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Technical Report

Determination of a Range of Concern for Mobile Source Emissions of Hydrogen Sulfide

by

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Summary

This paper describes an effort by the Emission Control Technology Division of the EPA to establish a range of concern for hydrogen sulfide (H_2S) emissions from mobile sources. In light of the action called for in section 202(a)(4) of the Clean Air Act (CAA)(1)* and due to a concern within industry as to what emission levels will be used as the basis for the evaluation of current and future technologies, a methodology was developed in order to bracket a range of concern for various unregulated pollutants(2). This paper coordinates the efforts from two EPA contracts in order to use this methodology specifically for an evaluation of hydrogen sulfide. Mathematical models were previously designed for various exposure scenarios (such as enclosed spaces, expressways, and street canyons) and were used to calculate the ambient air concentrations resulting from various mobile source hydrogen sulfide emission factors (grams/mile). In conjunction with this, a hydrogen sulfide health effects literature search was conducted by Midwest Research Institute under contract to EPA to aid in the determination of the final range of concern(3). Some of the typical health effects noted were eye and respiratory tract irritation, dizziness, nausea and headaches of various degrees depending on exposure. This search provides adequate evidence to support the chosen limits of the range.

The results of this analysis provide a range of concern for ambient hydrogen sulfide concentrations of 0.03 mg/m^3 to 14.0 mg/m^3. This corresponds to motor vehicle emission levels of from 10.5-4,900 mg/mile to 958.5-447,300 mg/mile on the road and 0.04-204 mg/min to 3.8-1,770 mg/min for garages, depending on the type of scenario chosen to represent public exposure. Under non-malfunction conditons or when the malfunction does not cause a rich mixture, high catalyst temperature and low exhaust space velocity, the resulting H_2S emissions are negligible (below the range of concern for any scenario).

The current estimated vehicle fleet emission factor for hydrogen sulfide, 0.34 mg/mile, is well below the lowest moving vehicle scenario range of concern of 10.5 mg/mile. For moving vehicles the controlling (lowest) ranges are those of the roadway tunnel scenarios. For this to result in ambient H_2S concentrations within the range of concern, it would require most of the vehicles to be malfunctioning in a way that would cause high H_2S emissions (over 10.5 mg/mi).

Under certain malfunction conditions, idling catalyst-equipped vehicles can emit H_2S at approximately 1.0 mg/minute. In personal or parking garage scenarios this would result in H_2S concentrations within the range of concern for severe situations. For this to present a possible problem in a parking garage scenario, a large percentage (50%) of the cars would have to be malfunctioning in this manner. However, for a severe case personal garage scenario, it would only take the one vehicle malfunctioning in this manner to cause a chronic repetitive exposure of the driver to a level of H_2S within the range of concern. Therefore, closer scrutiny of idle H_2S emissions is recommended to determine if production vehicle/catalyst systems could yield H_2S levels as high as those reported here (which were from experimental catalysts).

* Numbers in parentheses denote references listed at end of report.

I. Introduction

Emissions from gasoline engine vehicles have been characterized by industry, government and private researchers for many years. While federal motor vehicle regulations have been in effect since 1968 for HC, CO and NOx, there are a number of unregulated pollutants which are being characterized to see if they could represent an unreasonable risk to public health and welfare. One reason these other pollutants need to be studied is that it is possible for a new emission control system to increase an unregulated pollutant while decreasing the regulated ones. For instance, catalyst equipped vehicles can emit significantly more sulfuric acid than non-catalyst vehicles (4).

Hydrogen sulfide is an unregulated pollutant emission that has been found in various concentrations in some automotive emission tests (4,5,6,7). Due to its toxic properties and its disagreeable rotten-egg odor, tests have been conducted to characterize H_2S emissions as a function of driving cycle, emission control system, and sulfur content of fuel. The results of these tests along with health effects test data, as summarized later in this report, are used to determine the conditions under which automotive H_2S emissions could be of concern with respect to health and welfare.

Barnes and Summers of General Motors reported in 1975 that three conditions favored the formation of H_2S by Pt/Pd oxidation catalysts: (1) rich air/fuel ratio (i.e., a reducing condition); (2) low exhaust space velocity; and (3) high catalyst temperature. These conditions rarely occur simultaneously with properly tuned vehicles. However, malfunctioning vehicles or vehicles with maladjusted carburetors that run rich may meet these conditions and emit H_2S and COS. It should be noted that the reducing conditions that favor sulfide formation do not favor sulfate formation.

In the interest of establishing a range of concern for levels of H_2S in motor vehicle exhausts, Midwest Research Institute (MRI) compiled information on the health effects of hydrogen sulfide at different concentrations(3). The results of that work form the basis for the range of concern determined later in this report.

II. Background

When the Clean Air Act was amended in August 1977, the additions included sections 202(a)(4) and 206(a)(3) which deal with mobile source emissions of hazardous pollutants from vehicles manufactured after 1978. These sections are as stated below:

"(4)(A) Effective with respect to vehicles and engines manufactured after model year 1978, no emission control device, system or element of design shall be used in a new motor vehicle or new motor vehicle engine for purposes of complying with standards prescribed under this subsection if such device, system, or element of design will cause or contribute to an unreasonable risk to public health, welfare, or safety in its operation or function.

(B) In determining whether an unreasonable risk exists under subparagraph (A), the Administrator shall consider, among other factors, (i) whether and to what extent the use of any device, system, or element of design causes, increases, reduces, or eliminates emissions of any unregulated pollutants; (ii) available methods for reducing or eliminating any risk to public health, welfare, or safety which may be associated with the use of such devices, systems, or elements of design which may be used to conform to standards prescribed under this subsection without causing or contributing to such unreasonable risk. The Administrator shall include in the consideration required by this paragraph all relevant information developed pursuant to section 214."

206 (a) (3)

"(3) (A) A certificate of conformity may be issued under this section only if the Administrator determines that the manufacturer (or in the case of a vehicle or engine for import, any person) has established to the satisfaction of the Administrator that any emission control device, system, or element of design installed on, or incorporated in, such vehicle or engine conforms to applicable requirements of section 202(a)(4).

(b) The Administrator may conduct such tests and may require the manufacturer (or any such person) to conduct such tests and provide such information as is necessary to carry out subparagraph (A) of this paragraph. Such requirements shall include a requirement for prompt reporting of the emission of any unregulated pollutant from a system device or element of design if such pollutant was not emitted, or was emitted in significantly lesser amounts, from the vehicle or engine without the use of the system, device, or element of design."

Prior to these amendments, EPA's guidance to the manufacturers regarding hazardous unregulated pollutants were contained in the Code of Federal Regulations, Title 40, section 86.078-5b. This subsection is stated as follows:

"Any system installed on or incorporated in a new motor vehicle (or new motor vehicle engine) to enable such vehicle (or engine) to conform to standards imposed by this subpart:

(i) Shall not in its operation or function cause the emissions into the ambient air of any noxious or toxic substance that would not be emitted in the operation of such vehicle (or engine) without such system, except as specifically permitted by regulation; and

(ii) Shall not in its operation, function, or malfunction result in any unsafe condition endangering the motor vehicle, its occupants, or persons, or property in close proximity to the vehicle.

(2) Every manufacturer of new motor vehicles (or new motor vehicle engines) subject to any of the standards imposed by this subpart shall, prior to taking any of the action specified in section 203 (a)(1) of the Act, test or cause to be tested motor vehicles (or motor vehicle engines) in accordance with good engineering practice to ascertain that such test vehicles (or test engines) will meet the requirements of this section for the useful life of the vehicle (or engine)."

Before certification can be granted for new motor vehicles, manufacturers are required to submit a statement, as well as data (if requested by the Administrator), which will ascertain that the technology for which certification is requested complies with the standards set forth in section 86.078-5(b). This statement is made in section 86.078-23(d).

The EPA issued an Advisory Circular (AC) (4) in June 1978, to aid the manufacturers in complying with section 202 (a)(4). Manufacturers were asked to continue providing statements showing that their technologies did comply with the vehicle emission standards and also will not contribute to an unreasonable risk to public health. Another Advisory Circular (5) was issued in November of that year continuing these procedures for 1980 and later model years.

III. Methodology Overview

Along with the previously mentioned activities, EPA, with the input from several interested parties, has developed a methodology which is one possible approach to implementing section 202 (a)(4) of the CAA. This approach is explained in detail in EPA report number EPA/AA/CTAB/PA/81-2, "An Approach for Determining Levels of Concern for Unregulated Toxic Compounds from Mobile Sources" (6). Only a brief summary of this method will be presented in this report.

Under contract to EPA, Southwest Research Institute (SwRI), and Midwest Research Institute (MRI), have provided valuable information for this effort. SwRI developed or modified mathematical models for predicting ambient air concentrations of mobile source pollutants for a variety of exposure situations including enclosed spaces, street canyons, and expressways. Once vehicle emission factors for various vehicle categories have been determined for a particular pollutant, these models can then be used to calculate corresponding ambient air values for both severe and typical exposure situations for each scenario. A plot of ambient air concentrations vs. emission factors can then be designed for use in further steps of this methodology.

Health effects literature searches have been conducted by MRI in an attempt to aid EPA in the determination of a range of concern for various selected pollutants. With adequate information, the limits for this range can be chosen. The upper level of the range will be that value above which the studies show that the pollutant causes so great a hazard to human health as to require formal rulemaking action. The lower value of the range will be the lowest level at which there is evidence of adverse physiological effects. The region between these limits will be termed the "ambient air range of concern", indicating scattered data points providing evidence of adverse physiological effects caused by exposure to various concentrations of hydrogen sulfide. Using the ambient air vs emission factor plot developed earlier, any technology emitting a concentration of a pollutant (when converted to ambient air concentrations) falling within the range of concern will be subject to closer scrutiny. Technologies with emission levels falling below the lowest level of the range will constitute "no problem", implying a low level of effort monitoring. Technologies with emission levels which fall above the highest value of the range will be considered "dangerous" with respect to human health and, therefore, this will imply a necessity for regulation.

For the purpose of this report, this particular methodology has been used to develop a range of concern specifically for motor vehicle emissions of hydrogen sulfide.

IV. General Information

Hydrogen sulfide (H_2S) is a colorless gas having an odor of rotten eggs. It can result in severe toxic effects if inhaled at concentrations greater than about 200 ppm (280 mg/m^3), and various lesser effects at lower concentrations as detailed in the health effects section.

The gas must be handled carefully because of (1) its toxic properties (particularly dangerous because it may temporarily desensitize the olfactory nerves thus making it impossible to sense its presence), and (2) its explosive tendencies (low ignition temperature of 260°C and wide flammability range from 4.3 to 44% by volume in air).

Fluorine, chlorine, bromine and iodine react chemically with H_2S to form the corresponding halogen acid. Metal sulfides of varying solubilities are formed when H_2S is passed into solutions of the heavy metals, such as Ag, Pb, Cu, and Mn. This reaction is responsible for the tarnishing of Ag and is the basis for the separation of these metals in classical wet qualitative analytical methods. Hydrogen sulfide also reacts with many organic compounds.

The gas results from the decomposition of metal sulfides and albuminous matter and is found in the areas of mineral springs, sewers, and in some mines where it is referred to as "stink damp." H_2S also is a by-product of several industrial processes, including synthetic rubber, viscose rayon, petroleum refining, dyeing, and leather-treating operations. In the laboratory, H_2S usually is prepared by treating a sulfide with an acid, such as iron pyrites and HCl, or by heating thioacetamide $CH_3C(S)NH_2$. Three processes are used industrially to produce H_2S in large quantities:

(1) treating a sulfide with an acid,
$2NaHS + H_2SO_4 \rightarrow 2H_2S + Na_2SO_4$,

(2) reacting sulfur with an alkali,
$4S + 2NaOH + 2H_2O \rightarrow 2H_2S + Na_2S_2O_3$,

(3) directly reacting sulfur with hydrogen,
$S + H_2 \rightarrow H_2S$.

Large quantities of by-product H_2S usually are converted into elemental sulfur or H_2SO_4.

Industrial uses for H_2S incude (1) the preparation of sulfides, such as sodium sulfide and sodium hydrosulfide, (2) the production of sulfur-bearing organic compounds, such as thiophenes, mercaptans, and organic sulfides, (3) the removal of Cu, Cd, and Ti from spent catalysts where the gas acts to form a precipitate, (4) the formulation of extreme-pressure lubricants, and (5) the preparation of rare-earth phosphors used in color TV tubes(8).

In an automotive system, hydrogen sulfide is formed by the reduction of fuel sulfur as it passes through the exhaust system. Three-way catalyst systems oxidize the hydrocarbons and carbon monoxide to carbon dioxide and water, as do conventional oxidation catalysts; however, at the same time they reduce NOx to nitrogen. This reduction process provides a pathway for the formation of other reduced exhaust species such as ammonia, cyanide, organic amines, hydrogen sulfide and organic sulfides that would not be expected in significant quantities from conventional oxidation catalysts(9).

V. Emission Factors

H_2S exhaust emissions have been measured for a variety of vehicle types. The EPA recommended procedure for this measurement is described in an EPA report entitled, "Analytical Procedures for Characterizing Unregulated Pollutant Emissions from Motor Vehicles" (10). This basic procedure is what was used to obtain all the H_2S emission factors in this report. Small amounts of H_2S have been measured in the exhaust of gasoline-fueled vehicles equipped with either oxidation or three-way catalysts under normal operating conditions, at levels between 0.0 and 1.5 mg/mile. Under malfunction conditions, however, these emission rates can increase considerably. A reported emission rate for a malfunctioning vehicle operating with a 3-way catalyst was as high as 8.2 mg/km or 13.2 mg/mile, for the sulfate emission test (SET)* driving schedule (11).

Tests were run by EPA-ORD in order to evaluate the impact of low ambient temperatures on 3-way catalyst-equipped car emissions(12). These studies showed that H_2S emissions for the most part were not significantly affected by subambient temperature operation. Of the four vehicles tested, only one (Chevrolet Caprice) showed significant change due to the low test temperature, and this was mainly due to the cold-start portion of the test. For this first portion of the test, the H_2S emissions at the lower test temperature (60°F) were about 20 mg/mile as compared to 0.02 mg/mile at the higher (normal) test temperature (81°F). For the complete FTP, the maximum observed H_2S emission rate was 4.21 mg/mile, which was at 60°F for the vehicle mentioned above.

Average H_2S emission factors for various vehicle types were collected from several available sources. The values obtained are listed in Table I. These emission factors were compiled for the SET driving schedule, unmodified mode (i.e. properly tuned), as well as for various malfunction modes (when such data were available). Since the available data for some technologies list both an unmodified and a malfunction emission value, the final, average emission factor was weighted such that the value is 75% of the unmodified emission rate plus 25% of the malfunction rate. This calculation was based on the assumption that 25% of the vehicle fleet operates in the malfunction mode (i.e., rich idle, misfire, high oil consumption, etc.) at any given time (18). Further work may identify a more accurate percentage.

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*Also known as the Congested Freeway Driving Schedule (CFDS), which is a driving cycle with a 35 mph average speed designed to represent driving on congested freeways.

The emission factors obtained for the malfunction mode are especially important to this effort due to the fact that H_2S emissions tend to increase under malfunction conditions. Maximum emission rates have been listed below for three vehicle categories.

Maximum Reported H_2S Emission Rates under Malfunction Modes
(Highest Values Reported From Any Source on Any Single Test)

Vehicle Category	mg/mile
non-catalyst	SET 0
	FTP .08
oxidation catalyst	SET 6.9
	FTP 1.1
3-way catalyst	SET 13.2
	FTP 9.0

The reported emission factor for the 3-way catalyst vehicles under malfunction conditions is higher than those of the other two categories, and it is also much higher than any of the vehicle categories listed in Table I.

The driving cycles considered in this report were the Federal Test Procedure (FTP), the Sulfate Emission Test (SET), and idle testing. The results available for the Highway Fuel Economy Test were similar to SET values, but were usually slightly lower.

It may be more appropriate to choose driving cycles which would specifically simulate those scenarios under investigation (enclosed spaces, street canyons, etc.). At present, however, data do not exist to permit use of this approach for H_2S. It is not known at this point what percent of error is introduced by using emission factors from the standard test cycles.

Available H_2S idle emissions data were used to estimate H_2S exposures in parking garage situations, and will be discussed later in this report. One study by GM (5) investigated idle sulfide emissions as a function of oxidation catalyst temperature and air/fuel ratio. It was found that the mixture had to be richer than the correct setting, and catalyst temperature needed to be above 570°C to result in any detectable H_2S formation (greater than 0.05 ppm). Obtaining this condition required cruising the car at 96 km/hr for seven minutes (during which no detectable H_2S was emitted) and then decelerating to idle for the sample collection. This would be more representative of a situation like a freeway off ramp rather than a cold start in a garage.

Using the average H_2S emission factor data presented in Table I, it is possible to calculate a fleet average emission factor. The information necessary to make these calculations is listed in Table II. A fraction of the vehicle miles traveled (VMT) is listed for each vehicle class. These data were derived from information presented in the Pedco Report of 1978 (19), and the EPA report, "Mobile Source Emission Factors: For Low Altitude

Areas Only" (20). Each vehicle class VMT fraction is multiplied by the corresponding emission factor for that class, giving a fraction quantity of pollutant emitted from a particular vehicle category in comparison to other vehicle categories in the fleet. The EF X VMT fractions for each vehicle class are totaled and then averaged to obtain a total fleet average. For hydrogen sulfide emissions, this value is 0.34 mg/mile. This average takes into account only those vehicle classes listed in Table II. Of course, should any of these categories change, so would the total fleet average.

It is difficult to predict exactly what percentage of vehicle categories will make up the entire fleet at any one time. The most severe case, with respect to any pollutant emission, would be that case in which the entire vehicle fleet was comprised of all of the highest emitting technologies. In order to account for differing proportions of the highest H_2S emitting technologies, Table III was devised. The emission factor values presented here reflect hypothetical situations in which 25, 50, 75, and 100 percent of the vehicle fleet is comprised of the highest emitting technologies. The compiled emission factors listed in Table III will become an important tool in comparing vehicle emissions to the range(s) of concern. In subsequent steps, these values will be used to calculate ambient concentrations of H_2S for various fleet mixes of emission control technologies.

VI. Hydrogen Sulfide Health Effects

A literature review on the health effects of hydrogen sulfide was performed as an input to the determination of a range of concern for mobile source emissions of this compound(3,21). A summary of this literature search is included as an Appendix to this report.

As indicated in the methodology, in order to focus the health effects literature review, a preliminary range of ambient levels was selected to bracket the region of uncertainty with respect to hydrogen sulfide health effects. This range was determined to be 0.15 mg/m^3 - 14.0 mg/m^3 for H_2S. The lower end of this range was selected to approximate the lowest level at which adverse physiological effects could be detected. The preponderance of the evidence has shown little or no health effects at levels of hydrogen sulfide below this, although upon investigation a few instances of adverse reactions were found with chronic exposures as low as 0.05 mg/m^3 in adults and 0.03 mg/m^3 in babies.

The upper level of the preliminary range was chosen to be the threshold limit value (TLV) recommended by the ACGIH as 14 mg/m^3 (9). Above this level several studies had shown an adverse reaction in healthy subjects which could be harmful under repeated exposure.

The specific health effects that were found included irritations of the eyes and respiratory tract, dizziness, nausea and headaches of various degrees depending on the exposure level and duration. Chronic exposures resulted in more adverse effects than acute exposures for a given exposure level. More details of the relationship between health effects and exposures are included in Section VIII, "Determination of the Range of Concern."

VII. Hydrogen Sulfide Ambient Air Concentrations

The H_2S emission factor information provided in Table I through III can be used in conjunction wth the modeling techniques developed by Southwest Research Institute (SwRI) (see Reference 2), in order to calculate the ambient air concentrations produced by varying levels of H_2S vehicle emissions for different exposure situations. Future work may identify other scenarios which would also be appropriate for the assessment of human exposure to exhaust pollutants, but, for this task, only five exposure scenarios were investigated: personal garages, parking garages, roadway tunnels, street canyons, and urban expressways. A typical and severe case situation was developed for each of these scenarios. Each situation has been considered separately, and, therefore, no cumulative effects have been determined at this point. Reference (2) discusses the reasoning behind using these specific scenarios as well as the information used in the determination of the modeling techniques.

Table IV presents ambient air concentrations of hydrogen sulfide, as a function of vehicle emission rates, for eleven ambient situations. The vehicle emission rates correspond to those emission factors which were calculated for the various combinations of fleet categories found in Table III. This information will later be used to develop a plot which graphically represents the relationship between the emission factors for various scenarios and ambient air concentrations.

Each scenario is intended to represent a specific type of situation. The typical personal garage situation represents a 30 second vehicle warm-up time and the severe situation simulates a five minute vehicle warm-up time. Both of these cases, of course, take place within a residential garage, and are intended to correspond to summer and winter conditions, respectively.

The typical parking garage case simulates an above the ground, naturally ventilated garage in which it is assumed that a vehicle spends an equal amount of time on both the parking level and ramp level. The severe case represents an underground garage wherein the exposed population is assumed to be at parking level five (lowest level). It is also assumed that this exposure occurs 20 minutes after a major event in which the parking structure is essentially full. The initial concentration of H_2S is assumed to be low (0.001 mg/m^3).

In order to more closely assess public exposure to H_2S in a garage situation, idle emissions data were averaged from a limited number of sources. Although there was deviation depending on catalyst composition and type of malfunction, the available idle data indicate that vehicles with 3-way catalysts, operating in the malfunction mode can emit H_2S at rates ranging as high as 0.5 - 1.2 mg/min. For calculation purposes a rate of 1.0 mg/min. will be assumed.

In a worst case situation, where 100% of the vehicle fleet consists of automobiles with 3-way catalysts, operating in the malfunction mode, the H_2S ambient air concentrations for each of the garage situations would be as listed below. This, of course, might be a reasonable case for a personal garage situation in which a person starts his vehicle, equipped with a 3-way catalyst presently operating in the malfunction mode, in an enclosed garage.

H_2S Ambient Air Concentrations, mg/m^3

Fleet Make Up	Emission Factor	Personal Garage Typical	Personal Garage Severe	Parking Garage Typical	Parking Garage Severe
100% 3W	1 mg/min.	0.008	0.067	0.009	0.056

Since these values more accurately reflect the H_2S vehicle emissions in an actual garage situation, they should be used in the identification of those scenarios which may be of most concern to public health, with respect to exposure to H_2S. Due to limited data, idle emission values can only be evaluated for vehicles with 3-way catalysts (operating in the malfunction mode). In the future, when more idle data have been collected, it may be possible to evaluate other categories which would contribute to the vehicle fleet make up.

Two specific tunnel designs were chosen to estimate the two roadway tunnel cases. A newly designed, two lane roadway tunnel, with moderate traffic flow, is used for the typical condition, while an old design, heavily-traveled roadway tunnel is used for the severe condition. The street canyon situations are simulated by examining the parameters of two street canyons. The most sensitive parameter in this model appears to be the number of traffic lanes within the canyon. The typical condition is calculated for a two lane street canyon with a traffic load of 800 vehicles per hour and a sidewalk location of the exposed population. The severe condition is based on a six lane street canyon with a 2400 vehicles per hour traffic load, and the exposed population is located inside the vehicles.

Three different cases were considered in order to cover the possible range of exposures in an expressway situation. The off road case estimates an exposure involving a close proximity to the highway (i.e., living or working close to a heavily-traveled freeway). This case is calculated on a short term basis for a distance of 50 meters downwind of the roadway. The typical, on road exposure is based on a four lane expressway with a traffic load of 1400 vehicles per hour and a westerly wind (perpendicular to roadway) of 1.0 meter/second. In this situation, the exposed population is located inside the vehicle. The severe case represents a heavily-traveled (3600 vehicles/hour), ten lane freeway with a 1.0 meter/second westerly wind (perpendicular to roadway), and an in-vehicle location of the exposed population.

VIII. Determination of the Range of Concern

The range of concern for hydrogen sulfide emissions from automobiles is determined using the outputs from the previous three areas, emission factors, health effects and exposure estimation (the emission factors and exposure estimates have already been combined in Table IV). Using the preliminary range (0.15 mg/m^3 - 14 mg/m^3) as a stepping stone for this effort, along with the guidelines explained earlier in the methodology section of this report, an upper and lower value can be determined for the final range of concern.

The literature search reveals an epidemiological study (22) which shows that a chronic exposure concentration as low as 0.05 mg/m^3 caused a 50% higher morbidity rate as well as headaches, weakness, nausea, and vision problems in a group of apartment house residents.

There is also a study done in an occupational exposure setting involving the babies of nursing mothers who worked in a viscose (rayon) shop. During nursing these babies were exposed to hydrogen sulfide from the mothers' clothing at concentrations ranging from 0.028 - 0.055 mg/m^3. Compared to babies whose mothers worked in other shops without H_2S exposure, these babies were more poorly developed, vomited more after feeding, and were more susceptible to severe infectious diseases.

Since the nature of the exposure to automobile generated H_2S will not likely be comparable to the above exposure in that the exposure will more likely be of an acute or short term chronic nature (several hours per day repeatedly as a maximum), the upper level of the range of concern should be set at 14 mg/m^3. This exposure level corresponds to the TLV for hydrogen sulfide as set by the ACGIH for 8 hr. per day/40 hr. per week exposure to healthy workers.

Data concerning less severe exposures indicate that the minimum odor threshold was 0.005 mg/m^3. The level not affecting eye sensitivity to light was 0.008 to 0.010 mg/m^3, while light sensitivity-related eye responses were seen at 0.012 - 0.013 mg/m^3. Since 0.03 mg/m^3 is the lowest level at which any indications of adverse health effects were found, this is the recommended lower limit of the range of concern.

Between the chosen limits of this range, there are a few data points, some of which show adverse effects and some that do not. Therefore, this region has been termed the "range of concern" for hydrogen sulfide concentrations in the ambient air. This range can now be used in conjunction with the emission factor data to graphically present the conversion of hydrogen sulfide emissions to ambient air concentrations.

Once the literature search was completed and the appropriate information was tabulated for hydrogen sulfide, a table was prepared compiling all the information for the animal and human studies (3). These tables list the studies according to the exposure concentration of hydrogen sulfide. Using this health effects information along with the emission factor data presented in Table IV, graphs were composed representing the relationship between ambient air concentrations, emission factors, and the various types of public exposure situations (see Figures 2-6).

According to the methodology described earlier in the report, the lower and upper levels which comprise the health effects range of concern are compared to the mobile source situations to calculate the emission factor range of concern. The chief element of comparability between the health effects range and the ambient situations is exposure time. Most of the mobile source situations simulate short term exposures (durations of an hour or less per day) perhaps repeated several times per week over an extended period. The average exposure situations appear more likely to be repeated often, while the severe exposure conditions would likely only occur on infrequent occasions.

With the above information, the mobile source range of concern for hydrogen sulfide can be estimated for the different mobile source situations. Table V lists the vehicle emission factors which correspond to the high (14.0 mg/m^3) and low (0.03 mg/m^3) portions of the range of concern for hydrogen sulfide. Inspection of this table shows that the scenarios result in a wide range of emission factors corresponding to the health effects range of concern of 0.03 mg/m^3 to 14.0 mg/m^3.

Conclusions - Hydrogen Sulfide

1. The range of concern for ambient hydrogen sulfide concentrations is 0.03 - 14.0 mg/m^3.

2. This range of concern corresponds to motor vehicle emission rates ranging from 10.5 - 4,900 mg/mi to 958.5-447,300 mg/mile depending on the scenario of interest.

3 At higher concentrations (above 0.05 mg/m^3) the possible health effects range from minor eye and respiratory tract irritation to dizziness, nausea and headaches depending on degree of exposure and susceptibility.

4. With respect to the moving vehicle scenarios the controlling (lowest) ranges are those of the roadway tunnel scenarios. Some malfunctioning catalyst-equipped vehicles could emit H_2S at a level within, but not above, the range of concern for severe or typical tunnel scenarios. For this to result in ambient H_2S concentrations within the range of concern, it would require most of the vehicles to be malfunctioning in a way that would cause high H_2S emissions (over 10.5 mg/mi).

5. The current estimated vehicle fleet emission factor for hydrogen sulfide, 0.34 mg/mile, is well below the lowest moving vehicle scenario range of concern of mg/mile.

6. Under certain malfunction conditions, idling catalyst-equipped vehicles can emit H_2S at approximately 1.0 mg/minute. In personal or parking garage scenarios this would result in H_2S concentrations within the range of concern for severe situations. For this to present a possible problem in a parking garage scenario, a large percentage (50%) of the cars would have to be malfunctioning in this manner.

   However, for a severe case personal garage scenario, it would only take the one vehicle malfunctioning in this manner to cause a chronic repetitive exposure of the driver to a level of H_2S within the range of concern. Therefore, closer scrutiny of idle H_2S emissions is recommended to determine if production vehicle/catalyst systems could yield H_2S levels as high as those reported here (which were from experimental catalysts).

7. Under non-malfunction conditions or when the malfunction does not cause a rich mixture, high catalyst temperature and low exhaust space velocity, the resulting H_2S emissions are negligible (below the range of concern for any scenario).

Table I

Hydrogen Sulfide Emission Factors@

Vehicle Category	Hydrogen Sulfide (mg/mi) SET Schedule Average
Light Duty Diesel Vehicles	0.0*
Light Duty Diesel Trucks	0.0*
Heavy Duty Diesel Trucks	0.0**
Light Duty Gasoline Vehicles	
Non Catalyst; no air pump	0.00
Non Catalyst; air pump	0.02
Oxidation Catalyst; no air pump	0.31
Oxidation Catalyst; air pump	0.87
3-way Catalyst; no air pump	1.02
3-way Plus Oxidation Catalyst; air pump	0.44
Light Duty Gasoline Truck	
Non Catalyst, air pump	0.02
Catalyst, no air pump	0.31
Heavy Duty Gasoline Trucks	0.08***

@ References 13,14,15,16,17

* Below minimum limits of detection. (FTP)

** Not tested, but assumed insignificant due to light duty data.

***Due to a lack of sufficient data, this value is assumed to be the same as that given for non-catalyst, light duty gasoline vehicles, adjusted for approximate differences in fuel consumption.

Table II
Fleet Average Emission Factors -Hydrogen Sulfide
(Sulfate Emission Test Cycle)

Vehicle Class	Fraction VMT	Emission Factor (mg/mile)	EF x VMT Fraction
Light Duty Diesel Vehicles	0.015	0.0	0
Light Duty Diesel Trucks	0.002	0.0	0
Heavy Duty Diesel Trucks	0.027	0.0	0
Light Duty Gasoline Vehicles			
Non Cat.; no air pump	0.147	0.00	0.000
Non Cat.; air pump	0.098	0.02	0.002
Ox Cat.; no air pump	0.289	0.31	0.090
Ox Cat.; air pump	0.261	0.87	0.027
3-way Cat.; no air pump	0.012	1.02	0.012
3-way plus Ox Cat.; air pump	0.008	0.44	0.004
Light Duty Gasoline Trucks			
Non Catalyst	0.096	0.02	0.002
Catalyst	0.010	0.31	0.003
Heavy Duty Gasoline Trucks	0.035	0.08	0.003
Total Fleet Average			0.34 mg/mile

Table III

Hydrogen Sulfide Emission Factor - Compiled

Fleet Category	mg/mile
Fleet Average (FA)	0.34
75% FA + 25% OC*	1.2
50% FA + 50% OC	2.1
25% FA + 75% OC	2.9
100% OC	3.8
75% FA + 25% OC/3W+air*	1.7
50% FA + 50% OC/3W+air	3.1
25% FA + 75% OC/3W+air	4.5
100% 3W	5.9
75% FA + 25% 3W***	2.0
50% FA + 50% 3W	3.7
25% FA + 75% 3W	5.4
100% 3W	7.1

* Light Duty Gasoline Vehicles, without air pump, with oxidation catalyst under worst-case malfunction conditions.

** Light Duty Gasoline Vehicles, with air pump, with either oxidation catalyst or three-way catalyst under worst-case malfunction conditions.

*** Light Duty Gasoline Vehicles, without air pump, with three-way catalyst under worst case malfunction conditions.

NOTE: The malfunction emissions for this analysis are not the single one test results reported earlier. They are the average results from several test programs, the average being taken for those malfunctions producing the highest H_2S value.

Table IV

Ambient Air Scenarios

Hydrogen Sulfide Concentrations mg/m^3

Fleet Make up	Emission Factor mg/mile	Enclosed Spaces: Personal Garage* typical	Personal Garage* severe	Parking Garage* typical	Parking Garage* severe	Roadway Tunnel typical	Roadway Tunnel severe	Street Canyon typical	Street Canyon severe	Expressway off road	Expressway on road typical	Expressway on road severe
Fleet Average	0.34					.0004	.0010	(2)	.0001	.0001	(2)	.0002
75% FA** +25% OC***	1.2					.0013	.0034	(2)	.0004	.0002	.0001	.0006
50% FA +50%OC	2.1					.0024	.0060	.0001	.0007	.0004	.0003	.0010
25% FA +75% OC	2.9					.0033	.0083	.0001	.0010	.0005	.0004	.0025
100% OC	3.8					.0043	.011	.0001	.0013	.0006	.0005	.0033
75% FA +25%OC/3w+air@	1.7					.0019	.0049	.0001	.0006	.0003	.0002	.0015
50% FA +50% OC 3W+air	3.1					.0035	.0089	.0001	.0010	.0005	.0004	.0027
+75% OC/3W+air	4.5					.0051	.013	.0001	.0015	.0008	.0005	.0039
100% OC/3W+air	5.9					.0066	.017	.0002	.0020	.0010	.0007	.0051
75% FA +25% 3W[1]	2.0					.0023	.057	.0001	.0007	.0003	.0002	.0017
50% FA +50% 3W	3.7					.0042	.011	.0001	.0012	.0006	.0005	.0032
25% FA +75% 3W	5.4					.0061	.015	.0002	.0018	.0009	.0007	.0045
100% 3W	7.1					.0080	.020	.0002	.0024	.0012	.0009	.0062

** FA = fleet average.
*** OC = Light Duty Gasoline Vehicles - Oxidation Catalyst without air pump, worst case malfunction.
@ OC/3W+air = Light Duty Gasoline Vehicles - Three-way + Oxidation Catalyst with air pump.
1 3W = Light Duty Gasoline Vehicles - Three-way Catalyst without air pump, worst case malfunction.
2 = Less than 0.00005

Table V

Hydrogen Sulfide

Emission Factors Required to Result in Exposure Limits for the Ambient Air Range of Concern

Ambient Air Scenario*	Emission Factor (mg/mile) corresponding to a 0.03 mg/m^3 exposure	Emission Factor (mg/mile) corresponding to a 14.0 mg/m^3 exposure
Street Canyon - Typical	958.5	447,300
Expressway - Typical	246.0	114,800
Expressway - Close Proximity	177.0	81,900
Street Canyon - Severe	89.7	41,860
Expressway - Severe	60.6	28,280
Roadway Tunnel - Typical	26.7	12,460
Roadway Tunnel - Severe	10.5	4,900
Personal Garage - Typical**	3.8	1,770
Parking Garage - Typical**	3.4	1,588
Parking Garage - Severe**	0.5	252
Personal Garage - Severe**	0.4	204

* In order of increasing mg/m^3 concentration for 1 g/mile (or 1g/min) emission rate (excluding garage situations).

** Emission factors are given in mg/minute for garage exposures.

Figure 1

Pollutant Concentrations vs Emission Factors

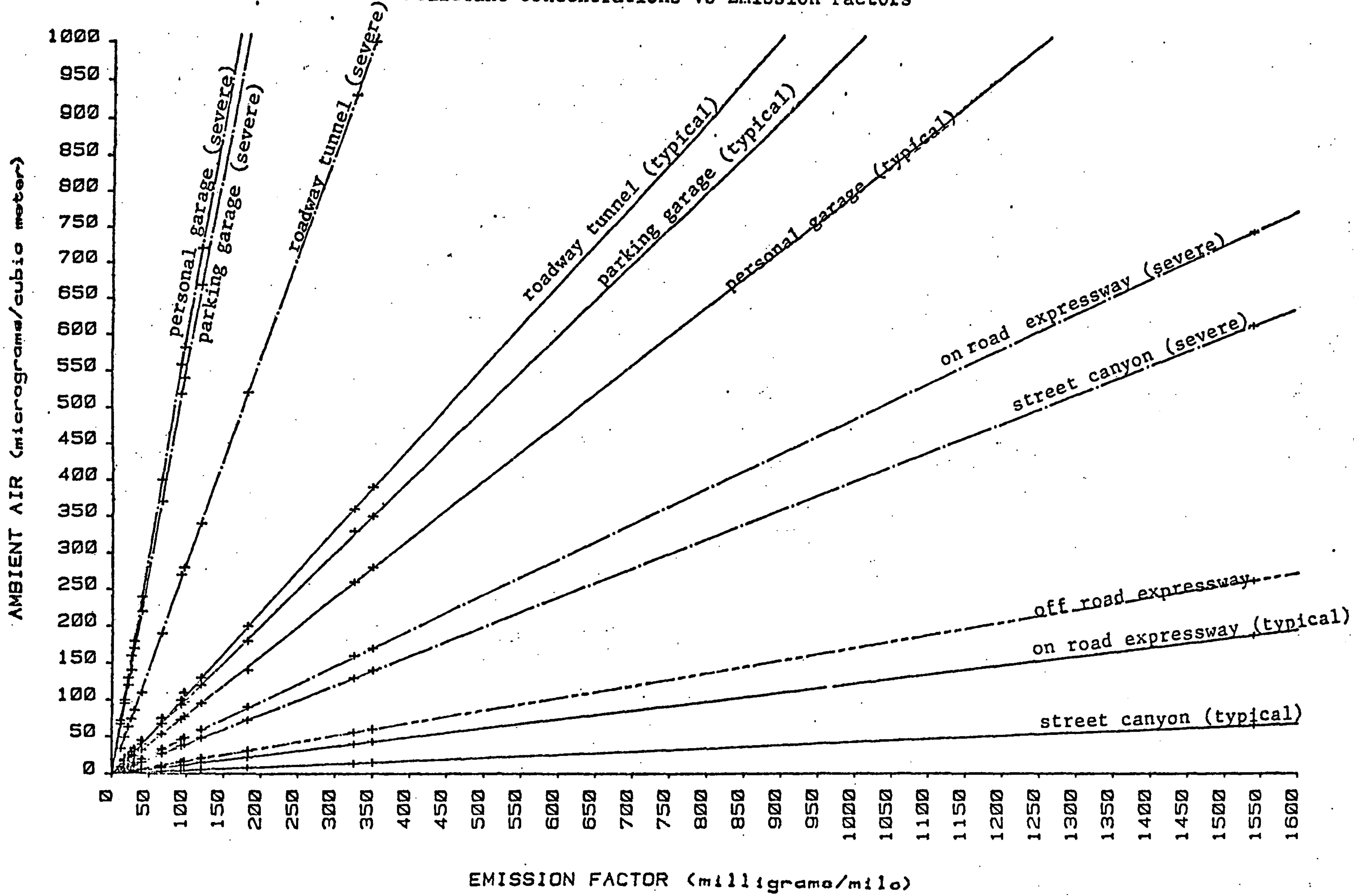
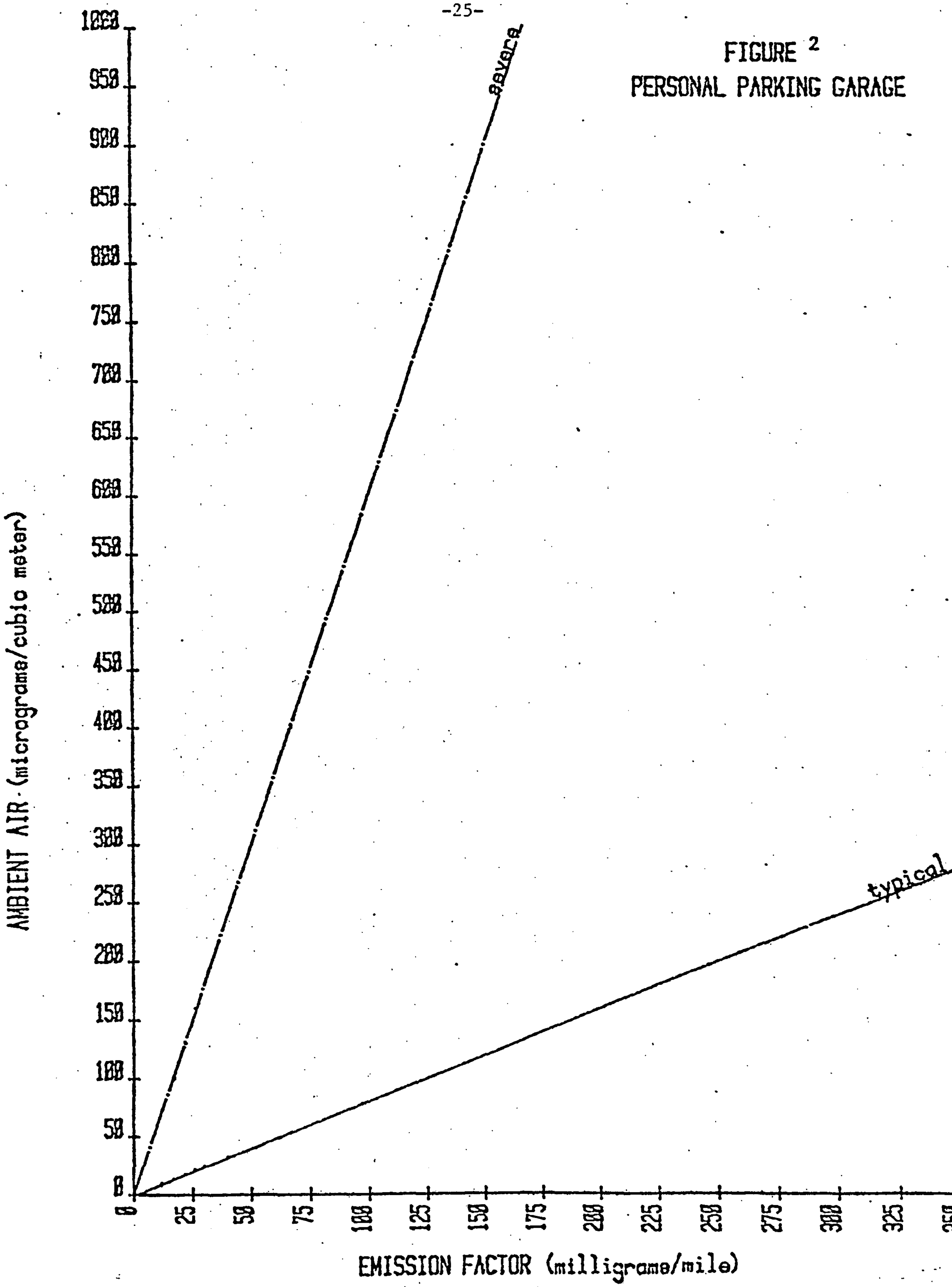


FIGURE 2

PERSONAL PARKING GARAGE



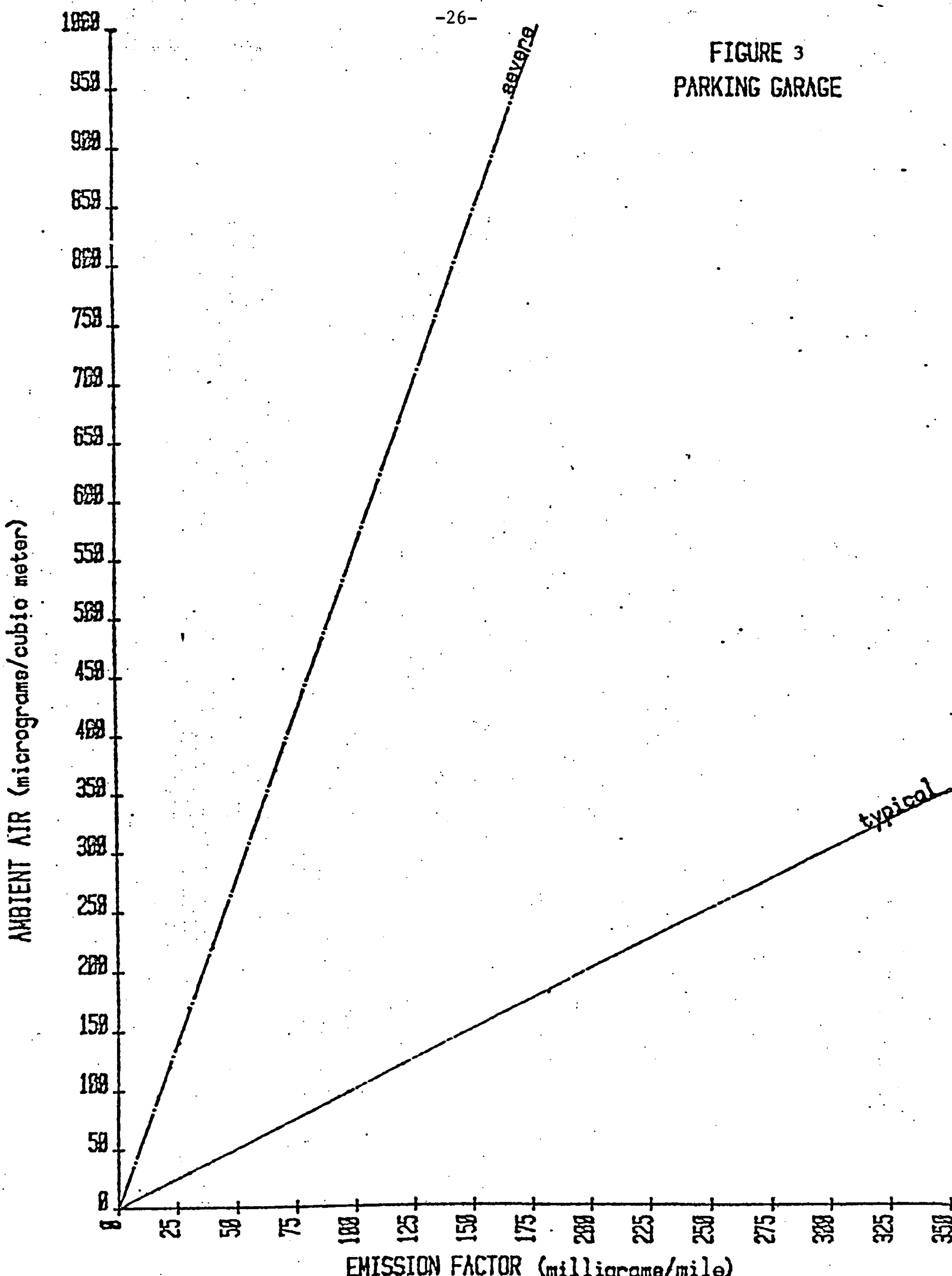


FIGURE 3
PARKING GARAGE

FIGURE 4
ROADWAY TUNNEL

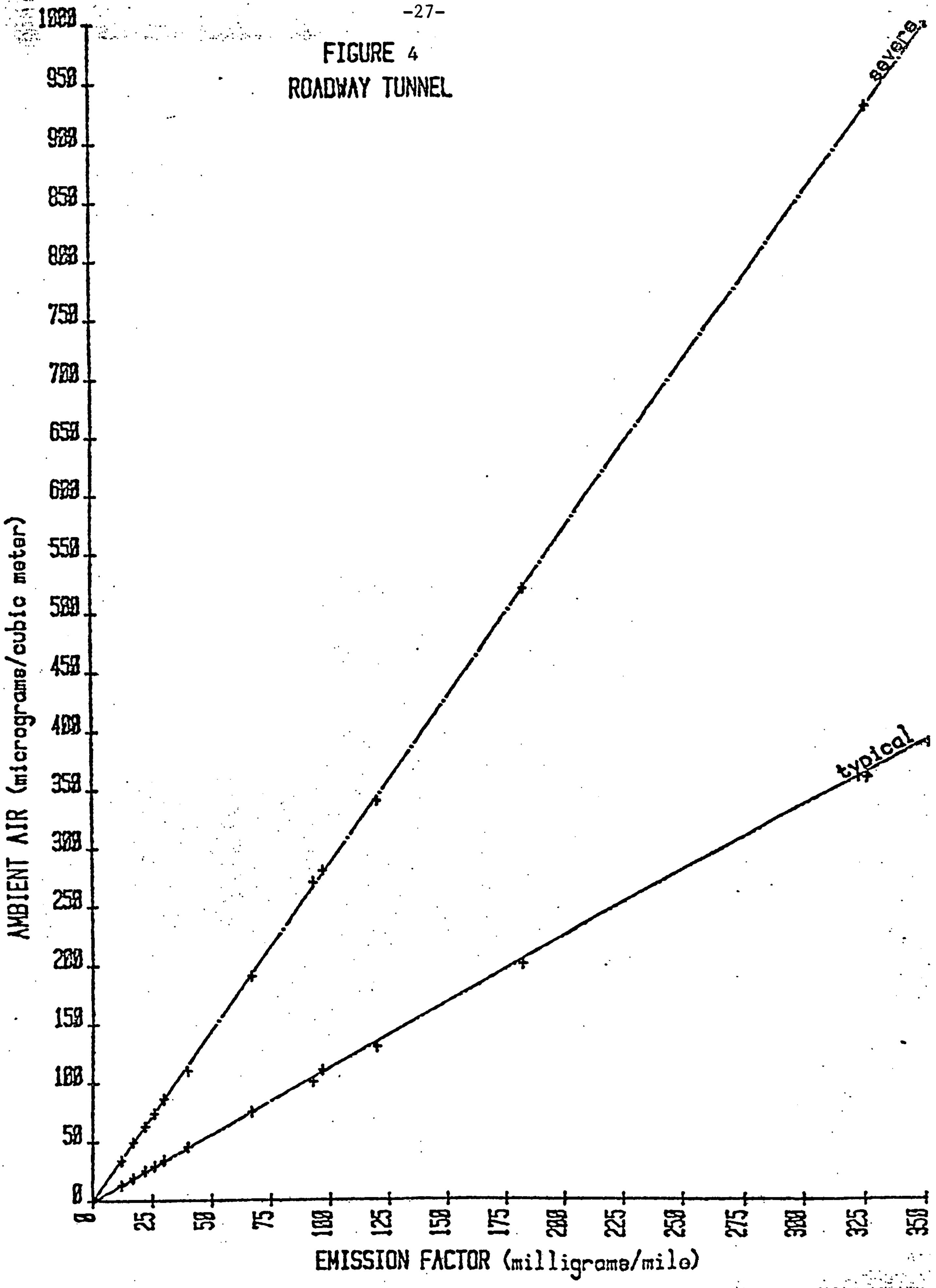


FIGURE 5

STREET CANYON

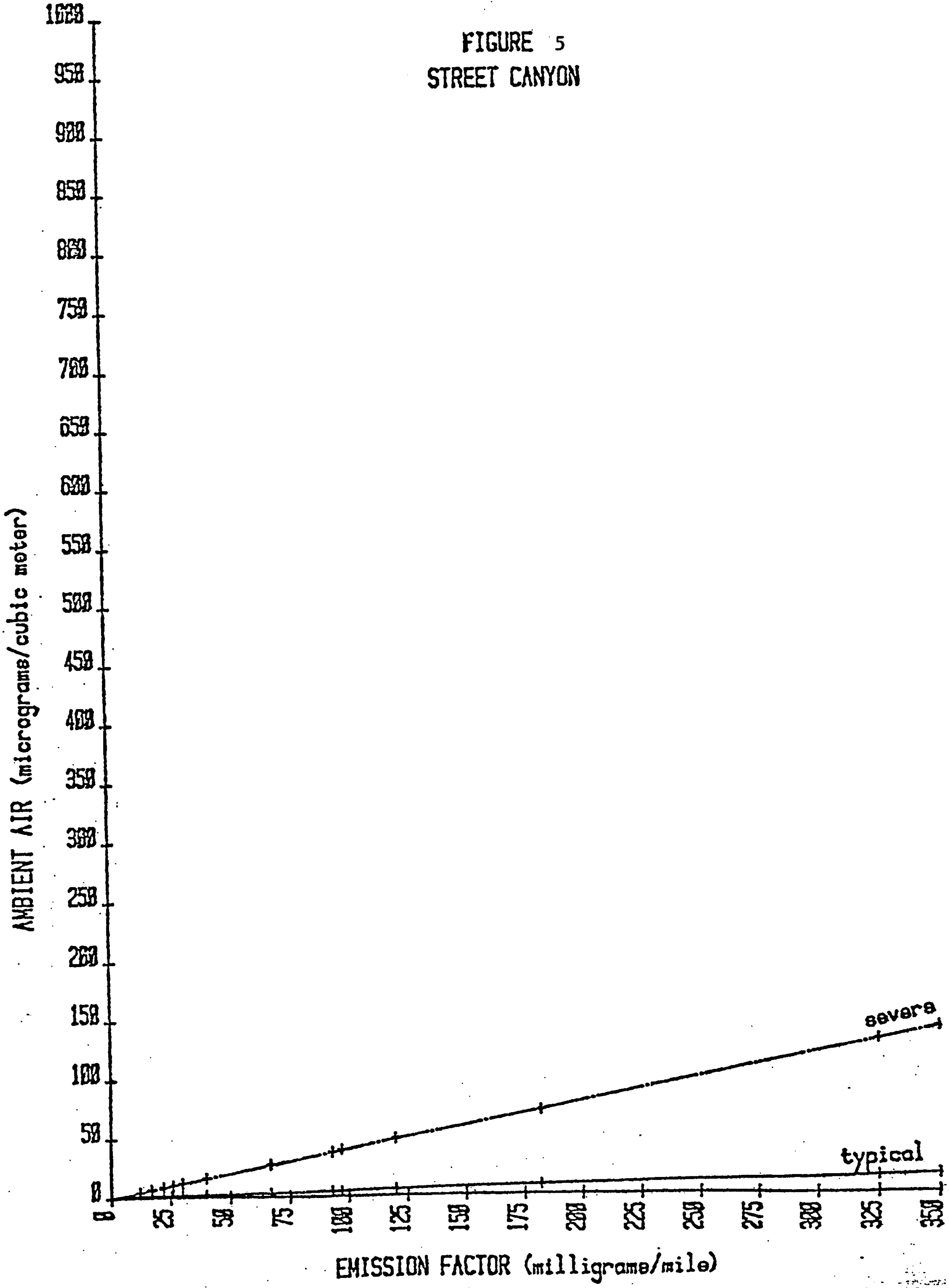


FIGURE 6
EXPRESSWAY

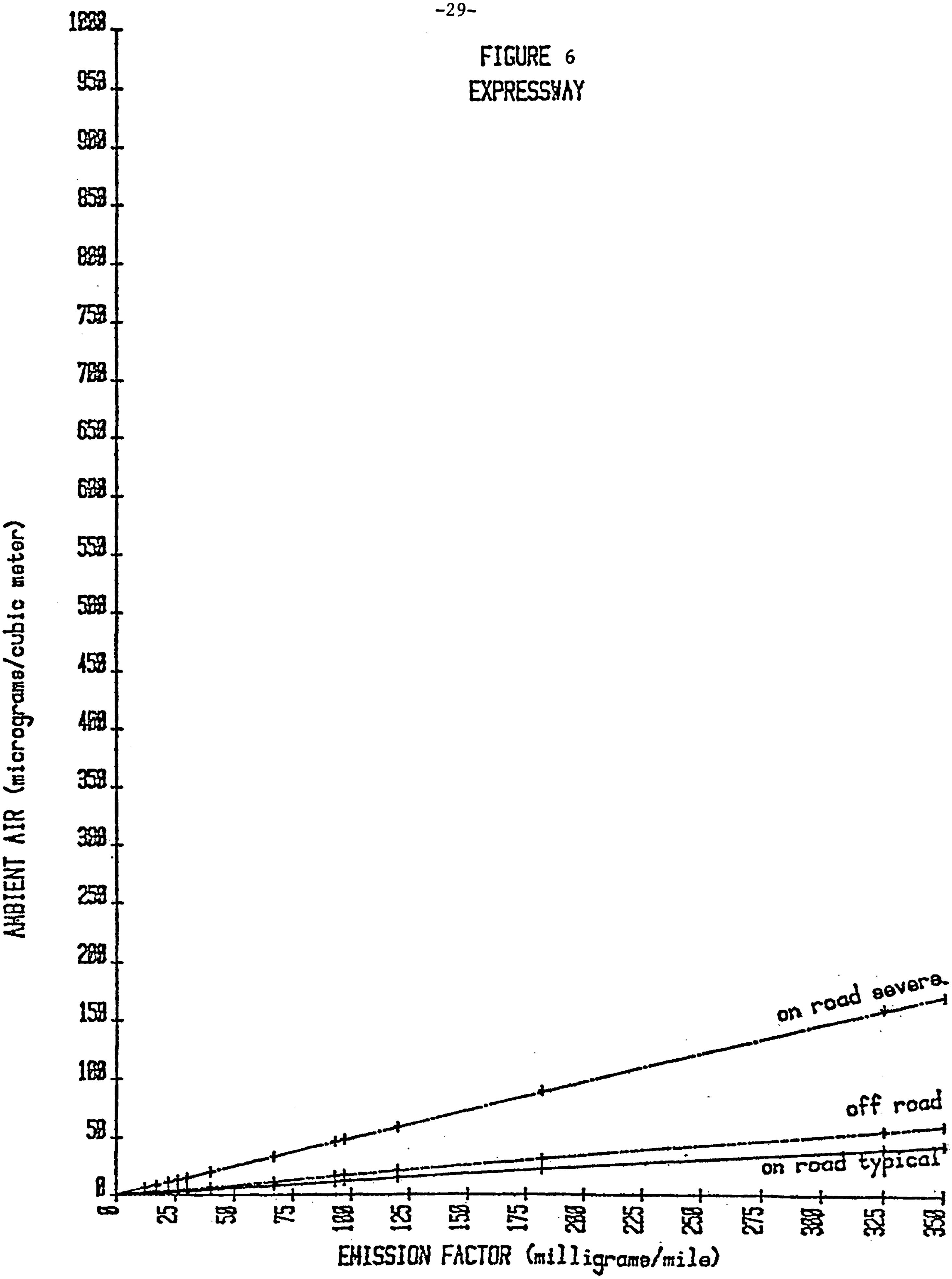


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TABLE S-2. SUMMARY OF HUMAN EXPERIMENTAL EXPOSURE TO H_2S

Level (mg/m^3)	Exposure	Table	Effects
3,499-8,165	Acute	IV-1	Eye, nose, and mouth irritations, leading to congestion and secretion. Higher exposures also caused dizziness, trembling, numbness, and heart palpitations. Afterwards, swollen and light-sensitive eyes, headache, fatigue, diarrhea, and bladder tenesmus lasting from several hours to a day.
1,420-4,700	Acute	IV-1	Irritation of eyes, nose, throat, and trachea, leading to tearing, swelling, and catarrh. Symptoms increased with increasing time and concentration. Sometimes irritation and headache continued for several hours after exposure stopped.
994-1,988	Acute	IV-1	Weak irritation of the eyes and throat at the lower levels. At the highest level, bronchitis, rhinitis, and heavy conjunctivitis lasted up to 4 d.
284-568	Acute	IV-1	No signs of irritation, as determined by cursory observation and subjective reaction.
0.20-0.96	Acute	IV-1	All people in the test group detected the odor.
0.08-0.50	Acute	IV-1	Range of odor thresholds within a group.
0.27	Acute	IV-1	Range of odor thresholds within a group.
0.15	Acute	IV-1	Threshold of objectionability (not odor).
0.1	Acute	IV-1	Most people in the test group detected the odor.
0.031-0.09	Acute	IV-1	Some of the people in the test group detected the odor.
0.012-0.03	Acute	IV-1	Range of odor thresholds within a group.

(continued)

TABLE S-2. (concluded)

Level (mg/m^3)	Exposure	Table	Effects
0.012 0.026	Acute	IV-1	Odor was not detected.
0.012- 0.013 (2 studies)	Acute	IV-1	Increased light sensitivity-related eye responses.
0.010 (2 studies)	Acute	IV-1	One study found significantly increased light sensitivity-related eye responses. The other study did not.
0.005- 0.009	Acute	IV-1	Range of "calculated" odor thresholds within several groups.
0.008	Acute	IV-1	No effect on the ability of the eye to adapt to darkness.
0.00067	Acute	IV-1	Lowest concentration at which all subjects recognized the odor.

TABLE S-3. SUMMARY OF OCCUPATIONAL AND EPIDEMIOLOGICAL EXPOSURES TO H_2S

Level (mg/m^3)	Exposure time	Table	Effects
≦ 28.4- > 852 (and low concns. of HCN, SO_2, CS_2, hydrocarbons)	"Acute"	V-1	Fatigue, dizziness, unconsciousness with or without respiratory failure. Rapid recovery (0.5 h) except for some nervous symptoms possibly lasting up to 1.5 mo.
326.6	~ 20 min	V-1	Unconsciousness, cramping, slow and shallow breathing, and low blood pressure. Fully recovered in 6 mo.
40-185	Acute, repeated	V-1	Within several hours, many signs of eye, nose, and throat irriation. Wide variation in individual responses.
~ 142	-	V-1	Within several hours, many signs of eye irritation. A wide variation in individual response, light cases recovering in a few hours, and severe cases in a week.
13.7-36.6	-	V-1	Eye irritation of varying severity, lasting from several hours to days. Some individuals had repeated episodes.
15-35	"Acute"	V-1	Nausea, weakness, and pain in the chest. Complete recovery within a week, no sequelae.
28.4 (often exceeded)	-	V-1	Fatigue, loss of appetite, irritability, headache, loss of memory, itching, and irritation of the eyes and respiratory tract.
7.1-14.2 (and SO_2 and lower aliphatic compounds)	-	V-1	Respiratory, gastroenteric, eye, and skin irritation.
7.1-14.2 (and SO_2)	5-15 y	V-1	Dermal symptoms suggestive of an allergic-type response. Some lung damage.
< 14.2	-	V-1	Weakness, nausea, dizziness, headache, nervousness, and occasional unconsciousness.

(continued)

TABLE S-3. (concluded)

Level (mg/m^3)	Exposure time	Table	Effects
0-9.94	3 d	V-1	Occasional slight and irregular changes in serum Fe and transferrin levels and in fractions of urinary sulfates.
∿ 0.03- ∿ 0.43	29 d	V-2	Mild symptoms of nausea, vomiting, headache, shortness of breath, burning eyes, respiratory tract irritation, gastrointestinal complaints, and disturbed sleep.
0.005- 0.300	Chronic	V-2	Headache, weakness, nausea, vision problems, and higher general morbidity rates in those households with ≧ 0.05 mg H_2S/m^3.
0.028- 0.055	Chronic	V-1	Babies were poorly developed, underweight, listless, anemic, dyspeptic, and more susceptible to infectious diseases.