

# Analysis of 1,3-butadiene Industrial Hygiene Data

SEPTEMBER 26, 2024

ToxStrategies

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## Acronyms

1,3-BD	1,3-butadiene
ACC	American Chemistry Council
AIHA	American Industrial Hygiene Association
APR	air purifying respirator with chemical cartridge
COU	conditions of use
EPA	U.S. Environmental Protection Agency
EHS	environmental health and safety
FID	flame ionization detection
GC	gas chromatography
KM	Kaplan-Meier
LCL	lower confidence level
LDAR	leak prevention, detection and repair program
LOD	limit of detection
NAICS	North American Industry Classification System
ND	non-detect
NIOSH	National Institute for Occupational Safety and Health
ONU	occupational non-user
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure limit
PPE	personal protective equipment
ppm	parts-per-million
SHE	safety health and environment
STEL	short-term exposure limit
TCE	trichloroethylene
TSCA	Toxic Substances Control Act
TWA	time-weighted average
UCL	upper confidence level
VOC	volatile organic chemical

## Executive Summary

The American Chemistry Council (ACC) 1,3-butadiene Toxic Substances Control Act (TSCA) Risk Evaluation Consortium (Consortium) is comprised of companies that manufacture or process 1,3-butadiene (1,3-BD). In an effort to inform the U.S. Environmental Protection Agency (EPA) risk evaluation of 1,3-BD as amended by the Frank R. Lautenberg Chemical Safety for the 21<sup>st</sup> Century Act of 2016 the Consortium compiled and analyzed existing industrial hygiene data to support EPA's exposure assessment of workers and occupational non-users (ONUs) associated with the Manufacturing and Processing (Processing as a Reactant) conditions of use, as described in EPA's Final Scope of the Risk Evaluation for 1,3-Butadiene (Scoping Document). The objective of the data collection and analysis was to provide EPA with a high-quality dataset that accurately represents the potential for exposures to workers and ONUs involved in the manufacturing and processing of 1,3-BD as a reactant.

The Consortium collected relevant exposure data through the use of a uniform data collection template. Information including type of company/operation, use and process information, product information, characteristics of the workplace, exposure controls and information about the air sampling campaigns were compiled. Upon receipt of the data, each file was reviewed for completeness and accuracy. Specific attention was focused on verification of analytical methods and detection limits, sample durations, job categories, task descriptions, operational status, work area descriptions, sample dates and PPE used during the task and sample collection. Following review and clarification, each Consortium member's data were blinded by company name and combined into one file for analysis. The Consortium exposure data were evaluated according to EPA's process described in the agency's Framework for Systematic Review and found to be of high quality.

The personal air samples were aggregated across all Consortium members and stratified to characterize exposures across jobs and tasks as well as exposure frequency and duration. Data designated by the companies as full shift were stratified by job group and one of three operational conditions of the workplace which describe exposure frequency and duration including routine, turnaround (planned, scheduled maintenance activities where equipment is repaired or replaced) and non-routine. Eight job groups were designated in the datasets:

- Infrastructure/Distribution
- Instrument/Electrical
- Laboratory Technician
- Machinery and Specialist Mechanical Group
- Maintenance
- Occupational Non-User (ONU)
- Operations On-site
- Safety Health and Environment (SHE)

Data designated by the companies as short term or task level air samples were stratified by task description, sample duration and one of the three operational conditions of the



workplace. Data were available for each of the tasks identified by EPA in the final Scoping Document:

- Unloading and transferring 1,3-butadiene to and from storage containers to process vessels
- Handling, transporting and disposing of waste containing 1,3-butadiene
- Cleaning and maintaining equipment
- Sampling chemicals, formulations, or products containing 1,3-butadiene for quality control
- Performing other work activities in or near areas where 1,3-butadiene is used

It should be noted that “repackaging chemicals, formulations or products containing 1,3-butadiene” was not included because that task is not conducted in the Manufacturing and Processing as a Reactant conditions of use.

The aggregated datasets were analyzed to determine the overall distribution of the data by the stratifications described in Sections 2.3.1 and 2.3.2. Statistical analysis was conducted using the statistical computing platform, R, and the analyses packages: *NADA* (Non-detects and Data Analysis for Environmental Data) and *tidyverse*. For each dataset, summary statistics were calculated from an empirical cumulative distribution function for the censored data using the Kaplan-Meier (KM) method (i.e. the minimum, maximum, 50<sup>th</sup> percentile, 90<sup>th</sup> percentile, 95<sup>th</sup> percentile, mean, standard error, and the 95<sup>th</sup> lower- and upper- confidence levels (LCL/UCL) on the mean). Summaries of the full dataset including all operational conditions, as well as alternative statistical analyses are included in Appendices C and D.

More than 6,000 air sample data points are available to characterize potential worker exposure to 1,3-BD under the Manufacturing and Processing as a Reactant conditions of use. The data analysis revealed highly censored datasets for all job groups and tasks with the full-shift datasets showing 65%-94% non-detect values and the task datasets showing 45%-100% non-detect values. However, an analysis of the detection limits associated with each sample indicated that they were less than 10% of the current OSHA Permissible Exposure Limit (PEL) and therefore sufficiently low to have confidence in the levels of exposure that can be inferred.

Of the full-shift samples, those collected during routine operations from workers in the SHE group had the highest 1,3-BD concentrations with a KM mean of 0.16 ppm and KM 95UCL of 0.23 ppm. Other groups such as Operations and Maintenance have similar routine full-shift exposure concentrations. Air samples collected on employees considered ONUs showed that their potential for exposure is very low with a KM mean of 0.012 ppm and KM 95UCL of 0.014 ppm. Table ES-1 provides a summary of the routine full-shift air concentrations

Of the short-term and task samples, personal samples collected during routine work associated with cleaning and maintaining equipment had the highest 1,3-BD concentrations with a KM mean of 3.9 and KM 95UCL 6.7 ppm. The Consortium dataset was also analyzed to understand the use of respirators and the analysis revealed that respirators were

indicated for all tasks, with types varying depending on the task and air concentrations measured. Table ES-2 provides a summary of the routine short-term air concentrations.

The Consortium dataset provides robust quantitative air concentration data for which occupational exposures to 1,3-BD in the Manufacturing and Processing as a Reactant COUs can be assessed. The central tendency measures of the data demonstrate that most workers in these COUs have routine full-shift exposures to 1,3-BD at levels 1 order of magnitude lower than the OSHA PEL of 1 ppm. Furthermore, even at the upper bound, the measures indicate worker full-shift exposures are lower than the OSHA PEL. The short-term data ( $\leq 15$  min) are similar in that at all of the central tendency measures are below the OSHA STEL of 5 ppm, as are all of the upper bound measures, except for the task of Cleaning and Maintaining Equipment. The activities where short-term exposures may exceed the STEL, engineering controls and personal protective equipment are used to reduce worker exposures. Table ES-3 provides a summary of respiratory protection used during the various tasks.

Risk assessment of the workers in the Manufacturing and Processing as a Reactant COU should be conducted using the routine full-shift and short-term, or task-based data provided herein. The designation of 'routine' for operational status reflects exposures that are may occur on a daily basis over the long-term. Therefore full-shift samples designated as routine should be used to characterize occupational exposures that may occur daily over a working lifetime. Short-term samples, designated as routine, should be used to characterize peak exposures that may occur regularly, for short durations, but may be variable in terms of frequency (weekly, monthly, quarterly, annually). However, in assessing short-term exposures, respirator use must be considered as the Consortium data indicate some type of respiratory protection is used for every short-term task activity where 1,3-BD may exposure occur.

**Table ES-1. Summary of Full-Shift Air Concentrations during Routine Operations**

Job Group	N Samples	% Non-Detects	Full Shift Personal Air Concentrations (ppm) - Kaplan Meier Statistics								
			Min	50th	90th	95th	KM-Mean <sup>1</sup>	SE	95LCL Mean	95UCL Mean <sup>2</sup>	Max
Infrastructure/Distribution Operations	455	78%	0.006	NA	0.210	0.450	0.12	0.038	0.045	0.193	16.400
Instrument and Electrical	313	91%	0.008	NA	0.021	0.160	0.068	0.033	0.003	0.133	10.000
Laboratory Technician	215	73%	0.006	NA	0.120	0.246	0.063	0.016	0.031	0.094	2.932
Machinery and Specialists Group	222	80%	0.008	NA	0.060	0.280	0.087	0.023	0.042	0.133	3.310
Maintenance	354	69%	0.001	NA	0.230	0.240	0.109	0.010	0.089	0.129	2.100
Operations Onsite	1952	88%	0.0001	0.001	0.037	0.190	0.074	0.016	0.043	0.105	16.000
Safety Health and Engineering	21	71%	0.038	NA	0.191	0.364	0.158	0.036	0.087	0.229	0.789
Missing Job Group Designation	378	94%	0.002	NA	NA	0.037	0.024	0.004	0.016	0.032	1.300
Occupational Non-User	39	77%	0.008	NA	0.013	0.033	0.012	0.001	0.010	0.014	0.038
<sup>1</sup> Recommended to characterize long term central tendency air concentrations											
<sup>2</sup> Recommended to characterize long term upper bound air concentrations											

**Table ES-2. Summary of Short-Term Air Concentrations during Routine Operations**

Task Code	Sample Duration (minutes)	N Samples	% Non-Detects	Short-Term Personal Air Concentrations (ppm) - Kaplan Meier Statistics								
				Min	50th	90th	95th	KM-Mean <sup>1</sup>	SE	95LCL	95UCL <sup>2</sup>	Max
<b>Unloading &amp; Loading</b>	<=15	89	45	0.044	1.0	8.1	17	2.7	0.52	1.7	3.7	26
	>15	158	45	0.024	0.73	8.0	18	3.6	0.77	2.1	5.1	89
<b>Handling Waste</b>	<=15	7	100	0.063	NA	NA	NA	NA	NA	NA	NA	1.6
	>15	10	90	0.081	NA	0.69	0.69	0.69	NA	NA	NA	3.7
<b>Cleaning &amp; Maintaining Equipment</b>	<=15	102	80	0.060	NA	2.7	15	3.9	1.4	1.1	6.7	120
	>15	159	73	0.022	0.063	2.6	8.3	1.8	0.77	0.28	3.3	110
<b>Sample Collection and Analysis</b>	<=15	187	89	0.030	NA	0.51	1.3	0.52	0.04	0.44	0.59	4.8
	>15	237	89	0.017	NA	0.36	2.10	0.49	0.12	0.25	0.74	18.0
<b>Other Tasks</b>	<=15	31	71	0.19	0.20	0.54	2.1	0.49	0.22	0.06	0.92	6.5
	>15	21	81	0.020	NA	0.17	3.7	0.49	0.31	-0.11	1.1	4.7
<sup>1</sup> Recommended to characterize short term central tendency air concentrations												
<sup>2</sup> Recommended to characterize short term upper bound air concentrations												

**Table ES-3. Summary of Respiratory Protection Used During Tasks**

<b>Task</b>	<b>Respirator</b>	<b>1,3-BD Air Concentration (ppm)</b>
<b>Unloading and Transfer</b>	Supplied air	<0.118 - 89
	Full Face APR	<0.06 - 36
	Half Face APR	<0.05 – 2.2
<b>Handling and Transporting Waste</b>	Full Face APR	<0.25 - <3.7
	Half Face APR	<0.08 - < 0.1
<b>Cleaning and Maintaining Equipment</b>	Supplied Air	<0.15 - 120
	Full Face APR	<0.02 - 110
	Half Face APR	<0.04 - <0.7
	No respirator	<0.4 - <0.7
<b>Sampling and Analysis</b>	Supplied Air	<0.52
	Full Face APR	<0.06 - 12
	Half Face APR	<0.09 - 7.3
	No respirator	<0.02 - 4.8
<b>Performing Other Work</b>	Supplied Air	0.27 - 4.7
	Full Face APR	<0.24 - <0.42
	Half Face APR	<0.2 - < 0.3
	No respirator	<0.39 - <0.67
<b>APR = Air purifying respirator with chemical cartridge</b>		

# 1 Introduction

The American Chemistry Council (ACC) 1,3-butadiene Toxic Substances Control Act (TSCA) Risk Evaluation Consortium is comprised of companies that manufacture or process 1,3-butadiene (1,3-BD). In an effort to inform the U.S. Environmental Protection Agency (EPA) risk evaluation of 1,3-BD under TSCA, the Consortium compiled and analyzed existing industrial hygiene data to support EPA's exposure assessment of workers and occupational non-users (ONUs) associated with the Manufacturing and Processing (Processing as a Reactant) conditions of use, as described in EPA's Final Scope of the Risk Evaluation for 1,3-Butadiene (Scoping Document)<sup>1</sup>. The objective of the data collection and analysis was to provide EPA with a high-quality dataset that accurately represents the potential for exposures to workers and ONUs involved in the manufacturing and processing of 1,3-BD.

In the final Scoping Document, EPA identified inhalation of vapors and potential dermal contact with liquids (containing low concentrations of 1,3-BD) as relevant exposure pathways and routes for workers and ONUs in the manufacturing and processing conditions of use. To characterize potential exposures via these routes, the members of the Consortium provided job and task descriptions and corresponding information related to the characteristics of the workplace operations, exposure controls, personal protective equipment (PPE) used or worn during work tasks, and associated air concentration measurements.

The quantitative exposure assessment strategies for each of the Consortium members are guided by compliance with the Occupational Safety and Health Administration (OSHA) butadiene standard (29 CFR 1910.1051), state of the art exposure assessment practices established by the American Industrial Hygiene Association (AIHA)<sup>2</sup> and best practices in the ACC Product Stewardship Manual.<sup>3</sup> The regulatory requirements and best practices are summarized in the following sections.

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<sup>1</sup> U.S. EPA (2020). Final Scope for the Risk Evaluation for 1,3-butadiene CASRN 106-99-0. EPA Document# EPA-740-R-20-11. August 2020.

<sup>2</sup> Jahn, S.D.; Bullock, W.H.; Ignacio, J.S. (Eds.). (2015). A Strategy for Assessing and Managing Occupational Exposures. 4<sup>th</sup> Edition. American Industrial Hygiene Association. Falls Church, VA

<sup>3</sup> American Chemistry Council (2019). Butadiene Product Stewardship Guidance Manual. American Chemistry Council. Washington, D.C.

## 1.1 Overview of 1,3-butadiene manufacturing and processing as a reactant

Butadiene is produced commercially by three processes:

- Steam Cracking of Paraffinic Hydrocarbons: In this process, butadiene is a co-product in the manufacture of ethylene (the ethylene co-product process)
- Catalytic Dehydrogenation of n-Butane and n-Butene (the Houdry process)
- Oxidative Dehydrogenation of n-Butene (the Oxo-D or O-X-D process)

These manufacturing processes are performed in closed systems. Each of these processes produces a stream commonly referred to as crude butadiene that is rich in 1,3-butadiene. Separation and purification of the butadiene stream is typically carried out by extractive distillation, since the boiling points of the various C<sub>4</sub> components are so close to each other. The final concentration in the purified butadiene product is typically <99 wt % pure and is stored liquefied in a pressurized sphere. Liquefied butadiene is shipped by pipelines, ships, barges, rail tank cars, tank trucks and bulk liquid containers to industrial customers who use it as a reactant or ingredient.

The immediate industrial users of 1,3 butadiene either polymerize the butadiene monomer or use it as a chemical intermediate. Common polymer intermediate products are shown under “Intermediates and Polymers” in Figure 1. It is important to note that these intermediates are subsequently sold to manufacturers who make final end products for consumers, listed in Figure 1 as “Uses.”

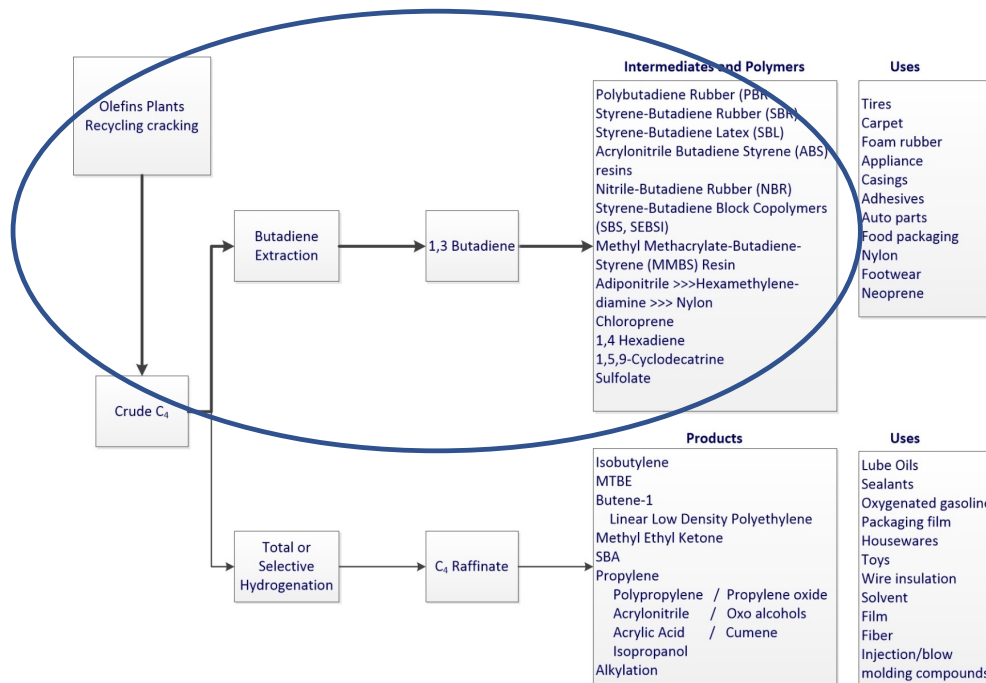


Figure 1. 1,3-Butadiene Supply Chain Overview

## **1.2 OSHA Butadiene Standard (29 CFR 1910.1051)**

Each of the Consortium members are obligated by the OSHA standard to characterize their employees' potential for exposure (1910.1051(d)). Specifically, the standard requires that determination of employee exposure be made from breathing zone samples (i.e. personal samples) that are representative of the 8-hour time weighted average (TWA) and 15 minute short term exposures for each employee. However, monitoring data are not required where objective data such as mathematical modelling or calculations based on composition, chemical and physical properties of a material, stream or product are available to demonstrate that 1,3-BD will not be released into air and result in airborne concentrations at or above the OSHA exposure limits (i.e., 8-hr TWA or STEL).

The OSHA butadiene standard also obligates manufacturers and processors to implement a variety of exposure controls to eliminate or reduce the potential for worker exposures. These controls include:

- Regulated Areas (1910.1051(e)(1))– Regulated areas must be established to restrict access to areas or operations where air concentrations of 1,3-BD may exceed the permissible exposure limit (PEL) or short-term exposure limit (STEL) to only authorized and trained personnel. As such, manufacturers and processors are required to anticipate, designate, and restrict entry to these areas. This required control significantly reduces the opportunity for butadiene exposures by ONUs.
- Engineering Controls (1910.1051(f)(1)) – A variety of engineering controls are specified by OSHA to reduce the potential for worker exposures including A program for maintaining the effectiveness of local exhaust ventilation systems and the use of pump exposure control technology such as, but not limited to, mechanical double-sealed or seal-less pumps. Additional engineering controls to minimize exposures include leak prevention, detection and repair program (LDAR), enclosed process sample boxes, line purging prior to opening for maintenance, remote tank gauging, and vapor recovery during cargo loading/unloading.
- Respirators (1910.1051(h)) – Respirators are required to be used by workers when engineering controls are insufficient to reduce butadiene exposures below the PEL (8-hr TWA or STEL). OSHA specifies the minimum respirator to be used depending on the air concentration.
- Dermal protection (1910.1051(j)) - Protective clothing and equipment must be provided to prevent eye contact and dermal exposure to 1,3-BD.

## **1.3 Exposure Assessment Strategy**

While the Consortium data were aggregated across nine member companies, each data set was generated from an industrial hygiene program whose exposure assessment strategy is based on the American Industrial Hygiene Association (AIHA) exposure assessment



strategy (EAS) guidance.<sup>4</sup> This guidance assists industrial hygienists in developing data that are representative of worker exposures, useful in prioritizing workers for additional evaluation or enhanced exposure controls and determining compliance with OSHA standards. Hallmarks of the strategy include qualitative assessments to prioritize exposure monitoring, development of similar exposure groups to allow for collection of representative samples, and sample program design to ensure sufficient sample size for decision analysis based on the collected data.

The AIHA guidance lists the following major steps in the strategy:

1. Establish strategy – Prepare a written program that includes roles, exposure assessment goals, decision criteria for acceptable exposures.
2. Basic Characterization – Collect information to describe the physical workplace, worker population, the work tasks performed, materials used and processes being run.
3. Exposure Assessment – Assess exposures in the workplace considering the information available on the workplace, workforce and environmental agents. The assessment outcomes include:
  - a. Groupings of workers having similar exposures,
  - b. Definition of an exposure profile for each group of similarly exposed workers relative to the appropriate occupational exposure limit (OEL), and
  - c. Judgements about the acceptability of each exposure profile – acceptable, uncertain, unacceptable
4. Further Information Gathering – Implement prioritized exposure monitoring or the collection of more information on health effects so that uncertain exposure judgements can be resolved with higher confidence.
5. Health Hazard Control – implement prioritized control strategies for unacceptable exposures
6. Reassessment – Periodically perform a comprehensive re-evaluation of exposures. Determine whether routine monitoring is required to verify that acceptable exposures remain acceptable.
7. Communication and Documentation – communication of exposure assessment findings and the maintenance of exposure assessment data are to be conducted throughout the implementation of the strategy.

To maximize available industrial hygiene resources, worker groups and tasks are prioritized for exposure assessment based on a relative exposure rating that is derived from qualitative and quantitative information. AIHA guidance recommends a rating scale of 0-

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<sup>4</sup> AIHA (2015). A Strategy for Assessing and Managing Occupational Exposures. American Industrial Hygiene Association, Falls Church VA.

4 based on an estimate of the 95<sup>th</sup> percentile of an exposure profile to the OEL. For example, if the 95<sup>th</sup> percentile exposure was less than 1% of the OEL, the rating would be 0 and if the 95<sup>th</sup> percentile of exposure was greater than 100% of the OEL, the rating would be 4. Therefore, most industrial hygiene programs do not prioritize exposure measurements for ONUs and when measurements are made, it is generally to confirm the low potential for exposure.

Based on the exposure assessment strategies used by the Consortium, this dataset, represents air concentrations of 1,3-BD for workers who are more likely than not to have exposure, rather than potential exposure to the whole worker population at a facility. In addition to characterizing exposures during routine operations, industrial hygienists target worst-case exposure scenarios such as during turnaround operations (a planned maintenance shutdown of a process unit) or process upsets (unplanned maintenance). These conditions occur infrequently and may not have engineering controls to minimize exposures. Thus, monitoring these exposure conditions allows for selection of proper PPE or other control measures.

## 2 Methods

### 2.1 Data Collection

The Consortium collected relevant exposure data through the use of a uniform data collection template. The components of the template are shown in Figure 2.

Company / Source characterization	Use Information/ Activities	Product Information	Characteristics of Workplace	Exposure Controls	Sampling Campaign
<ul style="list-style-type: none"> <li>• SIC/NAIC codes</li> <li>• Operation type</li> </ul>	<ul style="list-style-type: none"> <li>• Use Name</li> <li>• Activity</li> <li>• Amount Manufactured</li> <li>• Place of Use</li> <li>• Physical conditions of use (closed/open process, exposure controls)</li> <li>• Operating temperature</li> </ul>	<ul style="list-style-type: none"> <li>• Substance ID</li> <li>• Concentration of Substance in product</li> <li>• Physical form</li> </ul>	<ul style="list-style-type: none"> <li>• Work area</li> <li>• Job group</li> <li>• Task activity</li> <li>• Duration</li> <li>• Operation type (normal, turnaround, upset)</li> <li>• Employee type (Worker or ONU)</li> </ul>	<ul style="list-style-type: none"> <li>• Local exhaust ventilation</li> <li>• Dilution ventilation</li> <li>• Dermal protection</li> <li>• Respiratory protection</li> <li>• Other</li> </ul>	<ul style="list-style-type: none"> <li>• Date</li> <li>• Sampling Strategy</li> <li>• Sample type (full-shift or task)</li> <li>• Sample duration</li> <li>• Unit of measurement</li> <li>• Analytical method</li> <li>• Unsampled time</li> <li>• Time weighted average</li> <li>• Measurement below LOD</li> </ul>

**Figure 2. Components of Exposure Data Collection Template**

The Consortium also surveyed their membership on task-specific metadata (e.g., exposure time, task duration, number of shifts, number of workers per shift). The results of this survey and the survey template are reported in Appendix F and G, respectively.

## 2.2 Data Review and Quality Assessment

Upon receipt of the data, each file was reviewed for completeness and accuracy. Specific attention was focused on verification of analytical methods and detection limits, sample durations, job categories, task descriptions, operational status, work area descriptions, sample dates and PPE. Following review and clarification, each Consortium member's data were blinded by company name and combined into one file for analysis. The Consortium exposure data were evaluated according to EPA's process described in the agency's Framework for Systematic Review<sup>5</sup> and found to be of high quality. Each of the elements included in the assessment were considered and are described below.

**Methods:** Each individual data set included information on the sampling and analytical methods used in the air sampling programs. There were two methods used: NIOSH 1024 and OSHA 56. Both methods involve collection of an air sample using personal air sampling pumps, which draw air through a solid sorbent tube, followed by desorption using a solvent and analysis using gas chromatography (GC) coupled with flame ionization detection (FID). Passive sampling badges that do not require an air pump (e.g. [3M 3520, 3530](#)) are also used to collect personal air samples and demonstrated to meet OSHA's accuracy requirements. The NIOSH method has a stated working range of 0.02 to 100 ppm (0.04 to 220 mg/m<sup>3</sup>) and the OSHA method has a lower limit of quantification of 155 ppb (0.343 mg/m<sup>3</sup>). The NIOSH and OSHA methods are provided in Appendix A. The limits of detection for full-shift datasets by job category and the short-term datasets by task activity are provided. Lastly, all samples included in the Consortium dataset were analyzed by AIHA accredited laboratories.<sup>6</sup>

**Geographic Scope:** All of the data provided by the Consortium members are from their United States operations and therefore directly applicable to US workers. The data are from 47 sites throughout the US.

**Applicability to Condition of Use:** The Consortium member data are representative of Manufacturing and Processing as a Reactant conditions of use which are included in EPA's final Scoping Document. The NAICS codes for which the data are represented are:

- 324110 – Petroleum refineries
- 325110 – Petrochemical manufacturing
- 325199 – Other organic chemical manufacturing
- 325210 – Resin and synthetic rubber manufacturing
- 325211 – Plastic and resin manufacturing
- 325991 – Custom compounding of purchased resins
- 325998 – All other chemical product and preparation manufacturing

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<sup>5</sup> U.S. EPA (2018). Application of Systematic Review in TSCA Evaluations. Appendix D. EPA Document# 740-P1-8001. May 2018.

<sup>6</sup> [AIHA Laboratory Accreditation Programs, LLC | Homepage \(aihaaccreditedlabs.org\)](#)

**Temporal Representativeness:** All of the Consortium data were collected during the years of 2010 -2019 and therefore directly applicable to EPA’s risk evaluation.

**Sample Size:** The Consortium dataset is large; containing 5, 676 full-shift personal samples (workers and ONUs) and 1,051 short term and task level samples (workers).

**Accessibility and Clarity:** The Consortium data have been aggregated by job group, task, exposure frequency and duration. Additionally, ‘meta data’ including respiratory protection that is used in accordance with the requirements of the OSHA butadiene standard, and PPE to prevent skin contact with liquids containing low concentrations of butadiene are provided.

**Variability and Uncertainty:** The variability and uncertainty associated with the Consortium data are provided via full data distributions and summary statistics for the aggregated data sets. Overall, the dataset is highly censored (i.e., low detection frequency), but the limits of detection are sufficiently low to characterize potential exposure with respect to the OSHA PEL (8 hr TWA and STEL). The data at the high-end tail of the distributions represent jobs and tasks where engineering controls are not sufficient to reduce exposures and therefore OSHA mandated PPE is used.

## **2.3 Data Aggregation**

The personal air samples were aggregated across all Consortium members and stratified to characterize exposures across jobs and tasks as well as exposure frequency and duration. The data collection template provided standardized job groups and task descriptions used throughout the industry, however, some companies did not provide their industrial hygiene data mapped to the standardized job groups. As such, for four datasets, the company-specific job groups/titles were translated to the standardized groups as shown in Appendix B.

### **2.3.1 Full-Shift Air Samples**

Data designated by the companies as full shift (with sampling durations greater than four hours) were stratified by job group and one of three operational conditions of the workplace: routine, turnaround and non-routine, as shown in Figure 3 below.

Job Groups	Operational Condition
<ul style="list-style-type: none"> <li>•Infrastructure/Distribution</li> <li>•Instrument/Electrical</li> <li>•Laboratory Technician</li> <li>•Machinery and Specialist Mechanical Group</li> <li>•Maintenance</li> <li>•Occupational Non-User (ONU)</li> <li>•Operations On-site</li> <li>•Safety Health and Environment (SHE)</li> <li>•Missing or Unknown</li> </ul>	<ul style="list-style-type: none"> <li>•<b>Routine</b> <ul style="list-style-type: none"> <li>•Normal operations and routine maintenance</li> <li>•Exposure frequency = 5 day/wk, but varies</li> <li>•Exposure time = 8-12 hrs/day</li> </ul> </li> <li>•<b>Turnaround</b> <ul style="list-style-type: none"> <li>•Planned maintenance shutdowns of units</li> <li>•Exposure frequency = 2-4 weeks/5 yr</li> <li>•Exposure time = 8-12 hrs/day</li> </ul> </li> <li>•<b>Non-routine</b> <ul style="list-style-type: none"> <li>•Unplanned maintenance, process upsets</li> </ul> </li> </ul>

**Figure 3. Full-Shift Job Groups and Workplace Operational Conditions**

### 2.3.2 Short Term and Task Level Air Samples

Data designated by the companies as short term or task level air samples were stratified by task description, sample duration and one of the three operational conditions of the workplace, as shown in Figure 4 below. Data were available for each of the tasks identified by EPA in the final Scoping Document, except for “repackaging chemicals, formulations or products containing 1,3-butadiene” because that task is not conducted in the Manufacturing and Processing as a Reactant conditions of use. It should be noted that although some tasks are conducted a part of routine operations, the frequency of the task may be daily, quarterly or even annually.

Task	Sample Duration	Operational Condition
<ul style="list-style-type: none"> <li>•Unloading and transferring 1,3-butadiene to and from storage containers to process vessels</li> <li>•Handling, transporting and disposing of waste containing 1,3-butadiene</li> <li>•Cleaning and maintaining equipment</li> <li>•Sampling chemicals, formulations, or products containing 1,3-butadiene for quality control</li> <li>•Performing other work activities in or near areas where 1,3-butadiene is used</li> </ul>	<ul style="list-style-type: none"> <li>•≤ 15 minutes (relevant to compliance with OSHA STEL)</li> <li>•&gt; 15 minutes to characterize full task duration</li> </ul>	<ul style="list-style-type: none"> <li>•<b>Routine</b> <ul style="list-style-type: none"> <li>•normal operations and routine maintenance</li> <li>•Exposure frequency = 5 days/week</li> <li>•Exposure time = 15 – 239 min/task</li> </ul> </li> <li>•<b>Turnaround</b> <ul style="list-style-type: none"> <li>•planned maintenance shutdowns of units</li> <li>•Exposure frequency = 2 weeks/ 5yr</li> <li>•Exposure time = 15 – 239 min/task</li> </ul> </li> <li>•<b>Non-routine</b> <ul style="list-style-type: none"> <li>•unplanned maintenance, process upsets</li> </ul> </li> </ul>

**Figure 4. Short Term Task Designations, Durations, and Operational Conditions**

## 2.4 Data Analysis

The aggregated datasets were analyzed to determine the overall distribution of the data by the stratifications described in Sections 2.3.1 and 2.3.2. These statistics were computed using the statistical computing platform, R, and the analyses packages: *NADA* (Non-detects and Data Analysis for Environmental Data) and *tidyverse*. There are numerous methods for conducting statistical analyses of exposure data, and in this analysis, the Consortium evaluated three different approaches for characterizing the central tendency and high-end exposure potential. A summary of each is shown on Figure 5.

For each dataset, summary statistics were calculated from an empirical cumulative distribution function for the censored data using the Kaplan-Meier (KM) method (i.e., the minimum, maximum, 50<sup>th</sup> percentile, 90<sup>th</sup> percentile, 95<sup>th</sup> percentile, mean, standard error, and the 95<sup>th</sup> lower- and upper- confidence levels (LCL/UCL) on the mean). As alternative analyses, summary statistics were also calculated using the EPA's approach in the Risk Evaluation for trichloroethylene (TCE)<sup>7</sup>, which relies on substitution methods where non-detected values were substituted with one-half the limit of detection (LOD) or the LOD divided by the square root of 2. The "What-if Scenario", "Central Estimate" and "High-End Estimate" according to this approach, were assigned from the ½ LOD or LOD/sqrt (2) substitution-based statistics, depending on sample size cut-points and the geometric standard deviation for each stratified dataset.

Kaplan Maier Statistics	EPA Approach for TCE Risk Evaluation	General Summary Statistics
<ul style="list-style-type: none"><li>• Consistent with EPA approach in Superfund program to evaluate cancer risk of chemical substances the 95<sup>th</sup> UCL was computed to represent the High-End</li><li>• Kaplan-Meier Mean and Standard deviation</li><li>• 95<sup>th</sup> UCL of the mean</li><li>• 50<sup>th</sup> and 95<sup>th</sup> percentiles,</li><li>• Some groups did not contain a sufficient sample size and/or sufficient number of detects to compute all statistics</li></ul>	<ul style="list-style-type: none"><li>• Central Tendency represented by the 50<sup>th</sup> percentile, High-End represented by 95<sup>th</sup> percentile</li><li>• n=1: presented the value as a "what-if exposure"</li><li>• n=2: CT was midpoint, HE was maximum</li><li>• n = 3-5: CT was 50<sup>th</sup> percentile, HE was maximum</li><li>• n= 6+: CT was 50<sup>th</sup> percentile, HE was 95<sup>th</sup> percentile</li><li>• Censored data was included in the data analysis using standard substitution methods (i.e., ½ LOD or LOD/sqrt of 2)</li></ul>	<ul style="list-style-type: none"><li>• Summary statistics calculated using standard substitution methods (1/2 LOD or LOD/sqrt 2)</li><li>• 50<sup>th</sup> percentile</li><li>• Arithmetic mean</li><li>• 90<sup>th</sup> percentile</li><li>• Geomean</li></ul>

**Figure 5. Summary of Statistical Approaches**

<sup>7</sup> EPA (2020). Risk Evaluation for Trichloroethylene CASRN 79-01-6. U.S. Environmental Protection Agency. Office of Chemical Safety and Pollution Prevention. EPA Document #740R18008. November 2020.

Additionally, general statistics were computed (i.e. minimum, maximum, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup> and 95<sup>th</sup> percentiles and the proportion of non-detects reported between specific concentrations) using standard substitution methods for non-detected samples. The complete set of statistics for Full-Shift (stratified by job group and operational condition) and Short-Term (stratified by task, operational condition, and sampling time) personal air samples can be found in Appendices C and D, respectively.

### **3 Results**

More than 6,000 air sample data points are available to characterize potential worker exposure to 1,3-BD under the Manufacturing and Processing as a Reactant conditions of use. This section describes the results of the data analysis for the full-shift and short-term personal air samples, as well as exposure control measures, specifically PPE associated with the various job groups and tasks.

#### **3.1 Full-Shift Personal Air Concentration Data**

The Consortium members data included 5,676 full-shift personal samples collected from workers and ONUs. The sampling durations of this dataset ranged from as low as 4 hours to greater than 12 hours. All full-shift personal air concentrations were used as-is in the analysis and were not transformed into 8-hr TWA concentrations because the member companies indicated that the data were representative of full-shift exposures. The data analysis for each job group is described below.

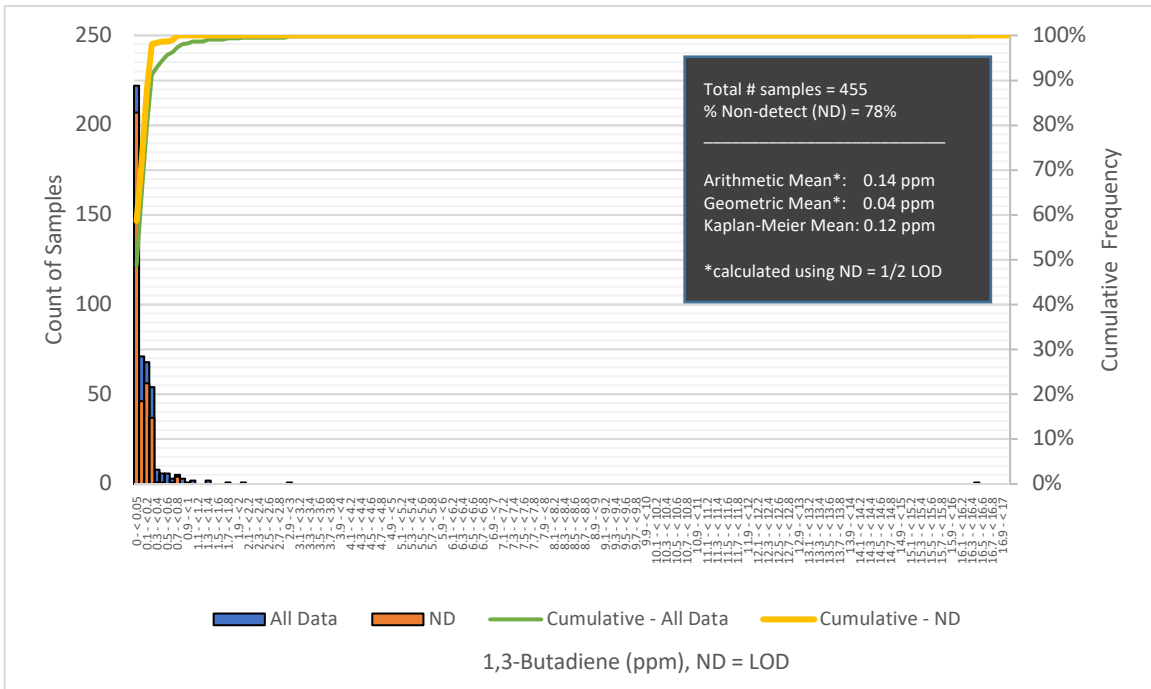
##### ***3.1.1 Infrastructure/Distribution Operations***

Workers in the Infrastructure/Distribution Operations job group are responsible for the infrastructure systems required to run the manufacturing and processing facilities including power utilities, water supply, wastewater treatment, as well as distribution of incoming raw materials or outgoing products. The activities carried out by these individuals include handling streams with low content of butadiene (such as utilities and waste streams) to potentially higher concentrations, when loading/unloading tanks/trucks. During their daily activities, workers might carry out tasks that involve opening process equipment, which, as described in the following section, tend to be controlled by the implementation of engineering controls and/or PPE. The tasks performed by workers in this job group include loading and unloading materials, sample collection, cleaning filters, and handling hoses. A summary of the sample data for this job group during routine operations is provided in Table 1 and the summary statistics for this job group and all operational conditions are provided in Appendix C.

**Table 1. Overview of dataset for Infrastructure/Distribution Operations (Routine)**

Job Group	N Samples	% Non-Detects	Range of Detection Limits (ppm)	KM Mean (ppm)	KM 95 UCL (ppm)
Infrastructure/ Distribution Operations	455	78%	0.006 – 0.7	0.12	0.19

The data for the routine operations describes the potential exposures that the workers in this job would experience on a day-to-day basis and long term over time. **Figure 6** is the overall distribution of routine full-shift personal air concentrations for the Infrastructure/Distribution job group.



**Figure 6. Distribution of Infrastructure/Distribution Routine Full-Shift Personal Air Concentrations**

As noted in Table 1 and as can be seen in Figure 6, the dataset is highly censored with 78% of the air concentrations for routine operations reported below the detection limits. The detection limits associated with this data set ranged from 0.006 – 0.7 ppm. The best descriptor of the central tendency air concentration for this job group is the Kaplan-Meier (KM) mean of 0.12 ppm and the best descriptor of the upper bound for this dataset is the KM 95<sup>th</sup> upper confidence limit on the mean (95 UCL) of 0.19 ppm.



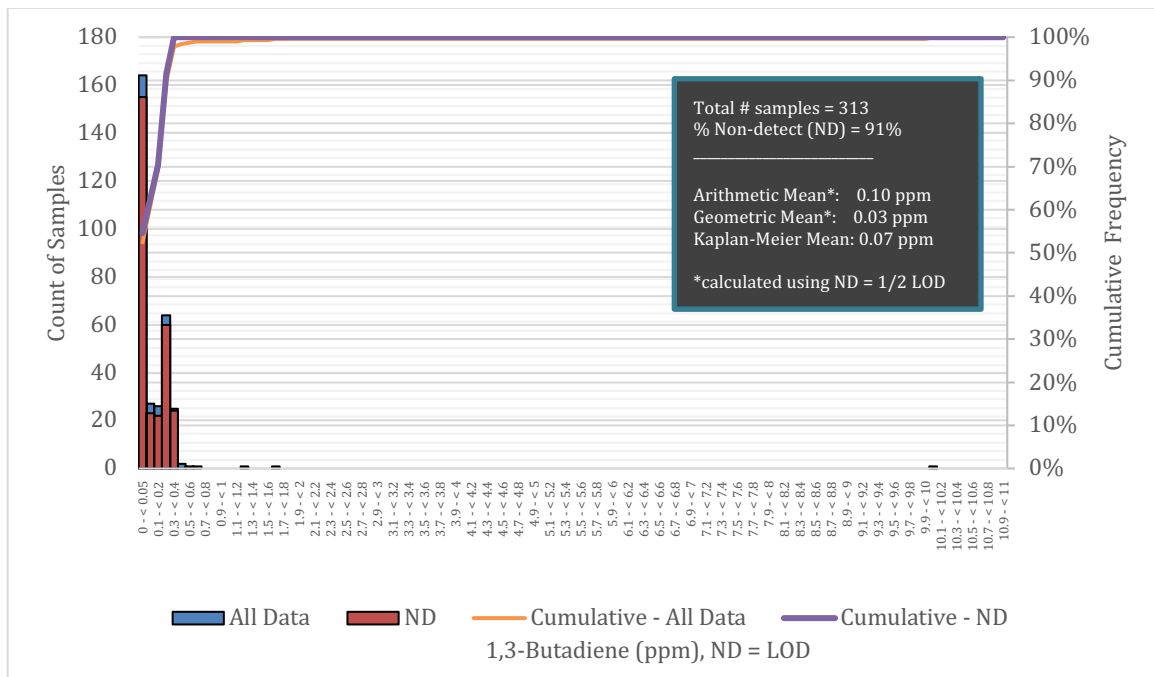
### 3.1.2 Instrument and Electrical

Workers in the Instrument and Electrical job group are responsible for the set up and maintenance of various electrical equipment including analyzers and various instruments throughout the facility. A summary of the sample data for this job group during routine operations is provided in Table 2 and the summary statistics for this job group and all operational conditions are provided in Appendix C.

**Table 2. Overview of dataset for Instrument and Electrical (Routine)**

Job Group	N Samples	% Non-Detects	Range of Detection Limits (ppm)	KM Mean (ppm)	KM 95 UCL (ppm)
Instrument and Electrical	313	91	0.008 – 0.35	0.07	0.13

The data for the routine operations describes the potential exposures that the workers in this job would experience on a day-to-day basis and long term over time. **Figure 7** is the overall distribution of routine full-shift personal air concentrations for the Instrument and Electrical job group.



**Figure 7. Distribution of Instrument and Electrical Routine Full-Shift Personal Air Concentrations**

As noted in Table 2 and as can be seen in Figure 7, the dataset is highly censored with 91% of the air concentrations for routine operations reported below the detection limits. The detection limits associated with this data set ranged from 0.008 – 0.35 ppm. The best descriptor of the central tendency air concentration for this job group is the Kaplan-Meier

(KM) mean of 0.07 ppm and the best descriptor of the upper bound for this dataset is the KM 95<sup>th</sup> upper confidence limit on the mean (95 UCL) of 0.13 ppm. As shown in these results, the majority of activities performed by workers in this job group result in minimal exposures, however, activities that involve opening the lines (like calibration and maintenance of equipment) may create an opportunity for exposure and as such requires the use of PPE for the duration of the task.

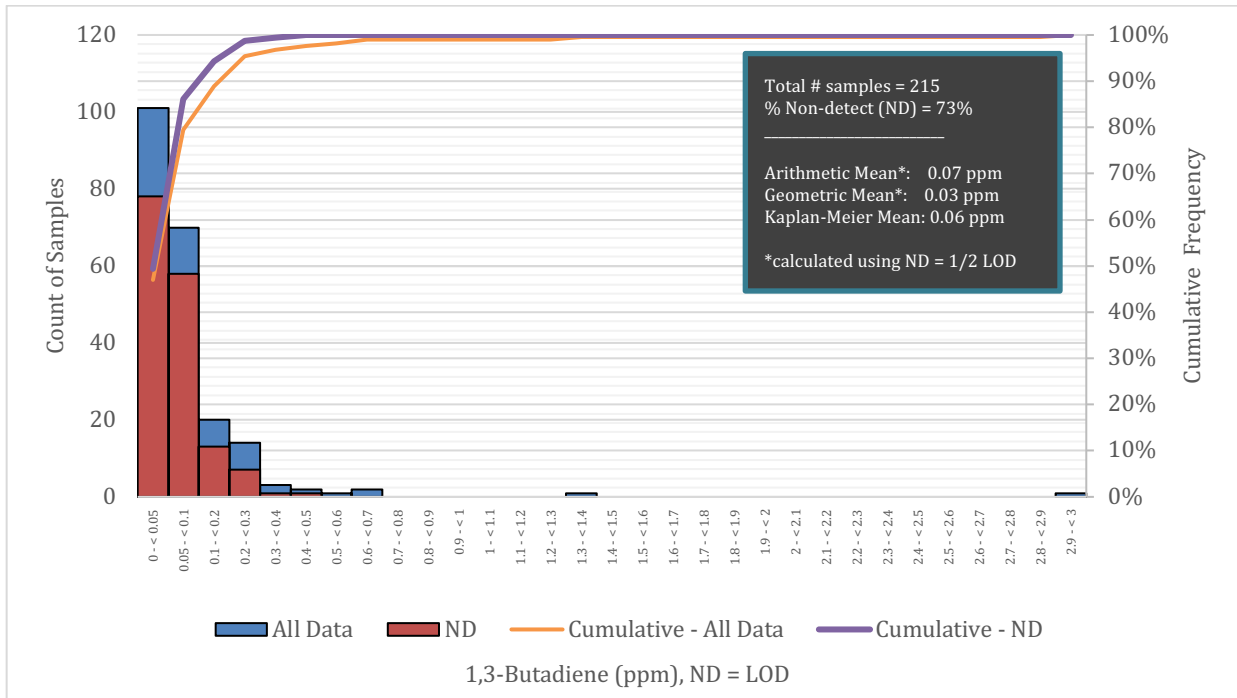
### 3.1.3 Laboratory Technician

Workers in the Laboratory Technician job group are responsible for sample collection and chemical analysis of process and product samples for the facility and conduct their work in laboratories. A summary of the sample data for this job group during routine operations is provided in Table 3 and the summary statistics for this job group and all operational conditions are provided in Appendix C.

**Table 3. Overview of dataset for Laboratory Technicians (Routine)**

<b>Job Group</b>	<b>N Samples</b>	<b>% Non-Detects</b>	<b>Range of Detection Limits (ppm)</b>	<b>KM Mean (ppm)</b>	<b>KM 95 UCL (ppm)</b>
<b>Laboratory Technician</b>	215	73	0.006 – 0.45	0.06	0.09

The data for the routine operations describes the potential exposures that the workers in this job would experience on a day-to-day basis and long term over time. **Figure 8** is the overall distribution of routine full-shift personal air concentrations for the Laboratory Technician job group.



**Figure 8. Distribution of Laboratory Technicians Full-Shift Personal Air Concentrations**

As noted in Table 3 and as can be seen in Figure 8, the dataset is highly censored with 73% of the air concentrations for routine operations reported below the detection limits. The detection limits associated with this data set ranged from 0.006 – 0.45 ppm. The best descriptor of the central tendency air concentration for this job group is the Kaplan-Meier (KM) mean of 0.06 ppm and the best descriptor of the upper bound for this dataset is the KM 95<sup>th</sup> upper confidence limit on the mean (95 UCL) of 0.09 ppm.

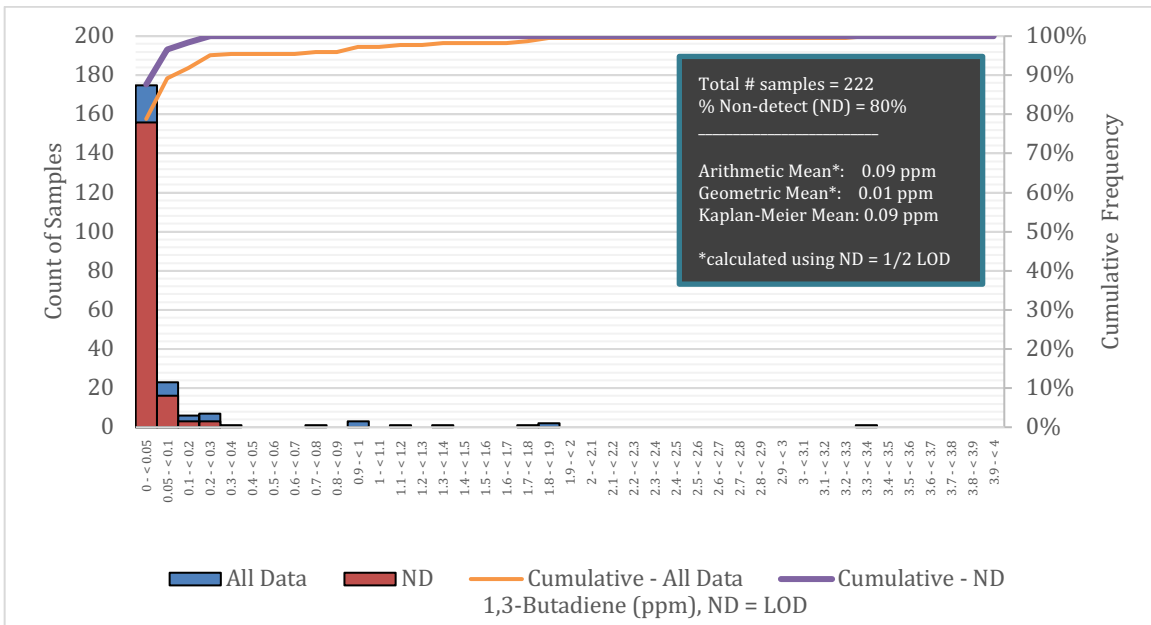
### 3.1.4 Machinery & Specialists Mechanical Group

Workers in the Machinery & Specialists Mechanical job group are skilled workers such as millwrights, boilermakers, pipefitters and welders who work throughout the manufacturing and processing facilities. In general, these workers perform activities in equipment that has been cleared and cleaned, especially because of the hazards associated with the heat/sparks generated during hot work such as welding and grinding. Exposures are typically associated with the brief activities involved in opening process equipment prior to maintenance activities. Because of the potential for exposures, these activities tend to be carried out with PPE (see task descriptions). A summary of the sample data for this job group during routine operations is provided in Table 4 and the summary statistics for this job group and all operational conditions are provided in Appendix C.

**Table 4. Overview of dataset for Machinery & Specialists Mechanical Group (Routine)**

Job Group	N Samples	% Non-Detects	Range of Detection Limits (ppm)	KM Mean (ppm)	KM 95 UCL (ppm)
Machinery & Specialists Mechanical	222	80	0.008 – 0.22	0.09	0.13

The data for the routine operations describes the potential exposures that the workers in this job would experience on a day-to-day basis and long term over time. **Figure 9** is the overall distribution of routine full-shift personal air concentrations for the Machinery & Specialists Mechanical job group.



**Figure 9. Distribution of Machinery & Specialists Mechanical Full-Shift Personal Air Concentrations**

As noted in Table 4 and as can be seen in Figure 9, the dataset is highly censored with 80% of the air concentrations for routine operations reported below the detection limits. The detection limits associated with this data set ranged from 0.008 – 0.22 ppm. The best descriptor of the central tendency air concentration for this job group is the Kaplan-Meier (KM) mean of 0.09 ppm and the best descriptor of the upper bound for this dataset is the KM 95<sup>th</sup> upper confidence limit on the mean (95 UCL) of 0.13 ppm.

### 3.1.5 Maintenance

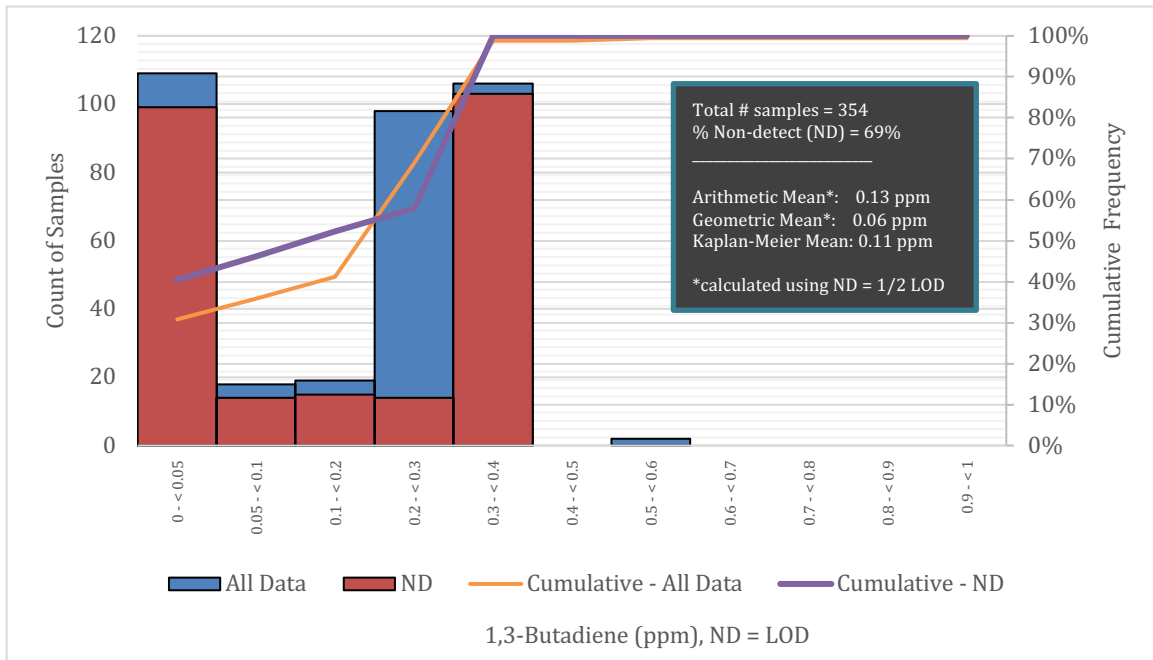
Workers in the Maintenance job group are responsible for a variety of preventative maintenance activities on process equipment, as well as addressing malfunctions. Some of the tasks performed by workers in this job group include connecting and disconnecting

lines, and draining, clearing and venting equipment. A summary of the sample data for this job group during routine operations is provided in Table 5 and the summary statistics for this job group and all operational conditions are provided in Appendix C. PPE used by these workers is described in Section 3.2.

**Table 5. Overview of dataset for Maintenance Job Group (Routine)**

Job Group	N Samples	% Non-Detects	Range of Detection Limits (ppm)	KM Mean (ppm)	KM 95 UCL (ppm)
Maintenance	354	69	0.0008 – 0.38	0.11	0.13

The data for the routine operations describes the potential exposures that the workers in this job would experience on a day-to-day basis and long term over time. **Figure 10** is the overall distribution of routine full-shift personal air concentrations for the Maintenance job group.



**Figure 10. Distribution of Maintenance Full-Shift Personal Air Concentrations**

As noted in Table 5 and as can be seen in Figure 10 the dataset is highly censored with 69% of the air concentrations for routine operations reported below the detection limits. The detection limits associated with this data set ranged from 0.0008 – 0.38 ppm. The best descriptor of the central tendency air concentration for this job group is the Kaplan-Meier (KM) mean of 0.11 ppm and the best descriptor of the upper bound for this dataset is the KM 95<sup>th</sup> upper confidence limit on the mean (95 UCL) of 0.13 ppm.

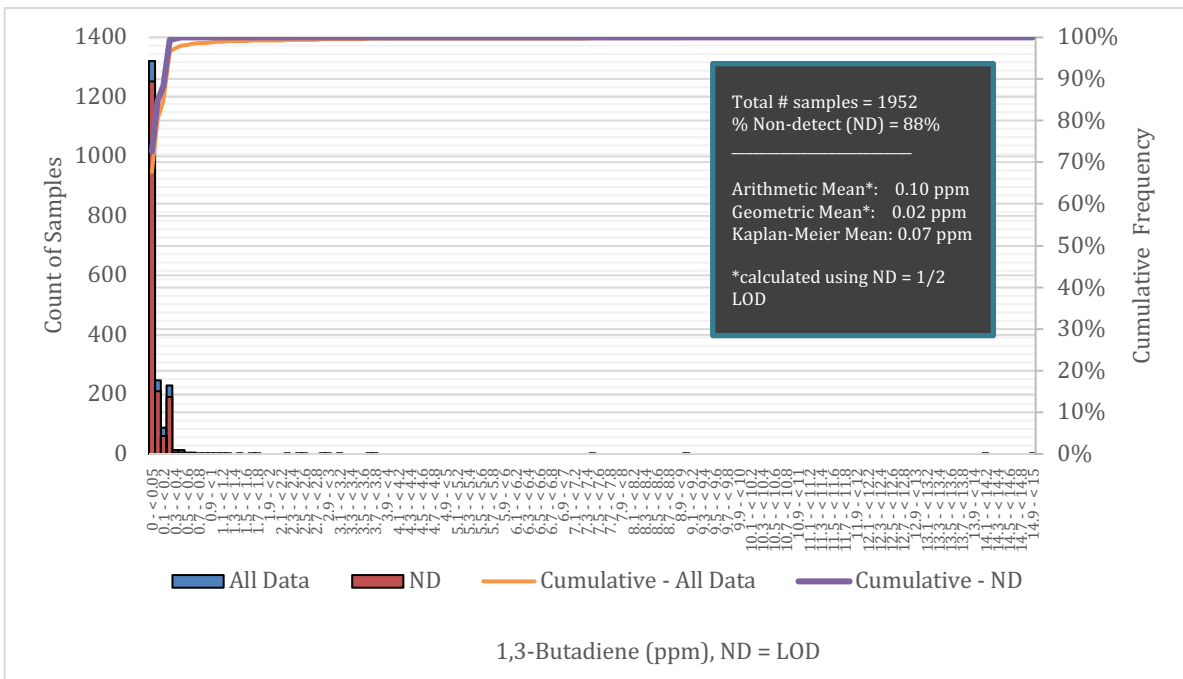
### 3.1.6 Operations Onsite

Workers in the Operations Onsite job group are responsible for operations of manufacturing and processing equipment throughout the facilities. These workers may be indoors inside of control rooms where they monitor chemical feeds, process temperatures, vessel pressure, etc. or outdoors where the process equipment is located to where they may collect process samples, drain/vent/clear process equipment and prepare it for maintenance. Additionally, workers in this job group may also assist the IH team in conducting air monitoring to establish the restricted areas. A summary of the sample data for this job group during routine operations is provided in Table 6 and the summary statistics for this job group and all operational conditions are provided in Appendix C.

**Table 6. Overview of dataset for Operations Onsite (Routine)**

Job Group	N Samples	% Non-Detects	Range of Detection Limits (ppm)	KM Mean (ppm)	KM 95 UCL (ppm)
Operations onsite	1952	88	0.004 – 0.45	0.07	0.10

The data for the routine operations describes the potential exposures that the workers in this job would experience on a day-to-day basis and long term over time. **Figure 11** is the overall distribution of routine full-shift personal air concentrations for the Operations onsite job group.



**Figure 11. Distribution of Operations Onsite Full-Shift Personal Air Concentrations**

As noted in Table 6 and as can be seen in Figure 11, the dataset is highly censored with 88% of the air concentrations for routine operations reported below the detection limits. The detection limits associated with this data set ranged from 0.004 – 0.45 ppm. The best descriptor of the central tendency air concentration for this job group is the Kaplan-Meier (KM) mean of 0.07 ppm and the best descriptor of the upper bound for this dataset is the KM 95 UCL value of 0.10 ppm.

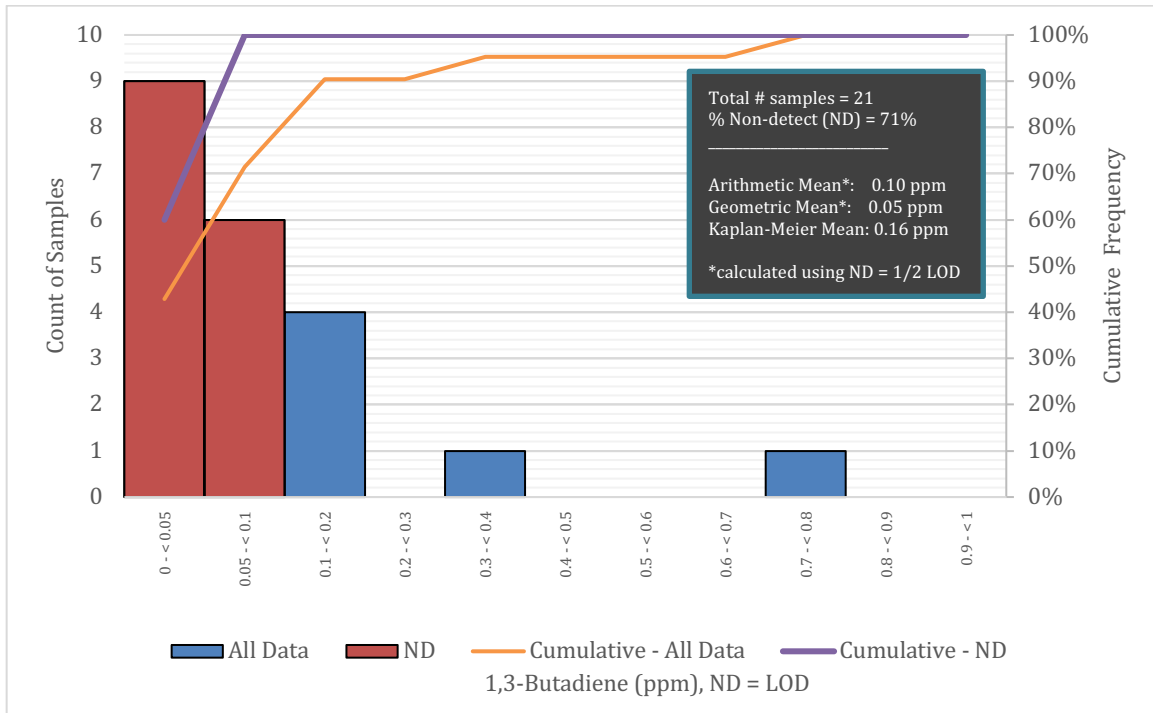
### 3.1.7 Safety, Health and Environment (SHE)

Workers in the Safety, Health and Environment (SHE) job group are responsible for assuring safety, health and environmental protection protocols are being followed in all areas of the facility. Workers in this job group may include industrial hygienists who conduct exposure assessments of workers in the various job groups, LDAR technicians, environmental engineers and safety technicians. The SHE workers may be indoors inside of offices or in various control rooms or outdoors where the process equipment is located to monitor other workers or processes. A summary of the sample data for this job group during routine operations is provided in Table 7 and the summary statistics for this job group and all operational conditions are provided in Appendix C.

**Table 7. Overview of dataset for SHE (Routine)**

Job Group	N Samples	% Non-Detects	Range of Detection Limits (ppm)	KM Mean (ppm)	KM 95 UCL (ppm)
SHE	21	71	0.04 - 0.06	0.16	0.23

The data for the routine operations describes the potential exposures that the workers in this job would experience on a day-to-day basis and long term over time. **Figure 12** is the overall distribution of routine full-shift personal air concentrations for the SHE job group.



**Figure 12. Distribution of SHE Personal Air Concentrations**

As noted in Table 7 and as can be seen in Figure 12, the dataset is highly censored with 71% of the air concentrations for routine operations reported below the detection limits. The detection limits associated with this data set ranged from 0.04 – 0.06 ppm. The best descriptor of the central tendency air concentration for this job group is the Kaplan-Meier (KM) mean of 0.16 ppm and the best descriptor of the upper bound for this dataset is the KM 95 UCL value of 0.23 ppm. It should be noted that the KM mean and 95 UCL values are influenced by two detected samples in a small dataset. It is unlikely that workers in the SHE group would have long term exposures to air concentrations greater than 0.1 ppm.

### 3.1.8 Occupational Non-Users

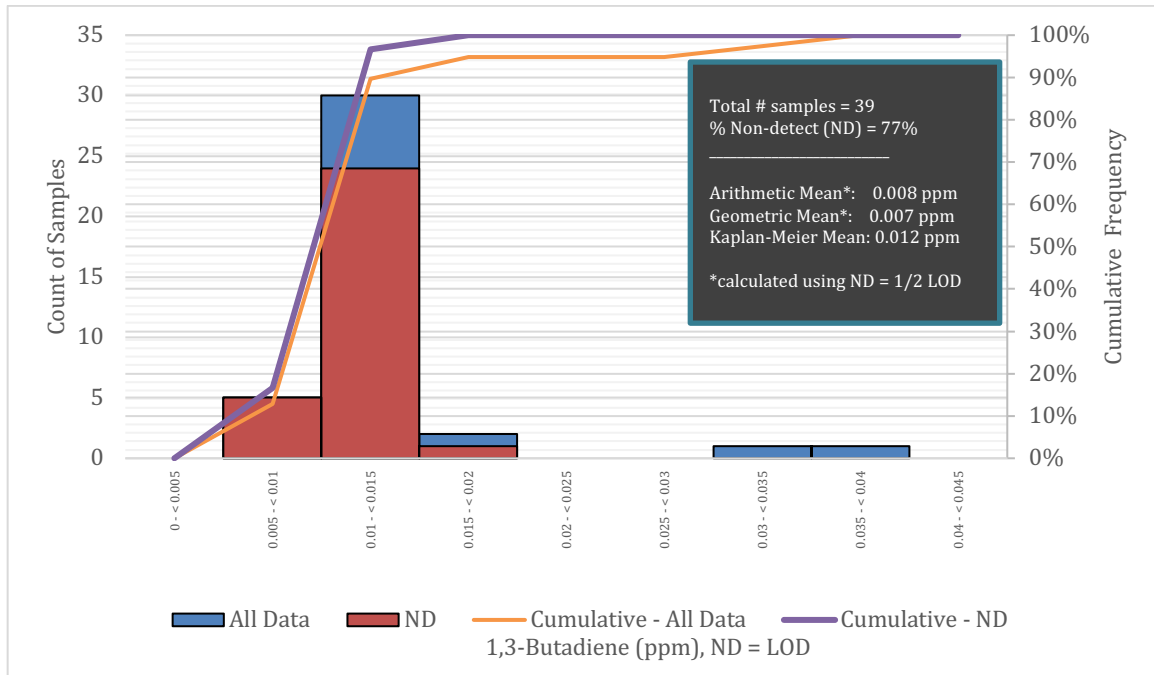
Workers in the Occupational Non-Users (ONU) job group are supervisory personnel associated with all of the worker job groups. In the Manufacturing and Processing as a Reactant conditions of use, administrative type employees (e.g. accountants, salespersons, etc.) do not access the operational parts of a facility. A summary of the sample data for this job group during routine operations is provided in Table 8 and the summary statistics for this job group and all operational conditions are provided in Appendix C.

**Table 8. Overview of dataset for ONU (Routine)**

Job Group	N Samples	% Non-Detects	Range of Detection Limits (ppm)	KM Mean (ppm)	KM 95 <sup>th</sup> percentile (ppm)
ONU	39	77	0.008 – 0.02	0.012	0.014



The data for the routine operations describes the potential exposures that the workers in this job would experience on a day-to-day basis and long term over time. **Figure 13** is the overall distribution of routine full-shift personal air concentrations for the ONU job group.



**Figure 13. Distribution of ONU Personal Air Concentrations**

As noted in Table 8 and as can be seen in Figure 13, the dataset is highly censored with 75% of the air concentrations for routine operations reported below the detection limits. The detection limits associated with this data set ranged from 0.008 – 0.02 ppm. The best descriptor of the central tendency air concentration for this job group is the Kaplan-Meier (KM) mean of 0.01 ppm and the best descriptor of the upper bound for this dataset is the KM 95<sup>th</sup> percentile value of 0.014 ppm.

### 3.2 Short Term and Task Air Concentration Data

The Consortium members data included 1,051 short term and task level samples collected from workers. Air samples collected to characterize potential exposures during tasks include those for OSHA compliance monitoring with the STEL (1-15 minutes in duration) or task level exposure characterization (16-240 minutes in duration). Generally, the compliance STEL samples are collected during periods of expected maximum or peak concentrations and compared to the OSHA STEL, which is the legal maximum average exposure for a 15-minute time period. The data associated with the durations 16-240 minutes are representative of the average exposure over the total duration of the task. The task level data are used to identify specific tasks that may contribute to a worker’s full-shift exposure throughout the workday and to target specific exposure controls and/or PPE selection to minimize exposure.

The data analysis for each task activity is described below. It should be noted that the air concentrations have not been time weighted and as such, the shorter duration samples have higher limits of detection. The distribution of detection limits by sample duration for the various task categories is provided on Table 9. As shown on Table 10, the vast majority of the detection limits for short term and task samples are below 1 ppm; it is rare (N=2) to have a detection greater than 5 ppm.

**Table 9. Overview of Sample Durations by Task for Routine Personal Samples**

Task	N Non-detects	DL [ $<0.1$ ppm]	DL [0.1 - $<0.5$ ppm]	DL [0.5 - $<1$ ppm]	DL [1 - $<5$ ppm]	DL [ $\geq 5$ ppm]
<b>Sample Duration <math>\leq 15</math> minutes</b>						
Unloading and Loading	40	10%	55%	13%	23%	0%
Handling of Waste	7	14%	71%	0%	14%	0%
Cleaning and Maintaining Equipment	81	1%	65%	25%	7%	1%
Sampling and Analysis	167	17%	37%	37%	10%	0%
Performing Other Work	22	0%	82%	14%	5%	0%
<b>Sample Duration <math>&gt;15</math> minutes</b>						
Unloading and Loading	71	11%	54%	11%	24%	0%
Handling of Waste	9	22%	33%	22%	22%	0%
Cleaning and Maintaining Equipment	109	19%	50%	15%	16%	1%
Sampling and Analysis	210	15%	62%	22%	0%	0%
Task	N Non-detects	DL [ $<0.1$ ppm]	DL [0.1 - $<0.5$ ppm]	DL [0.5 - $<1$ ppm]	DL [1 - $<5$ ppm]	DL [ $\geq 5$ ppm]
Performing Other Work	17	24%	71%	0%	6%	0%
Unloading and Loading	71	11%	54%	11%	24%	0%

The Consortium metadata reported in Appendix F includes information from member companies and five specific 1,3-BD tasks: unloading and loading, handling/transport/disposal of waste, general cleaning and maintenance, sample collection, and “other” tasks such as leak detection and tank gauging. In addition to task-specific metadata, site-specific controls, site-specific programs, and overarching regulatory requirements associated with each task are also reported.

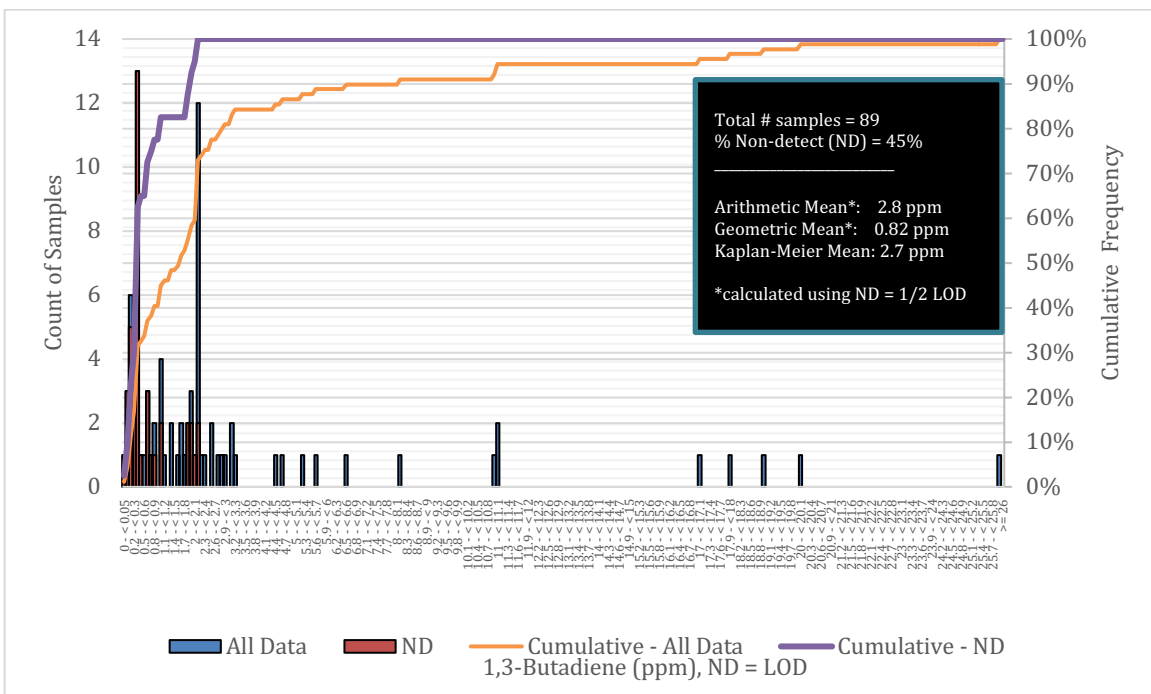
### **3.2.1 Unloading and transferring 1,3-butadiene to and from storage containers to process vessels**

This task is associated with the unloading and loading of product which involves opening of storage vessels, hose connections to truck tankers, rail cars or cargo vessels and pumping of pressurized liquid 1,3-BD. Workers in the job group Infrastructure/ Transportation operations perform this task. A summary of the sample data for this task during routine operations is provided in Table 10 and the summary statistics for this task and all operational conditions are provided in Appendix D.

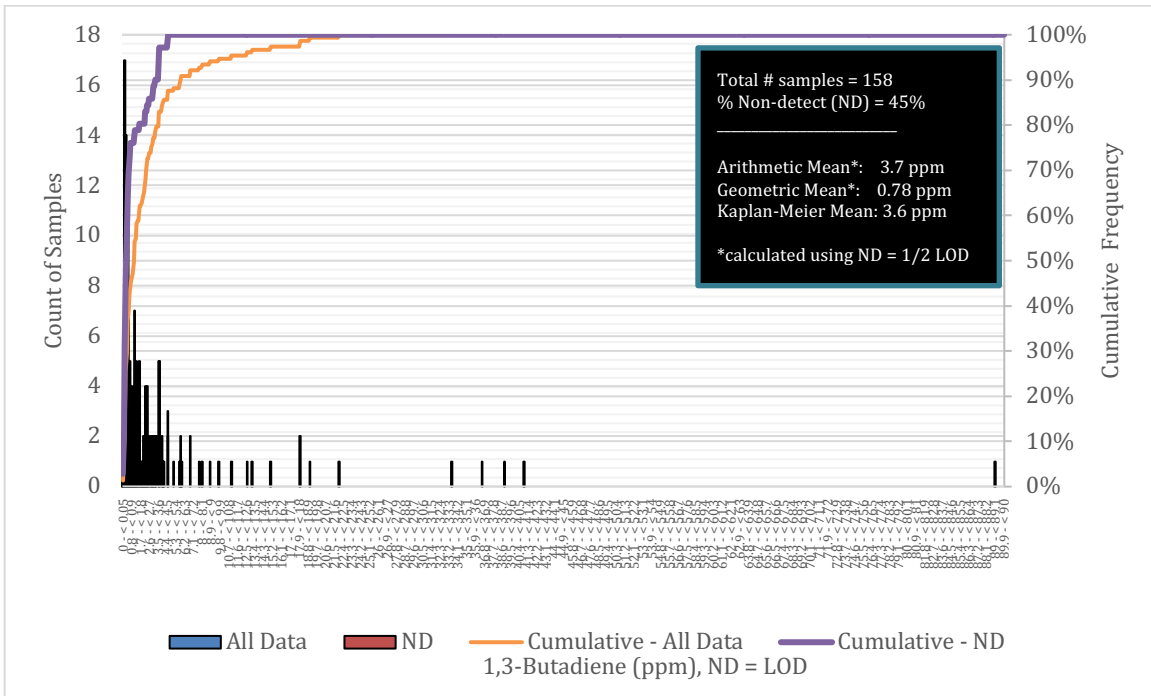
**Table 10. Overview of dataset for Unloading and Loading**

Task	N Samples	% Non-Detects	Range of Detection Limits (ppm)	KM Mean (ppm)	KM 95 UCL (ppm)
Unloading/Loading (≤15 minutes)	89	45	0.04 – 2.01	2.7	3.7
Unloading/Loading (15 - 239 minutes)	158	45	0.02 – 4.52	3.6	5.1

Figures 14a and 14 b are the overall distribution of routine short term and task level personal air concentrations for the Unloading and Loading task.



**Figure 14a. Distribution of Unloading/Loading Task Personal Air Concentrations, ≤ 15 minutes**



**Figure 14b. Distribution of Unloading/Loading Task Personal Air Concentrations, 15 - 239 minutes**

As noted in Table 10 and as can be seen in Figures 14a, b, the dataset is moderately censored with 45% of the air concentrations for this task reported below the detection limits. The detection limits associated with this data set ranged from 0.02 – 4.52 ppm, however, as can be seen from Figure 14a,b (and Appendix D), the 95<sup>th</sup> percentile value for the detection limits was 3.7 ppm. The best descriptor of the central tendency air concentration for this task activity are the Kaplan-Meier (KM) means of 2.7 ppm and 3.6 ppm and the best descriptors of the upper bound air concentrations for this dataset are the KM 95 UCL values of 3.7 ppm and 5.1 ppm.

### 3.2.1.1 Exposure Controls for Unloading and Loading Task

The exposure controls implemented for this task include: vapor recovery systems to capture 1,3-BD vapors at connection points, chemical protective gloves, suits and boots to prevent dermal contact, and respirators. The Consortium dataset included varying types of respirators used for this task depending on the air concentrations measured (Table 11).

**Table 11. Various Exposure Controls used for Unloading and Loading Task**

Task	Respirator	Concentration Range (ppm)
Unloading and Transfer	Supplied air	<0.118 - 89
	Full Face APR	<0.06 - 36
	Half Face APR	<0.05 – 2.2
APR = Air purifying respirator with chemical cartridge		

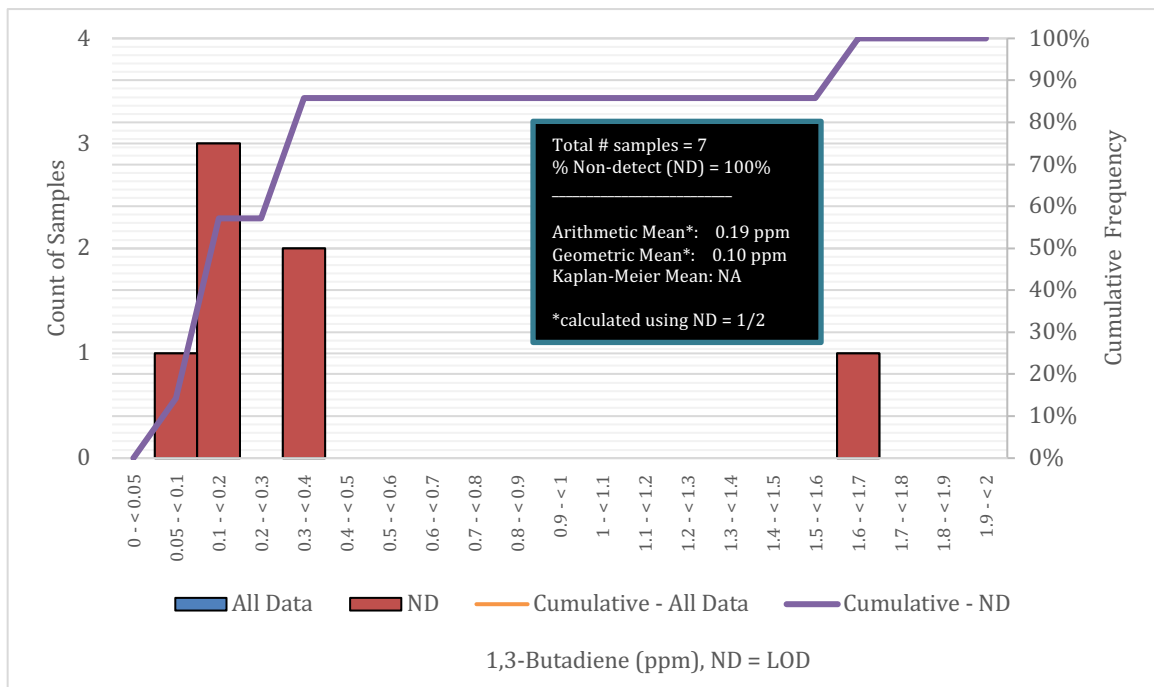
### 3.2.2 Handling, transporting and disposing of waste containing 1,3-butadiene

This task is associated with potential contact of facility waste streams containing 1,3-BD including disposing of analytical samples, loading of recycled oil, operations conducted at the onsite waste-water treatment plant. A summary of the sample data for this task during routine operations is provided in Table 12 and the summary statistics for this task and all operational conditions are provided in Appendix D.

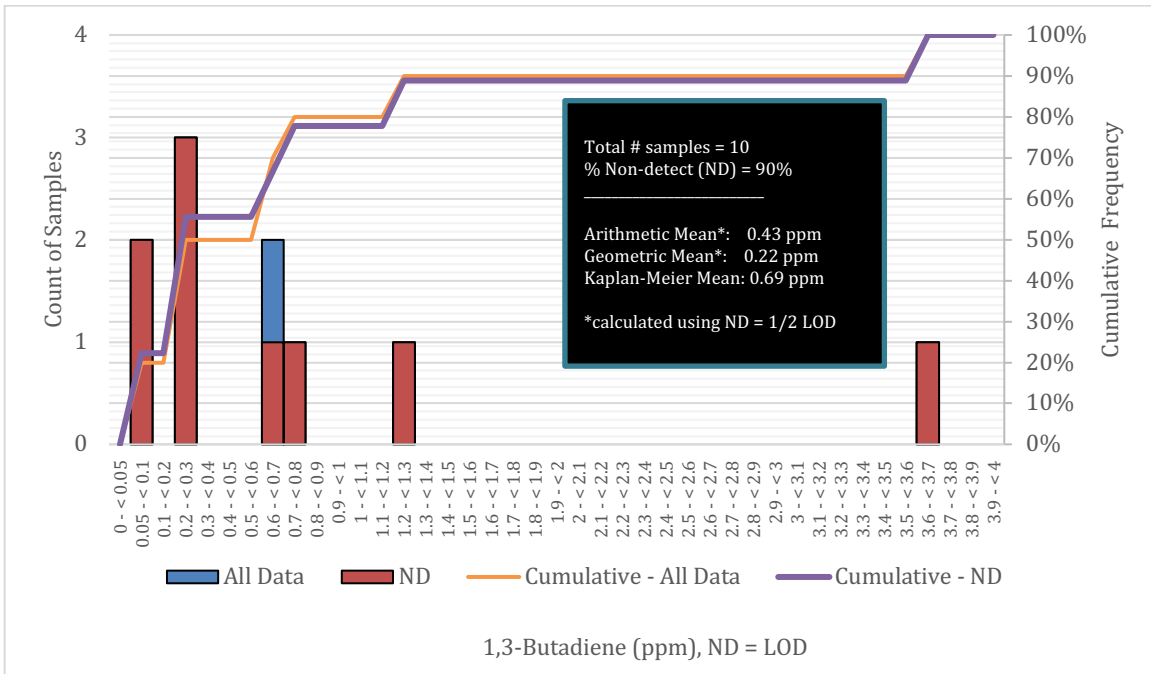
**Table 12. Overview of dataset for Handling of Waste**

Task	N Samples	% Non-Detects	Range of Detection Limits (ppm)	50 <sup>th</sup> percentile (ppm)	95 <sup>th</sup> percentile (ppm)
Handling of Waste (≤15 minutes)	7	100	0.06 – 1.6	0.05	0.61
Handling of Waste (15 - 239 minutes)	10	90	0.08 – 3.7	0.23	1.3

Figures 15a and 15b are the overall distribution of routine short term and task level personal air concentrations for the Handling of Waste task.



**Figure 15a. Distribution of Handling of Waste Task Personal Air Concentrations, ≤ 15 minutes**



**Figure 15b. Distribution of Handling of Waste Task Personal Air Concentrations, 15 - 239 minutes**

As noted in Table 12 and as can be seen in Figures 15a, b, the dataset is severely censored with 90 – 100 % of the air concentrations for this task reported below the detection limits. The detection limits associated with this data set ranged from 0.06 – 3.7 ppm, however as can be seen from Figure 15a,b (and Appendix D), the 95<sup>th</sup> percentile value for the detection limits was 2.7 ppm. The best descriptor of the central tendency air concentration for this task activity are 50<sup>th</sup> percentiles of 0.05 ppm and 0.23 ppm and the best descriptors of the upper bound air concentrations for this dataset are the 95<sup>th</sup> percentile values of 0.61 ppm and 1.3 ppm.

*3.2.2.1 Exposure Controls for Handling of Waste Task*

The exposure controls implemented for this task include: chemical protective gloves, suits and boots to prevent dermal contact, and respirators. The Consortium dataset included varying types of respirators used for this task depending on the air concentrations measured (Table 13).

**Table 13. Various Exposure Controls used for Handling of Waste Task**

Task	Respirator	Concentration Range (ppm)
Handling and Transporting Waste	Full Face APR	<0.25 - <3.7
	Half Face APR	<0.08 - < 0.1
APR = Air purifying respirator with chemical cartridge		

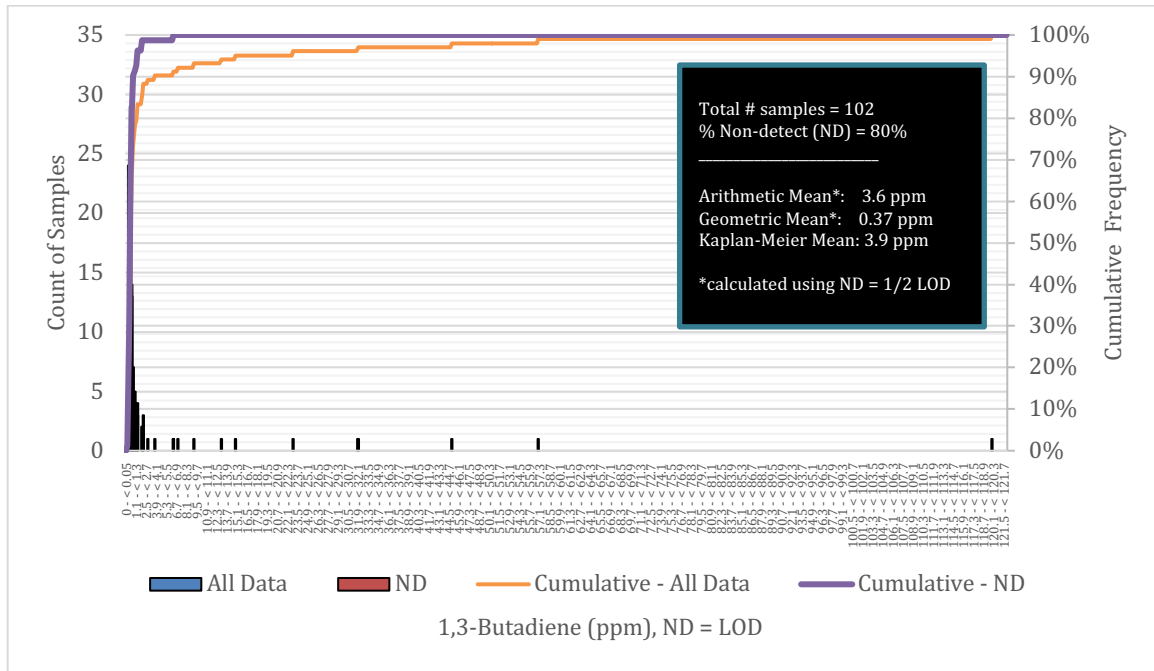
### 3.2.3 Cleaning and maintaining equipment

This task involves disassembly and re-assembly of process equipment (e.g. valves, pumps, and analyzers), tank cleaning, line purging, filter removal and cleaning, etc. Workers in the job groups Onsite Operations and Maintenance may perform this task. A summary of the sample data for this task during routine operations is provided in Table 14 and the summary statistics for this task and all operational conditions are provided in Appendix D.

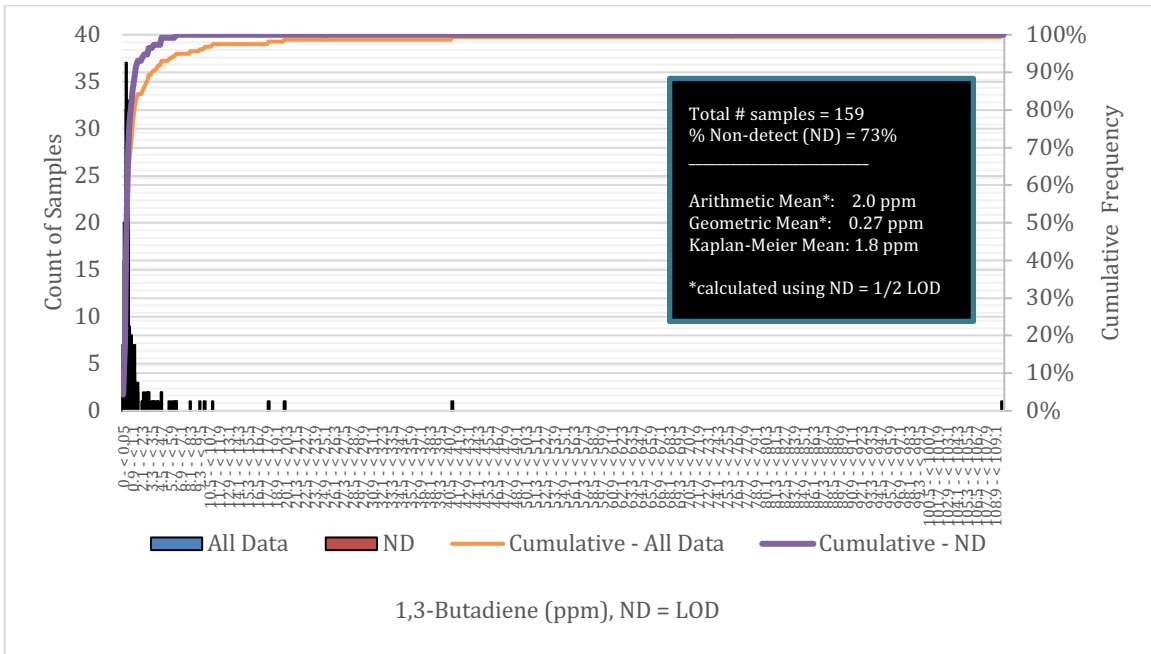
**Table 14. Overview of dataset for Cleaning and Maintaining Equipment**

Task	N Samples	% Non-Detects	Range of Detection Limits (ppm)	KM Mean (ppm)	KM 95 UCL (ppm)
Cleaning and Maintenance ( $\leq 15$ minutes)	102	80	0.06 – 6.3	3.9	6.7
Cleaning and Maintenance (15 - 239 minutes)	159	73	0.04 – 6.3	1.8	3.3

Figures 16a and 16b are the overall distribution of routine short term and task level personal air concentrations for the Cleaning and Maintaining Equipment task.



**Figure 16a. Distribution of Cleaning and Maintaining Equipment Task Personal Air Concentrations,  $\leq 15$  minutes**



**Figure 16b. Distribution of Cleaning and Maintaining Equipment Task Personal Air Concentrations, 15 - 239 minutes**

As noted in Table 14 and as can be seen in Figures 16a, b, the dataset is highly censored with 73 - 80% of the air concentrations for this task reported below the detection limits. The detection limits associated with this data set ranged from 0.04 – 6.3 ppm, however as can be seen from Figure 16a,b (and Appendix D), the highest 95<sup>th</sup> percentile value for the detection limits was 2.8 ppm. The best descriptor of the central tendency air concentration for this task activity are KM Means of 3.9 ppm and 1.9 ppm and the best descriptors of the upper bound air concentrations for this dataset are the KM 95 UCL values of 6.7 ppm and 3.3 ppm.

*3.2.3.1 Exposure Controls for Cleaning and Maintaining Equipment Task*

The exposure controls implemented for this task include: clearing lines and equipment prior to opening, chemical protective gloves, suits and boots to prevent dermal contact, and respirators. The Consortium dataset included varying types of respirators used for this task depending on the air concentrations measured (Table 15).

**Table 15. Various Exposure Controls used for Cleaning and Maintaining Equipment Task**

Task	Respirator	Concentration Range (ppm)
Cleaning and Maintaining Equipment	Supplied Air	<0.15 - 120



	Full Face APR	<0.02 - 110
	Half Face APR	<0.04 - <0.7
	No respirator	<0.4 - <0.7
APR = Air purifying respirator with chemical cartridge		

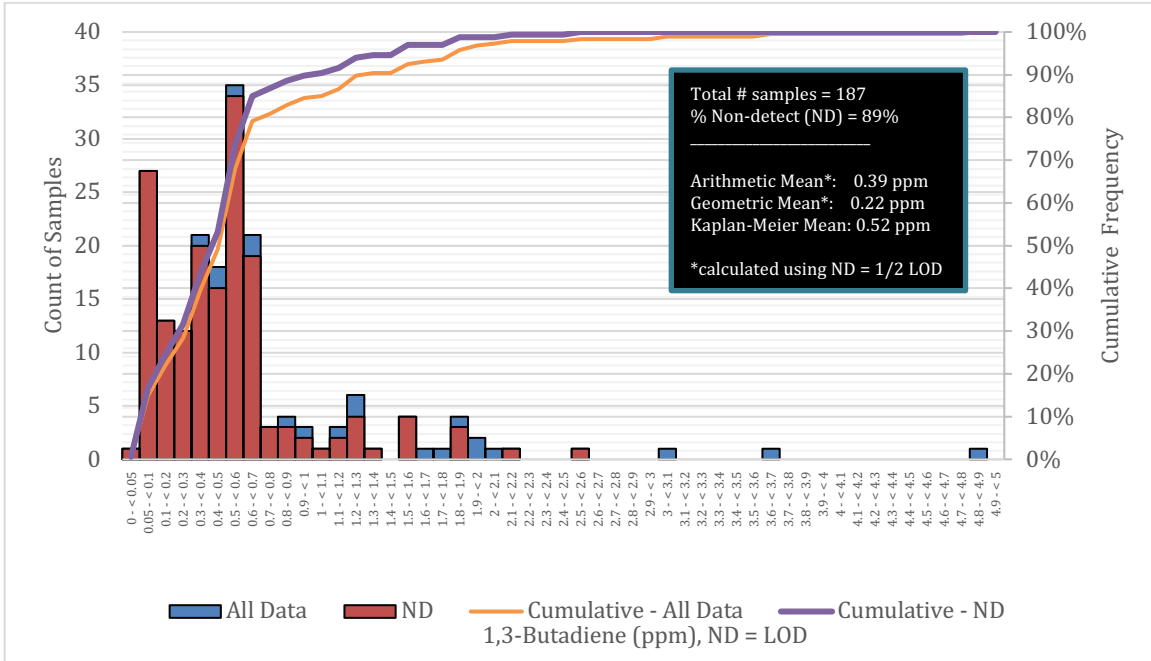
### 3.2.4 *Sampling chemicals, formulations, or products containing 1,3-butadiene for quality control*

This task involves collection of process stream samples and analysis for 1,3-BD. For gaseous samples, workers connect pressurized cylinders that have ports to allow the sample to flow in and also to allow excess gas to vent to safe location. Workers in many job groups may perform this task although most of the air samples are associated with workers in the Laboratory Technician and Onsite Operations job groups. A summary of the sample data for this task during normal operations is provided in Table 16 and the summary statistics for this task and all operational conditions are provided in Appendix D.

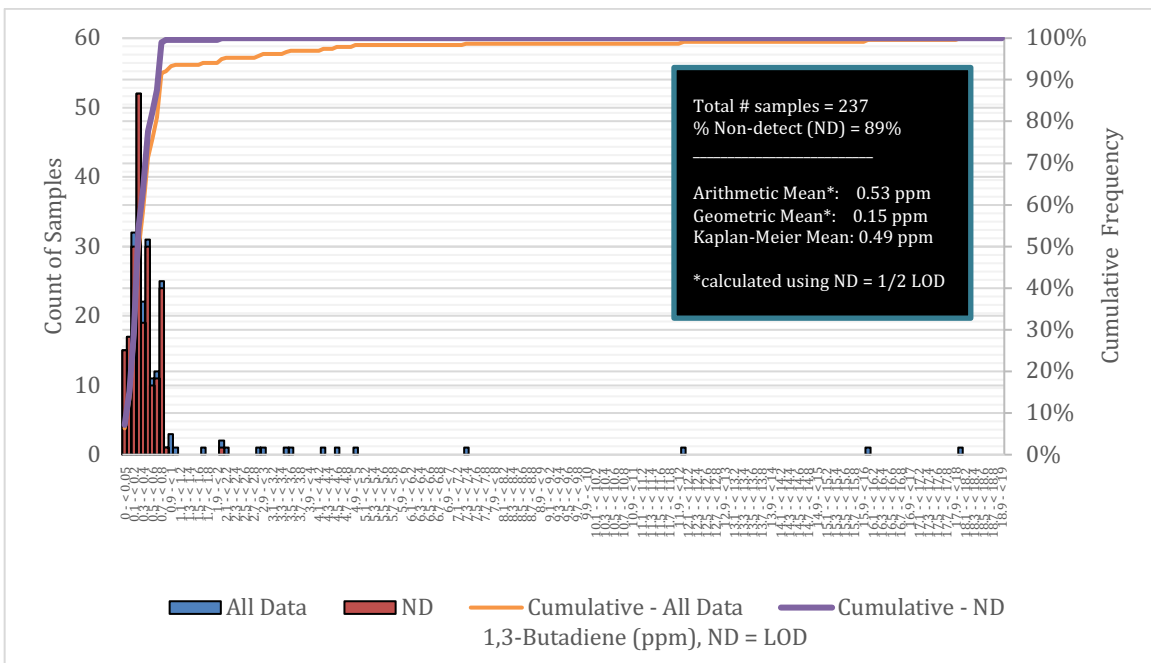
**Table 16. Overview of dataset for Collecting and Analyzing Process Samples**

<b>Task</b>	<b>N Samples</b>	<b>% Non-Detects</b>	<b>Range of Detection Limits (ppm)</b>	<b>KM Mean (ppm)</b>	<b>KM 95 UCL (ppm)</b>
<b>Collecting and Analyzing Samples (≤15 minutes)</b>	187	89	0.03 – 2.5	0.52	0.59
<b>Collecting and Analyzing Samples (15 - 239 minutes)</b>	237	89	0.02 – 2.0	0.49	0.74

**Figures 17a and 17b** are the overall distribution of routine short term and task level personal air concentrations for the Sample Collection and Analysis task.



**Figure 17a. Distribution of Sample Collection and Analysis Task Personal Air Concentrations, ≤ 15 minutes**



**Figure 17b. Distribution of Sample Collection and Analysis Task Personal Air Concentrations, 15 – 239 minutes**

As noted in Table 16 and as can be seen in Figures 17a, b, the dataset is highly censored with 89% of the air concentrations for this task reported below the detection limits. The

detection limits associated with this data set ranged from 0.02 – 2.5 ppm, however as can be seen from Figure 17a,b (and Appendix D) the highest 95<sup>th</sup> percentile value for the detection limits was 1.4 ppm. The best descriptor of the central tendency air concentration for this task activity are KM Means of 0.52 ppm and 0.49 ppm and the best descriptors of the upper bound air concentrations for this dataset are the KM 95 UCL values of 0.59 ppm and 0.74 ppm.

#### 3.2.4.1 Exposure Controls for Sample Collection and Analysis Task

The exposure controls implemented for this task include: chemical protective gloves, suits and boots to prevent dermal contact, enclosed sample boxes, pressurized sample containers, laboratory ventilation cabinets, and respirators. The Consortium dataset included varying types of respirators used for this task depending on the air concentrations measured (Table 17).

**Table 17. Various Exposure Controls used for Sample Collection and Analysis Task**

<b>Task</b>	<b>Respirator</b>	<b>Concentration Range (ppm)</b>
Sampling and Analysis	Supplied Air	<0.52
	Full Face APR	<0.06 - 12
	Half Face APR	<0.09 - 7.3
	No respirator	<0.02 - 4.8
APR = Air purifying respirator with chemical cartridge		

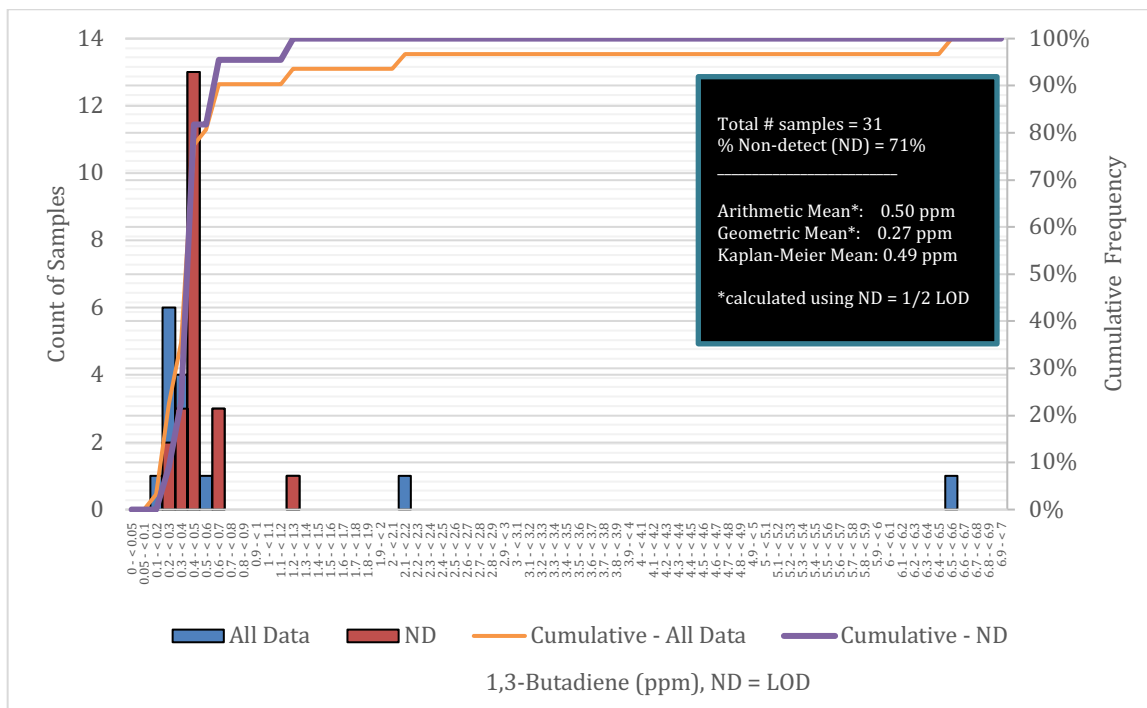
#### 3.2.5 Performing other work activities in or near areas where 1,3-butadiene is used

Most of the short-term or task samples were assignable to one of the four task categories described above. However, some samples were collected on workers that performed a variety of miscellaneous tasks that do not fall into the other categories identified by EPA. The tasks included air monitoring with direct reading instruments for VOCs during various maintenance activities (typically by EHS personnel) and routine visual inspections of operating areas. A summary of the sample data for this task during routine operations is provided in Table 18 and the summary statistics for this task and all operational conditions are provided in Appendix D.

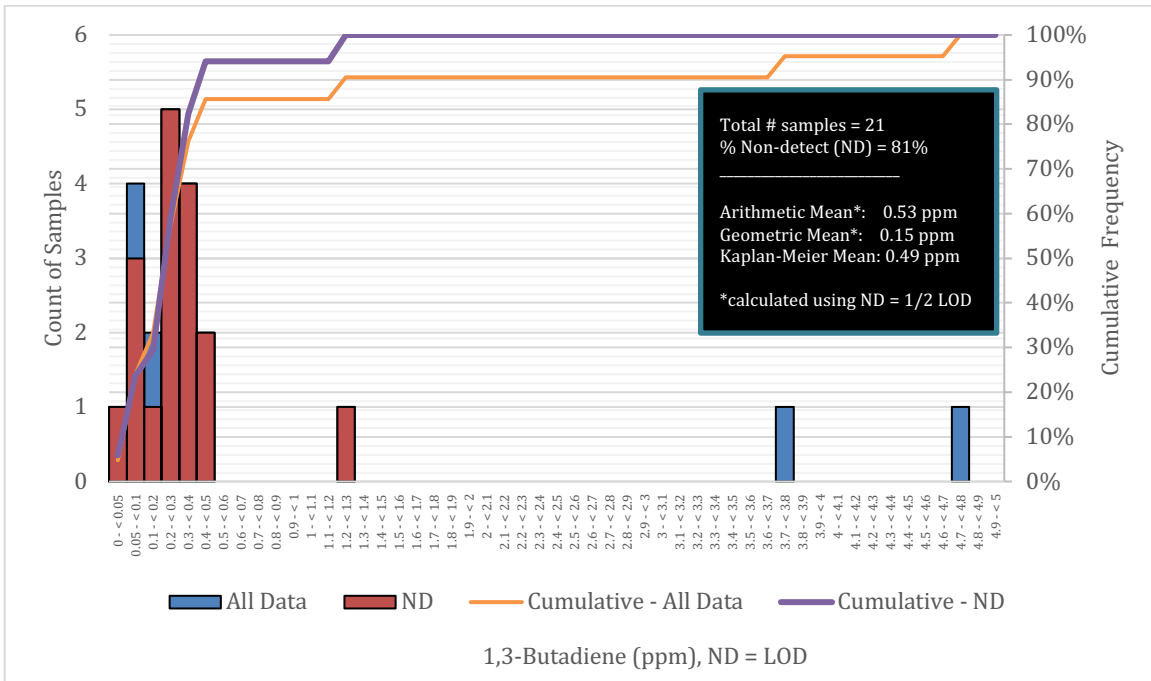
**Table 18. Overview of dataset for Performing Other Work Activity Tasks**

Task	N Samples	% Non-Detects	Range of Detection Limits (ppm)	KM Mean (ppm)	KM 95 UCL (ppm)
<b>Other Work Activities (≤15 minutes)</b>	31	71	0.2 - 1.2	0.49	0.92
<b>Other Work Activities (15 - 239 minutes)</b>	21	81	0.02 – 1.2	0.49	1.1

Figures 18a and 18b are the overall distribution of routine short term and task level personal air concentrations for the Other Work task.



**Figure 18a. Distribution of Other Work Task Personal Air Concentrations, ≤ 15 minutes**



**Figure 18b. Distribution of Other Work Task Personal Air Concentrations, 15 - 239 minutes**

As noted in Table 18 and as can be seen in Figures 18a, b, the dataset is highly censored with 71 - 81% of the air concentrations for this task reported below the detection limits. The detection limits associated with this data set ranged from 0.02 – 1.2 ppm. The best descriptor of the central tendency air concentration for this task activity are KM Means of 0.49 ppm and the best descriptors of the upper bound air concentrations for this dataset are the KM 95 UCL values of 0.92 ppm and 1.1 ppm.

### 3.2.5.1 Exposure Controls for Performing Other Work Tasks

The exposure controls implemented for this task include: chemical protective gloves, suits and boots to prevent dermal contact, and respirators. The Consortium dataset included varying types of respirators used for this task depending on the air concentrations measured (Table 19).

**Table 19. Various Exposure Controls used for Other Work Tasks**

Task	Respirator	Concentration Range (ppm)
Performing Other Work	Supplied Air	0.27 - 4.7
	Full Face APR	<0.24 - <0.42
	Half Face APR	<0.2 - <0.3
	No respirator	<0.39 - <0.67
APR = Air purifying respirator with chemical cartridge		

## 4 Discussion

The Consortium dataset provides robust quantitative air concentration data for which occupational exposures to 1,3-BD in the Manufacturing and Processing as a Reactant COUs can be assessed. The central tendency measures of the data demonstrate that most workers in this COUs have routine full-shift exposures to 1,3-BD at levels 1 order of magnitude lower than the OSHA PEL 8-hr TWA of 1 ppm. Furthermore, even at the upper bound, the measures indicate worker full-shift exposures are lower than the OSHA PEL. The short-term data ( $\leq 15$  min) are similar in that at all of the central tendency measures are below the OSHA STEL of 5 ppm, as are all of the upper bound measures, except for the task of Cleaning and Maintaining Equipment. It should be noted that the Cleaning and Maintaining Equipment task is considered routine because it is done frequently and on schedule, but is not necessarily a daily task.

As discussed in Section 2, the designation of ‘routine’ for operational status reflects exposures that are likely to occur regularly over the long-term. Therefore full-shift samples designated as routine should be used to characterize occupational exposures that may occur over a working lifetime. Short-term samples, designated as routine, should be used to characterize peak exposures that may occur regularly, for short durations during the course of a work week. It is important to note that some activities are not carried out on a daily/weekly basis, such as filter change-out, clearing/venting/opening process equipment, etc. These activities, although routinely scheduled, are infrequent (monthly, quarterly, or annually). These infrequent tasks are characterized as part of the exposure assessment program, and administrative controls or PPE are implemented to reduce exposures. Additionally, in assessing short-term exposures, respirator use must be considered as the Consortium data indicate some type of respiratory protection is used for every task activity where 1,3-BD may exposure occur.

As discussed throughout Section 3, all of the full-shift datasets are highly censored, meaning that 1,3-BD was not detected in most of the samples. This demonstrates the low exposure potential for most workers in the Manufacturing and Processing as a Reactant COUs and the effectiveness of engineering and operational controls to minimize worker exposures without the use of respirators. Furthermore, the upper bound values of the detection limits provide additional confidence that the non-detected values are truly reflective of very low exposure potential.

The short-term and task-based datasets were also highly censored although the upper bound range of detection limits was quite variable, particularly with short sample durations. Nevertheless, the Consortium dataset confirmed that respiratory protection is anticipated for all of the tasks and is used in compliance with the OSHA butadiene standard to minimize exposure to workers.

Risk assessment of the workers in the Manufacturing and Processing as a Reactant COU should be conducted using the routine full-shift and short-term or task-based data provided herein. Nevertheless, there are caveats associated with the data as it was collected and presented:

- The data are in inherently biased toward those activities or worker groups who are considered to have potential exposures in order to determine the need of PPE/Engineering controls and/or assess efficiency of those controls. As such, the data are representative of potential exposure for those workers who are more likely than not to have exposures.
- Consistent with AIHA Exposure Assessment Strategies guidance, full shift samples are likely to have been taken over time periods in which short term, or task level exposures might lead to exceedance of the PEL. However, during such a task, workers would be wearing PPE, which may not be documented with the full shift sample, but rather with the task sample dataset.
- Job groups are aggregated across member companies, but because the different industries handle process streams with low or high concentrations of 1,3-BD, the variability in the data are much higher than would exist at any given facility.
- Job groups are aggregated by similar names across facilities, but there may be different exposure potential depending on the site-specific activities. Nevertheless, the standard error (0.001 - 0.038) for the full-shift samples within each job group demonstrate that quantitatively, there is good precision around the mean exposure concentrations.
- Tasks are aggregated across industries and job groups. Operators at some facilities might carry out certain frequent maintenance activities (i.e. filter change-outs), while at other facilities maintenance operators might be involved in opening process equipment.
- Sample duration is not necessarily representative of the duration of the task. In some instances, the part of the task that leads to the exposure is short, but it might be impractical to start/stop the sampler at those times. On the other hand, the industrial hygienist might focus on the specific aspect of the full task that leads to the exposure (e.g. just the actual connection/disconnection of hoses during truck loading), which might bias high the estimated exposure for the whole task when there is no exposure.
- The database does not provide enough information to determine for a particular task how often the task occurs at facilities and of those occurrences, how often they are characterized at the high-end exposure value.
- Traditionally, dermal protection has not been reported as it is part of the basic hygiene programs at facilities included in the Manufacturing and Processing as a Reactant COUs to prevent contact with process streams. Furthermore, if there is potential for contact with 1,3-butadiene, the OSHA standard requires appropriate PPE.
- There are no standardized methods to assess dermal exposure to gases, or liquified gases of hydrocarbons in general. IH programs rely on the material compatibility and permeation information provided by the glove and protective clothing vendors.

The Consortium data indicate that air concentrations of 1,3-BD in workplaces representative of the Manufacturing and Processing as a Reactant COUs are well below the OSHA PEL and most of the short-term air concentrations are below the OSHA STEL.

Where worker tasks have the potential for exposure above the STEL, appropriate respiratory protection is used by the workers.

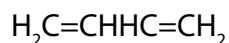


**APPENDIX A**

# **NIOSH and OSHA Sampling and Analytical Methods**

# 1,3-BUTADIENE

1024



MW: 54.09

CAS: 106-99-0

RTECS: EI9275000

METHOD: 1024, Issue 2

EVALUATION: FULL

Issue 1: 15 August 1987

Issue 2: 15 August 1994

OSHA: 1000 ppm  
 NIOSH: lowest feasible; suspect carcinogen  
 ACGIH: 10 ppm; suspect carcinogen  
 (1 ppm = 2.21 mg/m<sup>3</sup> @ NTP)

PROPERTIES: gas; vapor density 1.9 (air = 1); BP -4.4 °C;  
 explosive range 2.0 to 11.5% v/v in air

SYNONYMS: butadiene; biethylene; divinyl

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	SOLID SORBENT TUBE (coconut charcoal, 400- and 200-mg in separate tubes)	<b>TECHNIQUE:</b>	GAS CHROMATOGRAPHY, FID
<b>FLOW RATE:</b>	0.01 to 0.5 L/min	<b>ANALYTE:</b>	1,3-butadiene
<b>VOL-MIN:</b>	5 L @ 100 ppm	<b>DESORPTION:</b>	4 mL methylene chloride; 30 min
<b>-MAX:</b>	25 L	<b>INJECTION:</b>	1 µL
<b>SHIPMENT:</b>	separate front and back tubes, chill below -4 °C	<b>TEMPERATURE-INJECTION:</b>	200 °C
<b>SAMPLE STABILITY:</b>	at least two months for quality assurance blind spikes stored in a freezer	<b>-DETECTOR:</b>	250 °C
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>-COLUMN:</b>	see APPENDIX A
<b>ACCURACY</b>		<b>CARRIER GAS:</b>	helium
<b>RANGE STUDIED:</b>	0.19 to 19 mg/m <sup>3</sup> (25-L samples)	<b>MAKEUP GAS:</b>	nitrogen, 30 mL/min
<b>BIAS:</b>	0.1%	<b>COLUMNS:</b>	fused silica, 10 m × 0.50-mm ID, 1.8-µm CP WAX 57 CB (backflushable pre-column), and 50 m × 0.32-mm ID, Al <sub>2</sub> O <sub>3</sub> /KCI PLOT (see APPENDIX A)
<b>OVERALL PRECISION (<math>\hat{S}_r</math>):</b>	0.060	<b>CALIBRATION:</b>	vapor-spiked sampling media
<b>ACCURACY:</b>	±11.32%	<b>RANGE:</b>	1 to 480 µg per sample
		<b>ESTIMATED LOD:</b>	0.2 µg per sample
		<b>PRECISION (<math>\bar{S}_r</math>):</b>	0.025

APPLICABILITY: The working range is 0.02 to 100 ppm (0.04 to 220 mg/m<sup>3</sup>) for a 25-L air sample. At the higher levels, desorbed samples may require dilution. Below 0.9 mg/m<sup>3</sup> (0.4 ppm), the desorption efficiency falls below 75% and allowance should be made for decreased accuracy.

INTERFERENCES: Pentane, methyl acetylene, or vinylidene chloride may chromatographically interfere at high levels. High humidity (>80% RH) or other hydrocarbons present at permissible levels may significantly decrease the sampler's capacity for 1,3-butadiene.

OTHER METHODS: This revises Method S91 [1].

**REAGENTS:**

1. Methylene chloride,\* chromatographic quality with hydrocarbon (cyclohexene) preservative.
2. 1,3-Butadiene,\* 99.5%, in cylinder equipped for gas withdrawal, with needle valve.
3. Helium, purified.
4. Hydrogen, purified.
5. Air, purified.
6. Nitrogen, purified.
7. Water, distilled.

\*See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: Tandem charcoal tubes. Each tube is flame-sealed glass (8.5 cm long, 8-mm OD, 6-mm ID), has plastic caps for resealing, and contains activated coconut shell charcoal (such as SKC Lot 120) preceded by silylated glass wool and followed by a 3-mm urethane foam plug. The front tube holds 400 mg charcoal. The back tube holds 200 mg.
2. Personal sampling pump, 0.01 to 0.5 L/min, with flexible connecting tubing.
3. Refrigerant, bagged (e.g., Blue Ice or dry ice), and insulated shipping container.
4. Gas chromatograph, flame ionization detector, integrator, and column (see APPENDIX A).
5. Ice, wet.
6. Vials, 5-mL, 2-mL, 1-mL, and other convenient sizes, with PTFE-lined septum caps.
7. Pipettes, TD, 4-, 2-, and 1-mL.
8. Syringes, gas-tight, 250-, 100-, 25-, and 10- $\mu$ L.
9. Beaker, 150-mL.
10. Gas drying tube with serum cap to fit stem and 2-cm piece of plastic tubing to fit over serum cap.

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**SPECIAL PRECAUTIONS:** 1,3-Butadiene is a potential carcinogen, teratogen, and reproductive hazard [2]. Methylene chloride is toxic, very volatile, and a suspect carcinogen [3]. Work should be performed in a well-ventilated fume hood.

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**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Immediately before sampling, break ends of sampler tubes. Connect smaller tube to personal sampling pump with flexible tubing and to larger tube with a short piece of plastic tubing.
3. Sample at an accurately known flow rate of 0.01 to 0.5 L/min for a sample size of 5 to 25 L.
4. Separate the tubes, cap, and pack securely for shipment. Chill below  $-4^{\circ}\text{C}$  during shipment and storage.

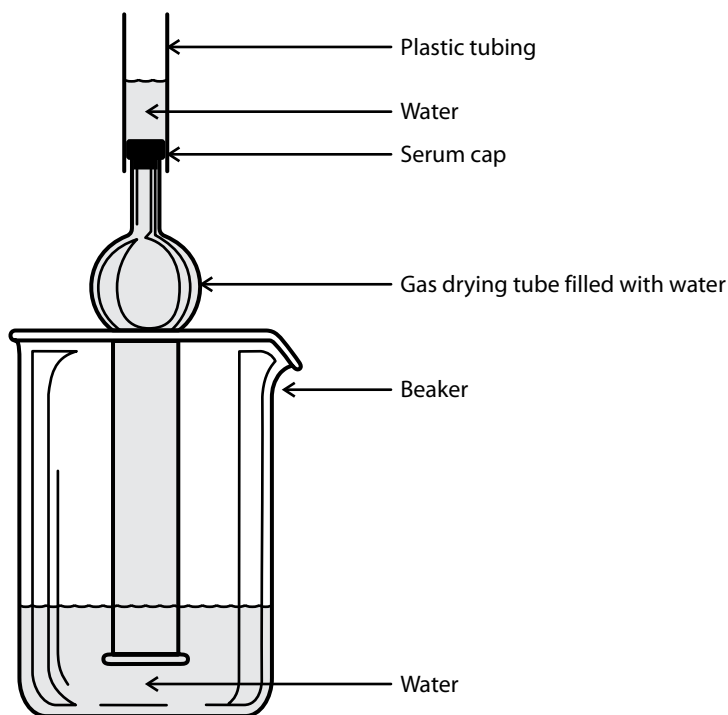
**SAMPLE PREPARATION:**

5. Add 4.0 mL methylene chloride to 5-mL vials and 2.0 mL to 2-mL vials. Loosely cap vials and thoroughly chill in ice.
6. Place front sorbent sections in 5-mL vials and back sections in 2-mL vials. Discard glass wool and foam plugs. Immediately cap each vial.
7. Remove from ice and allow to stand 30 min with occasional agitation.
8. Transfer sample solution to appropriate vial and cap if using an autosampler. Thoroughly chill solution and vial before making transfer.

**CALIBRATION AND QUALITY CONTROL:**

NOTE: The accurate measurement of pure 1,3-butadiene gas by gas-tight syringe is a critical step in the calibration. Even a slight obstruction (e.g., flakes of PTFE from the plunger tip which obstruct the needle) can cause 1,3-butadiene to be liquified as the plunger is depressed, making delivery incomplete. Bracketing gas samples with water, as described below, allows the volume taken to be approximately verified, and assures complete delivery. The precision of the analysis of multiple independent standards is another indicator of the accuracy of the volumes taken.

9. Make up stock solutions in triplicate at three concentration levels, e.g., 200  $\mu\text{L}$  of 1,3-butadiene gas in 1 mL solution, and both 200 and 50  $\mu\text{L}$  of gas in 4 mL solution:
  - a. Prepare a beaker and drying tube assembly as shown. Bubble 1,3-butadiene under the lower edge of the drying tube so that water is displaced and the gas is trapped in the tube.



- b. Pipet 1 or 4 mL of methylene chloride into a 1- or 5-mL vial, cap, and thoroughly chill.
  - c. Take a known amount (50 or 200  $\mu\text{L}$ ) of 1,3-butadiene from the drying tube with a 100- or 250- $\mu\text{L}$  gas-tight syringe. Bracket the gas in the syringe with small amounts of water (5 to 10% of syringe volume) taken from the area above the serum cap before and after withdrawing the gas. Do not take water from inside the drying tube, since it may contain a significant amount of dissolved 1,3-butadiene.
  - d. Slowly inject the 1,3-butadiene and water below the surface of the methylene chloride.
  - e. Agitate and continue to chill the vial to complete dissolution.
10. Calibrate daily with media blanks and triplicate independent media standards of at least six levels ranging from, e.g., 0.5 to 200  $\mu\text{L}$  1,3-butadiene gas per sample:
  - a. Break ends of larger sampler and attach to personal sampling pump with flexible tubing.
  - b. Take pure gas (50 or 200  $\mu\text{L}$ , as in step 9.c) for the higher levels, or 40  $\mu\text{L}$  of stock solution for lower levels.
  - c. Inject the gas and surrounding water plugs or the stock solution at a point inside the sampler near the glass wool plug while drawing clean air through tube at 0.05 L/min. Continue to draw air through the tube for 5 min or just until the stock solution evaporates.
  - d. Seal tube with plastic caps.

- e. Store at temperature below  $-4^{\circ}\text{C}$  overnight, then desorb (steps 5 through 8).
  - f. Analyze media standards and blanks together with samples (steps 13 and 14).
  - g. Convert gas volumes to masses, correcting for compressibility and water vapor (see APPENDIX B), and prepare a calibration graph (peak areas or heights vs. concentration of 1,3-butadiene taken in  $\mu\text{g}/\text{mL}$ ).
11. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in calibration range (step 10).
    - a. Dilute the stock solutions (step 9) with methylene chloride to extend the range of standards down to  $0.1 \mu\text{g}/\text{mL}$ . Avoid including water in the portions diluted.
    - b. Transfer solutions as in step 8 if using an autosampler, and analyze together with media standards (steps 13 and 14).
    - c. Convert gas volumes to masses, correcting for compressibility and water vapor (see APPENDIX B), and prepare DE calibration graph of peak area or height vs.  $\mu\text{g}/\text{mL}$  1,3-butadiene.
    - d. Read the concentrations,  $\mu\text{g}/\text{mL}$ , in media standards and blanks from DE calibration graph and multiply by the desorption volume to calculate the masses recovered.
    - e. Prepare a graph of DE vs.  $\mu\text{g}$  taken.  $\text{DE} = (\text{mass found} - \text{blank mass})/(\text{mass taken})$ .
  12. Analyze three quality control blind spikes to insure that calibration graph (step 10) is in control.

**MEASUREMENT:**

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1024-1. Inject sample aliquot manually using solvent flush technique or with autosampler.  
NOTE: If detector response is above range of working standards, dilute with methylene chloride, reanalyze, and apply appropriate dilution factor in calculations.
14. Measure peak area or height.  
NOTE: Vinylidene chloride, an impurity in methylene chloride, elutes just after 1,3-butadiene and may be used as an internal standard.

**CALCULATIONS:**

15. Determine the concentration,  $\mu\text{g}/\text{mL}$ , of 1,3-butadiene found in each sample front ( $W_f$ ) and back ( $W_b$ ) sorbent section from calibration graph (step 10), and multiply by desorption volume,  $D$ , mL, and dilution factor, if any, to calculate the mass,  $\mu\text{g}$ , found.  
NOTE 1: This calibration method corrects for media blank and DE. Do not duplicate corrections.  
NOTE 2: For any sampler with  $W_b > W_f/10$ , report breakthrough and possible sample loss.

$$C = \frac{(W_f + W_b) \times D}{V}, \text{ mg}/\text{m}^3.$$

**EVALUATION OF METHOD:**

The detector responses determined for triplicate standard solutions at each of five levels were linear over the range 0.3 to 440  $\mu\text{g}$  per sample. The pooled  $\bar{S}_r$  was 0.038. The estimated LOD was 0.02  $\mu\text{g}/\text{mL}$ .

The capacity of a 400-mg charcoal sorbent section was 31 L for a sample at 80% RH and approximately 56 ppm 1,3-butadiene. When exposed to 0.7 and 2.5 mL of pure 1,3-butadiene gas followed by 80% RH air, breakthrough occurred after 35 L and 28.5 L, respectively. The corresponding respective time-weighted average concentrations were 20 and 88 ppm.

For the analysis of media standards at levels of 1.1, 4.4, 18, 125, and 480  $\mu\text{g}$  per sample, the pooled  $\bar{S}_r$  was 0.025, and the desorption efficiencies were 67%, 68%, 75%, 102%, and 97%, respectively. Adding water to media standards just after spiking or during desorption had no significant effect on desorption efficiencies.

In a study of temperature effects on storage stability, 400-mg charcoal tubes were spiked with 26  $\mu\text{g}$  1,3-butadiene and stored either at ambient temperature or in a freezer below  $-4\text{ }^{\circ}\text{C}$ . Recoveries were measured relative to media standards stored overnight in the freezer. The recoveries (and days stored) were 94% (7), 93% (14), and 98% (21) for the frozen samples, and 95% (1), 76% (7), 61% (14), and 65% (21) for the ambient samples.

In a preliminary evaluation of precision and accuracy, charcoal tubes were spiked with 125  $\mu\text{g}$  1,3-butadiene via calibrated sampling valve. The recovery was 102.2% versus media standards (corrected for desorption efficiency) and 96.8% versus standard solutions (uncorrected for desorption efficiency); the  $\bar{S}_r$  of the response was 0.016. Subsequently, simulated samples were exposed to known amounts of approximately 10% 1,3-butadiene in helium, followed by 25 L of air at 80% RH. The 1,3-butadiene concentration was independently determined by packed column gas chromatography with thermal conductivity detection. Media standards were prepared via calibrated sampling valves. The recovery from six simulated samples at 463  $\mu\text{g}$  per sample was 101.6% versus media standards and 91.3% versus standard solutions; the  $\bar{S}_r$  of the response was 0.047. At 45.3  $\mu\text{g}$  per sample, the recovery was 112.3% versus media standards and 102.9% versus standard solutions; the  $\bar{S}_r$  of the response was 0.048. At 4.64  $\mu\text{g}$  per sample, the recovery was 80.3% versus media standards and 103.8% versus standard solutions; the  $\bar{S}_r$  of the response was 0.011. In the latter experiment, the two lowest levels of media standards appeared to be high, possibly due to absorption and release of 1,3-butadiene by internal parts of the sampling valve. The study was repeated at 4.71  $\mu\text{g}$ , with the three lowest levels of media standards prepared as in step 10. The recovery was 129.5% versus media standards and 91.2% versus standard solutions; the  $\bar{S}_r$  of the response was 0.023. The  $\bar{S}_r$  of the response pooled for all levels was 0.033. Assuming a sampling pump error of 0.05, the precision ( $\hat{S}_{rT}$ ) of the total sampling and analytical method was 0.060. For levels at and above 45  $\mu\text{g}$  (0.8 ppm in 25 L), apparent biases may be attributed to experimental errors in the preparation and analysis of standards and samples rather than a true bias in the method. At lower levels, based on the linear response and near-zero intercept observed for the standard solution calibrations and the higher than expected desorption efficiencies for the samples, there appeared to be a positive bias in the preparation of the simulated samples.

The method has been used in six industrial hygiene surveys, for a total of 621 samples, most of which were collected under conditions of high ambient temperature and humidity. Only two samples showed significant breakthrough ( $W_b > W_f/10$ ). Results for field samples at levels as high as 7.3 mg per sample were not significantly changed by dilution and reanalysis. In all, over 2000 analyses were made over a period of six months without any deterioration of the chromatographic columns. During the course of the analyses, twenty sets of standard solutions and media standards were prepared and analyzed, each set consisting of triplicates at each of five levels corresponding to 1.08 to 1.10, 4.32 to 4.40, 17.3 to 17.6, 108 to 110, and 432 to 441  $\mu\text{g}$  per sample. For the five levels of standard solutions, the respective pooled relative standard deviations of the observed responses were 0.093, 0.074, 0.059, 0.055, and 0.071. For each set of standard solutions, the deviations of the responses were determined relative to the line resulting from a weighted linear regression of response on concentration. The 95% confidence intervals for the mean relative deviations from linearity for the five levels were  $-0.002 \pm 0.003$ ,  $0.000 \pm 0.003$ ,  $-0.020 \pm 0.002$ ,  $0.002 \pm 0.002$ , and  $-0.019 \pm 0.002$ , respectively. For the media standards, the respective pooled  $\bar{S}_r$  for the observed responses at the five levels were 0.109, 0.080, 0.050, 0.064, and 0.037; the respective 95% confidence intervals for the mean percent recoveries relative to the standard solution calibrations were  $60.4 \pm 0.4$ ,  $66.4 \pm 0.3$ ,  $70.5 \pm 0.2$ ,  $86.2 \pm 0.3$ , and  $91.2 \pm 0.2$ .

The analysis of quality assurance blind spikes provided additional data indicating that samples were stable when stored below  $-4\text{ }^{\circ}\text{C}$ , and that average recoveries, calibrated against media standards, ranged from 96 to 107%. Seventy-seven blind spikes were prepared at six levels, 19.9 to 21.9, 48.6 to 52.6, 104 to 110, 199 to 219, 398 to 438, and 663  $\mu\text{g}$  per sample, stored in a freezer, and analyzed along with the field samples. The storage times ranged from 3 to 134 days; the average was 59 days. For the six levels of blind spikes, the respective relative standard deviations for recoveries were 0.210, 0.092,

0.054, 0.091, 0.126, and 0.056; the respective 95% confidence intervals for the mean recoveries were  $0.986 \pm 0.032$ ,  $0.961 \pm 0.014$ ,  $0.994 \pm 0.008$ ,  $1.029 \pm 0.015$ ,  $1.064 \pm 0.021$ , and  $1.074 \pm 0.021$ . Prior to linear regression of the recoveries versus the amounts spiked and/or days stored, three results, two high and one low, were determined to be outliers by application of one-sided Grubbs tests [4] at the 2.5% significance level and were dropped from the data set. Linear regression of percent recovery on days stored for the data segregated by level resulted in respective slopes and 95% confidence intervals of  $0.060 \pm 0.080$ ,  $0.005 \pm 0.128$ ,  $-0.003 \pm 0.092$ ,  $0.060 \pm 0.179$ ,  $0.249 \pm 0.188$ , and  $0.018 \pm 0.247$  percent per day. Thus, the only statistically significant correlation between recovery and days stored was at the next to highest level, for a gain rather than loss over time. Over all levels, the slopes and 95% confidence intervals for recovery versus amounts spiked and days stored were  $0.017 \pm 0.009$  percent per  $\mu\text{g}$  and  $0.045 \pm 0.051$  percent per day, respectively. Thus, according to the latter model: the recovery for the blind spikes increased at a rate corresponding to approximately 11% over the range prepared; as stored, the blind spikes appeared to be stable—the 95% confidence interval of the slope over time indicated a maximum gain of 5.7% or loss of 0.4% during the average 59-day storage period.

#### REFERENCES:

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- [2] NIOSH Current Intelligence Bulletin 41, "1,3-Butadiene," U.S. Department of Health and Human Services, Publ. (NIOSH) 84-105 (1984).
- [3] NIOSH Current Intelligence Bulletin 46, "Methylene Chloride," U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).
- [4] Grubbs, F. E. "Procedures for Detecting Outlying Observations in Samples," *Technometrics*, 11(1), 1–21, (February, 1969).
- [5] MacCallum, R. N., and J. J. McKetta. "Low-Pressure Zs of C<sub>4</sub> Hydrocarbons," *Hydrocarbon Process. Petrol. Refiner*, 42(5), 191–194 (1963).

#### METHOD WRITTEN BY:

R. Alan Lunsford, Ph.D., Yvonne T. Gagnon, NIOSH/DPSE, and John Palassis, NIOSH/DTMD.

#### APPENDIX A. GAS CHROMATOGRAPH COLUMN SELECTION, INSTALLATION, AND OPERATION:

Any column which separates 1,3-butadiene from the other substances present, and which otherwise provides satisfactory chromatographic performance, is acceptable. The column specified in NIOSH Method S91 [1] is 6 m  $\times$  3-mm OD stainless steel, packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS. It provides a convenient separation of 1,3-butadiene from the desorbing solvent. However, if other C<sub>4</sub> to C<sub>6</sub> hydrocarbons are present, interferences are likely. For the development of this method, a 50 m  $\times$  0.32-mm ID fused-silica porous-layer open-tubular (PLOT) column coated with Al<sub>2</sub>O<sub>3</sub>/KCl (Cat. # 7515, Chrompack, Bridgewater, NJ) was chosen as the analytical column because it provides a very efficient separation at temperatures above ambient. However, water from the samples deactivates the aluminum oxide, reducing retention times, and high-boiling or polar substances may accumulate on the column and irreversibly degrade the separation. The degradation was eliminated by using a backflushable pre-column, i.e., 10 m  $\times$  0.5-mm ID fused-silica CP Wax 57 CB (Cat. # 7648, Chrompack, Bridgewater, NJ). The pre-column allows light hydrocarbons to pass through, but water, methylene chloride, and polar or high boiling components are retained and can be backflushed. Eliminating the solvent peak significantly reduces the time required to complete the analysis.

Figures 1 and 2 schematically illustrate the installation and operation of the recommended columns in a Hewlett-Packard 5880A gas chromatograph with split-splitless capillary inlet systems installed in the "B" and "C" injector positions. The only change to the "B" system involves the normally closed (NC) port of

the "B" solenoid valve. Originally, it was connected to the capped port of the tee in the "B" septum purge line. (If desired, switching between normal operation of the "B" system and backflushable pre-column operation could be easily achieved by adding a manually operated three-way valve.) Replumb the components of the "C" system as shown, and extend lines from the normally open (NO) port of the "C" solenoid and the "C" backpressure regulator into the oven. Connect the lines and columns with a zero-dead-volume cross (e.g., Part # ZX1, Valco, Houston, TX) and graphite ferrules.

Set the initial oven temperature to 50 °C and the "C" backpressure regulator to 185 kPa. With the solenoid valves activated (inject mode), set the "C" flow control to 20 mL/min and the "B" controls so that the effluent from the analytical column and the "C" split vent total 10 mL/min. Then, with the solenoid valves deactivated (backflush or normal mode), adjust the "B" backpressure regulator until the flow from the "C" split vent returns to the value previously measured. This establishes a reverse flow of 10 mL/min through the pre-column. Program the oven to hold the initial temperature (50 °C) for 2 min, then rise to 120 °C at 20 °C/min, and hold for 8 min. Adjust the time from injection to backflush by injecting standards and progressively decreasing the time from 2 min until the methylene chloride peak is removed without attenuating the butadiene peak. It may be necessary to clear higher hydrocarbons from the analytical column by programming the oven to 200 °C at 30 °C/min and holding 4 min. Program the solenoid valves to be activated after each run to prepare for the next injection.

Using the backflushable pre-column, there remains a slight problem with retention drift. While in inject mode, the pre-column strips residual water from the carrier gas. This activates the aluminum oxide surface of the analytical column and causes retention to increase. The effect is most noticeable when starting up after the system has been idle. When beginning a sequence of samples, it is advisable to analyze solvent blanks until the retention drift (e.g., of vinylidene chloride) becomes tolerable.

## APPENDIX B. CONVERSION OF 1,3-BUTADIENE VOLUME TO MASS

MacCallum and McKetta [5] determined the compressibility factor,  $Z$ , which corrects for non-ideal behavior, for 1,3-butadiene at temperatures,  $T$ , ranging from 10 to 75 °C, and pressures,  $P$ , from approximately 420 to 1050 mm Hg. Multiple regression of the observed values against  $P$ ,  $PT$ , and  $PT^2$ , yields the following equation (standard error of the estimated  $Z$  is 0.000635 for 13 degrees of freedom):

$$Z = a + bP + cPT + dPT^2,$$

where:  $a = 1.00095$ ,  $b = -4.84089 \times 10^{-5}$ ,  $c = 4.44816 \times 10^{-7}$ ,  $d = -1.15744 \times 10^{-9}$ .

The mass,  $M$ , of 1,3-butadiene, corrected for compressibility and the presence of water vapor (when the gas is stored above water), may be calculated by the following equation:

$$M = \frac{(P - P_v) \times V \times 54.09}{Z \times 62.36 \times (T - 273.2)}, \mu\text{g},$$

where:  $P_v$  = vapor pressure of water @  $T$  °C (mm Hg),  
 $V$  = volume of 1,3-butadiene ( $\mu\text{L}$ ),  
 54.09 = molecular weight of 1,3-butadiene ( $\text{g}\cdot\text{mol}^{-1}$ ),  
 62.36 = gas constant ( $\text{mm Hg}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ),  
 273.2 = absolute temperature of 0 °C (K).



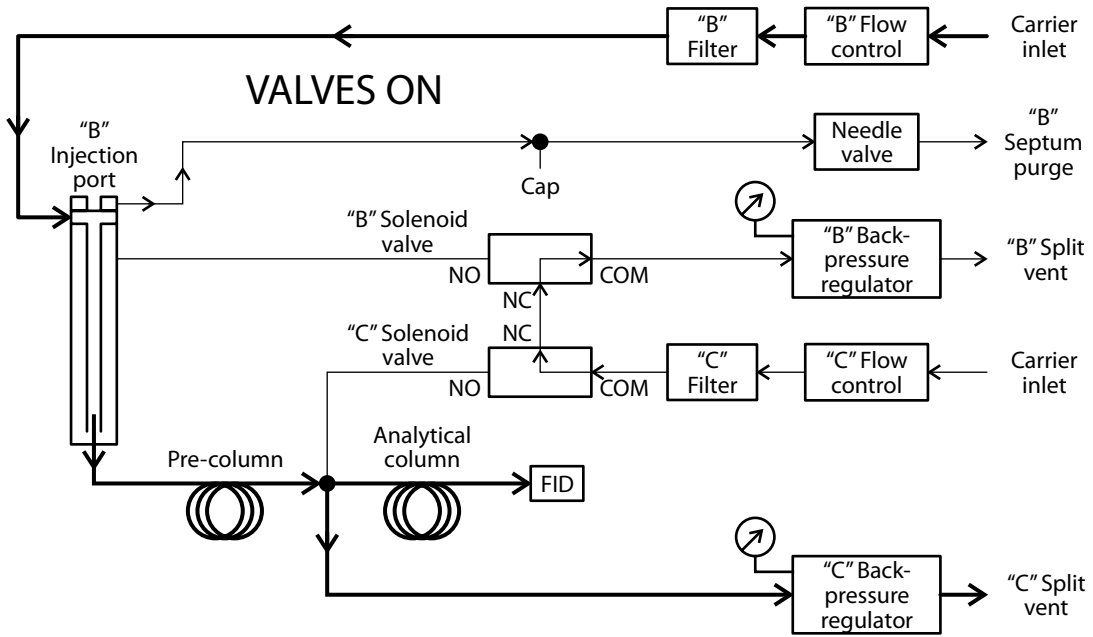


Figure 1. Flow diagram for pre-column system in inject mode.

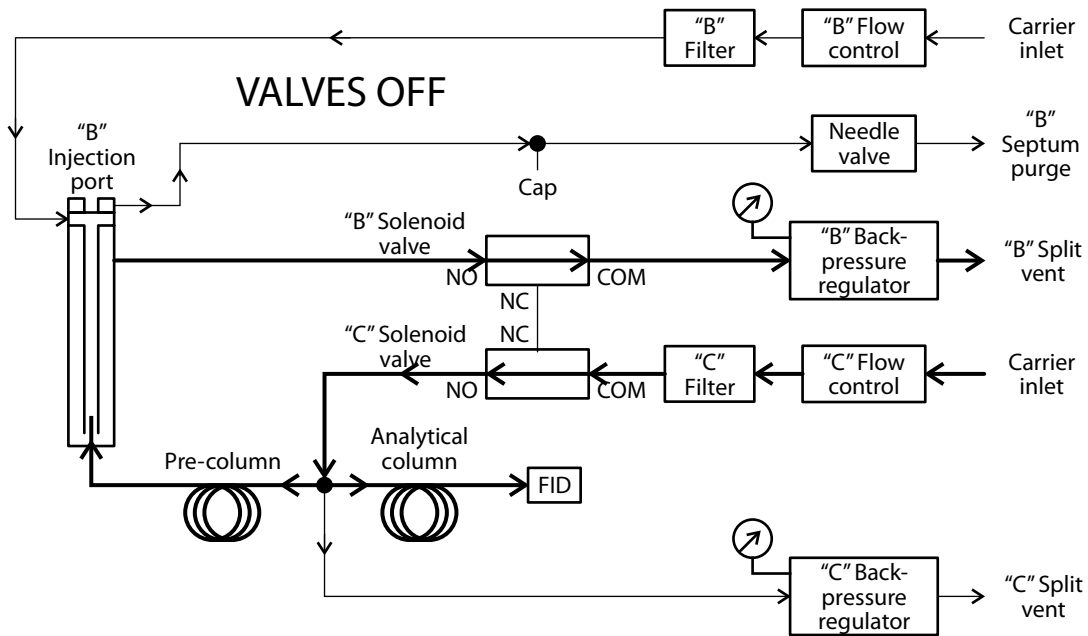


Figure 2. Flow diagram for pre-column system in backflush (normal) mode.



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*For problems with accessibility in using figures, illustrations and PDFs in this method, please contact the SLTC at (801) 233-4900. These procedures were designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.*

### 1,3-Butadiene

*Related Information: Chemical Sampling - [Butadiene](#)*

Method no.:	56
Matrix:	Air
Target concentration:	1 ppm (2.21 mg/m <sup>3</sup> )
Procedure:	Air samples are collected by drawing known volumes of air through sampling tubes containing charcoal adsorbent which has been coated with 4-tert-butylcatechol. The samples are desorbed with carbon disulfide and then analyzed by gas chromatography using a flame ionization detector.
Recommended air volume and sampling rate:	3 L at 0.05 L/min
Detection limit of the overall procedure:	90 ppb (200 µg/m <sup>3</sup> )
Reliable quantitation limit:	155 ppb (343 µg/m <sup>3</sup> )
Standard error of estimate at the target concentration: ( <a href="#">Section 4.6.1</a> )	6.5%
Special requirements:	The sampling tubes must be obtained from the Salt Lake City Analytical Laboratory. Collected samples should be stored in a freezer.
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.
Date: December 1985	Chemist: Warren Hendricks

Organic Methods Evaluation Branch  
OSHA Analytical Laboratory  
Salt Lake City, Utah

#### 1. General Discussion

##### 1.1. Background

###### 1.1.1. History

This work was undertaken to develop a sampling and analytical procedure for 1,3-butadiene at 1 ppm. The 1 ppm target concentration was selected in anticipation of a possible reduction in the current OSHA PEL of 1000 ppm. NIOSH has recently recommended that 1,3-butadiene be treated as a potential occupational carcinogen, teratogen and as a reproduction hazard. ([Ref. 5.1](#))

The current method recommended by OSHA for collecting 1,3-butadiene uses activated coconut shell charcoal as the sampling medium ([Ref. 5.2](#)). This method was found to be inadequate for use at low 1,3-butadiene levels because of sample instability ([Sections 4.5.2](#) and [4.6.2](#)).

The stability of collected samples has been significantly improved through the use of a specially cleaned charcoal which is coated with 4-tert-butylcatechol (TBC). TBC is a polymerization inhibitor for 1,3-butadiene ([Ref. 5.3](#)).

1.1.2. Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy).

Symptoms of human exposure to 1,3-butadiene include irritation of the eyes, nose and throat. It can also cause coughing, drowsiness and fatigue. Dermatitis and frost-bite can result from skin exposure to liquid 1,3-butadiene. ([Ref. 5.1](#))

NIOSH recommends that 1,3-butadiene be handled in the workplace as a potential occupational carcinogen. This recommendation is based on two inhalation studies that resulted in cancers at multiple sites in rats and in mice. 1,3-Butadiene has also demonstrated mutagenic activity in the presence of a liver microsomal activating system. It has also been reported to have adverse teratogenic and reproductive effects. ([Ref. 5.1](#))

#### 1.1.3. Potential workplace exposure

In 1984, 2.53 billion pounds of rubber grade butadiene were produced. This amount was only 3.7% less than the average yearly amount produced during the past decade of 1974-1984. In 1984, butadiene ranked 36th of the top 50 chemicals produced in the United States. ([Ref. 5.4](#)) About 80% of the 1,3-butadiene produced in the United States is a by-product of the manufacture of ethylene. The remaining 20% is produced by the dehydrogenation of n-butene and n-butane. ([Ref. 5.1](#))

About 90% of the annual production of 1,3-butadiene is used to manufacture styrene-butadiene rubber and polybutadiene rubber. Other uses include: polychloroprene rubber, acrylonitrile-butadiene-styrene resins, nylon intermediates, styrene-butadiene latexes, butadiene polymers, thermoplastic elastomers, nitrile resins, methyl methacrylate-butadiene-styrene resins and chemical intermediates. ([Ref. 5.1](#))

A NIOSH survey, that was conducted from 1972 to 1974, estimated that approximately 65,000 workers were potentially exposed to 1,3-butadiene. About 70% of this total was employed in chemical and chemical products occupations. Another 25% of the total was employed in work places which included: rubber and rubber products industries miscellaneous business services and miscellaneous manufacturing industries. ([Ref. 5.1](#))

#### 1.1.4. Physical properties ([Ref. 5.1](#))

CAS no.:	106-99-0
molecular weight:	54.09
appearance:	colorless gas
boiling point:	-4.41°C (760 mm Hg)
freezing point:	-108.9°C
vapor pressure:	2 atm at 15.3°C 5 atm at 47.0°C
explosive limits:	2 to 11.5% (by volume in air)
odor threshold:	1.3 ppm
structural formula:	H <sub>2</sub> C:CHCH:CH <sub>2</sub>
synonyms:	biethylene; bivinyl; butadiene; divinyl; buta-1,3-diene; alpha-gamabutadiene; erythrene; NCI-C50602; pyrrolylene; vinylethylene.

1.2. Limit defining parameters (The analyte air concentrations listed throughout this method are based on an air volume of 3 L and a desorption volume of 1 mL. Air concentrations listed in ppm are referenced to 25°C and 760 mm Hg.)

##### 1.2.1. Detection limit of the analytical procedure

The detection limit of the analytical procedure was 304 pg per injection. This was the amount of 1,3-butadiene which gave a measurable response relative to the interferences present in a standard. ([Section 4.1](#))

##### 1.2.2. Detection limit of the overall procedure

The detection limit of the overall procedure was 0.60 µg per sample (90 ppb or 200 µg/m<sup>3</sup>). This amount was determined graphically. It was the amount of analyte which, when spiked on the sampling device, would allow recovery approximately equivalent to the detection limit of the analytical procedure. ([Section 4.1.2](#))

##### 1.2.3. Reliable quantitation limit

The reliable quantitation limit was 1.03 µg per sample (155 ppb or 343 µg/m<sup>3</sup>). This was the smallest amount of analyte which could be quantitated within the limits of a recovery of at least 75% and a precision (±1.96 SD) of ±25% or better. ([Section 4.2](#))

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The reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of an analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

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##### 1.2.4. Sensitivity

The sensitivity of the analytical procedure over a concentration range representing 0.6 to 2 times the target concentration, based on the recommended air volume, was 387 area units per µg/mL. This value was determined from the slope of the calibration curve. ([Section 4.3](#)) The sensitivity may vary with the particular instrument used in the analysis.

##### 1.2.5. Recovery

The recovery of 1,3-butadiene from samples used in storage tests remained above 77% when the samples were stored at ambient temperature for 17 days, and above 94% when the samples were stored at refrigerated temperature for 18 days. These values were determined from regression lines which were calculated from the storage data. ([Section 4.6](#)) The recovery of the analyte from the collection device must be at least 75% following storage.

#### 1.2.6. Precision (analytical method only)

The pooled coefficient of variation obtained from replicate determinations of analytical standards over the range of 0.6 to 2 times the target concentration was 0.011. ([Section 4.3](#))

#### 1.2.7. Precision (overall procedure)

The precision at the 95% confidence level for the refrigerated temperature storage test was  $\pm 12.7\%$ . ([Section 4.6.1](#)) This value includes an additional  $\pm 5\%$  for sampling error. The overall procedure must provide results at the target concentrations that are  $\pm 25\%$  at the 95% confidence level.

#### 1.2.8. Reproducibility

Samples collected from a controlled test atmosphere and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The average recovery was 97.2% and the standard deviation was 6.2%. ([Section 4.7](#))

### 1.3. Advantages

1.3.1. The sampling and analytical procedure permits determination of 1,3-butadiene at low levels.

1.3.2. Samples are relatively stable following storage at ambient temperature for 17 days.

### 1.4. Disadvantage

The recommended sampling tubes must be obtained from the Salt Lake City Analytical Laboratory.

## 2. Sampling Procedure

### 2.1. Apparatus

2.1.1. Samples are collected by use of a personal sampling pump that can be calibrated to within  $\pm 5\%$  of the recommended 0.05 L/min sampling rate with the sampling tube in line.

2.1.2. Samples are collected with laboratory prepared sampling tubes. The sampling tube is constructed of silane-treated glass and is about 5-cm long. The i.d. is 4 mm and the o.d. is 6 mm. One end of the tube is tapered so that a glass wool end plug will hold the contents of the tube in place during sampling. The opening in the tapered end of the sampling tube is at least one-half the i.d. of the tube (2 mm). The other end of the sampling tube is open to its full 4-mm i.d. to facilitate packing of the tube. Both ends of the tube are fire-polished for safety. The tube is packed with 2 sections of pretreated charcoal which has been coated with TBC. The tube is packed with a 50-mg backup section, located nearest the tapered end, and with a 100-mg sampling section of charcoal. The two sections of coated adsorbent are separated and retained with small plugs of silanized glass wool. Following packing, the sampling tubes are sealed with two 7/32-in. o.d. plastic end caps. Instructions for the pretreatment and coating of the charcoal are presented in [Section 4.8](#) of this method.

### 2.2. Reagents

None required

### 2.3. Technique

2.3.1. Properly label the sampling tube before sampling and then remove the plastic end caps.

2.3.2. Attach the sampling tube to the pump using a section of flexible plastic tubing such that the large front section of the sampling tube is exposed directly to the atmosphere. Do not place any tubing ahead of the sampling tube. The sampling tube should be attached in the worker's breathing zone in a vertical manner such that it does not impede work performance.

2.3.3. After sampling for the appropriate time, remove the sampling tube from the pump and then seal the tube with plastic end caps. Wrap the tube lengthwise with an official OSHA seal (Form 21).

2.3.4. Include at least one blank for each sampling set. The blank should be handled in the same manner as the samples with the exception that air is not drawn through it.

2.3.5. List any potential interferences on the sample data sheet.

2.3.6. The samples require no special shipping precautions under normal conditions. The samples should be refrigerated if they are to be exposed to higher than normal ambient temperatures. If the samples are to be stored before they are shipped to the laboratory, they should be kept in a freezer. The samples should be placed in a freezer upon receipt at the laboratory.

2.4. Breakthrough (Breakthrough was defined as the relative amount of analyte found on the backup section of the tube in relation to the total amount of analyte collected on the sampling tube.)

Five-percent breakthrough occurred after sampling a test atmosphere containing 2.0 ppm 1,3-butadiene for 90 min at 0.05 L/min. At the end of this time 4.5 L of air had been sampled and 20.1  $\mu\text{g}$  of the analyte was collected. The relative

humidity of the sampled air was 80% at 23°C. ([Section 4.4](#))

Breakthrough studies have shown that the recommended sampling procedure can be used at air concentrations higher than the target concentration. The sampling time, however, should be reduced to 45 min if both the expected 1,3-butadiene level and if the relative humidity of the sampled air are high. ([Section 4.4](#))

#### 2.5. Desorption efficiency

The average desorption efficiency for 1,3-butadiene from TBC coated charcoal over the range of from 0.6 to 2 times the target concentration was 96.4%. The desorption efficiency was essentially constant over the range studied. ([Section 4.5](#))

#### 2.6. Recommended air volume and sampling rate

2.6.1. The recommended air volume is 3 L.

2.6.2. The recommended sampling rate is 0.05 L/min for 1 h.

#### 2.7. Interferences (sampling)

There are no known interferences to the sampling method.

#### 2.8. Safety precautions (sampling)

2.8.1. Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.

2.8.2. Follow all safety practices that apply to the work area being sampled.

### 3. Analytical Procedure

#### 3.1. Apparatus

3.1.1. A gas chromatograph (GC), equipped with a flame ionization detector (FID). A Hewlett-Packard Model 5840A GC was used for this evaluation. Injections were performed using a Hewlett-Packard Model 7671A automatic sampler.

3.1.2. A GC column capable of resolving the analytes from potential interferences. A 20-ft × 1/8-in. o.d. stainless steel GC column containing 20% FFAP on 80/100 mesh Chromosorb W-AW-DMCS was used for this evaluation.

3.1.3. Two milliliter glass vials with Teflon-lined caps.

3.1.4. Disposable Pasteur-type pipets, volumetric flasks, pipets and syringes for preparing samples and standards, making dilutions and performing injections.

#### 3.2. Reagents

3.2.1. Carbon disulfide. Fisher Scientific Company A.C.S. Reagent Grade solvent was used in this evaluation. The benzene contaminant that was present in the carbon disulfide was used as an internal standard (ISTD) in this evaluation.

3.2.2. Nitrogen, hydrogen, and air, GC grade.

3.2.3. 1,3-Butadiene of known high purity. Matheson Gas Products, CP Grade 1,3-butadiene was used in this study.

#### 3.3. Standard preparation

3.3.1. Prepare standards by diluting known volumes of 1,3-butadiene gas with carbon disulfide. This can be accomplished by injecting the appropriate volume of 1,3-butadiene into the headspace above the 1 mL of carbon disulfide contained in sealed 2-mL vial. Shake the vial after the needle is removed from the septum. A standard containing 7.71 µg/mL (at ambient temperature and pressure) was prepared by diluting 4 µL of the gas with 1 mL of carbon disulfide.

3.3.2. The mass of 1,3-butadiene gas which was used to prepare standards can be determined by use of the following equations:

$$MV = (22.41)(760/BP)(273+T)/(273)$$

where 22.41 = molar volume at STP  
MV = ambient molar volume  
BP = ambient barometric pressure  
T = ambient temperature

$$\mu\text{g}/\mu\text{L} = 54.09/MV$$

$$\mu\text{g per standard} = (\mu\text{g}/\mu\text{L})(\mu\text{L})(p)$$

where µg/µL = ambient density of 1,3-butadiene gas  
µL = µL of 1,3-butadiene used to prepare standard  
p = purity of 1,3-butadiene, (decimal form)

### 3.4. Sample preparation

3.4.1. Transfer the c section of the sampling tube to a 2-mL vial. Place the 50-mg section in a separate vial. If the glass wool plugs contain a significant amount of charcoal, place them with the appropriate sampling tube section.

3.4.2. Add 1 mL of carbon disulfide to each vial.

3.4.3. Seal the vials with Teflon-lined caps and then allow them to desorb for 1 h. Shake the vials by hand with vigorous force several times during the desorption time.

3.4.4. If it is not possible to analyze the samples within 4 h of desorption, separate the carbon disulfide from the charcoal, using a disposable Pasteur-type pipet, following the 1-h desorption time. This separation will improve the stability of desorbed samples. (Tables 4.5.1.2. and 4.5.1.3.)

3.4.5. Save the used sampling tubes to be cleaned and repacked with fresh adsorbent.

### 3.5. Analysis

#### 3.5.1. GC Conditions

column temperature:	95°C
injector temperature:	180°C
detector temperature:	275°C
carrier gas flow rate:	30 mL/min
injection volume:	0.80 µL
GC column:	20-ft × 1/8-in. o.d. stainless steel GC column containing 20%FFAP on 80/100 Chromosorb W-AW DMCS

3.5.2. Chromatogram See [Section 4.9.](#)

3.5.3. Use a suitable method, such as electronic integration or peak heights, to measure detector response.

3.5.4. Prepare a calibration curve using several standard solutions of different concentrations. Prepare the calibration curve daily. Program the integrator to report the results in µg/mL.

3.5.5. Bracket sample concentrations with standards.

### 3.6. Interferences (analytical)

3.6.1. Any compound with the same general retention time as the analyte and which also gives a detector response is a potential interference. Possible interferences should be reported to the laboratory with submitted samples by the industrial hygienist.

3.6.2. GC parameters (temperature, column, etc.) may be changed to circumvent interferences.

3.6.3. A useful means of structure designation is GC/MS. It is recommended that this procedure be used to confirm samples whenever possible.

### 3.7. Calculations

3.7.1. Results are obtained by use of calibration curves. Calibration curves are prepared by plotting detector response against concentration for each standard. The best line through the data points is determined by curve fitting.

3.7.2. The concentration, in µg/mL, for a particular sample is determined by comparing its detector response to the calibration curve. If any analyte is found on the backup section, this amount is added to the amount found on the front section. Blank corrections should be performed before adding the results together.

3.7.3. The 1,3-butadiene air concentration can be expressed using the following equation:

$$\text{mg/m}^3 = (A)(B)/(C)(D)$$

where A = µg/mL from Section 3.7.2.

B = desorption volume

C = liters of air sampled

D = desorption efficiency

3.7.4. The following equation can be used to convert results in mg/m<sup>3</sup> to ppm:

$$\text{ppm} = (\text{mg/m}^3)(24.46)/54.09$$

where mg/m<sup>3</sup> = result from Section 3.7.3.

24.46 = molar volume of an ideal gas at 760 mm Hg and 25°C

### 3.8. Safety precautions (analytical)

- 3.8.1. Avoid skin contact and inhalation of all chemicals.
- 3.8.2. Restrict the use of all chemicals to a fume hood whenever possible.
- 3.8.3. Wear safety glasses and a lab coat in all lab areas.

#### 4. Backup Data

##### 4.1. Detection limit data

###### 4.1.1. Detection limit of the analytical procedure

The injection size recommended in the analytical procedure (0.80 µL) was used in the determination of the detection limit for the analytical procedure. The detection limit of the analytical procedure was 304 pg per injection. This was the amount of 1,3-butadiene which gave a measurable response relative to interferences present in a standard. This detection limit was determined by the analysis of a standard containing 380 ng/mL of 1,3-butadiene in carbon disulfide. [Figure 4.1.1](#) is a chromatogram of the detection limit of the analytical procedure.

###### 4.1.2. Detection limit of the overall procedure

The injection size recommended in the analytical procedure (0.80 µL) was used in the determination of the detection limit of the overall procedure. 1,3-Butadiene was diluted for use in this study by adding the pure analyte to a sealed, silanized vial containing air and a few crystals of TBC. Samples were prepared by injecting 100-mg portions of TBC coated charcoal with appropriate amounts of the diluted 1,3-butadiene. The samples were stored in a freezer overnight before analysis to allow complete adsorption of the analyte. Each result is the average of at least 2 samples. The results of this study are presented in Table 4.1.2. and in [Figure 4.1.2](#).

Table 4.1.2.  
Detection Limit Data

sample number	µg spiked	µg recovered	percent recovered
1	0.38	0.26	68.4
2	0.58	0.34	58.6
3	0.76	0.48	63.2
4	0.96	0.67	69.8
5	1.2	1.0	83.3
6	1.4	1.3	92.8
7	1.9	1.9	100.0

The detection limit of the overall procedure was determined graphically ([Figure 4.1.2](#)) from the data in Table 4.1.2. This amount was 0.60 µg per sample.

##### 4.2. Reliable quantitation limit data

The recommended injection size of 0.80 µL was used in the determination of the reliable quantitation limit (RQL). The amount of 1,3-butadiene which provided a recovery of 75% from the sampling media was determined graphically ([Figure 4.2.1](#)) from the data in Table 4.1.2. This amount was 1.03 µg. A chromatogram of the RQL is presented in [Figure 4.2.2](#). Six samples were used to determine the precision at the RQL. The samples were prepared in a similar manner as those in [Section 4.1.2](#). The results of this study are presented below and in [Figure 4.2.1](#).

Table 4.2.  
Reliable Quantitation Limit Data

sample number	µg spiked	µg recovered	percent recovered
1	1.03	0.854	82.9
2	1.03	0.754	73.2
3	1.03	0.829	80.5
4	1.03	0.779	75.6
5	1.03	0.836	81.2
6	1.03	0.836	81.2
$\bar{x}$	1.03	0.815	79.1
			SD = 3.8
			1.96 SD = 7.4

##### 4.3. Sensitivity and precision (analytical method only)

The sensitivity and precision of the analytical procedure were evaluated by performing multiple injections of analytical standards at 0.6, 1, and 2 times the target concentration. The standards were prepared by injecting appropriate amounts of 1,3-butadiene gas diluted with carbon disulfide. The data are presented in Table 4.3. and also in [Figure 4.3](#). The ISTD data are the results of an internal standard calibration using the benzene contaminant present in carbon disulfide as the internal standard.

Table 4.3.  
1,3-Butadiene Sensitivity and Precision Data

	0.6×		1×		2×	
	3.86 µg/sample ISTD	area	6.75 µg/sample ISTD	area	13.5 µg/sample ISTD	area
	3.85	1332	6.66	2371	13.4	5190
	3.89	1509	6.73	2386	13.5	5167
	3.85	1507	6.78	2369	13.7	5076
	3.81	1345	6.78	2393	13.5	5097
	3.81	1416	6.86	2529	13.6	5045
	3.95	1354	6.75	2327	13.3	5087
$\bar{x}$	3.86		6.76		13.5	
CV	0.0138		0.00977		0.0105	
$\overline{CV} =$	0.011					

The sensitivity for 1,3-butadiene was 387 area counts per µg/mL.

#### 4.4. Breakthrough data

Breakthrough was defined as the relative amount of 1,3-butadiene found on the 50-mg sampling tube section in relation to the total amount collected on the sampling tube.

Three breakthrough studies were performed at twice the target level with the recommended air sampler. The test atmospheres were generated by diluting the effluent of a gas cylinder containing 100 ppm of 1,3-butadiene with humid air. The concentrations of the test atmospheres were determined by direct injection of the atmosphere into a gas chromatograph. The gas chromatograph was calibrated using 1,3-butadiene from another source that had been diluted with dry air in a Teflon gas bag. The average concentration of the test atmospheres was 2.0 ppm. The average relative humidity of these test atmospheres was 80% at 23°C. The sampling rates were about 0.05 L/min. The results of these studies are presented in Table 4.4.1.

Table 4.4.1.  
1,3-Butadiene Breakthrough at Twice the Target Concentration

sampling time, min	amt. on 100-mg section, µg	amt. on 50-mg section, µg	breakthrough, %
91	23.4	0.0	0.0
124	27.8	3.1	10.0
155	30.4	6.1	16.7
60	14.6	0.0	0.0
91	21.6	1.2	5.3
121	25.5	3.5	12.1
50	8.6	0.0	0.0
76	13.0	0.0	0.0
92	14.4	0.6	4.0
105	15.7	2.2	12.3
125	17.0	2.4	12.4

When the results of the three studies were combined, 5% breakthrough occurred after sampling for 90 min. The air volume sampled after this time was 4.5 L and the amount of 1,3-butadiene collected was 20.1 µg.

Additional breakthrough studies were performed at concentrations higher than twice the target level in order to determine if the recommended sampling procedure would be reliable at those concentrations. The test atmospheres used in these studies were generated and their concentrations were determined using the techniques previously described. Percent recovery values were calculated using sample results and the actual concentration of the test atmospheres. The sampling rates were about 0.05 L/min. The results of these studies are presented in Tables 4.4.2. through 4.4.4.

Table 4.4.2.  
1,3-Butadiene Breakthrough Study at 7.3 ppm  
(Relative Humidity = 77% at 22°C)



sampling time, min	air volume sampled, L	percent breakthrough	percent recovery
15	0.73	0.0	80.2
30	1.6	0.0	94.2
45	2.2	0.0	96.8
60	3.1	0.0	99.4
75	3.5	0.6	96.7
90	4.5	8.4	95.8

Five-percent breakthrough occurred after sampling for 84 min. At the end of this time, 4.2 L of air had been sampled and 68 µg of 1,3-butadiene had been collected.

Table 4.4.3.  
1,3-Butadiene Breakthrough Study at 32 ppm  
(Relative Humidity = 47% at 24°C)

sampling time, min	air volume sampled, L	percent breakthrough	percent recovery
15	0.71	0.0	87.3
46	2.3	0.0	87.2
60	3.2	0.0	91.2
90	4.3	0.0	94.8
105	5.2	0.0	95.0
120	6.3	0.0	97.5
155	8.2	0.0	93.0

No breakthrough was observed, even after sampling for 155 min. This data shows that, at low relative humidity, the recommended sampling media has considerable capacity for 1,3-butadiene.

Table 4.4.4.  
1,3-Butadiene Breakthrough Study at 36 ppm  
(Relative Humidity = 90% at 21°C)

sampling time, min	air volume sampled, L	percent breakthrough	percent recovery
36	1.9	0.0	105.8
47	2.2	0.0	98.8
60	3.0	21.6	90.2
75	3.9	30.0	96.0
90	4.3	30.6	76.4
105	5.8	32.1	57.6
121	6.3	31.1	56.7

It is apparent from the data in Tables 4.4.2. through 4.4.4. that the recommended sampling and analytical method can be used at 1,3-butadiene levels higher than the target concentration. The relative humidity of the sampled air has a significant effect on the ability of the sampling device to retain the analyte.

#### 4.5. Desorption efficiency and stability of desorbed samples

##### 4.5.1. Pretreated charcoal coated with TBC

The desorption efficiency of 1,3-butadiene was determined by injecting the gas onto 100-mg portions of the recommended collection medium. The samples were spiked and then stored in a freezer overnight prior to analysis. The average desorption efficiency over the range of 0.6 to 2 times the target concentration was 96.4%. The individual results are presented in Table 4.5.1.1.

The stability of desorbed samples was investigated by reanalyzing the target concentration desorption samples at various times after carbon disulfide addition. Freshly prepared standards were used for each analysis. The sample vials were resealed immediately after each analysis. The results of this study are presented in Table 4.5.1.2. The percent recovery is based on the theoretical amount of 1,3-butadiene added to the original samples.

Table 4.5.1.1.  
The Desorption Efficiency

of 1,3-Butadiene from Charcoal Coated with TBC

× target conc. µg/sample	0.6× 3.86	1× 6.75	2× 13.5
desorption efficiency, %	94.3 95.4 96.4 96.9 94.8 96.9 95.8	100.0 97.0 102.0 96.0 94.3 98.8 98.0	97.5 97.5 95.8 95.2 93.4 92.5 95.3
$\bar{x}$	95.8	98.0	95.3

Table 4.5.1.2.  
The Stability (% Recovery) of 1,3-Butadiene  
After Desorption from Charcoal Coated with TBC

time h	sample number						$\bar{x}$
	1	2	3	4	5	6	
1	100.0	97.0	102.0	96.0	94.3	98.8	98.0
4	98.7	95.1	97.7	89.0	88.6	87.4	92.8
9	90.2	89.4	92.2	88.7	88.0	89.4	89.6
16	84.2	92.2	84.1	81.3	80.3	86.6	83.1
24	82.4	76.8	79.7	76.6	72.3	79.0	77.8
58	66.8	50.4	52.3	61.5	60.6	64.2	59.3

To determine if the stability of desorbed samples could be improved, the following experiment was performed: twelve samples were prepared by injecting 1,3-butadiene gas, at the target concentration, onto 100-mg portions of the recommended sampling media. The samples were spiked and then stored in a freezer overnight prior to analysis. Following desorption and analysis, the carbon disulfide was separated from the charcoal for six of the samples. The other six samples were not separated. All of the samples were reanalyzed using freshly prepared standards and the results of this study are shown below.

Table 4.5.1.3.  
Effect of Charcoal on the Stability of Butadiene in CS<sub>2</sub>

storage time h	CS <sub>2</sub> /charcoal separated				CS <sub>2</sub> /charcoal not separated			
	1	2	3	$\bar{x}$	1	2	3	$\bar{x}$
6	93.1	91.8	93.5	92.8	93.6	91.3	93.1	92.7
28	88.9	90.1	92.4	90.5	76.8	74.0	76.2	75.7

It appears that the stability of desorbed samples can be improved by separating the carbon disulfide from the charcoal.

#### 4.5.2. Untreated charcoal

The desorption efficiency of 1,3-butadiene was also determined for untreated SKC, Inc. Lot 120 coconut shell charcoal in the same manner as used for the recommended medium. The average desorption efficiency over the range of 0.6 to 2 times the target concentration was 60.4%. The individual results are presented in Table 4.5.2.1.

The stability of 1,3-butadiene desorbed from untreated SKC, Inc. Lot 120 charcoal was investigated in the same manner as was the recommended medium. The results of this study are presented in Table 4.5.2.2.

Table 4.5.2.1.  
The Desorption Efficiency  
of 1,3-Butadiene from SKC, Inc. Lot 120 Charcoal

× target conc. µg/sample	0.6× 3.86	1× 6.75	2× 13.5
desorption efficiency, %	61.6 66.7 61.5 54.4 52.3 51.7	67.3 64.1 61.7 62.0 57.9 53.3	67.1 65.0 62.8 61.4 58.7 58.8
⊗	58.0	61.0	62.3

Table 4.5.2.2.  
The Stability of 1,3-Butadiene After Desorption  
From SKC, Inc. Lot 120 Charcoal (percent recovery)

storage time h	sample number						⊗
	1	2	3	4	5	6	
5	43.8	44.0	40.1	40.6	38.8	38.4	41.0

These data show that SKC, Inc. Lot 120 charcoal is inadequate for this application because of sample instability.

#### 4.6. Storage data

##### 4.6.1. Pretreated charcoal coated with TBC

The test atmosphere was generated by diluting the effluent of a gas cylinder, containing 100 ppm 1,3-butadiene, with humid air. The resultant atmosphere contained 1 ppm 1,3-butadiene, the relative humidity of the air was 75% and its temperature was 25°C. The 1,3-butadiene content of the test atmosphere was determined by direct injection of 100 µL of the atmosphere into a gas chromatograph. The gas chromatograph was calibrated using 1,3-butadiene from another source which had been diluted with dry air in a Teflon gas bag. Samples were collected, using the recommended method, and they were stored either at -25°C or at ambient temperature. The results of the storage test are presented in Table 4.6.1. and also in [Figures 4.6.1.1](#) and [4.6.1.2](#).

Table 4.6.1.  
1,3-Butadiene Storage Test Using TBC Coated Charcoal

storage time (days)	% recovery (ambient)			storage time (days)	% recovery (refrigerated)		
0	102.2	102.2	99.1	0	97.0	101.8	97.8
3	97.8	93.3	93.3	4	99.5	96.9	98.7
6	100.9	98.7	100.9	7	93.2	104.9	102.2
10	93.8	87.5	83.9	11	98.6	94.6	92.4
13	82.1	88.8	80.8	14	104.1	96.9	98.2
17	81.2	76.3	76.8	18	84.3	94.6	96.4

##### 4.6.2. Untreated charcoal

An additional ambient temperature storage test was performed using untreated SKC, Inc. Lot 120 charcoal as sampling media. The test atmosphere was generated and its concentration determined in the same manner as was used for the recommended method. The concentration of the test atmosphere was 1 ppm. The relative humidity of this atmosphere was 70% at 23°C. Sampling was performed at 0.05 L/min for 1 h. The results of this study are presented in Table 4.6.2. and also in [Figure 4.6.2](#).

Table 4.6.2.  
1,3-Butadiene Ambient Temperature  
Storage Test Using SKC, Inc. Lot 120 Charcoal

storage time days	% recovery
----------------------	------------

0	33.5	36.3	33.5
3	31.3	30.1	29.0
6	17.9	12.8	14.9
10	29.0	22.5	22.6
13	25.2	23.8	19.9
17	18.2	19.8	17.4

#### 4.7. Reproducibility data

Samples were collected from a test atmosphere which was generated by diluting the effluent of a gas cylinder, containing 100 ppm 1,3-butadiene, with humid air. The resultant atmosphere contained 1 ppm 1,3-butadiene and the relative humidity of the air was 84% at 23°C. The 1,3-butadiene content of the test atmosphere was determined by the direct injection of 100 µL of the atmosphere into a GC. The GC was calibrated using 1,3-butadiene, from another source, which had been diluted with dry air in a Teflon gas bag. The samples and a draft copy of this evaluation were given to a chemist unassociated with this work. The samples were analyzed after 3 days storage at reduced temperature. The results are presented in Table 4.7.

Table 4.7.  
Reproducibility

% recovery	statistics
100.0	
102.9	
100.5	$\bar{x} = 97.2$
98.0	$SD = 6.2$
96.6	
85.4	

#### 4.8. A procedure to prepare specially cleaned charcoal coated with TBC

##### 4.8.1. Apparatus

4.8.1.1. Magnetic stirrer and stir bar.

4.8.1.2. Tube furnace capable of maintaining a temperature of 700°C and equipped with a quartz tube that can hold 30 g of charcoal. A Lindberg Type 55035 tube furnace was used in this evaluation.

4.8.1.3. A means to purge nitrogen gas through the charcoal inside the quartz tube.

4.8.1.4. Water bath capable of maintaining a temperature of 60°C.

4.8.1.5. Miscellaneous laboratory equipment: One-liter vacuum flask, 1-L Erlenmeyer flask, 350-mL Buchner funnel with a coarse fritted disc, 4-oz brown bottle, rubber stopper, Teflon tape, etc.

##### 4.8.2. Reagents

4.8.2.1. Phosphoric acid, 10%, by weight, in water. "Baker Analyzed" Reagent grade was diluted with deionized water for use in this evaluation.

4.8.2.2. 4-tert-Butylcatechol (TBC). The Aldrich Chemical Company 99% grade was used in this evaluation. CAUTION- The bottle was labeled: Sensitizer! Severe irritant! Toxic! Refrigerate!

4.8.2.3. Specially cleaned coconut shell charcoal, 20/40 mesh. Specially cleaned charcoal (Lot number 482338) was obtained from Supelco, Inc. for use in this evaluation. The cleaning process used by Supelco is proprietary.

4.8.2.4. Nitrogen gas, GC grade.

##### 4.8.3. Procedure

Weigh 30 g of charcoal into a 500-mL Erlenmeyer flask. Add about 250 mL of 10% phosphoric acid to the flask and then swirl the mixture. Stir the mixture for 1 h using a magnetic stirrer. Filter the mixture using a fritted Buchner funnel. Wash the charcoal several times with 250-mL portions of deionized water to remove all traces of the acid. Transfer the washed charcoal to the tube furnace quartz tube. Place the quartz tube in the furnace and then connect the nitrogen gas purge to the tube. Fire the charcoal to 700°C. Maintain that temperature for at least 1 h. After the charcoal has cooled to room temperature, transfer it to a tared beaker. Determine the weight of the charcoal and then add an amount of TBC which is 10% of the charcoal, by weight. CAUTION- TBC is toxic and should only be handled in a fume hood while wearing gloves. Carefully mix the contents of the beaker and then transfer the mixture to a 4-oz bottle. Stopper the bottle with a clean rubber stopper which has been wrapped with Teflon tape. Clamp the bottle in a water bath so that the water level is above the charcoal level. Gently heat the bath to 60°C and then maintain that temperature for 1 h. Cool the charcoal to room temperature and then transfer the coated charcoal to a suitable container.

The coated charcoal is now ready to be packed into sampling tubes. The sampling tubes should be stored in a sealed container to prevent contamination. Sampling tubes should be stored in the dark at room temperature. The sampling tubes should be segregated by coated adsorbent lot number.

#### 4.9. Chromatograms

The chromatograms were obtained using the recommended analytical method. The chart speed was set at 1 cm/min for the first three min and then at 0.2 cm/min for the time remaining in the analysis.

Figures 4.2.2. and 4.9.2 are chromatograms of 1,3-butadiene desorbed from the recommended sampling media. The peak which eluted just before 1,3-butadiene is a reaction product between an impurity on the charcoal and TBC. This peak is always present, but it is easily resolved from the analyte. The peak which eluted immediately before benzene is an oxidation product of TBC.



Figure 4.1.1. Chromatogram of detection limit of the analytical procedure.

Peak identification was as follows:  
1, 1,3-butadiene; 2, carbon disulfide; 3, benzene.

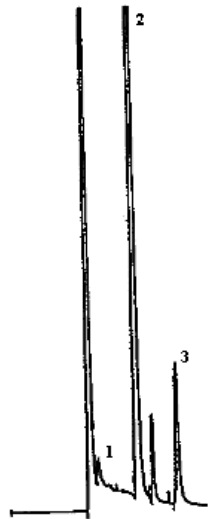


Figure 4.2.2. Chromatogram of the reliable quantitation limit.

Peak identification was as follows:  
1, 1,3-butadiene; 2, carbon disulfide; 3, benzene.

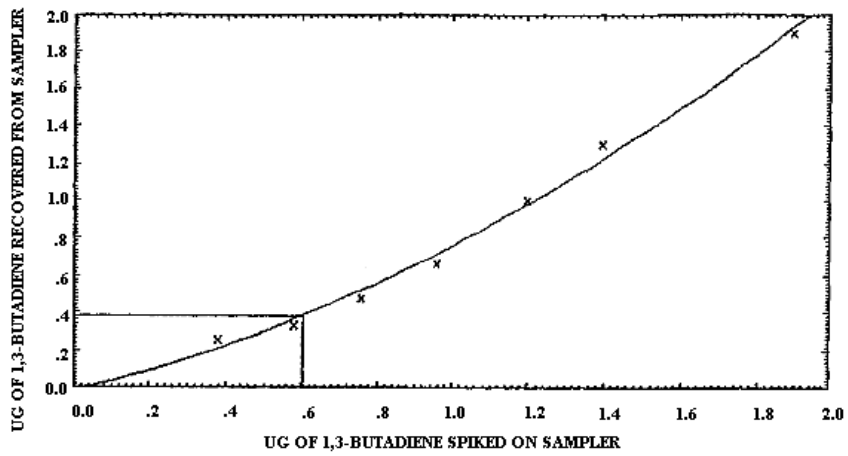


Figure 4.1.2. Determination of the detection limit of the overall procedure.

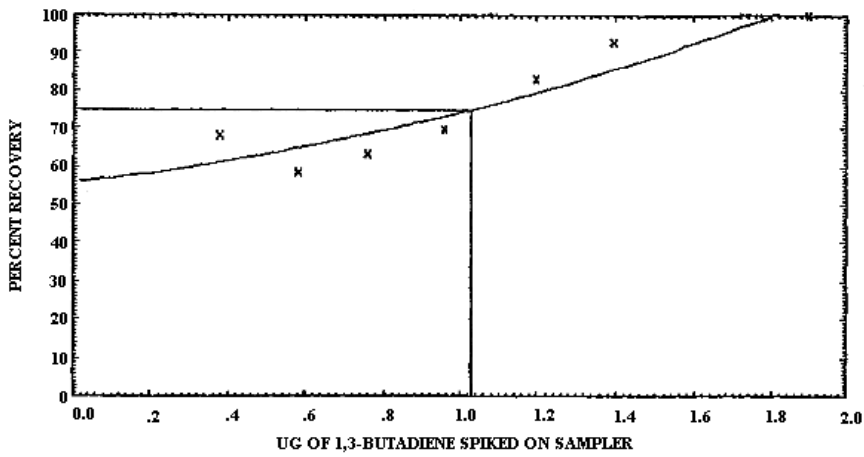


Figure 4.2.1. Determination of the reliable quantitation limit.

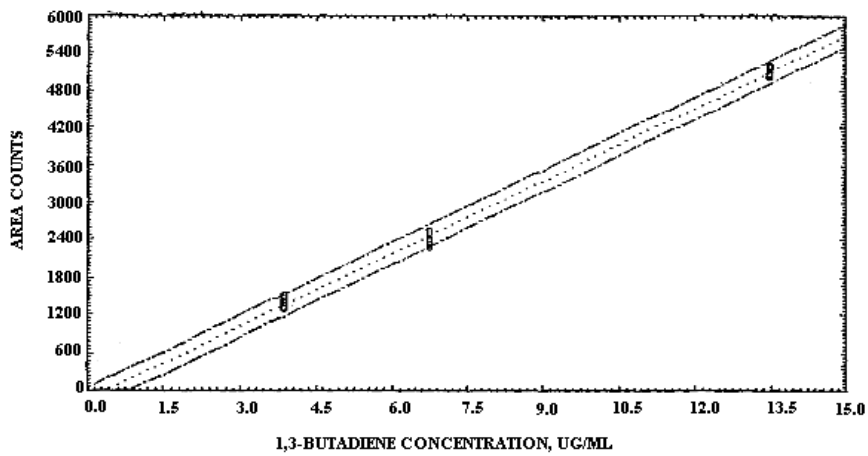


Figure 4.3. 1,3-Butadiene calibration curve.

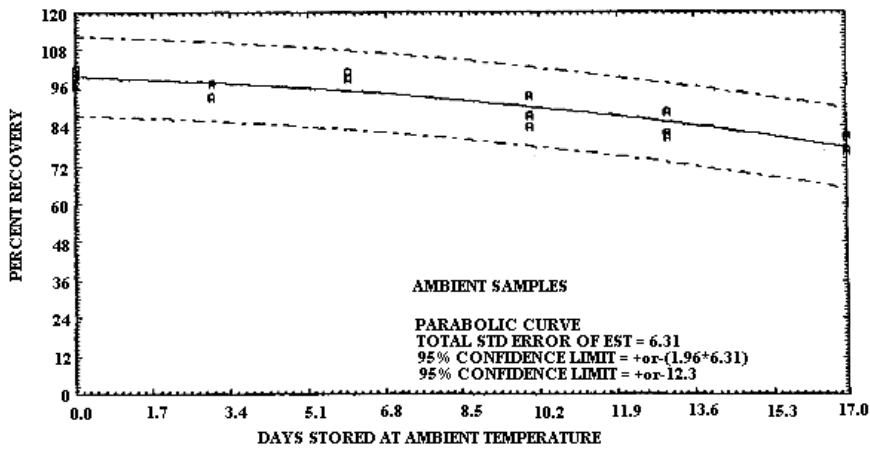


Figure 4.6.1.1. Ambient temperature storage test for 1,3-butadiene collected on TBC coated charcoal.

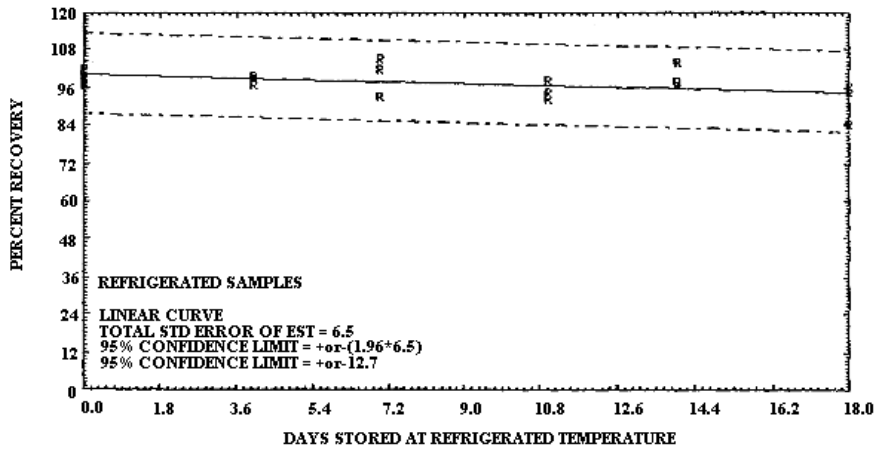


Figure 4.6.1.2. Reduced temperature storage test for 1,3-butadiene collected on TBC coated charcoal.

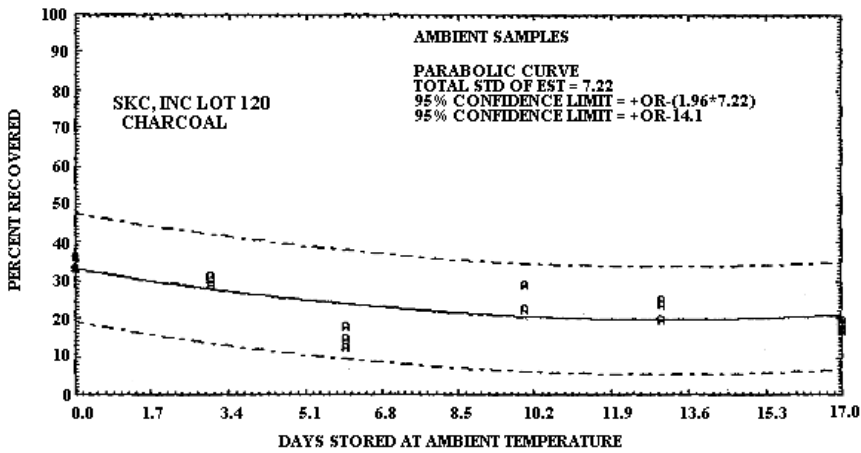


Figure 4.6.2. Ambient temperature storage test for 1,3-butadiene collected on untreated charcoal.

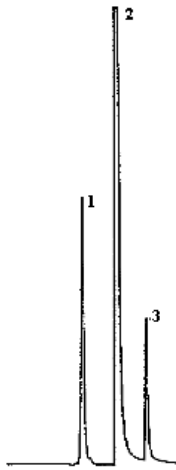


Figure 4.9.1. Chromatogram of a standard.  
Peak identification was as follows:  
1, 1,3-butadiene; 2, carbon disulfide; 3, benzene.

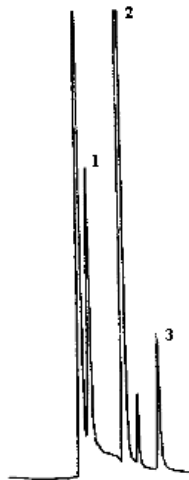


Figure 4.9.2. Chromatogram of a sample.  
Peak identification was as follows:  
1, 1,3-butadiene; 2, carbon disulfide; 3, benzene.

## 5. References

- 5.1. "Current Intelligence Bulletin 41, 1,3-Butadiene", U.S. Dept. of Health and Human Services, Public Health Service, Center for Disease Control, NIOSH.
- 5.2. "NIOSH Manual of Analytical Methods", 2nd ed.; U.S. Dept. of Health Education and Welfare, National Institute for Occupational Safety and Health: Cincinnati, OH. 1977, Vol. 2, Method No. 591 DHEW (NIOSH) Publ. (US), No. 77-157-B.
- 5.3. Hawley, G. G., Ed. "The Condensed Chemical Dictionary", 8th ed.; Van Nostrand Rienhold Company: New York, 1971; 139.
- 5.4. **Chem. Eng. News** (June 10, 1985), (63), 22-66.



**APPENDIX B**

**Standardized Job  
Groups and Titles**

<b>Work area</b>	<b>Original Job Group</b>	<b>Standard Job Group</b>
0	0	missing
0	0	missing
0	OPERATOR	Operations onsite
0	OPERATOR	Operations onsite
0	OPERATOR	Operations onsite
0	OPERATOR	Operations onsite
0	OPERATOR	Operations onsite
0	Pipe Fitter	Machinery & Specialists Mechanical Group
2 Plant	A Operator	Operations onsite
2 Plant	A Operator	Operations onsite
2 Plant	Operator Tech I	Operations onsite
2 Plant	Operator Tech I	Operations onsite
2 Plant	Operator Tech II	Operations onsite
2 Plant	Operator Tech II	Operations onsite
2 Plant	Operator Tech II	Operations onsite
2 Plant	Operator Technician Trainee	Operations onsite
2 Plant	Operator Technician Trainee	Operations onsite
2 Plant	Operator Technician Trainee	Operations onsite
4 Plant	0	Operations onsite
4 Plant	A Operator	Operations onsite
4 Plant	Operator Tech II	Operations onsite
4 Plant	Operator Tech II	Operations onsite
4 Plant	Operator Tech II	Operations onsite
4 Plant	Operator Tech II	Operations onsite
4 Plant	Operator Tech II	Operations onsite
4 Plant	Operator Technician Trainee	Operations onsite
4 Plant	Operator Technician Trainee	Operations onsite
Analytical Lab	Lab Technician III	Laboratory Technician
Analytical Lab	LABORATORY TECHNICIAN	Laboratory Technician
AREA NEXT TO CONTAINMENT	missing	missing
Block 10	OPERATOR	Operations onsite
Block 10	OPERATOR	Operations onsite
Block 12	0	missing
Block 12	0	missing
Block 12	0	missing
Block 12	BOILERMAKER	Machinery & Specialists Mechanical Group
Block 12	missing	Infrastructure / Distribution Operations
Block 12	missing	Infrastructure / Distribution Operations
Block 12	missing	Infrastructure / Distribution Operations
Block 12	missing	Infrastructure / Distribution Operations
Block 12	missing	Infrastructure / Distribution Operations
Block 12	missing	Infrastructure / Distribution Operations
Block 12	missing	Infrastructure / Distribution Operations
Block 12	missing	Infrastructure / Distribution Operations
Block 12	missing	Infrastructure / Distribution Operations
Block 12	missing	Infrastructure / Distribution Operations
Block 12	missing	Infrastructure / Distribution Operations
Block 12	OPERATOR	Operations onsite

<b>Work area</b>	<b>Original Job Group</b>	<b>Standard Job Group</b>
Block 12	OPERATOR	Operations onsite
Block 12	OPERATOR	Operations onsite
Block 12	OPERATOR	Operations onsite
Block 12	OPERATOR	Operations onsite
Block 13	OPERATOR	Operations onsite
Block 13	OPERATOR	Operations onsite
Block 13	OPERATOR	Operations onsite
Block 13	OPERATOR	Operations onsite
Block 13	OPERATOR	Operations onsite
Block 13	OPERATOR	Operations onsite
Block 13	OPERATOR	Operations onsite
Block 13	WEST GAUGER	Operations onsite
Block 13	WEST GAUGER	Operations onsite
Block 18	B Operator	Operations onsite
Block 18	OPERATOR	Operations onsite
Block 20	OPERATOR	Operations onsite
Block 20	OPERATOR	Operations onsite
Block 20	OPERATOR	Operations onsite
Block 20	OPERATOR	Operations onsite
Block 20	OPERATOR	Operations onsite
Block 20	OPERATOR	Operations onsite
Block 20	RIVER DOCK OPERATOR	Infrastructure / Distribution Operations
Block 20	RIVER DOCK OPERATOR	Infrastructure / Distribution Operations
Block 21	B Operator	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 21	OPERATOR	Operations onsite
Block 8	B Operator	Operations onsite
Block 8	NORTH GAUGER	Operations onsite
Block 8	NORTH GAUGER	Operations onsite
Block 8	Pipe Fitter	Machinery & Specialists Mechanical Group
Block 8	Pipe Fitter	Machinery & Specialists Mechanical Group
Block 9	B Operator	Operations onsite
Block 9	OPERATOR	Operations onsite
Block 9	OPERATOR	Operations onsite
Block 9	OPERATOR	Operations onsite
Block 9	OPERATOR	Operations onsite
Block 9	OPERATOR	Operations onsite
Block 9	OPERATOR	Operations onsite
Block 9	OPERATOR	Operations onsite
Block 9	SOUTH GAUGER	Operations onsite
Block 9	SOUTH GAUGER	Operations onsite

<b>Work area</b>	<b>Original Job Group</b>	<b>Standard Job Group</b>
DOCK	B Operator	Infrastructure / Distribution Operations
DOCK	B Operator	Infrastructure / Distribution Operations
DOCK	B Operator	Infrastructure / Distribution Operations
DOCK	LEAD OPERATOR	Infrastructure / Distribution Operations
DOCK	LEAD OPERATOR	Infrastructure / Distribution Operations
DOCK	LEAD OPERATOR	Infrastructure / Distribution Operations
DOCK	LEAD OPERATOR	Infrastructure / Distribution Operations
DOCK	LEAD OPERATOR	Infrastructure / Distribution Operations
DOCK	LEAD OPERATOR	Infrastructure / Distribution Operations
DOCK	LEAD OPERATOR	Infrastructure / Distribution Operations
DOCK	OPERATOR	Infrastructure / Distribution Operations
DOCK	OPERATOR	Infrastructure / Distribution Operations
DOCK	OPERATOR	Infrastructure / Distribution Operations
DOCK	OPERATOR	Infrastructure / Distribution Operations
DOCK	OPERATOR	Infrastructure / Distribution Operations
DOCK	OPERATOR	Infrastructure / Distribution Operations
DOCK	OPERATOR	Infrastructure / Distribution Operations
DOCK	OPERATOR	Infrastructure / Distribution Operations
DOCK	OPERATOR	Infrastructure / Distribution Operations
DOCK	OPERATOR	Infrastructure / Distribution Operations
East Terminal	A Operator	Infrastructure / Distribution Operations
East Terminal	missing	Operations onsite
East Terminal	missing	Operations onsite
East Terminal	Operator Tech I	Infrastructure / Distribution Operations
East Terminal	Operator Tech II	Infrastructure / Distribution Operations
F5 BLOCK 4	OPERATOR	Operations onsite
GAS LAB	LABORATORY TECHNICIAN	Laboratory Technician
GAS LAB	LABORATORY TECHNICIAN	Laboratory Technician
GAS LAB	LABORATORY TECHNICIAN	Laboratory Technician
missing	0	missing
missing	B Operator	Operations onsite
missing	LABORATORY TECHNICIAN	Laboratory Technician
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
missing	OPERATOR	Operations onsite
North Absorber/Vent	0	missing
North Absorber/Vent	A Operator	Operations onsite
North Absorber/Vent	A Operator	Operations onsite
North Absorber/Vent	missing	Operations onsite
North Absorber/Vent	Operator Tech II	Operations onsite

<b>Work area</b>	<b>Original Job Group</b>	<b>Standard Job Group</b>
North Absorber/Vent	Operator Tech II	Operations onsite
North Absorber/Vent	Operator Technician Trainee	Operations onsite
North Absorber/Vent	Operator Technician Trainee	Operations onsite
NORTH UNIT	0	missing
NORTH UNIT	0	missing
NORTH UNIT	A Operator	Operations onsite
NORTH UNIT	B Operator	Operations onsite
NORTH UNIT	B Operator	Operations onsite
NORTH UNIT	B Operator	Operations onsite
NORTH UNIT	CARPENTER	Infrastructure / Distribution Operations
NORTH UNIT	MACHINIST	Machinery & Specialists Mechanical Group
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
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NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing

<b>Work area</b>	<b>Original Job Group</b>	<b>Standard Job Group</b>
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	missing	missing
NORTH UNIT	OPERATOR	Operations onsite
NORTH UNIT	OPERATOR	Operations onsite
NORTH UNIT	OPERATOR	Operations onsite
NORTH UNIT	OPERATOR	Operations onsite
NORTH UNIT	OPERATOR	Operations onsite
NORTH UNIT	OPERATOR	Operations onsite
NORTH UNIT	OPERATOR	Operations onsite
NORTH UNIT	OPERATOR	Operations onsite
NORTH UNIT	OPERATOR	Operations onsite
NORTH UNIT	Pipe Fitter	Machinery & Specialists Mechanical Group
NORTH UNIT	Pipe Fitter	Machinery & Specialists Mechanical Group
NORTH UNIT	WELDER	Maintenance
NORTH UNIT	WELDER	Maintenance
NORTH UNIT	WELDER	Maintenance
NORTH UNIT	WELDER	Maintenance
NORTH UNIT	WEST GAUGER	Operations onsite
Plant Wide	INSTRUMENT-SPECIALIST	Instrument and Electrical
Plant Wide	INSTRUMENT-SPECIALIST	Instrument and Electrical
Plant Wide	MACHINIST	Machinery & Specialists Mechanical Group
Plant Wide	OPERATOR	Operations onsite
Plant Wide	OPERATOR	Operations onsite
Plant Wide	Pipe Fitter	Machinery & Specialists Mechanical Group
Plant Wide	Pipe Fitter	Machinery & Specialists Mechanical Group
Plant Wide	Pipe Fitter	Machinery & Specialists Mechanical Group
Plant Wide	Pipe Fitter	Machinery & Specialists Mechanical Group
Plant Wide	Pipe Fitter	Machinery & Specialists Mechanical Group
Plant Wide	Pipe Fitter	Machinery & Specialists Mechanical Group
QA LAB	0	Laboratory Technician
QA LAB	0	Laboratory Technician
QA LAB	0	Laboratory Technician
QA LAB	Head Lab Analyst (HNO)	Laboratory Technician
QA LAB	Head Lab Analyst (HNO)	Laboratory Technician
QA LAB	Head Lab Analyst (HNO)	Laboratory Technician
QA LAB	Head Lab Analyst (HNO)	Laboratory Technician
QA LAB	Head Lab Analyst (HNO)	Laboratory Technician
QA LAB	Head Lab Analyst (HNO)	Laboratory Technician
QA LAB	Head Lab Analyst (HNO)	Laboratory Technician
QA LAB	Head Lab Analyst (HNO)	Laboratory Technician
QA LAB	Lab Technician III	Laboratory Technician
QA LAB	Lab Technician III	Laboratory Technician
QA LAB	LABORATORY TECHNICIAN	Laboratory Technician
QA LAB	LABORATORY TECHNICIAN	Laboratory Technician
QA LAB	LABORATORY TECHNICIAN	Laboratory Technician
QA LAB	missing	Laboratory Technician
QA LAB	missing	Laboratory Technician

<b>Work area</b>	<b>Original Job Group</b>	<b>Standard Job Group</b>
QA LAB	missing	Laboratory Technician
QA LAB	missing	Laboratory Technician
QA LAB	Senior Chemist	Laboratory Technician
R&D Lab	Head Lab Analyst (HNO)	Laboratory Technician
R&D Lab	Head Lab Analyst (HNO)	Laboratory Technician
R&D Lab	Head Lab Analyst (HNO)	Laboratory Technician
R&D Lab	Head Lab Analyst (HNO)	Laboratory Technician
Rail Rack	missing	Infrastructure / Distribution Operations
Rail Rack	missing	Infrastructure / Distribution Operations
Rail Rack	OPERATOR	Infrastructure / Distribution Operations
Rail Rack	OPERATOR	Infrastructure / Distribution Operations
Rail Rack	RAIL RACK OPERATOR	Infrastructure / Distribution Operations
SOUTH 2	B Operator	Operations onsite
SOUTH 2	OPERATOR	Operations onsite
SOUTH 2	OPERATOR	Operations onsite
SOUTH 2	OPERATOR	Operations onsite
SOUTH 2	OPERATOR	Operations onsite
SOUTH 2	OPERATOR	Operations onsite
SOUTH 2	OPERATOR	Operations onsite
SOUTH 2	OPERATOR	Operations onsite
SOUTH 2	OPERATOR	Operations onsite
SOUTH 2	Pipe Fitter	Machinery & Specialists Mechanical Group
South Terminal	Operator Tech II	Infrastructure / Distribution Operations
South Terminal	Operator Tech II	Infrastructure / Distribution Operations
South Terminal	Operator Tech II	Infrastructure / Distribution Operations
South Terminal	Operator Technician Trainee	Infrastructure / Distribution Operations
SOUTH UNIT	0	missing
SOUTH UNIT	0	missing
SOUTH UNIT	0	missing
SOUTH UNIT	0	missing
SOUTH UNIT	0	missing
SOUTH UNIT	0	missing
SOUTH UNIT	0	missing
SOUTH UNIT	0	missing
SOUTH UNIT	A Operator	Operations onsite
SOUTH UNIT	B Operator	Operations onsite
SOUTH UNIT	B Operator	Operations onsite
SOUTH UNIT	B Operator	Operations onsite
SOUTH UNIT	B Operator	Operations onsite
SOUTH UNIT	CARPENTER	Infrastructure / Distribution Operations
SOUTH UNIT	CARPENTER	Infrastructure / Distribution Operations
SOUTH UNIT	CARPENTER	Infrastructure / Distribution Operations
SOUTH UNIT	CARPENTER	Infrastructure / Distribution Operations
SOUTH UNIT	CARPENTER	Infrastructure / Distribution Operations
SOUTH UNIT	ELECTRICAL SPECIALIST	Instrument and Electrical
SOUTH UNIT	ELECTRICIAN	Instrument and Electrical
SOUTH UNIT	missing	missing
SOUTH UNIT	missing	missing
SOUTH UNIT	missing	missing





<b>Work area</b>	<b>Original Job Group</b>	<b>Standard Job Group</b>
SOUTH UNIT	OPERATOR	Operations onsite
SOUTH UNIT	Operator Tech II	Operations onsite
SOUTH UNIT	Operator Tech II	Operations onsite
SOUTH UNIT	Operator Tech II	Operations onsite
SOUTH UNIT	Operator Tech II	Operations onsite
SOUTH UNIT	Operator Tech II	Operations onsite
SOUTH UNIT	Pipe Fitter	Machinery & Specialists Mechanical Group
SOUTH UNIT	Pipe Fitter	Machinery & Specialists Mechanical Group
SOUTH UNIT	Pipe Fitter	Machinery & Specialists Mechanical Group
SOUTH UNIT	Pipe Fitter	Machinery & Specialists Mechanical Group
SOUTH UNIT	Pipe Fitter	Machinery & Specialists Mechanical Group
SOUTH UNIT	WELDER	Maintenance
TANK FARM	LEAD OPERATOR	Operations onsite
TANK FARM	OPERATOR	Operations onsite
VAU	A Operator	Operations onsite
VAU	A Operator	Operations onsite
VAU	Operator Tech I	Operations onsite
VAU	Operator Tech II	Operations onsite
VAU	Operator Tech II	Operations onsite
VAU	Operator Tech II	Operations onsite
VAU	Operator Technician Trainee	Operations onsite
VAU	Operator Technician Trainee	Operations onsite
VAU	Operator Technician Trainee	Operations onsite
Water Treatment Plant	Pipe Fitter	Machinery & Specialists Mechanical Group
West Terminal	A Operator	Infrastructure / Distribution Operations
West Terminal	A Operator	Infrastructure / Distribution Operations
West Terminal	A Operator	Infrastructure / Distribution Operations
West Terminal	A Operator	Infrastructure / Distribution Operations
West Terminal	Operator Tech II	Infrastructure / Distribution Operations
West Terminal	Operator Tech II	Infrastructure / Distribution Operations
West Terminal	Operator Tech II	Infrastructure / Distribution Operations
West Terminal	Operator Tech II	Infrastructure / Distribution Operations
West Terminal	Operator Technician Trainee	Infrastructure / Distribution Operations

**Work area**

**Original Job Group**

**Standard Job Group**















































<b>Task</b>	<b>Process Type</b>	<b>Standard Job Group</b>
T034 : Relief Valve Repair & Testing	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T034 : Relief Valve Repair & Testing	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T034 : Relief Valve Repair & Testing	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T034 : Relief Valve Repair & Testing	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T300 : Working W/Manifold, Flanges, Piping, Etc	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T300 : Working W/Manifold, Flanges, Piping, Etc	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T301 : Repair Pump,Compressor,Valve,Equip.,Etc.	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T301 : Repair Pump,Compressor,Valve,Equip.,Etc.	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T301 : Repair Pump,Compressor,Valve,Equip.,Etc.	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T301 : Repair Pump,Compressor,Valve,Equip.,Etc.	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T301 : Repair Pump,Compressor,Valve,Equip.,Etc.	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T301 : Repair Pump,Compressor,Valve,Equip.,Etc.	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T301 : Repair Pump,Compressor,Valve,Equip.,Etc.	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T301 : Repair Pump,Compressor,Valve,Equip.,Etc.	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T301 : Repair Pump,Compressor,Valve,Equip.,Etc.	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T301 : Repair Pump,Compressor,Valve,Equip.,Etc.	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T301 : Repair Pump,Compressor,Valve,Equip.,Etc.	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T303 : Installing Blinds	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T303 : Installing Blinds	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
T303 : Installing Blinds	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
	CBW - MECHANICAL	Machinery & Specialists Mechanical Group
P011 : Routine Maintenance	CBW - OLEFINS MAINTENANCE LAB	maintenance
P012 : Routine Operations	CBW - OSBL	operations onsite
P012 : Routine Operations	CBW - OSBL	operations onsite
P012 : Routine Operations	CBW - OSBL	operations onsite
P012 : Routine Operations	CBW - OSBL	operations onsite
P012 : Routine Operations	CBW - OSBL	operations onsite



<b>Task</b>	<b>Process Type</b>	<b>Standard Job Group</b>
P012 : Routine Operations	CBW - OSBL	operations onsite
T021 : Operator Rounds	CBW - OSBL	operations onsite
	CBW - OSBL	operations onsite
	CBW - OSBL	operations onsite
P002 : Start-Up	CBW - QUENCH	operations onsite
P012 : Routine Operations	CBW - QUENCH	operations onsite
P012 : Routine Operations	CBW - QUENCH	operations onsite
P012 : Routine Operations	CBW - QUENCH	operations onsite
P012 : Routine Operations	CBW - QUENCH	operations onsite
T021 : Operator Rounds	CBW - QUENCH	operations onsite
	CBW - QUENCH	operations onsite
P012 : Routine Operations	CBW - RAIL RACK	Infrastructure / Distribution Operations
P012 : Routine Operations	CBW - RAIL RACK	Infrastructure / Distribution Operations
T031 : Loading Railcars	CBW - RAIL RACK	Infrastructure / Distribution Operations
T031 : Loading Railcars	CBW - RAIL RACK	Infrastructure / Distribution Operations
T031 : Loading Railcars	CBW - RAIL RACK	Infrastructure / Distribution Operations
T031 : Loading Railcars	CBW - RAIL RACK	Infrastructure / Distribution Operations
T031 : Loading Railcars	CBW - RAIL RACK	Infrastructure / Distribution Operations
T031 : Loading Railcars	CBW - RAIL RACK	Infrastructure / Distribution Operations
T031 : Loading Railcars	CBW - RAIL RACK	Infrastructure / Distribution Operations
T031 : Loading Railcars	CBW - RAIL RACK	Infrastructure / Distribution Operations
T031 : Loading Railcars	CBW - RAIL RACK	Infrastructure / Distribution Operations
T031 : Loading Railcars	CBW - RAIL RACK	Infrastructure / Distribution Operations
T031 : Loading Railcars	CBW - RAIL RACK	Infrastructure / Distribution Operations
T031 : Loading Railcars	CBW - RAIL RACK	Infrastructure / Distribution Operations
P012 : Routine Operations	CBW - UPPER FURNACE	Machinery & Specialists Mechanical Group
P012 : Routine Operations	CBW - UPPER FURNACE	Machinery & Specialists Mechanical Group
P001 : Shutdown		Machinery & Specialists Mechanical Group
P001 : Shutdown		Machinery & Specialists Mechanical Group

**APPENDIX C**

# **Statistical Analysis of Full-Shift Samples**

Full-Shift Personal Air Concentration Data Summary Statistics for 1,3 - Butadiene - All Durations >= 4 hr, concentrations given in ppm

Job Group	Operation Type	N Samples	% Non-Detects	N Detects	What-If Scenario	Central Estimate	High-End Estimate	% DL < 0.01ppm	% DL 0.01 to 0.25ppm	% DL 0.25 to 1ppm	% DL > 1ppm	Kaplan Meier Statistics									
												Min	50th	90th	95th	KM-Mean	SE	95LCL Mean	95UCL Mean	Max	
<b>Worker Personal Air Concentrations</b>																					
Infrastructure/Distribution Operations	ROUTINE	455	78%	102	--	0.03	0.45	7%	84%	9%	0%	0.0065	NA	0.210	0.450	0.12	0.038	0.045	0.193	16.400	
	NONROUTINE	3	33%	2	--	0.37	0.83	0%	100%	0%	0%	0.11	0.370	NA	NA	0.523	0.177	0.176	0.870	0.830	
Instrument and Electrical	ROUTINE	313	91%	29	--	0.02	0.16	9%	71%	20%	0%	0.0080	NA	0.021	0.160	0.068	0.033	0.003	0.133	10.000	
	NONROUTINE	5	100%	0	--	0.13	0.13	0%	100%	0%	0%	0.18	NA	NA	NA	NA	NA	NA	NA	0.190	
	TURNAROUND	4	50%	2	--	0.02	0.16	0%	100%	0%	0%	0.020	0.020	NA	NA	0.055	0.043	-0.029	0.139	0.160	
Laboratory Technician	ROUTINE	215	73%	57	--	0.03	0.24	11%	86%	3%	0%	0.0064	NA	0.120	0.246	0.063	0.016	0.031	0.094	2.932	
	NONROUTINE	1	0%	1	60.03	--	--	--	--	--	--	60.029	NA	NA	NA	60.03	NA	NA	NA	60.03	
Machinery and Specialists Group	ROUTINE	222	80%	44	--	0.01	0.28	12%	88%	0%	0%	0.008	NA	0.060	0.280	0.087	0.023	0.042	0.133	3.310	
	TURNAROUND	8	63%	3	--	0.01	0.01	40%	60%	0%	0%	0.009	0.009	NA	NA	0.010	0.001	0.008	0.011	0.013	
Maintenance	ROUTINE	354	69%	109	--	0.15	0.23	17%	37%	46%	0%	0.001	NA	0.230	0.240	0.109	0.010	0.089	0.129	2.100	
	NONROUTINE	2	50%	1	--	0.36	0.65	0%	100%	0%	0%	0.064	NA	NA	NA	0.650	NA	NA	NA	0.650	
	TURNAROUND	33	55%	15	--	0.03	4.92	28%	72%	0%	0%	0.009	0.019	3.001	5.700	0.792	0.328	0.148	1.435	8.001	
Operations Onsite	ROUTINE	1952	88%	229	--	0.02	0.20	24%	69%	7%	0%	0.000	0.001	0.037	0.190	0.074	0.016	0.043	0.105	16.000	
	NONROUTINE	38	95%	2	--	0.03	0.13	0%	100%	0%	0%	0.012	NA	NA	0.043	0.064	0.029	0.007	0.120	0.830	
	TURNAROUND	1633	93%	116	--	0.03	0.06	14%	86%	0%	0%	0.007	NA	0.017	0.060	0.111	0.028	0.057	0.166	39.000	
Safety Health and Engineering	ROUTINE	21	71%	6	--	0.04	0.36	0%	100%	0%	0%	0.038	NA	0.191	0.364	0.158	0.036	0.087	0.229	0.789	
Missing Job Group Designation	ROUTINE	378	94%	24	--	0.01	0.10	42%	57%	1%	0%	0.002	NA	NA	0.037	0.024	0.004	0.016	0.032	1.300	
<b>ONU Personal Air Concentrations</b>																					
Occupational Non-User	ROUTINE	39	77%	9	--	0.01	0.02	17%	83%	0%	0%	0.008	NA	0.013	0.033	0.012	0.001	0.010	0.014	0.038	

Abbreviations and Task Codes

DL = detection limit, KM - Kaplan-Meier, LCL - lower confidence limit, N - number, ND - non-detect, P = Personal, SD- standard deviation, SE - standard error,

Notes

1. NA = not available. Kaplan-Meier cannot be calculated on dataset with only non-detects. Standard deviation cannot be calculated on samples size =1.
2. Outliers have not been excluded from the statistics.
3. The selection of central and high estimates were modeled after the RISK EVALUATION FOR TCE. Specifically sample size cut-points and assignment of
  - N=1
  - N=2
  - N=3-5
  - N=6+

The selection of non-detect imputation values (i.e. LOD/sqrt(2) or LOD/2) was based on a review of GSD for the original data with ND = 1/2 LOD. If the geometric standard deviation (GSD) of the data is <3.0, then NDs were imputed using LOD/sqrt(2). If the GSD was 3.0 or greater, then NDs were imputed with LOD/2.

Statistics using 1/2 DL for ND									Statistics using DL/sqrt(2) for ND									
Min	50th	90th	95th	ArithMean	ArithSD	GeoMean	GeoSD	Max	Min	50th	90th	95th	ArithMean	ArithSD	GeoMean	GeoSD	Max	
0.003	0.025	0.210	0.449	0.140	0.802	0.039	3.749	16.400	0.005	0.035	0.211	0.495	0.154	0.802	0.051	3.458	16.400	
0.055	0.370	0.738	0.784	0.418	0.390	0.257	4.029	0.830	0.078	0.370	0.738	0.784	0.426	0.379	0.288	3.332	0.830	
0.004	0.020	0.152	0.160	0.104	0.577	0.028	4.421	10.000	0.006	0.028	0.215	0.226	0.124	0.578	0.038	4.292	10.000	
0.090	0.095	0.095	0.095	0.093	0.003	0.093	1.030	0.095	0.127	0.134	0.134	0.134	0.132	0.004	0.131	1.030	0.134	
0.013	0.017	0.118	0.139	0.052	0.072	0.027	3.297	0.160	0.018	0.020	0.118	0.139	0.054	0.070	0.033	2.892	0.160	
0.003	0.025	0.137	0.235	0.074	0.233	0.027	3.488	2.932	0.005	0.035	0.166	0.265	0.083	0.233	0.034	3.241	2.932	
60.03	60.03	60.03	60.03	60.029	NA	60.03	NA	60.03	60.03	60.03	60.03	60.03	60.03	60.03	NA	60.03	NA	60.03
0.004	0.006	0.077	0.277	0.089	0.341	0.015	4.055	3.310	0.006	0.009	0.077	0.277	0.094	0.340	0.020	3.707	3.310	
0.004	0.006	0.011	0.012	0.007	0.003	0.007	1.494	0.013	0.006	0.008	0.011	0.012	0.008	0.002	0.008	1.269	0.013	
0.000	0.152	0.230	0.234	0.132	0.169	0.062	4.677	2.100	0.001	0.210	0.230	0.240	0.156	0.173	0.078	4.367	2.100	
0.032	0.341	0.588	0.619	0.341	0.437	0.144	8.409	0.650	0.045	0.348	0.590	0.620	0.348	0.428	0.172	6.581	0.650	
0.004	0.029	2.721	4.919	0.793	1.849	0.062	9.367	8.001	0.006	0.042	2.721	4.919	0.798	1.847	0.074	8.405	8.001	
0.000	0.020	0.133	0.200	0.098	0.701	0.021	3.787	16.000	0.000	0.028	0.189	0.210	0.109	0.701	0.028	3.601	16.000	
0.006	0.023	0.095	0.095	0.056	0.132	0.030	2.410	0.830	0.008	0.032	0.134	0.134	0.070	0.132	0.042	2.323	0.830	
0.004	0.020	0.025	0.060	0.119	1.126	0.019	2.840	39.000	0.005	0.028	0.035	0.060	0.125	1.125	0.026	2.678	39.000	
0.019	0.027	0.191	0.364	0.098	0.179	0.045	2.928	0.789	0.027	0.038	0.191	0.364	0.106	0.176	0.058	2.531	0.789	
0.001	0.012	0.060	0.095	0.031	0.087	0.012	3.285	1.200	0.001	0.017	0.085	0.121	0.038	0.094	0.016	3.157	1.200	
0.004	0.006	0.013	0.017	0.008	0.007	0.007	1.678	0.038	0.006	0.008	0.013	0.017	0.010	0.006	0.009	1.486	0.038	

Review of Non-Detects and Detection Limits										
N ND	Min	25th	50th	75th	95th	Max	N_DL_lessthan_0.01ppm	N_DL_0.01to0.25ppm	N_DL_0.25to1ppm	N_DL_greaterthan1ppm
353	0.006	0.035	0.040	0.113	0.267	0.700	26	296	31	0
1	0.11	0.11	0.11	0.11	0.11	0.11	0	1	0	0
284	0.008	0.011	0.040	0.213	0.320	0.352	26	201	57	0
5	0.18	0.18	0.19	0.19	0.19	0.19	0	5	0	0
2	0.026	0.026	0.027	0.027	0.027	0.027	0	2	0	0
158	0.0064	0.018	0.050	0.060	0.202	0.452	17	136	5	0
NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
178	0.0080	0.010	0.011	0.040	0.068	0.220	21	157	0	0
5	0.0088	0.0095	0.010	0.011	0.011	0.011	2	3	0	0
245	0.0008	0.012	0.17	0.32	0.32	0.38	42	91	112	0
1	0.064	0.064	0.064	0.064	0.064	0.064	0	1	0	0
18	0.01	0.02	0.05	0.06	0.06	0.07	5	13	0	0
1723	0.0040	0.010	0.040	0.050	0.267	0.450	420	1189	114	0
36	0.012	0.038	0.045	0.081	0.190	0.190	0	36	0	0
1517	0.0071	0.030	0.040	0.040	0.050	0.640	216	1300	1	0
15	0.038	0.044	0.049	0.055	0.063	0.064	0	15	0	0
354	0.0019	0.0073	0.019	0.036	0.13	1.30	147	203	3	1
30	0.0080	0.010	0.011	0.011	0.012	0.018	5	25	0	0

**APPENDIX D**

# **Statistical Analysis of Short-Term and Task Samples**

Short-term Personal Air Concentration Data Summary Statistics for 1,3 - Butadiene (concentrations given in ppm)

Task Code	Operation Type	Sample Duration	N Samples	% Non-Detects	What-If Scenario	Central Estimate	High-End Estimate	% DL < 0.1 ppm	% DL 0.1 ppm to < 0.5	% DL 0.5 ppm to < 1 ppm	% DL 1 ppm to < 5	% DL > 5ppm	Kaplan Meier Statistics									
													Min	50th	90th	95th	KM-Mean	SE	95LCL	95UCL	Max	
<b>Personal Air Sampling</b>																						
1 - Unloading & Loading	ROUTINE	<=15	89	45	--	1.05	14.60	10%	55%	13%	23%	0%	0.044	1.0	8.1	17	2.7	0.52	1.7	3.7	26	
		>15	158	45	--	1.10	18.00	11%	54%	11%	24%	0%	0.024	0.73	8.0	18	3.6	0.77	2.1	5.1	89	
	OTHER	<=15	2	100	--	0.20	0.20	0%	100%	0%	0%	0%	0%	0.20	NA	NA	NA	NA	NA	NA	NA	0.20
		>15	2	50	--	0.53	1.00	0%	0%	0%	100%	0%	0%	0.051	0.051	0.051	0.051	0.051	NA	NA	NA	1.0
2 - Handling Waste	ROUTINE	<=15	7	100	--	0.05	0.61	14%	71%	0%	14%	0%	0.063	NA	NA	NA	NA	NA	NA	NA	1.6	
		>15	10	90	--	0.23	1.32	22%	33%	22%	22%	0%	0.081	NA	0.69	0.69	0.69	NA	NA	NA	3.7	
3 - Cleaning & Maintaining Equipment	ROUTINE	<=15	102	80	--	0.22	14.90	1%	65%	26%	7%	1%	0.060	NA	2.7	15	3.9	1.4	1.1	6.7	120	
		>15	159	73	--	0.21	6.23	18%	52%	15%	15%	1%	0.022	0.063	2.6	8.3	1.8	0.77	0.28	3.3	110	
	TURNAROUND	>15	1	0	0.11	--	--	--	--	--	--	--	--	0.11	NA	NA	NA	0.11	NA	NA	NA	0.11
	OTHER	<=15	14	71	--	0.35	4.47	0%	20%	60%	20%	0%	0%	0.010	0.010	0.010	NA	0.72	0.79	-0.83	2.3	10
>15		18	83	--	0.06	1.55	53%	27%	0%	20%	0%	0%	0.00010	0.010	0.63	2.4	0.19	0.17	-0.14	0.53	2.8	
4 - Sample Collection and Analysis	ROUTINE	<=15	187	89	--	0.37	1.60	17%	37%	37%	10%	0%	0.030	NA	0.51	1.3	0.52	0.04	0.44	0.59	4.8	
		>15	237	89	--	0.15	2.02	15%	62%	22%	0%	0%	0%	0.017	NA	0.36	2.10	0.49	0.12	0.25	0.74	18.0
	OTHER	<=15	1	100	0.32	--	--	0%	100%	0%	0%	0%	0%	0.32	NA	NA	NA	NA	NA	NA	NA	0.32
		>15	1	100	0.20	--	--	0%	100%	0%	0%	0%	0%	0.20	NA	NA	NA	NA	NA	NA	NA	0.20
6 - Other Tasks	ROUTINE	<=15	31	71	--	0.28	1.47	0%	82%	14%	5%	0%	0.19	0.20	0.54	2.1	0.49	0.22	0.06	0.92	6.5	
		>15	21	81	--	0.13	3.70	24%	71%	0%	6%	0%	0%	0.020	NA	0.17	3.7	0.49	0.31	-0.11	1.1	4.7
	OTHER	<=15	18	83	--	0.40	0.80	7%	7%	80%	7%	0%	0%	0.068	0.15	0.25	0.75	0.21	0.05	0.12	0.30	1.5
		>15	5	60	--	0.29	8.70	67%	0%	33%	0%	0%	0%	0.010	NA	NA	NA	2.0	2.1	-2.2	6.2	8.7

Abbreviations and Task Codes

DL = detection limit, KM - Kaplan-Meier, LCL - lower confidence limit, N - number, ND - non-detect, P = Personal, SD- standard deviation, SE - standard error, UCL - upper confidence limit

1 = Unloading and transferring 1,3-butadiene to and from storage containers to process vessels

2 = Handling, transporting and disposing of waste containing 1,3-butadiene

3 = Cleaning and maintaining equipment

4 = Sampling chemicals, formulations, or products containing 1,3-butadiene for quality control

5 = Repackaging chemicals, formulations, or products containing 1,3-butadiene

6 = Performing other work activities in or near areas where 1,3-butadiene is used

Notes

1. NA = not available. Kaplan-Meier cannot be calculated on dataset with only non-detects. Standard deviation cannot be calculated on samples size =1.

2. Outliers have not been excluded from the statistics.

3. The selection of central and high estimates were modeled after the RISK EVALUATION FOR TCE. Specifically sample size cut-points and assignment of

- N=1
- N=2
- N=3-5
- N=6+

The selection of non-detect imputation values (i.e. LOD/sqrt(2) or LOD/2) was based on a review of GSD for the original data with ND = 1/2 LOD. If the

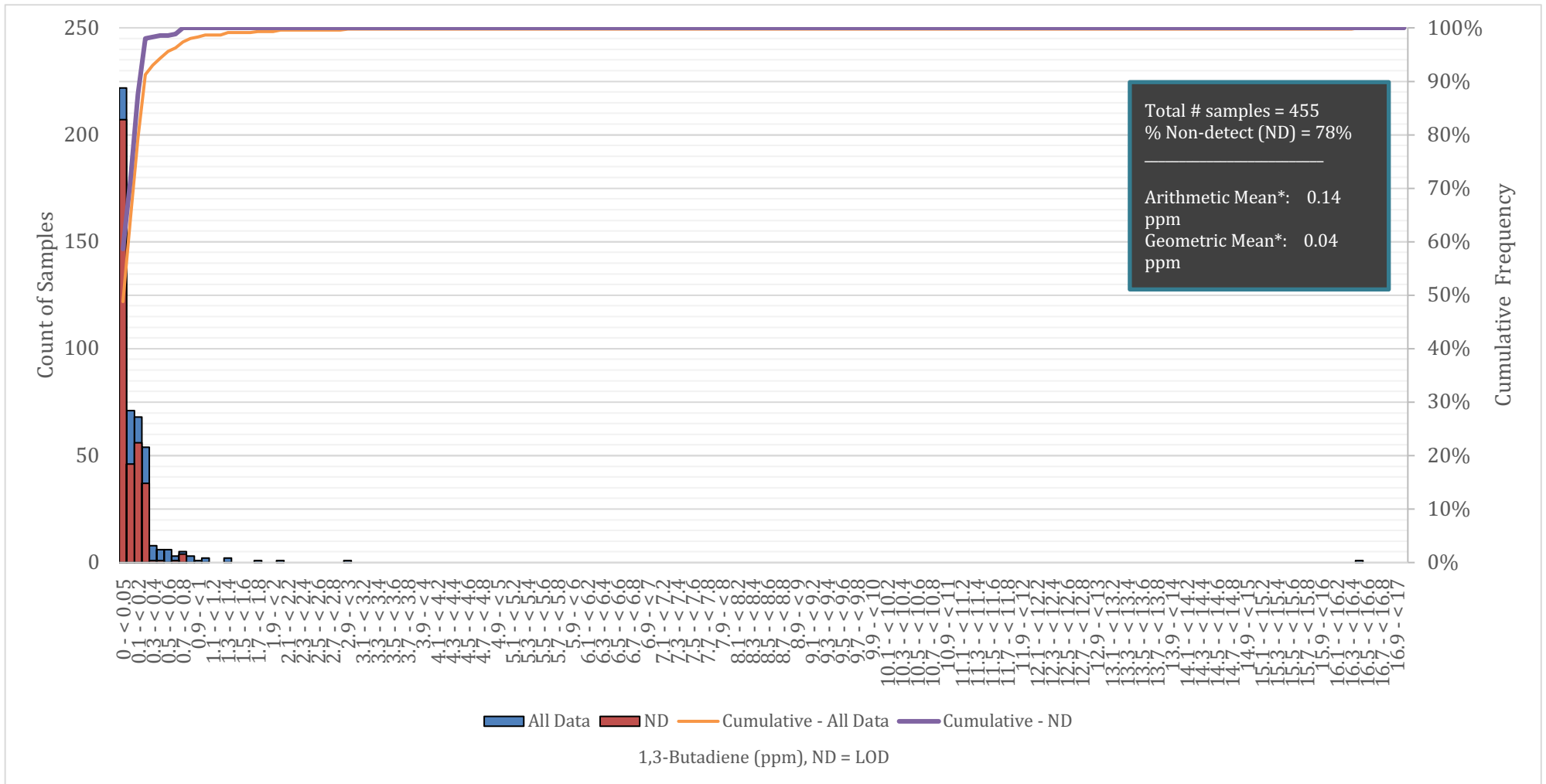
Statistics using DL/2 for ND									Statistics using DL/sqrt(2) for ND								
Min	50th	90th	95th	ArithMean	ArithSD	GeoMean	GeoSD	Max	Min	50th	90th	95th	ArithMean	ArithSD	GeoMean	GeoSD	Max
0.022	1.1	6.8	15	2.8	4.9	0.82	5.4	26	0.031	1.3	6.8	15	2.8	4.9	0.96	4.8	26
0.012	1.1	7.8	18	3.7	9.6	0.78	6.1	89	0.017	1.1	7.8	18	3.8	9.6	0.91	5.5	89
0.10	0.10	0.10	0.10	0.10	0	0.10	1.0	0.10	0.14	0.14	0.14	0.14	0.14	0	0.14	1.0	0.14
0.051	0.28	0.46	0.48	0.28	0.32	0.16	5.0	0.50	0.051	0.38	0.64	0.67	0.38	0.46	0.19	6.4	0.71
0.032	0.050	0.42	0.61	0.19	0.28	0.10	3.1	0.80	0.045	0.071	0.60	0.87	0.27	0.39	0.14	3.1	1.13
0.041	0.23	0.80	1.3	0.43	0.54	0.22	3.5	1.8	0.057	0.33	1.04	1.8	0.58	0.76	0.31	3.4	2.6
0.030	0.22	3.1	15	3.6	14.3	0.37	5.1	120	0.042	0.30	3.7	15	3.6	14.2	0.49	4.5	120
0.020	0.21	2.6	6.2	2.0	9.6	0.27	5.0	110	0.022	0.28	2.9	6.2	2.1	9.6	0.35	4.6	110
0.11	0.11	0.11	0.11	0.11	NA	0.11	NA	0.11	0.108	0.11	0.11	0.11	0.11	NA	0.11	NA	0.11
0.010	0.35	1.5	4.5	1.1	2.6	0.20	7.7	10.0	0.010	0.49	2.1	4.9	1.2	2.6	0.26	8.2	10.0
0.000050	0.062	1.2	1.6	0.41	0.67	0.07	12	2.4	0.000071	0.088	1.7	2.0	0.50	0.79	0.10	12	2.4
0.015	0.26	0.80	1.3	0.39	0.58	0.22	2.9	4.8	0.021	0.37	1.06	1.6	0.48	0.59	0.30	2.8	4.8
0.0085	0.15	0.38	2.0	0.53	1.9	0.15	3.5	18	0.0120	0.21	0.50	2.0	0.59	1.9	0.21	3.3	18
0.16	0.16	0.16	0.16	0.16	NA	0.16	NA	0.16	0.23	0.23	0.23	0.23	0.23	NA	0.23	NA	0.23
0.10	0.10	0.10	0.10	0.10	NA	0.10	NA	0.10	0.14	0.14	0.14	0.14	0.14	NA	0.14	NA	0.14
0.10	0.20	0.54	1.4	0.50	1.2	0.27	2.2	6.5	0.14	0.28	0.54	1.5	0.57	1.2	0.34	2.1	6.5
0.010	0.13	0.60	3.7	0.53	1.2	0.15	4.0	4.7	0.014	0.17	0.85	3.7	0.58	1.2	0.20	3.7	4.7
0.034	0.29	0.45	0.75	0.31	0.18	0.26	2.0	0.75	0.048	0.40	0.54	0.80	0.41	0.22	0.35	2.0	1.06
0.0050	0.29	5.3	7.0	1.9	3.8	0.17	16	8.7	0.0071	0.32	5.4	7.0	1.9	3.8	0.21	14	8.7



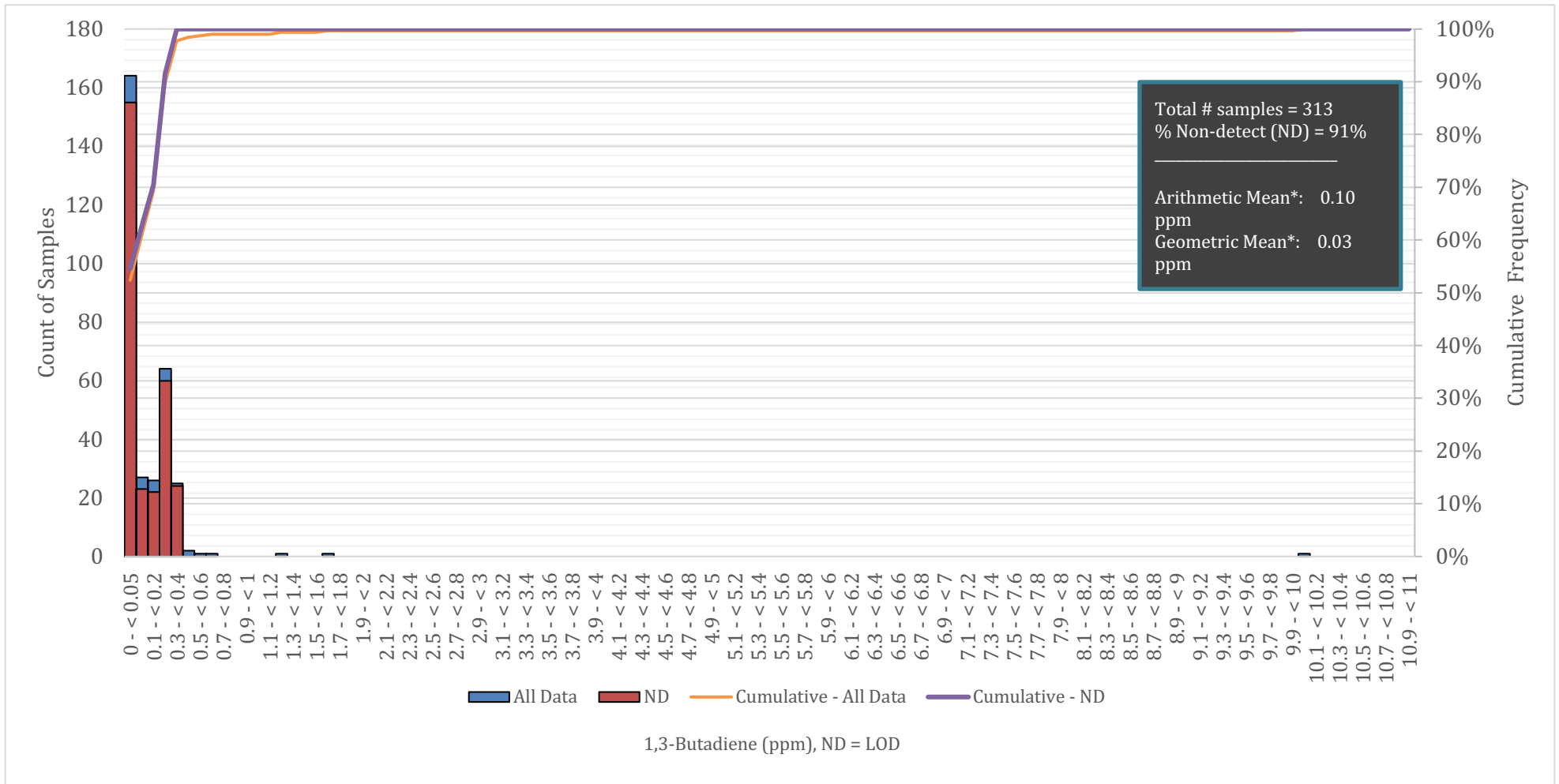
Review of Detection Limits for Non-Detected Observations											
N ND	Min	25th	50th	75th	95th	Max	N_DL_lessthan0.1ppm	N_DL_0.1tolessthan0.5ppm	N_DL_0.5tolessthan1ppm	N_DL_1to5ppm	N_DL_greaterthan5ppm
40	0.04	0.24	0.35	0.76	2.01	2.10	4	22	5	9	0
71	0.02	0.18	0.30	0.70	3.66	4.52	8	38	8	17	0
2	0.20	0.20	0.20	0.20	0.20	0.20	0	2	0	0	0
1	1.00	1.00	1.00	1.00	1.00	1.00	0	0	0	1	0
7	0.06	0.10	0.10	0.34	1.22	1.60	1	5	0	1	0
9	0.08	0.25	0.25	0.77	2.68	3.66	2	3	2	2	0
82	0.06	0.25	0.35	0.59	1.40	6.33	1	53	21	6	1
116	0.04	0.15	0.30	0.60	2.50	6.33	21	60	17	17	1
NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
10	0.15	0.70	0.70	0.70	2.91	3.00	0	2	6	2	0
15	0.00010	0.054	0.10	0.22	2.45	2.80	8	4	0	3	0
167	0.03	0.23	0.48	0.60	1.44	2.52	28	61	61	17	0
210	0.02	0.11	0.23	0.41	0.70	2.00	32	131	46	1	0
1	0.32	0.32	0.32	0.32	0.32	0.32	0	1	0	0	0
1	0.20	0.20	0.20	0.20	0.20	0.20	0	1	0	0	0
22	0.20	0.40	0.40	0.48	0.67	1.20	0	18	3	1	0
17	0.02	0.12	0.20	0.38	0.56	1.20	4	12	0	1	0
15	0.07	0.56	0.58	0.61	0.89	1.50	1	1	12	1	0
3	0.01	0.04	0.08	0.32	0.52	0.57	2	0	1	0	0

**APPENDIX E**

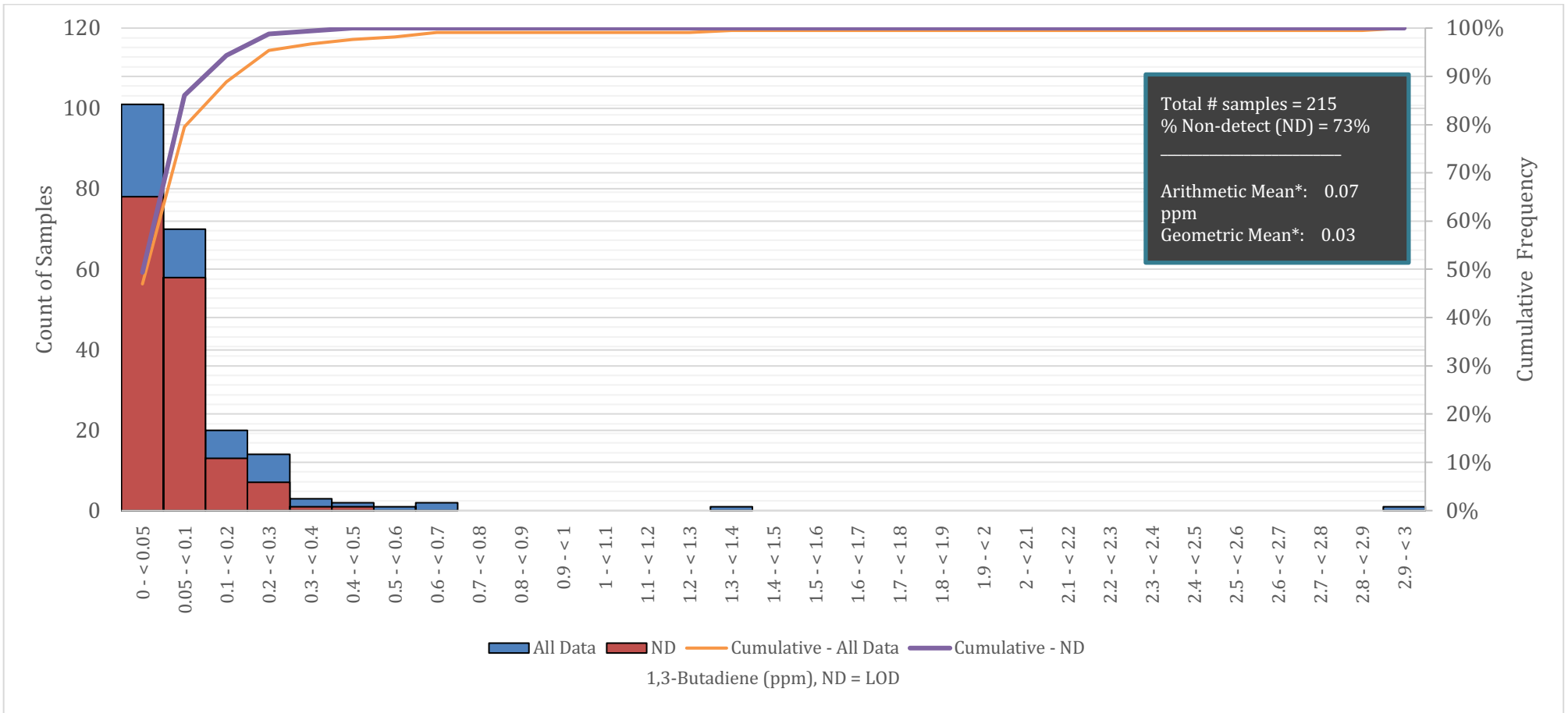
**Figures 6-18**



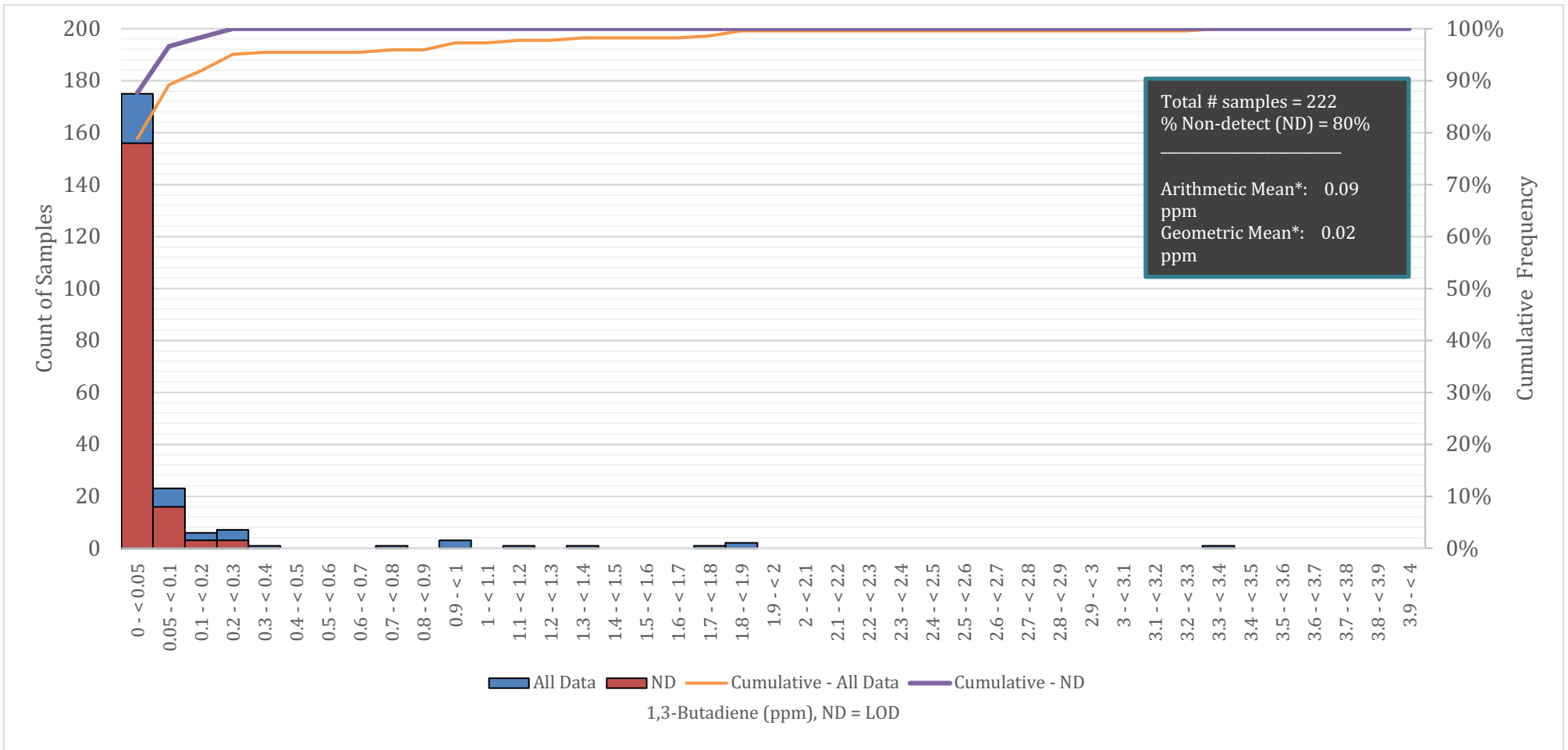
**Figure 6. Distribution of Infrastructure/Distribution Routine Full-Shift Personal Air Concentrations**



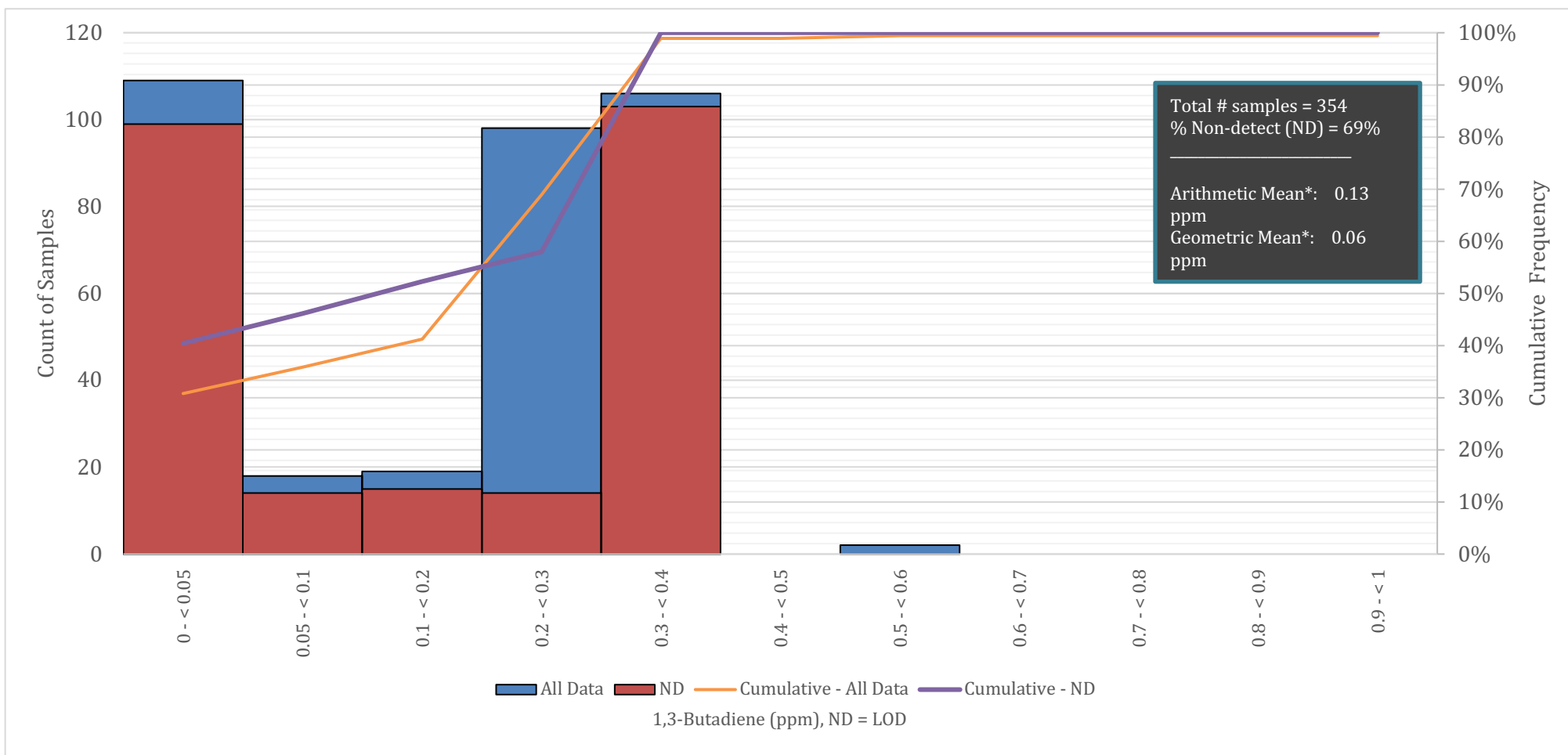
**Figure 7. Distribution of Instrument and Electrical Routine Full-Shift Personal Air Concentrations**



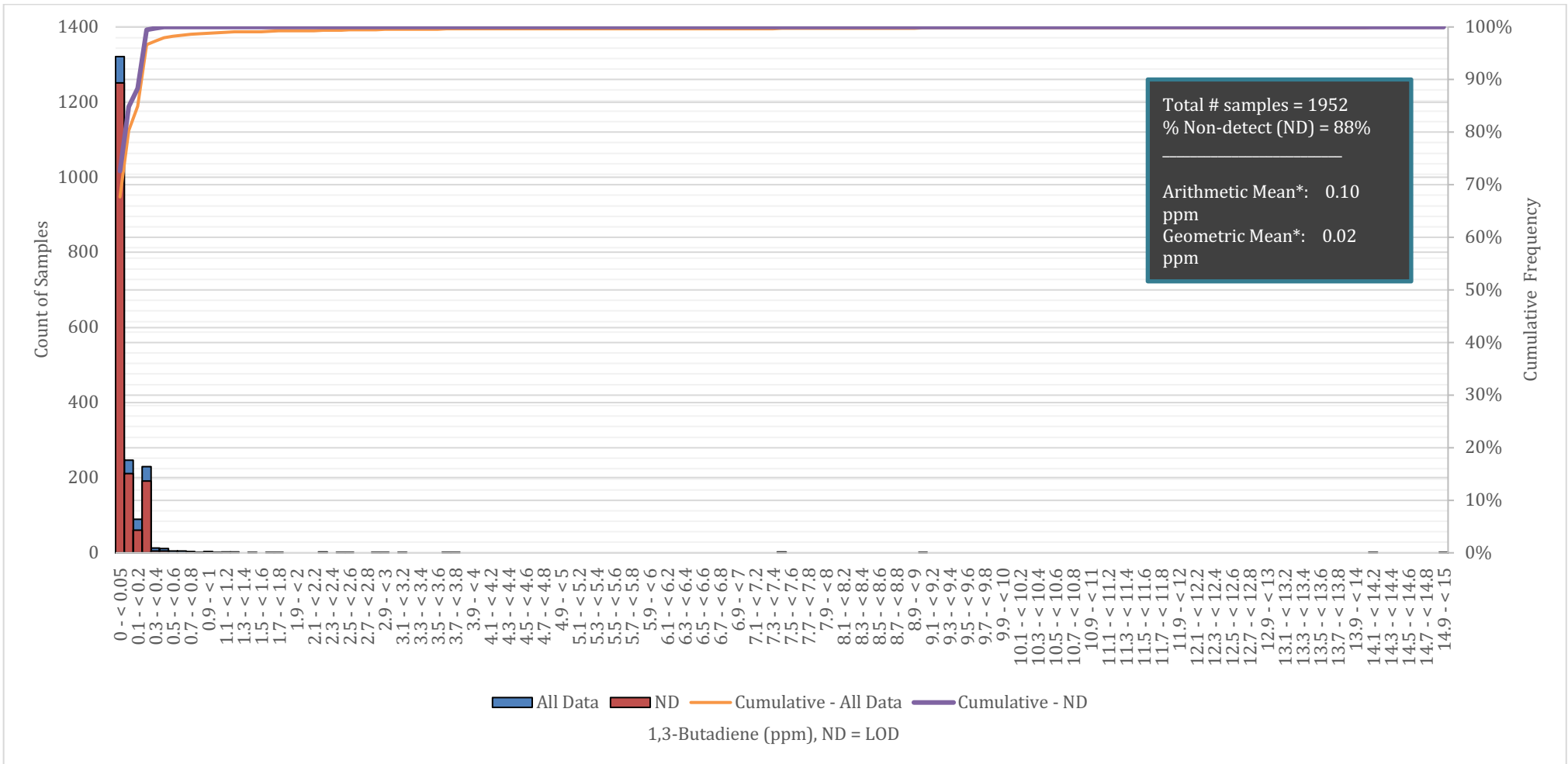
**Figure 8. Distribution of Laboratory Technicians Full-Shift Personal Air Concentrations**



**Figure 9. Distribution of Machinery & Specialists Mechanical Full-Shift Personal Air Concentrations**

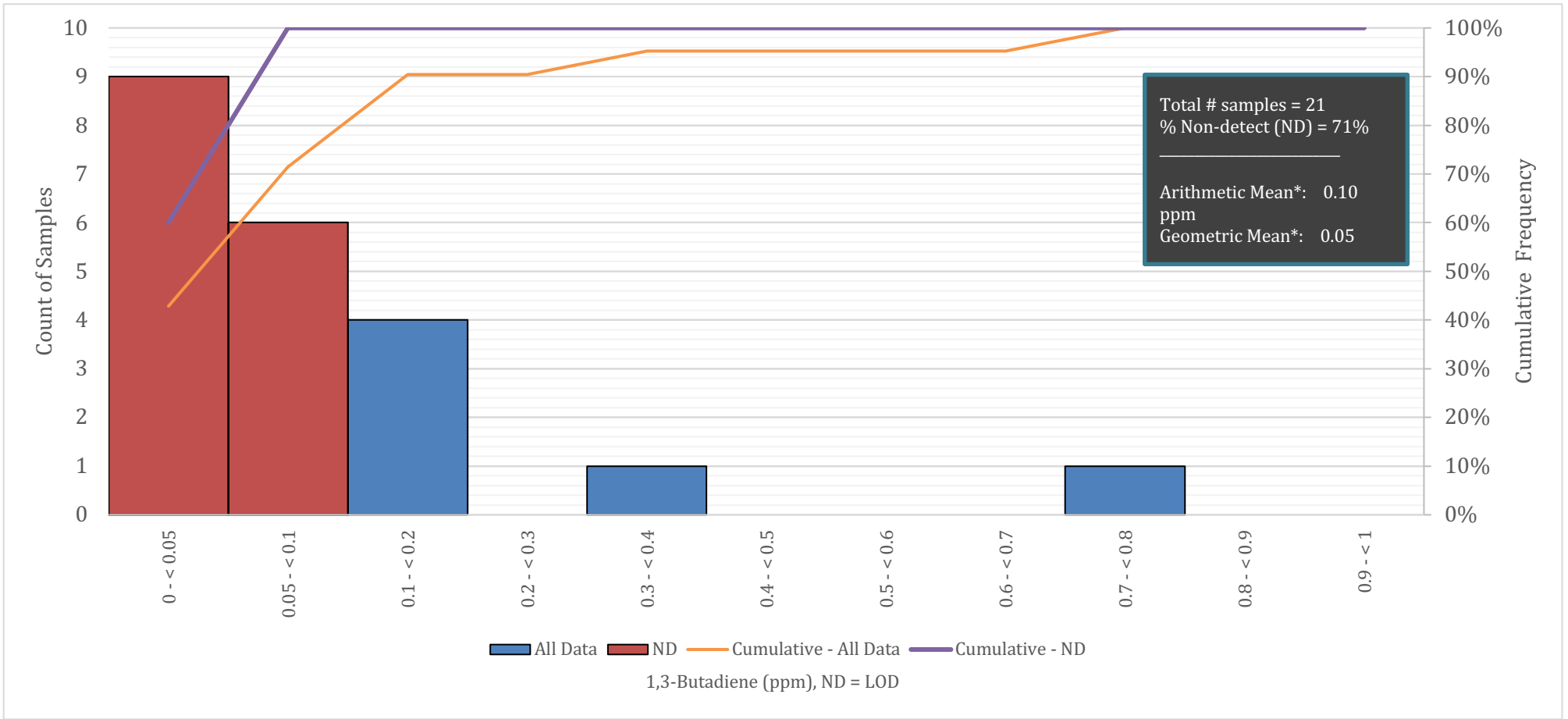


**Figure 10. Distribution of Maintenance Full-Shift Personal Air Concentrations**

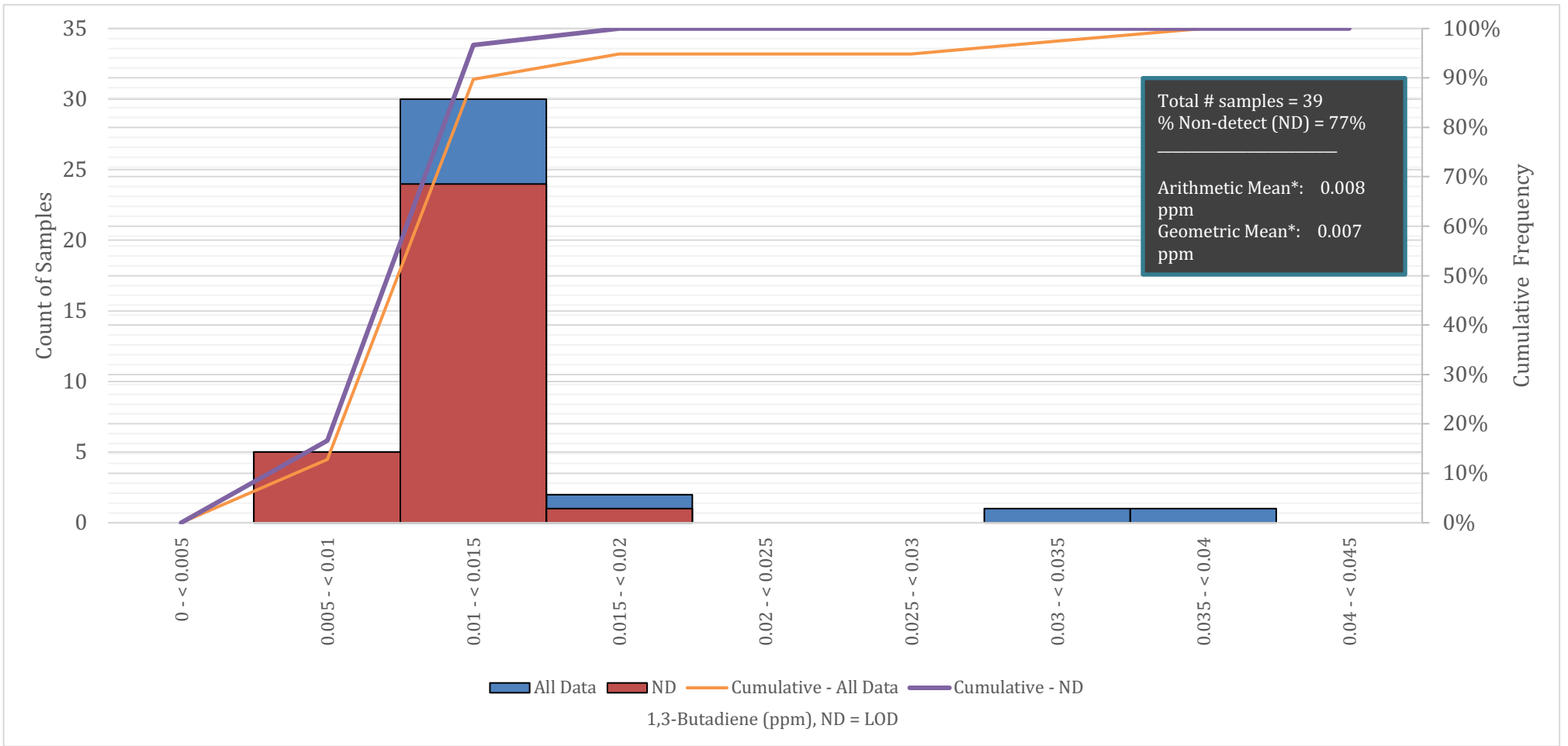


**Figure 11. Distribution of Operations Onsite Full-Shift Personal Air Concentrations**

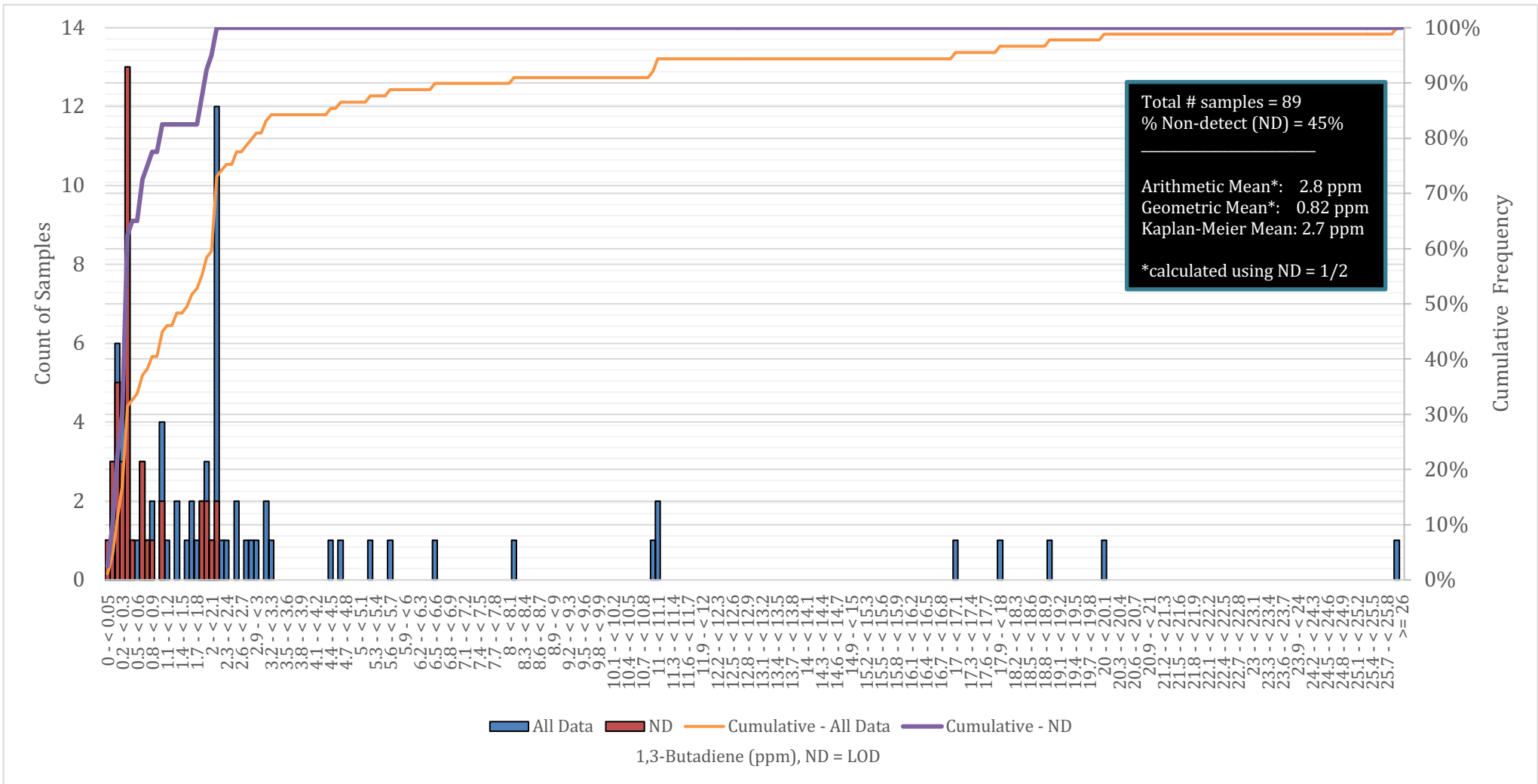




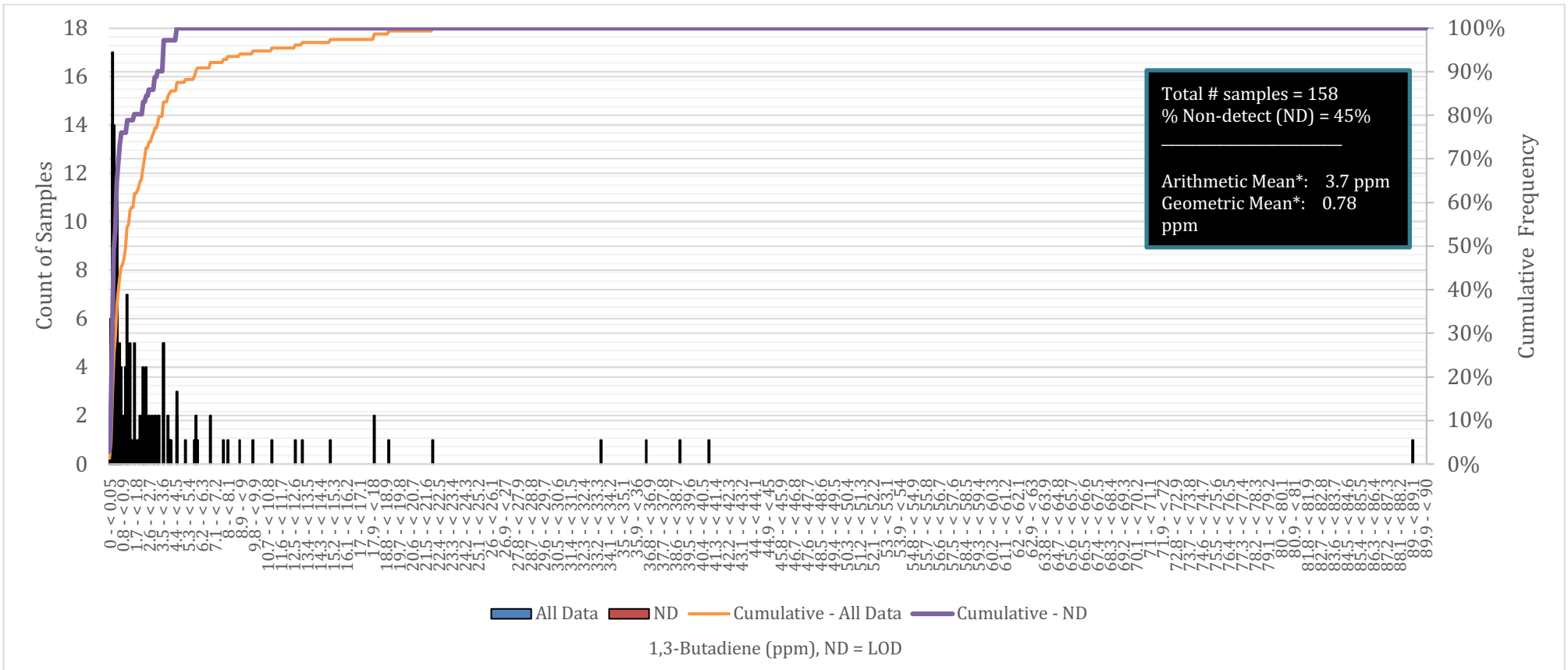
**Figure 12. Distribution of SHE Personal Air Concentrations**



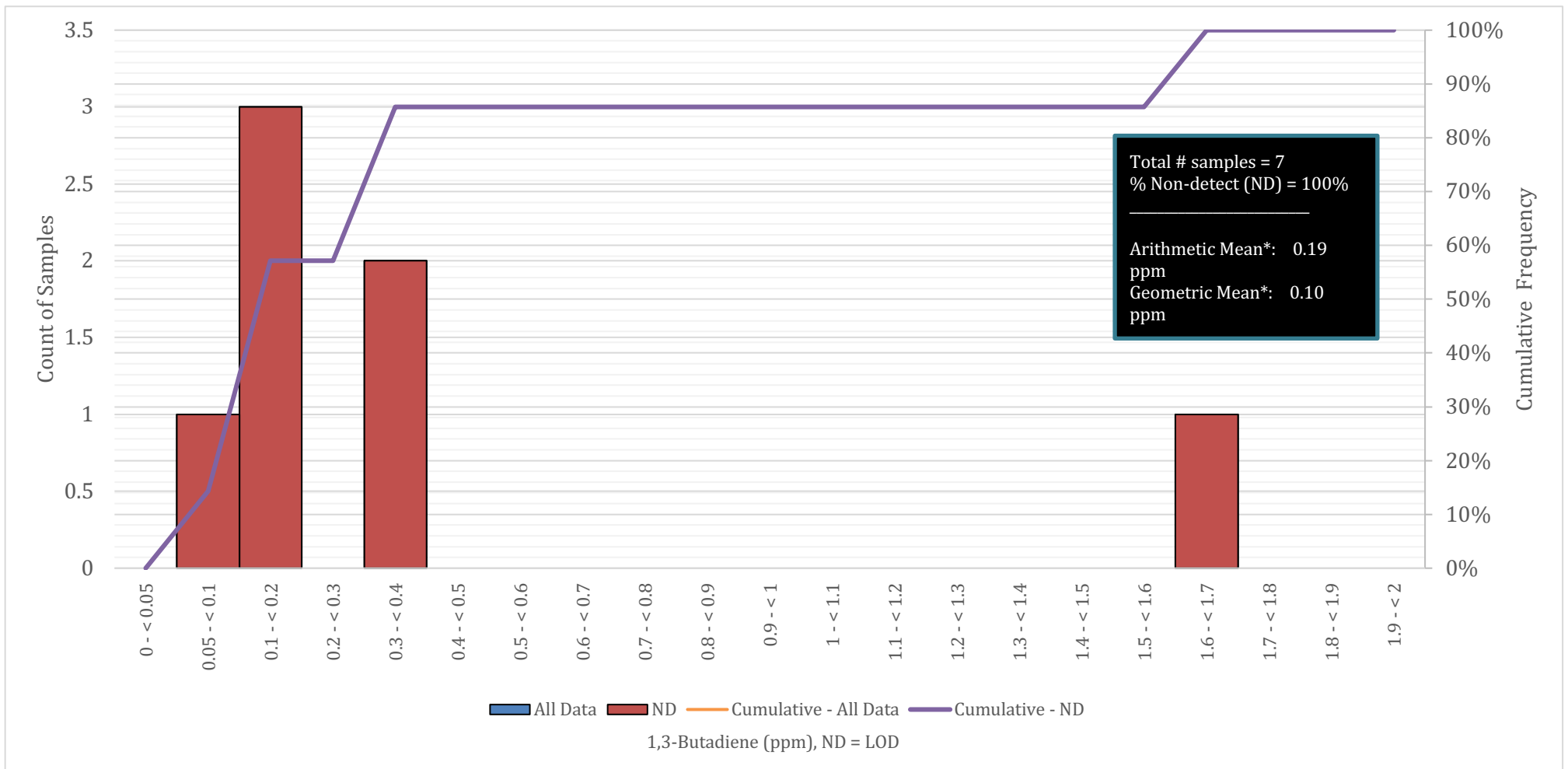
**Figure 13. Distribution of ONU Personal Air Concentrations**



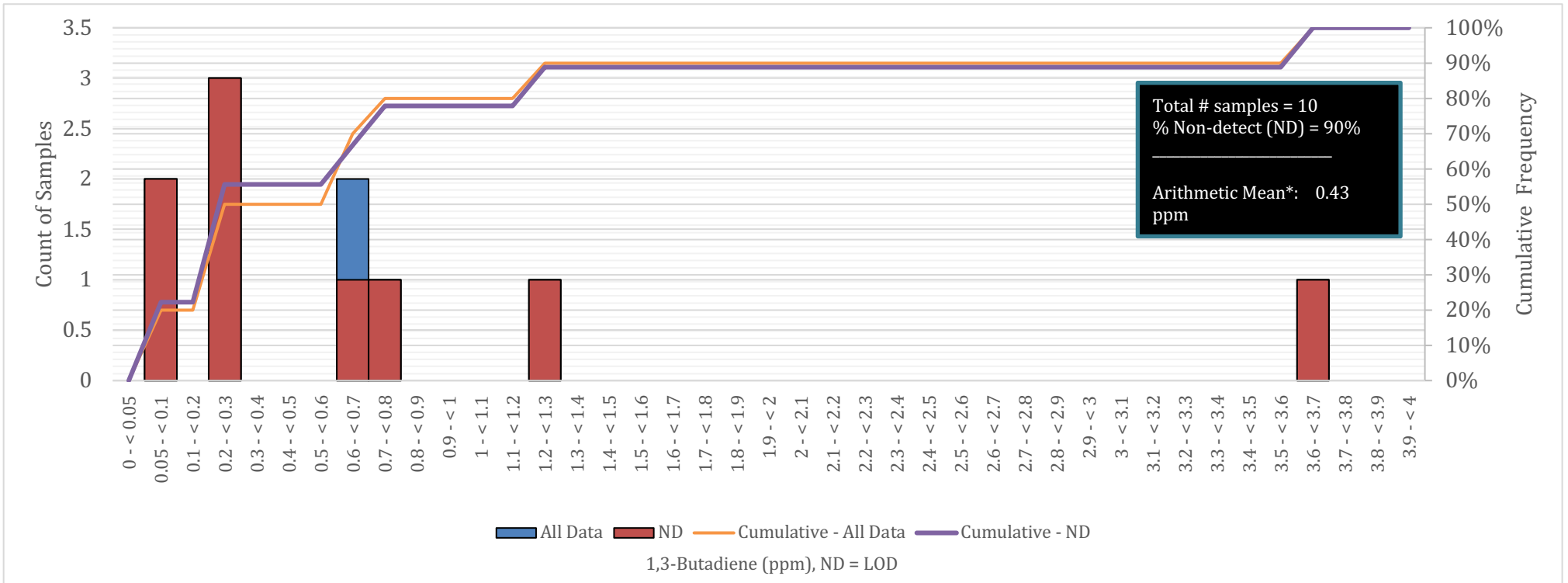
**Figure 14a. Distribution of Unloading/Loading Task Personal Air Concentrations, ≤ 15 minutes**



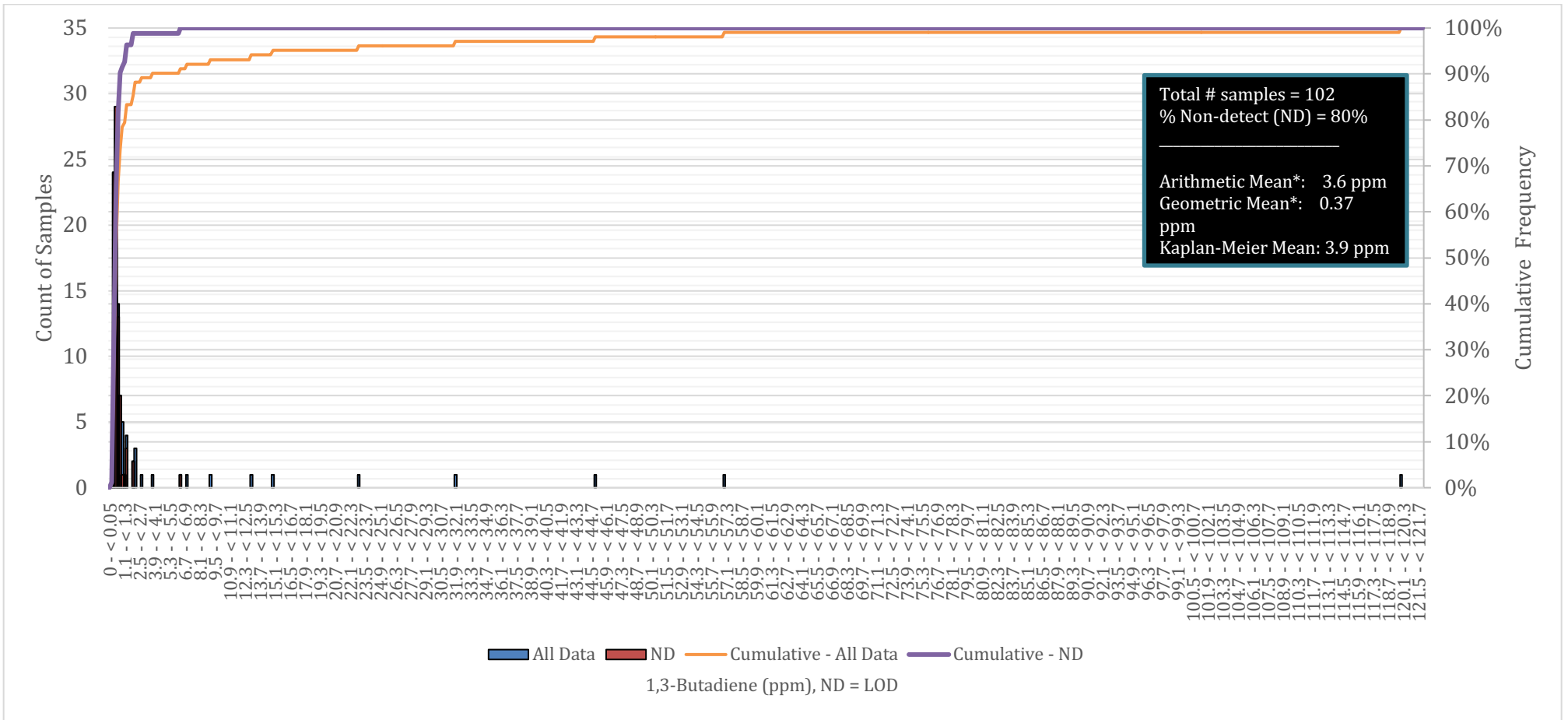
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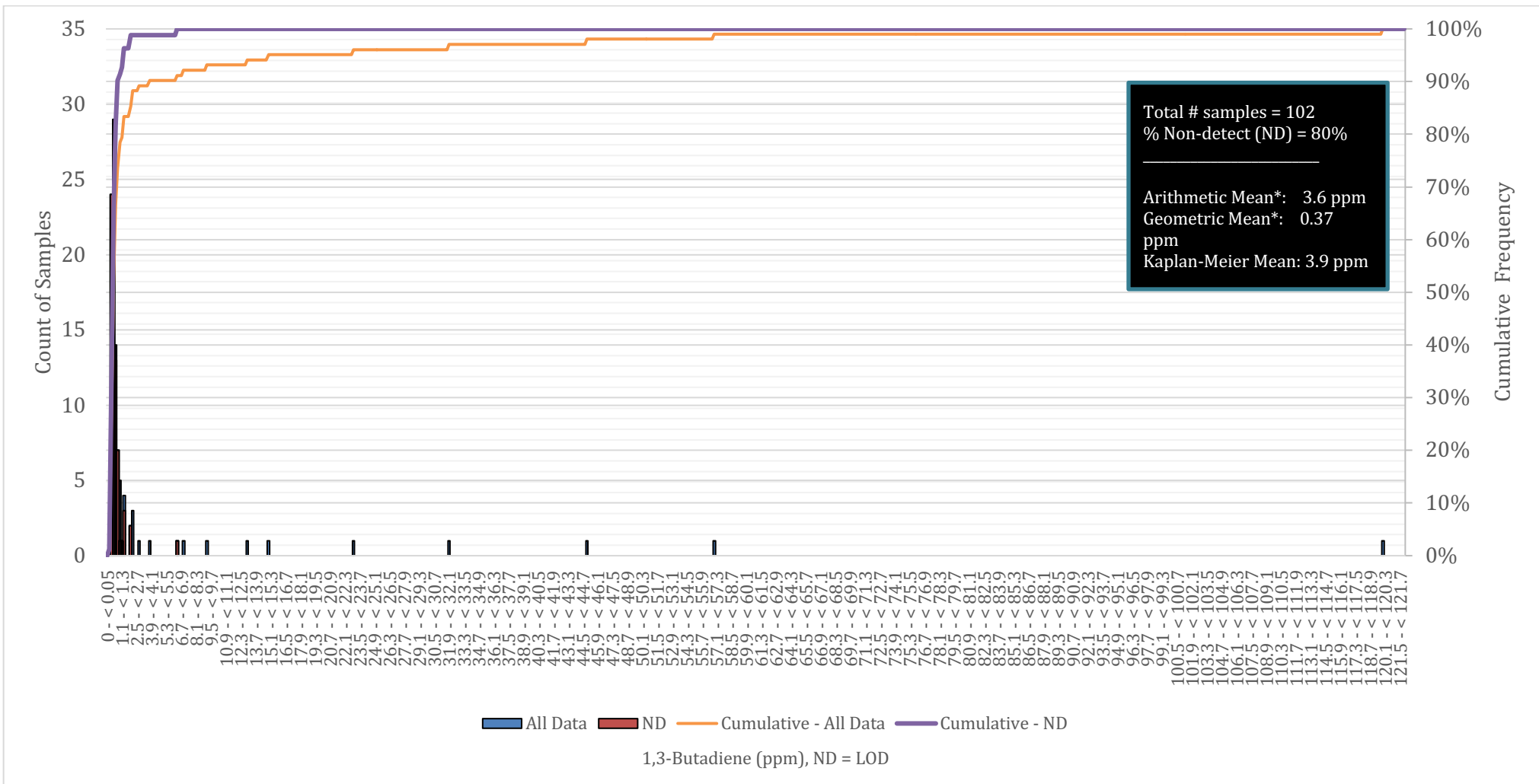
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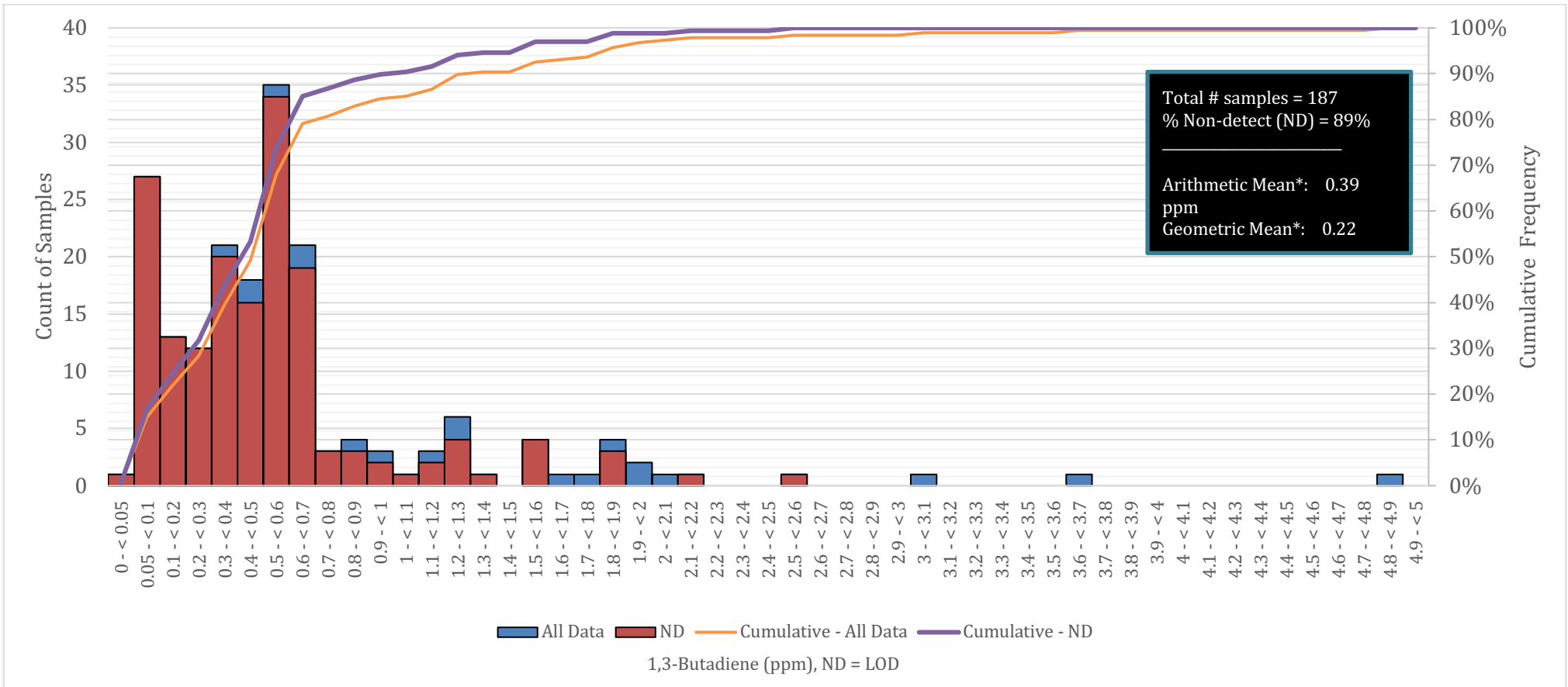


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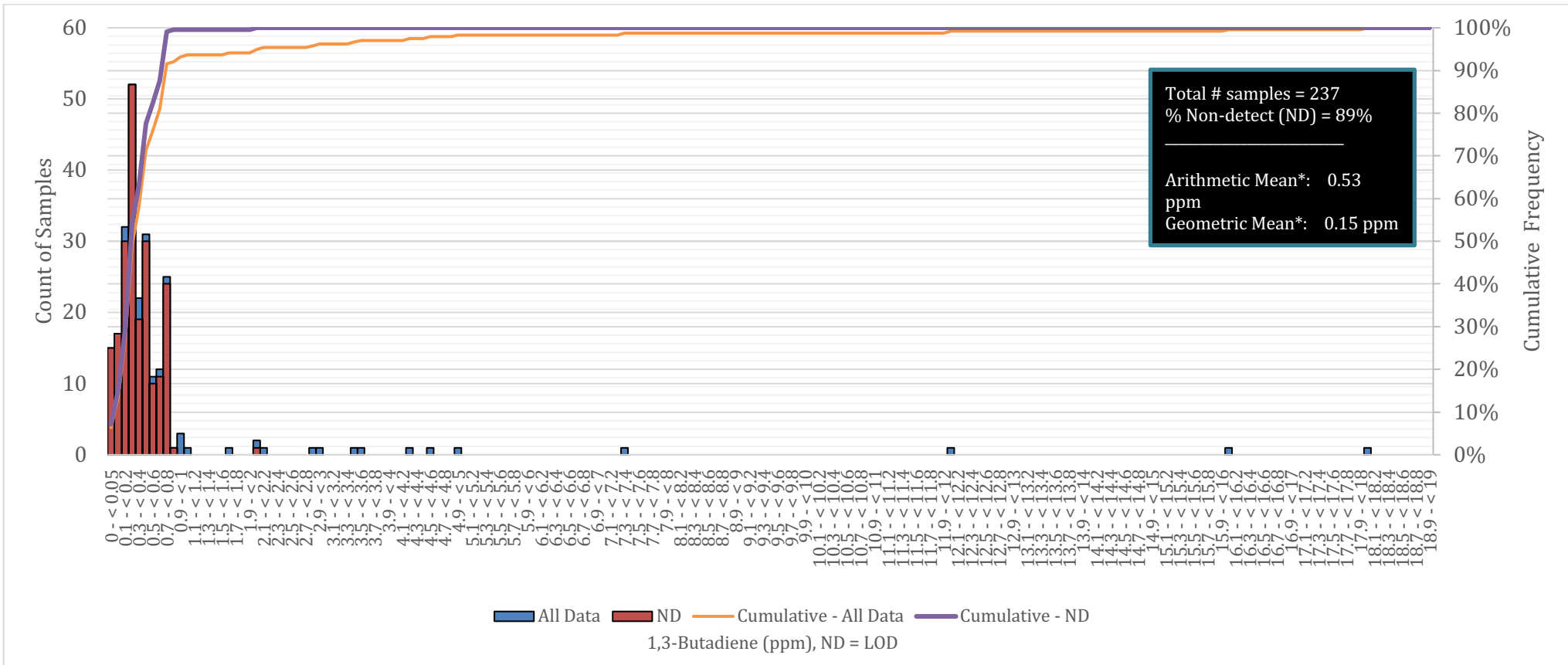


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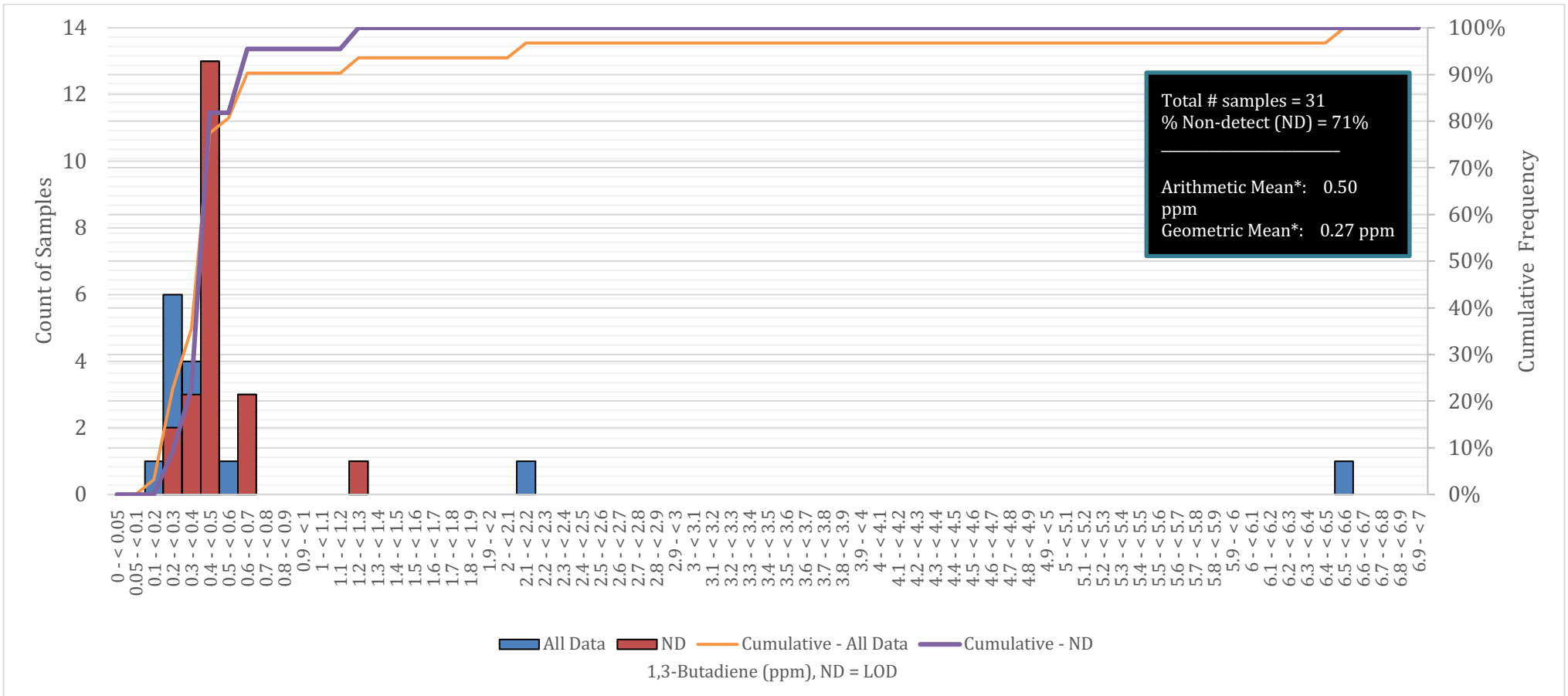




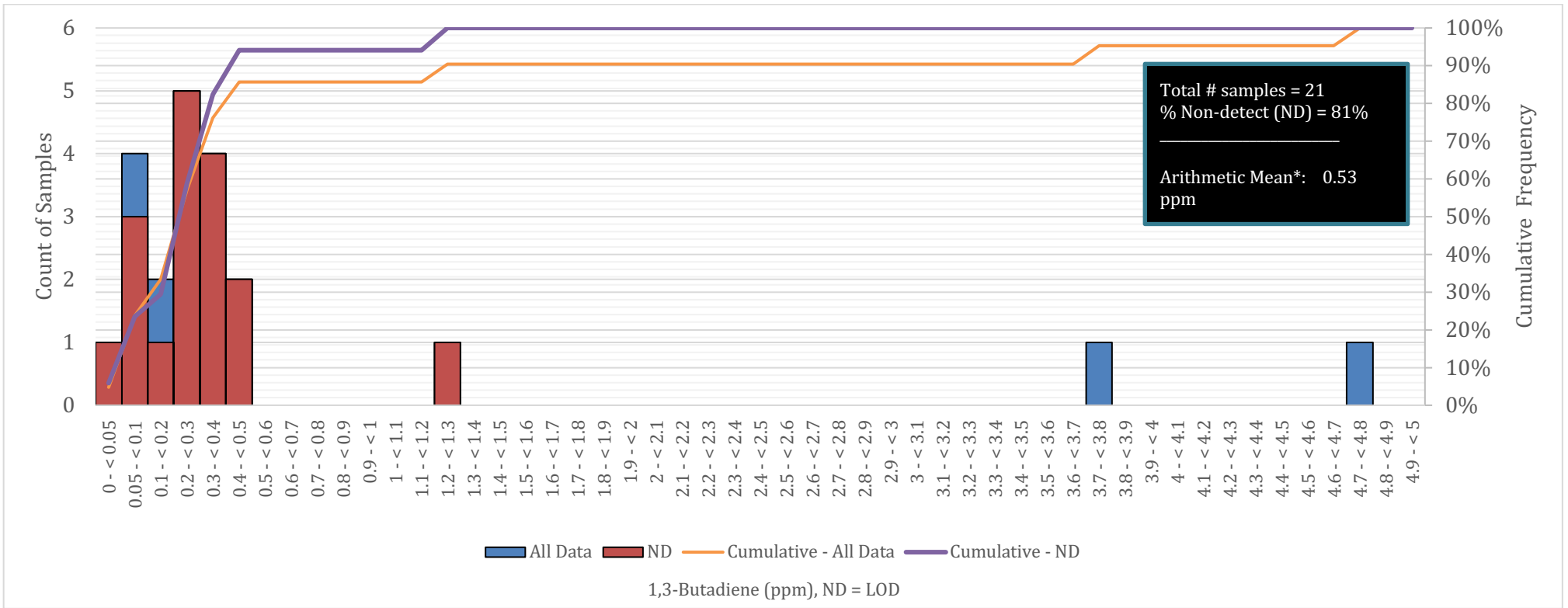
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**Figure 18b. Distribution of Other Work Task Personal Air Concentrations, 15 - 239 minutes**

**APPENDIX F**

# **IH Metadata Analysis**

# **Analysis of 1,3-Butadiene IH MetaData**

**SEPTEMBER 26, 2024**

**ToxStrategies**

Innovative solutions  
Sound science

# **White Paper: Analysis of 1,3-Butadiene IH MetaData**

**SEPTEMBER 26, 2024**

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## Acronyms

1,3-BD	1,3-Butadiene
ACC	American Chemistry Council
ANSI	American National Standards Institute
C4	Crude butylene concentration
CCPS	Center for Chemical Process Safety
CFR	U.S. Code of Federal Regulations
CoA	Certificate of Analysis
COU	Processing as a reactant conditions of use
CT	Connection Time
DOT	Department of Transportation
EHS	Environmental Health and Safety
EPA	U.S. Environmental Protection Agency
EF	Exposure Frequency
ET	Exposure Time
GHS	Globally Harmonized System
HAP	Hazardous Air Pollutant
HAZMAT	Hazardous Materials
HON	EPA's Hazardous Organic National Emissions Standards for Hazardous Air Pollutants
IH	Industrial Hygiene
LEV	Local Exhaust Ventilation
LDAR	Leak Detection and Repair Program
MOC	Management of Change
NESHAP	EPA's National Emissions Standards for Hazardous Air Pollutants
NFPA	National Fire Protection Association
OSHA	Occupational Safety and Health Administration
Oxo-D or O-X-D	Oxidative dehydrogenation of n-butene
PEL	Permissible Exposure Limit
PHA	Process Hazard Analysis
PPE	Personal Protective Equipment
ppmv	Parts per Million by Volume
PSM	Process Safety Management
RMP	EPA's Risk Management Program
SDS	Safety Data sheet
SOP	Standard Operating Procedure
TSCA	Toxic Substances Control Act
VOC	Volatile Organic Compound

# 1 Introduction

1,3-Butadiene (1,3-BD) is produced commercially by three processes: (1) steam cracking of paraffinic hydrocarbons (ethylene co-product process), (2) catalytic dehydrogenation of n-butane and n-butene (Houdry process), and (3) oxidative dehydrogenation of n-butene (Oxo-D or O-X-D process). These manufacturing processes are performed in closed systems (many of which operate at high pressure and low temperature). Each of these processes produce a stream, commonly referred to as crude butadiene, that is rich in 1,3-BD. Separation and purification of the butadiene stream typically is carried out by extractive distillation, because the boiling points of the various crude butylene concentration (C4) components are so close to each other. The final concentration in the purified 1,3-BD product is typically >99 wt% pure and is stored in liquid form in pressurized spheres. Liquefied 1,3-BD is shipped by pipelines, ships, barges, rail tank cars, tank trucks, and bulk liquid containers to industrial customers who use it as a reactant or ingredient. It is important to note that the storage and transport conditions are such that PPE must be used by workers and engineering controls must be implemented to minimize losses and promote safe operations.

Previously, the American Chemistry Council's (ACC) 1,3-BD Toxic Substances Control Act (TSCA) Risk Evaluation Consortium compiled industrial hygiene data related to potential worker exposures in the chemical manufacturing and processing as a reactant condition of use (COU). As part of that effort task level exposure data was collected and assessed for five major tasks: (1) unloading and loading, (2) handling of waste, (3) cleaning and maintaining equipment, (4) sampling and analysis, and (5) "other work". These data were reported to the U.S. Environmental Protection Agency (EPA) and published in a scientific peer-reviewed paper where high-level information regarding the task operations were provided (Panko et al., 2023). EPA has since requested additional details to better understand the potential for worker exposure during these tasks.

The objective of this white paper is to expand the information previously provided to EPA on short-term and task-level occupational exposure in the manufacture of 1,3-BD and processing as a reactant (COU). To that end, the Consortium has compiled available metadata associated with the tasks including the duration and frequency of the task during a given shift or day, demographics such as the number of workers per shift, number of shifts and number of sites where the task is conducted, and relevant controls to minimize exposures. Additionally, qualitative information regarding standard operating procedures were compiled in an effort to better inform EPA on how workers are made aware of the potential hazards of 1,3-BD, methods for protecting themselves during various tasks and other operational controls that may be specific to certain companies or sites, which are not covered in the [Butadiene Product Stewardship Manual \(ACC, 2024\)](#).

The data were collected using a simple survey template as shown in Appendix G. Five of the ten companies that provided the original 1,3-BD industrial hygiene (IH) data provided the associated metadata included in this white paper.

## 2 Overarching Programs for Worker Exposure Control

The industrial hygiene data reported in Panko et al. (2023) comes from 47 total sites where these 1,3-BD tasks take place. These 47 sites represent 100% of the 1,3-BD manufacturing in the United States; although not every site conducts every task. For example, some sites conduct loading/unloading tasks on barges while others conduct these tasks on railcars. Regardless, worker exposure to 1,3-BD in the manufacturing and processing as a reactant COU is minimized at the facility level through a variety of health and safety programs in their compliance with several EPA and Occupational Safety and Health Administration (OSHA) regulations, as well as companies' internal chemical management policies and programs that often exceed regulatory requirements. The primary programs are described below.

### 2.1 Hazard Communication

One tool to control exposures to 1,3-BD is the implementation of a robust hazard communication program as required by OSHA's hazard communication standard (29 CFR 1910.1200) and OSHA's chemical specific standard for 1,3-BD (29 CFR 1910.1051(l)). Under this program, workers are trained on chemical hazards, controls, and proper process procedures. Additionally, programs help ensure hazardous chemicals are not brought on-site without an approval process and all chemicals have an appropriate hazard warning label. Based on examples provided by participating companies, hazard communication programs typically include:

- Written hazard communication program
- Inventory of hazardous chemicals
- Globally Harmonized System (GHS) and National Fire Protection Association (NFPA) compliant labels
- Safety Data Sheets (SDS) for each hazardous chemical produced or brought on-site are readily accessible to workers
- Routine review process for maintenance of SDS's and written program
- New chemical review and approval process
- Procedure for employee communication
- Procedure for employee training, including protocols for new employees and general refresher training.
- Appropriate precautions for safe handling and use of chemicals

### 2.2 OSHA Occupational Exposure to 1,3-Butadiene Standard

OSHA's chemical-specific standard for 1,3-BD is included in [29 CFR 1910.1051](#). This standard is applicable to all the facilities in the 1,3-BD manufacturing and processing as a reactant conditions of use (COU). The standard sets forth strict requirements for exposure monitoring, regulated areas, engineering and work practice controls, personal protective equipment (PPE) including respiratory protection, medical surveillance, hazard communication, training, and recordkeeping. In addition, exposure monitoring results must

be communicated to the employees and any exposures over the permissible exposure limit (PEL) require written compliance plans to reduce exposure below the PEL by engineering or work practice controls. Subsequently, a written exposure goal program is required for those exposures greater than the action level but below the PEL. An exposure control program sets forth requirements to reduce exposures even further through programs for leak detection and repair (LDAR), local exhaust ventilation (LEV) effectiveness, as well as utilizing the most advanced exposure control technologies such as mechanical double sealed pumps, gauging devices, and unloading devices (OSHA, 2019).

### **2.3 OSHA Process Safety Management and EPA Risk Management Program**

OSHA's Process Safety Management regulation (29 CFR 1910.119) and EPA's Risk Management Program (RMP) rule (40 CFR Part 68) are two overarching regulations for 1,3-BD that aim to prevent releases of hazardous substances through implementation of engineering and administrative controls. Both regulations are triggered when a facility has greater than 10000 lbs of 1,3-BD on-site (CFR, 2019 and CFR, 1994). The requirements of these two regulations control 1,3-BD exposures through requirements such as strong hazard assessment procedures with employee participation, written operating procedures for all processes, and mechanical integrity requirements for equipment.

OSHA's Process Safety Management regulation (29 CFR 1910.119) contains requirements for preventing or minimizing the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals, which may result in toxic, fire, or explosion hazards. The regulation includes but is not limited to the following elements:

- Employee participation
- Written process safety information
- Process hazard analysis (PHA)
- Written operating procedures
- Employee training
- Employer responsibilities for contractors
- Pre-startup safety review
- Mechanical integrity requirements for different equipment such as pressure vessels, storage tanks, piping systems, relief and vent systems/devices, emergency shutdown systems, controls, and pumps.

EPA's RMP rule (40 CFR Part 68) requires facilities that use hazardous substances to develop a risk management plan which identifies potential effects of a chemical accident, identifies steps to prevent an accident, and outlines emergency response procedures should an accident occur. The RMP includes but is not limited to the following elements:

- Hazard assessment
- Worst-case and alternative release scenario analysis
- Defining of offsite impacts
- Documentation
- 5-year accident history
- Operating procedures

- Training
- Maintenance
- Process Safety Management (PSM), PHA, and Management of Change (MOC)
- Pre-startup safety reviews.

### 3 Task Specific Metadata

This section provides information received from the Consortium member survey related to each of the tasks for which industrial hygiene data was provided, along with a summary of relevant regulations corresponding to each task. It is important to note that not all tasks apply to all companies or sites and task-specific exposure factors and controls can vary by company or site.

#### 3.1 Unloading and Loading

Various controls, industry practices, and regulations promote the safe unloading and loading of 1,3-BD from transportation vehicles. Transfer operations for railcars, barges, tank trucks and process vessels containing 1,3-BD are regulated under EPA’s Hazardous Organic NESHAP (HON) regulations (CFR, 2024). Group 1 transfer racks are defined as “a transfer rack that annually loads greater than or equal to 0.17 million gallons of liquid products that contain organic Hazardous Air Pollutant (HAP) with a rack weighted average vapor pressure greater than or equal to 1.5 psia” (CFR, 2024). These Group 1 transfer racks must achieve a 98% reduction in the organic HAP or have an outlet concentration of 20 parts per million by volume (ppmv), or alternatively, a vapor balancing system can be utilized (CFR, 2024). The Department of Transportation (DOT) requires all hazardous materials to be properly classified, labeled, and packaged for transportation (CFR, 2010). In addition to federal regulations, there are also state regulations for unloading and loading of 1,3-BD from transportation vehicles. Since these vary by state, the specifics are not listed here.

##### 3.1.1 Railcars

The ACC Butadiene Product Stewardship Manual has an example procedure for unloading a rail tank car (ACC, 2023). The exposure factors associated with this task are shown on Table 1.

**Table 1. Exposure Factors Associated with Railcar Unloading and Loading**

Exposure Factor	Value	Unit
Exposure Time (ET)*	<0.25 – 0.75	Hours
Exposure Frequency (EF)	Range: 1-6 Average: 2.5	Per day
Number of Workers	1	Per shift
Number of Shifts	Range: 1-2	Per day

\*ET is the total time associated with the task including both connection and disconnection time

Based on participating company reports, the minimum PPE required when loading or unloading 1,3-BD from railcars is a half-facepiece respirator with organic vapor cartridges and chemical protective gloves or leather gloves for general protection when 1,3-BD exposure is not expected. When there is a splashing hazard or potential for trapped materials, a full face-piece respirator with organic vapor cartridges and chemical protective gloves are typically required, although one company reported requiring supplied air respirators during disconnection.

Additionally, the unloading and loading of rail tank cars are regulated by the Department of Transportation (DOT) 173.31 and 174.67 (CFR,1995a and 1995b). Safety requirements in 49 CFR 173.31, “Use of Tank Cars,” include that the tank car must be protected against movement or coupling, caution signs must be displayed on tank cars, and at least one wheel on tank car must be blocked against movement and the hand brake must be set. Safety requirements in 49 CFR 174.67, “Tank Car Unloading.” include maintaining written safety procedures that are available for employees, relieving interior pressure and proper removal of manway covers, use of safety precautions to prevent ignition of vapors, precautions for when unloading from the bottom outlet valve, requirements for hazardous materials (HAZMAT) employees to be present or a monitoring system monitored by HAZMAT employees, visual inspection of tank cars with hazardous materials, and no hazardous material residue on outside of package during transport (CFR, 1995b).

Another exposure control that is implemented when monitoring the loading/unloading of rail tank cars is the use of magnetic gauges, which are recommended over slip-tube gauges to prevent release of vapor into the air since magnetic gauges are a completely sealed metering system (Fajen, 1990). In the ACC Butadiene Product Stewardship Manual, magnetic gauge level gauges are visible in the images of typical butadiene rail tank car loading (ACC, 2023).

### **3.1.2 Barges**

In general, the barge loading procedure consists of the following seven steps:

1. Tugboat personnel moor barge
2. Tankerman prepares barge for loading
  - a. Barge securely tied, connect ground cable, proper grounding established
  - b. Communicate with team and complete declaration of inspection
  - c. Checks load arm for damage, checks condition of fittings
  - d. Verify vents/bleeds are closed and valve in correct position
3. Tankerman to remove blind flange from loading arm and connect to barge liquid header, ensures line and equipment opening precautions are followed
4. Test connection for leaks by opening nitrogen guard valve and closing when line is pressurized
5. Open instrument air supply guard valve to the barge
6. Manually reset solenoids at isolation valve
7. Test for shutdown, verify that all valves close

The exposure factors associated with this task are shown on Table 2.

**Table 2. Exposure Factors Associated with Barge Unloading and Loading**

Exposure Factor	Value	Unit
Exposure Time (ET)	Range: 0.2 – 1 Average: 0.5	Hours
Exposure Frequency (EF)	Range: : 1.5-8	Per month
Number of Workers	Range: 1-5	Per shift

Similar to railcar loading/unloading, based on participating company reports, the minimum PPE required when loading or unloading 1,3-BD from barges is a half-facepiece respirator with organic vapor cartridges and either leather, butyl rubber, fluoroelastomer, or nitrile gloves. Some companies also report requiring a full-facepiece respirator. Based on existing controls a splashing or trapped materials hazard is unlikely, however a full face-piece respirator and organic vapor cartridges and chemical-resistant gloves are typically required in those instances. One company utilizes a vapor destruction unit for hose disconnection, which leads to minimal to negligible exposure since this is a closed system.

Additionally, the loading and unloading of barges are regulated under 46 CFR 151.45-4. Requirements include a qualified person designated to oversee the transfer, the proper closing of all sea and ballast valves, precautions for connecting a cargo transfer, and inspection of the cargo prior to transfer. Additionally, barges with gas carrier shipments require inhibition or stabilization under 46 CFR 151.50-70.

### 3.2 Handling, Transporting, and Disposal of 1,3-Butadiene Waste

This task is associated with potential contact of facility waste streams containing 1,3-BD including disposing of analytical samples, loading of recycled oil, operations conducted at the onsite waste-water treatment plant. It is important to note that the presence of 1,3-BD in waste streams is highly dependent on facility operations, for example, some processing operations have no 1,3-BD in waste streams since nearly all of it is consumed in the processing and any residual is sent for destruction via flares or boilers. The exposure factors associated with this task are shown on Table 3.

**Table 3. Exposure Factors Associated with Handling, Transporting and Disposal of 1,3-Butadiene waste**

Exposure Factor	Value	Unit
Exposure Time (ET)	Range: 0.1 - 0.5 Average: 0.25	Hours
Exposure Frequency (EF)	Range: 1-3	Per day
Number of Workers	1-2	Per shift

Based on participating company reports, respiratory protection and eye/dermal protective equipment such as goggles, face shield, flame resistant (FR) smock and chemical protective gloves are typically required during the disposal of laboratory samples. Some companies send the sample back into the process or it is purged to flare, to prevent release of 1,3-BD



to the air. 1,3-BD is regulated as a hazardous waste (D001) under 40 CFR Part 261. Due to this, the transportation, storage, treatment, and disposal must be conducted in compliance with 40 CFR Parts 262, 263, 264, 268, and 270. Disposal can only occur in properly permitted facilities (CFR, 1996c).

### **3.3 General Cleaning and Maintenance**

This task involves disassembly and re-assembly of process equipment (e.g., valves, pumps, and analyzers), tank cleaning, line purging, filter removal and cleaning. Each of these activities involves a different set of steps, however, nearly all require some type of equipment shutdown. Therefore, preparation and safe work practices are implemented to prevent worker exposure to 1,3-BD as well as the control of hazardous energy.

Each facility has its own standard operating procedures (SOPs) for opening and isolating process lines and equipment, which also incorporate requirements for compliance with OSHA's Control of Hazardous Energy regulation, 29 CFR 1910.147, which sets minimum requirements for control of hazardous energy, as well as OSHA's permit-required confined space regulation, 29 CFR 1910.146, which establishes requirements for all confined space entries, where appropriate. Nevertheless, each of the SOPs incorporate the fundamental work steps outlined in the "Safe Work Practice: Line Opening guidance provided by the Center for Chemical Process Safety" (CCPS, 2024):

1. Identify work scope, materials and location and identify hazards along with possible controls.
2. Provide draining and cleaning procedures to workers and/or contractors
3. Complete physical isolation required for draining and cleaning. This includes installation of blinds or blocks
4. Drain and flush lines or equipment to remove hazardous materials. This may include steaming and inert gas purging.
5. Complete all other lockout/tagout activities in accordance with OSHA regulation 29 CFR 1910.147
6. Positively identify location of line break or equipment removal
7. Confirm that draining and energy isolation were successfully completed
8. Review the hazards of the line or equipment opening, ensure workers and contractors have the required PPE and safety equipment, and know the location of safety shower and eye wash
9. Issue line opening permit and execute the work
10. Clean the work area and return the permit after work is completed
11. Remove isolations and return the area to normal status

In general, use of respirators with organic vapor cartridges and chemical-resistant gloves appropriate for the job are used when performing maintenance-related activities on process equipment with 1,3-BD, and permanent connections to a closed drain header or provision for drain connection to a closed drain header are utilized for 1,3-BD drains, flushing, and cleaning connections (Fajen et al.,1990; Bowes, 2008). Based on participating company

reports, some companies report negligible 1,3-BD exposures during maintenance cleaning since they purge to flare.

### 3.3.1 Piping

Maintenance involving process piping is process-dependent and the actual frequency can be quite variable. Conducting maintenance requires precautions be taken for preventing fire and/or explosion hazards and exposure to workers by physically isolating the process and equipment to help ensure that butadiene is contained and the work behind the isolation is safe. The exposure factors associated with this task are shown on Table 4.

**Table 4. Exposure Factors Associated with Line or Pipe Maintenance or Cleaning**

Exposure Factor	Value	Unit
Exposure Time (ET)	Range: 0.25– 3 Average: 1	Hours
Exposure Frequency (EF)	Range: ≤1	Per week
Number of Workers	Range: 1-2	Per shift
Number of Shifts	Range: 1-2	Shifts per day

In general, the companies reported use of respirators with organic vapor cartridges during initial opening of a 1,3-BD line, as well as gloves and chemical protective suits depending on the specific situation.

As discussed in the ACC Butadiene Product Stewardship Manual, ANSI B31.1 sets standards for pressure piping. Additionally, OSHA’s flammable liquids regulation requires piping to be designed to minimize static electricity (CFR, 2016).

### 3.3.2 Pumps, Compressors and Valves

Maintenance tasks on pumps, compressors and valves may be conducted as part of routine maintenance or in case of equipment failure. The same general procedures for line opening are also followed for these pieces of equipment. The exposure factors associated with this task are shown on Table 5.

**Table 5. Exposure Factors Associated with Pump, Compressor and Valve Maintenance or Cleaning**

Exposure Factor	Value	Unit
Exposure Time (ET)	Range: 0.25– 12 Average: 4	Hours
Exposure Frequency (EF)	Range: 1 per day to 10 per year depending on the maintenance schedules	Per day or Per year
Number of Workers	Range: 1-8	Per shift
Number of Shifts	Range: 1-2	Shifts per day

According to company surveys, facilities typically have dual mechanical seals installed on pumps. Other controls for pumps, compressors, and valves include mechanical ventilation,

dripless fittings for bleeds, toxics air monitoring, and leak detection and repair (LDAR) programs.

Pumps containing 1,3-BD are regulated under EPA's National Emissions Standards for Hazardous Air Pollutants (NESHAP) regulations (40 CFR 63.163). Requirements are based on if the pump is an existing or a new source. Requirements include but are not limited to monthly monitoring of pumps for leaks, weekly visual inspection of pumps, prompt repair of pumps if a leak is detected, or exemption of these requirements if controls such as a dual mechanical seal system is in place.

Compressors containing 1,3-BD are regulated under 40 CFR 63.164. Requirements include but are not limited to a seal system on each compressor and a barrier fluid system equipped with a sensor.

Open ended valves containing 1,3-BD are regulated under 40 CFR Part H-63.167. Requirements include each open-ended valve or line to have a cap, blind flange, plug or second valve that seals the open end at all times except during maintenance unless there is an emergency shutdown system in place, or the material would autocatalytically polymerize or would present a serious hazard if a block and bleed system was utilized. Additionally, each open-ended valve or line that has a second valve is required to be operated in way so that the valve on the process fluid end closes before the second valve. Lastly, when utilizing a double block and bleed system, the bleed valve or line can remain open during required operations as long as the open-ended valve or line contains a cap, blind flange, plug, or second valve.

HON regulations also require work practice standards such as a leak detection and repair program to control equipment leak emissions (CFR, 2024). Valves are required to be monitored once per month at each process unit that has 2% or more of valves leaking (CFR, 2024).

Fajen et al. (1990) recommends that all process pumps contain dual mechanical seals to reduce pump leakage. For pump seals, Bowes (2008) recommends seal-less pumps, pressurized dual seals, or leakage alarms. For block valves, double packing without monitoring, double packing with leak detection, or special graphite packing with mandatory monitoring and maintenance are recommended for 1,3-BD (Bowes, 2008). For compressor seals, a contacting or thin film seal with buffer fluid is recommended and all emissions should be routed to a collection and disposal system (Bowes, 2008).

### ***3.3.3 Filters and Strainers***

Maintenance on filters and strainers are generally conducted as part of routine maintenance. The same general procedures for line opening are also followed in order to access these parts. The exposure factors associated with this task are shown on Table 6.

**Table 6. Exposure Factors Associated with Filters and Strainers Maintenance and Cleaning**

<b>Exposure Factor</b>	<b>Value</b>	<b>Unit</b>
Exposure Time (ET)	Range: 0.16 – 1.5 Average: 1.5	hours
Exposure Frequency (EF)	Range: <=1	Per day
Number of Workers	Range: 1-2	Per shift
Number of Shifts	Range: 1-2	Shifts per day

Filters and strainers may be permanent or temporary, where permanent types, have a permanent connection to a drain header and a way to flush the equipment before opening the housing for maintenance (Bowes, 2008) For either type however, PPE for respiratory and dermal hazards may be required based on air monitoring data (Bowes, 2008).

### 3.3.4 Storage Tanks

Storage tanks containing 1,3-BD require periodic cleaning as part of routine maintenance or when decommissioning a storage tank. The general tank cleaning steps include:

1. Obtain cleaning permit and approval
2. Pump the tank to the lowest acceptable level
3. Strip the remaining recoverable product from the lowest piping within the tank or utilize a method without requiring worker entry, such as tank flushing
4. Gauge the tank
5. Isolate all electrical equipment and isolate tank from live process service
6. Double block and bleed valves as necessary
7. Ensure tank is grounded
8. Follow equipment opening procedures
9. Use gas monitor to measure 1,3-BD, and degas tank if above applicable limits
10. Open tank and mechanically ventilate
11. Clean tank, using methods that do not require worker entry first
12. Once cleaned, test for oxygen, LEL and other toxics with gas meter. Levels must be meet applicable limits

The exposure factors associated with this task are shown on Table 7. Typical PPE required during washing tanks is chemical gloves and goggles.

**Table 7. Exposure Factors Associated with Cleaning Storage Tanks**

<b>Exposure Factor</b>	<b>Value</b>	<b>Unit</b>
Exposure Time (ET)	Range: 0.5 - 1	hour
Exposure Frequency (EF)	Range: 1-6	Per year
Number of Workers	Range: 2-4	Per shift
Number of Shifts	Range: 1-2	Shifts per day

### 3.4 Sample Collection

This task involves collection of process stream samples and analysis for 1,3-BD. For gaseous samples, workers connect pressurized cylinders that have ports to allow the sample to flow in and to allow excess gas to vent to safe location. Based on participating company reports, most samples are collected utilizing a closed loop system that includes the following steps:

1. Select sample cylinder (a sample bomb with a removable flow-through sampling container with quick disconnect fittings), block valve, and ensure sample station is in circulation
2. Place sample cylinder on sample point vertically
3. Verify valves are in appropriate positions
4. Collect sample and remove sample cylinder from point
5. Block sample point and install plug
6. Properly tag the sample cylinder

The exposure factors associated with this task are shown on Table 8.

**Table 8. Exposure Factors Associated with Sample Collection**

Exposure Factor	Value	Unit
Gas Sample Collection Exposure Time (ET)	Range: 0.03 – 0.33 Average: 0.18	Hours
Liquid Sample Collection Exposure Time (ET)	Range: 0.03 – 0.5 Average: 0.25	Hours
Gas Sample Exposure Frequency (EF)	Range: 0 – 3 Average: 1	Per day
Liquid Sample Exposure Frequency (EF)	Range: 1 per day – 1 per week	
Number of Workers (Gas Samples)	Range: 1-2	Per shift
Number of Workers (Liquid Samples)	Range: 1-16	Per shift
Number of Shifts (Gas Samples)	Range: 4-7	Shifts per day
Number of Shifts (Liquid Samples)	Range: 1-4	Shifts per day

A general example procedure for analyzing butadiene samples in a lab was provided as follows:

1. Bring butadiene cylinder under Class A hood, open cylinder valve slowly, check that butadiene is evaporating
2. Add boiling stones to a 100 mL graduated cylinder, open butadiene cylinder and measured out 50 mL
3. After the butadiene has evaporated, measured out 10 ML of n-Heptane and release into the graduated cylinder while rotating

4. Add 1 mL of 1000 ppm Eicosane in toluene internal standard to the n-Heptane solution and mix
5. Fill an auto sampler vial and place it on Channel 31N, and set up gas chromatograph
6. If the results from the run fall below set limits, have operations collect another sample and repeat the test again

The exposure factors associated with this task are shown on Table 9.

**Table 9. Exposure Factors Associated with Sample Analysis**

<b>Exposure Factor</b>	<b>Value</b>	<b>Unit</b>
Exposure Time (ET)	Range: 0.02 – 3 Average: 2	Hours
Exposure Frequency (EF)	1	Per day
Number of Workers	Range: 1-16	Per shift
Number of Shifts	Range: 1-2	Shifts per day

Based on participating company reports, most samples are collected utilizing a closed loop system. In general, nitrile or neoprene rubber gloves and goggles are required for collecting samples in a closed loop system. For a non-closed loop system, neoprene rubber gloves, goggles, and air purifying negative pressure respirators with organic vapor cartridges are required. When samples are analyzed, a fume hood is generally utilized with PPE including gloves and monogoggles.

Sample connection systems are regulated under NESHAP regulations (40 CFR 63.166). Each sampling connection system must have a closed-purge, closed-loop, or closed vent system. The sampling system must be designed to purge process fluid directly to the process line or collect and recycle the purged process fluid or designed to transport the fluid to a control device or collect, store, and transport the purged process fluid to a facility such as a waste management unit.

### **3.5 “Other” Tasks**

Some IH air samples were collected on workers that performed a variety of miscellaneous tasks that do not fall into the other four categories identified by EPA. The tasks included air monitoring with direct reading instruments for volatile organic compounds (VOCs) during various maintenance activities [typically by environmental health and safety (EHS) personnel], tank gauging and routine visual inspections of operating areas.

#### **3.5.1 Leak Detection or Other EHS Air Monitoring**

Leak detection or EHS air monitoring during various maintenance tasks is typically conducted by EHS personnel. The exposure time and frequency can be highly variable depending on the nature and purpose of the survey. Monitoring conducted as part of a leak response will require PPE specific to the type of leak that occurs.

### 3.5.2 Tank Gauging

Only 2 air samples were available for the tank gauging task in the industrial hygiene data set. This is not surprising because typically, tank gauging is performed with automatic tank gauge systems that do not require opening of the storage tanks to measure levels of the contents. However, if hand strapping of tanks (i.e., determine tank volume using a steel measuring tape or strap) is required, a full-face organic vapor respirator, chemical gloves, and chemical protective suit are typically required.

### 3.5.3 Routine Inspections

Routine visual inspections, also known as routine rounds, are conducted by process operators. The purpose of this task is to observe process operational parameters such as temperatures, pressures, check pumps and gauge levels, and make adjustments as necessary. The exposure factors associated with the routine inspections are shown on Table 10.

**Table 10. Exposure Factors Associated with Routine Inspections**

<b>Exposure Factor</b>	<b>Value</b>	<b>Unit</b>
Exposure Time (ET)	Range: 0.5 - 1	Hours
Exposure Frequency (EF)	2-3	Per day
Number of Workers	1	Per shift
Number of Shifts	2	Shifts per day

Based on participating company surveys, respirators are not typically worn during routine inspections.

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**APPENDIX G**

# **IH Metadata Survey Template**

