22. R. T. Ambron, J. E. Goldman, J. H. Schwartz, *Brain Res.* **94**, 307 (1975).
23. For previous reports of fast transport of lipid, see (*2*, *4*, *7*); A. McGregor, T. L. Jeffrey, J. D. Klingman, L. Austin, *Brain Res.* **63**, 466 (1973).
24. P. Siekevitz, *Annu. Rev. Physiol.* **34**, 117 (1972); G. Palade, *Science* **189**, 347 (1975); F. N. Katz, J. E. Rothman, V. P. Lingappa, G. Blobel, H. F. Lodish, *Proc. Natl. Acad Sci. U.S.A.* **74**, 3278 (1977); D. J. Morré in *The Synthesis, Assembly and Turnover of Cell Surface Components*, G. Poste and G. L. Nicolson, Eds. (Elsevier/North-Holland, New York, 1977), p. 1; U. Czichi and W. J. Lennarz, *J. Biol. Chem.* **252**, 7901 (1977).
25. S. Kruger, *J. Chromatogr.* **42**, 148 (1969).

26. Supported by research grants to J.H.S. from the National Science Foundation (BNS 77-16505) and from the National Institutes of Health (NS 12066). A.A.S. was supported by PHS medical scientist training grants GMO-1668 and GMO-7308; R.T.A. was a senior investigator of the New York Heart Association. We thank M. Gershon, E. R. Kandel, G. Kreibich, J. Oppenheim, and K. Pfenninger for criticism of the manuscript.

* Present address: Department of Microbiology, New York University School of Medicine, 550 First Avenue, New York 10016.

11 September 1978

Factors in Summer Ozone Production in the San Francisco Air Basin

In the recent report by Sandberg *et al.* (*1*) it is suggested that biogenic emissions are responsible for the high ozone levels observed in the San Francisco air basin.

First, for biogenic emissions to increase with previous winter rain, one would need to establish that summer vegetation is directly dependent on that rain. Miller and Cooper (*2*) find that tree-ring width is not correlated with previous winter weather. Furthermore, it does not necessarily follow that heavy winter rains will produce more summer vegetation since soil will reach saturation and any further rainfall will run off. One should therefore perform a detailed study of the types of vegetation in an area, their dependence on rainfall, and their emission patterns and then arrive at emission factors for the whole basin.

We have been concerned with the role of natural hydrocarbons in ozone production and have studied areas in the Midwest, Northeast, and Southeast, and we do not expect the San Francisco Bay Area to be significantly different. The greatest concentration of terpene we ever observed was in a pine forest in North Carolina, when the α-pinene carbon concentration was approximately 60 parts per billion (ppb), corresponding to ~50 percent of the total nonmethane hydrocarbon found in the canopy. A maximum pinene flux of ~67 μg/m^2-min was observed at this location; the temperature was ~34°C. If a simple line source diffusion model (*3*) is used with a forest 100 km in depth, the α-pinene carbon concentration in a city 1 km downwind will be 60 ppb at a high flux of 100 μg/m^2-min, assuming that the α-pinene is stable—that is, that there is no reaction with O_3 and OH radicals usually found in the atmosphere. With background O_3 and OH levels of 20 to 30 ppb and 10^5 cm^{-3}, respectively, the α-pinene concentration will be much lower. It is clear that even a high flux of 100 μg/m^2-min will not have a significant effect on the hydrocarbon concentration in a city downwind. The EKMA (empirical kinetic modeling approach) model (*4*) predicts that such low levels (60 ppb carbon) could, at the most favorable hydrocarbon/NO_x ratio, produce only approximately 15 ppb ozone.

Sandberg *et al.* state that the highest hydrocarbon levels are observed in the early morning (3 to 4 a.m.) and hypothesize that this is due to katabatic nocturnal drainage from the wooded hills. However, if the biomass is emitting the hydrocarbons in the early afternoon, as the authors suggest, they would be expected to react with ozone, which is present in high levels in the afternoon. This would be expected since most of the natural hydrocarbons are olefinic (isoprene and the terpenes) and would have a very high reaction rate with ozone. Therefore, hydrocarbons involved in katabatic nocturnal drainage would have to be emitted during the night, when biomass emissions are at a minimum. The emission levels given by Sandberg *et al.* are therefore gross overestimates. I suggest that if the authors consider the NO_x values along with the hydrocarbons they will also find the NO_x values elevated early in the morning. These high values are a result of two factors: anthropogenic emissions and the low mixing heights in the nighttime hours.

The authors found a high correlation (.81) between hydrocarbon and CO. Since they found no correlation between CO and rain but did observe a correlation between hydrocarbon and rain, it would appear that their data base changes from correlation to correlation.

Finally, Sandberg *et al.* ignored existing aerometric hydrocarbon data. We have studied a number of cities in the past decade and have never found a significant concentration of biogenically produced hydrocarbons (isoprene and the C_{10} terpenes). Much of the data has been published. All the published data show that the automotive contribution to hydrocarbons between 6 and 9 a.m. can vary from 40 percent (in Wilmington, Ohio, a rural site) to as much as 90 percent (in Manhattan, New York). The remainder is attributable to stationary sources.

JOSEPH J. BUFALINI
Gas Kinetics and Photochemistry Branch, Environmental Sciences Research Laboratory, Environmental Protection Agency, Research Triangle Park, North Carolina 27711

References

1. J. S. Sandberg, M. J. Basso, B. A. Okin, *Science* **200**, 1051 (1978).
2. H. G. Miller and J. M. Cooper, *Nature (London)* **260**, 697 (1976).
3. D. B. Turner, *Environ. Prot. Agency (U.S.) Publ. EPA-600/4-76-0306* (1976).
4. M. C. Dodge, *Environ. Prot. Agency (U.S.) Publ. EPA-600-3-77-048* (1977).

14 June 1978; revised 19 September 1978

The underlying assumptions that led Sandberg *et al.* (*1*) to the conclusion that there is a significant relationship between biomass increase during wet years and summer ozone excesses require a much more rigorous examination. First, in regard to the data displayed in their figure 1, the authors employed only a limited number of years to support their biomass hydrocarbon–ozone hypothesis. It would provide a much more stringent test of their hypothesis if data available from the whole span were used. We transferred the numbers for the whole span (1962 to 1977) from figure 1 and found a correlation coefficient of only .45 for the 16-year period. We also examined the annual averages of the maximum hourly average oxidant for the San Francisco Bay Area air basin for 1965 to 1974 (*2*). The correlation coefficient obtained for this average and the 2-year precipitation was .12. Thus, the totality of the data hardly justifies the strength of their claim for a rainfall-biomass-ozone interaction and erodes confidence in their suggestion that a single wet winter (1977 to 1978) will test it. The authors speak of ozone excesses, but that is not technically correct for the entire length of the air monitoring record. The instruments commonly in use until the last 3 years did not measure ozone specifically but responded also to other pollutants (positively to the peroxyacyl nitrates and NO_2 and negatively to SO_2); it is appropriate to distinguish between total oxidant and ozone data.

Second, no measurements were made to confirm that the kinds of hydrocarbons in the San Francisco Bay Area actually originated from biomass. The authors used estimates of hydrocarbon emissions based on a study of plants in a

0036-8075/79/0105-0081$00.50/0

closed atmosphere to propose what may be happening in a natural environment (*3*). Furthermore, there is more evidence than they acknowledged that nonmethane hydrocarbons (NMHC) from natural sources may never reach significantly high concentrations. For example, two recent studies (*4, 5*) showed that the total carbon from natural hydrocarbons did not exceed 0.1 part per million (ppm) in rural and remote areas. These studies were carefully designed to minimize calibration errors that would make it difficult to distinguish between natural and anthropogenic hydrocarbons. In other studies, whenever rural hydrocarbons were higher, there was evidence of contributions from anthropogenic sources (*6, 7*). Concerning the potential for oxidant formation from 0.1 ppm carbon NMHC, it should be recalled that the federal standard of 0.24 ppm carbon NMHC was established to achieve the oxidant air quality level of 0.08 ppm. Thus, an oxidant concentration of only a few hundredths of a part per million would be expected from an NMHC concentration of the order of 0.1 ppm carbon.

Third, the biomass hydrocarbon–ozone hypothesis does not take into account some important information which describes the spatial variation in ozone concentration as a function of photochemistry and the transport process (*8*). For example, at a suburban location such as Livermore, it is generally believed that higher oxidant concentrations are attributable to a delay in oxidant formation over urban areas because of higher NO concentrations; this can also explain the data of Coffey and Stasiuk cited by Sandberg *et al.* At locations in the downwind trajectory higher oxidant concentrations are to a significant extent due to reactions of NO_2 (formed by the quenching of ozone by NO emitted in the central areas) with anthropogenic hydrocarbons—not to addition of natural hydrocarbons. Because oxidant formation can be highly sensitive to hydrocarbon/NO_x ratios (*9, 10*), a hypothesis based only on total hydrocarbons (including methane) is too simplistic to be plausible, given our current knowledge of transport and transformations in photochemical air pollution.

In future examinations of the possible effects of biomass hydrocarbons on the photochemical synthesis of ozone, a critical assessment of meteorological factors is essential. Sandberg *et al.*'s suggestion that the nocturnal drainage from vegetated slopes concentrates biomass hydrocarbons in adjacent air basins implies the need for relatively stable nighttime conditions that are likely to be coupled with a low inversion and high temperature the following day. Indeed, our experience in the San Bernardino Mountains of southern California shows a clear relationship between ozone concentrations and mesoscale meteorological patterns at monitoring stations in the conifer forest zone. Thus, meteorological patterns typical of the summer season lead to the high ozone concentrations observed in the forest (*11*). We feel that even though the siting of our monitoring stations allows for the hypothetical participation of biomass hydrocarbons, there is no evidence that they could possibly be as important as the transport processes associated with the characteristic summer meteorological patterns.

Other factors to consider are that terpenes may act as ozone consumers as well as ozone producers in the troposphere (*12*) and that vegetation canopies also act as a sink for ozone (*13*). These suggestions further illustrate the complex nature of this problem.

In conclusion, we do not feel that Sandberg *et al.* have made a case for their hypothesis that annual changes of ozone concentrations in the San Francisco Bay Area air basin are strongly dependent on biomass hydrocarbon emissions. Rather, current accepted mechanisms for formation of photochemical air pollution (*14, 15*) provide an integrated view in which summer season meteorology, associated transport processes, photochemical transformations involving anthropogenic hydrocarbons, and the influence of hydrocarbon/NO_x ratios are important variables that determine the spatial and temporal trends in ozone concentrations in such an urban and suburban airshed.

PAUL R. MILLER
USDA, Forest Service
Pacific Southwest Forest and Range Experiment Station, Statewide Air Pollution Research Center, University of California, Riverside 92521
JAMES N. PITTS, JR.
ARTHUR M. WINER
Statewide Air Pollution Research Center and *Department of Chemistry, University of California, Riverside*

References and Notes

1. J. S. Sandberg, M. J. Basso, B. A. Okin, *Science* **200**, 1051 (1978).
2. Air Resources Board, State of California, *Air Pollution in California: Annual Report 1974* (Sacramento, 1975), p. 46.
3. R. A. Rasmussen, *J. Air Pollut. Control Assoc.* **22**, 537 (1972).
4. H. Westberg *et al., Environ. Prot. Agency (U.S.) Publ. 600/3-78-007* (1978).
5. R. A. Rasmussen, R. B. Chatfield, M. W. Holdren, E. Robinson, draft technical report to the Coordinating Research Council, Inc. (1976).
6. Research Triangle Institute, *Environ. Prot. Agency (U.S.) Publ. 450/3-75-036* (1975).
7. W. A. Lonneman, *Environ. Prot. Agency (U.S.) Publ. 600/3-77-001* (1977).
8. M. Corn, R. W. Dunlap, L. A. Goldmuntz, L. H. Rogers, *J. Air Pollut. Control Assoc.* **25**, 16 (1975).
9. E. L. Martinez, N. C. Possiel, E. L. Meyer, Jr., L. G. Wayne, K. W. Wilson, C. L. Boyd, *Environ. Prot. Agency (U.S.) Publ. 600/3-77-001b* (1977).
10. J. A. Eldon, J. C. Trijonis, K. Yuan, final report to California Air Resources Board, contract A5-020-87 (1978).
11. P. R. Miller *et al.*, *Environ. Prot. Agency (U.S.) Publ. 600/3-77-104* (1977).
12. L. A. Ripperton, O. White, H. E. Jeffries, *Proc. 147th Natl. Meet. Am. Chem. Soc.* (1967), pp. 54-57.
13. A. M. Townsend, *J. Am. Soc. Hortic. Sci.* **99**, 206 (1974).
14. K. L. Demerjian, J. A. Kerr, J. G. Calvert, *Adv. Environ. Sci. Technol.* **4**, 1 (1974).
15. B. J. Finlayson and J. N. Pitts, Jr., *Science* **192**, 111 (1976).

23 June 1978; revised 28 September 1978

We first wish to point out the verification of our prediction. Despite the overall 5 percent per year downtrend in the past decade of ozone data, a large increase was observed, as forecast, in 1978 although the magnitude was underestimated. In 1977 there were 40 days on which ozone levels exceeded the 80-ppb federal standard for 1 hour; 72 days were forecast (in March) for 1978 and 93 days were observed (as of 1 November 1978). The largest winter precipitation increase in 16 years of data was followed by the largest annual increase in ozone excesses, both in percentage and in number. Moreover, an increase in mean ozone values on meteorologically comparable days limits a purely summer-season meteorological explanation.

Bufalini's comments concerning tree rings were indirectly applicable. Miller and Cooper's results (*1*) relating tree-ring width to temperature and spring rains in northern Scotland may offer a good predictor of ozone in Aberdeen and a promising methodology for a more comparable climate, such as that in New England. However, we followed Fritts (*2*) in limiting our derived relationship to the precipitation-stressed Southwest states. We are aware of the geographic complexities in dendrochronology and find indications that fine-tuning of the relevant biomass indices would strengthen our basic correlation.

Bufalini discovered an inadvertent data-base shift in our simple and multiple correlations for San Jose. For the full 13 years of hydrocarbon data the comparable correlation coefficients (r) are: 2-year winter rain to summer quarter maximum-hour hydrocarbons, .69; 2-year winter rain to summer quarter maximum-hour CO, .36; summer quarter maximum-hour hydrocarbon to CO, .77. The resulting r^2 value for hydrocarbons

with CO implies a vehicular factor of nearly 60 percent in the variance, and that for hydrocarbons with rain implies a natural factor of more than 40 percent.

Published ambient hydrocarbon measurements are admittedly the strongest argument against the biogenic hypothesis. The data on a pine forest in North Carolina from Arnts *et al.* (*3*) cited by Bufalini are for measured fluxes above the forest canopy. They show the expected temperature inversion from canopy top to forest floor, and thus one might anticipate higher concentrations below the canopy. Because most of the California forested areas are in rugged terrain, a significant portion of the biogenic hydrocarbons emitted during the day would remain trapped below the canopy inversion and flow katabatically down the normal drainage channels, collecting finally in the valleys. Neither the flux measurements above the canopy nor the extended line-source model would be applicable to this flow. Direct measurements in wooded California terrain are needed, as we recommended in our report.

With regard to modeling, De Mandel *et al.* (*4*) concluded that the Environmental Protection Agency's standard EKMA diagram is inappropriate for urban centers in the San Francisco air basin, where measured hydrocarbon/NO_x ratios are very low. Such diagrams, however, do indicate that for these low ratios a hydrocarbon increment of 60 ppb would produce an ozone increment of about 30 ppb. Because mean summer ozone maxima at our usual receptor stations are near the 80-ppb federal standard, an increase of 30 ppb can result in an increase of more than 100 percent in days over standard.

Miller *et al.* first criticize our data-analysis rationale and question (i) our elimination of early data years, (ii) our neglect of annual averages, and (iii) our incorporation of ozone and total oxidant data. These are reasonable questions to those unfamiliar with our data base.

Our ozone-oxidant monitoring network grew from six stations in 1962 to 25 stations in 1977. Not until 1967 did we establish our first exurban downwind monitoring station (Livermore), where quenching by nitric oxide in an urban center was not an important factor. Thus the first 5 years (1962 to 1966) were excluded on the basis of comparability. An additional 15 stations were added in the following decade, but those established after 1970 made relatively minor percentage contributions to total excesses in the basin. Moreover, the increasingly stringent controls on anthropogenic emissions have increased the relative importance of natural emissions, particularly since 1970.

We have found annual averages for ozone-oxidant data to be of limited or negative value in northern California. Elevated afternoon ozone levels are measured at our major receptor stations on only 30 to 50 days per year compared to 150 to 200 days in the Los Angeles basin; thus our annual averages reflect the much more frequent days with background levels of 30 to 40 ppb. Moreover, a negative correlation between winter rain and winter ozone (reflecting zero ozone values on most rainy days) would counterbalance or outweigh the winter rain–summer ozone relation in annual means.

With respect to the comparability of our ozone and total oxidant data, we conducted parallel sampling for 2 years, at 11 long-term stations. We found the ozone slightly higher at two stations with some SO_2 interference and slightly lower at one station (San Jose) with the greatest vehicular influence, but the impact on overall basin data was less than 2 percent.

The second category of the Miller *et al.* critique, concerning hydrocarbon measurements, has been covered in large part in our reply to Bufalini. However, we emphasize that we did not simply assume that annual variations in total hydrocarbon concentrations were a function of biomass. We examined all the hydrocarbon data for our basin and found strong correlations that signaled such a relationship and called for further measurements. The existing measurements cited by Miller *et al.* appeared to have been taken at times and places that were not necessarily relevant.

We agree in general with the third category of their critique concerning the importance of transport and transformation processes and of hydrocarbon/NO_x ratios. We do not suggest that the urban ozone problem does not primarily result from anthropogenic sources or that long-range transport is not a very important consideration. We do suggest that the biogenic factor may also need to be included. For example, consider the data for the Los Angeles basin. The winter rain factor appeared to have no skill at the 80-ppb or even the 200-ppb ozone levels for the Los Angeles basin, but was strongly correlated at the 350-ppb level. Recent data showing an increase in the number of 350-ppb days from 7 in 1976 to 22 in 1978, in phase with heavy winter rains on the southern coast, appear to strengthen this relationship. It would be imprudent to overlook a factor that becomes more important on the days of greatest concern. On the other hand, the Los Angeles air basin data indicate an overwhelming anthropogenic base that would make a biogenic factor more difficult to detect.

Our own mobile monitoring data show that vegetation canopies as well as heavy traffic arteries are sinks for ozone. The reasons for the two kinds of sinks are, of course, different, but both may involve transport and incompletely understood transformations.

In conclusion, we concur that an integrated overview of the ozone problem is needed, incorporating summer-season meteorology, associated transport processes, photochemical transformations, and hydrocarbon/NO_x ratios. Pitts' work has demonstrated the importance of these ratios; we ask that the numerator as well as the denominator be more adequately determined.

J. S. SANDBERG
M. J. BASSO
B. A. OKIN

Bay Area Air Quality Management District, San Francisco, California 94109

References and Notes

1. H. C. Miller and J. M. Cooper, *Nature (London)* **260**, 697 (1976).
2. H. C. Fritts, *Tree-Rings and Climate* (Academic Press, New York, 1976).
3. R. R. Arnts, R. L. Seila, R. L. Juntz, F. L. Mowry, K. R. Knoerr, A. C. Dudgeon, "Measurement of fluxes from a loblolly pine," in *Proceedings of the 4th Joint Conference on Sensing of Environmental Pollutants* (New Orleans, La., 1977), pp. 829–833.
4. R. E. De Mandel, L. R. Robinson, J. S. Fong, R. Y. Wada, paper presented at the 71st Annual Meeting of the Air Pollution Control Association, Houston, June 1978.

13 November 1978