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The Determination of a Range of Concern for Mobile Source Emissions of Hydrogen Cyanide

by

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NOTICE

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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 cyanide (HCN) emissions from mobile sources. In light of the action called for in section 202(a)(4) of the Clean Air Act (CAA) 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. This paper coordinates the efforts from two EPA contracts in order to use this methodology specifically for an evaluation of HCN. 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 HCN emission factors (grams/mile). In conjunction with this, an HCN health effects literature search was conducted to aid in the determination of the final range of concern. This search provides adequate evidence to support the chosen limits of the range.

The results of this analysis provides a range of concern for HCN emissions from motor vehicles of from 38-3850 mg/mile to 2619-261,904 mg/mile or from 1.6-164 mg/minute to 13.9-1392 mg/minute depending on the type of scenario chosen to represent public exposure. The available emission factor data indicate that HCN emissions are not likely to present a problem to public health. Vehicles equipped with a 3-way catalyst operating under malfunction modes or low ambient temperatures may, however, make a greater contribution to any potential human exposure problem due to the increased emissions of HCN under these conditions.

I. Introduction

Bell Laboratories, in 1975, released the results of an experiment, which they had conducted, showing that HCN was formed by passing a mixture of nitrogen oxide (NO), carbon monoxide (CO), hydrogen (H_2), and varying amounts of water and sulfur dioxide (SO_2) over a heated platinum catalyst bed. The same study also showed that the addition of water and SO_2, typical of what would be expected in actual automobile exhaust, greatly supressed HCN production. Although the Bell work was done on a laboratory bench basis, not on cars, catalysts on engines, or even real automobile exhaust, the data were interpreted as meaning that catalyst-equipped cars may emit HCN. While there was some reason to question the significance of this experiment, as far as mobile sources are concerned (such as the sulfur content of gasoline and the water in exhaust), the data did suggest that further investigation was warranted(1)*.

The Environmental Protection Agency, in early 1976, found that vehicles using a 3-way catalyst could produce HCN under rich malfunction modes. Also, at this time, Volvo and Saab were certifying 3-way catalyst systems for use in California in 1977. Due to the possibility of significant emissions of various potentially harmful substances from 3-way catalyst systems, EPA requested information from the manufacturers and began a series of tests in an attempt to estimate the hazards of HCN from mobile sources. Tests were conducted by several organizations in order to support this effort.

Under contract to EPA, Exxon Research and Engineering Company investigated the effects of catalyst composition on HCN exhaust emissions (2). It was found that rhodium (Rh) containing 3-way catalysts tended to give significantly higher levels of HCN than did platinum or platinum-palladium catalysts. In-house EPA tests also verified this conclusion (3).

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* Numbers in parentheses indicate references at the end of the paper.

Of particular interest to EPA, with respect to HCN emissions, was the exposure situation which would be considered as a "worst case", such as levels of HCN that could occur in parking garages and on heavily-traveled roadways. After calculations were made, it was found that, in a closed environment situation, such as a parking garage, an upper bound of 5 ppm HCN could result from a maximum raw exhaust level of 10 ppm. At this level of HCN, the calculated level of CO would be as high as 6500 ppm. Because of this high CO value, it was concluded that the adverse health effects of CO would overshadow possible adverse health effects of HCN (by more than two orders of magnitude). Admittedly, this type of analysis could be characterized as the "HCN pot calling the CO kettle black" since an evaluation of HCN's effects was not made. With respect to the highway exposure situation, the "worst case" would result in a 1.1 ppm (1.2 mg/m^3) HCN level, a level which was not considered to have unacceptable health effects associated with it.

In 1978, the Office of Research and Development of EPA was asked once again to review the work which the Environmental Sciences Research Laboratory (EPA) had done earlier. They concluded that the information that they had reported earlier was still accurate, and that the HCN emission values presented did not constitute an unreasonable health hazard to the public (4,5).

While the reports mentioned previously did conclude that HCN from vehicles probably did not constitute a health hazard over and above that hazard posed by CO, no level of concern for HCN had been definitively determined. As a part of the Emission Control Technology Division's overall responsibility for the characterization of unregulated pollutants from mobile sources, an effort was started under contract with Southwest Research Institute (SwRI), and Midwest Research Insitute (MRI), to gather more information concerning various pollutants such as HCN and its health effects, to aid in the determination of levels or ranges of concern for HCN emissions from motor vehicles.

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.
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> (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 incorporatred 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 requiements 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) (6) in June 1978, to aid the manufacturers in complying with section 202 (a)(4). Manufactureres 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 (7) 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" (8). 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 and are being 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 HCN. 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 HCN.

IV. General Information

Hydrogen cyanide (HCN) is a flammable, toxic, and colorless liquid at room temperature which has the characteristic odor of bitter almonds. Other common synonyms used for this compound include hydrocyanic acid, prussic acid, and formonitrile. HCN is a very potent and fast acting poison which attacks the respiratory system by combining with the iron complex in the blood, stopping the oxidation processes in the tissue cells, and causing death by asphyxiation. In fact, in the past, HCN was one of the gases which was used for capital punishment executions.

Early symptoms of exposure to HCN may include weakness, headache, confusion, nausea, vomiting, and intially increased respiratory rate and depth. In later stages, breathing becomes slow, to the point of gasping. Acute poisoning at high levels of HCN produces almost immediate collapse and cessation of respiration. Chronic exposure can cause enlargement of the thyroid or goiter.

Humans are exposed to cyanide through various pathways such as diet and cigarettes, as well as occupational exposure (firefighters, jewelry plating operations, galvanizing shops, etc.). The common measure of cyanide exposure is the concentration of the cyanide metabolite thiocyanate in the urine or blood. This measurement can be misleading if the diet contains foods such as cherries, almonds, lima beans, and/or cabbage, which release thiocyanate or isocyanate in the body. Cyanide residues on food, due to fumigation, may also add to these concentrations.

Cigarettes can also contribute to the amount of hydrogen cyanide measured in the body. A two-pack-per-day smoking habit might contribute as much as 22 mg HCN to the daily intake (9-see also Appendix II).

Many occupational studies have not taken into consideration the contribution of diet or smoking to cyanide exposure. Each of these could be as important as occupational exposure to the urinary excretion of thiocyanate.

Three of the processes by which HCN is commercially produced consist of reacting methane, ammonia, and air over a platinum catalyst (1000-2000°C), reacting nitric oxide and gasoline (1400°C), and by reacting hydrocarbons, ammonia, and oxygen (600-1500°C). Although HCN can be produced by various other methods, it is reactions of this type which may be responsible for mobile source HCN exhaust emissions.

The following reaction equations represent the possible pathways by which HCN can be formed during engine combustion and catalytic conversion of the exhaust gas (10).

1) $CH_4^* + NH_3 + 3/2\ O_2 \longrightarrow HCN + 3\ H_2O$

2) $2\ CO + NH_3 \longrightarrow HCN + H_2 + CO_2$

3) $2\ CO + 3H_2 + 2\ NO \longrightarrow 2\ HCN + 2\ H_2O + O_2$

4) $CH_4 + NH_3 \longrightarrow HCN + 3\ H_2$

5) $1/3\ C_3H_8 + NH_3 \longrightarrow HCN + 7/3\ H_2$

6) $CO + NH_3 \longrightarrow HCN + H_2O$

7) $CH_4 + NO \longrightarrow HCN + H_2O + 1/2\ H_2$

8) $2\ C + H_2 + N_2 \longrightarrow 2\ HCN$

9) $C_2H_4 + 2\ NO \longrightarrow 2\ HCN + H_2O + 1/2\ O_2$

10) $C_2H_2 + 2\ NO \longrightarrow 2\ HCN + O_2$

*Not only CH_4 but all saturated and unsaturated hydrocarbons, radicals, and cracking products.

Considering, however, the equilibrium constant and kinetics for each of these reactions (in general, less HCN is formed by increased temperature), only reaction equations 1, 5, 7, 9 and 10 are significant for HCN formation during the engine combustion and catalytic conversion processes. These reactions can be further affected by factors such as catalyst poisoning, or the presence of water vapor.

V. Emission Factors

HCN exhaust emissions have been measured for a variety of vehicle types. The recommended procedure for this measurement is listed in two EPA reports entitled, "Analytical Procedures for Characterizing Unregulated Pollutant Emissions from Motor Vehicles" (11) and "Analytical Procedures for Characterizing Unregulated Emissions from Vehicles Using Middle-Distillate Fuels" (12). Apparently, this method has some cyanogen (C_2N_2) interference. Cyanogen is a flammable, toxic, and colorless gas at room temperature and like HCN has the characteristic odor of bitter almonds. Its physiological effect on living tissue is also similar to that of HCN. Attempts to analyze HCN and cyanogen separately have been unsuccessful and, therefore, cyanogen is included in all reported HCN emission factor values although it may not be specifically mentioned as such.

Small amounts of HCN have been measured in gasoline-fueled vehicle exhaust, under normal operating conditions, at levels around 1.0 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 112 mg/km or 179 mg/mile, for the FTP driving schedule(13).

Tests were run by EPA in order to evaluate the impact of low ambient temperatures on 3-way catalyst-equipped car emissions. These studies showed that HCN emissions also increased significantly during subambient temperature operation. One of the test vehicles, on the average, emitted 1.02 mg/mile of HCN at 78°F, while at 58°F, the same car emitted 22.53 mg/mile of HCN (over the FTP driving schedule). The maximum observed HCN emission rate for all tests was obtained at 61°F and was 38.02 mg/mile (14).

Average HCN 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 Federal Test Procedure (FTP) driving schedule, unmodified mode, as well as for various malfunction modes (when such data were available). Since the available data for some technologies list both an unmodified FTP and a malfunction emission value, the final, average emission factor was weighted such that the value is 75% of the unmodified FTP 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 (15). Further work may identify a more accurate percentage.

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

Maximum Reported HCN Emission Rates Under Malfunction Modes

Vehicle Category	mg/mile
non-catalyst	11.2
oxidation catalyst	9.6
3-way catalyst	179.2

The reported emission factor for the 3-way catalyst vehicle, which was obtained under malfunction conditions, is considerably higher than that of the other two categories. This value is also much higher than any of the vehicle categories listed in Table I, excluding Heavy Duty Gasoline Vehicles.

For the purpose of this report, only emission factors for the FTP driving cycle were considered, rather than values, or a combination of values, corresponding to various other cycles. This is due to the abundance of HCN emission data for this particular driving cycle, in comparison to other

TABLE I

Hydrogen Cyanide Emission Factors@

Vehicle Category	Hydrogen Cyanide (mg/mi) FTP Schedule Average
Light Duty Diesel Vehicles	3.2
Light Duty Diesel Trucks	3.2*
Heavy Duty Diesel Trucks	22.4
Light Duty Gasoline Vehicles	
Non Catalyst; no air pump	4.5
Non Catalyst; air pump	4.5**
Oxidation Catalyst; no air pump	2.4
Oxidation Catalyst; air pump	0.9
3-way Catalyst; no air pump	16.0
3-way Plus Oxidation Catalyst; air pump	24.7
Light Duty Truck	
Non Catalyst	4.5**
Catalyst, no air pump	2.4***
Heavy Duty Gasoline Vehicles	224.0[1]

@ References 13, 16, 17, 18, 19

* Due to a lack of sufficient data, this value is assumed to be the same as that given for Light Duty Diesel Vehicles.

** 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, without an air pump.

*** Due to a lack of sufficient data, this value is assumed to be the same as that given for light duty gasoline vehicles with oxidation catalyst and no air pump.

1 This value was derived from the emission factor test data from two heavy duty gasoline trucks operated over the 1983 HD transient cycle (see reference 19). Due to the questionability of this high emission factor value, its validity is suspect until more data become available such that this value can be verified.

driving schedules. It may be more appropriate to chose driving cycles which would most closely simulate those scenarios under investigation (enclosed spaces, street canyons, etc.). At present, however, data do not exist to permit use of this approach for HCN. The percent of error which is introduced by using the FTP emission factor is not known at this point. Available HCN idle emissions data were used to estimate HCN exposures in parking garage situations, and will be discussed later in this report.

Using the average HCN 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 (20), and the EPA report, Mobile Source Emission Factors: For Low Altitude Areas Only (21). 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 HCN emissions, this value is 11.4 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 HCN 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 one of the three highest emitting techologies. In this case, excluding heavy duty gasoline trucks, these three technologies include the three-way plus oxidation catalyst without air pump, three-way plus oxidation catalsyt with air pump, and a three-way catalyst under malfunction conditions. The compiled emission factors listed

Table II

Fleet Average Emission Factors - Hydrogen Cyanide*

Vehicle Class	Fraction VMT	Emission Factor (mg/mile)	EF x VMT Fraction
Light Duty Diesel Vehicles	0.015	3.2	0.048
Light Duty Diesel Trucks	0.002	3.2	0.006
Heavy Duty Diesel Trucks	0.027	22.4	0.605
Light Duty Gasoline Vehicles			
Non Cat.; no air pump	0.147	4.5	0.662
Non Cat.; air pump	0.098	4.5	0.441
Ox Cat.; no air pump	0.289	2.4	0.694
Ox Cat.; air pump	0.261	0.9	0.235
3-way Cat.; no air pump	0.012	16.0	0.192
3-way plus Ox Cat.; air pump	0.008	24.7	0.198
Light Duty Gasoline Trucks			
Non Catalyst	0.096	4.5	0.432
Catalyst	0.010	2.4	0.024
Heavy Duty Gasoline Trucks	0.035	224.0	7.840
Total Fleet Average			11.4 mg/mile

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20 21

Table III

Hydrogen Cyanide Emission Factor - Compiled

Fleet Category	mg/mile
Fleet Average (FA)	11
75% FA + 25% 3W*	12
50% FA + 50% 3W	14
25% FA + 75% 3W	15
100% 3W	16
75% FA + 25% 3W+OC**	15
50% FA + 50% 3W+OC	18
25% FA + 75% 3W+OC	22
100% 3W+OC	25
75% FA + 25% 3W***	53
50% FA + 50% 3W	95
25% FA + 75% 3W	137
100% 3W	179

* Light Duty Gasoline Vehicles - Three-way Catalyst without air pump

** Light Duty Gasoline Vehicles - Three-way + Oxidation Catalyst with air pump

*** Light Duty Gasoline Vehicles - Three-way Catalyst under malfunction condition in Table III will become an important tool in comparing vehicle emisions to the range(s) of concern. In subsequent steps, these values will be used to calculate ambient air concentrations of HCN for various fleet mixes of emission control technologies.

VI. Hydrogen Cyanide Health Effects

Midwest Research Institute (MRI), under contract to EPA, conducted a literature search of the health effects related to HCN, the results of which are contained in a report which is included as Appendix II to this paper.

The purpose of this literature search was to aid in the determination of a range of concern for HCN by providing supporting evidence for those levels at which adverse physiological effects have been detected from exposure to various concentrations of HCN. These scattered data points will be bracketed in order to set a final "range of concern". The lower value of this range will be selected to approximate the lowest level at which adverse physiological effects from exposure to HCN can be detected. Below this limit, the available literature shows little or no health effects, although some more sensitive subgroups of the population (asthmatics, etc.) may be affected by these levels.

The upper limit of the range is chosen to be that value above which the studies show such an adverse reaction in the exposed population from exposure to HCN, as to imply a necessity for regulation. The values selected for HCN and the rationale for chosing them are discussed in section VIII.

VII. Hydrogen Cyanide Ambient Air Concentrations

The HCN emission factor information provided in Table I through III, can be used in conjunction with the modeling techniques developed by Southwest Research Institute (SwRI) (see Appendix I), in order to calculate the ambient air concentrations produced by varying levels of HCN 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. Appendix I 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 cyanide, 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 HCN is assumed to be low ($1 \mu g/m^3$).

In order to more closely assess public exposure to HCN in a garage situation, idle emissions data were averaged from a limited number of sources (22, 23, 24, 25).

Table IV

Ambient Air Scenarios

Hydrogen Cyanide Concentrations $\mu g/m^3$

		Enclosed Spaces						Street Canyon		Expressway		
Fleet Make up	Emission Factor mg/mile	Personal Garage* typical	Personal Garage* severe	Parking Garage* typical	Parking Garage* severe	Roadway Tunnel typical	Roadway Tunnel severe	typical	severe	off road	on road typical	on road severe
Fleet Average	11					12	31	.47	4.4	1 8	1.3	5.4
75% FA** +25% 3W***	12					13	34	51	4 8	2 1	1 5	5 9
50% FA +50%3W	14					16	40	.60	5 6	2.4	1.7	6.9
25% FA +75% 3W	15					17	43	.64	6.0	2 6	1.8	7.4
100% 3W	16					18	46	.68	6.4	2.7	2.0	7.9
75% FA +25% 3W+OC@	15					17	43	.64	6.0	2.6	1 8	7.4
50% FA +50% 3W+OC	18					20	57	76	7 1	3 1	2 2	8.9
25% FA +75% 3W+OC	22					25	63	.93	8.7	3.8	2.7	10.9
100% 3W+OC	25					28	71	1.1	9.9	4.3	3.1	12
75% FA +25% 3W[1]	53					60	151	2.2	21	9.1	6.5	26
50% FA +50% 3W	95					107	271	4.0	38	16	12	47
25% FA +75% 3W	137					154	391	5.8	54	23	17	68
100% 3W	179					201	511	7.6	71	31	22	89
	2590					2910	7390	110	1030	450	320	1290

* These values are based on emission rates in grams/minute, and are discussed in detail in the body of the report.

** FA = fleet average.

*** 3W = Light Duty Gasoline Vehicles-Three-way Catalyst without air pump.

@ 3W+OC = Light Duty Gasoline Vehicles-Three-way + Oxidation Catalyst with air pump.

1 3W = Light Duty Gasoline Vehicles-Three-way Catalyst under malfunction condition.

Although there was some deviation, the available idle data appear to indicate that vehicles with 3-way catalysts, operating in the malfunction mode, emit HCN at a rate of approximately 1 mg/min.

In a worst case situation, where 100% of the vehicle fleet consists of automobiles with 3-way catalysts, operating in the malfunction mode, the HCN 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 and presently operating in the malfunction mode, in an enclosed garage.

HCN Ambient Air Concentrations ug/m^3

Fleet Make Up	Emission Factor	Personal Garage		Parking Garage	
		Typical	Severe	Typical	Severe
100% 3W	1 mg/min.	7.9	67	8.8	55.7

Since these values more accurately reflect the HCN 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 HCN. 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 of the vehicle.

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 meters/second. In this situation, the exposed population is located inside of 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

All of the information gathered up to this point is necessary input for the determination of a range of concern for HCN emissions from mobile sources. The health effects information will help to identify the limits of the range, while the emission factor data, along with the modeling techniques, will aid in the conversion of emission rates to ambient air concentrations so that it might be possible to focus upon the potential risks to public health (if any) from exposure to HCN exhaust emissions.

The upper value of the range has been chosen to be 11 mg/m^3 (11000 ug/m^3) (ambient air concentration). This level is the Threshold Limit Value (TLV) for hydrogen cyanide, which stands for the time-weighted average concentration for a normal 8-hour workday or 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effects. The evidence of adverse health effects above this level would be sufficient to support regulatory action.

The literature search does not reveal any one study in particular which supports a specific level which can be considered as the lowest level at which adverse physiological effects can be detected. In fact, very few of the studies are even appropriate for comparison with long-term, low-level exposure situations, as would be typical of human exposure to automobile exhaust. Due to a lack of supportive information at very low levels of exposure to HCN, the lower level of the range is, therefore, more difficult to determine.

Table V (Table IV-1 in Appendix II) is an excerpt from the MRI draft HCN report, which represents a collection of the human, acute dose-response data (MRI states that this information is usually generalized from the literature without original source attribution). This table indicates that 0.2 - 5.5 mg/m^3 (or 200-5500 ug/m^3)is considered to be the odor threshold level. Although this level does appear to have an effect on sensory perception, it cannot be definitely concluded that it would also cause any adverse physiological effects. The odor threshold might actually be considered a problem for those people who do not like the smell (i.e. welfare effects). The table also labels 0.11 - 0.99 mg/m^3 (or 110-990 ug/m^3) as the no effect level. There is not, however, enough concrete evidence in the literature search to support this statement.

The HCN health effects literature review emphasizes that there is <u>a very steep dose-response curve in many of the animal experiments</u>. For example, twice the no-observed-effect level can be lethal. Due to this type of response, it has been determined that a reasonable safety factor should be applied to the TLV in order to set a lower level for the range of concern. This approach is assumed to be suitable until more information concerning low level exposure to HCN is made available. The safety factor for this case has been chosen to be 100 (26), therefore, setting the lower level of the range at 0.11 mg/m^3, (110 ug/m^3) a concentration below which there is no available information definitely concluding that there are adverse physiological effects from exposure to HCN.

Between the chosen limits of the range (i.e. 110 ug/m^3 to 11000 ug/m^3), there are scattered data points providing evidence of adverse physiological effects caused by exposure to various concentrations of hydrogen cyanide.

Table V

HUMAN DOSE-RESPONSE DATA AS GENERALIZED IN THE LITERATURE[a]

Dose of HCN		
mg/m^3	ppm	Response
22,000	20,000	Even though breathing is through a gas mask, vertigo, weakness, and tachycardia occur after 8-10 min. Loss of work capacity for 2-3 d.
7,000-12,000	6,360-10,900	Level dangerous after 5 min even though a gas mask is used because of skin penetration.
5,000	4,500	Safe for 1 min.
3,750	3,410	Safe for 1.5 min.
3,600	3,410	Safe for 30 min with a gas mask.
2,500	2,270	Safe for 2 min.
1,000	909	Safe for an experienced, fumigator indefinitely.
550	500	No serious consequences after 1 min exposure
400	364	Tolerable for 1.5 min without vertigo.
300	270	Immediately fatal.* Lazarev (1971 [2-0144] stated that this concentration is tolerable for 2 min without headache. Lazarev (1956) [2-0145] stated a person at rest would withstand this concentration for 2 min without dizziness.
200	180	Fatal after 10 min.
150	140	Fatal after 0.5 h.
120-150	110-135	Fatal after 0.5-1 h.

*This statement in this reference does not seem to be consistent with the statement in other references for this HCN level.

(continued)

Table V (concluded)

Dose of HCN		
mg/m^3	ppm	Response
110	100	Fatal in 1 h.
50-60	45-54	Tolerated for 0.5-1 h without immediate or late effects
0.4-50	0.4-45	Headache, vertigo, nausea, regurgiation, heartburn, general weakness sensation of pressure in the epigastric region, sweating of the hands, instability of the autonomic nervous system, decrease in vascular tone, slowing of blood circulation.
20-50	18-45	Headache, nausea, vomitting, and tachycardia after several hours.
20-40	18-36	Slight symptoms (headache) after several hours.
5-20	4.5-18	Headache and vertigo.
11	10	Threshold limit value (ACGIH, 1979)
0.2-5.5	0.2-5.0	Odor threshold
0.11-0.99	0.1-0.9	No effect[b]

a Aghoramurthy and Mehta (1977), Dudley et al. (1942), Einhorn (1975), Flury and Zernik (1931), Henderson and Haggard (1943), Hamilton and Hardy (1949), Lazarev (1971) [most levels 300 mg/m^3], McNamara (1976).

b Attributed to Lazarev by Czechoslovak Committee of MAC (Wills et al., 1976)

Therefore, this region has been termed the "range of concern" for HCN 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 cyanide emissions to ambient air concentrations.

Once the literature search was completed and the appropriate information was tabulated for HCN, a large table was prepared compiling all the information for the animal studies (see Appendix III). This table lists the studies according to the exposure concentration of HCN (highest to lowest concentration). Using the health effects information along with the emission factor data, graphs were composed representing the relationship between ambient air concentrations, emission factors, and the various types of public exposure situations (Figure 1-5).

According to the methodology which will be used to establish a range of concern for non-zero threshold pollutants, the boundary limits of the ambient air range of concern (ug/m^3) are compared to the mobile source exposure scenarios in order to calculate the range of concern in vehicle emission factor units (mg/mi). Exposure time is the main element of comparison between the ambient air range and the mobile source exposure situations. Most of the exposure situations represent short term exposures (duration of an hour or less per day) perhaps repeated several times per week. The typical exposure situations are likely to be repeated often, while the severe exposure situations are more likely to occur on an infrequent basis.

With all of the collected information, a mobile source emission factor range of concern for hydrogen cyanide can be estimated for each scenario and situation as listed table VI and VII.

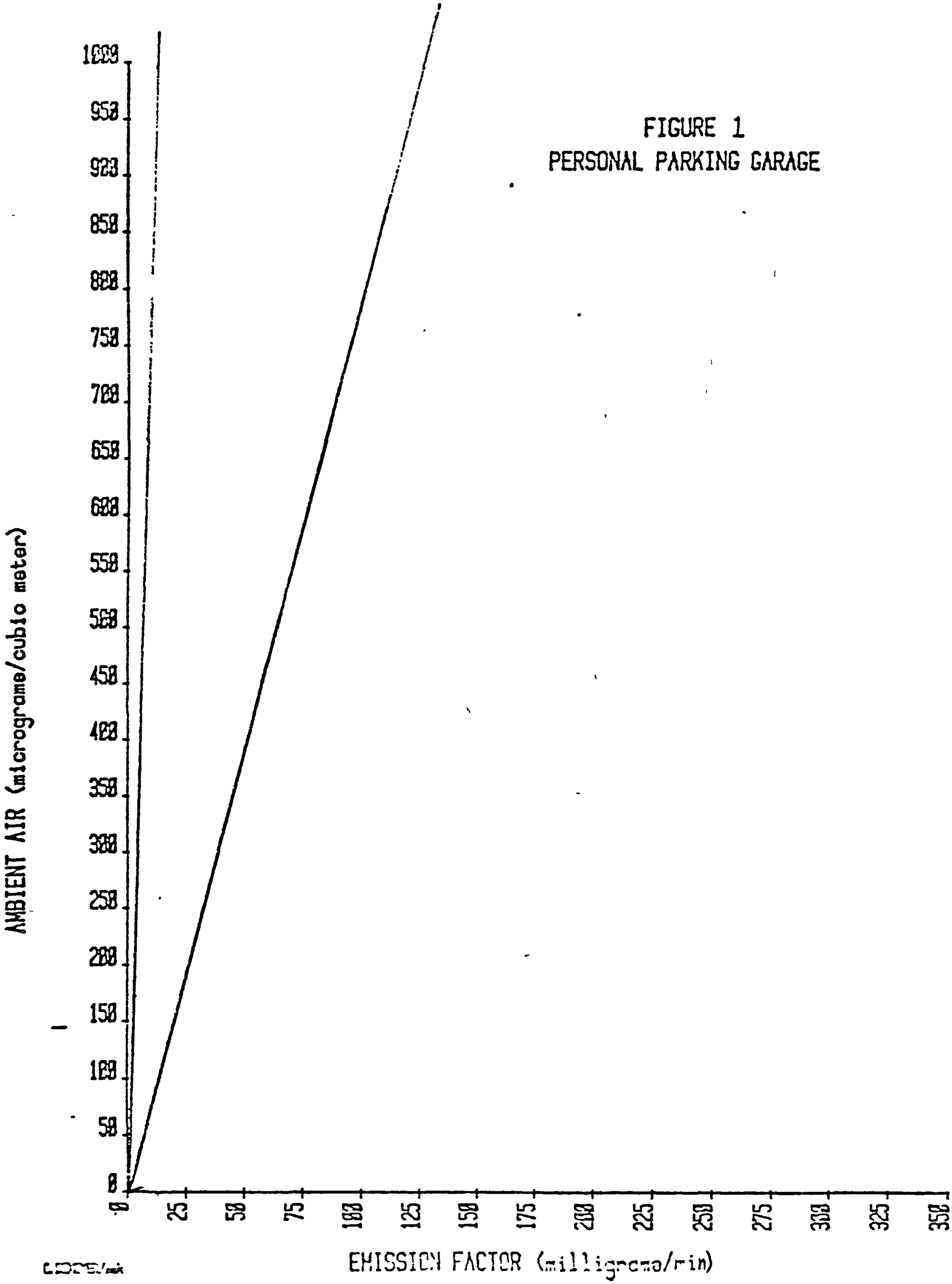

FIGURE 1
PERSONAL PARKING GARAGE
AMBIENT AIR (micrograms/cubic meter)
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
EMISSION FACTOR (milligrams/min)
0
25
50
75
100
125
150
175
200
225
250
275
300
325
350

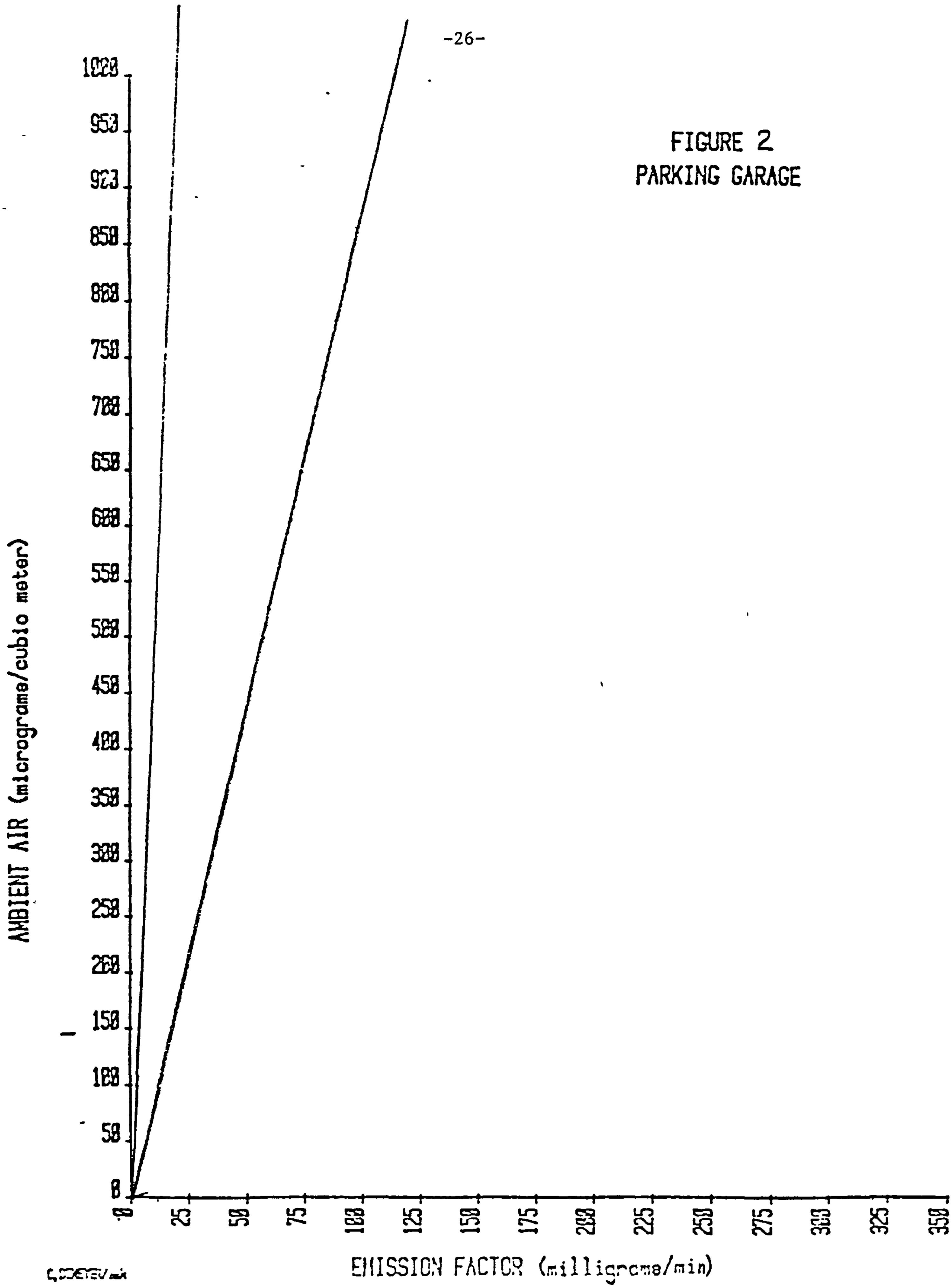
FIGURE 2
PARKING GARAGE
AMBIENT AIR (micrograms/cubic meter)
EMISSION FACTOR (milligrams/min)
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
25
75
125
175
225
275
325

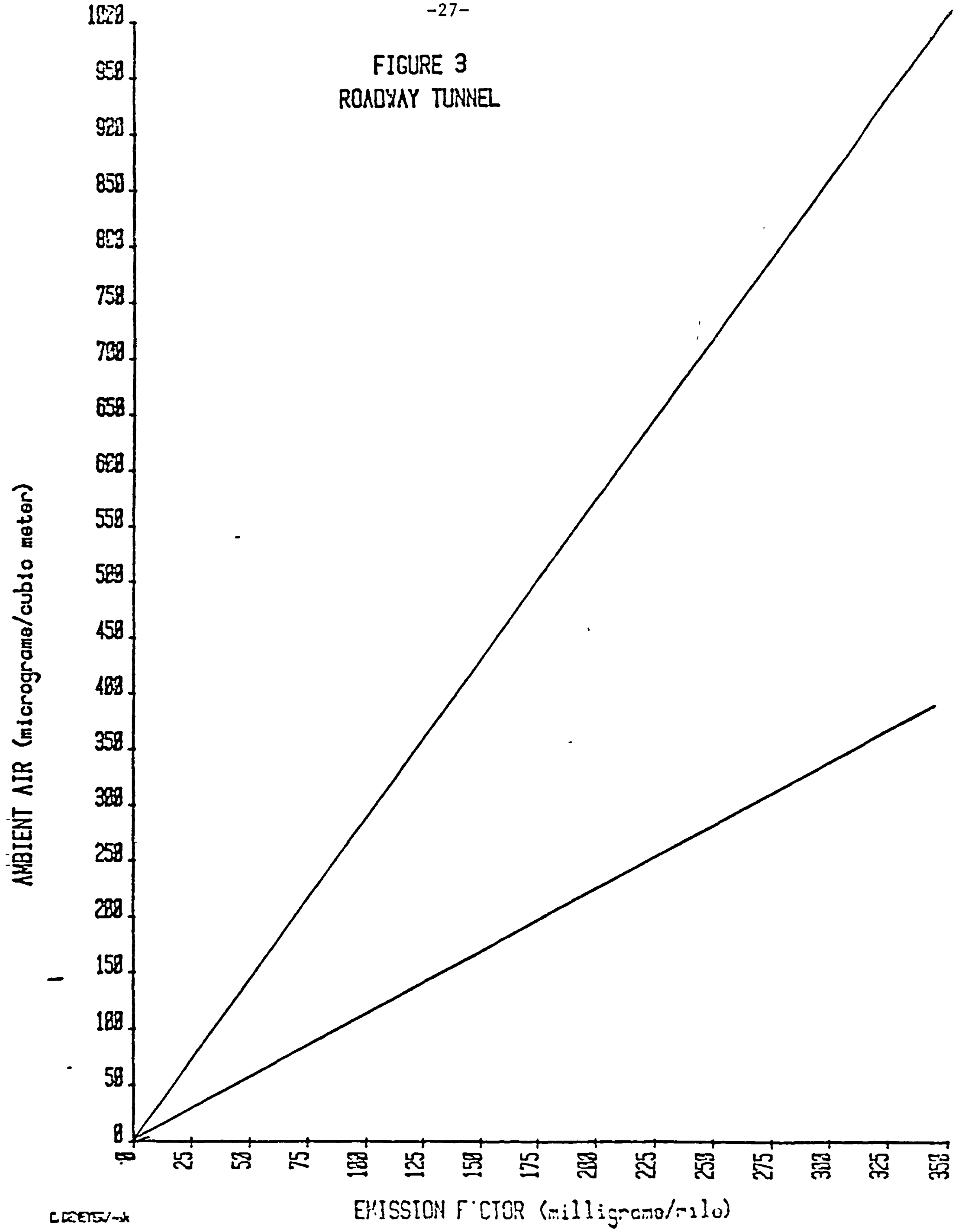
FIGURE 3
ROADWAY TUNNEL
AMBIENT AIR (micrograms/cubic meter)
EMISSION FACTOR (milligrams/mile)

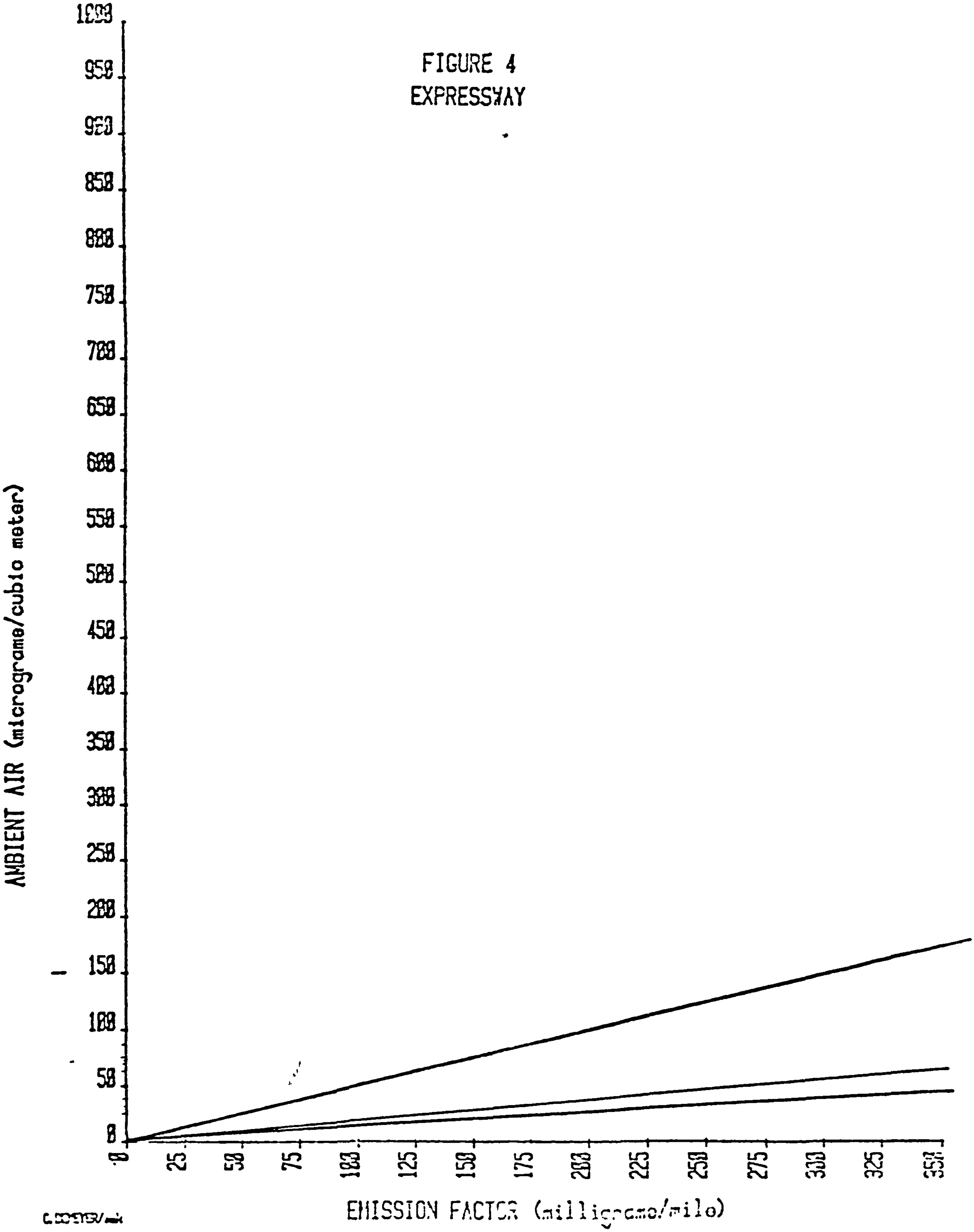
FIGURE 4
EXPRESSWAY
AMBIENT AIR (micrograms/cubic meter)
EMISSION FACTOR (milligrams/mile)
0
25
50
75
100
125
150
175
200
225
250
275
300
325
350
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000

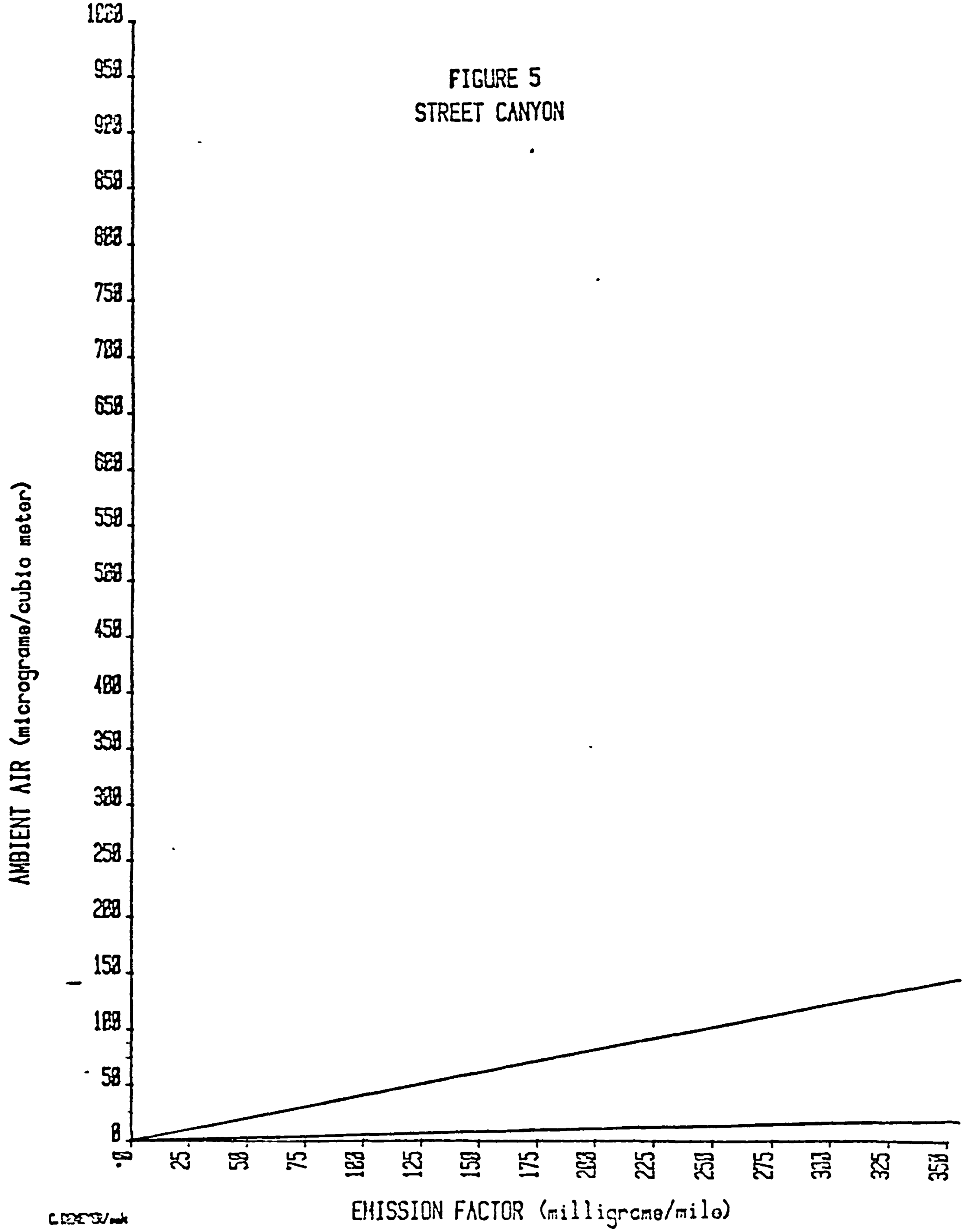
FIGURE 5
STREET CANYON
AMBIENT AIR (micrograms/cubic meter)
1000
950
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
EMISSION FACTOR (milligrams/mile)
0
25
50
75
100
125
150
175
200
225
250
275
300
325
350

Table VI

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 110 ug/m^3 exposure	Emission Factor corresponding to an 11,000 ug/m^3 exposure
Street Canyon - Typical	2619	261,904
Expressway - Close Proximity	1047	104,761
Expressway - Typical	887	88,709
Street Canyon - Severe	390	39,007
Expressway - Severe	217	21,739
Roadway Tunnel - Typical	98	9,800
Roadway Tunnel - Severe	38	3,850

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

Table VII

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

Ambient Air Scenario	Emission Factor (mg/min.) corresponding to a 110 ug/m^3 exposure	Emission Factor corresponding to an 11,000 ug/m^3 exposure
Personal Garage - Typical	13.9	1392
Parking Garage - Typical	28.2	2820
Parking Garage - Severe	2.4	239
Personal Garage - Severe	1.6	164

IX. Conclusions - Hydrogen Cyanide

Several conclusions could be drawn from the information provided in this report. These conclusions are listed below.

1) Table VI and VII indentifies a range of concern for each ambient exposure situation simulated. These ranges vary from 38 - 3850 to 2619 - 261,904 mg/mile for the moving vehicle situations (roadway tunnel, street canyons and expressways) and from 1.6 - 164 to 13.9 - 1392 mg/min for the stationary vehicle situations (personal and parking garages).

2) With respect to the moving vehicle situations the controlling (lowest) range is derived using the severe roadway tunnel situation. There is some question as to whether this scenario identifies a potential mobile source pollutant exposure problem. In other words, if the roadway tunnel scenario is identified as a potential problem with respect to a particular motor vehicle pollutant, then it is possible that the most appropriate solution would be to increase tunnel ventilation rather than to reduce vehicle emissions.

3) The hydrogen cyanide range of concern uses a safety factor of 100 in the determination of a lower level. In view of conclusion 5, it is possible that the inclusion of the roadway tunnel scenario (which seems to be the controlling factor) in the range of concern constitutes an additional margin of safety, but no specific factor has been calculated.

4) The current (estimated) vehicle fleet emission factor for hydrogen cyanide of 11 mg/mile or 1 g/min for 3 way catalysts equipped vehicles at idle, is well below the 38-3850 mg/miles or 1.6 - 164 mg/min range of concern for hydrogen cyanide emissions.

8) Specific emission control technologies or vehicle categories which appear to have emission factors that fall within the range of concern (referring to Table I) are heavy duty gasoline vehicles and malfunctioning 3-way catalyst vehicles.

As more information becomes available on long term, low level exposures to HCN, a lower level for the range of concern can be more accurately chosen. At this point, however, it was necessary to make some assumptions in order to assess a range of exposure concentrations for hydrogen cyanide, which may be of concern to public health. This range is intended to aid in the development of future technologies for mobile sources by providing a basis for exhaust emissions of hydrogen cyanide.

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