Reports

Trace Gas Analysis of Power Plant Plumes Via Aircraft Measurement: O_3, NO_x, and SO_2 Chemistry

Abstract. *The gaseous plume from an isolated 1000-megawatt power plant was systematically examined from a single engine aircraft to determine the extent to which* NO_x *and* SO_2 *chemistry occurs as a function of distance. The concentrations of ambient ozone, water vapor, and hydroxyl free radicals are indicated to be of major importance in defining the chemistry of power plant plumes during summertime conditions.*

Over the last decade, electric power generating plants have been considered as leading sources of SO_2 and H_2SO_4, and hence have been under increasing pressure to reduce their emissions of the primary pollutant SO_2. In most cases this is done by burning low-sulfur coal and oil, installing expensive stack gas scrubbing devices, or both. The trend toward tighter controls on power plant fuel quality and stack emissions would undoubtedly have continued until now if it had not been for the development of another major problem, the energy crisis. It is now apparent that energy and environmental control can no longer be treated as separate problems; any major decision on one will almost certainly affect the other. In this context, it is essential that the chemistry of power plant plumes be well understood.

Reported here are new findings on the chemistry of power plant plumes based on field studies with an airborne sampling platform and laboratory kinetic investigations. Of considerable significance in this work has been the identification of ambient ozone as a gas of major importance in defining the chemistry of the isolated power plant plume. Depletion of ambient ozone levels in the path of the plume was typically observed out to distances of 24 km from the plant; but of even greater significance was the fact that in nearly all cases during daylight hours (summer months) net ozone formation was seen beyond this point. Observed increases of 20 to 40 parts per billion downwind from the plant stack indicate that air quality standards for ozone are probably exceeded regularly during the summertime operation of large power plants (*1*). It is proposed that ozone is depleted primarily in the conversion of NO to NO_2, and that the ozone bulge at large distances is due to photochemically initiated free radical chemistry involving OH free radicals. This radical chemistry would also appear to explain the homogeneous gas phase conversion (*2*) of NO and SO_2 to HNO_3 and H_2SO_4. Calculations of conversion times suggest that HNO_3 formation is at least as great a potential health hazard as H_2SO_4 formation in power plant plumes.

The field studies reported here were carried out predominantly at the Morgantown power plant of the Potomac Electric Power Company, about 40 miles south of Washington, D.C. (more limited measurements were made at the Chalk Point and Dickerson power plants). The Morgantown plant is nominally rated at 1000 Mw, and the twin stacks of the station (cover) are about 200 m high (*3*). At present and when the data were collected (October 1973 to August 1974), the Morgantown plant burned a fuel mixture consisting of 75 percent oil (residual No. 6) and 25 percent coal.

Field data reported from October 1973 through 1 May 1974 were collected from a single engine Cessna 172 airplane. From May to August 1974 a single engine Cessna 205 airplane was employed. The sampling point on both aircraft was about 30 cm above the wing and directly over the cockpit (*4*). The sampling probe consisted of an aluminum conduit elbow 5 cm in diameter, which was mounted through the cabin roof and pointed forward to serve as a slight positive pressure sampling manifold.

Instrumentation flown during the study consisted of a Meloy SA-160R flame photometric SO_2 analyzer, a Monitor Labs 8410 chemiluminescence O_3 analyzer, and a Monitor Labs 8440 chemiluminescence NO-NO_2-NO_x analyzer (NO_x = NO + NO_2) (*5*). Whereas with the Cessna 172 only one instrument could be flown at a time, the Cessna 205 was capable of flying three or four instruments at once.

In sampling the Morgantown power plant over the altitude range 200 to 900 m, flights through the plume were made perpendicular to its center line. Since aircraft speeds ranged from approximately 95 to 105 m/hour, at distances as close as 1½ km sampling times were as short as 20 to 25 seconds. The time constants on all instruments were two to four times shorter than these sampling times.

During the sampling period of October 1973 to August 1974 extensive field data were collected on O_3, NO, NO_2, and to a lesser extent on SO_2. One of the first major observations made in the early flights was that the power plant plume had a significant effect on ambient O_3 concentrations. This effect can be seen in Fig. 1. Figure 1a shows O_3, which had an ambient concentration of 60 ppb, being totally depleted within the plume width out to 5 km from the plant. Beyond this distance, O_3 was totally depleted in portions of the plume, but the plume was observed to be breaking up and mixing with ambient air so that there were small regions with near-ambient O_3 concentrations. During another flight, as shown in Fig. 1b, O_3 depletion was again observed out to 24 km; but beyond this distance the O_3 concentration in the plume increased to a level exceeding that in ambient air by nearly 20 ppb. This O_3 bulge was still observed at 56 km (the excess being 25 ppb), which was the last point sampled. A total of ten flights on different dates during summer months have shown O_3 profiles similar to Fig. 1b. To the best

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of our knowledge, this is the first time such O_3 profiles in the plume of a power plant have been reported. That the O_3 bulge was, in fact, representative of the power plant plume is supported by the SO_2 profiles: as shown in Fig. 1b, significant negative or positive profiles of O_3 were observed only when positive SO_2 profiles were detected, thus marking the location of the plume. More recent summertime data show O_3 concentrations in the plume being pushed to levels as high as 40 ppb above ambient concentrations at distances of 70 km or greater.

We now consider the type of chemistry required to explain the O_3 profiles. In the case of O_3 depletion in the early stages of the plume, there are several possibilities: (i) loss of O_3 on aerosol particles, (ii) reaction of O_3 with SO_2, or (iii) reaction of O_3 with NO. The first possibility can probably be ruled out for large aerosol particles, since O_3 was depleted over large distances, and it is expected that this type of aerosol loading of the plume would be lost close to the stack. At present, the role of small aerosol particles (either directly from the stack or formed chemically in the plume) cannot be ruled out by any simple argument (*6*) [however, the evidence supporting possibility (iii) seems overwhelming]. Reaction of O_3 with SO_2 might be considered a very likely possibility because of the high concentrations of SO_2, but the rate constant for this process, $k \leq 2 \times 10^{-22}$ cm^3 molecule^{-1} sec^{-1} (*7*), shows that the lifetime of O_3 in the plume would be $\sim 2 \times 10^3$ days. This rules out the homogeneous O_3-SO_2 reaction (*6*). The final process listed, the O_3-NO reaction, was considered quite probable since its rate constant, $k = 1.66 \times 10^{-14}$ cm^3 molecule^{-1} sec^{-1} (*8*), gives an O_3 lifetime of only 5 seconds if the NO plume concentration is taken as 0.5 part per million (ppm). In fact, simultaneous measurements of the SO_2 and NO concentrations approximately 2.4 km downwind from the stack showed average values for these gases of 2.8 and 1.4 ppm, respectively.

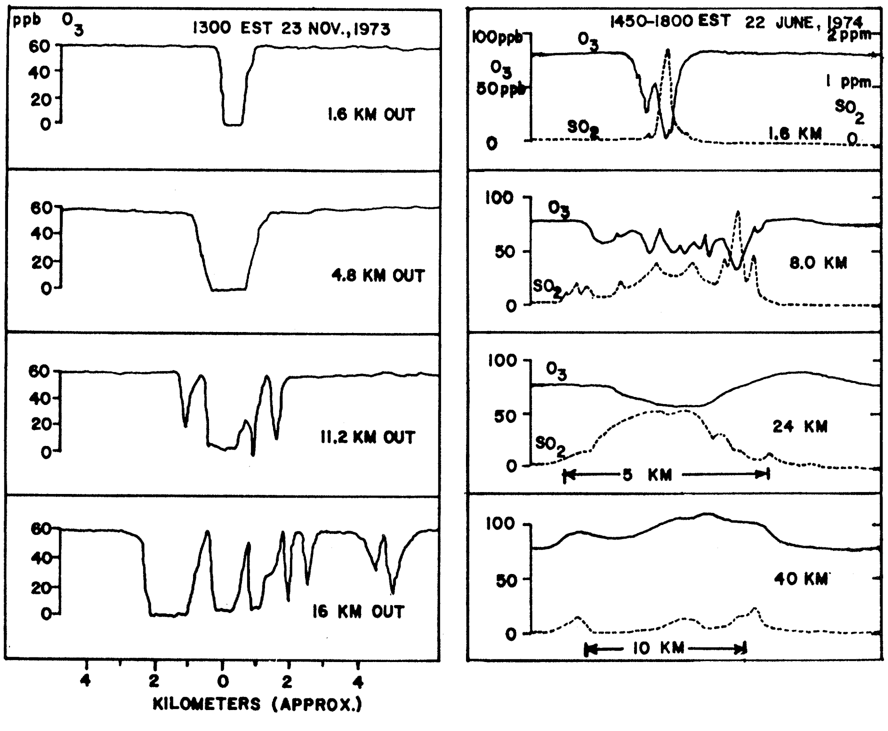


Fig. 1. (a) Profiles of plume O_3 concentrations measured downwind of the Morgantown power plant at ~600 m on 23 November 1973, 13:00 E.S.T. Each profile was determined by flying across the plume perpendicular to its center line. The abscissa is distance from the center line. Ambient air O_3 levels, 60 ppb. Meteorological conditions: winds at ~600 m, 19 to 22 km/hour; temperature, 285°K; humidity, 40 percent (*11*). (b) Plume O_3 profiles taken downwind of the Morgantown power plant at ~600 m on 22 June 1974, 14:50 to 15:50 E.S.T. Ambient air O_3 levels, 80 ± 4 ppb, background $SO_2 \simeq 6$ ppb. Meteorological conditions: winds at ~600 m, 24 km/hour, southerly; temperature, 300°K; humidity, 65 percent visibility, hazy (*11*). Variations in the background levels of O_3 beyond 1.6 km from the plant do not reflect actual variations in background O_3, which was found to be constant at 80 ± 3 ppb, but indicate extreme fragmentation of the plume over distances wider than those shown in some of the profiles of Fig. 1b. The diluted plume at its fringes also appears to be a source of net O_3 production (see 24 km profile), probably via reactions 5 through 8. The O_3 analyzer used in this work was calibrated at least once a week during this study; however, because of uncertainties in existing calibration methods, it is quite possible that the absolute O_3 concentrations quoted may be slightly in error. The relative changes observed in the O_3 concentration in and out of the plume should be highly reliable.

The conclusion that O_3 was most likely depleted by reacting with NO was shown to be correct in a series of field measurements in which both NO and NO_x were measured simultaneously; 12 separate flights were made to collect data of this type between October 1973 and August 1974. In processing the data from these flights, the effect of plume dilution on the concentration of NO was minimized by plotting the ratio of NO to NO_x against distance (*9*). As illustrated in Fig. 2, the NO/NO_x data show systematic conversion of NO to NO_2 (*10*), which strongly supports the O_3-NO reaction as the correct explanation for the O_3 depletion. When the measurements in Fig. 2 were made, the wind speed at ~ 450 m was 21 to 26 km/hour (*11*); these wind data give a 50 percent conversion time for NO going to NO_2 of ~ 17 minutes. [Pitts *et al.* (*12*) reported qualitative findings for a power plant near Long Beach, California, which also show a reasonably fast conversion of NO to NO_2.] The NO/NO_x data from the other 11 daytime flights show 50 percent conversion times ranging from 12 to 60 minutes. This range of values can be understood in terms of the observed variations in ambient O_3 concentrations, solar ultraviolet flux (<4000 Å), wind speeds, wind stability, and atmospheric stability. To further illustrate these points, one can examine the reaction scheme

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

$$NO_2 + h\nu \rightarrow NO + O \quad (2)$$

$$O + O_2 + M \rightarrow O_3 + M \; (M = N_2) \quad (3)$$

It is apparent that high ambient O_3 concentrations and low ultraviolet photon fluxes will enhance the rate of NO conversion to NO_2. This was illustrated during a scheduled nighttime flight in which a 50 percent conversion time of 12 minutes was found and the final ratio of NO to NO_2 was < 0.05. During daylight hours, the rate of photodecomposition of NO_2 at some point will be found to be just equal to the rate at which NO_2 is being formed by process 1. Under these conditions the system can be said to be in photochemical equilibrium (*13*), and NO/

NO_2 will be given by ($NO/NO_2 = J_2/k_1(O_3)$), when there is excess O_3 present. [In this equation J_2 is the photochemical rate constant for process 2 and k_1 is the bimolecular rate constant for reaction 1 (*14*)].

To explain the amount of excess O_3 generated downwind from the stack and the short time in which it developed (30 to 40 minutes), we suggest the importance of free radical chemistry. For example, it is now known that under daylight conditions and with excess CO and NO present, net O_3 can be generated by a chain reaction involving OH, HO_2, and H (*15, 16*) the initiating step being

$$OH + CO \rightarrow CO_2 + H \quad (4)$$

Other, more complex schemes can be written which involve hydrocarbons as major reactants (*17*); reactions of this type are believed to be the major source of O_3 in areas with high levels of photochemical smog. In the case of power plant plumes, however, hydrocarbon and CO emissions are extremely low because of the high-efficiency combustors employed (*18*) and it is difficult to see how either reactant could account for the observed O_3 buildup. The possibility that reactive hydrocarbons (nonmethane, ethane, and acetylene species) in the ambient air might be the explanation for the excess O_3 cannot be unequivocally ruled out at this time, but it appears unlikely considering their low estimated concentrations in nonurban air (< 3 ppb) and the short chain lengths for hydrocarbon-generated O_3.

The mechanism we favor for the O_3-generating stage of the plume involves the chemical interaction of NO_x with SO_2 via free radical chemistry and photochemistry, the first step of which would be

$$OH + SO_2 + M \rightarrow HSO_3 + M \quad (M = N_2) \quad (5)$$

Reaction 5 (*19*) could then be followed by

$$HSO_3 + O_2 + M \rightarrow HSO_5 + M \quad (M = N_2) \quad (6)$$

$$HSO_5 + NO \rightarrow HSO_4 + NO_2 \quad (7)$$

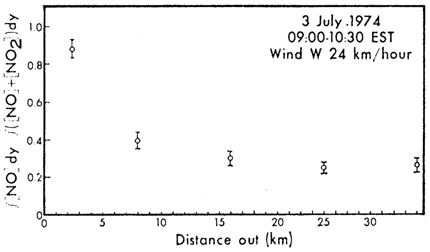
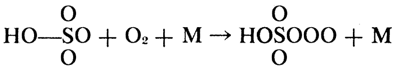


Fig. 2. Conversion of NO to NO_2 downwind from the stack of the Morgantown power plant at ~600 m on 3 July 1974, 09:00 to 10:30 E.S.T. The ordinate in this plot represents the ratio of the integrated NO concentration to the integrated NO_x concentration, where *dy* is the plume width at each distance from the stack. Error bars signify the total deviation observed in five to ten passes at each distance. Ambient air ozone levels, 80 ± 3 ppb, ambient $NO_x \simeq 10$ ppb (at 32 km typically $NO_x \simeq 25$ ppb above background).

Although the absolute rate constants for reactions 6 and 7 are not known, the rates of these reactions should be moderately high. Reaction 6 is a simple free radical O_2 scavenging reaction similar to a great many free radical reactions in the atmosphere; and even with a moderately low rate constant, the high concentration of O_2 in the atmosphere would produce a fast rate of consumption of HSO_3. Reaction 7 is a typical peroxide-NO reaction and should be moderately fast. The only likely competing reaction would be $HSO_5 + HO_2 \rightarrow H_2SO_5 + O_2$, but this should be ineffective since the NO concentration in the plume would be two or three orders of magnitude greater than the HO_2 concentration. A critical step in the production of O_3 via an effective chain process would involve the reaction of the free radical HSO_4 with an additional O_2 molecule; that is



$$HO\!-\!\overset{O}{\underset{O}{S}}O + O_2 + M \rightarrow HO\overset{O}{\underset{O}{S}}OOO + M \quad (8)$$

This new peroxide species could then react with NO to regenerate HSO_4 and two NO_2 molecules. Chain termination would probably result from reaction of HO_2 with HSO_4 to form H_2SO_4, reaction of HSO_4 with HSO_4, or reaction of HSO_4 with NO_2 to form HSO_4SO_2 (*20*). (The latter species would probably be photolyzed and returned to the chain cycle.) The NO_2 formed in the above reaction scheme would then lead directly to the generation of O_3 through reactions 2 and 3. As the ozone concentration increased, more OH would be generated (*15, 16*), and this would lead to still higher levels of ozone.

It is important to note, however, that on the basis of available rate data (*21*) the above O_3-generating process should be inhibited moderately close to the stack because of the temporary chain terminating step, $NO_2 + HSO_4$, the low levels of ozone present, and also because of the OH loss process

$$OH + NO_2 + M \rightarrow HNO_3 + M \quad (9)$$

In fact, in the middle stages of the developing plume (at 11 to 32 km), reaction 9 should be a significant source of nitric acid. First order calculations indicate 50 percent conversion times for NO_2 to HNO_3 of 2 to 3 hours during daytime in the summer. Because of the lower rate constant for process 5 (*19*) H_2SO_4 formation by homogeneous reactions (*2*) would probably require three to four times longer for 50 percent conversion.

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References and Notes

1. Although the plumes from only three large power plants have now been examined in terms of their O_3 generation characteristics, all evidence would point toward this phenomenon being common to all large power plants.
2. We do not contend that heterogeneous chemistry should be ruled out in power plant plumes. However, the study reported here was primarily aimed at elucidating the significance of homogeneous gas phase chemistry.
3. Each stack at the Morgantown plant is equipped with a Research Cottrell electrostatic precipitator, which has a guaranteed collection efficiency for fly ash of 99.5 percent.
4. The location of the sampling point directly over the cockpit was done after consultation with Cessna aeronautical engineers. All tests indicate that air sampled from this point is completely free from aircraft exhaust and propeller backwash.
5. The Monitor Labs 8440 chemiluminescence NO-NO_2-NO_x instrument was the only one on the market at the time which was capable of determining NO and NO_2 or NO and NO_x simultaneously. This feature is essential for obtaining quantitative conversion times for NO to NO_2.
6. S. A. Penkett [*Nature (Lond.)* **240**, 106 (1972)] suggested the possible importance of heterogeneous reactions in the conversion of SO_2 to H_2SO_4 in aerosol solutions containing SO_2, O_3, and H_2O. Whereas laboratory studies indicate that the reaction between O_3 and SO_2 in solution is measurable, we think these results can be extrapolated to power plant plumes only in a very qualitative way, and so do not constitute a satisfactory answer at this time to the ozone depletion question.
7. D. D. Davis, J. Prusaczyk, P. Kim, M. Dwyer, *J. Phys. Chem.* **75**, 1775 (1974).
8. D. Garvin and R. F. Hampson, Eds., ***NBSIR 74-430; Chemical Kinetics Data Survey VII. Tables of Rate and Photochemical Data for Modelling of the Stratosphere (Revised)*** (National Bureau of Standards, Washington, D.C., 1974).
9. If any NO_x is lost from the plume (for example, in reactions such as $NO_2 + OH + M \rightarrow HNO_3 + M$) the 50 percent conversion times for NO to NO_2 would be too long. However, on the basis of available rate data for this reaction, the error produced in measured NO to NO_2 conversion times of less than 30 minutes should be small and unimportant.
10. Integrated ratios (see Fig. 2) were found necessary because of the varying NO/NO_x ratios which resulted from limited segments of the plume mixing with ambient ozone.
11. Upper air winds, temperature, and relative humidity data were acquired from National Weather Service radiosonde observations at Sterling, Virginia, at 7:15 and 19:15 hours E.S.T. This weather station is located 70 km northwest of the Morgantown plant.
12. J. N. Pitts, Jr., H. R. Gloria, J. V. Behar, G. A. Bradburn, R. F. Reinisch, L. Zafonte,

Initial Survey of Major Air Basins in California (SAPRC Report No. 1, Statewide Air Pollution Research Center, Univ. of California, Riverside, 1972).

13. In the case of a power plant plume the NO-NO_2 system does not reach true photochemical equilibrium because the average ozone level in the plume slowly changes with distance due to the entrainment of ambient air by the plume and to free radical chemistry. It would be appropriate, therefore, to refer to the relatively constant ratio found for NO/NO_x at moderately long distances from the stack as indicative of a pseudo-photochemical equilibrium.
14. Values obtained for NO/NO_2 on several daytime flights from October 1973 to August 1974 ranged from 0.9 to 0.4. In each case these values were in reasonably good agreement with those calculated from the equation $NO/NO_2 = J_2/k_1[O_3]$ when J_2 was calculated from the expression $J_2 = 1 \times 10^{-2} \exp(-0.38 \sec X)$, where X is solar zenith angle, and plume O_3 concentrations were plugged in.
15. J. Heicklen, C. Westberg, N. Cohen, in *Chemical Reactions in Urban Atmospheres*, C. E. Tuesday, Ed. (Elsevier, New York, 1971), p. 95.
16. The reaction sequence suggested is

$$OH + CO \rightarrow CO_2 + H \qquad (a)$$
$$H + O_2 + M \rightarrow HO_2 + M \qquad (b)$$
$$HO_2\,NO \rightarrow NO_2 + OH \qquad (c)$$
$$NO_2 + h\nu \rightarrow NO + O \qquad (d)$$
$$\underline{O + O_2 + M \rightarrow O_3 + M} \qquad (e)$$
$$CO + 2O_2 \rightarrow CO_2 + O_3 \quad \text{(net reaction)}$$

However, the chain length for this sequence is strongly controlled by the ratio CO/NO_2. In all such chain processes the OH free radical is initially generated by the reaction sequence [H. Levy, *Science* **173**, 141 (1971)]

$$O_2 + h\nu\,(< 3100\ \text{A}) \rightarrow (^1D) + O_2 \qquad (f)$$
$$O(^1D) + N_2 \rightarrow O(^3P)\,N_2 \qquad (g)$$
$$O(^1D) + H_2O \rightarrow 2\,OH \qquad (h)$$

where $O(^1D)$ is a metastable state of atomic oxygen containing approximately 23 kcal/mole excess energy. Step g, which deactivates $O(^1D)$, reduces the overall efficiency of the OH-producing scheme, making the rate of production of OH linearly dependent on the absolute H_2O concentration. Thus, the rate of the O_3 generating chemistry should also depend linearly on the H_2O concentration, and hence on the season of the year.
17. Heicklen *et al.* (*15*). Although the hydrocarbon reaction scheme is much more complex, the key reactions which replace (b) and (c) in the above scheme are

$$R + O_2 \rightarrow RO_2 \qquad (i)$$
$$RO_2 + NO \rightarrow NO_2 + RO \qquad (j)$$

where R is a hydrocarbon free radical.
18. During several flights, CO and total hydrocarbons were measured as close as 1½ km from the Morgantown stack. The CO found was only 1 ppm above background and no hydrocarbons other than ambient methane could be detected.
19. W. Payne, L. Stief, D. D. Davis, *J. Am. Chem. Soc.* **95**, 7614 (1973); D. D. Davis, R. Schiff, W. Bollinger, S. Fischer, in preparation. At a N_2 pressure of 760 torr, $k_5 \sim 8 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1}.
20. The rate constant for the reaction of HSO_4 with O_3 has not yet been measured in the laboratory. We have suggested this process as one possible explanation for the observed O_3 bulge.
21. $k_9 = 7.5 \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1} ($M = N_2$). D. D. Davis, W. Bollinger, G. Machado, S. Fischer, in preparation.
22. Supported by NSF grant GI-36338X. The work reported is part of a thesis to be submitted by G. Klauber to Johns Hopkins University in partial fulfillment of the requirements for the Ph.D. degree in electrical engineering. The authors would like to express their appreciation to Dr. Hiram Levy for his many helpful suggestions.

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Counterclockwise Circulation in the Pacific Subantarctic Sector of the Southern Ocean

Abstract. *The distribution of isohalines in the upper 500 meters of Pacific subantarctic waters can be interpreted as evidence for an endemic counterclockwise circulation, the westward component of which is at 40 to 45 degrees south latitude. The distributions of a number of lanternfish species (family Myctophidae) lend support to such an interpretation.*

A recently completed analysis of the distribution of the oceanic fish family Myctophidae (lanternfish) in the World Ocean south of 30°S (*1*) required a detailed description of the hydrology of the Southern Ocean. An important part of that task included locating dominant hydrographic boundaries in the Southern Hemisphere, particularly the Subtropical Convergence (STC) and the Antarctic Polar Front (APF). Extensive published studies and knowledge of the APF (*2, 3*) facilitated its relatively precise location on a reference map. The region of the STC, however, has received less attention, and its extent and dynamics are poorly understood. Deacon (*2*), in his classical study of the Southern Ocean, defined the STC on the basis of surface temperature gradients and most subsequent workers have referred to his "line" as the Subtropical Convergence. The fact that the convergence between the southern anticyclonic gyres and the West Wind Drift is a broad and transitional region characterized by temporal and spatial variability, particularly in surface layers, makes such a line unrealistic. Inspection of a number of sources (*2, 4–6*) for more comprehensive parameters to identify the STC region resulted in selection of the isohalines of the 34.6 and 34.8 per mil at 200 m,

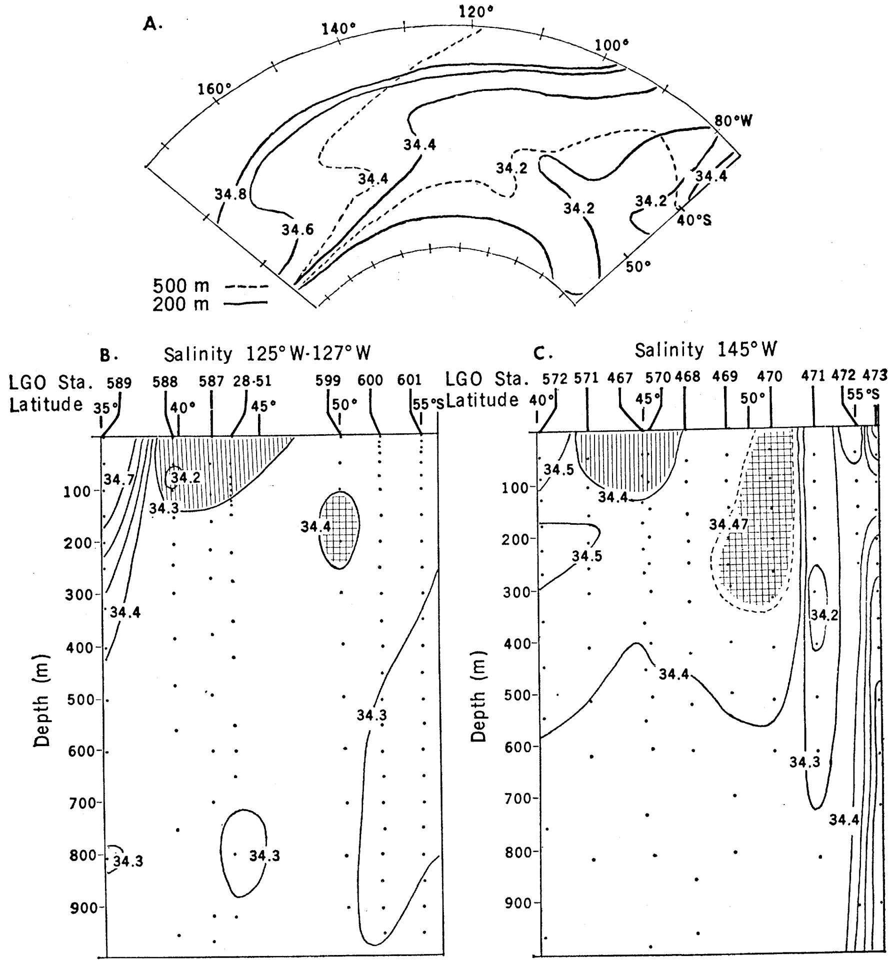

Fig. 1. Salinity distribution in Pacific subantarctic waters. (A) Isohalines at 200 and 500 m. (B) Profile at 0 to 1000 m, 125°W to 127°W. (C) Profile at 0 to 1000 m, 145°W. Salinity values are per mil. Vertical hatching indicates the region of relatively low salinity. Cross-hatching indicates the region of relatively high salinity. Abbreviation: LGO Sta., Lamont Geological Observatory Station. Based on data in (*6*).