PERGAMON

Atmospheric Environment 34 (2000) 3445–3451

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Short communication

Comparisons of weekday–weekend ozone: importance of biogenic volatile organic compound emissions in the semi-arid southwest USA

Jeremy E. Diem

Department of Geography and Regional Development, The University of Arizona, Tucson, AZ 85721, USA

Received 9 October 1999; received in revised form 15 November 1999; accepted 15 November 1999

Abstract

This paper examines differences between daily maximum weekday and weekend ambient ozone concentrations in the Tucson, AZ metropolitan area. Temporal variations in the Weekend Effect (i.e. weekend ozone concentrations are larger than weekday concentrations) are not explained entirely by changes in anthropogenic emissions of ozone precursor chemicals (i.e. nitrogen oxides and volatile organic compounds). A dramatic change from the Weekend Effect in June to the Weekday Effect (i.e. weekday ozone concentrations are larger than weekend concentrations) in July is associated with the onset of the North American Monsoon. A transition from a relatively dry atmosphere during the arid foresummer months of May and June to a relatively moist atmosphere during the monsoon months of July and August seems to explain the changes in ozone concentrations. Moist conditions are associated with increases in biogenic volatile organic compound (BVOC) emissions in the urban forest and surrounding desert areas. BVOC emissions appear to be an important source of VOCs, especially during the monsoon months. Therefore, an increase in ambient BVOC concentrations from June to July presumably reverses the sensitivity of ozone production in the Tucson area from VOC- to NO_x-sensitive.

Keywords: Air pollution; Ozone; Climatology; Biogenic emissions

1. Introduction

1.1. Overview of weekend vs. weekday comparisons

Differences between weekday and weekend ozone concentrations demonstrate the importance of day-to-day variations in emissions of ozone precursor chemicals (i.e. nitrogen oxides (NO_x) and volatile organic compounds (VOCs)). The Weekend Effect, which is defined as a weekend vs. weekday difference, is characterized by higher ozone concentrations occurring on the weekends in some locations. The Weekend Effect is present in areas where ozone production is VOC-sensitive (i.e. ozone concentrations increase with increasing ambient VOC concentrations and decrease with increasing ambient NO_x concentrations), such as metropolitan areas in California (Zeldin et al., 1989). Areas such as the southeastern US that are NO_x-sensitive (i.e. ozone concentrations increase with increasing ambient NO_x concentrations but show relatively little response to increased ambient VOC concentrations) do not usually experience the Weekend Effect (Walker, 1993).

In many areas, weekends usually have larger ambient VOC/NO_x concentration ratios than do weekdays, for NO_x and VOC emissions might drop by 30 and 10%, respectively, when moving from weekdays to weekends (Altshuler et al., 1993). As a result, areas where ozone production is VOC-sensitive have higher ozone concentrations on weekends than on weekdays. The detection of the Weekend Effect, and the subsequent linking of the phenomenon with emissions information, is an empirically based approach that provides a clue as to

E-mail address: diem@climate.geog.arizona.edu (J.E. Diem).

1352-2310/00/$ - see front matter
PII: S1352-2310(99)00511-7

whether ozone formation in an area is NO_x- or VOC-sensitive (Altshuler et al., 1995).

1.2. Purpose of study

This study illustrates the spatio-temporal variations in differences between weekday and weekend ozone concentrations in the Tucson, Arizona metropolitan area. These variations are related to changes in ozone precursor chemical emissions and, ultimately, to changes in atmospheric conditions, especially those resulting from the arrival of the North American Monsoon. The month-to-month differences in atmospheric conditions are explored further to describe the impact of biogenic VOC (BVOC) emissions.

1.3. Study area

Tucson is located at 32.25°N latitude and −111°W longitude, at approximately 700 m above sea level (a.s.l.) in southern Arizona. It is situated in a basin surrounded by four mountain ranges: the Rincon, Santa Catalina, Tortolita, and Tucson Mountains (Fig. 1). The Tucson metropolitan area has a hot, semi-arid climate. An average of slightly over 250 mm of precipitation is recorded each year with more than half of this falling during the summer season (Sellers and Hill, 1974). Ozone concentrations were monitored at five long-term sites (i.e. monitors that were in operation from 1995 to 1998). These five monitors are scattered throughout the metropolitan area (refer to Fig. 1), and have been placed in varying environments that include a rural, upwind area (Tangerine Road (TANG) in northwest Tucson), a city center area (Downtown (DT)), an urban/suburban area (22nd St. and Craycroft Rd. (22 & C)), and two downwind areas (Saguaro National Park East (SNP) and Pima County Fairgrounds (FG)).

2. Data and methods

2.1. Data

Data used in this study consist of hourly ozone concentrations, hourly and daily meteorological information, and

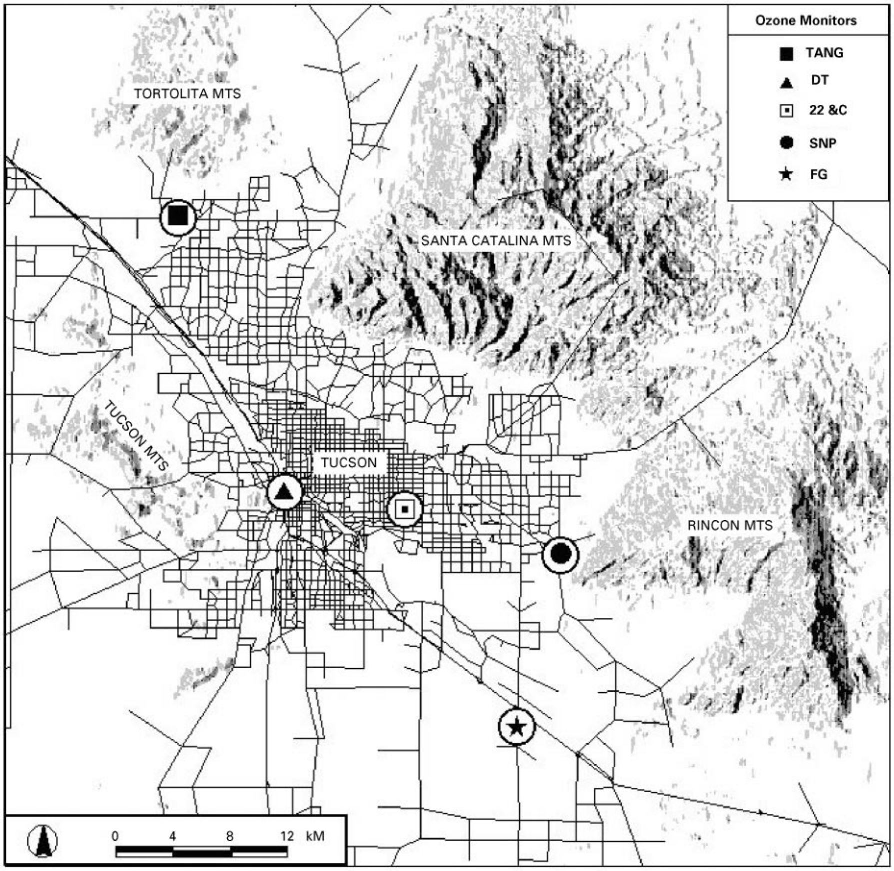

Fig. 1. Map of Tucson showing topography, road network, and locations of ozone monitoring stations (TANG = Tangerine; DT = Downtown, 22 & C = 22nd and Craycroft; SNP = Saguaro National Park East; and FG = Fairgrounds).

spatially varying estimates (i.e. maps) of average daily ozone precursor emissions estimates. Hourly ozone concentrations during the ozone season of April through September of 1995, 1996, 1997, and 1998 were obtained from the Environmental Protection Agency's (EPA) Aerometric Information Retrieval System (AIRS) for Tucson's five long-term ozone monitors. Hourly wind speed and direction data for the TANG and 22 & C monitors as well as hourly nitric oxide (NO) and nitrogen oxides data for the 22 & C monitor were also obtained from AIRS. Hourly temperature, relative humidity (RH), and insolation data were obtained from an Arizona Meteorological Network (AZMET) site located at The University of Arizona's Campus Agricultural Center in midtown Tucson. Daily temperature, wind speed, RH, and atmospheric pressure measurements at Tucson International Airport were obtained from the National Climatic Data Center (NCDC). Gridded weekday- and weekend-specific daily emissions estimates of VOCs and NO_x are described in Comrie and Diem (1999a).

2.2. Methods

These methods in the study include (1) calculating monthly variations in weekday and weekend daily maximum 1- and 8-h average ozone concentrations at each monitor, (2) determining the significance of month-specific weekday vs. weekend ozone differences using Student's *t*-test (a parametric test of the difference between two samples), (3) using a chemistry model to verify the association of the Weekend Effect with VOC-sensitive chemistry and the Weekday Effect with NO_x-sensitive chemistry, (4) relating the ozone differences to variations in ozone precursor chemical emissions from anthropogenic sources, and (5) relating ozone differences to meteorological values (i.e. daily temperature, precipitation, RH, insolation, and wind speed). The chemistry model used in this study is a modification of the Johnson (1984) Integrated Empirical Rate model based on photochemical simulations and environmental chamber experiments. Blanchard et al. (1999) provide a detailed description of the model. The model requires measurements of ozone, NO, and either NO_x or NO_y to calculate the extent of reaction (ratio of instantaneous to maximum smog production) and thus develop a qualitative understanding of the sensitivity of ozone formation to changes in VOC and NO_x concentrations. Situations in which the extent of reaction approaches one are NO_x-sensitive whereas situations where the extent of reaction is predominantly less than one are VOC-sensitive (Blanchard et al., 1999). Using this model, the sensitivity of ozone production at the 22 & C monitor is determined based on ozone, NO, and NO_x concentrations measured at the monitor.

3. Results

The Weekend Effect occurs throughout the Tucson region (Table 1, Figs. 2a and b). However, the phenomenon varies both spatially and temporally. Table 1 lists the average daily maximum 1 and 8-h average ozone concentrations at each of the five long-term monitors for weekdays and weekends during each month of the ozone season. Daily maximum ozone concentrations are compared at each station for the six months. Significant ($\alpha = 0.1$) positive differences between weekend and weekday ozone concentrations indicates the presence of the Weekend Effect. In April, the phenomenon is only present at the downtown monitor (DT). The event then expands eastward to 22 & C in May. By June, all monitors except for SNP, experience the Weekend Effect. In July, the situation reverses, for none of the monitors have significantly higher weekend concentrations. Instead, all monitors experience a Weekday Effect (i.e. significantly higher weekday concentrations) except for DT. August is nearly identical to July in that the Weekend Effect is missing. Finally, weekend concentrations are higher than weekday concentrations in September and the Weekend Effect returns to the two source-intensive stations, 22 & C and DT.

The presence of either the Weekend Effect or the Weekday Effect provides insight as to when and where ozone production in the Tucson metropolitan area is VOC- or NO_x-sensitive. In this study, the Weekend Effect and Weekday Effect are associated mostly with VOC- NO_x-sensitive chemistry, respectively. A general agreement between the chemistry model results, which tend to underestimate the extent of reaction, and the empirical ozone analyses was found. The basic month-to-month trend in extent of reaction is similar to changes in weekday vs. weekend ozone concentrations (Fig. 2c). The largest extent of reaction is related to NO_x-sensitivity while the smallest extent coincides with VOC-sensitivity.

VOC-sensitivity is present downtown only in April, but VOC-sensitivity is present throughout most of the metropolitan area by the end of June. A dramatic change from VOC-sensitive to either transitional (i.e. neither VOC nor NO_x-sensitive) or NO_x-sensitive ozone production occurs from June to July. None of the monitors have VOC-sensitivity in July. Similar conditions prevail in August while NO_x-sensitivity ceases to exist in September. In fact, VOC-sensitivity begins an eastward expansion out of the urban core by the end of the summer season. The occurrence of the Weekend Effect in source-intensive areas has also been observed in California's South Coast Air Basin (Elkus and Wilson, 1977; Zeldin et al., 1989).

The Weekend and Weekday Effects do not appear to be controlled entirely by variations in anthropogenic ozone precursor chemical emissions. Over the entire metropolitan area, the highest anthropogenic VOC/NO_x

Table 1
Weekday- and weekend-specific daily maximum 8-h and 1-hr average ozone concentrations (in ppm) at the five ozone monitoring stations from April through September. For each station, 8-h values (e.g., SNP8) are listed before 1-h values (e.g., SNP1). Weekday and weekend values in bold type are significantly different ($\alpha = 0.10$). Standard deviations for the 8- and 1-h average concentrations range from 0.006 to 0.014 and 0.007 to 0.015, respectively. Refer to Fig. 1 for monitoring station information

	SNP8	SNP1	TANG8	TANG1	FG8	FG1	22&C8	22&C1	DT8	DT1
April										
Weekday	0.058	0.062	0.056	0.060	0.056	0.059	0.055	0.061	**0.043**	**0.050**
Weekend	0.057	0.062	0.055	0.059	0.055	0.059	0.056	0.061	**0.051**	**0.056**
May										
Weekday	0.058	0.063	0.054	0.058	0.054	0.058	**0.056**	**0.062**	**0.042**	**0.050**
Weekend	0.058	0.064	0.055	0.059	0.055	0.060	**0.059**	**0.065**	**0.051**	**0.058**
June										
Weekday	0.056	0.061	**0.051**	**0.056**	0.052	**0.056**	**0.054**	**0.061**	**0.039**	**0.047**
Weekend	0.058	0.063	**0.055**	**0.059**	0.054	**0.059**	**0.058**	**0.064**	**0.050**	**0.056**
July										
Weekday	**0.059**	**0.068**	**0.052**	0.057	**0.053**	**0.060**	**0.059**	**0.069**	0.045	0.054
Weekend	**0.055**	**0.062**	**0.050**	0.055	**0.050**	**0.057**	**0.054**	**0.062**	0.046	0.054
August										
Weekday	0.062	**0.072**	0.054	0.060	0.055	**0.064**	0.060	**0.072**	**0.046**	0.057
Weekend	0.060	**0.067**	0.052	0.057	0.053	**0.059**	0.058	**0.066**	**0.049**	0.057
September										
Weekday	0.049	0.057	0.045	0.050	0.045	0.050	**0.047**	0.056	**0.033**	**0.043**
Weekend	0.052	0.059	0.046	0.051	0.045	0.052	**0.050**	0.058	**0.042**	**0.050**

($AVOC/ANO_x$) emission ratios occur in May and June (Fig. 2d). Increased NO_x emissions from power plants, associated with increased air conditioner use, causes the $AVOC/ANO_x$ ratio to drop markedly in July and August. The most NO_x-sensitive (least VOC-sensitive) chemistry, based roughly on anthropogenic emissions, should occur during May and June. However, the presence of a strong Weekend Effect at many of the monitors in June, the month with the largest $AVOC/ANO_x$ ratio, indicates that VOC-sensitivity occurs during that month. The abrupt change from the Weekend Effect in June to the Weekday Effect in July is not explained by variations in anthropogenic emissions. The anthropogenic emissions ratios also suggest that VOC-sensitivity should dominate the area in April, yet this only occurs at the downtown monitor.

The month-to-month variations are explained partially by variations in atmospheric conditions (Fig. 2e). A prevalent mountain–valley circulation results in consistent wind directions during the ozone season and it does not explain the month-to-month ozone variations. However, all month-to-month (e.g., April vs. May) differences in daily temperature, precipitation, insolation, and RH are significant ($\alpha = 0.1$). Only variations in precipitation and RH appear to explain the sharp contrast between June and July's sensitivities to ozone precursor chemicals. The effects of these variations appear to be secondary via increased BVOC emissions.

4. Discussion

It is hypothesized that BVOC emissions increase dramatically in July and August in the Tucson area thereby erasing the Weekend Effect. BVOCs might be an important component of the ozone production process for two reasons. BVOC production coincides with the time of maximum ozone concentrations, and BVOCs are typically more reactive than AVOCs (Abelson, 1988; Chameides et al., 1988). Based on BVOC emission algorithms, Tucson's relatively high summertime temperatures (between 35 and 40°C) and light intensities ($> 800\ \mu J\ m^{-2}\ s^{-1}$) are extremely favorable for high BVOC emissions (Guenther et al., 1993). In addition, the Tucson metropolitan area has a substantial amount of leaf biomass (Comrie and Diem, 1998). The urban forest is comprised of an assortment of both exotic (e.g., eucalyptus) and native species (e.g., mesquite and palo verde)

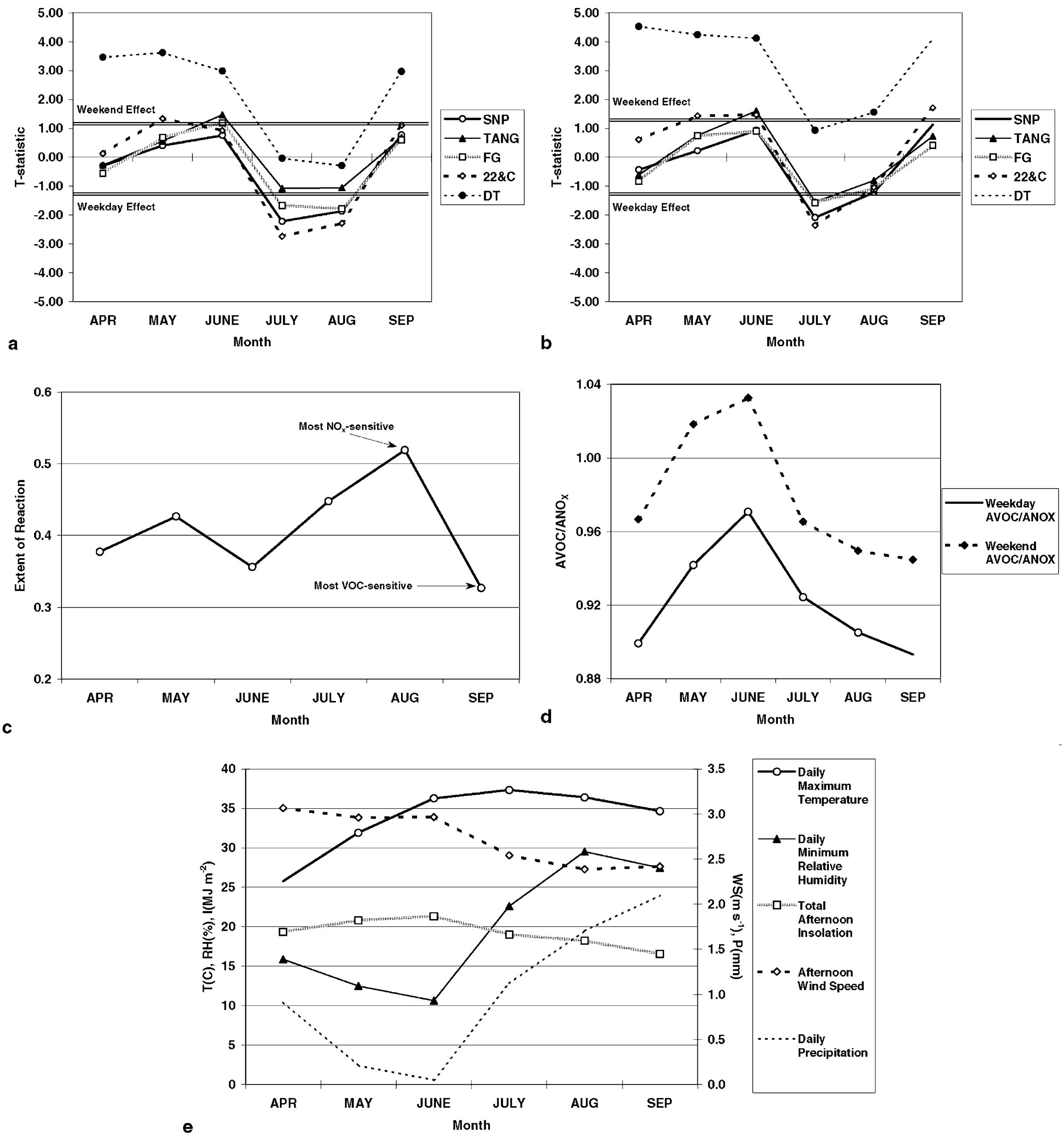

Fig. 2. Month-to-month changes in (a) weekend–weekday 1-h average ozone differences at the five ozone monitoring stations, (b) weekend–weekday 8-h average ozone differences at the five ozone monitoring stations, (c) extent of reaction at 2 PM, (d) anthropogenic VOC/NO_x (AVOC/ANO_x) emission ratios within the entire Tucson metropolitan area, and (e) atmospheric conditions (T = temperature, RH = relative humidity, I = insolation, WS = wind speed, and P = precipitation). Refer to Fig. 1 for monitoring station information.

while the surrounding desert lands are covered with shrubs, such as bursage and creosote-bush, and small trees, such as palo verde, acacia, and mesquite. Oaks, junipers, pines, and firs can be found at higher elevations. Decreased BVOC emissions during the arid foresummer months of May and June might contribute to the VOC-sensitive conditions in June while an abundance of BVOC emissions during the humid, summer months of July and August might be responsible for transitional to NO_x-sensitive conditions during those months.

Consequently, the smallest and largest total VOC/NO_x emission ratios should occur in May/June and July/August, respectively.

The North American Monsoon affects the southwestern United States in July, August, and September. This regional circulation advects low-level moisture into the Southwest from the eastern tropical Pacific Ocean and the Gulf of California while upper-level moisture is advected from the Gulf of Mexico (Adams and Comrie, 1997). Prior to the arrival of monsoonal moisture, important drought-deciduous plants at lower elevations, such as palo verde, triangle-leaf bursage, white-thorn acacia, creosote-bush, brittlebush, and even some sclerophyllic oaks at middle elevations in the Santa Catalina and Rincon Mountains lose some to most of their leaves during the arid foresummer (Turner et al., 1995; P. Jenkins, personal communication, The University of Arizona Herbarium, 1999). The rapid onset of moist conditions causes subsequent increases in leaf biomass for many of the Tucson region's xerophytic species. The associated increase in RH might also directly increase BVOC emissions. For example, Dement et al. (1975) found that camphor volatilization rates in California black sage nearly doubled when the RH was increased from 8 to 36% at 40°C. Similar afternoon temperatures and increases in RH are found in the Tucson region between June and August (Fig. 2e). Therefore, from June to July, the monsoon presumably takes the sensitivity of ozone production in the Tucson metropolitan area from a VOC-sensitive situation typical of summer-dry, coastal California to a NO_x-sensitive situation typical of the summer-wet, southeastern United States. Increased moisture levels point towards increased BVOC emissions and a consequent emergence and dominance of transitional/NO_x-sensitive chemistry during the peak monsoon months of July and August. BVOC emissions probably decrease substantially from August to September, thereby causing VOC-sensitivity. Results from a detailed biogenic emissions inventory that does not account directly for the effects of variations in relative humidity on vegetation indicate that BVOC emissions are approximately three times greater in July/August than in May/June (Diem and Comrie, 1998) Comrie and Diem, 1999b). This increase in BVOC emissions is certainly greater if relative humidity effects are considered. Although only circumstantial evidence has been presented, the monsoon mechanism appears to explain sufficiently the increased BVOC emissions given the significant effects that increased moisture levels have on vegetation growth in semi-arid areas.

BVOC emissions also appear to be a major factor in April. The AVOC/ANO_x emissions ratio in April at all of the sites is extremely small. VOC-sensitive atmospheres should prevail based on the anthropogenic emissions ratios. However, as mentioned previously, the Weekend Effect only occurs at the downtown monitor. It appears that most parts of the metropolitan area have transitional atmospheres. April is the peak month for the number of native species blooming in the Tucson region (M. Dimmitt, Arizona-Sonora Desert Museum, personal communication 1999). Blooming and bud break influence BVOC emission activity (Arey et al., 1991; Guenther et al., 1995; Monson et al., 1995). Many native species also have high leaf biomass values in the springtime (i.e. April) as a response to winter rains (Turner et al., 1995). Therefore, increased BVOC emissions in April seem to cause an increase in ambient VOC concentrations in many parts of the metropolitan area.

5. Conclusions

This study illustrates the importance of examining an air pollution phenomenon from both a spatial and a temporal perspective. The dramatic change from the Weekend Effect in June to the Weekday Effect in July suggests that the sensitivity of ozone production in the metropolitan area switches from VOC-sensitive during the arid foresummer to transitional/NO_x-sensitive during the monsoon months. Consequently, the optimal control strategies needed to reduce ozone levels in the Tucson metropolitan area probably vary over space and time. The proper selection of a precursor reduction strategy including VOCs, NO_x, or both depends not only on results from the above "natural experiments" but also on photochemical model simulations. Thus, this study is intended to complement intensive modeling studies. Temporal variations in the geography of NO_x-VOC chemistry over the course of a typical ozone season have been identified, and the likely impacts of BVOC emissions on ozone concentrations in a semi-arid area have been revealed.

Acknowledgements

This work was supported in part by the Pima Association of Governments (PAG). Many thanks to Darcy Anderson of PAG and Andrew Comrie of The University of Arizona for their useful comments on the manuscript.

References

Abelson, P.H., 1988. Rural and urban ozone. Science 241 (4873), 1569.

Adams, D.K., Comrie, A.C., 1997. The North American Monsoon. Bulletin of the American Meteorological Society 78 (10), 2197–2213.

Altshuler, S.L., Arcado, T.D., Lawson, D.R., 1995. Weekday vs. weekend ambient ozone concentrations – discussions and hypotheses with focus on northern California. Journal of the Air and Waste Management Association 45(12), 967–972.

Arey, J., Corchnoy, S.B., Atkinson, R., 1991. Emission of linalool from Valencia orange blossoms and its observation in ambient air. Atmospheric Environment 25 (7), 1377–1381.

Blanchard, C.L., Lurmann, F.W., Roth, P.M., Jeffries, H.E., Korc, M., 1999. The use of ambient data to corroborate analyses of ozone control strategies. Atmospheric Environment 33 (3), 369–381.

Chameides, W.L., Lindsay, R.W., Richardson, J., Kiang, C.S., 1988. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. Science 241, 1473–1475.

Comrie, A.C., Diem, J.E., 1998. System for management, observation, and GIS modeling of air pollution (SMOGMAP). Final Report, Phase 1. Pima Association of Governments, Tucson, AZ.

Comrie, A.C., Diem, J.E., 1999a. System for management, observation, and GIS modeling of air pollution (SMOGMAP). Final Report, Phase 2. Pima Association of Governments, Tucson, AZ.

Comrie, A.C., Diem, J.E., 1999b. System for management, observation, and GIS modeling of air pollution (SMOGMAP), First Quarter Report, Phase 3. Pima Association of Governments, Tucson, AZ.

Dement, W.A., Tyson, B.J., Mooney, H.A., 1975. Mechanism of monoterpene volatilzation in Salvia mellifera. Phytochemistry 14, 2555–2557.

Diem, J.E., Comrie, A.C., 1998. Development of a biogenic emissions inventory for a southwestern, semi-arid city. Preprints, Second Urban Environment Symposium, American Meteorological Society, Boston, MA.

Elkus, B., Wilson, K.R., 1977. Photochemical air pollution: weekend-weekday differences. Atmospheric Environment 11, 509–515.

Guenther, A., Zimmerman, P., Harley, P., Monson, R., Fall, R., 1993. Isoprene and monoterpene emission rate variability: model evaluation and sensitivity analysis. Journal of Geophysical Research 98 (D7), 12609–12617.

Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. Journal of Geophysical Research 100 (D5), 8873–8892.

Johnson, G.M., 1984. A simple model for predicting the ozone concentration of ambient air. Proceedings of the Eight International Clean Air Conference, Melbourne, Australia, 2 May, 1984, pp. 715–731.

Monson, R.K., Lerdau, M.T., Sharkey, T.D., Schimel, D.S., 1995. Biological aspects of constructing volatile organic compound emission inventories. Atmospheric Environment 29 (21), 2989–3002.

Sellers, W.D., Hill, R.H., 1974. Arizona Climate: 1931–1972. The University of Arizona Press, Tucson, AZ.

Turner, R.M., Bowers, J.E., Burgess, T.L., 1995. Sonoran Desert Plants: An Ecological Atlas. The University of Arizona Press, Tucson, AZ.

Walker, J.S., 1993. Tropospheric ozone concentration trends by day of week. Paper FM2-1116 presented at the International Conference and Course: Regional Photochemical Measurement and Modeling Studies. San Diego, CA, November 8–12.

Zeldin, M.D., Horie, Y., Mirabella, V.A., 1989. An analysis of weekend/weekday differences in the South Coast Air Basin of California. Presented at the 82nd Annual Meeting of the Air and Waste Management Association, Anaheim, CA, 25–30, June, Paper no. 89–125.6.