# *Original article*

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**Key terms:** airborne concentration; benzene; chemical plant; dock worker; exposure assessment; industrial hygiene; marine transport; refinery

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# Airborne concentrations of benzene for dock workers at the ExxonMobil refinery and chemical plant, Baton Rouge, Louisiana, USA (1977–2005)

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**Objective** Benzene is a natural constituent of crude oil and natural gas (0.1–3.0% by volume). Materials that are refined from crude oil and natural gas may contain some residual benzene. Few datasets have appeared in the peer-reviewed literature characterizing exposures to benzene at specific refineries or during specific tasks. In this study, historical samples of airborne benzene collected from 1977–2005 at the ExxonMobil Baton Rouge, Louisiana, USA, docks were evaluated.

**Methods** Workers were categorized into 11 job titles, and both non-task (≤180 minutes sample duration) and task-related (<180 minutes) benzene concentrations were assessed. Approximately 800 personal air samples (406 non-task and 397 task-related) were analyzed.

**Results** Non-task samples showed that concentrations varied significantly across job titles and generally resulted from exposures during short-duration tasks such as tank sampling. The contractor – tankerman job title had the highest average concentration [N=38, mean 1.4 parts per million (ppm), standard deviation (SD) 2.6]. Task-related samples indicated that the highest exposures were associated with the disconnection of cargo loading hoses (N=134, mean 11 ppm, SD 32). Non-task samples for specific job categories showed that concentrations have decreased over the past 30 years. Recognizing the potential for benzene exposure, this facility has required workers to use respiratory protective equipment during selected tasks and activities; thus, the concentrations measured were likely greater than those that the employee actually experienced.

**Conclusions** This study provides a job title- and task-focused analysis of occupational exposure to benzene during dock facility operations that is insightful for understanding the Baton Rouge facility and others similar to it over the past 30 years.

**Key terms** exposure assessment; industrial hygiene; marine transport.

Petroleum refineries have evolved since their initial operations in the mid-1800s to become complex facilities that process crude oil and related raw materials into a wide variety of more valuable intermediate or finished petroleum products. Modern refinery products include gasoline, fuels, gases, lubricants, waxes, asphalt, coke, and numerous compounds used by chemical plants for producing petrochemicals and petroleum-based products. While some refineries are located inland, many are located on oceans and navigable rivers to take advantage of marine transport of incoming crude oil, feed products, additives, and outgoing refinery products, byproducts, and waste. These refineries use dock facilities that are sometimes called wharfs or jetties. This paper focuses on airborne benzene concentrations measured at the ExxonMobil refinery dock facilities in Baton Rouge, Louisiana, USA. This study is part of a larger effort to understand the historical benzene air concentrations at all domestic ExxonMobil refineries and docks (1–4).

1 Sadly, Thomas Widner passed away on 19 July 2010; see In Memoriam, page 168.

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Benzene is a natural constituent of crude oil and natural gas, usually measuring between 0.1–3.0% by volume (5). Some products that are refined from crude oil and natural gas can retain small quantities of benzene because of the nature of the processes by which they are produced. An analysis of historical refinery worker benzene exposures at the ExxonMobil Baton Rouge facility has previously been completed for operational areas excluding the docks (4). Potential worker exposure to benzene can also occur during the loading and off-loading of ships, tankers, and barges containing gasoline and other benzene containing materials at refinery docks (6).

Dock workers at refineries are involved in several tasks that can result in potential short duration exposure to benzene, including connecting and disconnecting loading or off-loading hoses, working in areas near tank vents during cargo loading, gauging cargo vessel tanks, sampling products on cargo vessels, or repairing dock equipment that has contained cargo. Limited information regarding the potential benzene exposure associated with dock tasks has been reported (7–20). These papers reported potential exposure sources at docks, including venting of displaced vapors during material transfers, spills, and clothing contamination from contact or splashes (21). Loading cargo into barges generates hydrocarbon vapors in the vapor space of the cargo tank; these vapors historically have been either displaced to the atmosphere or collected by vapor-recovery systems installed at dock facilities. Potential exposure to these displaced vapors may occur if workers are in close proximity to tank vents or are near other potential vent points, such as tank hatches. In many cases, dock workers have been required to observe the liquid level in barge tanks near the end of the loading period to prevent tank overfill, resulting in potential worker exposure to hydrocarbon vapors exiting the cargo hatch.

Previous reports of benzene exposure at petroleum refineries have not fully characterized potential exposures to dock workers, as these analyses have included significant limitations, such as small sample sizes, characterization of a limited number of jobs or tasks, and limited presentation of data (such as providing only ranges or means). About half of the 144 petroleum refineries in the US have docks (22), resulting in potential benzene exposure of several thousand workers to dock-related operations. Thus, the results of this study might be applicable to more than 10 000 workers in the US (cumulatively over the past 30 years).

The purpose of this paper is to characterize historical benzene exposures for dock workers at the petroleum refinery in Baton Rouge, Louisiana, who might have been exposed to benzene from both refining and chemical operations. Measured benzene concentrations are provided by job title so that they can be used in future risk assessments or epidemiologic studies involving benzene. These data also provide a basis for determining potential longer term exposure to benzene for dock workers when used in conjunction with work history information.

The ExxonMobil Baton Rouge refinery is located on the Mississippi River in Baton Rouge, Louisiana, approximately 232 miles upriver from the Gulf of Mexico. One of the largest heritage Exxon refineries in the US, it is the second largest refinery in the US in terms of throughput, with a crude oil distillation capacity of approximately 501 000 barrels per day (22). The size of the refinery and the presence of the adjacent chemical plant, which utilizes the same dock facilities, are among the unique aspects of the Baton Rouge complex in terms of potential dock worker exposures. The refinery receives crude oil and other feed products via pipelines, barges, and ships. Using manufacturing processes that have been described in detail elsewhere (4), the refinery uses distillation, cracking/conversion, treating, and blending to produce 20 million tons annually of "clean products" (motor gasoline, heating oil, and similar products that require more refining than heavy fuels); 1.0 million tons of lubricants and waxes; 5.4 million tons of coke, fuels, and related products; and 4.6 million tons of gas oil, mixed olefins, and raffinate.

Located just north of the Baton Rouge refinery, the chemical plant receives some of the chemicals that it uses from barges and ships, and others from the refinery itself. Both the refinery and the chemical plant transport some of their products and byproducts in ships and barges. In 2001, the chemical plant produced 1.0 million tons of ethylene, 0.3 million tons of propylene, 0.3 million tons of benzene (6 700 barrels per day or 281 000 gallons/day based on 42 gallons/barrel), and 1.3 million tons of methyl ethyl ketone, isopropyl alcohol, plastics, rubber, and related materials together.

In chemical plants that are often adjacent to refineries, benzene from refinery streams is typically produced from catalytic reformate, pyrolysis gasoline, and toluene dealkylation for use in producing compounds such as ethyl benzene/styrene, cumene/phenol, cyclohexane, nitrobenzene, maleic anhydride, and alkyl benzene, which are used to manufacture resins, plastics, nylon, polyester, surfactants, detergents, insecticides, food additives, and other petroleum-based products (6).

The Baton Rouge dock facilities are located alongside the Mississippi River's left descending bank, west of the refinery. The refinery docks use these facilities to off-load crude oil and other cargo to the refinery and chemical plant and to load cargo onto ships and barges using four riverside berths that can accommodate ships up to 820 feet in length, and four other berths (one riverside and three inside) that can accommodate barges. A list of cargos that have commonly been transferred at the docks is presented in table 1.

A marine vapor recovery system was added to the Baton Rouge docks in the late 1980s, and is used when materials containing volatile organic compounds are being loaded; these are primarily those identified in table 2. Captured vapors are sent to shore, where they are thermally destroyed by flare systems.

In addition to crude oil and refinery cargo containing small quantities of benzene, from 1960–1991, benzene product manufactured at the chemical plant was occasionally loaded into barges at the Baton Rouge refinery docks. The loaded barges were typically of a 20 000-gallon capacity and loaded through a 6-inch line at berth 4. A 1988 report indicated that the refinery planned to discontinue loading benzene onto barges after 1991. Up to that point in time, about 50 benzene barges were loaded per year at the refinery dock. While these vessels were operated and inspected (including sampling and gauging) by employees under contract with the chemical plant, a refinery crew was responsible for making on-barge and on-dock load line connections and disconnections. Because these load lines contained residual cargo, workers were potentially exposed to benzene while disconnecting the transfer lines following cargo loading.

**Table 1.** Materials commonly transferred at Baton Rouge docks.

| Materials received | Materials shipped out |
|---|---|
| Crude oil (often from supertankers in the Gulf) | Spent caustic |
| Fresh caustic | Motor gasoline products |
| Motor gasoline ("mogas") components | Middle distillate (kerosene, jet fuel, diesel, heating oil) |
| Feeds to middle distillate facilities | Aviation fuels |
| Fuels feedstock for fluid catalytic crackers | Lubricant oil and grease products |
| Coker feed | Finished wax products |
| Chemical plant feed products (including heartcut reformate, butadiene, butylenes) | Chemical plant products (including benzene, isopropyl alcohol, methyl ethyl ketone, methyl tertiary butyl ether toluene, polymer feeds) |

**Table 2.** Chemicals for which a marine vapor recovery system has been used during material transfers (late 1980s to present).

| | |
|---|---|
| Motor gasolines ("mogas") | Low octane naphtha |
| 99.9% isopropyl alcohol | Reformer feed - heavy |
| Methyl ethyl ketone | Reformer feed - light |
| Methyl tertiary butyl ether | Heavy catalytically cracked naphtha |
| Aviation gasolines | Low severity reformate |
| Mixed gas oil | Alkylate |
| Toluene | Heartcut reformate |
| Steam cracked naphtha | Pyrolysis gasoline |
| Mixed xylenes | Light catalytically cracked naphtha |
| Raffinate | Natural gasoline |

A detailed summary of the ExxonMobil industrial hygiene program for benzene and monitoring strategy for the overall Baton Rouge Refinery is reported in Panko et al (4). This strategy aims to identify and characterize tasks or activities that may result in potential benzene exposure. To characterize potential worker exposure and verify engineering controls and personal protective equipment, tasks and activities that result in potential benzene exposure are often monitored more frequently than tasks with little or no potential benzene exposure. As a result of this focused monitoring strategy, the majority of available benzene monitoring results have been collected during tasks and activities with higher-than-typical potential for exposure.

A minimum of five personnel are on duty at all times for transfer operations at the Baton Rouge docks. Associated job titles are described in table 3. Other workers routinely work at the docks to perform equipment inspection, maintenance, and repair, in addition to various management and administrative activities. Cargo vessel crew members typically also perform activities onboard their vessels during cargo transfer.

## *Methods*

### Data collection

The industrial hygiene monitoring data reported in this paper were gathered from written survey reports and from three electronic databases used by ExxonMobil from 1977–2005: the Personal Computer Industrial Hygiene System (PC-IHS, 1977–1998), Medgate (1999–2003), and the Exposure Assessment Strategy and Database Application (EAS, 2004–2005). The accuracy of the information contained in all three databases was verified through an independent review of the corresponding

**Table 3**. Job titles and tasks evaluated for dock workers.

| Job title | Task |
|---|---|
| Dock connecting crew | Connect cargo hoses<br>Disconnect cargo hoses<br>Gauge cargo vessel tanks<br>Sample product on cargo vessel |
| Dock assistant operator | Load sulfidic caustic barge<br>Inspect cargo hose disconnection |
| Pipefitter/welder | Repair undrained equipment |
| Instrument technician | Repair undrained equipment |
| Contractor – gauging/inspection | Gauge cargo vessel tanks |
| Contractor – tankerman | Gauge cargo vessel tanks<br>Load benzene or gasoline barge<br>Load sulfidic caustic barge |

paper records associated with 25% of the air sample results. The results were then compared to an acceptable error rate, determined a priori, of ≤5% critical errors. An error was considered critical if it involved the sample result (concentration, lab result, units, qualifier). All other errors, including typographical errors, were considered non-critical, given that they would not lead to miscalculating the airborne concentration. Where possible, transcription errors were corrected by the authors prior to data analysis. Overall, based on the fact that there were <0.5% critical errors and 2.6% non-critical errors in the database, it was concluded that the database accurately reflected the original documentation.

ExxonMobil industrial hygienists conducted air sampling for benzene at the Baton Rouge refinery and dock facilities according to standard operating procedures involving using either 150 mg charcoal sorbent tubes or passive organic vapor badges. Samples were analyzed according to National Institute of Occupational Safety & Health (NIOSH), Occupational Safety and Health Administration (OSHA), or other methods consistent with internal standard operating procedures.

*Job/task descriptions.* Potential worker exposures to benzene-containing materials during refinery operations have been reported elsewhere (4). This paper focuses on tasks and activities resulting in potential benzene exposure during refinery dock operations, including the tasks and activities listed in table 3. Job titles for workers who typically performed monitored tasks included dock connecting crew, dock assistant operator, dock controller, pipefitter/welder, electrician, instrument technician, machinist, maintenance, contractor – tankerman, contractor – pipefitter, and contractor – gauging/inspection. Potential benzene exposures associated with the specific tasks performed by these workers are reported in this paper, including: connect cargo hoses, disconnect cargo hoses, gauge cargo vessel tanks, sample product on cargo vessel, load sulfidic caustic barge, inspect cargo hose disconnection, repair undrained equipment, and load benzene or gasoline barge.

*Personal protection.* The industrial hygiene air samples evaluated in this study represent measurements of benzene concentrations in air, without any adjustment for protective equipment or precautions that might have been taken by the worker. A review of current and historical practices indicates that respiratory protection is routinely worn by the dock workers while performing specific tasks.

The potential for dermal benzene exposure may exist for anyone working with an open benzene-containing process stream. A review of the current and historical refinery benzene and high boiling aromatic oils (HBAO) programs and dock operating procedures was performed to determine whether specific benzene-related jobs or tasks offered the opportunity for dermal exposure to benzene, and whether personal protective equipment was recommended for these tasks. Based on this review, dock workers have been required to wear protective clothing, including chemical resistant gloves, to prevent dermal exposure when there is a potential for skin contact with benzene-containing product streams. In addition, conversations with refinery industrial hygienists confirm that they could not recall instances in which more than incidental dermal exposure historically occurred. Furthermore, electronic industrial hygiene records indicate that >95% of the dock tasks and jobs monitored for benzene exposure did not involve dermal contact. Because it was judged to be de minimis, potential dermal exposure to benzene was not further evaluated in this study. In the era since OSHA's formation in 1971, the contribution of dermal absorption to the total dose (compared with the inhalation dose), is generally known to be rather small (23, 24).

## Data analysis

Air samples associated with work at the Baton Rouge docks were organized by job title and task description. Air samples were also classified by sampling duration (ie, <180 and ≥180 minutes) and type of sample (ie, personal and area). Samples <180 minutes in duration were considered task-related samples representative of peak or task-specific exposures, unless the industrial hygienist noted that routine work was performed. Samples of durations ≥180 minutes were considered non-task samples, as they most likely characterized more than one task performed by a worker as part of routine job duties, or were not specific to a single task. These could also be classified as classic "personal" samples that represent the typical time-weighted average (TWA) exposures of workers. Some samples were also classified as non-task samples when the sample collection time could not be determined.

Results for samples for which the laboratory result was below the analytical limit of detection were incorporated into the statistical analysis using the statistical software package ProUCL 4.0 (US Environmental Protection Agency, Washington, DC, USA) lognormal regression on order statistics (ROS) model. The ROS method was developed by Helsel & Cohn (25) and is the method that Hewett (26) refers to as the robust multiple censoring point log probit regression method, one of the censored data methods used in the IH DataAnalyst (IHDA) program. The ROS method was used because it is fairly robust even when the percentage of data below detection is fairly high (50–70%), and even with moderate deviations from the distribution assumptions (27–31). The benzene concentration data were tested for distribution fit using the Kolmogorov-Smirnov goodness-of-fit test for normal, lognormal, and gamma distributions. The data were found to fit none of these distributions ($P<0.05$) at a 95% confidence level. However, they were found to be approximately lognormally distributed based on probability plots. The natural log transformed sample results, including non-detect values estimated by the ROS model, were therefore used for non-task and task-related sample trend analyses. Summary statistics were calculated for the final job title categories and task bins.

Personal air samples were also classified by employment status (employee or contractor) to examine whether that was an important factor in potential exposure. Where possible, results were also classified by loading berth to support comparison of concentrations for berth 4 (which was most often used for loading gasoline and chemical plant benzene cargo) to concentrations at the other berths. To determine if there were trends over time by job title or task, pair-wise comparisons were made to identify statistical differences between samples collected from 1977–1989 and those collected from 1990–2005. The year 1990 was used as the cut-off point because regulations intended to reduce worker exposures and emissions from petroleum refineries were largely in place by 1990 (32, 33), and the vapor recovery system, which would be expected to reduce employee exposure to benzene at the docks, was installed in the late 1980s.

## *Results*

A total of 879 airborne benzene sampling results relevant to refinery dock workers were included in this analysis (4). Figure 1 presents a data breakdown of the benzene air samples taken at the docks. Of the dock worker samples, 75 were area samples and one was a source sample. These samples were not associated with any specific job titles or tasks, and were judged not to be representative of typical exposures of any dock facility employees, who routinely move between various areas while performing the tasks that have been characterized. As such, the area and source results were not considered further in this analysis. In total, there were 406 non-task samples and 397 task-related samples relevant to dock worker exposures available for analysis.

Limits of detection for non-task samples of airborne benzene taken at the docks ranged from 0.006–0.10 parts per million (ppm), with a median value of 0.020 ppm, geometric mean of 0.021 ppm, and geometric standard deviation of 1.8. Limits of detection for task-related samples taken at the docks ranged from 0.009–2.0 ppm, with a median value of 0.43 ppm, geometric mean of 0.37 ppm, and geometric standard deviation of 2.8.

### Non-task exposure estimates

Non-task airborne benzene concentrations are presented in table 4 and supplemental table A, which can be found in the Appendix at http://www.sjweh.fi/data_repository.php. The arithmetic mean of non-task samples was 0.28 ppm. The results from non-task samples were less than the analytical limit of detection (approximately 0.1 ppm for most samples) in 55% of the samples, resulting in a benzene detection frequency of 45%. Non-task air sampling data were available for 11 job titles, including 3 contractor jobs and 8 ExxonMobil jobs. Of these job titles, 7 had ≤10 samples, and were primarily associated with trade professionals (craftsmen) and maintenance personnel not solely assigned to the docks. As such, the benzene concentrations associated with these job titles while performing work at the docks are not fully characterized in this paper. For dock workers, all job titles except dock controller had a sufficient number of samples, from which non-task benzene concentrations could be characterized.

The contractor – tankerman job title was associated with the highest mean measured benzene concentration (1.4 ppm), with 36 of 38 samples (95%) having detectable airborne benzene concentrations, likely a reflection of the historical practice of the tankerman looking into an open cargo hatch while the tank was being filled to ensure the tank was not overfilled. The next highest overall mean of measured concentrations (0.30 ppm) was associated with the dock connecting crew job title. Forty-four percent of the non-task personal benzene air samples collected at the docks were associated with the dock connecting crew, reflecting the refinery's sustained efforts to characterize and control this potential source of worker exposure. Of the 179 non-task samples for the dock connecting crew, 102 (57%) reported concentrations above the benzene limits of detection. The highest measured air concentration for the dock connecting crew was 15 ppm, reported in a 200-minute sample collected in 1991. This result significantly skewed the mean value, as evidenced by the median value of 0.021 ppm. The sampling record confirmed that this sample was collected during a shift where unleaded gasoline barges were being loaded and product levels were being checked every 15 minutes. Only seven of the dock connecting crew samples exceeded 1 ppm. The lowest mean airborne concentration of 0.037 ppm was associated with the dock assistant operator and pipefitter/welder job titles. The samples associated with these job titles had detection frequencies of 27% and 23%, respectively.

Current and historical ExxonMobil respiratory protection standards were reviewed to identify those jobs and tasks that required respiratory protection over time. These standards included requirements applicable to dock workers. Examples of these requirements as of 2005 are presented in table 5. Three major types of

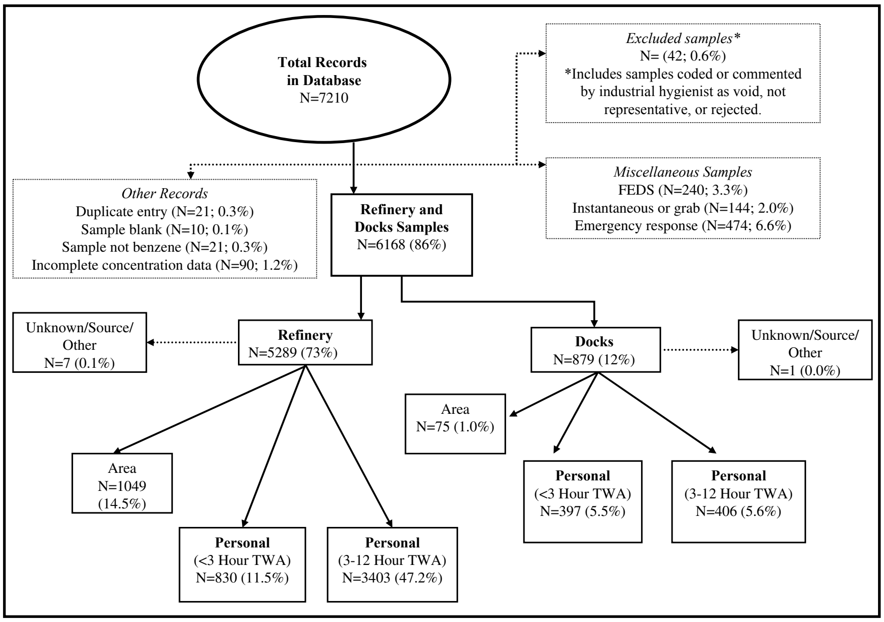


**Figure 1.** Data breakdown (1977–2005). For this analysis, only those personal samples associated with the dock facilities were considered. [TWA=time-weighted average; FEDS=Fugitive Emissions Detection Program.]

**Table 4.** Summary statistics for the non-task dataset by job category. [SD=standard deviation; NC=not calculated because more than 50% of the samples were below the limit of detection.]

| Job title | N | Detection frequency (%) | Benzene concentration (part per million) | | | | Sample duration (minutes) | |
|---|---|---|---|---|---|---|---|---|
| | | | Geometric mean | Geometric SD | Minimum detected | Maximum detected | 25th percentile | 75th percentile |
| Dock-specific employees | | | | | | | | |
| Dock connecting crew | 179 | 57 | 0.023 | 11 | 0.010 | 15 | 535 | 664 |
| Dock assistant operator | 123 | 27 | NC | NC | 0.010 | 1.3 | 510 | 720 |
| Dock controller | 3 | 0 | NC | NC | NC | NC | 705 | 720 |
| Other employees working at docks | | | | | | | | |
| Pipefitter/welder | 40 | 23 | NC | NC | 0.020 | 0.67 | 480 | 520 |
| Electrician | 6 | 0 | NC | NC | NC | NC | 460 | 500 |
| Instrument technician | 3 | 33 | NC | NC | 0.018 | 0.018 | 471 | 487 |
| Machinist | 2 | 0 | NC | NC | NC | NC | 500 | 543 |
| Maintenance | 1 | 0 | NC | - | NC | NC | - | - |
| Contract workers | | | | | | | | |
| Contractor – tankerman | 38 | 95 | 0.25 | 8.8 | 0.010 | 9.8 | 326 | 463 |
| Contractor – pipefitter | 7 | 0 | NC | NC | NC | NC | 523 | 558 |
| Contractor – gauging/inspection | 4 | 75 | 0.0086 | 7.8 | 0.0060 | 0.070 | 319 | 716 |
| Summary | | | | | | | | |
| Dock employees | 305 | 44 | NC | NC | 0.010 | 15 | 524 | 718 |
| Other employees | 52 | 19 | NC | NC | 0.018 | 0.67 | 480 | 515 |
| Contract workers | 49 | 80 | 0.11 | 13 | 0.0060 | 9.8 | 329 | 550 |
| All non-task samples | 406 | 45 | NC | NC | 0.0060 | 15 | 480 | 661 |

respiratory protection were typically worn by workers to protect against benzene exposure: half-face organic vapor respirators, full-face organic vapor respirators, and a self-contained breathing apparatus.

Contract workers were associated with only 12% of samples, but had higher detection frequencies and mean airborne benzene concentrations than ExxonMobil employees (table 4, supplemental table A). Detection frequencies were 44% for dock employees, 19% for employees not exclusively working on the docks, and 80% for contractors working at the docks. Mean airborne benzene concentrations were 0.19 ppm, 0.030 ppm, and 1.1 ppm, respectively. This observation is underscored by the fact that the majority of these contractor samples (9% of the total non-task samples) were associated with the contractor – tankermen job, and had higher detection frequencies and significantly greater airborne benzene concentrations ($P<0.0002$) than ExxonMobil employees and other contract workers (table 4, supplemental table A). Detection frequencies were 95% for contractor – tankermen, and 27% for other contractors working at the docks, while mean airborne benzene concentrations were 1.4 ppm and 0.015 ppm, respectively.

**Table 5**. Protective equipment and work practice requirements for operations with specific products at the Baton Rouge docks (circa 2000 to present). [SCBA=self-contained breathing apparatus.]

| Product | Task/situation | Respirator type | Work practice |
|---|---|---|---|
| All products | Hose connect or disconnect | Half-face respirator (organic vapor cartridge) | Required within 10 feet of:<br>• blanking or unblanking of cargo hoses before or after transfer operations<br>• handling of unblanked cargo hoses<br>• unblanked riser or presentation flange<br>• connecting or disconnecting cargo hoses |
| Heartcut reformate, pyrolysis gas/ resin oil, benzene hydrofiner feed/ product | Gauging or sampling | Full-face respirator (organic vapor cartridge) | Wear when gauging or sampling |
| Automobile gasoline | Sampling | Full-face respirator (organic vapor cartridge) | Wear when sampling |
| Sulfidic spent caustic | Onboard barge while loading | Half-face respirator (organic vapor cartridge) | Wear while loading<br>If within 2 feet of hatch, SCBA is required |
| Aviation gasoline | Sampling | Half-face respirator (organic vapor cartridge) | Wear when sampling |

Measured airborne benzene concentrations for dock connecting-crew personnel were higher at berth 4, where gasoline and benzene barges were most often loaded, than at berths 1, 2, 3, and 5 (table 6 and supplemental table B). The mean measured air concentration for the dock connecting crew while working at berth 4 was 0.71 ppm versus the mean value (0.019 ppm) of samples from berths 1, 2, 3, and 5. The mean of measured concentrations for the contractor – tankerman at berths 1, 2, 3, and 5 combined (N=8) was 0.12 ppm versus the 9.8 ppm measured air concentration in one sample from berth 4. However, mean airborne benzene concentrations for the dock assistant operator job title were lower for berth 4 (0.026 ppm) than for berths 1, 2, 3, and 5 (0.047 ppm).

A statistically significant decrease in measured airborne concentrations was observed for the dock connecting crew and dock assistant operator job titles for 1990–2005 compared to 1977–1989 (figure 2). The most likely cause of this decrease is the addition of the vapor recovery system in the late 1980s. A similar decrease was not apparent between those periods for the contractor – tankerman job title.

## Task exposure estimates

Results of the task-related personal air sampling are shown in table 7 and supplemental table C. As previously reported, in this study personal samples with durations of <180 minutes were considered task-related. Of the 397 task samples, 54 did not include descriptions that the authors could use to characterize specific dock-related tasks. Therefore, 343 task-related samples were available for this analysis. These data were used to characterize potential exposures during Baton Rouge dock tasks typically performed by two contractor job titles (gauging/inspection and tankerman) and four ExxonMobil job titles (dock connecting crew, dock assistant operator, instrument technician, and pipefitter/welder). Only 5 of these tasks had >10 personal task-related samples available for analysis: (i) disconnect cargo hoses, (ii) connect cargo hoses, (iii) gauge cargo vessel tanks, (iv) sample product on cargo vessel, and (v) repair undrained equipment.

The task that was sampled the most frequently (N=134) was the "disconnect cargo hoses" task, which had a mean concentration of 11 ppm. The maximum task-based concentration of 179 ppm was also associated with this task. The overall highest mean airborne benzene concentration, however, was associated with the "load benzene or gasoline barge" task (71 ppm). There were only three samples collected during this activity, though, and the mean is likely significantly skewed by the maximum detected value of 130 ppm. The lowest mean benzene concentration calculated for task-related samples with >10 samples (0.56 ppm) was associated with the "connect cargo hoses" task.

Mean airborne concentrations associated with the "disconnect cargo hoses" task collected in 1990–2005 were statistically significantly lower than mean concentrations found in samples collected in 1976–1989 (figure 3). The most likely cause of this decrease is the addition of the vapor recovery system in the late 1980s. A significant decrease in measured benzene concentrations was not observed between the pre-1990 data and the more recent data for the "connect cargo hoses" task, likely because it involved handling of hoses containing little or no residual product compared to hoses disconnected after cargo transfers. While the measured benzene concentrations for the "gauge cargo vessel tanks" task appears to have decreased significantly from 1976–1989 to 1990–2005, <10 samples from before 1990 were available for analysis, making the comparison uncertain.

**Table 6.** Summary statistics for the non-task dataset, by job category, for samples for which loading berth was reported. [SD=standard deviation; NC=not calculated because more than 50% of the samples were below the limit of detection].

| Job title | N | Detection frequency (%) | Benzene concentration (parts per million) | | | |
|---|---|---|---|---|---|---|
| | | | Geometric mean | Geometric SD | Minimum detected | Maximum detected |
| Berth 4 – gasoline/benzene barge loading | | | | | | |
| Dock connecting crew | 28 | 71 | 0.045 | 16 | 0.010 | 6.3 |
| Dock assistant operator | 15 | 27 | NC | NC | 0.010 | 0.14 |
| Contractor – tankerman | 1 | 100 | 9.8 | - | 9.8 | 9.8 |
| Berths 1, 2, 3, and 5 | | | | | | |
| Dock connecting crew | 19 | 32 | NC | NC | 0.018 | 0.10 |
| Dock assistant operator | 76 | 26 | 0.0056 | 9.1 | 0.010 | 1.3 |
| Dock controller | 1 | 0 | NC | - | NC | NC |
| Contractor – tankerman | 8 | 75 | 0.048 | 4.8 | 0.014 | 0.36 |

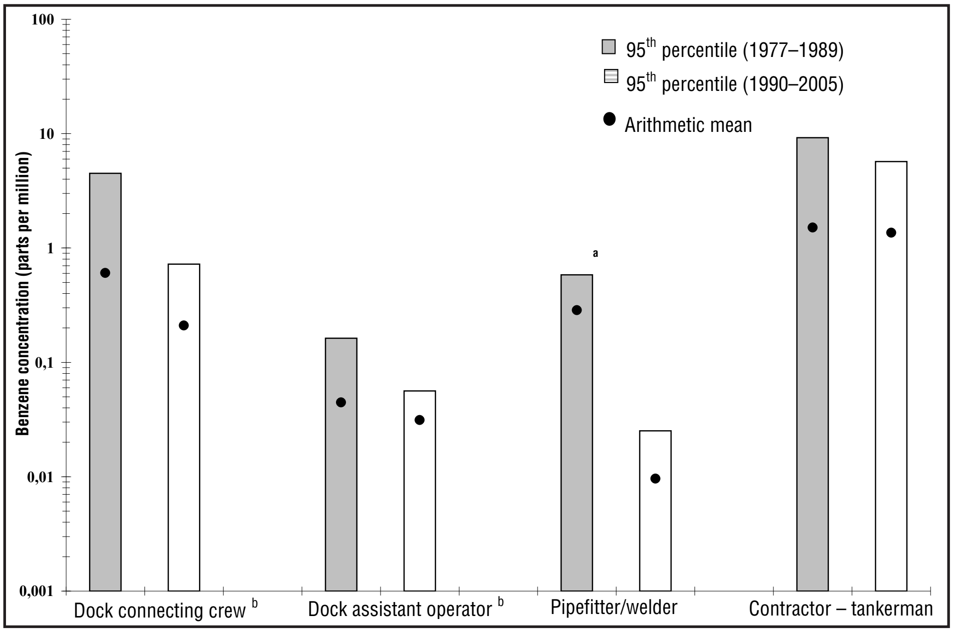


**Figure 2**. Distribution of non-task benzene air concentrations by job title and time period. [a] Sample size <10; [b] Statistically different by time period (P<0.05)

**Table 7**. Summary statistics for the task-related dataset, including task and job category. [SD=standard deviation; NC=not calculated because more than 50% of the samples were below the limit of detection].

| Task | Jobs | N | Detection frequency (%) | Benzene concentration (parts per million) | | | | Sample duration (minutes) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Geometric mean | Geometric SD | Minimum detected | Maximum detected | 25th percentile | 75th percentile |
| Disconnect cargo hoses | Dock connecting crew | 134 | 64 | 0.66 | 14 | 0.010 | 179 | 10 | 20 |
| Connect cargo hoses | Dock connecting crew | 87 | 38 | NC | NC | 0.10 | 14 | 15 | 25 |
| Gauge cargo vessel tanks | Contractor – gauging; Contractor – tankerman; Dock connecting crew | 65 | 29 | NC | NC | 0.080 | 99 | 10 | 20 |
| Sample product on cargo vessel | Dock connecting crew | 34 | 91 | 0.73 | 10 | 0.010 | 119 | 14 | 47 |
| Repair undrained equipment | Pipefitter/welder Instrument technician | 15 | 67 | 0.23 | 20 | 0.15 | 23 | 16 | 63 |
| Load benzene/gasoline barge | Contractor – tankerman | 3 | 100 | 22 | 14 | 1.0 | 130 | 15 | 124 |
| Load sulfidic caustic barge | Contractor – tankerman Dock assistant operator | 4 | 25 | NC | NC | 0.36 | 0.36 | 15 | 120 |
| Inspect cargo hose disconnection | Dock assistant operator | 1 | 100 | 8.7 | - | 8.7 | 8.7 | - | - |
| All task samples [a] | | 343 | 54 | 0.32 | 12 | 0.010 | 179 | 12 | 30 |

[a] Does not include 54 samples for which a task could not be assigned.

## Discussion

This paper presents historical industrial hygiene monitoring data representative of potential benzene exposure to Baton Rouge Refinery dock workers from 1977–2005. Prior to this study, no extensive analysis of historical industrial hygiene data for refinery dock workers had been performed, and, in particular, none had focused on the airborne concentrations in the workplace at specific refineries or for specific tasks. The previously published dock worker analyses (7–18, 20) addressed short study periods, small sample sizes, and lacked analyses that associated measurement results with the job titles and key tasks performed at the dock facilities.

The analysis by task bin is unique to this study, as other dock worker studies have focused primarily on long-term exposure estimates. Although using task-based exposure levels in epidemiology has its limitations (34), Verma et al (35) summarized data from several studies evaluating benzene exposure to employees in petroleum industries and explicitly recommended moving towards task-based exposure assessments as opposed to long-term time-weighted average estimates for the petroleum industry. This study addresses Verma et al's recommendation by providing a detailed task-level analysis of benzene air concentrations at the Baton Rouge docks. Task-based exposure distributions based on ≥10 samples are provided for five key tasks, including cargo hose disconnection, gauging, and sampling. Notable differences in exposures from hose connection and disconnection tasks are discernible in the results. Unique data regarding the types of product loaded (ie, gasoline/benzene versus other petroleum products) as a determinant of exposure are provided in table 6 and supplemental tables B and C. The results of this study, used in conjunction with work history information, provide a robust basis for determining exposures for dock workers.

Table 8 presents summaries of benzene personal air sampling results from 1977–2005 for the Baton Rouge Refinery (all areas other than the docks) and the associated dock facilities. When comparing these datasets, it is important to keep in mind that the refinery sampling program aggregates results from many operational units, some of which yielded mean benzene concentrations lower than samples from the docks, and some of which yielded higher mean concentrations. Sampling at the dock facilities was driven more by tasks of relatively short duration, likely resulting in more variable levels of potential exposure. Non-task samples indicate that mean airborne benzene concentrations associated with the dock workers were >2.5-times the mean benzene concentration associated with refinery workers (0.28 ppm versus 0.10 ppm), but the median concentrations were identical (0.01 ppm). Task-related samples collected from dock workers were associated with both higher mean and median benzene concentrations than those collected from refinery workers (means 6.6 versus 0.25 ppm and medians 0.26 ppm versus 0.02 ppm).

Results of sampling for airborne benzene in other published studies of exposures from marine handling of petroleum products and petrochemicals are presented in figure 4 and supplemental table D.1. Publications yielded 14 studies in Europe, the US, and Japan that

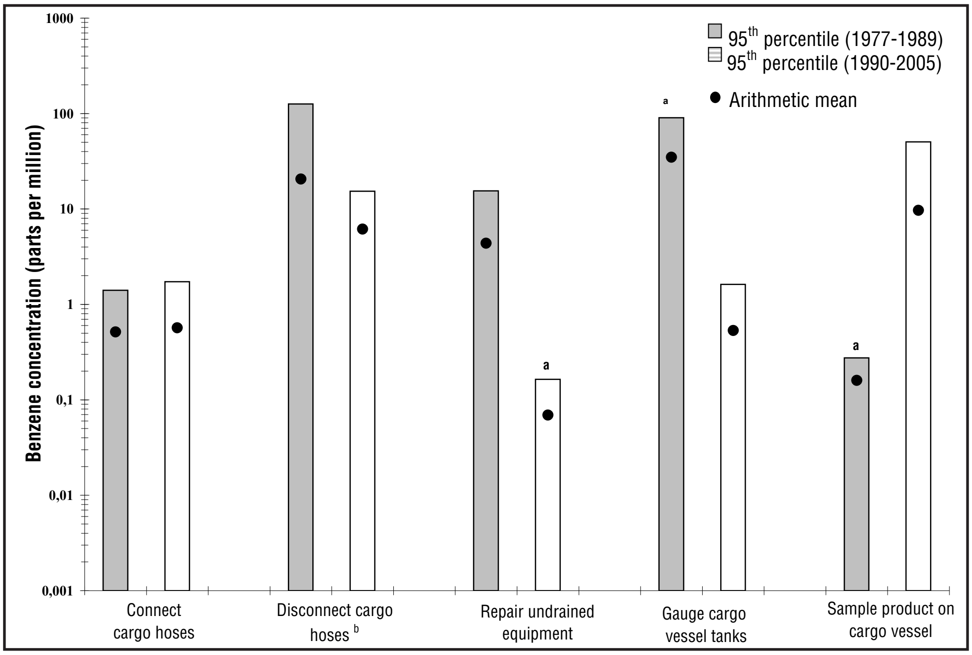


**Figure 3**. Distribution of benzene air concentrations by task and time period. [a] Sample size <10; [b] Statistically different by time period (P<0.05)

included ≥10 samples (8, 9, 11–20, 36, 37). Figure 4 shows the mean benzene concentrations for each dataset identified from these studies that used averaging times of ≥3 hours, along with maximum detected values when reported. More details regarding these and other relevant studies from the literature (10, 38–43) are presented in supplemental tables D.1 and D.2, including details regarding ongoing activities during the sampling campaigns, such as whether loading systems were closed (that is, vapor recovery was operational) or open (no vapor recovery), and other statistical parameters that were reported in some cases (such as geometric mean and median concentrations, arithmetic and geometric standard deviations, and ranges of results).

To facilitate comparison, figure 4 also shows the mean and maximum non-task airborne benzene concentrations for Baton Rouge dock workers from this study based on samples collected before 1990 (0.28 and 6.3 ppm, respectively) and for samples collected during 1990 and later years (0.15 and 15.3 ppm, respectively). The mean airborne benzene concentration for dock workers from this study based on non-task samples (0.28 ppm) lies within the range of means from the published studies, and below 82% of the mean concentrations reported from the studies depicted in figure 4, despite the fact that the Baton Rouge data set was targeted to over-represent benzene handling activities as discussed elsewhere (4). The mean airborne benzene concentration for dock workers from this study based on task-related samples (6.6 ppm) also lies within the range of means from the published studies, and below 29% of the mean concentrations reported for datasets included in supplemental table D.2.

This study characterizes potential benzene exposure for dock workers at the ExxonMobil facilities in Baton Rouge, Louisiana while loading and off-loading benzene-containing cargo from both the refinery and the chemical plant. This characterization will be useful for future dock worker exposure assessments, including epidemiology studies involving benzene. However, it is important to keep in mind that – although within the industrial hygiene program for the Baton Rouge complex – the docks were, in effect, an area of emphasis

**Table 8.** Detection frequencies and summary statistics for the non-task and task-related datasets from the Baton Rouge refinery and docks (1977–2005).

| Dataset | | N | Detection frequency (%) | Sample result (parts per million) | | |
|---|---|---|---|---|---|---|
| | | | | Arithmetic mean | 95th percentile | Maximum detected |
| Non-task | Refinery | 3403 | 43 | 0.095 | 0.30 | 24 |
| | Dock | 406 | 45 | 0.28 | 0.94 | 15 |
| Task | Refinery | 830 | 28 | 0.25 | 1.0 | 21 |
| | Dock | 343 | 54 | 6.6 | 26 | 179 |

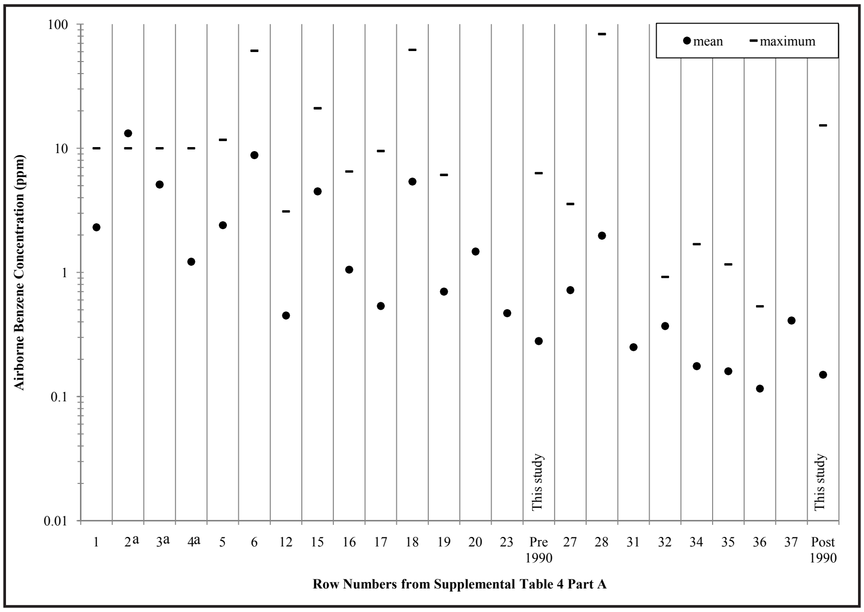


**Figure 4.** Arithmetic means and maximum detected values of airborne benzene concentrations from published studies of marine petroleum handling facilities and from this study. Studies from Supplemental table D.1 that included ≥10 samples are included here. Pre-1990: values based on dock connecting crew and dock assistant operator samples (1977–1989). Post-1990: values based on dock connecting crew, dock assistant operator, and dock controller samples (1990–2005).
[a] Maximum values stated as >10 parts per million.

for measurements of airborne benzene; sampling at the docks may have been more likely to occur when products containing benzene were being transferred. When considering these data for exposure reconstruction, then, it is especially important to bear in mind the nature of the samples analyzed in this dataset, which were primarily collected using a targeted strategy. As such, these data are likely to represent the upper tail of benzene air concentrations at the docks, rather than typical exposures. This study also demonstrates that task-related air concentrations are the primary source of potential exposure for refinery dock workers.

Despite the advantages that this study (which utilizes measurements spanning from 1977–2005) offers over existing studies of dock workers exposed to benzene, samples were not collected during each of those years for every job title or task. As a result, interpolation would be necessary to determine exposures during years for which no data was collected. While some samples were not well documented, considerable review of sample datasheets and consultation with ExxonMobil industrial hygienists and plant personnel helped to categorize relevant results.

Even with these limitations, though, this study provides an analysis of a very large dataset of benzene air concentrations at refinery docks, and characterizes a variety of job titles and tasks. Furthermore, an exhaustive independent review of the data was conducted to ensure data quality and accuracy with respect to original documentation. No other studies in the published literature to date have ensured this level of data quality and accuracy for such a large body of data. Based on a review of the literature, this study, then, appears to be the most robust analysis of the historical benzene exposure of this class of workers in the era since OSHA's formation in 1971.

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