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Day-of-Week Patterns in Toxic Air Contaminants in Southern California

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ABSTRACT

Day-of-week mean ambient concentrations were computed for six high-cancer-risk toxic air contaminants (TACs): 1,3-butadiene, benzene, acetaldehyde, formaldehyde, carbon tetrachloride (CCl_4), and perchloroethylene. Data from six urban sites in southern California, from 1989 through 2001, were analyzed. Graphical displays were used to search for repeated patterns. Benzene and 1,3-butadiene, emitted mainly by mobile sources, exhibit distinctly lower concentrations on Sundays and slightly lower concentrations on Saturdays and Wednesdays. Acetaldehyde and formaldehyde show some trace of a weekly pattern similar to that of benzene and 1,3-butadiene, but the pattern is not strongly marked. Perchloroethylene, used primarily as a dry-cleaning solvent, is also distinctly lower on Sundays. CCl_4 does not show a day-of-week pattern.

INTRODUCTION

With the recognition of the serious hazards to human health and the environment posed by toxic air contaminants (TACs), in the early 1980s, the state of California established an aggressive program to reduce toxic emissions to the air. The Toxic Air Contaminant Identification and Control Act of 1983 directed the California Air Resources Board (CARB) to identify, monitor, and control TACs.[1] The Act was subsequently strengthened by the enactment of toxic "Hot Spots" regulation, which required facilities to report toxic emissions and notify nearby residents of any risks.[2] Efforts are underway to use the information gathered through this effort to build emission inventories for TACs.[3] Because TAC problems can disproportionately impact residents of a small area such as a neighborhood, with the recent emphasis on environmental justice, TACs have become the subject of increasing interest.[4]

IMPLICATIONS

The seeming paradox that ozone (O_3) concentrations increase on weekends in some places while emissions of O_3 precursors presumably decrease has potential implications for O_3 control strategies. However, little information has hitherto been available on day-of-week patterns in ambient concentrations of TACs. This paper attempts to fill that gap. This analysis is presented not to elucidate day-of-week variations in O_3 concentrations but because TACs are of intrinsic interest because of their human health impacts.

Recent work has demonstrated the existence of a "weekend effect" in ambient ozone (O_3) concentrations in California's major urban areas, particularly Los Angeles and its environs.[5] In general, O_3 concentrations are higher on weekends than on weekdays, the effect being less pronounced at downwind sites. Oxides of nitrogen (NO_x), on the other hand, show reduced concentrations on weekends, primarily in the morning when motor vehicle activity is lower.[6] The reasons for this counterintuitive phenomenon are of great interest for their implications on air pollution control strategies.

Compared with criteria pollutants, relatively little published information is available on trends and temporal patterns in ambient concentrations of TACs. Most published studies tend to be of relatively short duration and limited spatial scale, which limits the possibilities for statistical analysis of temporal patterns. The most comprehensive published source of information on TAC concentrations in southern California currently available is the final report for the Multiple Air Toxics Exposure Study II.[7] Along with a wealth of background information, the report presents trends in regional average concentrations for several individual species and lumped categories of TACs. A scattering of information on ambient concentrations is available for other regions, mainly in the form of reports by public agencies and environmental organizations[8,9] and informal data summaries.[10,11] However, the subject of day-of-week patterns in TACs is unexplored. The goal of this analysis was to determine whether day-of-week patterns exist in ambient concentrations of important TACs in southern California.

Routine monitoring for TACs began in California in 1985. Today, approximately 70 compounds are measured at approximately 30 sites. Because data consist of 24-hr samples, collected once every 12 days, this data set does not have sufficient resolution to shed much light on

photochemistry and transport. However, because TACs have a significant human health impact, they are themselves of intrinsic interest.

The compounds represented in the data set come from a wide variety of sources, including motor vehicles, industrial plants, and waste disposal sites, among others. Emission patterns vary from one compound to another. Some compounds, such as those emitted primarily by on-road motor vehicles, can be expected to show a distinct day-of-week pattern.

METHODOLOGY

The study covered the Los Angeles area from 1989 through 2001. During that period, six CARB TAC network sites were operational in the Los Angeles area: Burbank, Los Angeles, North Long Beach, Riverside, Simi Valley, and Upland. Not all sites and compounds are represented for the entire study period. All data were taken from the CARB's official TAC database.[12]

The CARB laboratory implemented a suite of method changes in 1999 to improve accuracy at low concentrations. The changes were needed because of the steady decrease in ambient TAC concentrations. Before 1999, all aromatic and halogenated hydrocarbon compounds were measured using capillary column gas chromatography (GC) with a combination of a photoionization detector (PID) and electron capture detector. From 1999 on, aromatic compounds were measured with a modified GC/PID technique, and halogenated compounds were measured by GC and mass spectrometry. Calibration methods were also substantially revised to improve performance at the low end. While the difference in reported concentrations between the two methods is not pronounced, some caution should be exercised in interpreting the absolute magnitudes of the mean day-of-week concentrations because they represent an aggregation of two slightly disparate sets of data. However, comparisons between days of the week should not be affected by the method changes because data for all days of the week were affected equally.

Several candidate compounds were considered for the analysis, and six were ultimately chosen: 1,3-butadiene, benzene, acetaldehyde, formaldehyde, perchloroethylene (tetrachloroethylene), and carbon tetrachloride (CCl_4). The selection was made primarily on the basis of overall health risk, as measured by the total estimated excess lifetime cancer cases in California.[13] All six compounds are among the top ten in terms of cancer risk. Quality and quantity of data were also considered.

Other high-risk TACs that were not analyzed include diesel particulate matter (PM), *para*-dichlorobenzene, and hexavalent chromium (Cr). Diesel PM was not considered because ambient data were not available for the study period. *Para*-dichlorobenzene and hexavalent Cr were dropped from the analysis because most of the ambient measurements were below the limit of detection (LOD).

Data analysis fell broadly into four steps: data screening, adjustment for trend and seasonality, computation of day-of-week means, and statistical comparison. The four steps are described in more detail later. The open-source statistical software package R was used for most of the analysis. This software may be downloaded free of charge from the Internet.[14]

Data Quality Screening

One obvious outlier out of 11,110 observations was dropped from the analysis. Approximately 8% of the benzene data and 2% of the 1,3-butadiene data were reported as below LOD. No data were reported as below LOD for any of the other compounds. Where data were below LOD, two-thirds of the LOD was substituted, based on a linear approximation to the left tail of the data distribution. Investigations suggested that for a variety of assumed data distributions, this was a better choice than the conventional one-half LOD.

Adjustment for Trend and Seasonality

Because the data were relatively sparse and strong seasonal effects are present for most of the compounds analyzed, a few missing data points in one year could lead to a bias in the analysis. Moreover, TAC concentrations have generally decreased over the period of the study, which creates the potential for bias if certain days of the week are more heavily represented in early years. Therefore, the data were adjusted for seasonality and trend by taking residuals (differences between actual and fitted values) from a smoothing spline. Austin and Tran[5] employed a similar technique to preprocess O_3 data before computing day-of-week means.

A smoothing spline is a flexible regression curve that fits the data by striking a compromise between smoothness and fidelity to the data. The user chooses a "smoothness parameter" to adjust the balance between smoothness and fit. When the smoothing parameter is 0, the spline interpolates smoothly between the data points. As it approaches infinity, the spline curve tends toward a straight line, namely, the conventional least-squares linear regression fit. Splines have an advantage over other smoothing methods when applied to complex data sets in that their degree of smoothness is locally adaptive rather than being uniform over the range of the data.[15] Taking residuals from a spline fit with an appropriately chosen smoothness parameter effectively preserves high-frequency variation, such as day-of-week differences, while filtering out low-frequency variation, such as seasonality and trend.

The degree of smoothness was initially selected by generalized cross validation, then fine-tuned by eye, compound by compound, to yield a curve that followed the seasonal pattern and trend without excessive roughness (Figure 1). The residuals, henceforth referred to as the seasonally adjusted data, were largely serially uncorrelated and symmetrically distributed (Figure 2).

Computation of Day-of-Week Means and Standard Errors

Day-of-week means were computed treating the seasonally adjusted data for different days of the week as independent. The assumption of independence is reasonable because TAC samples are collected 12 days apart, which is long compared with the time scale of meteorological events that affect ground-level TAC concentrations.

Statistical Comparison

The comparison was performed graphically by examining error bar charts (Figure 3). The goal was to seek patterns, rather than contrast specific pairs of days. The width of the error bars was set in such a way that if the error bars for two days of the week do not overlap, the means for those days are significantly different at approximately a 95% confidence level. This was achieved by setting the width of the error bars to $1.96 \times 1.41/2 = 1.39$ times the standard error. Standard errors were computed by pooling variances for all days of the week, under the assumption that the variability for all days is similar. One should not place undue emphasis on the significance (or lack thereof) of the differences. A more meaningful question is whether particular patterns are repeated across several sites. The fact that a pattern occurs repeatedly is evidence that it is systematic and not random, even if pairwise differences between days are not significant at the chosen level of confidence. To ensure that the seasonal adjustment procedure did not introduce artifacts, "raw" means were computed without seasonal adjustment. While there were minor differences between the means of the raw and seasonally adjusted data, it did not change the overall conclusions.

To double-check the statistical results, the SAS general linear model (GLM) procedure was used to perform analysis of variance on day-of-week means, including fixed-effect terms (because this most closely approximates the effect of the spline filtering) for month within year to account for seasonality. To stabilize the error variance and reduce the effect of extreme observations, the data were transformed according to the relationship $y = \log(x + \mathit{offset})$, where *offset* varied from compound to compound. GLM significance levels for pairwise comparisons of days of week were compared against the error bar charts, and the results were comparable.

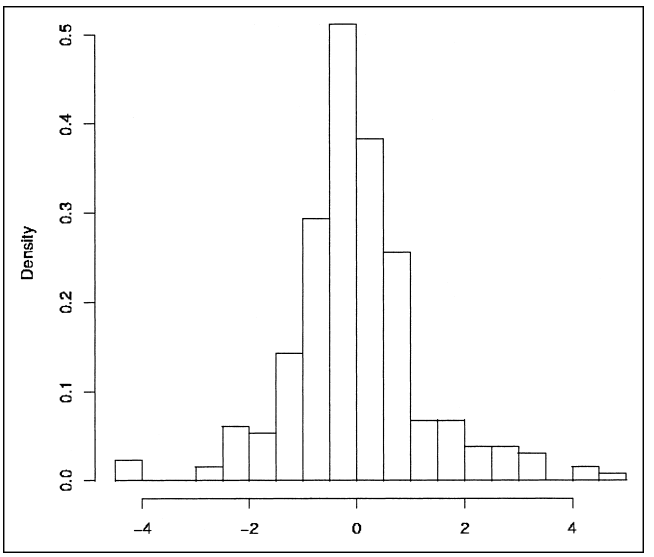

Figure 2. Histogram of residuals (seasonally adjusted concentrations) from the smoothing spline shown in Figure 1, showing a symmetric, bell-shaped distribution.

RESULTS

The error bar charts are presented in Figure 3. Sites are sorted geographically, from west to east. The following is a summary of the results:

1,3-Butadiene

Sunday is the lowest day of the week at all sites, sometimes significantly different from midweek days. The Saturday mean concentration is comparable to weekdays but generally slightly lower than Friday. Wednesdays also consistently show a dip relative to other weekdays. The

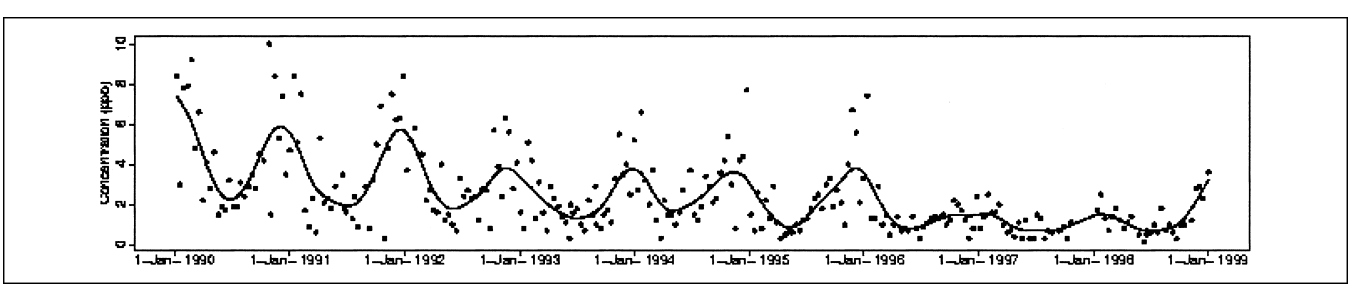

Figure 1. Ambient benzene concentrations at Burbank, 1990–1999. The solid line is the smoothing spline. Note the seasonality and decreasing trend.

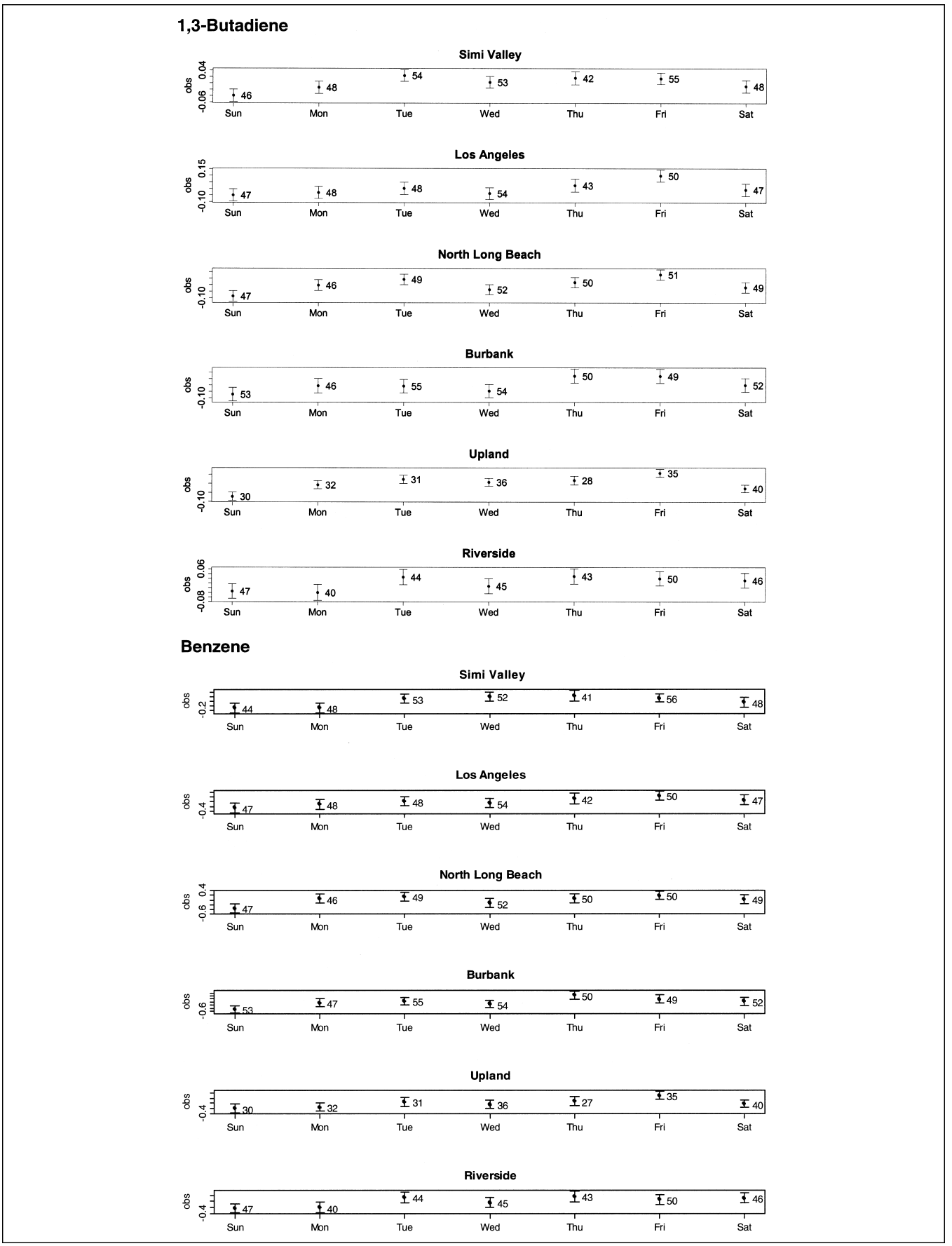

Figure 3. Weekly profiles for all six TACs.

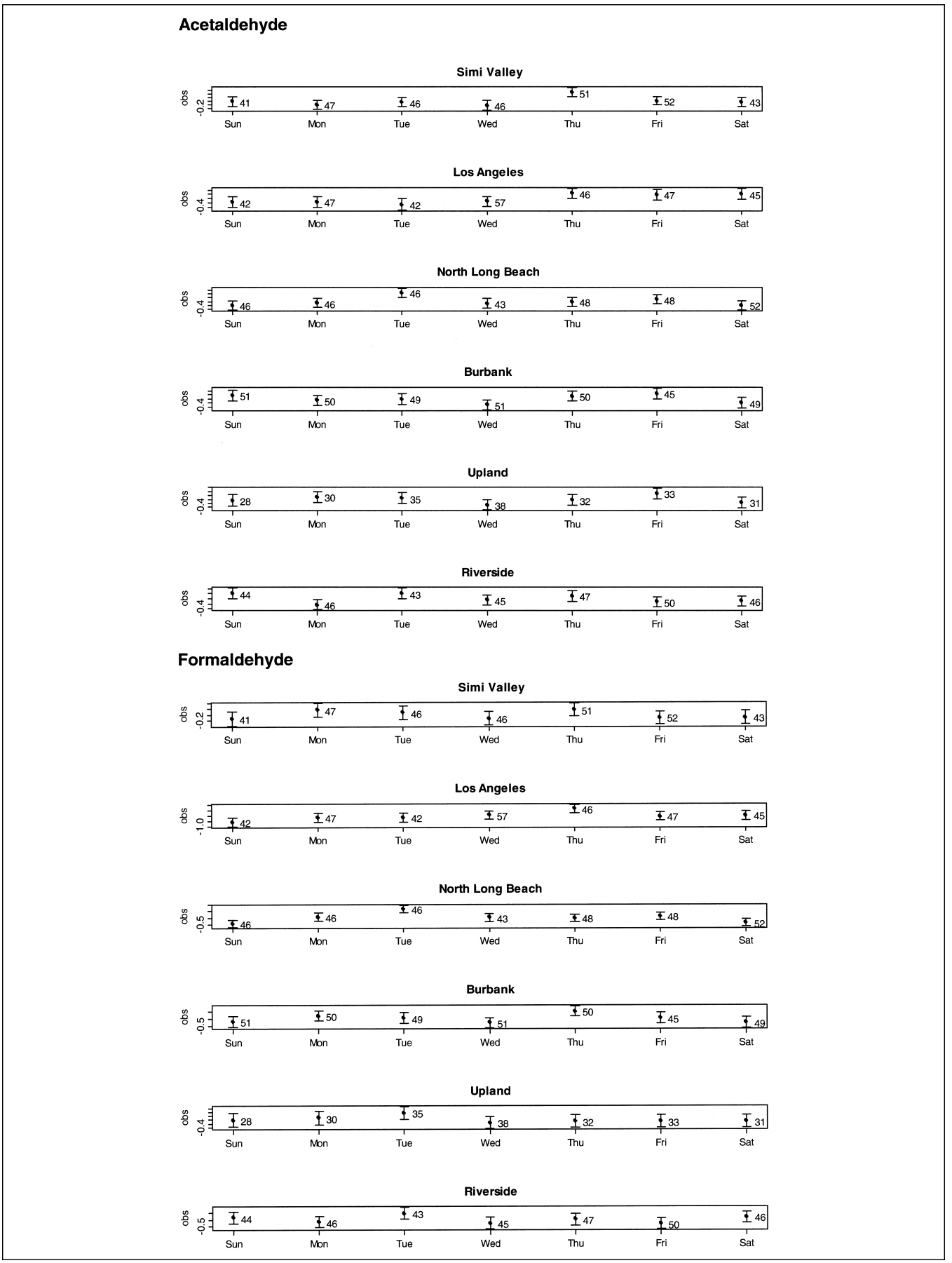

Figure 3. (cont.)

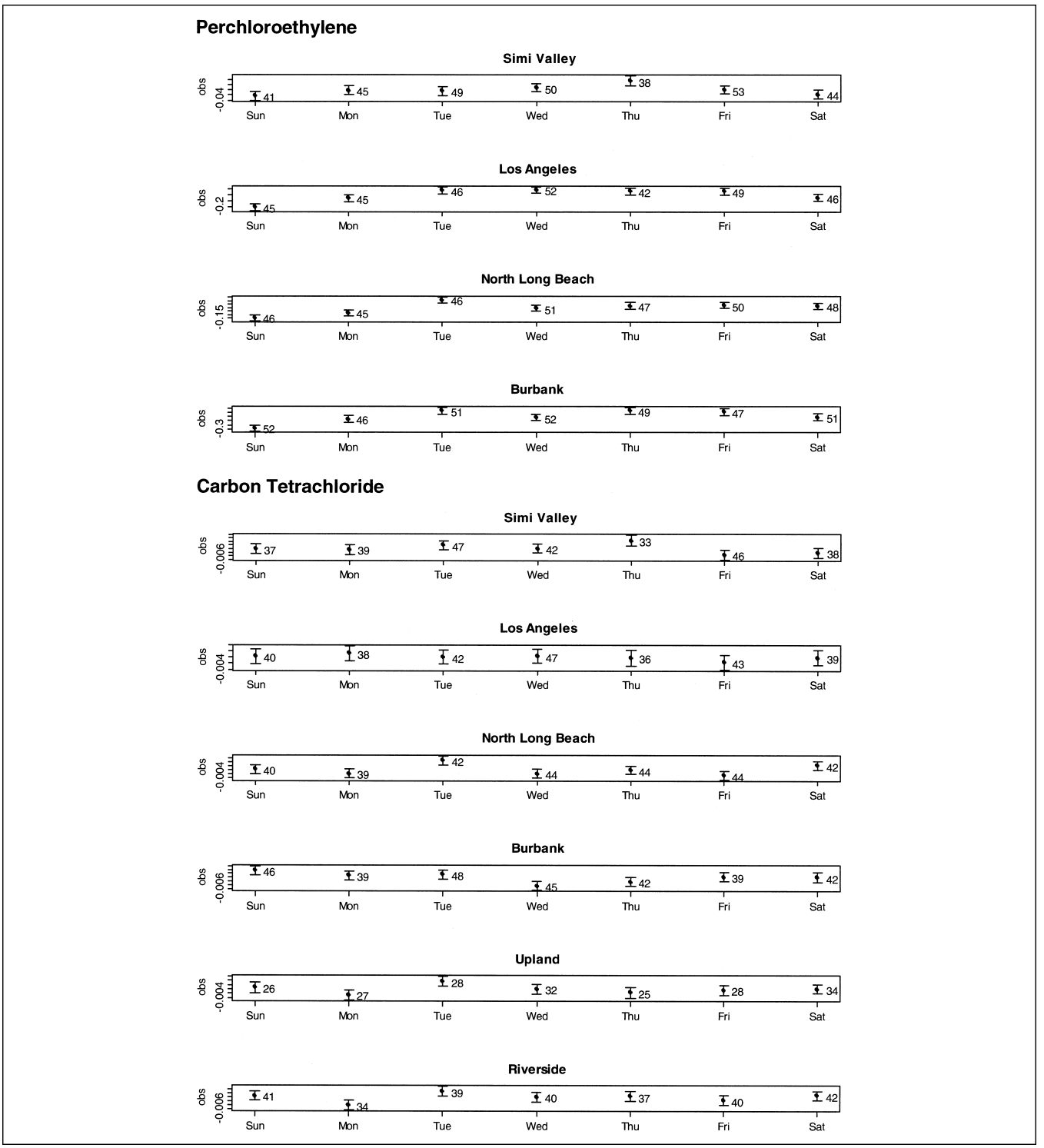

Figure 3. (cont.)

Wednesday dip is comparable in magnitude to the Saturday dip but not as pronounced as the Sunday dip. The overall effect is a very flattened "m" shape. Four of the sites, Long Beach, Upland, Burbank, and Simi Valley, show this behavior distinctly. Los Angeles differs in that Saturday is higher than Friday. The pattern is less apparent at Riverside.

Benzene

Site-by-site results are similar with 1,3-butadiene. Simi Valley fails to show a "Wednesday effect."

Acetaldehyde

Data were only available for 1996–2001. No day-of-week pattern is readily apparent. There is a suggestion of the

"m" shape apparent in benzene and 1,3-butadiene in the acetaldehyde data for Los Angeles, North Long Beach, and Upland. This is less evident in the other sites, however, primarily because Sundays seem to be comparable to or higher than weekdays.

Formaldehyde

Data were only available for 1996–2001. Similar to acetaldehyde, there is an echo of the "m" shape in the data for Los Angeles, North Long Beach, Burbank, and Upland, but this is less apparent at the remaining sites.

Perchloroethylene

Sunday is strikingly lower than other days of the week. Saturday is lower than weekdays, except at Long Beach, where it is comparable to weekdays.

Carbon Tetrachloride

No day-of-week pattern was discernable.

DISCUSSION

Benzene and 1,3-butadiene are mainly emitted by mobile sources. 1,3-Butadiene enters the atmosphere mainly through incomplete combustion of gasoline and diesel fuel. On-road motor vehicles are estimated to be responsible for approximately 70% of 1,3-butadiene emissions.[16] Benzene is a constituent of gasoline; together with other aromatic compounds, it is blended with gasoline to improve its combustion properties. Some of the benzene is emitted unburned in motor vehicle exhaust. It is also widely used in manufacturing as a solvent and raw material, but on-road motor vehicles are estimated to contribute approximately 60% of benzene emissions.[16]

1,3-Butadiene is highly reactive, with an atmospheric half-life of 1–9 hr in typical urban conditions.[16] Consequently, photochemical activity may cause weekly patterns in ambient concentrations to depart from emission patterns in a complicated way. Benzene, by contrast, is relatively unreactive, with a half-life of 8 days in typical urban conditions.[16] Therefore, a priori it is reasonable to expect benzene concentrations to follow a pattern that reflects fluctuating motor vehicle traffic volumes during the week.

Figure 4, taken from ref 6, shows traffic volume by hour of day for midweek (Tuesday–Thursday average) versus Saturday and Sunday, for a representative freeway site in the Los Angeles area. The significant feature of these data is that the traffic volume in the 5:00 a.m.–9:00 a.m. period is much higher in midweek. This coincides with stable atmospheric conditions, which give rise to high ground-level concentrations of primary pollutants. Ref 6 analyzed traffic data at numerous freeway sites throughout the Los Angeles area, and this behavior was consistent among all sites analyzed.

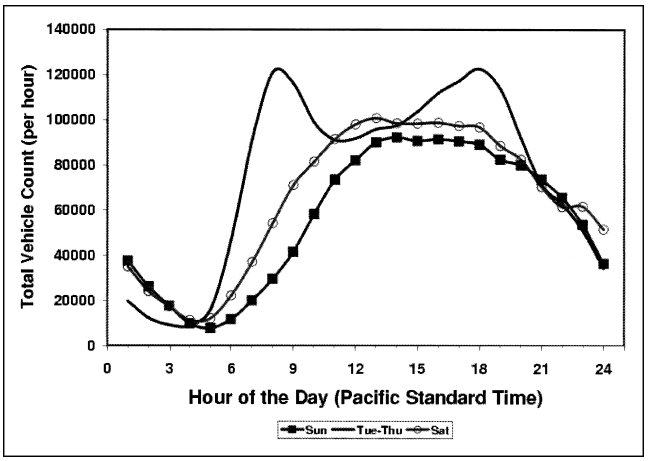

Figure 4. Hourly average freeway traffic volume by hour of the day for Burbank. Volumes were averaged over several counters located along the Interstate 5 and Interstate 134 freeways.

The analysis confirms that ambient concentrations of both 1,3-butadiene and benzene are lowest on Sunday, and Saturdays are low relative to Fridays. The Wednesday dip is an unexpected feature and may be connected with emission patterns or an as yet unexplained dynamic characteristic of the photochemical system. The similarity between 1,3-butadiene and benzene is also worth noting, given the difference in reactivity between the two compounds.

The question of how ambient concentrations of volatile organic compounds (VOCs) vary over the week in southern California has a broader significance in that it could help explain on the weekend effect in O_3 concentrations. At present, weekly patterns in VOCs are poorly characterized, partly because of sparse geographical coverage and the lack of year-round data. In this light, the results presented here for 1,3-butadiene and benzene may be a useful contribution to the discussion on the O_3 weekend effect.

The main source of acetaldehyde and formaldehyde is believed to be photochemical oxidation of hydrocarbon combustion products—primarily motor vehicle exhaust. As much as 67% of the acetaldehyde and 88% of the formaldehyde in urban air are believed to be photochemically derived.[16] The absence of day-of-week patterns for acetaldehyde and formaldehyde is therefore something of a surprise. One would expect the aldehydes to show a distinct weekly pattern of some sort, just as O_3 does.

While the analysis shows slight evidence of lower weekend aldehyde concentrations at some sites, the pattern is not as strong or consistent as one might expect. While the sample sizes are smaller than for the other compounds (because the data set only begins in 1996), it is unlikely that this could account completely for the discrepancy. It is also possible that, while secondary aldehyde formation is greater on weekends, higher primary

aldehyde emissions bring weekday concentrations up to weekend levels. However, to answer this question would require a data set with finer resolution than 24 hr.

Perchloroethylene is used primarily as a dry-cleaning solvent. It also finds application in a variety of industrial settings and consumer products, including degreasing operations, paints, adhesives, and inks.[16] The reduced concentrations on Sundays are consistent with a weekly work cycle with reduced emissions on weekends.

CCl_4, once widely used as a refrigerant, propellant, and industrial solvent in the United States, is currently being phased out. However, because of its long atmospheric persistence (50 years), tropospheric accumulation has created a global background concentration estimated at 0.11–0.15 ppb.[16] Ambient concentrations in California probably represent global background plus a minor contribution from local sources. It is therefore not surprising that CCl_4 fails to exhibit a day-of-week pattern.

CONCLUSIONS

With the exception of the aldehydes, the six TACs analyzed generally exhibited patterns consistent with a naïve expectation: lower concentrations on Sundays for benzene, 1,3-butadiene, and perchloroethylene, and no weekly pattern for CCl_4. Benzene and 1,3-butadiene, which are emitted mainly by on-road motor vehicles, show a strong relationship with traffic volume data. The "Wednesday effect" apparent in benzene and 1,3-butadiene is a mystery that warrants further investigation.

In the last two decades, ambient TAC concentrations in California have been impacted by a number of regulations, including some aimed specifically at reducing public exposure to toxic substances. Benzene emissions have been strongly impacted by the shift to cleaner-burning fuels. California's landmark Cleaner Burning Gasoline regulation, which took effect in the spring of 1996, imposes a direct limit on benzene content of gasoline.[17] Both benzene and 1,3-butadiene emissions have decreased as tailpipe VOC standards have become more stringent. The CARB adopted a control measure for perchloroethylene in 1993. The use of CCl_4, which in addition to being highly toxic is also responsible for depleting stratosperic O_3, is gradually being phased out throughout the world. The impact of regulation and technology changes upon aldehydes is more complex and is currently not well understood.

ACKNOWLEDGMENTS

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