

Recommendations for  
Twenty North Carolina Toxic Air Pollutants

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North Carolina Science Advisory Board on Toxic Air Pollutants

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**Table of Contents**

1.0 Executive Summary ..... 5

2.0 Background ..... 6

3.0 Evaluation Variables..... 8

    3.1 Date of most recent AAL review ..... 9

    3.2 New toxicological findings since establishment of AAL ..... 9

    3.3 Methodology used to derive AAL (and associated uncertainty factors) ..... 9

    3.4 Comparison of North Carolina AALs with comparable values from other federal/state agencies ..... 10

    3.5 Comparison of current ACGIH Threshold Limit Values (TLV) or Short Term Exposure Levels (STEL) with 1987 values ..... 10

    3.6 Emission and emission trends of twenty North Carolina TAPs ..... 11

4.0 NCSAB Discussion..... 13

5.0 Recommendations..... 13

    5.1 Acetic acid ..... 14

    5.2 Ammonia..... 14

    5.3 Bromine..... 15

    5.4 Dichlorodifluoromethane (CFC-12) ..... 16

    5.5 Dichlorofluoromethane (HCFC-21)..... 16

    5.6 Ethyl acetate ..... 17

    5.7 Ethyl mercaptan (ethanethiol)..... 17

    5.8 Ethylenediamine ..... 18

    5.9 Fluorides ..... 18

    5.10 Hexane isomers except n-hexane ..... 19

    5.11 Hydrogen sulfide ..... 20

    5.12 Methyl ethyl ketone (MEK) ..... 21

    5.13 Methyl mercaptan..... 22

    5.14 Nitric Acid ..... 22

    5.15 Sulfuric acid..... 23

    5.16 Tetrachloro-1,2-difluoroethane, 1,1,2,2- (CFC-112) ..... 24

    5.17 Tetrachloro-2,2-difluoroethane, 1,1,2,2- (CFC-112a)..... 25

    5.18 Toluene diisocyanate..... 25

    5.19 Trichloro-1,1,2-trifluoroethane, 1,2,2- (CFC-113) ..... 26

    5.20 Trichlorofluoromethane (CFC-11) ..... 26

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**FINAL DRAFT**

6.0 Conclusions ..... 27

7.0 References ..... 29

8.0 Appendices ..... 31

    Appendix A. Uncertainty factor decision tree ..... 31

    Appendix B. Comparison of North Carolina AALs for twenty TAPs with air levels established by other agencies ..... 32

    Appendix C. AAL basis summary for twenty North Carolina TAPs ..... 34

    Appendix D. North Carolina stationary source emissions data summary ..... 36

**List of Figures**

Figure 1. Comparative 2012 stationary source emissions of 20 North Carolina TAPs ..... 11

Figure 2. North Carolina Toxics Emission Trends for 1997-2012 for HAPs and TAPs ..... 12

Figure 3. Comparison of hexane isomers and n-hexane emissions between 1997 and 2012 ..... 19

**List of Tables**

Table 1. North Carolina air pollutants evaluated by the NCSAB ..... 7

Table 2. NCSAB assignments for North Carolina TAPs review ..... 8

Table 3. Comparison of acute and chronic sulfuric acid AALs ..... 24

Table 4. Pollutants recommended for delisting ..... 27

Table 5. NCSAB Recommendations ..... 28

## FINAL DRAFT

### List of Acronyms

AAL	Acceptable Ambient Level
ACGIH	American Conference of Governmental Industrial Hygienists
AEGL	Acute Exposure Guideline
ATSDR	Agency for Toxic Substances and Disease Registry
CAS	Chemical Abstracts
CFC-11	Trichlorofluoromethane
CFC-12	Dichlorodifluoromethane
CFC-112	Tetrachloro-1,2-difluoroethane, 1,1,2,2-
CFC-112a	Tetrachloro-2,2-difluoroethane, 1,1,1,2-
CFC-113	Trichloro-1,1,2-trifluoroethane, 1,2,2-
CNS	Central Nervous System
DAQ	Division of Air Quality
DENR	North Carolina Department of Environment and Natural Resources
EMC	Environmental Management Commission
EPA	Environmental Protection Agency
FEV <sub>1</sub>	Forced Expiratory Volume (1 second)
HAPs	Hazardous Air Pollutants
HCFC-21	Dichlorofluoromethane
HF	Hydrogen Fluoride
H <sub>2</sub> S	Hydrogen Sulfide
IRIS	Integrated Risk Information System
IUR	Inhalation Unit Risk
LRT	Lower Respiratory Tract
MEK	Methyl Ethyl Ketone
MRL	Minimum Risk Level
NESHAP	National Emissions Standards for Hazardous Air Pollutants
NOAEL	No Observed Adverse Effect Level
NCSAB	North Carolina Science Advisory Board on Toxic Air Pollutants
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Level
POD	Point of Departure
POM	Polycyclic Organic Material
RfC	Reference Concentration
RfD	Reference Dose
SCOEL	Scientific Committee on Occupational Exposure Limits

## FINAL DRAFT

STEL	Short-term Exposure Level
TAPs	Toxic Air Pollutants
TCDD	Tetrachlorodibenzo-p-dioxin
TERA	Toxicological Excellence for Risk Assessment
TLV	Threshold Limit Value
TWA	Time-Weighted Average
URT	Upper Respiratory Tract

## 1.0 Executive Summary

The North Carolina Department of Environmental and Natural Resources (DENR), Division of Air Quality (DAQ) tasked the North Carolina Science Advisory Board on Toxic Air Pollutants (NCSAB) with evaluating the relevancy of twenty chemicals included on the North Carolina toxic air pollutants (TAPs) list that are not included on the federal hazardous air pollutants (HAPs) list. This request was prompted by recent changes to the North Carolina Air Toxics Rules coupled with the review required by Session Law 2013-413.

The board qualitatively screened the compounds to determine if they should be retained or removed from the TAPs list. Several variables, including the date of the most recent Acceptable Ambient Level (AAL) review, identification of new and relevant toxicological research, comparison of North Carolina AALs with comparable values from other state/federal agencies and emission trends through 2012, were evaluated. Collectively, these variables were used to broadly assess whether North Carolina requires AALs for the TAPs and if so, what priority should be assigned for future evaluation.

Based on literature review of mainly secondary sources with referral to primary literature as necessary as well as discussion at convened meetings, the board recommends that fourteen of the twenty pollutants (acetic acid, ammonia, bromine, ethyl acetate, ethyl mercaptan, ethylenediamine, fluorides, hexane isomers, hydrogen sulfide, methyl ethyl ketone, methyl mercaptan, nitric acid, sulfuric acid, and toluene diisocyanate) remain on the list as TAPs. Of these, ammonia, hexane isomers, hydrogen sulfide, methyl mercaptan, and sulfuric acid were considered to be of higher priority for future review. Six pollutants characterized as ozone-depleting compounds (CFC-11, CFC-12, CFC-112, CFC-112a, CFC-113, and HCFC-21) were recommended for removal from the list. These compounds are effectively banned from use or production in the United States under the Montreal Protocol, although exemptions are possible. Emissions of these six pollutants have decreased 79-99 percent since 1997 and are expected to continue to decrease.

<u>Retain AAL, no change</u>	<u>Retain AAL, high priority review</u>	<u>Retain AAL, low priority review</u>
Acetic acid	Ammonia	Ethylenediamine
Bromine	Hexane isomers	Methyl ethyl ketone
Ethyl acetate	Hydrogen sulfide	Toluene,2,4 (2,6)-diisocyanate
Ethyl mercaptan	Methyl mercaptan	
Fluorides	Sulfuric acid	
Nitric acid		
	<u>Delist AAL</u>	
	Dichlorodifluoromethane (CFC-12)	
	Dichlorofluoromethane (HCFC-21)	
	Tetrachloro-1,2-difluoroethane, 1,1,2,2- (CFC-112)	
	Tetrachloro-2,2-difluoroethane, 1,1,1,2- (CFC-112a)	
	Trichloro, 1,1,2- trifluoroethane, 1,2,2-(CFC-113)	
	Trichlorofluoromethane (CFC-11)	

## 2.0 Background

The North Carolina Department of Environmental and Natural Resources (DENR), Division of Air Quality (DAQ) tasked the North Carolina Science Advisory Board on Toxic Air Pollutants (NCSAB) with evaluating twenty chemicals included on the North Carolina toxic air pollutants (TAPs) list that are not included on the federal hazardous air pollutants (HAPs) list (Table 1). Hexachlorodibenzo-p-dioxin (CAS # 57653-85-7), historically considered a North Carolina TAP, was excluded from this evaluation exercise. While this substance is not specifically singled out on the federal HAPs list, it is a dioxin-like compound, similar in structure to 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD). Dioxin-like compounds, including chlorinated dibenzofurans, are considered to be part of the polycyclic organic matter (POM) group<sup>1</sup> included on the federal HAPs list. Classification of hexachloro-p-dioxin as a HAP was confirmed by the US Environmental Protection Agency (EPA).<sup>2</sup>

North Carolina TAPs were identified in 1986/1987 from a survey of air pollutants released by North Carolina industries. From the survey results, the North Carolina Academy of Sciences selected 97 air pollutants deemed to have the greatest potential for causing adverse human health effects and developed AALs for each. AALs are airborne chemical concentrations below which a substance is not expected to have any adverse impacts on human health. They are used in pollution permitting to ensure that stationary source emissions do not add concentrations of toxic air pollutants to the air that may possibly be harmful to human health. Except for the 20 pollutants listed in Table 1, all North Carolina TAPs were later designated as federal HAPs by the 1990 amendments to the Clean Air Act.

Recent changes to the North Carolina Air Toxics Rules ([http://www.ncair.org/news/pr/2014/air\\_toxics\\_03132014.shtml](http://www.ncair.org/news/pr/2014/air_toxics_03132014.shtml)) coupled with the review required by Session Law 2013-413 prompted an evaluation of the relevancy of these twenty air pollutants under North Carolina's air quality permitting program. The AALs for the majority of the pollutants listed in Table 1 are based on acute or chronic health effects rather than carcinogenic effects. The AALs for most of these pollutants have not been reviewed since the inception of the Air Toxics program in 1987.

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<sup>1</sup> Section 112(b), Footnote (4), of the Clean Air Act defines Polycyclic Organic Matter (POM) as including "organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100°C."

<sup>2</sup> Email correspondence from Anne Pope of EPA dated June 26, 2014.

## FINAL DRAFT

**Table 1. North Carolina air pollutants evaluated by the NCSAB**

Air Pollutant	CAS Number
Acetic Acid	64-19-7
Ammonia	7664-41-7
Bromine	7726-95-6
Dichlorodifluoromethane (CFC-12)	75-71-8
Dichlorofluoromethane (HCFC-21)	75-43-4
Ethyl acetate	141-78-6
Ethyl mercaptan (ethanethiol)	75-08-1
Ethylenediamine	107-15-3
Fluorides <sup>1</sup>	Various
Hexane isomers except n-hexane <sup>2</sup>	Various
Hydrogen sulfide	7783-06-4
Methyl ethyl ketone	78-93-3
Methyl mercaptan	74-93-1
Nitric acid	7697-37-2
Sulfuric acid	7664-93-9
Tetrachloro-1,2-difluoroethane, 1,1,2,2- (CFC-112)	76-12-0
Tetrachloro-2,2-difluoroethane, 1,1,1,2- (CFC-112a)	76-11-9
Toluene diisocyanate, 2,4 and 2,6 isomers	91-08-7
Trichloro-1,1,2-trifluoroethane, 1,2,2- (CFC-113)	76-13-1
Trichlorofluoromethane (CFC-11)	75-69-4

<sup>1</sup> Fluorides refers to fluorine gas and inorganic, ionizable fluoride compounds, excluding HF. Included in this category class are compounds such as NaF, KF, CaF<sub>2</sub>, NH<sub>4</sub>F, and SiF<sub>4</sub>.

<sup>2</sup> Includes 2-methylpentane (CAS# 107-83-5), 3-methylpentane (CAS# 96-14-0), 2,2-dimethylbutane (CAS# 75-83-2) and 2,3-dimethylbutane (CAS# 79-29-8) or any combination of these.

The four-point charge to the NCSAB is detailed below:

- (1) Evaluate whether North Carolina should have AALs for the twenty pollutants listed in Table 1.
- (2) Recommend retention or deletion of each pollutant on the list.
- (3) For those substances retained, assign a low or high priority for future AAL review. Comprehensive AAL evaluations and revisions may be conducted at a later time.
- (4) Provide clear criteria and supporting rationales for each recommendation.

The evaluation may consider, but not be limited to, the known human health effects associated with inhalation exposures and whether the substance is currently emitted into the atmosphere from permitted North Carolina facilities. Additional resources may include toxicological evaluations conducted by the North Carolina Division of Air Quality (DAQ), the Agency for Toxic Substances and Disease Registry (ATSDR), EPA, or other regulatory or advisory agencies or bodies.

## FINAL DRAFT

Toxicological literature searches conducted according to the board member's assignments detailed in Table 2 formed the basis for the board's discussions and recommendations. Secondary sources (e.g. review articles, toxicological profiles) were mainly utilized with referral to primary literature (e.g. original research publications) as necessary. Findings for each pollutant were summarized in a standardized template.

**Table 2. NCSAB assignments for North Carolina TAPs review**

Dave Dorman	Acetic Acid (64-19-7) Nitric Acid (7697-37-2) Sulfuric Acid (7644-93-9)
Jane Hoppin	Dichlorodifluoromethane (CFC-12) (75-71-8) Dichlorofluoromethane (HCFC-21)(75-43-4) Trichlorofluoromethane (CFC-11) (75-69-4)
Elaina Kenyon	Hexane isomers excluding n-hexane (Various)
Ivan Rusyn	Ammonia (7664-41-7) Methyl Ethyl Ketone (78-93-3)
Tom Starr	Bromine (7726-96-6) Fluorides (Various)
Sandy Stopford	Ethyl Acetate (141-76-6) Ethyl Mercaptan (75-08-1) Methyl Mercaptan (74-93-1)
Not assigned	Ethylenediamine (107-15-3) Hydrogen Sulfide (7783-06-4) Tetrachloro-1,2-difluoroethane, 1,1,2,2- (CFC-112) (76-12-0) Tetrachloro-2,2-difluoroethane, 1,1,1,2- (CFC-112a)(76-11-9) Trichloro-1,1,1,2-trifluoromethane (CFC-113)(76-13-1) Toluene Diisocyanate (2,4 and 2,6 isomers)(91-08-7)

### 3.0 Evaluation Variables

Variables capable of influencing the recommendations to retain or remove pollutants from the list and assigning a priority for future AAL review were identified by the board. These included:

- Date of most recent AAL review
- New and relevant toxicological findings since the last AAL review
- Methodology used to derive AAL (and associated uncertainty factors)
- Comparison of North Carolina AALs with comparable values from other federal/state agencies
- Comparison of North Carolina AALs with current American Conference of Government Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) or Short Term Exposure Levels (STELs)
- Pollutant emission levels in pounds from North Carolina's permitted facilities in 2012
- Pollutant emission trends of pollutant in North Carolina from 1997 through 2012
- Critical human health endpoints

### 3.1 Date of most recent AAL review

The date of the most recent AAL review was considered a factor in assigning a relative priority for future evaluations. With the exception of hydrogen sulfide and toluene diisocyanate (2,4 and 2,6 isomers), the AALs for the remaining pollutants have not been reviewed or updated since their creation in 1987. The reasons for this are twofold. First, many of the compounds are classified as irritants (substances causing ocular, dermal, or respiratory irritation following exposure). Historical priorities for the NCSAB, established by the DAQ, have generally focused on pollutants associated with carcinogenicity and other chronic health effects rather than acute irritant effects. Second, there has been minimal new research published for many of these compounds since their original AALs were established.

### 3.2 New toxicological findings since establishment of AAL

The relative priority for future review of each pollutant was based primarily on the existence of new toxicological research findings. Review of the toxicological literature indicated that new and significant human health findings for the majority of compounds were lacking. The most notable exception was sulfuric acid. More rigorous literature searches were recommended for classes of compounds, such as hexane isomers, to ensure that a comprehensive evaluation of all possible combinations of individual components was considered.

### 3.3 Methodology used to derive AAL (and associated uncertainty factors)

The methodology used to derive the AALs was used as a surrogate for the point in time in which the AAL was established (similar to the date of the last AAL review). In the final analysis, the methodology used to derive the AALs did not greatly influence the board's recommendations.

The AALs established in 1987 were derived using a factored TLV approach. This methodology uses well-researched and peer-reviewed occupational exposure levels and divides these values by the product of several "uncertainty factors" to arrive at an exposure level expected to be free of adverse health effects for the general population. "Uncertainty factors" are used to account for potential interspecies differences in toxicity, inter-individual differences in sensitivity to toxicity, and to compensate for deficiencies in the data set with each such factor typically assigned a value ranging from one to ten. The multiplicative product of all the uncertainty factors is used as the final divisor.

## FINAL DRAFT

While more rigorous statistical analysis methods have been developed since 1987 to analyze toxicological study data, the factored TLV methodology is still used today, although to a much lesser extent.

Guidance for selecting uncertainty factors used in deriving North Carolina AALs is described in the North Carolina Academy of Sciences Report on the Recommendations of the Air Toxics Panel (1987/1987). A decision tree illustrating the stepwise logic used for selecting an uncertainty factor is included in Appendix A. Briefly, the report recommends the use of four independent factors to compensate for uncertainties associated with:

- Variation in population susceptibility ( $U_{\text{intraspecies}}$ ): Factor of 10
- Time conversion (8 hour work day to continuous exposure)( $U_{\text{time}}$ ): Factor of 4
- Experimental uncertainty associated with chronic studies ( $U_{\text{chronic}}$ ): Factor of 2
- Severity of effect (to be used in instances of irreversible or life threatening effects)( $U_{\text{severity}}$ ): Factor of 2

### **3.4 Comparison of North Carolina AALs with comparable values from other federal/state agencies**

North Carolina AALs were compared with air permitting levels established by California, Texas, Minnesota and Michigan and recommended air exposure levels established by the ATSDR and EPA (Appendix B). As expected, few TAPs had been evaluated by federal agencies. Only Texas had established air permitting levels for all of the North Carolina TAPs. Generally, North Carolina AALs were less restrictive than values established by other states. A comprehensive comparison of values is not feasible due to inconsistencies in averaging times associated with the values.

### **3.5 Comparison of current ACGIH Threshold Limit Values (TLV) or Short Term Exposure Levels (STEL) with 1987 values**

Comparison of 2013 ACGIH TLV/STEL values with 1987 values showed few differences. The STEL for bromine was reduced from 0.3 ppm to 0.2 ppm (lower value equivalent to 0.65 mg/m<sup>3</sup>) and the TWA for sulfuric acid was decreased by a factor of 5. Hydrogen sulfide was the only substance for which revisions had been made for both the TWA and STEL. Its TWA was reduced by a factor of 10 and its STEL was reduced by a factor of 3. The TWAs for two chlorofluorocarbons were also reduced: CFC-112 was reduced by a factor of 10 and the CFC-112a was reduced by a factor of 5. The lack of widespread changes to the AALs derived from ACGIH TLV or STEL values is

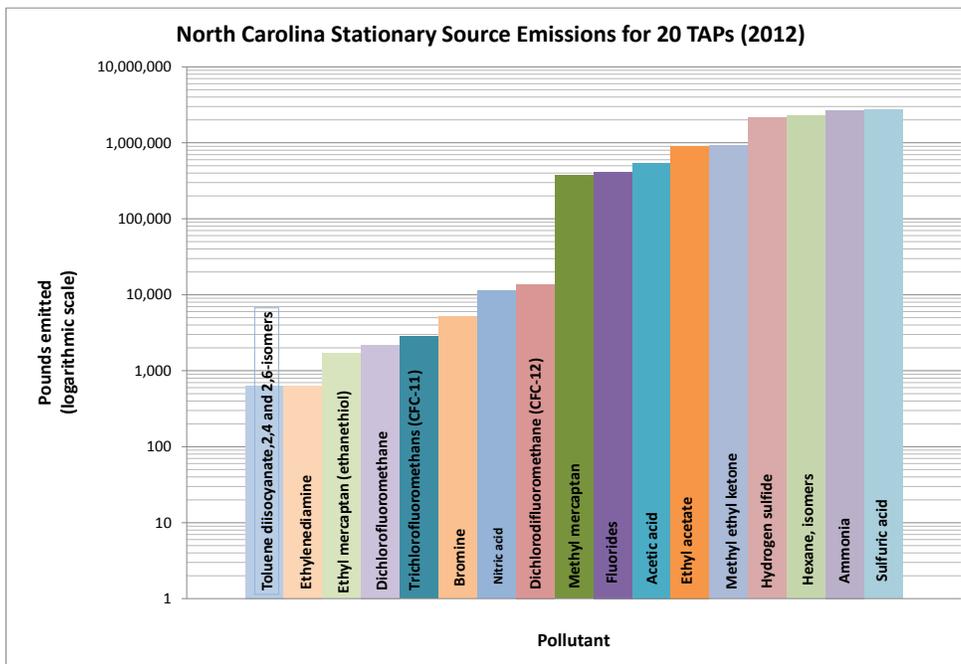
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attributable to the fact that there have been few newer significant toxicological findings for the majority of the twenty TAPs evaluated.

### 3.6 Emission and emission trends of twenty North Carolina TAPs

Yearly emissions and emission trends strongly influenced the board’s recommendations to retain or delist a North Carolina TAP and to a lesser extent, the priority for future review. Total yearly stationary source emissions for the twenty TAPs ranged from “none reported” to 2.7 million pounds. Emissions illustrated in Figure 1 (plotted using logarithmic scale) represent the sum total of emissions reported from facilities with air permits in 97 North Carolina counties for each of the twenty pollutants. Emissions from the three local air quality programs (Buncombe, Forsyth, and Mecklenburg) are not included.

Figure 1. Comparative 2012 stationary source emissions of 20 North Carolina TAPs



Four pollutants were emitted in excess of 2 million pounds per year in 2012. These were

- ammonia (2.7 million),
- hexane isomers excluding n-hexane (2.3 million),
- hydrogen sulfide (2.1 million) and
- sulfuric acid (2.7 million).

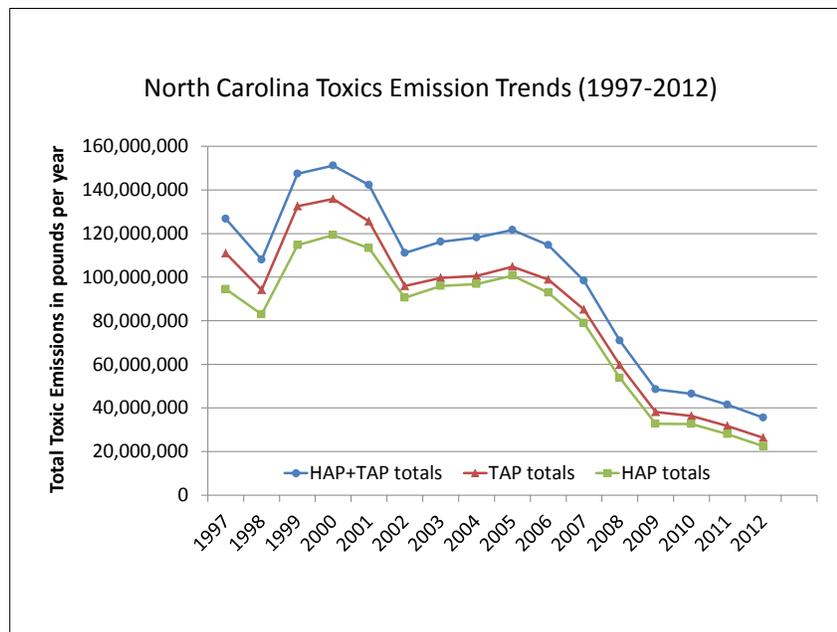
## FINAL DRAFT

No emissions were reported for tetrachloro-1,2-difluoroethane-1,1,2,2 (CFC-112) or tetrachloro-2,2-difluoroethane-1,1,1,2 (CFC-112a) in 2012. It is important to note that the de minimus reporting quantities for these substances is 1000 pounds. The lack of emissions reported to the inventory signifies only that emissions were below this 1,000 pound threshold and not necessarily zero.

Less than 1000 emitted pounds were reported for two pollutants on the list: ethylenediamine at 640 pounds and toluene diisocyanate, 2,4 and 2,6-isomers at 635 pounds.

A marked decrease in emissions from permitted stationary sources was noted for the majority of chemicals from 1997-2012 (Figure 2). Such reductions can be partially attributed to the implementation of the EPA's National Emissions Standards for Hazardous Air Pollutants (NESHAPs) that required installation of control devices and/or meeting work practice emission standards. The exceptions were hexane isomers and ethyl mercaptan. Emissions for hexane isomers increased from approximately 253,000 pounds to 2.3 million pounds (9-fold increase) during this time interval. Ethyl mercaptan emissions increased from approximately 340 pounds to 1680 pounds (5-fold increase). Increased emissions for hexane isomers were likely a result of increased production and their use as a substitute for the HAP n-hexane. Increased emissions for ethyl mercaptan is presumably due to the increase volume of waste in landfills and the increase in the number of landfills that are required to report emissions.

**Figure 2. North Carolina Toxics Emission Trends for 1997-2012 for HAPs and TAPs**



## 4.0 NCSAB Discussion

Each board member presented the results of their literature review and their recommendation for retaining or removing the pollutant from the TAPs list. Each pollutant was assigned to one of four categories:

1. Retain the AAL, no review necessary
2. Retain the AAL, high priority for AAL review
3. Retain the AAL, low priority for AAL review
4. Delist the AAL

In instances where the recommendation was to retain the pollutant on the TAPs list, further discussion was undertaken to assign a relative high/low priority for future AAL evaluation. In those instances where there was consensus about removing a substance from the list based on a lack of emissions, board members expressed concern about the public perception associated with removing a listed substance. They emphasized that their recommendation to remove a compound from the list should not be interpreted to mean that exposure to the compound was no longer associated with adverse health effects. Their recommendation was predicated on the lack of reported emissions and possible exposures from stationary sources. The risk of exposure (and possible associated adverse health effects) is expected to be small if there are no longer any emissions of these substances in North Carolina. However, the board emphasized that any future emissions of such substances may necessitate adding them back to the list. This is unlikely as the only pollutants that have been recommended for delisting (CFCs and HCFCs) have already been phased out of production and consumption under the Montreal Protocol.

## 5.0 Recommendations

The board recommends retaining fourteen of the twenty pollutants (acetic acid, ammonia, bromine, ethyl acetate, ethyl mercaptan, ethylenediamine, fluorides, hexane isomers, hydrogen sulfide, methyl ethyl ketone, methyl mercaptan, nitric acid, sulfuric acid, and toluene diisocyanate) on the TAPs list. Of these, ammonia, hexane isomers, hydrogen sulfide, methyl mercaptan, and sulfuric acid are considered to be of higher priority for future review. Six of the fourteen pollutants (acetic acid, bromine, ethyl acetate, ethyl mercaptan, fluorides, and nitric acid) lacked new toxicological data that would be useful in updating an AAL. Therefore, the board recommends no further AAL review for these substances at this time. The remaining three pollutants recommended for retention (ethylenediamine, methyl ethyl ketone, and toluene diisocyanate) were assigned a low priority for review. Six pollutants characterized as ozone-depleting compounds (CFC-11, CFC-12, CFC-112, CFC-112a, CFC-113, and HCFC-21) were recommended for removal from the list.

Summary information described in this section is provided in tabular form in Appendices B through D.

### 5.1 Acetic acid

**Recommendation: Retain the AAL**

**Priority: No review recommended at this time**

Acetic acid is emitted primarily from chemical manufacturers, dyeing companies, paper mills, tobacco companies, fiberglass products manufacturers, fabric/fiber-related manufacturing companies and coating and finishing operations in North Carolina. Its emissions have decreased by approximately 81 percent since 1997 (from 2.9 million pounds to approximately 543,000 pounds in 2012).

The current one-hour acute AAL for acetic acid, established in 1987, is 3.7 mg/m<sup>3</sup>. The critical human health endpoint upon which the AAL is based is eye and nasal irritation and changes in pulmonary function. The AAL was derived using a factored TLV method, a 15-minute STEL of 15 ppm (equivalent to 37 mg/m<sup>3</sup>), and an uncertainty factor (UF<sub>intraspecies</sub>) of 10.

Minimal new research on the human health effects associated with inhalation exposures to acetic acid has been conducted since 1997. Recent publications have identified mild human irritation effects in the range of 10 ppm (equivalent to 25 mg/m<sup>3</sup>) (Ernstgård et al, 2006, SCOEL, 2012). Acetic acid has not been tested for carcinogenicity.

The limited new toxicology data available for acetic acid suggests that the basis for the current AAL remains protective for human health. Therefore, the board recommends that acetic acid be retained on the North Carolina TAPs list. No further review is recommended at this time.

### 5.2 Ammonia

**Recommendation: Retain the AAL**

**Priority: High for review**

Statewide, ammonia is emitted primarily from phosphate fertilizer manufacturing facilities, pulp and paper mills and electric power generation units. Its emissions have decreased approximately 55 percent since 1997 (from 6 million pounds to 2.7 million pounds in 2012).

## FINAL DRAFT

Ammonia is an eye, skin, and respiratory irritant. Its one-hour acute AAL, established in 1987, is 2.7 mg/m<sup>3</sup>. The AAL was derived using a factored TLV method, a 15-minute STEL of 35 ppm (equivalent to 27 mg/m<sup>3</sup>), and an uncertainty factor (UF<sub>intraspecies</sub>) of 10.

The EPA has established a chronic RfC inhalation value for ammonia of 0.1 mg/m<sup>3</sup> and is currently in the process of revising this value under the EPA Integrated Risk Information System (IRIS). Its proposed RfC, which is undergoing public comment, is 0.3 mg/m<sup>3</sup>. The ATSDR has established both an acute and chronic inhalation value for ammonia of 1.2 and 0.07 mg/m<sup>3</sup> respectively. North Carolina does not have a chronic AAL for ammonia and its acute AAL is less restrictive than that proposed by the ATSDR.

Given that ammonia emissions have not decreased as dramatically compared with other pollutants and more recent inhalation values established or proposed by other authorities appear to be more stringent, the board recommends that the AAL for ammonia be retained. It also recommends that it be assigned a higher priority for review to determine if a chronic AAL is warranted.

### 5.3 Bromine

#### **Recommendation: Retain the AAL**

#### **Priority: No review recommended at this time**

Chemical manufacturing and pulp and paper mills comprise the predominant sources of stationary source bromine emissions in North Carolina. Bromine emissions have decreased approximately 73 percent since 1997 (from 19,271 pounds to 5,195 pounds in 2012).

Bromine is a mucous membrane and respiratory tract irritant. Its one-hour acute AAL, established in 1987, is 0.2 mg/m<sup>3</sup>. The AAL was derived using a factored TLV method, a 15-minute STEL of 0.3 ppm (equivalent to 2 mg/m<sup>3</sup>), and an uncertainty factor (UF<sub>intraspecies</sub>) of 10. While no EPA RfC or ATSDR MRLs are available for bromine, the EPA has established an Acute Exposure Guideline (AEG) for bromine. The AEG-1 value for bromine of 0.033 ppm (equivalent to 0.10 mg/m<sup>3</sup>) is the same as the bromine AAL. In the absence of new toxicological data or outside agency reviews, the board recommends that the AAL for bromine be retained. No further review is recommended at this time.

#### 5.4 Dichlorodifluoromethane (CFC-12)

**Recommendation: Delist the AAL**

**Priority: N/A**

North Carolina emissions of dichlorodifluoromethane (CFC-12) are almost exclusively from landfills. It had been used predominantly as a refrigerant and aerosol spray propellant until its manufacture was banned by the EPA in the United States in 1996 under the Montreal Protocol. Its ban was not predicated on its potential to cause adverse human health effects but rather its adverse impact the earth's ozone layer. Emissions have decreased approximately 79 percent since 1997 (from 64,188 pounds to 13,688 pounds in 2012).

Chronic exposures to dichlorodifluoromethane are associated with lung tissue injury in rats. The 24-hour chronic AAL, established in 1987, is 248 mg/m<sup>3</sup>. The AAL was derived using a factored TLV method, an 8-hour TLV of 1000 ppm (equivalent to 4950 mg/m<sup>3</sup>), and an uncertainty factor of 20 (UF<sub>intraspecies</sub> and UF<sub>chronic</sub>).

Based on its manufacturing ban in the United States, its expected continued reduction in emissions and its comparatively low toxicity potential, the board recommends that the AAL for dichlorodifluoromethane be removed from the North Carolina TAPS list.

#### 5.5 Dichlorofluoromethane (HCFC-21)

**Recommendation: Delist the AAL**

**Priority: N/A**

Similar to dichlorodifluoromethane (CFC-12), dichlorofluoromethane (HCFC-21) is predominantly released by landfills. It has been used as a refrigerant and propellant. Effective January 1, 2015, the EPA banned the manufacture and import of ozone-depleting HCFCs in support of the Montreal Protocol. Dichlorofluoromethane emissions have decreased approximately 95 percent since 1997 (from 39,865 pounds to 2,183 pounds).

Dichlorofluoromethane is hepatotoxic. The 24-hour chronic AAL, established in 1987, is 0.5 mg/m<sup>3</sup>. The AAL was derived using a factored TLV method, an 8-hour TLV of 10 ppm (equivalent to 40 mg/m<sup>3</sup>), and an uncertainty factor of 80 (UF<sub>intraspecies</sub>, UF<sub>chronic</sub>, and UF<sub>time</sub>).

Based on its anticipated phase-out in the United States and its expected continued reduction in emissions, the board recommends that the AAL for dichlorofluoromethane be removed from the North Carolina TAPS list.

## 5.6 Ethyl acetate

**Recommendation: Retain the AAL**

**Priority: No review recommended at this time**

Ethyl acetate is emitted primarily from coating and painting operations, furniture manufacturing, and packaging and textile facilities throughout the state. Its emissions have decreased by approximately 21 percent since 1997 (from approximately 1.2 million to 0.91 million pounds in 2012).

The current one-hour acute AAL for ethyl acetate, established in 1987, is 140 mg/m<sup>3</sup>. This value was derived using a factored TLV method with a TLV of 400 ppm (equivalent to 1,400 mg/m<sup>3</sup>) and an uncertainty factor of 10 (UF<sub>intraspecies</sub>). Mucous membrane irritation, the critical health effect identified in a human study dating back to the 1940's, is observed at the TLV. The 2013 ACGIH TLV remains unchanged since 1986, presumably due to a lack of new data. In the absence of new toxicological information or updated ACGIH values, the board recommends that ethyl acetate be retained on the North Carolina TAPs list and that its AAL does not require further evaluation at this time.

## 5.7 Ethyl mercaptan (ethanethiol)

**Recommendation: Retain the AAL**

**Priority: No review recommended at this time**

Ethyl mercaptan, formed from the biological digestion of wastes, is emitted almost exclusively from waste management facilities and landfills in North Carolina. Its emissions, primarily fugitive in nature, have increased by approximately four hundred percent since 1997 (from 342 pounds to 1,682 pounds in 2012).

The current one-hour acute AAL for ethyl mercaptan, established in 1987, is 0.1 mg/m<sup>3</sup>. This value was derived using a factored TLV method, a TLV of 0.5 ppm (equivalent to 1 mg/m<sup>3</sup>), and an uncertainty factor of 10 (UF<sub>intraspecies</sub>). Central nervous system (CNS) effects and mucous membrane irritation are the critical health effect identified in human studies dating back to 1968. The 2013 ACGIH TLV remains unchanged since 1986, presumably due to a lack of new data. In the absence of new data, the board recommends that ethyl mercaptan remain on the North Carolina TAPs list and that its AAL does not require further evaluation at this time.

## 5.8 Ethylenediamine

**Recommendation: Retain the AAL**

**Priority: Low for review**

Two thirds of the ethylenediamine released in North Carolina is from the manufacture of fabricated metal products. Glass manufacturing and chemical manufacturing each contribute approximately 15% towards the total yearly emissions. Emissions of ethylenediamine have decreased approximately 99 percent since 1997 (from 65,194 pounds to 640 pounds).

Ethylenediamine produces both corrosive and allergenic effects in humans. Ethylenediamine has both an acute and chronic AAL, both of which date back to 1987. The one-hour acute AAL is  $2.5 \text{ mg/m}^3$  and the 24-hour chronic AAL is  $0.3 \text{ mg/m}^3$ . Both the acute and chronic AAL were derived using a factored TLV method and an 8-hour TLV of 10 ppm (equivalent to  $25 \text{ mg/m}^3$ ). An uncertainty factor of 10 ( $UF_{\text{intraspecies}}$ ) was used for the acute AAL and an uncertainty factor of 80 ( $UF_{\text{intraspecies}}$ ,  $UF_{\text{chronic}}$ , and  $UF_{\text{time}}$ ) was used for the chronic AAL.

Based on its health effect profile, the board recommends retaining ethylenediamine on the North Carolina TAPS list. Due to its significant reduction in emissions combined with its minimal emissions reported in 2012, the board designates ethylenediamine as a lower priority for AAL review.

## 5.9 Fluorides

**Recommendation: Retain the AAL**

**Priority: No review recommended at this time**

Ninety eight percent of fluorides emissions in North Carolina result from phosphate fertilizer, glass, and brick manufacturing operations. Fluorides emissions have decreased approximately 81 percent since 1997 (from 2.1 million pounds to 0.42 million pounds in 2012).

Fluorides refers to a subset of compounds including fluorine gas and inorganic, ionizable fluoride compounds and excluding hydrogen fluoride (HF). Substances such as sodium fluoride (NaF), potassium fluoride (KF), calcium fluoride ( $\text{CaF}_2$ ), ammonium fluoride ( $\text{NH}_4\text{F}$ ) and silicon tetrafluoride ( $\text{SiF}_4$ ) are included in this chemical grouping. Fluorides have both an acute and a chronic AAL, both of which date back to 1987. Fluorides may cause eye, skin, and respiratory irritation following acute exposures and skeletal fluorosis following chronic exposures. The one-hour acute AAL is  $0.25 \text{ mg/m}^3$  and the 24-hour AAL is  $0.016 \text{ mg/m}^3$ . Both the acute and chronic AAL were derived using a factored

TLV method and an 8-hour TLV of 2.5 mg/m<sup>3</sup>. An uncertainty factor of 10 (UF<sub>intraspecies</sub>) was used for the acute AAL and an uncertainty factor of 160 (UF<sub>intraspecies</sub>, UF<sub>chronic</sub>, UF<sub>time</sub>, and UF<sub>severity</sub>) was used for the chronic AAL.

The ACGIH TLV for fluorides has not been revised since it was used as the basis for the North Carolina AAL in 1987. The TLV corresponds exactly with the EPA Acute AEGL-1 for fluorine (1.7 ppm equivalent to 2.5 mg/m<sup>3</sup>) suggesting that no new inhalation toxicological data exists for fluorides. In the absence of new toxicological data or outside agency reviews, the board recommends that fluorides be retained on the North Carolina TAPs list as the basis for the AAL has not changed. No review is recommended at this time.

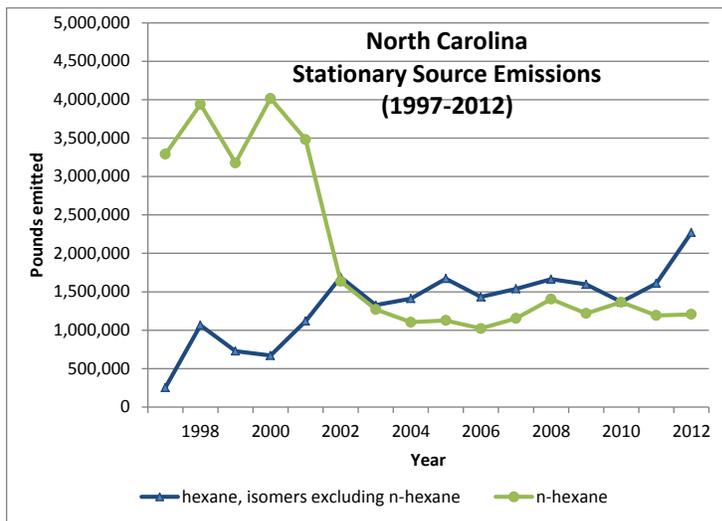
### 5.10 Hexane isomers except n-hexane

**Recommendation: Retain the AAL**

**Priority: High for expanded literature review**

Hexane isomers is a mixture composed of four structural isomers: 2-methylpentane, 3-methylpentane, 2, 2-dimethylbutane, and 2, 3-dimethylbutane or any combination of these in varying ratios. Three facilities account for 97 percent of total emissions statewide with a single facility responsible for 60 percent of emissions. These include a botanical extraction facility and two soybean processors. Emissions of hexane isomers has increased 800 percent since 1997 from 252,709 pounds to 2.3 million pounds in 2012. The marked increase in hexane isomers emissions is linked with increased production. The increase also appears to track with a decrease in n-hexane emissions during the same time interval suggesting possible industrial solvent substitution (Figure 3.)

**Figure 3. Comparison of hexane isomers and n-hexane emissions between 1997 and 2012**



## FINAL DRAFT

The current North Carolina one hour acute AAL for hexane isomers is 360 mg/m<sup>3</sup>. It was derived from an ACGIH STEL of 1,000 ppm (equivalent to 3600 mg/m<sup>3</sup>) and an uncertainty factor of 10 (UF<sub>intraspecies</sub>). The basis for the AAL is mucous membrane irritation and narcotic symptoms including dizziness, nausea, and headache.

Toxicological studies conducted on mixtures such as hexane isomers are sparse due to the complex and variable nature of such blends. Research studies are generally conducted with individual components and inferences are made for the mixture of interest. Review articles report that unlike n-hexane, hexane isomers is not associated with peripheral neuropathy in animal studies (Galvin and Bond, 1999a&b, Galvin and Panson, 1999). However, only 3-methyl pentane has been evaluated via the inhalation route in studies focusing on neurotoxic endpoints. Oral studies with 2-methylpentane and 2, 3-dimethylbutane demonstrated no dramatic differences in potency between the two substances . The EPA has not established an RfC or RfD for these compounds or for the mixture. However, hexane isomers is included in the Phase1 group of chemicals being evaluated for TOX 21, EPA's initiative to screen and prioritize thousands of chemicals for toxicity using robotic high-throughput screening assays. ATSDR has developed a toxicological profile for total petroleum hydrocarbons (which includes these compounds); however the composition of the mixtures tested is often unknown making extrapolation difficult.

Based largely on its increasing emissions and inclusion in future EPA testing, the board recommends that hexane isomers be retained on the North Carolina TAPs list. A more in-depth literature review to provide the necessary information to assign a priority level for future AAL review is recommended. For the interim, a high priority is assigned for an enhanced literature review for hexane isomers.

### 5.11 Hydrogen sulfide

#### **Recommendation: Retain the AAL**

#### **Priority: High for review**

Hydrogen sulfide is emitted primarily from phosphate fertilizer operations and pulp and paper mills in North Carolina. Its stationary source emissions have decreased by approximately 56 percent since 1997 (from approximately 4.8 million pounds to 2.1 million pounds in 2012).

The North Carolina AAL for hydrogen sulfide was reviewed by the NCSAB in 2001. The board recommended that it be changed from an acute 15-minute AAL of 2.1 mg/<sup>3</sup> to a chronic 24-hour AAL of 0.12 mg/m<sup>3</sup> based on nasal toxicity in animal studies. This recommendation was accepted by the Environmental Management

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Commission (EMC) in 2005. The board recommends retaining hydrogen sulfide on the North Carolina TAPs list based on its toxicity and significant statewide emissions. Although hydrogen sulfide has a relatively recent AAL review and update, the board recommends that it be assigned a higher priority for further review based on recent epidemiological research linking ambient hydrogen sulfide concentrations and adverse human health effects (Heaney et al, 2011; Drimal et al, 2010).

### 5.12 Methyl ethyl ketone (MEK)

**Recommendation: Retain the AAL**

**Priority: Low for review**

Methyl ethyl ketone (MEK) is released from several sources in North Carolina including plastics manufacturing, pulp and paper mills, and furniture manufacturing. Emissions have decreased approximately 91 percent since 1997 (from 4.3 million pounds to 0.37 million pounds).

Inhalation of methyl ethyl ketone causes nasal, ocular, and respiratory tract irritation. Methyl ethyl ketone has both an acute and chronic AAL, both of which date back to 1987. The one-hour acute AAL is 88.5 mg/m<sup>3</sup> and the 24-hour chronic AAL is 3.7 mg/m<sup>3</sup>. The acute AAL was derived using a factored TLV method, a 15-minute STEL of 300 ppm (equivalent to 885 mg/m<sup>3</sup>), and an uncertainty factor of 10 (UF<sub>intraspecies</sub>). The chronic AAL was derived using a factored TLV method, an 8-hour TLV of 200 ppm (equivalent to 590 mg/m<sup>3</sup>), and an uncertainty factor of 160 (UF<sub>intraspecies</sub>, UF<sub>chronic</sub>, UF<sub>time</sub>, and UF<sub>severity</sub>).

The EPA IRIS program evaluated the toxicological properties of methyl ethyl ketone in 2003 and recommended an RfC of 5 mg/m<sup>3</sup> based on skeletal variations observed in a rodent developmental study. The EPA concluded there were inadequate data for a human carcinogenic assessment of methyl ethyl ketone. The EPA delisted methyl ethyl ketone from the HAP list in 2005.

The board recommends retaining methyl ethyl ketone on the North Carolina TAPs list due to its acute irritant properties; however it is assigned a low priority for review based on its decreasing emissions and toxicity profile.

### 5.13 Methyl mercaptan

**Recommendation: Retain the AAL**

**Priority: High for review**

Eight-six percent of the statewide emissions of methyl mercaptan are produced by two paper mills although it is emitted from all paper mills. Its emissions have decreased by approximately 53 percent since 1997 (from 795,500 pounds to approximately 375,000 pounds in 2012).

The current one-hour acute AAL for methyl mercaptan, established in 1987, is 0.05 mg/m<sup>3</sup>. Methyl mercaptan is an irritant. Its AAL was based on pulmonary edema and respiratory effects although no specific levels of exposure were available at that time. The AAL was derived using a factored TLV method, a TLV of 0.5 ppm (equivalent to 1 mg/m<sup>3</sup>), and an uncertainty factor of 20 (UF<sub>intraspecies</sub> and UF<sub>severity</sub>). This uncertainty factor included an additional severity factor of two due to the seriousness of the critical health effect. It should be noted that while the acute toxicity of methyl mercaptan is comparable to that of hydrogen sulfide, its odor threshold is much lower and has been reported as 0.0016 ppm (equivalent to 0.003 mg/m<sup>3</sup>).

A 1981 chronic animal inhalation study demonstrating weight loss in animals exposed to 57 ppm methyl mercaptan (equivalent to 110 mg/m<sup>3</sup>) could potentially serve as a basis for a chronic AAL (Tansy et al, 1981). Although no new toxicological information is available for methyl mercaptan, there are new interpretations of the historical data for both acute and chronic exposures. In 2010, the OSHA PEL increased by a factor of 20 due to a court order that returned it to its previous level.

Given its toxicological properties and that its emissions are concentrated in two locations in the state, the board recommends retaining methyl mercaptan on the TAPS list. The board is receptive to establishing both acute and chronic AALs for methyl mercaptan based on new interpretations of historical data. Therefore, methyl mercaptan is assigned a higher priority for future review.

### 5.14 Nitric Acid

**Recommendation: Retain the AAL**

**Priority: No review recommended at this time**

In North Carolina, nitric acid is emitted primarily from pharmaceutical, fertilizer, and paper facilities as well as dye/fabric/textile manufacturers. Its emissions have decreased by approximately 74 percent since 1997 (from 42,904 pounds to approximately 11,350 pounds in 2012).

The current one-hour acute AAL for nitric acid, established in 1987, is 1.0 mg/m<sup>3</sup>. The critical human health endpoint upon which the AAL is based is eye and nasal irritation, similar to acetic acid. Dental erosion has also been observed in animal studies following exposures to high concentrations of nitric acid. The AAL was derived using a factored TLV method, a 15-minute STEL of 4 ppm (equivalent to 10 mg/m<sup>3</sup>), and an uncertainty factor of 10 (UF<sub>intraspecies</sub>).

Review of the literature post-1990 indicates no significant changes in toxicological findings for nitric acid evaluated by ACGIH. Hence, the original data used to establish the current AAL does not appear to have changed. Based on these preliminary findings, the board found no compelling reason to eliminate the nitric acid AAL from the North Carolina TAPs list. In the absence of new data to evaluate, the board considered it worthwhile to investigate the appropriateness of using short-term exposure data to extrapolate to long-term exposure guidelines. Therefore, the AAL for nitric acid was assigned low priority for further review.

### 5.15 Sulfuric acid

**Recommendation: Retain the AAL**

**Priority: High for review**

The primary emission sources of sulfuric acid in North Carolina are coal-fired power plants. Paper production represents the second most predominant source of emissions. Statewide sulfuric acid emissions have decreased approximately sixty-six percent since 1997 (from 7.9 million pounds to 2.7 million pounds in 2012).

Sulfuric acid emissions from coal-fired utilities are expected to continue to decline in future years although the magnitude of the reductions cannot be fully predicted. Future reduced emissions will result from sulfur dioxide emission controls installed to meet the 2013 compliance deadline for the North Carolina Clean Smokestacks Act and the requirements for the recently finalized EPA Mercury and Air Toxics (MATS) NESHAP. The final 2013 emissions inventory reflects an approximate 10 percent decrease relative to 2012 inventory results.

North Carolina currently has two AALs for sulfuric acid, both of which were established in 1987. Information associated with each value is detailed in Table 3.

**Table 3. Comparison of acute and chronic sulfuric acid AALs**

<b>Sulfuric Acid</b>	<b>Acute AAL</b>	<b>Chronic AAL</b>
Current NC Value	0.1 mg/m <sup>3</sup>	0.012 mg/m <sup>3</sup>
Critical Health Endpoint	Eye and nasal irritation	Impaired pulmonary function
Methodology	Factored TLV	Factored TLV
Uncertainty Factor <sup>1</sup>	10	80
1987 ACGIH TLV	1 mg/m <sup>3</sup>	1 mg/m <sup>3</sup>
2013 ACGIH TLV	0.2 mg/m <sup>3</sup>	0.2 mg/m <sup>3</sup>

<sup>1</sup> Uncertainty factors assigned in accordance with guidance included in 1986/1987 North Carolina Academy of Sciences: Report and Recommendations of the Air Toxics Panel.

The physical form of sulfuric acid has been linked with different adverse health effects (vapor vs. mist). An increasing literature base investigating the health hazards associated with sulfuric acid inorganic mists suggests that such mists may have carcinogenic potential (IARC, 2012; NTP, 2014). Board members concurred that the AAL for sulfuric acid should be assigned a higher priority for review based on the newer findings, publication of a more stringent ACGIH TLV than was used in 1987, and the fact that other states and agencies have established separate ambient exposure levels for different forms of sulfuric acid.

### **5.16 Tetrachloro-1,2-difluoroethane, 1,1,2,2- (CFC-112)**

**Recommendation: Delist the AAL**

**Priority: N/A**

No stationary source emissions were reported for tetrachloro-1,2-difluoroethane, 1,1,2,2 (CFC-112) in North Carolina in 1997 or any year since.

The 24-hour chronic AAL, established in 1987, is 52 mg/m<sup>3</sup>. The basis for the AAL is leukopenia (decreased white blood cells) and liver effects observed in rats following subchronic exposures of 1000 ppm. The AAL was derived using a factored TLV method, an 8-hour TLV of 500 ppm (equivalent to 4170 mg/m<sup>3</sup>) and an uncertainty factor of 80 (UF<sub>intraspecies</sub>, UF<sub>chronic</sub>, and UF<sub>time</sub>).

Based on the lack of historical emissions for CFC-112 and its phase-out in the United States under the Montreal protocol, the board recommends that its AAL be removed from the North Carolina TAPS list.

### 5.17 Tetrachloro-2,2-difluoroethane, 1,1,2,2- (CFC-112a)

**Recommendation: Delist the AAL**

**Priority: N/A**

No stationary source emissions were reported for tetrachloro-2,2-difluoroethane, 1,1,1,2 (CFC-112a) in North Carolina in 1997 or any year since.

The toxicological profile for CFC-112a mirrors that of tetrachloro-1,2-difluoroethane, 1,1,2,2 (CFC-112). The 24-hour chronic AAL, established in 1987, is 52 mg/m<sup>3</sup>. The basis for the AAL is leukopenia (decreased white blood cells) and liver effects observed in rats following subchronic exposures of 1000 ppm. The AAL was derived using a factored TLV method, an 8-hour TLV of 500 ppm (equivalent to 4170 mg/m<sup>3</sup>) and an uncertainty factor of 80 (UF<sub>intraspecies</sub>, UF<sub>chronic</sub>, and UF<sub>time</sub>).

Based on the lack of historical emissions for CFC-112a and its phase-out in the United States under the Montreal protocol, the board recommends that its AAL be removed from the North Carolina TAPS list.

### 5.18 Toluene diisocyanate

**Recommendation: Retain the AAL**

**Priority: Low for review**

The 2,4 and 2,6 isomers of toluene diisocyanate are released primarily from sites manufacturing urethane foam and rubber products. Their emissions have decreased approximately 46 percent since 1997 (from 1,172 pounds to 635 pounds).

Toluene diisocyanate is a potent human respiratory sensitizer. Occupational exposure studies have reported asthma and/or chemical bronchitis symptoms following exposures.

The North Carolina AAL for toluene diisocyanate was reviewed by the NCSAB in 1997. The board recommended that its 24-hour chronic AAL be changed from 0.07 ppb to 0.03 ppb (equivalent to 0.0002 mg/m<sup>3</sup>) based on adverse respiratory effects. This recommendation was accepted by the Environmental Management Commission (EMC) in 2002.

The board recommends retaining toluene diisocyanate on the North Carolina TAPS list due to its potency as a respiratory toxicant. Based on its relatively recent review and update, the board assigned a low priority for further review.

### 5.19 Trichloro-1,1,2-trifluoroethane, 1,2,2- (CFC-113)

**Recommendation: Delist the AAL**

**Priority: N/A**

Chemical manufacturing, military facilities, textile and fabric finishing, and tire and rubber manufacturing are the predominant stationary sources emitting trichloro-1,1,1-trifluoroethane (CFC-113) in North Carolina. Its emissions have decreased approximately 99 percent since 1997 (from 122,941 pounds to 1,441 pounds).

Trichloro-1,1-2-trifluoroethane, 1,2,2 is an acute cardiac sensitizer (increased cardiac sensitivity to epinephrine). Its one-hour acute AAL, established in 1987, is 958 mg/m<sup>3</sup>. The AAL was derived using a factored TLV method, a 15-minute STEL of 1250 ppm (equivalent to 9500 mg/m<sup>3</sup>), and an uncertainty factor of 10 (UF<sub>intraspecies</sub>).

Based on its significant reductions in emissions and its phase-out in the United States under the Montreal protocol, the board recommends that its AAL be removed from the North Carolina TAPs list.

### 5.20 Trichlorofluoromethane (CFC-11)

**Recommendation: Delist the AAL**

**Priority: N/A**

Trichlorofluoromethane (CFC-11) is emitted primarily in the state from tire and rubber manufacturing operations and electric power generation facilities. Its emissions have decreased approximately 94 percent since 1997 (from 47,382 pounds to 2,820 pounds).

Trichlorofluoromethane is a cardiac sensitizer. Its one-hour acute AAL, established in 1987, is 562 mg/m<sup>3</sup>. The AAL was derived using a factored TLV method, a 15-minute STEL of 1000 ppm (equivalent to 5600 mg/m<sup>3</sup>), and an uncertainty factor of 10(UF<sub>intraspecies</sub>).

Based on its significant reductions in emissions and its phase-out in the United States under the Montreal protocol, the board recommends that its AAL be removed from the North Carolina TAPs list.

## 6.0 Conclusions

The board recommends that fourteen of the twenty pollutants (acetic acid, ammonia, bromine, ethyl acetate, ethyl mercaptan, ethylenediamine, fluorides, hexane isomers, hydrogen sulfide, methyl ethyl ketone, methyl mercaptan, nitric acid and sulfuric acid) remain on the list as TAPs. Of these, ammonia, hexane isomers, hydrogen sulfide, methyl mercaptan, and sulfuric acid were considered to be of higher priority for future review. Six pollutants classified as ozone-depleting compounds (CFC-11, CFC-12, CFC-112, CFC-112a, CFC-113, and HCFC-21) were recommended for removal from the list. These compounds are effectively banned from use or production in the United States under the Montreal Protocol, although exemptions are possible. Emissions of these six pollutants have decreased 79-99 percent since 1997 and are expected to continue to decrease (Table 4). The NCSAB recommendations are summarized in Table 5.

**Table 4. Pollutants recommended for delisting**

Chemical Name	Synonym	Montreal Protocol Designation	US EPA Designation	Montreal Protocol Phase Out <sup>1</sup>	US EPA Phase Out	%Emissions Decrease
Trichlorofluoromethane	CFC-11	Annex A (Group 1)	Class 1 (Group 1)	January 1, 1996 (Non-article V party) January 1, 2010 (Article V)	January 1, 1996	94%
Dichlorodifluoromethane	CFC-12	Annex A (Group 1)	Class 1 (Group 1)	January 1, 1996 (Non-article V party) January 1, 2010 (Article V)	January 1, 1996	79%
Tetrachloro-1,2-difluoroethane, 1,1,2,2-	CFC-112	Annex B (Group 1)	Class 1 (Group 3)	January 1, 1996 (Non-article V party) January 1, 2010 (Article V)	January 1, 1996	N/A
Tetrachloro-2,2-difluoroethane, 1,1,1,2-	CFC-112a <sup>2</sup>	Annex B (Group 1)	Class 1 (Group 3)	January 1, 1996 (Non-article V party) January 1, 2010 (Article V)	January 1, 1996	N/A
Trichloro, 1,1,2- trifluoroethane, 1,2,2-	CFC-113	Annex A (Group 1)	Class 1 (Group 1)	January 1, 1996 (Non-article V party) January 1, 2010 (Article V)	January 1, 1996	99%
Dichlorofluoromethane	HCFC-21	Annex C (Group 1)	Class II	January 1, 2004 (Non-Article V) January 1, 2016 (Article V)	90% reduction by 2015 100% reduction by 2030	95%

<sup>1</sup> Article 5(1) Party is a Party classified at a meeting of the Parties as a developing country and whose annual per capita consumption of Annex A and Annex B substances are below the limits set in Article 5 of the Montreal Protocol.

<sup>2</sup> CFC-112a is an isomer of CFC-112 and therefore is treated the same under the Montreal Protocol.

## FINAL DRAFT

**Table 5. NCSAB Recommendations**

Air Pollutant	Recommendation	Review Priority
Acetic acid	Retain	No review recommended at this time
Ammonia	Retain	High
Bromine	Retain	No review recommended at this time
Dichlorodifluoromethane (CFC-12)	Delist	N/A
Dichlorofluoromethane	Delist	N/A
Ethyl acetate	Retain	No review recommended at this time
Ethyl mercaptan (ethanethiol)	Retain	No review recommended at this time
Ethylenediamine	Retain	Low
Fluorides	Retain	No review recommended at this time
Hexane isomers except n-hexane	Retain	High
Hydrogen sulfide	Retain	High
Methyl ethyl ketone	Retain	Low
Methyl mercaptan	Retain	High
Nitric acid	Retain	No review recommended at this time
Sulfuric acid	Retain	High
Tetrachloro-1,2-difluoroethane, 1,1,2,2- (CFC-112)	Delist	N/A
Tetrachloro-2,2-difluoroethane, 1,1,1,2- (CFC-112a)	Delist	N/A
Toluene diisocyanate,2,4 and 2,6- isomers	Retain	Low
Trichloro, 1,1,2- trifluoroethane, 1,2,2- (CFC-113)	Delist	N/A
Trichlorofluoromethane (CFC-11)	Delist	N/A

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Minnesota Department of Health (Air Values Table):  
<http://www.health.state.mn.us/divs/eh/risk/guidance/air/table.html>

North Carolina Academy of Sciences: Report and Recommendations of the Air Toxics Panel (1986/1987)

## FINAL DRAFT

North Carolina Division of Air Quality (Table of Toxic Air Pollutant Guidelines):  
<http://daq.state.nc.us/rules/rules/D1104.pdf>

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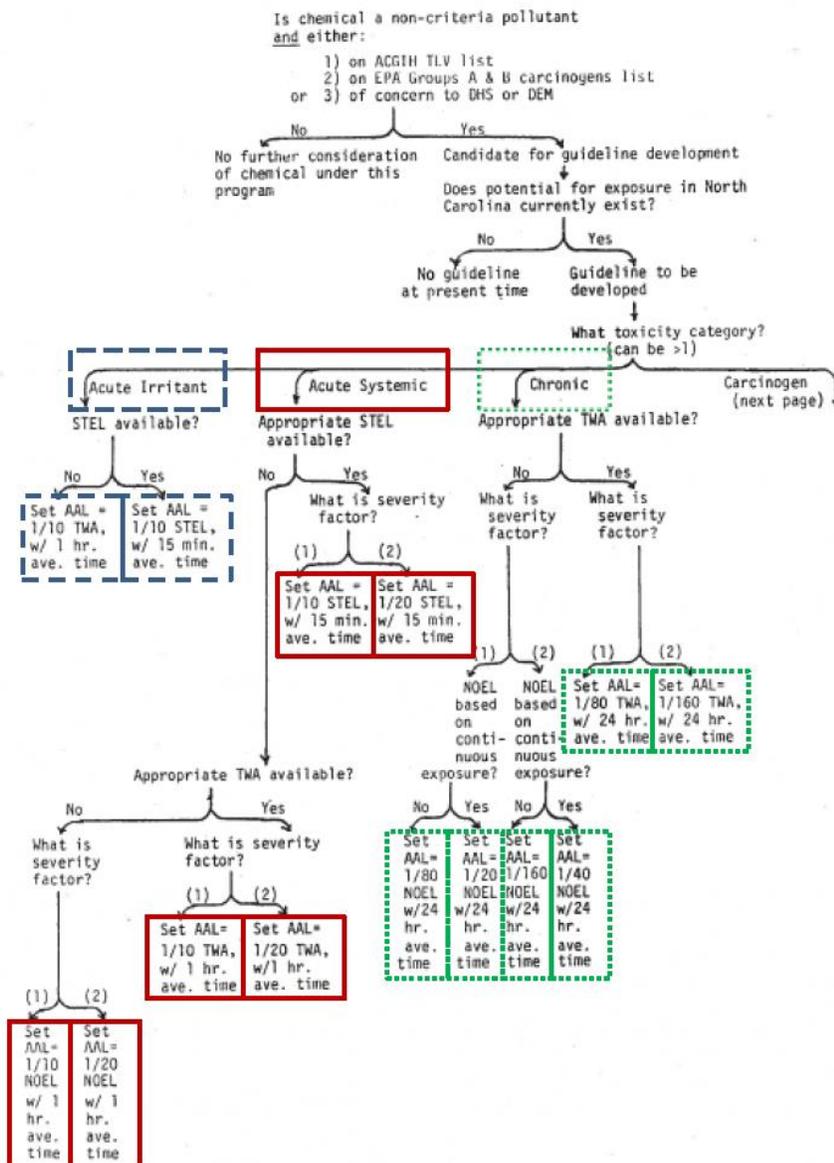
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<http://www.tceq.texas.gov/toxicology/esl/ESLMain.html>

## 8.0 Appendices

### Appendix A. Uncertainty factor decision tree



Source: North Carolina Academy of Sciences Report and Recommendations of the Air Toxics Panel (1987/1988)

## FINAL DRAFT

### Appendix B. Comparison of North Carolina AALs for twenty TAPs with air levels established by other agencies

Air Pollutants unique to North Carolina TAPs List	CAS No.	ATSDR (mg/m <sup>3</sup> ) <sup>1</sup>	IRIS (mg/m <sup>3</sup> )	Regulated State Air Concentration Levels (mg/m <sup>3</sup> )				
				North Carolina	California	Michigan	Minnesota	Texas
Acetic acid	64-19-7			3.7 (1 hour)		0.25 (8 hour)		0.015 (1 hour) 0.025 (annual)
Ammonia	7664-41-7	<u>1.2 (1 hour)</u> <u>0.07 (annual)</u> <u>2004</u>	<u>RfC= 0.1 (1991)</u> <u>Draft RfC = 0.3</u> <u>(2013)</u>	2.7 (1 hour)	3.2 (1 hour) 0.2 (annual)	0.1 (24 hour)	3.2 (1 hour) 0.080 (annual)	0.17 (1 hour) 0.017 (annual)
Bromine	7726-95-6			0.2 (1 hour)		0.007 ( 8 hour)		0.007 (1 hour) 0.0007 (annual)
Dichlorodifluoromethane (CFC-12)	75-71-8		<u>RfD (1995)</u>	248 (24 hour)		50 (8 hour)		50 (1 hour) 5 (annual)
Dichlorofluoromethane (HCFC-21)	75-43-4			0.5 (24 hour)				0.42 (1 hour) 0.042 (annual)
Ethyl acetate	141-78-6		<u>RfD (1998)</u>	140 ( 1hour)		3.2 (24 hour)		1.4 (1 hour) 1.44 (annual)
Ethyl mercaptan (ethanethiol)	75-08-1			0.1 (1 hour)				0.0008 (1 hour) .0013 (annual)
Ethylenediamine	107-15-3			2.5 (1 hour) 0.3 (24 hour)		0.00003 (annual)		0.25 (1 hour) 0.025 (annual)
Fluorides	Various	<u>0.01</u> <u>(1 hour MRL for</u> <u>fluorides as HF)</u> <u>2003</u>		0.25 (1 hour) 0.016 (24 hour)	0.24 (1 hour) 0.13 (annual)	0.14 (1 hour) 14 (annual) both HF	0.24 1 hour (HF)	hydrogen fluoride and soluble inorganic fluorides, as HF 0.018 (1 hour) .0087 (long -term)
Hexane isomers except n-hexane	Various			360 (1 hour)				
2-methylpentane	107-83-5					17.6 ( 8 hour)		3.5 (1 hour) 0.35 (annual)
3-methylpentane	96-14-0					3.5 (8 hour)		3.5 (1 hour) 0.35 (annual)
2,2-dimethylbutane	75-83-2							3.5 (1 hour) 0.35 (annual)
2,3-dimethylbutane	79-29-8					3.5 ( 8 hour)		1.48 (1 hour) 0.35 (annual)

## FINAL DRAFT

### Appendix B. Comparison of North Carolina AALs for twenty TAPs with air levels established by other agencies (cont.)

Air Pollutants unique to North Carolina TAPs List	CAS No.	ATSDR (mg/m <sup>3</sup> ) <sup>1</sup>	IRIS (mg/m <sup>3</sup> )	Regulated State Air Concentration Levels (mg/m <sup>3</sup> )				
				North Carolina	California	Michigan	Minnesota	Texas
Methyl ethyl ketone	78-93-3		<u>RfC= 5 (2003)</u>	88.5 (1 hour) 3.7 (24 hour)	13 (1 hour)	5 (24 hour)	10 (1 hour)	1.3 (1 hour) 2.6 (annual)
Methyl mercaptan	74-93-1	<u>No MRL</u> <u>Derived</u> <sup>2</sup> 1992		0.05 (1 hour)		0.01 (1 hour)		0.002 (1 hour) 0.001 (annual)
Nitric acid	7697-37-2			1 (1 hour)	0.086 (1 hour)	0.05 ( 8 hour)	0.13 (1 hour)	0.05 (1 hour) 0.005 (annual)
Sulfuric acid	7664-93-9	<u>No MRL</u> <u>Derived</u> <sup>2</sup> 1998		0.1 (1 hour) 0.012 (24 hour)	0.12 (1 hour) 0.001 (annual)	0.12 (1 hour) 0.001 (Annual)		TCEQ Reg Standard 0.7 (30 minute)
Tetrachloro-1,2-difluoroethane, 1,1,2,2-(CFC-112)	76-12-0			52 (24 hour)				4.2 (1 hour) 0.4 (annual)
Tetrachloro-2,2-difluoroethane, 1,1,1,2-(CFC-112a)	76-11-9			52 (24 hour)				8.3 (1 hour) 0.8 (annual)
Toluene diisocyanate,2,4 and 2,6-isomers	91-08-7		<u>RfC = 0.00008</u> <u>(1995)</u>	0.0002 (24 hour)	0.00007 (annual) 0.00009 (carcinogen)	0.00007 (annual) 0.00003 (annual-carcinogen)	0.00008 (annual)	0.0007 (1 hour) 0.0001 (annual)
Trichloro, 1,1,2-trifluoroethane, 1,2,2-(CFC-113)	76-13-1		<u>RfD (1996)</u>	950 (1 hour)		19 (24 hour)		38 (1 hour) 3.8 (annual)
Trichlorofluoromethane (CFC-11)	75-69-4		<u>RfD (1987)</u>	560 (1 hour)		56 (1 hour)		28 (1 hour) 5.6 (annual)

<sup>1</sup> ATSDR ppm values converted to ug/m3 using the formula [ppm \* Molecular weight]/ 24.45. Calculated values rounded to nearest 10.

<sup>2</sup> ATSDR document exists; however no MRL was derived or reported.

Source: Agency and state websites as listed under Section 7.0 (References).

**FINAL DRAFT**

**Appendix C. AAL basis summary for twenty North Carolina TAPs**

Air Pollutants unique to North Carolina TAPs List	CAS No.	NC AAL (mg/m <sup>3</sup> )	AAL Averaging Time	AAL Date	Critical Health Endpoint for AAL <sup>1</sup>	Methodology	NC Uncertainty Factor <sup>2</sup>	1987-1988 ACGIH TLV (mg/m <sup>3</sup> ) <sup>3</sup>	2013 ACGIH TLV (mg/m <sup>3</sup> ) <sup>3</sup>	Difference between 1987 and 2013 TLVs
Acetic acid	64-19-7	3.7	1 hour (acute) <sup>4</sup>	1987 (1997) <sup>4</sup>	URT and eye irritation, pulm function	Factored TLV (STEL)	10	37 (STEL) 25 (TWA)	37 (STEL) 25 (TWA)	No change
Ammonia	7664-41-7	2.7	1 hour (acute) <sup>4</sup>	1987 (1997) <sup>4</sup>	Eye damage, URT irritation	Factored TLV (STEL)	10	27 (STEL) 18 (TWA)	27 (STEL) 18 (TWA)	No change
Bromine	7726-95-6	0.2	1 hour (acute) <sup>4</sup>	1987 (1997) <sup>4</sup>	URT & LRT irritation, lung damage	Factored TLV (STEL)	10	2 (STEL) 0.7 (TWA)	1.3 (STEL) 0.7 (TWA)	STEL reduced from 0.3 to 0.2 ppm
Dichlorodifluoromethane (CFC-12)	75-71-8	248	24 hour (chronic)	1987	Cardiac sensitization	Factored TLV (TWA)	20	4,950 (TWA)	4,950 (TWA)	No change
Dichlorofluoromethane (HCFC-21)	75-43-4	0.5	24 hour (chronic)	1987	Liver damage	Factored TLV (TWA)	80	40 (TWA)	40 (TWA)	No change
Ethyl acetate	141-78-6	140	1 hour (acute)	1987	URT and eye irritation	Factored TLV (TWA)	10	1,400 (TWA)	1,400 (TWA)	No change
Ethyl mercaptan (ethanethiol)	75-08-1	0.1	1 hour (acute)	1987	URT irritation, CNS impariment	Factored TLV (TWA)	10	1 (TWA)	1 (TWA)	No change
Ethylenediamine	107-15-3	2.5 0.3	1 hour (acute) 24 hour (chronic)	1987	TLV basis not reported. NC doc indicates corrosivity and allergic potential. Fetotoxin	Factored TLV (TWA)	10 (acute) 80 (chronic)	25 (TWA)	25 (TWA)	No change
Fluorides	Various	0.25 0.016	1 hour (acute) 24 hour (chronic)	1987	Bone damage, fluorosis	Factored TLV (TWA)	10 (acute) 160 (chronic)	2.5 (TWA)	2.5 (TWA)	No change
Hexane isomers except n-hexane	Various	360	1 hour (acute) <sup>4</sup>	1987 (1997) <sup>4</sup>	CNS impairment, URT and eye irritation	Factored TLV (STEL)	10	3,600 (STEL) 1,800 (TWA)	3,600 (STEL) 1,800 (TWA)	No change
Hydrogen sulfide	7783-06-4	0.12 <sup>5</sup>	24 hour (chronic)	2006	Nasal lesions following 10 week exposure (rats) (Source: NC AAL document)	NOAEL	120 <sup>6</sup>	21 (STEL) 14 (TWA)	7 (STEL) 1.4 (TWA)	STEL reduced by a factor of 3 TWA reduced by a factor of 10
Methyl ethyl ketone	78-93-3	88.5 3.7	1 hour (acute) <sup>4</sup> 24 hour (chronic)	1987 (1997) <sup>4</sup>	URT irritation, CNS and PNS impairment	Factored TLV (TWA) Factored TLV (STEL)	10 (acute) 160 (chronic)	885 (STEL) 590 (TWA)	885 (STEL) 590 (TWA)	No change
Methyl mercaptan	74-93-1	0.05	1 hour (acute)	1987	Liver damage	Factored TLV (TWA)	20	1 (TWA)	1 (TWA)	No change
Nitric acid	7697-37-2	1	1 hour (acute)	1987 (1997) <sup>4</sup>	URT and eye irritation, dental erosion	Factored TLV (STEL)	10	10 (STEL) 5 (TWA)	10 (STEL) 5 (TWA)	No change

## FINAL DRAFT

### Appendix C. AAL basis summary for twenty North Carolina TAPs (cont.)

Air Pollutants unique to North Carolina TAPs List	CAS No.	NC AAL (mg/m <sup>3</sup> )	AAL Averaging Time	AAL Date	Critical Health Endpoint for AAL <sup>1</sup>	Methodology	NC Uncertainty Factor <sup>2</sup>	1987-1988 ACGIH TLV (mg/m <sup>3</sup> ) <sup>3</sup>	2013 ACGIH TLV (mg/m <sup>3</sup> ) <sup>3</sup>	Difference between 1987 and 2013 TLVs
Sulfuric acid	7664-93-9	0.1 0.012	1 hour (acute) <sup>4</sup> 24 hour (chronic)	1987	Pulmonary function	Factored TLV (TWA)	10 (acute) 80 (chronic)	1 (TWA)	0.2 (TWA)	TWA reduced by a factor of 5
Tetrachloro-1,2-difluoroethane, 1,1,2,2- (CFC-112)	76-12-0	52	24 hour (chronic)	1987	Blood and liver effects	Factored TLV (TWA)	80	4,170 (TWA)	417	TWA reduced by factor of 10
Tetrachloro-2,2-difluoroethane, 1,1,1,2- (CFC-112a)	76-11-9	52	24 hour (chronic)	1987	Blood and liver effects	Factored TLV (TWA)	80	4,170 (TWA)	833 (TWA)	TWA reduced by factor of 5
Toluene diisocyanate, 2,4 and 2,6-isomers	91-08-7	0.0002 <sup>7</sup>	24 hour (chronic)	2002	↓ FEV <sub>1</sub> in workers (Source = NC AAL document)	NOAEL	30 <sup>8</sup>	0.15 (STEL) 0.04 (TWA) *Applies to 2,4 isomer only	0.15 (STEL) 0.04 (TWA) *Applies to single or mixture of isomers	No change
Trichloro, 1,1,2- trifluoroethane, 1,2,2- (CFC-113)	76-13-1	950	1 hour (acute)	1987 (1997) <sup>4</sup>	CNS impairment, liver damage	Factored TLV (STEL)	10	9,500 (STEL) 7,600 (TWA)	9,500 (STEL) 7,600 (TWA)	No change
Trichlorofluoromethane (CFC-11)	75-69-4	560	1 hour (acute)	1987	Cardiac sensitization	Factored TLV (TWA)	10	5,600 (TWA)	5,600 (STEL)	Changed from TWA to STEL

<sup>1</sup> Source = ACGIH 2013 TLVs and BEIs except where noted.

<sup>2</sup> Uncertainty factors assigned in accordance with guidance described in the North Carolina Academy of Sciences Report and Recommendations of the Air Toxics Panel (1986/1987) except as noted.

<sup>3</sup> ACGIH ppm values for STELs and TLVs converted to mg/m<sup>3</sup> using the formula: [(ppm \* Molecular Weight) / 24.45].

<sup>4</sup> 1987(1997) The Environmental Management Commission (EMC) adopted the 15-minute averaging time AALs as 1-hour averaging time AALs in 1997.

<sup>5</sup> Original 1987 AAL= 2.1 mg/m<sup>3</sup>. Uncertainty factor of 10 used for acute effects.

<sup>6</sup> Uncertainty factors used: 4 for experimental time adjustment, 3 for interspecies variability, and 10 for interindividual variability.

<sup>7</sup> Original 1987 AAL = 0.014 mg/m<sup>3</sup> (acute) and 0.0005 mg/m<sup>3</sup> (chronic). Uncertainty factors used: 10 (Acute) and 80 (Chronic).

<sup>8</sup> Uncertainty factors used: 3 for experimental time adjustment and 10 for interindividual variation.

**FINAL DRAFT**

**Appendix D. North Carolina stationary source emissions data summary**

<b>Air Pollutants unique to North Carolina TAPs List</b>	<b>CAS No.</b>	<b>1997 Emissions (97 NC Counties) (pounds)</b>	<b>2012 Emissions (97 NC Counties) (pounds)</b>	<b>Deminimis Reporting Levels (pounds/year)<sup>1</sup></b>	<b>% Reduction in Reported Emissions from 1997</b>	<b>Facility Types for NC Emissions</b>
Acetic acid	64-19-7	2,920,786	542,872	100	81	Noncellulosic Organic Fibers, Textiles, Fiberglass, Synthetic Rubber
Ammonia	7664-41-7	6,005,138	2,689,284	100	55	Phosphate Fertilizer, Pulp & Paper
Bromine	7726-95-6	19,271	5,195	10	73	Noncellulosic Organic Fibers, Pulp & Paper
Dichlorodifluoromethane (CFC-12)	75-71-8	64,188	13,688	100	79	Landfills
Dichlorofluoromethane (HCFC-21)	75-43-4	39,865	2,183	100	95	Landfills
Ethyl acetate	141-78-6	1,149,207	909,043	10	21	Furniture, Autobody, Plastic Packaging
Ethyl mercaptan (ethanethiol)	75-08-1	342	1,682	10	392 (increase)	Landfills
Ethylenediamine	107-15-3	65,194	640	1	99	Fabricated Metal, Organic Chemicals, Fiberglass
Fluorides	Various	2,143,553	415,879	10	81	Phosphate Fertilizer, Fiberglass, Brick
Hexane isomers excluding n-hexane	Various	252,709	2,271,203	100	799 (increase)	Food and Oil Processing, Rubber
Hydrogen sulfide	7783-06-4	4,842,737	2,121,270	1	56	Phosphate Fertilizer, Pulp & Paper

**FINAL DRAFT**

**Appendix D. North Carolina stationary source emissions data summary (cont.)**

<b>Air Pollutants unique to North Carolina TAPs List</b>	<b>CAS No.</b>	<b>1997 Emissions (97 NC Counties) (pounds)</b>	<b>2012 Emissions (97 NC Counties) (pounds)</b>	<b>Deminimis Reporting Levels (pounds/year)<sup>1</sup></b>	<b>% Reduction in Reported Emissions from 1997</b>	<b>Facility Types for NC Emissions</b>
Methyl ethyl ketone	78-93-3	4,348,522	928,349	100	79	Plastics, Engine & Turbine, Pulp & Paper
Methyl mercaptan	74-93-1	795,477	374,500	1	53	Pulp & Paper
Nitric acid	7697-37-2	42,904	11,358	100	74	Motor Vehicle Parts, Glass Products, Pharmaceuticals
Sulfuric acid	7664-93-9	7,878,306	2,714,562	100	66	Electric Generation, Phosphate Fertilizer
Tetrachloro-1,2-difluoroethane, 1,1,2,2-(CFC-112)	76-12-0	NR <sup>2</sup>	NR <sup>2</sup>	1,000	NR <sup>2</sup>	None
Tetrachloro-2,2-difluoroethane, 1,1,1,2-(CFC-112a)	76-11-9	NR <sup>2</sup>	NR <sup>2</sup>	1,000	NR <sup>2</sup>	None
Toluene diisocyanate, 2,4 and 2,6-isomers	91-08-7	1172 <sup>3</sup>	635 <sup>4</sup>	1	46	Polyurethane Foam, Rubber and Plastic Hoses
Trichloro, 1,1,2-trifluoroethane, 1,2,2-(CFC-113)	76-13-1	222,941	1,441	100	99	Plastics, Textiles, Tires
Trichlorofluoromethane (CFC-11)	75-69-4	47,382	2,820	100	94	Landfills

<sup>1</sup> Deminimis reporting level defined as the recommended emission threshold for reporting to NC emission inventory. Emission quantities below threshold may or may not be reported (strictly voluntary).

<sup>2</sup> None reported.

<sup>3</sup> Emissions for only 2,4 isomer reported.

<sup>4</sup> Emissions reported as sum of both isomers.