Determination of a Range of Concern for Mobile Source Emissions of Ammonia

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 ammonia (NH<sub>2</sub>) emissions from mobile sources. In accordance with 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 NH2. Mathematical models were previously designed or adjusted for various exposure scenarios (such as enclosed expressways, and street canyons) and were used to calculate the ambient air concentrations resulting from various mobile source NH, emission factors. In conjunction with this, an NH, health effects literature search was conducted to aid in the determination of the final range of concern. search provides adequate evidence to support the chosen limits of the range.

The results of this analysis provide a range of concern for  $\mathrm{NH}_3$  emissions from motor vehicles of from 1260 mg/mile - 6302 mg/mile to 85,714 - 428,571 mg/minute or from 56 mg/minute - 268 mg/minute to 4811 mg/minute - 22788 mg/minute depending on the type of scenario chosen to represent public exposure.

The emission levels discussed above are based on the direct impact of  $\mathrm{NH}_3$  on human health. Ammonia as an  $\mathrm{NO}_2$  precursor and participant in subsequent photochemical reactions was not considered in the derivation of the limits discussed above. Ammonia emissions may become a photochemical oxidant concern before they become a directly emitted health hazard.

#### I. Introduction

As the vehicle emission standards have become more stringent, many automobile manufacturers developed new technologies aimed at reducing these emissions. In the early 1970's, the three-way catalytic converter was designed to reduce nitrogen oxides to molecular nitrogen. This new development raised some questions as to the potential for new tailpipe contaminants which might be produced by this system. One pollutant of concern was ammonia (NH<sub>3</sub>). While raw (untreated) automobile exhaust contains some NH<sub>3</sub>, the three-way catalyst can produce much greater quantitites than present in the raw exhaust.

During the time period around 1976, 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, the Environmental Protection Agency (EPA), as well as other concerned organizations, began to investigate the possible hazards of Among these efforts was an EPA NH<sub>3</sub> emissions from mobile sources. contract with Exxon Research and Engineering Company, which investigated the effects of catalyst composition on the emissions of various unregulated pollutants (1)\*. It was found that rhodium (Rh) - containing 3-way catalysts tended to give significantly higher levels of NH, than did platinum or platinum-palladium catalysts. In-house EPA tests also verified this conclusion (2). Exxon and other investigators also showed that three-way catalyst equipped vehicles operating under rich malfunction conditions emitted greater quantities of NH, than under normal operating conditions (1) (2).

Of particular interest to EPA at that time (1976-1978) with respect to automobile emission of  $\mathrm{NH}_3$  were exposure situations which could be considered to be "worst case" conditions wherein a combination of high vehicle emissions rates of  $\mathrm{NH}_3$ , adverse metorology, and sensitive populations coexisted at the same time and place. These early assessements

<sup>\*</sup>Numbers in parentheses indicate references at the end of the paper.

of ammonia concluded that even under adverse or "worst case" conditions ammonia emissions from three-way catalyst automobiles would not represent a public health hazard. The assessments were based on a mean ammonia concentration at the roadway of  $0.15~\text{mg/m}^3$  (0.22 ppm) and on an enclosed garage concentration of  $13~\text{mg/m}^3$  (19 ppm). The garage assessment was based on the simultaneous presence of CO in the garage at a concentration of  $3.9~\text{g/m}^3$  (5,700 ppm) which would constitute a much greater health hazard than NH<sub>3</sub>.

While the reports mentioned previously did conclude that  $\mathrm{NH}_3$  from vehicles probably did not constitute a health hazard over and above that hazard posed by CO, no level of concern for  $\mathrm{NH}_3$  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 Institute (MRI), to gather more information concerning various pollutants such as  $\mathrm{NH}_3$  and their health effects. This information would aid in the determination of levels or ranges of concern for  $\mathrm{NH}_3$  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.
- (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 un-

regulated 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); Ref. (3) 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 was issued in November of that year continuing these procedures for 1980 and later model years (4).

## 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" (5). 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.

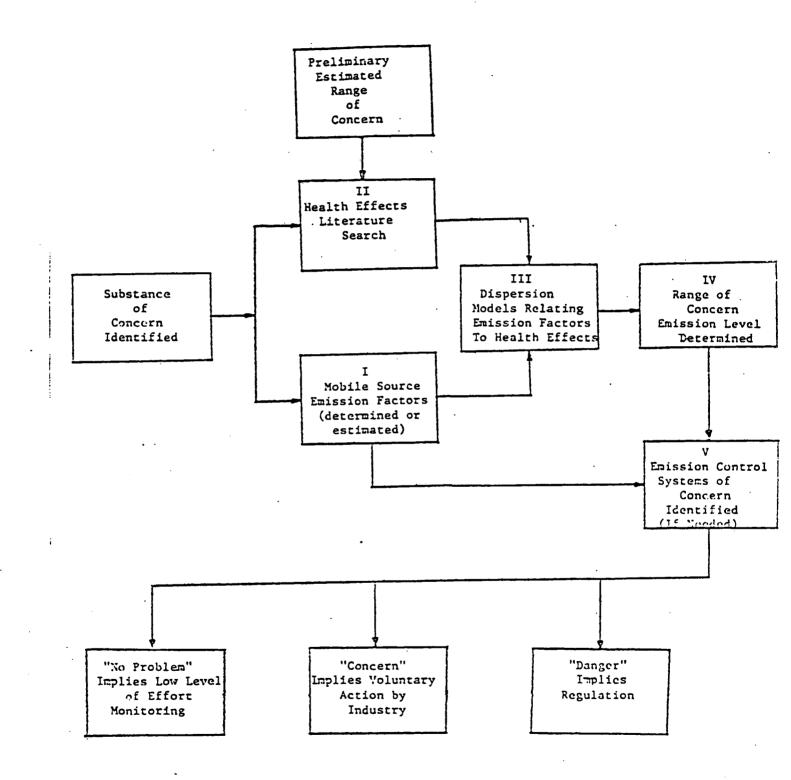
Health effects literature searches have been and are being conducted by MRI in an attempt to aid EPA in the determination of a range of concern for various selected pollutants. With adequate information, the limits for this range can be chosen. The upper level of the range will be that value above which available 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 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 NH2. Using the ambient air versus 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 Figure one graphically illustrates the logical flow of this pollutant assessment methodology.

For the purpose of this report, this particular methodology has been used to develop a range of concern specifically for motor vehicle emissions of  $\mathrm{NH}_{3}$ .

#### IV. General Information

Ammonia is a colorless, corrosive, and weakly alkaline gas with a distinctive pungent odor. This substance is known to be a respiratory and eye irritant but in large doses it may also be related to other various health problems such as chronic bronchitis, dyspnea (both associated with lung impairment), and decreased blood pressure. Although the basic pattern after exposure to NH<sub>3</sub> is irritative damage followed by a recovery period, some deaths have been reported (See Attachment I).

Figure 1
Flow Diagram - Toxic Pollutant Range of Concern



 $\mathrm{NH}_3$  was originally obtained as a by-product from the production of manufactured gas by the destructive distillation of coal. In later years, however, it was learned that  $\mathrm{NH}_3$  could be made by the direct combination of nitrogen ( $\mathrm{N}_2$ ) and hydrogen ( $\mathrm{H}_2$ ) in the presence of a catalyst and at high temperature and pressure. This is commonly known as the Haber process.

NH<sub>3</sub> is used in the production of a fertilizers and many other industrial organic synthetics, as well as in the preparation of numerous inorganic ammonium compounds, as an ingredient in cleaning and bleaching compounds, as a refrigerant, as an agent for the saponification of fats and oils, as an etching compound for metals (particularly aluminum), as a source of inert atmospheres for heat-treating and surface-hardening of metals, as an explosive, and as disinfectants and deodorants.

Another source of  $\mathrm{NH}_3$  exposure is cigarette smoke which is frequently an additional and confounding factor in many human health effects studies. Apparently, the amount of  $\mathrm{NH}_3$  in cigarette smoke varies with the type of tobacco and the investigator (See Attachment I). The ammonium ion is a normal constituent of body fluids, and it has been discussed that the human breath contains  $\mathrm{NH}_3$  in measurable, yet varying amounts.

It has been theorized that the variation in the ammonia levels in expired air between oral and nasal exhalation, which has been attributed to production of  $\mathrm{NH}_3$  by oral bacteria may be a greater  $\mathrm{NH}_3$  "exposure" than other low level chronic exposures such as automobiles.

#### V. Emission Factors

NH<sub>3</sub> 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" and "Analytical Procedures for Characterizing Unregulated Emissions from Vehicles Using Middle-Distillate Fuels" (6, 7).

Small amounts of NH<sub>3</sub> have been measured in gasoline-fueled vehicle exhaust, under normal operating conditions, at levels around 8.0 mg/mile. Under malfunction conditions, however, these emission rates can increase considerably. A reported emission rate for a malfunctioning vehicle equipped with a 3-way catalyst was as high as 518 mg/mile for the FTP driving schedule.

Average NH<sub>3</sub> 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 used in this report will be 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 (8). 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 NH<sub>3</sub> 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	26.2
oxidation catalyst	90.6
3-way catalyst	518.0

The reported maximum 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.

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 NH<sub>3</sub> emission data for this particular driving cycle, in comparison to other driving schedules. It may be more appropriate to chose driving cycles which would most closely simulate those scenarios under sufficient investigation (enclosed spaces, street canyons, etc.). At present, however, data do not exist to permit use of this approach for NH<sub>3</sub>. The percent of error which is introduced by using the FTP emission factor is not known at this point. Available NH<sub>3</sub> idle emissions data were used to estimate NH<sub>3</sub> 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 <u>fleet average</u> emission factor. The data necessary to make these calculations are 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 (9), and the EPA report, Mobile Source Emission Factors: For Low Altitude Areas Only (10). 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 NH<sub>3</sub> emissions, this value is 15.6 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 NH<sub>3</sub> emitting technologies,

TABLE I

## Ammonia Emission Factors@

Vehicle Category	Ammonia (mg/mi) Average
Light Duty Diesel Vehicles	13.1
Light Duty Diesel Trucks	6.1
Heavy Duty Diesel Trucks	52.4*
Light Duty Gasoline Vehicles	
Non Catalyst; no air pump	8.2
Non Catalyst; air pump	5.1
Oxidation Catalyst; no air pump	18.7
Oxidation Catalyst; air pump	11.2
3-way Catalyst; no air pump	123.0
3-way Plus Oxidation Catalyst; air pump	69.9
Light Duty Gasoline Truck	
Non Catalyst	8.2**
Catalyst, no air pump	18.7***
Heavy Duty Gasoline Trucks	32.8**

<sup>@</sup> References 11, 12, 13, 14

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

-13-Table II Fleet Average Emission Factors -Ammonia\*

Vehicle Class	Fraction VMT	Emission Factor (mg/mile)	EF x VMT Fraction
Light Duty Diesel Vehicles	0.015	13.1	0.019
Light Duty Diesel Trucks	0.002	13.1	0.02
Heavy Duty Diesel Trucks	0.027	52.4	1.41
Light Duty Gasoline Vehicles			
Non Cat.; no air pump	0.147	8.2	1.20
Non Cat.; air pump	0.098	5.1	0.50
Ox Cat.; no air pump	0.289	18.7	5.40
Ox Cat.; air pump	0.261	11.2	2.92
3-way Cat.; no air pump	0.012	123.0	1.47
3-way plus Ox Cat.; air pump		69.9	
3-way pius Ox Cat., air pump	0.000	09.9	0.55
Light Duty Gasoline Trucks			
Non Catalyst	0.096	8.2	0.78
Catalyst	0.010	18.7	0.18
Heavy Duty Gasoline Trucks	0.035	32.8	1.15
Total Fleet Average			
			15.6 mg/mile

<sup>\*</sup> References 9, 10, 11, 12, 13, 14

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 technologies. In this case these three technologies include the three-way 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 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 air concentrations of NH<sub>3</sub> for various automobile fleet mixes of emission control technologies.

#### VI. Ammonia Health Effects

Midwest Research Institute (MRI), under contract to EPA, conducted a literature search of the health effects related to NH<sub>3</sub>, the results of which are contained in a report which is included as Attachment I to this paper.

The purpose of this literature search was to aid in the determination of a range of concern for NH<sub>3</sub> by providing supporting evidence for those levels at which adverse physiological effects have been detected from exposure to various concentrations of NH<sub>3</sub>. 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 physiologial effects from exposure to NH<sub>3</sub> can be detected. Below this limit, the available literature shows little or no health effects.

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  $\mathrm{NH}_3$  as to imply a necessity for regulation. The values selected for  $\mathrm{NH}_3$  and the rationale for chosing them are discussed in section VIII.

## VII. Ammonia Ambient Air Concentrations

The NH<sub>3</sub> emission factor information provided in Table I through III, can be used in conjunction with the modeling techniques developed by Southwest

Table III

# Ammonia Emission Factors - Compiled

Fleet Category	mg/mile
Fleet Average (FA)	16
75% FA + 25% OC*	30
50% FA + 50% OC	43
25% FA + 75% OC	57
100% OC	70
75% FA + 25% 3W**	43
50% FA + 50% 3W	70
25% FA + 75% 3W	96
100% 3W	123
75% FA + 25% 3W***	142
50% FA + 50% 3W	267
25% FA + 75% 3W	393
100% 3W	518

<sup>\*</sup> Light Duty Gasoline Vehicles - Three-way plus oxidation catalyst with air pump.

<sup>\*\*</sup> Light Duty Gasoline Vehicle - Three-way Catalyst without air pump.

<sup>\*\*\*</sup> Light Duty Gasoline Vehicles - Three-way Catalyst under malfunction condition - Maximum Emission Rate.

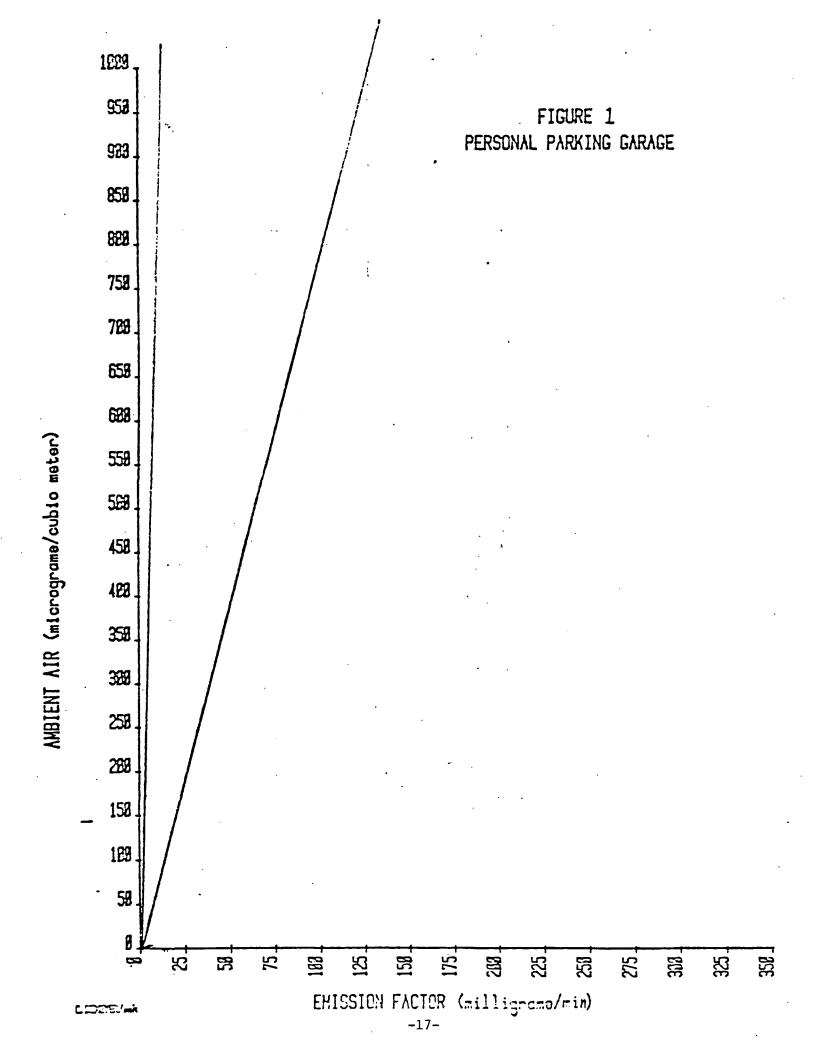
Research Institute (SwRI), in order to calculate the ambient air concentrations produced by varying levels of NH<sub>3</sub> vehicle emissions for different exposure situations. Future work may identify other scenarios which would also be appropriate for the assessment of human exposure to exhaust pollutants, 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 II discusses the reasoning behind using these specific scenarios as well as the information used in the determination of the modeling techniques. Figures 1-5 presents the exposure situations in a graphical manner.

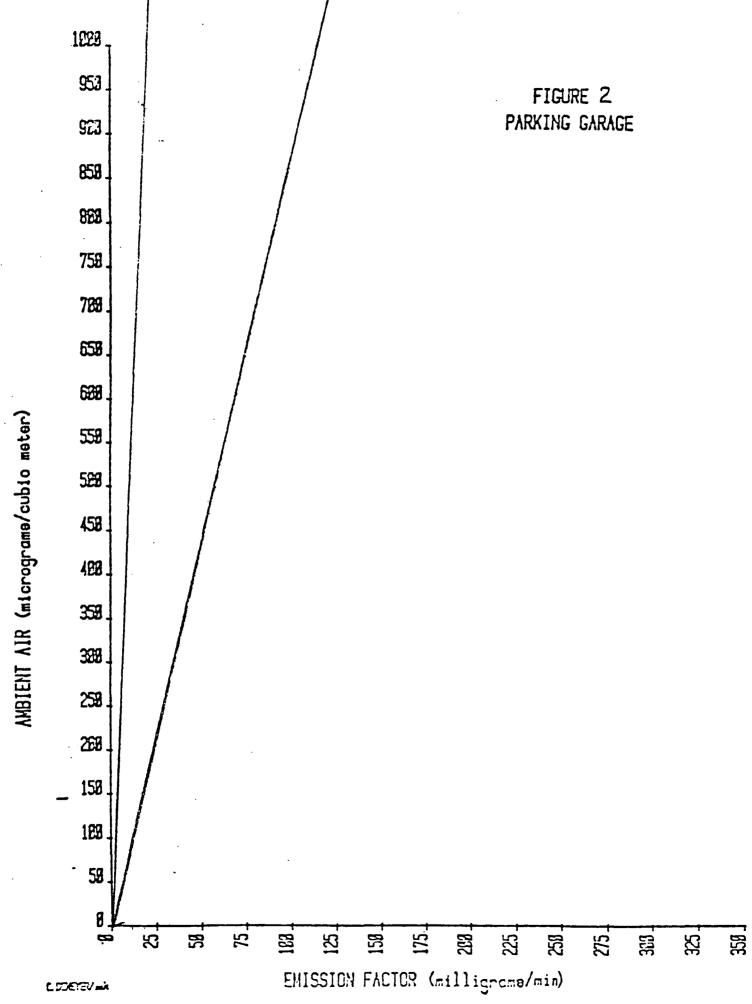
Each scenario is intended to represent a specific type of situation. The typical personal garage situation represents a 30 second vehicle warm-up time and the severe situation simulates a five minute vehicle warm-up time. Both of these cases, of course, take place within a residential garage, and are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

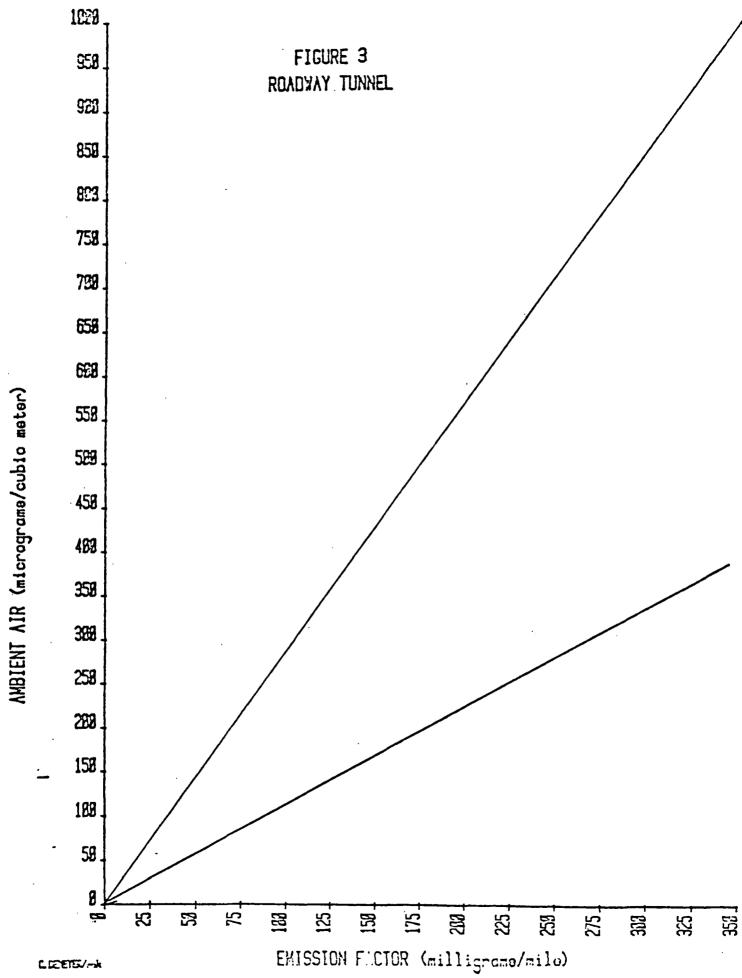
The typical, parking garage case simulates an above the ground, naturally ventilated garage in which it is assumed that a vehicle spends an equal amount of time on both the parking level and ramp level. The severe case represents an underground garage wherein the exposed population is assumed to be at 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 NH $_3$  is assumed to be low (1 ug/m $^3$ ).

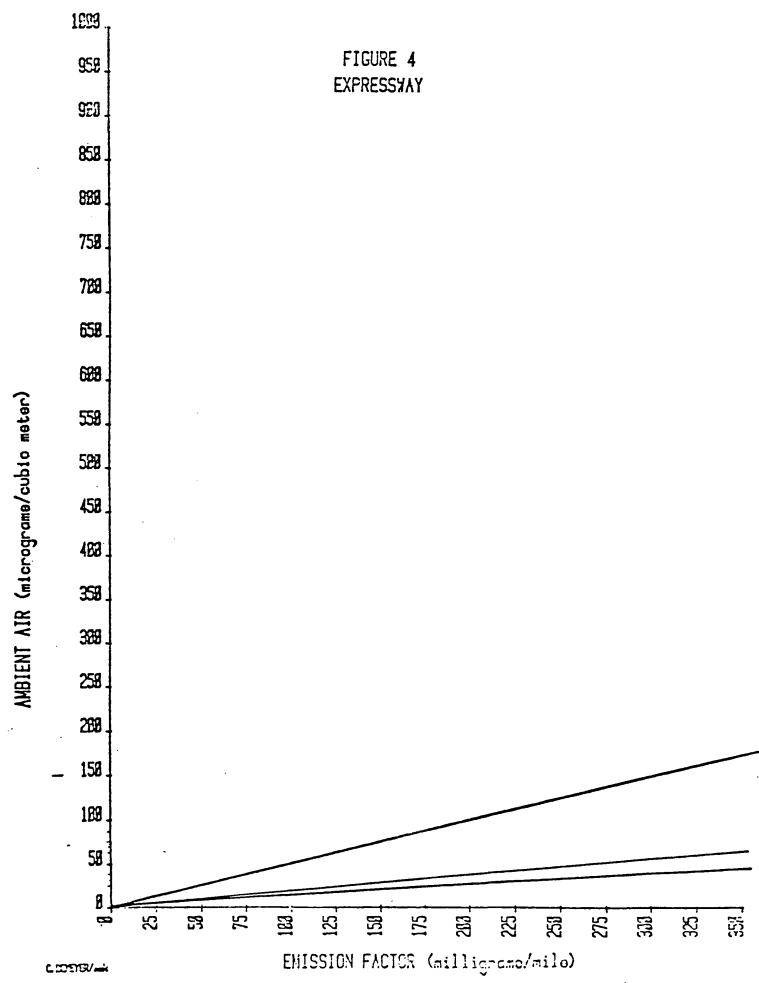
In order to more closely assess public exposure to  $NH_3$  in a garage situation, idle emissions data were averaged from a limited amount of data (15).

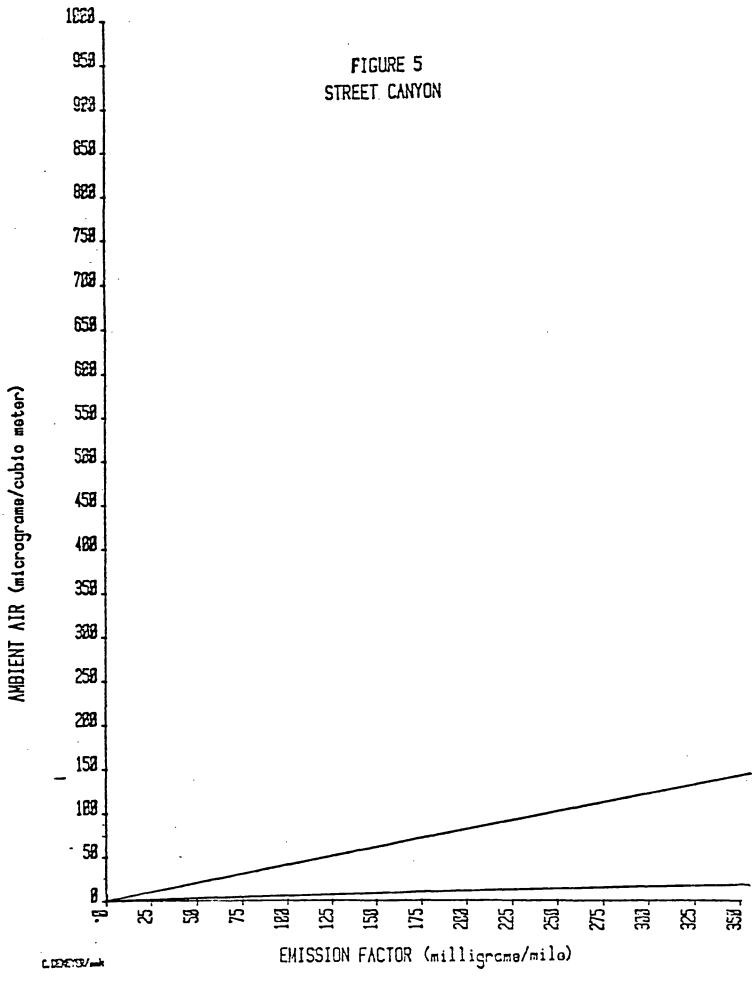
Idle data were readily available for only one vehicle (a 1977 Volvo 3-way prototype) tested at two laboratories. These emission factors average out











to be approximately 7 mg/min. This value appears to be relatively independent of vehicle operation condition, being constant under normal or malfunction conditions. This data point will be used to estimate the garage concentrations of ammonia, but it should be kept in mind that the lack of definitive data on these conditions make any of the resulting calculations subject to some doubt until more information on idle emissions for various vehicle emission control technologies.

In a worst case situation, where 100% of the vehicle fleet consists of automobiles with 3-way catalysts, the NH<sub>3</sub> 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 in an enclosed garage.

# NH<sub>3</sub> Ambient Air Concentration mg/m<sup>3</sup>

	Emission	Personal Garage	Parking Garage
Fleet Make Up	Factor	Typical Severe	Typical Severe
100% 3W	$\overline{7}$ mg/min.	0.06 0.47	0.06 0.39

As mentioned previously, due to limited data, idle emission values can only be evaluated for vehicles with 3-way catalysts. 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. The exposed population is located on the sidewalk.

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 100 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  $\mathrm{NH}_3$  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  $\mathrm{NH}_3$  exhaust emissions.

Health effects information on ammonia, as mentioned previously and as contained in detail in Attachment I, indicate that ammonia is chiefly an irritant gas particularly of the mucous membrances of the eye and respiratory tract. Recovery from nonfatal ammonia exposure is usually complete. Documentation of adverse physiological effects due to NH $_3$  exposure at low levels is poor, making the selection of a concrete range of concern difficult. Table IV (table IV-1 in Attachment II) is an excerpt from the MRI NH $_3$  report which represents a collection of the human, dose-response data. The ACGIH has given a value of 18 mg/m $^3$  as a time-weighted-average TLV for ammonia in order to prevent worker discomfort and lost work efficiency. This level seems appropriate as the high level of the range of concern for the general public exposure to automobile exhaust. The lower level of the range of concern is selected as 3.6 mg/m $^3$  which is the odor threshold according to

Level of Exposure (mg/m <sup>3</sup> )	Exposure Time	Effects
360-403.2 (several studies)	Acute	Blood pressure decreased; NH3 in the blood increased; rapdily reversible changes in lung functions; lacrimation but no coughing; widely varied subjective responses.
180-344	Acute	Changes in lung functions at rest and during exercise; changes in exercise cardiac frequency.
144	Acute	Lung function and slight cardiac changes.
96.5-106 (several studies)	Acute	Significant lung function and cardiac changes, at rest and exercise; some strong irritation of eyes, nose, mouth or throat, though others were relatively unaffected.
50-79.2 (several studies)	Acute	Slight lung function changes in some, reduced cardiac frequency changes in some, definite eye and throat irritation in some, though others relatively unaffected.
18-72	Repeated	Occasional mild irritation; increased Forced Expiratory Volume $^{\circ}$ l sec (FEV <sub>1</sub> ) but not other respiratory or blood pressure parameters; apparent adaptation in the ability to withstand brief excursions to 144 mg/m <sup>3</sup> .
51.8-57.6 (several studies)	Acute	Slight decrease in lung functions; definite eye and slight throat irritation at the higher level; slight irritation of some at the lower level; odor detected.
36 (several studies)	Acute	No lung function changes; slight to moderate irritation in some; odor detected.
36	Repeated	No significant changes in lung function, blood pressure, rate of irritation or neurological response.
33.7	Acute	Lowest concentration at which 4/4 detected the odor.
23	Acute	9/10 detected the odor; no irritation.

# Table IV, cont.

21.6	Acute	Faint irritation in some; odor detected.
13 ·	Acute	Increased NH $_3$ levels in blood and urine,; decreased $0_2$ consumption; no EKG changes; rapid recovery.
10	Repeated	Some changes in lung functions, heart rhythm, and odor sensitivity.
6.1	Repeated	No change in lung functions or heart rhythm; changes in odor sensitivity.
3	Acute	Tendency to decreased $\theta_2$ consumption; insignificant EKG changes; rapid recovery.
2.2	Repeated	Decreases in some lung functions and camphor odor the shold.
0.45-1.0	Acute	Range of thresholds of $\mathrm{NH}_3$ perception for 22 people.
0.32-0.76	Repeated	The upper range changed cerebral cortical activity; $0.32~\text{mg/m}^3$ was the subthreshold level.
0.32-0.65	Repeated	Upper levels decreased eye sensitivity to light; $0.32~\text{mg/m}^3$ was the subthreshold value for eye sensitivity.

consensus opinion. Below this level several studies have shown physiological effects, such as decreased eye sensitivity to light (about 0.5-0.7  $\,\mathrm{mg/m}^3$ ) or changed cerebral cortical activity (0.76  $\,\mathrm{mg/m}^3$ ) but rapid recovery was observed. It is not clearly known whether these measurements represent adverse physiological effects on just changed physiological parameters. Therefore, it is felt that a 3.6  $\,\mathrm{mg/m}^3$  level of NH $_3$  provided ample public safety when compared to the spectrum of NH $_3$  toxicity which seems moderate and reversible in non lethal exposures.

To contrast the 3.6 mg/m $^3$  - 18 mg/m $^3$  range of concern for ammonia to other levels of ammonia, it can be observed that the average baseline level of ammonia in urban air is about 0.014 mg/m $^3$ , and that the average level of ammonia in a healthy persons expired air may range from 0.1 - 1.5 mg/m $^3$  for nonsmokers and 0.4 - 1.93 mg/m $^3$  for smokers. There is also a marked difference in the level of ammonia between nasal or oral breathers because of bacteria present in the mouth.

Between the chosen limits of the range (i.e.  $3.6 \text{ mg/m}^3$  to  $18.0 \text{ mg/m}^3$ ), there are scattered data points providing evidence of adverse physiological effects caused by exposure to various concentrations of ammonia.

According to the methodology which has been used to establish a range of concern for non-zero threshold pollutants, the boundary limits of the ambient air range of concern  $(mg/m^3)$  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 V and VI.

Emission Factors Required to Result in

Exposure Limits for the Ambient Air Range of Concern

Table V

Ambient Air Scenario*	Emission Factor (mg/mile) corresponding to a 360 mg/m <sup>3</sup> exposure	Emission Factor mg/mile corresponding to an 18.0 mg/m <sup>3</sup> exposure
Street Canyon - Typical	85,714	428,571
Expressway - Close Proximity	34,285	171,428
Expressway - Typical	29,032	145,169
Street Canyon - Severe	12,765	63,829
Expressway - Severe	7114	428,571
Roadway Tunnel - Typical	3205	16,028
Roadway Tunnel - Severe	1260 mg/mile	6302 mg/mile
Personal Garage - Typical**	-	-
Parking Garage - Typical**	-	<b>-</b>
Parking Garage - Severe**	-	-
Personal Garage - Severe**	-	-

<sup>\*</sup> In order of increasing ug/m³ concentration for 1 g/mile (or 1g/min) emission rate (excluding garage situations).

<sup>\*\*</sup> These situations are based on emission rates in grams/minute, and are evaluated in Table VII.

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 3.8 mg/m <sup>3</sup> exposure	Emission Factor mg/mile corresponding to an 18.0 mg/m <sup>3</sup> exposure
Parking Garage - Typical	4811	22788
Personal Garage - Typical	974	4615
Parking Garage - Severe	82	390
Personal Garage - Severe	56	268

## Conclusions - Ammonia

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

- (1) Table V and VI identifies a range of concern in motor vehicle emission units (mg/mile) for each ambient exposure situation simulated. These ranges vary from 1,260 6,302 mg/mile to 85,714 428,571 mg/mile for the moving vehicle situations (roadway tunnel, street canyons and expressways) and from 56 268 mg/minute to 4811 22788 mg/minute 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 current estimated vehicle fleet emission factor for hydrogen cyanide of 16 mg/mile is well below the lowest moving vehicle situation range of concern of 1,260 6,302 mg/mile.
- (4) The current estimate emission rate for an idling vehicle (7 mg/minute) is well below the lowest stationary vehicle situation range of concern of 56 - 268 mg/minute.
- (5) The highest emission rate reported for ammonia (518 mg/mile) is far below the lowest level of the range of conern (1,260 mg/mile).
- (6) Not enough information is presently available to determine whether ammonia is hazardous to human health at levels below average odor threshold of 3.6  $mg/m^3$ . Since there are some indications of physiological changes at

lower levels of exposure, but no indications of adverse effects, future research may be needed if a closer resolution of the low level health effects of ammonia is desired.

As more information becomes available on long term, low level exposures to NH<sub>3</sub>, 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 asses a range of exposure concentrations for ammonia, 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 ammonia.

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