ner measurements in 1969 and 1971. This implies no significant change in the escape of H due to nonthermal mechanisms.

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Winter Rain and Summer Ozone: A Predictive Relationship

Abstract. *Insights from dendrochronology have provided a new seasonal predictor for air pollution meteorology. In the San Francisco Bay Area summer ozone excesses over the federal ozone standard are correlated (correlation coefficient* r = *.87) with precipitation for the two preceding winters, a factor related to tree-ring width in a precipitation-stressed climate. The hypothesis that reactive hydrocarbon emissions from vegetative biomass affects these ozone excesses was supported by a similar correlation between summer hydrocarbon average maximums and the two-winter precipitation factor, reaching* r = *.88 at suburban stations. A weak tendency for hot summers to follow wet winters (in 16 years of California data) explains only a minor part of the ozone-rain relationship in multiple correlations.*

In assessing long-term trends for boundary-layer ozone in the San Francisco air basin, a linear decrease of 5 percent per year was found to fit the basic data [days on which ozone levels exceeded the federal standard of 0.08 part per million (ppm) for 1 hour] from 1965 through 1977, but the trace was very noisy, with year-to-year variations frequently exceeding 30 percent (see Fig. 1).

A reporter's counterintuitive question led to an explanation of most of this variability. The question, "Did the drought have anything to do with our clean air in 1977?" led to an examination of rainfall data in conjunction with ozone data. The rare summer rains in California are associated with good vertical mixing and generally clean air. Thus a negative relationship between precipitation and ozone has been generally assumed to exist. The discovery of a strong positive relationship between winter rain and summer ozone, reinforced by a similar positive relationship between winter rain and summer hydrocarbon levels, has provided a seasonal predictor of summer ozone excesses.

Fortunately an excellent data base has been developed for the air basin in 16 years of continuous monitoring by the Bay Area Air Pollution Control District (BAAPCD). All data obtained before June 1975 have been adjusted in accord with the California Air Resources Board (CARB) calibration procedures of that date, and thus are comparable with later data. The monitoring network expanded from six urban stations in 1962 to 25 stations extending far into exurbia by 1975. The increase of ozone excesses in the period 1967 to 1969 was associated with the extension of the network to its first site (Livermore) away from urban centers, but in the downwind urban plume. Other new stations on the urban margins have added to the excess-day total in the air basin, but new stations in urban centers have had very little effect on observed ozone totals. The fact that excess days have decreased more than 60 percent in 12 years despite a fourfold amplification of the station network attests to both the reality of the decrease and the relative smoothness of the horizontal gradient of ozone. Precipitation is measured at about 70 stations in and near the San Francisco air basin, and monthly and annual totals are reported by the Environmental Data Service of the National Oceanic and Atmospheric Administration in *Climatological Data, Annual Summaries for California*. These data include an average for the Central Coast Drainage Basin, which is somewhat offset to the south of the San Francisco air basin, but encompasses the area where most ozone excesses occur.

Initial examination of the rainfall and ozone data sets (Fig. 1) and various exploratory correlations (Table 1) showed winter rainfall to be a strong leading indicator of summer ozone excesses. This counterintuitive relationship was then examined in detail, to seek out the strongest operational predictors and to examine the hypotheses that might explain it. These two goals were pursued concurrently, since predictors were developed through hypothesis testing.

Two major hypotheses were investigated. In hypothesis A, a purely meteorological relationship or forcing function, wet winters are precursors of hot stagnant summers that are conducive to photochemical oxidant formation. A corollary of A might include gradual rather than sudden advection of stratospheric ozone associated with strong subsidence during hot summers. In hypothesis B vegetative biomass increases with increased rainfall, leading to an increase of natural hydrocarbon emissions from this biomass.

Major features of the exploration of the ozone-rain relationship are summarized in Table 1. The independent variable of precipitation was first taken as an annual total from July through June in the California rainy season format, then narrowed to November through March in a non-ozone season format, and final-

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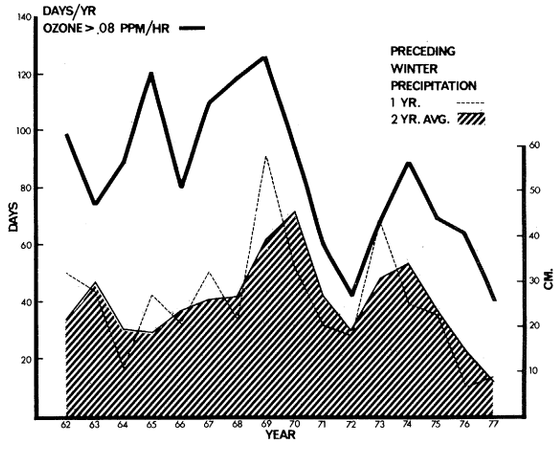

Fig. 1. Days per year on which the current federal 1-hour standard for ozone was exceeded in the San Francisco air basin (solid line) show a downward trend but with large year-to-year variation. A relationship is observed to the total precipitation during the preceding winter (dashed line). Precipitation for the two preceding winters (boundary of hatched area) is more strongly related to summer ozone excesses, particularly over the last 8 years, as anthropogenic hydrocarbon emissions have been sharply reduced and biomass emissions have become relatively more important.

ly narrowed to December through February in the winter-quarter format, which proved most effective as a predictor. The biomass-related format of two preceding winters was then added on the basis of dendrochronology, which further augmented the skill.

The dependent variable was usually ozone measured in terms of annual (primarily summer) days on which ozone levels exceeded various federal standards. Other dependent variables were summer-quarter means of daily maximum hourly average concentrations and summer weather parameters.

The correlation coefficients increased from .47 to .61 and .62 with the use of winter rather than annual precipitation. Surprisingly, the federal health advisory level for ozone, 20 parts per hundred million (pphm), was even more strongly correlated (r = .69) with winter rain. To test whether a local anomaly might be involved, an older Los Angeles Air Pollution Control District (LAAPCD) summary of 35-pphm days was correlated with winter rain in the South Coast Drainage Basin, and a correlation at r = .71 was found.

Hypothesis A (a meteorological link) was tested with data developed in our earlier trend studies. Warm days ($\geq$ 30°C) with low inversions ($<$ 305 m), tabulated as "trend" days, were correlated with winter precipitation, using trend days for San Jose as the long-term station of greatest activity. The value r = .32 showed that there was a positive but weak relationship. Then temperature alone was correlated (using San Jose summer days, $\geq$ 32°C). This correlation was stronger, with r = .51, $>$ 75 percent significance. These data suggest that there is some meteorological link, which should be further investigated by dynamic climatologists. It is interesting to note that the 3 years of maximum stratospheric sudden warming in the past 16 years, as reported by McGuirk (*1*), showed the dry-winter, cool-summer, low-ozone pattern in north central California.

Regarding hypothesis B (biomass), the field of dendrochronology provided invaluable insights. For the American Southwest (including California and probably extending into Texas, Oklahoma, and Kansas) the dominant growth-limiting factor evidenced in tree-ring width is precipitation. Moreover, as reported by Fritts (*2*), ring growth is strongly a function of food supplies photosynthesized and accumulated throughout the previous year as well as the current year. This suggested that average precipitation for the two preceding winters should be compared with ozone excesses to test the biomass hypothesis. The resulting correlation coefficients reached .86 and .87, $>$ 99 percent significance.

This hypothesis has been foreshadowed in the air-pollution literature. Coffey and Stasiuk (*3*) compared August ozone levels at urban and rural sites in New York State and found that the highest values frequently occurred at Whiteface, a remote mountain station, in a pattern which suggested that either stratospheric ozone or natural hydrocarbons were more important than anthropogenic emissions. Rasmussen (*4*), in chamber studies in Washington State, measured the reactive hydrocarbons (mainly monoterpenes) from trees, noting a strong temperature dependence. Extrapolating his measured emission rates, he estimated global forest hydrocarbon emissions as 175×10^6 metric tons per year, more than six times the anthropogenic total of 27×10^6 metric tons per year.

As an order-of-magnitude guide, we applied Rasmussen's emission rates to the San Francisco air basin, which has 7.3×10^3 km^2 of forest and 9.7×10^3 km^2 of farmland. The calculated hydrocarbon emissions of 198 metric tons per day from forests and 2.5 metric tons per day from farms may be compared with our emission inventory hydrocarbon values of 481 metric tons per day from stationary sources and 426 metric tons per day from mobile sources. Moreover, Rasmussen suggested that forest emissions may increase by a factor of 5 when the temperature exceeds 30°C. Thus the high-temperature emission rate would exceed 1000 metric tons per day, more than the combined total from all anthropogenic sources.

If the magnitudes of these calculated values are correct, then our long-term measurements of total hydrocarbons could reflect their influence, despite the relative grossness and complexity of the hydrocarbon data base. For total hydrocarbon measurements we used a flame ionization detector, which was calibrated against propane (C_3) through 1974 and against methane (C_1) since January 1975. If the mix of hydrocarbon species remained the same from year to year, the earlier data could be divided by 1.4 to compare them with the later data. The adjustment is appropriate for methane, which was overestimated by a factor of 1.4 in the early data, and background methane constitutes an important 1.4 ppm of the total hydrocarbon mix. However, the C_{10} terpenes and C_5 isoprenes, which should theoretically be most important in the biomass emissions, are more grossly underestimated by the C_1 calibration.

Consequently, we present the unadjusted data in Table 2, and make the correlations with precipitation for both unadjusted and adjusted hydrocarbon values, as raw material for photochemical modelers. The data in Table 2 are maximum hourly averages of total hydrocarbons averaged over the summer quarter (July through September) from the CARB air quality data summaries.

Total hydrocarbon measurements extend back to 1965 at San Francisco and San Jose, and were added at other stations as indicated in Table 2. The coefficients of the correlation between unadjusted summer hydrocarbon values for each of these stations and two-winter precipitation are quite high, and the station-to-station differences are closely related to the upwind balance of biomass and anthropogenic sources for normal summer trajectories. The lowest value, r = .56, occurs at Pittsburg, which lies downwind from a series of major petrochemical complexes. San Francisco and San Jose, which have high traffic densities, follow with r = .60 and .69, respectively. Remarkably high values are

Table 1. Examination of various precipitation measurements as the independent variable and ozone measurements or summer weather factors as the dependent variable with resulting correlation coefficients (r), percentage confidence, Spearman rank confidence, and data years covered.

Independent variable	Dependent variable	r	Confidence (%)	Rank confidence	Data years
One-year precipitation	Ozone or summer weather factors				
San Jose winter	Basin days > 8 pphm	.62	97.5	99	1965–1977
South Coast winter	LAAPCD days ≥ 35 pphm	.71	95	95	1957–1968
Central Coast winter	San Jose days ≥32°C	.51	75	95	1970–1977
Two-year precipitation	Ozone or hydrocarbon				
Central Coast winter	Ozone basin days >8 pphm	.87	99	99	1970–1977
La Honda winter	Ozone basin days >8 pphm	.86	99	99	1970–1977
Central Coast winter	San Jose ozone, summer mean of maximum hours	.64	95	95	1964–1977
Central Coast winter	San Jose hydrocarbon, summer mean of maximum hours	.69	95	95	1965–1977

found for Redwood City (r = .88), downwind from the heavily wooded Coast Range, and Santa Rosa (r = .87), downwind from extensive orchard country. The most surprising correlation, r = .81, is obtained for Livermore, a small city in a sheltered valley considered to be axially downwind from the San Francisco–Oakland urban plume. Nevertheless, 66 percent of the Livermore hydrocarbon variance (taken as r^2) appears to be related to biomass emissions, presumably in a 10- to 15-km trajectory over the wooded hills between Oakland and Livermore. When the hydrocarbon data are adjusted for the calibration change from C_3 to C_1 the same general patterns and relationships persist.

Since a strong effect of biomass hydrocarbon emissions is indicated both at Santa Rosa, one of the lowest-ozone stations, and at Livermore, generally the highest, other components of the urban plume might appear to be more important in an ozone control strategy. The oxides of nitrogen, particularly NO, appear to be the most likely candidates; but ozone development is very sensitive to hydrocarbon/NO ratios, and thorough determination of existing ratios and modeling of prospective changes (both including the temperature-dependent biomass emissions) should precede any revision of regulations. The role of the hydroxyl radical must also be carefully modeled.

Recent measurements of biomass emissions have been made by Zimmerman (5), who cautions that high emission tonnages over large areas do not necessarily lead to high concentrations. One clue to hydrocarbon buildups may exist in an unexplained idiosyncrasy of our hourly hydrocarbon data. Summer hydrocarbon maximums in the Bay Area generally occur at 3 or 4 a.m. and are difficult to relate to morning and evening traffic peaks. They are also difficult to relate to temperature-dependent biomass emissions, which presumably peak in the early afternoon. When this phenomenon was first noticed in 1965, we assumed that service-station gasoline storage tanks might routinely be filled in the predawn hours, but this was only rarely the case. Since the phenomenon is strongest in hot, stagnant summer weather, one might hypothesize that katabatic nocturnal drainage from the wooded hills flows into the collecting-basin valleys (where our stations with the highest hydrocarbon-rain correlations are located). The magnitude of the effect is indicated by the regression coefficient. At San Jose, for example, hydrocarbons increase 0.08 ppm for each centimeter of rain. The federal standard for reactive hydrocarbons (0.24 ppm as an average for 6 to 9 a.m., corresponding to the morning traffic peak) would appear to be violated with each 3 cm of winter rain, except for the minor time lag.

Since the hydrocarbons and carbon monoxide measured at community monitoring stations are generally attributed to vehicular sources and are thus assumed to vary together, it seemed appropriate to compare the CO maximum hourly summer-quarter averages with the 2-year rainfall averages. Selecting San Jose as the one station in the basin where both O_3 and CO standards are frequently exceeded, we found essentially

Table 2. Total hydrocarbon data (summer-quarter maximum hourly averages) are listed for two urban stations, San Francisco (SF) and San Jose (SJ), two suburban stations, Redwood City (RC) and Santa Rosa (SR), one suburban station assumed to lie in urban plume, Livermore (LI), and one industrial area station Pittsburg (PT). The Central Coast precipitation averaged for the two preceding winters is also listed with each summer's hydrocarbon data. For each station various hydrocarbon-precipitation relationships are calculated, first from the basic data and from data adjusted for a calibration change from C_3 to C_1 in 1975.

Year	Winter precipitation (cm)	Summer-quarter hydrocarbon average (ppm)						
		SF	SJ	RC	LI	SR	Five-station average	PT
1965	18.9	4.3	4.2					
1966	23.7	4.2	4.8					
1967	26.2	4.6	5.3					
1968	26.6	4.7	4.8					
1969	39.6	4.1	5.5	5.4		3.6		3.4
1970	45.5	4.6	5.6	4.6	4.1	3.1	4.4	3.6
1971	26.7	3.7	5.4	4.2	3.6		4.2	4.9
1972	19.0	3.1	4.6	3.1	3.4	2.5	3.3	3.0
1973	30.6	3.4	5.1	4.1	3.3	2.5	3.7	3.2
1974	34.1	3.4	3.7	4.2	3.2	2.6	3.4	3.0
1975	23.7	2.1	2.7	2.4	2.5	2.0	2.3	2.2
1976	14.6	2.2	2.1	2.5	2.8	2.2	2.4	2.1
1977	7.6	2.0	2.5	2.3	2.1	1.3	2.0	2.0
		Station hydrocarbon relation to winter rain						
Unadjusted								
Correlation coefficient		.60	.69	.88	.81	.87	.81	.56
Regression coefficient		.059	.083	.079	.043	.047	.059	.043
Significance (%)		95	99	99	98	99	98	85
Variance explained (%)		36	48	77	66	76	66	31
Adjusted								
Correlation coefficient		.53	.68	.84	.47	.64	.80	.34
Regression coefficient		.065	.104	.095	.027	.048	.063	.033
Significance (%)		90	98	99	75	90	97	65
Variance explained (%)		28	46	71	22	41	64	12

no correlation between summer CO and winter rain (r = .07). The absence of a precipitation effect on CO strengthens the biomass hypothesis and weakens the purely meteorological one. A multiple correlation coefficient of .92 was found for hydrocarbons with both CO and winter rain as independent variables, coefficients of the hydrocarbon-CO and hydrocarbon-rain simple correlations being .81 and .71, respectively. These values imply that at San Jose the biomass hydrocarbon emissions are not quite as important as the vehicular ones. However, the temperature-dependent biomass hydrocarbon emissions would vary more and therefore have a greater effect on ozone levels on hot days (as observed).

Further multiple correlations were used to examine the relative importance of hypotheses A and B. The best operating predictor of high ozone levels in the San Francisco air basin has been temperature. Thus, summer temperatures $\geq$ 32°C at San Jose and two-winter rain were compared with days of ozone levels $>$ 8 pphm as a dependent variable. The multiple correlation coefficient was .870, with rain and O_3 correlated at r = .869 and temperature and O_3 at r = .565. The contribution of temperature to the multiple correlation was only .001. We infer from these values that temperature does not affect ozone independently, but through the biomass factor.

In the recent survey of ozone and photochemical oxidants by the National Academy of Sciences (*6*), ozone was taken as an acceptable surrogate for the complex mix of noxious substances developed photochemically from urban emissions, and it was suggested that this surrogate role be periodically reevaluated (*6*, p. 127). The relationship indicated in these data should be considered in such a reevaluation.

The apparent influence of biomass hydrocarbon emissions on ozone should justify a major research effort to measure and model the species and interactions involved. However, the first phase in evaluating the biomass hypothesis may be undertaken with no need for grant applications or ad hoc conferences. Nature has provided California with a very wet year after two drought years. Based on the relationships observed over the past decade, one may predict a 60 to 70 percent increase of ozone excesses ($>$ 8 pphm) in the San Francisco air basin for 1978 compared to 1977, far outweighing the 5 to 6 percent annual decrease from control programs. Moreover, the increases should be most pronounced at outlying suburban stations and should also be reflected at the $\geq$ 20 pphm health advisory level. Since most of the western United States has had a similarly wet winter following a dry winter, the 1978 increases in ozone should be widespread. However, the quantitative aspects must be derived specifically for each air basin and watershed, possibly with guidance from locally knowledgeable dendrochronologists.

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Degraded Lignin Compounds Identified in Silicified Wood 200 Million Years Old

Abstract. *Degraded lignin compounds have been identified in Triassic age (about 200 million years) silicified wood from the Petrified Forest National Park in Arizona. The pyrolysis products from black carbonaceous samples include carbon dioxide, low-molecular-weight alkanes and alkenes, benzene, alkyl-substituted benzenes, phenol, cresol, xylenols, indenes, benzofurans, trimethylindanone, and naphthalenes. These compounds are also the primary pyrolyzates of modern lignin above 500°C.*

The Petrified Forest member of the Triassic Chinle Formation in Arizona contains a spectacular array of silicified wood embedded in friable clay-rich sandstones and shales. Analyses of the mineralized fossil wood indicate that organic material has been preserved in the black carbonaceous samples of silicified wood (up to 2.7 percent organic carbon), but that organic compounds are completely absent in the multicolored "woods" with no remaining biological structures. The well-preserved cell walls in the carbonaceous samples suggest that remnants of the original wood polymers have survived a 200-million-year history of silicification and diagenesis.

The principal components of wood cell walls are cellulose (~50 percent), hemicellulose (20 to 30 percent), and lignin (15 to 30 percent). Of these, lignin is the most resistant to decay (*1*) and was thus thought to be the most likely component to survive in the mineralized wood. Lignin is a complex three-dimensional polymer of phenylpropane derivatives (*2*), partially cross-linked by benzyl ether groups and connected to hemicellulose by covalent bonds (*3*). Lignin derivatives have been isolated from soils (*4*), unmineralized fossil wood, peat, and carbonaceous marine sediments (*5*). The results of these studies indicate that lignin degradation products are extremely stable with respect to time and that they can have long lifetimes in the geological record.

In this study, samples of the silicified (average 90 percent SiO_2) conifer *Araucarioxylon arizonicum* (the most abundant species of Chinle macrofossil) were analyzed by sequential high-vacuum (10^{-6} torr) pyrolysis and combined gas chromatography–mass spectrometry (GC-MS) as described in (*6*). Powdered samples were demineralized with concentrated HF at room temperature and washed first with cold distilled 6*N* HCl and then with triple glass-distilled water. A high-fired basalt was pretreated and analyzed in the same way as a check for organic contaminants in the extraction procedure. None were detected.

The samples were degassed at 150°C under high vacuum to remove adsorbed water and nonpolymeric organic fragments, and were pyrolyzed sequentially at 300°, 450°, and 600°C for 30 minutes at each step. An OS-138 (polyphenylether) support-coated tubular capillary column 45 m long and 0.05 cm in inside diameter was programmed from 40° to 190°C at 2.5°C per minute. The products were identified on the basis of their mass spectral fragment patterns and relative GC retention times. Brauns spruce lignin, a representative conifer lignin, was pretreated with HF, washed with 6*N* HCl and H_2O, pyrolyzed, and analyzed by GC-MS as a comparison for the fossil wood data.

The products released from interior sections of black silicified wood with preserved cell structures included a variety of alkyl-substituted phenolic and

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