



*Full Length Research Paper*

## **An assessment of occupational exposure to hydrogen sulfide (preliminary study – Libya pilot study)**

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### **ABSTRACT**

Hydrogen sulfide gas is a major gaseous pollutant associated with the oil and gas industry, with a direct toxic effect in the workplace in oilfields, and causing damage to the surrounding ecosystem. The Arabian Gulf Oil Company, which was established in 1965, is responsible to the Libyan government, and produces oil and gas in cooperation with international companies. The company has four fields spread over the Libyan desert, one of which was the location for this study. This field is located within 51 kilometers approximately of Oasis Gallo, and employs 650 workers, including engineers and technicians. However, hydrogen sulfide gases produced by oil and gas companies cause the most serious environmental damage to habitats and to aquatic populations. Release to the environment is primarily in emissions to the ambient air, where the chemical is likely to remain for less than 1 day, but may persist for as long as 42 days in winter. Hydrogen sulfide may evaporate easily from water, depending on temperature and PH; it is unlikely to bioconcentrate and biomagnify in the food chain. The concentration of hydrogen sulfide in air in unpolluted areas is very low, between 0.03 and 0.1  $\mu\text{g}/\text{m}^3$ . The samples were distributed in and around the field, and measurements were carried out at frequent intervals. The study focused on measuring the concentration levels of hydrogen sulfide. Sampling procedures were carried out according to regulations of the company, and were distributed around the different areas of the turbine plant site. Therefore, exposure doses among the workers depended on the exposure time according to internationally accepted standards. Consequently, the assessment of H<sub>2</sub>S in the field, are as follows: 100 ppm recorded near gas stations, 88 ppm in sections, 97ppm near the wells, and 33 ppm recorded after 1 kilometer away, east of the main terminal. Though, the length of time for which workers were exposed to the gas in those locations determined the severity of the risk of minimum values of H<sub>2</sub>S concentration being exceeded. but, the chronic daily intake assumed to be 1060 mg, and the risk will be  $1,1 \times 10^{-5}$ .

**Keywords:** Indoor, Outdoor, Chronic daily intake and Exposure.

### **INTRODUCTION**

Humans may be exposed to hydrogen sulfide from both endogenous and exogenous sources. Most endogenous production results from the metabolism of sulfhydryl containing amino acid (e.g. cysteine) by bacteria present in both the intestinal tract and the mouth. Hydrogen sulfide is also produced in the brain and several smooth muscles (e.g. thoracic aorta, ileum, and portal vein) by enzymes found in these tissues. In rats, the endogenous level of hydrogen sulfide is 50-160 $\mu\text{mol}/\text{litre}$  in the brain, and 1 mmol/litre in the ileum (Selene, 2003).

Human exposure to exogenous hydrogen sulfide is

principally via inhalation, and the gas is rapidly absorbed through the lungs. Hydrogen sulfide is metabolized through three pathways: oxidation, methylation, and reaction with metalloproteinase or disulfides containing proteins. Oxidation in the liver is the major detoxification pathway. The major oxidation product is thiosulfate, which is then converted to sulfate and excreted in the urine. Methylation pathways also serve as a detoxification route.

Hydrogen sulfide is a colorless gas that is known by its characteristic rotten egg like odor. Its toxicity is a result

of its reaction with metalloenzymes. In the mitochondria, cytochrome oxidase, the final enzyme in the respiratory chain, is inhibited by hydrogen sulfide.

Approximately 90 percent of the sources that emit hydrogen sulfide into the air are natural (EPA, 1993). Hydrogen sulfide is released into the air as a product of the decomposition of dead plant and animal material (DOM) which occurs especially in wet conditions with limited oxygen, such as in swamps. Hot springs, volcanoes, and other geothermal sources also emit H<sub>2</sub>S. Anthropogenic releases of H<sub>2</sub>S into the air result from industrial processes, primarily from the extraction and refining of oil and natural gas and from paper and pulp manufacturing (New York State Department of Health) but the gas is also present at sewage treatment plants, manure-handling plants, tanneries, and coke oven plants (Public Health Statement for Hydrogen Sulfide)

Release to the environment is primarily in emissions to the ambient air, where the chemical is likely to remain for less than 1 day, but may persist for as long as 42 days in winter. Hydrogen sulfide may evaporate easily from water, depending on temperature and PH; it is unlikely to bioconcentrate and biomagnify in the food chain. The concentration of hydrogen sulfide in air in unpolluted areas is very low, between 0.03 and 0.1 µg/m<sup>3</sup> (Selen)

Single inhalation exposure to high concentrations of hydrogen sulfide causes health effects in many systems. Health effects that have been observed in humans following exposure to hydrogen sulfide include death and respiratory, ocular, neurological, cardiovascular, metabolic, and reproductive effects.

There have been numerous case reports of human deaths after single exposures to high concentrations (≥700 mg/m<sup>3</sup>) of hydrogen sulfide gas (Beauchamp et al, 1984). Low concentration exposure to this gas can burn the respiratory tract and cause swelling around the eyes (ANSI, 1992). Most fatal cases associated with hydrogen sulfide exposure have occurred in relatively confined spaces; victim loses consciousness quickly after inhalation of hydrogen sulfide, sometimes after only one or two breaths ( the so called " slaughterhouse sledge hammer effect").

Many case studies have involved assumed accidental poisoning for which the exposure concentration and/or duration were not known. Death occurring after a single exposure to high concentration of hydrogen sulfide would appear to be the result of respiratory failure or arrest, with most cases initially presenting with respiratory insufficiency, non cardiogenic, pulmonary oedema, coma, and cyanosis (Selen). Outdoor workers are exposed to many types of hazards that depend on their type of work, geographic region, season, and duration of time they are outside.

Industry sectors with outdoor workers include the

agriculture, forestry, fishing, construction, mining, transportation, warehousing, utilities, and service sectors. Outdoor workers include farmers, foresters, landscapers, groundskeepers, gardeners, painters, roofers, pavers, construction workers, laborers, mechanics, and any other worker who spends time outside. Indoor environments are highly complex and building occupants may be exposed to a variety of contaminants (in the form of gases and particles) from office machines, cleaning products, construction activities, carpets and furnishings, perfumes, cigarette smoke, water-damaged building materials, microbial growth (fungal, mold, and bacterial), insects, and outdoor pollutants. Other factors such as indoor temperatures, relative humidity, and ventilation levels can also affect how individuals respond to the indoor environment (Center for Disease Control and Prevention, 2013).

The company has four fields spread over the Libyan desert, one of which was the location for this study. This field is located within 51 kilometers approximately of Oasis Gallo, and employs 650 workers, including engineers and technicians.

Exposure assessment is the step that quantifies the intake of an agent resulting from contact with various environmental media (e.g.; air, water, soil, food) , exposure assessment can address past, current, or future anticipated exposure, although uncertainties can become significant when attempting to anticipate what might have happened or what will happen. An exposure is considered chronic when it takes place over a substantial portion of the person lifetime (Theory and Practice, 2002).

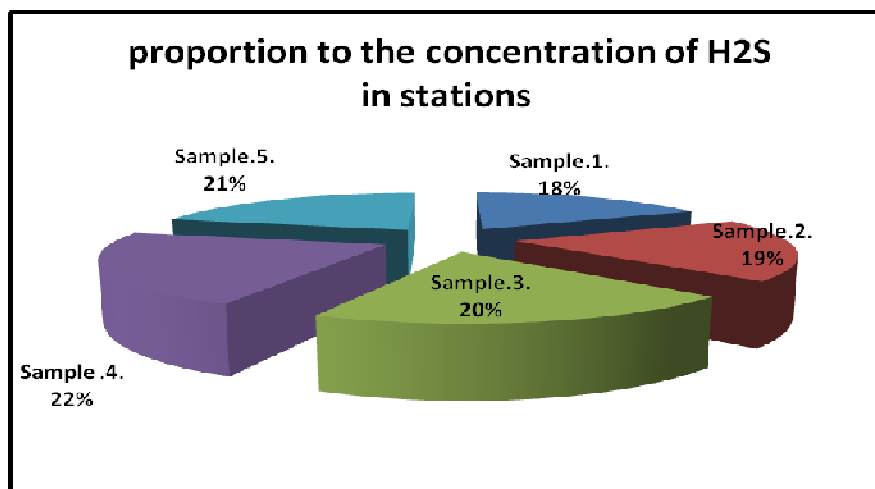
The samples were collected from different places in and around the field, and measurements were carried out at frequent intervals. The study focused on measuring concentrations of hydrogen sulfide. Sampling procedures were carried out according to company regulations, and were distributed around the different areas of the turbine plant site. The exposure doses among the workers depended on exposure time according to internationally accepted standards.

The period of time for which workers were exposed to levels of gas in those locations determined the severity of the risk of the minimum level of H<sub>2</sub>S concentration being exceeded.

Consequently, the assessment of H<sub>2</sub>S in the field, are as follows: 100 ppm recorded near gas stations, 88 ppm in sections, 97ppm near the wells, and 33 ppm recorded after 1 kilometer away, east of the main terminal. Though, the length of time for which workers were exposed to the gas in those locations determined the severity of the risk of minimum values of H<sub>2</sub>S concentration being exceeded. But, the chronic daily intake assumed to be 1060 mg, and the risk will be  $1,1 \times 10^{-5}$ .

**Table 1.** Shows the average concentration of H2S , in various stations

The average concentration P.P.M.				Sampling places	
Stations No.7	Stations No.4	Stations No.2.	Station no.1.		
96	96	66	86	Sample.1.	1
100	98	71	73	Sample.2.	2
92	100	73	81	Samole.3.	3
99	93	82	76	Sample .4.	4
90	89	78	74	Sample.5.	5



**Figure1.** Shows the proportion of concentration of different stations.

**Table 2.** indicate the concentration of H2S, near the oil and gas extractions wells.

Time of measurement (hr)	Ave. concentration P.P.M.	Place of samples	
08:30	95	Well no.171.	1
09:00	97	Well no. 206	2
09:30	73	Well no.192	3

**MATERIALS AND METHOD**

**Experimental set up:**

Company engineers placed the measuring devices in locations both inside and outside the field, in order to measure concentrations of H2S. Furthermore, this device is able also to measure concentrations of CO, O2 (The device called QRAE, consist of Covers diffusion pump models with firmware version, and automatically measures the gaseous, ranged from 2.05 to 100ppm), in and out work environment.

**RESULTS AND DISCUSSION**

Table 1 contains the results of measurements that were

taken near the stations in the field. The highest levels of concentration of H2S were recorded in station No. 7, and No.4, which is 100 ppm, due to this being the closest point to the turbine site. Meanwhile, the lowest level of concentration was recorded in gas station No. 2, and this indicates that the concentration of gas fell with increasing distance from the turbine site, i.e.17ppm. All the measurements taken in the stations exceeded the limit of exposure, for a period of 8 hours per working day. This confirms the risk of direct damage to workers in the workplace. Where figure 1. Shows the percentage of the concentration in accordance to their position from the stations.

There was a limited amount of variation among the readings in the concentration levels during the periods of regular measurement. This was due to the quantity and time of pumping oil out of the ground, as well as the

**Table 3.** The concentration of H<sub>2</sub>S near the oil reservoirs, in the field.

H <sub>2</sub> S concent. (P.P.M.)	Tanks volume(Lit)	Place of sampling	ت
28	35000	Tank1	1
25	31000	Tank2	2
31	43000	Tank3	3

**Table 4.** The concentration of H<sub>2</sub>S in site technical departments

Time of measurement	Ave. H <sub>2</sub> S conc. P.P.M.	Place of sampling	ت
08:00	47	operation division	-1
08:30	61	Maintenance department	-2
09:10	43	Petroleum Eng. Department	-3
09:55	88	Dep. of drying gas	-4
10:40	69	Dep. Of loss prevention	-5
11:20	77	Lab. sections	-6
12:00	53	Dep. Of drilling wells	-7

**Table 5.** The concentration of H<sub>2</sub>S outside the work environment (ppm).

P.P.M.	Sampling directions		
	Dist. From field ( meters)	Directions	
33	1000	East	.1
19	1000	West	.2
8	800	North	.3
11	1000	South	.4

depth of the well. Table 2. Shows the highest recorded, i.e. which is 97 ppm, and the lowest level which is 73ppm.

However, there was greater variation in the concentration of hydrogen sulfide near the oil storage reservoirs, as table 3 demonstrates. It indicates the concentration of hydrogen sulfide vs the quantity of oil in these tanks. The highest concentration was found near storage tank number 3, at 31 ppm; this reservoir held the largest amount of oil. There is a direct correlation between the amount of oil in the tank and the concentration of H<sub>2</sub>S.

On the other hand, different results were produced on the concentration of H<sub>2</sub>S in the working environment, while the lowest concentration of gas was found in sample (No. 3), which is 43ppm. In the Department where gas was dried, the gas contained hydrogen sulfide, with the same applying in the laboratory department, where analysis of oil and gas was taking place, and perhaps this is the main reason for the high level of concentration of hydrogen sulfide gas, and the low level of concentration of the gas in sections in different

locations. Hence, it was found that the technicians and engineers in this field were subject to H<sub>2</sub>S exposure, which in the long run will cause serious problems.

In comparison, concentrations of this gas in locations far from the field varied enormously. This was because the wind direction and sunlight hours also play a role in transferring pollutants. Table 5 indicates that to the east of the field, 1000 meters distant from the field, 33ppm was registered, whereas in the western part 19 ppm was registered, and the southern part registered 11.ppm. Nevertheless, measurement was made more difficult due to wind movement.

Therefore, the residents around this field are subject to H<sub>2</sub>S exposure and are consequently exposed to health problems, particularly relating to asthma and blood pressure.

Certainly, the concentrations of gas indoors and outdoors, exceed the limit, according to the World Health Organization guidelines, and exposure to this gas might cause health problems. Figure 2. Shows the concentration indoor and outdoor, which indicate that the exposure to the gas from the technician and engineering

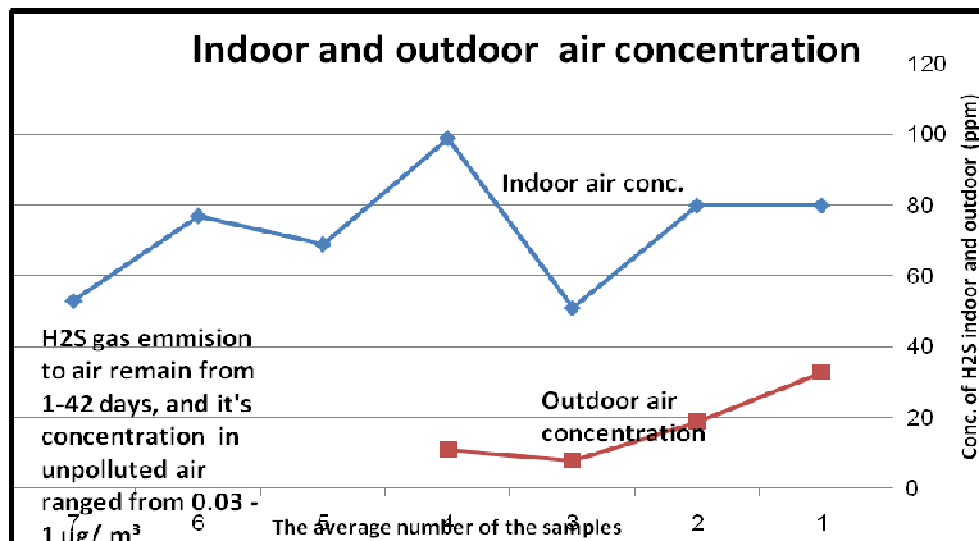


Figure 2. Indicted air concentration indoor and outdoor.

is higher in comparison with residents in Gallo.

Finally; the occupational exposure assessment according to this equation (Gillbert, 1991):

**Chronic daily intake (CDI) = total dose / body weight (kg) \* lifetime (days).**

We assume body weight is 70 kg , lifetime is 70 years , and potency factor 0,02.

Then, CDI equal to 0,000592 and the risk is  $1,1 \cdot 10^{-5}$

## CONCLUSION

Hydrogen sulfide is a highly toxic gas. It reacts with enzymes in the blood stream to inhibit cell respiration, and high concentrations of hydrogen sulfide can shut off the lungs. Hydrogen sulfide gases, produced by oil and gas companies can cause most serious environmental damage to habitats and to aquatic populations.

This is a preliminary study conducted in Libya, focusing on one of the four desert fields of the Arabian Gulf Oil Company, which produces oil and gas in cooperation with international companies.

This study identified high concentrations of H<sub>2</sub>S gas in the air, indoors and outdoors, and there is the probability that exposure to high levels of this gas increases the risk of exceeding the minimum level of H<sub>2</sub>S concentration.

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