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Retrieval and scientific interpretation of ecotoxicological information

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Sasol Group Services (Pty) Ltd

Toxicological Review for Hydrogen Sulphide

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Table of Contents

List of Tables

1 Introduction and terms of reference

Sasol Group Services (Pty) Ltd (“Sasol”) appointed INFOTOX (Pty) Ltd (“INFOTOX”) to conduct desktop reviews of data available (particularly locally for the Highveld and Vaal Triangle areas) that relate air quality parameters to adverse health effects. The intention is to review a number of air pollutants and to eventually rank the pollutants in terms of adverse health impacts. There is also a requirement to review publicly available health studies on domestic fuel burning to quantify relative impact, which will be attended to in future reports, where relevant.

Sasol requires INFOTOX to review the background methodology by which South African Ambient Air Quality Standards were derived and how this relates to international guidelines and standards. INFOTOX has to comment on and explain some of the assumptions factored into these standards, especially around exposure. Also, INFOTOX has to comment on the significance of ambient air concentrations exceeding the maximum allowable concentrations. However, there is not a South African Ambient Air Quality Standard for hydrogen sulphide.

This INFOTOX report is the first report in Phase 1 of the study and presents a toxicological review for hydrogen sulphide (H_2S).

2 Chemical description

Hydrogen sulfide is a colourless, flammable gas at ambient temperature and pressure. It has an odour similar to that of rotten eggs and is both an irritant and an asphyxiant. General chemical properties are listed below (ATSDR 2006):

Molecular weight	34.08 g/mol
Density in air at NTP	1.19 (air = 1.00) kg/m^3
Conversion factor	1 ppm = 1.4 mg/m^3 at 20 ºC
Water solubility	4.1 g/litre at 20 ºC

3 Overview of health effects

3.1 Carcinogenicity

Carcinogenicity studies on human exposure to hydrogen sulphide were not available in the scientific literature. However, no increase in cancer incidence was recorded in a cohort living downwind from natural gas refineries in Alberta, Canada, from 1970 to 1984 (ATSDR 2006). The US Department of Health and Human Services (DHHS), the International Agency for Research on Cancer (IARC), and the USEPA have not classified hydrogen sulfide for carcinogenicity (ATSDR 2006). The noncarcinogenic effects of hydrogen sulphide was thus assessed in this INFOTOX study.

3.2 Noncancer toxicity – acute exposures

While many organ systems have been assessed for potential effects exerted by hydrogen sulphide, the olfactory, respiratory and nervous systems appear to be most affected at low exposure concentrations (ATSDR 2006). The effects of hydrogen sulphide on several target organ systems suggest that it is a broad-spectrum toxicant.

The Concise International Chemical Assessment Document 53, published under the joint sponsorship of the United Nations Environment Programme, the International Labour Organization, and the World Health Organization, and produced within the framework of the Inter-Organization Programme for the Sound Management of Chemicals (WHO 2003), listed certain health effects that have been observed to occur at certain exposure levels of hydrogen sulphide in air. These are summarised in Table 3.2.1. Other references, as discussed below, support the general hierarchy of health effects associated with exposure levels.

Table 3.2.1: Key health effects documented at certain exposure concentrations of hydrogen sulphide in air (WHO 2003).

Concentration mg/m^3	Health effect	Reference
≥ 700	Death	Beauchamp et al. 1984
> 560	Respiratory distress	Spolyar 1951
> 140	Olfactory paralysis	Hirsch and Zavala 1999
28	Fatigue, loss of appetite, headache, irritability, poor memory, dizziness	Ahlhorg 1951
5 to 29	Eye irritation	IPCS 1981
7 to 14	Increased blood lactate concentration, decreased skeletal muscle citrate synthase activity, decreased oxygen uptake	Bhambhani and Singh 1991; Bhambhani et al. 1996, 1997
5.0	Increased eye complaints	Vanhoorne et al. 1995
2.8	Bronchial constriction in asthmatic individuals	Jappinen et al. 1990
0.011	Odour threshold	Amoore and Hautala 1983

There are several case reports of deaths due to exposure to hydrogen sulphide. Most fatalities occurred in relatively confined spaces (e.g., sewers, sludge tanks, cesspools, or hydrogen sulphide accumulated in buildings, pits or in dips on open land). The mechanism of hydrogen sulphide toxicity is cellular hypoxia, caused by inhibition of cytochrome oxidase, which is similar to the mechanism of cyanide toxicity (OEHHA 1999). Hydrogen sulphide inhibits the enzyme cytochrome oxidase, which prevents body cells from using oxygen. Thus, hydrogen sulphide impairs the body's ability to use oxygen and the primary target organs for acute toxicity are the central nervous system and the heart.

Although there is a large volume of published information on human exposure to hydrogen sulphide, in most cases the exposure levels and exposure durations are unknown or crudely estimated (Oesterhelweg and Püschel 2008; Knight and Presnell 2005; CHEMINFO 2005). For any indoor or outdoor source of hydrogen sulphide, the airborne concentrations at any time period in the vicinity of that source could vary by several to many orders of magnitude within short time periods.

Hirsch and Zavala (1999) reported olfactory paralysis at concentrations above 140 mg/m^3, but according to OEHHA (1999), olfactory fatigue may already prevent detection of hydrogen sulphide odour at concentrations exceeding 70 mg/m^3.

Clinical findings in case reports of overexposure situations and occupational studies confirm that neurotoxicity is the principal concern at high exposure levels of hydrogen sulphide. Several groups of investigators (referenced in USEPA 2003) reported long-term adverse neurological sequelae of hydrogen sulphide induced unconsciousness in humans during occupational, accidental, and chronic exposures including neuropsychological and neurobehavioural decrements, brain damage, and, in one instance, dementia (USEPA 2003).

Lee et al. (2009) reviewed a case in which a 24-year old male worker at a sewage disposal plant was transferred to the emergency medical center of a university hospital with myocarditis and acute myocardial infarction. The hydrogen sulphide concentration in air at the scene was reported as 95 mg/m^3 (rounded), but it was estimated that the actual exposure concentration could have been higher than 900 mg/m^3 over a period of ten minutes. The case showed good prognosis without neurological sequelae despite the high exposure, probably due to rapid detoxification by physiological oxidation reactions.

The IRIS database (IRIS 2003) for hydrogen sulphide highlighted that nasal tract and neurological effects may be elicited by hydrogen sulphide. Neurological alterations in animals noted at the lowest level of hydrogen sulphide exposure are regarded as possible indicators of a neurotoxic effect. Altered morphology of cerebellar Purkinje cells (Hannah and Roth 1991) at 28 mg/m^3 and altered neurotransmitter levels in the brains of postpartum rat pups exposed in utero and postpartum to 28 mg/m^3 hydrogen sulphide (Skrajny et al. 1992), are observed in the same hydrogen sulphide concentration range as noted for the clearly adverse nasal tract lesions reported by Brenneman et al. (2000). Brenneman and co-workers reported a no-observed-adverse-effect level (NOAEL) of 14 mg/m^3 hydrogen sulphide.

A well-controlled study by Jappinen et al. (1990) evaluated the effects of hydrogen sulphide exposure on the respiratory systems of asthmatic subjects. The study was conducted to evaluate the possible respiratory effects of hydrogen sulphide on pulp mill workers. 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 2.8 mg/m^3 hydrogen sulphide for 30 minutes. Three of the 10 volunteers complained of headache. 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 per cent, indicating bronchial obstruction. Although with some limitations, the study did indicate the potential for respiratory effects in sensitive individuals.

The closeness in exposure levels eliciting these effects indicate that the exposure range is in the critical transitional area in the exposure-dose-severity continuum for a variety of endpoints. Bhambhani and Singh (1985) reported that exposure of 42 individuals to 3.5 to 7 mg/m^3 hydrogen sulphide caused coughing and throat irritation after 15 minutes. No statistical alterations in lung function were observed in a group of 10 asthmatics exposed to 2.8 mg/m^3 hydrogen sulfide for 30 minutes, as compared to pre-exposure values. However, increased airway resistance and decreased specific airway conductance, implying bronchial obstruction, were observed in 2 out of the 10 subjects.

Generally, it has been found that health effects in human populations exposed for long periods to low levels of hydrogen sulfide cannot serve as a basis for setting tolerable concentrations, because of either co-exposure to several substances or insufficient detail on exposure characterisation (WHO 2003).

3.3 Noncancer toxicity – chronic exposures

The daily inhalation exposure of the human population to hydrogen sulphide that is likely to be without an appreciable risk of deleterious effects during a lifetime, the RfC, has been determined as 2 µg/m^3 (IRIS 2003). The RfC is an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure of the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from a no-observed-adverse-effect level (NOAEL), a lowest-observed-adverse-effect level (LOAEL), or benchmark concentration, with uncertainty factors generally applied to reflect limitations of the data used.

WHO (2003) derived a medium-term tolerable concentration of 20 µg/m^3 for exposure up to 90 days based on rat studies published by Brenneman et al. (2000).

Exposure to hydrogen sulphide in the Sasol study area is intermittent in nature, due to irregular short-term excursions into higher hydrogen sulphide concentrations, interspersed with longer episodes of low concentrations. It is known from the literature that health effects can occur as a result of short-term exposure; therefore, it was considered appropriate to conduct the risk assessment on the basis of short-term exposure considerations.

4 Hydrogen sulphide odour and health concerns

4.1 Study focus

Data on low-level environmental exposures to hydrogen sulphide are more limited than studies of severe effects and mortality at high exposure levels, as has been discussed above in this section. Most studies of non-lethal effects at environmental levels have been conducted in the parts-per-million (mg/m^3) range in ambient air. These concentrations are much higher than the levels where the unpleasant hydrogen sulphide odour results in the expression of annoying discomfort.

Aside from the higher concentration ranges, the potential for development of adverse health effects in individuals exposed to hydrogen sulphide at concentrations in the parts-per-billion (µg/m^3) range (where odour is an annoyance factor) is of concern. This is an important consideration in the overall assessment of the impacts of hydrogen sulphide on community health, but these have not been described as conclusively as the effects at higher exposure levels. As will be indicated in Section 5 below, control of exposures of communities to hydrogen sulphide through consideration of the odour threshold and annoyance level has been applied in setting ambient air quality guidelines in certain jurisdictions.

The focus of this study is primarily on low concentration exposures at or slightly above the odour annoyance level.

4.2 Odour and sensory perception

The sensory perception of odorous substances has four major components, namely, detectability, intensity, character and hedonic tone (Cha 1991).

Two types of thresholds are distinguished. Firstly, the odour detection threshold is the lower limit of the perceived odour intensity range that can be detected. It refers to the minimum concentration of a substance that would elicit a sensory response in the olfactory receptors of a specified percentage of a given population, usually 50 percent of the cases where the odour is present. Secondly, the odour recognition threshold refers to the lowest concentration at which the sensory effect can be recognised correctly in 50 per cent of the cases in the test group.

Odour intensity refers to the perceived strength of the odour sensation. The intensity increases as a function of concentration according to the relationship in Equation 4.2.1:

$$I = k C^n \qquad (4.2.1)$$

Where:

I	Perceived intensity of the odour sensation
k	A constant: the y-intercept of the psychophysical function
C	Concentration of the substance
n	Slope of the psychophysical function

The slope and intercept vary with the type of odorous substances with the parameter *n* varying typically between 0.2 and 0.8. A ten-fold decrease in concentration for a substance with a value of *n* = 0.2 would lead to a reduction in odour intensity of 1.6, whereas for *n* = 0.8, the reduction in intensity would be a factor of 6.3. Hydrogen sulphide is a so-called low-*n* substance (Niessen 2002). Due to the exponential relationship between the perceived odour intensity and the concentration of the substance (Equation 4.2.1), a reduction in hydrogen sulphide concentration of a specific magnitude has less influence on the odour intensity than does a reduction of the same magnitude for substances with high *n*-values, such as ammonia and aldehydes. The implication of this is that relatively large reductions in source concentrations of hydrogen sulphide have to be achieved to reach a noticeable reduction in the intensity of the perceived odour sensation.

The third characteristic of odour is described as its character, namely, its characteristic smell. The odour of hydrogen sulphide is described as *"rotten eggs"*.

The fourth dimension of odour is its hedonic tone. This is a categorical judgement of the relative pleasantness or unpleasantness of the odour. Perception of hedonic tone is influenced by such factors as subjective experience, frequency of occurrence, odour character, intensity and duration. These factors determine when a specific odour becomes a nuisance to an individual. The nuisance threshold is defined as the concentration at which not more than a small percentage of the affected population (not more than 5 per cent) experiences annoyance for a small part of the time (less than 2 per cent). Because odour annoyance is influenced by a number of socio-economic psychological factors, WHO (2000) advised that a nuisance threshold cannot be determined on the basis of concentration alone.

The terminology described above is not followed consistently in the literature. For example, a review of odour threshold data for hydrogen sulphide concluded that 68 per cent of the general population would be expected to have a detection threshold for hydrogen sulphide in air of 10 µg/m^3 (Amoore and Hautala 1983), representing the geometric mean of all available published data. It is uncertain whether this referred to a detection threshold or a recognition threshold. The geometric mean recognition threshold reported by CHEMINFO (2005) is 6.3 µg/m^3. It was suggested that age, sex, medical conditions and smoking habits would affect the detection threshold, but no specific detail was provided by Amoore and Hautala (1983).

Willhite and Dydek (1991) pointed out that widely variable odour thresholds are probably the result of variances in the test protocol, consideration of a single compound at a time as opposed to mixtures of contaminants in ambient air, the relationship between a laboratory-derived threshold and practical community odour perception, etc. These authors developed a guideline for predicting off-site odour impacts of sources from an odour impact model study that reported relationships between detection thresholds and complaint levels. It was indicated that compounds with an unpleasant odour have the potential to cause annoyance at concentrations exceeding three-times the detection threshold. Applying this 3-fold multiplier to the mean detectable level of 10 µg/m^3 results in a mean annoyance threshold of 30 µg/m^3 for hydrogen sulphide.

More recently, Collins and Lewis (2000) reviewed several studies that have been conducted to establish the ratio of discomforting annoyance threshold to detection threshold for unpleasant odours. The geometric mean of the ratios determined in these studies was a ratio of 5. According to these studies an unpleasant odour should result in annoying discomfort when it reaches an average concentration of 5 times its detection threshold. Applying the 5-fold multiplier to the mean detectable level of 10 µg/m^3 results in a mean annoyance threshold of 56 µg/m^3 for hydrogen sulphide.

4.3 Description of symptoms at low exposure levels

The types of symptoms and observations that may be reported by individuals exposed to hydrogen sulphide at low exposures are listed below (Fiedler et al. 2008). Reference to haematopoietic effects is from Legator et al. (2001). These descriptions are of interest in the interpretation of controlled studies and case reports of exposure to hydrogen sulphide and have been used in questionnaires for community surveys in situations of low levels of exposure.

Type of symptom	Manifestation
Central nervous system	Headache Fatigue Lightheaded Drowsy Nausea
Haematopoietic	Clotting disorder Bruising Anaemia

Cognitive	Difficulty in concentrating Disoriented/confused Dizzy
Eye irritation	Burning, dryness or itching Runny or watery eyes
Anxiety	Feel jittery in body Feel nervous Heart palpitations Feel tense Worried
Upper respiratory tract	Sneeze Nasal congestion Choking Throat irritation (burning or dryness) Nose irritation (dryness or itching)
Lower respiratory tract	Shortness of breath Wheeziness Chest tightening Chest pain Coughing
Somatic control[1]	Skin irritation or dryness Stomach ache Numbness Ear ringing Leg cramps Back pain Sweating Body aches

5 Responses to low levels of hydrogen sulphide in ambient air

As described by Jon-Fang Don (1999), direct action of hydrogen sulphide on mucous membranes is usually observed first by symptoms of eye irritation, resulting from local inflammation of the conjunctiva and cornea. Acute inflammation of conjunctiva accompanied by lacrimation and mucopurulent exudate often occurs. Corneal erosion with blurred vision may also occur. Occasionally, corneal ulceration may occur, resulting in impaired vision. Since the cornea is affected together with the conjunctiva in many instances, the ophthalmologic effects of hydrogen sulphide exposure is more accurately described as keratoconjunctivitis, rather than conjunctivitis. In general, irritation of the eyes occurs at a concentration of hydrogen sulphide of 70 µg/m^3; however, conjunctivitis or "sore eyes" have been observed upon exposures in the range of 7 to 140 µg/m^3.

The current California Ambient Air Quality Standard (CAAQS) for hydrogen sulfide is 42 µg/m^3, averaged over one hour. The standard was adopted in 1969 and was based on the geometric

[1] The section of the nervous system responsible for sensation and control of the skeletal muscles.

mean odour threshold measured in adults. The purpose of the standard was to decrease odour annoyance in communities (OEHHA 1999). At this concentration the odour would be detectable by 83 per cent of the population and would be discomforting to 40 per cent of the population (Amoore 1985). These "theoretical" estimates have been substantiated by odour complaints and reports of nausea and headache (Reynolds and Kamper 1984, cited in Roth and Goodwin 2003) at 42 µg/m^3 hydrogen sulphide exposures from geyser emissions. Most information on hydrogen sulphide toxicity was obtained from studies that assessed exposure levels of hydrogen sulphide orders of magnitude above the standard and the concentration of 42 µg/m^3 can thus not be interpreted as a threshold in terms of health effects without supporting information to this end.

Collins and Lewis (2000) reviewed several studies with the aim of establishing whether or not this CAAQS of 42 µg/m^3 would be adequately protective against adverse health effects. The review also included a discussion of whether significant adverse health effects would reasonably be expected to occur especially amongst infants and children at exposure concentrations below the CAAQS. The report is rather inconclusive, stating that the CAAQS is well below the no-observed-adverse-effect levels (NOAELs) from animal experiments where exposure lasted weeks to months. According to the authors, comparison with the OEHHA reference exposure level of 8 µg/m^3 chronic exposure was also not helpful. The fact that the authors conducted a detailed review of available literature but was still unable to come up with unambiguous conclusions demonstrates the paucity of studies from which clear exposure-response interpretations can be made at these low concentrations.

Campagna et al. (2004) examined the possible relationship between ambient levels of hydrogen sulfide and total reduced sulfur (TRS) and hospital visits among residents of Dakota City and South Sioux City, Nebraska. Total reduced sulfur is the combined concentrations of hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Air monitoring data in this study indicated that hydrogen sulfide was the primary constituent of the total reduced sulfur. A high TRS or hydrogen sulfide level was defined as a 30-minute rolling average of ≥ 42 µgm^3. Among children younger than 18 years, positive associations were found between hospital visits for all respiratory disease (including asthma) and high hydrogen sulfide level the previous day. Such associations were also found with high levels of TRS on the previous day. Positive associations were found between and the previous day's high hydrogen sulfide level in adults, while the previous day's total reduced sulphur was related to hospital visits for asthma in children. The study also reported some high levels of hydrogen sulphide as ≥ 90 ppb (≥ 125 µg/m^3) and it is thus not possible to draw a clear correlation between the hospital visits and actual exposures over selected periods of exposure. Given the cut-off of ≥ 42 µgm^3 for high exposures in the study, it can be interpreted that the focus was on low-level exposures in the µg/m^3 range, although the upper limit was not actually stated.

Fiedler et al. (2008) studied sensory and cognitive effects of acute exposure to hydrogen sulphide. The study was based on concentrations of 70, 700 and 7 000 µg/m^3. The study did not report on zero exposures to hydrogen sulphide as a point of reference and the data were thus reported relative to the three concentrations, mostly with reference to the 70 µg/m^3 exposure level. The assessed concentrations were relatively high and it is not possible to draw conclusions from this study that would assist in the assessment of effects of hydrogen sulphide levels in air at the low end of the range of exposures.

Legator (2001) conducted a study of multi-symptom effects of chronic low-level exposures to hydrogen sulphide. Areas with relatively high ambient hydrogen sulphide exposures were identified at Odessa in Texas and at Puna in Hawai. At Odessa, measured exposure levels were 500 to 750 µg/$m^3$for maximum 8-hour exposures, 150 to 300 µg/m^3 for highest daily exposures and 3 to 40 µg/m^3 for annual average exposures. At Puna, a peak concentration of 421 µg/m^3 was recorded. Periodic releases of hydrogen sulphide were also measured in the range 280 to 700 µg/m^3. Considering reference to hourly recordings of data in the text of the report, it is inferred that these excursions were expressed as hourly averages.

Three reference communities were selected where concentrations of hydrogen sulphide were insignificant. Trained interviewers used a specially designed, menu-based computer questionnaire to conduct a multi-symptom health survey.

Legator (2001) listed several limitations of the study, but concluded that the two selected exposed communities were very similar in terms of the reported adverse health outcomes. When comparing the responses of the exposed communities to responses of the unexposed reference communities, 9 out of 12 symptom categories had iterated odds ratios above 3. The highest odds ratios (and therefore the strongest statistical relationships) were for central nervous system, respiratory and haematopoietic systems at the exposure concentrations.

Kilburn and Warshaw (1995) assessed an exposure scenario involving sulfide gases, including hydrogen sulphide, downwind from the processing of "sour" crude oil. The authors studied 13 former workers and 22 neighbours of a California coastal oil refinery who complained of headaches, nausea, vomiting, depression, personality changes, nosebleeds, and breathing difficulties. Limited off-site air monitoring (one week) in the neighborhood measured average levels of 14 µg/m^3 hydrogen sulphide (with peaks of 139 µg/m^3), but also dimethylsulfide, and mercaptans. The mercaptans were not specified. The authors concluded that neurophysiological abnormalities were associated with exposure to reduced sulfur gases, including hydrogen sulphide, from crude oil desulfurisation. However, because exposures were to a mixture of sulphur compounds, the interpretations cannot be regarded as conclusive for exposure to hydrogen sulphide. Although not discussed by the authors, it is important to note that there were peaks almost ten times the weekly average concentration and, most likely, the responses would have been associated with the peak (short-term) higher concentrations of hydrogen sulphide (139 µg/m^3). The authors did not state the durations of these peaks.

Haahtele et al. (1992) measured hydrogen sulphide concentrations for two days at a monitoring station during the implementation of a new processing technique at a near-by paper mill. This new process caused temporary increases in the measured ambient air concentrations of hydrogen sulphide. The 4-hour averaged concentrations during the high exposure period were 4 to 5 times higher and the maximum concentration 20 times higher than the concentrations before and after the excursion during the implementation. The highest 4-hour concentration was 135 µg/m^3 and the 24-hour averages for the two days were 35 and 43 µg/m^3, respectively. It was noted that sulphur dioxide concentrations were very low, but that mesityloxide was also noticeable, although it was not measured. Generally, the emission of mesityloxide from paper mills is of much less concern that the generation of hydrogen sulphide. It is therefore judged that the focus by Haahtele et al. (1992) on exposure to hydrogen sulphide is of primary value. An open-ended questionnaire was administered during the high concentration period and was repeated four months after the event during a reference period of two days four months after the event. Observations of difficulties in breathing, irritation of the eyes, headache and nausea were recorded during the high exposure period, but not during the reference period. Mental symptoms were also reported during the high exposure period. The authors stated that the prevalence of these symptoms was significantly higher during the high exposure period than during the reference period.

In a study by TNRCC (1998), six workers were exposed to a mean concentration of 125 µg/m^3 hydrogen sulphide for approximately 5 hours in a monitoring van downwind from an oil refinery. Persistent odours were reported and eye and throat irritation, headache and nausea were reported by these workers. This report concurs with other observations, such as those reported by Haahtela et al. (1992).

In a review of the literature by Roth and Goodwin (2003), reference was made to anonymous reports of nausea and vomiting near manure lagoons where hydrogen sulphide was present in the air. Two of the tests showed mean hydrogen sulphide levels of more than 139 µg/m^3, with one of the sites measuring 187 µg/m^3. Eight out of 32 tests showed mean hydrogen sulphide concentrations greater than 70 µg/m^3. These are assumed to be direct readings not reflecting time-averaged concentrations. Although somewhat anecdotal, these observations also support the reports by TNRCC (1998) and Haahtela et al. (1992).

Following the findings of a number of peer-reviewed studies, the Implementation & Monitoring Unit of the Air Quality Section of the Nebraska Department of Environmental Quality derived a reference concentration of 0.1 ppm (140 µg/m^3) for respiratory effects averaged over a 30-minute period (NDEQ 1997). Although the reference concentration was developed for TRS, the Department has concluded that, from a toxicological standpoint, TRS and hydrogen sulphide are interchangeable. The reference concentration is included in this review because the derivation is well supported in that it followed US Environmental Protection Agency (USEPA) methodology for deriving ambient air reference concentrations, using either animal or human health studies (USEPA 1989).

In order to avoid substantial complaints about odour annoyance among the exposed population, the World Health Organization (WHO 2000) recommended that hydrogen sulfide concentrations should not be allowed to exceed 7 µg/m^3, based on a 30-minute averaging period. This is much lower than the California Ambient Air Quality Standard (CAAQS) for hydrogen sulfide of 42 µg/m^3, averaged over one hour. A health-based guideline value of 150 µg/m^3 with an averaging time of 24 hours was proposed by WHO (2000), based on eye irritation.

Logue et al. 2001 conducted health studies in an elementary school affected by hydrogen sulphide from composting facilities and in a school in Chester County, southeastern Pennsylvania, as well as in a school not affected by hydrogen sulphide as a control. The surveys were conducted in spring and in autumn. Oudoor and indoor concentrations were monitored by the State Environmental Agency. A school health questionnaire was developed that covered symptoms of eye irritation (burning), dry or sore throat, skin irritation or rash, tightness in the chest, runny nose, asthma (worsening of), cough, wheezing or other breathing problems, dizziness, headache, nausea of vomiting and other symptoms.

Hydrogen sulphide concentrations ranged between <14 and 95 µg/m^3 for indoor air and between 17 and 82 µg/m^3 as one-hour averages for the spring survey. For the autumn survey, the concentrations ranged between <14 and 110 µg/m^3 for indoor air and between 25 and 180 μg/m^3 as one-hour averages. No consistent association was found between exposure to these low one-hour averaged concentrations and recorded symptoms in the study. However, it must be noted that ambient differences between spring and autumn could have introduced other factors besides hydrogen sulphide exposure, and hence the lack of statistical significance.

Heaney et al. (2011) conducted a study on the relation between malodour, ambient hydrogen sulphide and health in a community bordering a landfill. Although ambient hydrogen sulphide concentrations were associated with reports of landfill odour, even the highest hourly average concentrations of hydrogen sulphide were at or below the detection threshold. The landfill odour represents a complex mixture of several gaseous compounds and the observed health effects can thus not be attributed to hydrogen sulphide on its own.

6 Long-term health effects of exposure to hydrogen sulphide

Roth and Goodwin (2003) reviewed studies on long-term health effects of hydrogen sulphide, which are expanded on in this section. Long-term exposure of children to low levels of sulfur compounds (annual average hydrogen sulphide of 1 to 8 μg/m^3; daily average of 15 to 100 μg/m^3) has been associated with increased cough and nasal symptoms (Martilla et al. 1994, cited by Roth and Goodwin 2003) and upper respiratory tract infections (Jaakkola et al. 1991, cited by Roth and Goodwin 2003).

Exposure of adults to total reduced sulfur compounds near a pulp mill at annual mean concentrations of 2 to 3 μg/m^3 was associated with increased cough, nasal symptoms and respiratory infections (Partti-Pellinen et al. 1996, cited by Roth and Goodwin 2003).

Roth and Goodwin (2003) also reviewed a study that reported increased nervous system symptoms in a cross-sectional study of citizens living near an industrial wastewater treatment pond and geothermal processing facility (Legator et al. 2001, referred to previously in Section 5). Partti-Pellinen et al. (1996) reported an increased risk of headache or migraine in a community exposed to TRS compounds at an annual mean concentration of 2 to 3 μg/m^3. Roth and Goodwin (2003) referred to an abstract of a publication by Boev et al. (1998) in which it was reported that agents emitted by a sulphide-containing gas processing plant had adverse effects on the functional status of children who resided in the vicinity of the plant, namely, decreased vital capacity of the lung, decreased mental performance, retarded sensory-motor responses and alterations of the enzymatic system.

The conclusions from these studies have to be contextualised. It is not inferred simplistically that adverse health effects as described would develop at low annual averaged hydrogen sulphide concentrations. The premise of the studies is that the communities that were the subject of investigations resided in areas where hydrogen sulphide was present in ambient air as a result of a specific source or sources. It is also evident that short-term peaks in exposure levels occurred, although the measure of exposure was a long-term average concentration. Therefore, in the vicinity of sources of hydrogen sulphide it is likely that adverse health effects may develop in members of the community even though annual averaged concentrations may be low – even below the odour detection threshold. It is possible that the adverse health effects were associated with the short-term peaks, although these peaks were not apparent from the low annual averaged hydrogen sulphide concentrations. It should be concluded that averaging of concentrations over longer periods may mask peak exposures, while the peak exposures may contribute to long-term health effects.

7 Summary of concentrations and effects of exposure to hydrogen sulphide

Table 7.1 lists ambient air concentrations of hydrogen sulphide selected from the literature review presented in this documented. Where available, averaging times are presented and the most pertinent observations are presented.

The intention of this table is to provide a framework for the health-risk based interpretation of ambient air concentrations recorded in the Sasol study area. The exposure concentrations and health observations in the table have been collated from a review of the scientific literature, as presented in the preceding sections.

Table 7.1: Selection of concentrations for exposure to hydrogen sulphide in ambient air and key observations.

Concentration (µg/m^3)	Averaging time	Observation/endpoint/symptom	Reference
6.3	Not specified	Geometric mean odour recognition threshold	CHEMINFO (2005)
7	30 minutes	Protection against odour	WHO 2000
10	Not specified	Odour detection threshold for 68 per cent of the population	Amoore and Hautala 1983
30	Not specified	Mean odour annoyance threshold	Willhite and Dydek 1991
42	1 hour	California Ambient Air Quality Standard Odour detectable by 83 per cent of the population and would be discomforting to 40 per cent of the population	OEHHA 1999 Amoore 1985
56	Not specified	Mean odour annoyance threshold	Collins and Lewis 2000
125	5 hours	Persistent odour, eye and throat irritation, headache and nausea	TNRCC 1998
135 35 to 43	4 hours 24 hours	Difficulties in breathing, irritation of the eyes, headache and nausea	Haahtele et al. 1992
139	30 minutes	Nebraska ambient air quality guideline Respiratory effects	NDEQ 1997
150	24 hours	Eye irritation in humans	WHO 2000

8 Situation assessment

Table 8.1 lists reported ambient air concentrations for various averaging times at specific locations in the Sasol study area. The data illustrate a situation of low average hourly concentrations, while it is clear that high concentration peaks occur, as indicated by the hourly maximum concentrations that are higher than the average by orders of magnitude.

Table 8.1: Measured hydrogen sulphide concentrations in ambient air (Sasol data).

Location	Monthly (max)	Daily (max)	Hourly (max)	Hourly (average)
	µg/m^3			
Amersfoort	30.1	34.3	118	2.77
Secunda - Sasol Club	8.2	32.6	164	5.31
Langverwacht	12.1	67.3	237	6.94
Springs	12.5	46.4	188	3.23
Grootvlei	10.2	23.8	81	1.23
Rosebank	5.4	20.9	77	4.96

It is clear that exposure in the Sasol study area is manifested as intermittent in nature due to irregular short-term excursions into higher hydrogen sulphide concentrations, interspersed with longer episodes of low concentrations. This scenario would typically concur with short-term reports of odour annoyance and some health symptoms as described in the publications reviewed in Section 5.

Odour annoyance is likely to be registered by exposed individuals at hourly maximum concentrations in the region of 30 to 60 µg/m^3 and above (Table 7.1). This concentration range covers practically all receptor locations (Table 8.1). It is, however, uncertain how frequently these maximum hourly values are recorded. It is thus necessary to determine the frequency of higher peaks in order to assess odour impacts and the likelihood of complaints by communities.

In terms of health effects, INFOTOX is of the opinion that the WHO 24-hour guideline concentration (150 µg/m^3) is not adequately protective of exposed communities. Averaging of concentrations over 24 hours has the potential to mask high short-term excursions that may occur over one or more hours. It can thus not be ruled out that compliance with this guideline would prevent the recognition of adverse health responses. The WHO guideline appears insufficiently protective, considering reports of eye and throat irritation, difficulties in breathing, headache and nausea associated with exposures in the range of 125 to 135 µg/m^3 over a period of 4 to 5 hours (Table 7.1).

The selection of air concentration guidelines for managing hydrogen sulphide exposure should take cognisance of what is known and not known of low-level hydrogen sulphide exposures and health outcomes, as discussed in this document. The published information provided somewhat limited, but convincing evidence that exposures should be limited to lower excursion concentrations over shorter averaging times than the WHO guideline. It is clear that the selection of a lower guideline air concentration averaged over a period shorter than 24 hours is warranted. The establishment of a practicable management guideline, stipulating both an air concentration and averaging period should be determined by taking into consideration costs of reduction of hydrogen sulphide emissions and potential health benefits achieved by such curtailment.

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