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Original Scientific Article

Photochemical Pollution Indicators in the Subtropics

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Abstract. Indicators evaluated from the long-term hourly averages of ozone volume fractions at air monitoring sites are proposed as measures of the photochemical pollution exposure at those sites. These indicators are based on the average of the daily maximum-to-minimum ratio during the period of maximum ozone production and are corrected a), for the average maximum to average total ozone ratio (indicator P_1) and b), for the number of hours the limit ozone volume ratio limit of 80 ppb was exceeded (indicator P_2). These indicators are then combined into P_3 as their geometrical mean. The rationale for the introduction of a new set of indicators is based on the suspicion that ozone volume fractions do not provide information either on the total daily ozone that is produced or on the fraction of it that has produced other photochemical pollution components despite that ozone correlates quite well with some of them. Unlike the European stations, where every case in excess of the 80 ppb limit occurs within the April to September "growth period", stations in the subtropics have longer periods (*e.g.* at Greater Baton Rouge (GBR), USA, for 2001 to 2008) are shifted towards later months June to November (*e.g.* the Pearl River Delta (PRD) in China for 2006). While GBR and the rural PRD stations exhibit indicators close to those of polluted stations in northern Italy (Po Valley), the (sub)urban PRD stations have high photochemical pollution indicators. However, a surprisingly low indicator level occurs for the coastal Hong Kong stations for reasons possibly attributable to the prevailing easterly winds which bring fresh air and airborne sea-salt particulates. (doi: 10.5562/cca1807)

Keywords: ambient ozone, photochemical pollution, pollution indicators

IMPLICATIONS

The proposed indicators represent a new approach to photochemical pollution problems and they permit a very different view of the air quality at particular sites. The proposed pollution indicators might be of interest to law- and policy-makers in that they give a better representation of pollution-related problems than do simple limiting values. Such indicators should also function well in different climatic zones.

INTRODUCTION

A considerable rise of tropospheric ozone in the subtropics is predicted[1,2] over the next 100 years. Ozone is a strong oxidant that affects living cells and their constituents, especially those involved in photosynthesis and respiration processes, and, hence, vegetation and human health in general. It also affects numerous other materials prone to oxidation.

Ozone, a typical pollutant in the atmospheric boundary layer of regions with substantial sunshine and vehicle traffic, is relatively easy to measure and has been monitored at many sites for long periods of time. We have recently shown that by a systematic comparison of the accumulated and now widely available 1-hour averages of ambient ozone data from sites in Europe,[3] particularly ones in the central Mediterranean region (Italy, Slovenia, Croatia),[4] valuable information on photochemical pollution can be obtained using newly proposed indicators (vide infra). Actually the new indicators are more relevant for photochemical pollution than traditional ozone indices based on daily average or hourly maximum. Since ozone formation is initiated by photo-dissociation of NO_2 and since its further production and destruction is facilitated by the presence of volatile organic compounds (VOCs) and particles,[5] its volume fraction (or mass concentration) shows a pronounced diurnal variation with peak values in the early afternoon and minimum values during rush-hours and

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night. The daily maximum hourly or longer-term values are used to define indices, limits, directives and standards for air quality with respect to ozone. However, these entities provide little or no information on the total amount of ozone produced daily nor on the amounts of other photochemical pollution components that are subsequently produced in further reactions of ozone with other pollutants present in the air. Ozone concentrations do correlate quite well with some photochemical indices[6] but these generally represent reactants (precursors) and not the products of reactions with ozone. It is not unusual, for example, that higher altitude stations in remote areas record higher hourly and long-term (8 hours or more) averages than do stations in urban and suburban sites where the significant destruction of ozone decreases the average but often leads to further deterioration of the air quality. Consequently, ozone fractions, on their own, are not valid indicators of photochemical pollution. By assuming that ozone reaction products (*e.g.* aldehydes, peroxides, radicals and secondary organic aerosols (SOA)[7]) represent very potent pollution components of the ambient air, new pollution indicators were devised by considering the typical diurnal variation of ozone volume fractions. The indicators are based on calculating the ratios of daily maximum-to-minimum hourly average ozone fractions, the maxima being representative of ozone formation and the minima of ozone destruction and, hence, of the formation of potentially hazardous compounds. The average of such daily ratios over time periods of interest (*e.g.* growth season 1 April – 30 September), yields a valid indication of the ozone load along with its reaction products in air. A further correction factor was also applied in order to give a higher weight to the peak ozone values. This was done in two ways: (1), the average ratio is multiplied by the seasonal average of daily maxima divided by the mean for the whole season (indicator P_1) or (2) by accounting for the total time a chosen limiting value (*e.g.*, 80 ppb) was exceeded (indicator P_2).

One further problem with this procedure had to be solved. When the daily minimum hourly value was measured as zero, thus preventing the calculation of the max/min ratio, the ratio was set to 1.25 times the maximum value. This factor was obtained by considering the detection limit and precision of used ozone monitors. Originally, the minimum value was set at 0.4 instead of 0 ppb, based on the 1 ppb precision of the monitors[4] which proved to be too large and yielded very high ratios. Setting the zero value to 0.8 ppb, which is equivalent to multiplication of the daily maximum by 1.25, was found to be a more appropriate correction factor because frequent zero values in the data were often a result of imprecise measurements at very low volume fractions.

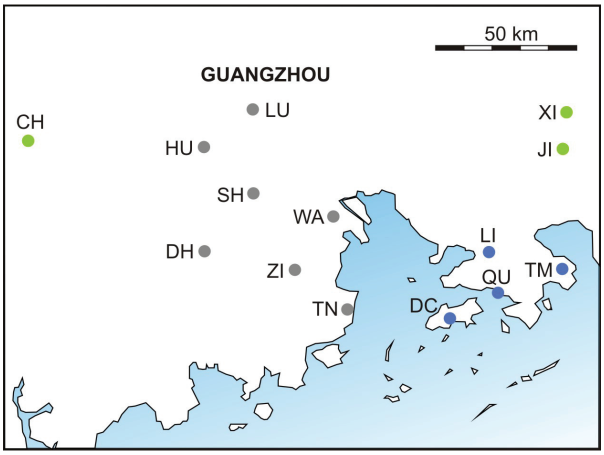

Figure 1. Map of PRD sites indicating rural (green), maritime (blue) and suburban (grey) location.

In order to investigate the incidence of high-ozone episodes at latitudes closer to the tropics, we have analyzed the data for the whole year and compared them with those consecutive six months, the "growth season" in mid-latitudes, that would cover most of the high pollution events. Thus by analyzing ambient ozone data for many European stations,[3,4] it was found that the 80 ppb ozone limit had been rarely, if ever, exceeded outside the April–September period. One would expect a different seasonal distribution at lower latitudes. Present investigation is aimed to find out how do the new indicators perform in the subtropics, concerning both their value and their seasonal (and growth-seasonal) dependence. It should be mentioned that in the Fourier transform frequency analysis of long-term ozone data the ratio of yearly to daily frequency intensities correlates nicely with the *R*-value of investigated monitoring stations.[8,9]

EXPERIMENTAL METHODS

The two indicators: $P_1 = RM/A$ and $P_2 = R(1+168\,t_{exc}/N)$, where R is the average of daily maximum-to-minimum ratios, M and A the seasonal average daily maximum and average values, t_{exc} the time in hours the limit of 80 ppb was exceeded and N the number of measured hourly average fractions. The scaling factor 168 represents the number of hours per week and was chosen so as to multiply R by two when the limiting value was exceeded for one hour per week on the average. The two indicators have been applied here in the analysis of data from three stations Capitol (CAP), Louisiana State University (LSU) and Port Allen (PAL) in the Greater Baton Rouge (GBR) area[9] in USA for 2001–2008 (http://www.deq.louisiana.gov/portal/Default.aspx?tabid =2420) and fourteen stations in the Pearl River

Table 1a. Ozone data for the Baton Rouge area stations for the whole years 2001 to 2008.
(source: http://www.deq.louisiana.gov/portal/Default.aspx?tabid=2420)

JAN – DEC									
	Year	A/ppb	R	M/ppb	t_{exc}/h	P_1	P_2	P_3	N
Capitol	2001	23.5	29.2	47	56	58.5	62.1	60.3	8364
	2002	21.8	26.9	44	34	54.3	44.8	49.3	8592
	2003	21.5	30.4	44	58	62.1	65.0	63.5	8524
	2004	22.8	23.6	43	35	44.5	39.9	42.1	8530
	2005	24.7	20.1	46	48	37.4	39.0	38.2	8546
	2006	23.9	16.7	46	42	32.1	30.3	31.2	8585
	2007	23.1	16.3	45	31	31.8	26.2	28.9	8604
	2008	23.6	20.7	42	5	36.8	22.8	29.0	8028
	CAP	**23.11**	**22.98**	**44.6**	**38.8**	**44.7**	**41.3**	**42.8**	**67 773**
Louisiana State Univ.	2001	23.4	21.6	46	48	42.6	42.2	42.4	8472
	2002	22.4	27.2	45	34	54.6	45.2	49.7	8607
	2003	23.8	30.2	49	92	62.3	85.3	72.9	8514
	2004	26.1	27.3	49	98	51.2	80.4	64.2	8439
	2005	28.6	27.0	54	138	50.9	100.4	71.5	8506
	2006	28.5	16.6	53	89	30.9	45.7	37.6	8546
	2007	26.4	17.5	50	74	33.1	42.7	37.6	8601
	2008	25.4	24.4	46	17	44.2	33.1	38.2	8074
	LSU	**25.57**	**23.96**	**49.0**	**74.1**	**46.2**	**59.5**	**51.8**	**67 759**
Port Allen	2001	23.1	31.7	47	54	64.5	65.7	65.1	8463
	2002	23.9	18.5	46	49	35.6	36.7	36.1	8393
	2003	24.0	29.5	49	105	60.2	90.1	73.6	8583
	2004	24.6	24.0	47	70	45.9	56.9	51.1	8595
	2005	26.5	26.2	50	56	49.5	55.1	52.2	8555
	2006	26.6	16.3	50	101	30.6	48.4	38.5	8617
	2007	23.4	16.9	45	30	32.6	26.9	29.6	8564
	2008	23.3	20.2	43	7	37.3	23.2	29.4	8110
	PAL	**24.44**	**22.87**	**47.0**	**59.3**	**44.5**	**50.4**	**47.0**	**67 880**

Delta (PRD) region in southern China for the year 2006. The latter data were collected within the Program of Regional Integrated Experiments on Air Quality over the Pearl River Delta: (PRIDE-PRD-2006). All stations (Figure 1) were provided by automatic ozone monitors and were logged as average hourly volume collected at all fractions. All stations (PRD 21.5° – 24° N, GBR around 30° N) fulfill the subtropical condition. The indicator $P_3 = \sqrt{P_1 \cdot P_2}$, introduced recently[4] as more robust to variations than P_1 and P_2, is also given.

RESULTS

The results for all stations consist of the following annualized items: averages of the ozone volume fraction (A/ppb), the corresponding average of the daily maximum-to-minimum ratios (R), the average of daily maxima (M/ppb), the time (in hours) the 80 ppb limit is exceeded (t_{exc}/h), the calculated photochemical pollution indicators P_1 and P_2, their geometric mean $P_3 = \sqrt{P_1 \cdot P_2}$ and the number of hourly values (N) for a, the whole year and for b, the six consecutive months with the highest photochemical pollution are given for the GBR area in Tables 1a and 1b and for the Pearl River Delta area in Tables 2a and 2b, respectively.

The chosen mid-latitude growth season (1 April to 30 September) covers almost all the events (91 %) within which the 80 ppb limit was exceeded at the three (sub)urban stations in the GBR area and the data are similar to those from polluted sites along the river Po in

Table 1b. Ozone data for the Baton Rouge area stations for the period 1 April to 30 September with highest photochemical pollution (source: http://www.deq.louisiana.gov/portal/Default.aspx?tabid=2420)

APR – SEP									
	Year	A/ppb	R/ppb	M/ppb	t_{exc}/h	P_1	P_2	P_3	N
Capitol	2001	26.7	33.1	53	54	65.8	104.4	82.9	4213
	2002	25.6	34.6	53	34	71.5	80.5	75.9	4307
	2003	24.4	35.3	51	43	73.6	95.2	83.7	4255
	2004	25.9	26.0	49	33	49.2	59.6	54.2	4292
	2005	30.0	19.8	56	40	36.9	50.7	43.3	4295
	2006	27.6	19.8	54	42	38.8	52.4	45.1	4295
	2007	26.9	18.9	52	31	36.5	41.6	39.0	4316
	2008	25.7	21.5	47	5	39.4	26.1	32.1	3970
	CAP	**26.61**	**26.14**	**51.9**	**35.48**	**51.5**	**64.0**	**57.1**	**33 943**
Louisiana State Univ.	2001	26.8	19.1	51	47	36.3	54.2	44.4	4285
	2002	26.3	32.8	53	34	66.0	76.2	70.9	4315
	2003	27.5	33.4	56	75	67.9	131.3	94.4	4304
	2004	30.4	29.4	58	88	56.2	132.8	86.4	4212
	2005	34.4	36.0	65	127	67.9	218.1	121.7	4211
	2006	32.2	19.0	61	83	36.1	80.8	54.0	4294
	2007	30.1	19.8	58	71	38.1	74.4	53.2	4312
	2008	27.6	25.1	50	15	45.6	41.9	43.7	3783
	LSU	**29.42**	**26.83**	**56.6**	**68.09**	**51.8**	**101.7**	**71.3**	**33 716**
Port Allen	2001	25.2	39.5	51	43	80.0	105.8	92.0	4303
	2002	27.2	25.7	54	49	51.1	75.6	62.2	4242
	2003	26.9	33.1	55	84	67.8	141.9	98.1	4300
	2004	27.3	27.2	52	61	51.8	92.0	69.0	4296
	2005	30.4	36.9	58	45	70.5	102.3	84.9	4272
	2006	30.3	20.0	58	101	38.2	98.4	61.3	4321
	2007	26.9	19.7	53	29	38.7	42.0	40.3	4299
	2008	25.1	25.2	47	7	47.1	32.9	39.4	3817
	PAL	**27.45**	**28.45**	**53.6**	**53.06**	**55.8**	**87.1**	**68.8**	**33 850**

northern Italy.[4] When the period was shifted by one month from 1 May to 31 October no significant change was observed. The reason is that both in April 2003 and October 2005 unusually high ambient ozone fractions were measured. It seems, however, that a longer period such as 7 months covering April to October, would take into account all the pollution episodes in any given year.

The data for the 14 PRD-stations (Figure 1) during 2006 reveal three types of sites: first, the rural type stations CH, XI and JI which lie at some distance both from the heavily polluted Guangzhou area as well as from the sea; second, the coastal type stations LI, TM, QU and DC within the Hong Kong area; and third, the (sub)urban stations within or affected by the greater metropolitan area of Guangzhou (Table 2).

Ozone data at the rural stations CH, JI and XI show a similar behaviour to the Baton Rouge stations. However, the frequency of high ozone events (above 80 ppb) outside the mid-latitude growth season (April-September) is much higher here (some 30 %) but reduces to 15 % when the six-months period is shifted to June-November. Both the USA and the China data suggest that the period of frequent high ozone events at lower latitudes is shifted to later months compared to the European April-September growth season. In addition, the data indicate that the spread of high ozone events becomes wider the further south one goes: the April-September period covers over 95 % of such events in Europe,[4,5] the same period 91 % in Louisiana, but in the most high ozone abundant June-November

Table 2a. Ozone data for the Pearl River Delta area (Figure 1, at right) for the whole year 2006

JAN – DEC 2006									
	Site	A/ppb	R/ppb	M/ppb	t_{exc}/h	P_1	P_2	P_3	N
Rural	CH	21.7	16.4	47	124	35.6	60.2	46.3	7830
	XI	24.7	22.4	51	133	46.3	82.1	61.7	8363
	JI	32.5	13.8	57	172	24.1	65.1	39.6	7750
		26.2	**17.7**	**51.6**	**142.7**	**35.6**	**69.4**	**49.5**	**23 943**
Coastal	LI	19.1	21.2	41	83	45.5	61.1	52.7	7417
	TM	34.4	7.0	55	183	11.2	32.5	19.1	8503
	QU	12.5	10.9	28	19	24.3	15.0	19.1	8527
	DC	18.6	19.7	40	77	42.2	50.2	46.0	8334
		21.2	**14.5**	**41.0**	**90.8**	**30.2**	**38.9**	**33.5**	**32 781**
Suburban	LU	15.4	51.5	47	139	157.3	213.3	183.2	7436
	HU	17.7	30.4	52	215	89.3	174.4	124.8	7630
	SH	19.0	26.6	53	285	74.2	187.0	117.8	7946
	WA	21.1	34.6	54	316	88.6	259.6	151.7	8164
	DH	17.2	24.5	44	180	62.9	117.6	86.0	7969
	ZI	21.2	41.0	55	269	106.0	302.9	179.2	7073
	TN	23.2	19.3	51	297	42.5	146.5	78.9	7578
		19.3	**32.3**	**50.8**	**243.6**	**88.1**	**199.1**	**130.8**	**53 796**

Table 2b. Equivalent data for the period 1 June to 30 November with highest photochemical pollution

JAN – DEC 2006									
	Site	A/ppb	R/ppb	M/ppb	t_{exc}/h	P_1	P_2	P_3	N
Rural	CH	25.3	17.3	55	112	37.6	102.2	62.0	3841
	XI	26.4	22.3	56	107	47.3	119.9	75.3	4110
	JI	32.3	16.7	59	118	30.5	97.5	54.5	4105
		28.1	**18.8**	**56.7**	**112.3**	**38.5**	**106.6**	**64.0**	**12 056**
Coastal	LI	21.5	14.9	46	66	31.9	59.5	43.6	3709
	TM	34.5	7.7	56	153	12.6	54.3	26.2	4274
	QU	13.7	12.2	31	16	27.5	19.8	23.3	4268
	DC	20.3	20.1	44	65	43.7	72	56.1	4232
		22.5	**13.7**	**44.2**	**75.4**	**28.8**	**51.1**	**37.0**	**16483**
Suburban	LU	18.4	61.2	57	122	189.7	403.5	276.7	3662
	HU	21.6	36.5	63	181	106.8	324.4	186.1	3860
	SH	23	37.9	66	250	108.7	432.8	216.9	4028
	WA	25.6	37.3	66	263	96.1	436.3	204.8	4129
	DH	20.4	25.5	52	161	65	201.3	114.4	3923
	ZI	25	38.6	64	230	98.7	415.3	202.5	3954
	TN	29.1	25.4	64	255	55.9	307.7	131.2	3858
		23.4	**37.3**	**61.8**	**210.2**	**102.2**	**360.9**	**189.9**	**27 414**

period only 84 % of the events in the PRD. It should be stated that June-July is at PRD the typical "wet" season, while October the "dry" and "polluted" season. It is typical of the subtropics that after a long "winter" a short "spring" is followed by a long "summer" characterized by transport of clean and wet ocean air inland. This is more pronounced at lower latitudes (GBR *vs.* PRD). Three stations LI, TM, QU and DC at the coast

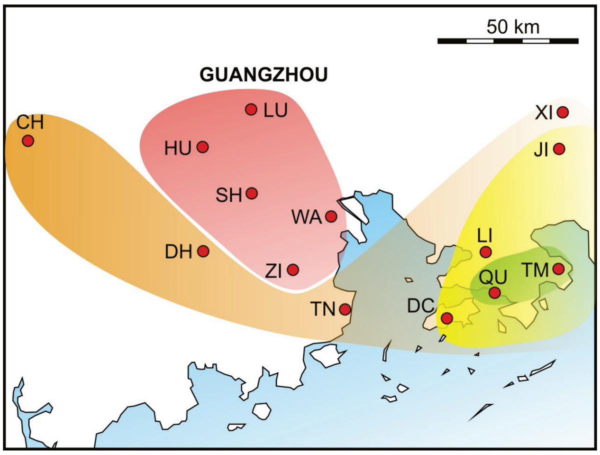

Figure 2. Assessment of photochemical pollution at PRD sites according indicator P_3 for the whole year 2006.

of Hong Kong have the lowest photochemical pollution indicators, being quite stable throughout the year. In addition to a possibly cleaner atmosphere, which is supported by the prevailing easterly winds from the sea and other unpolluted areas, a further reason could also be due to ozone destruction on airborne sea-salt particles. The remaining stations HU, LU, SH, DH, TN, WA and ZI, termed "suburban" here, are characterized by high indicator values P_1, P_2 and P_3 with LU (190, 404 and 277), SH (109, 433 and 217), and the not much lower WA and ZI exceed the highest values reported so far (*i.e.*, for the Italian station Montelibretti (128, 268 and 185)[3]). They show both higher maximum-to-minimum ratios over the season and the limiting value of 80 ppb is exceeded much more frequently. An assessment of the photochemical pollution according the indicator P_3 values for PRD stations during 2006 is shown in Figure 2. The seven different parameters (*i.e.* excluding *N*) of Table 2a were taken into consideration to create clustering using PCA procedure. Prior to modeling all data were centered to the mean value. The best clustering was obtained using PC1 and PC2 The suburban stations form visibly distinct cluster on the other hand rural and coastal station show greater similarity. The main contribution to PC1 can be accounted to descriptors t_{exc}, P_1, P_2 and P_3, the main contributors to PC2 are P_1 and P_3 and negative contribution of t_{exc}.

CONCLUSIONS

The subtropics experience the highest ozone values and will find it difficult to comply with any stricter ozone standards[10]. The new indicators presented here perform also in the subtropics when their seasonal characteristics are considered and show to be more, or at least equally, relevant to assess photochemical pollution than traditional ozone indices and should be recommended for air quality management tasks.

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