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Trends, Distribution and Frequency Analysis of Ozone Data from Three Monitoring Stations in Baton Rouge, Louisiana for the Years 1995 to 2005*

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Troposphere ozone concentrations exhibit pronounced, characteristic diurnal and seasonal cycles. These cycles are usually well defined. However, additional oscillations also occur; these are generally much smaller in amplitude than the 1-day or 1-year cycles and they might be attributable to anthropogenic influences (*e.g.*, specific man-induced meteorological and chemical influences on an individual monitoring station, periodic maintenance activities, *etc.*). Indeed, it is possible that the spectral analysis of photochemical pollution data could pinpoint hidden conditions that affect particular monitoring stations. Such an analysis, one based on Fourier transform methods, was applied to long-term data from 3 American monitoring stations. As would be expected, strong signals were found for the 1-day and 1-year periods; however, some weaker signals, ones probably associable with anthropogenic affairs, were also observed. A principal component analysis (PCA) was applied to the transformed data sets in order to identify these periods. Periods of 3.5-days and 7-days, as well as a number of other cycles, were found and can be considered to be markers of anthropogenic influences. European and American data will be compared and the effects of Hurricane Katrina will be examined.

Keywords
ozone
frequency analysis
long-term data
PCA

INTRODUCTION

California and the south and southeastern states of the US are the areas with perennial ozone compliance problems *vis-à-vis* Air Quality Standards. Greater Baton Rouge (population over 700,000) is one such area; its difficulties are usually attributed to rather high population and traffic, to oil refineries and the petrochemical industry and to copious sunshine, all of which provide ideal conditions for ozone formation. The Louisiana Department of Environmental Quality (LDEQ) is attempting to keep levels low by controlling the emission of precursors and by continuous monitoring of air quality and meteorological parameters at three locations: station Port Allen (PAL) in the west, station Capitol (CAP) in downtown Baton Rouge and station Louisiana State University (LSU) in the south. Eleven years (1995–2005) of ozone data, used as average 1-hour volume fractions per individual station, were provided to us by LDEQ and are an-

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* Dedicated to Prof. Nikola Kallay on the occasion of his 65th birthday.

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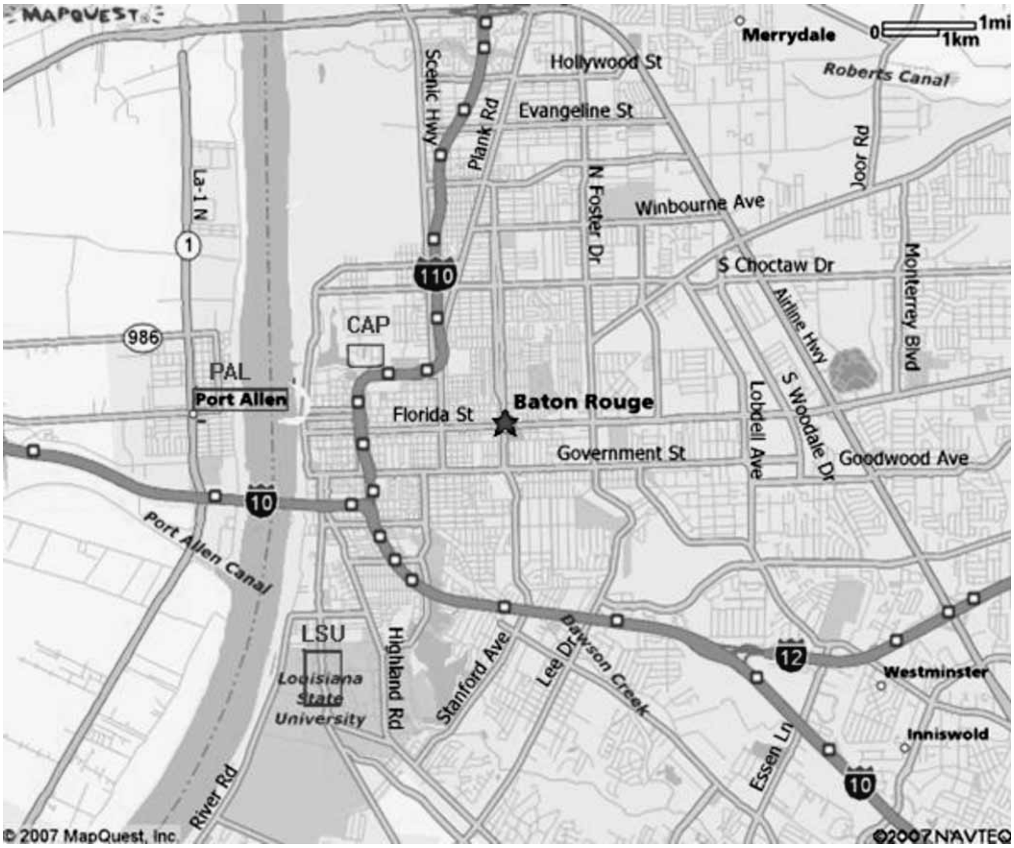

Map 1. Map of Greater Baton Rouge area with monitoring stations indicated.

alyzed here. We are particularly interested in the yearly and monthly mean values, their trend over the years, the distribution of measured ozone data, and the information that might be contained in a long-term frequency analysis of these 1-hour averages. Because Hurricane Katrina devastated this region on Aug. 29, 2005, we will attempt to analyze its effects on ozone levels. We will also try to assess the extent of air pollution at these sites and provide their ranking on the basis of a Principal Component Analysis.

EXPERIMENTAL

Long term ozone data were collected from 3 stations in the Greater Baton Rouge area: Station LSU (LSU) and Station Capitol (CAP), both on the eastern bank of the Mississippi, are located approximately 4 km apart; the third station, Station Port Allen (PAL), is 2 km to the north from LSU on the western river bank (see map 1; the airport, refineries and chemical industries are a few kilometers to the north). Data were collected with commercial UV photometric instruments. The raw data were averaged into hourly values for purposes of trend, distribution and FT analyses.

Missing values were estimated and inserted for the FT analysis. The number of missing values, fortunately, was very small and quite random. After testing several data sets using different »missing value estimation« methods (*e.g.*, zero, average value, the average of corresponding values, *etc.* at the same hour and day for the preceding and following years) and comparing the results, we conclude that there is no significant difference in the main FT peaks. Therefore, we used »padding with average value« methods for all sites. A principal component analysis (PCA)[1] was performed on these and other data sets obtained from the FT analysis[2] in order to identify any patterns in the frequency space that might be caused by anthropogenic activities.

RESULTS AND DISCUSSION

The LDEQ data for each station represents nearly 100,000 hourly averages of ozone volume fractions for the 1995–2005 period. The LSU data are shown in Figure 1 for illustrative purposes. It indicates that contamination exceeds the national ambient air quality standard of an 8-hour-average of 80 ppb and that transgression of the more severe standard of 60 ppb that is now under discussion[3] is frequent.

Before the files were corrected by »padding« for any missing values, the average monthly mean values of ozone concentration for each of the stations for the period 1995–2005 were calculated and are shown in Figure 2. Two maxima, Spring and Fall in Apr/May and Aug/Sep respectively, are obvious; such behavior is seen quite often in certain European locations.[4]

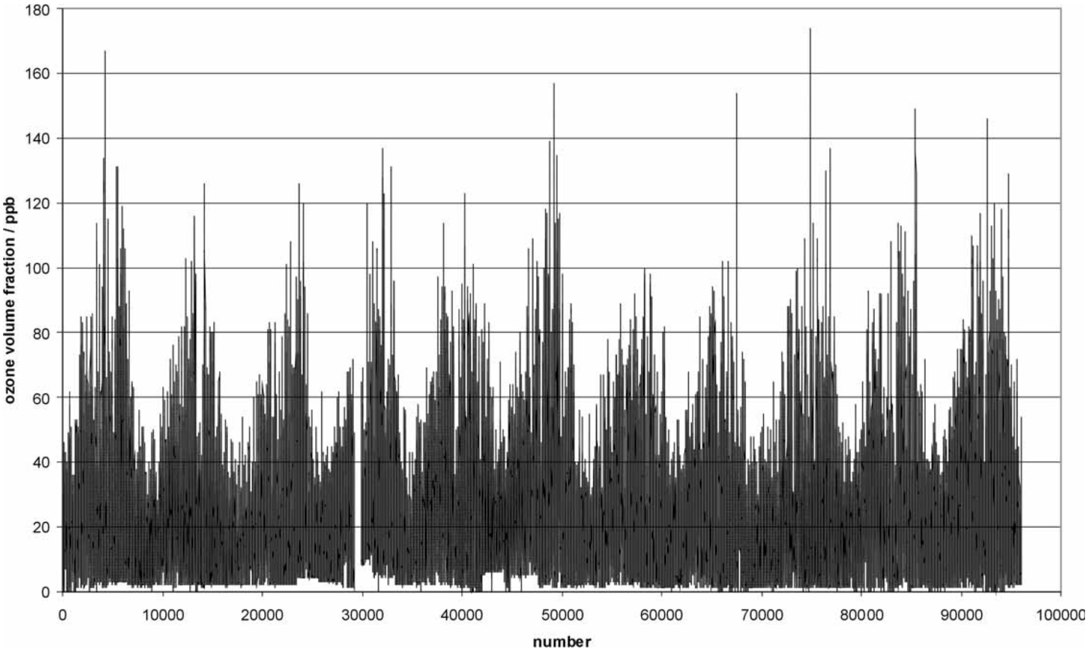

Figure 1. Hourly mean values of ozone concentrations for the period 1995–2005 at Station LSU.

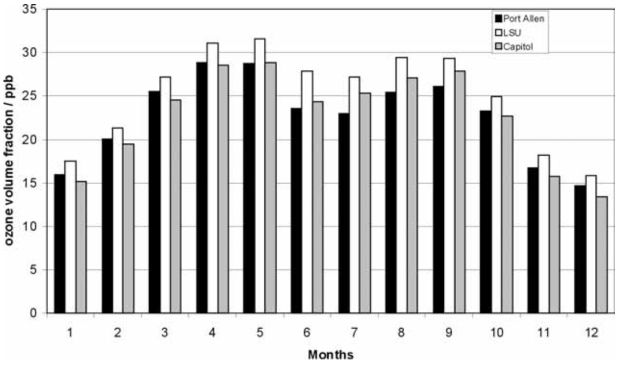

Figure 2. Seasonal variation from average monthly volume fractions for 1995–2005 at the three Greater Baton Rouge stations.

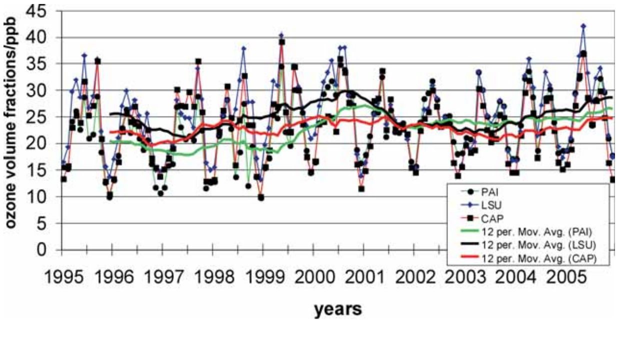

Figure 3. Monthly ozone levels at LSU, CAP and PAL based on a 12 month moving average.

Monthly averages of the ozone volume fractions and their trends (based on a 12 month moving average) for 1995–2005 for the 3 Greater Baton Rouge stations are shown in Figure 3. The trend analysis for the three stations on the basis of the calculated 12 months moving averages indicates an upward trend from 1995 to 2001, a significant drop until 2003, followed by a slow recovery (as shown in Figure 3; according to the Directive 2002/3/EC relating to ozone in ambient air[5] the calculated mean concentration is assigned to the month on which it ends). With few exceptions, (CAP in spring 1995, summer 1997 and spring 2000), the measured values at all three stations correlate quite well. The LSU site is generally highest, whereas PAL is generally lowest indicating either more ozone production at the former or more destruction at the latter. Interestingly, for most years, the distribution of the monthly mean ozone volume fractions exhibits a double maximum which, over the 11-year period, shows a shift from higher Fall values (*e.g.*, '95, '97, '98, '00) towards higher Spring values (*e.g.*, '01, '02, '03, '04, '05). However, the average yearly values, at least compared to Europe,[6] are rather low: below 30 ppb (PAL 23, LSU 25 and CAP 23), indicating considerable ozone destruction by other pollutants.

The distribution of the hourly values (Figure 4) is typical for polluted sites. The most abundant values are low ozone volume fractions of 5–10 ppb, indicative of the consumption of ozone by other pollutants throughout the night and early morning. This is nicely demonstrated by examining and comparing the distributions at LSU for 5–10 h, 10–17 h, 18–22 h and 22–5 h periods over the years. The daytime values have a nearly normal distribution because ozone production is the governing factor. In the evening, ozone destruction starts, low values become more frequent and the median shifts to lower values, a process that continues through the night and

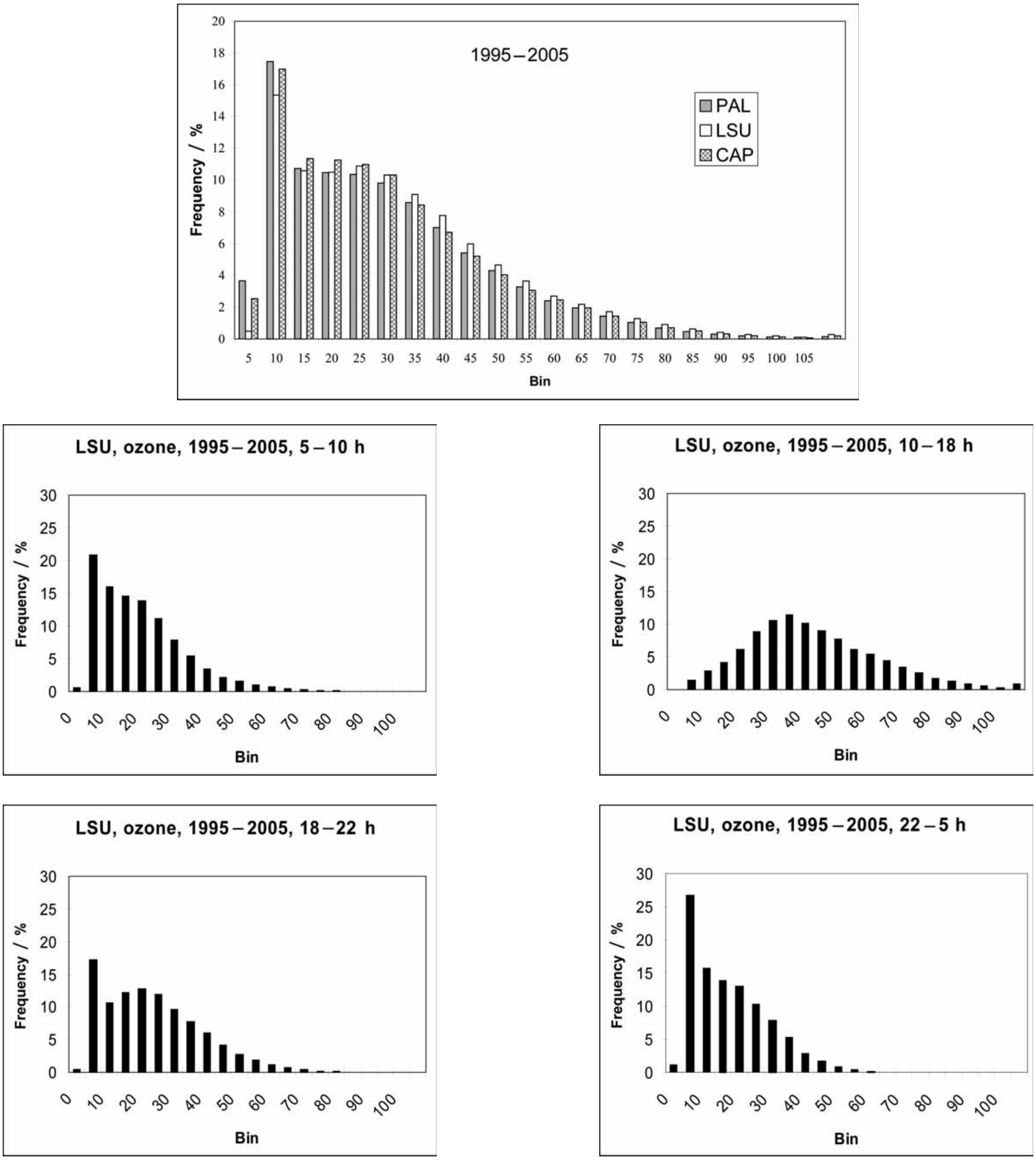

Figure 4. Distribution of mean 1-hour ozone data at LSU, CAP and PAL for 1995–2005 (upper) and distributions at LSU for the 5–10 h, 10–18 h, 18–22 h and 22–5 h intervals.

early morning, at which point ozone production begins to dominate once more. From the relative heights of the low concentration peaks in Figure 4, one might classify PAL as the most polluted site and LSU as the least polluted site because it shows that ozone destruction pollutants are the culprits at PAL site.

Troposphere ozone has been recognized as an atmospheric pollutant and has been investigated for 14 years (1988–2002) within the purview of the EUROTRAC/TOR project. A Tropospheric Ozone Research (TOR) network[7] of more than 20 monitoring stations distributed throughout Europe was established. This network generated a data bank of +10 years, which was used to find out why boundary layer ozone started to rise in the 20th century and what might be done to understand that rise. One of the recent results from EUROTRAC/TOR was a spectral analysis of ozone data at 12 stations.[2,8,9] It showed, in addition to the expected frequencies corresponding to the 1-day and 1-year time periods (the latter accompanied by »harmonics« of 182.5, 121.8 and 91 days), that a number of other statistically significant frequencies occur in the 7–40-day range. While the 7-day period and its 3.5-day harmonic point to an obvious anthropogenic origin, the others remain unexplained. These authors

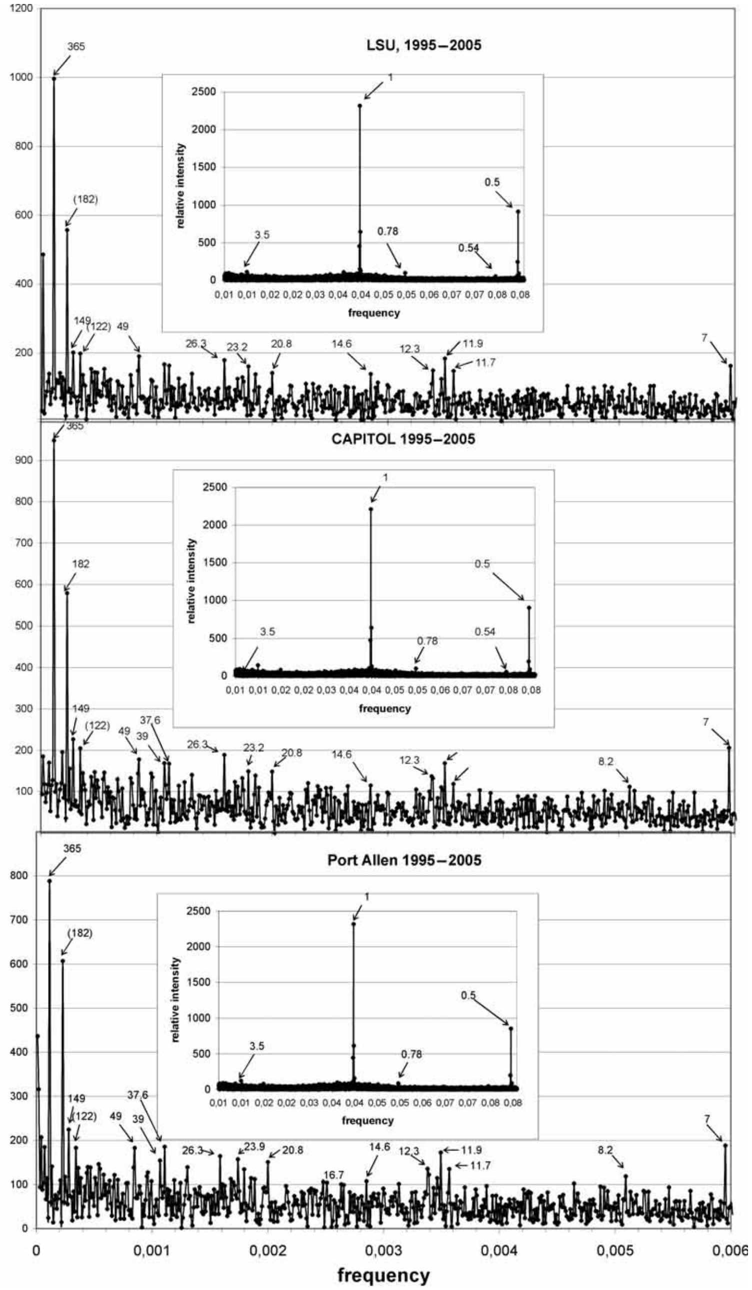

Figure 5. The Fourier transformation of the ozone data of Figure 1. The number of days corresponding to the statistically significant frequency peaks are denoted by arrowed numbers.

also found that the relative intensity of 1-day *vs.* 1-year peaks at a given monitoring station was a good index of the pollution levels at that site. Indeed, Cvitaš and Klasinc[10,11] suggested that the mean value of max/min ratios of the daily ozone volume fractions over a period of time be adopted as a pollution index for that site. Index values below 10 indicated »very clean«, up to 50 »moderately clean« and over 100 »heavily polluted«.[12]

Upon Fourier transformation of the ozone data from the 3 Greater Baton Rouge area stations, the frequency spectra shown in Figure 5 were obtained. The statistically significant (90 % confidence) frequency peaks are shown in Figure 5, and their periods (in days) and their intensities are listed in Table I. The double maximum characteristic of the monthly averages over the year is reflected in the increased intensity of the 2nd harmonics (1/2 year period) and appearance of a new 149 d period corresponding to the average distance between the spring-fall maxima. Thus the 182.5 days period may well be partly »real« too.

However, it is already clear that the relative 1d/1y frequency ratios of the Greater Baton Rouge stations do not correlate with the simple pollution index.[12] The reason probably lies in the choice of EUROTRAC/TOR

TABLE I. Significant periods (in days) and their relative intensities, as found by Fourier analysis

LSU		CAP		PAL	
period	rel. intensity	period	rel. intensity	period	rel. intensity
365.3	995.9	365.3	948.0	365.3	788.4
182.6	557.5	182.6	579.0	182.6	606.7
121.8	199.0	121.8	204.4	121.8	183.1
149	201	149	226	149	225
53.6	136.0	53.6	132.7		
49.0	190.4	49.0	178.0	49.0	183.3
31.9	139.9	31.9	140.6	37.6	185.8
26.3	179.7	26.3	189.0	26.3	164.6
22.4	138.5			20.8	151.2
20.8	142.0	15.7	112.8		
14.6	139.1	14.6	114.9		
12.3	149.4	12.8	105.2		
11.9	183.8	11.9	168.6	11.9	172.4
11.7	147.9	11.7	118.8	11.7	135.0
		11.3	91.6	11.3	93.5
11.0	90.6	11.0	103.0	10.7	96.4
9.2	105.0			9.0	102.5
				8.2	119.1
		7.6	97.6	7.6	93.5
		7.4	97.7	7.4	85.5
7.0	162.7	7.0	205.9	7.0	188.4
6.6	94.5			6.4	48.4
6.3	58.7				
6.2	58.9				
6.1	83.9	6.1	75.1	6.1	77.0
		6.0	85.7		
5.2	55.0	5.2	52.8	5.3	85.1
				5.1	65.6
				4.8	69.9
5.0	80.8	5.0	82.3	4.6	68.6
		4.9	51.5	4.5	64.4
		4.2	60.5	4.4	47.5
				4.3	65.8
4.0	79.0	4.0	83.6	4.0	82.2
		4.0	47.5		
		3.9	65.6		
3.9	74.8	3.9	74.5	3.9	62.4
		3.7	54.0	3.7	58.2
				3.6	51.3
3.5	115.5	3.5	143.3	3.5	122.0
				3.5	43.7
3.4	77.2	3.4	58.1	3.4	72.1
1	2318	1	2210	1	2318

stations, all of which were relatively unpolluted (*i.e.*, not significantly influenced by nearby emissions, but still representative of large land areas). This may well be correct because some polluted European sites do not follow this correlation either. The observed periodicities of ozone data can have various sources. Thus, they show dependency on geographical altitude and latitude and on anthropogenic emissions of ozone precursors as well as the influence of general atmospheric circulation and its oscillations on total and surface ozone content.[13] Spontaneous chemical oscillations in tropospheric compositions with such periodicities have been proposed by Hess and Madronich.[14] Also movement of air masses over long distances involving their interaction with surface may create periodic behavior on the observed scale(s).[15] A recent analysis by spectral windowing of surface ozone periodicities in data from 83 EMEP monitoring stations[16] links the scales of 31–90,19–30, 8–18 and 0–7 days to ozone seasonal cycle, planetary waves with low wave number, change of ozone with weather patterns caused by planetary waves propagation with high wave numbers and to synoptic and local scale variability, respectively. Since we are now interested in anthropogenic effects, we have, in addition to the 12 TOR stations[8] used data from two urban (Zagreb and Ljubljana) as well as the three US stations. A correlation of these observations with those from the European stations will appear separately.[17]

In that approach, largely based on 1-d/1-y intensity ratios, to find some measure of the degree of ozone pollution, a PCA that included the set of significant frequencies corresponding to the periods between 7 and 40 days was performed. In an orthogonal PC1-PC2 coordination system, where PC1 contains 90 % of the 1-day and 10 % of the 1-year frequency and PC2 is a linear combination of a dominant 1-year frequency with a small contribution of all other frequencies and an even smaller negative contribution of the 1-day frequency, one generates Figure 6. All stations lie on a diagonal line, seemingly ranked by degree of pollution. The LSU station has consistently higher ozone values, yet it is deemed by PCA analysis to be the least polluted site.

Finally, we essay a few words on the influence of Hurricane Katrina on ozone concentrations. Katrina was the most costly natural disaster ever to strike the USA and one of the strongest storms during the last 100 years with sustained winds of over 200 km/h at landfall.[18] It began as a tropical depression on Aug 23 strengthened into a tropical storm moving through the Bahamas and became a hurricane after entering and moving westwards in the Gulf of Mexico. It reached the highest Category 5 status on Aug 28 and advanced toward Louisiana during the night making landfall close to the mouth of Mississippi River as a Category 3 storm but accompanied by a horrific surge of over 6 m across a path of 30 km.

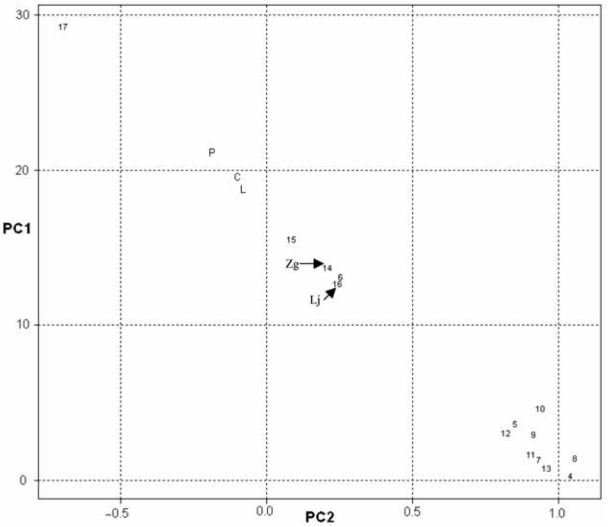

Figure 6. Ranking of the LSU (L), Capitol (C) and Port Allen (P) stations together with 12 EUROTRAC/TOR (numeration from Ref. 17) and stations Zagreb (Zg) and Ljubljana (Lj) according to a principal component analysis. Station Iskrba, Slovenia (Nr. 17, data obtained from Slovenian Environmental Agency, ARSO) is added for comparison.

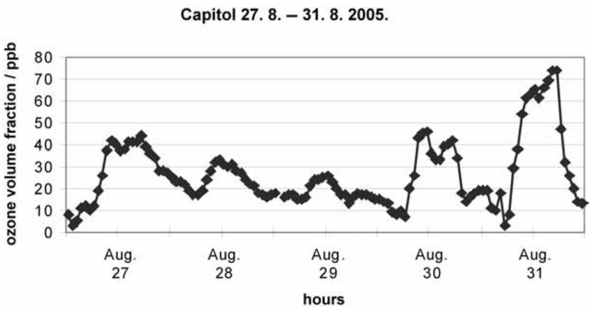

Figure 7. Average 1-h ozone volume fractions measured in downtown Baton Rouge (CAP) during hurricane Katrina in 2005.

The main impact of Katrina occurred on Aug 29, 2005. Unfortunately two stations, LSU and PAL did not generate data for Katrina. The ozone volume fractions in the period Aug 27 to 31 demonstrate the effects: the incoming hurricane decreased the ozone readings, only to be followed by a quite rapid recovery.

CONCLUSIONS

Frequency analysis of long-term air pollution data may reveal and explain many of the periodic properties in the lower atmosphere. Some of these may result from human activities as demonstrated by an attempted ranking of monitoring sites regarding ozone pollution. Comparison of such analyses from various locations, such as performed here, should generate a useful analytical tool.

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SAŽETAK

Usmjerenost, raspodjela i frekvencijska analiza ozonskih podataka s tri stanice u Baton Rougeu, Louisiana od 1995. do 2005. godine

Leo Klasinc, Nenad Kezele, Matevz Pompe i Sean P. McGlynn

Koncentracije troposferskog ozona pokazuju izražene, karakteristične dnevne i sezonske cikluse. Ti ciklusi obično su dobro definirani. Međutim, događaju se i dodatni ciklusi; oni su u pravilu mnogo niže amplitude od 1-dnevnog i 1-godišnjeg ciklusa i mogu se povezati s ljudskim utjecajem (npr. specifični čovjekom izazvani meteorološki i kemijski utjecaji na pojedinu mjernu stanicu, periodične servisne aktivnosti i dr.). No spektralna analiza podataka fotokemijskog onečisćenja može i ukazati na skrivene uvjete koji utječu na određenu mjernu stanicu. Takva analiza koja se temelji na metodi Fourierove transformacije primijenjena je na dugogodišnje podatke s 3 američke mjerne stanice. Prema očekivanju nađeni su jaki signali za 1-dnevni i 1-godišnji period te periodi od tri i pol i sedam dana kao i neki slabiji signali s periodima između 7 do 90 dana koji su vjerojatno povezani s antropogenim djelovanjem. Primjena metode analize glavne komponente (Principal Component Analysis, PCA) na te periode dala je rangiranje stanica obzirom na ozonsko onečišćenje. Europski i američki podaci su uspoređeni te istraženi efekti orkana Katrina na ozonske podatke.