INVESTIGATION OF ATMOSPHERIC DISPERSION PROBLEMS BY MEANS OF A TRACER TECHNIQUE

Thesis by

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To Sue,

who pulled up her roots

in my pursuit of knowledge.

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(With apologies to Bob Dylan)

You don't need a weatherman
to know which way the wind blows.
(All you need is sulfur hexafluoride.)

ABSTRACT

The purpose of this thesis was to extend the capabilities of an existing atmospheric tracer technique and to demonstrate the sensitivity and usefulness of this technique by investigating a number of complex atmospheric dispersion problems. These problems ranged from a fairly small scale of about one meter to a quite large scale of about 100 kilometers. The tracer used was sulfur hexafluoride, an inert non-toxic gas detected by means of electron-capture gas chromatography; the air sampling and analysis techniques were developed to permit a minimum detection limit of one part SF_6 in 10^{12} parts of air. Four main atmospheric dispersion problems of environmental significance were studied in detail: ventilation systems in buildings; air flow within the wake downwind of a building; dispersion from an urban highway; and large-scale transport and dispersion over the Los Angeles area.

Tracer experiments involving SF_6 were used to obtain quantitative data regarding actual residence time distributions in rooms and hallways, and contamination caused by reentry of laboratory fume hood hood exhausts into a building. Application of a mixing factor was found useful in room ventilation tests, and measured values ranged from 0.3 to 0.7 in small rooms without fans. In one experiment with a roof fume hood exhaust located only 16 feet from the main ventilation intake of a building, 20% of the fumes exhausted were found to reenter the ventilation system.

Sulfur hexafluoride was used to probe the air flow within the wake downwind of a 12 meter high, three-story building. A reverse-flow circulation was observed with a longitudinal extent downwind of about three building heights; the extent of the recirculation on the roof was confined to less than one-half the width of the building from the downwind edge. The recirculating velocities in the wake were estimated to be about 0.1 - 0.3 those of the prevailing wind at the top of the building. The wake downwind of the building was found to be well-mixed in all three dimensions and exhibited a characteristic exponential dilution time of approximately one minute.

A number of quasi-instantaneous line source releases of SF_6 were made by an automobile moving along an urban highway in Los Angeles. Concentrations at various distances from 0.4 km to 3.2 km downwind of the highway were recorded at ground level as a function of time. The tracer data were used to test the validity of several theoretical models which can be used in predicting the dispersion from an instantaneous crosswind line source. The model based upon the semi-empirical turbulent diffusion equation, using a power-law vertical velocity profile and a power-law vertical eddy diffusivity profile, was found to provide the best agreement with the data.

Finally, sulfur hexafluoride was used as a tracer in a large-scale test over the urban region near Los Angeles. On July 19, 1973, 33.5 kg of SF_6 was released over a period of 45 minutes from the city of Anaheim. The transport and dispersion from Anaheim was traced in five neighboring communities including Palm Springs, which at 124 km away was the furthest location tested. A preliminary analysis of the data indicated that the cities of Riverside and Palm Springs possibly lie in a direct path of the pollutant transport from Anaheim.

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PROPOSITION

1. INTRODUCTION

1.1 Philosophy of thesis

Of great practical concern on a number of scales is how atmospheric contaminants from real sources spread and dilute over distances and in time. However, in many cases air flow is so complicated that theoretical solutions of the governing fluid mechanics equations prove intractable. Experimental tracer studies become a necessity in these cases, providing basic concentration data for the formulation of new ideas and equations describing the dispersion process.

The purpose of this thesis was to extend the capabilities of an existing atmospheric tracer technique, sulfur hexafluoride, and to demonstrate the sensitivity and usefulness of this technique in studying a wide range of complex environmental air flow problems. In contrast with a normal dissertation, the emphasis was not on studying one small problem in great detail, but rather on demonstrating the sensitivity and breadth of the tracer technique. Four main atmospheric dispersion problems on a number of scales were studied in some detail, and in addition, four minor tracer studies were made. The extreme sensitivity of the tracer, which could be measured at one part in 10^{12} parts of air, was necessary in the larger scale tracer tests. As an example of the sensitivity of this technique, if only 100 pounds of SF_6 were allowed to evenly disperse up to a height of 1/4 mile, the tracer could be detected over an area of 8000 square miles, which is approximately the area of the state of Massachusetts.

A large amount of theoretical work has been done concerning atmospheric turbulence and diffusion, with an emphasis on formulating prediction models for the spreading and dilution of pollutants. However, before any theory of atmospheric dispersion can be considered valid, it must be compared with experimental observations of a tracer substance which moves and disperses with the main air flow. As Monin and Yaglom(1) state in their largely theoretical treatise on turbulence: "the theory developed in the preceeding section will be relevant only when certain elements of the fluid are marked; that is, have some properties which are distinguishable from the properties of the surrounding fluid."

1.2 Atmospheric structure

1.21 Stability

Before various atmospheric dispersion theories can be discussed, some basic facts about the structure of the atmosphere must be known. Due to the large length scales involved, atmospheric flow is almost always turbulent. Above a certain height known as the planetary boundary layer, frictionless flow can be assumed; the resulting wind, known as the geostrophic wind, is the result of a balance between the horizontal pressure gradient and the Coriolis force due to the earth's rotation. The planetary boundary layer is of the order 500-1000 meters,(2) and various methods of estimating this height have been proposed.(3,4) Close to the ground, approximately 50-100 meters in height, is the surface boundary layer, where frictional forces dominate and constant shear stress can be assumed.

Flow in the planetary boundary layer is greatly influenced by the vertical temperature gradient. If transport processes occur adiabatically in dry air, the thermodynamic result is an adiabatic temperature lapse rate equal to about -1° C/100 meters. An atmosphere with this temperature gradient is called neutrally stable or neutral. A negative vertical temperature gradient larger than the adiabatic lapse rate results in unstable conditions; a negative temperature gradient smaller than the adiabatic one results in stable conditions. A positive temperature gradient, in which the temperature increases with height, is known as a temperature inversion. Edinger(5,6) discusses in some detail the characteristics of the temperature inversion layer which occurs over the Los Angeles basin.

Pasquill(7) has defined six general stability categories, A-F, which have received widespread use: class A represents very unstable conditions, class D corresponds to neutral stability, and class F represents very stable conditions. These stability categories can be very easily determined from estimates of only wind speed and amount of insolation. A more meaningful estimate of the stability condition is from the variance or standard deviation of the horizontal wind direction, since this quantity is directly related to the intensity of turbulence. The variance of the wind direction can be easily calculated from the output of a recording wind vane. Luna and Church(8) have shown that the Pasquill stability categories correspond fairly well to stability conditions determined by the standard deviation of the wind direction.

1.22 Velocity profiles

Various vertical velocity profiles have been proposed within the planetary boundary layer. In general, they can be divided into two classes, those which include the effect of the Coriolis force due to the earth's rotation and those which neglect this effect. If the Coriolis force is included, wind profiles are obtained which are not unidirectional, but turn with height. For example, in the classic Ekman spiral velocity profile,(9) the wind direction at the ground is at a 45° angle from the geostrophic wind direction. However, due to their complexity, such profiles are rarely used to model atmospheric dispersion problems; studies have shown that the Coriolis effect is negligible for distances less than about 25 km.(10,11) Normally, wind velocity profiles are assumed which have a height dependence but flow in one direction only, neglecting the Coriolis effect.

The simplest velocity profile is one which is unidirectional and constant with height; this very simple profile has received widespread use in atmospheric diffusion theories. In the surface boundary layer, where constant shear stress can be assumed, a logarithmic velocity profile derived from dimensional analysis has been shown to fit wind data quite well under neutral stability conditions and over flat land.(12,13) This profile is usually written in the form

$$u = \frac{u_*}{k} \ln \left(\frac{z+z_o}{z_o} \right) \tag{1}$$

where u_* is the friction velocity, k is von Karman's constant, and z_o is the roughness parameter of the surface. A simple method for estimating the roughness parameter z_o has been described by Lettau.(14)

For non-neutral stability conditions, a similarity argument has led to a so-called "log-linear" velocity profile,(15,16) usually written as

$$u = \frac{u_*}{k}\left[\ln\left(\frac{z+z_o}{z_o}\right) + \frac{\alpha z}{L}\right] \tag{2}$$

where α is a constant and L is the Monin-Obukhov length, a parameter which is positive for stable conditions, negative for unstable conditions, and goes to infinity for neutral stability. This velocity profile has been shown to be fairly accurate under stable conditions,(17) but not very accurate for unstable conditions.(13,18)

Power-law velocity profiles have been introduced in order to have a simple expression which will hold throughout the planetary boundary layer:

$$u = a\ z^p \tag{3}$$

Deacon(19) assumed that the exponent varied with stability conditions. Experiments by DeMarrais(20) over rough terrain showed that Deacon was right; the exponent p increased with increasing stability. Jones et al.(21) have shown that a power-law profile applies over an urban area (Liverpool, England); p was found to be about 0.2 in neutral conditions and increased linearly with increasing stability. Theoretical work(22) has also demonstrated that the exponent p should increase with increasing stability.

A comparison of the velocity profiles in equations (1), (2), and (3) is shown in Figure 1. As can be seen, a typical logarithmic profile can be represented quite well by a power-law profile with a 1/7 exponent. Likewise, a typical "log-linear" velocity profile under stable conditions (positive L) can be represented quite well by a power-law

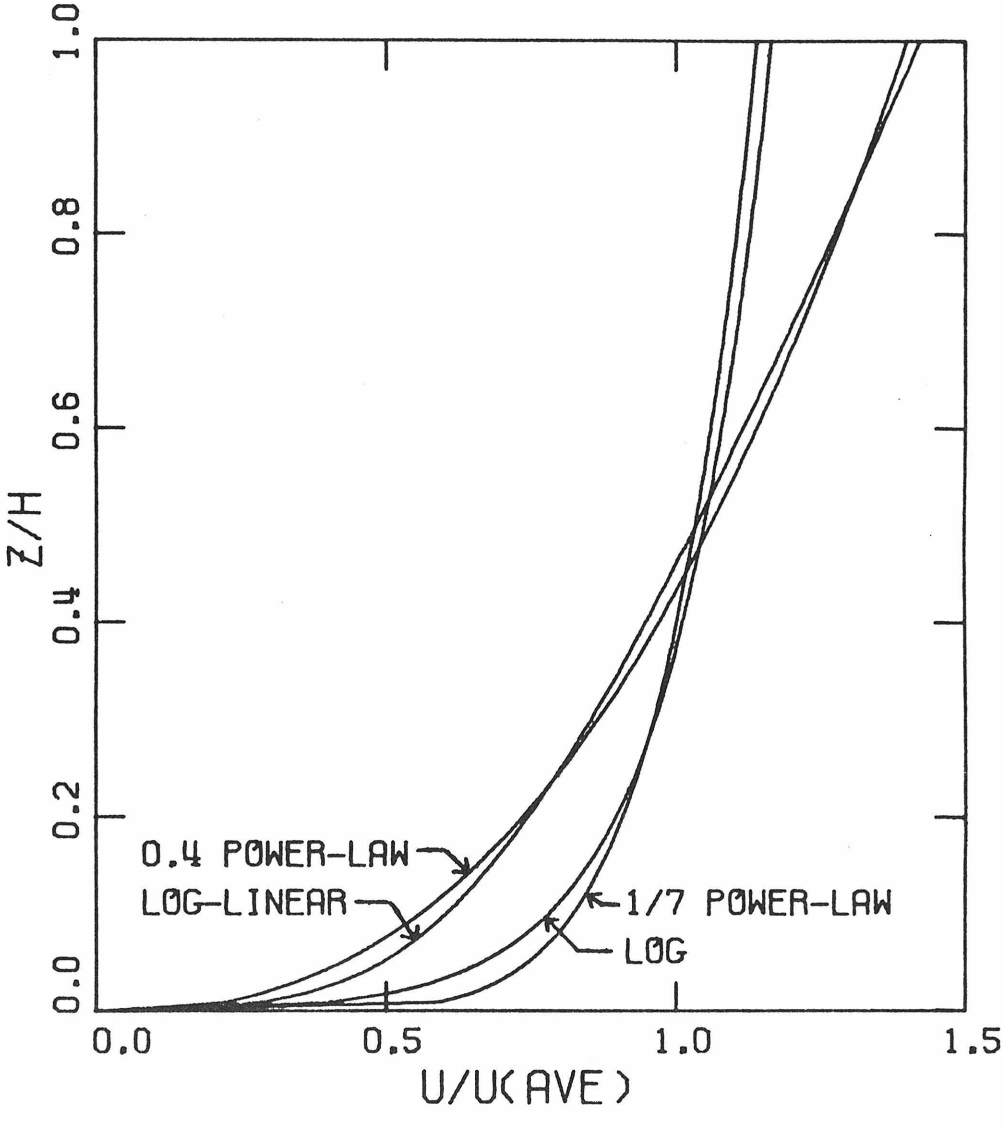

Figure 1. Comparison of vertical velocity profiles.

profile with a 0.4 exponent. It should be noted that with increasing stability, velocity profiles approach a linear dependence with height; with decreasing stability, a profile which is constant with height is approached.

1.3 Atmospheric diffusion theories

1.31 Gaussian plume model

In general, models for predicting atmospheric dispersion of pollutants can be divided into two classes: those which assume that concentrations vary in a Gaussian manner, commonly known as Gaussian plume models, and those which use the concept of an eddy diffusivity, commonly known as K-theory. Reviews of atmospheric dispersion theories have been presented by Slade(23) and Hoffert(24). The validity of any theoretical model must of course be tested by comparison with experiment.

The Gaussian plume model has been attributed mainly to Pasquill(7, 25) and Gifford,(26) although Cramer(27) had earlier suggested an almost identical modeling scheme. A typical Gaussian plume equation for ground-level concentrations from a continuous point source is

$$c = \frac{Q}{\pi \sigma_y \sigma_z \bar{u}} \exp \left[- \left(\frac{y^2}{2\sigma_y^2} + \frac{h^2}{2\sigma_z^2} \right) \right] \tag{4}$$

where Q is the source strength, h is the source height, $\bar{u}$ is the average wind velocity, and σ_y and σ_z are the standard deviations of the plume concentration in the crosswind and vertical directions respectively. This model assumes a wind velocity which is constant with height and downwind distance. Values of σ_y and σ_z for continuous point source releases are tabulated as empirical functions of downwind distance and stability conditions.(28,29) Gaussian equations similar to equation (4) can be written for instantaneous or continuous point, line, and area sources.

This model has received widespread usage in the analysis of experimental tracer data and in the prediction of atmospheric dispersion of pollutants. Tracer experiments involving continuous point source releases over relatively flat terrain have shown good agreement with the model.(23) Gaussian plume equations have been used to predict pollutant concentrations from a highway,(30) and have been extensively used in urban diffusion models involving multiple sources.(31-37)

1.32 K-theory

The other widely used approach is the gradient transport assumption applied to the equation of turbulent diffusion, commonly known as K-theory or the semi-empirical turbulent diffusion equation.(1) Neglecting molecular diffusion, and using time-averaged velocities and concentrations, the basic equation is

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} + w\frac{\partial c}{\partial z} = \frac{\partial}{\partial x}\left(K_x \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial c}{\partial z}\right) \qquad (5)$$

where K_x, K_y, and K_z represent the eddy diffusivities in the x, y, and z directions respectively. Although atmospheric turbulence cannot be accurately described by a gradient transport process, this approach has received widespread use because of its generality. Analytical and numerical solutions of equation (5) can take into account different velocity and eddy diffusivity profiles, various boundary conditions, varying ground terrain, and the addition of chemical reactions. A good summary of the application of K-theory to atmospheric dispersion can be found in Monin and Yaglom.(1)

Analytical solutions of equation (5) have in general been confined to steady-state, unidirectional flow with the assumption of various velocity and eddy diffusivity profiles(38-45) or simple unsteady-state diffusion with no advection.(46,47) Dilley and Yen(48) derived an analytical solution for steady-state flow with the addition of a locally-induced vertical velocity due to the urban heat-island effect. Heines and Peters have presented analytical solutions of steady-state flow with the addition of a temperature inversion aloft(49) and the addition of a first-order chemical reaction.(50)

Saffman(51) introduced the use of moments in analyzing the unsteady-state case and derived results for the spread of an instantaneous source using power-law velocity and eddy diffusivity profiles. Saffman's analysis has been extended,(52,53) and other analyses using moments have considered a logarithmic velocity profile with a linear eddy diffusivity,(54) an Ekman spiral velocity profile with constant K_z,(55, 56) and a log-linear velocity profile with a constant-stress equivalent eddy diffusivity.(57) Numerical solutions of equation (5) have considered complicated eddy diffusivity profiles and varying ground terrain.(58-63) With the addition of chemical reactions, numerical solutions using the K-theory concept have modeled photochemical smog formation in urban areas.(64-67)

There are some practical problems in the application of the eddy diffusivity concept to atmospheric diffusion problems. First of all, values of eddy diffusivities and vertical K_z profiles are not known accurately. As Richardson(68) observed in 1926, the value of the eddy diffusivity depends on the length scale involved. Values of eddy diffusivities have been determined experimentally by correlation of fluctuating velocity components,(69-72) by dispersion of balloons,(73,74) and from naturally-occurring radon-222 concentration profiles.(75-78) A technique involving electrical measurements of the air has been suggested.(79) A review of experimental values of eddy diffusivities on a number of scales has been presented by Bauer.(80)

One problem of experimental measurements of eddy diffusivities in the planetary boundary layer is the fact that K_z is not constant but must vary with height, increasing from zero at ground level and decreasing to zero or a small value at the geostrophic wind level, since frictionless flow is assumed there. A large number of theoretical K_z profiles which apply throughout the planetary boundary layer have been proposed.(9,81-89) Another problem in the use of K-theory for atmospheric dispersion calculations is the fact that values of eddy diffusivity are highly dependent on stability; Guedalia et al.(78) found that K_z values varied from 10^3 to 10^6 cm^2/sec depending on the vertical temperature gradient.

1.33 Other theories

In addition to the Gaussian plume model and the K-theory model, a number of other theories have been proposed for the prediction of atmospheric dispersion of pollutants. Sutton(90,91) in 1932 proposed a model similar to the Gaussian plume model, but including an empirical stability parameter which could be related to the velocity profile; for some reason, this model never received widespread acceptance. Use of dimensional arguments in the surface boundary layer has resulted in what is commonly known as Lagrangian similarity theory;(92-94) however, due to unknown functional relationships, this theory is very difficult to apply to atmospheric dispersion experiments.

Hanna(95,96) has proposed a very simple model for estimating dispersion from urban sources, namely that the concentration of pollutant is simply proportional to the source strength divided by the average wind speed. A good review of mainly empirical formulas for the calculation of the rise of hot pollutant plumes has been presented by Briggs.(97) A large amount of work has recently been done on numerical simulation of atmospheric turbulence without resorting to the eddy diffusivity assumption; Orszag and Israeli(98) present a review of this work. Bullin and Dukler(99) recently used a Monte Carlo method to numerically simulate turbulent diffusion and found good agreement with experimental dispersion data.

1.4 Review of tracer techniques

1.41 Particulate tracers

Many different types of tracers have been used to experimentally study atmospheric dispersion. Following the comments of Pasquill,(100) tracer techniques can be divided into three general categories: optical outline methods, trajectories of individual markers, and chemical tracer substances which disperse along with the flow. The earliest tracer experiments(25) at Porton, England in 1923 used smoke as an optical tracer; a smoke cloud was photographed at different times to establish plume dimensions. Oil-fog, a dense black smoke, has been commonly used in optical outline tracer tests.(101-103) Probert et al.(104) used a soap bubble solution as a visual tracer to study the wakes behind cylindrical tanks. The problem with optical outline methods is that they are limited to close distances from the source and dilution factors can be only roughly estimated from photographs.

The trajectories of balloons equipped with radar transponders can be individually followed over fairly long distances. Neutrally-buoyant tetrahedral balloons, commonly known as tetroons, have been used as individual markers in tracing air currents over the Los Angeles basin;(105-107) the shift from land to sea breeze can be clearly seen. However, balloons can be used for only wind speed and direction data; information on the dilution of pollutant concentrations is not possible.

For accurate dilution information, chemical tracer substances which disperse along with the main flow must be used; they can be divided into two general categories, particulates and gases. Probably the most widely used tracer substance has been a fluorescent particulate one, a mixture of zinc and cadmium sulfide,(108) sometimes referred to simply as FP tracer. After release of the tracer, the analysis involves drawing an air sample through filter paper, and then under ultraviolet light, counting the number of fluorescent particles trapped on the filter paper. Zinc-cadmium sulfide has been used as an atmospheric tracer over flat rural land,(109-111) over mountainous terrain,(112) and over various cities: Los Angeles,(113) San Francisco,(114) St. Louis,(115,116) Ft. Wayne, Indiana,(117,118) and Johnstown, Pennsylvania.(119) Sehmel(120) used zinc sulfide as a tracer to measure particle resuspension from an asphalt road caused by automobile traffic.

Although it has been widely used as a tracer, the use of zinc-cadmium sulfide should decline for two reasons. One is that the tracer has been classified as toxic,(121) "which limits its use in heavily populated areas." Spomer(122) has presented a detailed discussion and others(123-125) have commented on the toxicity hazard of zinc-cadmium sulfide. The other problem with this tracer is that the particles settle out; comparison of zinc-cadmium sulfide with gaseous tracers has shown that at distances of 60-70 km, 50% to 80% of the particles had been lost.(126,127)

Another commonly used fluorescent particulate tracer is uranine dye;(128-131) the collection and analysis procedure is similar to that for zinc-cadmium sulfide. Particulate tracers have been used which are simply collected on an adhesive substance and counted under a microscope; these have included lycopodium spores(132-134) and glass microspheres.(135) Particulates which serve as ice nuclei have been proposed as atmospheric tracers; these have included silver iodide(136,137) and lithium stearate.(138) Detection is accomplished by drawing an air sample into a cold chamber and counting the number of ice crystals which form.

The use of tree pollen and ragweed pollen has been suggested as a naturally-occurring atmospheric tracer for studying dispersion over the ocean.(139) One study used as a tracer particulate matter generated from large-scale field burning in the Willamette Valley in Oregon.(140) An interesting particulate tracer which has been studied is the use of either antimony oxide powder(141,142) or indium oxide powder.(143,144) After air samples are collected, they are irradiated with neutrons in a nuclear reactor; concentrations are determined by the amount of a radioactive isotope (antimony-122 or indium-116) which has formed.

1.42 Gaseous tracers

Gaseous tracers have a distinct advantage over particulate tracers since they do not settle out due to gravitational forces. Radioactive gaseous tracers which have been used have included argon-41,(145-148) krypton-85,(149-151) xenon-133,(126) and tritiated water vapor.(152) Argon-41 emitted from a stack at Brookhaven, New York was traced for 160 miles over the ocean.(146) The use of various radioactive tracers in testing small-scale ventilation problems has been reviewed by Gerrard.(153) The problem with radioactive tracers is, of course, that they cannot be used over populated areas. Even when used in dilute amounts for testing the ventilation in a room, the experimenter must monitor concentrations remotely from another room.

Sulfur dioxide, since it is released continuously from power station smoke stacks, has been used to monitor dispersion downwind of a power plant.(154-156) Problems included sensitivity of measurement and interference from existing background SO_2 concentrations. A well-known tracer test commonly referred to as Project Prairie Grass used SO_2 as a tracer over flat prairie land near O'Neill, Nebraska in 1956.(157) Sulfur dioxide has also been used as a tracer in wind tunnel studies of dispersion around buildings.(158,159) A recent study suggested measuring sulfur-32 to sulfur-34 isotope ratios with a mass spectrometer as a method for tracing stack emissions of SO_2.(160) This method is dependent on the fact that the isotope ratios in the fuel are different from those in the ambient air.

In small enclosures, high levels of tracer gas concentration can be introduced in order to overcome sensitivity problems in the analysis. Various tracer gases with low sensitivity have thus been used to test ventilation rates in structures. Helium has been used as a tracer gas to determine the infiltration rate of outside air into a closed house;(161,162) sensitivity is such a problem that the house must be initially filled with 0.5% helium in order to follow its change with time. Helium has also been used as a tracer gas in wind tunnel studies of turbulence.(163,164) Nitrous oxide (N_2O) has been used as a tracer to test ventilation in a mine(165) and in a hospital room.(166) Lidwell and Lovelock(167) used various evaporated organic solvents detected by ultraviolet absorption as tracers for studying ventilation rates in rooms.

2. EXPERIMENTAL TECHNIQUE

2.1 Electron-capture detector

Recent advances in analytical chemistry have made possible extremely sensitive measurements of certain gaseous halogenated compounds. The principle of detection is based on the fact that these gases have a very high affinity for capturing electrons, and thus if these gases are introduced into a small electric current, the measured current will decrease. Schultz(168) in 1957 used a simple concentric electrode detector to measure concentrations of freon-12 (CCl_2F_2) from a field tracer release. Lovelock and Lipsky(169) in 1960 introduced a detector with a radioactive source which provided a low electron density, and thus a greatly increased sensitivity. This electron-capture detector was soon improved by pulsing the applied voltage to allow more efficient capture of electrons.(170) Use of this detector has grown steadily in gas chromatography studies, principally in the area of detection of halogenated pesticides. Lovelock(171) and more recently Aue and Kapila(172) have presented good reviews of the operation and applications of the electron-capture detector in gas chromatography.

There are two electron-emitting radioactive sources which are commonly used in electron-capture detectors, tritium and nickel-63. Tritium, which is fairly inexpensive, is normally chemically bonded to a titanium substrate, however this source has the drawback of emanation of tritium gas when operated at temperatures above 200° C.(173,174) Recently, a scandium substrate for tritium has been proposed which can be operated at 300° C with negligible tritium loss.(175,176) Nickel-63, which is a solid, is normally used for high temperature operation in pesticide work. Promethium-147 has been proposed as an alternative radioactive source which has properties similar to nickel-63, but is much less expensive.(177,178) Shoemake et al.(179) have proposed other candidates for radioactive sources in electron-capture detectors: technetium-99, radium-226, and americium-241; these sources can all be operated at high temperature, but are relatively expensive.

The operating characteristics of the electron-capture detector are not completely understood at the present time. Chen and Wentworth(180) have noted that for some compounds the detector temperature can affect sensitivity by a factor of 10^3, while for other compounds the detector temperature does not affect sensitivity. A number of studies have examined optimum operating conditions for the electron-capture detector,(181-184) however some of these studies are contradictory. For example, using a nickel-63 source and argon-methane carrier gas, Simmonds et al.(181) found that the standing current decreased with increasing temperature; in a similar study, using the same source and carrier gas, Devaux and Guiochon(182) found that the standing current increased with increasing temperature. Recent studies(185,186) have shown that very small quantities of oxygen or water vapor in the carrier gas can have a large effect on the electron-capture detector; Van de Wiel and Tommassen(185) very carefully excluded any oxygen from entering a nickel-63 detector and found that the standing current was independent of temperature.

2.2 Sulfur hexafluoride as a tracer gas

Tabulation of the sensitivity of the electron-capture detector for a large number of halogenated compounds(187) showed that sulfur hexafluoride, an inert non-toxic gas, had one of the highest responses. Simmonds et al.(188) have demonstrated that optimum pulsing of an electron-capture gas chromatograph can lead to a detection limit of 2×10^{-13} parts SF_6 per part of air. Clemons et al.,(189) by concentrating SF_6 in an activated charcoal trap, showed that sensitivity could be increased to one part in 10^{14}. Sulfur hexafluoride is chemically inert at normal temperatures and is stable to ultraviolet light;(190) it is extremely insoluble in water.(191,192)

Lester and Greenberg(193) have demonstrated that sulfur hexafluoride is non-toxic. Animals were exposed to atmospheres consisting of 80% SF_6 and 20% O_2 for periods of 16 to 24 hours; no indications of intoxication, irritation, or any other symptoms were observed during the exposures or at any time thereafter. Eagers(194) has concluded that SF_6 "appears to be physiologically inert when pure." Wood et al.(195) recently tested pulmonary ventilation in human subjects by having them breathe a mixture of 90% SF_6 and 10% O_2 under a pressure of 2 atmospheres. In a similar study, Martin et al.(196) tested dogs which breathed a mixture of 95% SF_6 and 5% O_2 at a pressure of 4 atmospheres. No mention of any abnormal or toxic effects was made in either of the latter two studies.

Thus, since it is gaseous, physiologically inert, chemically inert, and easily detectable in extremely low concentrations, sulfur hexafluoride is an excellent atmospheric tracer. Short range dispersion tests using SF_6 as a tracer have been made from continuous point source releases.(197,198) Longer range studies have shown that SF_6 can be detected up to 75 miles away from a continuous point source.(127,189) Recently, portable electron-capture gas chromatographs which can be used in aircraft have shown good results detecting sulfur hexafluoride in preliminary field tests.(199,200) Dietz and Cote(200) have developed a technique which can continuously monitor SF_6 concentrations for a period of about 40 seconds.

One problem in the use of sulfur hexafluoride as an atmospheric tracer is that SF_6 is also used as an insulator in high voltage underground electrical cables,(201) and thus there must be a small ambient concentration. Lovelock(202) recently measured in Ireland ambient SF_6 and CCl_3F concentrations carried by winds from European industrial areas and found an ambient SF_6 concentration level of 10^{-13}. If this level increases significantly in the next few years, there are many other gaseous halogenated compounds with high sensitivity which could be used as alternative atmospheric tracers.

Sulfur hexafluoride was used as a tracer gas in all the atmospheric dispersion experiments described in sections 3-7. Air samples were taken in most cases by 250-ml polyethylene squeeze bottles; the sampling technique is discussed in detail in section 2.3. The analysis procedure by electron-capture gas chromatography and the calibration procedure are described in detail in section 2.4. The limit of detection under operating conditions was one part SF_6 in 10^{12} parts of air.

2.3 Air sampling methods

In the atmospheric tracer studies described in sections 3-7, it was necessary in most cases to obtain a series of air samples and return them to the laboratory for analysis. In one study, two portable, battery-operated electron-capture gas chromatographs were used to make immediate analyses in the field; these chromatographs will be described in section 2.4. To obtain ambient air samples, sometimes called "grab" samples, previous studies have used evacuated stainless steel cylinders,(198) plastic bags,(203,204) and plastic squeeze bottles.(197) Evacuated stainless steel cylinders are probably best for SF_6 samples, since there is low adsorption and the time of sampling can be easily adjusted; however, stainless steel cylinders are expensive and quite bulky. Plastic bags are relatively inexpensive, however they are also bulky and require a hand pump which can contaminate an air sample.

Plastic squeeze bottles are inexpensive, take up little space, and can be easily cleaned for reuse. 250-ml polyethylene squeeze bottles were used for air sampling in all the tracer tests. The sampling procedure was to squeeze a bottle hard ten successive times, one squeeze a second. Field tests showed a reproducibility of 5%, and SF_6 samples could be contained in the bottles for a period of at least two weeks without change. The averaging time in sampling with squeeze bottles was approximately 10 seconds. Concentrations can be compared with those for other sampling times by the one-fifth power law suggested by Cramer(27) and Hino,(205)

$$\frac{c_{t_1}}{c_{t_2}} = \left(\frac{t_1}{t_2}\right)^{-1/5} \tag{6}$$

where t_1 and t_2 are averaging times in sampling. This relation applies for sampling times less than 10 minutes, but may not be valid in all situations.

One problem encountered with the polyethylene squeeze bottles was that sulfur hexafluoride at concentrations above 2×10^{-9} adsorbed on the polyethylene surface. The standard cleaning technique which was adopted for used bottles was to evacuate them for 5 minutes in a vacuum dessicator and then fill them with high-purity compressed air; this procedure was repeated three times. It was found that this cleaning procedure using three short evacuations was as effective as one long evacuation overnight. However, polyethylene bottles which had contained SF_6 concentrations of 2×10^{-9} or higher could not be effectively cleaned by this procedure; small but measurable residual SF_6 concentrations of order 5×10^{-4} of the original concentrations remained inside the bottles after cleaning. To insure accuracy in the tracer experiments, bottles which had contained an SF_6 concentration of 2×10^{-9} or higher were never reused. It is possible that evacuation at high temperature or treatment by liquid solvents may clean contaminated bottles, however these procedures were not tried.

Polyethylene syringes, of capacities 20 ml to 50 ml, were found to take air samples as well as the squeeze bottles if the syringes were capped immediately and analyzed within 18 hours. Preliminary tests indicated an SF_6 contamination problem similar to that described above for the polyethylene bottles. A remote, self-contained, sequential air sampling unit was developed which incorporated polyethylene syringes; this automatic sampling device is described in detail in Appendix A-5. The sampling unit contains a number of spring-loaded syringes which are released sequentially by the motion of a rotary mechanical timer. Field tests indicated that the sampling device could take accurate sequential air samples automatically and contain each sample without leakage for at least a period of 18 hours in an outdoor environment.

2.4 Analysis and calibration procedures

The instrument used for analysis in most of the tracer studies was an Analytical Instrument Development Inc. (Avondale, Pa.) Model 510 electron-capture gas chromatograph equipped with a 1-ml loop gas sampling valve. The detector, of parallel-plate design, contained a 200-millicurie tritiated titanium foil which under operating conditions produced a standing current of about 5×10^{-9} amps. The AID chromatograph was adapted by attaching an external pulser which produced a 34 volt pulse of 1-μsec duration. For optimum sensitivity to SF_6, the pulse period was adjusted to 200 μsec; Simmonds et al.(188) found for a similar chromatograph an optimum pulse period for SF_6 sensitivity of 180 μsec. The carrier gas was prepurified nitrogen which was run at a flow rate of 90 ml/min. A molecular sieve trap was used to remove any residual water vapor from the carrier gas before it entered the chromatograph.

The column used to separate SF_6 was 8 ft x 1/8 inch stainless steel packed with 80-100 mesh 5A molecular sieve. Under operating conditions, this column caused the SF_6 to elute first as a sharp peak in about 20 sec after injection, followed by a large oxygen peak which appeared in about 45 sec after injection; a typical separation of a low SF_6 concentration and oxygen is shown in Figure 2. The column and detector were operated at 50° C. The electrometer output from the chromatograph was monitored by an Esterline Angus Model T171B strip-chart recorder (1 megohm input impedance). A low-pass RC filter with a time constant of

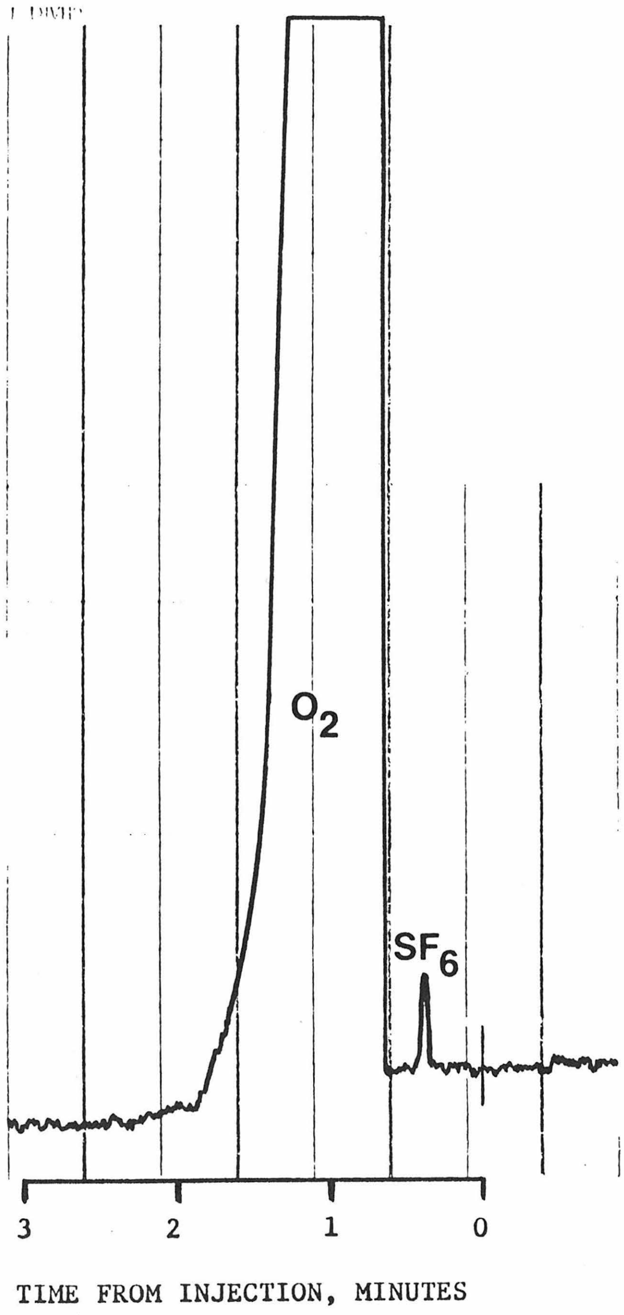

Figure 2. Typical separation of SF_6 and oxygen, showing the SF_6 peak eluting before the large oxygen peak. The SF_6 concentration was 5.0×10^{-12} parts SF_6 per part of air.

about 0.5 sec was used to reduce high frequency noise. Integration of the SF_6 peak was accomplished by an Infotronics Model CRS-100 digital electronic integrator. For analysis of the squeeze bottle samples, a cap for the bottles was mounted on the inlet of the gas sampling valve of the chromatograph. A sample was analyzed by attaching the polyethylene bottle, squeezing the bottle and thus flushing at least 10 ml through the 1-ml sampling loop, and injecting the sample before releasing the squeeze on the bottle.

In the large-scale field study described in section 6, two portable, battery-operated electron-capture gas chromatographs were used to make immediate field analyses of SF_6 concentrations. The two chromatographs were similar to the one used by Simmonds et al.(206) to measure ambient levels of halogenated hydrocarbons over the Los Angeles basin. Each chromatograph contained a detector of concentric cylindrical design with a 200-millicurie tritiated titanium foil. The detector was pulsed at 38 volts for a 1-μsec duration; the pulse period was adjusted to 200 μsec for optimum SF_6 sensitivity. Each instrument contained a 3.5 ft x 1/4 inch stainless steel column packed with 80-100 mesh 5A molecular sieve; the carrier gas was prepurified nitrogen. The column and detector were operated at ambient temperature. The electrical output of each chromatograph was monitored by an Esterline Angus Model T171B battery-operated strip-chart recorder; an RC filter with a time constant of 0.3 sec was used to reduce high frequency noise. For field analysis, a 50-ml syringe was used to draw in an ambient air sample through a 1-ml loop gas sampling valve. Each analysis system consisting of carrier gas bottle, chromatograph, and recorder was completely self-contained and could be easily operated within an automobile.

Calibration of the AID chromatograph and the two portable chromatographs was accomplished by a well-mixed exponential dilution system, similar to that suggested by Lovelock(207) and used by Saltzman et al.(190) A 6 x 6 x 6 inch Lucite cube was built with a magnetically-driven propeller positioned inside. An initial concentration of approximately 1 ppm of sulfur hexafluoride was introduced inside the cube. A slow flow rate of high-purity compressed air was then started which resulted in one complete air change in about 30 min. If the system were well-mixed, the dilution should follow the equation

$$c = c_o e^{-N} \qquad (7)$$

where c_o is the initial concentration and N is the number of air changes. A graph of log peak area versus the number of air changes should thus yield a slope of -1. Figure 1 in Drivas et al.(208) and in Appendix A-1 shows that the dilution system was indeed well-mixed.

A typical calibration curve of integrated peak area versus SF_6 concentration is shown in Figure 2 of Appendix A-1. The minimum detectable SF_6 concentration, defined as three times the peak-to-peak noise level, was about 1.0×10^{-12} for the AID chromatograph and 1.5×10^{-12} for the two portable gas chromatographs. All chromatographs had a linear dynamic range of approximately 10^3, from SF_6 concentrations of 10^{-12} to 10^{-9}. At higher concentrations, the electron-capture detector became overloaded; however, with electronic digital integration, a calibration curve is possible up to 1 ppm SF_6 if standard operating conditions are maintained. This extremely large operating range of 10^6 in tracer concentration proved quite useful in some experiments, for example, the building wake tests described in section 4.

An interesting operating feature of the electron-capture gas chromatographs was that the tritiated titanium foils became contaminated with use, resulting in a dip below the normal baseline after a large peak which increased analysis time. The origin of the contamination is not known; a suggested cause is adsorption of a high molecular weight impurity from the carrier gas or air samples.(209) After approximately three months of operation, a used tritium foil was subjected to a cleaning procedure similar to those suggested by Holden and Wheatley(210) and Claeys and Farr;(211) the cleaning procedure is described in detail in Appendix A-6. The cleaning procedure restored fairly new foils, however after approximately one year of operation, the cleaning procedure was no longer effective and the tritiated titanium foil had to be replaced. Also at three month intervals, at the same time the detector was disassembled for cleaning, the molecular sieve column and the carrier gas molecular sieve trap were regenerated by heating at 300° C for three hours while purging with a flow of prepurified nitrogen.

3. CHARACTERIZATION OF VENTILATION SYSTEMS IN BUILDINGS

Adequate ventilation in a building is important for both personal comfort and safety. Also of major concern is the amount of contamination caused by toxic emissions from laboratory fume hood exhausts, which reenter the original building and may contaminate surrounding buildings. In extreme cases, buildings have been evacuated because of the reentry of toxic exhaust fumes.(212) Tracer experiments, involving sulfur hexafluoride, were used to obtain quantitative data regarding actual residence times in rooms and hallways, and contamination caused by reentry of laboratory fume hood exhausts into a building. These studies are described in detail in Appendix A-1 and in Drivas et al.(208)

The tracer experiments found that ventilation in rooms and hallways could be described by an exponential decay with time of an initial concentration of tracer, as found by Lidwell and Lovelock.(167) This exponential behavior could be represented by a well-mixed theory with the addition of a "mixing factor" to account for the non-idealities in mixing, as is commonly done for calculations of actual ventilation rates in structures.(213,214) Measured values of the "mixing factor" ranged from 0.3 to 0.7 in small rooms without fans.

Experiments on the reentry of fume hood exhausts into buildings showed some surprising results. One fume hood, although satisfying the Los Angeles County building code,(215) was located only 16 ft from the main air intake of the ventilation system of a three-story building, as shown in Figure 6 of Appendix A-1. In one test of this fume hood, about 20% of the exhausted fumes reentered the ventilation system. Another experiment involved a roof fume hood exhaust on a three-story building with ventilation intakes both at ground level and on an adjoining building roof. In this test, more of the exhaust reentered the ground level intake of the same building as compared to the roof intake of the adjoining building.

4. PROBING THE AIR FLOW WITHIN THE WAKE DOWNWIND OF A BUILDING

Knowledge of the air flow dynamics around a building is essential to good planning of its ventilation system. A sketch of a typical air flow pattern around a building(159) is presented in Figure 1 of Appendix A-2. One main characteristic of the side view is the large eddy or cavity which forms downwind in the wake behind the building, causing a reverse flow from ground level to the roof of the building. Investigation of this recirculation is important, since pollutants emitted near the ground level from automobiles may be transported directly to a roof intake vent, and toxic gases exhausted from the roof may be transported to ground level where people may be present and where ventilation intakes may be located.

Sulfur hexafluoride was used as a tracer to probe the air flow and dispersion patterns within the wake downwind of a 12 meter high, three-story building. Specifically, the extent and velocities of the recirculation in the wake were investigated and a characteristic exponential dilution time for the wake was determined. Also, some practical contamination problems relating to the wake were examined, including direct infiltration of the tracer into the building. These studies are described in detail in Appendix A-2.

A reverse-flow circulation was observed with a longitudinal extent downwind of about three building heights; wind tunnel tests on a scale-model building of similar shape indicated that the extent of the downwind eddy was about 3.75 building heights.(216) The extent of the recirculation on the roof was confined to less than one-half the width of the building from the downwind edge. The recirculating velocities in the wake were estimated to be about 0.1 - 0.3 those of the prevailing wind at the top of the building. These values are consistent with recirculating velocities associated with other wake flows; for example, Grove et al.(217) investigated the velocities within the wake behind a circular cylinder and found that the recirculating velocities were about 0.1 - 0.3 those of the free-stream velocity.

The wake downwind of the building was found to be well-mixed in all three dimensions and exhibited a characteristic exponential dilution time of approximately one minute, as shown in Figures 5 and 6 of Appendix A-2. It was noted during the course of the experiments that the tracer could be detected inside the building, presumably drawn in through the main intake vents on the roof. However, in one test, integration of the concentration recorded at the intake vents resulted only in one-fifth the concentration level recorded inside the building; possibly, direct infiltration from the wake into the building had occurred.

5. DISPERSION OF AN INSTANTANEOUS CROSSWIND LINE SOURCE OF TRACER RELEASED FROM AN URBAN HIGHWAY

As discussed in section 1.3, there are two main methods at present of characterizing dispersion from pollutant sources in urban areas; one is the Gaussian plume model and the other is the use of the semi-empirical turbulent diffusion equation, commonly referred to as K-theory. In order to test various forms of these models, sulfur hexafluoride was used as a tracer in a quasi-instantaneous line source release by an automobile moving along an urban highway in Los Angeles. Concentrations at various distances from 0.4 km to 3.2 km downwind of the highway were recorded at ground level as a function of time. These tracer concentration data were used to test the validity of the above theories in predicting the dispersion from an instantaneous urban ground-level crosswind line source. This study is described in detail in Appendix A-3.

Runs were made along a section of Interstate 405 (commonly known as the San Diego Freeway) which runs parallel to the Pacific Ocean coastline about 6 km inland; during the afternoon a brisk sea breeze normally blows inland perpendicularly across the highway. Typical SF_6 concentration vs. time curves at various distances downwind of the line source release are shown in Figures 1 and 2 of Appendix A-3. The curves spread with increasing distance downwind and exhibit a skewness to the right which also increases with increasing downwind distance. A most interesting feature is that the apparent average velocity in each run, calculated from the average travel time at each distance, increases with increasing downwind distance, as shown in Table 2 of Appendix A-3.

The Gaussian model equation for concentration from an instantaneous crosswind line source was tested in order to compare this theory with the experimental data. The comparison showed two major discrepancies: one, the peak concentrations were overestimated by a factor of 20, and two, the times associated with the movement of the concentration peak downwind were in error. This latter result is due to the fact that the Gaussian model assumes a constant average velocity for the movement of the peak concentration; the experimental data show an apparent velocity which increases with time.

The experimental results of non-Gaussian concentration profiles and an apparent velocity which increases with time can be interpreted by the effect of wind shear, i.e. a horizontal wind velocity which increases with height. As the cloud of tracer grows vertically with time, the effective mean wind velocity which is transporting the cloud increases. Integral moment analyses by Chatwin(54) and Saffman(51) were used to compare K-theory approaches using vertical velocity profiles with the experimental results. Saffman's analysis of the semi-empirical turbulent diffusion equation, using a power-law vertical velocity profile and a power-law vertical eddy diffusivity profile, was found to more accurately predict the experimental results than the other models tested.

6. POLLUTANT TRANSPORT AND DISPERSION OVER THE LOS ANGELES AREA

There has been a long-term and growing interest in the meteorology associated with pollutant transport through the area surrounding Los Angeles, California.(5,218) Angell et al.(106,107) have used tetroons to study wind trajectories in the Los Angeles basin. Use of chemical tracers can characterize the dispersive power of the atmosphere in addition to tracing wind trajectories. Zinc-cadmium sulfide has been used as a tracer over Los Angeles,(113) however preliminary results indicate that little of the tracer could be measured. In a large-scale test, sulfur hexafluoride was used as a tracer over the urban area near Los Angeles in order to study pollutant transport and dispersion over distances up to 124 km. This study is described in detail in Appendix A-4.

On July 19, 1973, sulfur hexafluoride was released at a rate of 750 g/min for a period of 45 min from ground level in Anaheim, California. During the time of the release, the base of the temperature inversion was reported to be 550 meters near the ocean and 750 meters inland near Pomona. The wind in Anaheim was mainly from the southwest, blowing inland. Dispersion data well above the minimum detectable concentration limits were obtained in five neighboring communities up to 124 km (78 miles) away: Pomona, Riverside, San Bernardino, Cajon Pass, and Palm Springs. Two portable, battery-operated gas chromatographs, as described in section 2.4, were operated within automobiles and used to locate the tracer cloud as it passed through the geographical regions. One chromatograph was used to follow the tracer north along the route encompassing Riverside, San Bernardino, and Cajon Pass; the other was used to follow the tracer east from Pomona to Palm Springs. Individuals were left behind to collect air samples when the tracer began to appear at Pomona, Riverside, and San Bernardino.

The concentration versus time data obtained at each location are shown in composite form in Figure 7 of Appendix A-4. The data were analyzed by two methods: one, by use of the Gaussian plume model, as summarized in Table 1 of Appendix A-4; and two, by numerical integration over time of the concentration recorded at each location, as summarized in Table 2 of Appendix A-4. Both approaches indicated that the cities of Riverside and Palm Springs possibly lie in a direct path of the pollutant transport from Anaheim. Palm Springs, which at 124 km from Anaheim was the furthest location sampled, received eight times the amount of the tracer recorded in Cajon Pass, and half the amount recorded in Pomona, which was only 34 km distant from the release point in Anaheim. This work demonstrated the applicability of the SF_6 tracer technique in studies of large-scale urban regions. The entire test was quite inexpensive, and all data were analyzed and graphs prepared within 24 hours after the end of the test.

7. MISCELLANEOUS TRACER TESTS

7.1 Gas transport in the human lung

Many attempts have been made to relate experimental data on gas residence times in the human lung to a theoretical model. Five and six compartment models of the lung which require a computer have been recently suggested.(219,220) These models have found good agreement with data obtained by the standard nitrogen washout technique (breathing pure oxygen and analyzing the decrease in nitrogen with each breath). However, these models are so complex that their use in practice is severely limited. Since concentration curves from nitrogen washout experiments show a predominantly exponential behavior, a simple single-compartment model of the lung is proposed.

If a single compartment is well-mixed, concentration will decrease as

$$\frac{c}{c_o} = e^{-N/N_T} \tag{8}$$

where c_o is initial concentration, N is the number of breaths, and N_T is the theoretical number of breaths for one air change. Since lungs are not perfectly well-mixed, a mixing factor k is introduced to account for variations from the well-mixed model, as was done for room ventilation in section 3,

$$\frac{c}{c_o} = e^{-k \frac{N}{N_T}}$$

where $0 \leq k \leq 1$. The theoretical number of breaths for one air change, N_T, can be defined as

$$N_T = \frac{FRC + \left(V_T - V_D\right)}{\left(V_T - V_D\right)} \tag{10}$$

where FRC is the functional residual capacity, V_T is the tidal volume, and V_D is the alveolar dead space. These quantities can be measured by standard experimental techniques.

An experiment was conducted using sulfur hexafluoride as a tracer gas in the human lung. A small volume of dilute SF_6 was inhaled, and the decrease in concentration was measured with every breath. The results are shown in Figure 3. The number of breaths, N_{exp}, required for the concentration to decrease by a factor of 1/e can be calculated from the graph. The ratio of N_{exp} to the theoretical number of breaths for one air change (N_T) gives the value of the mixing factor:

$$k = \frac{N_T}{N_{exp}} \tag{11}$$

This model was used to analyze data for both healthy and diseased lungs, and the results are shown in Table 1. The experimental data were obtained from the papers which propose the multicompartment models.(219,220) An interesting result is the fact that healthy lungs are quite close to being completely well-mixed (i.e., having a mixing factor close to 1). While the use of SF_6 as a tracer is not proposed as an alternative to the standard nitrogen washout technique, the proposed model is quite useful in its ease of interpreting experimental data.

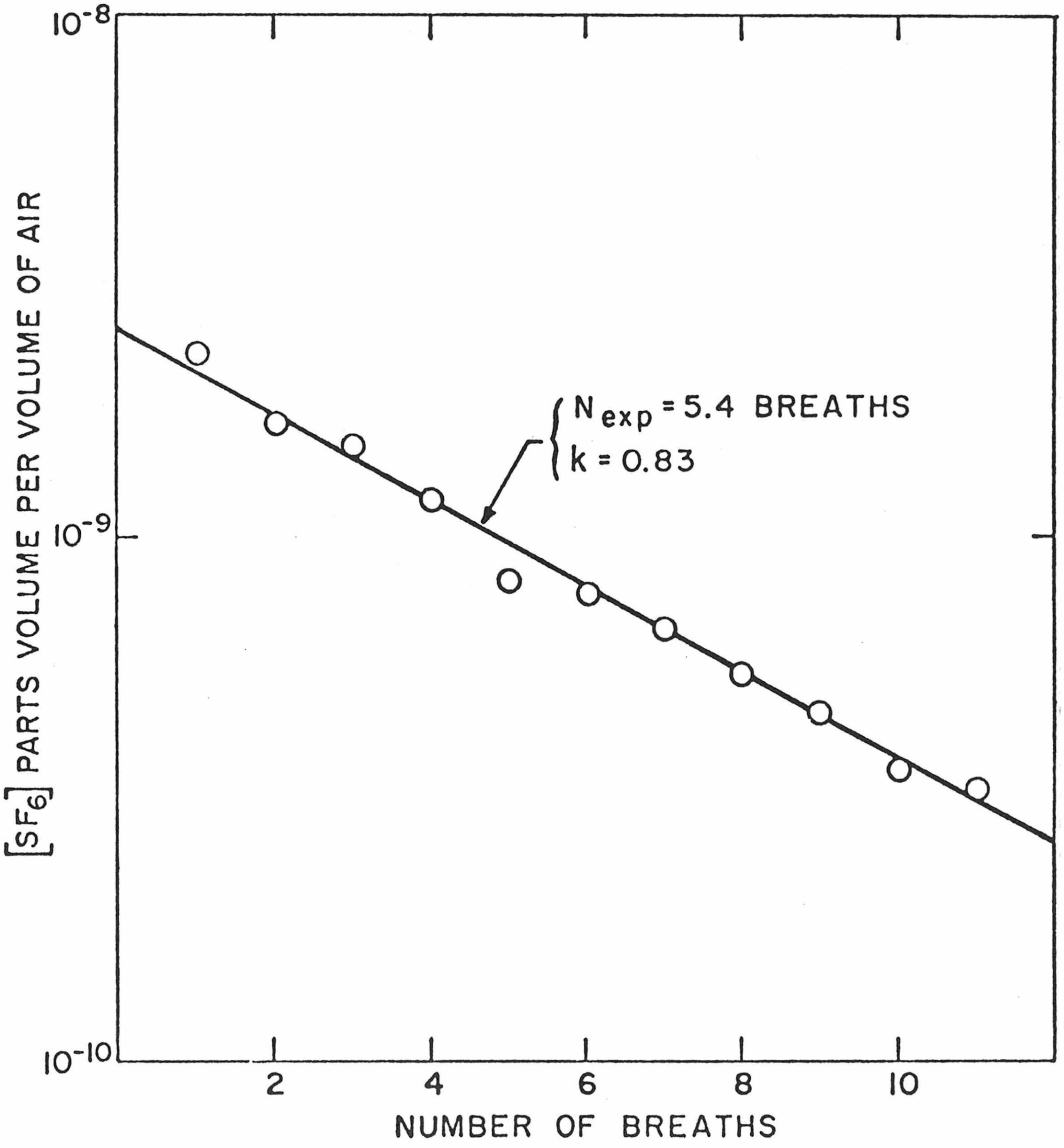

Figure 3. Decrease in tracer concentration as a function of number of breaths in healthy lung.

Table 1. Comparison of healthy and diseased lungs.*

Source	Lung condition	ϕ	N_T	N_{exp}	k
Saidel, et al.(220) Fig. 2B	Diseased	0.20	6.6	12.3	0.54
Hashimoto, et al.(219) Fig. 6	Diseased	0.11	12.6	19.5	0.65
Saidel, et al.(220) Fig. 2B	Healthy	0.20	7.8	9.1	0.86
Present work	Healthy	0.33	4.5	5.4	0.83

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* $\phi = V_T/FRC$; V_D was estimated as 150 ml.(221).

7.2 Air infiltration rates into a moving automobile

An experimental investigation using sulfur hexafluoride as a tracer gas was conducted to determine the infiltration rate of outside air into a moving closed automobile. This information is vital in case a leak develops in the exhaust system which bleeds carbon monoxide into the passenger section of a car. Also, in traveling through automobile tunnels, which usually contain high concentrations of carbon monoxide, knowledge of infiltration rates is important for the comfort and well-being of car passengers.

As mentioned previously, air infiltration rates into closed houses have been measured using helium as a tracer gas.(161,162) These studies found that the experimental air change rate per hour increased linearly with increasing wind velocity. A simple theoretical discussion will add credence to this observation.

Consider the stagnation pressure built up by wind velocity on the side of a house or the front surface of a moving car. From conservation of mechanical energy,

$$\frac{p_s - p_o}{\rho} = \frac{u_o^2}{2} \qquad (12)$$

where p_s is the stagnation pressure, p_o is atmospheric pressure, ρ is the air density (assumed constant), and u_o is the wind or car velocity. This stagnation pressure in turn forces outside air through the small tortuous openings in a house or car. Since a large amount of frictional resistance is encountered, conservation of mechanical energy yields

$$\frac{p_s - p_o}{\rho} = \frac{u^2}{2} + \frac{u^2}{2} F \qquad (13)$$

where u is velocity through the opening, and F is a frictional factor which depends on the geometry and roughness of the opening and the Reynolds number of the flow. However, for turbulent flow, the Reynolds number dependence is small, and F will stay approximately constant with a change in wind velocity. Equating the right hand sides of equations (12) and (13) yields:

$$u = \frac{u_o}{\sqrt{F + 1}} \tag{14}$$

Thus, the velocity through the small opening, and consequently the air change rate, should vary linearly with the wind or car velocity, as found experimentally in the house studies.

In this study we used a 1969 Volkswagen sedan, a car noted for its airtightness, with 52,000 miles on the odometer. A small amount of SF_6 was released inside the car, and after well-mixing, the decrease in SF_6 concentration with time was measured as a function of car speed. All windows and vents were kept closed and all samples were taken in the center of the car. The results are shown in Figure 4. From the graph, the experimental time for one complete air change, t_{exp}, can be calculated; it ranged from 5.9 minutes at 60 miles per hour to 21 minutes at 15 miles per hour.

The above theoretical discussion predicts that the time for one air change (t_{exp}) should be inversely proportional to the car velocity. Figure 5 verifies this theoretical prediction. Thus, the initial intake rate of atmospheric pollutants is directly proportional to the car speed. Whether the experimental residence times found are typical for most cars, or above average, is a question to be decided by

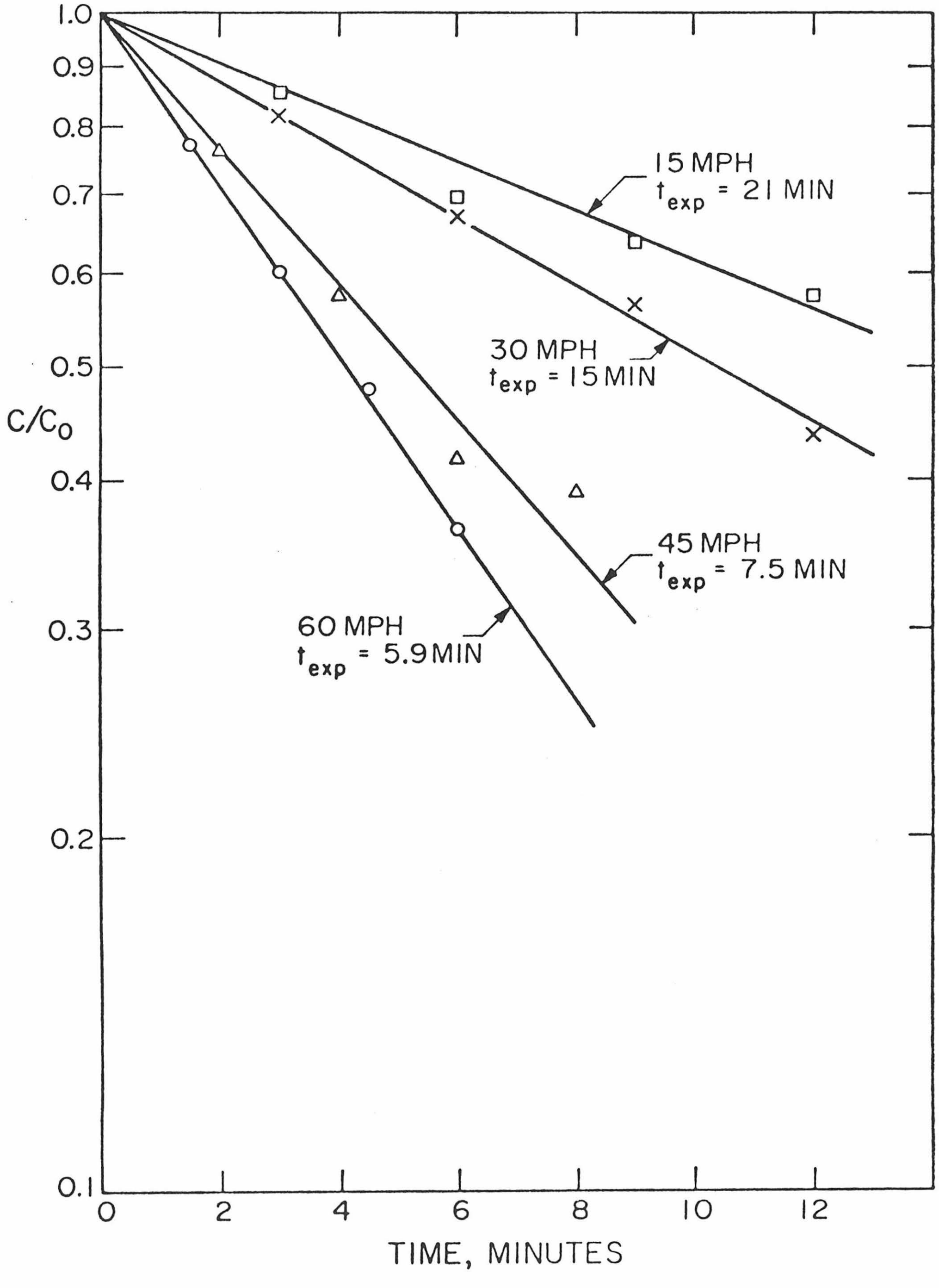

Figure 4. Decrease in tracer concentration as a function of time for various speeds in a 1969 Volkswagen sedan.

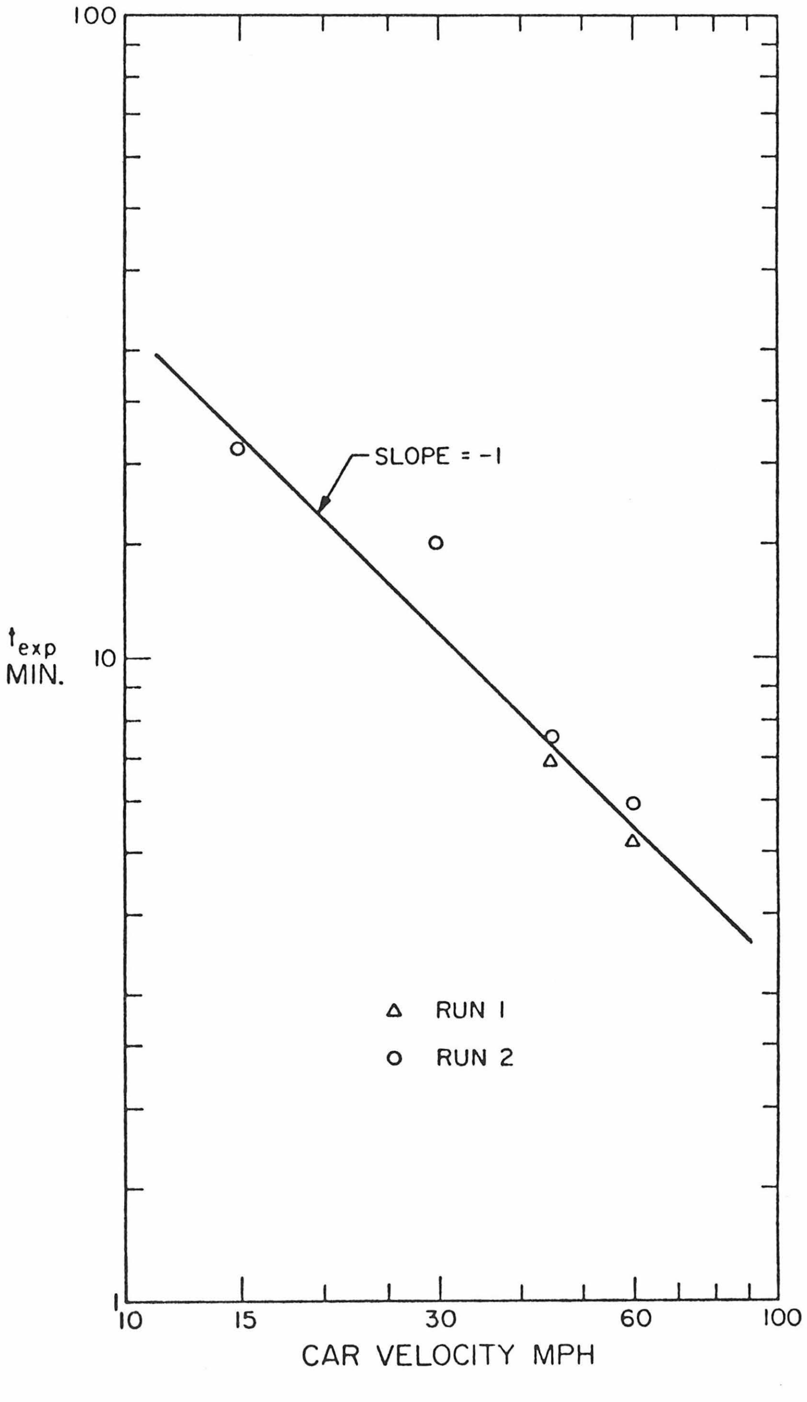

Figure 5. Exponential decrease time versus car velocity for a 1969 Volkswagen sedan.

more extensive tracer studies on different makes and models of automobiles.

7.3 Dispersion in an automobile tunnel

As discussed in section 7.2, the intake of pollutants while driving through tunnels is a function of the automobile speed. Another factor which must be considered is how the concentration level of the pollutant itself varies in a tunnel. Dispersion of pollutants in an automobile tunnel is fairly complicated, since the movement of the cars possibly has a great influence on air mixing.

A tracer test using sulfur hexafluoride was conducted in a two-way traffic automobile tunnel. The tunnel was straight and 240 ft long with fairly rough walls. The tunnel was about 30 ft wide and thus had room for two lanes of traffic, one lane moving in each direction. The shape of the tunnel was roughly semi-circular, with a maximum height of about 30 ft. The tunnel was located near Malibu, California about one-half mile from the ocean; ventilation was accomplished by a natural sea breeze flow in one direction.

About one liter of SF_6 was released as an instantaneous point source in the center of the upwind end of the tunnel. Air samples were taken on catwalks on both sides of the tunnel near the downwind end. The amount of traffic was about 4-5 cars/min in each direction, with estimated speeds of about 30 miles per hour. The results of the tracer test are shown in Figure 6.

The one striking result is that dispersion in the automobile tunnel was not uniform; the traffic flow direction had a large effect on

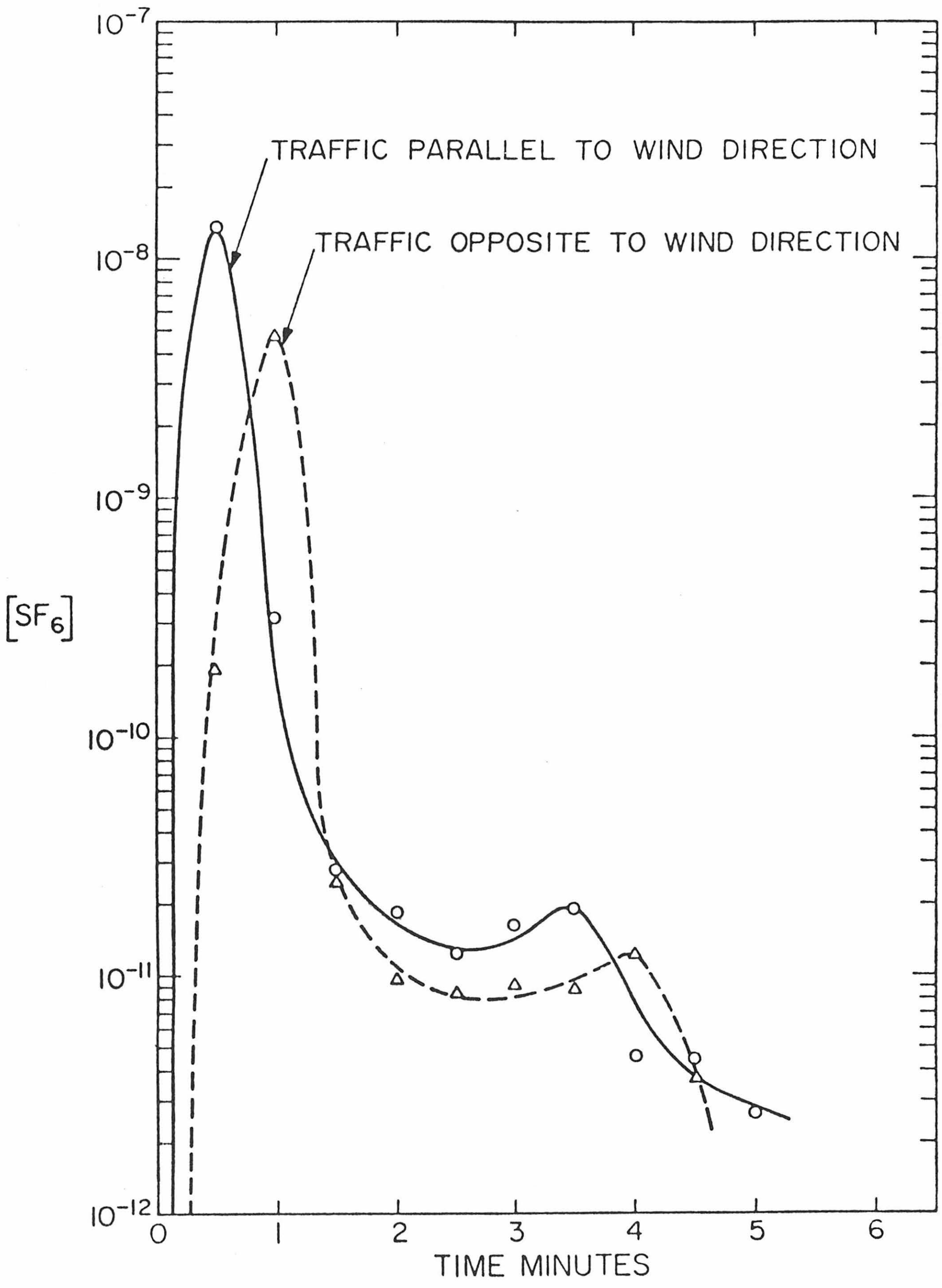

Figure 6. Tracer concentration as a function of time for each side of a two-way traffic automobile tunnel.

the concentration distribution. Two distinct peak heights were recorded; from the peak heights, the apparent average wind velocity in the traffic lane parallel to the wind was 5.2 mph and in the lane opposite to the wind direction was 2.7 mph. These results indicate that a possible simple way of modeling flow in a two-way traffic automobile tunnel is to use a linear velocity profile across the width of the tunnel to approximate the effect of the traffic flow direction. Much more work is needed to characterize the effects of traffic density and automobile speed on the dispersion of pollutants in both one-way and two-way traffic tunnels.

7.4 Dispersion in a complex of buildings

During the building wake studies described in section 4, some contamination problems arose due to a student in a nearby building using sulfur hexafluoride in an unrelated experiment. Preliminary sampling indicated that this student, who was inadvertently releasing SF_6 from the roof of Guggenheim, was contaminating a large section of the Caltech campus downwind. It was decided to make a similar test, releasing a known amount of sulfur hexafluoride, to determine how dispersion occurs in a fairly complicated complex of buildings, the Caltech campus.

Sulfur hexafluoride was released as a continuous point source at a rate of about 350 ml/min from the roof of Guggenheim. During the afternoon, the prevailing wind was from the south-southwest, carrying the tracer over a large section of the Caltech campus. It was found that SF_6 concentrations in buildings downwind reached a steady-state in about 30 min. All air samples were taken inside buildings downwind after the tracer had been released for at least 30 min; SF_6 was released continuously during the entire time of sampling. Two runs were made, Run 1 on August 28, 1973 and Run 2 on October 4, 1973.

The two runs are summarized in Table 2. Guggenheim, from whose roof the tracer was released, recorded the highest concentrations inside; concentrations in all other buildings were normalized to the concentrations recorded in Guggenheim. It can be seen from Table 2 that the reproducibility, except for a few cases, was quite remarkable for a complicated flow in a complex of buildings; in most cases, concentrations were within a factor of two. This excellent reproducibility is probably due to the fact that the air samples were taken inside buildings whose relatively long residence times have a smoothing effect on the highly fluctuating concentrations outdoors.

Figure 7 shows the relative concentration levels recorded over the Caltech campus for the two runs. It should be noted that the concentrations decrease relatively rapidly downwind of the release point. Comparison with the Gaussian plume model for very unstable conditions showed that the recorded concentrations were lower by about a factor of ten than the calculated concentrations, i.e. the Gaussian model overestimated the concentrations by about a factor of ten. Munn and Cole (130) used uranine dye as a tracer to study dispersion 500-1000 ft downwind of a fairly large building and also found that the Gaussian plume model overestimated recorded concentrations by about a factor of ten. It appears that the Gaussian plume model, while used mainly for dispersion over flat land, can certainly be used as an upper bound for calculating dispersion in a complex of buildings.

Table 2. Dispersion in a complex of buildings.

Campus location	Fraction of Guggenheim concentration Run 1	Run 2
Guggenheim	1.00	1.00
Thomas	0.36	0.31
Firestone	0.18	0.26
Spalding Laboratory	0.19	0.18
Winnett Lounge	0.13	0.16
Cafeteria	0.075	0.079
Keck Laboratory	0.062	0.062
Booth	0.070	0.058
Baxter	0.015	0.056
Keck House	0.020	0.050
Campus Architect	0.023	0.046
Steele	0.033	0.040
Dabney Hall	0.048	0.033
Central Warehouse	0.030	0.020
Lauritsen	0.0002	0.018
Marks House	0.0009	0.0028
Sloan	0.0023	0.0012
Ruddock House	0.017	0.0011
Fleming House	0.0011	0.0005
Crellin	0.0002	0.0004
Noyes	0.0015	0.0004

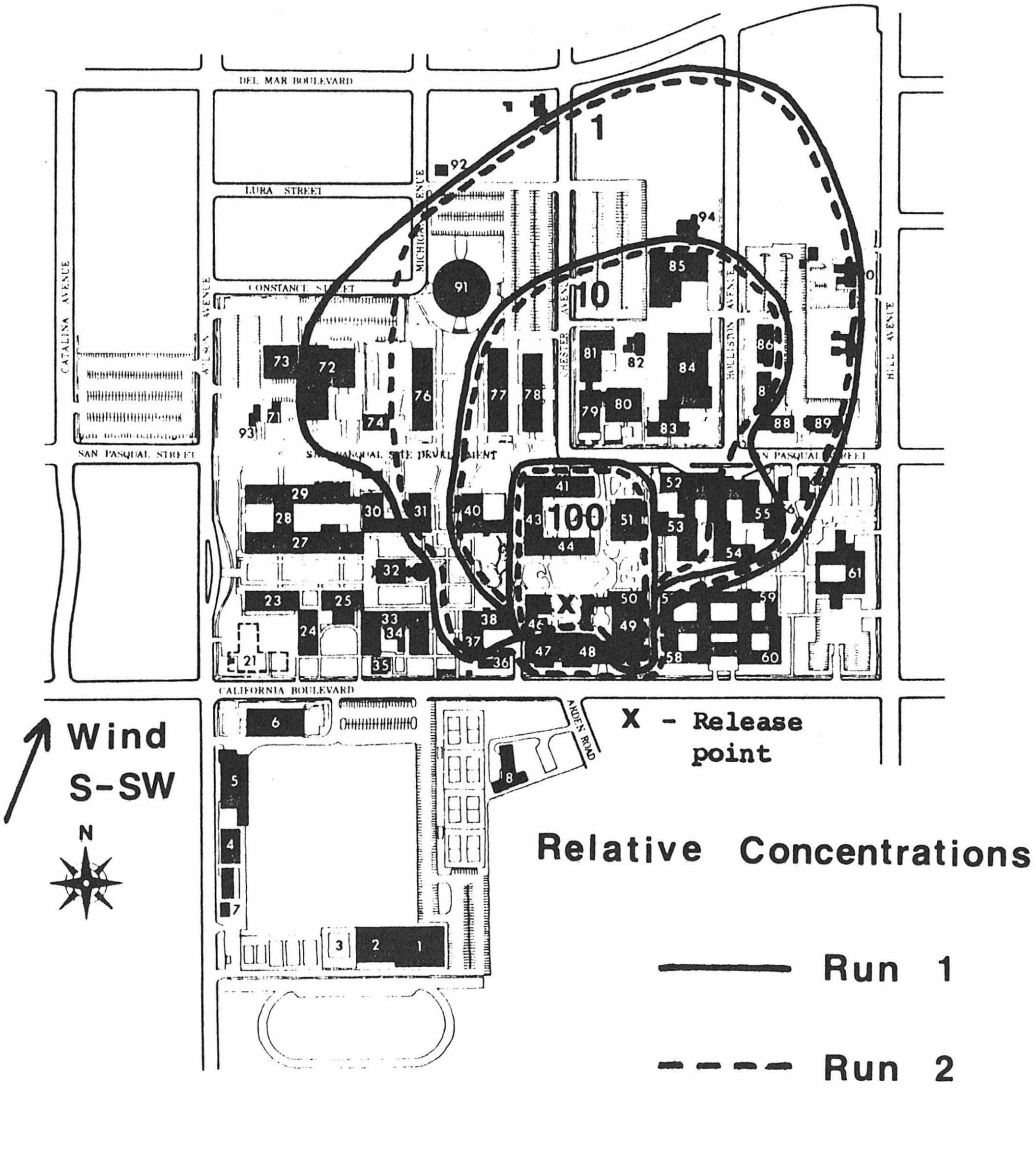

Figure 7. Isopleths of relative tracer concentration for dispersion in a complex of buildings.

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APPENDIX A-1. EXPERIMENTAL CHARACTERIZATION OF VENTILATION SYSTEMS IN BUILDINGS

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Experimental Characterization of Ventilation Systems in Buildings

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■ Tracer experiments, involving sulfur hexafluoride, were used to obtain quantitative data regarding actual residence time distributions in rooms and hallways, and contamination caused by reentry of laboratory fume hood exhausts into a building. Application of a mixing factor, k, was found to be of use, and measured values ranged from 0.3 to 0.7 in small rooms without fans. One experiment involved a roof exhaust with ventilation intakes both on an adjoining roof and at ground level; in this experiment more of the exhaust reentered the ground level intake of the same building as compared to the roof intake of an adjoining building. In another experiment, 20% of the fumes exhausted were found to reenter the ventilation system.

The air quality of urban atmospheres is being widely discussed. In spite of the fact that a significant portion of a person's life is spent within buildings, the air quality within buildings has been relatively overlooked. Accurate characterization of airflow through buildings is important for both personal comfort and safety. Of major importance in various facilities is the length of time required for purging until the concentration of toxic species lowers to a safe level. Also of major concern is the degree of contamination caused by emissions from laboratory fume hood exhausts, which reenter the original building and surrounding buildings. In extreme cases, buildings have been evacuated because of the reentry of toxic exhaust fumes (Clarke, 1965).

Probably the most useful method of characterizing the effectiveness of room and hallway ventilation is the mixing factor guide reported by Constance (1970). If the room under consideration is ideally well-mixed, then following a spill of a pollutant, the concentration will decrease due to purging as indicated by the equation:

$$c = c_0 e^{-(Q/V)t} \tag{1}$$

Some time ago Lidwell and Lovelock (1946) noted that if the room is not well-mixed, then the rates of decay will not necessarily be logarithmic nor will the decay rates be the same in all parts of the room. Lidwell and Lovelock also noted that in practice it is usually possible to fit a curve of the type:

$$c = c_0 e^{-Kt} \tag{2}$$

where K is a constant. This idea is identical to that used by Constance in his use of the mixing factor k:

$$c = c_0 e^{-k(Q/V)t} \tag{3}$$

Values of k are normally estimated to be from $^1/_3$ to $^1/_{10}$. Using a tracer-gas technique, values of k can be experimentally measured and thus accurately characterize room ventilation.

A number of studies have considered airflow around buildings and the location of fume exhausts to minimize reentry. Almost all these studies have required the building of scale models and have used smoke or chemical tracers in controlled wind and water tunnel experiments. Fan and Brooks (1968) made water tunnel tests of a scale model of the west campus of the California Institute of Technology using a dye tracer; they showed that the intake vent of Crellin—a chemistry laboratory—is presently located in possibly the worst place for contamination by reentry of exhaust fumes. Evans (1957) made extensive wind tunnel tests with a smoke tracer on a larger number of building and roof shapes showing the eddy formation downwind. Halitsky (1962, 1963) used SO_2 as a tracer in wind tunnel studies of scale model buildings to determine the dilution factor from exhaust vents to intake vents. Halitsky (1965) and Fan and Brooks (1968) have also theoretically modeled plume behavior to estimate exhaust stack heights to limit contamination of building air intakes. Davis and Moore (1964) made wind tunnel tests using a smoke tracer on a scale model of a tall nuclear reactor building. They found that the transition from a steady plume to a turbulent wake depended on the ratio of the exhaust velocity to wind velocity. Clarke (1965) also commented on the significance of this ratio and the importance of having a large exhaust velocity. Munn and Cole (1967) released a fluorescent tracer, uranine dye, from an actual building exhaust stack and measured concentrations 500–1000 ft downwind. Likewise, Turk et al. (1968) released SF_6, the tracer used in the present experiment, from an actual building stack and measured concentrations 650–1000 meters downwind.

To the authors' knowledge, no experimental tracer tests have been made to determine the effectiveness of ventilation in rooms and the contamination resulting from reentry of fume hood exhausts under real conditions. The goal of this investigation was to gain quantitative knowledge in these two areas. No legal standards exist for the design and location of fume hood exhausts. Thus, these measurements are vital for the safety of personnel working in any building which exhausts toxic fumes.

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Experimental

The analytical technique involved a gas tracer detected by electron capture gas chromatography. The electron capture detector was similar to that first developed by Lovelock and Lipsky (1960). Sulfur hexafluoride (SF_6) was used as the tracer gas. Lester and Greenberg (1950) have shown that SF_6 is completely nontoxic; rats were kept for 24 hr in an atmosphere of 80% SF_6 and suffered no ill effects. Previous studies (Collins et al., 1965; Clemons and Altshuller, 1966) have shown that SF_6 can be detected in concentrations of 1 part in 10^{11} using the technique of electron capture gas chromatography. Thus, since it is physiologically inert and easily detectable in low concentrations, sulfur hexafluoride is an excellent atmospheric tracer. Clemons et al. (1968) traced air movements over distances of 75 miles from a location where pure SF_6 was released at 1 lb/min for 1 hr.

The instrument used in this study was a portable electron capture gas chromatograph (Analytical Instrument Development, Inc., West Chester, Pa.) equipped with a 1-ml loop gas sampling valve. The detector contained a 200-mCi tritium foil which under operating conditions produced a standing current of 4×10^{-9} A. An 8 ft × 1/8 in. stainless steel column was packed with 80-100-mesh 5A Molecular Sieve. This column caused the SF_6 to elute first, followed by an oxygen peak; any water vapor was adsorbed by the Molecular Sieve. The carrier gas was prepurified nitrogen which was run at 120 ml/min. The column and detector were kept at 55°C. Integration of the SF_6 peak was accomplished by an Infotronics Model CRS-100 digital electronic integrator.

Due to the difficulty in making prepared standards with an SF_6 concentration of 10^{-11}, calibration was accomplished by means of a well-mixed exponential dilution system, similar to that used by Saltzman et al. (1966). A 6 × 6 × 6-in. Lucite cube was built with a magnetically driven propellor positioned inside. A slow airflow rate of 104 ml/min resulted in one air change every 33.5 min and thus assured good mixing. If the system were well-mixed, the dilution would follow that equation:

$$c = c_o e^{-N} \tag{4}$$

where c_o is the initial concentration and N is a number of air changes. A graph of peak area vs. number of air changes should thus yield a slope of −1, as shown in Figure 1. Figure 2 shows the relationship between peak area and actual SF_6 concentration. The minimum detectable SF_6 concentration under the operating conditions was 3×10^{-12}. The detector has a linear dynamic range of approximately 10^3 below SF_6 concentrations of 2×10^{-9}. At higher concentrations, the detector becomes overloaded; however, a calibration curve is possible up to 1 ppm if standard operating conditions are maintained.

Air samples were taken by dry 250-ml polyethylene bottles using the technique reported by Collins et al. (1965). The sampling procedure was to squeeze the bottle hard 10 successive times, one squeeze a second. Field tests showed excellent reproducibility, and samples could be contained in the bottles for at least a period of two weeks. For analysis, a cap for the bottles was mounted on the inlet of the gas sampling valve of the chromatograph. A sample was analyzed by attaching the polyethylene bottle, squeezing the bottle and thus flushing at least 10 ml through the 1-ml sampling loop and injecting the sample before releasing the squeeze on the bottle. Although polyethylene bottles proved quite useful in sampling, surface adsorption of SF_6 was a problem. For example, if a bottle contained an SF_6 concentration of 10^{-7}, after cleaning by rapid flushing with pure air, desorption of SF_6 produced concentrations up to 5×10^{-10}, which limited reuse of the bottle.

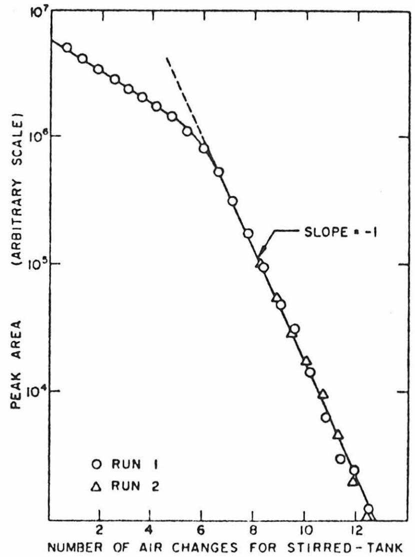

Figure 1. SF_6 peak area vs. number of air changes in the well-stirred dilution apparatus

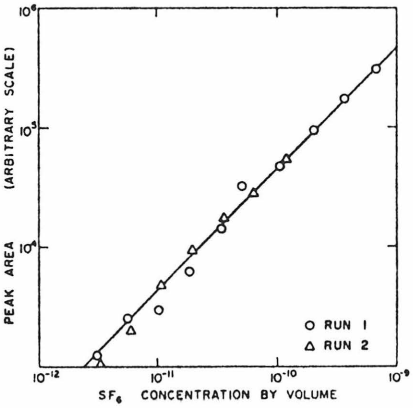

Figure 2. SF_6 calibration curve calculated from the exponential dilution

Room and Hallway Ventilation Tests and Results

The first step was to test the theory for a well-mixed room. A small (16 × 10 × 9) rectangular room, Room 27, was chosen in the basement of Caltech's Spalding Laboratory. The basement and room have a simple in-out ventilation system with no recirculation. From measuring the volumetric flow rate, Q, at the intake vent of the room and the room volume, V, as shown in Table I, the theoretical characteristic

Table I. Theoretical Residence Times for Basement Rooms

Room	Q, ft^3/min	V, ft^3	τ, min
25	384	1440	3.8
27	316	1440	4.6
31	328	1440	4.4

time, τ, for one air change can be calculated:

$$\tau = V/Q \tag{5}$$

For Room 27, τ = 4.6 min.

Four large fans were placed strategically in the room to provide good mixing. One-tenth ml of pure SF_6 was injected in front of one of the fans, and air samples were taken every 2 min in the center of the room and in one corner of the room near the exhaust vent. The results are shown in Figure 3. The two locations in the room gave essentially identical results. The dotted line represents the best fit of a straight line through the data points. The negative reciprocal of the slope of this line gives the effective residence time, t_{exp}, for one air change (the time required for concentration to decrease by $1/e$). From the graph, t_{exp} = 5.1 min. The solid line indicates the theoretical well-mixed residence time, τ = 4.6 min. The mixing factor as used by Constance (1970) can thus be defined:

$$k = \frac{\tau}{t_{exp}} \tag{6}$$

In this case, k = 0.90; thus, the fans produced almost complete well-mixing. Without the fans, the mixing factor can be much less, as will be shown below.

An important point is that the integrated concentration-time curve, multiplied by the flow rate Q, should equal (theoretically) the initial amount of tracer injected into the room:

$$Q\int_0^\infty c\,dt = v_0 \tag{7}$$

where v_0 is the initial volume of tracer. In this case, integration produced a total volume of 0.092 ml, quite close to the injected volume of 0.10 ml. Thus, essentially all the injected tracer was measured, and no erroneous readings were caused by previous contamination of the room.

A larger scale test was made to determine the efficiency of the ventilation system of the entire basement of Spalding Laboratory. The basement has one main intake vent which distributes fresh air to all the rooms. Air from the rooms is exhausted into the hallway, and one large vent exhausts the hallway air. There is no recirculation. Pertinent ventilation data are given in Table I for three of the rooms.

One liter of pure SF_6 was injected into the intake vent of the basement system, and SF_6 concentrations were sampled in the above three rooms and at both ends of the hallway. Rooms 25 and 27 were sampled at the center of the room and Room 31 was sampled 3 ft from one corner of the room. Figure 4 shows the results for these three rooms. Concentrations peaked very quickly in all three rooms. By coincidence, the data for Rooms 25 and 27 fell on the same straight line; thus, both rooms had essentially the same actual residence time. Calculations for the three rooms are summarized in Table II.

Table II. Experimental Residence Times and Mixing Factors for Basement Rooms

Room	Location	t_{exp}, min	k
25	Center of room	6.7	0.56
27	Center of room	6.7	0.68
31	Corner of room	14.6	0.30

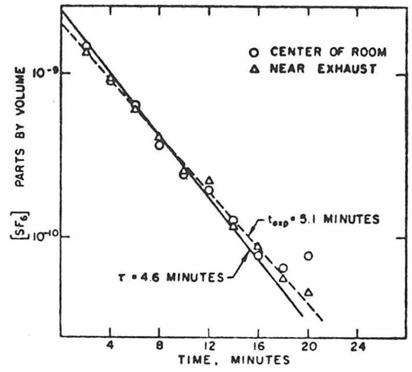

Figure 3. Results of the well-mixed ventilation test in Spalding, Room 27

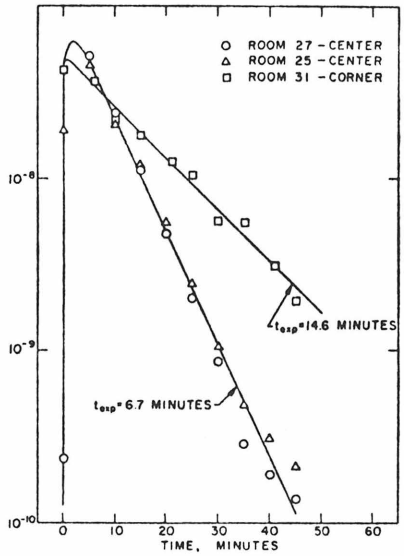

Figure 4. Results of the Spalding basement ventilation test for Rooms 25, 27, and 31

The mixing factors in the center of the room are quite high; however, the corner of Room 31 had a mixing factor slightly less than $^1/_3$. Thus, the normal estimate of k = $^1/_3$ to $^1/_{10}$ is reasonably valid. The rooms tested were rather small (16 × 10 ft) and larger rooms would presumably have worse mixing in corners and thus lower mixing factors.

Data from the two ends of the hallway are shown in Figure 5. Again, the concentrations peak rapidly. The break in slope of the curve for the west end of the hallway is difficult to explain since all rooms exhaust into the hallway and thus airflow is quite complicated. However, using the lower part of both curves, t_{exp} = 18.0 min for the east end and 22.8 min for the west end of the basement hallway. Thus, we can assume one complete air change takes place in the basement roughly every 30 min, to be on the safe side. If a sudden leak developed which flooded the basement with a 10^{-3} concentration of chlorine gas, the basement would have to be evacuated since the recommended safe threshold limit for chlorine gas is 1 ppm (Committee on Threshold Limit Values, 1962). Seven air changes would be needed to reach 1 ppm ($e^{-7} \cong 10^{-3}$) and thus, the time required for this dilution would be 7 × 30 min or 3.5 hr.

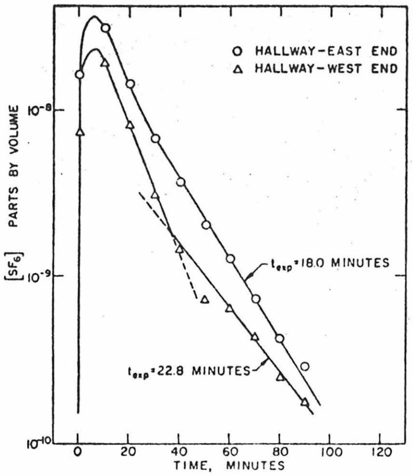

Figure 5. Results of the Spalding basement ventilation test for the east and west ends of the basement hallway

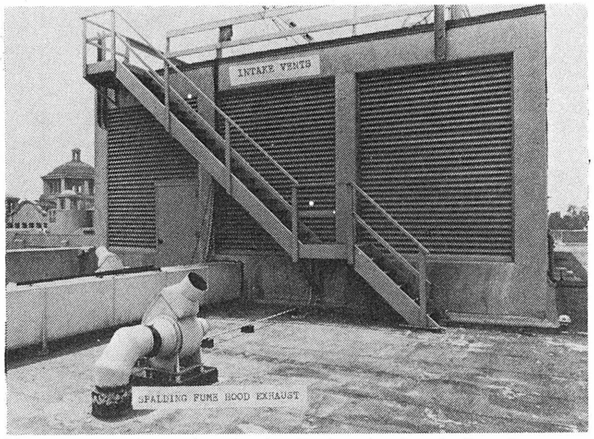

Figure 6. Roof of Spalding, showing the fume hood outlet from Room 236 and the main ventilation intakes

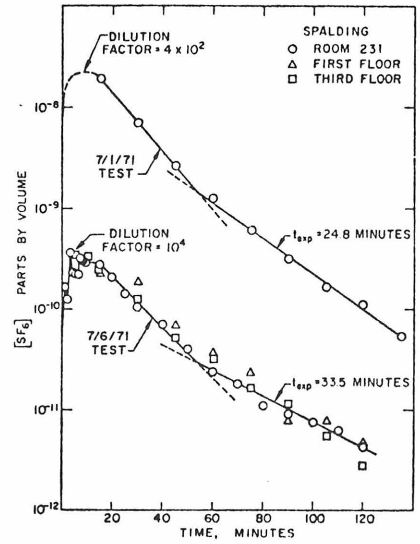

Figure 7. Results of two fume hood releases of SF_6 from Spalding, Room 236

Fume Hood Tests and Results

As mentioned previously, most studies concerning dilution of exhaust gases from buildings have used scale models in controlled wind and water tunnel experiments. In the present study, SF_6 was released inside a laboratory fume hood and the amount reentering the building after leaving the exhaust was measured in several locations inside the building.

Two tests were made from a fume hood in Room 236 in Spalding Laboratory; the room is a chemical engineering research laboratory. Spalding is a rather large, rectangular three-story building with the main ventilation intake and exhaust on the roof along with 10 fume hood exhausts. The roof ventilation system has some recycle and serves the first three floors; the basement has an independent ventilation system. Surprisingly, the fume hood exhaust for Spalding 236, shown in the foreground of Figure 6, was located only 16 ft from the main intake of the ventilation system (the three large panels in the background).

In the first test, pure SF_6 was released at a rate of 144 ml/min for 10 min into a fume hood which had a flow rate of 590 ft^3/min. Therefore, the exhaust SF_6 concentration was 8.7×10^{-6}. Measurements of the amount of SF_6 which reentered the building were taken in Room 231 of Spalding; the door was kept closed to prevent any direct contamination from Room 236, the release point. Wind direction was not measured for this test.

Results are shown in the upper curve of Figure 7. Surprisingly high concentrations were reached in the building. A dilution factor, D, can be defined:

$$D = \frac{\text{Exhaust concn}}{\text{Max. concn recorded in building}} \qquad (8)$$

For this case, $D = 400$. The minimum value of D, because of the large area of the intake vents, would occur if the entire fume exhaust reentered the intake vent. Since the flow rate of the intake vent is approximately 50,000 ft^3/min and the fume hood exhaust is 590 ft^3/min, the minimum dilution factor would be:

$$D_{min} = \frac{50{,}000}{590} = 85 \qquad (9)$$

Thus, in this case, 85/400 or about 20% of the exhaust fumes reentered the ventilation system. The intake vent in this case had such a large area (14 × 24 ft) it could easily accommodate the width of a plume from the exhaust duct even under very unstable conditions.

A second test from the same fume hood was made releasing pure SF_6 at a rate of 58 ml/min for 10 min. The exhaust concentration in this case was 3.5×10^{-6}. Measurements were made in 231 Spalding and also in the first and third floor hallways of Spalding. The wind direction was from the south, blowing in gusts in the same direction as the fume hood exhaust (Figure 6). Results are shown by the lower curve of Figure 7.

The dilution factor D (exhaust concn/max. concn inside) in this test was about 10^4. Thus, wind conditions are extremely important in determining contamination: in this test, the wind blew most of the exhaust fumes away from the intake; in the first test, 20% of the fumes reentered (wind direction was not measured).

Samples taken on each of the three floors were almost identical, indicating that any exhaust fumes reentering the building were well-mixed after entering the intake vent. Both tests showed a break in the slope of the curves for the 231 Spalding

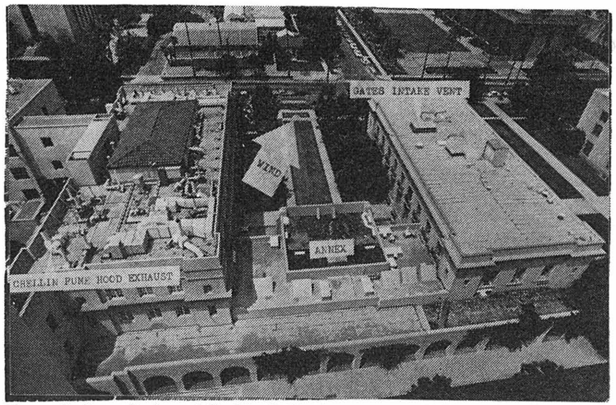

Figure 8. Overall view of Crellin (left), the annex, and Gates, showing the fume hood outlet from Crellin, Room 357 and the ventilation intake of Gates

Figure 9. West side of Crellin, showing the fume hood outlet from Room 357 and the ground-level ventilation intake

data at about 50 min; this phenomena is probably due to small eddies in corners of the room. The experimental residence times, t_{exp} = 24.8 min and 33.5 min, are quite long, indicating that recirculation is not desirable in buildings with fume hood exhausts.

One additional fume hood release test was made in Crellin—an organic chemistry laboratory. Crellin is a rectangular three-story building joined by an annex to Gates, an older two-story chemistry building, as shown in Figure 8. The main exhaust vent and 31 fume hood outlets are on the roof of Crellin; the main intake vent is at ground level, as shown in Figure 9. The intake and exhaust of Gates are both located on the roof.

On the day of the test, there was a variable wind blowing from the south-southwest, as shown in Figure 8. Seventy-six ml/min of pure SF_6 was released from a fume hood in Room 357 Crellin for 20 min. This fume hood exhaust is located in the southwest corner of Crellin as indicated in the photographs and has a flow rate of 690 ft^3/min. Thus, the exhaust concentration in this case was 3.9×10^{-6}. Samples were taken in the first-floor hallways of Crellin and Gates and in the annex hallway between Crellin and Gates. Results are shown in Figure 10.

The highest concentrations were recorded in Crellin and the lowest in Gates, contrary to intuition which suggested the wind direction would carry exhaust fumes over to the Gates inlet vent. Results are summarized in Table III. The dilution factors are relatively high, due mainly to the fact that the intake vent of Crellin is not on the roof (where the fume exhausts are), but at ground level.

To illustrate the usefulness of dilution factors, consider a student in Spalding running a reactor with chlorine gas, for which the minimum safe level is 1 ppm. Using a minimum dilution factor of 100, the fume hood exhaust should have no higher concentration than 10^{-4}. Since a typical fume hood flow rate is 10^7 ml/min, the student should not be allowed to run chlorine gas at any flow rate higher than 1000 ml/min.

Table III. Results of Crellin Fume Hood Release

Location	Dilution factor	t_{exp}, min
Crellin, first floor	4×10^4	12
Annex, first floor	1.4×10^5	17
Gates, first floor	6×10^5	37

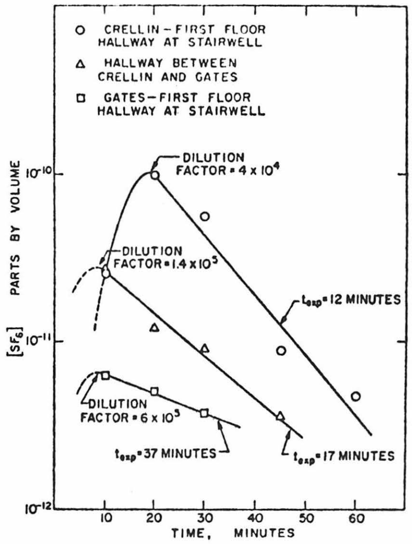

Figure 10. Results of the fume hood release of SF_6 from Crellin Room 357

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APPENDIX A-2. PROBING THE AIR FLOW WITHIN THE WAKE DOWNWIND OF A BUILDING BY MEANS OF A TRACER TECHNIQUE

(by P. J. Drivas and F. H. Shair)

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ABSTRACT

Sulfur hexafluoride, an inert, gaseous tracer detected by means of electron-capture gas chromatography, was used to probe the air flow within the wake downwind of a 12 m high, three-story building. A reverse-flow circulation was observed with a longitudinal extent downwind of about three building heights; the extent of the recirculation on the roof was confined to less than one-half the width of the building from the downwind edge. The recirculating velocities in the wake were estimated to be about 0.1 - 0.3 those of the prevailing wind at the top of the building. The wake downwind of the building was found to be well-mixed in all three dimensions and exhibited a characteristic exponential dilution time of approximately one minute. Some practical contamination problems relating to the wake were also examined, including direct infiltration of the tracer into the building.

1. INTRODUCTION

The transport of outdoor pollutants into a building by way of ventilation and infiltration is of considerable concern (McCormick, 1971; Benson et al., 1972; Sabersky et al., 1973; Derham et al., 1974; Shair and Heitner, 1974; Hales et al., 1974). The influence of the air flow patterns around buildings upon ventilation systems has long been of interest to engineers (ASHRAE Guide and Data Book: Applications, 1971). One important consideration is the location of ventilation inlets and outlets which minimizes the reentry of contaminated exhaust air (Clarke, 1965). Another important consideration is the location of the ventilation inlet which tends to minimize the entry of contaminants arising from parking lots and streets.

Several studies have investigated air flow around buildings, although most have used wind and water tunnel tests on scale models of buildings (Evans, 1957; Halitsky, 1962, 1963; Davies and Moore, 1964). Scorer (1963) concisely cites the limitations of wind tunnel experiments in the study of air flow around buildings; although possessing limitations, such studies can certainly be of use in the planning and designing of new buildings and building complexes.

In order to determine the air flow and dispersion of pollutants around real buildings, field studies involving atmospheric tracers are quite useful. Munn and Cole (1967) used a fluorescent particulate tracer, uranine dye, to investigate the dilution of a building exhaust 150-300 meters downwind. Caput et al. (1973) also used uranine dye to study the transport of air over a thin wind-break. Probert et al. (1973) used a soap bubble solution as a visual tracer to investigate the separation angle associated with wakes behind cylindrical tanks. Using sulfur hexafluoride as a tracer, Drivas et al. (1972) investigated the reentry of fume hood exhausts into a building; in one case it was found that 20% of the exhausted fumes reentered the ventilation system of the building.

A sketch of a typical air flow pattern around a building (Halitsky, 1963) is presented in Figure 1. One main characteristic of the side view is the large eddy or cavity which forms downwind in the wake behind the building, causing a reverse flow from ground level to the roof of the building. Investigation of this recirculation is important since (1) pollutants emitted near the ground level from automobiles may be transported directly to a roof intake vent and (2) toxic gases exhausted from the roof may be transported to the ground level where people may be present and where ventilation intakes may be located.

Knowledge of the air flow dynamics around a building is essential to good planning of its ventilation system. In this work, sulfur hexafluoride was used as a tracer to probe the air flow and dispersion patterns within the wake downwind of a three-story building. Specifically, the extent and velocities of the recirculation in the wake were investigated and a characteristic exponential dilution time for the wake was determined. Also, some practical contamination problems relating to the wake were examined, including direct infiltration of the tracer into the building.

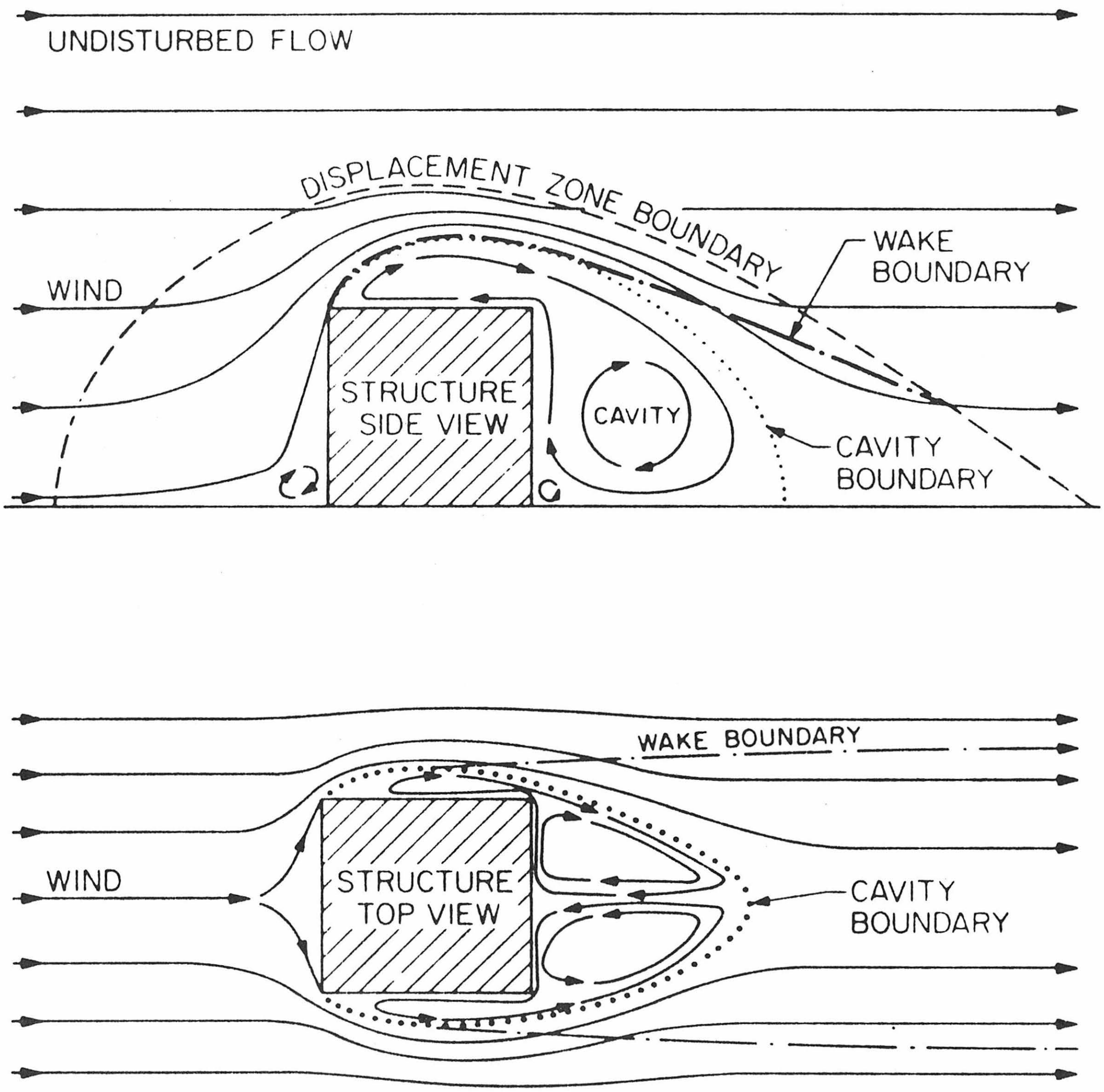

Figure 1. Sketch of the air flow patterns around a building, showing the recirculating cavity region (Halitsky, 1963).

2. EXPERIMENTAL PROCEDURE

Since the development of the electron-capture detector for gas chromatography by Lovelock and Lipsky (1960), several suitable tracers have been used in various meteorological studies (Collins et al., 1965; Saltzman et al., 1966; Lovelock, 1971). The tracer used in this work was sulfur hexafluoride; since it is gaseous, physiologically inert, chemically inert, and easily detectable in extremely low concentrations, SF_6 is an excellent air flow tracer. Preliminary field tests using SF_6 as a tracer have shown quite successful results (Turk et al., 1968; Dietz and Cote, 1973). Current analysis techniques have reached detection limits of 2×10^{-13} parts SF_6 per part of air (Simmonds et al., 1972).

In this work, the tracer was released in most tests as an instantaneous point source (i.p.s.) by bursting a single balloon which contained approximately one liter of SF_6. In one test, a quasi-instantaneous line source release from an automobile exhaust was used. Samples were collected by the squeeze bottle technique and analyzed by the electron-capture gas chromatography procedure described by Drivas et al. (1972). The concentrations of SF_6 which were detected ranged from 10^{-6} to 1.5×10^{-12} parts SF_6 per part of air, an extremely large detection range of about 10^6.

The wake tested was that downwind of a three-story building (the Caltech Spalding Laboratory of Chemical Engineering) which is 12 m high, 17 m in width, and 64 m long, as shown in Figure 2. The intake and exhaust vents of the ventilation system for the first three floors are housed in a small penthouse on the roof, as shown in Figure 2; a photograph showing the detail of the penthouse intake vents can be found in

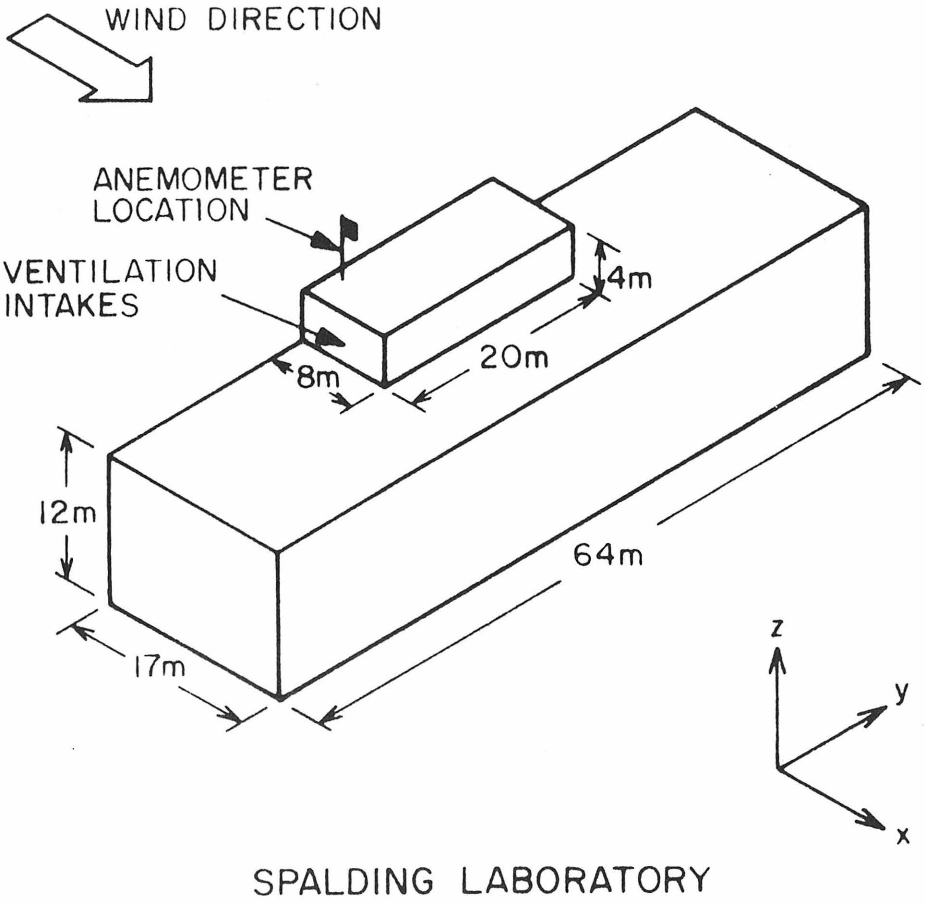

Figure 2. Spalding Laboratory, the three-story building tested, showing the wind direction and coordinate system.

Drivas et al. (1972). Since the intake flow rate is about 1.4×10^6 l/min and the building volume is about 1.3×10^7 l, the characteristic time for mixing in the building is about 9 min. In general, a test was conducted by releasing an instantaneous point source of SF_6 within the wake downwind of this building and monitoring the concentration of tracer at various points within the wake, on the roof, and inside the building.

The velocity and direction of the wind blowing over the building were measured at 18 m above ground level by an anemometer located on top of the penthouse. During the afternoon, the normal prevailing wind direction was perpendicular to the length of the building, with the penthouse on the upwind side; thus a wake formed downwind of the building in the x direction, as shown in Figure 2. For most of the tests, the average wind velocity was approximately 2.5 m/sec, although rapid fluctuations in any one test could vary from zero wind velocity to greater than 5 m/sec. Based on a wind velocity of 2.5 m/sec and the height of the building (12 m), the characteristic Reynolds number was approximately 2×10^6. The stability conditions varied from moderately unstable to neutrally stable, corresponding to the Pasquill stability categories B-D. It should be noted that the building tested was located in a complex of other buildings, however there were no buildings directly downwind which could influence the dimensions of the wake.

3. PRESENTATION AND DISCUSSION OF RESULTS

An important consideration in the analysis of experimental data in general is the reproducibility of repeated experiments. Four instantaneous point source (i.p.s.) releases were made at 6 m downwind of the building and 1.2 m above ground level; for each test the concentration of tracer was monitored on the roof, 1.5 m from the downwind edge, in a direct line from the release point in the x direction. Figure 3 shows the results of the two tests which had the largest difference in the tracer peak concentration. Also in Figure 3 are shown the results of two i.p.s. releases made at 6 m downwind of the building and 0.3 m above ground level; as above, the tracer concentrations were monitored on the roof, 1.5 m from the downwind edge.

As can be seen in Figure 3, the quantitative reproducibility was not especially good, since the peak concentrations on the roof for the two releases at 1.2 m above ground level varied by a factor of 100. However, the qualitative similarity of the two curves is quite evident, with a sharp primary peak followed by a somewhat oscillatory decay to a relatively constant value after about 5 min. Likewise, a quite distinct qualitative difference exists between the two releases at 1.2 m above ground level and the two releases at 0.3 m above the ground; the significance of this difference will be discussed below. Thus, although tracer concentrations in any repeated tests could vary by a factor of ten or more, the extremely large range of detection (from 1 to 10^{-6} ppm of tracer) allowed significant qualitative differences to become observable.

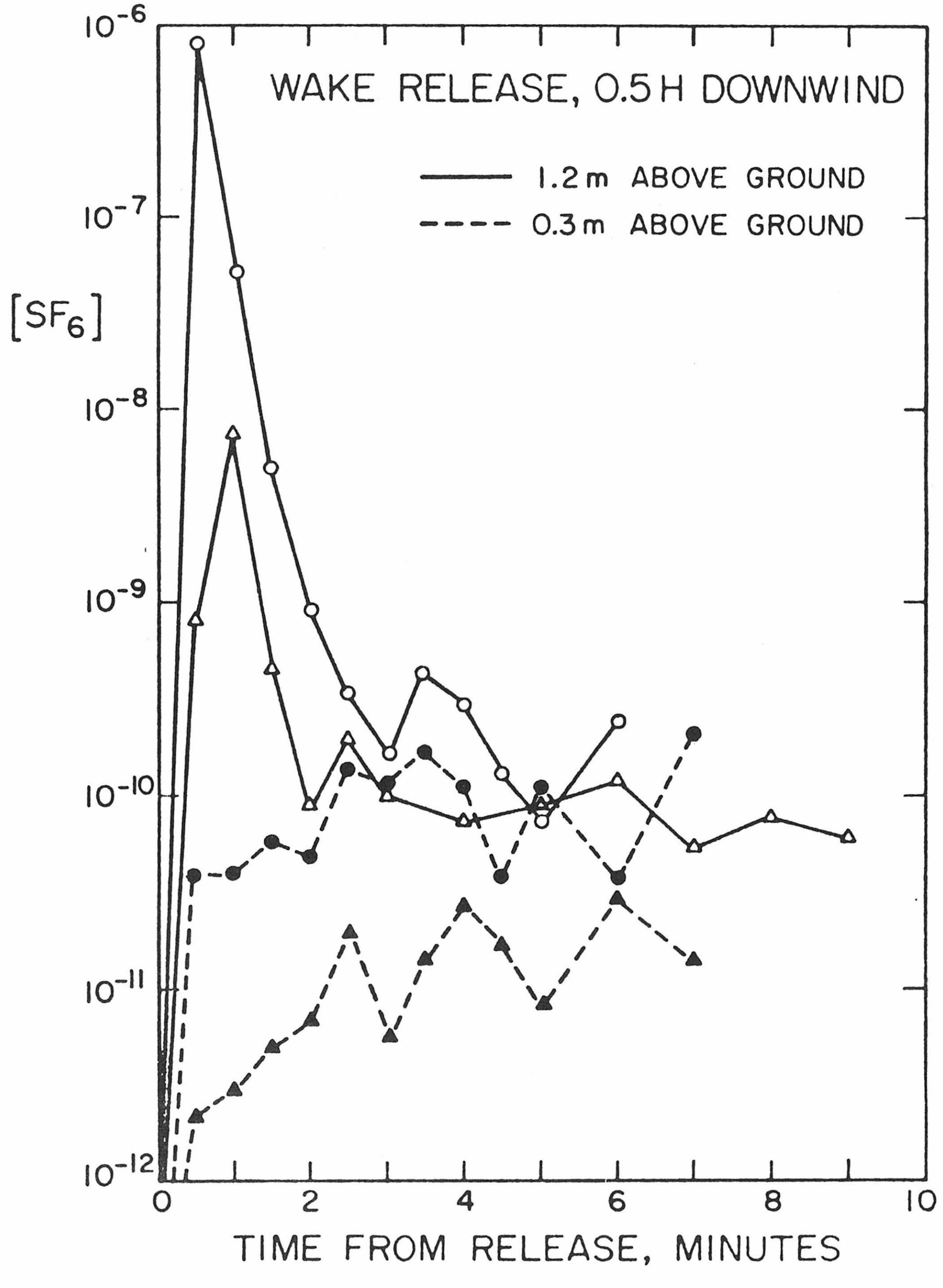

Figure 3. SF_6 concentration on the downwind edge of the roof as a function of time from releases made 6 m downwind at 1.2 m and 0.3 m above ground level.

An important feature of the two releases at 1.2 m above ground level in Figure 3 is that significant concentrations were recorded on the roof within 30 - 60 sec, indicating a reverse flow carrying the tracer from ground level to the roof. The effect of buoyancy was considered as a cause, however measurement of ambient temperatures indicated no temperature differences between 0.3 m above ground level, 1.2 m above ground level, and roof level. In fact, on days with strong sunshine, the wake of the building was in shade up to 12 m downwind and thus slightly cooler than roof level, possibly introducing a local stabilization. Thus, the experimental evidence suggests the existence of a recirculating eddy in the wake downwind of a building, in agreement with previous investigations (Evans, 1957).

Calculation of the velocities necessary to initially carry the tracer from the ground to roof level yielded values of 0.3 m/sec for a 60 sec transit time and 0.6 m/sec for a 30 sec transit time. Since the average free-stream wind velocity was about 2.5 m/sec, the circulation velocities within the wake can be estimated to be 0.1 - 0.3 those of the upstream prevailing wind. These values are consistent with recirculating velocities associated with other wake flows; for example, Grove et al. (1964) investigated the velocities within the wake behind a circular cylinder and found that the recirculating velocities were about 0.1 - 0.3 those of the free-stream velocity. Recently Caput et al. (1973) estimated that the recirculation velocities behind a thin wall were less than 50% of the free-stream velocity at the top of the wall.

To determine the longitudinal extent of the recirculating eddy in the x direction, a series of i.p.s. releases were made at 1.2 m above ground level at increasing downwind distances from the building. Tracer concentrations were monitored on the roof, 1.5 m from the downwind edge; thus, any measurable concentrations recorded on the roof would be indicative of a reverse circulation. Releases made at four building heights (4H) downwind and at greater distances yielded no measurable tracer concentrations on the roof. Releases made at 3H downwind (H = 12 m) resulted in irregular but measurable concentrations on the roof. Releases at downwind distances less than 3H yielded quite high tracer concentrations on the roof, as will be shown below. Thus, the longitudinal extent of the recirculating eddy in the x direction appeared to be about three building heights downwind, or 3H. Wind tunnel tests on a scale-model building of similar shape indicated that the extent of the downwind eddy was about 3.75 H (Evans, 1957).

To determine the extent of the recirculation on the roof, an i.p.s. release was made in the wake, 6 m (0.5 H) downwind from the building and 1.2 m above ground level. Concentrations were monitored at 1.5 m from the downwind edge of the roof, at the center of the roof near the main intake vents, and 1.5 m from the upwind edge of the roof. The results are shown in Figure 4. A large peak concentration was recorded at the downwind edge, much less at the center of the roof, and even less at the upwind edge during the first three minutes. Apparently, the extent of the recirculation on the roof was mainly confined to a region somewhat less than one-half the width of the building from the downwind edge. It should be noted in Figure 4 that after about 5 min, all three locations on the roof reached a relatively constant concentration; this effect was thought to be due to the contamination from the main building

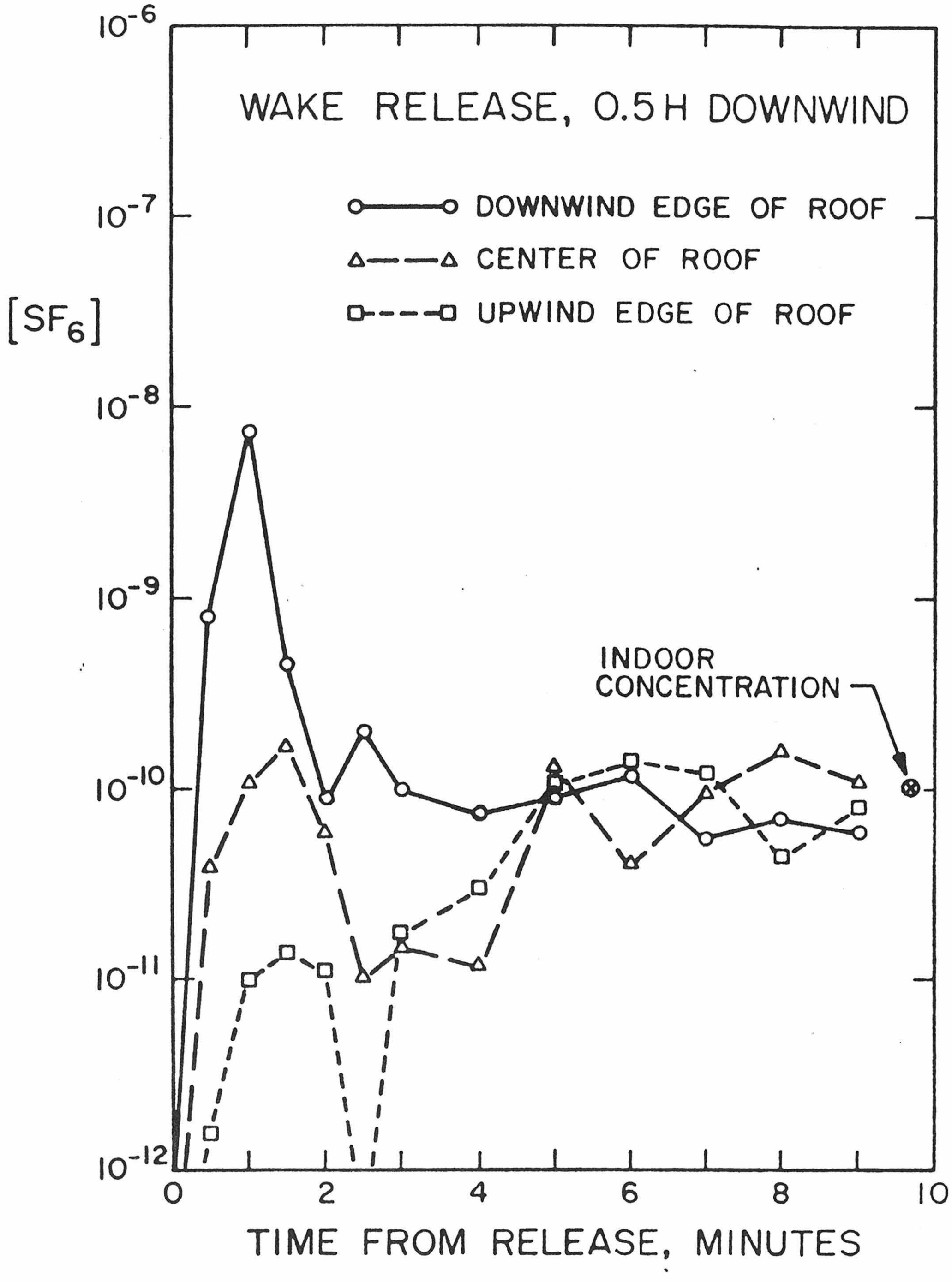

Figure 4. SF_6 concentration at three locations on the roof as a function of time from a release made 6 m downwind at 1.2 m above ground level.

exhaust and will be discussed below.

Tracer measurements were made in the wake itself to investigate if the wake became well-mixed and to determine a characteristic exponential dilution time. One i.p.s. release was made 0.5 H downwind from the building, 1.2 m above ground level, and near the center of the building on the y axis. Concentrations were monitored at the release point, on the roof (1.5 m from the downwind edge) above the release point, and in the wake at 0.5 H downwind, 1.2 m above ground level, and 1 H from the end of the building in the y direction. As shown in Figure 5, in all three locations similar concentrations were recorded, in most cases within a factor of two. Thus, the wake appeared fairly well-mixed both vertically and along the axis of the length of the building (the y direction). Using the data from only the first 5 min in Figure 5, a computer linear least-squares fit resulted in a characteristic exponential dilution time of 1.0 min. As will be discussed below, after about 5 min, contamination from the main building exhaust is thought to have occurred.

A similar test was made to determine if the wake was well-mixed longitudinally downwind (in the x direction). An i.p.s. release was made in the same location as the previous test; concentrations were monitored in the wake at 1.5 H and 2.5 H downwind in the x direction at 1.2 m above ground level. The results are shown in Figure 6. As in the previous test, after 60 seconds, both locations had similar concentrations, indicating that the wake was also well-mixed longitudinally downwind (along the x axis). Using the data from only the first 5 min in Figure 6, a computer linear least-squares fit resulted in a characteristic exponential dilution time of 1.0 min. Thus, using this tracer

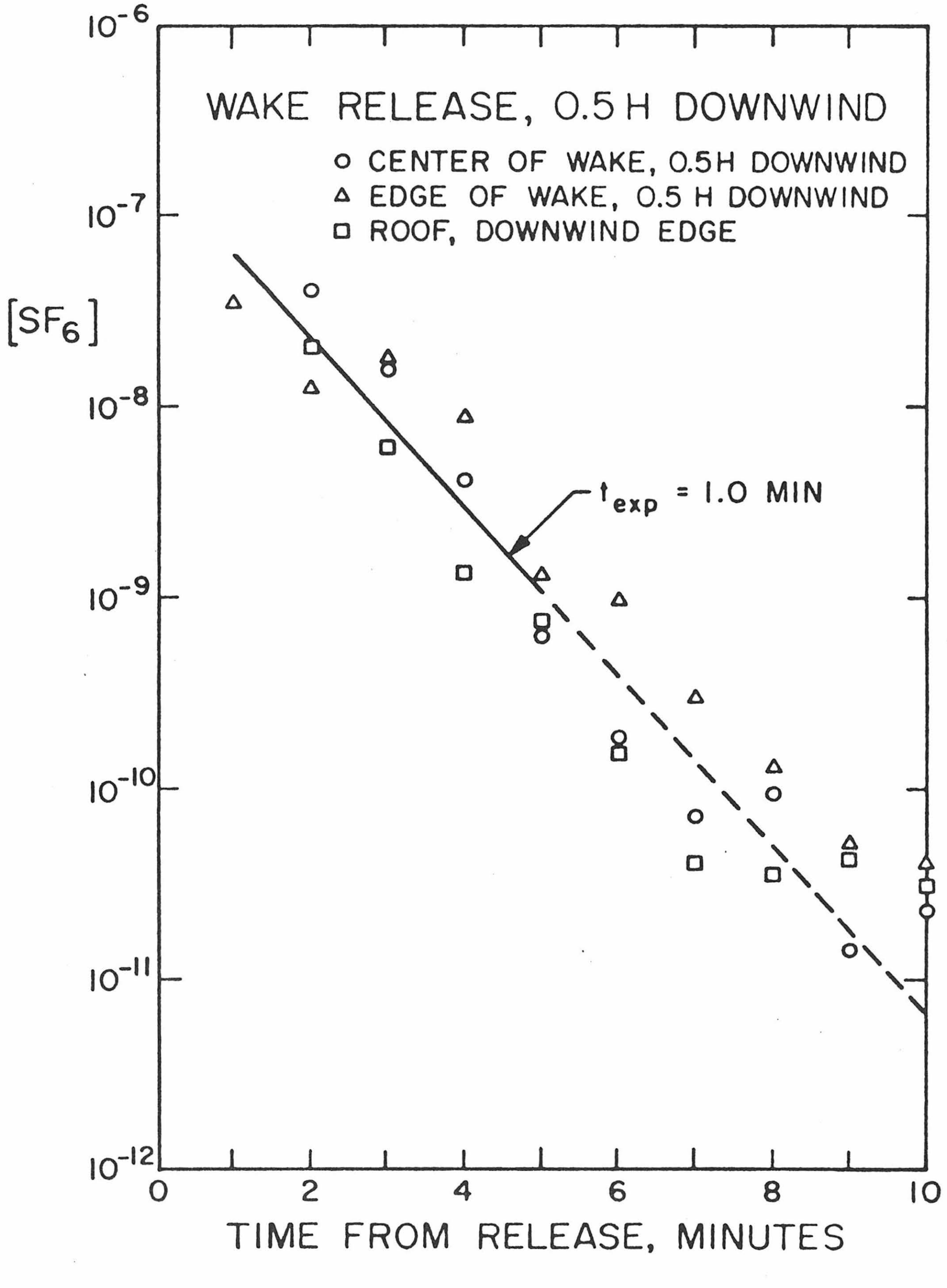

Figure 5. SF_6 concentration at the center of the wake, the edge of the wake, and on the downwind edge of the roof as a function of time from a release made 6 m downwind at 1.2 m above ground level.

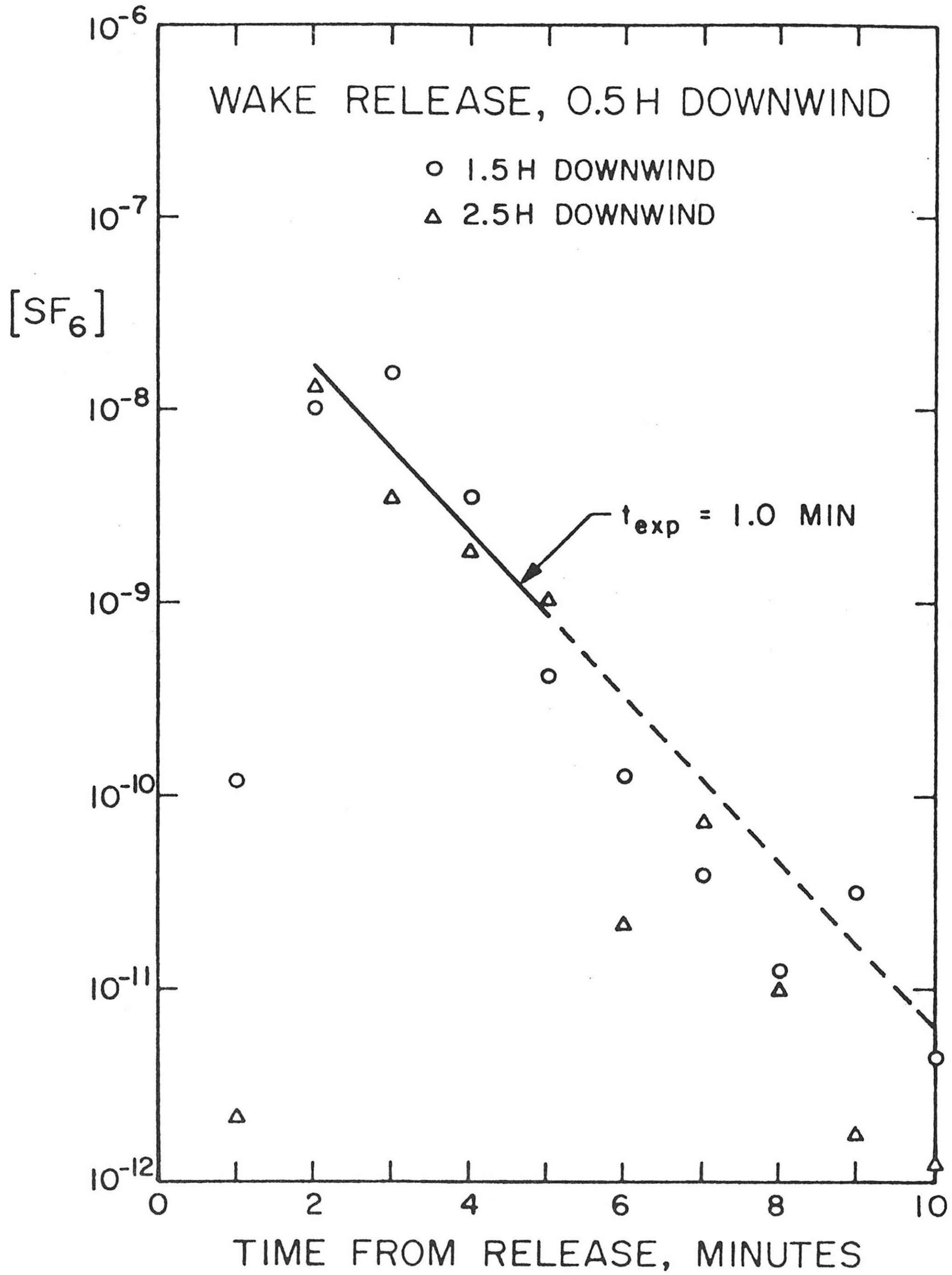

Figure 6. SF_6 concentration in the wake at 18 m and 30 m downwind as a function of time from a release made 6 m downwind at 1.2 m above ground level.

technique, it could be determined that the wake under investigation became well-mixed in all three dimensions in a period of about 2 minutes and had a characteristic exponential dilution time of approximately one minute.

Figures 7 and 8 show the relative influences of the height and downwind distance of a ground-level release on the peak concentrations recorded on the roof. An i.p.s. release was made at 0.5 H, 1.0 H, and 1.5 H downwind of the building at 1.2 m above ground level in Figure 7 and at 0.3 m above ground level in Figure 8. The tracer concentration was monitored in each case on the roof, 1.5 m from the downwind edge, in a direct line from the release point in the x direction. As can be seen, a distinct qualitative difference exists between the 1.2 m releases in Figure 7 and the 0.3 m releases in Figure 8; this same difference is also evident in Figure 3. These data possibly suggest the existence of different flow regimes between 1.2 m and 0.3 m above ground level. Certainly, the height of the releases was more influential than the downwind distance in the wake when considering the peak concentrations observed on the roof.

A quasi-instantaneous line source release of tracer by an automobile moving within the wake was conducted to determine if mixing caused by the wake of the moving automobile could influence pollutant transfer. About 1.5 l of tracer was released in the wake of the building from the automobile exhaust which was 0.3 m above ground level; the automobile was driven at a speed of 40 km/hr parallel to the length of the building in the y direction and 1 H downwind of the building. The concentration of tracer was monitored on the roof, 1.5 m from the downwind edge. As

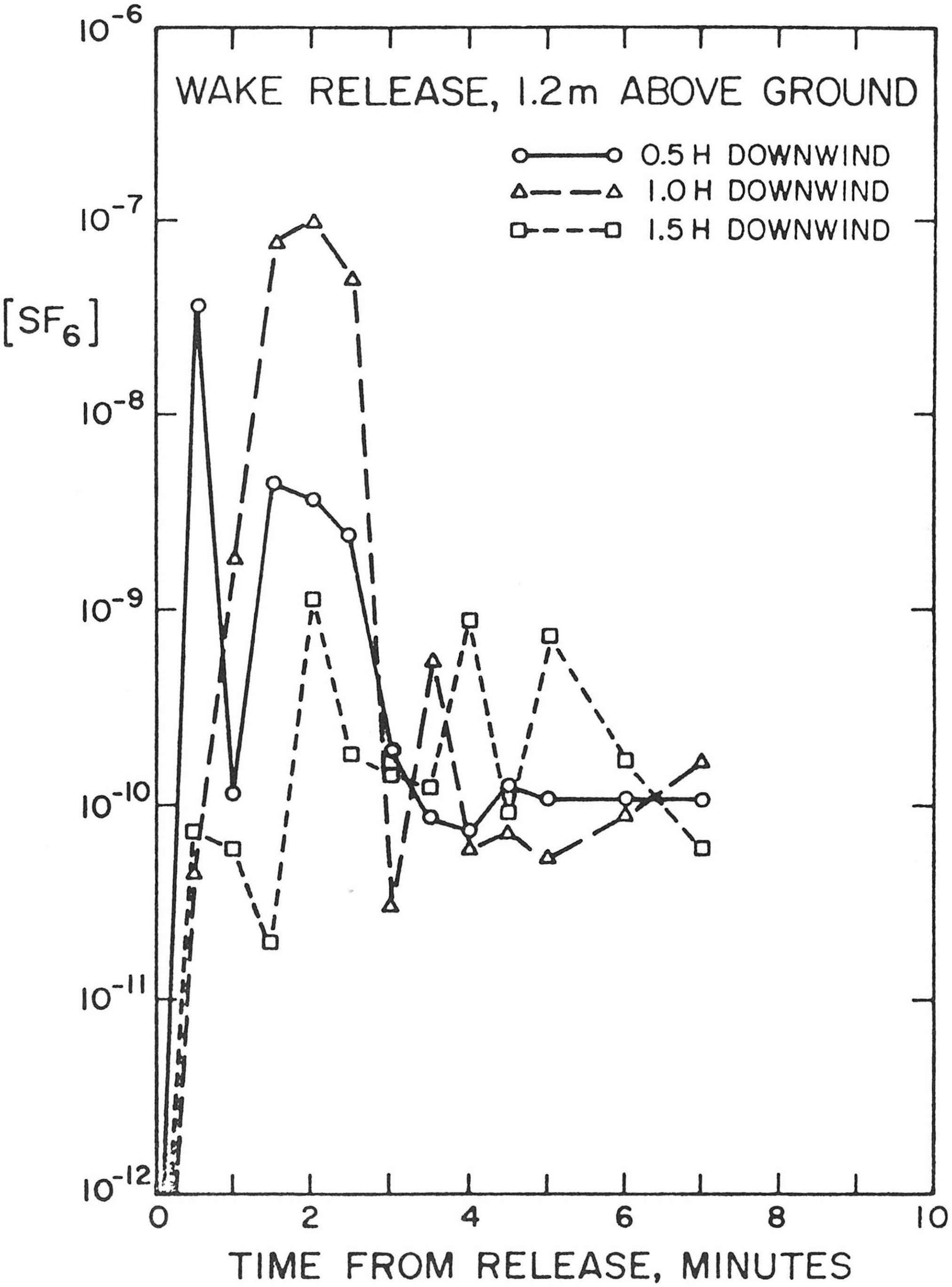

Figure 7. SF_6 concentration on the downwind edge of the roof as a function of time from releases made 1.2 m above ground level at different distances downwind.

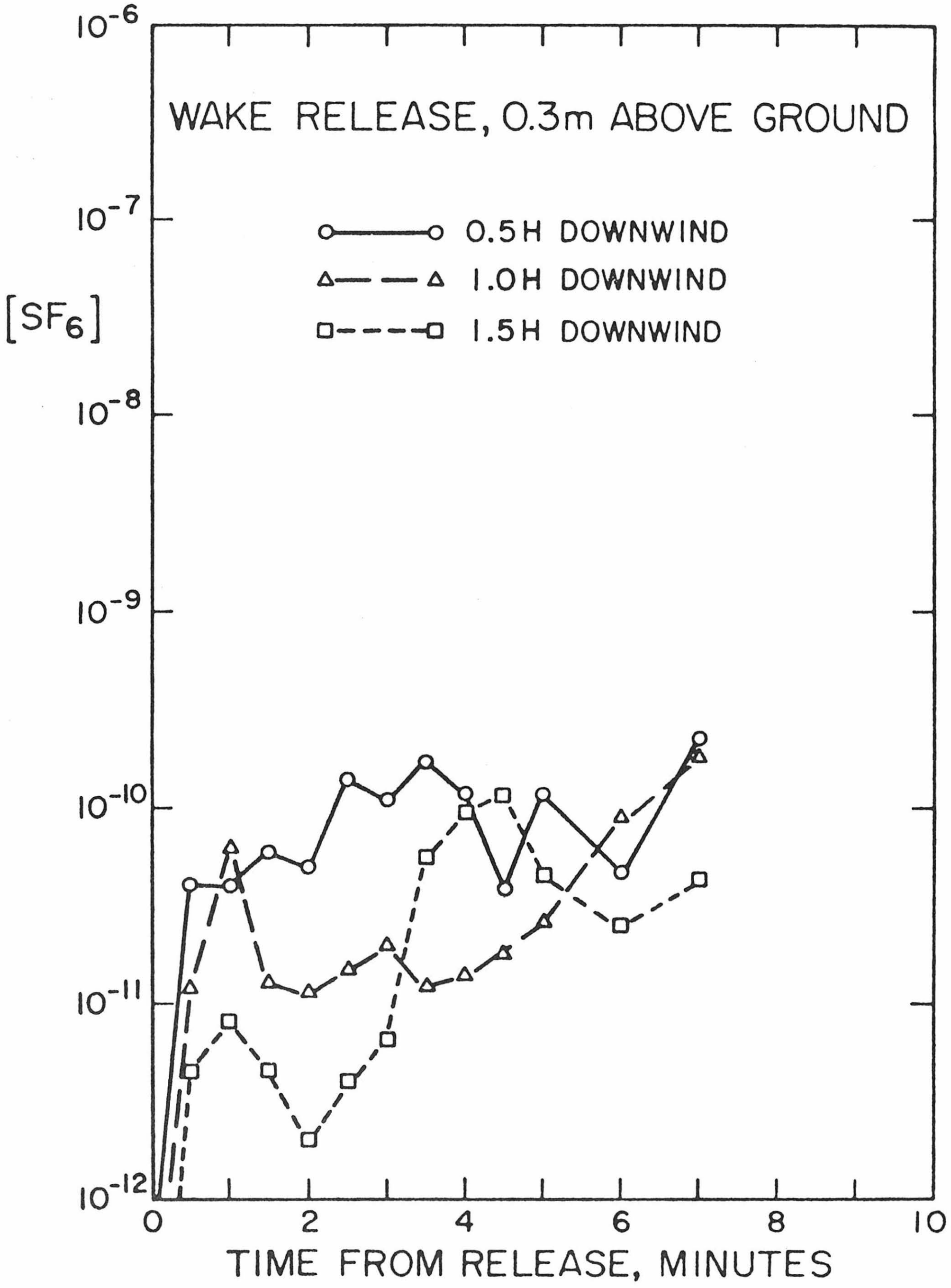

Figure 8. SF_6 concentration on the downwind edge of the roof as a function of time from releases made 0.3 m above ground level at different distances downwind.

shown in Figure 9, the tracer curve exhibits some of the characteristics of a release 1.2 m above ground level, although the actual release height was 0.3 m above the ground. Apparently some mixing of the tracer did occur initially in the wake behind the moving automobile.

It had been noted during the course of the experiments that the tracer could be detected inside the building, presumably drawn in through the main intake vents on the roof. In Figure 4, the data taken at the center of the roof represents the amount of tracer which could enter the main intake vents. If this curve is integrated over time for the first 3 minutes, the resulting tracer concentration in the building, assuming that the building is well-mixed, is about 2×10^{-11}. However, as shown in Figure 4, the tracer recorded indoors reached a concentration level of about 10^{-10}. Possibly, direct infiltration from the wake into the building had occurred.

An important feature of the tracer concentration curves, especially clear in Figure 4, is that after about 5 min from the tracer release, concentrations on the roof approached a relatively constant value. A test was conducted to determine if contamination due to the main ventilation exhaust on the roof was likely to occur. About 10 cm^3 of SF_6 were released inside the main ventilation intake, and concentrations were monitored inside the building on each floor and also outside on the roof near the main intake vents. The results are shown in Figure 10. The initial portions of the indoor curves indicate differences which occur between floors in the air distribution system. However, it should be noted that after about 5 minutes, the building became fairly well-mixed. Also, after about 5 minutes, the roof indeed became contaminated due to

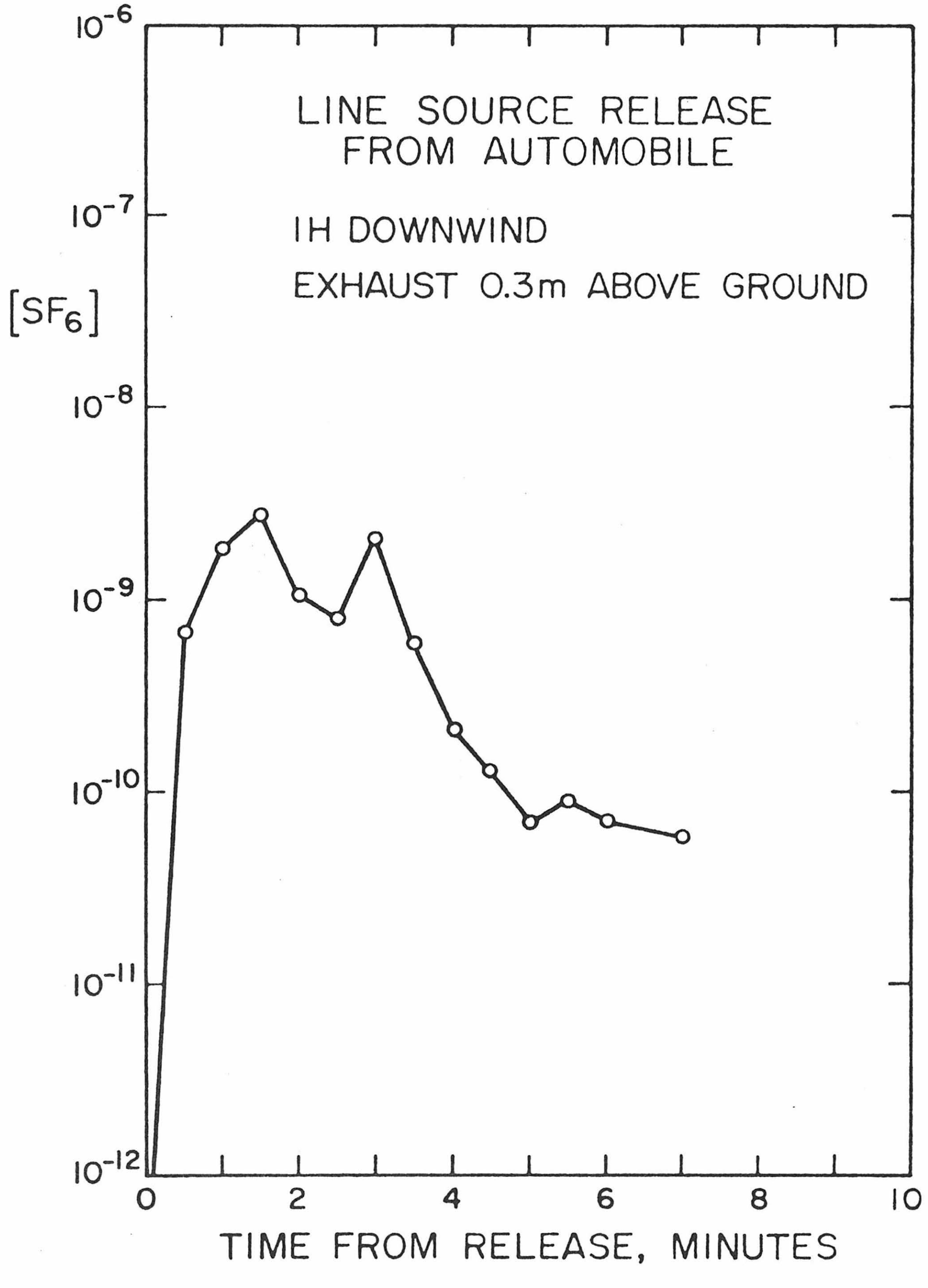

Figure 9. SF_6 concentration on the downwind edge of the roof as a function of time from a line source release by automobile made 12 m downwind at 0.3 m above ground level.

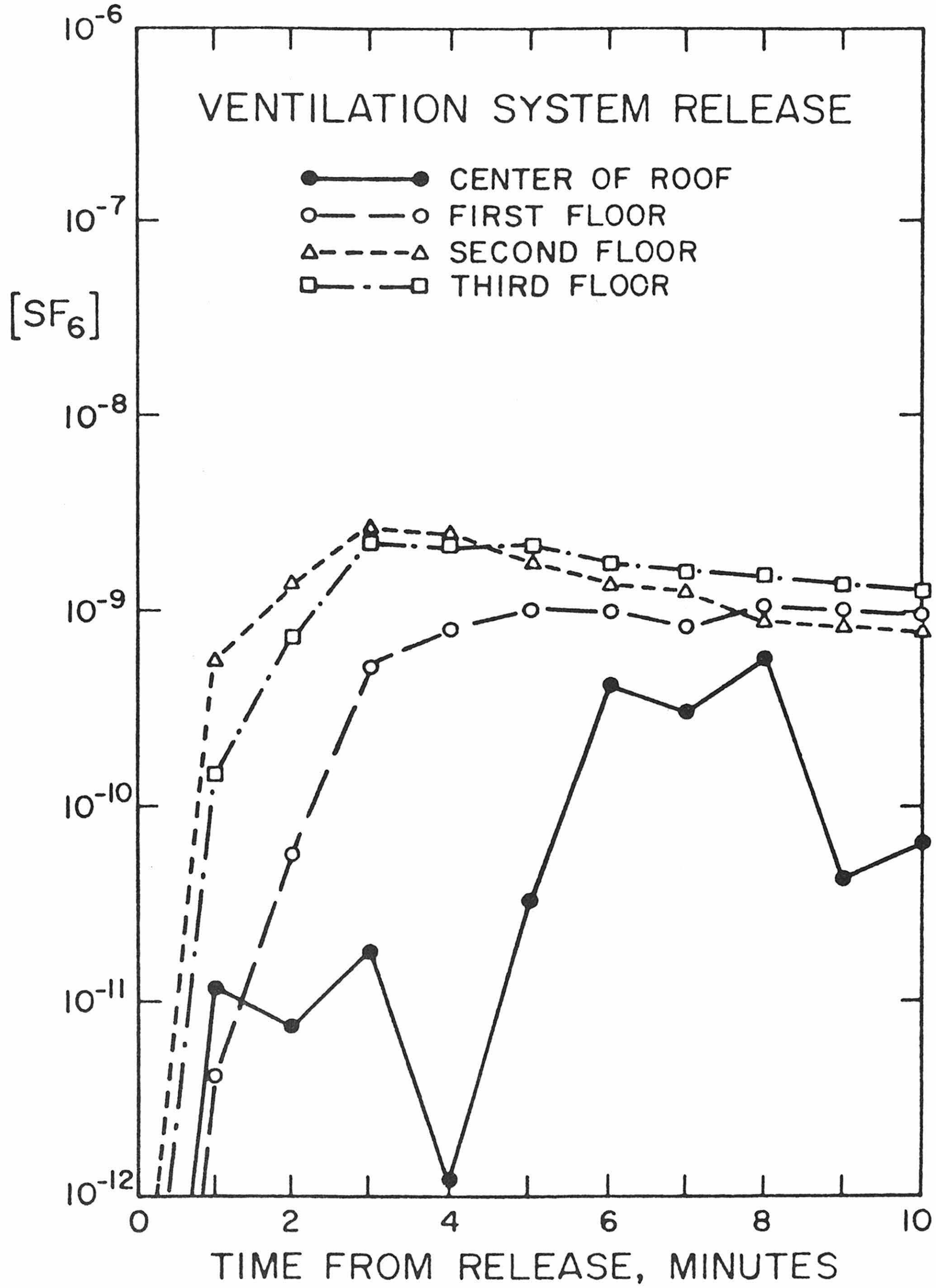

Figure 10. SF_6 concentration inside the building and at the center of the roof as a function of time from a release made inside the ventilation intake.

the building air being exhausted on the roof. Thus, only the data taken within about 5 minutes of a release can be attributed solely to the air flow patterns in the wake.

4. CONCLUSION

This work was not meant to completely characterize the dynamics and dispersion associated with air flow around buildings. In this work, an inert, gaseous tracer, detected by means of electron-capture gas chromatography, was used to probe the characteristics of air flow and dispersion of pollutants around a specific building. Using SF_6 as a tracer, some basic characteristics of the wake downwind of a three-story building were investigated. The experiments determined, among other factors, the extent of the recirculating eddy and the characteristic exponential decrease time in the wake. An important point is that only one specific building shape and size was studied; tracer tests on many other buildings are necessary before any generalization of the experimental results can be made. It is anticipated that future use of this tracer technique can be quite useful in elucidating the dynamics of air flow around urban buildings and building complexes.

ACKNOWLEDGEMENT

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APPENDIX A-3. DISPERSION OF AN INSTANTANEOUS CROSSWIND LINE SOURCE OF TRACER RELEASED FROM AN URBAN HIGHWAY

(by P. J. Drivas and F. H. Shair)

In press, Atmospheric Environment.

ABSTRACT

Sulfur hexafluoride was used as a gaseous tracer in a quasi-instantaneous line source release by an automobile moving along an urban highway in Los Angeles. Concentrations at various locations from 0.4 km to 3.2 km downwind of the highway were recorded at ground level as a function of time. The tracer data were used to test the validity of several theoretical models which can be used in predicting the dispersion from an instantaneous crosswind line source. The model based upon the semi-empirical turbulent diffusion equation, using a power-law vertical velocity profile and a power-law vertical eddy diffusivity profile, was found to provide the best agreement with the data.

1. INTRODUCTION

At present there are two main methods of characterizing dispersion from pollutant sources in urban areas; one is the Gaussian plume model (Pasquill, 1962), and the other is the use of the so-called semi-empirical equation of turbulent diffusion (Monin and Yaglom, 1971). Most tracer experiments in urban areas have focused exclusively on continuous point source releases and correlation of the data with the Gaussian plume model (Smith, 1968; McElroy, 1969; Sandberg et al., 1970). Hilst and Bowne (1971) used an instantaneous line source of tracer released by airplane and correlated the data with a Gaussian plume model. Various urban diffusion models based on this concept have appeared in the literature (Turner, 1964; Clark, 1964; Miller and Holzworth, 1967).

The semi-empirical equation of turbulent diffusion (sometimes called K-theory) uses the concept of an eddy diffusivity and offers greater generality. A common form of this equation for diffusion from a cross-wind line source is

$$\frac{\partial c}{\partial t} + \bar{u}\,\frac{\partial c}{\partial x} = \frac{\partial}{\partial z}\left(K_z\,\frac{\partial c}{\partial z}\right) + \frac{\partial}{\partial x}\left(K_x\,\frac{\partial c}{\partial x}\right) \tag{1}$$

where c is time-averaged concentration, $\bar{u}$ is time-averaged horizontal wind velocity, and K_z and K_x are respectively the eddy diffusivities in the vertical and the along-wind horizontal directions. Analytical and numerical solutions of this equation can take into consideration different velocity and eddy diffusivity profiles, various boundary conditions, varying ground terrain, and chemical reactions. The literature abounds with analytical solutions of this equation; Monin and Yaglom (1971) contains a good summary. Numerical solutions have ranged from calculation of carbon monoxide diffusion very close to a highway (Danard, 1972) to complex models of photochemical smog formation in the Los Angeles basin (Sklarew et al., 1972; Lamb and Seinfeld, 1973).

The main drawback of this approach is the gradient transport assumption, which is essentially an analogy from molecular Fickian diffusion and should not strictly apply to mass transport by turbulent eddies. However, values and profiles of eddy diffusivities are empirically derived to take into account the effects of atmospheric stability and ground terrain in much the same way as the empirical constants in the Gaussian plume model. Thus, both approaches are dependent on experimental diffusion data for their basic numerical constants.

In this work, we tested the ability of the Gaussian plume model and various forms of the semi-empirical diffusion equation to predict the dispersion of an instantaneous tracer release. Specifically, sulfur hexafluoride was used as a tracer in a quasi-instantaneous line source release by an automobile along an urban highway in Los Angeles; concentrations at various locations from 0.4 km to 3.2 km downwind of the highway were recorded at ground level as a function of time. These tracer concentration data were used to test the validity of the above theories in predicting the dispersion from an instantaneous urban ground-level crosswind line source.

2. EXPERIMENTAL PROCEDURE AND RESULTS

Sulfur hexafluoride, the tracer used in the experimental program, is an inert, non-toxic gas which can be detected in extremely low concentrations by electron-capture gas chromatography (Collins et al., 1965; Saltzman et al., 1966). Field tests have shown that SF_6 is an ideal atmospheric tracer (Turk et al., 1968; Clemons et al., 1968). Concentrations were determined as a function of time by sampling with a squeeze bottle technique and analyzing the samples with an electron-capture gas chromatograph, as described in detail in Drivas et al. (1972). The measured concentrations ranged from 10^{-8} to 2×10^{-12} parts SF_6 per part of air.

A quasi-instantaneous line source of sulfur hexafluoride was released from the exhaust of an automobile moving along a Los Angeles highway. The length of the release was approximately 2.4 km in most of six runs. Rates of sulfur hexafluoride release and speeds of the releasing automobile are shown in Table 1. The section of the highway used, Interstate 405 (locally known as the San Diego Freeway), runs parallel to the Pacific Ocean coastline about 6 km inland. During the afternoon a brisk sea breeze normally blows inland perpendicularly across the highway. SF_6 measurements were obtained as a function of time at various locations along a wide cross street, Venice Boulevard, which runs inland in a straight line perpendicular to the highway for over 6 km. The street, approximately 25 meters wide, is located in a flat urban region comprised mainly of one and two-story residences. All samples were taken on Venice Boulevard approximately 1.5 meters above ground level.

Table 1. Description of Experimental Runs.

Run No.	Date	Rate of SF_6 Release (l/min)	Car Speed (km/hr)	Weather Conditions	Temperature* Inversion Height (m)	σ_θ (degrees)
1	8/21/72	31	80	sunny, smoggy	271.	5.6
2	8/28/72	33	80	sunny, smoggy	230.	21.2
3	12/1/72	44	88	partly cloudy	none	8.6
4	1/10/73	31	80	sunny, clear	none	10.1
5	1/12/73	31	80	overcast	510.	9.4
6	1/17/73	36	96	sunny, clear	none	9.8

* Data obtained from the U.S. Weather Bureau station at Los Angeles International Airport. The airport is about 8 km from the testing site and the temperature inversion readings were taken about 2 hours before each experimental run.

Six runs were made in the afternoon when the sea breeze was blowing inland, two runs during the summer and four runs during the winter. The dates, general weather conditions, and heights of temperature inversions (if any) are given in Table 1. The horizontal wind direction was measured during each run by means of an anemometer wind vane 2 meters above ground level. From the recorded wind direction data, the standard deviation (σ_θ, as shown in Table 1) was calculated using a 3 second averaging period and a 10 minute sampling time.

Typical SF_6 concentration vs. time curves at various distances downwind of the line source release are shown in Figures 1 and 2; these data represent Runs 3 and 4 respectively. As might be expected, the peak concentrations decrease and the curves spread with increasing distance downwind. A most interesting feature is that, except for the shortest downwind distance at 0.4 km, the curves are decidedly non-Gaussian; they exhibit a skewness to the right. This skewness increases with increasing downwind distance.

A summary of the sampling locations and peak SF_6 concentrations recorded in all the runs is presented in Table 2, along with four factors which were computed for each location from the recorded concentration curves. In all runs, the along-wind horizontal standard deviation (σ_x, calculated in the normal manner) increases while the total area under each curve decreases with increasing distance downwind. The average time of travel (t_{ave}) was calculated at each location by:

$$t_{ave} = \frac{\int_o^\infty ctdt}{\int_o^\infty cdt} \tag{2}$$

The corresponding apparent average velocity ($\bar{u}$) was calculated by dividing the downwind distance by the average time of travel. It should be noted that, except for one point in Run 2, the apparent average velocity in each run increases with increasing distance downwind.

Variations in the actual wind velocity are not believed to cause this phenomenon.

Table 2. Summary of Experimental Results

Run No.	Downwind Distance (km)	Peak $[SF_6]$ (ppb)	t_{ave} (min)	$\bar{u}$ (m/sec)	σ_x (meters)	Total Area (Arbitrary Units)
1	0.4	4.75	3.05	2.18	49.4	46.3
	0.8	2.35	4.92	2.71	86.8	19.3
	1.6	0.882	7.52	3.55	215.	15.5
2	0.4	1.81	2.55	2.62	57.2	15.5
	0.8	0.623	5.38	2.48	134.	9.58
	1.6	0.365	8.58	3.11	217.	5.77
3	0.4	12.0	3.10	2.15	57.8	160.
	0.8	3.02	6.04	2.21	110.	51.5
	1.6	0.990	9.24	2.89	183.	19.2
	2.4	0.500	12.2	3.29	339.	15.3
	3.2	0.229	15.5	3.44	508.	11.4
4	0.4	2.32	3.57	1.87	74.5	34.8
	0.8	0.382	6.53	2.04	179.	12.1
	1.6	0.126	9.97	2.68	365.	3.61
	2.4	0.0565	14.7	2.72	407.	2.72
5	0.8	1.02	6.46	2.06	122.	22.8
	1.6	0.610	11.1	2.41	242.	13.7
	2.4	0.305	15.3	2.61	345.	11.6
6	0.8	0.285	7.97	1.67	102.	7.12
	1.6	0.0855	14.2	1.88	214.	3.50
	2.4	0.0478	18.1	2.21	323.	2.74
	3.2	0.0294	22.9	2.33	377.	1.77

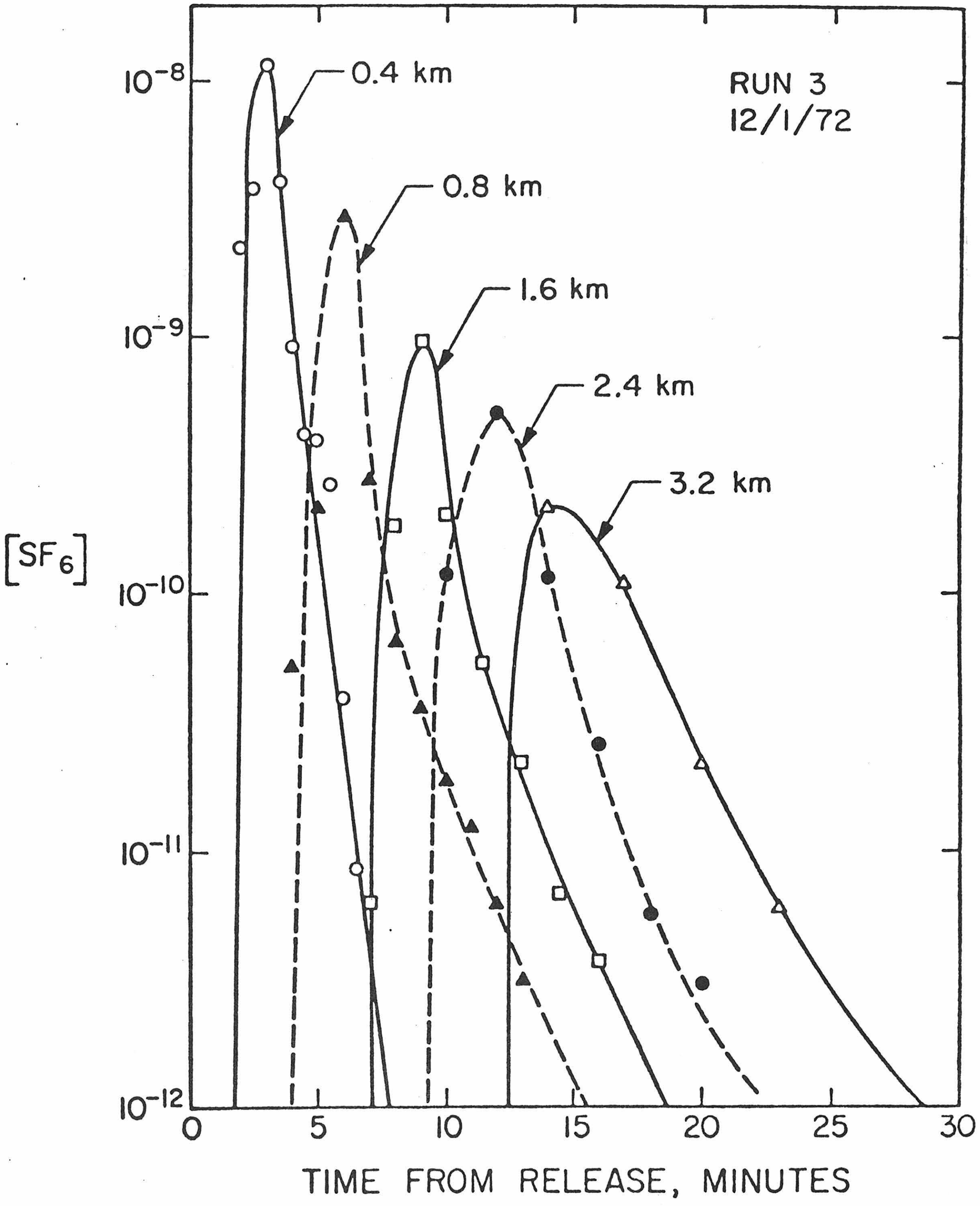

Figure 1. SF_6 concentration at the five downwind distances tested in Run 3 as a function of time from the automobile line source release.

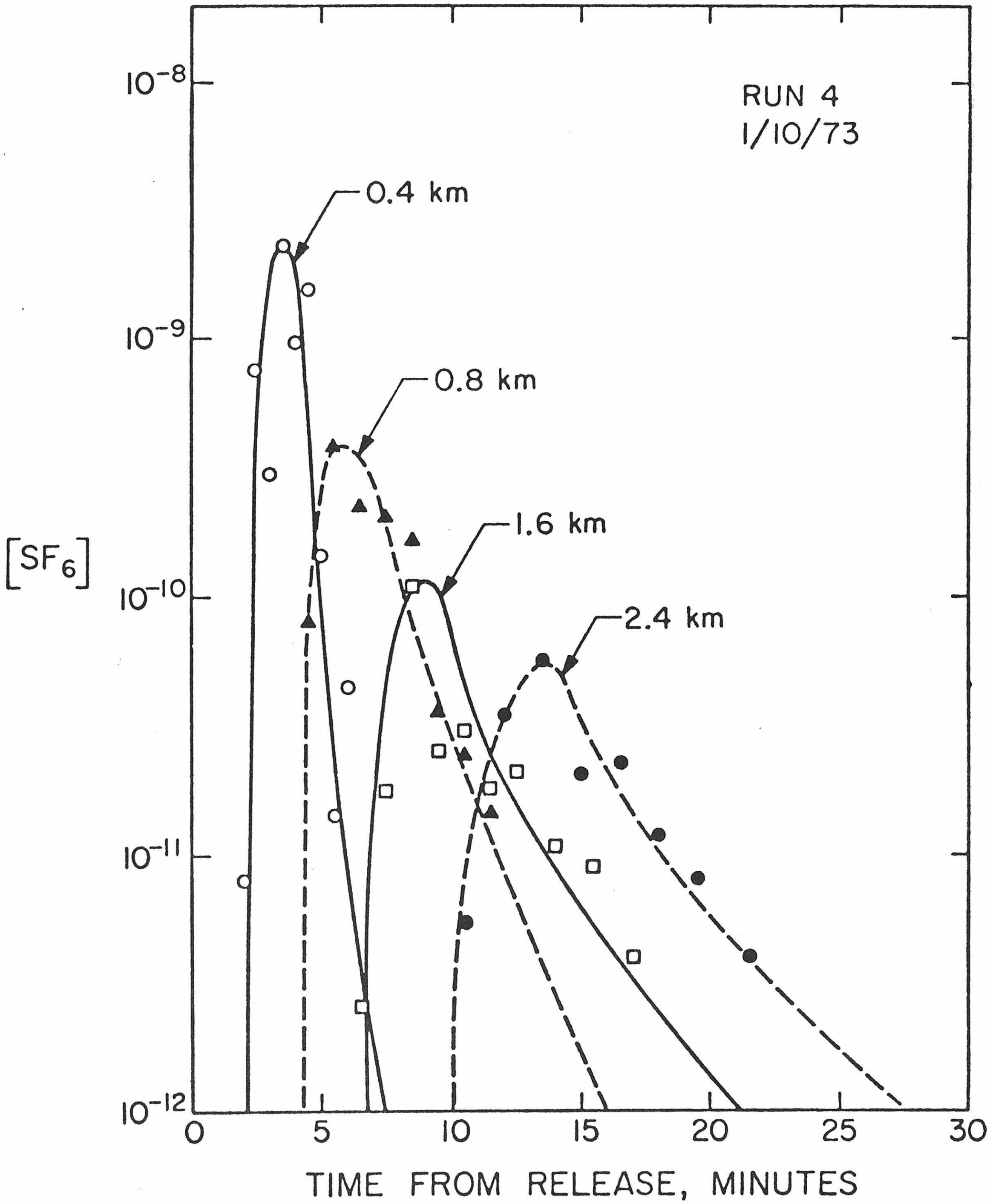

Figure 2. SF_6 concentration at the four downwind distances tested in Run 4 as a function of time from the automobile line source release.

3. COMPARISON WITH THEORY

The Gaussian model equation for concentration from an instantaneous crosswind line source was tested in order to compare this theory with the experimental data. The equation used and suggested values of the variables were taken from Slade (1968). Details of the calculation are given in the Appendix to this paper. The results showed two major discrepancies: one, the peak concentrations for the case tested (Run 4) were overestimated by a factor of 20; and two, the time associated with the movement of the concentration peak downwind was grossly in error. This latter result is due to the fact that the model predicts a constant average velocity for the movement of the peak concentration; the experimental data show an apparent velocity which increases with time. Thus, the Gaussian model does not provide a good description of the dispersion from an instantaneous line source. However, it should be noted that the Gaussian model does provide an adequate description of dispersion from continuous source releases (Slade, 1968).

Most analytical solutions of the semi-empirical equation of turbulent diffusion are for the steady-state case. A transient solution of equation (1) exists for the simplified case of a constant average velocity $\bar{u}$, independent of height, and constant values of the eddy diffusivities, $K_x = K_z = K$, which are taken to be independent of time or position. The solution for an instantaneous ground level line source, simplified from Monin and Yaglom (1971), with the boundary conditions $\frac{\partial c}{\partial z} = 0$ at $z = 0$ and $c \to 0$ as $x, z \to \infty$ is,

$$c(x, z, t) = \frac{Q}{2\pi Kt} \exp\left[\frac{-(x - \bar{u}t)^2 - z^2}{4Kt}\right] \tag{3}$$

where Q is the source strength of the line source. This solution, however, exhibits the same drawbacks as the Gaussian plume model, namely that it predicts Gaussian concentration curves and assumes a constant average velocity, both of which are inconsistent with experimental observations.

The above analytical solution assumes an unbounded atmosphere above ground level and an infinitesimally small line source. In three of the experimental runs, however, a temperature inversion was present; in fact, the inversions were fairly low for the two cases in the summer (see Table 1). Also, the fast-moving traffic may provide some mixing of the line source release, perhaps to an initial zone with dimensions of highway width and automobile height. To test the influence of an inversion height and an initial well-mixed zone, a finite-difference computer solution of equation (1) with constant $\bar{u}$ and constant $K_x = K_z = K$ was developed, with the boundary condition of $\partial c/\partial z = 0$ at the inversion height. For a low inversion height of 200 meters and a large initial well-mixed zone 20 meters wide by 20 meters high, the computer results were essentially identical to the analytical solution (3) from 0.4 km to 4.0 km downwind. Heines and Peters (1973) also concluded that the effect of an inversion height is negligible for sources close to the ground. Thus, an unbounded atmosphere and an infinitesimally small line source appear to be valid assumptions, at least for the downwind distances tested experimentally.

The experimental results of non-Gaussian concentration profiles and an apparent velocity which increases with time can be interpreted by the effect of wind shear, i.e. a horizontal wind velocity which increases with height. As the cloud of tracer grows vertically with time, the effective mean wind velocity which is transporting the cloud increases. The semi-empirical diffusion equation can account for this effect; however, at the present time analytical solutions of the time-dependent equation (1) have not yet been developed for the case of $\bar{u}$ as a function of z in the atmospheric surface layer. One approach to the problem is the use of analysis by integral moments (Aris, 1956) to obtain information about the shape and spreading of tracer concentration curves.

Chatwin (1968) used the technique of moments to analyze equation (1) for the case of an instantaneous ground-level line source tracer release, an unbounded upper atmosphere, a logarithmic velocity profile ($\bar{u} = k_1 \ln z$) and a linear vertical eddy diffusivity profile ($K_z = k_2 z$). He neglected the axial eddy diffusivity term in equation (1), an assumption which appears to be valid (Walters, 1969). Chatwin obtained a very simple result for the ground-level spreading of the tracer concentration curve:

$$\sigma_x \sim t \tag{4}$$

A linear least-squares fit of $\ln \sigma_x$ vs. $\ln t_{ave}$ from the data in Table 2 yielded slopes (which represent a power-law exponent, $\sigma_x \sim t_{ave}^b$) of 1.11 to 1.47, as shown in Table 3 and in Figure 3 for three of the runs. Thus the experimental curves spread slightly faster than Chatwin's theoretical prediction.

Saffman (1962) used the technique of moments to analyze equation (1) for the more general case of an instantaneous source and an unbounded upper atmosphere with power-law velocity and vertical eddy diffusivity profiles, namely:

$$\bar{u} = k_1 \, z^a \; ; \quad K_z = k_2 \, z^c \tag{5}$$

Neglecting the contribution of the axial diffusion term, his basic results for the ground-level apparent velocity and spreading were:

$$\bar{u} \sim t^{\frac{a}{2-c}} \; ; \quad \sigma_x \sim t^{1 + \frac{a}{2-c}} \tag{6}$$

A linear least-squares fit of ln $\bar{u}$ vs. ln t_{ave} from the data in Table 2 yielded slopes or values of a/(2−c) of 0.13 to 0.55, as shown in Table 3 and in Figure 4 for three of the runs. A comparison of the $\bar{u}$ and σ_x time exponents for each run in Table 3 with the theoretical predictions of equation (6) exhibits excellent agreement. The power-law model thus accurately predicts the increase with time of both the spreading and the apparent average wind velocity. Also, Saffman's analysis of the third-order moment

Table 3. Comparison of Experimental Results with Theory

Run No.	Exponent: $\bar{u} \sim t^b_{ave}$	Exponent: $\sigma_x \sim t^b_{ave}$	Constant Stress Region a_{ave}	c_{ave}	σ_θ(degrees)
1	0.55	1.47	1.04	−0.04	5.6
2	0.13	1.11	0.14	0.86	21.2
3	0.33	1.22	0.38	0.62	8.6
4	0.30	1.33	0.46	0.54	10.1
5	0.28	1.22	0.33	0.67	9.4
6	0.33	1.29	0.45	0.55	9.8

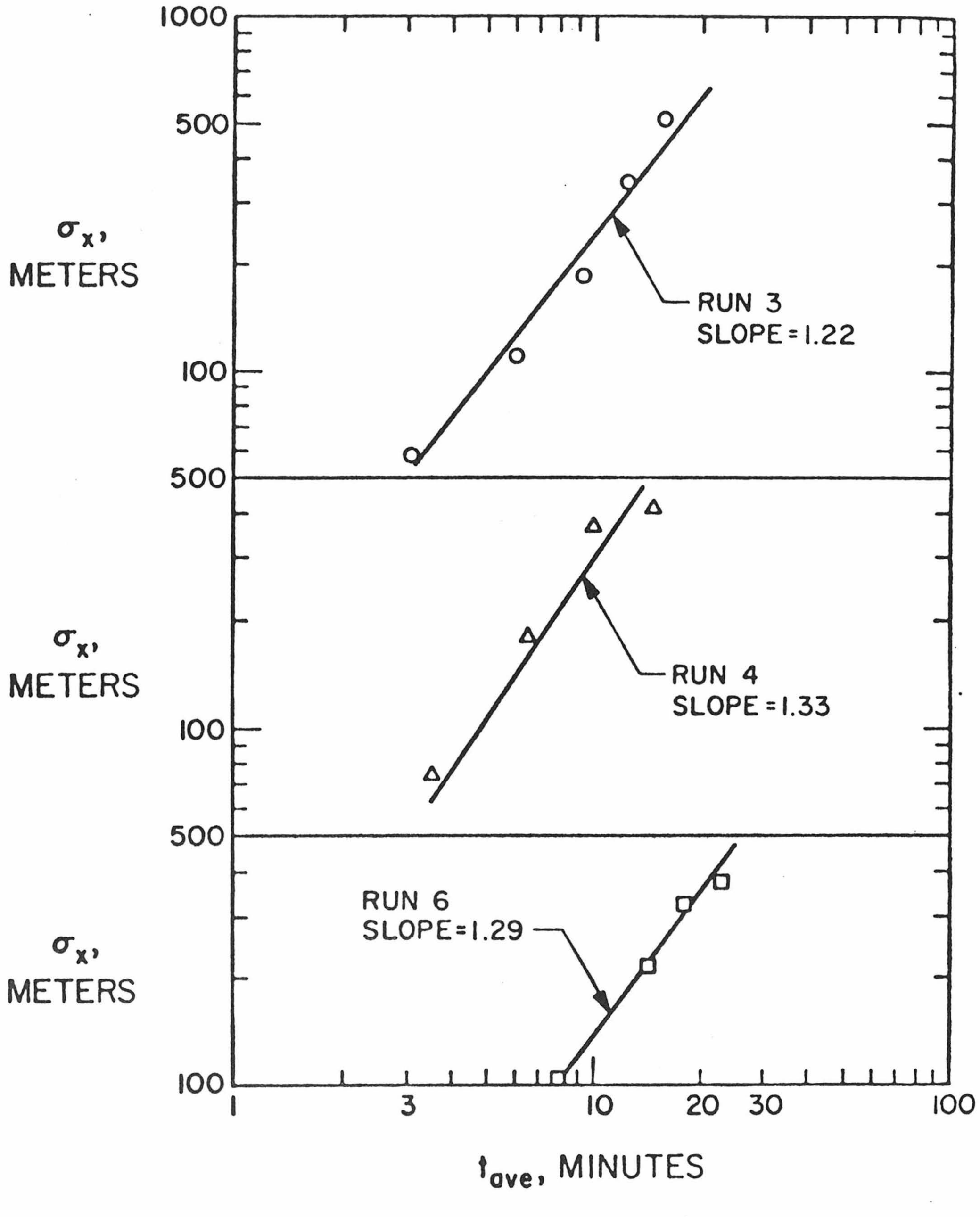

Figure 3. Linear least squares fit on log-log coordinates of the along-wind horizontal standard deviation versus the average time of travel for Runs 3, 4, and 6.

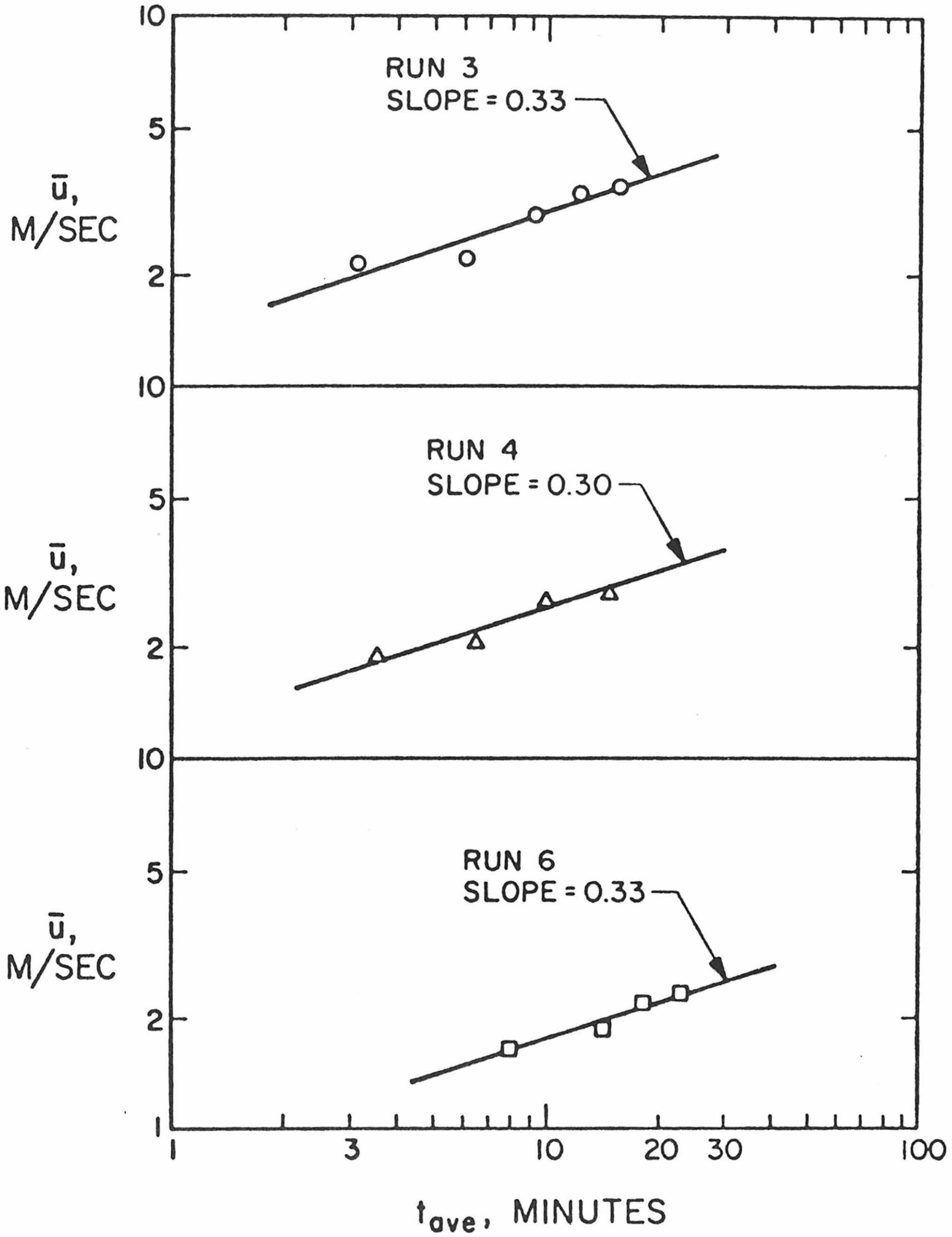

Figure 4. Linear least squares fit on log-log coordinates of the apparent average velocity versus the average time of travel for Runs 3, 4, and 6.

yields the theoretical prediction that the skewness of the tracer curves should increase with time, a prediction which is verified by the experimental curves. Thus, the semi-empirical diffusion equation, using power-law velocity and eddy diffusivity profiles, works quite well in predicting dispersion from an urban ground-level crosswind line source.

One further result from Saffman's theory is that the total area under the curves, actually the zero-order moment, should decrease proportionally as time to the power -1/(2-c). Analysis of the total area data with this relationship and use of the values of a/(2-c) in Table 3 yielded values of a and c which resulted in the quantity $(a + c - 1) > 0$ in five of the six runs, a relationship which indicates that the shear stress is not maximum at the ground but increases with height. A probable explanation for this anomaly is the fact that the original line source was released with a finite velocity, and deformation of the line source by the wind as it was released resulted in crosswind diffusion, which reduced the experimental areas more than predicted by the theory. Crosswind diffusion, however, would not affect the spreading along the direction of the wind, and the results of equation (6) would still be valid.

Use of the constant shear stress assumption $(c = 1 - a)$ and the above values of a/(2-c) yielded average values of a and c as shown in Table 3. Run 1, which occurred under the most stable conditions tested (the lowest value of the wind direction standard deviation) resulted in essentially a linear velocity profile and a constant vertical eddy diffusivity. Run 2, which occurred under the largest turbulent intensity tested, resulted in a velocity exponent of about one-seventh. The relationship between the constant shear stress average velocity exponent and the wind direction standard deviation is shown in Figure 5.

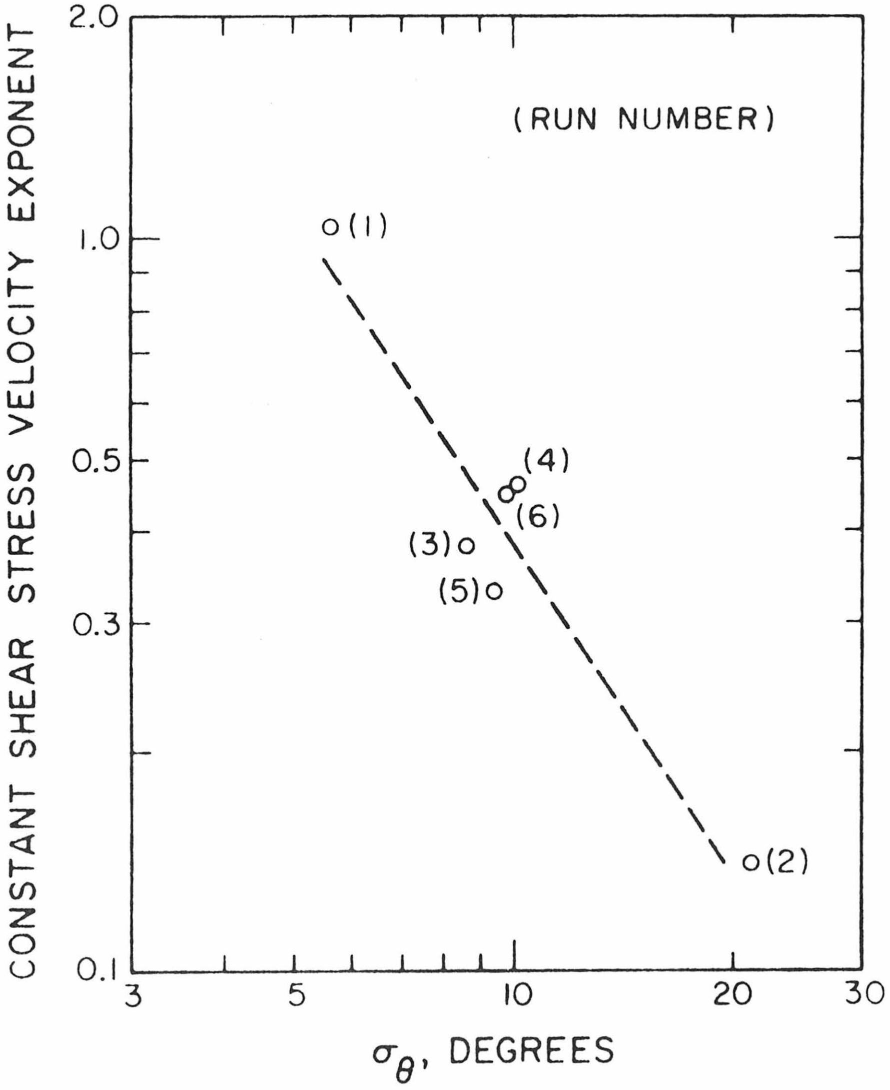

Figure 5. Average constant shear stress velocity exponent as a function of the horizontal wind direction standard deviation.

4. A PRACTICAL APPLICATION

An important application of the above results is to determine how much distance from a heavily-travelled highway is required for automobile pollutants to have dispersed to ambient concentration levels. This information is important in deciding how close to a highway residential housing can be built without being exposed to high concentrations of automobile pollutants, particularly carbon monoxide. Since a heavily-travelled highway can be treated as a continuous line source, an analytical solution of equation (1) (without the time-dependent and axial-diffusion terms) exists for the case of an unbounded upper atmosphere and power-law velocity and eddy diffusivity profiles. Using the constant shear stress assumption,

$$\bar{u} = u_1 z^a \; ; \quad K_z = K_1 z^{1-a} \tag{7}$$

the solution, simplified from Calder (1949), for the ground-level concentration from a continuous, ground-level crosswind line source is

$$c(x) = \frac{(2a + 1)Q}{u_1 \Gamma\left(\frac{a+1}{2a+1}\right)} \cdot \left[\frac{u_1}{(2a+1)^2 K_1}\right]^{\frac{a+1}{2a+1}} \cdot x^{-\frac{a+1}{2a+1}} \tag{8}$$

where Q is the source strength of the line source.

A value of the source strength for carbon monoxide emission from a heavily-travelled highway will be used for the following calculations. Using the emission-speed correlation in Roberts et al. (1973), the average carbon monoxide emission from an automobile travelling 96 km/hr is 24.8 gm/km. A typical noontime traffic density for the section of highway tested, Interstate 405, is 8750 cars/hr (Roberts et al., 1971). The resulting value of Q is then 0.523 cm^3 CO/cm-sec.

A typical value of the velocity profile exponent a of 0.25 will be used in the sample calculation. To estimate a value for u_1, a velocity value u_o = 3 m/sec will be assumed to apply at z_o = 10 m. In a recent study of radon-222 vertical concentration profiles, Cohen et al. (1972) estimated that for near neutral conditions, a value $K_o = 2 \times 10^5$ cm^2/sec applies at z_o = 100 m; these values will be used to calculate a value for K_1. Using the above numerical values, equation (8) becomes

$$c(x) = 0.150 \, x^{-0.833} \qquad (9)$$

where x is in km, and c represents the ground-level carbon monoxide concentration in parts per million.

Using a relatively close distance of 100 meters (0.1 km), the resulting carbon monoxide concentration from equation (9) is 1.02 ppm. Thus, only 100 meters away from a heavily-travelled highway, the carbon monoxide concentration resulting from the highway automobile traffic is predicted to be below normal ambient levels in the Los Angeles basin. At closer distances, equation (8) may not apply, since the assumption of an infinitesimally small line source becomes unjustifiable; a numerical solution may be necessary to take into account the dimensions of the highway.

5. CONCLUSION

Tracer experiments, involving a release of sulfur hexafluoride, were used to test the validity of the Gaussian plume model and various forms of the semi-empirical equation of turbulent diffusion in predicting various characteristics associated with the dispersion from an instantaneous ground-level crosswind line source. The model based upon the semi-empirical diffusion equation, using a power-law vertical velocity profile and a power-law vertical eddy diffusivity profile, was found to provide a consistent interpretation of the data. Saffman's analysis using this model was found to more accurately predict the experimental results than the other models tested. It should be noted that these results apply only for an instantaneous crosswind line source.

APPENDIX

Using the Gaussian model, the ground-level concentration downwind of a ground-level instantaneous crosswind line source is given by (Slade, 1968):

$$\chi = \frac{Q_L}{\pi \sigma_{xI} \sigma_{zI}} \exp\left[- \frac{(x - \bar{u}t)^2}{2\sigma_{xI}^2} \right] \tag{A-1}$$

The following estimates will be used for the σ_{xI} and σ_{zI} factors; these estimates apply for neutral conditions in the range 100-4000 meters downwind (Slade, 1968):

$$\sigma_{xI} = 0.06(x)^{0.92} = 0.06(\bar{u}t)^{0.92}$$

$$\sigma_{zI} = 0.15(x)^{0.70} = 0.15(\bar{u}t)^{0.70}$$

For Run 4, which occurred under nearly neutral conditions, 31 l/min of SF_6 were released for 100 sec or 1.67 min; thus, the total amount of SF_6 released was 52 liters. Since the density of SF_6 at 25°C and 1 atm is 6.42 g/l, the total mass released was 330 g. The length of the release, 80 km/hr for 100 sec, was 2200 m. Therefore, Q_L--the mass released per unit length--was 0.15 g/m.

For an estimate of the average surface wind velocity, $\bar{u}$, a value of 1.87 m/sec will be used; this value was calculated from the arrival of the concentration peak at the closest distance, 400 m. Using the above values, concentrations were calculated from equation A-1 for x = 400 meters and x = 2400 meters. The concentrations were converted from g/m^3 to the experimentally measured [SF_6], parts SF_6 per part of air, by the relation $[SF_6] = \chi/5.86 \times 10^3$. The comparison of the theoretical curves calculated from equation A-1 with the experimental data taken at

400 meters and 2400 meters is shown in Figure 6.

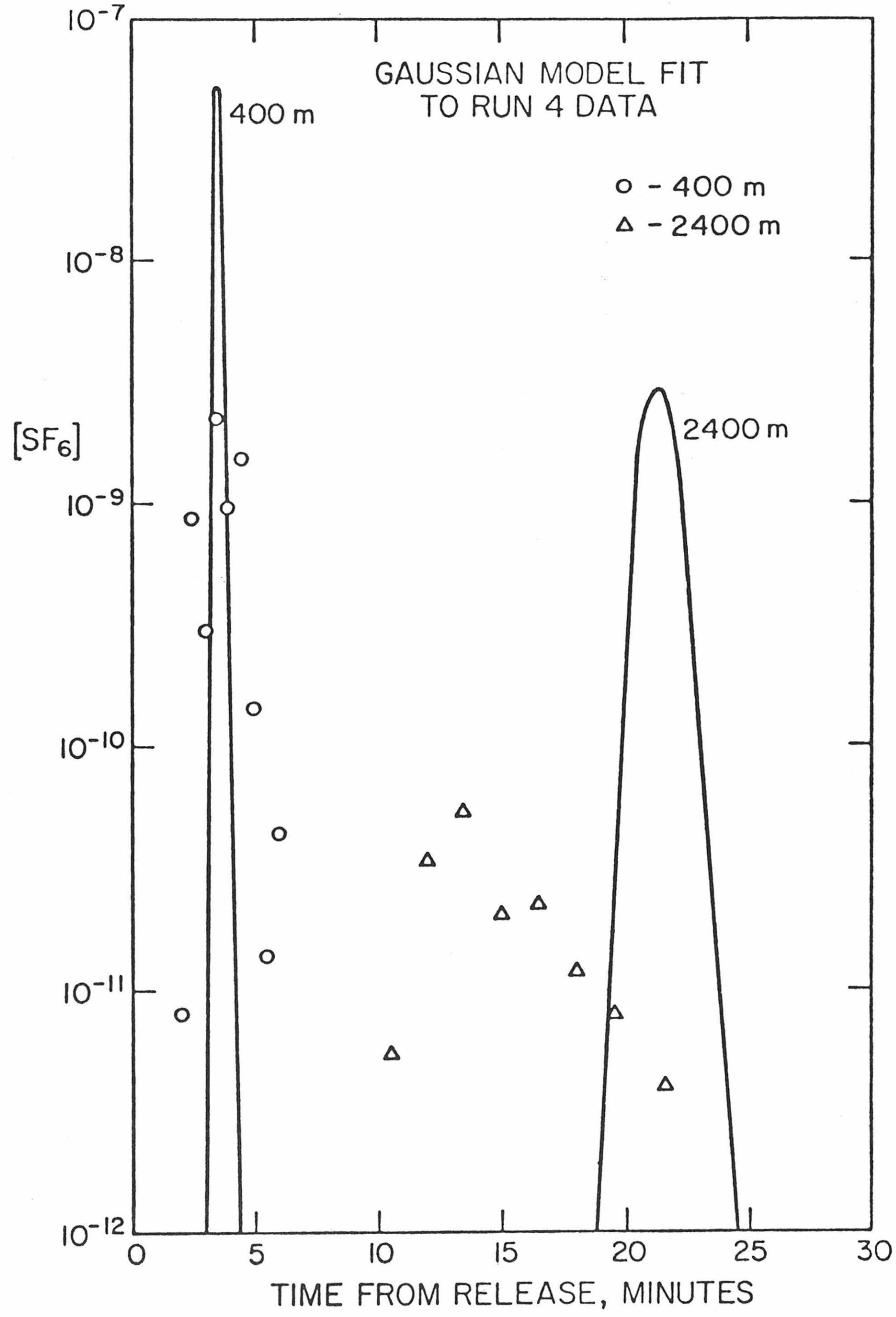

Figure 6. Comparison of Gaussian model with experimental data points from Run 4.

Table 4. Experimental data for Runs 1, 2, 5, and 6.

Run 1

0.4 km		0.8 km		1.6 km	
Time (min)	$[SF_6]$	Time (min)	$[SF_6]$	Time (min)	$[SF_6]$
2.0	$9.70\mathrm{x}10^{-12}$	4.0	$8.00\mathrm{x}10^{-11}$	7.0	$8.82\mathrm{x}10^{-10}$
2.5	$1.10\mathrm{x}10^{-9}$	5.0	$2.35\mathrm{x}10^{-9}$	8.0	$5.75\mathrm{x}10^{-10}$
3.0	$4.75\mathrm{x}10^{-9}$	6.0	$1.11\mathrm{x}10^{-10}$	9.0	$1.02\mathrm{x}10^{-10}$
3.5	$3.07\mathrm{x}10^{-9}$	7.0	$3.60\mathrm{x}10^{-11}$	10.0	$4.30\mathrm{x}10^{-11}$
4.0	$2.05\mathrm{x}10^{-10}$	8.0	$1.40\mathrm{x}10^{-11}$	11.0	$5.50\mathrm{x}10^{-11}$
4.5	$1.52\mathrm{x}10^{-11}$	9.0	$2.60\mathrm{x}10^{-12}$	12.0	$6.05\mathrm{x}10^{-12}$
5.0	$3.50\mathrm{x}10^{-12}$			13.0	$2.40\mathrm{x}10^{-12}$

Run 2

0.4 km		0.8 km		1.6 km	
Time (min)	$[SF_6]$	Time (min)	$[SF_6]$	Time (min)	$[SF_6]$
1.5	$1.30\mathrm{x}10^{-11}$	4.0	$2.40\mathrm{x}10^{-11}$	8.0	$3.65\mathrm{x}10^{-10}$
2.0	$3.40\mathrm{x}10^{-10}$	5.0	$6.23\mathrm{x}10^{-10}$	9.0	$8.00\mathrm{x}10^{-11}$
2.5	$1.81\mathrm{x}10^{-9}$	6.0	$1.60\mathrm{x}10^{-10}$	10.0	$5.80\mathrm{x}10^{-11}$
3.0	$2.40\mathrm{x}10^{-10}$	7.0	$1.85\mathrm{x}10^{-11}$	11.0	$1.05\mathrm{x}10^{-11}$
3.5	$3.50\mathrm{x}10^{-11}$	8.0	$5.50\mathrm{x}10^{-11}$	12.0	$1.30\mathrm{x}10^{-11}$
4.0	$3.15\mathrm{x}10^{-11}$	9.0	$6.10\mathrm{x}10^{-12}$	13.0	$7.80\mathrm{x}10^{-12}$
4.5	$5.60\mathrm{x}10^{-12}$			14.0	$2.40\mathrm{x}10^{-12}$

Run 5

0.8 km		1.6 km		2.4 km	
Time (min)	$[SF_6]$	Time (min)	$[SF_6]$	Time (min)	$[SF_6]$
4.0	4.10×10^{-12}	9.0	3.20×10^{-11}	11.5	4.20×10^{-12}
5.0	9.00×10^{-11}	10.0	6.10×10^{-10}	13.0	7.80×10^{-11}
6.0	1.02×10^{-9}	11.0	2.28×10^{-10}	14.5	3.05×10^{-10}
7.0	2.55×10^{-10}	12.0	1.20×10^{-10}	16.0	1.92×10^{-10}
8.0	5.80×10^{-11}	13.0	6.50×10^{-11}	17.5	5.05×10^{-11}
9.0	6.50×10^{-11}	14.5	2.75×10^{-11}	19.0	5.50×10^{-11}
10.0	4.60×10^{-11}	16.0	1.13×10^{-11}	21.0	1.07×10^{-11}
11.0	2.15×10^{-11}	17.5	4.10×10^{-12}	23.0	4.25×10^{-12}
12.0	9.70×10^{-12}				
13.0	6.20×10^{-12}				

Run 6

0.8 km		1.6 km		2.4 km		3.2 km	
Time (min)	$[SF_6]$	Time (min)	$[SF_6]$	Time (min)	$[SF_6]$	Time (min)	$[SF_6]$
6.0	7.20×10^{-11}	9.0	2.50×10^{-12}	14.5	2.55×10^{-11}	19.0	9.50×10^{-12}
7.0	8.80×10^{-11}	11.0	1.40×10^{-11}	16.0	2.85×10^{-11}	21.0	2.50×10^{-11}
8.0	2.85×10^{-10}	12.0	3.90×10^{-11}	17.5	2.78×10^{-11}	23.0	2.94×10^{-11}
9.0	5.30×10^{-11}	13.0	3.28×10^{-11}	19.0	4.78×10^{-11}	25.0	1.23×10^{-11}
10.0	1.95×10^{-11}	14.5	8.55×10^{-11}	21.0	1.40×10^{-11}	28.0	3.70×10^{-12}
11.0	1.72×10^{-11}	16.0	2.70×10^{-11}	23.0	5.40×10^{-12}		
12.0	7.10×10^{-12}	17.5	1.12×10^{-11}				
13.0	8.80×10^{-12}	19.0	4.10×10^{-12}				

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APPENDIX A-4. A TRACER STUDY OF POLLUTANT TRANSPORT AND DISPERSION IN THE LOS ANGELES AREA

(by P. J. Drivas and F. H. Shair)

In press, Atmospheric Environment.

ABSTRACT

Sulfur hexafluoride was used as a tracer in a large-scale test over the urban region near Los Angeles, California. On July 19, 1973, 33.5 kg of SF_6 was released over a period of 45 minutes from the city of Anaheim. The transport and dispersion from Anaheim was traced in five neighboring communities including Palm Springs, which at 124 km away was the furthest location tested. A preliminary analysis of the data indicated that the cities of Riverside and Palm Springs may possibly lie in a direct path of the pollutant transport from Anaheim.

1. INTRODUCTION

There has been a long-term and growing interest in the meteorology associated with pollutant transport throughout the area surrounding Los Angeles, California (Edinger, 1959; Pitts, 1969). Edinger (1973) has measured the vertical distribution of the photochemical smog in this region. Angell et al. (1966, 1972) have used tetroons to track wind trajectories in the Los Angeles area.

Use of atmospheric tracers can characterize the dispersive power of the atmosphere in addition to tracing wind trajectories. The most common tracer which has been used in urban areas is a fluorescent particulate one, zinc-cadmium sulfide (Leighton et al., 1965). This tracer has been used over the San Francisco Bay area (Sandberg et al., 1970), over Los Angeles (Dreyfuss, 1972), over St. Louis (Pooler, 1966; McElroy, 1969), over Johnstown, Pennsylvania (Smith, 1968), and over Ft. Wayne, Indiana (Hilst and Bowne, 1971). Continued use of this tracer over urban areas is somewhat perplexing, in view of the fact that cadmium sulfide is classified as toxic, "which limits its use in heavily populated areas" (American Chemical Society, 1969). The toxicity of this fluorescent particle tracer has been discussed in more detail by Spomer (1973) and commented on by Nordberg (1973), Mitchell (1973), and Lewis (1973). Another problem with this tracer is that the particles settle out; comparison of zinc-cadmium sulfide with a gaseous tracer, sulfur hexafluoride, showed that a distance of 70 km, 50% to 80% of the particles had been lost (Niemeyer and McCormick, 1968).

Sulfur hexafluoride has also been suggested as an ideal tracer (Collins et al., 1965). The gas is chemically inert at normal temperatures and is stable to ultraviolet light (Saltzman et al., 1966); it is extremely insoluble in water (Ashton et al., 1968). The method of detection by electron-capture gas chromatography, as first reported by Lovelock and Lipsky (1960), has been continually improved. Currently, it is possible to detect SF_6 in concentrations lower than 10^{-12} parts SF_6 per part of air (Simmonds et al., 1972; Dietz and Cote, 1973). Preliminary field tests using SF_6 as a tracer have shown quite successful results (Clemons et al., 1968; Turk et al., 1968; Hawkins et al., 1972; Dietz and Cote, 1973).

Due to the growing concern as to the possible health hazards associated with atmospheric tracers, it is not inappropriate to carefully document the information regarding the toxicity of sulfur hexafluoride. Apparently the first experiments aimed at determining possible toxic effects associated with the inhalation of SF_6 were reported by Lester and Greenberg (1950). Animals were exposed to SF_6 concentrations up to 80% by volume for periods up to 24 hours. No indications of intoxication, irritation or any other disturbances were observed during these exposures or at any time thereafter. SF_6 is not hydrolyzed or otherwise altered in the body, with the formation of substances which might possibly have some toxic actions. Eagers (1969) has concluded that SF_6 "appears to be physiologically inert when pure." A brief survey of the recent literature indicates that SF_6 is finding use in various pulmonary ventilation studies (Wood et al., 1969; Martin et al., 1972). The first study involved human subjects who breathed mixtures of 10% O_2 and 90% SF_6 under a pressure of 2 atmospheres. Some of the experiments in the second study involved dogs which breathed a mixture of 5% O_2 and 95%

SF_6 (by volume) under a pressure of 4 atmospheres. No mention of any toxic effects was noted in either of the above mentioned articles, or in any other studies of which the authors are aware.

In this study, sulfur hexafluoride was used as a tracer to study pollutant transport and dispersion throughout the large urban area near Los Angeles. About 33.5 kg (74 pounds) of SF_6 were released in Anaheim between noon and 12:45 p.m. during July 19, 1973. Air samples were collected throughout the afternoon in five communities which were thought to be somewhat downwind of Anaheim during the afternoon of the test. The purpose of this work was to demonstrate the applicability of the SF_6 tracer technique in studies of large-scale urban regions.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

From 12:00 noon until 12:45 p.m. (PDST) on July 19, 1973, sulfur hexafluoride was released at a rate of 750 g/min near the intersection of Katella Avenue and Lewis Street in Anaheim, California. The release was made using a single 1A cylinder with the second stage of the two-stage regulator set at 2.1 kg/cm^2 (30 p.s.i.g.). The total amount of SF_6 released, 33.5 kg, was thermodynamically limited. The liquid SF_6 in the tank became progressively colder throughout the release and eventually froze; at this point, about 75% of the SF_6 in the cylinder had been released. The height of the release point was about 1 meter. The terrain near the release point was level with no buildings closer than about 100 meters.

During the afternoon, a SW sea breeze normally occurs in Anaheim. The Orange County Air Pollution Control District station in Anaheim was located 2 km north of the release point; this station reported a steady SW surface wind (measured at a height of 8 meters) from noon until 12:33 p.m. at about 2 m/sec. However, from 12:33 until 12:37 p.m. the wind direction shifted to SE, and then shifted back to SW from 12:37 until 12:45 p.m. During the rest of the afternoon, the surface wind in Anaheim was constant from the SW at a speed of 3 m/sec. During the time of the release, the base of the temperature inversion was reported to be 550 meters near the ocean and 750 meters inland near Pomona. The day was sunny and all locations except Cajon Pass had considerable build-up of smog.

Analysis in the field was accomplished by two portable, battery-operated electron-capture gas chromatographs. The electrical output of each gas chromatograph was connected to a portable, battery-operated recorder (Esterline Angus T171B). Each chromatograph employed a cylindrical detector equipped with a 200 millicurie tritiated foil. The carrier gas was prepurified nitrogen. The column was 1.1 meters long and made from 0.6 cm (1/4-inch o.d.) stainless steel tubing; the column was packed with 80-100 mesh 5A molecular sieve and operated at ambient temperature. The flow rate of the carrier gas was adjusted to permit the SF_6 peak to appear in 20 seconds after injection; the large oxygen peak appeared about 45 seconds after injection. Optimum SF_6 response was obtained with a pulse period of 200 μsec and a pulse width of 1 μsec. Ambient air samples were drawn in through a sample valve with a 50 ml syringe. The volume of the sample loop was 1 ml.

Calibration of each chromatograph with a well-mixed exponential dilution system indicated that the output signal of each instrument was linear from 10^{-9} to about 10^{-12} parts SF_6 per part of air; the limit of detection for each instrument, determined as three times the peak-to-peak noise level, was about 1.5×10^{-12} parts SF_6 per part of air, which corresponds to about 10^{-8} g SF_6/m^3.

The portable gas chromatographs, operated within automobiles, were used to locate the tracer cloud as it passed through various geographical regions. One chromatograph was used to follow the tracer cloud north along a route encompassing Riverside, San Bernardino, and Cajon Pass; the other was used to follow the tracer east from Pomona to Palm Springs. The locations sampled and the general wind directions are shown on Figure 1. The shortest distances from the release point in Anaheim to the sampling locations are given in Table 1.

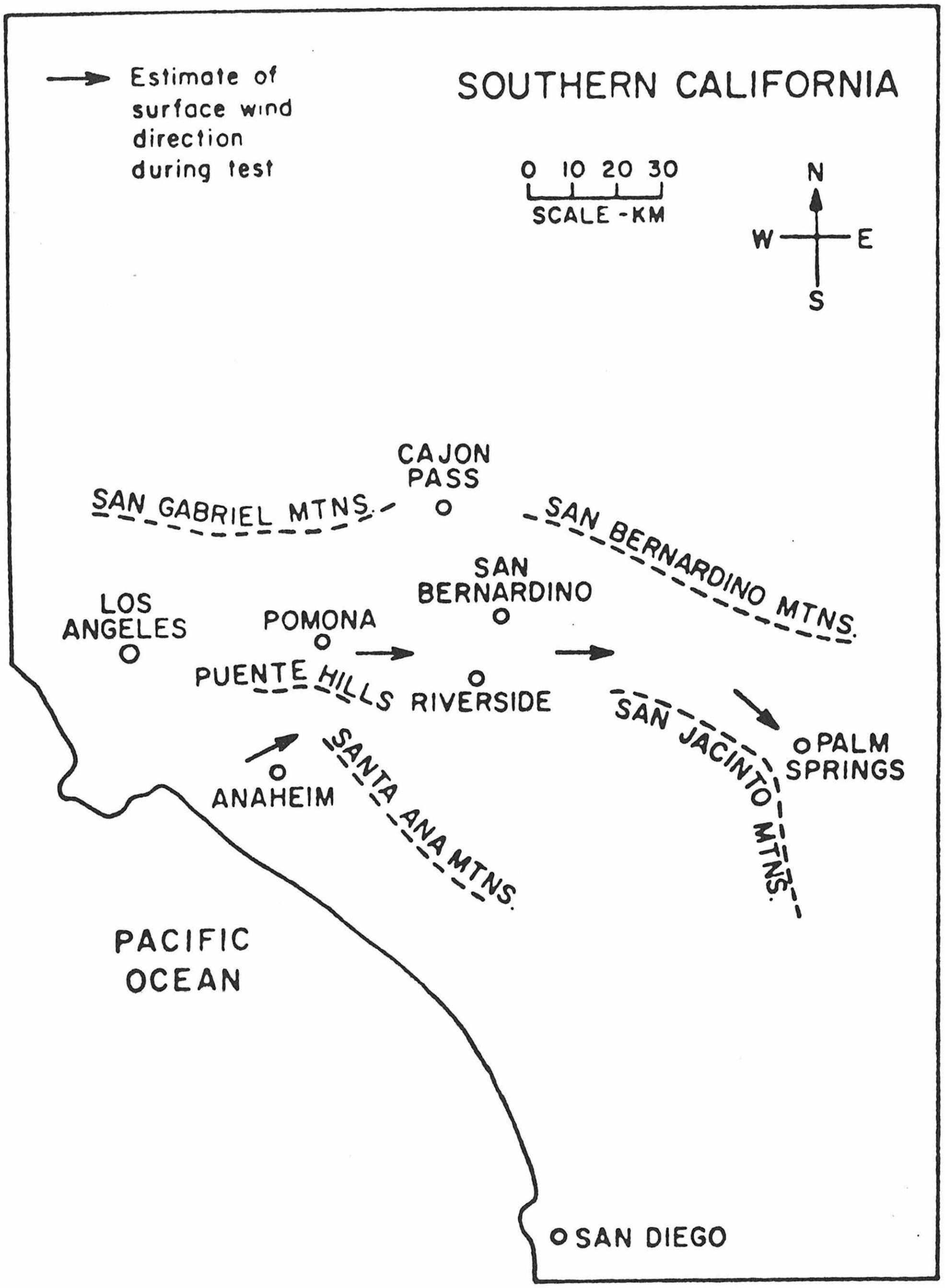

Figure 1. Geographical points of interest associated with the tracer test conducted July 19, 1973.

When the SF_6 tracer began to appear in Pomona, Riverside and in San Bernardino, individuals were left behind to collect air samples every 12 or 15 minutes by the squeeze bottle method described by Drivas et al. (1972). The averaging time for sampling was about 10 sec; if necessary, the concentration data could be adjusted to represent longer sampling times (Cramer, 1959; Hino, 1968). The bottle samples were analyzed in the laboratory during the day after the field test was conducted. All air samples were taken about 1 meter above ground and in open spaces (generally in public parks) with no buildings in the immediate vicinity. Ambient air sampling, two days before the field test with the portable gas chromatographs, indicated no detectable SF_6 concentrations in each of the locations.

3. PRESENTATION AND DISCUSSION OF RESULTS

The concentration versus time data obtained at each location are shown in Figures 2-6, and a composite of the results is shown in Figure 7. Although the base of the temperature inversion at 750 meters near Pomona around noon was somewhat higher than usual (typical heights during the summer are close to 300 meters), all locations except Cajon Pass had concentrations well above the minimum detectable level. It is reasonable to expect that higher peak concentrations would be observed with lower inversion heights when wind velocities are similar. In order to facilitate discussion of the data, pertinent results are listed in Table 1.

The Pasquill-Gifford dispersion graphs, as described by Turner (1970), probably do not apply to these data because (1) the graphs are based on experimental data associated with relatively smooth terrain in rural surroundings and (2) these graphs are based upon data for a continuous point source (i.e. for release times greater than the time required for the tracer to travel between the release point and the sample point). However, it is still instructive to discuss our data with respect to the quantity $\chi_p U_2/Q$, where χ_p is the peak value of the tracer observed in grams SF_6/meter^3, U_2 is an average velocity associated with the movement of the concentration peak, and Q is the release rate of SF_6 in Anaheim. It is reasonable to expect that the Pasquill-Gifford graphs represent an upper bound to dispersion experiments for finite release time of tracers over urban areas. Thus, the values of $\chi_p U_2/Q$ can be expected, in general, to be lower than the values of $\chi U/Q$ reported in Figures 3.5A-3.5F of Turner (1970).

As indicated in Figure 2, the tracer reached Pomona quite rapidly; however, the tracer peaked at a relatively low value of concentration. As shown in Table 1, the value of $\chi_p U_2/Q$ for Pomona was 9.7 x 10^{-9} meters^{-2}; the only situations for which this value could be a downstream value would be if the Pasquill stability were category A with an inversion height near 5000 meters. Since the inversion height in Pomona was certainly below 2000 meters, we suggest that the Pomona data simply reflect the fact that it was not directly downwind of Anaheim during the time of our release of tracer. Among the locations sampled, the highest concentration peak was observed in Riverside, which is located 55 km northeast of Anaheim. As shown in Table 1, the value of $\chi_p U_2/Q = 2.8 \times 10^{-8}$ meters^{-2}; this value of $\chi U/Q$ corresponds to a distance 55 km directly downwind in the Pasquill stability class A with an inversion height of 2000 meters. Although the inversion height at Riverside during the test was unknown, the inversion height generally increases with increasing distance inland and with increasing time during the afternoon (Edinger, 1959). Consequently, it is not unreasonable to suggest that Riverside may have been directly downwind of Anaheim during the day of this tracer study. The value of $\chi_p U_2/Q$ for San Bernardino also suggests that it was not directly downwind of the tracer release. Of all the locations sampled, Cajon Pass received the lowest peak value. Two distinct concentration peaks were recorded in Palm Springs which, at 124 km from Anaheim, was the furthest location sampled. This phenomenon may be due to two separate paths associated with the wind pattern from Los Angeles to Palm Springs. The value of $\chi_p U_2/Q$ associated with the second peak is in agreement with a downwind position in the Pasquill stability

Table 1. Comparison of data with Gaussian plume model.

Location	L(1) (meters)	t_1(2) (seconds)	t_2(3) (seconds)	U_1(4) $\frac{\text{meters}}{\text{second}}$	U_2(5) $\frac{\text{meters}}{\text{second}}$	χ_p(6) $\frac{\text{g } SF_6}{\text{meter}^3}$	χ_p(7) $\frac{\text{g } SF_6}{\text{meter}^3}$	$[\chi_p U_2/Q]$(8) (meter^{-2})
1. Pomona	34,000	<3,600	5,490	>9.4	6.2	4.4×10^{-8}	1.9×10^{-8}	9.7×10^{-9}
2. Riverside	55,000	5,400	11,250	10.2	4.9	1.6×10^{-7}	7.0×10^{-8}	2.8×10^{-8}
3. San Bernardino	66,000	13,500	14,490	4.9	4.6	6.8×10^{-8}	3.0×10^{-8}	1.1×10^{-8}
4. Cajon Pass	74,000	19,800	19,800	3.7	3.7	9.3×10^{-9}	4.1×10^{-9}	1.2×10^{-9}
5. Palm Springs	124,000	16,740	16,650(9)	7.4	7.4	2.6×10^{-8}	1.1×10^{-8}	7.0×10^{-9}
			20,250		6.1	5.0×10^{-8}	2.2×10^{-8}	1.1×10^{-8}

(1) Approximate direct line distance from location to release point in Anaheim.

(2) Minimum transit time defined as the time from the beginning of the release to the time at which the concentration of the tracer reaches the limit of detection.

(3) Transit time for peak measured from midpoint of the release to the time at which the concentration peak passes the location.

(4) U_1 represents a lower bound of maximum velocity determined from the data = L/t_1.

(5) U_2 represents an average velocity associated with the movement of the concentration peak = L/t_2.

(6) $\chi_p = 5.8 \times 10^3 [SF_6]_p$ where $[SF_6]_p$ is the concentration of SF_6 at the peak; the units of $[SF_6]_p$ are parts SF_6/part of air.

(7) Values of χ_p adjusted to represent 10 min sampling times by the one-fifth power law relationship (Cramer, 1959).

(8) χ_p values representing 10 min sampling times used to compute $\chi_p U_2/Q$.

(9) Note that two separate peaks were observed in the data from Palm Springs.

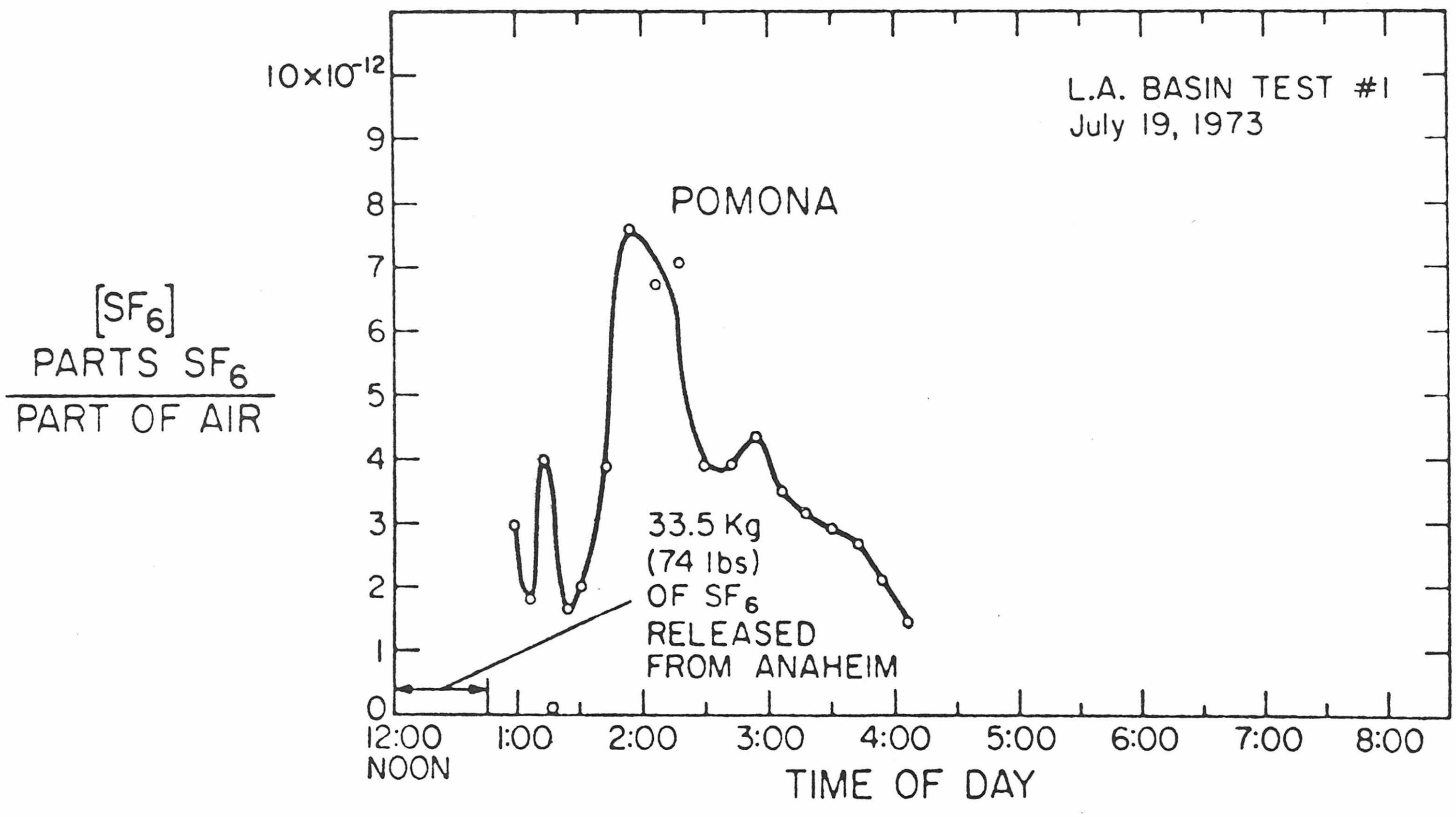

Figure 2. SF_6 concentration versus time curve for Pomona.

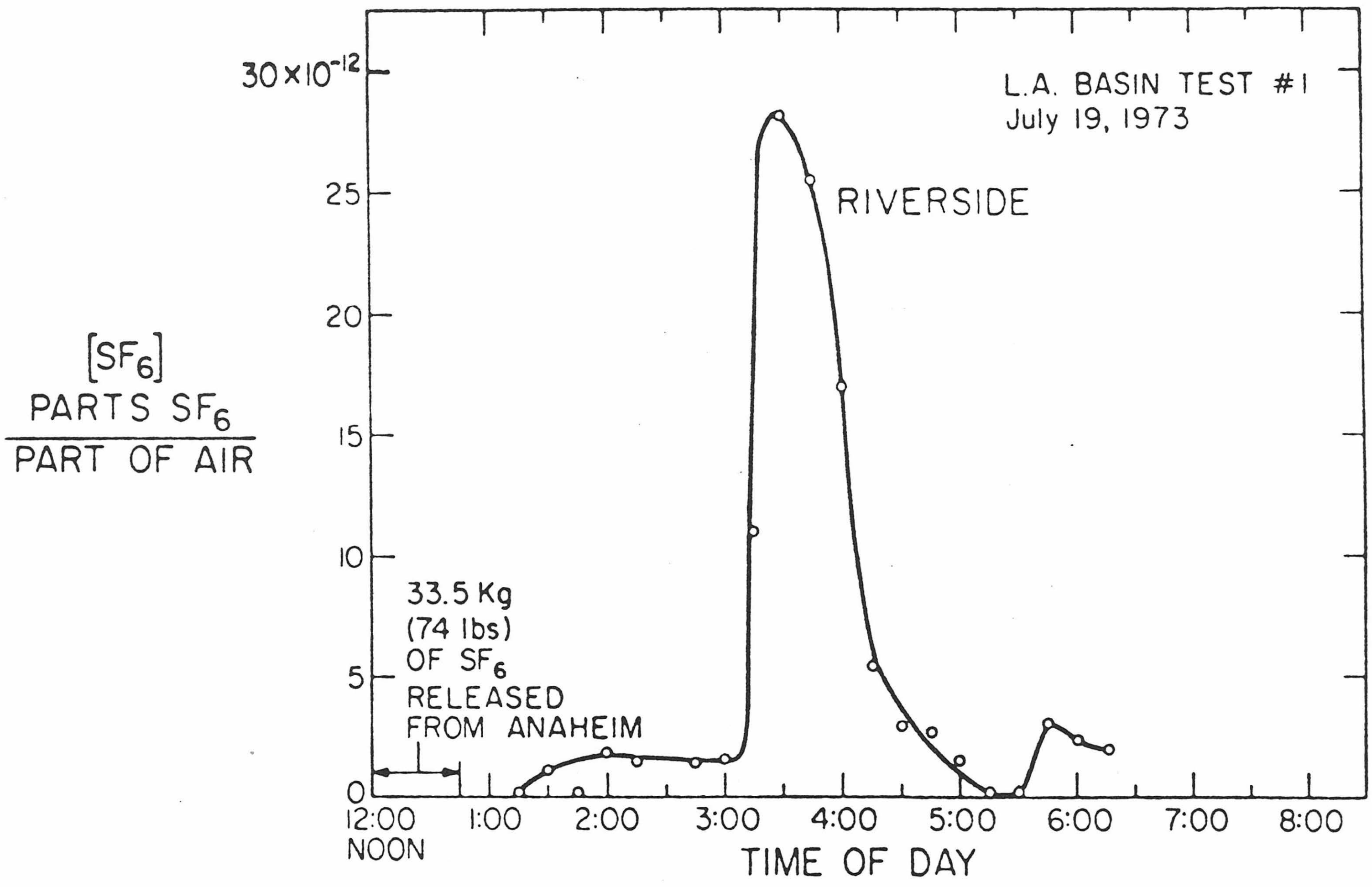

Figure 3. SF_6 concentration versus time curve for Riverside.

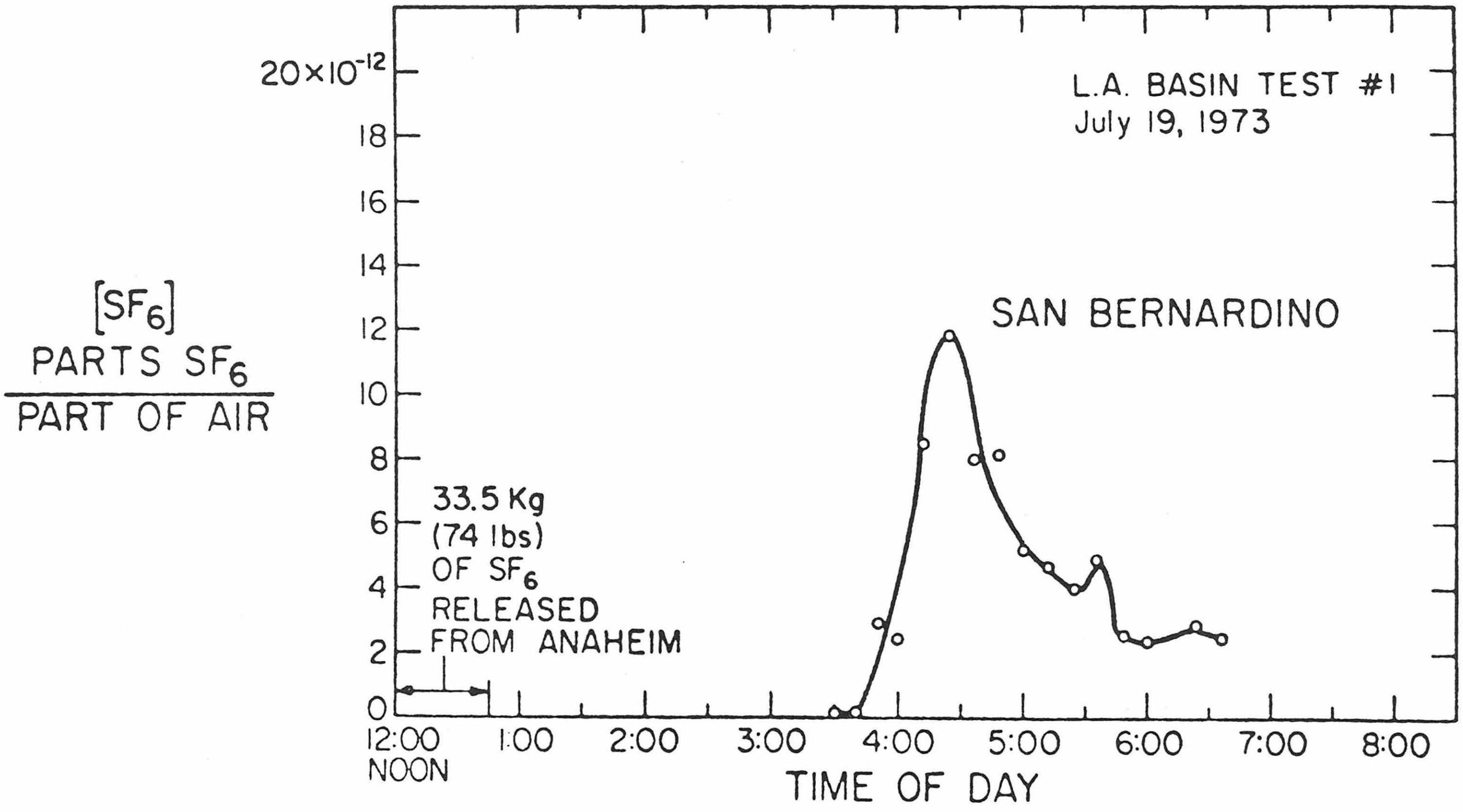

Figure 4. SF_6 concentration versus time curve for San Bernardino.

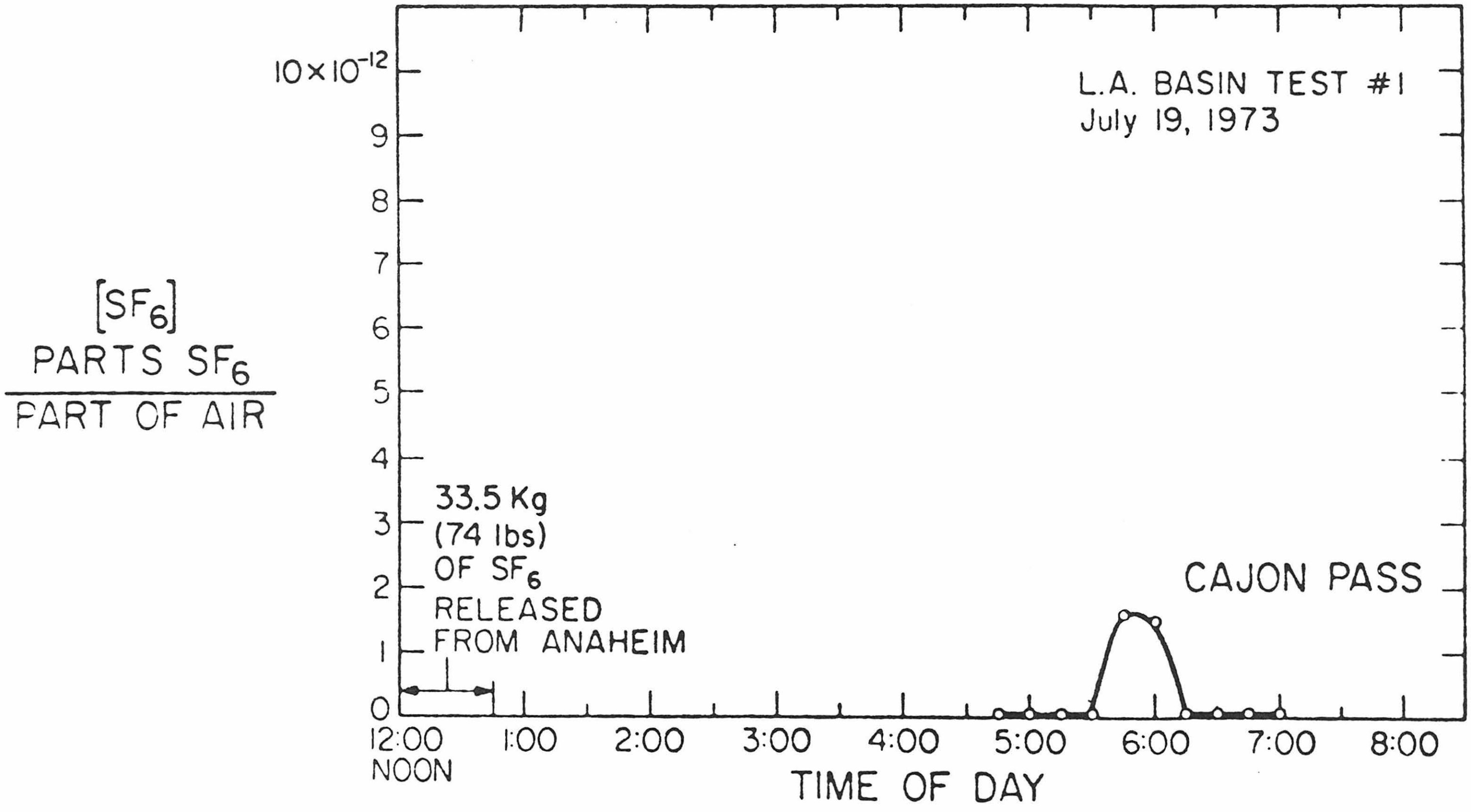

Figure 5. SF_6 concentration versus time curve for Cajon Pass.

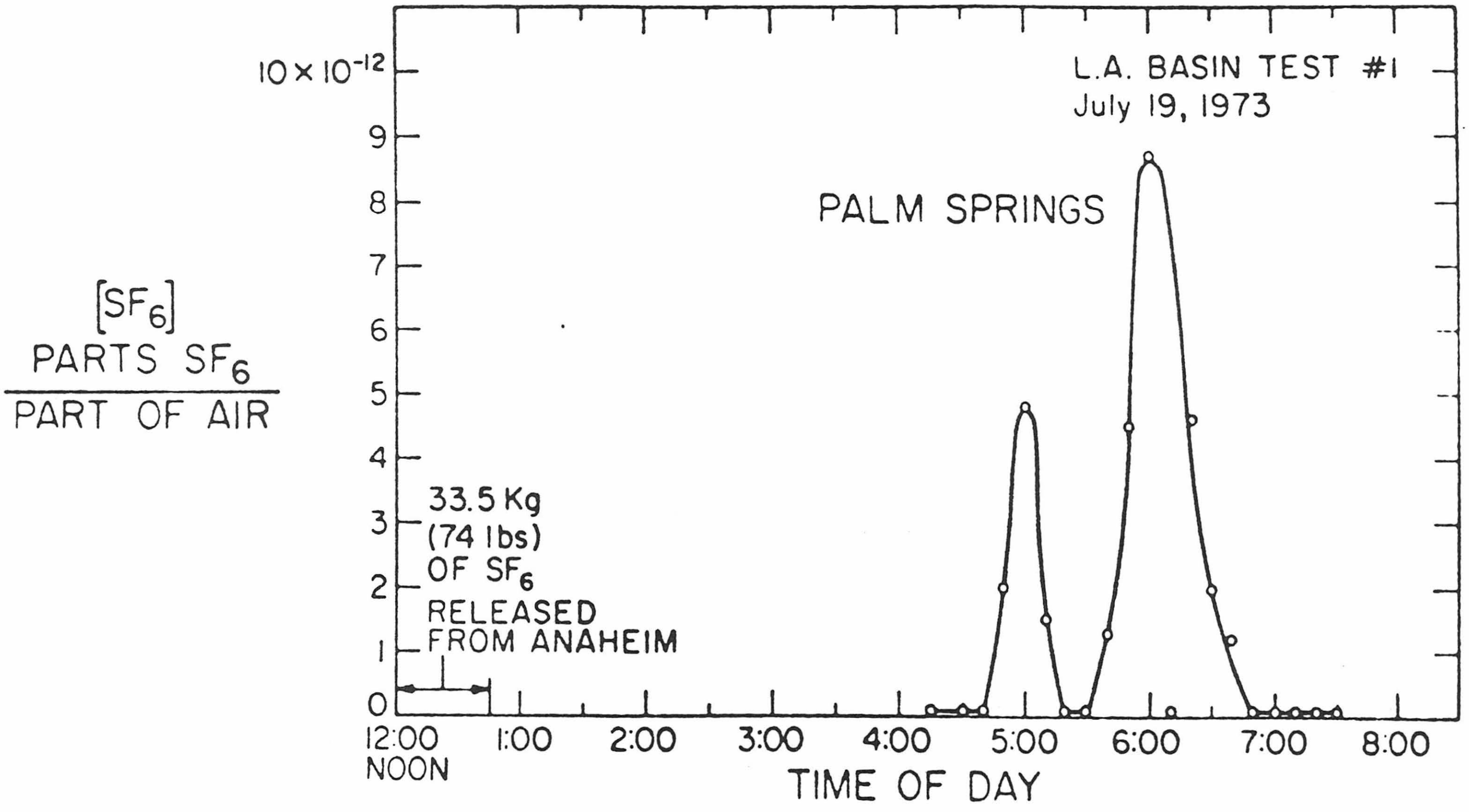

Figure 6. SF_6 concentration versus time curve for Palm Springs.

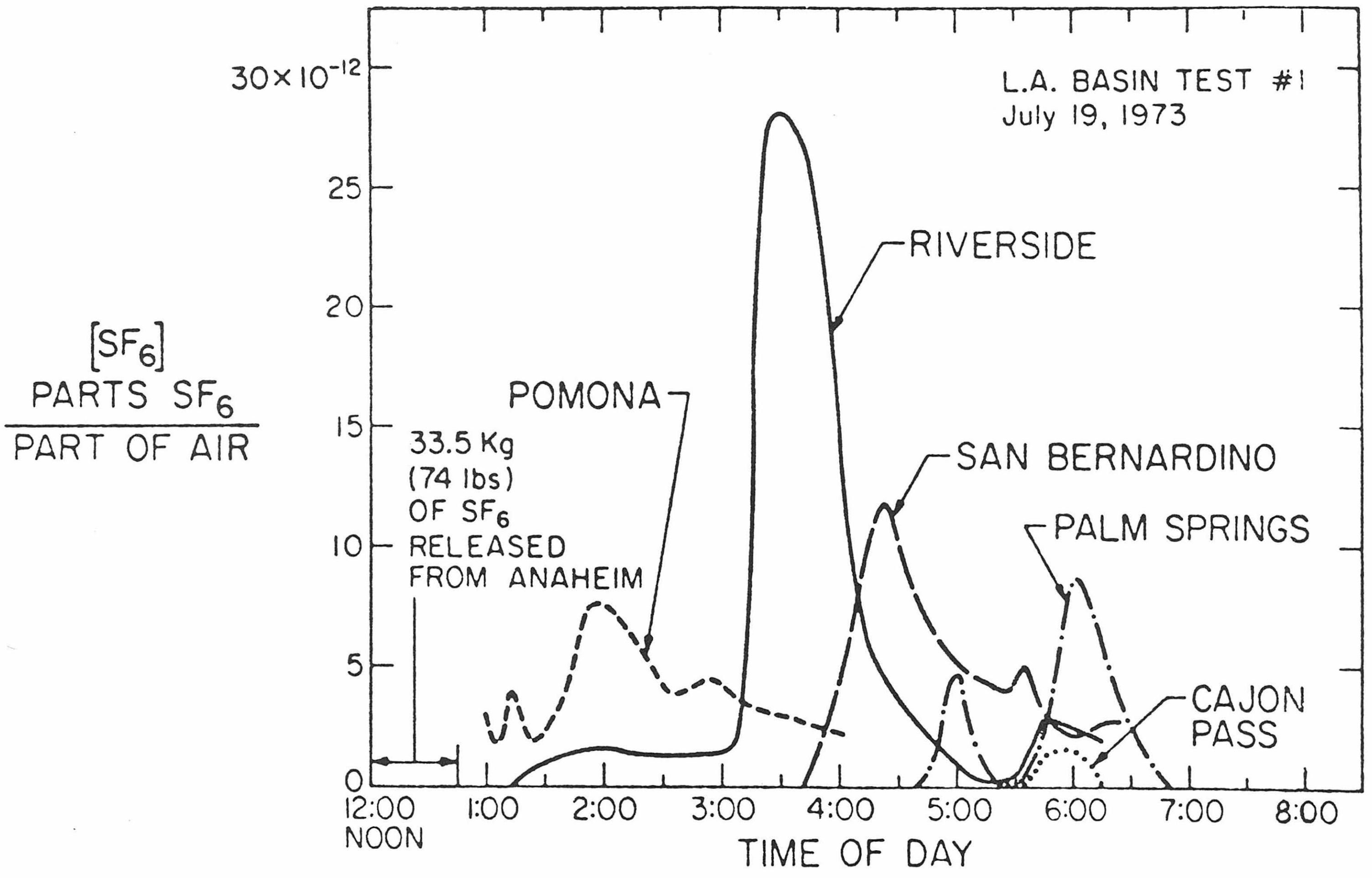

Figure 7. Compilation of SF_6 concentration versus time curves associated with the tracer test conducted July 19, 1973.

class A with an inversion height of about 3000 meters. The atmospheric conditions during the day of the test were estimated in stability categories A-B (Turner, 1970).

The concentration curves in Figures 2-6 were numerically integrated over time in order to determine the fractional contribution at each location of the original amount of tracer released in Anaheim. The results of this calculation are given below in Table 2. The fraction of tracer recorded at each location is defined as:

$$\text{Fraction} = \frac{\left[\int_{-\infty}^{\infty} c\,dt\right]_{\text{sampling location}}}{\left[\int_{-\infty}^{\infty} c\,dt\right]_{\text{release point}}}$$

Table 2. Fraction of tracer recorded at each location.

Location	Fraction of original amount released
Riverside	38.4×10^{-12}
San Bernardino	19.6×10^{-12}
Pomona	16.4×10^{-12}
Palm Springs	8.3×10^{-12}
Cajon Pass	1.0×10^{-12}

It should be noted that Palm Springs, at 124 km distance, received eight times the amount of the tracer recorded in Cajon Pass, and half the amount recorded in Pomona, which was only 34 km distant from the release point in Anaheim. These data further verify that the main urban air mass from Anaheim flows along the Riverside-Palm Springs route.

In the data for Pomona, Riverside, and San Bernardino, a small secondary peak occurred after the main peak (see Figures 2-4). This observation is possibly due to the fact that near the end of the tracer release, the wind direction in Anaheim shifted away from the normal SW direction for 4 minutes, and then shifted back to SW during the last 8 minutes of the release.

As shown in Table 1, these data indicate the existence of winds ranging in speed from at least 3.7 to over 10 meters/second even though the surface wind at Anaheim was measured between 2 and 3 meters/second. This is not inconsistent with typical velocity profiles (Jones et al., 1971; Turner, 1970); by using a one-fifth power law velocity profile, a velocity of 3 m/sec at 8 m gives rise to a velocity of 7.5 m/sec at a height of 750 m.

Certainly these data are subject to other interpretations and many questions raised here will be answered only through future investigations. However, this study clearly demonstrates that SF_6 is eminently useful as a tracer in probing the air flow within and around the Los Angeles basin. Other compounds suitable for electron-capture detection, which are emitted from industrial sources, may also be useful tracers in probing the air flow away from the Los Angeles basin (Simmonds et al., 1974).

It is of some interest to note several economic aspects of this study. The cost of material associated with the tracer release (the SF_6 gas cylinder plus a two-stage regulator) was $300. Six persons were involved in this test, one for the release and five for sampling. Four of the persons were trained during the morning of the test after pertinent meteorological data had been received and a decision to conduct the test had been made. All the data were analyzed and graphs prepared during the following day by one person. Thus, about 56 man-hours were required to conduct the test and to obtain the data. If a larger number of sampling points were desired during a test, it may be possible to reduce costs through the use of remote sequential air samplers.

4. CONCLUSION

The applicability of the sulfur hexafluoride tracer technique was demonstrated in a large-scale test over the Los Angeles area. A release of 33.5 kg of SF_6 from Anaheim over a period of 45 minutes permitted dispersion data well above the minimum detectable concentration limits to be obtained in five neighboring communities up to 124 km away: Pomona, Riverside, San Bernardino, Cajon Pass, and Palm Springs. A preliminary analysis of the data indicated that the cities of Riverside and Palm Springs may possibly lie in a direct path of the pollutant transport from Anaheim. Since the tracer is non-toxic and the entire test was relatively inexpensive, sulfur hexafluoride appears to be an ideal tracer for studying the transport and dispersion of pollutants over urban areas.

ACKNOWLEDGEMENT

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APPENDIX A-5. AN INEXPENSIVE REMOTE SEQUENTIAL AIR SAMPLER

(by G. A. Griffith, P. J. Drivas, and F. H. Shair)

In press, Journal of the Air Pollution Control Association.

ABSTRACT

A remote sequential air sampling unit has been developed which is compact, lightweight, and quite inexpensive. The sampling device contains a number of spring-loaded syringes which are released sequentially by the motion of a rotary mechanical timer. Field tests indicate that the sampling device can take accurate sequential air samples automatically and contain each sample without leakage for at least a period of 18 hours in an outdoor environment.

1. INTRODUCTION

In atmospheric tracer studies and air pollutant monitoring, a need often exists to obtain a series of ambient air samples and return them to a laboratory for analysis. Due to the economic consideration of manpower cost, a self-contained sequential air sampling device is desirable. However, the only currently available sequential sampling instruments are for collection of particulate matter in air or for absorption of a specific gaseous compound in a liquid solution; most units are not portable and are fairly expensive (American Conference of Governmental Industrial Hygienists, 1972). A few studies have adapted such instruments for remote use, but again only for sampling particulates or absorbed gases (Beddoes, 1967; Chatfield, 1967; Labdon, 1967).

To obtain manual ambient air samples (sometimes called grab samples), previous studies have used evacuated stainless steel containers (Turk et al., 1968), plastic bags (Conner and Nader, 1964; Schuette, 1967), and plastic squeeze bottles (Collins et al., 1965; Drivas et al., 1972). However, none of these methods can be easily or inexpensively adapted to an automated sampling system. The purpose of this note is to describe a new, inexpensive, and fairly simple device which functions as a remote sequential air sampler.

2. DESCRIPTION OF SAMPLING DEVICE

The sampling device consists basically of a number of spring-loaded syringes which are released sequentially by the motion of a rotary mechanical timer. As shown in Figure 1, four 20-cc plastic syringes were used; larger syringes could be used if a greater air volume is required for analysis, and a larger number of syringes could be incorporated by extending the length of the device. The syringes are attached by a thumb-screw mechanism to the outside of a 12-inch length of a 5-inch wide aluminum channel. The plunger of each syringe is attached to a strong spring which is anchored at the rear of the aluminum channel.

To spring-load each syringe, the spring is extended across the entire width of the channel and latched at the forward edge of the channel by a metal pin held in place by an L-shaped lever arm (in Figure 1, the two syringes at the rear are fully spring-loaded). The rotary mechanical timer is connected to a shaft with four adjustable metal arms. As the timer turns, the extended arms sequentially push each L-shaped lever arm forward and thus release the metal pin which latches the spring; the spring thus pulls back the syringe plunger and takes in an ambient air sample (in Figure 1, the two syringes at the front have taken samples). A 60-minute rotary mechanical timer was used for this device; shorter or longer desired time periods could be accommodated with a different timer.

Near the end of the sampling process for each syringe the same spring which operates the syringe plunger pulls back a guided brass rod assembly which forces a rubber septum against a needle on the front of each syringe (as shown in Figure 1 for the two syringes at the front).

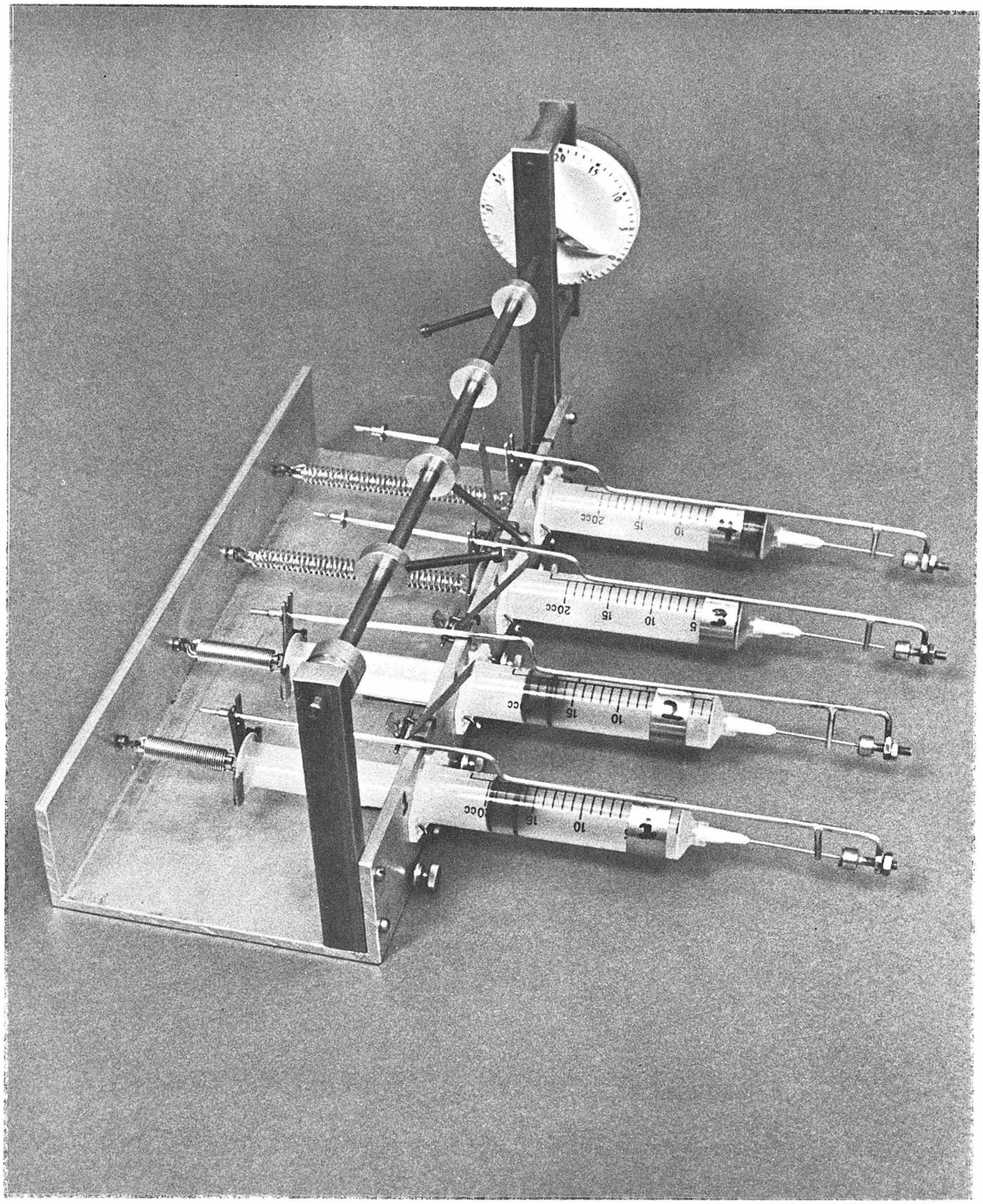

Figure 1. View of the sampling device. The front two syringes have taken samples, while the two syringes in the rear are in the spring-loaded position.

The needle ends have been squared off to form a tight fit against the septums. Thus, each syringe automatically closes itself, using a small amount of spring tension to provide a good seal between the end of the syringe needle and the rubber septum. The amount of closing tension is adjustable by means of a screw thread on the forward end of the brass rod assembly (Figure 1).

The total cost of the materials (not including labor) for the sampling device was under $12.00. The device is completely mechanical, requiring no batteries or external source of power. The total dimensions of the device in Figure 1, including the syringes, are 15 in. x 13 in. x 7 in. The sampling device is quite portable, weighing only about 3 pounds.

3. FIELD TEST

An experimental study of the time for room ventilation was used to test the sampling unit, operating completely automatically. Sulfur hexafluoride, an inert, non-toxic gas which can be detected in extremely low concentrations, was used as a tracer; the analysis procedure by electron-capture gas chromatography is described in detail in Drivas et al. (1972). A small amount of the tracer (0.1 ml) was well-mixed in a room and its decay with time caused by the room ventilation air flow was followed. The sampling device was set to release the syringes sequentially at ten minute intervals. As the sampling unit was automatically operating, simultaneous manual squeeze bottle samples were taken. The squeeze bottle technique has been shown to be an accurate manual air sampling method (Drivas et al., 1972).

At the end of the test, the sampling device with its four closed-off syringe samples was set outdoors on a building roof for 18 hours, experiencing a maximum temperature of 86° F in the afternoon and a minimum temperature of 56° F overnight. The squeeze bottle samples were kept inside the laboratory during this time period. Analysis of both sets of samples the following morning produced the results shown in Figure 2.

The sequential syringe samples were essentially identical to the manual squeeze bottle samples, proving that no leakage occurred on experiencing temperature fluctuations outdoors for 18 hours. The room ventilation test showed a characteristic decay time (the time required for an initial concentration to decrease by a factor of 1/e) of approximately 15 minutes. Thus, the sampling device can take accurate sequential air samples automatically and contain each sample without leakage

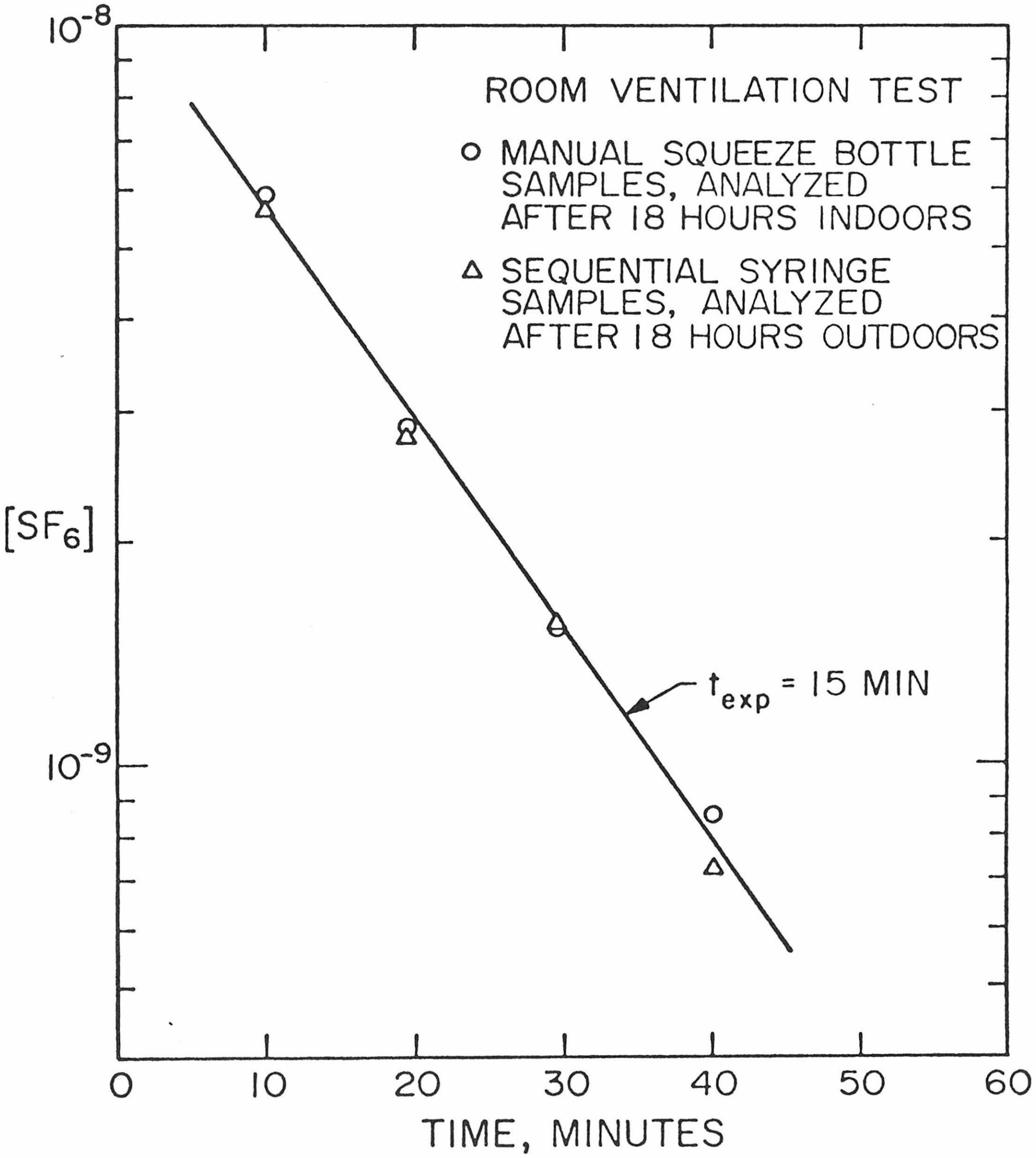

Figure 2. Tracer concentration versus time for the room ventilation test; the sequential syringe samples are compared with manual squeeze bottle samples.

for at least a period of 18 hours in an outdoor environment.

4. APPLICATIONS

An important application of the remote sequential air sampling unit is in the fields of atmospheric tracer studies and routine air pollutant monitoring, where automated sampling would produce a considerable saving in manpower cost. The remote sampling device would be ideal in areas where toxic or explosive gases are present, for example in gaseous mines. An added safety feature to sampling in mines is the fact that the sampling unit is completely mechanical; there is no electrical hazard which might trigger an explosion. Finally, since the sampling device is extremely compact and lightweight, it could be suspended or supported in areas where manual sampling would be very difficult, for example within a few feet of fast-moving highway automobile traffic.

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APPENDIX A-6. CLEANING PROCEDURE FOR TRITIUM FOIL

At three month intervals, a tritiated titanium foil was subjected to a cleaning procedure similar to those suggested by Holden and Wheatley (1967) and Claeys and Farr (1968). The tritiated surface of the foil should never be touched with the fingers, since natural perspiration can contaminate the foil; a tweezers or needle nose pliers should be used to handle the foil. No attempt was made to optimize the following cleaning procedure:

1. Immerse foil for 3 minutes in boiling 5% potassium hydroxide in 95% ethanol (5 g KOH/100 ml 95% ethanol).
2. Wash foil twice in hot 95% ethanol.
3. Wipe foil gently with pipe cleaner dipped in Amway paste metal cleaner.
4. Clean off excess metal cleaner with pipe cleaner dipped in acetone.
5. Wash foil in:
    (1) hot acetone
    (2) hot 95% ethanol
    (3) methanol
    (4) acetone

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APPENDIX A-7. DISCUSSION: "MULTIPLE BOX MODEL FOR DISPERSION OF AIR POLLUTANTS FROM AREA SOURCES"

In press, Atmospheric Environment.

DISCUSSION

MULTIPLE BOX MODEL FOR DISPERSION OF AIR POLLUTANTS FROM AREA SOURCES*

In his recent paper, Ragland (1973) stated that "The surface layer extends to $z = ku_*/f$ for neutral stability," and used this value in the calculation of eddy diffusivity profiles. However, this height is a normal estimation not of the surface boundary layer but of the planetary boundary layer or Ekman layer (Blackadar and Tennekes, 1968; Hanna, 1969). If values for u_* under neutral conditions are taken from Table 3 of the paper and the values $k = 0.4$ and $f = 10^{-4}$ $\sec^{-1}$ are used, the resulting values for the height of the "surface layer" range from 920 to 4000 meters. However, in Figure 3 of the paper, surface layer heights are used which are lower than the above values by a factor of about ten. Thus, the surface layer values used in Figure 3 are reasonable, but it is unclear how they were estimated.

In addition, there appears to be an error in the integration leading to equation (33) in the paper. The correct equation should be

$$u = \frac{u_*}{k} (1 + \alpha) \ln\left(\frac{z + z_o}{z_o}\right)$$

There are also some obvious typographical errors in equations (25), (27), (30) and (34).

Peter J. Drivas

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* Ragland K. W. (1973) Atmos. Environ., 7, 1017-1032.

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AUTHOR'S REPLY

Here is my reply to P. J. Drivas regarding my paper entitled "Multiple Box Model for Dispersion of Air Pollutants from Area Sources."

For the calculations I assumed that the surface layer for a neutral atmosphere extends to 10% of the planetary boundary layer thickness. The text on page 1024 should read, "The surface layer extends to $z = 0.1\ ku_*/f$ for neutral stability."

Equation 33 is obtained by setting $z = L$ in Eq. 32. Since Eq. 33 is really an empirical relationship, it is perhaps better not to specify ϕ_M in this particular instance.

Regretably the following typographical corrections should be made.

Eq. 25 $$K_M = \frac{ku_* z}{1 + \alpha z/L}$$

Eq. 27 $$K_M = ku_* z\left(1 - \frac{15z}{L}\right)^{.25}$$

Eq. 28 $$K_M = 0.1\ k^2 u_*^2/f \quad \text{for } z > 0.1\ ku_*/f$$

Eq. 29 $$K_M = \frac{0.1k^2 u_*^2}{f}\left(1 - \frac{1.5ku_*}{fL}\right)^{0.25} \quad \text{for } z > 0.1\ ku_*/f$$

Eq. 34 $$u = \frac{u_*}{k}\int_{z_o}^{z+z_o} \frac{dz}{z(1 - 15z/L)^{.25}}$$

Kenneth W. Ragland
Associate Professor

PROPOSITION

ON THE DESENSITIZATION OF PHOTOGRAPHIC EMULSIONS BY OXYGEN AND WATER VAPOR

The proposition entitled:

"On the Desensitization of Photographic Emulsions by Oxygen and Water Vapor"

submitted by Peter J. Drivas

was approved on May 22, 1974.

George R Gavalas
G. R. Gavalas, reviewer

W. H. Corcoran
W. H. Corcoran, reviewer

J. H. Seinfeld, reviewer

ABSTRACT

Oxygen and water vapor are known to separately desensitize photographic films and plates. An examination of the characteristic times involved demonstrates that the desensitizing process must be diffusion-controlled. An analysis technique is proposed which uses this desensitizing property to obtain an effective diffusion coefficient for oxygen or water vapor through a photographic emulsion layer. Experimental data on the loss of photographic sensitivity with time due to water vapor showed good agreement with the theory. Comparison of this effective diffusion coefficient with a normal diffusion coefficient through a non-photosensitive emulsion may yield basic information on the mechanism of desensitization, in particular the stability and perhaps the fraction of the oxygen or water vapor which reacts to cause the desensitization.

1. INTRODUCTION

The desensitizing effects of oxygen and water vapor on photographic emulsions have been known for some time. In 1878 Abney(1) noted that photographic exposures made in "atmospheres free from oxygen" showed greater sensitivity to light than exposures made in air. Blau and Wambacher(2) in 1934 found that the sensitivity of photographic film was increased by reducing the air pressure or by substituting pure nitrogen for air. Recently, a number of studies have examined in some detail the effects of the environment on the sensitivity of photographic emulsions to light, on the onset of low-intensity reciprocity failure, and on the stability of the latent image.

The important environmental factors affecting photographic emulsions were found to be oxygen, water vapor, and temperature.(3) Films which had been evacuated and then exposed either in vacuum or in dry nitrogen or helium showed much higher sensitivity than films exposed in room air. Addition of either dry oxygen or oxygen-free water vapor desensitized photographic emulsions; the combination of oxygen and water vapor desensitized more strongly than either alone.(4,5) In general, exposure in vacuum greatly reduced or eliminated low-intensity reciprocity failure.(6) For this reason, Lewis *et al.*(7) suggested for more sensitive astronomical photography that plates be evacuated and then exposed in dry helium and also at low temperature.* Latent-image stability

* In general, lowering the temperature increases sensitivity; this effect is separate from the effects of oxygen and water vapor.

was found to be greater in a vacuum than in either dry oxygen or room air.(8,9) A good review of the environmental effects on sensitivity has recently been presented by James.(3)

Photographic emulsions normally consist of sensitized silver bromide grains in a hardened gelatin supporting medium. The mechanism by which oxygen and water vapor separately desensitize emulsions is thought to be the formation of O_2^- or H_2O^- on the surface of the silver bromide grains in the emulsion:(3)

$$O_2 + e_t^- \rightleftharpoons O_2^- \tag{1}$$

$$H_2O + e_t^- \rightleftharpoons H_2O^- \tag{2}$$

The oxygen and water vapor react with trapped electron sites (e_t^-) on the silver bromide which would normally promote the formation of the latent image. The electrons are trapped by a silver bromide crystal defect or by an impurity center caused by chemical sensitization.(10) For oxygen and water vapor acting together, more complicated desensitization mechanisms have been proposed.(5)

Of some interest is the rate at which oxygen and water vapor desensitize a photographic emulsion which has been initially evacuated. Babcock et al.(5) present data relating the decreasing sensitivity of a film to the time of exposure to oxygen-free water vapor; they concluded that after 80 min, the sensitivity of emulsions up to 11 μm thick had been lowered to a constant level. The main purpose of this proposition is to demonstrate how such sensitivity-time data can be used to obtain some basic information on the mechanism of photographic desensitization, in particular whether the mechanism is diffusion-controlled or reaction-controlled and possibly the stability and fraction of the total oxygen or water vapor which reacts to cause the desensitization.

2. THEORY

2.1 Diffusion-controlled reaction

Rate constants for reactions (1) or (2) have not been measured, however a simple analysis of characteristic times can decide whether the desensitization process is diffusion-controlled or reaction-controlled. Experiments involving a series of short intermittent exposures have demonstrated that trapped electrons have a relatively short lifetime, of the order of a few seconds, before they recombine with positive holes in the silver bromide crystals. Maerker(11) found lifetimes of trapped electrons ranging from 3 to 10 sec for various types of emulsions. In more recent work, Tamura *et al.*(12) found lifetimes ranging from less than a second to a maximum of 6 sec for various emulsions in dry air. Thus, a characteristic time for trapped electrons to react with oxygen or water vapor must be of the order of one or two seconds. However, the data of Babcock *et al.*(5) on the rate at which oxygen-free water vapor desensitizes an initially-evacuated photographic emulsion indicates a characteristic time of about 5 min for the desensitization process. Thus, since the reaction is relatively rapid, the desensitization process must be controlled by the rate of diffusion of oxygen or water vapor through the emulsion layer.

2.2 Diffusion through a thin layer

Normal diffusion of a single gas through a thin layer of homogeneous solid can be described by a one-dimensional Fickian diffusion equation,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{3}$$

with the important assumption that the gas does not interact with the solid.(13) For diffusion of a multicomponent gaseous mixture through a homogeneous solid, the same equation applies for each gaseous component, since the concentrations of the diffusing species are very low compared to the solid concentration. This simple Fickian diffusion approach has been used extensively in the measurement of diffusion coefficients of gases through solids by standard techniques such as time-lag measurement(14,15) or steady-state counterdiffusion.(16)

For the case of water vapor diffusion through a photographic emulsion, some adsorption takes place in the gelatin supporting medium. For the diffusion of water vapor in a hydroscopic medium, Barrer(17) suggested using a diffusivity which is concentration-dependent. A better description of the adsorption process would be the addition of a loss term in equation (3):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \frac{\partial c_a}{\partial t} \qquad (4)$$

If the amount adsorbed, c_a, is related to the water vapor concentration by Henry's law, i. e. $c_a = kc$, and the process is diffusion-controlled, then equation (4) reduces to:

$$\frac{\partial c}{\partial t} = \left(\frac{D}{1+k}\right) \frac{\partial^2 c}{\partial x^2} \qquad (5)$$

Thus, standard techniques of measuring water vapor diffusion which use equation (3) would result in an effective diffusivity which is somewhat lower than a diffusivity without adsorption. In the following analysis, equation (3) will be assumed to apply for both oxygen and water vapor; for the case of water vapor, the diffusivity D will represent an effective diffusivity which includes the effects of adsorption.

Photographic film consists of a thin emulsion layer (of order 10 μm) on top of a relatively thick base; diffusion through the base will be assumed negligible. If the film is initially evacuated and then exposed to a constant outside concentration c_1, diffusion through a thin layer of thickness L can be described by the following boundary conditions: $c(x) = 0,\ t < 0$; $c(L) = c_1,\ t \geq 0$; $(\partial c/\partial x) = 0$ at $x = 0$. The solution of equation (3) with these boundary conditions can be found in Crank(18) and the analogous heat-transfer case in Carslaw and Jaeger;(19) the solution for

$t \geq 0$, $0 \leq x \leq L$ is:

$$\frac{c}{c_1} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos\frac{(2n+1)\pi x}{2L} \exp\left(\frac{-Dt}{L^2}(2n+1)^2\pi^2/4\right) \qquad (6)$$

The important quantity when desensitization of the film is considered is the average concentration through the photosensitive emulsion layer. Since in general a photographic film can have a thin gelatin overcoat which is not photosensitive, the average concentration should apply only through a photosensitive emulsion thickness L_e, where $L_e \leq L$:

$$\left(\frac{c}{c_1}\right)_{ave} = \frac{1}{L_e} \int_0^{L_e} \left(\frac{c}{c_1}\right) dx \qquad (7)$$

Substituting equation (6) into (7) yields:

$$\left(\frac{c}{c_1}\right)_{ave} = 1 - \frac{8L}{\pi^2 L_e} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \sin\frac{(2n+1)\pi L_e}{2L} \exp\left(\frac{-Dt}{L^2}(2n+1)^2\pi^2/4\right) \qquad (8)$$

As can be seen, if the ratio (L_e/L) is known, the average concentration is a function only of the dimensionless group, Dt/L^2.

2.3 Stability of reacted species

Equation (3) does not accurately describe the desensitization process, since the oxygen and water vapor react to form O_2^- and H_2O^-. Since it has been shown that the desensitizing process is diffusion-controlled, the assumption will be made that reaction (1) or (2) is at equilibrium. An equilibrium constant for equation (1) can be defined as

$$K = \frac{(O_2^-)}{(O_2)(e_t^-)} \tag{9}$$

where (e_t^-) is the number of trapped electron sites on the silver bromide crystals where the reaction can take place. Since

$$(O_2) + (O_2^-) = c_t \tag{10}$$

where c_t is the concentration of total oxygen, then:

$$(O_2^-) = \left[\frac{K(e_t^-)}{1 + K(e_t^-)}\right] c_t \tag{11}$$

This can be written simply as

$$c_r = f\, c_t \qquad (0 \leq f \leq 1) \tag{12}$$

where c_r is the reacted (O_2^-) concentration and f is the fraction of the total oxygen which reacts to cause desensitization of the photographic emulsion. Likewise, $c_u = (1-f)c_t$, where c_u is the unreacted concentration. The above equations (9-12) are of course similar for desensitization by water vapor.

As will be shown in section 3, photographic data on the loss of sensitivity with time can be used to calculate an effective diffusion coefficient for oxygen or water vapor, using equation (8). However, an important point which is not clear in the photographic literature is whether the reacted species (O_2^- or H_2O^-) can recombine quickly with positive holes in the same manner as trapped electrons or whether the reacted species are stable and relatively immobile on the silver bromide crystals. These two cases will be considered separately; in each case, an effective diffusion coefficient can be calculated.

Case 1. Unstable reacted species. If the reacted molecules can recombine with positive holes in the silver bromide as quickly as trapped electrons, with a lifetime of only a few seconds, then this recombination will be fast compared to the diffusion process. Thus, the reaction will not hinder the diffusion process and an equation for the total diffusion can be written:

$$\frac{\partial c_t}{\partial t} = D \frac{\partial^2 c_t}{\partial x^2} \tag{13}$$

Analysis of photographic data on the loss of sensitivity with time should yield an effective diffusion coefficient identical with a normal diffusion coefficient through a non-photosensitive emulsion.

Case 2. Stable reacted species. For a long-lived reacted species, the unreacted oxygen or water vapor concentration would decrease through the thin layer due to adsorption of the reacted species on the silver bromide crystals:

$$\frac{\partial c_u}{\partial t} = D \frac{\partial^2 c_u}{\partial x^2} - \frac{\partial c_r}{\partial t} \tag{14}$$

Expressing this equation in terms of the total oxygen or water vapor concentration, with the assumption that the fraction f is relatively independent of concentration, yields:

$$\frac{\partial c_t}{\partial t} = (1-f)\ D\ \frac{\partial^2 c_t}{\partial x^2} \tag{15}$$

Thus, analysis of photographic data on the loss of sensitivity with time, using equation (8), should yield an effective diffusion coefficient:

$$D_e = (1-f)\ D \tag{16}$$

Comparison with a normal diffusion coefficient D through a non-photosensitive emulsion can yield the fraction of the total oxygen or water vapor which reacts to cause the desensitization. Note, however, that if f is very small, this case is indistinguishable from case 1.

3. COMPARISON WITH EXPERIMENT

Babcock *et al.*(5) present data showing the decrease in photographic density at constant exposure of an initially-evacuated film as a function of time of contact with oxygen-free water vapor (35% relative humidity in nitrogen). The corresponding case of exposure to dry oxygen has not been studied in such detail. The film tested had a 1-µm thick silver bromide emulsion layer covered with a 10-µm thick gelatin overcoat; thus, in equation (8),

$L_e/L = 1/11$. The film had a 175-μm base which can be assumed to have effectively stopped diffusion from the other side. The temperature was controlled at 20° C.

It will be assumed that the photographic density decrease from the evacuated condition is directly proportional to the average concentration of water vapor in the photosensitive emulsion layer. After 80 min, no further density decrease was observed; the density difference will be normalized on this point (i. e., 80 min represents $c/c_1 = 1$). The following data in Table 1 are taken from the straight-line region of Figure 3.III of Babcock *et al.*(5) Photographic density (d) is a dimensionless quantity, defined as the logarithm of a transmitted light intensity ratio.

Table 1. Desensitization due to oxygen-free water vapor.

Time(min)	Density(d)	$d_o - d$	c/c_1
0	0.805	0	0
5	0.725	0.080	0.308
10	0.610	0.195	0.750
20	0.575	0.230	0.885
40	0.555	0.250	0.962
80	0.545	0.260	1.000

To compare these data with theory, equation (8) was solved numerically for $L_e/L = 1/11$; the result is the solid line plotted as c/c_1 as a function of Dt/L^2 in Figure 1. From Table 1, the point at 5 min was fixed near the correct concentration at a value of $Dt/L^2 = 0.25$. The other points were then plotted as the corresponding values of Dt/L^2 (i.e., 0.5, 1.0, 2.0, and 4.0). The data points are compared with the theory in Figure 1. Considering the large number of assumptions in the analysis technique, agreement is quite good. The resulting effective diffusion coefficient is approximately 1.0×10^{-9} cm^2/sec.

Ideally, a comparison of this figure with a normal diffusion coefficient for water vapor through a hardened gelatin layer could determine the stability of the reacted molecules and possibly reveal the fraction of the total water vapor which causes the desensitization, using equation (16). Unfortunately, since water vapor adsorbs on most substances, it is rarely studied in diffusion experiments; diffusion studies through gelatin are apparently also rare. Some studies on the diffusion of aqueous solutions into semi-liquid gelatin pastes exist,(20,21) but have questionable applicability.

Since hardened gelatin shows a structural behavior quite similar to a semicrystalline polymeric material like polyethylene,(22) diffusion studies through thin polyethylene layers may be used for comparison. Michaels and Bixler(23) studied by means of a time-lag technique the diffusion of eleven relatively small molecules (but not including water vapor) through semicrystalline polyethylene and found diffusion coefficients ranging from 10^{-7} to 10^{-9} cm^2/sec. Since water vapor adsorbs on gelatin, its diffusion coefficient

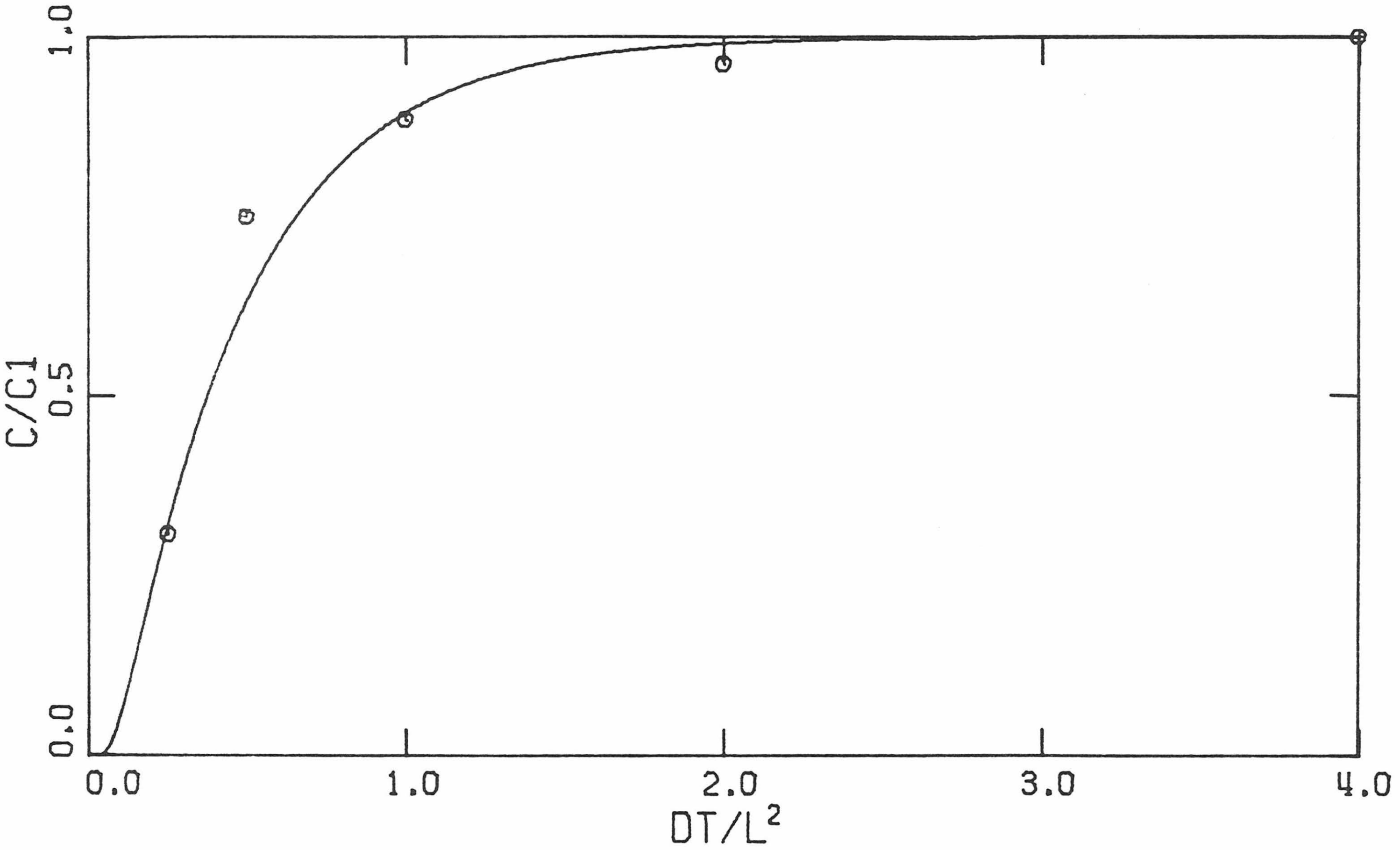

Figure 1. Comparison of diffusion-controlled reaction theory (solid line) with experimental data (open circles) on photographic desensitization by oxygen-free water vapor.

through a non-photosensitive emulsion might be expected to fall in a low range due to adsorption, as discussed in section 2.2. The low values of diffusivities found by Michaels and Bixler and the low value of 10^{-9} cm^2/sec found by the analysis technique may indicate either an activated solid diffusion process or a Knudsen diffusion process through small and very tortuous pores.

4. CONCLUSION

Due to the lack of data on normal diffusion of water vapor, it is not possible to make any statements about the mechanism of water desensitization. However, it has been shown that the desensitization process in general is diffusion-controlled and that the analysis technique appears valid for obtaining an effective diffusion coefficient through a photographic emulsion from data on the loss of sensitivity with time. Future work should certainly include basic diffusion data for oxygen and water vapor through non-photosensitive emulsions taken by standard diffusion-measurement techniques.(14-16) Comparison of these data with some systematic experiments on desensitization rates may answer some very basic questions on the stability and fraction of the oxygen or water vapor which reacts to cause photographic desensitization.

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