On Photochemical Air Pollution Potential in Southern California Derived from Ozone Data from 16 Monitoring Stations

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Abstract. Average hourly ozone volume fractions from ten automatic monitoring stations in the Los Angeles and six in the Riverside area for the April through September season in the years 2000 to 2005 have been analysed on the basis of recently introduced photochemical pollution (PP) indicators. Although considerably high indicator values were found for almost all the stations, surprisingly, some (*e.g.* Palm Springs) exhibit low daily maximum-to-minimum ratios of hourly ozone values which is crucial for assessment of a low PP by the given indicator method, despite the overall high ozone concentrations recorded. At such stations, in contrast to elsewhere, a characteristic quasi normal distribution of all ozone hourly volume fractions exists which could be a consequence of poor vegetation or some special meteorological conditions there. Compared with a similar assessment in central Europe and the Mediterranean region, the present analysis shows that PP problems in California are significant. (doi: 10.5562/cca2008)

Keywords: photochemical pollution, pollution indicators, ambient ozone, average hourly ozone data, ozone precursors, growth season

INTRODUCTION

Despite the enormous importance of ozone in the atmosphere for protecting life on Earth's surface by blocking Sun's UV radiation, because of its oxidizing capacity, elevated ozone concentrations in the planetary boundary layer are harmful to the most life forms. Its natural sources there are transport from the stratosphere by intrusions and from electric discharges that can break oxygen molecules into atoms, but most of it is a consequence of human activities releasing nitrogen dioxide which photolytically yields oxygen atoms to combine with molecular oxygen into ozone. Nitrogen dioxide concentrations in the atmosphere are normally very low (however, its natural sources being wildfires and lightning can under circumstances become quite substantial).[1] Considerably increased concentrations in ambient air can invariably be associated with human activities (energy production, chemical industry, transport and combustion processes) the increase in ozone volume fractions observed worldwide nowadays (or even the whole amount) is generally considered as pollution. It is also predicted that, most probably, further rise in the tropospheric ozone concentrations will occur in the future[2] and have effect on crops.[3] Ozone can be easily

and reliably monitored and based on measured average hourly ozone volume fractions a number of indices, directives, air quality standards and limits have been put forward in order to quantify the air quality affecting humans, vegetation and materials.[4,5] In spite of ozone being the most abundant species in the hazardous atmospheric condition known as photosmog, there are numerous other components present in this reactive brew which cause adverse effects. Based on long-term ozone monitoring results at various locations over Europe[6] we realized that along with a high daily value the extent of the diurnal variation expressed as the average of daily maximum-to-minimum ratio (R) gives a much better insight into the atmospheric condition arising from ozone formation in a polluted atmosphere that we call photochemical pollution (PP). Since ozone reaction products – aldehydes, peroxides, radicals, secondary organic aerosols[7–10] – represent very potent pollution components, new pollution indicators have been devised that take into account corrections of R for the amount of daily ozone production (P_1) and the number of hours the hourly average exceeded a chosen limiting value over a given period (P_2) (usually the vegetation growth season).[6,11] Also a third indicator defined as their geometrical mean was introduced to take care for possibly

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larger differences between P_1 and P_2, and is therefore chosen to be the principal photochemical pollution indicator in our recent analyses.[12,13] The ozone data from monitoring stations in California seemed to be a good example to test the approach on a really tough problem – assessment of PP at the cradle of Los Angeles smog. The proposed indicators for identification of sites prone to PP have shown good predictive power in the case of central European, Mediterranean (Italy, Slovenia, Croatia), a UK set of stations[14] and even some stations in the subtropics (Louisiana, Hong Kong).

METHODS

All the data used, were obtained from the California Environmental Protection Agency (http://www.arb.ca.gov/adam/hourly/hourly1.php) and US Environmental Protection Agency (http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm). The locations of all monitoring sites are given in Table 1 and shown on the map in Figure 1. All data, originally shown vol-

ume fractions in ppm, were simply converted to volume fractions in ppb.

The calculation method has been described previously[6,11,12] and was developed by analysing ten years of ozone data from twelve EMEP (European Monitoring and Evaluation Programme) stations over Europe. The indicators are defined as:

$$P_1 = RM / A \tag{1}$$

$$P_2 = R\left(1 + 168 \cdot t_{exc} / N\right) \tag{2}$$

$$P_3 = \sqrt{P_1 \cdot P_2} \tag{3}$$

where R is the average of daily maximum-to-minimum ratios, M is the seasonal average of daily maximum values, A is the average of all seasonal data, t_{exc} is the duration in hours the limit of 80 ppb was exceeded ("excess time") and N is the total number of hourly averages of ozone volume fractions measured over some period
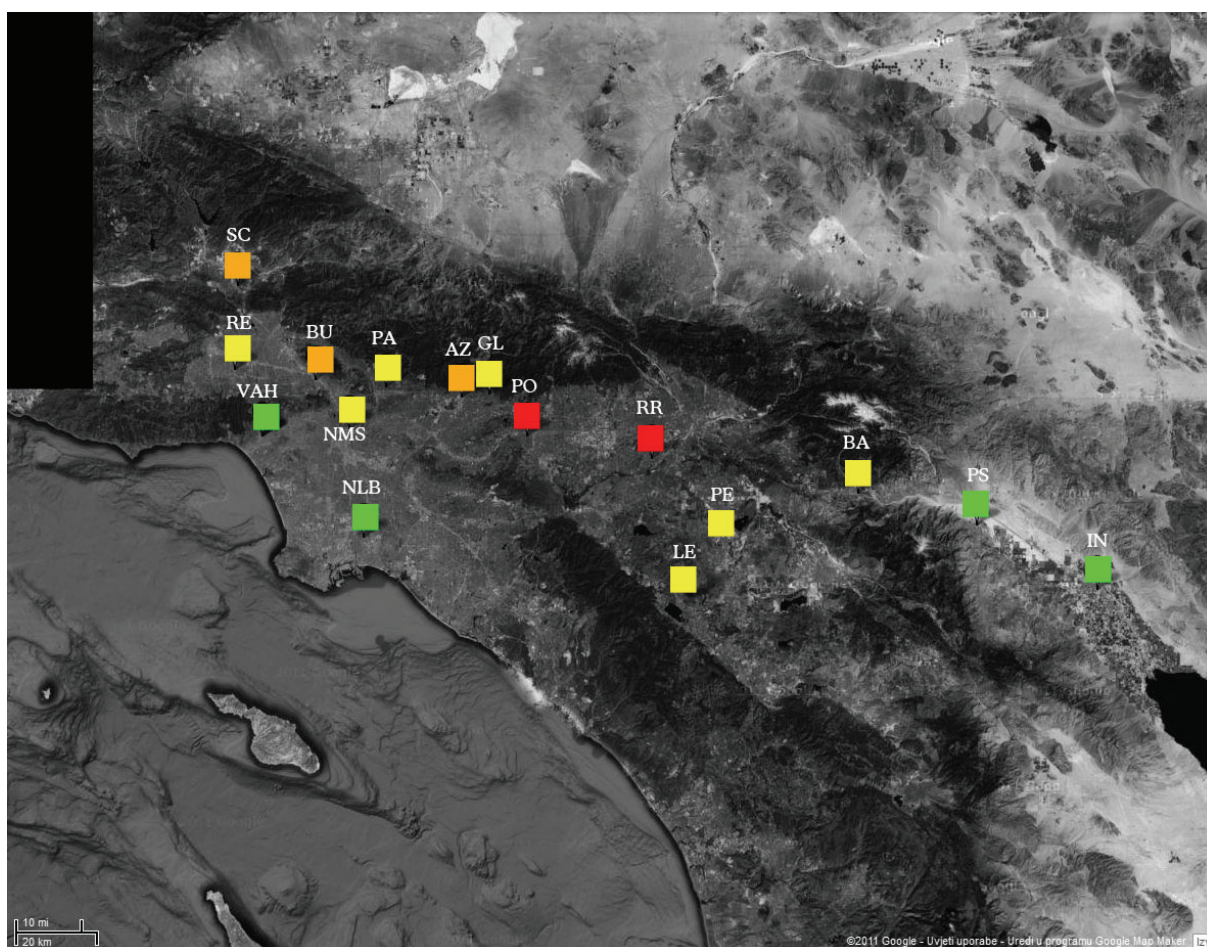
Figure 1. Map of the Greater Los Angeles Area with indicated monitoring sites. The colour codes for the P_3-indicators are as follows: green ($P_3 < 70$), yellow ($70 < P_3 < 140$), orange ($140 < P_3 < 210$) and red ($P_3 > 210$). The names of the stations, abbreviations and their geographical coordinates are given in Table 1.

Table 1. Geographical coordinates of 16 investigated monitoring sites

Monitoring station	Abbreviation	N Latitude / °	W Longitude / °	Altitude / m
Azusa	AZ	34.136	117.924	182
LA VA Hospital	VAH	34.051	118.457	61
Santa Clarita	SC	34.383	118.528	375
Burbank	BU	34.176	118.317	10
Glendora	GL	34.144	117.850	84
LA North Main Street	NMS	34.066	118.227	87
North Long Beach	NLB	33.824	118.189	6
Pasadena	PA	34.133	118.127	250
Pomona	PO	34.067	117.750	270
Reseda	RE	34.199	118.533	69
Indio	IN	33.708	116.216	–4
Palm Springs	PS	33.853	116.541	171
Lake Elsinore	LE	33.676	117.331	1449
Banning Airport	BA	33.921	116.858	473
Perris	PE	33.789	117.228	442
Riverside-Rubidoux	RR	34.001	117.415	250

of time (usually the growth season). The 168 factor in P_2 arises from the arbitrary 1 hour / week average excess time that, if present, would double the R value.

Both indicators are based on daily maximum-to-minimum ratios. The minimum value is set to 0.8 if recorded as zero in accordance with the detection limit of the instruments.

All indicators depend crucially on the value of R. Since R is the ratio of daily maximum and minimum hourly volume fractions, thus indirectly reflecting the daily ozone turnover, the indicators may also be a valid measure for adverse effects on living organisms and materials. However, especially the low, close to zero, values affect the average ratio strongly and hence the indicator values. This may also be seen from the frequency distribution of measured values which were analysed here, as well.

RESULTS AND DISCUSSION

The results for all the mentioned stations are shown in Table 2. Data in the table include (in the order of the columns) location, name of the station followed by corresponding average values of the ozone volume fraction (A / ppb), average of daily maximum-to-minimum ratios (R), average of daily maxima (M / ppb), average excess time during which the 80 ppb limit was exceeded (t_{exc} / h) and averages of indicators P_1, P_2 and P_3. The last column gives the total number of recorded and validated hourly average ozone volume fractions. Data in the table include period from April to September in each year. For every station except Perris, 6-year

period from 2000 to 2005 has been covered. (Perris had not enough data for 2005 and this year was excluded). Annual differences between data from the same station do not indicate any significant trend neither toward lower nor to higher values of ozone in the atmosphere.

One can observe that indicators P_1 and P_2 often contribute to P_3 very differently – the influence of P_2 being much higher in almost all cases (with the exception of LA VA Hospital). It was found previously[6] that for stations in moderate climate regions the values of P_1 and P_2 did not differ much for a given station and the number of hours above the threshold of 80 ppb was usually quite low.

Table 2 shows that photochemical pollution in California is substantial indeed. According to our previous analysis[6] sites with indicator values greater than 40 should be classified as medium polluted, and those with indicator values above 100 as polluted. During the seasonal period, only two of the 16 investigated stations: Palm Springs and NLB, have a P_3-indicator value (as 6 years average) lower than 40, while 10 of them exceeded the value of 100. An alternative grouping of the sites in ranges of 70 units for P_3 yields four as low to medium ($P_3 < 70$), seven as substantially ($70 < P_3 < 140$), three as heavily ($140 < P_3 < 210$) and two as extremely polluted sites ($P_3 > 210$): Pomona with 220 and Riverside-Rubidoux with 300. For comparison, P_3-values for three Louisiana stations (8-year averages), which are at similar latitude, were between 57 and 71, while the highest value determined for the Pearl River Delta station at Luhu Guangzhou (China) for months June – November 2006 was 277.[12]

Table 2. Characteristic parameters of ambient ozone fractions obtained for the growth season at 16 monitoring sites in the Greater Los Angeles area

Monitoring station	A / ppb	R	M / ppb	t_{exc} / h	P_1	P_2	P_3	N
Azusa	28.4	42.6	71	185	110	350	190	25 140
LA VA Hospital	31.7	31.0	59	41	60	70	63	25 058
Santa Clarita	38.8	31.8	85	423	70	580	200	24 600
Burbank	27.9	44.2	68	147	110	280	180	24 948
Glendora	34.9	19.4	78	281	44	230	99	25 079
LA North Main Street	26.2	35.3	60	60	83	120	97	24 597
North Long Beach	28.6	12.5	50	9	22	18	20	25 129
Pasadena	30.7	26.2	70	172	60	190	110	25 099
Pomona	25.6	50.9	67	158	130	380	220	25 143
Reseda	35.3	25.3	73	255	53	260	110	25 158
Indio	47.8	13.5	72	270	21	160	56	25 394
Palm Springs	55.4	4.5	81	502	6.5	94	25	25 029
Lake Elsinore	42.6	25.1	80	366	47	380	130	24 744
Banning Airport	48.7	21.2	85	516	37	480	130	24 528
Perris	42.1	19.0	84	462	39	380	120	21 183
Riverside-Rubidoux	36.8	48.6	82	413	110	850	300	24 963

The variations in the indicator values from year to year are not very large and usually within 30 to 40 % expressed as relative standard deviations. This means that only two figures in the indicator values can be taken as significant. Variations for very large displacements of sites are, of course, larger, but too little is known (too few data analyzed) at present to allow us to draw meaningful conclusions.

It needs to be noted that two of the stations with the lowest P_3 values – Palm Springs and Indio – are located in the desert valley surrounded by mountains, while the other two – NLB and LA VA Hospital – are located close to the sea. Lack of vegetation and local conditions (*e.g.* lack of nitrogen oxides at night)[15] may be the reasons; unusually low P_3-values were also found for the coastal stations in Hong Kong.[12]

The low P_3-values are a consequence of low R values at Palm Springs and Indio stations. In spite of the yearly average of over 500 hours with ozone fractions in excess of 80 ppb which occur here, the P_3-values remain low because of the small difference between the daily maximum and minimum values. The high values could be a consequence of ozone and ozone-precursor transport from neighbouring locations, yet no significant destruction takes place owing to scarce vegetation and hardly any deposition to desert sand.[16] Consequently, although experiencing high ozone values, these sites, because of comparatively low ozone destruction, exhibit relatively low P_3-values and belong to medium PP according to the described scheme.

On the other hand, sites such as Azusa, Santa Clarita, Riverside-Rubidoux and Pomona have extremely high P_3-values indicative of photochemically most polluted sites, such as some found in the Pearl River Delta (PRD) area.[12] High daily ozone production in this area is accompanied with high ozone consumption by volatiles and aerosols in the air.

If average data for the whole years are compared with seasonal values in Table 2, the monthly averages and averages of daily maxima of ozone concentrations for all stations are significantly lower (30 %) and more than 95 % of excess time is observed during the growth season (compared with 95 % in Sicily, Italy, 91 % in Louisiana, USA, but only 84 % in PRD, China).[12] Because low values of average ozone hourly data do critically affect the R-value and finally the PP assessment we compared the shape of the ozone data frequency distribution during the growth season with the indicator P_3 calculated here for the California stations.

The frequency distributions of ozone volume fractions are represented by histograms of a box-width of 5 ppb, Figure 2. For sites with low P_3-values the distribution shows a quasi-normal (Gaussian) shape while for sites with high P_3-values a much higher frequency of low ozone volume fractions can be seen. Analogously the cumulative probability distribution generally following a sigmoidal curve becomes more spread out as the P_3-indicator increases. This is to be expected since the indicators are largely determined by the average daily maximum-to-minimum ratio, R, which increases with the spread of measured values.
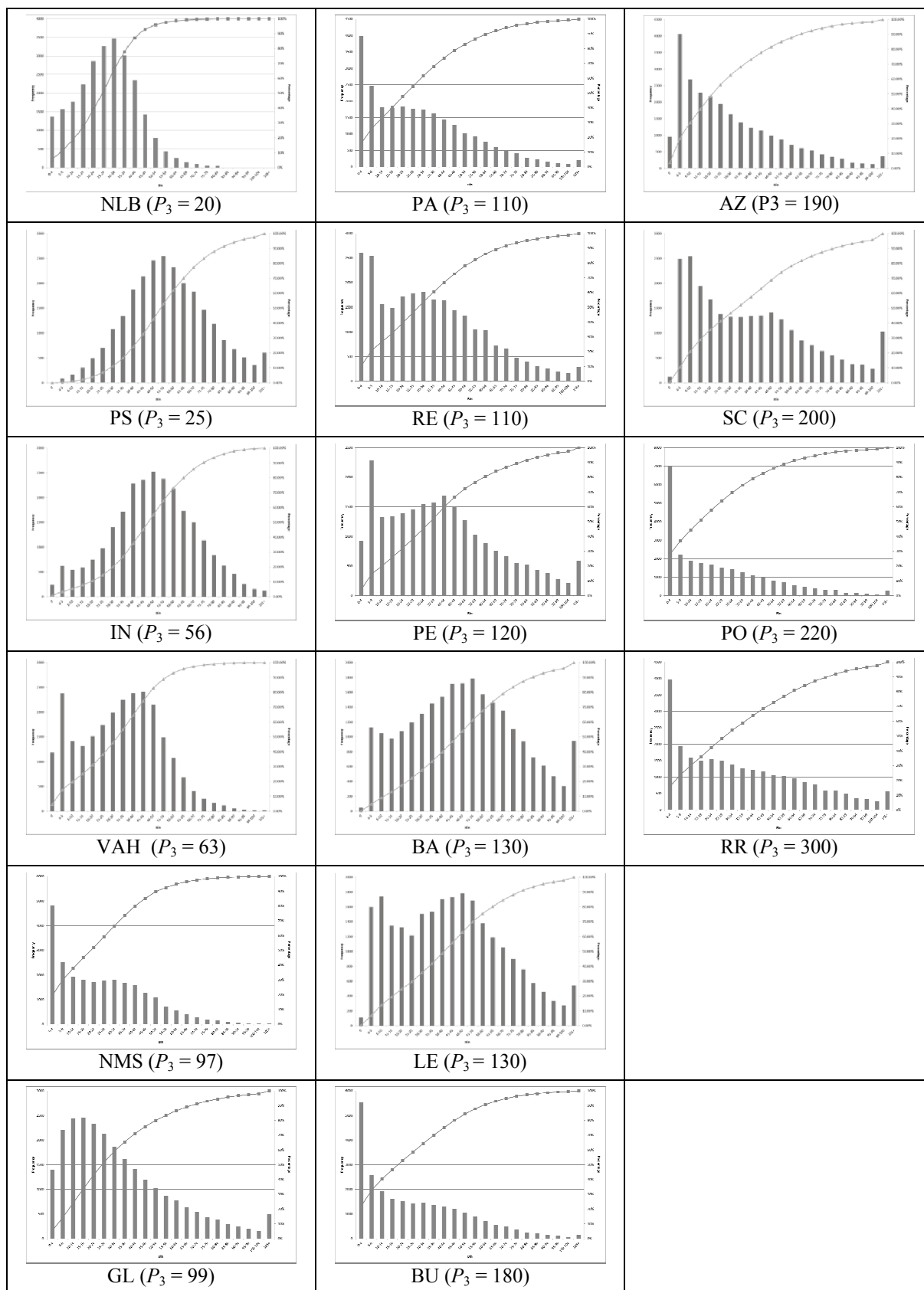
Figure 2. Histogram representations of frequency distributions of seasonal ambient ozone fractions (in 5 ppb intervals) and calculated P_3-indicator values for 16 Californian stations. Station abbreviations are given in Table 1.

CONCLUSION

The present assessment of PP at some stations in the Los Angeles and Riverside regions during the growth season from April through September based on indicator determination from ozone data between 2000–2005 shows the sites to be prone to PP, however, with relatively large differences found (*e.g.* for Palm Springs and Riverside) between them. The comparison with the data for the whole year shows that the growth season has been adequately chosen because less than 5 % of the measured ozone volume fractions exceeding the 80 ppb threshold occur outside the season similar as in Europe, and less than in Louisiana where it is ca. 15 % or the Pearl River Delta region where 30 % of the excess times lie outside the April to September period. Although the indicator values do differ for years at a station as well as between the stations a general pattern of high PP in the region is clearly observable (see Map). The indicators reflect the distribution of hourly average ozone volume fractions. High indicator values are associated with a high frequency (significantly higher than in a normal distribution).

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