Stolthaven New Orleans Terminal Flooding

Proposed:
Revised Air Sampling and Monitoring Work Plan
Vs 1.6

Prepared On Behalf Of:
Stolthaven New Orleans

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Prepared By:

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	Name/Position	Signature	Date Signed
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Reviewed By:	Nathan Williams		10/04/2012
Approved By:	Dr. Mike Berg		10/04/2012

September 1, 2012 (Revised 10/04/2012)

Changes From Version 1.0 to Version 1.1

- *Section 3 – Added formic acid and styrene to the Occupational and Community Exposure Guidelines.*
- *Section 4 – Added formic acid and styrene to the Real-Time Monitoring methods section.*
- *Section 4, Table 4.3 – Based on additional information from site conditions, updated octane to octene for colorimetric detector tube detection.*

	Name/Position	Signature	Date Signed
Prepared By:	Nathan Williams		9/2/2012
Approved By:	Dr. Phil Goad		9/2/2012

Changes from Version 1.1 to 1.3 (1.2 was skipped)

- *Section 3 – Added chlorobenzene, diethanolamine, and hydrogen sulfide* to the Occupational and Community Exposure Guidelines.*
- *Section 4 – Added chlorobenzene and hydrogen sulfide* to the Real-Time Monitoring methods sections.*
- *Section 5 – Added analytical sampling methods for hydrogen sulfide* and diethanolamine.*
- *Section 5.1 – Added number of analytical stations. Added analytical station locations. Added list of analytes being sampled for at each location.*

** Hydrogen Sulfide was added based on the potential for hydrogen sulfide emissions from floodwater impacted soils and surface water. Hydrogen sulfide remains un-related to the Stolthaven New Orleans Terminal facility.*

	Name/Position	Signature	Date Signed
Prepared By:	Nathan Williams		9/18/2012
Approved By:	Dr. Phil Goad		9/18/2012

Changes from Version 1.3 to Version 1.4

- *Section 4.3 – Added language describing the newly implemented AreaRAE fixed-station monitoring network located inside the Stolthaven New Orleans Terminal facility. 12 stations were added and the AreaRAEs were equipped with 11.7 eV lamps.*

	Name/Position	Signature	Date Signed

Prepared By:	Nathan Williams		9/19/2012
Approved By:	Dr. Phil Goad		9/19/2012

Changes from Version 1.4 to Version 1.5

- *Section 4.3 – AreaRAEs were previously equipped with 11.7eV lamps to detect formic acid. Due to excessive, confirmed sensor drift, the 11.7eV lamps were replaced with 10.6eV lamps. MultiRAEs used in the area of the formic acid scrubbers will remain equipped with 11.7eV lamps for added detection capability.*
- *Table 4.3 – Table was updated to reflect the change from 11.7eV lamps to 10.6eV lamps. The corresponding detection limits were adjusted to reflect the detection limit capability of the 10.6eV lamp.*
- *Table 3.1 was updated to include occupational and workplace exposure limits for 1-hexene and 1-octene.*
- *Table 3.2 was updated to include community exposure guidelines for 1-hexene.*
- *Table 4.1 and 4.3 received updated chemical-specific detection limits for real-time instruments including 1-hexene.*
- *Table 5.1 – Analytical method for methyl acrylate media was updated to include XAD-2 Sorbent Tubes*

	Name/Position	Signature	Date Signed
Prepared By:	Nathan Williams		9/23/2012
Approved By:	Dr. Phil Goad		9/23/2012

Changes from Version 1.5 to Version 1.6

- *Section 1 – Removed "Monitor air within the adjacent community to assess potential off-site impact odors from airborne contaminants originating from the terminal once the area is assessable."*
- *Section 1 – Changed "incident command" to "Stolthaven and all required stakeholders"*
- *Section 1 – Changed "regulatory approval" to "approval"*
- *Section 2 – Removed "locations throughout adjacent community or residential areas,"*
- *Section 4 – Changed "real time monitoring will be conducted…" to "real time monitoring may be conducted.."*
- *Section 4.1 – Removed 11.7 eV PID lamp monitoring within the community; 11.7 eV lamp will continue to be monitored for VOCs within the work area.*
- *Section 4.2 – Removed chlorobenzene*
- *Table 4.2 – Removed chlorobenzene*
- *Section 4.3 – Removed Section 4.3, Real Time Monitoring Locations*
- *Table 5.1 – Removed summary of Radiello badge sampling for H2S and Diethanolamine*
- *Section 5.1 – Removed ", co-located with AreaRAE real-time instruments"*
- *Section 5.1 – Replaced "As of 9/18/2012, thirteen analytical stations have been established. Stations 1-4 were established along the levee between the Stolthaven facility and the Mississippi River on 9/1/2012. Stations 10-13 were established along Highway 39, adjacent from the Stolthaven facility, on 9/6/2012. Stations A, B, and C were established along Highway 39, as community stations, on 9/8/2012. Stations 14 and 15 were established near B-Tank Farm on 9/16/2012" with "Perimeter monitoring will include analytical air sampling at the existing, fixed ambient air quality stations 2, 3, 4, 12, and 13. These stations provide coverage at representative points along the facility perimeter"*
- *Section 5.1 – Deleted stations 1, 10, and 11; "Hydrogen Sulfide (as of 9/18/2012)*
- *Chemicals Sampled at Stations A, B, and C*
- *Methyl Acrylate*

- *VOCs*
- *Diethanolamine (at stations A and C only)*
- *Hydrogen Sulfide (as of 9/18/2012)*
- *Chemicals Sampled at Stations 14 and 15,*
- *Diethanolamine,*

Hydrogen sulfide was added on 9/18/2012 to address potential hydrogen sulfide emissions from floodwater impacted soils and standing water, unrelated to Stolthaven processes or products"

	Name/Position	Signature	Date Signed
Prepared By:	Nathan Williams		9/23/2012
Approved By:	Dr. Mike Berg		9/23/2012

1 Introduction and Purpose

- This work plan addresses air monitoring and sampling in response to a failure in the levee surge protection system resulting in flooding at the Stolthaven New Orleans terminal. The purpose of this monitoring and sampling plan includes the following:
- Monitor air at the perimeter of the terminal to protect the community and response workers in close proximity.
- Monitor air inside the terminal to protect the workers and other personnel located within the terminal.
- Provide toxicology, industrial hygiene, and environmental consulting to support and assist with compliance with exposure standards and guidelines.
- All sampling data will be summarized as soon as available and presented for review onsite.
- This work plan will be implemented immediately upon approval by Stolthaven and all required stakeholders. This plan may be modified to reflect the changing nature of onsite work conditions; however, no changes will be made without prior approval.

2 Air Sampling and Monitoring Locations

- Real-time[1] air and analytical air sampling [2] will be performed at the following locations:

[1] The term "real–time air monitoring" generally refers to using handheld, portable direct reading instruments that rapidly detect and display the airborne concentration of a chemical.

- in and around areas near the Stolthaven New Orleans terminal,
- selected locations that will address potential off-site receptors, accounting for possible changes in wind-direction,
- selected locations that will address potential on-site receptors in regards to workers.
- In addition to fixed position monitoring, CTEH® will provide air monitoring assistance to address community concerns of odors or the presence of chemicals associated with the release site.

3 Exposure Standards and Guidelines

- The Occupational Safety and Health Administration (OSHA) establishes workplace standards to protect the safety and health of workers. The American Conference of Governmental Industrial Hygienists (ACGIH) and National Institute for Occupational Safety and Health (NIOSH) have also established exposure guidelines to protect workers from hazards on the job. Table 3.1 lists the OSHA and ACGIH values for all chemicals of interest. When applicable, sampling data results will be compared to health- and risk-based ambient air and exposure guidelines such as Minimal Risk Levels from the Agency for Toxic Substances and Disease Registry, Acute Exposure Guideline Levels from the EPA, and Emergency Response Planning Guidelines from the American Industrial Hygiene Association.

[2] The term “analytical air sampling” refers to air sampling methods that involve collection of air samples over a specified period, followed by analysis at a laboratory. The results of these samples represent the average airborne concentration for the sample period. These methods typically involve passing a known volume of air through a collection medium (e.g. charcoal sample tube or filter cassette) that efficiently traps and retains the compound until it can be analyzed by the laboratory. By knowing the volume of air collected, and the quantity of chemical absorbed onto the collection medium, the average air concentration can be calculated.

Table 3.1 Occupational Exposure Standards and Guidelines*

Chemical*	OSHA			ACGIH		Additional
	PEL-TWA (ppm)	PEL-STEL (ppm)	PEL-CEIL (ppm)	TLV-TWA (ppm)	TLV-STEL (ppm)	
Methyl Acrylate	10	-	-	2	-	IDLH of 250ppm
Styrene	100	-	200	20	40	IDLH of 700ppm
Formic Acid	5	-	-	5	10	IDLH of 30ppm
Hydrogen Sulfide***	NE	NE	20	1	5	IDLH of 100ppm
Chlorobenzene	75	350	NE	10	46	IDLH of 1000ppm
1-Octene**	NE	NE	NE	NE	NE	NE
1-Hexene	-	-	-	50	-	NE
Diethanolamine	-	-	-	0.2 IFV	-	IFV= inhalable fraction and vapor

NE= Not Established

*chemical values are in parts per million (ppm)

**CTEH using the Workplace Environmental Exposure Level (WEEL) of 75 ppm values as an occupational exposure standard for 1-Octene.

*** CTEH has added hydrogen sulfide based on the potential presence of H2S generated by floodwater impacted soils and surface water. Hydrogen sulfide is not associated with the Stolthaven facility.

a. OSHA PEL-TWA = The permissible concentration in air of a substance that shall not be exceeded in an 8-hour work shift or a 40-hour work week (OSHA 29 CFR: 1910.1000).
b. OSHA PEL-STEL = The time-weighted average exposure that should not be exceeded for any 15-minute period (OSHA 29 CFR: 1910.1000).
c. OSHA PEL-Ceiling = The exposure limit that shall at no time be exceeded. If instantaneous monitoring is not feasible, then the ceiling shall be assessed as a 15-minute time-weighted average (TWA) exposure, which shall not be exceeded at any time during the working day. (OSHA 29 CFR: 1910.1000).
d. ACGIH TLV-TWA = The Threshold Limit Value-TWA is the concentration for a normal 8-hour workday and a 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect (ACGIH, 2012c).
e. ACGIH TLV-Ceiling = The ceiling exposure limit is the level to which workers cannot be exposed to for any period of time (ACGIH, 2012c).

f. ACGIH TLV-STEL = The STEL exposure limit is a 15 minute time weighted exposure that should not be exceeded at any time during a work day. (ACGIH, 2012c).

3.2 Community Exposure Guidelines

- The American Industrial Hygiene Association (AIHA) establishes Emergency Response Planning Guidelines (ERPGs) to protect communities from the adverse effects of chemicals. USEPA has developed Acute Exposure Guideline Levels (AEGLs) to protect communities in the event of emergency chemical releases. The Department of Energy's (DOE) Subcommittee on Consequence Assessment and Protective Action (SCAPA) developed Temporary Emergency Exposure Limits (TEELs) and Protective Action Criteria (PAC) for over 1,250 chemicals for which ERPGs have not been developed. In cases where AEGL or ERPG values exist, SCAPA adopts the AEGL or ERPG values for the PAC-1, PAC-2, and PAC-3 values. TEEL values should be used only when an ERPG is not available for a given chemical. If an AEGL or ERPG value exists, the TEEL is the same as the AEGL or ERPG. Table 3.2 lists the PAC, ERPG, and ATSDR Acute MRL values for chemicals of interest.

Table 3.2 Community Exposure Guidelines*

Exposure Guideline	PAC-1[a] (ppm)	PAC-2[b] (ppm)	PAC-3[c] (ppm)	ERPG-1[d] (ppm)	ERPG-2[e] (ppm)	ERPG-3[f] (ppm)	ATSDR Acute MRL[g] (ppm)
Methyl Acrylate	6	170	1000	NE	NE	NE	NE
Styrene	20	130	1100	50	250	1000	5
Formic Acid	3	25	250	3	25	250	NE
Chlorobenzene	10	150	400	NE	NE	NE	NE
Hydrogen Sulfide	0.51	27	50	0.1	30	100	0.07
Octene (ppm)	40	800	2000	40	800	2000	NE
Hexene	50	500	5000	NE	500	5000	NE
Diethanolamine*	3 mg/m3	5.1 mg/m3	130 mg/m3	NE	NE	NE	NE

NE=Not Established
DOE/SCAPA 2012; AIHA, 2012; ATSDR, 2012

*Any detectable diethanolamine may be addressed with some form of action to be determined based on the resultant measured air concentrations of the samples collected.

Agency for Toxic Substances and Disease Registry Acute Minimal Risk Levels An estimate of daily human exposure to a substance that is likely to be without an appreciable risk of adverse noncarcinogenic effects over an acute exposure period (14 days or less)

Emergency Response Planning Guidelines: Emergency Response Planning Guidelines (ERPGs) are established by the American Industrial Hygiene Association (AIHA) and are intended to provide estimates of concentration ranges where one reasonably might anticipate observing adverse effects as a consequence of exposure to a specific substance. ERPGs may be expressed in three ways:

a. PAC-1 is the maximum concentration in air below which it is believed nearly all individuals could be exposed without experiencing other than mild transient health effects (DOE/SCAPA, 2012).

b. PAC-2 is the maximum concentration in air below which it is believed nearly all individuals could be exposed without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action (DOE/SCAPA, 2012).

c. PAC-3 is the maximum concentration in air below which it is believed nearly all individuals could be exposed without experiencing or developing life-threatening health effects (DOE/SCAPA, 2012).

d. ERPG-1 = The maximum concentration in air below which it is believed nearly all individuals could be exposed for up to 1 hr without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odor (AIHA, 2011).

e. ERPG-2 = The maximum concentration in air below which it is believed nearly all individuals could be exposed for up to 1 hr without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action (AIHA, 2011).

f. ERPG-3 = The maximum concentration in air below which it is believed nearly all individuals could be exposed for up to 1 hr without experiencing or developing life-threatening health effects (AIHA, 2011).

g. ATSDR Acute MRL= An estimate of daily human exposure to a substance that is likely to be without an appreciable risk of adverse noncarinogenic effects of an acute exposure period (14 days or less) (ATSDR, 2012)

4 Real-Time Monitoring

- Real-time air monitoring will be performed during the CTEH® air monitoring activities.
- The term “real–time” refers to direct reading instruments that allow nearly instantaneous determinations of a chemical concentration in air. Real-time measurements provide immediate information for worker and community exposure scenarios and, with the use of appropriate site safety measures, help prevent overexposures. Real-time measurements are not directly comparable to OSHA or ACGIH 8-hour TWA values or to community exposure standards or guidelines. Instantaneous real-time samples do not necessarily represent conditions experienced

throughout the workday and can substantially underestimate or overestimate exposures potentially experienced by workers. Direct reading instruments perform sampling and analyses within the instrument and concentration readings can usually be obtained immediately. These instruments have fast response times and can follow rapid changes in concentration.

- CTEH® will monitor at locations in response to incident site changes and/or community concerns or requests. There will be manually logged fixed real-time monitoring stations set up in the nearby community. Real-time monitoring will be conducted using the Rae Systems MultiRAE Plus, AreaRAEs, and the Gastec GV-1000 piston pump with colorimetric detector tubes. Additionally, the MultiRAE plus photo ionization detector (PID) and AreaRAE will be equipped with PID with 10.6eV lamp, oxygen, and LEL sensors.
- Real-time air monitoring instruments may be used to determine air quality at the incident site or within the community. These instruments include the AreaRAE 5-gas monitor, the MultiRAE plus PID, and the Gastec GV-100.

Table 4.1 Summary of Real-time Instrument Detection Limits

Instrument	Analyte	Energy Lamp (eV)	Detection Limit
MulitRAE, AreaRAE PID	VOCs	10.6	0.1 ppm
MulitRAE, AreaRAE PID	Methyl Acrylate	10.6	.37ppm
MulitRAE, AreaRAE PID	Octene	10.6	0.1 ppm*
MulitRAE, AreaRAE PID	Styrene	10.6	0.1 ppm*
MultiRAE, AreaRAE PID	Formic Acid	11.7	0.1 ppm*
MultiRAE, AreaRAE PID	Hexene	10.6	0.1 ppm*
RAE Systems Oxygen Sensor	Oxygen	NA	0.1 %
RAE systems LEL Sensor	LEL	NA	1%

*Correction factor is <1. Detectible when PID reads 0.1 ppm VOC.

4.1 Photo Ionization Detectors

MultiRAE and AreaRAE are used to measure airborne concentrations of volatile organic compounds (VOCs). Photo ionization is a nondestructive technique that is somewhat specific through selection of ultra-violet (UV) lamps of varying energies. PIDs use high energy UV light from a lamp housed within the detector to provide energy needed for ionizing VOCs. Ions are collected in an ionization chamber with accelerating and collecting electrodes designed to measure current. Current produced during VOC ionization is proportional to VOC concentrations.

PIDs are not specific for any chemical and can be affected by atmospheric humidity. PIDs often need to account for background readings and need to be coupled with other real-time instruments. A 10.6 eV PID lamp will be used to monitor for VOCs in the community and both 10.6 and 11.7 eV PID lamps will be used to monitor for VOCs in the work area.

4.2 Colorimetric Detectors

- Gastec colorimetric detector tubes will be used to determine concentrations of methyl acrylate, styrene, formic acid, hydrogen sulfide, and octene. Gastec detector tubes contain detecting reagents specifically designed to detect the target chemical. These thin glass tubes have printed calibration scales, which allow the user to directly read airborne concentrations of the substances being measured. Gastec detector tubes are hermetically sealed, the inner diameters are controlled, and detecting reagents with long-term stability are selected. All detector tubes undergo stringent quality control, and each production lot is independently tested and calibrated.

Table 4.2 Colorimetric Tubes and Detection Limits

Instrument	Analyte	Tube Name	Detection Limit	Sampling Volume
Gastec GV100	Methyl Acrylate	Ethyl Acetate #141L	5 ppm	200 mL
Gastec GV100	Octene	Hydrocarbons (Higher Class) #105	20 ppm	200 mL
Gastec GV100	Styrene	#124L	0.5 ppm	400 mL
Gastec GV100	Formic Acid	Acetic acid #81	0.2 ppm	200 mL
Gastec GV100	Hydrogen Sulfide	Hydrogen Sulfide # 4LL	0.1 ppm	1000 mL

5 Analytical Air Sampling

Analytical air sampling will be conducted for the purpose of collecting data that represents TWA concentrations of contaminants throughout the day. When applicable, sampling will be conducted and analyzed for Volatile Organic Compounds specifically, methyl acrylate and octene (additional VOCs if necessary). This sampling may be further developed, according to laboratory data, to include additional constituents identified at or near levels of concern. Monitoring will be responsive to onsite activities and may require additional locations.

All samples will be held according to method/laboratory requirements and will be shipped to an AIHA accredited laboratory for subsequent analysis. Analytical air sampling methods for the compounds below are available in Appendix A. Table 5.1, on the following page, includes sample method information.

Table 5.1 Summary of Analytical Air Sampling Methods

Analyte	Analytical Method	Sample Media	Flow Rate (mL/min)	Max Volume (L)
Methyl Acrylate	Modified NIOSH 2537	XAD-2 Sorbent Tube	10 - 50	8
Volatile Organic Compounds	EPA TO15+TICs	1 Liter Mini-Can	-	1L

5.1 Analytical Air Sampling Stations

- Analytical sampling will occur at fixed stations at the incident site perimeter and when applicable, in locations of specific interest. These fixed stations will be comprised of active sampling pumps. Perimeter monitoring will include analytical air sampling at the existing, fixed ambient air quality stations 2, 3, 4, 12, and 13. These stations provide coverage at representative points along the facility perimeter. Each sample will be positioned at breathing zone levels away from potential air path obstructions.
- Chemicals Sampled at Stations 2, 3, 4, 12, and 13
  - Methyl Acrylate
  - VOCs

6 Data Management

- All analytical air samples will be sent to Galson Laboratories, an AIHA Accredited Laboratory located in East Syracuse, N.Y.
- A request for complete data packages will be made to the laboratory for all samples analyzed.
- The data packets will be reviewed and the data will undergo a data validation process.
- All real-time instruments will be calibrated according to the manufacturer recommendations or as determined necessary by CTEH® personnel.
- Calibration logs will be completed daily.
- Real-time readings will be documented by handwritten notes, handheld PDA, or by the use of data logging capabilities of the instrument, if available.

- Real-time data will be entered onsite and drafts made available upon request.

7 Project Organization

- CTEH® will be responsible for the following:
- Air monitoring
- Toxicology support/Industrial Hygiene Monitoring
- Quality Assurance/Quality Control
- Data evaluation
- Reporting
- CTEH® site management:
- Nathan Williams – Air Sampling Manager
- Dr. Phillip Goad – Partner/Principal Toxicologist

8 Equipment Decontamination

- If required, equipment will be decontaminated by the decontamination group where all entries and exits occur. The decontamination will be with damp cloths as the equipment cannot be submerged under water.

9 Field Documentation

- During the project, the team members will maintain various field books, reports, electronic database, and logs. Each of the components of the field documentation is described below.

10 Calibration and Maintenance of Field Instruments

- The calibration and maintenance of field equipment and instrumentation will be in accordance with each manufacturer's specifications or applicable test/method specifications, and shall be documented in the calibration logs or site safety and health logbooks.

11 Sample Labels and Chain of Custody (COC)

- All sample labels used on sample containers will include, at a minimum, a sample identification code, the date of the sample, and the analyte. Each sample will be identified on a chain of custody record. The analytical sample numbering system will include site name, date, analyte, and identification code unique to each sample.

12 Packaging and Shipping

- Packaging and shipping of samples will vary depending upon sample media, contaminant concentration, preservation technique, and sample container. The person packaging the samples is responsible to ensure that the sample packaging is in suitable condition for shipping.

13 References

ACGIH. Documentation of the TLVs and BEIs with Other Worldwide Occupational Exposure Values. CD-ROM 2011. Cincinnati, Ohio: American Conference of Governmental Industrial Hygienists; 2011.

AIHA. 2011 Emergency Response Planning Guidelines (ERPG) and Workplace Environmental Exposure Level (WEEL) Handbook. Fairfax, VA: American Industrial Hygiene Association; 2011.

ATSDR. Minimal risk levels (MRLs). Atlanta, GA: Agency for Toxic Substance and Disease Registry; 2012 Feb. http://www.atsdr.cdc.gov/mrls/index.asp

DOE/SCAPA. Protective Action Criteria (PAC): Chemicals with AEGLs, ERPGs & TEELs: Rev. 27. Washington, DC: U.S. Department of Energy; 2012 Feb. http://www.atlintl.com/DOE/teels/teel.html

HSDB (Hazardous Substance Data Bank) [TOXNET]. Bethesda, MD: National Library of Medicine, National Toxicology Information Program; 2012. http://toxnet.nlm.nih.gov/

New Jersey Department of Health and Senior Services. Hazardous substance fact sheet: ammonia. Trenton, NJ: New Jersey Department of Health and Senior Services, Right to Know Program, 2007 Sep; RTK Substance number: 0084. http://nj.gov/health/eoh/rtkweb/documents/fs/0084.pdf

NIOSH. NIOSH Pocket Guide to Chemical Hazards. Cincinnati, Ohio: National Institute for Occupational Safety and Health; 2005 Sep; DHHS (NIOSH) Publication No.2005-149.

OSHA. Air contaminant--permissible exposure limits. 29CFR1910.1000

USEPA. Health effects test guidelines. OPPTS 870.2500 Acute Dermal Irritation. Washington DC: Office of Prevention, Pesticides, and Toxic Substances, U.S. Environmental Protection Agency; 1998 Aug; EPA/712/C-98/196.

USEPA. IRIS (Integrated Risk Information System). Washington, DC: U.S. Environmental Protection Agency; 2011. http://www.epa.gov/iris/index.html

Appendix A
Analytical Methods
(Available upon request)

Appendix B
Proposed Work Area AreaRAE Stations