Technical Basis for a
Total Reduced Sulfur
Ambient Air Quality Standard

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Nebraska Department of Environmental Quality
Air Quality Section
Implementation & Monitoring Unit

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Preface

The Nebraska Department of Environmental Quality (NDEQ) is proposing to establish an ambient air quality standard for total reduced sulfur. The NDEQ is planning to present the proposal to the Environmental Quality Council at the June 1997 meeting. The purpose of this paper is to present the proposed standard and to provide supporting information. The paper was prepared based on information obtained through a scientific literature search which primarily focused on exposure to hydrogen sulfide and total reduced sulfur by way of the inhalation pathway. The literature search deliberately focused on low-level toxic effects as these are the concentrations that are expected to be encountered in ambient air. In addition, NDEQ located and reviewed all available current well-documented and well-controlled studies and information related to associated exposures.

This paper contains findings from numerous occupational, epidemiological, animal, and welfare studies. A number of on-line databases, several library searches and state surveys were used in preparing this document. Interviews were conducted with the leader of the University of Alberta research team, and with personnel from the Agency for Toxic Substances and Disease Registry, and the Nebraska Department of Health and Human Services.

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List of Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
CFR	Code of Federal Regulations
Cl_2	Chlorine
COS	Carbonyl Sulfide
CS_2	Carbon Disulfide
ERPG	Emergency Response Planning Guide
H_2S	Hydrogen Sulfide
HEC	Human Equivalency Concentration
ISA	Instrumentation Society of America
LOAEL	Lowest Observed Adverse Effect Level
MF	Modifying Factor
MSHA	Mine Safety and Health Administration
NDEQ	Nebraska Department of Environmental Quality
NDHHS	Nebraska Department of Health and Human Services
NEPA	Nebraska Environmental Protection Act
NIOSH	National Institute of Occupational Safety and Health
NO_2	Nitrogen Dioxide
NOAEL	No Observed Adverse Effect Level
OEL	Occupational Exposure Level
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Level
POMS	Profile of Mood States
PPM	Parts Per Million
RfC	Reference Concentration
SO_2	Sulfur Dioxide
STEL	Short Term Exposure Limit
TLV	Threshold Limit Value
TRS	Total Reduced Sulfur
TSP	Total Suspended Particulates
TWA	Time Weighted Average
UF	Uncertainty Factor
WHO	World Health Organization

Definitions

Acute Exposure: A one-time or short-term exposure with a duration of less than or equal to 24 hours.

Critical Effect: The first adverse effect, or its known precursor, that occurs as rate of exposure increases.

Chronic Exposure: Multiple exposures occurring over an extended period of time or a significant fraction of the exposed individual's lifetime.

Lowest-Effect Level (LEL): Lowest-Observed-Adverse-Effect Level.

Lowest-Observed-Adverse-Effect Level (LOAEL): The lowest exposure level at which there are statistically or biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group.

Modifying Factor (MF): An uncertainty factor that is greater than zero and less than or equal to 10; its magnitude reflects professional judgment regarding scientific uncertainties of the database or study design not explicitly treated by the uncertainty factors (e.g., the number of animals tested). The default value is 1.

No-Observed-Adverse-Effect Level (NOAEL): An exposure level at which there are statistically or biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group. Some effects may be produced at this level, but they are not considered as adverse or precursors to specific adverse effects.

Reference Concentration (RfC): An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily concentration received by the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. The inhalation reference concentration is for continuous inhalation exposures and is expressed typically in mg/m^3.

Subchronic Exposure: Multiple or continuous exposures occurring over about 10% of an experimental species' lifetime, usually at least 3 months.

Threshold: The dose or exposure below which a significant adverse effect is not expected (non-carcinogenic only).

Uncertainty Factor (UF): One of several, generally 10-fold factors, used in operationally deriving the RfD from experimental data. UFs are intended to account for (1) the variation in sensitivity among the members of the human population; (2) the uncertainty in extrapolating animal data to humans; (3) the uncertainty in extrapolating from data obtained in a study that is of less-than-lifetime exposure; (4) uncertainty in using LOAEL data rather than NOAEL data; and (5) the inability of any single study to adequately address all possible adverse outcomes in humans.

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1. Introduction

Total Reduced Sulfur (TRS) consists of the total sulfur from the following compounds: hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide ($(CH_3)_2S$), and dimethyl disulfide (CH_3SSCH_3) (87). These TRS compounds occur naturally in the environment. H_2S makes up the greatest proportion of TRS. As much as 90 percent of all H_2S found in the environment is naturally occurring. Naturally occurring air concentrations of H_2S are estimated to be between 0.00011 and 0.00033 parts per million (ppm) (72). The Department has concluded that from a toxicological standpoint TRS and H_2S are interchangeable. A detailed examination of this issue is found in Section 5. Throughout the document references will be made to both TRS and H_2S. When H_2S is used, it is primarily because the information NDEQ examined specifically referenced H_2S.

TRS compounds are also present in the gases from numerous industrial manufacturing processes. Levels exceeding these typical ambient concentrations have been measured in the ambient air in the Dakota City, Nebraska, area. In order to protect the public health and welfare, the NDEQ is proposing to establish ambient air quality standards for TRS. The NDEQ is planning to present the proposal to the Environmental Quality Council at the June 1997 meeting.

2. NDEQ's Regulatory Authority

The NDEQ is responsible for ensuring that all Nebraskans are not exposed to unacceptable levels of contaminants in the ambient air. In creating the Department of Environmental Quality, the Legislature declared their purpose in the opening statement of the Nebraska Environmental Protection Act (NEPA). Section 81-1501 states:

> ***Whereas the water, land, and air of this state are among its most precious resources and the pollution thereof becomes a menace to the health and welfare of each person, and the public in general, in this state and whereas pollution of these resources in this state is likewise a concern in adjoining states, the public policy of this state is hereby declared to be ...***
>
> ***to achieve and maintain such a responsible degree of purity of the natural atmosphere of this state that human beings and all other animals and plants which are indigenous to this state will flourish in approximately the same balance as they have in recent history and to promulgate laws, rules and regulations and enforce uniformly the same in such a manner as to give meaningful recognition of the protection of each element of the environment, air, water, and land***

In Section 81-1504 of NEPA, the Department is given the following express power and duty:

> ***to develop comprehensive programs for the prevention, control and abatement of new or existing pollution of the air, waters, and land of the state***

2.1 Air Pollution

Air pollution is defined in Title 129-Nebraska Air Quality Regulations as:

> **the presence in the outdoor atmosphere of one or more air contaminants or combinations thereof in such quantities and of such durations as are or may tend to be injurious to human, plant, or animal life, property, or the conduct of business**

2.2 Air Contaminants

Air contaminants are defined in Title 129 as:

> **the presence in the outdoor atmosphere of any dust, fume, mist, smoke, vapor, gas, other gaseous fluid, or particulate substance differing in composition from or exceeding in concentration the natural components of the atmosphere**

2.3 Ambient Air

Ambient air is defined in Title 129 as:

> **the portion of the atmosphere, external to buildings, to which the general public has access**

To fulfill the obligations of the statute, the Department is proposing to establish ambient standards for TRS. These ambient standards will ensure that the public throughout the state will be protected from adverse health and welfare effects caused by exposures to TRS.

3. Purpose of the Ambient Air Quality Standards

Ambient standards protect the public from adverse health and welfare effects associated with air pollutants. Federal standards exist for particulate matter, ozone, carbon monoxide, lead, nitrogen dioxide, and sulfur dioxide. No federal ambient air quality standards exist for TRS or H_2S, the primary component of TRS. A survey of 49 states conducted by the NDEQ reveals that 27 states currently have standards for H_2S (see Section 10.0)

3.1 Need for Establishing a Total Reduced Sulfur Standard

Over the last several years the NDEQ has received numerous complaints pertaining to odor in the Dakota County area. The NDEQ does not regulate odors and is not proposing to regulate odors. Odors and nuisances are typically addressed by local governments. In June 1994 the NDEQ began receiving complaints specific to H_2S exposures in the Dakota County area. A joint inspection conducted by NDEQ and the Nebraska Department of Health and Human Services (NDHSS) (formerly the Nebraska Department of Health) in August 1994 found evidence of H_2S emissions. This evidence included health complaints consistent with the effects of exposure to H_2S and visible corrosion on buildings and other outdoor structures. Subsequently, complaints specific to H_2S exposures were received from Omaha, Wakefield, and Lexington. Consistent with statutory obligations, the NDEQ in

1995 initiated an H_2S ambient monitoring program in Dakota County and found levels above what normally would be expected in the environment. Instantaneous readings were recorded as high as 47 parts per million (ppm). A review of existing state standards showed that levels detected in Dakota County exceeded other states' standards. The monitoring network was expanded in February 1996, October 1996, and again in March 1997.

In the course of monitoring, NDEQ learned that the instrumentation was subject to interferences from mercaptans. NDEQ researched alternative monitoring methods but could find no reliable, viable method specific to H_2S. While there are analytical methods to measure H_2S emissions from point sources, these methods are not applicable for ambient monitoring for two primary reasons--expense and long-term reliability. Reliable and viable methods do exist for TRS. The NDEQ reviewed information on the health effects of TRS, the physical and chemical properties of TRS, and the literature references of typical TRS emission sources. This information was compared to that of H_2S, and the NDEQ concluded that TRS is a reasonable substitute for H_2S (see Section 5.0).

Citizens in Dakota County, as well as other areas of the state, continue to express concerns over exposure to TRS. While the NDEQ has not directly correlated the reported problems with monitored levels, the symptoms reported in terms of both health and welfare are consistent with what is commonly experienced when humans are exposed to TRS.

3.2 Summary of Monitored Levels

The Department initiated ambient monitoring in Dakota County during August 1995. The instrumentation used was a Jerome 631-X portable H_2S sampler. The instrument was set up to take an instantaneous sample every five minutes. The purpose of the monitoring was to establish what levels of H2S existed in the ambient air in the Dakota City/South Sioux City area. Hydrogen sulfide levels as high as 47 ppm (instantaneous sample) have been recorded in the ambient air with the Jerome instrument. Monitoring was expanded in February 1996 to include a meteorological station. Monitoring was expanded again in October 1996 to include a continuous H_2S ambient monitor (Dasibi 4108). The Dasibi provided one-minute and one-hour averages. The Jerome and the Dasibi both were subject to interferences from mercaptans. In March 1997, the Department installed a continuous TRS ambient monitor (API 102A).

Since installing the Dasibi H_2S monitor in October 1996, the highest one-minute level the Department has recorded as of May 7, 1997, was 3.26 ppm in April 1997. Accordingly, the NDEQ has not recorded any one-minute averages that exceed the proposed health standard of 10 ppm for a one-minute timeframe.

The highest 30-minute average the Department has recorded--1.68 ppm--occurred April 25, 1997. This was well above the 0.10 ppm proposed health standard. In March 1997, 30-minute averages were commonly as high as 0.40 ppm, and in April 1997, several 30-minute averages were above 1.0 ppm. Of 30-minute averages recorded by the Department in April 1997, approximately 30 exceeded 1.0 ppm and 165 exceeded 0.40 ppm. The proposed 30-minute health standard has been exceeded routinely.

The highest 30-day average--0.012 ppm--occurred in January 1997. This was above both the 0.005 ppm and 0.01 ppm proposed 30-day standards. Although NDEQ has not established a monitoring program for relative humidity, it is expected that the relative humidity in the Dakota County area is greater than 60 percent.

The NDEQ has not yet established a monitoring program for other communities in the state. The NDEQ has plans to initiate a monitoring program in the city of Lexington during the summer of 1997.

4. Physical and Chemical Characteristics

The proposed definition of TRS in Title 129, Nebraska Air Quality Regulations, is the sum of the compounds: hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide ($(CH_3)_2S$), and dimethyl disulfide ($CH_3\ SSCH_3$) (87). The TRS compounds are often referred to as malodorous sulfur compounds. Hydrogen sulfide is a highly odorous and colorless gas with a characteristic rotten egg smell at low concentrations. Methyl mercaptan has been described as having a garlic or rotten cabbage odor. Dimethyl sulfide and dimethyl disulfide also have a pervasive and offensive odor (29). The odor perception threshold for H_2S varies considerably with individual sensitivities but is usually in the range of 0.003 to 0.012 ppm (parts per million). The odor threshold is even lower for methyl mercaptan at 0.0016 ppm (128). The California Air Resources Board contracted for an extensive study of the perception of H_2S odor. The contractor determined that at 0.03 ppm 83 percent of the population detected the odor and 40 percent experienced annoyance (99).

The following conversion is assumed for TRS: 1 ppm = 1.417 mg/m^3 (EPA CFR 40 Subpart BB).

4.1 Hydrogen Sulfide

H_2S has a chemical structure of H-S-H. The molecular weight is 34.08. It is flammable in air and can explode (96). Hydrogen sulfide dissociates in water as well as several other polar organic solvents. It is readily oxidized by several agents including: hydrogen peroxide, oxygen, ozone, and sulfur dioxide. H_2S may also react with metals and acids (73). Hydrogen sulfide has a tendency to be released from water when pH levels are slightly to very acidic (6.0 and below). As the temperature increases, the solubility in water decreases. Unless sufficiently high heats are applied in the industrial process, H_2S remains the single-largest TRS compound found in the environment. H_2S has a specific gravity of 1.19 compared to air, and therefore tends to accumulate in low-lying areas (127). This characteristic accounts for the number of poisonings resulting from oil drilling, manure sewage handling, and wastewater treatment processes (80).

4.2 Methyl Mercaptan

Methyl mercaptan has a chemical structure of CH_3-S-H and a molecular weight of 48.11. It is soluble in water and alcohol. Methyl mercaptan has a specific gravity of 0.867 and therefore is slightly lighter than air. It is volatile with a boiling point of 43° F (127). Depending upon factors such as pH and temperature, the ratio of methyl mercaptan to H_2S usually is between 1:50 and 1:100 from wastewater systems (98).

4.3 Dimethyl Sulfide

Dimethyl sulfide has a chemical structure of CH_3-S-CH_3 and a molecular weight of 62.13. It is not soluble in water but is soluble in alcohol and ether. Like methyl mercaptan, it is lighter than air. It is not volatile with a boiling point of 99° F under standard pressure (127). Dimethyl sulfide is not expected to be found in the environment in significant quantities.

4.4 Dimethyl Disulfide

The chemical structure for dimethyl disulfide is CH_3-S-S-CH_3. The molecular weight is 94.2. It is not volatile with a boiling point of 242° F (47).

4.5 Conclusion

The formation of the heavier organic sulfides such as dimethyl disulfide is not favored over the formation of H_2S (98). For practical purposes, H_2S will be the only TRS compound found in significant quantities in the environment in Nebraska.

5. TRS as a Surrogate for H_2S

A prerequisite to any ambient air quality standard is the availability of a reliable ambient monitoring method. The monitoring equipment must be selective for the compound of concern and not subject to interference from other compounds. Furthermore, the equipment must be able to operate for extended periods of time in field conditions. While there is monitoring equipment which can quantify H_2S, that equipment is designed to be used for source emissions and not applicable to continued operation in ambient environments. The ambient monitoring equipment used in many H_2S applications is subject to interferences from mercaptans. Because of the limitations of available H_2S ambient monitoring equipment, and because of the toxicological similarities of H_2S and TRS, the NDEQ elected to propose an ambient standard for TRS.

5.1 Toxicological Considerations for Using TRS as a Surrogate for H_2S

Of the compounds that make up TRS, the most studied is H_2S. Hydrogen sulfide is one of the leading causes of sudden death in the workplace and is both an irritant and a toxic asphyxiant (13). Hydrogen sulfide reversibly inhibits the cytochrome oxidase system, thereby blocking aerobic metabolism. Hydrogen sulfide poisoning symptoms are similar to cyanide except that H_2S also produces signs--such as conjunctivitis of the eyes or pulmonary edema--of an irritant gas (12).

Little information is available on the toxic effects of TRS as a whole in the ambient environment. Most human studies on TRS involve the kraft pulp and paper industry. The Department in conjunction with the Department of Health and Human Services has reviewed toxicological information to see what relationship exists among the four TRS compounds. The following are toxicological considerations for using TRS as a substitute for H_2S:

- H_2S and methyl mercaptan affect the body by a similar mechanism, causing inhibition of cellular respiration which is the precursor to asphyxiation (11, 42, 55, 56).

- Individuals exposed to TRS report similar symptoms as those exposed to H_2S. These symptoms include eye, nose and respiratory irritation, and headaches (29).
- In terms of lethal effects occurring from a short-term exposure, methyl mercaptan, dimethyl disulfide and hydrogen sulfide are of the same order of magnitude (54).
- In an LC_{50} test, an equimolar mixture of methyl mercaptan, dimethyl disulfide, and methyl sulfide was as toxic as H_2S (54). This suggests that TRS has a similar toxicity as H_2S.
- All of the TRS compounds are toxic to the respiratory system. There is experimental evidence that the nasal passages are the most sensitive part of the respiratory system for H_2S (26) and dimethyl sulfide (124). It is also suggested that the nasal passages would be sensitive targets for dimethyl sulfide and methyl mercaptan (124).

An epidemiological study on the health effects of TRS emissions from pulp mills showed that the occurrence of eye and nasal symptoms and cough was greater among those exposed to levels up to 0.07 ppm (daily average) than those not exposed to TRS emissions (29). These symptoms are similar to those reported from H2S exposure. Other epidemiological studies conducted in Finland in communities with elevated levels of TRS emissions report similar findings. Partti-Pellin distributed a self-administered questionnaire and concluded that those in the TRS-exposed community reported coughs, respiratory infections, and headaches in excess of the unexposed community (36). The relative risk for headache was significantly greater in the exposed community. In a 1992 study Haahtela found that during periods of exposure at levels above 0.025 ppm (daily average), reports of eye and respiratory symptoms were greater than during a reference period (21).

5.2 Physical Characteristics

As described in Section 4.0, the term TRS is used to refer to the total concentration of sulfur from hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide ($(CH_3)_2S$), and dimethyl disulfide ($CH_3\ SSCH_3$) (87). These compounds are the primary constituents that cause a pervasive and offensive odor in the ambient air (36). Of these four compounds, H_2S is the most likely to become gaseous in the ambient environment. Methyl mercaptan is the only TRS compound other than H_2S which may be emitted in measurable quantities. Depending upon temperature and pH, the ratio of mercaptan to H_2S is usually between 1:50 and 1:100 for waste water treatment facilities (98). In order for the compounds other than H_2S to be released into the environment, the application of heat is typically required.

5.3 Monitoring Considerations

In response to complaints of hydrogen sulfide and after review of other state standards, the Nebraska Department of Environmental Quality initiated a monitoring program for hydrogen sulfide. Subsequently, we learned the instrumentation was subject to interferences from other reduced sulfur compounds, such as mercaptans. These interferences could cause the instrument to be biased on the high side. The Department examined existing H_2S monitoring methods and found that there are no available methods which are continuous, reliable, and practicable. In order to demonstrate compliance with the standards, methods which accurately measure the compound(s) of concern must be used. Total reduced sulfur (TRS), of which H_2S is the primary constituent, can be measured in an accurate and precise manner. Monitoring for TRS eliminates interferences as all compounds are taken into consideration. As previously explained, while it is expected there will be insignificant amounts of, if any, mercaptans present in samples for H_2S, in order to address the interference issue the Department

elected to monitor for TRS. Given the physical and toxicological characteristics, monitoring for TRS accomplishes the Department's objectives to protect the public health and welfare from H_2S.

The Department conducted side-by-side monitoring in Dakota County which demonstrate that TRS is a reasonable surrogate for H_2S.

6. Potential Sources of TRS

TRS occurs naturally as a result of microbial degradation of sulfates under anaerobic conditions and the bacterial decomposition of proteins. A combination of an anaerobic environment and organic material containing sulfates will result in the production of TRS compounds (13). Hydrogen sulfide may also be produced by the action of dilute acids of iron sulfide or other sulfides, by heating sulfur with paraffin, or by the direct combination of sulfur and hydrogen. Hydrogen sulfide is present naturally in the gases from volcanoes, coal pits, gas wells (sour gas), sulfur springs, petroleum, and stagnant bodies of water. TRS may occur in sewage as a result of industrial discharges (22).

Several types of industry use hydrogen sulfide in the manufacture of products. It is used as a reagent in the production of inorganic sulfide to make dyes, plastics, leather products, pharmaceuticals, organosulfur products and rubber chemicals. It is used in metallurgical waste treatment and recovery processes to separate metals. Hydrogen sulfide used commercially in the United States is primarily derived from crude oil refining (in which sulfides occur naturally) or from "sour" natural gas. When sulfides are removed from crude oil, sulfur compounds are converted to H_2S. Most of this H_2S is converted to sulfuric acid and elemental sulfur (22). Hydrogen sulfide has been used in the production of heavy water for nuclear reactors (12). TRS can be found in the emissions from kraft pulp paper plants and tanneries.

Typical Nebraska sources that produce TRS compounds include packing plants, leather tanneries, municipal and industrial sewage treatment plants, livestock waste control facilities, composting operations, animal rendering plants, sugar beet processing plants, and oil and natural gas extraction sites.

7. Workplace and Ambient Concentrations

According to estimates provided by EPA (73), the concentration of H_2S in some selected workplaces are:

0.002-0.016 ppm	sewage treatment plant
0.054 ppm	sulfate paper mill
0.216-0.933 ppm	sewage treatment plant of a sulfate paper mill
< 15 ppm	viscose rayon plant

Ambient air is the air outside of buildings to which the public has access. Naturally occurring ambient levels of H_2S tend to be on the order of 0.00011 to 0.00033 ppm (parts per million) (73).

8. Health Effects

Relatively little information is available regarding long term exposure to low-level concentrations of TRS or its components. Exposure to TRS compounds has been studied most frequently in occupational

settings. Regarding the health effects of TRS compounds, hydrogen sulfide is the most studied due to the fact that H_2S is the most prevalent TRS compound found in the environment.

TRS compounds have documented effects on the central nervous system, the respiratory system, the mucous membranes, and the olfactory system. The human body can tolerate certain levels of TRS exposure. Oxygen will oxidize the sulfur compounds into thiosulfates which are excreted through the kidneys. If too much thiosulfate is present, the body cannot keep pace and cells may not receive sufficient oxygen to survive. For purposes of human exposures, this is the first adverse health effect, or critical effect. Hydrogen sulfide interacts with enzymes and other macromolecules, including the hemoglobin and myoglobin. These macromolecules are held together by disulfide bonds which are disrupted when exposed to sulfide in an aqueous solution. The critical target enzymes are the cytochrome oxidase which are needed to supply cells with sufficient oxygen. The effect of H_2S can be best described as asphyxiation. This is similar to how cyanide effects the body (20). Studies indicate that in healthy, moderately exercising men, inhibition of cytochrome oxidase occurs at levels of exposure above 2 ppm (8).

Long-term exposure to low-level concentrations may cause chronic health effects (13). TRS compounds produce their toxic effects from inhalation rather than from absorption through the skin (13). TRS also may decrease the body's ability to withstand infection (13). Based on available data, TRS is not considered a human carcinogen (73).

Acute exposure to higher concentrations has been well documented to cause adverse health effects. Asthmatics experienced bronchial obstruction after being exposed to 2 ppm for 30 minutes. Exposure to 10 ppm for four to seven hours causes eye irritation (conjunctivitis) to occur. After one hour of exposure to 50 ppm, eye and respiratory tract irritation is noticeable. The olfactory nerves fatigue after exposure to 100 ppm. The nerves are paralyzed at 150 ppm. Prolonged exposure to a concentration of 250 ppm may cause pulmonary edema. Breathing stops after a few minutes of exposure at 500 ppm. Respiratory paralysis and rapid collapse occurs at exposure to 1,000 ppm of H_2S. Death is imminent at 5,000 ppm (88). The following table summarizes the acute health effects:

ACUTE HEALTH EFFECTS OF TRS EXPOSURE LEVELS (88)

Clinical Effects	Exposure Level (PPM)
Bronchial obstruction in asthmatics after 30 minutes	2 (31)
Inhibited enzyme activity after 30 minutes	>2 (8)
Conjunctivitis (eye irritation) after 4-7 hours	10
Eye and respiratory irritation after 1 hour	50
Olfactory nerves fatigue after 2-5 minutes	100
Pulmonary edema after prolonged exposure	250
Breathing stops after 2-15 minutes	500
Respiratory Paralysis	1,000
Imminent Death	5,000

8.1 Human Health Studies

Although there is relatively little information available regarding long term exposure to low-level concentrations of TRS or its components, studies indicate that health effects are present when humans are exposed to low levels for a length of time. In Terre Haute, Indiana, atmospheric concentrations of H_2S reached .3 ppm (1-hour mean) due to the biodegradation of an industrial waste lagoon. As a result, there were 41 health related complaints reported. Some of the symptoms included nausea, loss of appetite, loss of sleep, headaches and shortness of breath (43). Studies surrounding pulp mills in Finland indicate that residents exposed to daily averages exceeding 0.028 ppm TRS (40 ug/m^3) were more susceptible to subjective symptoms such as headaches, depression, tiredness, and nausea (36). Another study in Finland concluded that the World Health Organization (WHO) recommendation of 0.1 ppm (daily average) did not provide protection from health effects such as cough and throat irritation (21). A case study involving a 20-month-old infant exposed to levels up to 0.6 ppm of H_2S for one year showed signs which suggested toxic encephalopathy. Ten weeks after the infant's removal from exposure the symptoms were reversed (18).

These type of epidemiological studies must be examined with caution. Most of these studies contain possible confounding factors such as stress, bias, poor exposure data, and exposure to other pollutants which may have synergistic effects. Confounding factors interfere with establishing a clear cause and effect relationship between pollutant exposure and documented health effects. Although these type of studies are not the sound scientific studies upon which an ambient air quality standard can be based, they provide good information in support of the establishment of a standard.

Well-controlled human studies were conducted by a team of researchers led by Dr. Yagesh Bhambhani of the University of Alberta, Canada. Following the Alberta Oil Well Blowout in 1982, the Bhambhani team began studying the health effects of H_2S on humans. The team conducted well-controlled studies of the effects of hydrogen sulfide on healthy, exercising men and women. The results of these studies indicate that there are significant physiological effects from short-term hydrogen sulfide exposure above 2.0 ppm (8). Specifically, the blood lactate levels in subjects were significantly increased, indicating inhibition of cytochrome oxidase activity. Cytochrome oxidase is an enzyme responsible for the electrochemical transfer of oxygen from the blood to the cells. Inhibition of this enzyme's activity results in cells' not receiving adequate oxygen and may ultimately result in asphyxiation.

Another well-controlled study evaluated the effects of H_2S exposure on the respiratory systems of asthmatic subjects (31). Although the author concluded that there were no significant changes in the respiratory capacity of the asthmatics when exposed to 2 ppm hydrogen sulfide, two of the 10 subjects experienced an increase of more than 30 percent in airway resistance and a decrease of more than 30 percent in specific airway conductance indicative of bronchial obstruction.

Table 8.1 lists each study the Department evaluated as part of development of this standard. Exposure parameters and results are provided where available.

Table 8.1: Human Health Studies & Evaluations Summary

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Adelson (2)	1966	Acute--worker exposure (levels unknown)	This was an evaluation of occupational exposures. Three people died as a result of exposure to H_2S gas in sewers. Autopsies reported each person to have hemorrhagic pulmonary edema and a greenish cast to the blood and viscera. Brain tissues were greenish purple in color. Gas chromatograph analyses of blood samples showed significant levels of hydrogen sulfide. Authors cautioned that no person should enter into an environment with H_2S gas without taking safety precautions.
Andrae (4)	1988	Chronic--children (levels of TRS unknown as they were not monitored)	The researchers distributed questionnaires to parents of 5301 children aged 6 months to 16 years. Responses were received for 4990 of the questionnaires. Children living near a paper pulp plant (source of TRS) more often had symptoms suggesting bronchial hyperreactivitiy and allergic asthma. Researchers looked at children with other environmental factors such as damp homes or exposure to second-hand smoke. The author suggests that the results indicate that various moderate environmental pollutants may have synergistic effects to increase bronchial hyperreactivity and allergy in children with a family history of allergies.
Bhambhani (8)	1991	Acute--healthy men exposed to 0, 0.5, 2, & 5 ppm H_2S on four separate occasions while exercising	The men exercised between 16 and 25 minutes, depending on their level of fitness. The study found that blood lactate levels and oxygen uptake were significantly increased when subjects were exposed to 5.0 ppm H_2S over control conditions. Subjective symptoms such as headache were eliminated by exposing the subjects to the gas through a mouth tube. The subjects were not able to detect the gas. Although the authors concluded that the men could safely exercise at maximum levels while exposed to 5.0 ppm H_2S, they also stated that the increased blood lactate levels were indications of inhibited cytochrome oxidase activity. The significant increases in blood lactate levels occurred at exposure between 2.0 and 5.0 ppm.

Table 8.1: Human Health Studies & Evaluations Summary (Cont.)

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Bhambhani (7)	1995	Acute--healthy men and women exposed to 10 ppm for 15 minutes while exercising	The results indicated that no significant changes in respiratory parameters occurred as a result of oral inhalation. The authors noted that the subjects may not be representative of the worker populations which may be exposed to H_2S in an occupational setting. The subjects were aerobically fit, had higher pulmonary functions than typical for their ages, and had not been exposed previously on multiple occasions.
Bhambhani (9)	1996	Acute--healthy men and women exposed to 5 ppm for 30 minutes while exercising	The results showed that the concentration of an enzyme (citrate synthase) significantly decreased. Although not significant, there was a tendency for the blood lactate and lactate dehydrogenase concentrations to increase and cytochrome oxidase concentration to decrease. The author noted that the fact that short-term exposures to 5 ppm had an impact on the aerobic metabolism in the study group may have implications on current occupational exposure limits.
Burnett (11)	1977	Chronic--review of hospital records (levels unknown)	The study looked at 5 years of hospital records, employee and employer reports, and coroner office records. A total of 221 cases were reviewed. Most exposures were in workplace settings. Of the 221 exposures, 78% required hospital evaluation, 75% were unconscious after exposure, and 13% were still unconscious upon hospital arrival. Most of the subjects exhibited neurological symptoms. Fourteen (14) of the 221 died as a result of the exposure. The respiratory system was affected in 39% of the cases.

Table 8.1: Human Health Studies & Evaluations Summary (Cont.)

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Brooks (10)	1993	Acute--risk assessment from acute exposure to levels between 0.04 and 12.8 ppm H_2S (1-hr max)	Review of literature suggested that no serious adverse health effects are expected in these exposures for a duration less than 4 hours. Temporary eye irritation are the primary health effect. Author stated subjective symptoms such as headache and nausea may result. Other factors may increase the sensitivity of the community.
Dales (73)	1989	Chronic--population within 300 sq. miles of a natural gas source (levels unknown)	Found increased respiratory symptoms in young, but not older population. Symptoms included irritation and inflammation of the respiratory mucosa. Other pollutants (sulfur dioxide and particulate matter) were present. Authors concluded more investigation was needed on the health effects of chronic low-level exposure.
Donham (15)	1995	Chronic--swine confinement workers exposed to unknown levels	Swine manure degradation is a source of TRS compounds. In this study swine confinement workers were evaluated for respiratory diseases. The authors reported that significantly more confinement workers reported chronic bronchitis than the control group. Other pollutants may have contributed.
Gaitonde (18)	1987	Chronic--20 month old infant exposed to levels up to 0.6 ppm for one year	Child was reported to have tonic deviation of the eyes, involuntary movements and frequent falls. Tomograms of the brain showed signs which suggested toxic encephalopathy. Ten weeks after the infant's removal from the exposure, the symptoms were reversed. No respiratory disease or other abnormalities found.

Table 8.1: Human Health Studies & Evaluations Summary (Cont.)

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Haahtela (21)	1992	Acute--residents exposed to peak concentrations for 2 days. The highest 4-hr concentration of H_2S was 0.095 ppm. The 24-hr averages for the 2 days were 0.025 ppm and 0.030 ppm.	Symptoms reported during the 2-day peak exposure period were compared to symptoms reported during lower level days. On the "control" days, the 4-hr H_2S concentrations were between 0.00007 and 0.002 ppm. Large portions of the population reported breathlessness and mental symptoms during the peak exposure period compared to no reports of such symptoms during the "control" period. Eye symptoms, cough, and throat irritation were reported significantly more often during the peak exposure period. The author concluded that the WHO guideline of 0.10 ppm 24 hour average is too high and does not provide protection from adverse health effects.
Higashi (23)	1983	Subchronic--worker exposure to 0.3 - 7.8 ppm (average 3.0 ppm) H_2S	Compared to "non-exposed" workers (exposed to levels less than 0.1 ppm H2S). Found no significant difference in 8-hour pulmonary function between two groups.
Jaakkola (29)	1990	Chronic--residential exposure to TRS compounds. Levels up to: Annual means: H_2S = 0.006 ppm CH_3SH = 0.002 ppm Daily means: H_2S = 0.070 ppm CH_3SH = 0.024 ppm	Chronic bronchitis and asthma were prevalent slightly more in the moderately polluted and severely polluted communities than in the non-polluted community. Childhood eczema was more prevalent in the non-polluted community. Eye and nasal symptoms and cough were found significantly more often in the polluted communities. The occurrence of symptoms was dose related. The people in the severely polluted community had more symptoms than those in the moderately polluted community. The authors concluded that the WHO standard of 0.1 ppm - 24 hour average does not protect against these type of adverse health effects.

Table 8.1: Human Health Studies & Evaluations Summary (Cont.)

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Jaakkola (30)	1991	Chronic--children exposed to ambient H_2S levels 0.001 ppm -annual mean and 0.125 ppm -max 1/2 hour	Infants showed a higher rate of respiratory infection than the reference city infant population. Synergistic effects of all pollutants present may have been a contributing factor.
Japinnen (31)	1990	Acute--Pulp mill workers exposed to 1-11 ppm H_2S; and asthmatics at rest exposed to 2 ppm H_2S for 30 minutes	Workers reported no subjective symptoms after exposure. A volunteer group of 10 asthmatics was also exposed. Three of the 10 complained of headaches after exposure. No significant changes in respiratory function for pulp mill workers, some changes in asthmatic subjects.
Jappinen & Tola (73)	1990	Chronic--worker exposure (levels unknown)	Found slightly increased mortality rate over what would be expected. Pulp mill workers were area of focus.
Kangas (32)	1984	Acute-Chronic--worker exposure to 0-15 ppm methyl mercaptan, 0-15 ppm dimethyl sulfide, 0-1.5 ppm dimethyl disulfide and 0-20 ppm H_2S	Surveyed workers and found that the workers complained of headaches and a decrease in the capacity to concentrate more often than the control group. The number of sick leaves was greater in the exposed workers than among the controls.
Kilburn (33)	1995	Chronic--refinery worker exposure ambient 24-hr averages of 0-8 ppm H_2S and 6.1-70.7 ppm TRS between April 1987 to January 1991	Questionnaires were completed by residents, former workers, and controls. Author found that the exposed individuals were statistically significantly abnormal for two-choice reaction time, balance, color discrimination, digit symbol, trail-making A and B, and immediate recall of a story when compared to controls.

Table 8.1: Human Health Studies & Evaluations Summary (Cont.)

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Klingburg (34)	1988	Subchronic--worker exposure to organic sulfides (H_2S not measured) < 0.2 ppm methyl mercaptan and <0.05 ppm dimethyl sulfide and dimethyl disulfide	Study suggested that exposure to low levels of organic sulfides may disturb iron metabolism. H_2S was not measured.
Nesswetha (73)	1969	Subchronic--worker exposure to 10 ppm H_2S for 6-7 hours and 14 ppm H_2S for 4-5 hours	Found eye irritation in workers at these levels and durations. Other confounding factors were present.
Parra (35)	1991	Acute/Subchronic--30-year-old man (smoker) exposed to unknown levels	Patient after being exposed to H_2S gas in a toilet facility connected to a manure pit continued to have reduced lung capacity 5 months after the accident. Author believed the reduced lung capacity was due to mild fibrosis as a result of the exposure. Author concluded that the case illustrates a pulmonary injury due to H_2S inhalation which appears as a subacute illness and develops into a chronic functional disability.
Partti-Pellinen (36)	1996	Chronic--general population exposure to TRS (up to 0.1 ppm 24-hr).	Distributed a self-administered questionnaire. Authors conclude that those in the exposed community reported coughs, respiratory infections, and headaches in excess of the unexposed community. The relative risk for headache was significantly greater in the exposed community. Stated that more headaches, depression, tiredness, and nausea were reported on days when the 1-hr or daily averages exceeded 0.028 ppm TRS (40 ug/m^3) (cited from Evans, 1967; Jaakkola, 1990; Vikka, 1991). Both communities were exposed to similar levels of SO_2.

Table 8.1: Human Health Studies & Evaluations Summary (Cont.)

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Poda (86)	1966	Chronic--worker exposure (levels unknown)	Author concluded that those who have been over-exposed more than once did not become more or less sensitive to H_2S. Concluded that no pathological findings were found in over-exposed individuals which could be attributed to H_2S. Those who consumed alcohol 16 to 24 hours before work were more sensitive to H_2S. Persons with neuropsychiatric problems were more effected by exposure to H_2S. The author concluded that people with hay fever, vasomotor rhinitis, mild seasonal asthma or migraine could work safely while exposed to H_2S.
Richardson (37)	1995	Chronic--WWTP workers compared to sewer workers	Author suggests that workers exposed to H_2S experience a decrease in lung function, in particular those with the highest exposure (sewer workers).
Rubin & Arieff (39)	1945	Chronic--worker exposure to an average of 1-5.5 ppm for 3 months to 17 years	Found no significant increase in health effects of the 100 workers evaluated. Stress could have been a factor.
Rossi (38)	1993	Chronic--occurrence of asthma attacks in relation to air pollution events. Daily (24-hr) H_2S levels were as follows: mean = 0.002 ppm range = 0-0.024 ppm Highest 1-hour levels: mean = 0.011 ppm range = 0-0.121 ppm	Significant correlations were found between asthma attacks at an emergency room in Hawaii and levels of NO_2, SO_2, TSP (total suspended particulates) and H_2S. Pollen levels did not show a correlation with asthma attacks. Temperature had a small association with attacks.

Schiffman (40)	1994	Chronic--residential exposure to odor emissions from swine operations (levels unknown)	Swine operations emit odorous TRS compounds. The study evaluated the POMS (profile of mood states) of 44 nearby residents and compared them with controls. The experimental group reported significantly more tension, depression, anger, fatigue, confusion, and less vigor than the control group.

Table 8.1: Human Health Studies & Evaluations Summary (Cont.)

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Tenhunen (42)	1982	Pulp mill workers exposed to levels ranging as follows (8-hr averages): H_2S = 0.05 - 5.2 ppm CH_3SH = 0.07 - 2.0 ppm $(CH_3)_2S$ = 0.03 - 3.2 ppm	In a clinical survey of subjective symptoms, the workers were comparable to the control group. Sick leave absences were on average 5 days per year more than the control group. The authors found that heme synthesis was inhibited in the worker population. It was not known whether the inhibition was due to low-level chronic exposure or due to cumulative effects of occasional peak exposures.
U.S. Public Health Service--Terre Haute Study (43)	1964	Acute/Subchronic--general population exposure to levels exceeding 0.3 ppm	Health effects such as nausea, eye irritation, shortness of breath, loss of sleep were reported.

8.2 Animal Studies

In studying cause and effect relationships related to exposures to air pollutants, there are a number of advantages to using animal studies. The primary advantage is that animal studies can be highly controlled and documented. There also are disadvantages. The majority of the H_2S studies use rodents. The nasal passage anatomy, biochemistry, and physiology of rodents do not lend themselves to compare well with humans. Although rodents are not appropriate to use for studying possible effects on humans via the inhalation pathway, the rodent studies may be used to support establishment of an ambient air quality standard. A discussion of the animal studies reviewed by NDEQ are presented in Table 8.2.

The effects of H_2S on rats has been well studied. Hannah and Roth found that low levels of H_2S may cause severe alteration in cells within the central nervous system, putting the rat at risk for birth defects (46). Lopez found that at 400 ppm rats showed signs of clinical lethargy and epiphora (51). Lopez concluded that high doses of H_2S cause pulmonary edema and severe transient injury to the nasal cavities. In a different study Lopez concluded that the inhalation of H_2S has a poor exposure-response relationship and once the threshold is reached, nasal lesions may rapidly form (52).

Khan reported that H_2S inhibited cytochrome oxidase activity at levels of 50 ppm and higher in rats (49). Cytochrome oxidase is an enzyme which is crucial for supplying oxygen to cells. Vahlkamp studied the effects of methyl mercaptan and dimethyl sulfide on enzyme activity (55). Methyl mercaptan inhibits cytochrome oxidase and mitochondrial electron transfer in the liver and the brain. This is similar to how cyanide effects cytochrome oxidase. Dimethyl sulfide was much less effective as an inhibitor of mitochondrial respiration.

Torrans and Clemens studied the effects of H_2S on cytochrome oxidase activity in fish (130). Fathead minnows and channel catfish were exposed to 1.0 mg/L H_2S at 20 degrees C, water pH 8.0. After the fish were exposed for periods less than 25 minutes (13 to 23 minutes for the channel catfish and 9 to 15 minutes for the fathead minnows), ventilation ceased, and the fish were examined for enzyme activity. Cytochrome oxidase activities were inhibited by as much as 55 percent in the kidneys of the fathead minnows. Brain enzymes were inhibited as much as 28 percent and heart enzymes as much as 66 percent in the catfish. As the exposure to H_2S increased, the reduction in enzyme activity increased. The blood lactate levels increased as the cytochrome oxidase activity decreased (130). This finding is consistent with the findings of Bhambhani in the 1991 study on healthy exercising men.

A study of TRS compound by Tansy assessed the 50 percent lethal concentration of the TRS compounds (54). The following LC50 values were determined:

- methyl mercaptan--675 ppm
- dimethyl sulfide--40,250 ppm
- dimethyl disulfide--805 ppm
- hydrogen sulfide--444 ppm
- equimolar mixture of methyl mercaptan, dimethyl sulfide and dimethyl disulfide--550 ppm

Table 8.2 provides a summary of the animal studies the NDEQ reviewed during the standard development process.

Table 8.2: Animal Studies & Evaluations Summary

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Curtis (44)	unknown	Subchronic--Pigs exposed to 2 ppm of H_2S	Levels at higher than normal had little effect on the growth performance of healthy pigs. Ammonia and particulates were involved.
Drumond Sour Gas Well Blowout (73)	1984	Chronic--Farm animal exposure of 0.01 to 3.5 ppm of H_2S	Reports of eye irritation, pneumonia, reduced exercise tolerance and reproductive failure.
Hannah & Roth (46)	1990	Chronic--Rats exposed to 10 and 20 ppm	Produced severe alterations in cells within the central nervous system.
Hayden (47)	1990	Subchronic--Rat dams and pups exposed to levels < or = 75 ppm H_2S from day 1 of gestation to day 21 postpartum	Evaluated blood glucose levels. Levels were significantly elevated in maternal blood on day 21 postpartum at all exposure levels. Possible decreases in serum triglycerides in pups and dams on day 21 postpartum. Elevated glucose levels (chronically) can produce retinopathy, neuropathy, and nephropathy and can increase severity of cardiac and peripheral atherosclerosis. The pups showed subtle changes in development. There was a decrease in time of ear detachment and hair development.
Khan (49)	1989	Acute--Rats exposed for 4 hrs to various levels of H_2S	There were no changes in lung mitochondrial respiratory chain enzymes at an exposure of 10 ppm. Significant changes were noted at exposures of 50-400 ppm.
Khan (50)	1991	Acute--Rats exposed for 4 hrs to 0, 50, 200, 400 ppm H_2S	Respiratory rates were reduced in rats exposed to 200-400 ppm. Significant decrease in cell viability was observed in rats exposed to 400 ppm.
Lodgepole Blowout Inquiry Panel	1984	Farm animals exposed to 10-15 ppm (duration unknown from citation)	Owners reported their animals had runny noses & eyes, coughing, decreased appetite, diarrhea, red stools & urine, and low weight gain. Some people noted that wild animals disappeared for a period of time.

Table 8.2: Animal Studies & Evaluations Summary (Cont.)

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Lopez (52)	1987	Acute--Rats exposed for 4 hrs to 0, 10, 200, or 400 ppm H_2S	At 400 ppm, rats showed signs of clinical lethargy and epiphora. Lesions were noted in the nasal cavity at levels greater than 200 ppm.
Lopez (51)	1987	Acute--Rats exposed for 4 hrs to 0, 10, 200, or 400 ppm H_2S	Author concluded that high doses of H_2S cause pulmonary edema and severe transient injury to the nasal cavities. Inhalation of H_2S appears to have a poor exposure-response relationship and when the threshold is reached, lesions rapidly form.
Nordstrum (73)	1976	Calves exposed to 20 ppm (duration unknown from citation)	Distress, lethargy, restlessness, diarrhea, vomiting, coughing, dyspnea, photophobia, keratitis corneal opacity, nasal irritation and epistaxis reported.
Rogers & Ferin (73)	1981	Acute--Rats exposed to 45 ppm for 2, 4 or 6 hrs, then exposed to bacteria	Rats exposed for 4 hours had a 6.5-fold greater percent of colony forming units (bacteria colonies) and those exposed for 6 hours had a 52-fold greater percent of bacteria colonies.
Siegal (41)	1986	The ambient levels of H_2S at Sulphur Bay Wildlife area on Lake Rotorua, New Zealand typically exposes shore and water birds to concentrations of 0.125 to 3.9 ppm.	Due to higher oxygen utilization rate and ventilation rate in birds than mammals of human size, it was believed by the authors that these birds' exposure would be higher than for a human at the same concentrations. Populations in the wildlife area have thrived, as measured by an increasing number of nests found for several species in the preserve, indicating the levels of H_2S naturally occurring in that area are not detrimental to these animals. No other parameters of exposure were measured on a population level or an individual level in this study.

Table 8.2: Animal Studies & Evaluations Summary (Cont.)

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Skrajny (53)	1992	Chronic--Rats exposed to 20 ppm and 75 ppm during prenatal development	Author suggests that H_2S may cause irreversible changes in monoamine levels in the developing central nervous system of rats. H_2S-induced alterations of monoamine levels may produce long-term morphological and neurochemical changes in the central nervous system. Impaired cognitive and perceptual functions and memory loss may be explained by H_2S exposure.
Tansy (54)	1981	Acute--Rats exposed to levels of methyl mercaptan and other reduced sulfur compounds for 4 hrs to determine the 24-hr LC50 values.	The following LC50 values were determined: methyl mercaptan--675 ppm dimethyl sulfide--40,250 ppm dimethyl disulfide--805 ppm hydrogen sulfide--444 ppm equimolar mixture of methyl mercaptan, dimethyl sulfide and dimethyl disulfide--550 ppm A discussion of the effects on rats after 3 months of exposure to concentrations of 2, 17 and 57 ppm methyl mercaptan was also provided. Body weight was significantly reduced and followed a dose-related trend. Some liver damage was noted.
Torrans and Clemens (130)	1982	Fish exposed to H_2S at various levels	Cytochrome oxidase activities were inhibited by as much as 55 percent in the kidneys of the fathead minnows. Brain enzymes were inhibited as much as 28 percent and heart enzymes as much as 66 percent in the catfish. As the exposure to H_2S increased, the reduction in enzyme activity increased. The blood lactate levels increased as the cytochrome oxidase activity decreased

Table 8.2: Animal Studies & Evaluations Summary (Cont.)

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Vahlkamp (55)	1978	Acute--rats exposed to methyl mercaptan, ethyl mercaptan, and dimethyl sulfide	Methyl mercaptan inhibits cytochrome oxidase and mitochondrial electron transfer in the liver and the brain. Such inhibition decreases cellular respiration and leads to coma. This is similar to how cyanide effects cytochrome oxidase. Dimethyl sulfide was much less effective as an inhibitor of mitochondrial respiration.
Waller (56)	1976	Acute--rat study on inhibitive effects of methyl mercaptan	Methyl mercaptan is a strong inhibitor of rat liver mitochondrial respiration by reacting with cytochrome oxidase. The effect was dose-related.

9. Welfare Effects

Welfare effects are defined as those not associated with human health, such as effects on plant life, animal life, or property. As required by the Nebraska Environmental Protection Act Sections 81-1501, 81-1502 and 81-1504, the Department is responsible for developing programs which prevent, control, and abate air pollution in order to protect public health and welfare (see Section 2.0). The NDEQ is proposing to establish air quality standards which address welfare concerns.

9.1 Animal Life

Few studies exist that attempt to measure natural or accidental exposure of wildlife to TRS or to determine its effects. One investigation examined the ambient levels at the Sulfur Bay Wildlife area near Lake Rotorua, New Zealand, where shore and water birds were exposed to total reduced sulfur (TRS) of geothermal origin in concentrations of 0.125 to 3.90 ppm (41). In spite of theses high levels, the wildlife thrived in this area. Other studies looked at the short-term effect of exposure to TRS fumes from gas well blowouts in Canada. These studies found no significant impact on local waterfowl, small mammals or large ungulates such as elk (73).

9.2 Vegetation

Young, growing plant tissues were found to be the most susceptible to injury. Plants exposed to TRS concentrations of 20-400 ppm for five hours in the middle of the day displayed a wide range of injury. Eight species showed no injury at 400 ppm, and other species displayed visible injury at less than 40 ppm (73).

Plants exposed to low concentrations of TRS (0.03 to 30 ppm) over long periods of time showed considerably more damage than those exposed for shorter durations. A wide range of sensitivity to TRS was evident across plant species. Of the plants studied, radish, soy bean, clover, kidney bean, buckwheat, cucumber and tomato were determined to be the most sensitive. Kentucky bluegrass and pepper were intermediately sensitive plants. Exposures of 0.03 ppm for 28 to 35 days were found to significantly increase yields for alfalfa, while exposures between 0.3 and 3 ppm resulted in reduced yield (73).

9.3 Corrosion

When present in low concentrations and under certain conditions, active sulfur compounds (including hydrogen sulfide, elemental sulfur, and organic sulfur compounds such as the mercaptans) rapidly attack copper, silver, aluminum and iron alloys. Below exposures of 0.005 ppm the corrosive effects are minimal and do not reduce equipment reliability. At levels as low as 0.01 ppm for one month, the corrosive effects on metals can be measured and may be a factor in determining electronic equipment reliability. At concentrations up to 0.05 ppm there is a high probability of corrosive attack. At greater than 0.05 ppm severe corrosion can be expected. An environment classified as severe would contain contaminates at levels which cause reliability of electronic equipment to be expressed in terms of months rather than years (61).

TRS is corrosive to metal such as iron, zinc, copper, lead and cadmium. Copper contacts and components of electrical systems may be rapidly oxidized to black copper sulfate in the presence of 4 to

8 ppm of TRS, resulting in a weakened, poorly conducting material. Oxidation is the most familiar type of corrosion and is readily observable in the form of rust. A buildup of oxide on a metal surface acts as insulation to reduce further corrosion on chromium, aluminum, and nickel metals. Some oxides, such as iron oxide, are more porous and therefore more susceptible to chemical attack by TRS (62).

Franey evaluated the degradation of copper and copper alloys by atmospheric sulfur (63). Franey found that pure copper was very sensitive to sulfur-containing gases. He found that hydrogen sulfide was four orders of magnitude more corrosive than SO_2 or carbon disulfide (63). Unless H_2S is absorbed by vegetation or soil, it is partially oxidized in the atmosphere to form a sulfurous acid in the presence of moisture. It may also be oxidized to free sulfur, a reactive form of sulfur. The sulfurous acid or free sulfur may attack copper to form a copper sulfide (66).

TRS is a precursor to the formation of sulfuric acid which corrodes lead-based paint, concrete, metals and other materials. The State of Pennsylvania based their welfare standard (0.005 ppm) for H_2S on its effect on the darkening of exterior lead-based paint. "New," lead-free paint was found to be insensitive to TRS exposure for at least 10 months at levels that caused older surface coatings to darken overnight. This discoloration was found to be temporary (71).

The presence of moisture and small amounts of inorganic chlorine compounds greatly accelerate sulfide corrosion (61). Because there are areas of Nebraska where the availability of moisture is limited, the NDEQ investigated the levels of relative humidity needed for corrosion to occur. The NDEQ found that there is a direct relationship between the average relative humidity, TRS, and the acceleration of corrosion. At relative humidities above 60 percent, corrosion rates of copper rapidly increase (67).

A discussion of studies of welfare effects reviewed by the NDEQ is presented in Table 9.0.

Table 9.0: Welfare Effects Studies & Evaluations Summary

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Sitting (126)	1974	0.053 ppm H_2S for a few hrs	Darkened paint
Rapaport (115)	1988	0.003-0.050 ppm H_2S over a 1 mo period	Corrosion to sensitive electronic parts can occur at 0.003 ppm H_2S, and severe corrosion may occur at 0.05 ppm H_2S.
EPA (73)	1993	5-10 ppm H_2S for several hrs with higher peak exposures	Alfalfa and hay crops reported 1/2 to 1/3 of their normal yield after exposure. No comparison to unexposed crops was made, and other confounding factors such as seasonal parameters were not ruled out.
McCallan (73)	1936	20-400 ppm H_2S for 5 hrs	Some species of vegetation or weeds showed injury at less than 40 ppm. Young tissues were the most susceptible to injury.
Benedict & Breen (73)	1955	Unknown--higher levels than the McCallan study	Younger tissues were more vulnerable to damage than older.
Heck (73)	1970	Divided plants into sensitive, intermediate and resistant groups	Sensitive: kidney bean, buckwheat, clover, cucumber, soybean, tobacco, and tomato Resistant: apple, cherry, mustard, strawberry
Thompson & Kats (73)	1978	Various crops and forest plants fumigated in continuous long-term low-level exposures (246 days)	Threshold for significant injury was between 0.03 and 0.30 ppm for most plants except the Douglas fir which was between 0.03 and 0.1 ppm. The study showed that plants exposed to low concentrations of H_2S over long periods of time experienced considerably more damage. Alfalfa showed damage after 5 days of exposure to 3 ppm H_2S. Yield was reduced at 3 ppm and 0.3 ppm, but not at 0.01 ppm. Exposure at 0.03 ppm increased yields. Ponderosa pine exposed to 3 ppm showed no visible effect after 4 to 6 weeks of exposure, but at 8 weeks defoliation occurred. Tip burn could be seen at 0.3 ppm after 8 weeks of exposure. The California buckeye, sugar beet, and lettuce were resistant to damage and at exposures to 0.3 ppm growth was in fact stimulated in sugar beet and lettuce.
Faller and Linser (73)	1972	SO_2 and H_2S were exposed to sunflowers grown in a sulfur-free environment. Plants were exposed for 3 wks to levels ranging from "a few" ppm to 200 ppm	Growth was stimulated compared with the plants grown in the sulfur-free environment.

Table 9.0: Welfare Effects Studies & Evaluations Summary

Reference	Year of Study	Exposure Parameters	Results/Discussion of Study
Abbott, W.H. (57)	1983	1 ppm--30 ppb H_2S per wk	Showed that low-levels in combination with other environmental variables can reduce equipment reliability.
Franey, L. (63)	1988	Exposure to H_2S and/or ozone and/or light. H_2S between 2.1-2.3 ppm. Ozone between 0-0.2 ppm.	SO_2, H_2S and COS cause major corrosive reaction with copper and copper alloys. Temperature, relative humidity, ozone and light have accelerating effects on reaction rates. H_2S and COS were found to be four orders of magnitude more corrosive than SO_2 or CS_2 for pure copper.
Rice (67)	1981	Exposure to H_2S, Cl_2, SO_2/NO_2, and ozone of various levels and relative humidities.	Copper corrosion is sensitive to relative humidity. Corrosion rates are dramatically increased when the relative humidity is above 60%. Copper corrosion is also influenced by the SO_2, H_2S, Cl_2 and O_3 concentrations.

10. Existing State Standards

In July 1996, the NDEQ conducted a survey of the 49 other states. The survey revealed 27 states which have standards for H_2S or TRS. The NDEQ requested information from these states to determine how they arrived at their standards, how they enforce their standards, and what compliance issues they have faced. The Department also requested information on regulatory development packages. NDEQ found that caution must be used when examining other state standards. States have based standards on odor or nuisance, welfare effects or health effects. The averaging periods also vary from state to state. For these reasons, comparison of state standards has been difficult. The NDEQ found that the majority of existing standards were written in the early years of the air quality regulatory program (early 1970s). For this reason, there was little information regarding the rationale associated with the other state standards. In addition, the issues of monitoring methods and mercaptan interference had not been addressed.

Table 10.1 summarizes the survey results. Where available, the basis and year of establishment for such standard are provided.

Table 10.1: Summary of State H_2S/TRS Standards

State	Concentration (ppm)	Averaging Time	Allowances	Basis for Standard (Year Established)
Alabama	20	30-min		unknown (1976)
Alaska	0.035	30-min		unknown (1982)
Arizona	0.08	24-hr		welfare--policy, not rule
	0.13	1-hr		welfare--policy, not rule
California	0.03	1-hr		nuisance (1969)
Colorado	0.10	1-hr		welfare, nuisance (1979)
Delaware	0.06	3-min	never to exceed	survey of states with H_2S standard (health & nuisance)
	0.03	60-min	never to exceed	
Georgia	15			OSHA PEL--guideline only
Hawaii	0.025	1-hr	never to exceed	health--Lopez et al. (1987) enforced as a nuisance standard (1996)
Idaho	0.05			health--ACGIH TLV divided by 20
Illinois	0.01	8-hour		health-- reports of nausea, loss of appetite and fatigue at 0.08 ppm and eye effects at 0.7 ppm and due to sensitive populations-- odor and welfare not considered (1974)
Michigan	0.0045	10-min		nuisance (1992)
	0.0007	24-hr		unknown (1992)
Minnesota	0.05	30-min	not to exceed twice per yr	nuisance (1968)
	0.03	30-min	not to exceed twice in 5 consecutive days	nuisance (1968)

Table 10.1: Summary of State Standards (Cont.)

State	Concentration (ppm)	Averaging Time	Allowances	Basis for Standard (Year Established)
Missouri	0.05	30-min	not to exceed twice per yr	nuisance
	0.03	30-min	not to exceed twice in 5 consecutive days	nuisance
Montana	0.05	1-hr		unknown (1980)
Nevada	0.08	1-hr		unknown (early 1970s)
New Hampshire	0.03	24-hr		unknown (1990)
New Mexico	0.01	1-hr		unknown (early 1970s)
New York	0.01	1-hr		unknown (1972)
	0.0007	1-yr		unknown (1972)
North Carolina	1.5	15-min		health & welfare
North Dakota	10	instantaneous	never to exceed	health--NIOSH 10 min standard and converted to instantaneous (1990)
	0.2	1-hr	not to exceed once per mo	health--studies showing that at 0.3 ppm headaches, nausea, and other minor health effects occur; for a degree of safety elected to use 0.2 ppm (1990)
	0.1	24-hr	not to exceed once per yr	health--WHO recommendation 1983 (1990)
	0.02	90-day		welfare--crop damage information (1990)
Oklahoma	0.1	30-min		unknown (1972)

Table 10.1: Summary of State Standards (Cont.)

State	Concentration (ppm)	Averaging Time	Allowances	Basis for Standard (Year Established)
Pennsylvania	0.1	1-hour		welfare (1971)
	0.005	24-hour		welfare (1971)
South Carolina	0.1	24-hour		health -- ACGIH TLV divided by a safety factor (1991)
Tennessee	20	12-hour		unknown (1995)
Texas	0.08 (screening level)			health and nuisance
Vermont	0.02	24-hour		health (1989)
Wyoming	0.05	30-minutes	not to exceed twice per yr	nuisance (1970)
	0.03	30-minutes	not to exceed twice in 5 consecutive days	nuisance (1970)

11. Occupational Standards and Other Guidelines

Exposure to H_2S is regulated by the Occupational Safety and Health Administration (OSHA). Other occupational organizations also have recommendations for H_2S limits. It is important to note that these occupational standards are for narrowly defined healthy working populations and circumstances. The occupational organizations as well as EPA do not recommend using these standards to protect the general population (see Section 12.4). Table 11.1 details occupational standards and other guidelines for H_2S.

11.1 Occupational Safety and Health Administration

In July 1992, the 11th Circuit Court of Appeals in its decision in *AFL-CIO vs. OSHA 965 F.2d 962*, vacated standards set by OSHA in 1989 for 212 hazardous compounds. Hydrogen sulfide was one of the affected compounds. The primary reason the Court repealed the standards was OSHA's failure to follow the required process in establishing the revised standards. When the Court rendered its ruling, the 1971 standards were reinstated. The current OSHA standard (1971) is an acceptable ceiling concentration of 20 ppm averaged over 15 minutes. Although OSHA has a secondary provision which allows levels to reach a maximum peak of 50 ppm over 10 minutes, this maximum peak can only occur provided that no other measurable exposure occurs during the workday.

11.2 National Institute for Occupational Safety and Health

The National Institute for Occupational Safety and Health (NIOSH), a division of the United States Department of Health and Human Services, has a recommendation of 10 ppm, 10-minute average per week for H_2S. This recommendation is based on eye irritation effects. NIOSH develops and periodically revises recommended limits for exposure to hazardous compounds found in an occupational setting. The recommendations are then published and transmitted to the Occupational Safety and Health Administration (OSHA) and the Mine Safety and Health Administration (MSHA) for their use in promulgating occupational standards.

11.3 World Health Organization

The World Health Organization (WHO) reviewed information on health effects and recommended a daily (24-hour) value of 0.1 ppm H_2S. This value was based on the eye irritation effects at 10 ppm and a safety factor of 100. WHO noted that changes in heme synthesis were found at 1 ppm in pulp mill workers. Since the WHO made its recommendation in 1983, Bhambhani and Jappinen have conducted studies which indicate that eye irritation is not the most sensitive critical health effect.

Table 11.1: Occupational Standards and Other Guidelines

Regulating Authority	Concentration (ppm)	Averaging Time	Purpose of Standard or Recommendation
National Research Council/ National Academy of Sciences (81)	50	10-min	Recommended for narrowly defined occupational groups and not intended for application in general industrial settings or as exposure limits for the general public. These recommended values do not take into consideration the possible effects of exposures for hypersensitive persons.
	10	24-hr	Recommended for narrowly defined occupational groups and not intended for application in general industrial settings or as exposure limits for the general public. These recommended values do not take into consideration the possible effects of exposures for hypersensitive persons.
	1	90-day	Recommended for narrowly defined occupational groups and not intended for application in general industrial settings or as exposure limits for the general public. These recommended values do not take into consideration the possible effects of exposures for hypersensitive persons.
American Industrial Hygiene Association (82)	100	1-hr (ERPG-3)	Level at which nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.
	30	1-hr (ERPG-2)	Level at which nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.
	0.1	1-hr (ERPG-1)	Level at which nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor.

Table 11.1: Occupational Standards and Other Guidelines (Cont.)

Regulating Authority	Concentration (ppm)	Averaging Time	Purpose of Standard or Recommendation
Occupational Safety and Health Administration (80)	20	15-min	An acceptable ceiling concentration
	50	10-min	A secondary level. This maximum peak can only occur provided that no other measurable exposure occurs during the workday.
American Conference of Governmental Industrial Hygienists (79)	10	Time weighted average (TWA) 8-hr work day and 40-hr work wk	ACGIH does not recommend extending the use of these levels to other applications, such as applying them to different populations other than the worker population or developing new exposure/recovery time models.
	15	Short-term exposure limit (STEL)	
National Institute for Occupational Safety and Health (80)	10	10-min TWA	
	100	Immediately dangerous to life and health	
World Health Organization (92)	0.1	24-hr	Recommendation based on a lowest-adverse-effect level of 10 ppm (eye irritation) and a safety factor of 100. Noted that a report of change in heme synthesis at about 1ppm should be considered.

12. Procedures Used to Derive an Ambient Standard

The purpose for an ambient standard is to protect against unacceptable levels of the pollutant of concern. The unacceptable levels are defined as those that cause adverse health and welfare effects. The levels at which relevant thresholds are set are determined by the associated cause and effect relationship. For purposes of establishing health-based standards, the cause is the level of exposure to the pollutant of concern that results in an adverse health impact--the effect.

The U.S. Environmental Protection Agency (EPA) has established a method for deriving an ambient standard using either animal or human health studies in *Interim Methods for Development of Inhalation Reference Doses* (74). The Department relied on this document in establishing the health based ambient air quality standard.

12.1 Guidelines for Selecting Key Health Studies

Before developing an ambient standard, evidence must be gathered to determine if the pollutant poses a risk to public health. Studies are of two types: human studies and experimental animal studies.

Utilizing human studies offers great advantages as doing so eliminates much uncertainty and the need to extrapolate from animals to humans. The three types of human studies usually used are epidemiological studies, clinical studies or controlled exposure experiments, and case reports. Factors which need to be considered when using these studies include the following: accuracy of exposure measurements and durations; elimination of exposures to other pollutants that may have confounding or synergistic effects with the pollutant of concern; comparison to control (unexposed) populations; elimination of subjective health effects, and control of variations among the exposed population. The health studies used by the NDEQ satisfactorily meet these criteria in that exposures were only to H_2S; the studies were well designed and contained a control group; and subjective health effects caused by odor were eliminated because subjects were exposed through the mouth.

When appropriate human data is not available, animal studies (usually mammals) are typically utilized. The animals most often used include the rat, mouse, guinea pig, hamster, rabbit, monkey and dog. One of the benefits of animals studies is that they usually are conducted under controlled conditions on a homogeneous population and that bias or subjective data do not enter into the experiment. Factors to consider when using animal studies include: the appropriateness of the animal species as a model for humans, the study design, and the validity of the study for humans. The scientific animal studies NDEQ found were conducted on rats and mice. Rodents are not the preferred animal species to compare to humans due to differences in nasal passage anatomy, physiology, and biochemistry.

After all toxicological, epidemiological, experimental, and supporting data has been reviewed and evaluated, a key or critical study is selected which contains the most appropriate information on the critical effect. The critical effect is the first adverse effect or its precursor that is caused by exposure to the pollutant of concern. The effect will become more pronounced as the exposure increases. This is referred to as a exposure-response relationship. This is a critical component of the establishment of a standard. It represents the cause and effect relationship that determines the appropriate level for the ambient standard.

When selecting a critical study, the criteria to consider include: variations in species, delineation of all toxic effects and associated exposure levels, and multiple toxic endpoints. Multiple toxic endpoints are the adverse health effects of a chemical on more than one system in the body (e.g., nervous system and respiratory systems). In the case of multiple toxic endpoints, the critical effect is the effect on the most sensitive system. If the critical effect is prevented, all adverse effects will be prevented.

12.2 Calculation of the Reference Concentration

After the critical effect is identified, an exposure level that represents the highest level tested in which the critical effect was not demonstrated is established. This is the NOAEL (No-Observed-Adverse-Effect-Level). If an experimental animal study is utilized, a conversion is made to account for dosimetric differences between the animal and the human species. This becomes the human equivalent concentration (NOAEL-HEC). If a NOAEL-HEC is calculated, then a lower uncertainty factor to account for dosimetric differences may be used. If a NOAEL-HEC is not calculated, then an uncertainty factor of 10 is used.

The inhalation reference concentration is derived by applying uncertainty factors (UFs) to the NOAEL-HEC. These factors account for uncertainties associated with determining a reference concentration from different human or animal databases. An additional factor called the modifying factor (MF) (see Table 12.1), reflecting professional judgment of the entire database available on the specific chemical, may be applied. The below equation illustrates the derivation:

$$RfC_i = \frac{NOAEL\text{–}HEC}{UF * MF}$$

where:

RfC_i = inhalation reference concentration (mg/m^3 or ppm)

NOAEL-HEC = human equivalent NOAEL accounting for dosimetric differences between species (mg/m^3 or ppm)

UF = uncertainty factor (unitless)

MF = modifying factor, default is 1 (unitless)

Table 12.1 Uncertainty and Modifying Factors (74)

Uncertainty Factor or Modifying Factor	Guideline on Usage
Standard Uncertainty Factors	
Human to Sensitive Human	Use a 10-fold factor to account for variations in sensitivity among members of the human population.
Animal to Human	Use an additional 10-fold factor to account for the uncertainties in extrapolating animal data to the case of average healthy humans.
Subchronic to Chronic	Use up to an additional factor of 10 to account for uncertainties in extrapolating to chronic NOAELs from less than chronic NOAELs.
LOAEL to NOAEL	Use up to an additional factor of 10 to account for extrapolating from a lowest-observed-adverse-effect-level (LOAEL) to a NOAEL.
Incomplete to Complete Database	Use up to an additional factor of 10 to account for any single animal study to adequately address all possible adverse outcomes in humans.
Modifying Factor	
	Use professional judgment to assess other uncertainties in the study and database not addressed by an uncertainty factor, above. The default value is 1. The maximum value is 10.

It is important to note that if the database on humans is adequate, the total uncertainty factor will be much lower than if an animal database is used. Whenever possible, a human study should be selected as the key study to avoid extrapolation uncertainties between the animal species and humans.

12.3 Calculation of an Ambient Air Quality Standard

When the reference concentration has been calculated, it may be expressed in parts per million (ppm) as follows:

$$ppm = \frac{RfCi}{1.417}$$

where:

ppm = parts per million volume of air

RfCi = inhalation reference concentration (mg/ m^3)

1.417 = conversion factor ((mg/ m^3)/ppm)

This is the value for the ambient standard expressed in ppm, over the duration "equivalent" to the exposure period of the key study. For example, if the key study was a 24 hour exposure for rats, the standard would likely be expressed in ppm over a 24 hour period. However, there will be instances where the duration will be shortened or lengthened depending on the appropriateness of the exposure period of the study to human population exposure.

12.4 Limitations of Occupational Exposure Limit Values

When relevant information has been lacking for ambient air exposures, occupational exposure limits (OELs), such as those recommended by the American Conference of Governmental and Industrial Hygienists (ACGIH), Occupational Safety and Health Administration (OSHA), and the National Institute of Occupational Safety and Health (NIOSH) have been used as surrogates. The standards recommended by these occupational groups are based on documented toxicological, epidemiological, and clinical information pertaining to the healthy human worker population. The US EPA and the occupational organizations do not endorse the utilization of these values for ambient air considerations. These values are limited in that the OELs may use outdated health information and seldom consider sensitive populations. In spite of the recommendations not to use occupational standards, many states indicated they have utilized occupational standards to some degree. An example calculation is shown below:

The ACGIH recommends a 10 ppm 8-hour workday average in a 40-hour work week. To extrapolate to a 30-day ambient exposure, the following factors could be used:

4.2 exposure duration increasing from 40 hours to 168 hours.

10 uncertainty factor to account for sensitive populations

2.5 modifying factor to account for uncertainties in going from healthy worker to general population

Rounding the total uncertainty factor to 100 results in a value of 0.1 ppm (dividing 10 ppm by 100) 8-hour average in one week.

13. Proposed Standard Summary

The NDEQ proposes the following ambient levels for TRS:

10 parts per million TRS, one-minute average;

0.10 parts per million TRS, 30-minute rolling average;

0.01 parts per million TRS, 30-day rolling average when the average relative humidity is 60 percent or less;

0.005 parts per million TRS, 30-day rolling average when the average relative humidity is greater than 60 percent.

10 ppm, one minute average

The NDEQ proposes to convert the NIOSH recommended ceiling of 10 ppm, 10-minute time weighted average to a one-minute average. This ceiling limit would protect against concentrations reaching those levels at which deleterious health effects are imminent. Derivation of this standard is explained in Section 13.1.

0.10 ppm level, 30-minute average

While there is a considerable amount of information available on occupational exposures, there is relatively little epidemiological information on low-level ambient exposures. The information that is available lacks consistency due to confounding factors such as varying exposure times, exposures to other pollutants, stress, inaccurate monitoring information and human biases. These types of studies may be used to support a standard once derived. The Department has relied on well-controlled human studies to develop the standard and has substantiated it with epidemiological information. Derivation of this standard is explained in Section 13.2.

0.01 ppm and 0.005 ppm levels, 30-day rolling average

In order to protect against welfare effects such as vegetation damage and corrosion, the Department is proposing a two-tiered 30-day standard. The Department recognizes that the availability of moisture in the air will affect the rate of corrosion. Therefore, a lower standard for those areas in the state with higher relative humidities is proposed. Based on the literature the Department has reviewed, establishing a standard to minimize corrosion effects will also address concerns related to damage to vegetation. Corrosion effects occur at lower levels than those levels which result in damage to vegetation. Derivation of this standard is explained in Section 13.3.

13.1 Derivation of 10 ppm Standard

The NDEQ is proposing a 10 ppm (parts per million) one-minute average ambient air quality standard. This standard was developed from occupational guidelines which are based on deleterious health effects, specifically eye irritation, of healthy workers.

Upon reviewing occupational information, the NDEQ determined the need for a ceiling limit which should never be exceeded in the ambient air. This ceiling limit would protect against concentrations' reaching levels at which deleterious health effects may be imminent.

The NDEQ utilized information from the National Institute for Occupational Safety and Health (NIOSH). NIOSH makes a recommendation of 10 ppm, 10-minute average per week for hydrogen sulfide. The NDEQ believes that the NIOSH recommended limit is an appropriate basis as it relies on more recent information than the 1971 OSHA standard.

Occupational standards are established to protect healthy people who are exposed during the workday in an occupational setting. It is important to remember that the NDEQ must protect the general population. The general population includes sensitive people who are more susceptible to experiencing adverse health effects when exposed to hazardous compounds. These people may include children, elderly and those with compromised respiratory function, such as asthmatics.

To arrive at the 10 ppm, one-minute standard, the NDEQ used the following steps:

1. The NDEQ calculated the equivalent exposure and concentration which would be inhaled over a one-minute period. The exposure is calculated using the following equation:

Concentration ∗ Time = Exposure

The equivalent exposure received over 10 minutes when exposed to 10 ppm is:

10 ppm ∗ 10 minutes = 100 ppm ∗ minute

The one-minute concentration is calculated:

Exposure ÷ Time = Concentration

100 ppm•minute ÷ 1 minute = 100 ppm

2. Next, to account for sensitive populations, the NDEQ applied an uncertainty factor of 10. The use of this uncertainty factor is based on EPA standard procedures for deriving ambient air quality standards. The standard is calculated as follows:

$$\frac{100ppm}{10} = 10.0ppm$$ averaged over a 1-minute period

13.2 Derivation of 0.10ppm Standard

The NDEQ is proposing a 0.10 ppm (parts per million) 30-minute average ambient air quality standard. Like the 10 ppm standard, it was developed based on the cause and effect relationship between TRS and health effects.

The NDEQ reviewed 45 animal and human health studies to collect information on the level of H_2S and/or TRS which will cause adverse health effects in humans. The human body can tolerate exposure to certain amounts of TRS by naturally changing it to less harmful compounds and removing them from the blood through the excretory system. If too much TRS is present, removal cannot occur quickly enough. When this happens, the first physiological effect that is noted is a reduction in the activity of cytochrome oxidase enzymes. Cytochrome oxidase enzymes are needed to transfer oxygen from blood to cells. At this point, cells may not receive enough oxygen to survive. This is the critical effect.

13.2.1 Critical Study

The study which best illustrates the critical effect was conducted by a team of researchers from the University of Alberta led by Dr. Yagesh Bhambhani (8). Subsequent to a large oil well blowout in Alberta in 1982, the team began studying the health effects of H_2S on humans. The work done by the University of Alberta research team was among the first research conducted directly on human subjects. Dr. Bhambhani and his team conducted controlled and well-documented studies of the effects of H_2S on healthy exercising men and women. These studies have been thoroughly peer-reviewed and published in reputable journals including the *Journal of Occupational and Environmental Medicine*, the *Journal of Applied Physiology,* and the *American Industrial Hygiene Association Journal*.

The critical study NDEQ selected was conducted in 1991. The research team exposed 16 healthy men to H_2S while they were cycling. The men were exposed to 0, 0.5, 2.0, and 5.0 ppm on four separate occasions. The men exercised between 16 and 25 minutes depending on their level of fitness. The study found that the blood lactate levels and the oxygen intake were significantly increased when the men were exposed to 5.0 ppm hydrogen sulfide over control conditions. Importantly, subjective symptoms such as headache were eliminated by exposing the subjects to the gas through a mouth tube. This eliminated possible effects of sensitivity to odors. Although the authors concluded that the men could safely exercise at maximum levels while exposed to 5.0 ppm H_2S, they stated that the blood lactate levels were indicative of inhibition of cytochrome oxidase activity. Hydrogen sulfide, by inhibiting the enzymes responsible for supplying cells with oxygen, causes the body to shift to anaerobic metabolism with a resultant build-up of lactate in the blood. This finding is consistent with the Torrans and Clemons study on fish (130). Torrans and Clemens found that as cytochrome oxidase activity was inhibited, blood lactate levels increased in fish. The significant increases in blood lactate levels occurred between exposure to 2.0 ppm and 5.0 ppm. At 2.0 ppm there were no significant increases observed, suggesting that the lowest-observed-adverse-effect-level (LOAEL) was 5.0 ppm, and the no-observed-adverse-effect-level (NOAEL) was 2.0 ppm.

Using the steps outlined in Section 12.0, the NDEQ arrived at the 0.10 ppm standard as follows:

1. Identify the key health study which contains the best information on the critical effect. After reviewing 45 animal and human studies the NDEQ concluded that the 1991 Bhambhani study was the study which best illustrated the critical cause and effect relationship that defines the H_2S level at which the enzyme activity is inhibited. Furthermore, the study showed a exposure-response relationship. As concentration increased, the negative effect was increased.

2. Identify the highest level at which the critical effect is not seen. The NOAEL for the study was 2.0 ppm. Since the study was on humans, an adjustment to account for interspecies differences was not necessary.

3. Calculate the reference concentration by considering factors to account for uncertainties in the data. Since the study was conducted on humans, only one of the uncertainty factors outlined in EPA standard procedures was necessary, allowing for a lower overall uncertainty factor. The only uncertainty factor NDEQ needed to apply was that related to sensitive populations. An uncertainty factor of 10 was used to protect against adverse health effects in sensitive populations which include children, elderly, and those with compromised respiratory functions.

The only other variable which needed to be utilized in the derivation of the standard was the modifying factor. A value of between one and ten is assigned as the modifying factor to account for any uncertainties in the critical study and the related database not already taken into consideration. The NDEQ used a modifying factor of two because the research conducted by the University of Alberta research team was very well controlled, well documented, and subjected to extensive peer review.

The reference concentration was calculated as follows:

$$\frac{2.0\,ppm}{2*10} = 0.10\,ppm$$

4. **Convert the reference concentration into parts per million (ppm) and express over the duration equivalent to the exposure period of the key study.** The reference concentration did not require a conversion to ppm. The NDEQ is proposing to set the ambient standard at the reference concentration level derived from the 1991 Bhambhani study. EPA has derived a reference concentration based on a 1983 study conducted on mice. As stated earlier, rodents are not the most appropriate animal to use to represent human exposures due to differences in the nasal passageways. Furthermore, human studies should be used whenever possible. The NDEQ has concluded that the 1991 Bhambhani study is the most appropriate study from which to derive an ambient air quality standard. The EPA RfC is for a daily exposure period. The Bhambhani studies show that adverse health effects may occur after exposure to levels above 2 ppm for 30 minutes. The NDEQ concludes that to adequately protect the public health an ambient standard with a shorter exposure period is more appropriate than a daily exposure period. The exposure duration in the 1991 Bhambhani study was

between 16 and 25 minutes, depending on the subject's level of fitness. This exposure period is close to 30 minutes and subsequent studies conducted on healthy exercising men and women were for a period of 30 minutes. We assumed a period of 30 minutes for the standard.

13.2.2 Supporting Human Studies

Bhambhani 1994 (6)

A 1994 Bhambhani study suggested that healthy men and women could be exposed to 5.0 ppm H_2S for 30 minutes without experiencing adverse health effects (6). It was reported that blood lactate levels did not significantly increase due to exposure to H_2S. The author noted that the blood samples were taken from an artery as opposed to a vein which may account for lower blood lactate levels. Although the increases were not considered significant, there was some increase in blood lactate levels in 70% of the men and 83% of the women exposed to hydrogen sulfide compared to control conditions.

The NOAEL for the study was 5.0 ppm. Like the critical study, the 1994 study was conducted on humans; therefore only one of the uncertainty factors required by EPA standard procedures was needed, allowing for a lower overall uncertainty factor. The only uncertainty factor NDEQ needed to apply was that related to sensitive populations. An uncertainty factor of 10 is used to protect against adverse health effects in sensitive populations.

The study was well-controlled and subjected to significant peer review, but it lacked a exposure-response evaluation, as there was only one level of exposure. The author noted that the blood sampling location was not the most appropriate for evaluating enzyme activity and blood lactate levels. The study also focused on the respiratory system instead of the cytochrome oxidase activity. The respiratory system is not the most sensitive system. For these reasons the NDEQ utilized a modifying factor of 5.

The reference concentration was calculated as follows:

$$\frac{5.0\,ppm}{5*10} = 0.10\,ppm$$ averaged over a 30-minute period

The exposure period for the study was 30 minutes.

Bhambhani 1996 (7)

In 1996 the Bhambhani research team looked at the effects of H_2S on the respiratory system (7). They exposed 19 healthy men and women to 10 ppm for 15 minutes while they were exercising on bicycles. The subjects exercised at 50% of their maximum aerobic power. The researchers found that respiratory function was not affected as a result of the exposure. Although this study did not focus on enzyme activity, it does represent effects on respiratory function.

The NOAEL for the study was 10.0 ppm. The study was conducted on humans; therefore only one of the uncertainty factors required by EPA standard procedures was needed, allowing for a lower overall uncertainty factor. The only uncertainty factor NDEQ needed to apply was that related to sensitive

populations. An uncertainty factor of 10 is used to protect against adverse health effects in sensitive populations.

The study was well-controlled and subjected to significant peer review, but lacked a exposure-response evaluation, as there was only one level of exposure. For these reasons, the NDEQ utilized a modifying factor of 5.

The reference concentration was calculated as follows:

$$\frac{10.0\,ppm}{5*10} = 0.20\,ppm$$ averaged over a 15-minute period

In order to compare this with the 30 minute proposed level, an equivalent standard over a 30-minute period is calculated. This is done using the equations outlined in Section 13.1:

> The NDEQ calculated the equivalent exposure and concentration which would be inhaled over a 30-minute period. The exposure is calculated using the following equation:
>
> **Concentration * Time = Exposure**
>
> The equivalent exposure received over 15 minutes when exposed to 0.20 ppm is:
>
> **0.2 ppm * 15 minutes = 3.0 ppm•minutes**
>
> The 30-minute concentration is calculated:
>
> **Exposure ÷ Time = Concentration**
>
> **3.0 ppm•minute ÷ 30 minutes = 0.10 ppm**

This is comparable to the results obtained by using the 1991 and 1994 Bhambhani studies.

Jappinen (1990) (31)

In 1990 a study was conducted to evaluate the possible respiratory effects of H_2S on pulp mill workers (31). Along with the pulp mill workers, a group of 10 asthmatic volunteers (3 men, 7 women) was assessed for respiratory effects as a result of exposure to 2.0 ppm H_2S for 30 minutes. The subjects were exposed through the nose and mouth; therefore subjective effects could occur. In the asthmatic subjects, the airway resistance was increased and the specific airway conductance was decreased. Even though the author concluded that the overall results were not statistically significant, two subjects experienced changes greater than 30%, indicating bronchial obstruction. Although this study did not focus on enzyme activity, it does represent respiratory effects in sensitive populations.

Although the author concluded that overall the results were not statistically significant, the NDEQ considers the changes experienced by two of the subjects to be a health effect. Therefore, the NDEQ concluded that the LOAEL for the study was 2.0 ppm. Like the Bhambhani studies, the study was conducted on humans; therefore only one of the uncertainty factors required by EPA standard procedures was needed, allowing for a lower overall uncertainty factor. The Jappinen study was conducted on asthmatics who are considered a sensitive population. Therefore, the uncertainty factor for sensitive populations was not needed. The only uncertainty factor NDEQ needed to apply was consideration that a NOAEL was not derived in the study. The maximum uncertainty factor of 10 is used to extrapolate from a lowest observed adverse effect to a no observed adverse effect level.

Like the critical study, the Jappinen study was well-controlled, well-documented, and subjected to peer review. Consistent with the critical study, the NDEQ utilized a modifying factor of 2.

The reference concentration was calculated as follows:

The LOAEL for the study was 2.0 ppm. The exposure duration was for 30 minutes. The reference concentration was calculated as follows:

$$\frac{2.0\,ppm}{2*10} = 0.10\,ppm$$ averaged over a 30-minute period

13.3 Derivation of 0.01 ppm and 0.005 ppm Standards

The Nebraska Department of Environmental Quality (NDEQ) is proposing a 0.01 ppm (parts per million), 30-day rolling average ambient air quality standard for TRS when the average relative humidity is 60 percent or less. The NDEQ is also proposing a 0.005 ppm, 30-day rolling average standard when the average relative humidity is greater than 60 percent. This standard was developed based on the welfare effects of TRS on structures, specifically corrosion.

13.3.1 Corrosive Effects

Corrosion is the deterioration of a substance, usually a metal, because of a reaction with its environment (61). Air pollution is one of several factors which may contribute to metal corrosion. Other factors include humidity, temperature, and synergistic effects of pollutants. H_2S and TRS are sulfurous compounds which have corrosive effects on metals (62). H_2S is an aggressive corrosive in the aqueous

phase. H_2S will dissociate in solution to form sulfide anions which allow hydrogen atoms to attack metal surfaces. If the solution is a pH of 8 or above, H_2S will normally not attack steel.

The NDEQ reviewed information on the corrosive effects of TRS. Long-term, low-level exposure to TRS probably has the most noticeable effect on certain metals, primarily copper, silver, zinc, lead and iron. According to the Instrumentation Society of America (ISA), at levels as low as 0.01 ppm for one month, moderate corrosive effects on these metals can be detected, usually in the form of rust or tarnish. Tarnish is a film on the surface of the metal. Typically, tarnish detracts from the metal's appearance. In the case of electrical contacts, tarnish formed by TRS compound reaction with the metal surface can lead to problems with resistance and arching. This is typically in an enclosed environment and applies to sensitive electronic equipment (62). Controlling the humidity, air recirculation, pressurization, and minimizing the pollutants within an enclosed environment are key to maintaining reliable electronic equipment (58).

In a study conducted by Rice, copper and silver were exposed to 0.015 ppm and 0.038 ppm H_2S in environments with varying levels of relative humidity (67). The corrosion rate of silver was unaffected by relative humidity and was only slightly higher when the level of H_2S was 0.038 ppm. The corrosion rate of copper increased with increasing relative humidity at both levels of exposure.

13.3.2 Vegetative Effects

The effects of long-term exposure of TRS on vegetation are limited, with a wide range of sensitivity to TRS being seen across plant species. There was no apparent damage to plants exposed to levels as low as 0.03 ppm for long periods. Some species, such as alfalfa, actually exhibited growth stimulation at these lower levels. At levels above 0.3 ppm for 30 days, alfalfa yields were reduced. Based on this information, corrosion will occur before vegetation is threatened.

13.3.3 Relative Humidity

The NDEQ gathered information from the University of Nebraska to ascertain the relative humidity levels across the state. The following table summarizes the average monthly relative humidity values for 1996.

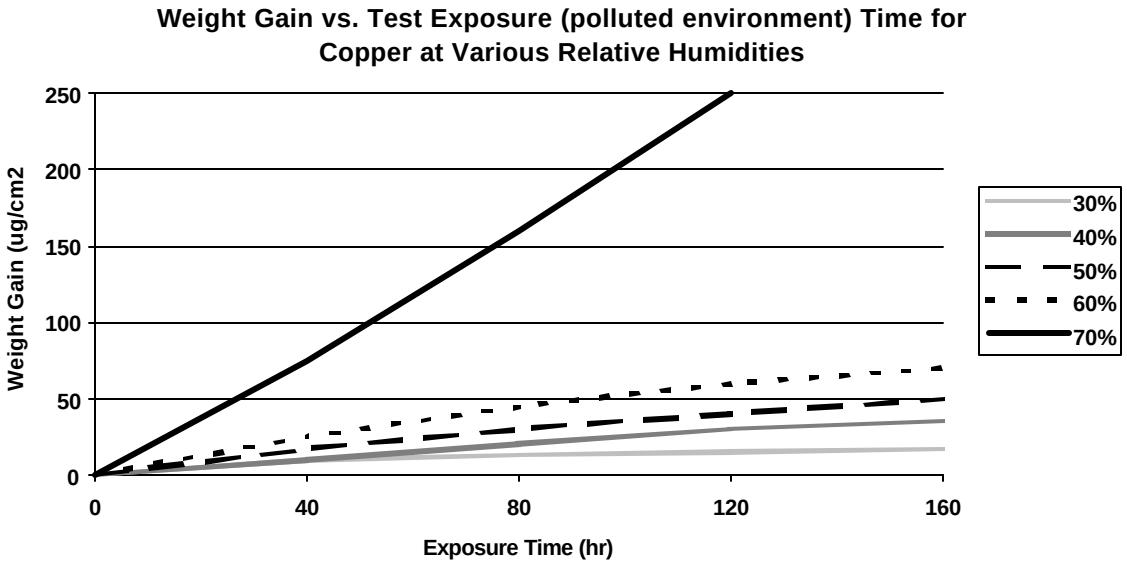
Table 13.1 Average Relative Humidities for Select Sites in Nebraska

City	January	February	March	April	May	June	July	August	September	October	November	December
Grand Island	69	70	66	61	64	63	65	67	67	63	69	71
Lincoln	70	72	69	64	67	65	65	69	70	67	72	73
Norfolk	70	72	69	62	63	64	66	69	66	64	70	73
North Platte	71	68	64	**60**	64	65	64	65	63	62	68	70
Eppley	72	71	66	62	65	66	70	71	72	67	71	74
North Omaha	69	69	66	62	64	64	71	72	70	65	71	73
Scottsbluff	66	62	**60**	**57**	**58**	**58**	**57**	**58**	**56**	**56**	63	65
Valentine	68	69	66	**59**	61	**60**	**59**	**59**	**57**	**57**	64	67

13.3.4 Derivation

Copper is a metal sensitive to TRS exposure. The NDEQ believes that copper is the metal of most concern. Ensuring that copper materials are protected from accelerated corrosion serves to address welfare concerns. Copper materials and alloys may be found in the ambient environment in such things as air conditioning coils and outdoor light fixtures.

According to Rice, corrosion rates dramatically increase when relative humidities are above 60 percent. The following graph illustrates:



The Instrumentation Society of America information indicated corrosion could be measured at 0.01 ppm over a period of one month. This recommendation was based on sensitive instrumentation such as fine gauge computer filaments. The draft proposal which the NDEQ sent out for public input included an uncertainty factor of 2 which resulted in a standard level of 0.005 ppm.

Many commentors indicated that corrosion occurs regardless of TRS levels due to other environmental factors such as moisture, light and other pollutants. In drier parts of the state, metals may tolerate higher levels of TRS. Subsequent to receiving this comment the NDEQ reviewed information regarding relative humidity and how it affects corrosion rates.

Based on this information the NDEQ agrees that the more arid parts of the state may tolerate higher concentrations of TRS compounds. Similarly, the more humid parts of the state are more susceptible to corrosion from TRS exposure. Therefore, in order to minimize the corrosive effects in more humid areas, the NDEQ applied an uncertainty factor of 2 to the Instrumentation Society of America's value of

0.01 ppm to arrive at the 0.005 ppm proposed standard for the areas of the state which have average relative humidities of greater than 60 percent. Correspondingly, for the areas of the state which have average relative humidities of 60 percent or less, the NDEQ is proposing to use the ISA's recommendation of 0.01 ppm.

14. Monitoring Methods for TRS

TRS is measured using a pulse-UV fluorescence SO_2 analyzer equipped with a TRS thermal converter. The machine scrubs all sulfur dioxide from the air stream sample and pumps the remaining air to the TRS converter where it is thermally oxidized into sulfur dioxide. The air is then pumped back to the analyzer where it is measured for sulfur dioxide. This is done by measuring the ultraviolet light absorbed by the sulfur dioxide. The results are reported as TRS in parts per million. As there is no federal ambient air quality standard for H_2S or TRS, there is no related EPA-approved monitoring method. However, there are monitoring methods available, such as those chosen by the Department, which are proven, accurate and precise. In the conduct of the TRS monitoring program, NDEQ will utilize the Quality Assurance and Quality Control methods prescribed in the NDEQ's Quality Assurance Project Plan.

Compliance with each tier of the standard will be demonstrated using the above described method. The instruments continuously monitor for TRS and are equipped to read out in 1-minute averages. Typically, ambient air quality standards are enforceable regardless of the risk, or lack thereof, associated with possible exposures. The NDEQ is proposing that the ambient standard for TRS be enforced only if there is an accompanying human exposure. Therefore, monitoring will typically occur at the nearest point of human exposure in the ambient air.

15. Other Regulatory Provisions

During the regulatory development process, the NDEQ received many comments and suggestions and much information from the concerned public, other state agencies, and the regulated community. These comments have been beneficial in the development of the proposal.

In March 1997, the NDEQ presented a preliminary draft proposal to interested parties in a series of stakeholder meetings. In the draft proposal the NDEQ included a three-tier standard:

10 ppm	**1-minute**
0.1 ppm	**30-minute rolling average**
0.005 ppm	**30-day rolling average**

The proposal which will be presented to the Environmental Quality Council in June 1997 was revised as follows:

- change to the form of the welfare-based standard to consider the effects of relative humidity (discussed in Section 13.3.4);
- addition of a provision which states that the standards apply only where human exposure occurs; and
- addition of an exception for concentrations of TRS emissions due to the seasonal turnover of lakes and lagoons.

15.1 Human Exposure

The NDEQ has taken a unique approach to implementing and enforcing the standards. The standards shall apply only where human exposure occurs. Typically, ambient standards apply anywhere the public has access. Using the risk-based management approach allows the NDEQ to use limited resources to respond to instances of TRS exposure where human exposure occurs. If there is a violation of one of the standards in a location where human exposure does not occur, the NDEQ will not be required to pursue mitigative action.

15.2 Exception for Seasonal Events

The NDEQ recognizes that there are certain events that occur infrequently for which there is no reasonable control measure available. Specifically, the NDEQ is excepting the seasonal turnover of lakes and lagoons which results in the release of TRS emissions.

15.2.1 Lakes

In the spring and early summer the combination of solar heating and wind mixing of water layers brings about the warming of the upper portion of a body of water causing thermal stratification. There are essentially three types of layers which are formed. The epilimnion is a warmer, less dense layer which floats on a cooler, denser water layer called the hypolimnion. Between these two layers is a zone of water of changing temperature and density called the metalimnion (129).

Thermal stratification influences the process occurring in a lake and may result in dissolved oxygen depletion, nutrient release, and the formation of H_2S. When turnover of the layers occurs, the H_2S may be released to the atmosphere. Turnover is dependent upon the stability of the stratification. Deeper lakes that are protected from the wind will have stable stratification persisting through much of the summer. Shallow waters are unstable due to wind influences. In shallow waters the layers may be easily mixed. In Nebraska lakes tend to either be dimictic or monomictic. Dimictic refers to having two

mixing periods each year, once during the spring and again during the fall. During the winter months the waterbody is covered with ice and becomes stagnant. As the spring warms the waterbody, the stratification becomes unstable, resulting in the spring turnover. Summer stratification begins and continues until the onset of colder weather. The cooling of the water breaks up the stratification and causes the fall turnover. During fall turnover, the waterbody continues to cool until the whole lake is uniform in temperature (about 4 degrees C). Ice is formed on the surface, and stagnation occurs until the spring turnover. Deep bodies of water such as Lake McConaughy, Merritt Reservoir, and deep sandpits are dimictic (129).

Monomictic refers to having only one mixing period which occurs during the spring. The majority of Nebraska's lakes are monomictic. Like dimictic waterbodies, monomictic bodies become stagnant during winter ice cover and mix in the spring when the stratification is no longer stable. Monomictic bodies stay mixed during the summer, warming but never stratifying. Spring turnover will typically occur three to four weeks after ice-out. The duration of the turnover is usually a few days to one week (129).

15.2.2 Lagoons

In wastewater treatment lagoons the turnover will depend upon the type of treatment provided by the lagoon.

Aerobic lagoons are those in which oxygen is utilized to biologically degrade contaminants. The cells are often shallow (2-4 feet) but can be deep (10-15 feet) and are equipped with appurtenances used to produce dissolved oxygen for bacteria respiration and to mix the lagoon contents. Due to the mixed conditions, the water temperature tends to remain constant throughout the profile, and stratification is unlikely to occur.

Facultative lagoons are those in which a combination of aerobic, facultative (functioning as neither aerobic or anaerobic) and anaerobic bacteria is utilized to biologically degrade the contaminants. Near the bottom of the lagoon cell oxygen is absent, and anaerobic bacteria function to decompose the settleable solids, etc. Near the surface, aerobic bacteria use dissolved oxygen to decompose any liquid or gaseous intermediate products. Facultative lagoons are typically 3 to 6 feet deep, and raw wastewater is delivered to the center of the bottom of the cell to allow for uniform dispersion. In the spring after ice-out, a weak stratification occurs, and eventually the less dense warmer water at the bottom rises to the surface, often carrying unstabilized particles. In lagoon operation and maintenance this is known as "spring turnover". TRS compounds may be associated with the spring turnover event. If the lagoon has not been organically overloaded, turnover lasts only a few days to a week. Facultative lagoons will not stratify during the summer months; therefore only one turnover event is expected annually.

Anaerobic lagoons are those lagoons which are designed to biologically degrade organic matter in the absence of dissolved oxygen. These lagoons are often used as a roughing process for high (organic) strength waste prior to further treatment. Anaerobic cells are often 10 to 15 feet deep and designed to retain heat which enhances treatment and removal. Often greases, oils, and scum form a layer or

"crust" on the surface which further insulates the cell. Due to the design and loadings to anaerobic cells, stratification and turnover are unlikely to occur.

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