Association of Non-Marine Sulfate Aerosol with Sea Breeze Circulation in Tampa Bay

GEORGE S. YOUNG AND JOHN W. WINCHESTER

Florida State University, Tallahassee 32306

(Manuscript received 25 June 1979, in final form 16 December 1979)

ABSTRACT

Peak concentrations of aerosol sulfur in Tampa, Florida may be the result of either regional-scale transformation and transport processes or local-scale transport from nearby air pollution sources. The existence of the latter has been demonstrated in Tampa through correspondence of sulfur with sea breeze circulation patterns and the resulting chloride concentration maxima (which serve as indicators of the marine aerosol), vanadium concentration maxima (which indicate times of high concentrations of certain plume constituents), and the locations of sources favorable for high concentrations of air pollution-derived sulfate during occurrences of the sea breeze. The analysis indicates that locally derived sulfate in the Tampa atmosphere, which may be less abundant than sulfate due to regional-scale processes, can be identified by the use of combined meteorological and chemical tracer interpretation.

1. Introduction

It is important to be able to resolve air pollution sulfate in an urban area into components due to local sources and to the regional-scale sulfate arising from the transformation of sulfur dioxide to sulfate during atmospheric transport on the 100–1000 km distance scale. Commonly used air pollution control strategies direct attention primarily to the emissions within a few kilometers of the receptor site. However, the relative effect on local air quality of longer range transport from sources outside the control area may not be small compared to that of nearby local sources. Therefore, in order to implement air quality control measures, there is a need to evaluate local source contributions to air quality in the presence of regional or larger scale air pollution effects. Inasmuch as Florida lies at the edge of a large eastern U.S. source region for air masses generally contaminated by sulfur oxides from fossil fuel combustion, Florida's air quality is determined by a combination of this regional air pollution transport and additions from local sources (Ahlberg *et al.*, 1978; Leslie *et al.*, 1978). Preliminary evidence indicates that the regional sulfate component substantially exceeds the local source component except for short time periods when transport of sulfates by local meteorological circulations may predominate over transport by synoptic-scale air masses. However, the reliable identification of such time periods cannot be made by a superficial scanning of sulfate concentration variability with time. Instead, a careful analysis of the associations of periods of maximum aerosol sulfate concentration with atmospheric dynamic and chemical tracer indicators is required. In this paper such an analysis is applied to the Tampa Bay area.

2. Experimental

Measurements were made of the concentrations of sulfur and associated trace elements at a near-ground sampling station on Davis Island off Tampa for a 2-week period, 1–15 November 1976. The sampling device used, the time-sequence streaker filter sampler (Nelson, 1977), permitted discrete measurements of concentration to be made at 2 h intervals by particle-induced x-ray emission (PIXE) analysis of two week-long Nuclepore filter strips (Johansson *et al.*, 1975). The geographic setting of Tampa Bay on the west coast of Florida is shown in Fig. 1, with an indication of the sampling site and the locations of major air pollution sources from fossil fuel combustion, mostly oil.[2] In this paper we report the concentration measurements made for S, Cl, Si, K, Ca, Ti, V, Fe, Zn, Br and Pb.

3. Results

Fig. 2 presents the observed concentrations of aerosol sulfur (assumed to be predominantly in sulfate form) as a function of time over the 2-week

[2] E. Pfetzing, 1976: Air quality modeling in Hillsborough, Pinellas and Polk counties, Florida, Vols. 1 and 2. PEDCo-Environmental, Cincinnati, Ohio.

0021-8952/80/040419-07$05.75

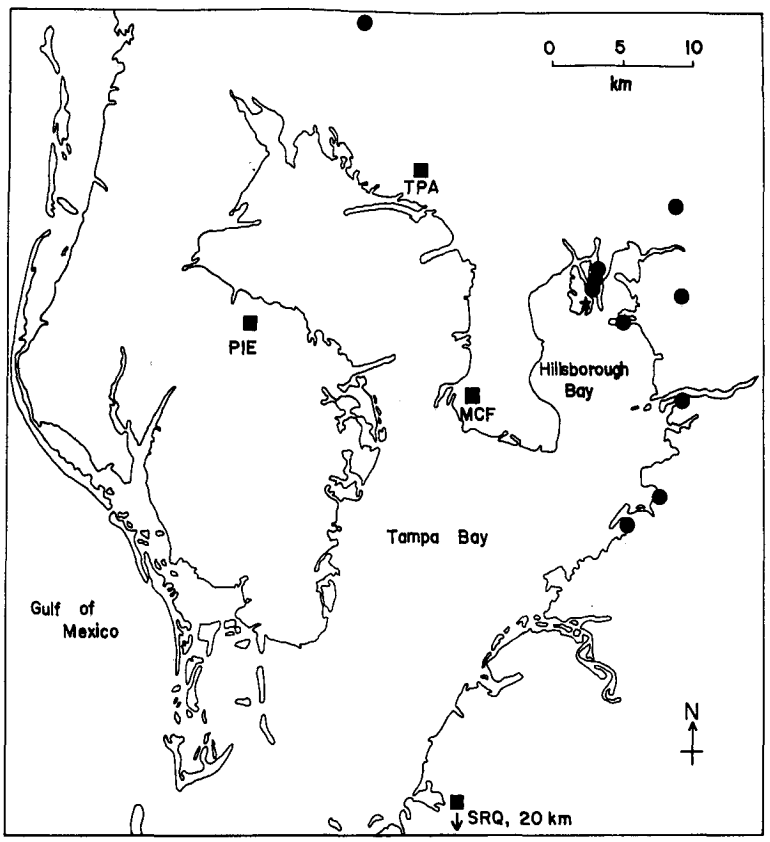

FIG. 1. Map of Tampa Bay area showing major local sulfur pollution sources (circles), airports providing wind records (squares), and the sampling site on Davis Island (star).

sampling period. Concentrations range from 500 to 4000 ng m^{-3}, or a factor of 8. Most commonly concentrations lie between 1000 and 2000 ng m^{-3} but with finestructure showing sharp decreases and increases in concentrations occurring within a few hours of time. On the average most of the sulfur occurs in <1 μm aerodynamic diameter particles (Ahlberg *et al.*, 1978) and is attributed to the atmospheric transformation of gaseous sulfur dioxide to aerosol sulfate, ultimately of air pollution origin. Sea spray sulfate occurs primarily in coarser particles, and biogenic and other natural fine aerosol sulfur is unlikely to exceed 100 ng m^{-3} (Lawson and Winchester, 1979). The maxima may be due either to local or to larger scale atmospheric transport, and it is the task of this paper to identify the times when local effects predominate. The approach will be based on an empirical examination of patterns of the variability of sulfur and other aerosol constituents with time, in the light of variable meteorological conditions during sea breeze episodes. An alternative statistical approach to studying Tampa aerosol composition relationships by time series analysis is given by Zinsmeister and Redman (1979).

Fig. 2 also shows the observed Cl concentrations in the same aerosol samples. Cl varies from less than the detection limit of 50 ng m^{-3} to nearly 4000 ng m^{-3} and is considered to be primarily a sea spray constituent. Even during times of maximum Cl concentration the S/Cl weight ratio is much higher than in seawater, where S/Cl = 0.0467 (Riley and Chester, 1971), and that typically found in marine aerosol (Meinert and Winchester, 1977). In general, the Cl maxima appear more prominently than do those for S, suggesting predominantly local effects governing the atmospheric concentration of Cl. Such effects are expected in the Tampa Bay area owing to the variability of the path of the air over land or sea before reaching the sampling site. After midday on Tuesday through Friday, 9–12 November, sea breeze circulations were well-defined and Cl maxima are correspondingly sharp. Sulfate maxima also occur nearly synchronously.

Fig. 2 also shows times when V was measured at concentrations above its detection limit of 30 ng m^{-3}; most of these occurrences are during the four sea breeze circulation days. Vanadium is a constituent of petroleum and may serve as a tracer of local plume trajectories from fuel oil combus-

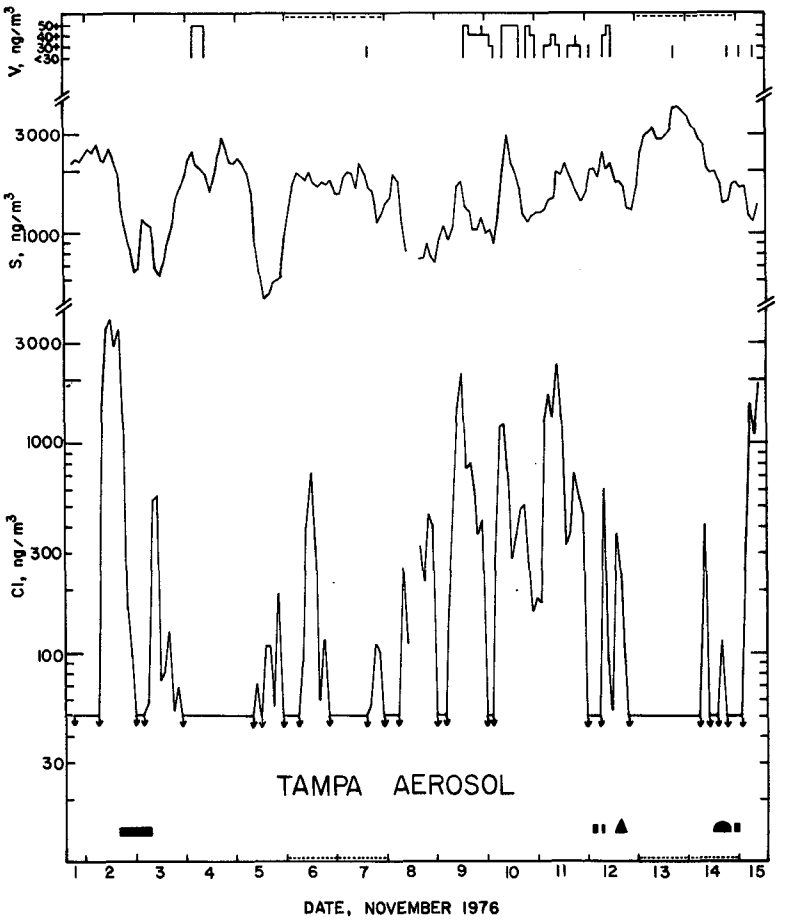

FIG. 2. Aerosol sulfur and chlorine concentrations presented as functions of time for the period 1–15 November 1976. Vanadium concentrations are shown along the top as a bar graph with 10 ng m^{-3} resolution. Precipitation (thick bar), cold frontal passage (triangle), and warm frontal passage (half-circle) are depicted along the bottom of the figure. Weekends (dashed lines) are indicated along the time axis.

tion sources. Chemical tracers must be used since the circulations involved in bay breezes involve considerable vertical transport which would invalidate any computed constant level trajectory. In Fig. 2, indications are given of the occurrence of precipitation and cold and warm frontal passages, but these do not occur during the first three sea breeze circulation days; on the fourth day a cold front, preceded by some precipitation, marked the end of the sea breeze.

Fig. 3 is a superposition of the sulfur concentration pattern of variability with time for the first and second sampling weeks. The lack of a significant correspondence between the two patterns indicates that the patterns are not predominantly diurnal or linked to weekly cycles of human activity. However, the contrary is observed for Ca, shown in Fig. 4, where a marked diurnal pattern is observed, with maxima at midday, lower values at the weekends, and a great similarity between the two weeks. Atmospheric concentrations of Ca are apparently governed by local cycles of human activity, including the generation of surface dust and emissions from industrial processes. This is apparently not the case for sulfate.

The pattern of variability of lead concentration is shown in Fig. 5. Concentrations are lowest at night and on the weekends. High concentrations during the day exhibit finestructure, often showing maxima in the morning and afternoon, but correspondences between the two weeks are not close. The contribution of emissions from automobile traffic near the sampling site may be large and highly dependent on local advection and mixing, which are variable. Fig. 5 also shows the variability in Br/Pb weight ratios in the aerosol. Although the variability is slight, ranging from about 0.1 to 0.3, the lowest values often occur at night, suggesting somewhat older average aerosol age and more extensive volatility loss of Br from particles. Longer night-

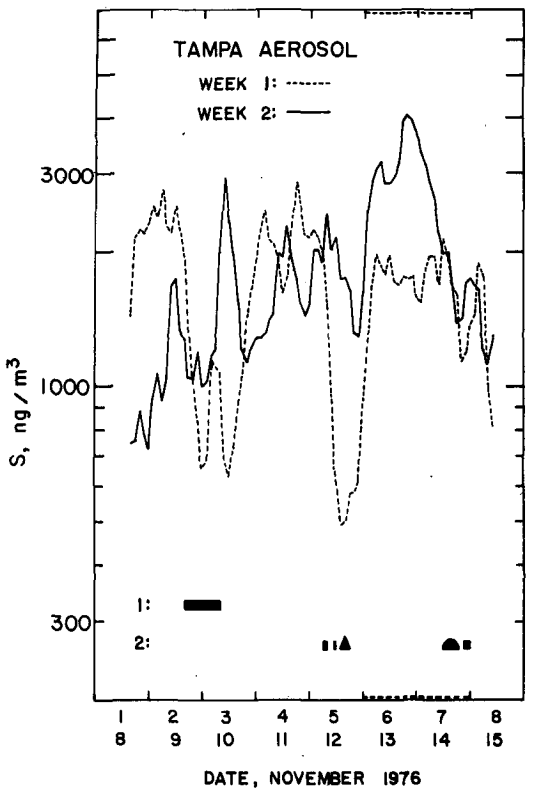

FIG. 3. Time variation of sulfur concentrations (ng m^{-3}) shown with week 1 and week 2 superimposed. Weather and weekends are depicted as in Fig. 2.

time aging times following emission of automotive exhaust could result from the decreased nighttime emissions near the sampling site so that the sample contains aged daytime aerosol and aerosol transported over greater distances to the site. For both night and daytime, however, the lead and bromine data are consistent with Tampa area source, transport and transformation processes being dominant for these elements.

Figs. 6–10 portray the patterns of variability with time for the elements K, Si, Fe, Ti and Zn in the same aerosol samples. In all cases the patterns of concentration variability with time exhibit marked fluctuations, but they are not correlated significantly with those of S, Cl, V, Ca, Pb or Br. Some elements (e.g., Si, Fe and Ti), may be constituents predominantly of terrestrial dust or fly ash silicate material. K may be of mixed origin, for example, dust or organic constituents of fuels. Zn may be from still another anthropogenic and natural sources, not as yet clearly identified in the case of Tampa. The lack of correspondence between these elements and S in the same aerosol samples indicates that the transport pathways of S are not closely related to those of terrestrial dust or other aerosol sources in the Tampa area.

4. Discussion

The correspondences between S, Cl, V, and surface wind patterns, indicated briefly above, suggest that a sea breeze circulation model may be used to describe the transport of pollution sulfate aerosol from sources in the Tampa area to the sampling site. Such a model may help distinguish between such locally produced sulfate air pollution and the large regional background of air pollution sulfate characteristic of the atmosphere over the eastern United States. Fig. 11 presents surface wind observations made hourly at four airport stations for two days which are typical of the meteorological conditions during the 2-week sampling period: 1 November

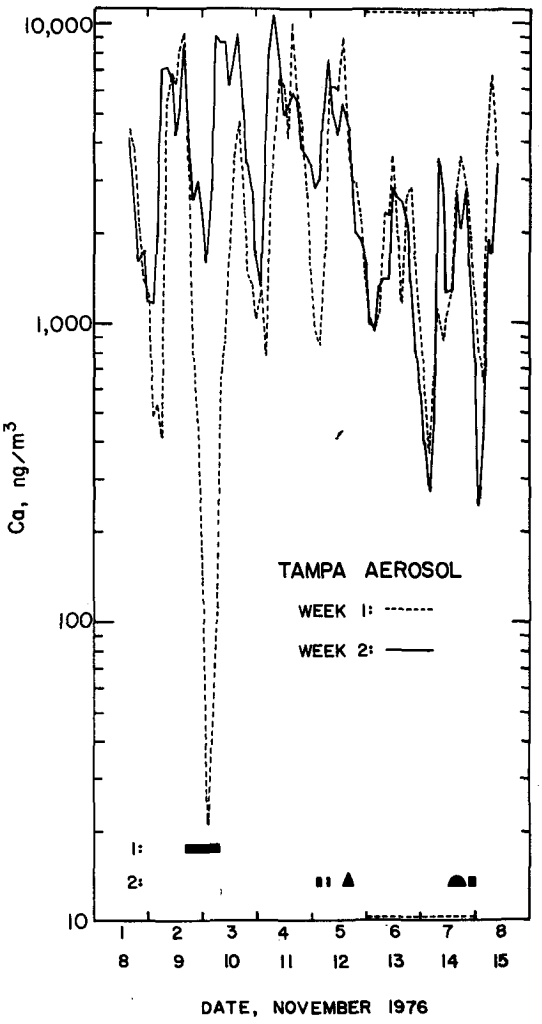

FIG. 4. As in Fig. 3 except for calcium concentrations.

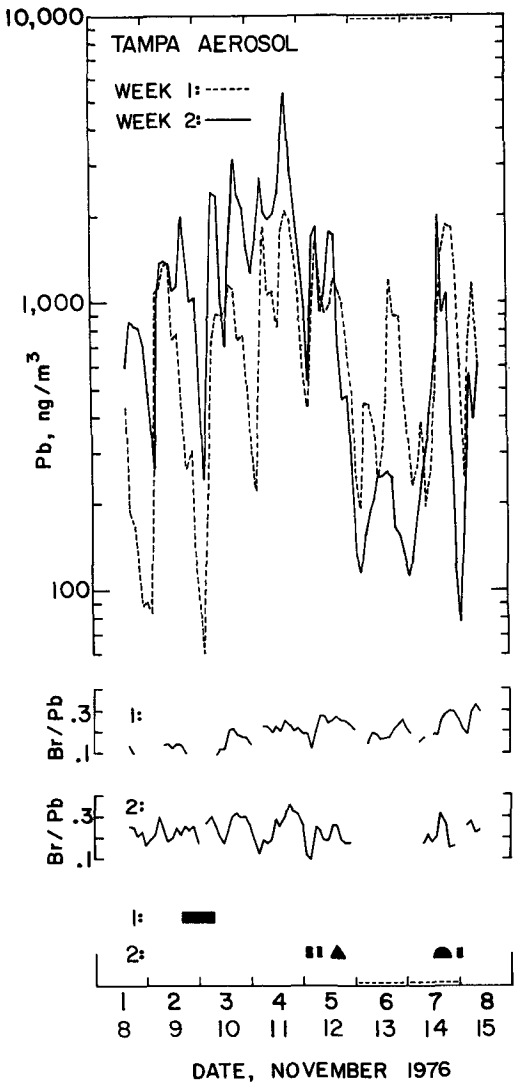

FIG. 5. As in Fig. 3 except for lead concentrations (ng m^{-3}) and Br/Pb weight ratios.

when the sea breeze circulation was not well developed, and 9 November which is one of four days with a well-developed sea breeze circulation. In the latter example, all four airport stations report a marked shift in wind direction in early afternoon. At most stations a shift from predominantly northeasterly flow to westerly flow is observed during early afternoon. Such a shift near the sampling site means a shift of airflow from an over-land to an over-water trajectory providing an opportunity for sea spray to be transported to the sampling site. Thus Cl in the aerosol may be a sensitive indicator of the exact time of the onset of sea breeze circulation at the sampling site (Hall, 1954).

The combined meteorological and aerosol chemical data suggest a three-dimensional air pollution circulation model to account for the occurrence of locally derived sulfate at the sampling site during times of well-developed sea breeze circulation (Kauper, 1960; Edinger and Helvey, 1961; Findlater, 1963, 1964; Anthes, 1978). Fig. 12 is a diagram of two such conceptual models for sea breeze circula-

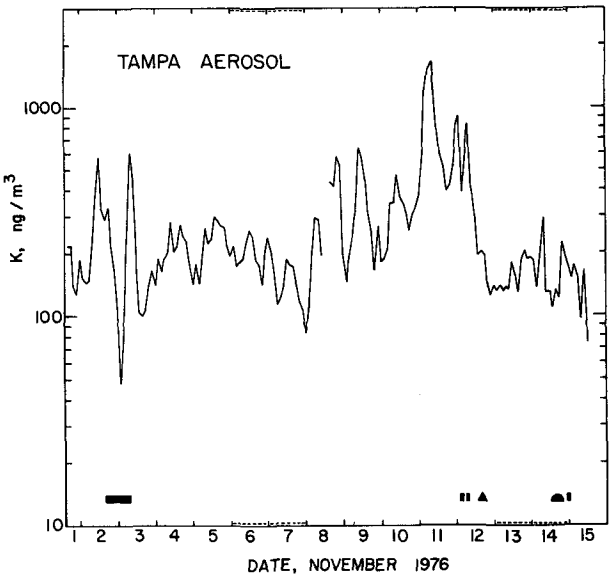

FIG. 6. As in Fig. 3 except for potassium concentrations.

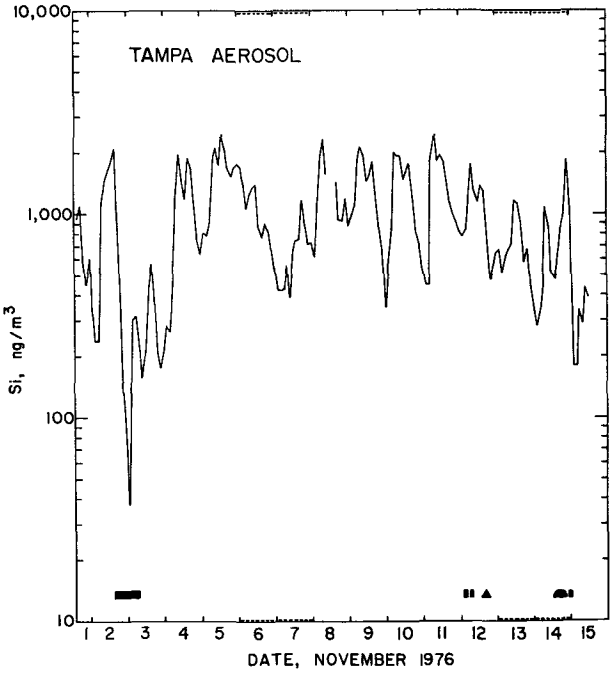

FIG. 7. As in Fig. 3 except for silicon concentrations.

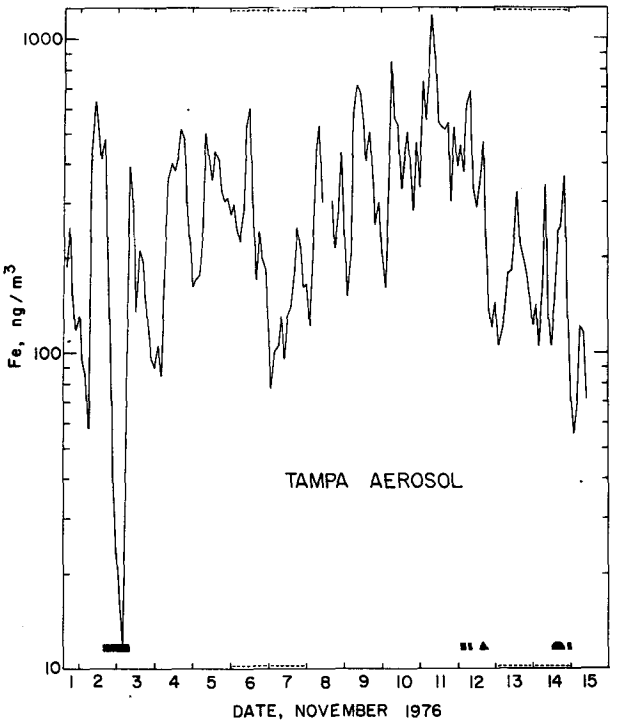

FIG. 8. As in Fig. 3 except for iron concentrations.

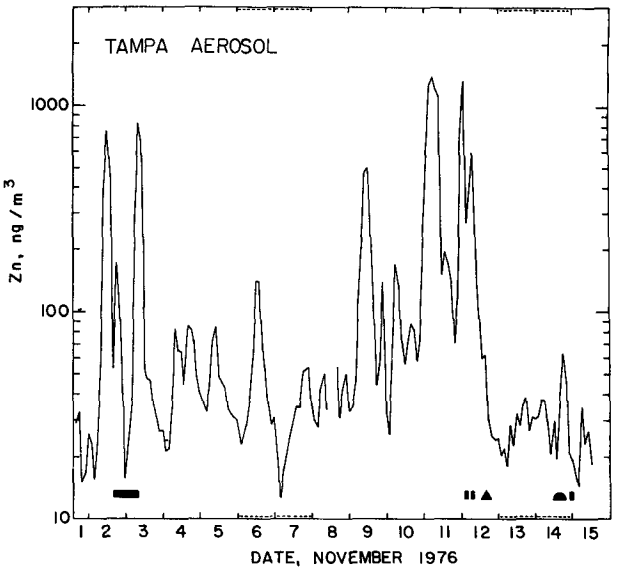

FIG. 10. As in Fig. 3 except for zinc concentrations.

tion (Lyons, 1972, 1975; Lyons and Olsson, 1972). Fig. 12a is the turbulent mixing case, while Fig. 12b is the trapping case. In turbulent mixing, a tall stack pollution source is seaward of the receptor site and sea-to-land breezes carry the plume inland to a point where it enters the turbulent internal boundary layer and may be mixed downward to the sampling site. The pollution aerosol may continue to be advected inland until it reaches the sea breeze frontal boundary where it can flow up the frontal surface (Wallington, 1959) in the return flow and subside over the bay. From this position it may be advected back in over the coast for a second pass across the sampling site.

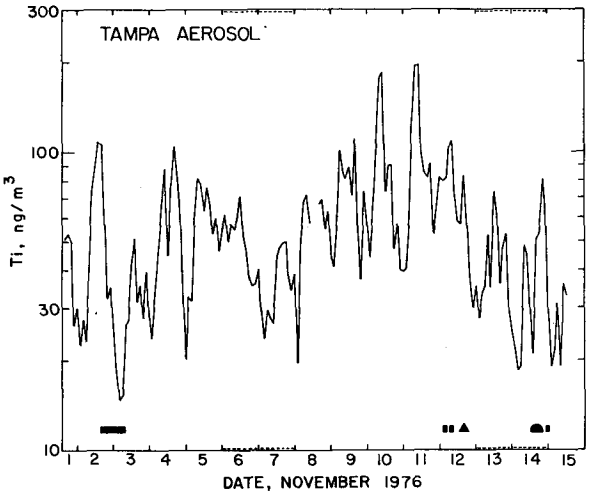

FIG. 9. As in Fig. 3 except for titanium concentrations.

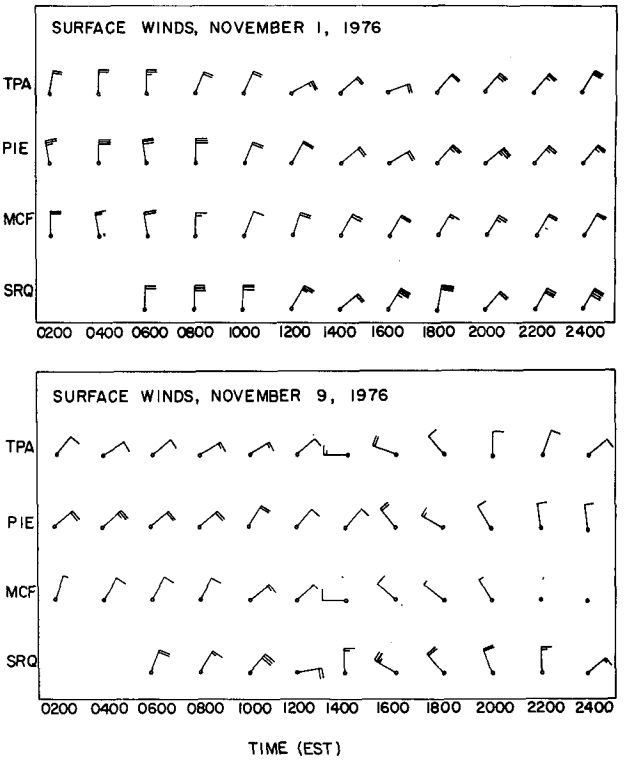

FIG. 11. Wind arrows every 2 h for four airports in the Tampa Bay area, shown in Fig. 1. The orientation of the arrow indicates the wind direction, each full barb represents 2.5 m s^{-1} (5 kt); no barb indicates calm conditions. No data were available at SRQ for 0200 and 0400.

Fig. 12b is an alternative conceptual model which may in fact be more relevant to the Tampa Bay situation. This case represents the trapping of a plume from a tall stack inland of the sampling site. The pollution aerosol may be advected to the sea breeze front and move up the frontal surface in the return flow. Then pollution aerosol can subside over the bay and be advected in across the coast in the sea breeze to reach the sampling site. The trapping case corresponds to the second pass mentioned following the mixing in Fig. 12a.

The results of this study suggest that sulfate from local air pollution sources, although on the average over long time periods not necessarily dominant over long-range transported sulfate, may be significant over short time periods. The satisfactory identification of such periods, however, requires a demonstrated correspondence between times of sulfate concentration maxima and meteorological or chemical tracer indicators of air movement from local sources. In Tampa Bay the available weather data permit a general indication of air movements which may transport high concentrations of locally derived pollution sulfate to the sampling site, but the chemical tracers of Cl and V, together with a comparison of other elemental constituents of the aerosol, were crucial in the precise definition of the local episodes.

Acknowledgments. This work was supported in part by the U.S. Environmental Protection Agency and the Florida Sulfur Oxides study. The authors are indebted to A. C. D. Leslie who carried out the aerosol sampling and elemental analyses on which this study was based, to W. H. Mach for comments on meteorological interpretation, and to Margaret Dancy for assistance in manuscript preparation.

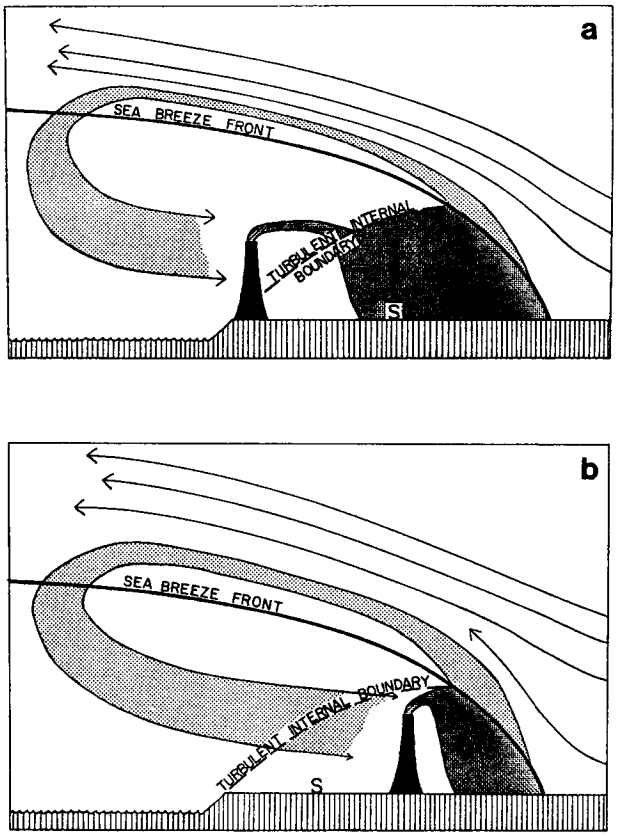

FIG. 12. (a) the pollution plume for the hypothetical turbulent mixing case. (b) The pollution plume for the hypothetical trapping case. The wind trajectory components normal to the coast and significant internal atmospheric boundaries are indicated. S represents the sampling site relative to a hypothetical tall stack air pollution source.

REFERENCES

Ahlberg, M. S., A. C. D. Leslie and J. W. Winchester, 1978: Characteristics of sulfur aerosol in Florida as determined by PIXE analysis. *Atmos. Environ.*, **12**, 773–777.

Anthes, R. A., 1978: The height of the planetary boundary layer and the production of circulation in a sea breeze model. *J. Atmos. Sci.*, **35**, 1231–1239.

Edinger, J. G., and R. A. Helvey, 1961: The San Fernando convergence zone. *Bull. Amer. Meteor. Soc.*, **42**, 626–635.

Findlater, J., 1963:: Some areal explorations of coastal airflow. *Meteor. Mag.*, **92**, 231–243.

——, 1964: The sea breeze and inland convection—an example of their interrelation. *Meteor. Mag.*, **93**, 82–83.

Hall, C. D., 1954: Forecasting the lake breeze and its effects on visibility at Chicago's Midway Airport. *Bull. Amer. Meteor. Soc.*, **35**, 105–111.

Johansson, Thomas B., Rene E. Van Grieken, J. William Nelson and John W. Winchester, 1975: Elemental trace analysis of small samples by proton-induced X-ray emission. *Anal. Chem.*, **47**, 855–860.

Kauper, E. K., 1960: The zone of discontinuity between land and sea breezes and its importance to southern California air pollution. *Bull. Amer. Meteor. Soc.*, **41**, 410–422.

Lawson, D. R., and J. W. Winchester, 1979: Atmospheric sulfur aerosol concentrations and characteristics from the South American continent. *Science*, **205**, 1267–1269.

Leslie, A. C. D., M. S. Ahlberg, J. W. Winchester and J. W. Nelson, 1978: Aerosol characterization for sulfur oxide health effects assessment. *Atmos. Environ.*, **12**, 729–733.

Lyons, W. A., 1972: The climatology and prediction of the Chicago lake breeze. *J. Appl. Meteor.*, **11**, 1259–1270.

——, 1975: Turbulent diffusion and pollutant transport in shoreline environments, *Lectures on Air Pollution and Environmental Impact Analyses*, Amer. Meteor. Soc., 136–208.

——, and L. E. Olsson, 1972: Mesoscale air pollution transport in the Chicago lake breeze. *J. Air Pollut. Control Assoc.*, **22**, 876–881.

Meinert, D. L., and J. W. Winchester, 1977: Chemical relationships in the North Atlantic marine aerosol. *J. Geophys. Res.*, **82**, 1778–1782.

Nelson, J. William, 1977: Proton-induced aerosol analyses: Methods and samplers. *X-ray Fluorescence Analysis of Environmental Samples*, Thomas G. Dzubay, Ed., Ann Arbor Science Publishers, 19–34.

Riley, J. P., and R. Chester, 1971: *Introduction to Marine Chemistry*. Academic Press, 465 pp.

Wallington, C. E., 1959: The structure of the sea breeze front as revealed by gliding flights. *Weather*, **14**, 263–270.

Zinsmeister, A. R., and T. C. Redman, 1980: A time series analysis of aerosol composition measurements. *Atmos. Environ.*, **14**, 201–215.