U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ... Health Service
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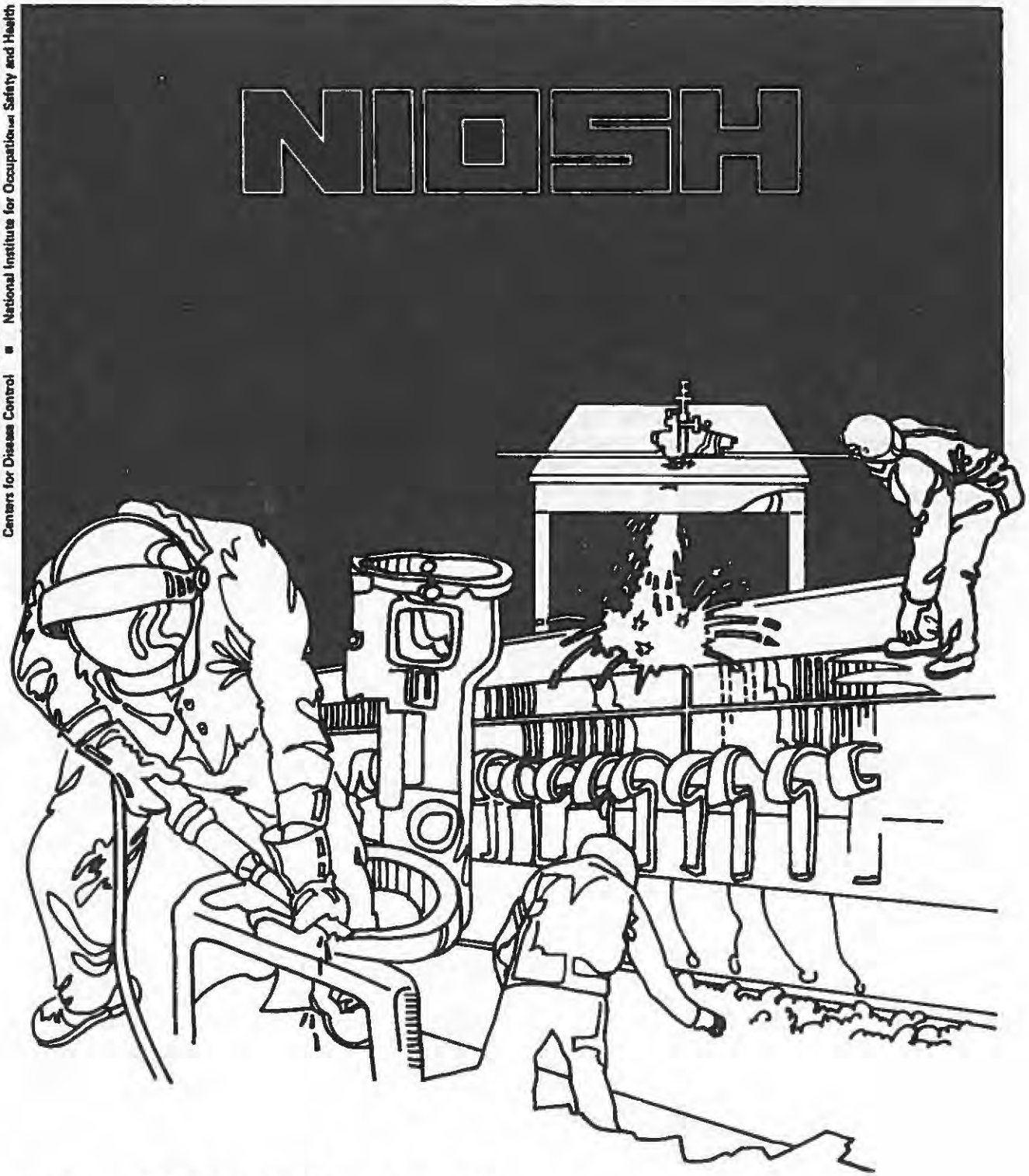

Health Hazard Evaluation Report

HETA 81-327-1161
CARRIBEAN GULF REFINING CORPORATION
BAYAMON, PUERTO RICO

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial nygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

HETA 81-327-1161
August 1982
Carribean Gulf Refining Corporation
Bayamon, Puerto Rico

NIOSH INVESTIGATORS:
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I. SUMMARY

In July and October 1981, a Health Hazard Evaluation was conducted by the National Institute for Occupational Safety and Health at the Carribean Gulf Refining Corporation in Bayamon, Puerto Rico, to evaluate employee exposures to tetraethyl lead, hydrogen sulfide and other refinery contaminants. General air samples were obtained for measurement of polycyclic aromatic hydrocarbons, nitrosamines, hydrogen sulfide, carbon monoxide, volatile organic vapors and tetraethyl lead. Personal air samples were obtained for measurement of exposure to hydrocarbons and hydrogen sulfide. Health questionnaires were completed on 47 exposed workers and 19 office workers as controls. Medical records were reviewed on 45 workers with current or previous exposure to tetraethyl lead.

Hydrogen sulfide exposure represents a potential health hazard at open maintenance ports at the gas compressors of the Gulfiner Unit (50 ppm, 10 feet downwind of the open ports) and the flare knock-out drum (50-200 ppm). Personal monitors showed highest exposures, 10 and 14.3 ppm, to maintenance personnel cleaning the roof above the gas concentration unit. NIOSH recommends a 10 minute ceiling of 10 ppm.

A direct reading instrument for carbon monoxide indicated levels at flanges and blanks in the piping system at peak potential exposures of 600 ppm. NIOSH recommends worker's exposures be limited to 35 ppm as a 10 hr. TWA, and a 200 ppm ceiling.

Two personal air samples for benzene exceeded the NIOSH recommended standard of 3.2 mg/M^3. One was obtained during maintenance activities (placing of blanks in the platformer unit) and one was obtained during process sampling at the platformer unit. Analysis of air samples for tetraethyl lead, toluene, xylene, nitrosamine, aliphatic hydrocarbons and aromatic hydrocarbons did not show concentrations above NIOSH recommended criteria.

Personal samples of sulfates ranged from 10-26 ug/M^3 with a mean concentration of 18 ug/M^3. There are no NIOSH recommended criteria for exposure to sulfates.

The health questionnaires revealed that statistically significant excesses of reported throat and eye irritation were reported most frequently in maintenance workers. Symptoms of intoxication while at work were reported most frequently among both maintenance and operations workers when compared with office workers controls.

Review of medical records revealed no workers with history of elevated blood or urine lead values.

On the basis of data obtained in this evaluation, NIOSH determined that a health hazard to hydrogen sulfide existed at the Gulfiner Unit, and benzene at the Platformer Unit at the Carribean Gulf Refining Corporation in Bayamon. Workers in these areas were exposed to concentrations above the NIOSH recommended standards for these substances. In addition, a potential exposure to carbon monoxide existed at the CO Boiler. Health and safety recommendations are offered in the body of the report.

KEYWORDS: SIC 2911,hydrogen sulfide, carbon monoxide, benzene.

II. INTRODUCTION

On May 26, 1981, the National Institute for Occupational Safety and Health (NIOSH) received a request for a Health Hazard Evaluation from the President of the Union de Trabajadores de la Industria del Petroleo representing workers at Carribean Gulf Refining Corporation in Bayamon, Puerto Rico. The request expressed concern about potential lead poisoning among workers exposed to tetraethyl lead, about eye and nose irritation experienced by workers throughout the plant, respiratory diseases in workers in the sulfur unit and about exposures to hydrogen sulfide in other areas of the plant.

On July 13-14, 1981 NIOSH conducted an initial site visit and preliminary survey. An opening conference was held with union and company representatives in which the nature and scope of the request and plans for the survey were discussed. Additional concerns were raised by union representatives about maintenance workers exposed to the water cooling towers, skin problems at the waste treatment facility, and lack of air conditioning in the waste treatment control room and laboratory.

The initial evaluation included a walk-through of the plant and general area air sampling for polynuclear aromatic hydrocarbons (PNA's), nitrosamines, H_2S, CO , volatile organic vapors, and tetraethyl lead. Confidential interviews were performed with 14 of the 200 production workers.

NIOSH distributed Interim Report #1 for this investigation in September 1981. Interim recommendations centered on improved maintenance practices and respiratory protection to reduce potential exposures to H_2S and CO, and improved personal protective devices to provide skin protection in areas of potential skin irritant exposure.

A follow-up survey was conducted on October 14-16, 1981 to collect personal air samples for hydrocarbons and H_2S. In addition, exposures at the sulfur plant were evaluated during teardown and maintenance activities. Medical questionnaires were administered to 52 of the 325 workers involved in maintenance, operators, office work, laboratory work and work with tetraethyl lead. Company medical records on workers exposed to tetraethyl lead were also reviewed.

III. BACKGROUND

The Carribean Gulf Refinery plant is located on the Bay of San Juan in Catano near Bayamon, Puerto Rico. It was constructed in 1955. It currently employs 325 workers, including 110 production (operations) workers on 3 shifts, 90 maintenance workers on day shift primarily, and 125 technical, supervisory and clerical workers.

The capacity of the refinery is 40,000 barrels of crude oil per day, and the refinery is currently operating at 26,000 barrels per day, exclusively using Venezuelan crude containing approximately 1% sulfur.

Crude oil is unloaded from tankers at a docking facility, transported to tanks for storage, then processed using the following units:

1. Crude Distillation. Two crude distillation columns are used to produce the following products: light ends, straight run gasoline, naptha, intermediates (kerosene, diesel) and heavy ends.

2. Vacuum Distillation. One unit separates heavy crude from residual oil and heavy gas oil. Top ends from vacuum distillation are sent to the Fluid Catalytic Cracker (FCC), low ends go to the asphalt plant.

3. FCC Unit. Diesel oil and gas oil are cracked by the fluid catalytic cracker using a silica and aluminum catalyst. Regeneration of the catalyst produces large amounts of carbon monoxide waste (CO) used as a fuel in the CO Boiler.

4. Gas Concentration Unit. Recovers various hydrocarbons as pure products.

5. Pretreater and Platformer. Removes sulfur compounds and then makes more compact aromatics to improve the octane rating of gasoline.

6. Gulfiner unit. Removes sulfur from diesel oil, resulting in a gaseous stream that may be up to 35% H_2S at 200 PSI.

7. Amine unit. Uses monoethanolamine to remove sulfur from intermediates (kerosene, diesel). H_2S is then sent to the sulfur plant where H_2S and SO_2 are reacted to produce elemental sulfur and water.

8. Tetraethyl lead addition unit. Tetraethyl lead is added to gasoline in a batch process by weighing quantities in a large tank then mixing the TEL in line with the gasoline which is then sent to the tank farm for storage. Other areas include an asphalt plant, loading racks for gasoline and asphalt, laboratory, and waste water treatment plant.

IV. METHODS

A. Environmental

1. Initial Survey

On the initial survey, air samples were collected for PNA's, nitrosamines, hydrocarbons, tetraethyl lead, H_2S and CO. A bulk sample of the catalyst used in the FCC was obtained for laboratory analysis of free silica.

Six general area air samples for PNA's were collected at the FCC unit and the asphalt loading dock. Air samples for PNA's were collected on glass fiber/silver membrane filters with a porous polymer backup tube using portable pumps at a flow rate of 2.0 liters per minute (lpm). They were extracted with benzene for benzene soluble analysis, evaporated to dryness, then reconstituted with acetonitrile for analysis by high performance liquid chromatography.

Five general area air samples for nitrosamines were collected on thermasorb tubes at the amine unit by means of portable pumps operating at a flow rate of 1.5 lpm. They were desorbed by backflushing with 2 ml of acetone and analyzed by gas chromatography/thermal electron analysis using a 10% carbowax 20 M + 2% KOH column.

Five air samples for hydrocarbons were collected on 3M Organic Vapor Monitors (OVM) in several areas of the refinery. 3M OVM badges operate on the principle of passive adsorption of organic vapors onto activated carbon. They were desorbed in carbon disulfide and analyzed qualitatively by gas chromatography using a 10% SP-1000 column and a flame ionization detector.

Four personal and area samples for tetraethyl lead were collected during a blending operation at the organic lead blending building on SKC 226-30-03 porous polymer tubes at a flow rate of 1.0 lpm. These samples were analyzed according to NIOSH Method S383 by gas chromatography with a photoionization detector.

A direct reading Ecolyzer 6000 H_2S personnel monitor was used to conduct a hydrogen sulfide survey at selected locations in the refinery. A direct reading Ecolyzer 6000 CO personnel monitor was used to conduct a carbon monoxide survey at the CO boiler.

2. Follow-up Survey

On the follow-up survey 26 personal air samples (breathing zone) and one area sample were collected for benzene, toluene, xylene, aliphatic hydrocarbons and aromatic hydrocarbons by means of charcoal tubes and portable pumps which were calibrated at 50cc and 200cc per minute. They were desorbed with 0.5 ml carbon disulfide and analyzed according to NIOSH Method P&CAM 127.

Personal air samples for hydrogen sulfide were collected on long term detector tubes and an MDA Chronotox system. Four personal air samples were collected on cellulose ester membrane filters in the sulfur plant using portable battery operated pumps at a flow rate of 1.5 lpm. These samples were analyzed by ion chromatography for sulfates and sulfites.

B. Medical

1. Initial Survey

Workers from the departments of Operations and Maintenance were selected at random to participate in the medical evaluation from the seniority list provided by the company. Several additional individuals with suspected cases of occupational disease known to the union were also asked to participate. Each worker was interviewed privately in either Spanish or English using a questionnaire concerning past medical history, symptoms, social history and occupational history.

2. Follow-up Survey (October 1981):

Workers involved in maintenance, operations, planning and services (laboratory) and plant management (office controls) were selected at random for the medical study from a list of current employees provided by the company. Alternates were selected if the original employee was not available during the dates of the survey. In addition, all workers who had previous or current exposure to tetraethyl lead were requested to participate. Company medical records of all workers with regular known contact to tetraethyl lead were reviewed.

Participants were interviewed privately in either Spanish or English. The interviews consisted of questions regarding past medical history, current symptoms, respiratory problems, social history and occupational history.

C. Evaluation Criteria

1. Hydrogen Sulfide

Hydrogen sulfide is an irritant of the eyes and respiratory tract at low concentrations. At high concentrations, it rapidly causes respiratory paralysis with consequent asphyxia. Inhalation of 1000 ppm can cause a coma after a single breath and can be rapidly fatal. 300 ppm is considered immediately hazardous to life and health. Prolonged exposure to 250 ppm causes pulmonary edema. Exposure to levels above 50 ppm for one hour can produce acute conjunctivitis with pain, lacrimation, and photophobia. In severe form, this can lead to keratoconjunctivitis and vesiculation of the corneal epithelium (surface of the eye). Prolonged exposure to 50 ppm also causes rhinitis, H_2S pharyngitis, bronchitis and pneumonitis. The lower limit of odor detection is 0.02 ppm. At about 100 ppm it may not be detectable due to olfactory fatigue. Thus, the odor cannot be relied upon as a warning of dangerous H_2S concentrations. The OSHA acceptable ceiling concentration for H_2S is 20 ppm, with an acceptable maximum peak of 50 ppm for 10 minutes once if no other measurable exposure occurs. The NIOSH recommended criteria for exposure to H_2S is a ceiling concentration no greater than 10 ppm as determined by a 10 minute sampling period. NIOSH recommends evacuation of an area if the concentration of H_2S equals or exceeds 50 ppm. No published litertaure is available concerning the extent of low-level chronic and acute exposures among refinery workers.

2. Carbon Monoxide

Carbon monoxide is an odorless, colorless gas. It causes tissue hypoxia by preventing the blood from carrying sufficient oxygen. Carbon monoxide combines reversibly with the oxygen-carrying sites on the hemoglobin molecule with an

affinity ranging from 210-240 times greater than that of oxygen. Since CO causes damage by hypoxia, symptoms are seen in those tissues with the greatest oxygen consumption -- the brain and the heart.

With exposure to high concentrations such as 4000 ppm and above, transient weakness and dizziness may be the only signs before collapse. 1500 ppm is considered immediately dangerous to life and health. Exposures to concentrations of 500-1000 ppm causes headache, rapid heart beat, nausea, weakness, dizziness, mental confusion, and in some cases, hallucinations. Exposure to 50 ppm for 90 minutes may cause aggrevation of angina pectoris. The OSHA personal exposure limit is 50 ppm (for an 8 hour time weighted average). NIOSH recommends 35 ppm with a 200 ppm ceiling.

V. RESULTS

A. Environmental

The results of the initial H_2S survey utilizing a direct reading instrument are presented in Table 1. They indicate several point sources of the gas in the refinery. Open maintenance ports at the off-gas compressors of the Gulfiner Unit (not in operation at the time of the survey) were point sources of H_2S. Levels were as high as 50 ppm 10 feet downwind of the open ports. The Gulfiner strips H_2S from diesel fuel. Presumably, the levels would be higher if the unit were in operation. H_2S levels at the flare knockout drum ranged from 50 ppm at the drum pit to 200 ppm at the flare knockout drain valve. There was also a strong ammonia-like odor in the air during the knockout drum draining operations. Open ports at the gas concentration units' gas compressors were also determined to be significant sources of H_2S (greater than 250 ppm).

The results of the personal and area samples for H_2S taken during the follow-up survey are contained in Table 2. Concentrations ranged from below the limit of detection to 14.3 ppm. The highest personal exposures (TWA of 14.3 and 10 ppm) were obtained from maintenance personnel who were cleaning and painting the roof above the gas concentration unit. (NIOSH recommends personal exposure of less than 10 ppm for a 10 minute period.)

The carbon monoxide survey at the CO boiler is presented in Table 3. CO passes from the catalytic regeneration unit of the fluid catalytic cracker to the CO boiler where it is used as fuel. Leaks were detected at flanges (greater than 600 ppm) and stops (blanks) in the piping system.

The results of the personal and area samples taken for hydrocarbons are presented in Table 4. One personal air sample for benzene (7.3 mg/M^3) taken during maintenance activities (the placing of blanks in the platformer unit) was above the NIOSH recommended criteria of 3.2 mg/M^3. No personal air samples for benzene exceeded the OSHA

standard for benzene (32 mg/M^3). One short-term personal air sample (30 minutes) taken while process samples were collected from the platformer unit had a concentration of 3.3 mg/M^3. Analysis of the remaining air samples for toluene, xylene, aliphatic hydrocarbons and aromatic hydrocarbons did not demonstrate any air concentrations which exceeded OSHA or NIOSH recommended criteria/standards on the days of the survey.

Table 5 contains the results of personal air samples collected for sulfates and sulfites in the sulfur plant during maintenance and cleaning activities. Personal breathing zone concentrations of sulfates ranged from 10 to 26 ug/M^3 with a mean concentration of 18 ug/M^3. No sulfites were observed above the limit of detection (2 ug/M^3). There are no OSHA or NIOSH recommended standards/ criteria concerning sulfates and sulfites.

The limit of detection for tetraethyl lead is 0.650 ug/sample. None of the air samples collected on the day of the survey were above the limit of detection.

Analysis of PNA general area air samples for benzo(a)pyrene, chrysene, pyrene, benz(a)anthracene, fluoranthene and benzene solubles indicated no levels of benzene solubles greater than 0.02 mg/M^3. The OSHA standard is 0.2 mg/M^3. Of the above PNA's, only pyrene was detected (at 0.06 ug/M^3 on two samples). On the basis of these results, no further air samples for PNA's were collected on the follow-up survey.

The detection limit for nitrosamines was 5 ng/sample, the limit of quantitation was 10 ng/sample. In the amine stripping unit, only one of the general area air samples which was collected (at the still column, 5 feet above ground level) was above the limit of detection for dimethylnitrosamine. However, this sample remained below the limit of quantitation and, therefore, cannot be reported as an air concentration. Since no significant levels of nitrosamines were observed during the initial survey, no additional samples were collected on the follow-up survey.

Bulk sample analysis of the catalyst used in the fluid catalytic cracker by X-ray diffraction revealed no levels of quartz or cristobalite (free silica) which were above the level of detection (1.5% of the bulk sample).

B. Medical

1. Initial Survey

All 14 workers who were selected to participate agreed to be interviewed. Ages ranged from 22-64 with a mean of 42 years. Eleven males and 3 female workers were interviewed. Two workers had a history of hypertension, and two workers had histories of ulcers of the stomach or duodenum. Frequency of symptoms reported are in Table 6. The most prominent symptoms are those of mucous membrane irritation, particularly of the eyes and throat

(71%). Half of those interviewed reported episodic intoxication from work exposures. Four workers had symptoms suggestive of chronic bronchitis (all 4 were current or past smokers, however). Five workers, all operators, reported episodic feelings of chest discomfort or difficulty breathing. Four workers reported episodes of wheezing.

Five workers reported skin problems. One worker, an operator in the waste treatment area, reported suffering itching rashes on arms and legs associated with pouring soda ash from bags into ponds using short rubber gloves and wearing low top shoes.

2. Follow-up Survey

A total of 52 active employees (16%) participated in the follow-up study. A breakdown of the study participation by department is shown below.

Department	Total	selected		participants		alternates	total participants			
	#	#	%	#	%	#	#	%	M	F
Maintenance	90	20	22	9	10	4	13	14	13	0
Operators	110	38	35	12	10	7	19	17	18	1
Office	125	20	16	15	12	4	19	15	14	5
Lab		1		1		0	1		1	0
Totals	325	84		37		15	52		46	6

Frequencies of reported symptoms is shown in Table 6. Statistically significant excesses compared with office and management controls were noted in eye irritation and sore throat in maintenance workers, and symptoms of intoxications while at work among both operators and maintenance workers.

These differences could not be explained on the basis of smoking, mean age or duration of employment among the three groups since the three groups did not differ significantly in these parameters.

Smoking history	Maintenance	Operators	Office Controls
Never smoked	5	8	6
Previously smoked	3	4	5
Currently smokes	5	7	8
Mean age	40 yrs.	39 yrs.	42 yrs.
Mean seniority	12 yrs.	9 yrs.	14 yrs.

Sex distribution was different between the three groups, however, and may explain some of the observed differences.

Sex	Maintenance	Operators	Office Controls
Male	13	18	14
Female	0	1	5

(p=.02 when Maintenance and Operators are combined and compared with Office Controls using Fishers Exact Test).

No trends were observed in prevalence of reported location of work for any of the symptoms reported.

With the assistance of the company medical department, medical records of workers with known or potential tetraethyl lead (TEL) exposures were reviewed. The periodic company evaluation of TEL exposed workers was previously performed by Ethyl Corporation physicians, but since 1980 has been performed by company physicians. This periodic evaluation includes a physical examination, and blood and urine tests. In particular, medical records of five currently exposed workers who are certified by the company for work in the TEL area revealed no cases of elevated blood or urine leads, or reported symptoms suggestive of TEL exposure. Five other workers had previous evaluations which led to their rejection from further certification for work with TEL due to medical conditions which might be exacerbated by exposure to TEL: diabetes mellitus, kidney disease and stomach disorders.

VI. DISCUSSION

A. Environmental

The environmental results indicate that hydrogen sulfide exposure represents a potential health hazard in several areas of the refinery. Significant point sources were measured at the gas concentration unit, the Gulfiner unit and at the flare knockout drum. Several of the point sources were greater than 250 ppm (the maximum reading obtainable on the direct reading instrument). At least one of the personal samples repeatedly exceeded both the OSHA ceiling concentration of 20 ppm and the NIOSH recommended criteria of a 10 ppm ceiling concentration as determined by a 10 minute sampling period. This sample was collected on 10-16-81 while a painter was working under the roof of the gas concentration unit. For this sample, the MDA Chronotox unit indicated an air concentration for the duration of sampling for H_2S which was 10 ppm. However, analysis of the MDA Chronotox printout (which presents concentrations for each 15 minute sampling period, then averages them) for this sample indicated that 5 of the 15 minute sampling periods measured hydrogen sulfide levels which were equal to or exceeded the OSHA ceiling concentration of 20 ppm. Nine of the 15 minute sampling periods on this sample exceeded the NIOSH recommended ceiling of 10 ppm for a 10 minute sampling period. Analysis

of the air sample collected on the wastewater treatment operator on 10-15-81 indicated an average concentration of 1.5 ppm, however, the MDA Chronotox printout demonstrated that one of the 15 minute sampling periods had an average concentration of 25 ppm, while a second 15 minute sampling period had a concentration of 11 ppm. This suggests exposure to one of the point sources (possibly the flare knockout drum) located near the wastewater treatment plant.

The flare knock-out drum has an automatic pump which should drain it, but the float mechanism which triggers the pump frequently sticks in the on position causing the pump to continue pumping even when the drum is empty. This has caused many pump failures and necessitates manual draining of the pump. Operators stated that the H_2S gases released during these manual draining operations are extremely irritating. H_2S was also detected at 10-15 ppm at the wastewater treatment plants' primary separator following the draining of the flare knockout drum into the sewer drainage system.

Repair of the flare knock-out drum system and control of the point sources located during this survey should be priority items for the health and safety department.

Significant point sources of carbon monoxide were also measured at the CO boiler. Leaks were detected at several of the stops (blanks) which were inserted in the pipes. The purpose of the stops (blanks) in the system is to prevent the passage of CO while work is performed downstream of the stops. Therefore, these leaks represent a potentially serious health hazard for maintenance people working on the system or entering boilers to perform routine maintenance.

Personal air samples for hydrocarbons indicated one area of interest -- the platformer unit, where one of the benzene samples was above the NIOSH recommended criteria, but below the OSHA standard. Vigilance in this area, especially during maintenance activities should mitigate any potential health problems. None of the other hydrocarbons sampled for approached the NIOSH or OSHA standards/recommended criteria on the days of the survey.

Maintenance activities were observed at the sulfur plant during the rodding and steam cleaning of boiler condenser tubes which had become plugged with sulfur. Numerous employee complaints were received on both the initial and followup surveys concerning exposures at the sulfur plant. Workers complained about respiratory and skin irritation when working in the area. There are no standards/criteria which address occupational exposure to elemental sulfur, sulfates or sulfites; however, they will react with water to form sulfuric acid which is a severe respiratory and skin irritant. Inhalation of any of the above sulfur compounds would be likely to form sulfuric acid in the respiratory tract. Similarly, reaction of these compounds with sweat could also form sulfuric acid and lead to skin irritation. Therefore, the use of personal protective equipment in this area is highly recommended.

B. Medical

The results of both the initial and follow-up questionnaire surveys indicate an excess of reported symptoms of mucous membrane irritation among maintenance workers and of intoxication-like symptoms among both maintenance workers and operators when compared to office controls.

Possible explanations for these findings include:

(1) Exposure to hydrogen sulfide sources demonstrated in the environmental sampling, particularly in maintenance workers in areas such as the Gulfiner unit and involved in the repair and maintenance of the gas concentration unit.

(2) Exposure to refined petroleum solvents such as benzene in the platformer unit.

(3) Chance is unlikely to account for these results since statistically significant excesses were seen.

(4) Bias, in particular selection bias, due to the high proportion of unavailable and therefore non-participating workers in the questionnaire survey. Confounding due to the different proportion of female workers in the study and control groups may also have played a role.

VII. RECOMMENDATIONS

1. Cover maintenance ports at compressors in the Gulfiner Unit and gas concentration unit to prevent leakage of H_2S.

2. Repair flanges and stops at the CO Boiler which are allowing escape of carbon monoxide. Evaluate effectiveness of blanks when they are installed prior to beginning maintenance procedures.

3. Repair pump float at flare knockout drum.

4. When tetraethyl lead blending has been completed, the blender should change his clothing. He should not enter eating or common use areas with clothes which are potentially contaminated with TEL.

5. Repair floating roof seals on tanks # 404 and #405. Install stairways over aboveground pipes in the tank farm.

6. Install a backup electrical power system to maintain operations during power outages.

7. Workers should be provided long gloves and high-top shoes for use while pouring soda ash in the waste treatment area.

8. Maintenance workers in areas which have been identified as having high CO or H_2S levels should have appropriate respiratory protection.

9. Maintenance workers and operators in the sulfur unit should be provided with adequate skin and respiratory protection.

VIII. AUTHORSHIP

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IX. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati address. Copies of this report have been sent to:

1. Carribean Gulf Refining Corp.
2. Union de Trabajadores de la Industria del Petroleo
3. NIOSH, Region II
4. OSHA, Region II

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

TABLE I

HYDROGEN SULFIDE SURVEY

CARRIBEAN GULF REFINING CORPORATION
BAYAMON, PUERTO RICO
HETA 81-327

July 13, 1981

Location	Approximate H_2S Concentration (ppm)
Perimeter survey of sulfur plant	BLD
Platform above sulfur plant	BLD
Gulfiner Unit, open port at off-gas compressor	50
Gulfiner Unit, 10 ft. downwind of off-gas compressor	50
Gulfiner Unit, recycle and makeup compressors	BLD
Flare knockout drum pit	50
Flare knockout drain valve	200
Waste treatment plant, primary separator	10-15
Perimeter survey of sour water stripper	BLD
Gas Concentration Unit, at open port of gas compressor B	>250
Gas Concentration Unit, at open port of gas compressor C	>250
4 ft. downwind of gas compressor C in gas concentration unit	7-8

* BLD = below limit of detection (1 ppm)

TABLE II

AIR SAMPLING FOR HYDROGEN SULFIDE
(ALL CONCENTRATIONS REPORTED IN PARTS PER MILLION)

CARIBBEAN GULF OIL REFINING CORPORATION
BAYAMON, PUERTO RICO
HETA 81-327

October 14-16, 1981

Job/Location	Date	Type Sample	Sample Period	Sample Volume (l)	Concentration (PPM) Long-Term Detector Tubes	Concentration (PPM) MDA Monitox
Gas Concentration GE-1A (west side)	10/14	A	1437-0833	19.6	1.1 PPM	-
Gas Concen. Compressor West Compressor	10/14	A	1441-0414	12.5	4.8 PPM	-
Gas Concen. Below Large Gas Compressor	10/14	A	1447-0842	21.9	0.2 PPM	-
Gas Concentration GE-1A (east side)	10/14	A	1451-0834	18.1	0.7 PPM	-
SWAT Maintenance	10/15	P	0657-1140	Pump malfunction. Sample invalidated.		
Maintenance, Boiler #1	10/15	P	0714-1501	9.3	ND	-
General Maintenance invalidated.	10/15	P	0702-1515	3.0	Pump malfunction. Sample	
Maintenance, Boiler #1	10/15	P	0727-1502	5.2	ND	
Gas Concen. Unit, 3ft. above west compressor	10/15	A	0838-1516	8.0	9.4 PPM	Overloaded
Wastewater Treatment Operator	10/15	P	0824-1443	6.2	1.5 PPM	1.5
FCC Operator	10/15	P	0803-1405	5.7	ND	Unit Malfunction
Crude Unit Operator	10/15	P	0805-1417	6.5	ND	ND
Gas Concen. Unit, 3ft. above east compressor	10/15	A	0846-1257	4.2	>14.2 Detector tubes above full scale	Unit Malfunction
Painter #1, Above Gas Concen. Unit	10/15	P	1350-1520	1.6	6.3	-
Painter #2, Above Gas Concen. Unit	10/15	P	1350-1520	1.4	14.3	-
Maintenance, Cleanout of Sludge Tank in Wastewater Treatment Area	10/16	P	0746-1524	6.3	ND	-
Operator Wastewater Treatment	10/16	P	0759-1559	4.5	ND	Unit Malfunction
Painter #1, Above Gas Concen. Unit	10/16	P	0924-1500	7.1	0.4	1.1
Gas Concen. Unit 10 ft. In Front of West Compressor Unit and 6 ft. Above Deck	10/16	A	0934-1458	6.1	ND	0.5 PPM
Maintenance, Installing Stops In Platformer	10/16	P	0736-1507	7.6	0.3	-
Trainee-Operator In Wastewater Treatment Plant	10/16	P	0756-1424	7.2	ND	-
Painter #2, Above Gas Concen. Unit	10/16	P	0921-1444	6.3	7.1	10.0
Maintenance, Installing Stops In Platformer	10/16	P	Pump malfunction. Sample invalidated.			
Maintenance, Installing Stops In Platformer	10/16	P	0730-1517	8.0	ND	-
Maintenance, Installing Stops In Platformer	10/16	P	0805-1517	6.8	ND	-
Gas Concen. Unit, 10 ft. In Front of East Gas Compressor 4 ft. Above Deck	10/16	A	0931-1501	4.7	1.5	3.8 PPM

OSHA PEL - 20 PPM ceiling concentration; maximum peak of 50 PPM for 10 minutes.
NIOSH Recommended Criteria - 10 PPM ceiling concentration as determined by a 10 minute sampling period.

TABLE III

CARBON MONOXIDE SURVEY

CARRIBEAN GULF REFINING CORPORATION
BAYAMON, PUERTO RICO
HETA 81-327

July 14, 1981

Location	CO Concentration (ppm)
CO boiler, operators panel	*1-2
Below CO boiler line	2-6
At flange on feed pipe from FCC to CO boiler #4	>600
At stop (blank) in line on feed pipe to CO boiler #4	350
10 ft. downwind of leaking flange on pipe to CO boiler #4	10-20
Above horizontal diversion pipe to CO boiler #5 (second floor level)	2
Junction between compressor and vertical pipe stack diversion to CO boiler #5	400-425
3 ft. downwind of above measurement	250
Flange at compressor leading to diversion to CO boiler #5	200-500
Upwind of vertical pipe stack to CO boiler #5	0
Downwind (at face) of vertical pipe stack to CO boiler #5	100
3 ft. downwind of above measurement	50

* Background concentrations were 1-2 ppm

TABLE 1.

AIR SAMPLING FOR BENZENE, TOLUENE, XYLENE, ALIPHATIC HYDROCARBONS AND AROMATIC HYDROCARBONS
(All Concentrations Expressed As mg/M^3)

CARIBBEAN GULF REFINING CORPORATION
BAYAMON, PUERTO RICO
HETA 81-327
October 14-16, 1981

Location-Activity	Date of Sample	Time Of Sample	Type Of Sample	Benzene	Toluene	Xylene	Aliphatic Hydro-Carbons	Aromatic Hydro-Carbons*
PROCESS SAMPLE TAKING								
Poly Unit	10/15/81	0338-0404	P	BLD	BLD	BLD	8.0	BLD
Gas Treatment Unit	10/15/81	0340-0418	P	BLD	BLD	BLD	26.6	BLD
Platformer	10/15/81	0400-0432	P	3.3	5.0	3.3	150.	6.7
Crude Unit #2	10/15/81	0355-0424	P	1.6	BLD	BLD	4.9	BLD
FCC Unit	10/15/81	0335-0409	P	BLD	BLD	BLD	46.8	BLD
Tank Farm (Tanks #409, 410, 501)	10/15/81	0435-0516	P	BLD	BLD	BLD	42.1	BLD
Crude Unit #1	10/15/81	0357-0424	P	BLD	BLD	BLD	BLD	BLD
GASOLINE LOADING RACKS								
Central Loading Rack	10/15/81	0458-1118	A	2.2	6.5	8.3	56.7	2.0
Gas Loader - Lane 1	10/15/81	0454-1123	P	2.6	6.3	5.8	184.	6.8
Gas Loader - Lane 2	10/15/81	0455-1117	P	2.6	4.7	4.7	157.	4.7
Gas Loader - Lane 3	10/15/81	0456-1120	P	2.7	5.4	4.4	163.	6.0
LABORATORY								
Tester B - Batch #203	10/14/81	0750-1426	P	BLD	0.5	BLD	19.7	BLD
Tester B - Batch #415	10/14/81	0746-1428	P	BLD	0.5	1.1	16.4	BLD
Tester A - Batch #311	10/14/81	0751-1427	P	BLD	0.5	BLD	23.0	BLD
Tester B - Batch #203	10/16/81	0828-1415	P	2.5	5.0	3.5	55.0	2.5
Tester B - Batch #415	10/16/81	0823-1415	P	0.5	4.5	2.5	20.0	13.9
Tester A - Batch #311	10/16/81	0826-1415	P	BLD	BLD	BLD	0.6	BLD
MAINTENANCE								
Placing Stops in Platformer Unit	10/16/81	0730-1510	P	7.3	11.6	12.8	140.	10.4
Placing Stops in Platformer Unit	10/16/81	0736-1537	P	3.1	8.2	8.7	132.	4.6
Operator-Wastewater Treatment	10/16/81	0758-1559	P	0.4	0.4	0.8	0.8	BLD
Placing Stops In Platformer Unit	10/16/81	0730-1517	P	BLD	0.9	1.3	31.0	BLD
Trainee-Wastewater Treatment	10/16/81	0756-1426	P	BLD	0.6	1.1	22.7	BLD
Tank Cleaning-Tank #1000, API Sludge	10/16/81	0746-1527	P	1.7	3.0	4.3	38.3	4.3
Placing Stops In Boiler #1	10/15/81	0714-1501	P	BLD	BLD	BLD	BLD	BLD
General Plant Maintenance	10/15/81	0657-1514	P	BLD	BLD	BLD	1.6	0.8
Repairing Boiler #1	10/15/81	0727-1503	P	BLD	BLD	BLD	BLD	BLD
General Plant Maintenance	10/15/81	0702-1515	P	BLD	BLD	BLD	16.2	BLD
Limit of Detection				0.01	0.01	0.02	0.03	0.02
OSHA PEL				32	753	435	2.9	+
NIOSH Recommended Criteria				3.2	376	435	350	+

BLD = Below limit of detection
* Total aromatic hydrocarbons excluding benzene, toluene and xylene
+ No existing standards or criteria (based on individual aromatic compound and for group class)
P = Personal
A = Area

TABLE V

AIR SAMPLING FOR SULFATE AND SULFITE

CARRIBEAN GULF REFINING CORPORATION
BAYAMON, PUERTO RICO
HETA 81-327

October 16, 1981

Location-Activity	Time Of Sample	Type Of Sample	Sulfate ug/M^3	Sulfite ug/M^3
Sulfur Plant - Maintenance	0958-1533	P	26	BLD
Sulfur Plant - Maintenance	1001-1537	P	22	BLD
Sulfur Plant - Maintenance	0959-1530	P	14	BLD
Sulfur Plant - Maintenance	1005-1530	P	10	BLD
Limit of Detection			5 ug/sample	2 ug/sample

BLD = Below limit of detection

P = Personal

Table VI
Frequencies of
reported symptoms
Survey 1 (July 1981)

Carribean Gulf Refining Corporation
HETA 81-327

Symptoms reported	Number reporting	%
Skin peeling	3	21
Irritation of eyes	10	71
Frequent fatigue	5	36
Nasal allergies (rhinitis)	5	36
Anxiety while at work	7	50
Acne	6	43
Skin cancer	0	
Corneal ulcer	1	7
Difficulties hearing	3	21
Nose bleeds	0	
Erruptions of skin	4	29
Anemia	0	
Backache	4	29
Sore throat	9	64
Intoxication from exposures at work	8	57
Dizziness	7	50
Mental confusion	2	14
Depression	4	29
Numbness	2	14
Blisters of skin	1	7
Blurred vision	4	29
Elevated blood lead	1	7
Metalic taste in mouth	1	11
Pain in stomach	3	33
Nausea or vomiting	4	44
Loss of appetite	4	44
Difficulty sleeping	4	44
Headache	2	22
Cough	4	29
Phlegm production	4	29
Chest discomfort	5	36
Wheezing	4	29
Shortness of breath	3	21

Table VII
Frequencies of
reported symptoms
Survey 2 (Oct. 1981)

Carribean Gulf Refining Corporation
HETA 81-327

Symptoms reported	Controls #	Controls %	Maintenance #	Maintenance %	Maintenance Sig*	Operators #	Operators %	Operators Sig*
Skin peeling	3	16	2	15	NS	3	16	NS
Irritation of eyes	4	21	8	62	*	6	32	NS
Frequent fatigue	8	42	3	23	NS	3	16	NS
Nasal allergies (rhinitis)	6	32	6	46	NS	7	37	NS
Anxiety while at work	5	26	5	38	NS	2	11	NS
Acne	1	5	2	15	NS	2	11	NS
Skin cancer	0	0	0	0	NS	0	0	NS
Corneal ulcer	0	0	0	0	NS	0	0	NS
Difficulties hearing	3	16	5	38	NS	3	16	NS
Nose bleeds	0	0	0	0	NS	1	5	NS
Dermatitis	4	21	3	23	NS	4	21	NS
Anemia	1	5	0	0	NS	0	0	NS
Backache	7	37	3	23	NS	5	21	NS
Sore throat	4	21	8	62	*	4	21	NS
Intoxication from exposures at work	0	0	5	38	**	7	37	**
Dizziness	2	11	3	23	NS	6	32	NS
Depression	0	0	1	8	NS	1	5	NS
Numbness	1	5	0	0	NS	0	0	NS
Cough in a.m.	2	11	3	23	NS	3	16	NS
Cough day or night	2	11	3	23	NS	3	16	NS
Cough greater than 2 yrs	1	5	2	15	NS	2	11	NS
Phlegm in a.m.	2	11	4	31	NS	0	0	NS
Cough with phlegm for more than 3 months per year and more than 2 years	1	5	2	15	NS	0	0	NS
Shortness of breath on climbing a small hill	1	5	4	31	NS	2	11	NS
Wheezing	2	11	0	0	NS	0	0	NS

*Significance test (Fisher's Exact Test) p less than 0.05
** p less than 0.01

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