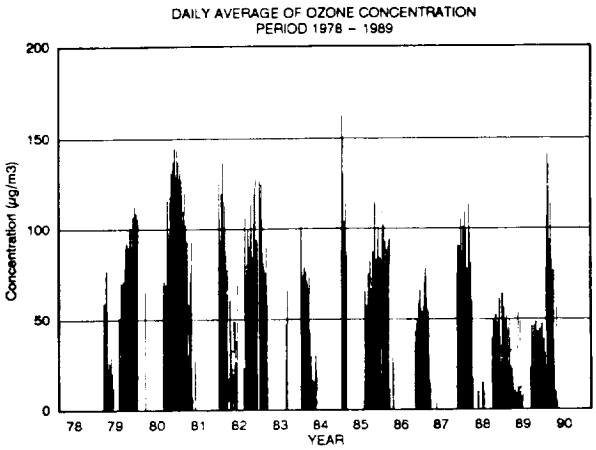

Fig. 3. Daily averages of ozone concentration (1978-1989).

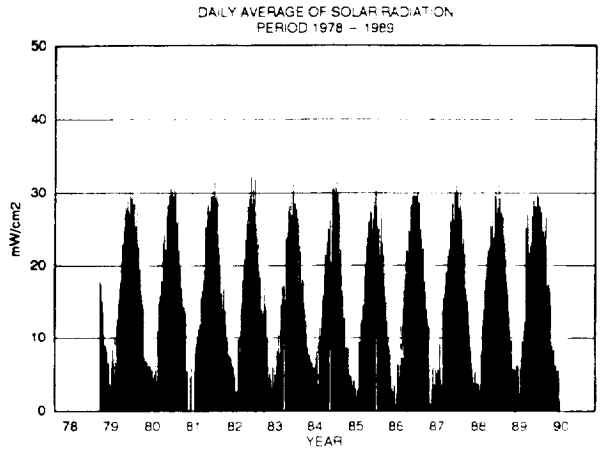

Fig. 4. Daily averages of nitrogen oxides concentration (1978-1989)

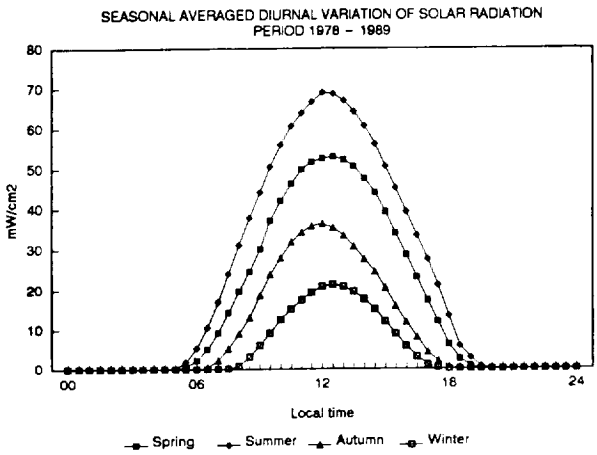

Fig. 5 Seasonal diurnal variation of solar radiation.

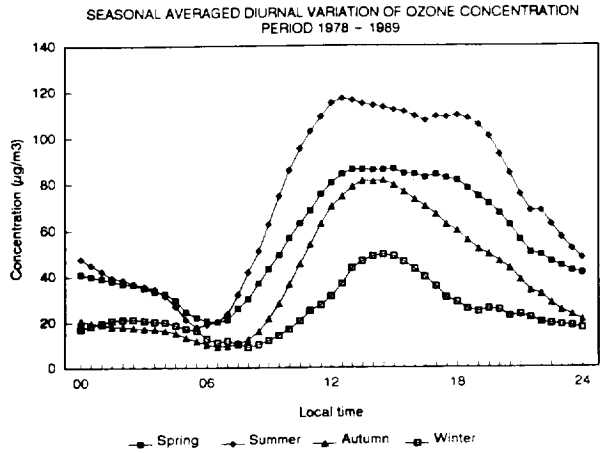

Fig. 6. Seasonal diurnal variation of O_3 concentration.

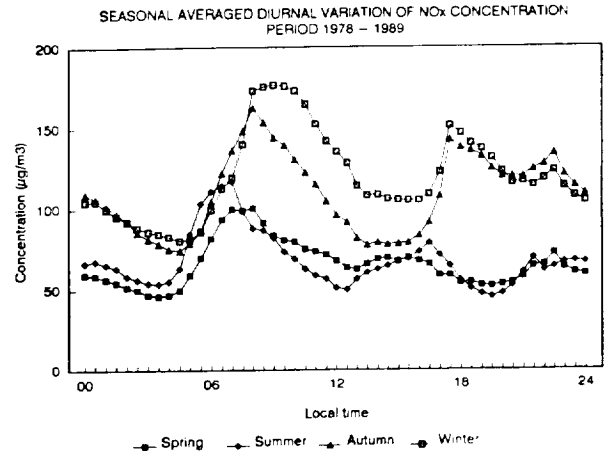

Fig. 7. Seasonal diurnal variation of NO_x concentration.

3. CONCLUSIONS

The high summer values of ozone concentration in Ravenna's industrial region, are to a great extent determined by emission of such pollutants as nitrogen oxides in conjunction with remarkable amount of solar radiation. The strong correlation of O_3 concentrations to the latter and the comparison with relative intensities indicate that solar radiation rathen than high concentrations of primary pollutants drives the formation of ozone. Transport phenomena due to the presece of topographic discontinuities can notably alter the duration of high level concentrations in this area.

Budgets show how during the warm seasons the air quality is subject to frequent episodes of photo-oxidation reactions, resulting in high concentration values of secondary pollutants. The simultaneous presence of hydrocarbons and ozone in atmosphere which can produce free radicals, is more likely in the summer.

ACKNOWLEDGEMENT

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