(37) Muller, D.; Jaenicke, L. *FEBS Lett.* **1973**, *30*, 137–9.
(38) Cook, A.; Elvidge, J.; Bentley, R. *Proc. R. Soc. London, Ser. B* **1951**, *138*, 97–114.
(39) Whittle, K. J.; Blumer, M. In "Organic Matter in Natural Waters"; Hood, D. W., Ed.; University of Alaska: College, AK, 1970; pp 495–508.
(40) Mitchell, J.; Fogel, S.; Chet, I. *Water Res.* **1972**, *6*, 1137–40.
(41) Young, L.; Mitchell, R. *Appl. Microbiol.* **1973**, *25*, 972–5.
(42) Muller, D. In "Marine Natural Products Chemistry"; Faulkner, D., Fenical, W., Eds.; Plenum Press: New York, 1977; pp 351–60.
(43) Ahern, D. G.; Meyers, S. P. "The Microbial Degradation of Oil Pollutants"; Center for Wetland Resources, Louisiana State University: Baton Rouge, LA, 1973; Publication No. LSU-56-73-01.
(44) Walker, J. D.; Cooney, J. J. *J. Bacteriol.* **1973**, *115*, 635–9.
(45) Kikuchi, T.; Mimura, T.; Moriwaki, Y.; Ando, M.; Negoro, K.-I. *Chem. Pharm. Bull.* **1974**, *22*, 945–9.
(46) Collins, R.; Kalnins, K. *Int. J. Air Water Pollut.* **1965**, *9*, 501–4.
(47) Schauenstein, E.; Esterbauer, H.; Zollner, H. "Aldehydes in Biological Systems. The Natural Occurrence and Biological Activities"; Pion: London, 1977; p 192.
(48) Ackman, R.; Tocher, C.; McLachlan, J. *J. Fish. Res. Board Can.* **1968**, *25*, 1603–20.
(49) Chuecas, L.; Riley, J. *J. Mar. Biol. Assoc. U.K.* **1969**, *49*, 97–116.
(50) Fisher, N.; Schwarzenbach, R. *J. Phycol.* **1978**, *14*, 143–50.
(51) Rasmussen, R. *Tellus* **1974**, *26*, 254–60.
(52) Banwart, W.; Bremner, J. *Soil Biol. Biochem.* **1974**, *6*, 113–5.

(53) Jenkins, D.; Medsker, L.; Thomas, J. *Environ. Sci. Technol.* **1967**, *1*, 731–5.
(54) Reid, E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Co.; New York, 1958; pp 118–26.
(55) Challenger, F. "Aspects of the Organic Chemistry of Sulphur"; Academic Press: New York, 1959; pp 5–6.
(56) Kadota, H.; Ishida, Y. *Annu. Rev. Microbiol.* **1972**, *26*, 127–38.
(57) McMillan, F.; King, J. *J. Am. Chem. Soc.* **1948**, *70*, 4143.
(58) Vineyard, B. *J. Org. Chem.* **1966**, *31*, 601–2.
(59) Wratten, S.; Faulkner, D. *J. Org. Chem.* **1976**, *41*, 2465–7.
(60) Moore, R. *J. Chem. Soc., Chem. Commun.* **1971**, 1168–9.
(61) Roller, P.; Au, K.; Moore, R. *J. Chem. Soc., Chem. Commun.* **1971**, 503–4.
(62) Moore, R.; Mistysyn, J.; Pettus, J., Jr. *J. Chem. Soc., Chem. Commun.* **1972**, 326–7.
(63) Maroulis, P.; Bandy, A. *Science* **1977**, *196*, 647–8.
(64) Friend, J. In "Chemistry of the Lower Atmosphere"; Rasool, S. I., Ed.; Plenum Press: New York, 1973; Chapter 4.
(65) Murray, A.; Riley, J. *Nature (London)* **1973**, *242*, 37–8.
(66) Burreson, B.; Moore, R.; Roller, P. *Tetrahedron Lett.* **1975**, *7*, 473–6.
(67) Helz, G.; Hsu, R. *Limnol. Oceanogr.* **1978**, *23*, 858–69.
(68) MacKinnon, M. *Mar. Chem.* **1979**, *8*, 143–62.

Volatile Organic Compounds at a Coastal Site. 2. Short-Term Variations[#]

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■ Virtually all volatile organic compounds (VOCs), monitored at a coastal northeastern U.S.A. site, showed similar levels of variability (relative standard deviation ~80%), chiefly attributable to short-term (i.e., daily to weekly) fluctuations. Two related examples are a "summer weekend effect" and a "winter week effect" in alkylbenzene levels, explained by invoking a step-function change in the (anthropogenic) source. The reaction of the shallow coastal seawater is controlled by the rapid air–sea exchange process. If air–sea exchange dominates all other sinks for many VOCs, concentration measurements and air–sea exchange data would permit estimation of in situ source functions. Multivariate statistical techniques, applied to the more extensive winter survey, revealed over 50 significant positive correlations and showed 4 significant subgroupings (10 alkylbenzenes and total VOCs, 4 saturated hydrocarbons, 3 aldehydes, and 2 alkanes with 1 aldehyde). The significance of these groupings and their interpretation is discussed.

Introduction

It has been shown by Gschwend et al. (1) that major year-round changes in the concentrations of individual volatile organic compounds (VOCs) of a dynamic coastal site may be accounted for by major seasonal changes in the sources, the sinks, and the processes affecting these compounds. However, it is clear both from the dynamics of gas exchange in shallow coastal waters and also from the "day of the week" correlation found previously (1) that there is underlying short-term (i.e., day-to-week time scale) variability of VOC concentrations which needs to be better understood. In this paper, we examine the results of more intensive surveys of VOCs designed to determine the extent and possible causes of their short-term variability. Additionally, we have sought to improve our utilization of the large and diverse data set (a kind presently becoming very common with the use of powerful analytical tools such as glass capillary gas chromatography) by using a range of powerful multivariate statistical techniques to examine VOC interrelations, expecting these to be indicative of the processes controlling their cycling.

Methods

Several surveys of VOCs were carried out at Chemotaxis Dock (CD), in Vineyard Sound, MA. These included (a) a series of short-duration studies of the weekend variations of alkylbenzenes during the summer of 1978 and (b) a longer-term investigation into the variability of most VOCs identified previously (1). This latter survey consisted of a time series based on a 3–4-day sampling frequency carried out over a 12-week period (December 19, 1978 to March 19, 1979). Extraction and analysis of VOCs in the seawater samples was carried out immediately after sampling. For logistical reasons, it was possible to analyze only a fraction of these samples for the suite of environmental variables. For a discussion of the analytical procedures used in the determination of the volatile organic com-

pounds and associated environmental variables, the reader is referred to Schwarzenbach et al. (2) and Gschwend et al. (1). For the purpose of this paper, we reemphasize that the overall reproducibility of the combined operations of sampling, stripping, elution, and gas-chromatographic analysis of the VOCs between three independent workers and between replicate samples was 14% and 9% (relative standard deviation), respectively, at the 5 ng/kg level.

In addition to the normal qualitative interpretations of the data, a variety of statistical analyses was also performed on the winter data set. This data set constituted a matrix of 28 observations on 34 VOCs. This matrix had few missing data values (distributed throughout the matrix). The second matrix is a less regularly sampled set of 15 associated environmental variables (time of sampling, salinity, temperature, precipitation, chlorophyll a, phaeopigments, NO_3^-, NO_2^-, Si, PO_4^{3-}, total phytoplankton cell counts, and cell counts of the four major phytoplankton species). This second set averaged only 14 observations per variable. For this reason, estimation of correlations within this set and between it and the VOC variables is substantially less accurate than correlations estimated within the VOC data set; therefore, this paper focuses on the latter relationships.

The Pearson product moment correlation coefficient (r) was calculated for all 1176 pairs of variables, including the subset of 561 pairs of organic compounds. It is important to note that individual correlations cannot formally be tested for "significant" departure from zero by using standard statistical tables, since the latter are based on the assumption that a *single* test is being performed, whereas 561 (nonindependent) tests are being carried out simultaneously. The extent to which it is possible to generate large spurious correlations, simply by calculating enough coefficients, seems to be poorly understood in the literature. The problem is particularly acute when the number of observations is small in relation to the number of variables being measured, as is often the case in high-resolution molecular organic chemistry of natural waters. Thus, if a standard multivariate normal model were fitted to the VOC matrix, a total of 629 parameters would need to be estimated from our approximately 950 data. This relative scarcity of data rules out classical procedures such as factor analysis and multivariate time series analysis.

The statistical approach adopted in this paper is to obtain an overall picture of the relationships between individual organic compounds using the nonparametric techniques of clustering (3) and multidimensional scaling (4). These are evaluated by using correlation profile analysis (5) which allows a simple graphical comparison of the ordered correlation coefficients obtained for all pairs of measured variables with a similar set of coefficients from simulated random matrices of sizes identical with that of the original data matrix. In effect, this technique is a global test of whether there are any significantly nonzero correlations in the data and, if so, roughly how many.

"Weighted average link" hierarchial cluster analysis (5) was performed on the VOC data, by first constructing a "dissimilarity" matrix with the (i,j)th element, δ_{ij}, equal to $(1 - |r_{ij}|) \times 100\%$, where r_{ij} is the observed correlation of the ith and jth variables. The results of cluster analysis of VOCs are graphically summarized in similarity dendrograms.

The dissimilarity matrix was also used to construct a multidimensional scaling (MDS) plot performed by the nonparametric procedure described by Kruskal (4). This is a more flexible form of principle coordinate analysis in which the chemicals are viewed as points in two (or higher)
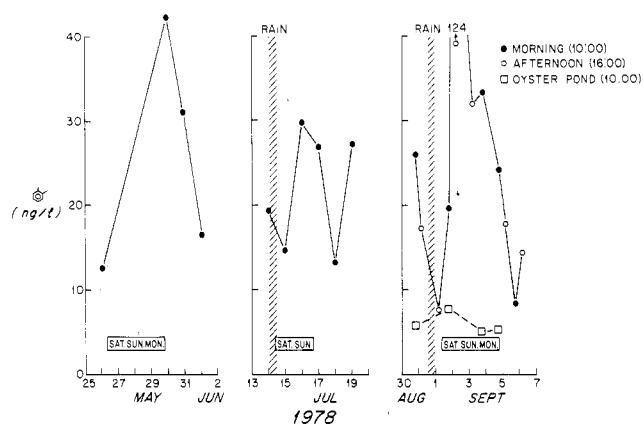

Figure 1. The "summer weekend effect" at Chemotaxis Dock and Oyster Pond, illustrated for 1,2-dimethylbenzene.

dimensional space, whose proximity reflects the interrelationship between chemicals. The procedure requires complex iterative computation, but the essentials are as follows: (a) An initial configuration of chemicals in the MDS space is needed. We have random starting positions and repeated the iterations several times with different starts to assess the stability of the solution. (b) The set of distances (d_{ij}) between points, i and j, in the current MDS space is related to the corresponding set of dissimilarities (δ_{ij}) by a general nonparametric regression approach, allowing the distance–dissimilarity relationship to be an arbitrary monotonic increasing function. (This flexibility is one of the key advantages of MDS over other methods.) (c) The adequacy of this regression—and thus the "goodness of fit" of the current MDS configuration to the dissimilarities—is assessed by a normalized residual sum of squares, "the stress factor", S,

$$S = [\sum_{ij}(d_{ij} - \hat{d}_{ij})^2/\sum_{ij}d_{ij}^2]^{1/2}$$

where $\hat{d}_{ij}$ is the fitted distance from the regression corresponding to the dissimilarity, δ_{ij}. (d) S is iteratively minimized by using the method of steepest descent to obtain successively improved configurations in the MDS space.

In short, MDS summarizes the correlations in the data by representing chemicals as points in the two-dimensional MDS space; the closer the two chemicals are, the stronger the correlation between them. Note that the procedure is a function only of the rank orders of the dissimilarities; thus, the origin, the orientation, and the scale of the MDS plot are arbitrary.

Results and Discussion

Since our seasonal data suggested that alkylbenzene concentration variations occurred on a time scale of less than 1 week and that these variations were particularly prominent immediately after summer weekends, we investigated these aromatic hydrocarbons in CD seawater samples collected approximately daily during three 1978 summer weekends. The alkylbenzene concentrations rose sharply during each of these periods (as shown for 1,2-dimethylbenzene in Figure 1), thus supporting our interpretation of the seasonal data. That is, dramatically intensified activities associated with tourism on summer weekends on Cape Cod probably supplied large quantities of alkylbenzenes to coastal seawater. Additionally, the three 1978 weekends revealed the time scale needed to deplete the alkylbenzenes to preweekend levels: approximately 2–3 days. These data thus also corroborate our estimate based on the year-round data. As discussed in
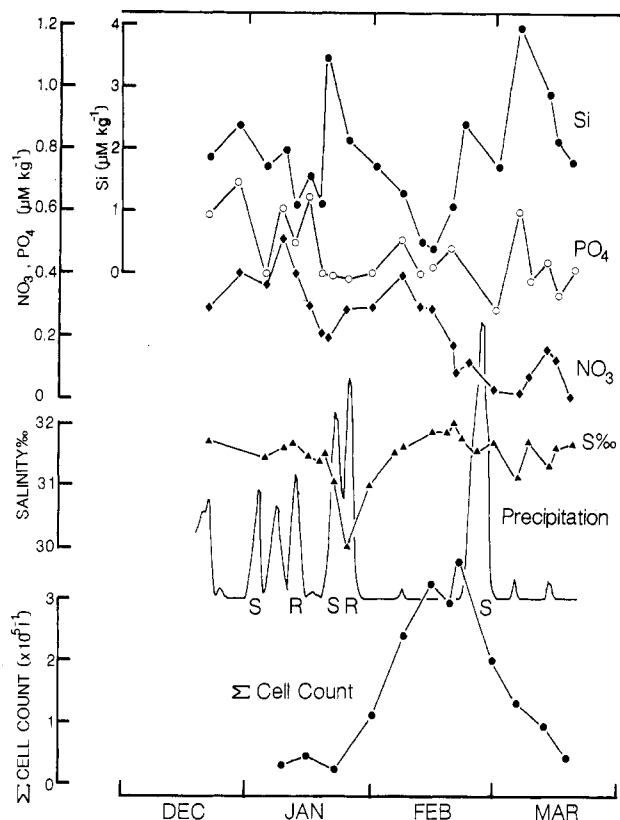
Figure 2. Time series data of selected environmental variables at Chemotaxis Dock, December 1978–March 1979. Snow and rain showers are indicated by S and R, respectively.

Gschwend et al. (1), air–sea exchange almost certainly suffices to account for the rapid decline in alkylbenzene concentrations.

In conjunction with the third summer weekend sample series, samples were collected from Oyster Pond, a shallow, brackish water pond separated from Vineyard Sound by a narrow strip of land. Oyster Pond is free of motorboat traffic but serves as a conduit for runoff flow into the coastal seawater (6). Water samples collected from the pond before, during, and after the weekend always contained much less of the alkylbenzenes than the seawater samples collected concurrently (Figure 1). Consequently, we conclude that the large summertime alkylbenzene deliveries to the coastal seawater were primarily from boats, and not from cars via the atmosphere or runoff. These data support the contention of Clark et al. (7) that motorboats are an important source of petroleum pollution to the coastal marine environment.

These data provide the first direct evidence of very short-term fluctuations of alkylated benzene levels. Based on these observations, a winter study period was selected in order to minimize the effects of strong local sources on the basic factors that control the short-term variability of all of the VOCs. The results of the time series survey of a representative selection of VOCs and environmental variables are shown in Figures 2–6. The mean concentrations and standard deviations were remarkably similar to those observed in the seasonal study (Table I of ref 1).

Environmental Variables. The concentrations of nitrate, phosphate, and silicate together with salinity, atmospheric precipitation, and total phytoplankton cell counts recorded throughout the survey at CD are shown in Figure 2. An average salinity of 31.65 ± 0.41‰ was maintained throughout the 3-month survey except in late January, when the salinity dropped to 30.04‰ following a rapid thaw of accumulated snowfall on Cape Cod. This
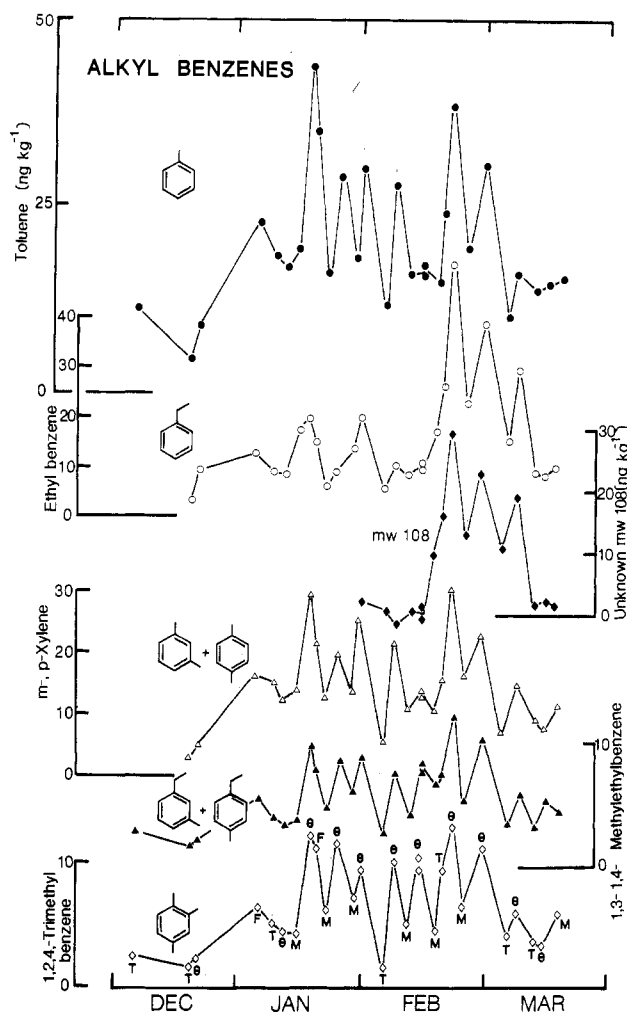
Figure 3. Temporal variation of selected C_1–C_3-alkylbenzenes and the unknown compound (mol wt 108) at Chemotaxis Dock, December 1978–March 1979. The day of the week on which samples were taken is indicated as follows: Monday (M), Tuesday (T), Thursday (Θ), and Friday (F).

thaw preceded an unusually dry and sunny February when the wind averaged 15 mph and blew consistently offshore (WNW at Boston's Logan Airport (8)). These conditions apparently stimulated a small bloom of diatoms at CD and a concomitant decrease in the nutrient concentrations. However, this bloom, composed of *Asterionella glacialis* (formerly *japonica*) (38%), *Thallasiosira nordenskioeldii* (32%), *Skeletonema costatum* (25%), *Thallasionema nitzschioides* (3%), and a *Chaetoceros* sp. (2%), was short-lived, reaching a maximum cell count of only 3.4 × 10^5 cells/kg. The subsequent decrease in the diatom population at the end of February coincided with the resumption of heavy snow and rainfall, which decreased the temperature of these shallow waters from 3.0 to −1.6 °C and caused occasional ice slush, but no permanent ice cover. The levels of chlorophyll *a* averaged 5.5 ± 2.1 μg/kg (not shown in Figure 2) but did not correlate with the diatom bloom ($r = 0.31$) or any other variable. The apparent random chlorophyll *a* trend may be influenced not only by diatoms but also by plant debris originating from terrestrial sources or periodic washup of sea grass (*Zostera*) following storm activity. Although there were several correlations within the matrix of environmental variables, these almost always corresponded to a priori interdependent variables, e.g., *T. nordenskioeldii* sp. vs. total phytoplankton cell count, $r = 0.90$; Si vs. total cell count, $r = -0.92$.
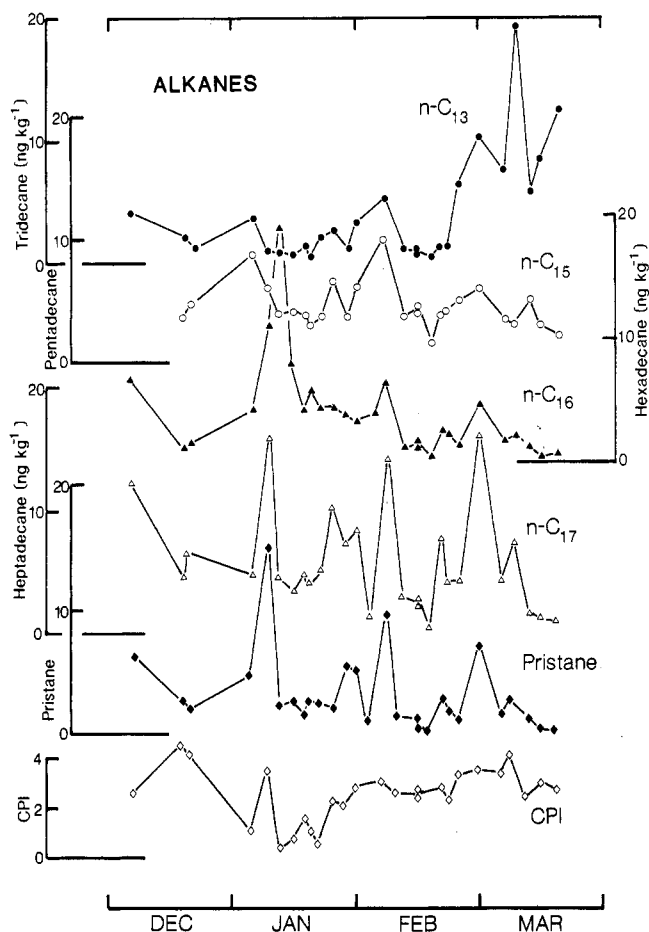
Figure 4. Temporal variation of selected *n*-alkanes, pristane, and alkane carbon preference index (CPI = $(n\text{-}C_{15} + n\text{-}C_{17})/(n\text{-}C_{14} + n\text{-}C_{16})$) at Chemotaxis Dock, December 1978–March 1979.

The correlation profile analysis (CPA) plot of the cross correlations between the environmental data set and the VOC data set is shown in Figure 7. The CPA profiles resulting from 50 simulations of random data are also included; these show, for example, that of the 525 possible correlations up to 6 have $[r] > 0.6$ and are spurious; there are none for $[r] > 0.7$. When this criterion is used, it is clear from Figure 7 that the eight or nine environmental VOC correlations with $[r] > 0.7$ are not spurious. Most prominent is *Asterionella* sp. vs. the unknown of molecular weight 108 (see Gschwend et al. (*1*)) $r = 0.93$, which lends further support to the hypotheses in the preceding paper on the source and role of this fascinating compound. However, other correlations were curious and not immediately explicable, e.g., octanol vs. precipitation, $r = 0.70$; NO_3^- vs. pristane, $r = 0.71$. The general absence of correlations between the environmental variables and the VOCs points to the complexity of the system under investigation and/or to the low specificity of our selected environmental variables.

VOC Covariability. The average concentration and the relative standard deviation (RSD) of individual VOCs were remarkably similar to the values reported for the seasonal survey (*1*) and therefore will not be discussed here. The exceptions were dimethyl disulfide and octanal, which averaged 463 ± 312 and 43.9 ± 29.0 ng/kg, respectively. These elevated concentrations may have been caused by increased storm activity and disturbance of shallow sediments rich in these compounds (*1*). The alkylnaphthalenes were generally less than 4 ng/kg (see Figure 6), confirming the absence of oil pollution events during this survey. It is clear from Figures 3–6 that there is
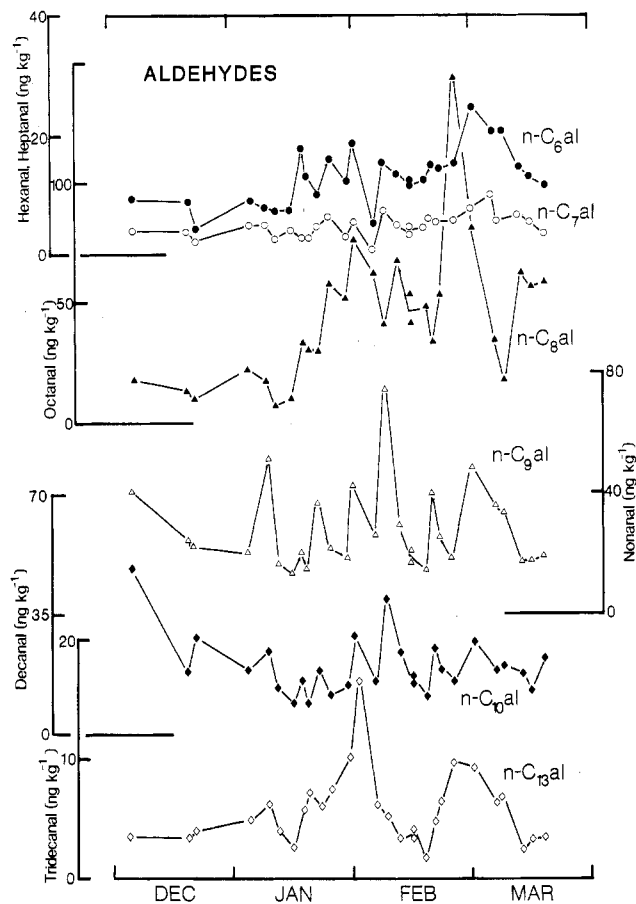

Figure 5. Temporal variation of selected aldehydes at Chemotaxis Dock, December 1978–March 1979.
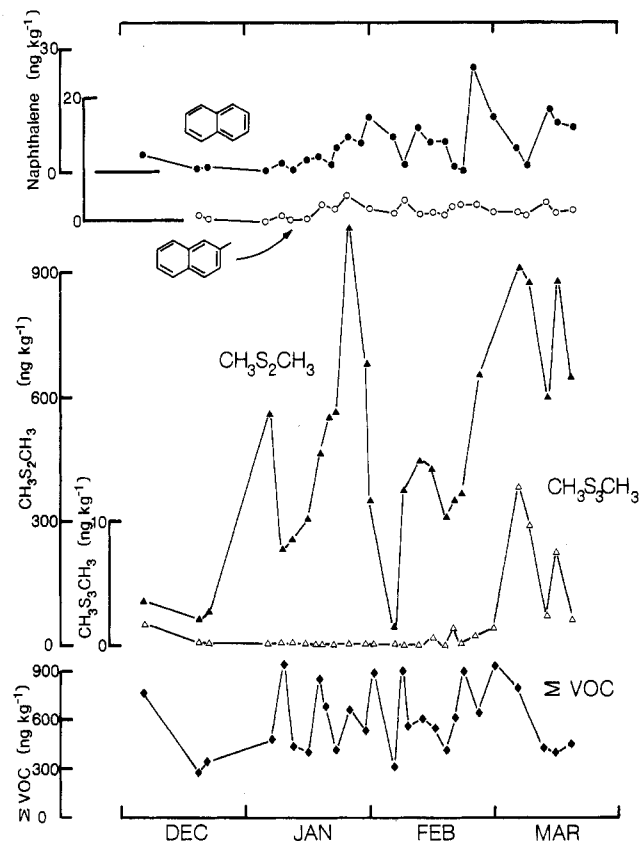

Figure 6. Temporal variation of naphthalene, 2-methylnaphthalene, dimethyl disulfide (strip + restrip), dimethyl trisulfide, and total volatile organic compounds at Chemotaxis Dock, December 1978–March 1979. Note different concentration scales.
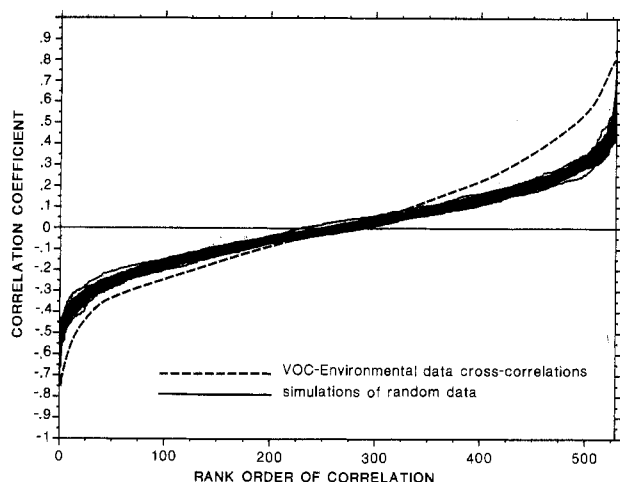
Figure 7. Correlation profile analysis of the cross correlations between environmental data and VOC (– – –) as well as the results of 50 simulations of random data sets.
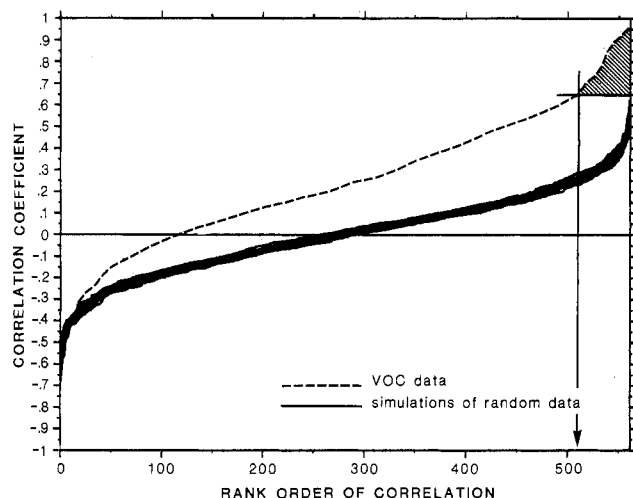

Figure 8. Correlation profile analysis of the VOC data set (– – –) and 50 simulations of random data sets (superimposed curves). VOC correlations with $r > 0.65$ are indicated by the hatched region located above $r = 0.65$.

considerable temporal variability in VOCs (RSD range, 40–204%; mean = 80%), and, since no more than 14% can be attributed to analytical imprecision, most of this variability must be environmental.

The extent to which individual compounds covaried can be estimated from their CPA plot in Figure 8. Because of very low concentrations (<1 ng/kg) or incomplete records, the variability of tetrachloroethylene, the unknown of molecular weight 108 (see ref 1), propylbenzene, and alkylnaphthalenes were excluded from the statistical analyses. A total of 50 random data matrices were simulated, each having 28 rows (observations) and 34 columns (VOC variables) with missing data exactly as for the original VOC data matrix. By definition, all calculated correlation coefficients from this matrix are spurious; the largest of these was approximately 0.65. It is therefore apparent from Figure 8 that the positive correlations in the VOC data are radically different from any generated by chance. In fact, a formal Monte Carlo test would clearly show that the hypothesis of total absence of correlations in the VOC data can be rejected at the 2% significance level. A conservative estimate of the number of nonspurious correlations is approximately 50. In addition, Figure 8 demonstrates that the negative correlations observed in the VOC data are probably spurious, since at the negative end of the range the correlation profile for these data

matches that for the random simulations.

The overwhelming presence of positive correlations in the VOC data is interesting, in that, quite independent of any chemical knowledge, the statistical analysis suggests the presence of a process(es) or property(ies) common to many compounds—possibly gas exchange and volatility. Figure 9 presents the dendrogram of the cluster analysis of the 34 organic compounds (see Methods). The 50 or so nonspurious correlations in Figure 8 can be identified with the major clusters occurring at similarities > 0.65. Figure 10 presents the corresponding multidimensional scaling (MDS) plot for the VOC data. The stress factor of 0.24 (4) is not particularly low, indicating that a two-dimensional representation of the similarities between the organic compounds is a little oversimplified. Nevertheless, the groups of compounds delineated by the cluster analysis show up well on this plot, as can be seen by the circumscription of the major clusters formed at similarity level > 0.65. It is immediately evident that the significant clusters are *chemical* groupings of isomers or homologues (with the single exception of decanal grouping with tetradecane and pentadecane), indicating that the factors that force variability at CD operate through physicochemical, chemical, or common-source mechanisms and not, for example, by dominant coproduction or consumption of chemically diverse assemblages, e.g., by biological activities. It is therefore appropriate to consider the major clusters in terms of their molecular structures.

Aromatic Hydrocarbons. The concentrations of toluene, ethylbenzene, 1,3- and 1,4-dimethylbenzene, 1,3- and 1,4-methylethylbenzene, and 1,2,4-trimethylbenzene (Figure 3) illustrate the variability typical of alkylbenzenes. The alkylated C_1–C_4 benzenes dominated the spectrum of volatile compounds observed in this study and accounted for 90% of all hydrocarbons with toluene being apparently the most abundant aromatic compound (20 ± 9.2 ng/kg). Similar observations were made by Sauer et al. (9, 10) in the Caribbean Sea and the Gulf of Mexico. However, in the latter part of this survey, when GC separations were also carried out on a Pluronics 121 column to resolve benzene from the CH_2Cl_2 solvent front, concentrations of benzene invariably were found to be 20–50% in excess of toluene. With the exception of ethylbenzene, the determination of which was affected by the coelution of the unknown of molecular weight 108 (1), all of the alkylated benzenes cofluctuated ($r = 0.86$–0.96), indicating a compositionally constant source and similar transport process(es) for all alkylated benzenes. This is confirmed by the tight clustering of the alkylated benzenes in the MDS plot of Figure 10. The size of this cluster provides a good relative measure of the behavioral similarity of an extremely similar group of compounds that are known to have relatively low biological reactivity and a diffuse (anthropogenic) source. Petroleum fuel is the most probable source.

There is a remarkable weekly regularity in the fluctuations of alkylbenzene levels during during late January and through February. During this period, low concentrations always coincided with Monday or Tuesday samples and highs with Thursdays or Fridays (see, e.g., 1,2,4-trimethylbenzene in Figure 3). Thus, a weekly varying source function for alkylbenzenes, such as the one observed during the summer weekend survey, is implicated; however, the phase has shifted from weekend highs to lows. It is unlikely that locally polluted waters are responsible for this variation, since the previous study showed that offshore gradients in the concentrations of alkylbenzenes at CD are absent (1). Also, any tidal periodicities transporting waters
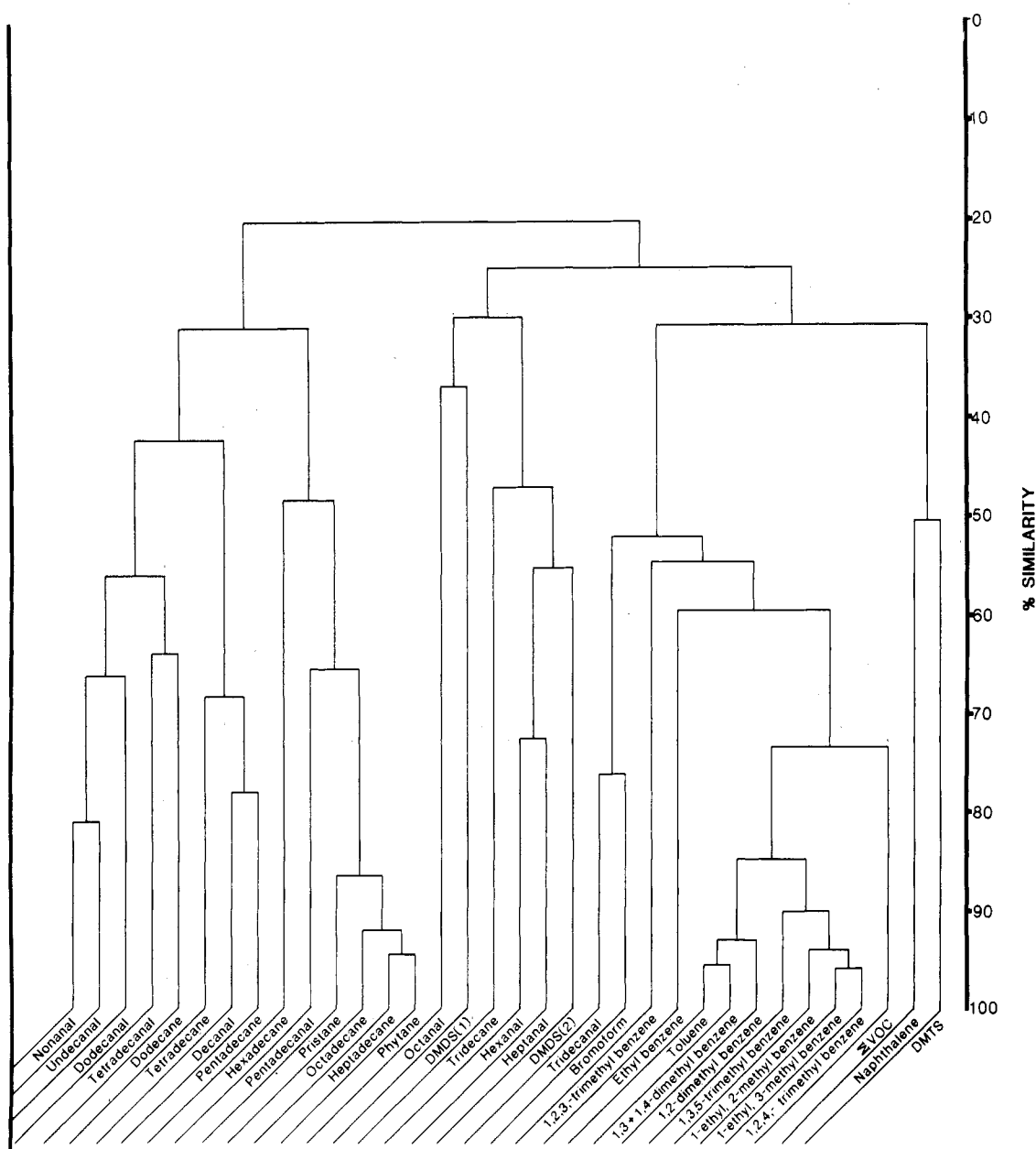
Figure 9. Similarity dendrogram resulting from the cluster analysis of the VOC data.

of fluctuating alkylbenzene content to CD would go out of phase with the observed concentration patterns within this period. An atmospheric source of alkylated benzenes is more likely. The alkylbenzenes are present in the water at levels not far from equilibrium with their *expected* atmospheric concentrations. Throughout this period the weather pattern was unusually stable, characterized by steady winds from the west (15 mph and WNW at Boston's Logan Airport but very likely SW at Woods Hole) that transport suburban/urban air offshore. For example, Cleveland et al. (*11*) have shown that urban air from the highly industrialized metropolitan area of New York travels to New England. Pulses in gasoline emissions from such a NE U.S. regional source would take 0–1 day to reach Cape Cod and approximately another day (*1*) for effective gaseous exchange with the waters at CD. Since traffic emissions should decrease on weekends in winter, this 1–2-day lag could give rise to the observed low-level winter fluctuation pattern (Monday/Tuesday < Thursday/Friday) of Figure 3.

Alkanes. The alkane cluster, composed of *n*-heptadecane, *n*-octadecane, pristane (2,6,10,14-tetramethyl-

pentadecane), and phytane (2,6,10,14-tetramethylhexadecane), identified in the MDS plot (Figure 10) corresponds to a group of petrogenic alkanes as indicated by their pristane/phytane and n-C_{17}/pristane ratios of 0.9 and 1.8 (*12*). The source may be chronic input of trace concentrations of these alkanes into the waters, rather than any oil pollution event. However, there may also be a biogenic contribution to the alkanes since there was a marginal predominance of odd- to even-numbered carbon chains ((n-C_{15} + n-C_{17})/(n-C_{14} + n-C_{16}) = 2.6 ± 1.6, Figure 4) (*13, 14*).

There is a general increase in the concentration of alkanes with increasing molecular weight (molar volume) which is opposite to the trend of their solubility behavior as *extrapolated* from data on lower molecular weight members (*15–17*) using molar volume–solubility relationships (*18, 19*). The estimated degree of saturation increases from ~0.1% for dodecanes up to ~180% for *n*-octadecane. Thus, the undersaturated alkanes could possibly be truly dissolved, whereas those above saturation must be at least partially in micellar or adsorbed forms. Supersaturated concentrations of hydrocarbons can be accom-
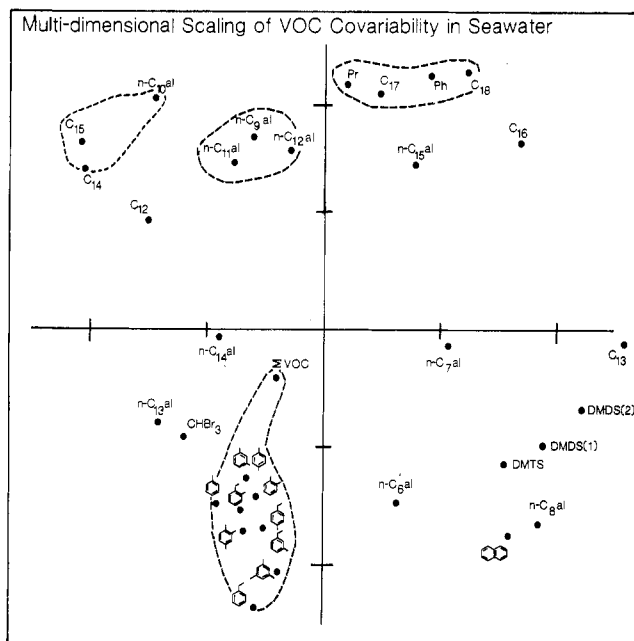
Figure 10. Multidimensional scaling of the volatile organic compounds plotted in two-dimensional configuration with reference to rotationally arbitrary axes (22 iterations, stress = 0.238 (5)). Proximity of compounds is a measure of similarity in environmental behavior. The four groups of compounds circumscribed in the MDS plot correspond to the major clusters in Figure 9 and possess similarities (correlation coefficients) of >0.65.

modated in seawater in various forms, including micellar aggregates, hydrophobic complexes with dissolved organic matter, or by adsorption onto particulate matter (20, 21). However, only truly dissolved forms of hydrocarbon exert vapor pressure and are thus available for gaseous exchange. The matter is further complicated by reported solubilities (22) (physical form not specified) which are much higher for high molecular weight compounds than those obtained from the extrapolation used above. Sauer et al. (9, 10), using helium to strip volatile alkanes from seawater, obtained concentrations remarkably similar to our work.

Aldehydes. The statistically derived cluster of nonanal, undecanal, and dodecanal constitutes a group of chemically similar compounds. We note that autooxidation of monounsaturated fatty acids can theoretically give rise to consecutive alkanals (23). The group shown in Figure 10 may arise this way. However, the scattered distribution of other aldehydes in Figure 10 strongly suggests that as a group their sources and sinks are by no means simple. The strong covariance of aldehydes and chlorophyll a observed previously (1) was not seen in this study. This was undoubtedly due to the relative weakness of the February 1979 phytoplankton bloom (20 times lower cell density than 1978) and the insensitivity of chlorophyll a values to this difference (maximum values in 1978 were only twice those in 1979). It is worth adding that aldehydes at CD may also have originated from aldehyde-rich sediments (1), which are invariably disturbed during sporadic storm activity.

Other Compounds. The absence of significant covariability between naphthalene and the alkane and alkylbenzene clusters implies separate sources or different processes. However, the coincidence of the naphthalene and octanal peaks with the heavy snowfall in late February (see Figures 2 and 6) may indicate a runoff or atmospheric inputs. The dimethyl polysulfides show no easily explainable pattern either on the similarity dendrogram or on the MDS plot. Dimethyl disulfide (DMDS) "restrip"

concentrations do not correlate with the concentration in the first strip, indicating that the previously reported (2) capacity for DMDS formation is not consistent in the CD samples.

Conclusions

This and preceding papers (1, 2) report the results of intensive studies of a structurally diverse variety of organic compounds at a coastal site. The study location—chosen primarily for year-round accessibility and for uncontaminated sampling—is clearly an extremely complex one encompassing a multiplicity of sources, sinks, and processes. For example, the 15 classical "environmental" variables monitored proved almost irrelevant in explaining VOC variability (Figure 7). Nevertheless, several points that may be generally valid and that transcend a mere inventory of the VOC structures present have emerged. First, as stressed in the preceding paper, the theoretically expected dominance of air–sea exchange (1, 2, 9, 10) as a sink mechanism (especially in shallow waters without very high organic carbon sediment/particulate levels) is confirmed by the observations. The short-term variability of the alkylbenzenes, a nearly ideal case with a fairly well-known, diffuse source function and a low biochemical and adsorptive reactivity, requires a major atmospheric sink. The conclusion that the air–sea exchange sink dominates can tentatively be extended to most of the other compounds by noting that the relative standard deviations of most compound concentrations (Table I, ref 1) were very similar to those of the alkylbenzenes (Table I, ref 1). If a single sink dominates the variability in the short term of nearly all VOCs, then concentration data combined with the steady-state assumption can yield source strength estimations, a type of information practically unavailable by other approaches.

A second conclusion, revealed with especial clarity by the statistical treatment of this paper, is that the closest interrelations among compound behaviors follow quite strictly classical chemical classifications (i.e., the groups of Figure 10 are isomeric/homologous chemical families). Early expectations that VOC data would tend to reflect ecological units of organization (i.e., algal excretions, benthic products, bioturbational releases) are not supported. Instead, fundamentally *chemical* parameters somehow dominate—whether by physical chemistry (e.g., air–sea exchange), chemistry (e.g., controls on alkane composition of oils), or biochemistry (lipid oxidations to aldehydes).

Future studies of volatiles should therefore focus on these suggested relationships and applications. To realize the full potential of such relationships, it is imperative that hydrodynamically simpler environments be chosen, that a more closely correlated set of environmental variables be measured concurrently, and that atmospheric concentrations of VOCs be monitored concurrently.

Literature Cited

(1) Gschwend, P. M.; Zafiriou, O. C.; Mantoura, R. F. C.; Schwarzenbach, R. P.; Gagosian, R. B. *Environ. Sci. Technol.*, preceding paper in this issue.
(2) Schwarzenbach, R. P.; Bromund, R. H.; Gschwend, P. M.; Zafiriou, O. C. *Org. Geochem.* 1979, *1*, 93–107.

(3) Everitt, B. "Cluster Analysis"; Heinemann: London, 1974.
(4) Kruskal, J. B.; Wish, M. "Multidimensional Scaling"; Sage Publications: Beverly Hills, CA, 1978.
(5) Kruskal, J. B. In "Mathematical Methods for Digital Computers"; Enslein, K.; Ralston, A.; Wilt, H. S., Eds.; Wiley-Interscience: New York, 1977; Vol. 3, pp 296–339.
(6) Emery, K. O. "A Coastal Pond Studied by Oceanographic Methods"; Elsevier: New York, 1972.
(7) Clark, R. C.; Finley, J. S.; Gibson, G. G. *Environ. Sci. Technol.* **1974**, *8*, 1009–14.
(8) NOAA. "Local Climatological Data. Boston, Massachusetts"; Environmental Data and Information Service: Asheville, NC, 1978 and 1979.
(9) Sauer, T. C., Jr.; Sackett, W. M.; Jeffrey, L. M. *Mar. Chem.* **1978**, *7*, 1–16.
(10) Sauer, T. C., Jr. *Limnol. Oceanogr.* **1980**, *25*, 338–51.
(11) Cleveland, W. S.; Kleiner, B.; McRae, J. E.; Warner, J. L. *Science* **1976**, *191*, 179–81.
(12) Erhardt, M.; Blumer, M. *Environ. Pollut.* **1972**, *3*, 179–94.
(13) Bray, F. E.; Evans, F. E. *Geochim. Cosmochim. Acta* **1961**, *22*, 2–15.
(14) Farrington, J. W.; Meyers, P. A. In "Environmental Chemistry"; Eglinton, G. Ed.; Chemical Society: London, 1975; Vol. 1, 109–35.
(15) McAuliffe, C. *J. Phys. Chem.* **1966**, *70*, 1267–75.

(16) McAuliffe, C. *Science* **1969**, *163*, 478–9.
(17) Button, D. *Geochim. Cosmochim. Acta* **1976**, *40*, 435–40.
(18) Hermann, R. B. *J. Phys. Chem.* **1972**, *76*, 2754–9.
(19) Reynolds, J. A.; Gilbert, D. B.; Tamford, C. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 2925–7.
(20) Boehm, P. D.; Quinn, J. G. *Geochim. Cosmochim. Acta* **1973**, *37*, 2459–77.
(21) Shaw, D. G. In "Fate and Effects of Petroleum Hydrocarbons in Marine Organisms and Ecosystems"; Wolfe, D. A., Ed.; Pergamon Press: Elmsford, NY, 1977; pp 8–18.
(22) McAuliffe, C. In "Petroleum in the Marine Environment"; Petrakis, L., Weiss, F. T., Eds.; Advances in Chemistry Series, American Chemical Society: Washington, DC, 1980; p 203.
(23) Schauenstein, E.; Esterbauer, M.; Zollner, H. "Aldehydes in Biological Systems: Their Natural Occurrence and Biological Activity"; Pion: London, 1977; p 192.

Computer Modeling Study of Photochemical Ozone Formation in the Propene–Nitrogen Oxides–Dry Air System. Generalized Maximum Ozone Isopleth

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■ Computer simulation for the propene–nitrogen oxides–dry air system was performed by using a detailed reaction model in order to represent previous experimental results. The proportional relationships between $[O_3]_{max}$ and $[O_3]_{ps}$, $[NO_x]_0^{1/2}$, and $k_1^{1/2}$ were successfully reproduced by the model. Based on the calculated data, the plot of $[O_3]_{max}/[O_3]_{ps}$ vs. $[C_3H_6]_0/[NO_x]_0$ was found to fall on a single common curve, which is called a generalized maximum ozone isopleth. In the falloff region of the above plot, an approximate linear relationship between $[O_3]_{max}/[O_3]_{ps}$ and $([C_3H_6]_0/[NO_x]_0)^{1/2}$ was obtained, implying that $[O_3]_{max}$ is linear with $[C_3H_6]_0^{1/2}$ in the NO_x-excess region.

In order to characterize ozone formation in photochemical air pollution, many attempts (*1-8*) have been made to correlate the maximum ozone concentration attained in smog-chamber experiments with the reaction parameters such as light intensity, initial concentrations of hydrocarbons and nitrogen oxides, temperature, or hydrocarbon reactivity. In our previous papers (*1-3*) on smog-chamber studies of the olefin–nitrogen oxides system, an approximate, proportional relationship

$$[O_3]_{max} \propto [O_3]_{ps} \qquad (I)$$

was proposed to hold in the hydrocarbon-excess region, where $[O_3]_{max}$ is the maximum ozone concentration ultimately reached and $[O_3]_{ps}$ is the photostationary ozone concentration parameter in the absence of hydrocarbon.

The same relationship has also been suggested to hold in the irradiation of sampled ambient air (*4*). On the other hand, in the flow reactor study of the cyclohexene–nitrogen dioxide–air system, Shen et al. (*7*) have proposed that $[O_3]_{max}/(k_1[NO_x]_0/k_2)^{1/2}$ depends only on the ratio of the initial concentrations of the hydrocarbon and the nitrogen oxides and presented normalized maximum ozone concentration curves. Here k_1 and k_2 are the rate constants for the photolysis of NO_2 and the reaction of NO and O_3, respectively.

Since a detailed mechanism for the photooxidation of the propene–NO_x system based on the knowledge of chemical kinetic data has been reported (*9*) recently, it is of great interest to determine whether computer modeling can reproduce the above experimentally obtained relationship. For the purpose of establishing an ozone control strategy based on smog-chamber data with the aid of computer simulation, substantiation of the experimental data by means of the "theoretical" prediction and vice versa should be of key importance.

This study presents the reaction model which can reproduce our previously reported C_3H_6 (3 ppm)–NO_x (1.5 ppm)–dry air runs where reaction products were fully analyzed by a long-path Fourier transform infrared spectrometer (*10*). Lower-concentration runs were then simulated by using the same reaction model to obtain the theoretical relationship between $[O_3]_{max}$ and $[C_3H_6]_0$, $[NO_x]_0$, and the light intensity. The computer modeling was found to predict eq I successfully, and the proposal