Phase 3 Report

Risk-Based Evaluation of Exploration & Production Wastes

Prepared for

Louisiana Department of Natural Resources Office of Conservation Baton Rouge, Louisiana

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A. EXECUTIVE SUMMARY

Non-Technical Summary

Compliance Solutions, Inc. (CSI) was retained by the Louisiana Department of Natural Resources (DNR) to provide toxicological and risk assessment support with regard to the disposal and treatment of exploration and production (E&P) wastes. Based on analytical data collected under a DNR-mandated testing program, it was determined that the only chemical constituent of these wastes that need be addressed from a workplace or public health point-of-view is benzene. This is because benzene is volatile, and has been found to cause a type of leukemia in individuals exposed repeatedly to high concentrations of benzene vapor at their workplace. This report describes the process by which CSI determined the maximum concentration of benzene allowable in each type of E&P waste such that the health of workers and the public are protected.

Worker Health: CSI conducted interviews with DNR staff and employees of companies involved in the treatment, transfer and disposal of E&P wastes. It was determined that the type of employee with the greatest potential for exposure to benzene vapor as a result of his job is the contract worker who washes out cuttings boxes after the E&P waste they contain is emptied into the open hold of a transport barge. For such a worker, the U.S. Occupational Safety & Health Administration (OSHA) requires that he be exposed to a benzene vapor concentration that is no more than 3.242 mg/m³ (expressed as an average over an 8-hour period).

CSI used two commonly accepted mathematical models to simulate the volatilization on benzene vapor from the waste in the barge (Farmer's Model) and the dispersion of benzene in the breathing zone of the worker (Open-Box Model). While more sophisticated mathematical models are available, these models were selected because the assumptions on which they are based are readily apparent and understood by a technical reader, and because they are health-conservative (i.e., any inaccuracies from the use of these models tend to err on the side of protecting health). In addition, a number of health-conservative assumptions were used by CSI in this analysis including a) that a total of 32 cuttings boxes are emptied and rinsed out during the 8-hour period (i.e., one box every 15 minutes); b) that each cuttings box is filled with the E&P waste to a level 6 inches from the top; c) that the wind blows at a speed of only 2 m/sec (about 4.5 miles per second = half of average wind speed for Louisiana; wind removes benzene vapor from breathing zone); and d) that summer conditions apply (i.e., average temperature is 90°F. Using these assumption, CSI used the combined environmental models to calculate the maximum benzene concentration allowable in each type of E&P waste such that the concentration of benzene vapor in the breathing zone of the Cuttings Box Washer is no more than the OSHA limit. This maximum concentration is called by CSI the Industrial Maximum Permissible Concentration (MPC_{Ind}).

Community Health: Because residential areas are located near commercial waste treatment, transfer and disposal facilities, CSI also evaluated the health risks associated with community exposures to benzene vapor emitted from these operations. As a result of interviews with DNR staff and employees of commercial facilities, it was determined that the type of operation most likely to result in sustained community exposures to benzene vapor was land treatment.

CSI utilized risk-based formulas and assumptions recommended by the U.S. Environmental Protection Agency (EPA). These model assumes that a hypothetical resident (weighing 154 lbs) is exposed to a specific concentration of benzene vapor, 24 hours per day, 350 days per year for 30 years, and then evaluates the resulting increase in cancer risk (called the incremental lifetime cancer risk or ILCR) over that person's expected 70 year lifespan. The EPA and other regulatory agencies accept a maximum ILCR ranging from one-in one million, to one-in-10,000. Stated technically, a one-in-one million ILCR means that if one million adults, each weighing 154 lbs, is exposed to that specific concentration of benzene vapor, 24 hours per day, 350 days per year for 30 years, we are 95% certain that no more than one of those individuals will develop cancer as a result. On that basis, CSI used the EPA risk formula to calculate that the concentration of benzene vapor that results in a one-in-one million ILCR for the hypothetical resident is 0.000294 mg/m^3 . In order to be health-conservative, it was assumed that this concentration was generated by the benzene emissions from each type of E&P waste placed in a 5-acre treatment pond, that 100% of the benzene in the waste volatilizes to the atmosphere during a six-month treatment period, and that the hypothetical resident lives 500 feet from the edge of the treatment pond. Using a commonly accepted vapor dispersion model, it was determined that 289 lbs of benzene must volatilize annually from each type of waste to generate that concentration of benzene vapor at the air breathed by the resident. Based on the historical volumes of each type of E&P waste land-treated in Louisiana, it is then possible to calculate the maximum allowable concentration of benzene in each waste type such that the ILCR criterion of one-in-one million is not exceeded following 30 years of exposure. That maximum concentration is called by CSI the Residential Maximum Permissible Concentration (MPC_{Res}).

E&P Wastes Recommended for Regulation by DNR: Both the MPC_{Ind} and the MPC_{Res} could be adopted by DNR for the regulation of all types of E&P wastes. Both are considered to be based on extremely health-protective assumptions and models, although the MPC_{Res} was found to be more stringent than the MPC_{Ind}. However, because enforcement of regulations requires the expenditure of manpower and resources, CSI used data previously collected under DNR's testing program to evaluate the likely regulatory impact of these potential criteria. It was found that the benzene content of most types of E&P waste are low and generally do not exceed the MPC criteria. Only four types of E&P waste were found to exceed the MPCs at a rate greater than 5% --Waste 05 (Production Pit Sludge), Waste 06 (Production Tank Sludge), Waste 07 (Produced Sand & Solids), and Waste 12 (Gas Plant Waste). CSI recommends that DNR adopt the MPC_{Res} as the regulatory standard for each of the four waste types. Specifically it is recommended that waste generators or commercial facility operators should demonstrate that each batch of waste contains no more than the appropriate MPC_{Res} in order to be accepted for land treatment within the State of Louisiana.

Technical Summary

Compliance Solutions, Inc. (CSI) was retained by the Louisiana Department of Natural Resources (DNR) to provide toxicological and risk assessment support with regard to the disposal and treatment of exploration and production (E&P) wastes. This work was divided into three phases:

- Phase 1 of the project consisted of a review of available toxicological and analytical data on oilfield wastes and recommendation of analytical tests to be required by DNR in an Emergency Rule issued under Statewide Order 29-B. As a result of this Emergency Rule, oil and gas producers and disposal facilities located throughout the state generated analytical data on 16 categories of E&P wastes as defined by DNR. These data were compiled and analyzed by the Hazardous Substance Research Center at Louisiana State University (LSU).
- In Phase 2 of the project, CSI conducted a quality assurance audit of the E&P waste data as compiled in LSU's database, and analyzed the validated analytical data with regard to specific chemical constituents found in each type of E&P waste. CSI concluded that benzene was the only analytical parameter of regulatory concern based

on the EPA's Toxicity Characteristic Leaching Procedure (TCLP), and identified 10 categories of benzene-containing E&P wastes that required a more detailed evaluation in Phase 3 (see Table A-1 below). It is noteworthy that if Waste 01 is excluded from the list, the remaining wastes account for only 6.6% of all of the waste produced in Louisiana during 1998.

Table A-1

Waste	Description	Waste	Description
01	Salt Water / Produced Brine	08	Produced Formation Fresh Water
04	Workover / Completion Fluids	12	Gas Plant Processing Waste
05	Production Pit Sludge	13	BS&W Waste
06	Production Tank Sludge	14	Pipeline Test / Pig Water
07	Produced Sand / Solids	15	Commercial E&P Waste

List of E&P Wastes Selected for Risk-Based Evaluation in Phase 3

Phase 3 is the subject of the present report. In this phase, CSI conducted interviews with DNR staff and the staff of various waste disposal facilities to evaluate how various types of E&P wastes are handled and to identify potential receptors and exposure pathways. Based on these interviews, CSI used the risk-based approaches described below to define recommended Maximum Permissible Concentrations (MPCs) for benzene in each category of E&P waste:

MPC_{Ind}: Industrial MPCs were calculated for each of the priority E&P waste categories identified in Phase 2. The receptor with the greatest potential exposure to benzene was judged to be a Cuttings Box Washer at a commercial transfer facility, who spends approximately eight hours of his workday rinsing out cuttings boxes over a barge hold into which the boxes have been emptied. Based on interviews with representatives from a commercial waste transfer company, CSI made several health-conservative assumptions including a) that 32 cuttings boxes filled with a specific category of E&P waste would be emptied and rinsed out during this 8-hour period; b) that the operation would take place at an atmospheric temperature of 90°F, and c) that the wind speed is only 2 m/sec. A combination of Farmer's Model (volatilization from the waste) and an Open Box Model (dispersion in air) was then used to define the Industrial Maximum Permissible Concentration (MPC_{Ind}) of benzene in a waste such that the concentration of benzene vapor in the breathing zone of such a hypothetical cuttings box washer

would not exceed the Permissible Exposure Limit (PEL) for benzene (1 ppm = 3.242 mg/m^3 as an 8-hour time-weighted average) as established for daily workplace exposures by the U.S. Occupational Safety & Health Administration (OSHA). [see Table A-2 below].

MPC_{Res}: Because commercial waste treatment and disposal facilities are found near residential areas, CSI also considered the potential for waste-derived benzene exposures to a hypothetical residential neighbor (i.e., the receptor). Because of the large volumes of E&P wastes that are placed in land treatment cells (up to 15,000 bbl per acre), it was decided that all waste types (i.e., not just the 10 waste streams identified in Phase 2) should be included in the residential exposure scenario regardless of apparent benzene content. Risk-based formulas and assumptions as specified by the U.S. Environmental Protection Agency (EPA) were used to define the average daily benzene vapor concentration (i.e., daily exposure level) that would produce a one-in-one million (10^{-6}) incremental lifetime risk of cancer. A Gaussian air-dispersion model (API DSS) was then employed to calculate the amount of benzene that must be released from a specific type of E&P waste in a treatment cell in order to result in that daily exposure level for a receptor living 500 feet from the edge of a 5-acre treatment cell (health-conservative assumptions). It was determined that an E&P waste would have to generate 131 kg (289 lbs) of benzene vapor annually for 30 years to increase the lifetime cancer risk of the receptor by 10^{-6} . Based on ten years of quarterly data submitted to DNR by a commercial waste treatment company, the mass of each waste type in a representative treatment cell was calculated.

The volume of Waste 15 (commercial facility waste) was found to be surprisingly large (almost 26% of total E&P wastes received for land treatment), compared to the number of batches received during the Phase 2 program (2 validated samples). It was determined by DNR that Waste 15 comprises solids that are received or generated (e.g., gravity separation of solids) by a commercial transfer facility and sent to a commercial facility for land treatment. For purposes of calculating the Residential Maximum Permissible Concentration (MPC_{Res}) of benzene allowable in each waste category, it was assumed that the amount of Waste 15 received for land treatment was in proportion to the solids content and relative volume of the other waste types received by the commercial transfer station. A portion of Waste 15 was therefore added to each of the other waste categories for the calculation of the MPC_{Res} criteria. For example, a 5-acre treatment cell was assumed to contain on average 580,924 kg of Waste 06 (including 7,374 kg from Waste 15) per treatment cycle. Based on the results of air dispersion modeling, 131 kg of benzene can be released during each 12-month period (i.e., two treatment cycles) for 30 years, without exceeding the 10^{-6} risk target. The MPC_{Res} is therefore 131,000,000 mg of benzene / (2 cycles x 580,924 kg of Waste 06 per cycle) = 113 mg/kg. Stated more directly, the MPC_{Res} is the maximum concentration of benzene permitted in a specific E&P waste such that the incremental lifetime cancer risk (ILCR) for a hypothetical resident living 500 feet from a 5-acre treatment cell will not exceed one in one million (10^{-6}) after 30 years of exposures to benzene vapor derived from that type of E&P waste. As shown in Table A-2 below, the derived MPC_{Res} is substantially more stringent than the MPC_{Ind} criterion for each waste type.

The MPC_{Ind} and MPC_{Res} criteria are Total Benzene concentrations. In order to get an understanding of how regulations based on these criteria would likely impact the treatment and/or disposal of E&P wastes, the TCLP Benzene data submitted to DNR during the Phase 2 program were used to derive an estimate of the Total Benzene content of each sample. This estimate was calculated based on two assumptions: a) that the solids/liquid content of each category of E&P waste is constant; b) that because of the way that the TCLP test is conducted, the Total Benzene content of the waste can be estimated by the formula

Total Benzene = $(1 \times \%Liquid + 20 \times \%Solid) \times TCLP$ -Benzene.

In the real world, both of these assumptions are simplistic. However, based on the estimated Total Benzene values, it is clear that the benzene content of most types of E&P wastes is low, and the expected ILCR for the hypothetical receptor is substantially lower than 10^{-6} for each waste type. Only four categories of E&P waste were found to have more than 5% of submitted samples exceed the MPC_{Ind} and/or MPC_{Res} criteria -- Waste 05 (Production Pit Sludge), Waste 06 (Production Tank Sludge), Waste 07 (Produced Sand / Solids), and Waste 12 (Gas Plant Waste). CSI recommends that DNR adopt the MPC_{Res} as the regulatory standard for each of the above four waste types. Specifically it is recommended that waste generators or commercial facility operators should demonstrate that the benzene content of each batch of E&P waste be no more than the appropriate MPC_{Res} in order to be accepted for land treatment within the State of Louisiana.

Table A-2

MAXIMUM PERMISSIBLE CONCENTRATIONS (MPCs) FOR E&P WASTES

				Occupational Scenario			Residential Scenario		
Waste Code	Description	Validated Samples	MPC _{ind} (mg/kg)	MPC _{ind} Exceedances	Percent MPC _{Ind} Exceedances	MPC _{Res} (mg/kg)	MPC _{Res} Exceedances	Percent MPC _{Res} Exceedances	
02	Oil-Based Drilling Mud & Cuttings	148				104	1	0.7%	
03	Water-Based Drilling Mud & Cuttings	218				12	2	0.9%	
04 *	Drilling, Workover & Completion Fluids	274	1026	2	0.7%	239	3	1.1%	
05 *	Production Pit Sludges	20	1007	0		43	1	5.0%	
06 *	Production Storage Tank Sludge	162	1007	15	9.3%	113	35	21.6%	
07 *	Produced Oily Sands & Solids	147	1007	4	2.7%	97	9	6.1%	
12 *	Gas Plant Waste	4	1015	1	25.0%	1214	1	25.0%	

* Recommended by CSI for risk-based evaluation (Phase 3 of DNR program).

NC = Not Calculated (Based on Phase 2 evaluation).

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DNR Phase 3 Report
C. BACKGROUND

The history of Louisiana's governmental interest in the regulation of oilfield waste disposal facilities dates back to July 20, 1980, when the Department of Natural Resources (DNR) added Paragraph 13 to Section XV of Statewide Order No. 29-B. This paragraph contained the first rules issued in the United States governing commercial oilfield waste disposal facilities and began a succession of increasingly more stringent regulatory controls designed to protect human health and the environment.

While other states were promulgating regulatory controls on the disposition of Exploration and Production (E&P) wastes, the federal government was conducting studies to determine the potential for adverse health and environmental effects posed by E&P wastes. The 1987-1988 study conducted by the United States Environmental Protection Agency concluded that many of these wastes did not pose a significant hazard when properly managed and subsequently certain oil and gas wastes were exempted from hazardous waste regulations under the Resource Conservation and Recovery Act (RCRA).

The limited testing required by DNR under Statewide Order No. 29-B for wastes received at commercial storage, treatment, and disposal facilities was considered to be consistent with the national exemption for E&P waste under RCRA. The adequacy of DNR's testing requirements were brought into question in March of 1994 when Exxon transported 81 loads of gas plant waste from their Escambia, Alabama gas plant to the DNR-permitted disposal facility at Campbell Wells (US Liquids) near Houma, Louisiana. This odiferous waste prompted the residents of the nearby community of Grand Bois to file suits against Campbell Wells and Exxon alleging adverse health effects from toxic emissions from the waste treatment facility.

Governor M.J. "Mike" Foster became aware of the intensity of local concern over the US Liquids facility during the 1997 legislative session and his concern prompted several environmental initiatives in response to the Grand Bois situation. One of these initiatives was the review of existing state regulations regarding "non-hazardous oilfield waste" (NOW; the term then applied to RCRA-exempt E&P wastes) and a reevaluation of the testing requirements of waste prior to unloading at commercial waste disposal facilities. In

October of 1997, Governor Foster announced that the state would begin the testing of oilfield waste prior to disposal and DNR Secretary Jack Caldwell began the planning necessary to implement the testing.

Secretary Caldwell retained Dr. Ben Thomas of Compliance Solutions, Inc. (CSI) to serve as a toxicological consultant to DNR. A three-phase program was outlined:

- <u>Phase 1</u>: The Phase 1 program evaluated available published literature concerning the chemical composition of each category of E&P waste, and recommended analytical testing requirements for DNR's 29-B test program. The testing program included the analysis of benzene, toluene, ethylbenzene, xylene (volatile constituents in crude oil and natural gas condensates; collectively referred to as BTEX) and metals using the Environmental Protection Agency's (EPA) Toxicity Characteristic Leaching Procedure (TCLP). Analysis of Total Sulfur and Reactive Sulfur, as well Oil & Grease content were also required for certain types of E&P wastes.
- <u>Phase 2</u>: Evaluation of the analytical results submitted to DNR under their 29-B testing program and identification of highpriority E&P wastes and constituents; and
- <u>Phase 3</u>: Development of recommended Maximum Permissible Concentrations (MPCs) for high-priority E&P wastes.

Continued public concern over the issue of potential adverse health effects resulting from E&P wastes warranted the issuance of the May 1, 1998 Emergency Rule amendment to Statewide Order 29-B by the commissioner of conservation. A second Emergency Rule was issued on August 29, 1998 for the purpose of extending the period of testing. This extension of the sampling and testing period was necessary to acquire additional analytical data, thereby strengthening the validity of conclusions reached during the interpretation of this data.

The lead role in the analysis of the voluminous data collected during the sampling program was undertaken by the Hazardous Substance Research Center at Louisiana State University. The Center issued a March 29, 1999 report entitled "TCLP Characterization of Exploration and Production Wastes in Louisiana." It was at this point that Compliance Solutions, Inc. (CSI), which had previously provided toxicological support during the development of the 29-B Emergency Rule, began its independent quality assurance audit of the analytical data and statistical procedures used in the LSU report.

The audit of the 541 sample batches revealed a high degree of accuracy on the part of the LSU staff. Refinements of their techniques employed by CSI did not significantly alter the validity of the statistical analyses that they performed. On August 13, 1999, this phase of the project culminated in CSI's issuance of its *Phase 2 Report on the Quality Assurance Audit and Statistical Analysis of the E&P Waste Database*.

Based on our analysis of the data submitted to DNR as part of the 29-B emergency test program, CSI concluded that benzene (a known human leukemogen) was the only analyte from the 29-B test program that was of regulatory concern. It was recommended that the following ten wastes undergo a more detailed risk-based evaluation in Phase 3 of the program:

- Waste 01 (Salt Water / Produced Brine)
- Waste 04 (Drilling, Workover & Completion Fluids)
- Waste 05 (Production Pit Sludge)
- Waste 06 (Production Tank Sludge)
- Waste 07 (Produced Sand / Solids)
- Waste 08 (Produced Formation Fresh Water)
- Waste 12 (Gas Plant Processing Waste)
- Waste 13 (Basic Sediment & Water Waste)
- Waste 14 (Pipeline Test Water / Pipeline Pig Water)

• Waste 15 (E&P Waste Generated by Commercial Facilities)

The objective of the Phase 3 work was to determine how E&P wastes are treated and/or disposed, who might be exposed to benzene from those wastes, and how that exposure might occur. In the case of potential industrial exposures, this was accomplished through interviews with the staff of four different types of commercial waste treatment facilities to define relevant exposure pathways. Because land treatment cells are required by DNR to be lined with at least 12 inches of a "slowly permeable" soil (LAC 43: XIX.129.M.7.c.i and ii), contamination of groundwater by benzene is unlikely. Therefore, air emissions modeling provided the means to quantify the potential exposures to benzene vapor for a worker at a commercial facility and for a hypothetical residential receptor. Such an understanding is critical for development of risk-based regulations for E&P wastes.

DNR Phase 3 Report D. EXPLORATION AND PRODUCTION WASTES

General E&P Waste Classification

The Exploration & Production (E&P) industry produces a large number of waste streams during the production of crude oil and natural gas. Although some of these waste streams may contain hazardous substances, the concentrations of these hazardous constituents are relatively low. The Environmental Protection Agency (EPA) classifies E&P wastes into two categories, namely exempt and non-exempt wastes.

An exempt waste is a waste that is generated during an operation that is uniquely associated with the production of oil and gas. These wastes are sometimes referred to as non-hazardous oilfield waste (NOW). An example of NOW would be produced water. A non-exempt waste, on the other hand, is a waste that is generated during an operation that is not uniquely associated with the production of oil and gas. An example would be painting wastes that are generated while painting a tank or vessel.

Generally, the EPA believed these large volumes of waste are lower in toxicity than other materials being regulated as hazardous waste under RCRA. Subsequently, Congress exempted these wastes from the RCRA Subtitle C hazardous waste regulations pending a study and regulatory determination by the EPA. The EPA has given jurisdiction to the individual states to develop disposal criteria for these wastes. However, non-exempt wastes must comply with RCRA.

The following is a list of exempt and non-exempt wastes published by the EPA.

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Exempt E & P Wastes

- Produced water
- Drilling fluids
- Drill cuttings

- Cooling tower blowdown
- Spent filters, filter media, and backwash (assuming the filter itself is not hazardous

- Rigwash
- Drilling fluids and cuttings from offshore operations disposed of onshore
- Geothermal production fluids
- Hydrogen sulfide abatement wastes from geothermal energy production
- Well completion, treatment, and stimulation fluids
- Basic sediment and water and other tank
 bottoms from storage facilities that hold
 product and exempt waste
- Accumulated materials such as hydrocarbons, solids, sand, and emulsion
 from production separators, fluid testing vessels, and production impoundments
- Pit sludges and contaminated bottoms from storage or disposal of exempt wastes
- Gas plant dehydration wastes, including glycol-based compounds, glycol filters, • filter media, backwash, and molecular sieves
- Gas plant sweetening wastes for sulfur
 removal, including amines, amine filters, amine filter media, backwash, precipitated
 amine sludge, iron sponge, and hydrogen sulfide scrubber liquid and sludge
- Workover wastes

and the residue in it is from an exempt waste stream)

- Pipe scale, hydrocarbon solids, hydrates, and other deposits removed from piping and equipment prior to transportation
- Produced sand
- Packing fluids
- Hydrocarbon-bearing soil
- Pigging wastes from gathering lines
- Wastes from subsurface gas storage and retrieval, except for the nonexempt wastes listed below
- Constituents removed from produced water before it is injected or otherwise disposed of
- Liquid hydrocarbons removed from the production stream but not from oil refining
- Gases from the production stream such as hydrogen sulfide and carbon dioxide, and volatilized hydrocarbons
- Materials ejected from a producing well during the process known as blowdown
- Waste crude oil from primary field operations
- Light organics volatilized from exempt wastes in reserve pits or impoundment or production equipment

Nonexempt E & P Wastes

- Unused fracturing fluids or acids
- Gas plant cooling tower cleaning wastes
- Painting wastes
- Waste solvents
- Oil and gas service company wastes such as empty drums, drum rinsate, sandblast media, painting wastes, spent solvents, spilled chemicals, and waste acids
- Vacuum truck and drum rinsate from trucks and drums transporting or containing nonexempt waste
- Refinery wastes
- Liquid and solid wastes generated by crude oil and tank bottom reclaimers
- Used equipment lubricating oils
- Waste compressor oil, filters, and blowdown

Louisiana Exempt E&P Waste Classification

- Used hydraulic fluids
- Waste in transportation pipeline related pits
- Caustic or acid cleaners
- Boiler cleaning wastes
- Boiler refractory bricks
- Boiler scrubber fluids, sludges and ash
- Incinerator ash
- Laboratory wastes
- Sanitary wastes
- Pesticide wastes
- Radioactive tracer wastes
- Drums, insulation, and miscellaneous solids

In the state of Louisiana, the exempt waste streams are classified by DNR into 18 different categories as discussed below. Table D-1 is a summary of the relative proportion of solids and liquid that is characteristic of each waste type, and has been assumed by CSI in its Phase 3 evaluations. This table also provides the weight of each waste type, a parameter that is used in the exposure modeling discussed in Section F.

The primary chemical of concern in E&P wastes is benzene (LSU 1999; CSI 1999). In the Phase 2 testing program, benzene was analyzed by EPA's Toxicity Characteristic Leaching Procedure (TCLP) method (see Section G), and results were compared to the

regulatory criterion of 0.5 milligrams per liter (mg/L). The following paragraphs describe E&P wastes and discuss the frequency that TCLP-Benzene was seen to exceed the 0.5 mg/L criterion in each waste.

Waste Code 01 -- Salt Water (Produced Brine)

Water produced from an oil or gas well, where the concentration of chloride ion in the water is greater than 500 parts per million (ppm) is referred to as Produced Brine. A certain amount of "salty" formation water is present in many oil or gas reservoirs. The quantity of water produced depends on the recovery method, the nature of the formation being produced, and the length of time the field has been producing. Generally, the ratio of produced water to oil or gas increases over time; it may exceed 90 percent of the total produced volume. The Total Dissolved Solids (TDS) in produced water ranges from several hundred parts per million to over 150,000 ppm. In addition to petroleum hydrocarbons and metals, produced brine may also contain biocides, coagulants, corrosion inhibitors, cleaners, dispersants, and emulsion breakers. As shown in Appendix Tab A, the concentration of TCLP-Benzene in this waste exceeds the TCLP criterion of 0.5 milligrams per liter (mg/L) in 10-30% of samples.

Waste Code 02 -- Oil-Based Drilling Mud & Cuttings

Oil-based mud is a thick, heavy liquid that is circulated through the drilling well to carry pieces of rock (bit cuttings) from the drill bit to the surface. They are used when water sensitive

formations are drilled, high temperatures are encountered, pipe sticking occurs, or when it is necessary to protect against severe drill string corrosion. After being used, oil-based drilling fluids are composed of water-in-diesel oil emulsion, bentonite clays, and drilled solids. Also present are additives for control of fluid properties such as viscosity. Since fluid stability is necessary, additives such as fluid loss control materials, thinners, and weighting agents are used. The concentration of TCLP-Benzene in this waste rarely exceeded the TCLP criterion of 0.5 milligrams per liter (mg/L) [see TCLP-Benzene data compiled in Appendix Tab B].

Waste Code 03 -- Water-Based Drilling Mud & Cuttings

Water-based muds can be made with fresh or saline water and are used for most types of drilling. Water-based fluids are composed of fresh water, naturally occurring clays, drilled solids and additives for fluid loss control, viscosity, thinning, pH control, and weight control. These additives are necessary to maintain down-hole fluid properties and for fluid stability. This waste stream also contains reactive solids like bentonite clays, and weight-control solids such as barite. The concentration of TCLP-Benzene in this waste rarely exceeded the TCLP criterion of 0.5 milligrams per liter (mg/L) [see TCLP-Benzene data tabulated in Appendix Tab C].

Waste Code 04 -- Drilling, Workover & Completion Fluids

Drilling fluids primarily consist of spent hydraulic fluids that are a result of the drilling operation. Workover fluids and completion fluids are primarily fresh water or saltwater based fluids with additives for special purposes. These fluids include well completion, treatment, and stimulation fluids; inert materials originating from downhole, such as produced sand, formation and pipe scale, and cement cuttings; and pieces of downhole equipment such as sealing elements and pumping equipment. This waste stream comprises salts, organic polymers, corrosion inhibitors, and petroleum hydrocarbons. The concentration of TCLP-Benzene in this waste exceeds the TCLP criterion of 0.5 milligrams per liter (mg/L) in 10-30% of samples [see TCLP-Benzene data tabulated in Appendix Tab D].

Waste Code 05 -- Production Pit Sludges

Pit sludge is generally composed of drilling mud and cuttings, rigwash and spent completion fluids. Materials found in pit sludges include accumulated hydrocarbons, solids, sand, and emulsions. Pits are open to the atmosphere except when flooded with water. It should be noted that these sludges contain populations of microbes that feed on petroleum hydrocarbons. The result of this biological action is a reduction in the amount of hydrocarbon present, a process called biodegradation. The concentration of TCLP-Benzene in

this waste exceeds the TCLP criterion of 0.5 milligrams per liter (mg/L) in 10-30% of samples [see TCLP-Benzene data tabulated in Appendix Tab E].

Waste Code 06 -- Production Storage Tank Sludge

Tank bottoms are basic sediment and water (BS&W) and other materials that collect in the bottom of tanks at production treatment, separation and storage facilities. The term "tank" may refer to production separators, fluid treating vessels, crude oil stock tanks, and production impoundments. Although open production impoundments are occasionally called "tanks", sludges originating from impoundments are more correctly called Production Pit Sludge (Waste 05). In any case, the use of open production pits is no longer practiced. Materials found in tank bottoms include accumulated heavy hydrocarbons, solids, sand, emulsions, and mineral scale. As mentioned above for Waste 05, biological activity is present in these hydrocarbons, resulting in a steady decrease in hydrocarbon concentration. The concentration of TCLP-Benzene in this waste exceeds the TCLP criterion of 0.5 milligrams per liter (mg/L) in more than 30% of samples [see TCLP-Benzene data tabulated in Appendix Tab F].

Waste Code 07 -- Produced Oily Sands & Solids

Produced oily sands and solids comprises sand, drilling debris, and other solids produced during the drilling process and/or from the operation of a producing well. These materials may also contain crude oil, salts, organic polymers, and corrosion inhibitors. The concentration of TCLP-Benzene in this waste exceeds the TCLP criterion of 0.5 milligrams per liter (mg/L) in more than 30% of samples [see TCLP-Benzene data tabulated in Appendix Tab G].

Waste Code 08 -- Produced Formation Fresh Water

Produced formation fresh water contains petroleum hydrocarbons, metals, biocides, coagulants, corrosion inhibitors, cleaners, dispersants, and emulsion breakers. Produced formation fresh water is defined as water originating from oil and gas production containing less than 500 parts per million (ppm) of Total Dissolved Solids (TDS). This waste displayed low concentrations of TCLP-Benzene in the available sample batches but there are insufficient samples for reliability [see TCLP-Benzene data tabulated in Appendix Tab H].

Waste Code 09 -- Rainwater

Rainwater (storm water) can become contaminated upon contact with hydrocarbon leaks or spills. To prevent this from taking place, good housekeeping practices, spill/leak prevention, containment, and cleanup procedures must be observed. When contamination of rainwater occurs, is must be handled as a waste and treated accordingly. The concentration of TCLP-Benzene in this waste rarely exceeded the TCLP criterion of 0.5 milligrams per liter (mg/L) [see TCLP-Benzene data tabulated in Appendix Tab I].

Waste Code 10 -- Washout Water

Washout water is generated from the cleaning of vessels (barges, tanks, etc.) that transport E&P waste, and are not contaminated by other regulated chemicals. These regulated (non-exempt) chemicals include those controlled by the EPA under the Resource Conservation & Recovery Act (RCRA). This waste displayed low concentrations of TCLP-Benzene in the available sample batches but there are insufficient samples for reliability [see TCLP-Benzene data tabulated in Appendix Tab J].

Waste Code 11 -- Washout Pit Water

Water from oilfield-related carriers that are only permitted to haul non-hazardous oilfield waste. Washout pit waste is regulated under RCRA if it is contaminated with hazardous chemicals originating from sources outside of oil and gas exploration and production. This stream would contain the residue (solids, sludges, etc.) present in the washout pit. The concentration of TCLP-Benzene in this waste exceeds the TCLP criterion of 0.5 milligrams per liter (mg/L) in 10-30% of samples [see TCLP-Benzene data tabulated in Appendix Tab K].

Waste Code 12 -- Gas Plant Waste

Natural gas plant processing waste that is or may be commingled with produced formation water. The concentration of TCLP-Benzene in this waste exceeds the TCLP criterion of 0.5 milligrams per liter (mg/L) in more than 30% of samples [see TCLP-Benzene data tabulated in Appendix Tab L].

Waste Code 13 -- Basic Sediment & Water (BS&W) Waste

BS&W consists of waste from approved salvage oil operators who only receive waste oil from oil and gas leases. The concentration of TCLP-Benzene in this waste exceeds the TCLP criterion of 0.5 milligrams per liter (mg/L) in more than 30% of samples [see TCLP-Benzene data tabulated in Appendix Tab M].

Waste Code 14 -- Pipeline Test Water

This stream contains water that does not meet discharge limitations established by the state. This waste fluid is generated from the cleaning and pressure testing of hydrocarbon pipelines. The concentration of TCLP-Benzene in this waste exceeds the TCLP criterion of 0.5 milligrams per liter (mg/L) in more than 30% of samples [see TCLP-Benzene data tabulated in Appendix Tab N].

Waste Code 15 -- Commercial Facility Waste

This waste stream is believed to consist of three types of materials received or generated at commercial transfer facilities: 1) waste barge loads received by commercial transfer facilities and trans-shipped (unaltered) to a commercial land treatment facility; 2) solids remaining in barges returning from waste shipments to Texas processing facilities; and 3) sludge material accumulating from gravity separation and liquid decantation of solids-laden washout water. This waste displayed low concentrations of TCLP-Benzene in the sample batches submitted during the Phase 2 program, but there were insufficient samples to confidently conclude that benzene is not an issue with this waste [see TCLP-Benzene data tabulated in Appendix Tab O].

From the data provided by a commercial land treatment company, it became apparent that over the past few years, commercial facilities have taken these solids and re-manifested them simply as Waste 15. As a result, Waste 15 accounted for approximately 26% of all E&P waste accepted for land treatment in Louisiana during the past 10 years, and any reference to the original waste type was lost. After discussion with DNR staff, it was decided that Waste 15, for the purposes of the Phase 3 evaluation, should be distributed among other waste categories in proportion to their solids content and their relative volume (as received by the commercial waste transfer company). Volume data that had been provided to CSI early in the Phase 3 program by a commercial waste transfer company (representing total receipts during six months in 1999) were compared with receipt data available from DNR's regulatory database for the first three months of 2000. As summarized in Table D-2, the relative percentage of total receipts represented by each category of E&P waste were similar between the two data sets and therefore CSI combined the industry and DNR data to use as the basis for reallocating Waste 15.

Waste Code 16 -- Oil Spill Waste

Wastes that are generated from crude oil spill clean-up operations are classified as oil spill wastes. This waste stream will contain constituents that will depend on the nature of the spilled material(s) and the materials used to clean up the spill. The concentration of TCLP-Benzene in this waste rarely exceeded the TCLP criterion of 0.5 milligrams per liter (mg/L) [see TCLP-Benzene data tabulated in Appendix Tab P].

Waste Code 50 -- Waste Containing Salvageable Crude / Hydrocarbons

This waste stream contains waste crude that still has hydrocarbons that can be recovered. This can be shipped to a salvage operator or can be disposed of as a waste. This stream usually contains a mixture of constituents including heavy hydrocarbons and sludges. Wastes do not generally appear at treatment facilities coded with this number. The analytical data collected from oil and gas operators and submitted to DNR did not contain any code 50 information.

Waste Code 99 -- Other E&P Wastes

This waste stream contains other E&P wastes not specifically identified above but determined to be exempt from the requirements of RCRA according to the Form UIC-23 process. This waste displayed low concentrations of TCLP-Benzene in the available sample batches but there are insufficient samples for reliability [see TCLP-Benzene data tabulated in Appendix Tab Q].

Table D-1

Waste Code	Waste Type Soli		uids Ratio netric)	Waste Weight (Kg/Bbl)	
01	Salt Water (Produced Brine)	1:99	1022.5	162.6	
02	Oil-Based Drilling Mud & Cuttings	10:90	1044.1	166.0	
03	Water-Based Drilling Mud & Cuttings	10:90	1044.1	166.0	
04	Drilling, Workover & Completion Fluids	5:95	1032.0	164.1	
05	Production Pit Sludges	50:50	1140.0	181.2	
06/15	Production Storage Tank Sludge	50:50	1140.0	181.2	
07	Produced Oily Sands & Solids	50:50	1140.0	181.2	
08	Produced Formation Fresh Water	3:97	1027.3	163.3	
09	Rainwater	1:99	1022.5	162.6	
10	Washout Water	5:95	1032.0	164.1	
11	Washout Pit Water	5:95	1032.0	164.1	
12	Gas Plant Waste	30:70	1092.0	173.6	
13	Basic Sediment and Water (BS&W)	10:90	1044.1	166.0	
14	Pipeline Test Water	3:97	1027.3	163.3	
16	Oil Spill Waste	50:50	1140.0	181.2	

Assumed Weight per Barrel of E&P Waste

Abbreviations: Kg - Kilograms m³ - Cubic meters

m^o - Cubic meters Bbl - Barrel (42 gallons)

	Comparison of DNR and Newpark Waste Volumes							
Waste	Description	% of	f Received V	/aste		Solids (Waste 15)	
		DNR*	Newpark*	Combined	Content	W15 Factor	Bbl of W15	Kg to Add*
01	Salt Water (Produced Brine)	2.31%	3.15%	2.73%	0.01	0.0003	0.64	11
02	Oil-Based Drilling Mud & Cuttings	13.63%	13.83%	13.73%	0.10	0.0137	31.98	5,79
03	Water-Based Drilling Mud & Cuttings	40.16%	37.21%	38.68%	0.10	0.0387	90.10	16,32
04	Drilling, Workover & Completion Fluids	10.35%	13.32%	11.84%	0.05	0.0059	13.79	2,49
05	Production Pit Sludges	0.62%	0.55%	0.58%	0.50	0.0029	6.79	1,23
06	Production Storage Tank Sludge	1.71%	5.28%	3.49%	0.50	0.0175	40.69	7,37
07	Produced Oily Sands & Solids	3.08%	3.13%	3.10%	0.50	0.0155	36.12	6,54
08	Produced Formation Fresh Water	0.03%	0.09%	0.06%	0.03	0.0000	0.04	
09	Rainwater	0.22%	4.48%	2.35%	0.01	0.0002	0.55	9
10	Washout Water	26.27%	15.23%	20.75%	0.05	0.0104	24.17	4,37
11	Washout Pit Water	0.27%	0.84%	0.55%	0.05	0.0003	0.65	11
12	Gas Plant Waste	0.47%	0.11%	0.29%	0.30	0.0009	2.04	36
13	Basic Sediment and Water (BS&W)	0.29%	0.26%	0.28%	0.10	0.0003	0.64	11
14	Pipeline Test Water	0.06%	1.25%	0.66%	0.03	0.0002	0.46	8
15	Commercial Facility Waste	0.00%	0.68%	0.34%	0.50			
16	Oil Spill Waste	0.54%	0.55%	0.54%	0.50	0.0027	6.35	1,15
99	Other E&P Waste	0.00%	0.03%	0.01%	0.50			
Total		100.00%	100.00%	100.00%		0.1095	255.00	46,20
Available	data includes waste receipts from a commercial transfer with solids content, to allocate Waste 15. W15 Factor =	company (Jan - J	lune 1999) and fr	om DNR's regulat		Jan - Mar 2000). Th	hese data were av	

** Amount of Waste 15 (kg) to be allocated to other waste cateories, assuming a 5-acre treatment cell.

DNR Phase 3 Report **E. EXPOSURES TO E&P WASTES**

OCCUPATIONAL EXPOSURES

Based on information gained during Phase 2 of this program, it became apparent that there are two broad categories of E&P wastes -- a) liquid wastes and b) waste slurries (i.e., containing a significant portion of solids). Liquid wastes are generally stored, transported, and disposed of (injected into deep wells) in closed systems that largely prevent human exposures. Solids, on the other hand, are transported and/or treated in systems that allow volatilization of chemical constituents (e.g., benzene vapor) and dispersion in the air. As a result, it was primarily the solids-containing E&P wastes (i.e., those having a significant portion of submitted TCLP Benzene data above the EPA's screening level) that were recommended for risk-based evaluation in this Phase 3 program.

In order to understand a) how E&P wastes are handled, transported, treated and disposed of, and b) who and how people are potentially exposed to benzene vapor from those processes, CSI interviewed experts at DNR, as well as representatives from Louisiana's commercial transfer and treatment facilities. The following summarizes the results of those interviews.

Commercial Transfer Facilities

Contract Worker - In CSI's opinion, the receptor with potentially the greatest workplace exposures to benzene from E&P wastes is a contract worker who washes out cuttings boxes at a transfer facility. During the transfer operations, cuttings boxes are hoisted from the deck of a barge or workboat, and inverted over the open hold of the transfer barge. A contract worker stands on a catwalk extending across the hold and washes residue out of the inverted box into the hold. It is our understanding that such a worker would be engaged in this activity for eight hours of his usual 12-hour shift. Benzene present in the waste will volatilize and a certain portion of the generated vapor will reach the worker's breathing zone. In addition to inhalation, other exposure pathways were considered by CSI including ingestion of particulate (dust or small droplets of mud), inhalation of mist (small droplets of liquid), dermal contact with particulate, dermal contact with vapor, dermal contact with mist, dermal contact with liquid, and ingestion of liquid. These additional pathways were therefore not considered further in this risk-based evaluation.

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Site Manager - This individual stands outside near the operations that fill the transfer barges. He may be supervising the contract workers on the deck of the transfer barge or watching the unloading of vacuum trucks into the barge hold. This person is also exposed to benzene vapors but this exposure is more limited than that of the contract worker because he is standing off to the side of the barge hold, not directly above it as with the contract worker. The site manager's activities also take him away from the barge loading area, further reducing the likelihood of exposure. Inhalation of particulate and mists and dermal contact with liquid and mist were considered in the pathway assessment but were discounted for the reasons cited above.

Vacuum truck driver – The vacuum truck driver transports several different types of predominantly liquid wastes that are pumped through the truck's discharge hose directly into the open barge hold. The splashing of wastes into the hold generates vapors and mists. In addition, this worker may come into contact with some liquids during handling of the pump hose and he may have some dermal exposure to mists. However, these pathways present negligible opportunity for exposure to benzene. Spillage from the discharge hose is infrequent and mists are mainly confined to the hold of the barge. Except for minimal inhalation of vapor during unloading, no other pathways appear to present a significant health risk.

Commercial Land Treatment Facilities

Truck Driver (Open and Vacuum) - This individual is responsible for dumping solid wastes from open trucks or pumping liquid wastes directly into the treatment cells. The major pathway of exposure is through inhalation of vapor. This receptor might also be exposed through inhalation of particulate but the potential benzene concentrations in the particles are expected to be very low. As stated above, E&P wastes are generally wet and not likely to produce dusty conditions during unloading.

Bulldozer Operator – After wastes have been deposited at the edge of a treatment cell, this individual is responsible for spreading the wastes evenly over the bottom of the cell. The bulldozer operator is potentially exposed through inhalation of vapors, inhalation of particulate, ingestion of particulate, and dermal contact with particulate. As mentioned above, the major pathway of exposure is through inhalation since other pathways offer little chance of contact with benzene. After the cell is fully loaded, it is flooded so that hydrocarbons may be skimmed off. Although the bulldozer operator does not spend as much time working in the cell as the

eggbeater operator, this receptor's potential for exposure is higher since the spreading of wastes in the cell involves working with fresh E&P wastes. In the commercial treatment cell facilities, this individual has the highest potential for exposure. However, the magnitude of this exposure is still lower than that of the contract worker discussed above.

Eggbeater Operator- This individual is responsible for churning the contents of the treatment cell in an enclosed vehicle. As with other receptors, several potential exposure pathways were considered, including ingestion of particulate, inhalation of mist, inhalation of particulate, dermal contact with particulate, dermal contact with liquid, and dermal contact with mist. When the eggbeater is operating, the cell is flooded and would not give rise to dusty conditions. In addition, the cab of the eggbeater is enclosed which further reduces the likelihood of exposure to mists or particulate. Dermal contact with liquid is not expected to occur with any regularity and is not considered a contributing factor to benzene exposure. As noted for other receptors, the major pathway of exposure is through inhalation.

Offsite Receptor- This individual is usually a resident that lives in a nearby subdivision. The major pathway of exposure is through inhalation of vapor. The assumptions built into the air dispersion modeling for the residential receptor included a 5-acre treatment cell loaded twice a year with 62,083,462 kg of E&P waste. The receptor is located 500 feet from the edge of the treatment cell. Since the waste in the treatment cell is either wet or under water, the likelihood of exposure due to particulate inhalation is very low. Particulate emissions in the form of blowing dust may be occasionally generated from site roadways but this particulate will have negligible benzene content.

Site Manager - The site manager is potentially exposed to benzene vapors but the opportunity for exposure is limited. Other site workers have a much higher potential for exposure to fresh E&P wastes.

Analyst – The analyst catches samples of incoming waste streams for analysis at the onsite analytical laboratory. This task does not entail the duration of exposure necessary to be considered as a receptor with a significant potential inhalation of vapors.

Tank Washer – The tank washers enter boat tanks after their contents have been pumped out to the transfer barge. They are generally wearing appropriate personal protective gear and therefore have a low exposure risk. Other workers have a much higher potential for exposure.

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Commercial Crude Oil Reclamation Facilities

Truck Driver - This individual is responsible for pumping recyclable liquid wastes from a vacuum truck into the slop tank for separation. Since the system is closed, there is little opportunity for exposure to the driver.

Yard Man - Oversees site operations at the recycling facility. The yardman moves around within the site and is not situated near emissions sources for long periods of time. The exposure risk to this receptor from inhalation of vapor is very low.

Site Operators - The site operator and operator's helper gauge tanks and change filters and therefore have an opportunity to be exposed to benzene through inhalation of vapor. However, these tasks are only performed for approximately one hour every day. The frequency and duration of exposure, although higher than that for other workers at the facility, are not considered to be significant.

Commercial Waste Processing Facilities

Truck Driver - This individual is responsible for dumping solid wastes on a staging pad for placement into the hopper that begins the treatment process. The vacuum truck driver pumps liquid wastes into a holding barge. The truck drivers have the potential to be exposed via inhalation of vapor but the level of exposure is expected to be low. Other receptors at the facility have a higher potential for exposure.

Excavator Operator – This individual excavates solids from the holding barge that were not able to be pumped to the slab. This individual has low potential for exposure since the excavator controls are located approximately 20 feet from the waste, reducing the potential for benzene exposure in this receptor. In addition, the waste has already been agitated in the holding barge, which would reduce significantly the amount present in the waste this worker is handling.

Centrifuge Operator – The centrifuge operator is located 30 to 40 feet from the material being processed and is expected to encounter low concentrations of vapors infrequently.

The waste has already been subjected to agitation and other handling operations, reducing its potential to produce benzene vapors.

Loader Operator – The loader operator places wastes dumped on the staging slab into the process hopper. This operation places the worker in close proximity to the wastes but the fact that wastes have already been agitated reduces their potential to produce benzene vapors. The degree of exposure through inhalation of vapor is expected to be low for this receptor.

Site Operator - The site operator is not present in the vicinity of fresh wastes for significant time periods and therefore is not likely to accumulate a significant exposure. Other workers at this type of facility have a higher potential for exposure while working with the wastes.

Summary -- Exposures at Commercial Facilities

Compliance Solutions, Inc. (CSI) conducted extensive interviews with representatives from the four major types of commercial facilities. The interviews were conducted with the goal of identifying the single receptor with the highest potential for exposure to benzene. At the conclusion of these interviews, it was clear that the contract worker washing out cuttings boxes was the most susceptible receptor for benzene exposure. The determining factors for this receptor were position and proximity to fresh wastes and the length and duration of the exposure. The major pathway for benzene exposure was by inhalation of vapors. Other pathways were either incomplete or contributed only negligible amounts to the exposure scenario.

RESIDENTIAL EXPOSURES

In order to ascertain the risk posed by the handling and treatment of waste at commercial land treatment facilities, it was necessary to determine the degree to which residential receptors may be exposed to benzene vapors. This determination requires the use of an emissions model to back-calculate the concentration of benzene in a waste such that the target cancer risk (one in one million or 1×10^{-6}) is not exceeded at the receptor point. A detailed explanation of the assumptions and results of this modeling is given in Section F.

Exposure pathways for residential receptors were considered, and inhalation of vapor was the only complete pathway available for the transport of benzene to a residential receptor. The inhalation pathway is modified by various parameters such as distance from the source to the receptor, wind speed, and wind direction. All of these parameters are entered into the risk-based exposure model.

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The Louisiana Department of Natural Resources has issued regulatory guidance that established a limit of 500 feet as the minimum distance from a residence that a treatment cell may be constructed at a commercial facility. Louisiana Administrative Code (Title 43, Part XIX, Section 129.M.2.d.i.) states the following:

"Commercial facilities and associated saltwater disposal wells may not be located in any area where the disposal well or related storage tanks, pits, treatment facilities or other equipment are within 500 feet of a residential, commercial, or public building..."

The emissions modeling that was performed as part of the exposure assessment assumed a distance of 500 feet from the edge of the land treatment cell (assumed to be square) to a hypothetical residential neighbor.

The length of exposure for residential receptors is a value provided in regulatory guidance issued by the Environmental Protection Agency. Various population mobility studies have shown that the 50^{th} and 90^{th} percentile values for years living in a home are close to that found by the U.S. Bureau of the Census which determined these values to be 9.1 and 32.7 years respectively. The value that is recommended by EPA for risk assessments is the 95^{th} percentile, which is 30 years (EPA, 1997 Table 15-176). This is the value used for exposure duration (ED) in the calculation of a risk-based concentration of benzene that is protective of residents (see discussion in Section F below).

Another exposure pathway that was considered was inhalation of particulate. It was determined that this pathway would result in a negligible exposure to benzene for three reasons:

- The wastes that are deposited in treatment cells are kept moist or wet to enable the natural biodegradation of petroleum hydrocarbons. Since the content of the cells are moist (if not actually under water), there is little opportunity for dusts to form. Roadways at treatment facilities at wetted to prevent dust formation, but occasionally dusty roadways may occur.
- If dusts are formed, they originate from mixtures of different waste types, not solely from wastes with elevated benzene content. In addition, the wastes that are potentially capable of producing an exposure constitute a fraction of the total waste volume handled. Therefore, if dusts are formed, they most likely originate from mixtures of innocuous waste types.

• Perhaps the strongest argument for discounting the effects of particulate inhalation is the observation that benzene evaporates very quickly. Given the fact that dusts are dry by definition, it is unlikely that significant levels of benzene would be present on dust particles.

Table E-1 WASTE HANDLING PROCEDURES Commercial Treatment Facilities

Waste Transport	Wastes Handled	Handling Procedure
Barge Barge Hold	1*,2,3,4*,5*,6*,7*,8,9, 10,12*,13*,14*,15*,16	Barges offloaded with pumps if waste sufficiently wet, otherwise removed with an excavator and placed in dump trucks. Waste placed in treatment cell at a maximum rate of about 15,000 barrels per acre (about 2 feet deep). Waste is spread over floor of cell by dozer operator. Cell is then flooded to allow hydrocarbon to be skimmed off for recycling. After initial drying period, eggbeater operator agitates wastes in cell to accelerate biodegradation. Flooding, skimming, eggbeating operations continue until waste meets criteria for reuse. Receptors Considered: Truck driver, analyst, barge washer, dozer operator, eggbeater operator, offsite receptor
		Receptor Chosen: None. Receptors at other facilities have higher potential for exposure.
Boat Tank	1*,2,3,4*,5*,6*,7*,8,9, 10,12*,13*,14*,15*,16	Very infrequently handled. Receptors Considered: Truck driver, analyst, tank washer, dozer operator, eggbeater operator, offsite receptor Receptor Chosen: None. Receptors at other facilities have higher potential for exposure.
Vacuum Truck	1*,4*,5*,6*,7*,8,9,10, 11,12*,13*,14*,15*,16	Vaccuum trucks with produced water unload into storage tanks prior to injection. Trucks with uninjectable wastes discharge directly into treatment cell. Wastes then treated as described above. Receptors Considered: Truck driver, analyst, dozer operator, eggbeater operator, offsite receptor
		Receptor Chosen: None. Receptors at other facilities have higher potential for exposure.
Open Truck	2,3,7*,12*,16	Predominantly solid wastes received in open trucks or roll-off boxes are placed directly into treatment cell. Wastes then treated as described above. Receptors Considered: Truck driver, analyst, dozer operator, eggbeater operator, offsite receptor Receptor Chosen: None. Receptors at other facilities have higher potential for
Cuttings Boxes	1*,2,3,4*,5*,6*,7*,8,9, 10,11,12*,13*, 14*,15*,16	exposure. Wastes are not received in cuttings boxes. Receptors Considered: Not applicable Receptor Chosen: Not applicable
Drums	12*	Very infrequently handled. Receptors Considered: Truck driver, analyst, dozer operator, eggbeater operator, offsite receptor. Receptor Chosen: None. Receptors at other facilities have higher potential for exposure.
Notes: * - Wastes ch	osen for risk assessment.	Wastes and waste handling based on experience of US Liquids.

Table E-2

WASTE HANDLING PROCEDURES Commercial Transfer Facilities

Waste Transport	Wastes Handled	Handling Procedure
Davas	4* 0 0 4* 5* 0* 7* 0 0	Waste received from incoming barge is pumped from incoming barge into transfer barge. Liquids are pumped directly while more solid wastes are slurried if possible prior to pumping. Solids not pumpable are removed by crane operator.
Barge Barge Hold	1*,2,3,4*,5*,6*,7*,8,9, 10,12*,13*,14*,15*,16	Receptors Considered: Contract worker, site manager, offsite receptor
		Receptor Chosen: <u>Contract worker</u> (longest exposure duration and most frequent exposure, see Table 3).
	4* 0 0 4* 5* 6* 7* 0 0	Waste received from incoming boat is pumped into transfer barge. Liquids are pumped directly while more solid wastes are slurried prior to pumping. More solid wastes (e.g., cuttings) primarily arrive in cuttings boxes.
Boat Tank	1*,2,3,4*,5*,6*,7*,8,9, 10,12*,13*,14*,15*,16	Receptors Considered: Contract worker, site manager, offsite receptor
		Receptor Chosen: <u>Contract worker</u> (longest exposure duration and most frequent exposure, see Table 3).
	4* 4* 5* 6* 7* 0 0 40	Vacuum trucks arrive at barge dock, hook up discharge hose to mounting flange, and pump directly into open transfer barge hold. Truck driver responsible for washing vacuum tank.
Vacuum Truck		Receptors Considered: Contract worker, site manager, offsite receptor
		Receptor Chosen: <u>Contract worker</u> (longest exposure duration and most frequent exposure, see Table 3).
		Truck dumps into receiving pit and is excavated into barge.
о т .	0.0.40	Receptors Considered: Contract worker, site manager, offsite receptor
Open Truck	2,3,16	Receptor Chosen: Contract worker (longest exposure duration and most frequent exposure, see Table 3).
	1*,2,3,4*,5*,6*,7*,8,9,	Cuttings boxes arrive by work boat or barge. Contract workers hook up box which is crane-hoisted for upending over open transfer barge hold. Contract worker on catwalk above barge hold rinses inverted box contents into hold.
Cuttings Boxes	10,11,12*,13*,	Receptors Considered: Contract worker, site manager, offsite receptor
	14*,15*,16	Receptor Chosen: <u>Contract worker</u> (longest exposure duration and most frequent exposure, see Table 3).
		Wastes are mostly liquids and are commingled with other wastes in the transfer barge. Drums go back to the generator. Limited volumes are handled - one shipment a month or less.
Drums	12	Receptors Considered: Contract worker, site manager, offsite receptor
		Receptor Chosen: <u>Contract worker</u> (longest exposure duration and most frequent exposure, see Table 3).

Notes: * - Wastes chosen for risk assessment. Wastes and waste handling based on experience of Newpark Environmental Services

Table E-3

WASTE HANDLING PROCEDURES Commercial Recycling / Reclamation Facilities

Waste Transport	Wastes Handled	Handling Procedure
Barge Barge Hold	1*,4*,5*,6*,7*,13*,14*	Wastes arrive in closed-hold barges and sampled to detemine solids content. Liquid wastes then centrifuged and pumped to holding tank for deep well injection. Wastes with high solids content are pumped to oil/water slop tank for settling and phase separation. Separated oil is drawn off for heat treatment to remove BS&W then pumped to 10,000 barrel sales tank. Receptors Considered: Truck driver, site operator Receptor Chosen: None. Receptors at other facilities have higher potential for exposure.
Boat Tank	No wastes are received in boat tanks.	No wastes are handled from boat tanks. Receptors Considered: Not applicable Receptor Chosen: Not applicable
Vacuum Truck	1*,4*,5*,6*,7*,13*,14*	Wastes arrive in vacuum trucks and are sampled to detemine solids content. Remaining process as described above. Receptors Considered: Truck driver, site operator Receptor Chosen: None. Receptors at other facilities have higher potential for exposure.
Open Truck	No wastes are received in open trucks	No wastes are handled from open trucks. Receptors Considered: Not applicable Receptor Chosen: Not applicable
Cuttings Boxes	No wastes are received in cuttings boxes	No wastes are handled in cuttings boxes. Receptors Considered: Not applicable Receptor Chosen: Not applicable
Drums	No wastes are received in drums	No wastes are handled in drums. Receptors Considered: Not applicable Receptor Chosen: Not applicable

Notes: * - Wastes chosen for risk assessment. Wastes and waste handling based on experience of Philips Services

Table E-4

WASTE HANDLING PROCEDURES Commercial Reuse Facilities

Waste Transport	Wastes Handled	Handling Procedure
Barge	2,3,4*,5*,6*,7*,9, 10,11,12*,13*,14*,15*,	Wastes pumped to 10,000 barrel holding barge. After agitating, wastes pumped to desanders, desilters, and centrifuge. Liquids go through water treatment process and are discharged into city sewer system. Solids removed from staging pad with front- end loader and placed into hopper/conveyor. Wastes then have drying agent added and are spread on drying pad by excavator operator. Dried wastes collected by excavator for truck shipment to BFI landfill.
Barge Hold	16,99	Receptors Considered: Truck driver, centrifuge operator, site operator, excavator operator, loader operator
		Receptor Chosen: None. Receptors at other facilities have higher potential for exposure.
		Boat tank pumped into holding barge. Remaining process as described above.
Boat Tank	2,3,4*,5*,6*,7*,9, 10,11,12*,13*,14*,15*,	Receptors Considered: Truck driver, centrifuge operator, site operator, excavator operator, loader operator
	16,99	Receptor Chosen: None. Receptors at other facilities have higher potential for exposure.
	4*,5*,6*,7*,9,10,	Vacuum truck pumped into holding barge. Remaining process as described above.
Vacuum Truck		Receptors Considered: Truck driver, centrifuge operator, site operator, excavator operator, loader operator
	11,12*,13*,14*,15*,16	Receptor Chosen: None. Receptors at other facilities have higher potential for exposure.
		Open truck dumps wastes on staging pad for placement into hopper. Remaining treatment as described above.
Open Truck	2,3,7*,12*,16	Receptors Considered: Truck driver, centrifuge operator, site operator, excavator operator, loader operator
		Receptor Chosen: None. Receptors at other facilities have higher potential for exposure.
		Cuttings boxes are either dumped directly into hopper/conveyor or, if sufficiently wet, pumped into treatment process as described above.
Cuttings Boxes	2,3,7*	Receptors Considered: Truck driver, centrifuge operator, site operator, excavator operator, loader operator
		Receptor Chosen: None. Receptors at other facilities have higher potential for exposure.
		No drum handling occurs at site.
Drums	No wastes are received in drums	Receptors Considered: Not applicable
		Receptor Chosen: Not applicable

Notes: * - Wastes chosen for risk assessment. Wastes and waste handling based on experience of Environmental Treatment Team.

Table E-5

Receptors and Exposures - Waste Code 01 and 08

Produced Brine and Produced Formation Fresh Water

Exposure Issue	Transfer	Injection	Cell Treatment	Reuse/ Recycle
Receptor	Truck Driver	Truck Driver	NA	Truck Driver
Types of Exposure	IHV, IHM, DCL,DCM	IHV, DCL	NA	IHV, DCL
Duration of Exposure	20 minutes load/unload 15 minutes truck wash	20 minutes load/unload	NA	20 minutes offload
Frequency of Exposure	6-8 loads per day 1 wash per day	6-8 loads per day	NA	4 loads per day 2-3 times per week
Receptor	Site Manager	NA	NA	Site Operator
Types of Exposure	IHV, IHM, DCL,DCM	NA	NA	IHV, DCL
Duration of Exposure	12 hours/day 183 days/year	NA	NA	1 hour/day
Frequency of Exposure	Daily (7 on - 7 off)	NA	NA	7 days/week
Receptor	NA	NA	NA	NA
Types of Exposure	NA	NA	NA	NA
Duration of Exposure	NA	NA	NA	NA
Frequency of Exposure	NA	NA	NA	NA

Abbreviations: IHP - Inhalation Particulate; IGP - Ingestion Particulate; IGL - Ingestion Liquid; INV - Inhalation Vapor; IHM - Inhalation Mist; DCP - Dermal Contact Particulate: DCL - Dermal Contact Liquid; DCM - Dermal Contact Mist

Table E-6 Receptors and Exposures - Waste Code 04 Workover / Completion Fluids

Exposure Issue	Transfer	Injection	Cell Treatment	Reuse/ Recycle
Receptor	Truck Driver	Truck Driver	NA	Truck Driver
Types of Exposure	IHV, IHM, DCL,DCM	IHV, DCL	NA	IHV, DCL
Duration of Exposure	20 minutes load/unload 15 minutes truck wash	20 minutes load/unload	NA	20 minutes offload (for injection)
Frequency of Exposure	6-8 loads per day 1 wash per day	1 load per day 3 times per week	NA	4 loads per day 2-3 times per week
Receptor	Site Manager	NA	NA	Site Operator
Types of Exposure	IHV, IHM, DCL,DCM	NA	NA	IHV, DCL
Duration of Exposure	12 hours/day 183 days/year	NA	NA	1 hour/day
Frequency of Exposure	Daily (7 on - 7 off)	NA	NA	7 days/week
Receptor	NA	NA	NA	NA
Types of Exposure	NA	NA	NA	NA
Duration of Exposure	NA	NA	NA	NA
Frequency of Exposure	NA	NA	NA	NA

Abbreviations: IHP - Inhalation Particulate; IGP - Ingestion Particulate; IGL - Ingestion Liquid; INV - Inhalation Vapor; IHM - Inhalation Mist; DCP - Dermal Contact Particulate: DCL - Dermal Contact Liquid; DCM - Dermal Contact Mist

Table E-7

Receptors and Exposures - Waste Code 05 Production Pit Sludges

Exposure Issue	Transfer	Injection	Cell Treatment	Reuse/ Recycle
Receptor	NA	NA	Egg-Beater Operator	Truck Driver
Types of Exposure	NA	NA	IGP, IHV, IHM, IHP DCP, DCL, DCM	IHV, DCL
Duration of Exposure	NA	NA	6 hours/day 1hour wash	20 minutes offload
Frequency of Exposure	NA	NA	4 days/week 1 wash/week	4 loads per day 2-3 times per week
Receptor	Site Manager	NA	Dozer Operator	Site Operator
Types of Exposure	IHV, IHM, DCL,DCM	NA	IGP, IHV, IHP, DCP	IHV, DCL
Duration of Exposure	4 hours/day	NA	6 hours/day	1 hour/day
Frequency of Exposure	4 days/year	NA	1-2 days/week	7 days/week
Receptor	Contract Worker	NA	Offsite Residential	Excavator Operator
Types of Exposure	IGP, IHV, IHM, DCP, DCV, DCM	NA	IHV, IHP	IHV
Duration of Exposure	4 hours/day	NA	24 hours/day	12 hours/day
Frequency of Exposure	4 days/year	NA	365 days/year	5 days/week

Abbreviations: IHP - Inhalation Particulate; IGP - Ingestion Particulate; IGL - Ingestion Liquid; INV - Inhalation

Vapor; IHM – Inhalation Mist; DCP - Dermal Contact Particulate: DCL - Dermal Contact Liquid; DCM - Dermal Contact Mist

Table E-8

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Receptors and Exposures - Waste Code 06

Production Storage Tank Sludge

Exposure Issue	Transfer	Injection	Cell Treatment	Reuse/ Recycle
Receptor	Truck Driver	NA	Egg-Beater Operator	Truck Driver
Types of Exposure	IHV, IHM, DCL,DCM	NA	IGP, IHV, IHM, IHP DCP, DCL, DCM	IHV, DCL
Duration of Exposure	20 minutes load/unload 15 minutes truck wash	NA	6 hours/day 1hour wash	20 minutes offload
Frequency of Exposure	6-8 loads per day 1 wash per day	NA	4 days/week 1 wash/week	4 loads per day 2-3 times per week
Receptor	Site Manager	NA	Dozer Operator	Site Operator
Types of Exposure	IHV, IHM, DCL,DCM	NA	IGP, IHV, IHP, DCP	IHV, DCL
Duration of Exposure	12 hours/day 183 days/year	NA	6 hours/day	1 hour/day
Frequency of Exposure	Daily (7 on - 7 off)	NA	1-2 days/week	7 days/week
Receptor	Contract Worker	NA	Offsite Residential	Excavator Operator
Types of Exposure	IGP, IHV, IHM, DCP, DCL, DCM	NA	IHV, IHP	IHV
Duration of Exposure	8 hours/day rinsing 183 days/year	NA	24 hours/day	12 hours/day
Frequency of Exposure	Daily (7 on - 7 off)	NA	365 days/year	5 days/week

Abbreviations: IHP - Inhalation Particulate; IGP - Ingestion Particulate; IGL - Ingestion Liquid; INV - Inhalation Vapor; IHM - Inhalation Mist; DCP - Dermal Contact Particulate: DCL - Dermal Contact Liquid; DCM - Dermal Contact Mist

Table E-9 Receptors and Exposures - Waste Code 07 Produced Oily Sands and Solids

Exposure Issue	Transfer	Injection	Cell Treatment	Reuse/ Recycle
Receptor	Truck Driver	NA	Egg-Beater Operator	Truck Driver
Types of Exposure	IHV, IHM, DCL,DCM	NA	IGP, IHV, IHM, IHP, DCP, DCL, DCM	IHV, DCL
Duration of Exposure	20 minutes load/unload 15 minutes truck wash	NA	6 hours/day 1hour wash	20 minutes offload
Frequency of Exposure	6-8 loads per day 1 wash per day	NA	4 days/week 1 wash/week	4 loads per day 2-3 times per week
Receptor	Site Manager	NA	Dozer Operator	Site Operator
Types of Exposure	IHV, IHM, DCL,DCM	NA	IGP, IHV, IHP, DCP	IHV, DCL
Duration of Exposure	12 hours/day 183 days/year	NA	6 hours/day	1 hour/day
Frequency of Exposure	Daily (7 on - 7 off)	NA	1-2 days/week	7 days/week
Receptor	Contract Worker	NA	Offsite Residential	Excavator Operator
Types of Exposure	IGP, IHV, IHM, DCP, DCL, DCM	NA	IHV, IHP	IHV
Duration of Exposure	8 hours/day rinsing 183 days/year	NA	24 hours/day	12 hours/day
Frequency of Exposure	Daily (7 on - 7 off)	NA	365 days/year	5 days/week

Abbreviations: IHP - Inhalation Particulate; IGP - Ingestion Particulate; IGL – Ingestion Liquid; INV - Inhalation Vapor;

IHM - Inhalation Mist; DCP - Dermal Contact Particulate: DCL - Dermal Contact Liquid; DCM - Dermal Contact Mist

Table E-10 Receptors and Exposures - Waste Code 12 Gas Plant Waste

Exposure Issue	Transfer	Injection	Cell Treatment	Reuse/ Recycle
Receptor	NA	NA	Egg-Beater Operator	NA
Types of Exposure	NA	NA	IGP, IHV, IHM, IHP DCP, DCL, DCM	NA
Duration of Exposure	NA	NA	6 hours/day 1hour wash	NA
Frequency of Exposure	NA	NA	4 days/week 1 wash/week	NA
Receptor	Site Manager	NA	Dozer Operator	NA
Types of Exposure	IHV, IHM, DCL,DCM	NA	IGP, IHV, IHP, DCP	NA
Duration of Exposure	4 hours/day	NA	6 hours/day	NA
Frequency of Exposure	1 day/month	NA	1-2 days/week	NA
Receptor	Contract Worker	NA	Offsite Residential	Excavator Operator
Types of Exposure	IGP, IHV, IHM, DCP, DCL, DCM	NA	IHV	IHV
Duration of Exposure	4 hours/day	NA	24 hours/day	12 hours/day
Frequency of Exposure	1 day/month	NA	365 days/year	5 days/week

Abbreviations: IHP - Inhalation Particulate; IGP - Ingestion Particulate; IGL - Ingestion Liquid; INV - Inhalation Vapor; IHM - Inhalation Mist; DCP - Dermal Contact Particulate: DCL - Dermal Contact Liquid; DCM - Dermal Contact Mist

Table E-11 Receptors and Exposures - Waste Code 13

BS&W Waste

Exposure Issue	Transfer	Injection	Cell Treatment	Reuse/ Recycle
Receptor	Truck Driver	NA	Egg-Beater Operator	Truck Driver
Types of Exposure	IHV, IHM, DCL,DCM	NA	IGP, IHV, IHM, IHP DCP, DCL, DCM	IHV, DCL
Duration of Exposure	20 minutes load/unload 15 minutes truck wash	NA	6 hours/day 1hour wash	20 minutes offload
Frequency of Exposure	6-8 loads per day 1 wash per day	NA	4 days/week 1 wash/week	4 loads per day 2-3 times per week
Receptor	Site Manager	NA	Dozer Operator	Site Operator
Types of Exposure	IHV, IHM, DCL,DCM	NA	IGP, IHV, IHP, DCP	IHV, DCL
Duration of Exposure	12 hours/day 183 days/year	NA	6 hours/day	1 hour/day
Frequency of Exposure	Daily (7 on - 7 off)	NA	1-2 days/week	7 days/week
Receptor	Contract Worker	NA	Offsite Residential	Excavator Operator
Types of Exposure	IGP, IHV, IHM, DCP, DCL, DCM	NA	IHV, IHP	IHV
Duration of Exposure	8 hours/day rinsing 183 days/year	NA	24 hours/day	12 hours/day
Frequency of Exposure	Daily (7 on - 7 off)	NA	365 days/year	5 days/week

Abbreviations: IHP - Inhalation Particulate; IGP - Ingestion Particulate; IGL - Ingestion Liquid; INV - Inhalation Vapor; IHM - Inhalation Mist; DCP - Dermal Contact Particulate: DCL - Dermal Contact Liquid; DCM - Dermal Contact Mist

Table E-12Receptors and Exposures - Waste Code 14

Pipeline Test Water / Pigging Wastes

Exposure Issue	Transfer	Injection	Cell Treatment	Reuse/ Recycle
Receptor	Truck Driver	NA	Egg-Beater Operator	Truck Driver
Types of Exposure	IHV, IHM, DCL, DCM	NA	IGP, IHV, IHM, IHP DCP, DCL, DCM	IHV, DCL
Duration of Exposure	20 minutes load/unload 15 minutes truck wash	NA	6 hours/day 1hour wash	20 minutes offload
Frequency of Exposure	6-8 loads per day 1 wash per day 70 loads/year	NA	4 days/week 1 wash/week	4 loads per day 2-3 times per week
Receptor	Site Manager	NA	Dozer Operator	Site Operator
Types of Exposure	IHV, IHM, DCL, DCM	NA	IGP, IHV, IHP, DCP	IHV, DCL
Duration of Exposure	12 hours/day 100 days/year	NA	6 hours/day	1 hour/day
Frequency of Exposure	Daily (7 on - 7 off)	NA	1-2 days/week	7 days/week
Receptor	Contract Worker	NA	Offsite Residential	Excavator Operator
Types of Exposure	IGP, IHV, IHM, DCP, DCL, DCM	NA	IHV, IHP	IHV
Duration of Exposure	8 hours/day rinsing 100 days/year	NA	24 hours/day	12 hours/day
Frequency of Exposure	Daily (7 on - 7 off)	NA	365 days/year	5 days/week

Abbreviations: IHP - Inhalation Particulate; IGP - Ingestion Particulate; IGL - Ingestion Liquid; INV – Inhalation Vapor; IHM - Inhalation Mist; DCP - Dermal Contact Particulate: DCL - Dermal Contact Liquid; DCM – Dermal Contact Mist

OCCUPATIONAL SCENARIO

<u>Development of Maximum Permissible Concentrations Protective of Workers Exposed</u> to E&P Wastes (MPC_{Ind})

Physical Setting

The worker of concern (i.e., the receptor) is a contract worker who washes out cuttings boxes at a transfer facility. During the transfer operations, cuttings boxes are hoisted from the deck of a barge or workboat and inverted over the open hold of the transfer barge. The worker stands on a catwalk extending across the hold and washes residue out of the inverted box into the hold. According to information provided to CSI by representatives from a commercial transfer company, such a worker would likely perform this task for eight hours out of a 12-hour shift. Because he stands directly above freshly dumped wastes for eight hours suggests that this worker has the highest potential exposure to benzene, compared to other workers we considered. Regulatory policies that protect the cuttings box washer would therefore also protect all other types of workers who may be exposed to benzene-containing E&P wastes.

The relevant regulatory standard applicable to this receptor is the Occupational Safety & Health Administration (OSHA) Permissible Exposure Limit for benzene (PEL = 1 ppm = 3.242 mg/m^3 as an 8-hour time-weighted average). This is the maximum allowable workplace concentration of benzene vapor in air (expressed as the average concentration over an 8-hour period) to which a worker may be exposed according to OSHA.

The dimensions of each cuttings box are $6 \ge 6 \le 4$ feet. CSI assumed that each box is filled to a level that is 6 inches from the top. CSI has also assumed that the relative weight of the solids in a waste is 10 pounds per gallon (1.208 kg/L), and that of liquids in the wastes is 8.5 pounds per gallon (1.027 kg/L). These assumptions allow us to estimate the mass of waste that is emptied into the transfer barge during an 8-hour period.

Estimation of Benzene Concentration in the Breathing Zone

The following assumptions and approach were used in the estimation of benzene concentration in the breathing zone:

- Only one type of E&P waste will be emptied into the barge during the workday (i.e., all the benzene vapor is due to the processing of that category of benzene waste);
- ii. All cutting boxes are filled with the same batch of E&P waste and the concentration of benzene in the waste is the same in each cuttings box;
- iii. Each cuttings box requires 15 minutes to empty and wash (i.e., a total of 32 cuttings boxes will be processed during an 8-hour period;
- iv. The average temperature during the work period is 90°F;
- v. Each time a cuttings box is emptied into the barge, the contents distribute evenly over the entire cross section of the barge;
- vi. The waste in the barge, after the cuttings box washing, is a slurry with a continuous aqueous film on the surface;
- vii. The air immediately above the waste is in equilibrium with the aqueous film;
- viii. The release of benzene into and within the barge air-space occurs solely by diffusion;
- ix. Since the contents of the barge are replenished every 15 minutes, diffusion is limited to the newly formed layer of waste; and
- x. The concentration of benzene in the waste is the same in each cuttings box.

The following approach is used to model the volatilization of benzene from the waste and to estimate the airborne concentration of benzene in the breathing zone of the worker:

Step 1: Benzene concentration in the aqueous-phase is related to the benzene concentration in the waste, using mass balance and equilibrium relationships.
Step 2: Benzene concentration in the air immediately above the waste will be calculated using the aqueous phase concentration and Henry's Law.
Step 3: Farmer's Model will be used to represent the benzene emission rate.
Step 4: Benzene concentration in the breathing zone of the worker, above the barge hold,

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will be represented by an open box model.

This approach uses two common environmental models --Farmer's model (characterizes the volatilization of benzene from the waste) and an Open Box Model (characterizes the concentration of benzene vapor to which the worker is exposed). The equations of these two models are expressed in the form stating that the amount of benzene vapor being volatilized from the waste must equal the amount of benzene vapor sustaining the airborne concentration at the OSHA PEL. The Total Benzene concentration in the waste that is necessary to generate and sustain a 1 ppm PEL is then calculated for each waste category. This Total Benzene concentration is the Industrial Maximum Permissible Concentration (MPC_{Ind}) for that waste. A more detailed explanation follows.

Step 1: Calculation of Benzene Concentration in the Aqueous Phase

Since Step 2 in the process utilizes aqueous phase-air equilibrium, it is necessary to estimate the aqueous phase concentration from the total concentration in the waste.

Benzene concentration in the aqueous phase (assuming the waste is a slurry that is saturated with aqueous solution -- that is, there are no pore spaces filled with benzene vapor within the waste) was calculated using the following mass balance and equilibrium equations:

Total benzene = benzene in the solid phase + benzene in the aqueous phase

$$V_w C_w = V_w \theta_s C_s \rho_s + V_w \theta_w C_{aq}$$
⁽¹⁾

or

$C - a C r \perp a C$	
$C_w = \boldsymbol{q}_s C_s \boldsymbol{r}_s + \boldsymbol{q}_w C_{aq}$	(2)

Where:

$V_{\rm w}$	=	Volume of waste [L of waste]
C_{w}	=	Benzene concentration in the waste [mg of benzene/L of waste]
θ_{s}	=	Volumetric fraction of solids in the waste [L of solids/L of waste]
Cs	=	Benzene concentration in the solids phase [mg-benzene/kg of waste]
$ ho_{s}$	=	Density of the solids phase [kg of solids/L of waste]

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$\theta_{ m w}$	=	Volumetric fraction of aqueous phase in the waste [L of aqueous liquid/L of
		waste]
\mathbf{C}_{aq}	=	Benzene concentration in the aqueous phase [mg of benzene/L of aqueous
		liquid]

Refer to Table F-1 for a list of the parameters and their values.

From soil-water equilibrium, we have

$$C_s = k_d C_{aq} \tag{3}$$

Where:

 k_d = Soil-water partitioning coefficient of benzene [cm³/g]

Combining Equations 2 and 3, we get,

$$C_{w} = C_{aq} \left(\rho_{s} k_{d} \theta_{s} + \theta_{w} \right) \tag{4}$$

or

$$C_{aq} = \frac{C_w}{\left(\rho_s k_d \theta_s + \theta_w\right)} \tag{5}$$

Step 2: Benzene Concentration in the Air Immediately Above the Waste

Henry's Law states that, for dilute solutions, the concentration of a solute in the vapor phase is proportional to the concentration in the aqueous phase. The constant of proportionality is called the Henry's Law Constant. Hence, we have,

$$C_{air-waste} = C_{aq}H \tag{6}$$

Where:

Cair-waste	=	Benzene concentration in the air at the waste surface [mg of benzene/L of air]
Н	=	Henry's Law coefficient for benzene []

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Step 3: Benzene Emission Rate – Farmer's Model

The transport of benzene from the air just above the waste surface to the top of the barge hold is assumed to occur solely by diffusion. Therefore, the emission rate of benzene is equal to the diffusional transport rate and is estimated using the Farmer's Model as given below.

$$M_{bz} = D_{bz} A \frac{\left(C_{air-waste} - C_{air-openend}\right)}{d \times 10^3}$$
(7)

Where:

M_{bz}	=	Benzene emission rate [mg of benzene/s]
D _{bz}	=	Diffusivity of benzene in air [cm ² /s]
А	=	Horizontal cross sectional area of the barge hold [cm ²]
Cair-openend	=	Benzene concentration in air at the top of the barge hold [mg of benzene/L of
		air]
d	=	Average distance from the waste surface to the top of the barge [cm]
10^{3}	=	Conversion factor [cm ³ /L]

Step 4: Benzene Concentration in Air at the Worker's Breathing Zone – Open Box Model

Benzene vapors that reach the top of the barge mixes with the ambient air. The volume of air that is available for this mixing process depends on the wind speed. Higher wind speeds mean larger volumes of air per unit time are carried across any given plane vertical to the wind direction. This type of mixing process with the ambient air is called an open box model because the volume of air available for mixing in a given period of time can be replaced by the volume of an open box with hypothetical boundaries; the cross section of the box being the cross section of the vapor source and the length of the box being the distance the wind travels in that given period of time. Therefore, based on

the open box model, we have,

$$C_{air-bzone} = \frac{M_{bz}}{v_{wind}W_b h}$$
(8)

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where:	

Cair-bzone	=	Benzene concentration in the breathing zone [mg of benzene/m ³ of air]
Vwind	=	Wind speed [m/s]
$\mathbf{W}_{\mathbf{b}}$	=	Width of the barge [m]
h	=	Height of the breathing zone [m]

Estimation of Maximum Permissible Concentration (MPC) in the Waste

The Permissible Exposure Limit (PEL) in the breathing zone stipulated by OSHA is 3.242 mg/m^3 for benzene. Therefore, the MPC_{Ind} in the waste can be back-calculated using the above equations and substituting the OSHA PEL for C_{air-bzone}.

Alternative Worker Exposure Model

It should be noted here that following the completion of CSI's analysis, Dr. Danny D. Reible of the LSU Hazardous Substance Research Center proposed an alternative model of worker exposure (see Appendix 2). This model assumes that each emptied cuttings box delivers its equivalent volume of benzene-equilibrated air to the breathing zone of the Cuttings Box Washer -- an assumption that results in a higher value for M_{Bz} . Both conceptual models have their technical merits, and empirical data do not exist to determine which model has greater validity. For that reason, CSI has retained its already health-conservative approach to its evaluation of potential worker exposures to benzene vapor. We note that even if there were an order of magnitude difference in the derived value of the MPC_{Ind} criterion, it would not change the ultimate conclusions of this report, and the MPC_{Ind} values that are derived using the LSU model are within this order of magnitude.

RESIDENTIAL SCENARIO

<u>Development of Maximum Permissible Concentrations Protective of Residents</u> (<u>MPC_{Res})</u>

The health implications to residential neighbors of a commercial E&P land treatment facility were evaluated using EPA exposure assumptions and a common type of vapor dispersion model to characterize likely exposures to a hypothetical receptor. This individual is assumed to be an adult who lives 24 hours per day for a total of 30 years at a point that is 500 feet from the closest

edge of a 5-acre land treatment cell. It should be noted that 5 acres was used here because it is a more health-conservative assumption than using the average size of a land treatment cell in Louisiana (3.73 acres; range: 2.1-6.46 acres). Contributions from benzene emissions from other land treatment cells to the total exposure of the residential receptor were assumed to be negligible because a) the increased distance of the receptor from adjacent cells greatly reduces his exposure to the to benzene vapor from these sources; b) the wind directions assumed by CSI would further reduce the benzene vapor contributions from these sources; and c) the values of other parameters assumed by CSI in its air dispersion modeling (discussed more fully below) is believed to provide adequate additional conservatism in the calculation of the MPC_{Res} to ensure protection of the hypothetical receptor.

In this analysis, the increase in lifetime cancer risk due to benzene exposure associated with any category of waste treated during that 30-year period was limited by CSI at no more than 10^{-6} (1 in 1 million). The mathematical model used by CSI calculates the amount of benzene that must volatilize from each type of treated E&P waste such that the increased lifetime cancer risk of 10^{-6} is not exceeded for a residential neighbor assuming 30years of daily exposure. The cumulative cancer risk (from all types of treated E&P wastes) will not exceed 10^{-4} after 30 years of daily exposure, even if the land treatment cell were loaded with E&P wastes all containing benzene at the MPC_{Res}. These target risk levels are consistent with the regulatory policies established by the U.S. Environmental Protection Agency (EPA), the Lousiana Department of Environmental Quality (LDEQ), and other agencies. CSI used historical data on the average volume of each type of E&P waste that is land-treated in Louisiana in order to calculate the MPC_{Res} for each waste. A more detailed description of this process follows.

Approach:

The Maximum Permissible Concentration (MPC_{Res}) of benzene in the waste protective of residents in the downwind direction of the land treatment facility was estimated using the following steps:

- **Step 1**: Estimation of allowable risk-based concentration of benzene in air for residents living approximately 500 ft from a 5-acre treatment unit.
- **Step 2**: Estimation of allowable benzene emission rate from the waste so that the receptor point concentration of benzene would not exceed the risk-based value.

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Step 3: Estimation MPC_{Res} of benzene in the waste assuming a 100% volatilization of benzene from the waste during treatment and using the emission rate from Step 2.

Step 1: Estimation of Risk-Based Concentration of Benzene in Air

Risk-based concentration of benzene in air was calculated using the equation,

$$C_a = \frac{TR \times BW \times AT_c \times 365}{ED \times EF \times IR_a \times SF_i} \tag{1}$$

Where:

C _a =	=	Risk-based concentration of benzene in air [mg of benzene/m ³ of air]
TR =	=	Target risk []
BW =	=	Body weight [kg]
$AT_c =$	=	Averaging time for carcinogens [years]
365 =	=	Conversion factor [days/year]
ED =	=	Exposure duration [years]
EF =	=	Exposure frequency [days/year]
IR _a =	=	Inhalation rate [m ³ of air/day]
SF _i =	=	Slope factor for inhalation [risk per (mg of benzene/kg body wt-day)]

See Table F-2 for the values of the parameters used. The concentration of benzene vapor that will yield an incremental lifetime cancer risk of 10^{-6} to the residential receptor after 30 years of daily exposure is 0.000294 mg/m³.

Step 2: Estimation of Allowable Benzene Emission Rate

A Gaussian dispersion model was used to estimate the allowable benzene emission rate from the waste so that the risk-based receptor point concentration would not be exceeded.

Model Description:

Gaussian Dispersion Models are the most commonly used tools to estimate the steady-state concentration of chemicals down-wind from a source. Such models also form the basis of the Industrial Source Complex Short-Term (ISCST) and Industrial Source Complex Long-Term (ISCLT) models typically used by the EPA. The model implementation requires three

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meteorological inputs: (i) wind speed, (ii) wind direction, and (iii) atmospheric stability. In these models, wind speed and atmospheric stability are each divided into six classes and the wind direction into sixteen sectors each of 22.5 degrees. This results in a total of 6x6x16=576 combinations of atmospheric conditions. Thus, at any time, the atmospheric conditions are described by one of these 576 conditions. The long-term average concentration at any point is computed by estimating the concentration for each atmospheric condition and then time-weighting these concentrations.

The above approach requires a large volume of data. The American Petroleum Institute's Decision Support System (API DSS) (API, 1994) and the EPA's MULTIMED model (EPA, 1990) have developed simplified versions assuming that the wind speed is constant in the direction of the receptor for a specified fraction of the year. In the API DSS model (used by CSI), the steady state concentration at the receptor is computed for each stability class and the annual average concentration is derived by time-weighting the concentrations for each stability class.

The sector-averaged (16 sectors of wind direction) form of the Gaussian model is derived by averaging the concentration profile across a single sector (22.5 degrees). For a specified stability class, the steady-state ground level concentration is computed using the following equation (API, 1994):

$$C_j = 10^3 \frac{16}{2\boldsymbol{p}x} \times \frac{2QDP_i}{u\boldsymbol{s}_j \times (2\boldsymbol{p})^{0.5}}$$

where:

C_j	=	steady-state concentration at distance x for stability class j [mg/m ³]
Х	=	distance from the source to the receptor [m]
Q	=	emission rate [g/s]
\mathbf{P}_{i}	=	fraction of the year that wind blows in the direction of the receptor from the
		source [dimensionless]
u	=	mean annual wind speed at source release height [m/s]
σ_{j}	=	vertical dispersivity for stability class j [m]
D	=	term for atmospheric decay of the chemical [dimensionless]
10^{3}	=	conversion factor [mg/g]

Atmospheric chemical decay D in Equation (2) can be estimated using the equation (API, 1994):

$$D = \exp\left(-k\frac{x}{u}\right) \tag{3}$$

where

k = first order decay rate constant $[s^{-1}]$

The vertical dispersivity σ_j in Equation (2) can be estimated from the equation (API, 1994):

$$\boldsymbol{s}_{j} = a\boldsymbol{x}^{b} + c \tag{4}$$

Where a, b, and c are constants associated with the six stability classes. The specific values are listed in Table F-3.

The annual average receptor point concentration is estimated by frequency-weighting as given below (API, 1994):

$$C_{avg} = f_j C_j \tag{5}$$

where:

$$C_{avg}$$
 = annual average receptor point concentration [mg/m³]
 f_j = fraction of the year the atmosphere is represented by stability class j
[dimensionless]

The Gaussian air dispersion model Version 1.30 as described in the American Petroleum Institute Decision Support System (API DSS) was used in this modeling effort.

Input Parameters:

This section discusses the various input parameters used to implement the API DSS model. The specific values used are listed in Table F-2.

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Meteorological Inputs:

- <u>Mean wind speed</u>: The mean annual wind speed listed in API DSS for Shreveport in Louisiana is 3.9 m/s, and this value was assumed for the hypothetical land treatment cell modeled here.
- <u>Frequency of stability classes</u>: Stability classes reflect the vertical temperature patterns in the atmosphere. These temperature patterns indicate the extent of vertical movement of air in the atmosphere and, hence, the extent of dilution of chemicals due to mixing. Stability class A is extremely unstable, B is moderately unstable, C is slightly unstable, D is neutral, E is slightly stable, and F is moderately stable. Stability classes A to F have been assigned frequencies of 0.05, 0.1, 0.15, 0.25, 0.3, and 0.15 respectively. These values keep the atmosphere at stable or near stable conditions most of the time. A high frequency of stable conditions is more conservative because it results in less dispersion and higher receptor point concentrations.
- <u>Fraction of the time wind blows in the direction of the receptor</u>: A conservative value of 0.25 (wind blows in the direction of the receptor 25% of the time) was assumed.

The Source/Receptor Parameters:

- <u>Emission rate</u>: An iterative procedure was used to estimate the emission rate of benzene so that the down-wind concentration at the receptor would not exceed the risk based value estimated in Step 1. See Figure F-1 for the calculation of benzene emission rate.
- <u>Area of the source</u>: Area of the land treatment unit of $20,234 \text{ m}^2$ (5 acres) was used.
- <u>Distance to the receptor</u>: A site-specific distance of 500 ft (152 m) from the edge of the land treatment unit (142 m x 142 m) to the nearest residence was used in the model simulations (i.e., approximately 223 m = 732 feet from the center of the cell to the receptor). A distance of 500 feet is the minimum allowed by DNR from the edge of a commercial land treatment cell to the nearest residence.

• <u>Treatment cycle of 6 months</u>: Based on data provided by a commercial land treatment company, CSI assumed that it requires 6 months to load a land treatment cell to its maximum permitted capacity (15,000 bbl per acre), treat the waste, and empty the cell to allow the next cycle to begin without delay. It was assumed that this cycle would be repeated for 30years (note: EPA statistics indicate that 95% of people in the United States live at a specific residence for less than 30 years, and to be health-conservative, they recommend that risk evaluations assume this duration of exposure for a residential receptor). It was further assumed that 100% of the benzene content of the waste will volatilize from the treatment cell during each 6-month treatment cycle.

Chemical-Specific Parameter:

• <u>Atmospheric decay</u>: A conservative assumption of no decay was used. Note that because the estimated concentrations are for steady-state conditions, no other chemical-specific property (like molecular weight and diffusivity) is required.

Model Assumptions:

- i. Source is at ground elevation,
- ii. The chemical emissions at the source are steady and continuous,
- iii. The distribution of chemicals within the plume is Gaussian (binormal) in the vertical and cross-wind directions,
- iv. Longitudinal (down-wind) dispersion is negligible,
- v.Wind speed is steady in a constant direction; short-term fluctuations in wind are not accounted for,
- vi. Atmospheric dispersion can be characterized by six stability classes (A,B,C,D,E, and F) and are used to estimate the dispersivity values,
- vii. No dispersion of chemicals or particles occurs during transport,
- viii. The model assumes a flat terrain, and
- ix. The model assumes a point source of emission, i.e., a relatively small source area. Thus, the Gaussian model is more appropriate when the distance to the receptor is large relative to the size of the source.

Step 3: Estimation of MPC_{Res} of Benzene in the Waste

The benzene MPC_{Res} for each category of E&P waste is calculated using the estimated allowable emission rate and making three assumptions: a) that the land treatment cell is filled to maximum capacity (15,000 bbl per acre); b) that over the 30-year period the proportion of each specific waste type treated in that cell will be the same as seen during the past 10 years (based on DNR records); c) that the mass of each type of E&P waste per barrel is constant (see Table D-10); and d) that 100% of benzene in the specific category of waste will volatilize into the atmosphere during each 12-month treatment cycle.

$$C_w = \frac{E_{bz}}{M_w} \tag{6}$$

Where:

\mathbf{C}_{w}	=	Concentration of benzene in the waste [mg/kg]
$E_{bz} \\$	=	Allowable benzene emission rate [mg/year]
M_{w}	=	Total mass of waste treated in the unit [kg/year]

MPC Values for Industrial and Residential Scenarios

Employing the above methods for calculating the MPCs results in values that represent the concentration of benzene in a waste above which an unacceptable exposure to benzene vapors may occur. The MPCs for the industrial and residential scenarios are based on models assumptions that are health-conservative, and are summarized in Table F-5.

TABLE F-1				
PARAMETERS USED IN THE CALCULATION C	OF MPCs OCCU	JPATIONA	AL SCENARIO	
Parameter	Symbol	Units	Value	
Concentration in the waste	C _w	mg/L	Reported	
Concentration in the solid phase	Cs	mg/kg	Estimated	
Concentration in the aqueous phase	C _{aq}	mg/L	Estimated	
Concentration in the air at the waste surface	Cair-waste	mg/L	Estimated	
Concentration in the air at the open end of the barge hold	Cair-openend	mg/L	3.242 mg/m ³	Steady-state con
Concentration in the air in the breathing zone	C _{air-bzone}	mg/m ³	Estimated	
Horizontal cross sectional area of the barge	А	cm ²	$L_b x W_b x_{10}^4$	
Mean distance from the waste surface to the open end of the barge	d	cm	222.5	Repres
Volume of waste	Vw	L	L _{cb} xW _{cb} xH _{w-cb} x10 ³	Volu
Fraction of solids in the waste	θ_{s}		Variable	The waste is a slurr
Fraction of aqueous phase in the waste	θ_{aq}		Variable	1
Density of the solids	ρ _s	g/cm ³	2.6	
Wind speed	Vw	m/s	2	
Height of breathing zone	h	m	2	
Chemical Specific Properties - Benzene				
Soil-water partitioning coefficient	k _d	cm ³ /g	0.37	Based of
Henry's Law Constant	Н		0.228	
Diffusivity in air	D _{bz}	cm ² /s	0.092	
Dimensions of the barge				
Length	L _b	m	13.4	
Width	W _b	m	8.53	
Height	H _b	m	2.74	
Dimensions of the cutting box				
Length	L _{cb}	m	1.83	
Width	W _{cb}	m	1.83	
Height	H _{cb}	m	1.22	
Height of waste in the cutting box	H _{w-cb}	m	1.07	

* Mean of the distances between the waste surface and the barge open-end after unloading the first cutting box and the 32nd cutting box (at the beginning and the end of

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Parameter Data for estimating maximum acceptable concentration of benzene va Farget risk Body weight Averaging time for carcinogens	Symbol por TR	Unit	Value Used	Re
Target risk Body weight	-			
Body weight	TR			
	IK		1x10 ⁻⁶	Default target risk, LDEQ
Averaging time for carcinogens	BW	kg	70	Adult body weight, LDEQ
	ATc	year	70	Default averaging time, LD
Exposure duration	ED	year	30	For resident adult, LDEQ (
Exposure frequency	EF	days/year	350	For resident adult, LDEQ (
inhalation rate	IRa	m³/day	20	For resident adult, LDEQ (
Cancer slope factor for inhalation for benzene	SFi	mg/(kg-day) ⁻¹	0.029	LDEQ (1998)
Data for API DSS model simulations				
Source Data				
Area of source	А	m ²	20234	5 acres, size of the treatment
Emission rate	Q	kg/year	variable	Maximum allowable emissi
Chemical data				
First order decay rate in air	k	1/s	0	Conservatively assumed (no
Receptor data				
Distance from the source to receptor	Х	m	223	Distance from center of trea
Metereologic Data				
Mean annual wind speed	u	m/s	3.9	Annual average for Shrever
Frequency of occurrence for each stability class:				
A (extremely unstable)	f_A	-	0.05	Conservatively assumed.
B (moderately unstable)	f_B	-	0.10	Conservatively assumed.
C (slightly unstable)	$f_{\rm C}$	-	0.15	Conservatively assumed.
D (neutral)	f _D	-	0.25	Conservatively assumed.
E (slightly stable)	f_E	-	0.30	Conservatively assumed.
F (moderately stable)	$f_{\rm F}$	-	0.15	Conservatively assumed.
Fraction of the time wind blows in the direction of the receptor from the source	Pi	-	0.25	Conservatively assumed.
Data for estimating benzene MPC in the waste				
Allowable benzene emission rate	E _{bz}	mg/year	Estimated	From API DSS model simu
Mass of waste treated in the unit	M _w	kg/year	Estimated	Approximate total mass of

TABLE F-2

Equals the distance from the center of a 5-acre square source area to a receptor located at 500 ft away from the edge of the source area.

LDEQ (1998): Risk Evaluation/Corrective Action Program (RECAP), December 1998, Louisiana Department of Environmental Quality.

*

Table F-3

Constants for Pasquill-Gifford Curves for Each Stability Class

> 1000 m								
			> 1000 III					
Stability =	A	В	C D E		F			
а	0.001	0.0476	0.119	2.61	52.6	33.6		
b	1.89	1.11	0.915	0.45	0.15	0.14		
С	9.60	2.00	0.00	-25.5	-126	-75.00		
		10	0 m - 1000	m				
Stability =	А	В	С	D	E	F		
а	0.001	0.0476	0.119	0.187	0.1345	0.362		
b	1.89	1.11	0.915	0.755	0.745	0.55		
С	9.60	2.00	0.00	-1.40	-1.10	-2.70		
			< 100 m					
Stability =	А	В	С	D	E	F		
а	0.1742	0.1426	0.1233	0.0804	0.06	0.0434		
b	0.936	0.922	0.905	0.881	0.854	0.814		
С	0.00	0.00	0.00	0.00	0.00	0.00		

Table F-4

COMPARISON OF MODELED RECEPTOR POINT CONCENTRATIONS WITH RISK-BASED ALLOWABLE CONCENTRATION FOR BENZENE FOR VARIOUS EMISSION RATES

Source area = 5 acres; distance to receptor from the edge of the source = 500 feet.

Benzene Emission Rate [kg/yr]	Concentration in Air at the Receptor Point [mg/m ³]	Risk-Based Allowable Concentration [mg/m ³]
50	1.13E-04	2.94E-04
100	2.25E-04	2.94E-04
131	2.95E-04	2.94E-04
150	3.38E-04	2.94E-04



	Table F-5									
Calcu	Calculation of Maximum Permissible Concentrations - Residential (MPC _{Res})									
Waste	Description	Kg of Waste	Kg from Waste 15	Total Kg	MPC _{Res} (mg/kg)					
01	Salt Water (Produced Brine)	299,483	115	299,599	219					
02	Oil-Based Drilling Mud & Cuttings	626,271	5,795	632,066	104					
03	Water-Based Drilling Mud & Cuttings	5,399,127	16,327	5,415,453	12					
04	Drilling, Workover & Completion Fluids	271,756	2,498	274,254	239					
05	Production Pit Sludges	1,513,008	1,231	1,514,239	43					
06	Production Storage Tank Sludge	573,551	7,374	580,924	113					
07	Produced Oily Sands & Solids	671,180	6,544	677,724	97					
08	Produced Formation Fresh Water	47,568	8	47,576	1,377					
09	Rainwater	1,317,074	99	1,317,173	50					
10	Washout Water	1,095,336	4,379	1,099,715	60					
11	Washout Pit Water	393,918	117	394,035	166					
12	Gas Plant Waste	53,574	369	53,943	1,214					
13	Basic Sediment and Water (BS&W)	94,851	116	94,967	690					
14	Pipeline Test Water	71,868	83	71,951	910					
16	Oil Spill Waste	171,137	1,150	172,287	380					
	Total in Hypothetical 5-acre Cell/Cycle	12,599,700	46,206	12,645,906						

Table F-6

MAXIMUM PERMISSIBLE CONCENTRATIONS (MPCs) FOR E&P WASTES

Waste Code	Waste Type	Validated Samples	MPC _{Ind} (mg/kg) **	MPC _{Res} (mg/kg) ***
01 *	Salt Water (Produced Brine)	59	NA ****	219
02	Oil-Based Drilling Mud & Cuttings	148	NC ****	104
03	Water-Based Drilling Mud & Cuttings	218	NC	12
04 *	Drilling, Workover & Completion Fluids	274	1026	239
05 *	Production Pit Sludges	20	1007	43
06 *	Production Storage Tank Sludge	162	1007	113
07 *	Produced Oily Sands & Solids	147	1007	97
08 *	Produced Formation Fresh Water	4	NA	1,377
09	Rainwater	7	NC	50
10	Washout Water	5	NC	60
11	Washout Pit Water	44	NC	166
12 *	Gas Plant Waste	4	1015	1,214
13 *	Basic Sediment and Water (BS&W)	12	NA	690
14 *	Pipeline Test Water	11	NA	910
16	Oil Spill Waste	13	NC	380
99	Other	8	NC	NC

* Recommended by CSI (Phase 2) for risk-based evaluation in Phase 3 of DNR program.

- ** MPC_{Ind} = Maximum Permissible Concentration of benzene in a waste such that the OSHA Permissible Exposure Limit (PEL = 3.242 mg/m³ as 8-hr time-weighted average) will not be exceeded for a worker washing 32 emptied cuttings boxes of that waste during his shift (barge loading operation).
- *** MPC_{Res} = Maximum Permissible Concentration of benzene in a waste such that the incremental lifetime cancer risk for a hypothetical resident living 500 ft from a treatment cell will not exceed one-in-one million (10⁻⁶) after 30 years of exposure.
- **** NC = Not Calculated (Based on Phase 2 evaluation). NA = Not Applicable (Waste is not, or is only rarely transported in cuttings boxes).

G. MPCs vs. DATA FROM 29-B EMERGENCY RULE

In order to evaluate the potential regulatory implications of the proposed MPCs for Total-Benzene in each category of E&P waste, a crude estimate of Total Benzene content was derived from the TCLP-Benzene data submitted to DNR under the 29-B Emergency Rule.

Although different batches of each E&P waste may vary significantly with regard to solids and liquids content, CSI assumed for the purpose of deriving a crude estimate of Total Benzene that each waste type has a characteristic solids-to-liquids ratio (see Table D-1). In the TCLP method, solids are analyzed by first extracting volatile components from the wastes by agitation in 20 weight equivalents of acidified water. In order to interpret what the total benzene concentration in the waste might be, it is a standard practice to multiply the TCLP value by 20 to account for the dilution during the extraction step. Liquid wastes generally do not have to be extracted and therefore a multiplier of 1 is used on the TCLP results to arrive at the total benzene concentration. The reported TCLP-Benzene value is the sum of the analytical results on the solids extract and liquid portion of the tested batch, and was calculated by assuming that a simple one-to-one relationship existed between the percentage of liquids (TCLP multiplier of 1) and the percentage of solids (TCLP multiplier of 20). For example, a waste that was 10% liquid and 90% solid would have a TCLP multiplier calculated in the following manner:

TCLP Multiplier = (10% x 1) + (90% x 20) = (0.1 + 18) = 18.1

Table G-1 gives the results of this calculation for each of the 16 waste categories. As shown by this table, wastes that are nearly all liquid have multipliers close to 1. The multiplier increases with increasing solids content. As summarized in the Appendix 1 the TCLP-Benzene content of each batch of E&P waste submitted to DNR and validated by LSU was used to derive an estimate of Total Benzene by multiplying the TCLP value by the appropriate multiplier from Table G-1.

It must be emphasized that the Total Benzene concentration as derived in this manner from TCLP data should be considered to be a crude estimate of benzene content. In many cases (see Appendix 1), the calculated Total Benzene value is impossibly high (i.e., above the solubility limit of benzene in water). For example, the single batch of Waste 12 that exceeds the MPC_{Res} exhibits an estimated Total Benzene concentration (17,822 mg/L) -- ten times higher than the maximum solubility of benzene in water (1800 mg/L). The same is true for 14 of 43 exceedances for Waste 06 (estimated Total Benzene 2401 to 157,500) and 4 of 13 exceedances

for Waste 07 (estimated Total Benzene 2163 to 26,250). Such findings indicate that the TCLP assay must be conducted carefully -- for example, inadequate separation procedures may leave small droplets of oil in the water extract from the TCLP analysis giving artificially high values of TCLP-Benzene. The frequency and extent to which the TCLP procedure tends to overestimate Total Benzene content is unclear, and this analytical problem may have affected other batches of E&P wastes (even those in which the estimated Total Benzene content does not exceed benzene's solubility limit).

In spite of the limitations of the Total Benzene estimates derived from the 29-B test data, the derived values do provide data useful for evaluating the regulatory impact of the proposed MPC criteria, and are used here only for that purpose. As summarized in Table G-2, only four categories of E&P waste are seen to have more than one-in-20 (5%) exceedences of the MPC_{Ind} and/or MPC_{Res} criteria -- Waste 05 (Production Pit Sludge), Waste 06 (Production Tank Sludge), Waste 07 (Produced Sands/Solids) and Waste 12 (Gas Plant Waste).

The one-in-20 criterion used here is considered to be a reasonable basis for determining which categories of E&P waste should receive regulatory attention with regard to benzene content for two reasons. First, as noted above, use of TCLP-Benzene data tends to overestimate Total Benzene content in a waste, increasing the likelihood that a batch will exceed the MPC (i.e., use of a one-in-20 criterion is reasonable considering data quality). Second, E&P wastes meeting a one-in-20 criterion means that <u>at least</u> 19 of every 20 batches are expected to contain benzene that is less than the MPC_{Res} and the cancer risk to the hypothetical resident assumed in our model will therefore be less than 10^{-6} (i.e., use of a one-in-20 criterion remains health-protective). Although not directly relevant to the present case, many readers will recognize that a one-in-20 criterion (p < 0.05) is the standard used by scientists when evaluating the results of statistical tests. For these reasons, CSI has applied a one-in-20 criterion to the Total Benzene estimates for each waste type (see data tables in Appendix 1), and recommends that DNR focus regulatory attention only on the four waste types listed above.

Table G-1

TCLP Multiplier Based on Solids:Liquids Content of E&P Waste

Waste Code	Waste Type	Solids %	Liquids %	TCLP Multiplier
01	Salt Water (Produced Brine)	1%	99%	1.19
02	Oil-Based Drilling Mud & Cuttings	10%	90%	2.90
03	Water-Based Drilling Mud & Cuttings	10%	90%	2.90
04	Drilling, Workover & Completion Fluids	5%	95%	1.95
05	Production Pit Sludges	50%	50%	10.50
06	Production Storage Tank Sludge	50%	50%	10.50
07	Produced Oily Sands & Solids	50%	50%	10.50
08	Produced Formation Fresh Water	3%	97%	1.57
09	Rainwater	1%	99%	1.19
10	Washout Water	5%	95%	1.95
11	Washout Pit Water	5%	95%	1.95
12	Gas Plant Waste	30%	70%	6.70
13	Basic Sediment and Water (BS&W)	10%	90%	2.90
14	Pipeline Test Water	3%	97%	1.57
15	Commercial Facility Waste	50%	50%	10.50
16	Oil Spill Waste	50%	50%	10.50

Table G-2

EXCEEDANCES OF MAXIMUM PERMISSIBLE CONCENTRATIONS (MPCs) FOR E&P WASTES

			lı	ndustrial Scena	rio	R	esidential Scen	ario
Waste Code	Waste Type	Validated Samples	MPC _{Ind} (mg/kg) **	MPC _{Ind} Exceedances	Percent MPC _{Ind} Exceedances	MPC _{Res} (mg/kg) ***	MPC _{Res} Exceedances	Percent MPC _{Res} Exceedances
01 *	Salt Water (Produced Brine)	59	NA ****			219	0	
02	Oil-Based Drilling Mud & Cuttings	148	NC ****			104	1	0.7%
03	Water-Based Drilling Mud & Cuttings	218	NC			12	2	0.9%
04 *	Drilling, Workover & Completion Fluids	274	1026	2	0.7%	239	3	1.1%
05 *	Production Pit Sludges	20	1007	0		43	1	5.0%
06 *	Production Storage Tank Sludge	162	1007	15	9.3%	113	35	21.6%
07 *	Produced Oily Sands & Solids	147	1007	4	2.7%	97	9	6.1%
08 *	Produced Formation Fresh Water	4	NA			1377	0	
09	Rainwater	7	NC			50	0	
10	Washout Water	5	NC			60	0	
11	Washout Pit Water	44	NC			166	0	
12 *	Gas Plant Waste	4	1015	1	25.0%	1214	1	25.0%
13 *	Basic Sediment and Water (BS&W)	12	NA			690	0	
14 *	Pipeline Test Water	11	NA			910	0	
16	Oil Spill Waste	13	NC			380	0	
99	Other	8	NC			NC		
	ommended by CSI for risk-based evaluat		•	•				

** MPCInd = Maximum Permissible Concentration of benzene in a waste such that the OSHA Permissible Exposure Limit (PEL = 3.242 mg/m3 as 8-hr time-weighted average) will not be exceeded for a worker washing 32 emptied cuttings boxes of that waste during his shift (barge loading operation).

*** MPCRes = Maximum Permissible Concentration of benzene in a waste such that the incremental lifetime cancer risk for a hypothetical resident living 500 ft from a treatment cell will not exceed one-in-one million (10-6) after 30 years of exposure.

**** NC = Not Calculated (Based on Phase 2 evaluation). NA = Not Applicable (Waste is not, or is only rarely transported in cuttings boxes).

DNR Phase 3 Report
H.DISCUSSION

The Phase 3 study conducted by Compliance Solutions, Inc. was designed to identify E&P wastes with the potential to create an unacceptable exposure to benzene vapor, and to propose appropriate criteria to limit exposures to waste-derived benzene vapor in both occupational and residential settings. CSI has used risk-based approaches to calculate what we consider to be reasonable, health-protective criteria called Maximum Permissible Concentrations (MPCs) that represent the maximum acceptable concentration of Total Benzene in each category of E&P waste from an occupational and from a residential perspective. The derived MPC_{Res} value is more stringent than the corresponding MPC_{Ind} for each waste category. CSI believes that the MPC_{Res} [see Table G-2] are protective of health in a conservative manner, and should be adopted by DNR as the regulatory criterion for the maximum Total Benzene content in those types of E&P waste that may contain significant concentrations of benzene.

Using crude estimates of Total Benzene content (derived from the TCLP data submitted to DNR under the 29-B Emergency Rule), only four categories of E&P waste were found to have more than one exceedance of the MPC_{Res} per every 20 submitted samples -- Waste 05 (Production Pit Sludge), Waste 06 (Production Tank Sludge), Waste 07 (Produced Sand / Solids), and Waste 12 (Gas Plant Waste) [see Table G-2]. Although some of these exceedances appear to be due to problems in the TCLP analytical procedure, CSI recommends that these four waste categories be the focus of any change in DNR's regulatory approach.

It is appropriate to acknowledge a recent study, sponsored by the American Petroleum Institute (API), of the offsite cancer risks associated with benzene emissions from a large, single, hypothetical E&P waste treatment facility (Willis et al., in preparation). These authors have used a combination of methods to demonstrate that the community cancer risks are low -- that is, the ILCR is less than 2.5-in-100,000 even under extremely conservative assumptions. As discussed above (see p. F-7), this value of the ILCR is within the range considered to be acceptable by the EPA and other agencies. While the API investigators did not develop an equivalent to our MPCRes, CSI's evaluation generally supports the API conclusion that community cancer risk from land treatment operations is generally low. However, CSI believes that batches of the four types of E&P waste listed above may contain levels of benzene that warrant specific regulatory attention.

DNR now has a variety of regulatory approaches to consider with regard to benzene in E&P wastes. These approaches range from banning Wastes 05, 06, 07, and 12 from DNR-permitted transfer/treatment facilities in Louisiana, to requiring analytical data demonstrating that each batch of E&P waste complies with the MPC_{Res} criteria prior to its acceptance at a DNR-licensed transfer/treatment facility. Alternatively (recommended by CSI), DNR could allow the regulated community to decide for their specific operating situation how best to handle each type of E&P waste in order to comply with DNR's waste criteria (i.e., the MPC_{Res}). Regardless of the regulatory approach DNR takes, CSI believes that these risk-based MPCs provide all parties with a technical basis on which to develop appropriate measures to protect the health of the citizens of Louisiana, as well as that of workers at DNR-permitted E&) waste transfer/treatment facilities.

DNR Pha	se 3 Report
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APPENDIX 2

Alternative Worker-Exposure Model

Compliance Solutions, Inc.

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Suggested by

Dr. Danny D. Reible, Director Hazardous Substance Research Center/South & Southwest Louisiana State University



Correspondence

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From: Danny D. Reible, Director Chevron Professor of Chemical Engineering Date: July 24, 2000

To: Ben Thomas Compliance Solutions, Inc. 11011 Richmond, Suite 650 Houston, TX 77042

Re: Comments on the Report "Risk-Based Evaluation of Exploration and Production Wastes"

You had requested additional information on the model that I had prepared to compare to your model of releases from the barge for the purposes of assessing worker exposure. The approach that I employed is attached. This is a slightly revised version of the previous approach.

Estimation of cutting box worker exposure (with additional clarification as requested.):

Assumptions:

- The bulk of the vapors giving rise to exposure are released during cutting box cleaning and the vapors emanating from the barge are negligible. This underestimates the total emissions but I believe the bulk of the emissions to be during cleaning of the box.
- The agitation associated with the cleaning of the cutting box maintains the air space within the cutting box in equilibrium with the waste (i.e. the vapor space is maintained at C_{air mete}).
- The cleaning of the cutting box results in the release of one box volume of vapors at the concentration, C_{air-waste}. This does not necessarily mean that the full cutting box has a vapor space equal to its own volume or that the vapors are released only when the cutting box is almost empty. The conceptual model that I employed is that the agitation of the wastes associated with cleaning out the box effectively keeps the cutting box vapors equilibrated with the waste until the box is completely empty. That is, when the box is half empty, the remaining half of the box is equilibrated vapors, etc:. Similar models are used in AP-42 to determine emissions during filling and emptying operations. I believe this conceptual model is most applicable to solids in which wash water is used to assist removal from the cutting box. If the waste is mostly liquid and pours out of the cutting box without agitation, it may be appropriate to only consider the vapors originally in the air space within the box. In this instance, however, the emissions from the barge (as you estimated previously) are important and should be added to the total emissions
- The dimensions of the cutting box are 1.8 m X 1.2 m X 1.2 m
- One box is cleaned every 15 minutes
- The emissions from either the cutting box or the barge (or both) are used to estimate an MPC as
 per your previous approach.

Results:

The release rate of benzene is given by

$$M_{Bz} = \frac{C_{atr-waste} V_{box}}{\tau_{box}}$$

where $C_{air-waste}$ is in mg/L, V_{box} is the volume of the box and τ_{box} is the time to clean the box. Substituting numerical values and employing the appropriate unit conversions.

$$M_{Bz} = \frac{C_{air-watte} (1.8 m) (1.2 m) (1.2 m) (10^{3} L/m)}{(15 min) (60 sec/min)}$$

= 2.88 C_{atr-watte} [mg/sec]