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FIELD PROGRAM DESIGNS FOR VERIFYING PHOTOCHEMICAL DIFFUSION MODELS

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FIELD PROGRAM DESIGNS FOR VERIFYING PHOTOCHEMICAL DIFFUSION MODELS

by

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1 INTRODUCTION

1.1 MOTIVATION FOR DESIGNING EXPERIMENTS TO AID MODEL DEVELOPMENT

Computer simulation models adequate to predict air quality in terms of emissions and meteorology must be improved in terms of fidelity if they are to be useful in testing implementation strategy plans. Observational evidence forms a substantial basis for the models we presently possess; these existing models have each been tested (to a greater or lesser extent) against the available body of measured data. Because the experimental community now stands at the threshold of fielding elaborate measurements programs, such as the Los Angeles Reactive Pollutant Program (LARPP) and the Regional Air Pollution Study (RAPS), the time is at hand for modelers to lay out specific data needs.

Recommendations for field programs must address themselves to achieving specific design goals based on modeling needs. The first step in accomplishing this is to identify gaps in the model calculations, recognizing that gaps may exist in the input data, in the phenomenology underlying the governing equations, or in the adequacy of the air quality measurements. Next, the variables to be measured must be designated and any special conditions of the experimental setting specified. As a final step, details of instrumentation, precision, sampling rate, and data displays must be specified. Much of the current content of field programs embodies our earlier recommendations; however, the present report refines and extends these recommendations to address newly identified problems.

To be sure, we have not attempted to carry through all of these steps in the present study. In some areas we lack answers either because we are unable to conduct a meaningful experiment or because a reliable instrument does not exist. In other areas, specifying a comprehensive program design will depend on active collaboration with the experimenter in the planning phases.

1.2 OBJECTIVES OF CURRENTLY PLANNED FIELD MEASUREMENTS

1.2.1 Regional Air Pollution Study (RAPS/St. Louis)

The overall objective of RAPS is directed to the development of air quality simulation models that are useful for predicting the effects of emission controls on air quality in a region. In achieving this broad objective, the program has been structured to achieve a set of complex and interacting subgoals.[1] The structuring of RAPS follows relatively fundamental lines to enhance our understanding of related phenomena. It also has specific tasks for test and evaluation of the simulation models.

Among the fundamental objectives of RAPS are the characterization of atmospheric motion in the urban airshed and the refinement of chemical mechanisms to describe transformation or losses. Laboratory experiments and rate constant measurements are considered as adjuncts to the successful pursuit of the program. Tests of the assembled models as well as of their components are listed among the RAPS/St. Louis subgoals.

In approaching this set of objectives, the RAPS planners envisioned six broad work areas:

1. Emission Inventory
2. Atmospheric Transformations
3. Atmospheric Structure and Dispersion
4. Removal Processes
5. Mathematical Simulations
6. Control Economics

The philosophy of the RAPS approach recognizes the deficiency of past programs due both to a lack of definite goals and to the fact that data acquisition has been limited by the available measurement instruments. Rather than relying on targets of opportunity as in the past, the regional study plan recognizes the need to treat the problem on an extended scale, both in geographical space and scientific complexity. In the final analysis RAPS will try to facilitate the development of control strategies having general applicability. The stated implications touch on social and economic considerations that must be understood in order to implement actual control strategies.

1.2.2 Los Angeles Reactive Pollutant Program (LARPP)

The measurements phase of this program is scheduled to begin in August 1973. The LARPP objectives are more limited than those of RAPS; however, the orientation toward modeling is the same. For these reasons, this discussion can be far more specific than that for RAPS. LARPP, however, is by no means a simple program.

To describe the program directly it is useful to quote the first sentence of the program plan:[2]

> Most simply stated, the objective of the Los Angeles Reactive Pollutant Program (LARPP) is to provide a data package suitable for developing and subsequently validating computer models which effectively simulate the photochemically induced reactions causing smog.

This is in response to recommendation from a joint (CAPA-3/CAPA-7) committee of the Coordinating Research Council, Inc. (CRC). In September 1972, CRC set as a major goal of future field programs the task of acquiring a data base for reactive pollutant models. They proposed to exploit the moving coordinate system concept by moving an instrument package along with an air mass to the extent possible.

The embodiment of these objectives in LARPP is built around a helicopter/tetroon* system for air sampling and tracking. Gas species, tracer density, and meteorological data will be measured by two helicopters that follow tetroon clusters across the Los Angeles basin. Radar tracking, mobile van

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*A neutral-buoyancy, lighter-than-air vehicle which flies freely, presumably following the path of air motion.

sampling, and laboratory analyses constitute the main ground support capabilities. Fixed wing aircraft missions will collect data on winds, moisture, and temperature.

1.3 APPROACH OF THIS STUDY

In this paper we follow a chronological sequence in ordering the major sections. First our recommendations developed in early 1970 for CRC are reviewed and placed into the present context of test plans (Sec. 2). The following section (Sec. 3) gives three specific conceptual plans that can be pursued to shed further light on certain key questions that remain unanswered. Using the LARPP design as a prototype, the next section (Sec. 4) presents a data management plan that aids ongoing program direction in addition to providing an archive for modelers. We close (Sec. 5) with a discussion of areas for future field programs. In contrast with the specific conceptual plan section, this overview of the future is heuristic in nature. Its incompleteness is unavoidable because of limitations both in theory and instrumental technique.

REVIEW OF OUR PREVIOUS RECOMMENDATIONS*

Some years ago, in an effort to improve the communication between theoretical and field programs, we suggested new directions for future field measurements of air pollution (under Coordinating Research Council sponsorship). Although many of these suggestions have since been implemented, there is a continued need for the fulfillment of their objectives. It may be noted that LARPP will be a proving ground for some of the methods proposed in the recommendations. The results from LARPP may help to achieve an understanding of the physical and chemical processes that determine air quality under specific emission source conditions and meteorological settings using tested methodologies.

2.1 SUMMARY OF PREVIOUSLY SUGGESTED ELEMENTS OF NEW EXPERIMENTS

The philosophy underlying the approaches initially suggested emphasized experimental design rather than after-the-fact analysis of available data. Although the RAPS philosophy does not rule out new instrumental development to achieve its goals, our current experimental design recommendations emphasize new uses and configurations of available measurement technology. In considering novel techniques it is profitable first to summarize the main features of program innovations that were suggested earlier.

Considering the air over a city as a dispersion and reaction region for air pollutants, we observe that the data from ground-based fixed monitoring stations may be hampered by "wall effects." For assessing potential damage to receptors, current ground level measurements are essential; however, for gaining a deeper understanding of atmospheric processes, ground-based data provide only a small part of the needed information. Thus, in our recommendations we emphasized airborne measurements over a few typical days at the possible expense of extensive statistics at a few fixed stations in order to control program costs. Photochemical modeling studies[3] have shown that this shift in emphasis is essential for regional studies.

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*Based on work sponsored by CRC-APRAC Project No. CAPA-7.

Vertical profiles of temperature and concentration hold the key to the ultimate effects of air pollution in an urban area and its vicinity. A combination of modern monitoring instruments and available airborne platforms can supply the needed measurements. To this end we asked that helicopters or tethered balloons fitted with compact measuring equipment be utilized more extensively than in prior programs. This approach permits achieving two important goals.

1. Vertical profiles can be obtained over a meaningful height interval near the ground (measurements at 1000 feet and above usually give only the conditions at the upper edge of the mixing layer).

2. Air masses can be tracked in the micrometeorological environment of an urban airshed (the wind seldom carried the pollutants over just those ground-based stations where pertinent quantities are being measured). To improve this aspect of the work, we suggested improved ways to follow tetroons with a helicopter, using tetroon <u>and</u> helicopter transponders, along with a voice-link.

All of the advanced air pollution simulation models consider stability effects on dispersion, horizontal advection, and the vertical spread of pollutants after they are emitted. Many useful check points are obtained by arranging for flights of instrument packages through the polluted layers of air. Therefore, gathering data arrayed in three dimensions is essential to the validation of the models.

Chemical concentrations of interest are carbon monoxide, hydrocarbons, oxides of nitrogen, and ozone. Because of its slow reactions, CO acts as a tracer and indicates the advective and diffusive spread of pollutants. It is also rather specific to vehicular sources. For the same reasons, acetylene should also be considered as a candidate for a tracer material. For hydrocarbons we would recommend eliminating detailed analyses, which resolve individual compounds, in favor of more frequent readings of a coarser chemical resolution. The breakdown only needs to include broad reactivity classes (even if they have to be as coarse as total hydrocarbons and methane).

Total oxides of nitrogen would help in solving the puzzle of the nitrogen balance, which continues to be manifested in observations and which we indicated in our early studies.[3] Individual measurements of oxides of nitrogen, of course, indicate the degree of conversion from NO to NO_2. This, combined with the ozone measurement, holds the key to determining the progress of the main transformations involved in photochemical smog. Among our suggestions on the chemical techniques were tests of bag samples for aging effects that might shift the composition and tests for rotor downwash interference with sampling from a helicopter.

We also offered recommendations on improved data communications. The use of modern computer/telecommunications interfaces could provide a real-time data base of "quick look" assessments of the measurements program. Prescribed standardized data formats would allow analysts to design input/output portions of computer models that would allow fast-response feedback to the field program. This would greatly enhance rapid transmission of the results to the community at large and encourage wider participation in the study.

2.2 SUMMARY OF PREVIOUSLY RECOMMENDED AUXILIARY DATA ANALYSES

The analysis of data taken in previous field programs remains incomplete. Specifically, the measurements made by Scott Research Laboratories in their Los Angeles Basin and New York City programs contain information which could be of use in RAPS planning. Since this information has been available for so long, it is not likely that its analysis will receive much attention. There is valuable information yet to be gleaned from these data. The ultraviolet statistics from both programs should be studied in conjunction with weather records to determine if attenuation of UV radiation due to smog aerosol is a significant feature that should be added to photochemical/diffusion models and to field programs designed to validate them. This is especially true of the airborne ultraviolet data (sparse as it is).

Presumably the composition of the St. Louis atmosphere will be somewhere between that of Los Angeles and New York. (The former is characterized more by photochemical oxidant, and the latter by sulfur dioxide and particulates.) For this reason it seems essential to process the (Scott) New York City data to at least the same extent as we did for the 1968 and 1969 Los Angeles Basin programs.[4] This entails calculating diurnal histories of hydrocarbon reactivity statistics. Profiles of reactivity distribution would show the composition variation of the hydrocarbon as it is attacked. Key ratios give important clues regarding material balances in the atmosphere. We examined CO/NO_x and C_2H_2/NO_x ratios for Los Angeles; however, it would be of interest to add SO_x to the ratio tests for New York City. Some surprising departures were observed in the quasi-equilibrium test, leading to the hypothesis of turbulent mixing interference explained in the appendix. The processing codes for these analyses are still intact and operative from the previous work. It is mainly a matter of identifying the work plan and modest resources needed to complete these tasks.

These same codes can be integrated into the software for a quick-look capability to back up either LARPP or RAPS data acquisition in a real-time mode. With appropriate data links, the various contaminant concentration ratios and reactivity indices can be fed back to the control center to assist in planning future actions and in diagnosing any current problems. Other pre-RAPS analyses should be directed toward a feasibility study for running air quality simulation models nearly in real time, parallel to the program of measurements. Side-by-side calculations using various available models may enhance this aspect of the study by employing a tightly coupled interaction between simulations and field data. The purpose would be to relate the future-time situation map to the present-time situation map in order to deploy mobile sampling units and special test instruments. The real-time operation would, therefore, provide guidance for testing certain special aspects of a model (e.g., pollutant behavior at convergences or division of flow around terrain features). Practically on-line operation of a model is also useful in that it provides a timely assessment of the adequacy of the data base to serve the model development efforts.

3 CONCEPTUAL DESIGNS OF SOME FIELD EXPERIMENTS

3.1 AUTOMOTIVE EMISSIONS ALONG MAJOR HIGHWAYS

The determination of emission rates of the three pollutants CO, HC, and NO_x along major highways can be done in two steps: the first is computational and the second is an experimental verification.

In the computational approach, certain basic measurements must be used for inputs. These basic data are traffic statistics, vehicle emission statistics by model year, and a vehicle age/mileage distribution. The traffic statistics need not be finer than hourly vehicle counts and average traffic speeds; the time resolution of meteorological data is seldom better than this. Ten-minute resolution intervals would be warranted probably for special tests to verify emissions experimentally.

Vehicle emission statistics are usually available in terms of a standard driving cycle. The mean of a sample should be used for each individual model year. Speed corrections and removal of cold-start emissions must be applied to the standard emission factors to approximate more nearly the driving modes on a major highway. This procedure has been well established in our recent EPA evaluation studies of photochemical/diffusion modeling.

An aggregate emission factor is derived from the vehicle age/mileage distribution by taking a weighted average of the mean model year factors. The weighting coefficients are formed from a composite function of both the percentage of the vehicles and the average annual mileage put on a vehicle in the particular age bracket in question. This combination provides the likelihood of finding a vehicle within each age bracket and hence a certain mean emission factor. Multiplying the aggregate emission factor (corrected for cold-start and speed) by the traffic density gives the roadway emission intensities.

Refinements can be applied to this procedure, but the data volume needed would be beyond the scope of most field programs. One of the refinements involves using a traffic velocity distribution function to account for the spread in emissions around that at the mean speed. Another would be to use specially measured mode emission factors (e.g., acceleration from 50 to 60 mph, cruise at 65 mph, and deceleration from 70 to 60 mph) along with mode distributions for the traffic dynamics.

A spot check field program should be used to verify the computational emissions model. This is best done along a stretch of major highway at grade level, with few or no other emission sources nearby, and with a direction nearly perpendicular to the prevailing wind. Simultaneous car counts, traffic speed estimates, meteorological measurements, and air quality measurements should be taken at the chosen site. The objective of the experimental check is to run a mass balance between pollutants in (from computations based on traffic dynamics) and pollutants out. Part of the input will be pollutant advected in. Meteorological measurements and air quality measurements will be taken around the periphery of an Eulerian (ground-fixed) control volume aligned along the roadway. The choice of crosswind conditions eliminates the difficulty of accounting for advection in and out of the ends of this imaginary box.

Assessment of the computational approach will be expressed as a percentage deviation between measured and computed pollutant fluxes. To be sure, this is not an absolute test of the computational approach because the experimental checkout results will also contain some assumptions (e.g., profile shape, quasi-steadiness, and the like). The assessments should be made for a variety of sites, wind speeds, and traffic flows. The computational model may turn out to show systematic biases. For the purposes of emission modeling, such biases may form the bases of correction factors. The use of the computational model for other roadways will, therefore, eliminate the need for further extensive measurements.

3.2 PLAN FOR STUDYING PHOTOCHEMICAL TRANSFORMATIONS*

Since the Lagrangian coordinate frame (moving with the air mass) is intrinsic to air pollution modeling, it seems natural to track an air mass with an aircraft. Previous attempts at this have suffered from basic logistical difficulties. Air traffic restrictions prevented flights at altitudes and headings of interest in some cases. The use of tetroons for marking air movement required visual tracking of the tetroons by a helicopter, which was often impossible because of limited visibility. Consequently, data in previous programs often had a series of air samples being taken along a totally different flight path than that followed by the air.

Remedies to these problems should be implemented in field programs. Use of government aircraft may permit more altitude flexibility than before because of exceptions to flight rules that may be made. Mounting a transponder on the helicopter <u>as well as</u> on each of the tetroons will allow simultaneous tracking by ground-based radar. Differences between the tracking signals can be used to guide the helicopter by voice communication link.

Multiple tetroons flying simultaneously will enhance the certainty as to the mass center location of the air parcel. Also, if a tetroon hangs up on a building or hits the ground, the remaining tetroons can still complete the mission. The auxiliary use of stratified multicolored particulate tracers affords a means of checking out the multi-tetroon approach. The feasibility of these techniques will have been established by the Metronics, Inc., tracer project now under way in the Los Angeles Basin under sponsorship of the state of California.

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*Much of this subsection stems from discussions with Dr. William A. Perkins, Jr., on the experimental designs for LARPP. Consequently, many elements of that program are found here since the documents were written simultaneously.

Although it may still be difficult, the airborne measurement of carbon monoxide is an essential part of the program to follow air parcels. The photochemical modeler uses this information to check out the diffusion portions of his code. The rapidly reactive pollutants are also of interest. It is difficult to list them in any order of importance, but ozone, oxides of nitrogen, and nonmethane hydrocarbons (as an aggregate group) are of interest.

An important adjunct to the flight program should be a highly localized study of the balance among oxides of nitrogen in a three-dimensional Eulerian control volume. This subprogram takes a form closely resembling that of the CO-balance studies conducted by Stanford Research Institute in San Jose, California.[5] The ground area intercepted by the control volume will be selected as one that has an excellent source-emissions data base. The airspace of the "side walls" of the control volume will be selected so that they are readily accessible for helicopter transects. The thermal inputs and terrain near the control volume should be uniform enough that wind data from a multiplicity of stations in the area can be interpreted with some degree of confidence.

Because they may reveal the removal processes, nitric oxide, nitrogen dioxide, nitrous acid, and organic nitrates should be measured in the gas phase in helicopter samples and in samples collected from ground-based fixed intakes near rooftop height. Particulate analyses and test surface analyses* must be made simultaneously to aid in ascertaining the fate of oxides of nitrogen in the urban airshed. Determining this is not only crucial from the standpoint of receptor dosages of certain of these oxides, but is essential to understanding the role of surface reactions in causing ozone buildup by removing nitric oxide (which would react rapidly with O_3 to form $NO_2 + O_2$).

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*Typical urban surface material samples could be exposed and analyzed for NO_x uptake in comparison with unexposed control samples. This could be coordinated with laboratory studies.

3.3 A SPATIALLY INTEGRATED SAMPLING TECHNIQUE

Three reasons present themselves immediately for testing spatially averaged measurements of gas phase pollutants:

1. Photochemical/diffusion models have coarse space resolution; hence, spatially averaged readings afford a more reliable comparison than do highly localized readings.
2. Correlation with health effects demands some degree of averaging over space as well as time to build confidence in the results.
3. Simultaneous collection and mixing from a spatially separated array of sampling inlets can avoid the reaction rate errors due to chemical times being shorter than turbulent mixing times.

The advantages presented by the first two reasons are self-evident, but the merit of the third is somewhat subtle.

Addressing the question of mixing interference with the $NO + O_3$ reaction, we can follow two sampling rules to avoid time averaging errors in computing reaction rates (or conversely in comparing with model-derived average concentrations). The first rule is to take simultaneous mixed samples from points separated by more than the correlation length (integral scale) of the local atmospheric turbulence. The second rule is that the multiple samples must be rapidly mixed and allowed to equilibrate at the ambient temperature and sunlight intensity conditions.

A device that should satisfy the two rules is the OASIS (Octopus Air Sampler In Situ). The OASIS has eight horizontal sampling tubes, each about one meter long, extending radially from a central mixing chamber. The mixing chamber must be transparent to the ultraviolet NO_2 dissociation bands and will contain a nozzle cluster fed by the sampling tubes to assure fast mixing. The volume of the OASIS mixing chamber must be consistent with the steady sampling flow in such a way that photochemical equilibration will be nearly achieved in the typical detention time for a gas element entering the chamber. Samples withdrawn from the mixing chamber can be analyzed with available chemiluminescence detection equipment.

The purpose of the OASIS design is to mix and react uncorrelated samples of a polluted atmosphere. The analysis of the reacted gas mixture will then correspond more nearly to the concentrations predicted by models. If these steps are not taken, the product of time-averaged NO and O_3 concentrations can correspond to much higher reaction rates than those that actually occur (see Appendix).

4.1 ADVANCE PLANNING

The efforts should begin with meetings with the test working group whose responsibilities have been delineated. These meetings will permit the group to plan in detail the test procedures, data collection procedures, data formats, and to fill in any other details and gaps that may exist in the preliminary program design. Each of the agencies that collect data should be visited by the data manager so that the data collection plans can be reviewed and understood. Tape formats must be planned down to the bit level so that programs can be written to extract the data.

Detailed arrangements must be made to provide the program director with quick-look data so that he can determine how well the tests are going and whether to institute changes in the procedures. Even though test procedure design may be conceptually complete, many finishing touches are usually needed to coordinate data acquisition with data management requirements. The data manager must work actively during the planning phase to establish standardized procedures for data acquisition and communication. Moreover, he may provide further assistance in the test program planning outside of the area of data management.

It is extremely important that this task be allowed sufficient lead time, since a great deal of development is required before implementation of computer programs can begin. Many of the programs must be written and completely validated before the beginning of data acquisition.

4.2 REPORTS TO THE PROGRAM DIRECTOR

During the conduct of a field pollutant measurement program, the director must be able to know that optimum procedures have been followed with regard to flight plans, sampling frequencies, and scheduling times. He must also be able to assess the adequacy of sampling data including measurement sensitivity, equipment reliability, and calibration. In ascertaining that each operation has met its specific test objectives, he may find it necessary that certain changes be brought about in the test procedures.

Essential to the achievement of these objectives is a systematic compilation of test results in the form of "quick-look" readable displays that can be provided to the program director very shortly after the collection of the data (preferably within 24-36 hours after each operation). One effective means for displaying this information is an on-line terminal located in the program director's office.

An example of such a terminal is the Control Data 711 Cathode Ray Tube (CRT) Display Terminal. This terminal, shown in Fig. 1, is one of a family of low-cost, stand-alone remote terminals designed for communications with a computer in a conversational mode over telephone lines. This common-carrier compatibility of the 711 Terminal and its freedom from

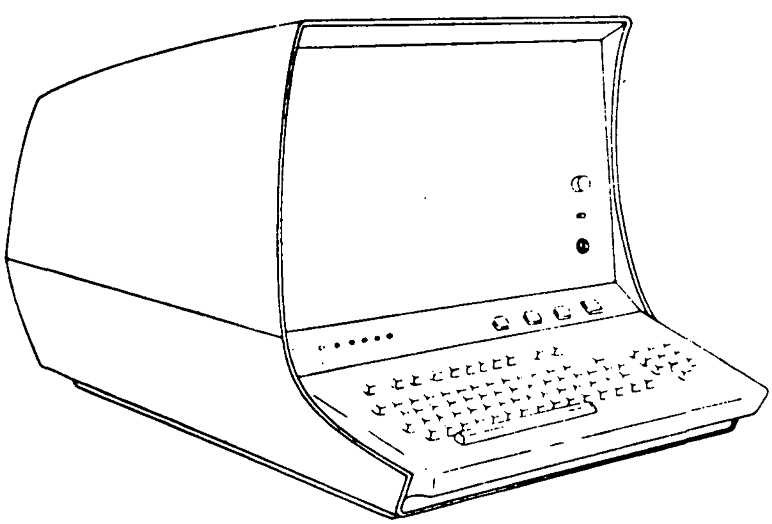

Figure 1. CRT Display Terminal

space-consuming external control units makes interactive computer-communication easy to install wherever there is a telephone outlet.

The keyboard is electronic and has a standard typewriter layout with a 10-key adding-machine-type cluster plus user's choice of additional eight special-function keys for device and communications control.

The CRT is a modified television display module, accepting EIA Standard composite video images from the device's self-contained logic. Characters are dot-formed and generated by TV raster scan. Input is via control interface. Viewing area is 8 inches high by 10 inches wide and displays 16 lines of 80 characters.

4.2.1 Quick-Look Data

If the central element in the program design is a body of helicopter measurements, these data and radar tetroon tracking data should be available to the program director on the shortest possible lead time following the collection of the information. Specifically, flight plan logs, the profiles of tracer concentration, tetroon location with respect to tracer material, carbon monoxide, ozone, nitric oxide, nitrogen dioxide, temperature, and ultra-violet intensity will be provided using data which have undergone preliminary reduction. This means that nominal calibration factors should be used for quick conversion of the raw data into approximate and unedited displays. At the same time, the data will be undergoing full correction and editing. As those results become available, they should be placed in the project director's data file to replace the approximate, unedited values.

Examples of the kinds of displays that could be made available to the program director are shown in the photographs of Figs. 2-7 and are drawn from ideas for the Los Angeles Reactive Pollutant Program.[2] These examples, using fictitious numbers, were created by typing directly onto the display screen.

The following six pages (pre-printed, and thus unnumbered) contain Figs. 2-7.

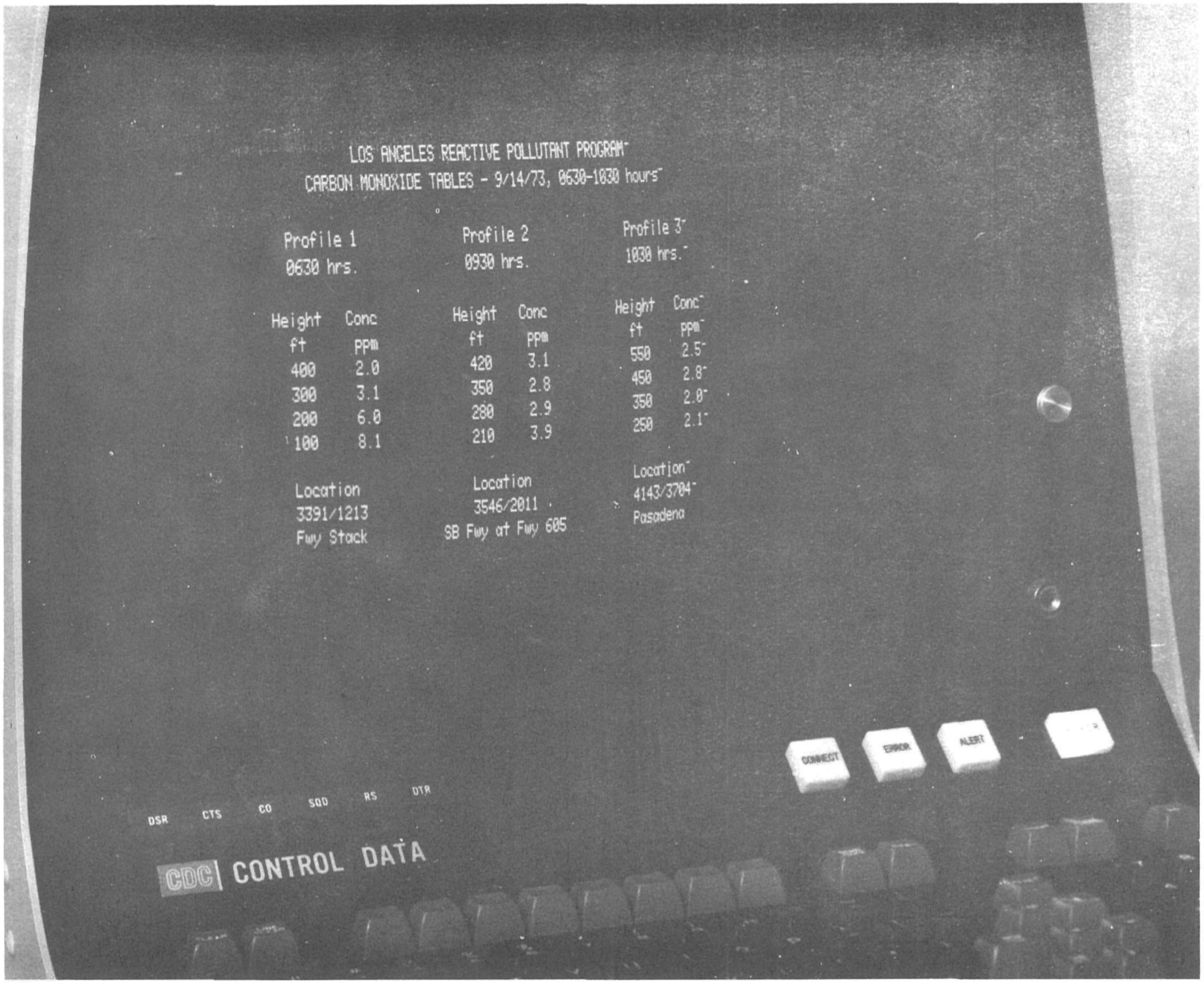

Figure 2. Carbon Monoxide Tables

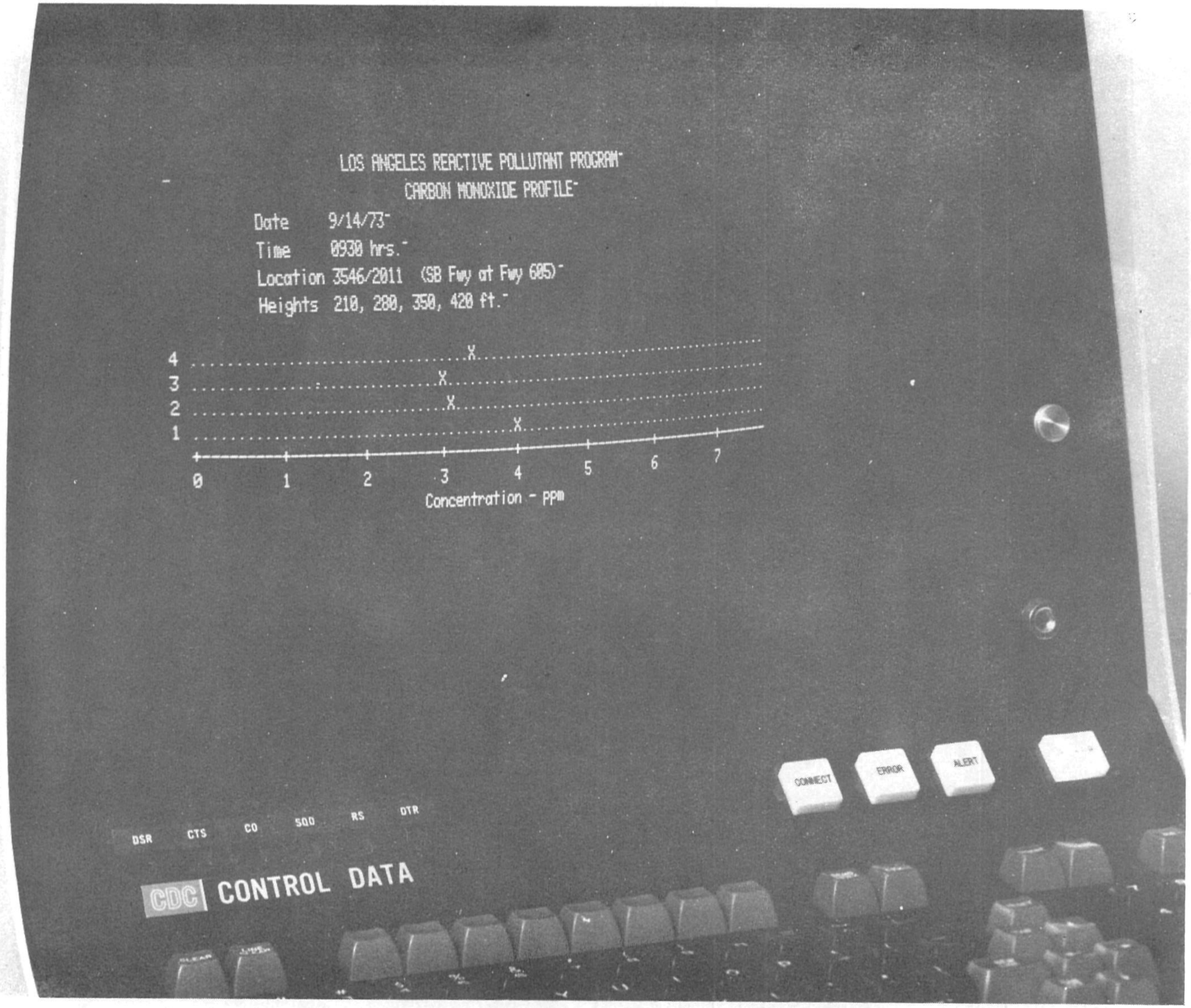

Figure 3. Carbon Monoxide Profile

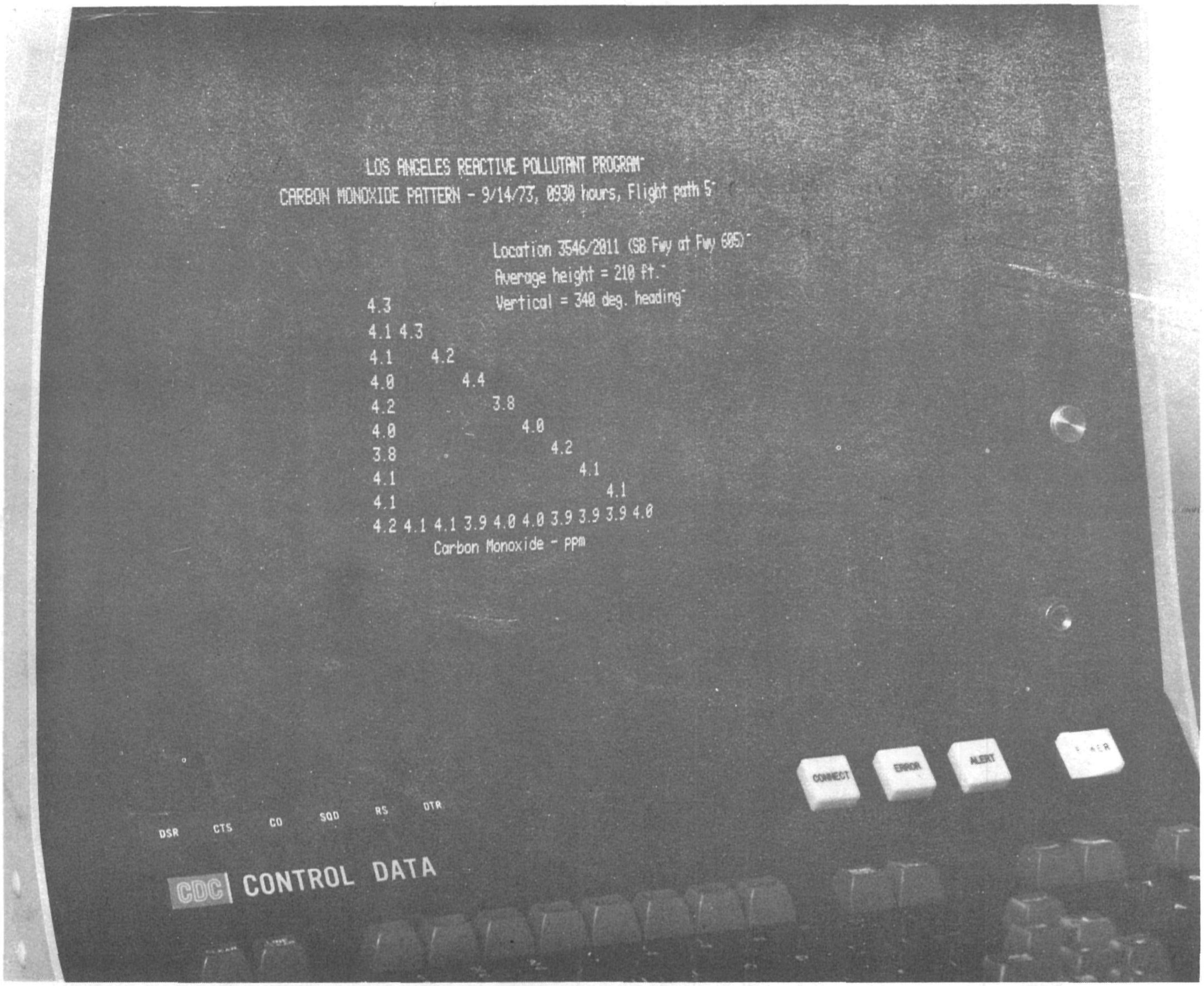

Figure 4. Carbon Monoxide Pattern

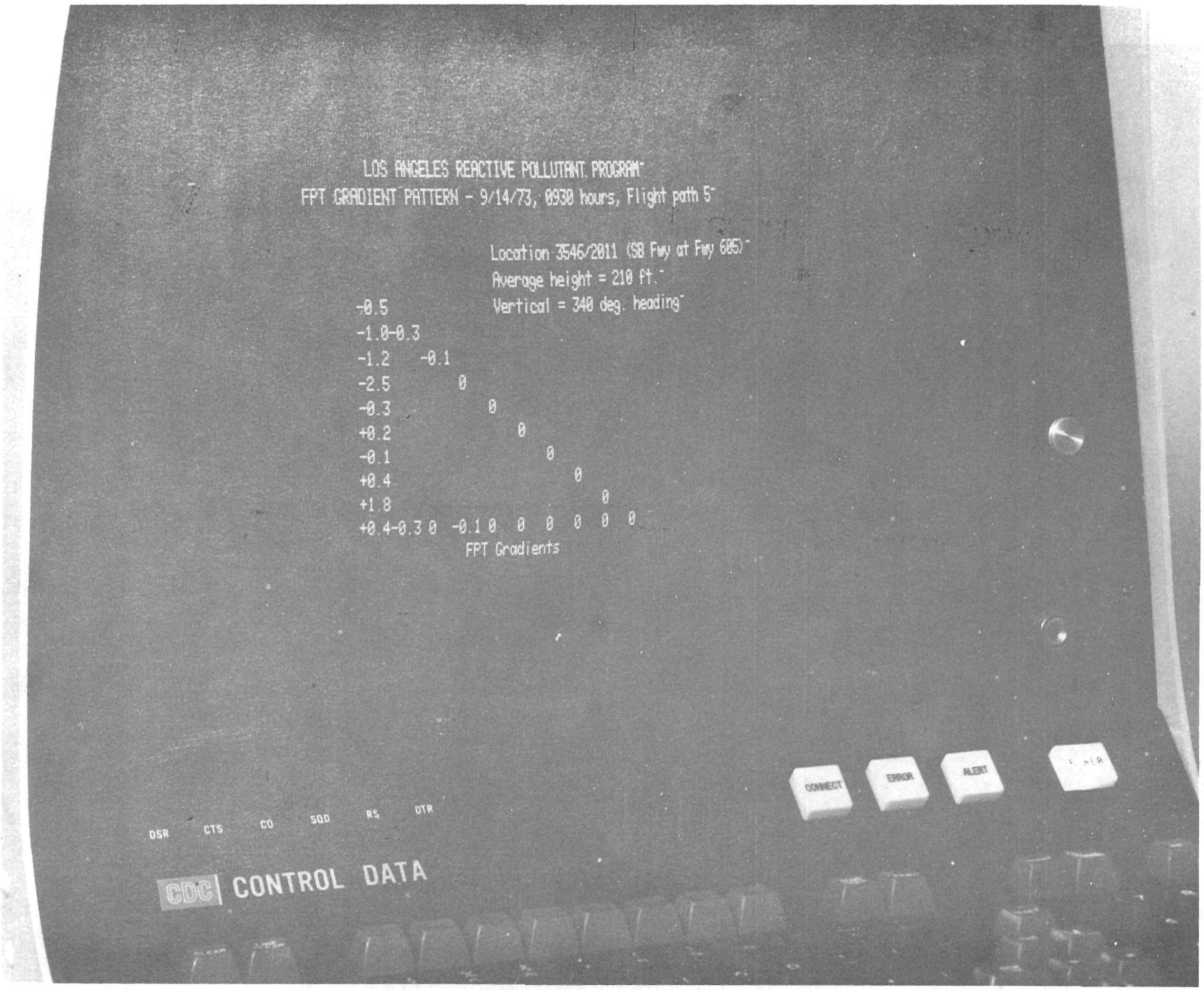

Figure 5. FPT Gradient Pattern

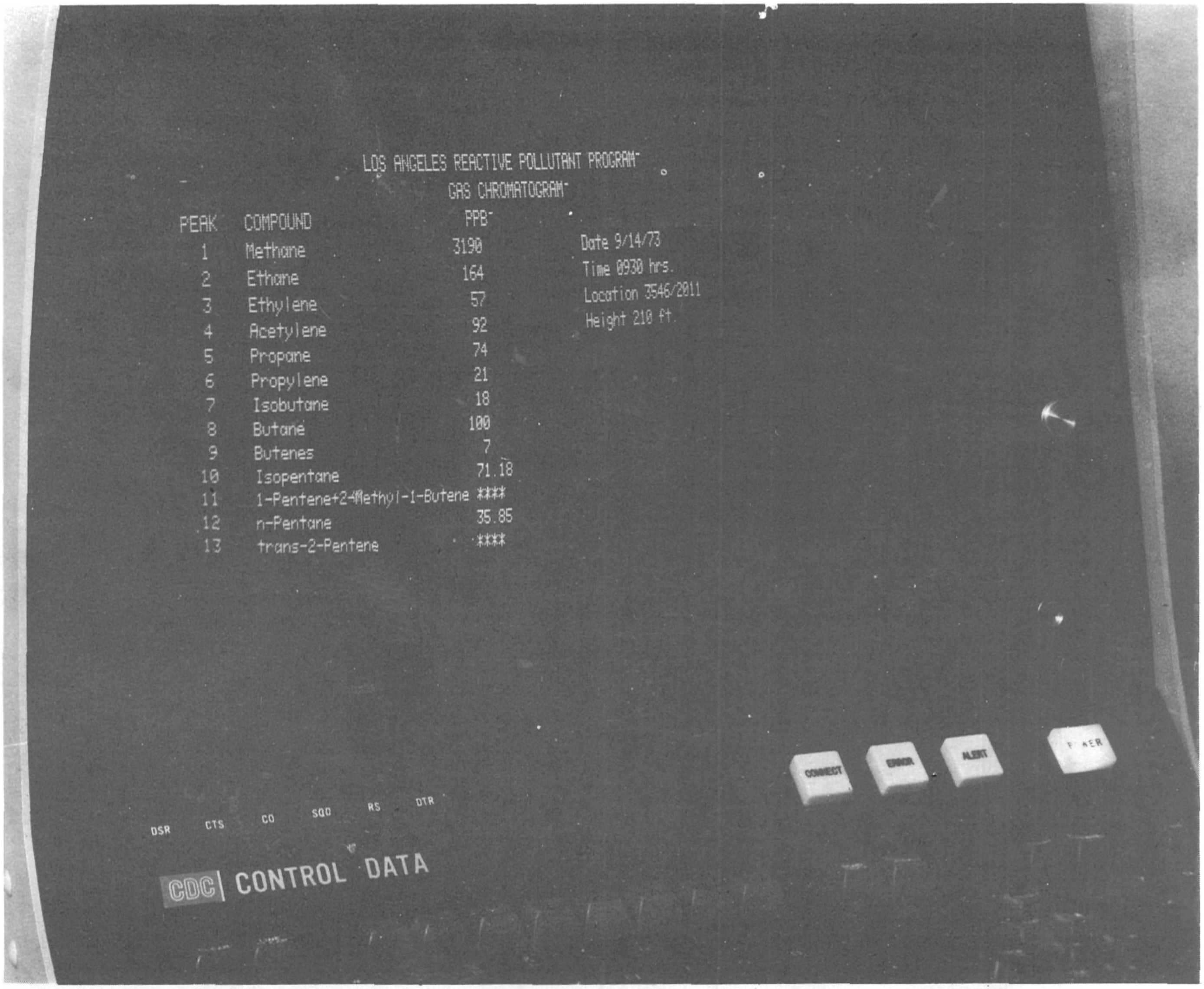

Figure 6. Gas Chromatogram, Peaks 1-13

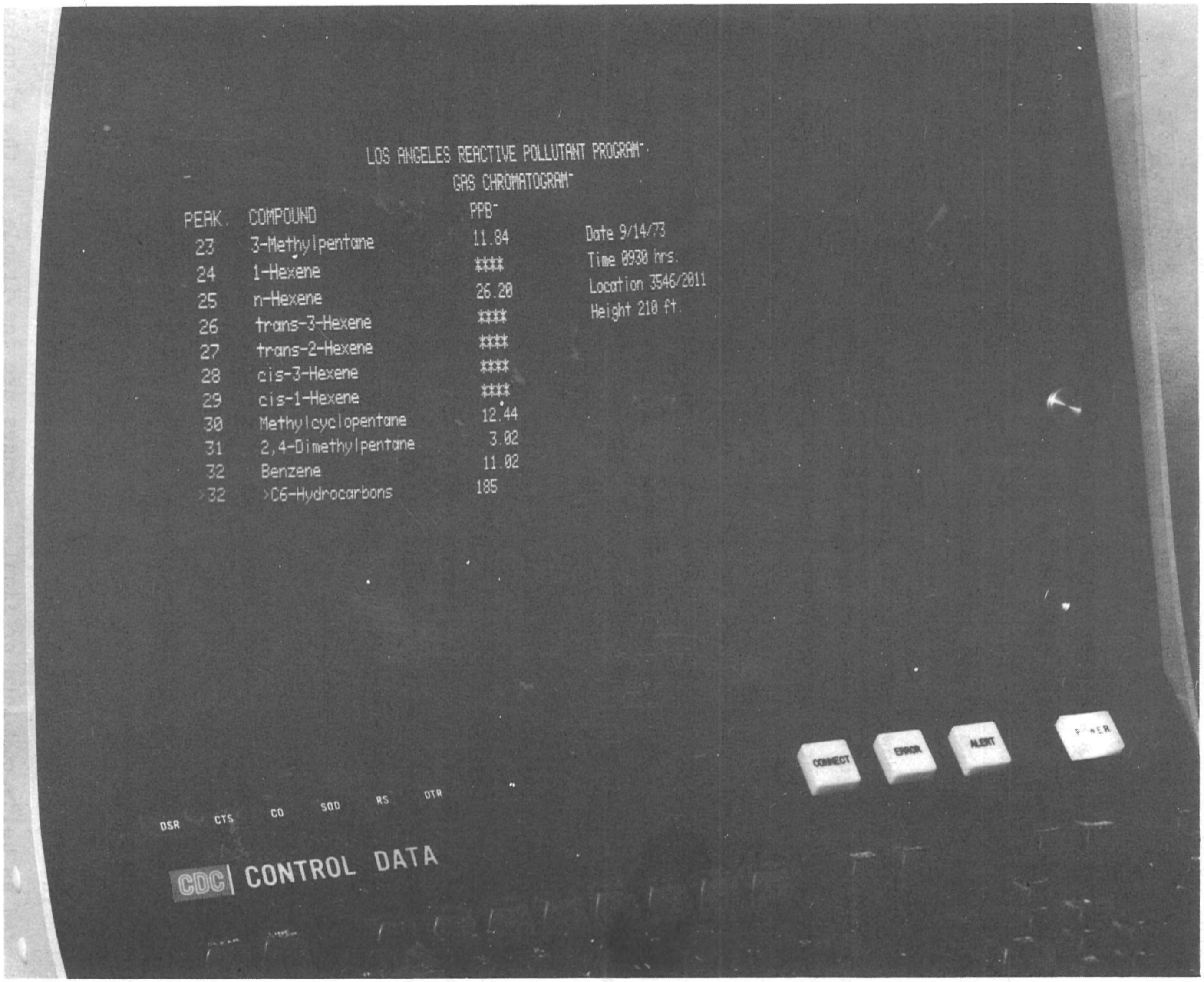

Figure 7. Gas Chromatogram, Peaks 23-32

Figure 2 is a photograph of an actual Control Data 711 CRT display of three carbon monoxide profiles in tabular forms (from helicopter measurements). Headings show identification numbers and times. Below the height-above-ground concentration entries are locational data in the form of coordinates and key words from the helicopter log.

Figure 3 shows a plot option as applied to the second profile tabulated in Fig. 2. Height station is the vertical coordinate and concentration is the horizontal coordinate. The points, each denoted by an "x", are averages of the flight path around the tetroons at each height.

Figure 4 shows more detail for one of the flight paths averaged on the previous figure. The triangular pattern indicates the shape of the flight path (denoted by the identification number "5" in the heading) and the numbers are locally averaged co-readings. If CO levels are recorded every 5 seconds and a leg of the flight path takes 2 minutes, a smoothing and interpolation operation is used to get ten concentration values per leg, as shown. The vertical reference is 340 degrees on the compass for this particular pattern.

The display in Fig. 5 is very similar to that in Fig. 4 except gradients of fluorescent particle tracer (FPT) are shown. The numbers show that the helicopter flight pattern (which is presumably around the centroid of the tetroons) is somewhat to the east of the apparently highest concentration of the FPT cloud. This is clearly an important diagnostic for the project director in planning future flight missions.

Figures 6 and 7 show tabulations of gas chromatographic data. Because of laboratory requirements, this type of information will not be available as rapidly as the helicopter data. Hand-recorded logs add to the communication lag time.

The displays in Figs. 2-7 are given as examples and are not represented as being complete or final. Changes are inevitable in the planning phase of the work when the data manager interacts with the project director to come up with the optimum forms of data presentation for the "quick-look" feedback function.

4.2.2 Data System Procedures

The system proposed could function as follows: The quick-look raw data will be picked up by the on-site data manager and transmitted to a data center. There are several alternative means of doing this. One simple approach is to take it by courier to the processing center.

Some of the quick-look data that are not in machine-readable form. such as the plotted helicopter positions, certain calibration information not on the tapes, and some log information, can be entered into the computer through the on-line terminal by typing the data on the keyboard.

A goal of the data manager (providing the helicopter tapes are made available to him immediately after the tests) should be to have all of the quick-look data entered into the computer by midnight of the test day. Programs can then be run that perform a rough data reduction (how rough is to be determined--perhaps considerable machine editing can be performed at this time), and a merging of data from different sources including data entered via the terminal. The data can be stored in an on-line random-access disk file for use by the program manager on the morning following the test.

The program manager will access the file and obtain displays created from the file by typing certain coded commands on the keyboard of the 711 terminal (which can be on or next to his desk) and sending the commands (simply by pressing a key) to the computer. The computer will then access the required data in the file (if available), format the requested display, and transmit the display to the terminal over the phone line. The on-site data manager can help the program manager as needed.

Details in operations for obtaining the data for both the quick-look file and the archival file must be worked out when more definite plans are finalized by the agencies acquiring the data. In general, the issuance of signed receipts should be required with endorsements any time data change hands. Copies of these receipts will be retained by the data manager, given to the data acquisition agency, and filed in the program office. This will minimize misunderstandings regarding where certain data are in the system.

Another data management function is the provision of project status reports to the program director. These should be statistical in nature, outlining the number of hours flown for the week and for the program. They will also provide information on the time lag between data acquisition and data reduction for all missions. This will highlight any serious scheduling problems to the program director, and will provide him with an up-to-date view of how much of the resources in time and equipment have been expended.

At least four months should be scheduled prior to initiation of the field program to allow for program preparation and establishment of data links for this rapid reporting system that will be provided to the program director. An on-site representative of the data manager should be provided at all times during the operation of the field program. It will be his responsibility to obtain the data from the various agencies and to send it to the data center. As the file of reports is refined and updated, it will be placed in permanent storage so that it will form a part of the modelers' archives.

4.2.3 Computer Program Development

As a part of this task, the data manager must specify, design, code and validate the computer programs that read-in the quick-look data, merge data from various sources, create the quick-look on-line file, and, in response to commands from the terminal, format displays. A telecommunications package will be needed to allow interactive communication with the terminal. The same displays that will be sent to the terminal screen can also be printed on either the printers in the data center or one of the printers attached to various remote terminals in the test area as backup.

4.3 ARCHIVES FOR MODELERS

Investigators who develop simulation models for prediction of air quality generally use two types of data:

1. Input data that specify the needed meteorological parameters.
2. Test data which consist of air quality measurements that the model output must be checked against.

LARPP will be collecting both types of data for the purpose of broadening the base for simulation model development. In performing this task to establish archives for the modelers, machine readable records should be utilized to minimize errors throughout. In this way numerous key punch errors in transcription from printed books will be avoided. Standard magnetic tape files should be used and detailed documentation in catalogs must be provided. As part of this documentation, the measurement methods, the data reliability, the limitations in its use, and calibration information that might affect the application of these results to modeling tests all must be described. The catalog part of the documentation will first provide the modeler with some indication of the types of days and the types of flight programs conducted. Summary graphs and tabulations will provide a guide to the selection of the appropriate tape files. Codes and formats for the tapes will be given in full detail in the documentation so that, using the catalog, the modeler can order the magnetic tapes that are best suited to his purposes.

A number of measurements not represented in the quick-look reports to the program director should be included in the archives files. The aircraft wind field and meteorological data from the fixed-wing aircraft equipped with an INS or doppler system will be included in this file. This will round out the data sample and provide additional information for those modelers who do not utilize a moving coordinate system concept. Also, greater details in the hydrocarbon analysis will be entered in the final version of the data archives. Finally, other data sources may be utilized such as the five CHESS stations and the Los Angeles Air Pollution Control District stations. Lidar information will give further checks on the mixing layer depth and structure if it becomes available. Similar information might be provided by acoustic sounder data. One of the data manager's responsibilities is the editing of these peripheral bits of information as to their relevance and utility to the modeling effort.

The data manager will act as custodian for these archives during the life of the proposed program. At the conclusion of the program the complete documentation and data files that have resulted from the program should be delivered and made available to users.

4.3.1 Data Sources and Volume

In order to size the data management problem we have estimated the total number of data points to be recorded on the archival files. We do not presently have enough information to know how accurate our estimate is, but the estimate serves as a reasonable point of departure.

The estimates given in Table 4.1 show approximately 13 million data points. Assuming an average of 10 BCD characters per data point (a conservatively high estimate), the archival file will contain approximately 130 million characters.

A single 2400-foot reel of magnetic tape recorded at a normal 556 bpi with record gaps can hold about 12 million characters. Therefore the entire file will fit on about 11 reels of magnetic tape. This is the most convenient method of storing archival files. However, if desired, each day can be put on a separate small reel for certain applications.

TABLE 4.1

ESTIMATE OF TOTAL DATA POINTS PER DAY IN LARPP

Data Source	Rate	Duration	Quantity	Records	Variables per Record	Data Points[†]
Helicopters	1800/hr[*]	6.4 hr	2 helicopters	23,000	~15	~345,000
Radar	120/hr	6 hr	3 targets	2,160	5	10,800
Fixed Wing	8400/day[**]	---	1 plane	~8,400	6 (t, θ, z, V, T, H_2O)	~50,000
Van	200/hr	6 hr	1 van	1,200	14 (t, x, y, FPT, UV, O_3, NO, NO_2, CO, HC, SO_2, nephelometer, T, H_2O)	~16,000
Bag Samples	30/day	---	---	30	37 (t, x, y, z, 33 peaks)	1,140
Other Sources	---	---	---	1,000	10 ---	10,000
Totals per day				35,790		433,000
Totals per 30 days				1,000,000		13,000,000

[*] Data every 2 seconds for 20-minute profile, up to three profiles per hour.

[**] Assumes 700 miles per sortie, one sortie per day, 12 measurements per mile.

[†] Includes one extra point per record for record type and index information.

4.3.2 Archival File Format

The archival file should be on magnetic tape. The retrieval program, described later, could generate records for users on seven-track tape with a variety of selection and formatting options.

One possible format of the file is as follows: The file will be a serial file ordered by time. Each day's file will consist of (1) a header record giving the date and other pertinent information, (2) a time-ordered series of data records from all sources, followed by (3) a series of log entry records.

The data records from each source will have this format:

Time	Record Type	Indexes to Log Entries	Variable 1	Variable 2	. . . .	Variable n

The Record Type indicates the source of the data and the data record type. For example, a record from the radar could be designated as Record Type No. 1, and could have as Variable 1 the object the data is on (e.g., tetroon 1), Variables 2, 3, and 4 could be the position. A different record type would contain data from the helicopters. For fast processing, each record type has a fixed number of variables in a fixed format. (If it turns out to be required, in some cases a variable-length format can be used.) Variables for which data is missing are filled in with a "no data" character.

The Indexes to Log Entries point to appropriate records containing the third type of information stored on each day's file, the log entries. These records contain text from the various logs that were produced during the day. For convenience in data processing, it is recommended that all log entries have a prescribed format consisting of (1) time of entry, (2) text of any kind, (3) a code that indicates which type of data records are affected (e.g., an "H1" to indicate that the records from helicopter

1 are affected), (4) a list of the variables that might be affected, and (5) the beginning and end times during which the log entry affects data.

The reason for the above information is so the data entries can be automatically keyed to the log entries that might affect the data. During retrieval of data for a particular modeler, the appropriate footnotes (in the form of log-entry text) can then be automatically retrieved for just the data that the modeler requires.

The proposed variable-length format for the log entries is:

Log Entry Number	Time	L_1	Text	T_1	T_2	R	V_1	. . .	V_n	$

where Log Entry Number is a unique number assigned by the computer to each log entry for the day

Time is the time of the log entry

L_1 is the variable length of the text

T_1 is the first time this log entry applies

T_2 is the last time this log entry applies

R is the record type number to which this log entry applies

V_1, ..., V_n are the variables to which this record applies

R is a delimiter

Additional sets of record types and variables can follow the delimiter (represented here by $), each set separated by a delimiter.

The <u>Log Entry Number</u> is the same number that appears in the data records called "Indexes to Log Entries." These indexes are generated automatically by the computer from the trailing information in the log entries.

The reasoning behind the proposed organization of the archival file will become more evident under the later discussion on data retrieval.

4.3.3 Supplementary Data Files

Two additional archival data files should be constructed along with the principal file described in the previous subsection. Both of these files will be in essentially the same format and can be created at relatively small additional expense. One of the files will contain all raw data from the field measurement program; the other will be a much abbreviated file containing the smoothed (and possibly interpolated) data that many modelers will require.

Following most field measurements programs, the raw data are set aside and frequently lost unless some conscious effort is made to preserve and catalog these files. There is no better time for this activity than during and following the program itself. Usually the experimenter is so busy with the operational and logistical aspects of the program that this detail is overlooked. It is for these reasons that the data manager should create and maintain a raw data bank. This raw data bank will provide a source of basic information to those who would investigate special aspects of the field program at some future date. For example, it may be discovered that a certain type of interference occurred in one piece of instrumentation. With the raw data and all of the independent measurements, it may be possible to correct and refine even further the information that was obtained during the program. Also, in the course of evaluating the data for modeling purposes, it is sometimes useful to be able to go back to the original raw data. The accomplishment of this task would begin by preparing and designing a record structure that would contain the various types of data that are collected and recorded. The information included may, for practical purposes, be limited to the information recorded on magnetic tape or on punched paper tape.

It might be anticipated that since the retrieval system can smooth certain data, different modelers will need the same smoothed data. Rather than perform the same smoothing operations over and over, or requiring each modeler to smooth his own data, there should be a much shortened file of selected smoothed data.

4.3.4 Retrieval of Archival Data

An archival data bank is useful in direct proportion to the flexibility and quality of the retrieval programs. The above file and record structure is designed with convenient and versatile retrieval as the uppermost criteria.

Retrieval programs are needed to permit the modeler to access only those parts of the data required in the format desired. After consulting the archival-file documentation, the modeler will specify (1) the day(s) of interest, (2) the start and end times during the day(s) of interest, (3) the record types of interest, and (4) the variables of interest. Then a tape will be created using one of the options described below that contains exactly the data requested. Because of the data log indexing method described above, the log entries that pertain to the data requested, and only the data requested, will also be included on the modeler's tape.

Several options should be made available to the modeler so that the data are in a form most useful to him. These options include (1) within the requested time span get all of the actual data in the selected records every time it appears in the data bank, (2) get actual data at the recorded time nearest to a desired time (e.g., request data every 10 minutes, get actual data at a closest time available to 10-minute rate), (3) get interpolated data at exact time increment specified, (4) get interpolated data that has also been smoothed.

4.3.5 Documentation

The documentation of the archival tapes should describe each test day in detail, preceded by an appropriate summary. This summary describes the experimental design objectives and details the types of data obtained. A discussion of experimental data accuracy aids the modeler in using the archives to the best advantage. A data catalog shows tetroon trajectories, helicopter positions, and coarse concentration data. It includes log comments on the day's operations and certain meteorological data. The data available on the archival tapes are described in detail, including types of files on the tapes.

A separate section (or volume) describes the formats of the archival files in detail, and emphasizes a treatment of the available retrieval capabilities and the simple steps that modelers need to follow to extract the required data.

4.3.6 Data Security

Whenever a data bank is being created and stored, procedures must be instituted to ensure that the data are not irretrievably lost by any of the many ways data banks are destroyed: fire, riot, sabotage, stray magnetic fields, operator error, etc. The data manager should make two copies of each source data and store the extra copy in a secure place. All lost tapes can then be recreated from the copy. If the data manager is permitted to keep and store the original tapes, then these should be stored in the secured area rather than copies. In no cases should original data tapes be used for other than making copies.

4.3.7 Computer Program Development

The data manager will specify (in cooperation with appropriate agencies), design, code and validate all of the software required to perform this task, including reading and formatting software for the various sources, creation of the data files, and software to perform the retrieval functions.

5 BRIEF OVERVIEWS OF FUTURE FIELD PROGRAM OBJECTIVES

5.1 DEFINITION OF THE ROLE OF AEROSOLS IN ATMOSPHERIC CHEMISTRY

Those modelers who have been engaged in photochemical validation tests over the past several years have noted deficits in the gas-phase oxides of nitrogen. A worthwhile goal of any field program is a systematic search for the pathways whereby NO_x leaves the gas-phase system. Certainly this has received attention in the smog chamber work, and we have now reached the point where field programs can no longer ignore this problem. Two gas-solid reaction possibilities immediately come to mind regarding the fate of NO_x. One involves the aerosol and the other surfaces on or near the ground. Rough calculations of nitrate in aerosol suggest that these effects cannot account for much of the loss. Urban surfaces, however, may take up much of the oxides of nitrogen before they mix upward.[6]

Aerosol formation causing reduced visibility is probably the most obvious manifestation of photochemical smog. The physicochemical phenomena governing these reactions should be investigated in sufficient detail at least to give a bulk reaction rate to put in air quality simulation models. A broad recommendation in this area was recently drafted and adopted by the Photochemistry and Transformation Modeling Panel at the Third AEC/EPA Chemist Meteorologist Workshop (Ft. Lauderdale, Florida, January 15-19, 1973). The recommendation is:

> It is recommended that models be tested by field measurements. For aerosols these measurements should include (a) light scattering (b) concentration in terms of particle number density (c) concentration in terms of mass per unit volume (d) particle size distribution, and (e) composition (significant for heterogeneous catalysis, health effects, or as needed to test models). For gases the measurements should include (a) identification of chemical compounds and (b) concentrations. The meteorological measurements will include (a) temperature (b) turbulence (c) relative humidity and (d) wind vector. Vertical

distributions should be obtained. The measurements will be made with respect to both a ground-fixed and air-fixed coordinate system. It is important that the measurements attempted in any given field program be limited to the needs of the program and be sufficient to test the model involved.

Another particulate interaction of potential significance is attenuation of ultraviolet radiation. The attenuation goes up with decreasing wavelength so that even though total solar input is only slightly reduced, shorter wavelengths in the NO_2-dissociation band may be cut down. Certainly some data exist on this from previous Los Angeles basin programs. They must be analyzed prior to designing new field experiments.

5.2 FURTHER UNDERSTANDING OF GAS PHASE PROCESSES AFFECTING REACTION RATES

Nonuniformities in concentrations arise because of incomplete mixing in the atmosphere. Non-zero correlations between fluctuations of reactant species-pairs lead to errors in chemical calculations if the reaction-time is smaller than (or equal to) the mixing time.[6] The large effects of this interference were exhibited by the 1969 Los Angeles data and were documented in our 1970 data analysis report.[4] It must be an objective of any second-generation field program (such as LARPP or RAPS) either to investigate this effect in detail or to circumvent it by devising physical arrangements that average properly over space or time (like the OASIS sampling technique described in Sec. 3). The 1973 AEC Chemist-Meteorologist Workshop drafted and adopted the following recommendation that was suggested by presentations by G. Hilst and by A. Eschenroeder:

> Turbulent mixing corrections to reaction rate terms should be evaluated. Spatial nonuniformity in the gas phase concentration may lower the reaction rates of species that are being mixed together; this behavior is expected at plume boundaries. In models this must be reflected as a "mixedness" correction.

As developments in basic theory become available, it will be necessary to approximate certain terms. For example, in a second-order closure scheme for two reactive species, there can be nine partial differential equations to be solved. For a ten-species mechanism, more representative of atmospheric chemistry, there can be 120 such simultaneous differential equations. A laboratory program should be conducted in parallel with the model improvements to test the validity of turbulent reaction theory.

Efforts should be directed toward the development of new transport and diffusion formulations that are suited for reacting gas flow.

The possibility of using wind tunnels to physically model diffusion and the behavior of chemically reactive systems should be thoroughly investigated.

APPENDIX

THE DEPENDENCE OF APPARENT REACTION RATES ON TURBULENT MIXING PROCESSES

A.1 INTROCUTION

Heterogeneities appear in the atmosphere as sources emit gases that take some time to mix on a microscopic scale. Large blobs of newly emitted gas break up into smaller blobs by the turbulent cascade mechanism. When small enough scales are attained, molecular scale diffusion smears out the nonuniformity. If the emitted pollutant is a potential atmospheric reactant, this final microscopic mixing must take place before the reaction can begin. If the reaction is fast compared with mixing, then the rate of reaction is controlled by the turbulent cascade process. Consequently, if concentrations of reactants are averaged over many turublent blobs (as they are in most models), the reaction rates calculated from these average values can be greatly overestimated. The overestimation occurs because the calculation assumes that the reactants are homogeneously mixed. In this appendix we assess the significance of the inhibition of reactions by turbulent mixing process in atmospheric photochemical calculations.

Our specific approach is the calculation of the parameter called r which is a ratio of reeaction time to mixing time. (This is simply the reciprocal of the first Dämkohler number for the convective and diffusive structure of the turbulence.) If r is smaller than unity, mixing can be the rate controlling process and inhomogeneities can cause errors in the reaction rate calculation. If the reverse is true, then the reaction is not hindered seriously by mixing (the greater r is than unity, the less is the hindrance).

A.1.1 Atmospheric Kinetics and Concentrations Typical of Photochemical Smog

Recent extensions of our earlier work[7] on photochemical diffusion simulation suggest that the lumped-parameter mechanism in Table A.1 gives a high degree of consistency for atmospheric modeling. The main improvement is the addition of hydroxyl radical reactions which are now thought to dominate the organic chains.

Although Donaldson and Hilst[8] assign concentrations of 1 ppm to each species, it is preferable to use observed and calculated values for a polluted atmosphere. The levels in Table A.2 will be used to evaluate r in this appendix.

A.1.2 Calculation of Turbulent Mixing Time

Mixing time consists of two components: one for the convective breakup of large inhomogeneities into fine structure; and another for diffusive smearing of fine structure into homogeneity. The first process needs to occur before the second one can proceed. We will show here which one is rate-controlling and how long the total mixing process takes.

The convective breakup time is easily estimated by using turbulence cascade time[9] τ_c given by

$$\tau_c \simeq k^{-3/2}E^{-1/2} \tag{A.1}$$

where k is turbulence wave number and E is the turbulence energy spectrum function. The highest intensity of large scale inhomogeneities is at the spectral peak. Using the peak properties we can relate E and k to bulk variables of the turbulence. A turbulence spectrum solution[15] gives the following values at the peak:

$$k \simeq 2/\Lambda \qquad \text{and} \qquad E \simeq u'^2\Lambda/5 \tag{A.2}$$

TABLE A.1

PHOTOCHEMICAL KINETIC MECHANISM FOR ATMOSPHERIC POLLUTION

Rate constants are in $ppm^{-1} \cdot sec^{-1}$ except where noted

	Reaction	Rate Constants Used in Model: Early Time	Rate Constants Used in Model: Late Time*	Sources
1.	$h\nu + NO_2 \rightarrow NO + O$	8.3(-4)***	$5.0(-3) sec^{-1}$	Ref. 10
1a.	$O + O_2 + M \rightarrow O_3 + M$	$2.2(-7) ppm^{-2} sec^{-1}$		Ref. 11
2.	$NO + O_3 \rightarrow NO_2 + O_2$	4.4(-1)		Ref. 12
3.	$O + HC \rightarrow 8RO_2$	4.6(0)		**
4.	$OH + HC \rightarrow 8RO_2$	1.7(+2)		**
5.	$O_3 + HC \rightarrow RO_2$	6.7(-5)		**
6.	$RO_2 + NO \rightarrow NO_2 + (1/8)OH$	1.7(+3)		**
7.	$RO_2 + NO_2 \rightarrow PAN$	3.3(0)		**
8.	$OH + NO \rightarrow HONO$	2.5(+1)		Ref. 13
9.	$OH + NO_2 \rightarrow HNO_3$	5.0(+1)		Ref. 14
10.	$h\nu + HONO \rightarrow OH + NO$	3.1(-6)	$1.9(-5) sec^{-1}$	**
11.	$NO + NO_2 \xrightarrow{H_2O} 2HONO$	1.7(-5)		**
12.	$NO_2 + O_3 \rightarrow NO_3 + O_2$	8.3(-5)		Ref. 10
13.	$NO_3 + NO_2 \rightarrow N_2O_5$	7.5(+1)		**
14.	$N_2O_5 \rightarrow NO_3 + NO_2$	2.3(-1)		Ref. 10
15.	$N_2O_5 \xrightarrow{H_2O} 2HNO_3$	$1.0(0) sec^{-1}$		**
16.	NO_2 + particulates $\rightarrow$ products			

*Early time refers to 0630-0700 LST and late time to ∿1300 LST. Photochemical rate constants are continuously varied with the solar zenith angle; therefore, values given for photolysis rates are typical for the times shown only.

**Where values are either uncertain or unreported, estimates are made based on smog chamber results.

***Parentheses after a number are defined as follows (a) ≡ × 10^a, i.e., 8.3(-4) = 8.3 × 10^{-4}.

TABLE A.2

MEASURED AND MODELED POLLUTANT CONCENTRATIONS IN THE LOS ANGELES BASIN

Species	Typical Concentrations in ppm	
	Early Time (0630-0700 LST)	Late Time (1300 LST)
NO	1(-1) to 5(-1)	1(-2)
NO_2	2(-1) to 4(-1)	1(-1)
HC	5(-1)	1(-1) to 2(-1)
RO_2	1(-8)	1(-6)
OH	1(-8)	1(-7)
HNO_2	1(-2)	1(-2)
NO_3	1(-8)	1(-7)
N_2O_5	1(-8)	1(-6)
O_3	2(-3)	2(-1) to 4(-1)

where Λ is the longitudinal integral scale and u'^2 is the mean square fluctuation velocity. Therefore

$$\tau_c \simeq 4\Lambda/5u' \tag{A.3}$$

In the atmospheric boundary layer, the RMS fluctuation velocity is 20% or 30% greater than the friction velocity,[16] and the scale for energy-containing eddies is approximately 20% of the height above ground:

$$u' - 5u^*/4 \tag{A.4}$$

For the lower atmosphere, an RMS fluctuation of 40 $cm \cdot s^{-1}$ is typical so that $\tau_c \simeq 4$ s at a height of 10 meters.

The time τ_d for diffusive smearing of fine structure may be estimated as one random-walk time scale over a dissipation length

$$\tau_d \simeq \lambda_d^2/2D \tag{A.5}$$

where λ_d is a dissipation length scale and D is the molecular diffusion coefficient. Priestley[17] points out that λ_d is about fifteen[18] length scales so that

$$\lambda_d \simeq 15\nu^{3/4}\varepsilon^{-1/4} \tag{A.6}$$

where ν is kinematic viscosity and ε is the turbulence dissipation rate. Since $\varepsilon \propto u'^3$ and $\lambda_d \propto u'^{-3/4}$, we can derive a velocity scaling law to get Priestley's empirical curve for a 5 ms^{-1} wind speed down to 1 ms^{-1} which is more typical for a day with high air pollution. Because air Schmidt numbers are near unity, $D \simeq \nu \simeq 15\ cm^2 \cdot s^{-1}$. At 10 meters above the ground this gives us $\tau_d \simeq 63.5$ s.

A.13 Calculation of Chemical Time

In calculating r for a multicomponent mixture, each species can be assigned a chemical time that can be defined by the concentration divided by absolute value of the reaction rate. Donaldson and Hilst[8] applied their binary mixture model to reactions occurring in a multicomponent system. They thereby had an r for each reaction. The species actually mix and react (rather than the reactions); therefore, it seems physically meaningful to define an $\dot{r}$ for each species.

The use of species chemical times requires that we compute only the binary or tertiary reaction terms since those are the ones that can be affected by inhomogeneities. For stationary state species, both forward and reverse rates are large but their difference is small. In these cases, we used averages between absolute values of forward and reverse rates. It should be noted that the expected stationary state balances are not precisely satisfied by using the concentrations in Table A.2 in the mechanism in Table A.1. This is to be expected because the concentrations were assigned only rough order-of-magnitude values in the cases of highly active species.

A.1.4 Discussion of Values of r

Table A.3 gives values of the r-parameter. Only hydrocarbon, nitrogen dioxide, and nitrous acid vapor are relatively unaffected. It is significant that Reaction 2 can affect either nitric oxide or ozone with respect to hindrance by insufficient mixing. This is in contrast to the findings of Donaldson and Hilst who employed a rate constant a few orders of magnitude smaller.

This finding has considerable consequences for predicting pollutants in photochemical smog because Reactions 1 and 2 are the dominant inorganic

TABLE A.3

RATIOS OF CHEMICAL TIMES TO MIXING TIMES AT 10 meters HEIGHT IN A 1 $m \cdot s^{-1}$ WINDFIELD

	Early Time (0630-0700 LST)	Late Time (1300 LST)
NO	1.6(+1)	1.2(-1)
NO_2*	5.0(+2)	2.6(+2)
O_3	1.2(-1)	3.3(0)
O	3.1(-7)	3.2(-7)
HC	8.3(+3)	4.0(+2)
RO_2	4.4(-5)	2.2(-4)
OH	8.1(-3)	2.6(-2)
HONO*	1.9(+3)	1.3(+3)
NO_3	1.1(-3)	8.9(-4)
N_2O_5	1.2(-3)	1.7(-2)

*Only binary reactions were considered in chemical times.

cycle. Indeed, we have cited[6] atmospheric observations made several years ago in the Los Angeles basin which tend to bear this out. Figure A.1 shows the logarithm of the rate ratio of Reaction 1 to Reaction 2.* It is plotted versus ozone level. Photochemical quasiequilibrium theory would say that the ratio should be near unity (i.e., the logarithm should be near zero); however, we have surmised that inhomogeneous effects inhibit Reaction 2 enough to drive the points distinctly negative at high ozone levels. This could occur because of fresh NO being introduced into an atmosphere high in ozone, but no reaction takes place until they are intimately mixed. It is described in our paper cited above how Mast meter inaccuracies, NO inaccuracies at low NO-levels, reaction interferences, and sampling tube dark reactions can all be eliminated as causes of the large departures. Although positive evidence is not yet available, the small values of r(i.e., 1.2×10^{-1}) for either NO or O_3 suggest that turbulent inhomogeneities are responsible for the apparently anomalous behavior.

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*Reaction 1a is so fast that an ozone molecule forms almost immediately following a photolysis of a nitrogen dioxide molecule.

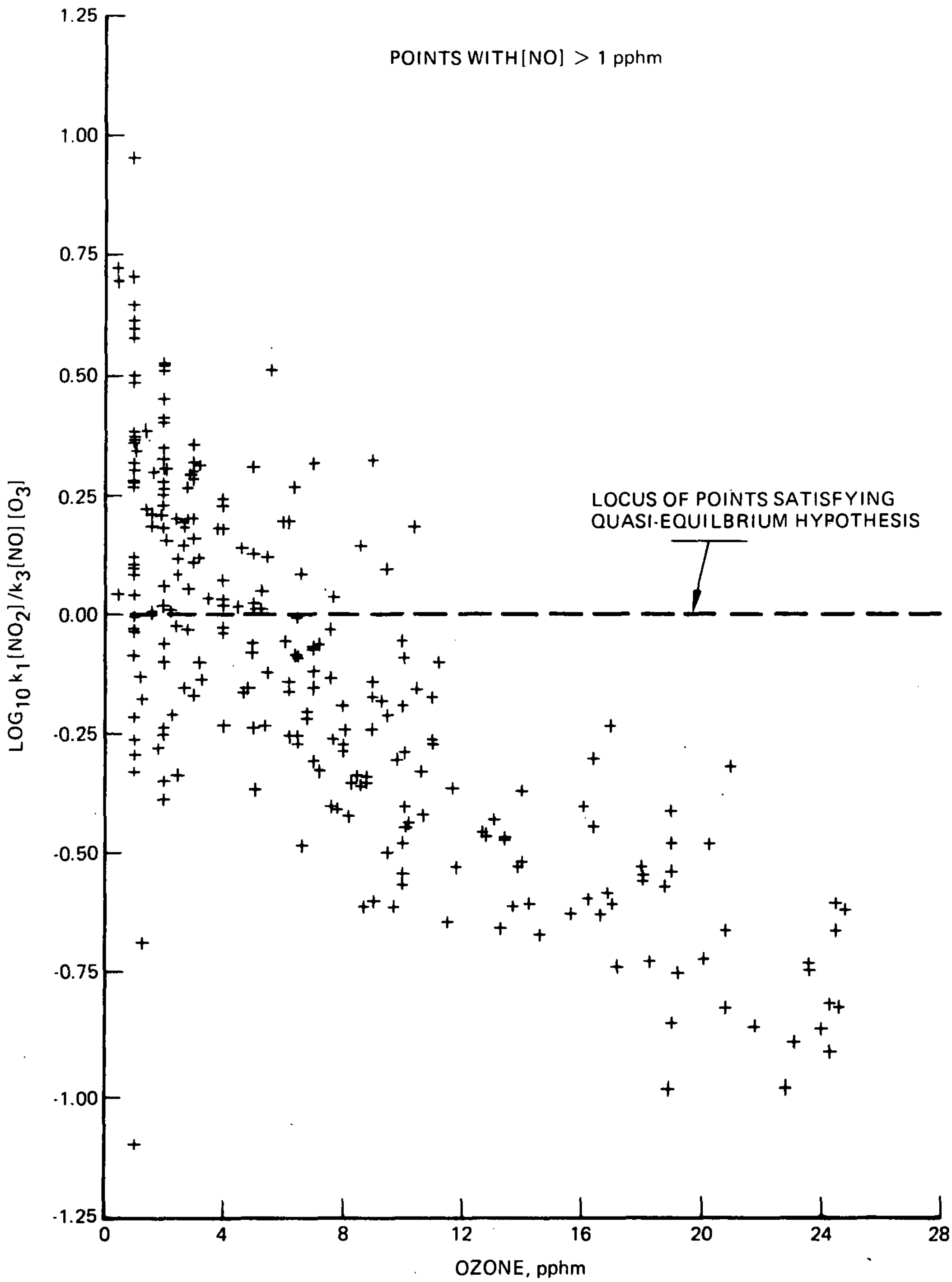

Figure 8. Possible Turbulence Effects on the Ozone Quasiequilibrium for 1969 Ground Data at El Monte--High NO Levels

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16. Abstracts

Carefully designed experimental measurement programs are necessary to the task of collecting the extensive data base needed for testing air pollution models. In this paper a series of recommendations is offered as input for field measurement programs. These recommendations update and refine suggestions made earlier. Some specific techniques and instrumentation are called for in certain cases, but in others only conceptual objectives are set forth. The report presents three specific conceptual plans. A description is presented of a data management system using the Los Angeles Reactive Pollutant Program (LARPP) as a prototype. It is concluded that future field programs must be structured to meet specific goals. The specific goals discussed here include verifying emissions models for vehicle populations, following photochemical transformations in a moving air mass, searching for turbulent reaction inhomogeneities in the atmosphere, and characterizing the interaction of gas phase species with aerosols.

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