Assessment of Air Emissions
at the
U S Liquids Exploration and Production Land Treatment Facility

Grand Bois, Louisiana

FINAL PROJECT REPORT

Submitted to:

Department of Energy
Petroleum Technology

By

John H. Pardue and K.T. Valsaraj
Department of Civil & Environmental Engineering
Department of Chemical Engineering
Louisiana State University
Baton Rouge, LA 70803-7511

December 2000

TABLE OF CONTENTS

Section **Page**

Appendices

Activity Log

DEQ Air Record

List of Tables

List of Figures

Acknowledgements

We would like to acknowledge the assistance of the employees of the US Liquids facilities in Bourg, LA and Bateman Island, LA. Special thanks to Troy LeBoeuf and Jerry Brazzelle for cooperating on logistical matters for the on-site measurements.

We would also like to thank the Office of Conservation, Department of Natural Resources for their collaboration throughout the study period. Special thanks to Carroll Wascom and Gary Snellgrove for their help.

Additionally we would like to thank the Department of Environmental Quality for providing matching funds for the study in the form of the air measurements made at the Bourg facility and the community of Grand Bois.

Finally, we would like to acknowledge the support of the graduate students and post-doctoral associates at Louisiana State University who contributed to this study: Won Sik Shin, Sangjin Lee, Eun-Ju Lee, Erin Watson, Ricky Zaepfel, Cesar Gomez-Hermosillo, and Gabriel Kassenga.

1.0 Executive Summary

1.1 Non-technical executive summary

This project was initiated to make the first set of measurements documenting the potential for emissions of pollutants from exploration and production (E&P) waste disposal facilities at Bourg, Louisiana and Bateman Island, Louisiana. The objective of the project was to quantify the emissions and to determine whether the measured emissions were potentially harmful to human health of workers and the adjacent community. The study, funded by the Department of Energy (DOE) is designed to complement additional studies funded by Louisiana Department of Natural Resources (LADNR) and the American Petroleum Institute (API). The distinguishing feature of this study is that actual, independent field measurements of emissions were used to assess the potential problems of this disposal technology.

Initial measurements were made at the Bourg, LA facility, adjacent to the community of Grand Bois in late 1998-early 1999. Emission measurements were performed using aluminum chambers placed over the surface of the landfarm cells. Air was pulled through the chambers and the concentration of the contaminants in the air exiting the chambers was measured. The contaminants of interest were the “BTEX” compounds (benzene, toluene, ethylbenzene and xylene), commonly found in E&P wastes and hydrogen sulfide, a noxious gas present naturally in many E&P wastes and crude oils. Measurements indicated that emissions were measurable using the techniques developed for the study. However, when the air concentrations of these contaminants that developed above the landfarm cells were compared with standards for workers (from the Occupational and Safety and Health Association “OSHA”) and for communities (Louisiana’s ambient air standards), levels were not of concern. Since amounts of wastes being processed by the Bourg facility were considerably lower than normal, a decision was made to continue the study at the Bateman Island facility near Morgan City, LA. This facility was receiving more normal loadings of E&P wastes.

Additional emission measurements were made at the Bateman Island facility within cells over a range of “ages’, from those most recently loaded with E&P wastes to cells that have not received wastes for 9 months or more. As expected the greatest chance for emissions when the cell is most recently loaded. Again, measured fluxes did not produce air concentrations that were of concern. As expected, the highest fluxes were observed in the cells that had recently received wastes and older cells had very low emissions.

Measurements of emissions of hydrogen sulfide (H_2S) were also conducted at these two facilities. Levels of emissions were similar to the range observed in the literature for natural salt marshes that surround these facilities. Production of sulfide within the cells was also measured by the most sensitive techniques available and measured sulfide production rates were low in the samples tested. The only potential concern at the facility with regards to sulfide was the levels of sulfide emitted from the sumps.

The facility logbook at Bourg was analyzed to determine a time sequence of activities over 1998-1999. The Louisiana Department of Environmental Quality conducted a time-series of air concentrations for hazardous air pollutants during this period at the fenceline of the Bourg facility. These data were characterized by periods of static concentrations interspersed with peaks. A series of peaks were analyzed and compared with logbook records for the activities occurring at the time. In reverse fashion, a set of activities documented by the logbook was examined and the concentrations of benzene that developed from these activities were documented. No direct correlation could be made with the observed peaks and any activities suggesting that concentrations of benzene at the fenceline may be the result of a complex suite of activities including onsite activities not documented in the logbook (loading of the cells by truck haulers) and offsite activities (automobile traffic).

Based on these results several recommendations were made. These include maintaining loading of wastes at rates observed during the study period and further evaluating sulfide emissions from the sump system. A scientifically based cell management approach that would maintain benzene levels below levels of concern is possible based on the simple emission models calibrated during this study. However, measured emission rates and long-term records of air concentrations near the facilities suggest that this is not necessary at present.

1.2 Technical Executive Summary

Emission flux measurements were conducted at landfarm cells containing exploration and production (E&P) wastes at the U.S. Liquids facilities in Bourg and Bateman Island, Louisiana. Flux measurements were conducted using dynamic emission flux chambers with a special design for the consistency of these wastes. Measurements were targeted at BTEX VOCs (benzene, toluene, ethylbenzene and xylene) and sulfides. The primary objectives of the study were to identify and quantify emissions of hydrocarbons and H_2S from the landfarm process at US Liquids facilities and to identify operational activities associated with these emissions. In addition, am objective was to determine whether the magnitude and extent of these emissions pose a threat to human health and the environment.

Fluxes of BTEX were measurable and ranged from 2 to 200 mg/m^2/day. The relative magnitude of the fluxes was consistent with toluene>*o*-xylene>*m*-, *p*-xylene>ethylbenzene>benzene. Flux measurements were used to predict the overlying air concentrations using a simple impoundment model using some relatively conservative assumptions for wind speed. In all cases, the impoundment model well-predicted the concentrations of benzene in the air above the cells (~1 ppb). The measurements demonstrated that while BTEX emissions were measurable from the landfarm cells, they did not produce concentrations that exceeded OSHA or Louisiana ambient air standards. Since the Bourg facility was receiving reduced volumes of E&P wastes at the time of these measurements it was decided to move the study to the Bateman Island facility, a location that was receiving more typical loadings of a commercial facility.

Fluxes ranged from a low of non-detectable for a benzene measurement to 327 mg/m^2/day for a measured toluene flux. Again the relative magnitude of the fluxes was consistent with toluene>*o*-xylene>*m*-, *p*-xylene>ethylbenzene>benzene. Although one measurement produced BTEX fluxes that were higher than the Bourg facility, the bulk of the flux measurements were of similar magnitude, indicating limited risk. There was a strong relationship between cell age and the magnitude of the flux. After the cells were closed to further waste loadings, emissions of BTEX dropped considerably. Again, the simple impoundment model was effective at predicting air concentrations of benzene, which were also around 1 ppbv.

Measured fluxes at the Bourg facility varied over one several orders of magnitude from 0.02 to ~6 mg of S/m^2-hr. At Bateman Island, measured sulfide fluxes were much less variable and ranged from 0.01-0.16 mg/m^2-hr. These fluxes are comparable to the natural fluxes observed from salt marshes. Again, the simple impoundment model predicted the ambient sulfide air concentrations that were below 80 ppbv, which is the restrictive Texas ambient air standard. The only concern with regard to sulfide was the results of a walking tour of the Bourg, LA facility with the sulfide meter. While ambient levels of sulfide were below the Texas standard of 80 ppb, air concentrations directly over a sump indicated ppmv concentrations, suggesting that the sumps are a major source of sulfide emission at these facilities.

The facility log-book at Bourg was analyzed to determine a time sequence of activities for 1998-1999. The Louisiana Department of Environmental Quality conducted a time-series of air concentrations for hazardous air pollutants during this period at the fenceline of the Bourg facility. These data were characterized by periods of static concentrations interspersed with peaks. A series of peaks were analyzed and compared with logbook records for the activities occurring at the time. In reverse fashion, a set of activities documented by the logbook was examined and the concentrations of benzene that developed from these activities were documented. No direct correlation could be made with the observed peaks and any activities suggesting that concentrations of benzene at the fenceline may be the result of a complex suite of activities including onsite activities not documented in the logbook (loading of the cells by truck haulers) and offsite activities (automobile traffic).

Based on these results several recommendations were made. These include maintaining loading of wastes at rates observed during the study period and further evaluating sulfide emissions from the sump system. A scientifically based cell management approach that would maintain benzene levels below levels of concern is possible based on the simple emission models calibrated during this study. However, measured emission rates and long-term records of air concentrations near the facilities suggest that this is not necessary at present.

In conclusion, fluxes of BTEX and sulfide were measurable at the US Liquids facilities and were predictable from simple impoundment models and more complex mass transfer models. These measurements provide a scientific basis for establishing a “loading factor” procedure for managing these facilities based on the expected benzene concentration of each waste type. However, existing loading of wastes at the Bourg and Bateman Island facility did not produce fluxes of BTEX and sulfide of concern. This gives several regulatory options for reducing the risk of the emissions of these waste components.

2.0 Introduction

2.1 Background

Disposal of exploration and production (E&P) wastes is a major obstacle for cost-effective oil production. E&P wastes encompass a cross-section of waste types including cuttings, drilling fluids and produced waters (Table 2.1). These wastes have been exempted from classification as a hazardous waste under the Resource Conservation and Recovery Act and its subsequent amendments. Currently, the disposition of these wastes is regulated at the state level. In Louisiana, the Department of Natural Resources (LADNR) regulates these wastes under Statewide Order 29-B (Table 2-2). This order provides regulatory guidance on the operation of commercial facilities for disposal of these wastes and the closure of production pits, the historical method of E&P waste disposal.

Land disposal remains one of the most cost-effective disposal options despite uncertainty about the long-term effects of these disposal practices. At present, land disposal facilities like the US Liquids facilities in Bourg, Louisiana and Morgan City, LA operate in a similar fashion. Liquid and solid wastes are off-loaded via a barge or truck into a series of earthen cells. These cells ranged in surface area from 2-4.5 acres with a depth of 5-6 feet. Wastes are placed in these cells for a maximum of 30 days at which point the cell is closed. Following closure, several operations are performed. These include the siphoning off of free oil from the surface of the cells, a washing/mixing procedure described in more detail below designed to reduce the salt content of the solids and the offloading of the solids onto reuse piles where the remaining solids are dried. In each case, the water removed from the cell is deep-well injected on site. The life cycle of a single cell from loading to offloading (Figure 2-1) can be one year or longer. Each of these facilities has multiple (>12) cells.

Typical mixtures of E&P wastes in commercial facilities meet most of the reuse standards immediately after placement in the cells. These include naturally-occurring radioactive material (NORM), oil and grease, metals content and pH standards. The salinity or conductivity requirement is where these wastes require the primary treatment.

The design of the facilities is based on the need to reduce the salt content of these wastes in the most economical method possible. The potential problems with this method of disposal are the potential of release of these other constituents including volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene and xylenes and hydrogen sulfide gas. These contaminants would be readily volatilized during the operation of these cells and could potentially cause human health problems near these facilities. At present, virtually nothing is known about the magnitude of the flux of BTEX and sulfide gas from these cells.

2.2 Project Objectives

Based on this need, the project objectives were:

1) To identify and quantify emissions of hydrocarbons and H_2S from the landfarm process at Bourg and to identify operational activities associated with these emissions
2) To determine whether the magnitude and extent of these emissions pose a threat to human health and the environment
3) To recommend changes in the operating procedures at the US Liquids facility to mitigate any harmful emissions
4) To implement these changes and measure the outcomes

2.3 Flux measurements

Emission measurements are generally conducted by determining the transfer of contaminants from one location to another. In this case, the interest is in the release or emission of BTEX and hydrogen sulfide from the cell water and waste material to the air overlying the cells. By definition, emission measurements determine a *flux* or a mass transfer per unit area per unit time (i.e., $mg/m^2/day$) (Figure 2-2). When the flux is multiplied by the area of the cell, an estimate of the total emission (in kg/day or lb/day) can be made. Measurement of fluxes is important than simply measuring air concentrations because it directly and unambiguously establishes the source and magnitude of the emissions. However, modeling calculations must often accompany flux measurements to predict air concentrations. Details of these calculations are presented below.

Emission measurements can be accomplished by a number of methods including static and dynamic chamber techniques (reviewed in Rolston, 1986; Wesley et al., 1989; Majewski et al., 1990; Denmead et al., 1993). Chamber techniques are based on the same general approach. A chamber is placed over the surface of the soil, water or sediment enclosing a known surface area. In static chambers, .the emissions are measured by analyzing changes in concentrations in contaminants of concern in the headspace of the chambers. While static chambers provide estimates of emissions, they suffer from numerous limitations including unrealistically high air concentrations in the chamber headspace. Dynamic chambers provide a marked improvement over static chambers by better mimicking the actual emission process and preventing the build-up of unnaturally high concentrations in the chamber, itself. Since dynamic chambers represent the current state of the art, they were selected as the measurement method of choice in this study.

Emissions of sulfides provide a different challenge because of the potential for production of sulfides in the cells as well as emissions. While sulfide emissions can also be measured using dynamic chamber techniques, the potential to *produce* sulfides must also be determined. Sulfides are produced by groups of anaerobic bacteria, the sulfate-reducing bacteria, which reduce sulfate to sulfide as an alternate electron acceptor. The state of the art method for measuring sulfate reduction potential is through the use of radiolabeled sulfate where the sulfate-reducing bacteria are provided with tracer quantities of $^{35}S\text{-}SO_4^{2-}$ in the laboratory and the formation of radioactive sulfide is measured over time.

2.4 Organization of the report

The report is organized as follows: Following the introduction, the methods utilized to make the measurements are described in full detail. Results and discussion follow the methods and some conclusions and recommendations complete the report.

Table 2-1

Classification of E&P Wastes (Data from Reible et al., 1999)

Waste Code	Title	% TCLP Exceedence for Benzene
01	Salt Water (Produced Brines)	10-30
02	Oil-based Drilling Mud & Cutting	Rarely
03	Water-based Drilling Mud & Cuttings	Rarely
04	Drilling, Workover, & Completion Fluids	10-30
05	Production Pit Sludges	10-30
06	Production Storage Tank Sludge	>30
07	Produced Oily Sands and Solids	>30
08	Produced Formation Fresh Water	Uncertain
09	Rainwater	Rarely
10	Washout Water	Uncertain
11	Washout Pit Water	10-30
12	Gas Plant Waste	>30
13	Basic Sediments & Water	>30
14	Pipeline Test Water	>30
15	Commercial Facility Waste	Uncertain
16	Oil Spill Waste	Rarely
50	Waste Containing Salvagable Crude/Hydrocarbons	Uncertain
99	Other E&P Wastes	Uncertain

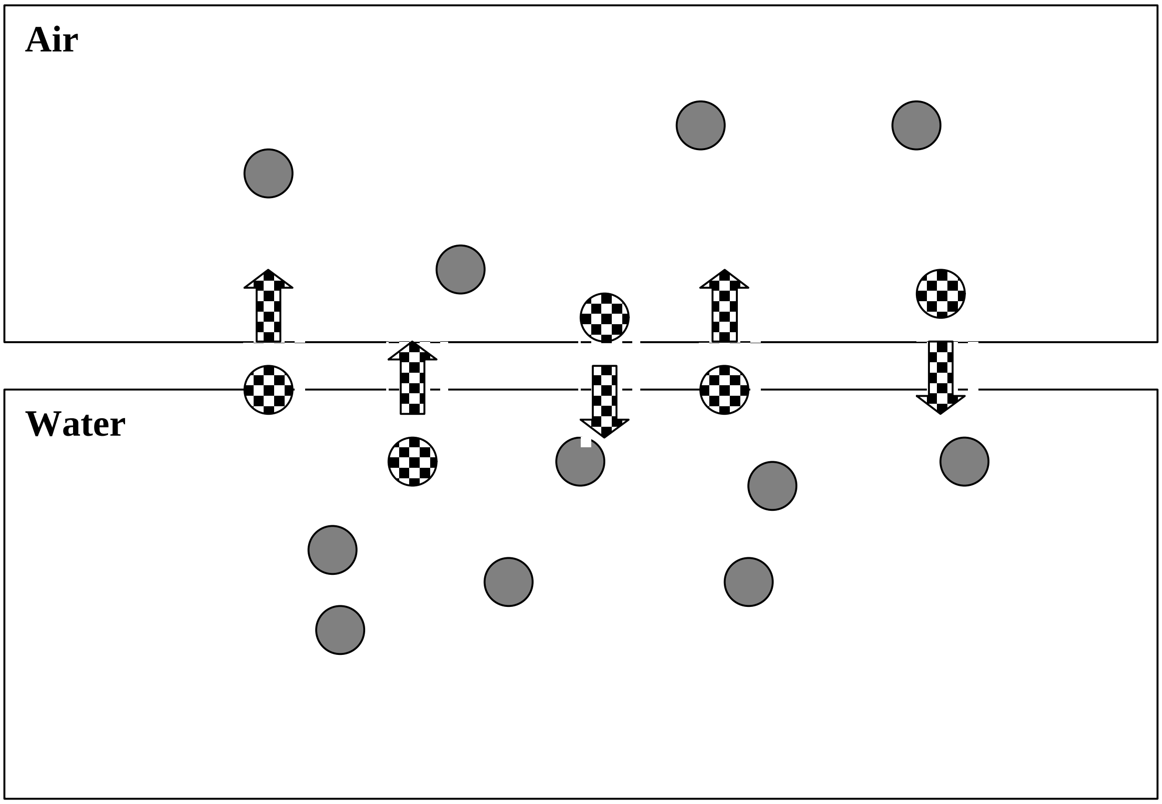


Figure 2-1. What is a flux? A flux is a net transport of chemical across a interface.

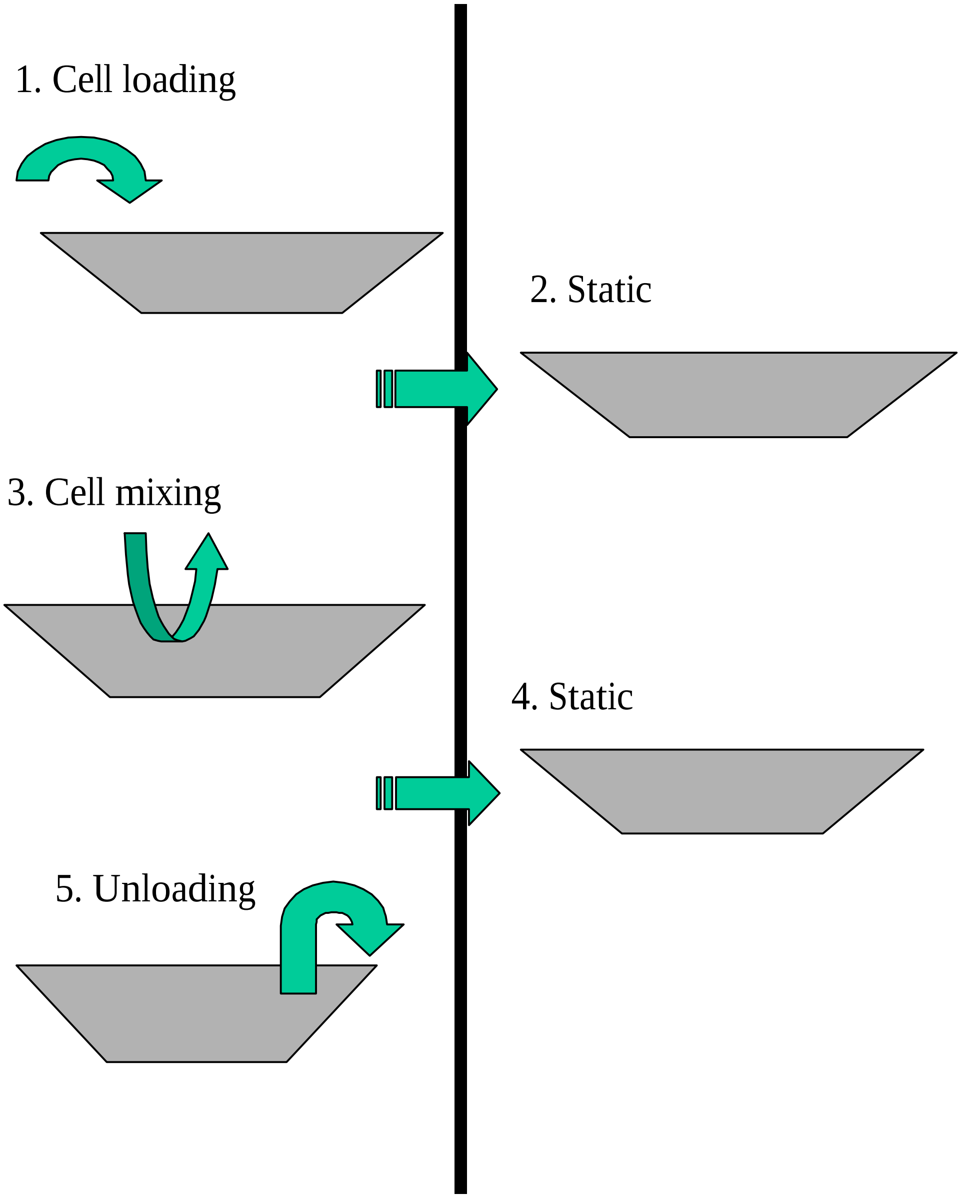


Figure 2-2. Life cycle of US Liquids waste pit

3.0 Materials and Methods

3.1 Flux chamber methods

VOC flux measurements from the landfarm cells were performed using a dynamic flux chamber method modified for use in the oily cell material. A dynamic flux chamber measures emissions by enclosing a portion of the impoundment or landfarm cell leaving a small air space. Air is pulled through the chamber and the hydrocarbons leaving the chamber are trapped using activated carbon. The flux is calculated using the following equation:

$$J = \frac{Q}{A}\left(\overline{C}_{out} - \overline{C}_{in}\right)$$

where J is the mass flux (i.e., mg/m^2-day), Q is the constant flow rate through the chamber (m^3/day), A is the enclosed surface area of the chamber (m^2), C_{out} is the concentration of the target compounds in the outflowing gas and C_{in} is the concentration of the target compounds in the incoming gas.

The design of the chambers was based on one described in Gao et al. (1997) (Figure 3-1). Flux chambers were constructed from 20-gauge galvanized sheet metal with a skeleton of 1” angle iron to provide rigidity. The dimensions of the rectangular top of the chamber (40 cm x 40 cm) define the area over which the flux is measured. Air flowing across the chamber passes through a series of baffles constructed of 26-gauge galvanized sheet metal. These baffles prevent dead spaces in the chamber providing for efficient flow of air. A collar constructed of the same 20-gauge sheet metal was used initially used to implace the chamber into the cell material. The purpose of the collar was two-fold, to isolate the area for flux measurement, preventing air exchange from around the edges of the chamber and secondly, to keep the chamber stable during the flux measurement. During several test measurements it was determined that the density of the cell material was highly variable, and a float was added to provide further stability.

For each set of measurements in the landfarm cells, three flux chambers were utilized. The three chambers were spaced out evenly in the landfarm cell. Each chamber was connected to a separate vacuum pump (Cole-Parmer, Inc.) on the levee surrounding the cell. The vacuum pump was connected to the chamber via thick-walled Tygon tubing across a trap containing 5 grams of activated carbon (Supelco, Inc.). The vacuum pump pulled air through the chamber and subsequently through the trap. Contaminants found in the trap were a combination of those from background and the VOC flux across the water-air interface. Background air was pulled through the chamber since air completely scrubbed of VOCs gives an unrealistic elevated flux. This background contribution was measured using a personal air sampler (Buck Scientific) with a similar activated carbon trap. The personal air sampler was mounted on top of the chamber and measured background concentrations of VOCs. Photographic details of the measurements are provided in Figure 3-2. For reference, a map of the Bourg, LA facility is presented in Figure 3-3.

3.2 Sulfide measurements

Sulfide measurements were conducted simultaneously with BTEX flux measurements using the dynamic chambers described above. For these measurements, a Y-connection was placed in the exit air stream from the chamber and a gold-foil sulfide analyzer (Arizona Instruments) was connected with a short piece of Teflon tubing to the analyzer. The sulfide analyzer operates on the following principle. At a preprogrammed time, the analyzer pumps a volume of air through the instrument. The sulfide interacts with a piece of gold foil in the instrument to produce an electrical signal and a “concentration” is measured based on a previous calibration. For the purposes of these emission flux measurements, the instrument was programmed to make a measurement every 5 minutes during the period the emission flux measurements were being performed. Background sulfide measurements were made before and after every time period.

3.3 Measurement of sulfate reduction rates

For the measurement of sulfate reduction rates, sediment was collected from the cell and transported to the laboratory under anaerobic conditions. A slurry was prepared from cell sediment and site water and placed in a 60 mL serum bottle sealed with a butyl rubber cap. Anaerobic conditions were assured using the Hungate method.

A single-step method (Fossing and Jorgensen, 1989) was used to determine sulfate reduction rate. Sulfate reduction rates were measured in undisturbed sediments using the direct injection of tracer quantities of $^{35}SO_4^{2-}$ (Jorgensen, 1978). The radiosulfate was purchased from Amersham Co. (Arlington Heights, IL) as a form of $Na_2{}^{35}SO_4$. A volume of 30 µl carrier-free $^{35}SO_4^{2-}$ (1.75 µCi) was injected into the serum bottle with a Hamilton micro-syringe. Serum bottles were incubated in a constant temperature room for 48 hours. Sulfate reduction was terminated by freezing at -65^{o}C. To prevent sulfide oxidation, samples from the serum bottles were removed in an anaerobic chamber and placed in deoxygenated N_2 flushed gastight centrifuge bottles. Each bottle contains 70 ml of 20% (w/v) zinc acetate (ZnAc). This quantitatively binds the soluble sulfides and prevents further bacterial transformations (Howarth and Jorgensen, 1984). The sediment was centrifuged and the radioactivity of residual $^{35}SO_4^{2-}$ was measured from a subsample of the supernatant. One ml of the supernatant was mixed with 10 ml of liquid scintillation cocktail (Ultima Gold, Packard Co., Meriden, CT) and the radioactivity of the $^{35}SO_4^{2-}$ was measured using liquid scintillation counting. The sediment pellet was washed twice with deoxygenated sea water to remove the remaining $^{35}SO_4^{2-}$. The washed sediment was homogenized and 1-2 g of subsample was transferred to a round-bottom boiling flask and mixed with 5 ml of distilled water and 5 ml of ethanol. The reaction flask was fitted with a condenser and a port for N_2. The condenser was connected to two ZnAc traps in series. Each trap contains 10 ml of 5% (w/v) ZnAc buffered with 0.1% acetic acid and a drop of antifoam (Antifoam B, Sigma Chemical Co., St. Louis, MO.). The reaction flask was degassed for 20 min with N_2 and 16 ml of 1 M Cr^{2+} (in 1 N HCl) and 8 ml of 12 N HCl were added. The sediment slurry was gently boiled and the H_2S was flushed for 40 min with continuous magnetic stirring. The total reduced inorganic sulfur (TRIS = acid volatile sulfur, AVS + chromium reducible sulfur, CRS) was distilled simultaneously with HCl and Cr^{2+} and the amount of $^{35}SO_4^{2-}$ reduced was calculated from the total $H_2{}^{35}S$ released. After distillation, the two ZnAc traps were pooled. The $Zn^{35}S$ precipitate was then suspended using a vortex mixer, 5 ml of subsample was withdrawn, mixed with 10 ml of the Ultima Gold scintillation fluid (Packard Co., Meriden, CT.) and the radioactivity of ^{35}S was assayed with a liquid scintillation counter (Beckman LS 6000SC).

The Sulfate Reduction Rate (SRR) was calculated by following equation:

$$SRR = \frac{1.06 \cdot 24 \cdot a \cdot \left[SO_4^{\ 2-}\right]}{(A + a) \cdot t}$$

where a is the radioactivity of sulfide (ZnS), A is the total radioactivity of sulfate SO_4^{2-}after incubation, [SO_4^{2-}] is the sulfate concentration in nmol per cm^3 sediment, t is the incubation time in hours, and 1.06 is the correction factor for the expected isotope fractionation (Jorgensen and Fenchel, 1974).

3.4 BTEX measurements

Benzene, toluene, ethylbenzene and xylene sorbed onto activated carbon were extracted using techniques described in NIOSH Method. Briefly, the traps were disassembled in the laboratory and the carbon separated into 0.1 g aliquots. Pesticide-grade carbon disulfide (CS_2) (2 mL) was added to each aliquot of carbon. After a period of extraction the samples were analyzed using a gas chromatograph-mass spectrometer. A 1 uL aliquot of the extract was injected in a splitless mode. The column is an HP-5MS (Hewlett-Packard) with 5% phenyl methyl siloxane. The oven temperatures were as follows: inlet temperature, 250 °C, initial oven temperature, 0 °C for 2 minutes, ramped to 260°C at a rate of 10°C/minute. The following ions were monitored in selected ion monitoring mode by the mass spectrometer: 78 for benzene, 91 for toluene and for ethylbenzene and 106 for *o*-xylene, *m*-xylene and *p*-xylene. The surrogate was 4-bromofluorobenzene and an ion of 95 was monitored for that compound. The internal standard was 1,2-difluorobenzene (ion = 114).

3.5 Additional measurements

Additional measurements were performed on water and sediment from selected waste pits to gain further information on the waste properties. Biochemical oxygen demand (BOD) and pH were determined using probes using EPA Method 360.1 and 150.1, respectively. Dissolved sulfides were measured using Standard Method 4500-S-D. Sulfate was measured using Standard Method 4500-SO42-E. Chloride was measured using Standard Method 4500-Cl-C. Conductivity was measured using Standard Method 2510 B. Reactive sulfides were measured using method described in Sec. 7.3 1310. Acid volatile sulfides were measured using the diffusion method of Brouwer and Murphy. Toxicity characteristic leaching procedure tests were performed on overlying landfarm cell soil using SW 846 Method 1311.

3.6 QA/QC

Full details on quality assurance/quality assurance procedures are presented in the details of the references listed above. All data included in the report passed appropriate QA/QC criteria including blanks, calibration checks, matrix spikes, matrix spike duplicates and surrogate recovery.

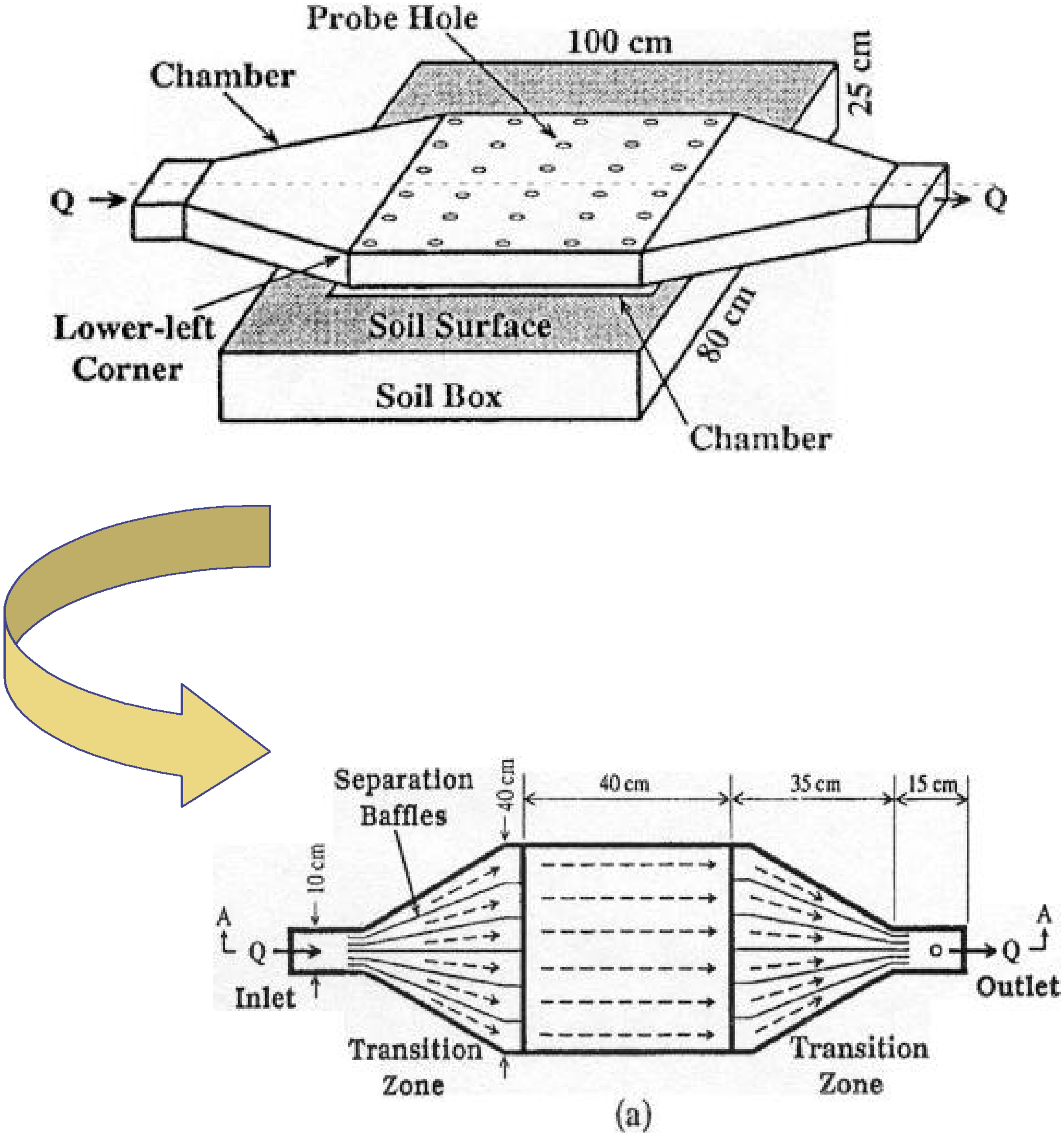


Figure 3-1. Details of flux chamber (adapted from Gao et al., 1997)

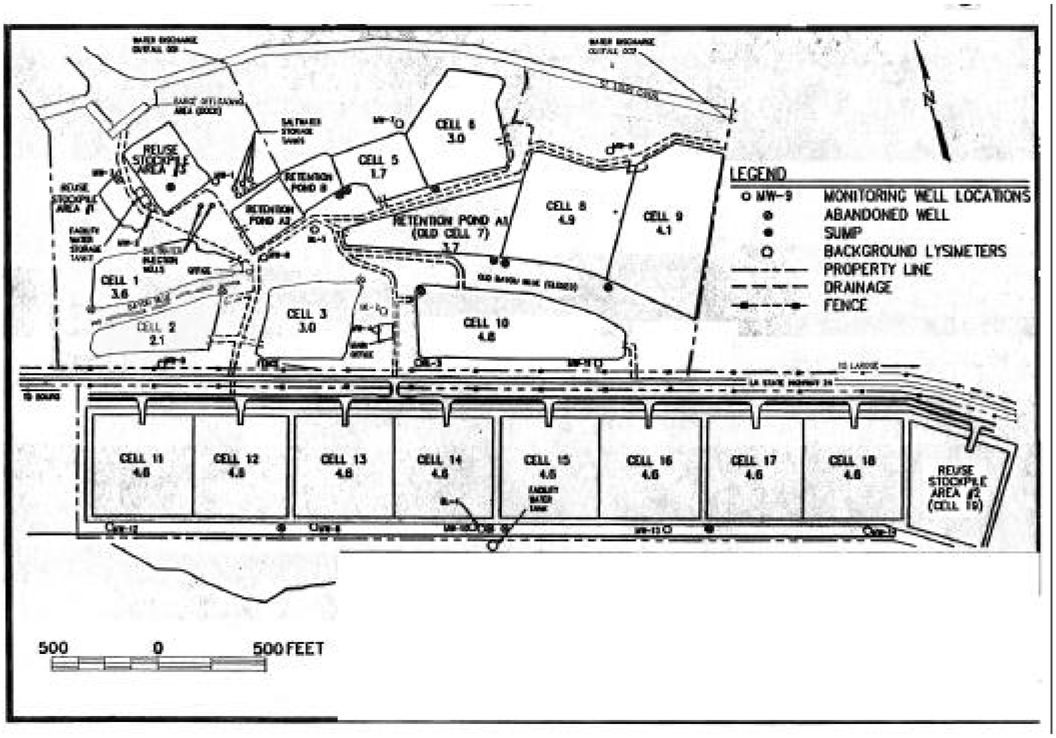


Figure 3-3 Map of Bourg, LA US Liquids Facility

Figure 3-2 A. Landfarm cells at Bateman Island facility

Figure 3-2 B. Dewatering of cell at Bateman Island facility

Figure 3-2 C. Placement of a flux chamber in a cell at Bateman Island

Figure 3-2 D. Close-up of placement of a flux chamber in a cell in Bateman Island

4.0 Results and Discussion

4.1 BTEX fluxes at Bourg, LA facility

Flux measurements were conducted on two dates in December 1998 at the US Liquids facility at Bourg, LA. These measurements were conducted after 3 trips to the site to test equipment, standardize sampling techniques and train graduate students on sampling procedures. Fluxes, expressed as mg of compounds per meter squared of surface area of the cells per day (mg/m^2/day) are given in Table 4-1. Measurable fluxes were determined for benzene, toluene, ethylbenzene and *o*-,*m*-,and *p*-xylenes. No additional compounds on the 8260B list were detected.

The relative magnitude of the fluxes was consistent with toluene>*o*-xylene>*m*-, *p*-xylene>ethylbenzene>benzene. Fluxes ranged from a low of 2.7 mg/m^2/day for a benzene measurement to 165 mg/m^2/day for a measured toluene flux. Within cell variability was large for flux measurements taken in cell 6 (coefficient of variation of ~100%). As expected, higher fluxes were measured near the area of the cell where the waste was off-loaded. The variability in the most recently closed cell, cell 10 taken 2 weeks later indicated much less variability (coefficient of variation of ~25%) presumably due to mixing of the cell contents as part of normal cell operations.

When these flux measurements are multiplied by the surface area of the cells, estimates of whole cell emissions are in the range of 0.11 to 2.95 lbs per day of toluene to 0.17 to 0.41 lbs per day of benzene (Table 4-2). This assumes that average meteorological conditions, cell loading conditions and composition are similar throughout the year. Although fluxes provide valuable information magnitude and confirmation of the source, they do not, of themselves, allow for predictions of risk. Since risk-based standards are expressed in air concentrations of the chemicals, it is necessary to make parallel air measurements or use simple modeling expressions to compute air concentrations. At the Bourg site, both methods were utilized.

A number of atmospheric dispersion models have been developed for the purpose of estimating downwind air concentrations. These are reviewed in Hanna et al. (1982) or Zanneti (1990). For the purposes of this study, however, long-average concentrations adjacent to the cells may be of more interest than the rapidly changing fluxes that would occur with different atmospheric conditions. Reible () developed a simple mass balance model based on average meteorological conditions, which average pollutant concentration over depth. This model is given by:

$$C_{A1} = \frac{\dot{N}_A LW}{HW < U >}$$

where N_A is the emission flux from a source of length L and width W. H is the height over which the contaminant is approximately well-mixed and <U> is the height-averaged wind velocity.

Using several other assumptions including specifying the roughness height gives:

$$C_A = 27N_A/U$$

where C_A = air concentration (moles/m^3), N_A is the flux in moles/m^2-sec and U = average wind velocity in m/s.

Utilizing the model equations specified above, air concentrations in a well-mixed box above the cell can be predicted (Table 4-3). These predictions were based on an assumption of a wind speed of 1 m/s. This is within the range of wind speeds reported at the site. These results are very comparable to actual air concentrations measured using personal air samplers directly above the cells (Table 4-3). In all cases, measured and predicted air concentrations are less than the two established standards, an OSHA standard for benzene of 1 ppmv for 8 consecutive hours and the Louisiana ambient air standard of 3.76 ppbv.

Remarkably, both the measured and predicted air concentrations for these compounds are very similar to air concentrations measured at Louisiana Department of Environmental Quality air monitoring stations at the fenceline of the Bourg facility. A sequence of these concentrations taken over the same frame. These measurements, taken over the same time frame, were made with different analytical techniques and in separate laboratories, yet they both indicate that concentrations of between 1-5 ppbv are routinely observed in the air around this facility. These data are discussed in more detail later.

The ancillary measurements taken in the cells at this location also shed some light on conditions within the cells during this time period (Table 4-4 and Table 4-5). Measured water concentrations and TCLP measurements indicate that only BTEX compounds are present from those on the analyte list. Concentrations are in the ppb range. The pH of the water in these cells is near neutrality and the overlying water is anoxic, as expected. Measured values of water concentrations coupled with the flux measurements can be used to calibrate a predictive flux model that can be used to insure that ambient air standards are not exceeded. This approach is discussed in a later section.

The conclusions from the flux measurements from the Bourg facility are as follows:

- Measureable fluxes of benzene, toluene, ethylbenzene and xylene were observed. These fluxes ranged from approximately 2 to 200 mg/m^2/day.
- The relative magnitude of the fluxes was consistent with toluene>*o*-xylene>*m*-, *p*-xylene>ethylbenzene>benzene.
- Measured air concentrations and those predicted by a simple impoundment model were very similar. Neither observed or predicted air concentrations of the contaminant of regulatory concern, benzene, exceeded ambient air standards or OSHA standards.

The conclusions were supported by relatively limited measurements (6 individual flux chambers on two dates) and the relatively low loading rates occurring at the Bourg facility created questions about the relevance of the data to other sites. It was proposed therefore to move the study to US Liquids Bateman Island facility near Morgan City to determine whether similar flux measurements are observed in facilities where higher loadings of E&P wastes are occurring.

4.2 BTEX fluxes at Bateman Island facility

Flux measurements were conducted over 6 dates from March 1999 to April 1999 at the US Liquids facility at Bateman Island, LA. Techniques developed at the Bourg facility were utilized directly in these similar cells. Fluxes, expressed as mg of compounds per meter squared of surface area of the cells per day (mg/m^2/day) are given in Table 4-6. As observed previously at the Bourg facility, measurable fluxes were determined for benzene, toluene, ethylbenzene and *o*-,*m*-,and *p*-xylenes. No additional compounds on the 8260B list were detected.

The relative magnitude of the fluxes was consistent with toluene>*o*-xylene>*m*-, *p*-xylene>ethylbenzene>benzene. Fluxes ranged from a low of non-detectable for a benzene measurement to 327 mg/m^2/day for a measured toluene flux. Within cell variability was large on flux measurements taken from newer cells. Variability decreased as the cells increased in age presumably due to mixing and the previous history of fluxes in these older cells. When these flux measurements are multiplied by the surface area of the cells, estimates of whole cell emissions are in the range of 0.05 to 1.49 lbs per day of toluene to below detection to 0.6 lbs per day of benzene (Table 4-7). This assumes, crudely, that meteorological, loading and mixing conditions are similar over the course of the day.

A steady decrease in contaminant flux was observed as the cells aged (Table 4-8). This is expected as the cells are mixed and the initial load of BTEX is reduced from volatilization and probable biological degradation processes occurring in the cells. The variability in the flux across the cell also decreased over the lifetime of the cell as indicated by decreases in the standard deviation between the three measurements taken in each cell (Table 4-8). Clearly, aging has an effect on the magnitude and duration of emission and near the end of the life cycle of the cell, fluxes are extremely low and pose little risk.

We conclude that fluxes of BTEX are measurable in the Bateman Island cells using these techniques but do they result in air concentrations that exceed established risk-based standards? Since risk-based standards are expressed in air concentrations of the chemicals, it is necessary to make parallel air measurements or use simple modeling expressions to compute air concentrations. Similar to the Bourg site, both methods were utilized at Bateman Island.

Utilizing the simple impoundment model discussed above, air concentrations in a well-mixed box above the cell can also be predicted (Table 4-7). These predictions were based on an assumption of a wind speed of 1 m/s. This is within the range of wind speeds reported at the site. With the exception of the first set of measurements made in Cell 4B (the cell that was being loaded during this period of the study), results were very comparable to actual air concentrations measured using personal air samplers directly above the cells (Table 4-9). In all cases but the measurement taken initially at 4B, measured and predicted air concentrations are less than the two established standards, an OSHA standard for benzene of 1 ppmv for 8 consecutive hours and the Louisiana ambient air standard of 3.7 ppbv. There is no clear indications of why the initial measurements in Cell 4B were high. There were no obvious differences in the condition of the cells during that period. The lack of the agreement with the impoundment model and the mass transfer model discussed below suggest that the results from this sampling event should be viewed with caution. However, we have no conclusive reason to discount these measurements completely.

Again, measured and predicted air concentrations for these compounds are very similar to air concentrations measured at Louisiana Department of Environmental Quality air monitoring stations at the fenceline of the Bourg facility. Both sets of measurements indicate that concentrations of between 1-4 ppbv are routinely observed in the air around these facilities.

The ancillary measurements taken in the cells at this location also shed some light on conditions within the cells during this time period (Table 4-10 and Table 4-11). TCLP measurements on the soils indicate that only BTEX compounds are present from those on the analyte list. Concentrations are in the ppb range. The pH of the water in these cells is near neutrality and the overlying water is anoxic, as expected. Measured values of water concentrations coupled with the flux measurements can be used to calibrate a predictive flux model that can be used to insure that ambient air standards are not exceeded. This approach is discussed in a later section.

The conclusions from the flux measurements from the Bateman Island facility are as follows:

- Measurable fluxes of benzene, toluene, ethylbenzene and xylene were observed. These fluxes ranged from approximately 2 to 200 mg/m^2/day.

- With the exception of one set of flux measurements, predicted air concentrations did not indicate exceedance of applicable air standards in air just above the cells.
- Fluxes decrease as the cells age.
- Air concentrations are similar to the measurements observed at the Bourg facility.

Flux measurements at Bateman Island established the magnitude of BTEX fluxes under these static conditions. The measurements also established the differences in flux magnitude and variability as the cells age through their life cycle. Clearly, it is possible to load enough wastes with high VOC concentrations to produce emissions of concern, however that has not been observed at these loading rates. Managing the cells to ensure that benzene emissions do not exceed applicable standards is a possible approach. This is discussed in more detail below.

4.3 Mass transfer coefficients determination

Although the simple impoundment models have been effective at predicting air concentrations, it has limited use as a management tool since the model does not relate water concentrations and the flux. Since distributions of aqueous benzene concentrations are available for the waste types, it may be possible to estimate loadings of categories of wastes that would produce undesirable water concentrations of benzene. For example, volumes of various categories of wastes would be allowed into a cell to minimize the possible benzene concentrations. By definition, these “undesirable” concentrations are those that would produce a flux of benzene, creating air concentrations exceeding any applicable standard (OSHA or the Louisiana ambient air standard).

Several models for predicting volatilization have been developed (Thibodeaux, 1996). One applicable model has the following form:

$$N_A = K_L\,(C_w - C_a / H_c) \tag{3}$$

Where N_A is the flux of compound A from the cell (mg/m^2.h), C_w is the concentration of the compound in water (mg/m^3), C_a is the concentration of the compound in air (mg/m^3), and H_c represents the Henry's constant for the compound (dimensionless). K_L is the average mass transfer coefficient for the compound (m/h). Note that this model requires inputs of aqueous and air concentrations and knowledge of flux to calculate the mass transfer coefficient. Fluxes and aqueous concentrations of BTEX were used to estimate a mass transfer coefficient for each cell type. Results are presented in Table 4-12. Mass transfer coefficients for BTEX compounds can be predicted from available correlations such as those presented in the literature (Thibodeaux, 1996) for air emissions from non-aerated surface impoundments. The mean, high and low values of K_L predicted are also listed in Table 4-12. In general, observed mass transfer coefficients are similar to those observed previously in the non-aerated portion of impoundments with one exception. The initial measurement made at the Bateman Island facility (3/17/99) had the highest measurable flux, however, the mass transfer coefficient predicted from the model fit was larger than literature values. This provides additional evidence that the BTEX concentrations observed were anomalous.

Measured mass transfer coefficients can be used to relate potential fluxes to aqueous concentrations and to the allowed waste oil concentrations. This provides a potential approach for regulating these landfarm cells. As an example, consider the case of benzene. Let us assume an average maximum flux to air of 20 mg/m^2.d (= 0.83 mg/m^2.h). Consider the average predicted mass transfer coefficient of 9.4 cm/h (=0.094 m/h) for benzene. The Henry's constant for benzene is 0.22. If the air concentration of benzene is to be kept below the Louisiana ambient standard of 3.8 ppbv (= 0.011 mg/m^3), then the average water concentration can be obtained from equation (3) for flux: C_w = (0.83/0.094) + (0.011 / 0.22) = 9 mg/m^3. Data generated on TCLP tests for benzene from oil field waste indicates that the TCLP leachate concentration of benzene can be related to the total concentration of benzene in the waste oil through a multiplier that depends on the composition of the waste (Thomas, 2000). If such a multiplier is estimated for a given waste, then the total maximum allowable concentration of benzene in that waste can be estimated.

This model requires inputs of aqueous concentrations and knowledge of a mass transfer coefficient, K_L (cm/hr). Fluxes and aqueous concentrations of BTEX were used to predict a mass transfer coefficient for each cell type. Results are presented in Table 4-12. In general, observed mass transfer coefficients are similar to those observed previously in the non-aerated portion of impoundments with one exception. The initial measurement made at the Bateman Island facility (3/17/99) had the highest measurable flux, however, the mass transfer coefficient predicted from the model fit was larger than literature values. This provides additional evidence that the BTEX concentrations observed were anomalous.

Measured mass transfer coefficients can be used to predict relate aqueous concentrations to potential fluxes. This provides a potential approach for regulating these landfarm cells.

4.4 Conclusions of BTEX Flux Measurements

Several important conclusions can be drawn from the BTEX flux measurements. The most important conclusion is that the waste composition and loading occurring in the cells between December 1998 and April of 1999 do not result in emissions of BTEX that violate ambient air or OSHA standards. Importantly, this was in air immediately above the cells themselves. Air which has dispersed and been transported away from the immediate facility would be expected to have lower concentrations. Simple impoundment models appear to predict the air concentrations reasonably well and the data obtained here have been used to calibrate a more sophisticated mass transfer model that could be used to manage cell loading.

Table 4-1

BTEX fluxes at U.S. Liquids Facility at Bourg, LA

	Flux, mg/m^2/day				
Cell	**Toluene**	**Benzene**	**Ethylbenzene**	**o-xylene**	**m,p-xylene**
6	164.7	20.8	74.5	159.4	49.3
6	33.5	6.0	9.7	22.0	23.5
6	19.8	3.1	3.8	15.3	14.5
6 (avg)	72.67	9.97	29.33	65.57	29.10
6 (std dev.)	80.00	9.49	39.23	81.33	18.06
6 (C.V %)	110.09	95.25	133.73	124.04	62.07
10	29.7	5.4	6.3	15.2	14.5
10	19.3	2.7	4.4	11.3	10.5
10	29.4	4.5	7.9	19.1	18.0
10 (avg)	26.13	4.20	6.20	15.20	14.33
10 (std. Dev.)	5.92	1.37	1.75	3.90	3.75
10 (C.V., %)	22.65	32.73	28.26	25.66	26.18

Cell 6

Table 4-2

Estimated Mass Flux for U.S. Liquids Bourg Facility

			Flux (lbs/day)		
Cell	Toluene	Benzene	Ethylbenzene	o-xylene	m,p-xylene
6	2.95	0.41	1.19	2.66	1.19
10	0.11	0.17	0.25	0.62	0.59

*for each 4.6 acre landfarm cell

Table 4-3

Predicted and Measured Air Concentrations at the Bourg, LA Facility

Cell	Benzene, ppbv, estimated	Benzene, ppbv, measured
6	2.03	
6	0.59	0.31
6	0.30	
10	0.52	
10	0.26	0.42
10	0.44	

Table 4-4
Measured water and soil concentrations at the Bourg, LA facility

Date	Cell	Benzene	Toluene	Ethylbenzene	Xylene
		µg/L			
12/11/98	6	85.19	67.11	7.9	34.84
12/11/98	6	74.92	58.23	6.16	31.22
12/18/98	10	123.22	35.16	3.92	26.11
12/18/98	10	109.22	28.22	2.4	18.84

Table 4-5
Ancillary measurements at the Bourg, LA facility

Date	Cell	pH	BOD	Sulfide	Chlorides	Sulfate	Conductivity	AVS	Sulfide, reactive
		S.U.	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L
12/11/98	6	6.84	NA	0.073	13,845	83.2	41.8	0.27	0.41
12/18/98	10	7.13	NA	0.10	14,114	152.4	40.2	0.18	0.28

Table 4-6

Bateman Island Fluxes

	Flux, mg/m^2/day				
Cell	Toluene	Benzene	Ethylbenzene	o-xylene	m,p-xylene
10	35.7	19.3	5.7	11.1	12.5
10	21.5	9.9	3.1	6.1	6.7
10	15.4	4.7	5.8	12.5	14.1
10 (avg)	24.20	11.30	4.87	9.90	11.10
10 (std dev.)	10.42	7.40	1.53	3.36	3.89
10 (C.V %)	43.04	65.49	31.45	33.99	35.08
9	20.1	6.7	10.7	26.3	45.1
9	34.2	14.4	10.5	11.2	20.0
9	54.6	22.6	14.8	21.3	36.2
9 (avg)	36.30	14.57	12.00	19.60	33.77
9 (std. Dev.)	17.35	7.95	2.43	7.69	12.73
9 (C.V., %)	47.78	54.59	20.22	39.25	37.69

Cell 6

Table 4-6 (cont.)

Bateman Island Fluxes

	Flux, mg/m^2/day				
Cell	Toluene	Benzene	Ethylbenzene	o-xylene	m,p-xylene
4A	14	9.0	7.8	15.7	13.1
4A	6.6	4.8	5.5	10.5	9.8
4A	8.5	5.4	5.3	9.8	10.0
4A (avg)	9.70	6.40	6.20	12.00	10.97
4A (std dev.)	3.84	2.27	1.39	3.22	1.85
4A (C.V %)	39.62	35.49	22.41	26.86	16.87
3B*	0.0	1.5	0.02	0.03	0.04
3B	0.0	1.0	0.08	0.22	0.18
3B	0.0	1.3	0.0	0.0	0.02
3B (avg)	0.00	1.27	0.03	0.08	0.08
3B (std. Dev.)	0.00	0.25	0.04	0.12	0.09
3B (C.V., %)	0.0	19.87	124.90	143.16	108.97

Table 4-6 (cont.)

Bateman Island Fluxes

	Flux, mg/m^2/day				
Cell	Toluene	Benzene	Ethylbenzene	o-xylene	m,p-xylene
4B*	327	108	67	140	97
4B	314	113	60	124	91
4B (avg)	320.50	110.50	63.50	132.00	94.00
4B (std dev.)	9.19	3.54	4.95	11.31	4.24
4B (C.V %)	2.87	3.20	7.79	8.57	4.51
4B	18.4	8.9	5.5	13.1	10.4
4B	12.1	7.2	2.2	5.0	3.3
4B	29.6	12.9	10.3	22.6	18.9
4B (avg)	20.03	9.67	6.00	13.57	10.87
4B (std. Dev.)	8.86	2.93	4.07	8.81	7.81
4B (C.V., %)	44.24	30.27	67.88	64.93	71.88

Table 4-7

Estimated mass flux for Bateman Island

	Flux (lbs/day)*				
Cell	**Toluene**	**Benzene**	**Ethylbenzene**	**o-xylene**	**m,p-xylene**
10	0.99	0.46	0.20	0.41	0.45
9	1.49	0.60	0.49	0.80	1.38
4A	0.40	0.26	0.25	0.49	0.45
4B	0.82	0.40	0.25	0.56	0.45
3B	0.00	0.05	0.00	0.00	0.00

* for each 4.6 acre cell

Table 4-8

Relationship Between Cell Age and Magnitude of Benzene Flux

Cell age (time after closure)	Mean Benzene Flux ($mg/m^2/day$)	Standard Deviation of Flux ($mg/m^2/day$)
Current	14.5	7.9
1 week	11.3	7.4
3 month	9.7	2.9
6 month	6.4	2.2
9 month	1.3	0.24

Table 4-9

Predicted and Measured Air Concentrations at the Bateman Island, LA Facility

Cell	Benzene, ppbv, estimated	Benzene, ppbv, measured
4B -1	10.6	
4B-1	11.1	0.82
4B-2	0.87	
4B-2	0.70	
4B-2	1.26	1.11
10	1.89	
10	0.98	1.28
10	0.46	
9	0.66	
9	1.41	1.90
9	2.21	

Table 4-10

TCLP measurements made at Bateman Island

Date	Cell	Benzene	Toluene	Ethylbenzene	Xylene
			mg/L		
3/17/99	4B	0.12	0.12	0.04	0.18
3/26/99	4B	0.06	0.11	0.03	0.10
4/9/99	4A	0.06	0.14	0.06	0.24
4/16/99	3B	<0.05	<0.05	<0.05	<0.05
4/23/99	10	0.06	0.004	0.01	0.05

Date	Cell	As	Ba	Cd	Cr	Pb	Hg	Se	Ag
3/17/99	4B	0.008	1.75	<0.01	0.04	0.03	<0.0005	0.03	<0.01
3/26/99	4B	0.027	1.61	<0.01	0.95	0.07	<0.0005	<0.001	<0.001
4/9/99	4A	0.002	9.02	<0.01	0.29	0.17	0.002	0.17	<0.01
4/16/99	3B	<0.001	6.7	<0.01	0.06	0.11	0.001	<0.001	<0.01
4/23/99	10	0.002	2.6	<0.01	0.05	0.02	0.001	<0.001	<0.01

Table 4-11.
Additional data for Bateman Island

Date	Cell	pH	BOD	Sulfide	Chlorides	Sulfate	Conductivity	AVS	Sulfide, reactive
		S.U.	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L
3/17/99	4B	7.01	3.4	0.088	15,995	113.5	43.8	0.11	0.04
3/26/99	4B	6.04	3.6	0.098	15,795	122.9	43.5	0.29	0.31
4/9/99	4A	7.46	4.1	0.132	6,848	86.89	19.5	0.15	0.07
4/16/99	3B	7.84	5.4	0.112	7,098	46.78	21.75	0.08	0.04
4/23/99	10	6.69	5.1	0.339	19,994	115.6	51.00	0.03	0.03

Table 4-12

Mass transfer coefficients for BTEX compounds from the Morgan City and Grand Bois Oil Field Waste Air Emission Study.

Date	**Cell #**	**Cell Age**	**Mass Transfer Coefficient, K_L (cm/hr)**			
Bateman Island Results:			Benzene	Toluene	Ethyl benzene	o-xylene
3/17/99	4B	3 mon.	25.6 ± 18.1	74.4 ± 52.6	44.0 ± 31.3	22.9 ± 16.3
3/26/99	4B	3 mon.	6.7 ± 1.6	7.6 ± 2.7	8.3 ± 4.6	5.1 ± 2.7
4/09/99	4A	6 mon.	3.7 ± 4.4	2.4 ± 2.7	4.3 ± 0.8	2.1 ± 0.5
4/16/99	3B	9 mon.	2.1 ± 2.1	N/A	N/A	0.14 ± 0.16
4/23/99	10	1 wk.	7.8 ± 4.2	10.1 ±3.5	1.8 ± 0.4	8.2 ± 2.3
Bourg Results:			Benzene	Toluene	Ethyl benzene	o-xylene
1/15	6	1 wk.	5.5 ± 4.3	52.2 ± 46.9	21.0 ±21.7	8.8 ± 8.9
1/29	10	1 wk.	2.3 ± 0.6	18.8 ± 3.5	4.3 ± 1.0	20.4 ±4.3
Predicted values from Literature (range)			2.6 to 18.0	2.4 to 16.6	2.3 to 16.0	2.1 to 14.8
	(Mean)		9.4	8.6	8.3	6.2
Predicted values from Literature (range)			2.6 to 18.0	2.4 to 16.6	2.3 to 16.0	2.1 to 14.8

Note: Average and standard deviations are given for K_L. Literature values are obtained from data for methanol (Thibodeaux, 1996) by correcting for the diffusivities.

4.5 Sulfide Flux measurements at Bourg and Bateman Island

Sulfide flux measurements were conducted on one date in December 1998 and two dates in January 1999 at the US Liquids facility at Bourg, LA. At both dates, flux measurements were conducted in the currently loaded cell. As before with the BTEX flux measurements, sulfide flux was measured after 3 trips to the site to test equipment, standardize sampling techniques and train graduate students on sampling procedures. Fluxes, expressed as mg of compounds per meter squared of surface area of the cells per day ($mg/m^2/hr$) are given in Table 4-13. The Arizona Instruments sulfide meter measures hydrogen sulfide with a detection limit of 1 ppbv but is also less sensitive to other reduced sulfur gases (sensitivity listed in Appendix 1). Therefore, these measurements are somewhat conservative. The sulfide analyzer measured sulfide concentrations leaving the flux chamber every 5 minutes, therefore a time-series record of sulfide release is also available (Figure 4-1).

Measured fluxes at the Bourg facility varied over one several orders of magnitude from 0.02 to ~6 mg of S/m^2-hr. Fluxes were not related to temperature or any observed condition of the cells. It is expected that fluxes of sulfides would be variable in the currently loaded cell as wastes with different sulfide content are loaded. Patterns of sulfide emissions from the Grand Bois samples are presented in Figure 4-1. For the sampling date in December 1998, a relatively consistent flux of sulfide was observed over the sampling period. For the two dates in January, emissions were very variable with spikes of sulfide against a very low background. This pattern is suggestive of short-term releases of sulfide-rich bubbles (ebullition), a dominant mechanism of sulfide release in marshes.

At Bateman Island, measured sulfide fluxes were much less variable and ranged from 0.01-0.16 mg/m^2-hr (Table 4-14). Again, the age of the cell appeared to impact the magnitude of the flu with lower fluxes observed in cells of increasing age (Table 4-15). Patterns of sulfide emission are presented in Figure 4-2. Again, ebullition appears to be the dominant mechanism based on the observed pattern of sulfide release, spikes in sulfide concentration against a very low background.

How does these sulfide fluxes compare to those measured in other systems? A large amount of literature is available concerning the estimation of fluxes of reduced sulfide gases from various components of the environment and the atmosphere. Reviewed below is the current state of knowledge for fluxes of H_2S from wetland environments and petroleum facilities, two of the most likely sulfide sources near the US Liquids landfarms.

4.6 Review of Wetland Sulfide Fluxes

H_2S is generated in salt marshes as the result of microbially-mediated sulfate reduction by specialized bacteria such as *Desulfovibrio*. Sulfate reduction rates have been measured in these environments and representative rates are X and X. The sulfide generated by this process can be *retained* in the wetland (i.e., through precipitation as FeS and subsequent conversion to pyrite), can be *oxidized* to elemental sulfur and sulfate by oxygen at the sediment-water interface, or *emitted* to the atmosphere by diffusion or by formation of sulfide-rich bubbles (*ebullition*). Because reduced sulfur gases could be significant greenhouse gases, much effort has been directed at estimating the magnitude of fluxes of H_2S from wetland environments.

Biogenic sulfide fluxes from a variety of environments in the eastern and southeastern U.S. were measured during a 4-year study by Adams and others (1981a,b). This study established the range of potential fluxes in various freshwater, brackish and saline wetland environments in addition to other soil types (Table 4-16). Fluxes were highly variable in the saline marshes ranging from 0.02-602 g S/m^2-year. Several measurements were made in Louisiana near Jeanrette, La (ΣS flux = 0.031 g S/m^2-yr) and at the Rockefeller National Wildlife Refuge (H_2S flux = 0.09 g S/m^2-year). Without further detail on the types of marshes, implacement of the chambers, and other factors it is difficult to specify further what caused the fluxes of H_2S from salt marshes to vary over several orders of magnitude.

Subsequent studies have identified other measurements for comparison. Fluxes of H_2S from selected Florida wetlands (mangrove swamp, freshwater marshes, swamps, and saline marshes) ranged from 0.004 (freshwater swamp)-0.106 (mangrove swamp) g S/m^2-yr (Castro and Dierberg, 1987). The average flux measurement was 0.008 g S/m^2-yr.

Additional measurements in Florida Spartina alterniflora marshes reveal spatial variability ranging from 0.0008 g S/m^2-yr to 0.08 g S/m^2-yr. Additional short-term measurements have been made in a Florida *Spartina alterniflora* marsh over a tidal cycle (Cooper et al., 1987, 1989). Results varied over 4 orders of magnitude from 10^{-1} to 10^2 g S/m^2-yr with the highest fluxes during high tide. Fluxes from a salt-water marsh in New Hampshire were 0.008 to 0.044 g S/m^2-yr (Goldberg et al., 1981).

More detailed seasonal sulfide flux measurements have been conducted at the Great Sippewissett Marsh in Falmouth, MA (Steudler and Peterson, 1984, 1985). These results revealed fluxes of H_2S of 5.8 g S/m^2-year with peak releases in May and October. Results indicated that H_2S accounted for about 35% of the sulfur emitted from the marsh while dimethyl sulfide accounted for 49% of the total. Results were used to extrapolate globally to estimate the contribution of salt marshes to the total atmospheric sulfur budget. Dimethylsulfide (DMS) is an important component of sulfur flux from salt marshes due to the presence of an important precursor (dimethylsulphoniopropionate) in the tissues of *Spartina alterniflora* (Dacey et al., 1987; Morrison and Hines, 1990). DMS is liberated from the leaves of the plants rather than from sediments. The opposite is true for H_2S fluxes which originate in the sediments and often display maxima just prior to high tide due to tidal pumping (Hansen et al., 1978; Jørgensen and Okholm-Hansen, 1985; Cooper et al., 1987).

Direct air measurements of sulfide species at ground level have also been conducted near wetlands including several sites in Louisiana (Thibodeaux, Rockefeller Wildlife Refuge, Cocodrie and Caillou Bay, LA) (Berresheim, 1993). H_2S concentrations were in the range of 200-900 ppt (parts per trillion) in these recent measurements.

Using the simple impoundment model of Reible described above, the sulfide concentration in air can be estimated from the magnitude of these fluxes, coupled with some simple assumptions of possible wind speeds (e.g., 1 m/s). These results are presented in Table 4-17. From the range of potential fluxes presented in Tables 4-13 and 4-14, air concentrations of sulfide exceeding the Texas ambient air standard (80 ppb) are possible resulting from when the emission flux exceeds 150 g of S/m^2/year (Table 4-18). Although several measurements of sulfide emissions from wetlands have exceeded this value, the bulk of salt marsh sulfide fluxes would produce lower ambient air concentrations than the Texas sulfide standard.

Based on these results the following conclusions can be drawn about sulfide fluxes from wetlands:

- Measured sulfide vary over several orders of magnitude
- Measured sulfide fluxes are within the range of those observed in natural saline wetlands
- Using a simple impoundment model, measured fluxes of sulfides from wetlands would not normally produce air concentrations over the marsh that exceeds 80 ppbv.

4.7 Review of Sulfide Emissions from Petroleum Facilities

In addition to biogenic sulfide production, other sources include the naturally present H_2S in crude oil and natural gas. H_2S content in crude oil exploration and production is enhanced by water injection that enhances growth of sulfate-reducing bacteria in oil-producing strata. Few published studies have quantified sulfide emissions from oil field. A recent study (Tarver and Dasgupta, 1997) of sulfide emissions from West Texas oil fields provides an excellent discussion and data set. Several findings have application to the current problem. Emission from tank batteries represented very large sources of H_2S emission due to the high concentrations of H_2S in the tank headspace that ranged from 15-20% (v/v). Based on turnover of oil from the tanks and the subsequent displacement of the tank vapor, fluxes from a tank battery were on the order of 1-3 x 10^6 g of S/yr. Compared with areal fluxes from marshes, this would obviously be a major source of H_2S. By comparison, a rectangular section of marsh or a landfarm cell 30 m by 30 m (900 m^2) emitting sulfide at 50 g/m^2-year, would result in 4.5 x 10^4 g of S/yr, two orders of magnitude less than a single tank battery.

The study by Tarver and Dasgupta (1997) also documented a strong diurnal pattern of sulfide concentration in the air surrounding the oil E&P areas in West Texas. H_2S concentrations peaked early in the morning (5 AM) and decreased to very low levels during sunlight hours. Concentrations were 2-3 times higher at nighttime when compared with daylight levels. Several potential explanations were used to explain this diurnal pattern. These include convective transport of the H_2S to higher altitudes during daylight hours, an increase in the boundary layer height during the day and oxidation of H_2S by $HO^{\cdot}$ and $HO_2^{\cdot}$ radicals. The relative importance of each mechanism could not be determined despite experimentation. Clearly, however, the strong diurnal pattern of sulfide excursions (high concentrations measured at night) documented at the US Liquids facility has a precedent from this West Texas oilfield study.

4.8 Comparison of measured fluxes with published values in wetlands

Measured sulfide fluxes from the land treatment cells at Bourg and Bateman Island were within the range observed in wetlands such as salt marshes. Observed fluxes were generally of low magnitude and were generally near the detection limit of the instrument. Based on the magnitude of these fluxes, it can be concluded that fluxes from the landfarm cells when they are in static mode (not mixed or loaded) are similar in magnitude to the brackish and saline marshes surrounding these facilities. As before, the simple impoundment model can be used to estimate air concentrations of H_2S that would result in a well-mixed box of air above the cell. These estimates are provided in Table 4-17. Most of the observed fluxes (all of those from Bateman Island and the January sampling dates from the Bourg, LA facility) would result in ambient air concentrations less than 1 ppbv . This agrees with the very low background air concentrations measured on those dates. The highest ambient background concentration measured (55 ppbv), corresponded to the highest predicted air concentration (31 ppbv) at the December 1998 sampling at the Bourg facility. Again, the simple impoundment model effectively linked the observed air concentrations with the measured fluxes.

4.9 H_2S surveying

In addition to measured fluxes, survey measurements were made at the Bourg, La site using the Arizona Instruments meter. A walking tour around Cell 6 was made and 8 separate measurements were made at 1-minute intervals. Measured concentrations had an average of 53 ppb with a standard deviation of 10 ppbv. In addition, to the area directly around the cell, measurements were made at an open manhole near Cell 6 leading from the subsurface sumps draining the cells. The inlet from the sulfide analyzer was placed over the outlet of the manhole and the concentration measured. Concentrations were 14.4, 13.1 and 13.3 ppmv after three separate measurements. Clearly the survey indicates that the manholes leading from the sumps are a major source of sulfide in the system.

Where does the observed sulfide originate? Several possibilities exist that would require further investigation. Drainage of water with moderately high sulfide concentrations would be one possibility. Since the drainage system represents an enclosed or confined space, Henry's Law can be used to predict the water concentration that would produce air concentrations of this magnitude. Assuming an equal volume of water and air in the sump and a dimensionless Henry's Law constant of $10^{-0.99}$ M/atm, a water concentration of 55 ppbw could generate an air concentration of 15 ppmv. Even though relatively low concentrations of sulfides were observed in these measurements, it is possible that small production of sulfide could be responsible for the observed air concentration near the sumps. A second possibility is that sulfide generation occurs at deeper depths in the waste material than were sampled for this study. A more detailed coring of waste material in the landfarm cells would be necessary to resolve this. Air leaving the sumps would be relatively straightforward to treat.

4-10 Sulfate reduction rates

Measured sulfate reduction rates were consistently below 50 $\mathrm{nmol/cm^3/day}$. These low measured rates indicate that sulfide would be generated *in situ* very slowly, at least in the surface waste pit material sampled in these studies. Low observed sulfate reduction rates are consistent with the low concentrations of reactive sulfides and acid volatile sulfides measured in the sediments and waters. These low rates are also support the low sulfide fluxes that were measured in the study.

4-11 Conclusions from Sulfide Measurements

Sulfide flux measurements were conducted on landfarm cells at both Bourg and Bateman Island, LA.US Liquids facilities. Measured fluxes at the Bourg facility varied over one several orders of magnitude from 0.02 to ~6 mg of S/m^2-hr. At Bateman Island, measured sulfide fluxes were much less variable and ranged from 0.01-0.16 mg/m^2-hr. These fluxes are comparable to the natural fluxes observed from salt marshes. Measured fluxes varied over several orders of magnitude but this was not unexpected given the variable sulfide content of E&P waste. Again, the simple impoundment model predicted the ambient sulfide air concentrations that were below 80 ppbv, which is the restrictive Texas ambient air standard. Measured air concentrations were generally less than detection (1 ppbv). The only concern with regard to sulfide was the results of a walking tour of the Bourg, LA facility with the sulfide meter. While ambient levels of sulfide were below the Texas standard of 80 ppb, air concentrations directly over a sump indicated ppmv concentrations, suggesting that the sumps are a major source of sulfide emission at these facilities.

Table 4-13

Measured sulfide fluxes at US Liquids, Bourg, LA facility

e	Sulfide Flux	
Cell	(mg/m^2/day)	g of S/m^2/year
6	143.4 (12/17/98)	52.3
10	2.71 (1/29/99)	0.99
6	0.49 (1/15/99)	0.18

Table 4-14

Measured sulfide fluxes at US Liquids Bateman Island, LA facility

	Sulfide flux	
Cell	(mg/m^2/day)	g of S/m^2/year
3/17	0.01	0.088
3/26	0.09	0.75
4/9/99	0.04	0.33
4/16/99	0.16	1.4

Table 4-15

Effect of cell age of sulfide emissions

Cell age (time after closure)	Mean Benzene Flux ($mg/m^2/day$)	Standard Deviation of Flux ($mg/m^2/day$)
Current	14.5	7.9
1 week	11.3	7.4
3 month	9.7	2.9
6 month	6.4	2.2
9 month	1.3	0.24

Table 4-16
Measured H_2S fluxes from Wetlands

	Average sulfur flux, g of S/m^2/yr	
Soils/locales	**H_2S**	**ΣS**
Saline marshes		
Aransas W.R. Tx	0.06	0.52
Cedar Island, NC (10/77)	0.02	0.029
Cedar Island, NC (5/78)	0.02	0.079
Cedar Island, NC (7/78)	0.16	1.82
Cox's Landing (11/77)	139.5	152.4
Cox's Landing (7/78)	502.9	518.3
E. Wareham, MA	-	0.65
Everglades, N.P.	74.61	75.7
Georgetown, SC	0.94	1.69
Jeanerette, LA	-	0.031
Lewes, DE	0.096	0.66
Rockefeller W.R., LA	0.09	0.12
St. Marks W.R., FL	1.31	3.80
Sanibel Island W.R., FL	601.6	650.9
Wallops Island, VA	-	4.45

Table 4-17

Predicted and Observed Sulfide Concentrations at Bourg and Bateman Island US Liquids Facilities

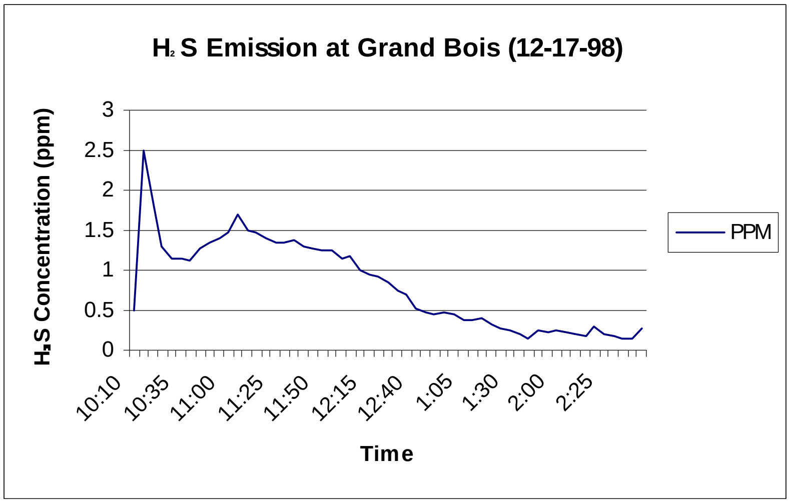
Location/Date	Observed Flux g S/m^2/year	Predicted sulfide air concentration, ppbv	Observed sulfide air concentration, ppbv
Bourg, LA 12/17/98	52.3	30.8	54
Bourg, LA 1/15/99	0.99	0.58	<1
Bourg, LA 1/29/99	0.18	0.11	<1
Bateman Island, 3/17/99	0.088	0.05	<1
Bateman Island, 3/26/99	0.75	0.44	<1
Bateman Island, 4/9/99	0.33	0.20	<1
Bateman Island, 4/16/99	1.4	0.82	<1

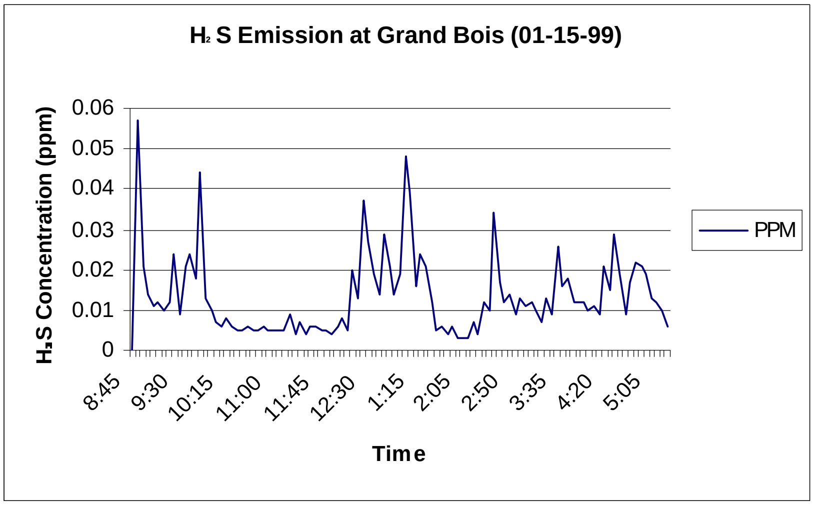
Table 4-18

Predicted sulfide air concentrations from a range of theoretical fluxes

Sulfide Flux (g/m^2-year)	Predicted air concentration, ppbv
0.02	0.012
0.05	0.029
0.1	0.059
1	0.588
10	5.88
100	58.8
150	88.2
200	117.6
500	294.1

*Texas Ambient Air Standard- 80 ppbv





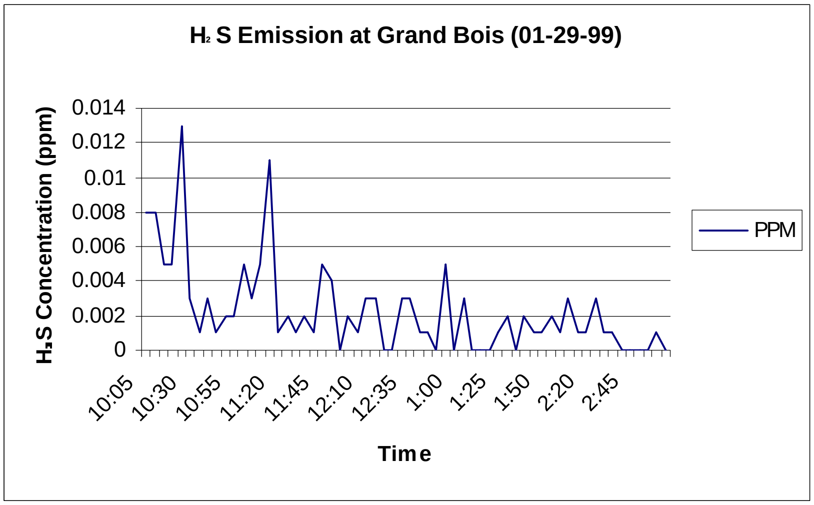
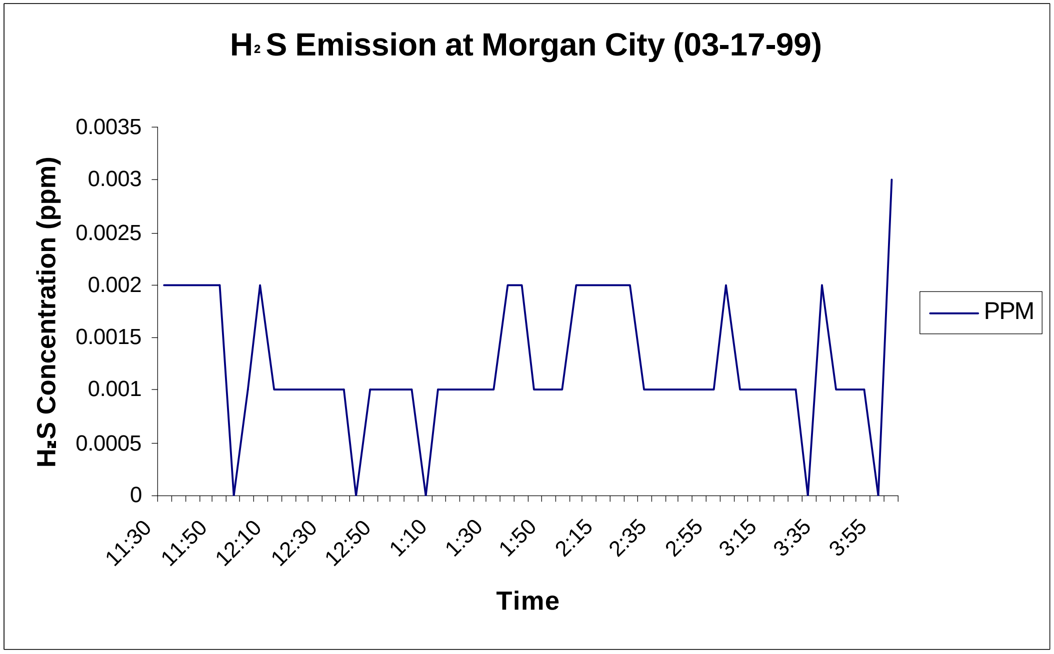


Figure 4-1. Patterns of sulfide emission at the Bourg, LA facility



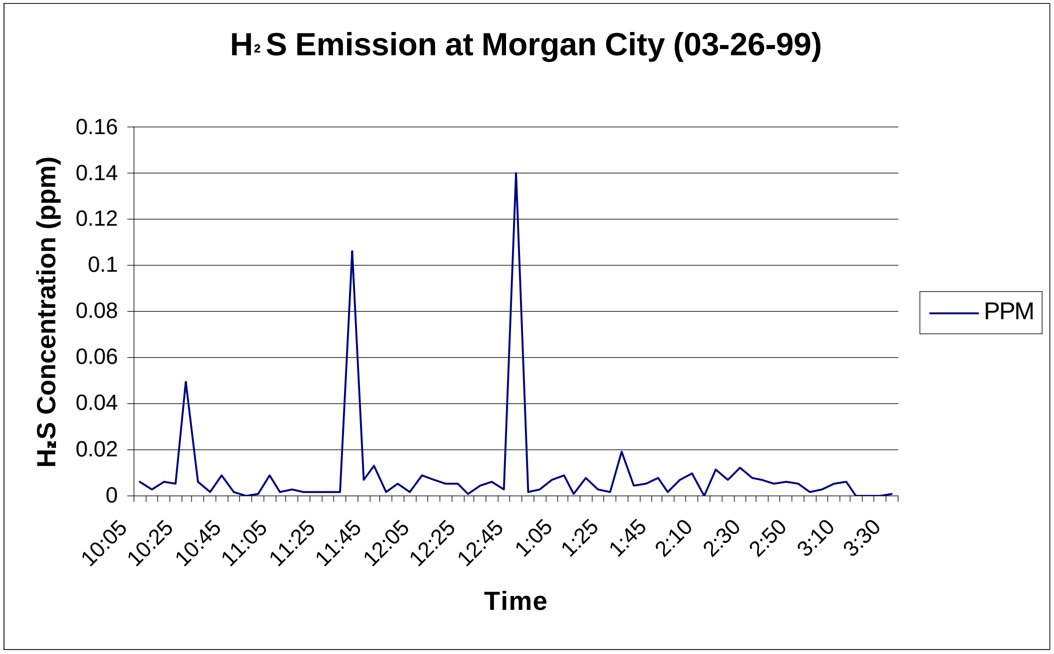


Figure 4-2 H_2S emission patterns from Bateman Island, LA facility

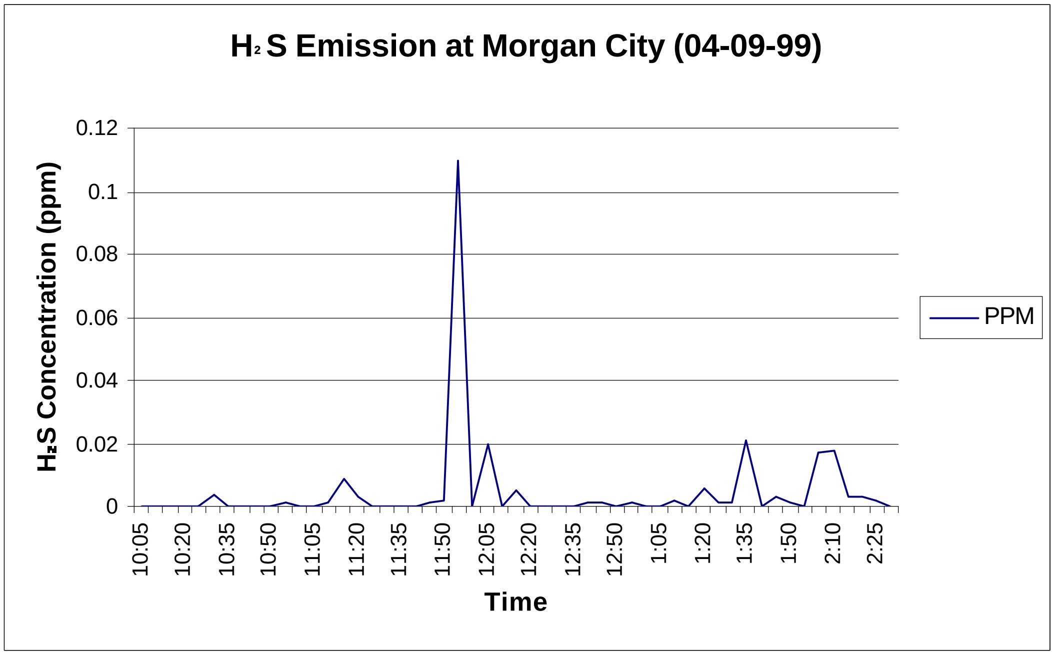


Figure 4-2 (cont.) H_2S emission patterns from Bateman Island, LA facility

5.0 Identification of site activities associated with emissions

5.1 Simultaneous air measurements of sulfide and VOCs

Coincident with this study, measurements of VOCs and sulfide were conducted by the Louisiana Department of Environmental Quality at stations just at the fenceline of the Bourg facility and at a second station within the community of Grand Bois near the Acadian Shipyard. These measurements provide an independent check on the measured and predicted concentrations observed in the present study. Since sampling for these contaminants was performed remotely, they provide a longer and more complete seasonal record of air concentrations near the landfarm cells.

The benzene, toluene, ethylbenzene and xylene data records from the sampling station at the fenceline are presented in Figures 5-1 to 5-4. In these graphs, data are presented with varying scales since the data vary over several orders of magnitude. Importantly, the graph with the smaller scale indicates that ambient air concentrations of BTEX measured by DEQ are similar to those measured by the current study (ranging from less than 1 to several ppb for benzene). These data provide some additional confirmation on the precision of our results given that the DEQ and LSU analyses were performed in separate laboratories.

In the graph with the expanded scale, data indicate that these relatively low BTEX concentrations are interspersed with spikes of higher concentrations. It can be hypothesized that these spikes are associated with some activity at the US Liquids Bourg, LA facility. Activities that might lead to these spikes would include the offloading of wastes from a closed cell, cell loading of E&P wastes or some other activity. To examine this hypothesis, logbooks from the Bourg facility were obtained and transcribed. Logbooks at the facility are used to check out and record the use of heavy equipment at the site. From the log books, various mixing, waste transfer and other related activities can be associated with approximate time intervals and locations within the facility. The complete transcribed logbooks, from June 1998-February 1999, are given in the Appendix.

Based on the benzene data in Figures 5-1, and the available logbook records, two approaches will be taken to link observed BTEX air concentrations at the Bourg facility with cell activities: 1). Identifying peak concentrations and looking for associated activities over a similar time frame and 2). Looking at large scale site activities that occurred during the period of record and observing the associated changes in the air concentrations.

During the period of record, June 1998-February 1999, five periods of elevated benzene concentrations have been identified: three periods of elevated concentrations (>2X background) and two large spikes (>10X background). Each of these periods are discussed in some detail below:

9/6/1998 (Large benzene spike)

A large spike of benzene was observed on 9/6/98 as seen in Figure 5-5. Also presented on the Figure are the activities one week prior to the spike. On 9/6/98, the benzene levels rose to 137 ppbv from a typical background level of 1-2 ppbv. On 9/6/98, the super-sucker truck was at the dock working with the “Houma oil treater” possibly offloading a load of waste or cleaning out a barge. On the several days prior to 9/6, the backhoe was at several of the cells and pumps were being used to dewater several cells. Either of these groups of activities could have resulted in the observed benzene peak.

10/30/98 (Large spike)

A large spike of benzene was observed on 10/30/98 as seen in Figure 5-6. Also presented on the Figure are the activities one week prior to the spike. On 10/30/98, the benzene levels rose to 82 ppbv from a typical background level of 1-2 ppbv. On 10/30/98, the backhoe was used at several of the cells to set-up and move pumps used to wet and dewater cells. A barge was off-loaded on 10/28/98 and the barge was cleaned the following day again using the super-sucker truck. As before, a spike in benzene concentration followed the barge offloading and cleaning. In addition, the watering/dewatering of cells was common to both of the time periods. The possibility that the barge activity or watering/dewatering is responsible for these spikes in concentration in examined further below.

8/5-8/6 1998(Small spike)

A moderate spike of benzene was observed on 8/5-8/6 1998 (Figure 5-7). Also presented on the Figure are the activities one week prior to the spike. On 8/5/98, the benzene levels rose to 11.2 ppb from a typical background level of 1-2 ppbv. On 8/6/98, the benzene levels were at 6.1 ppbv. Several activities were conducted during this period. A series of earthmoving activities with the CAT machine were conducted on the day prior to the peak including “cleaning out the road between the stockpiles, and working the levee at cell 6”. Since none of these activities involve the waste, directly, it is difficult to ascribe any of the benzene spike to these activities. On the first day of the spike, additional earthmoving activities were occurring including “cleaning out the road between the stockpiles and working a new ramp at cell 6”. In addition the “stockpile 3 was worked with the CAT 325 longarm”. Since this was the only operation that directly involved waste this may have resulted in the observed concentrations. The possibility that stockpile working was responsible for elevated benzene concentrations will be examined in more detail below.

11/20-11/21 (Small spike)

A moderate spike of benzene was observed on 11/20-11/21 (Figure 5-8). Also presented on the Figure are the activities one week prior to the spike. On 11/20/98, the benzene levels rose to 12.7 ppbv from a typical background level of 1-2 ppbv. On 11/21/98, benzene levels were at 14.2 ppbv. Examining the activities prior to the spike indicates that several activities could be responsible for the benzene peak. The pumps were run on several cells (2, 5, 6B, and 10) on the 19th and 20th presumably to wet or dewater the cells. On the 19th, the CAT.320 dock machine was used to work on cell 17. Since this is near the air monitoring station, this activity is also potentially responsible.

12/20/98 (Small spike)

A moderate spike of benzene was observed on 12/20/98 (Figure 5-9). Also presented on the Figure are the activities one week prior to the spike. On 12/20/98, the benzene levels rose to 37 ppbv from a typical background level of 1-2 ppbv. Two activities were identified that could be potentially responsible for the spike: On 12/17/98 the CAT.320 dock machine was used to “work on cell 17”. This presumably could mean mixing or reworking of cell material. On 12/19/98, pumps were again used on cells 6B and cell 18. These activities have also been identified above as potentially responsible for the benzene spikes.

Based on analysis of these spikes and the associated activities, several activities at the US Liquids facility have been identified as potentially responsible for the observed concentrations. These include the following:

a). Unloading or cleaning of barges- both large benzene spikes

b). Watering and dewatering of cells via use of pumps- small benzene spikes on 11/20/98 and 12/20/98

c). Working the stockpile- small benzene spike on 8/5/98-8/6/98

Presumably, these activities are common ones at the site and this should be reflected in the logbook record. This is investigated below. At present the link between each activity and the observed air concentration is tenuous since the record is so short. However, additional information should be obtained by doing the reverse analysis, examining the number of times each activity occurred and determining the associated air concentration.

5.2 Air concentrations associated with US Liquids activities of interest

In addition to the air concentrations associated with individual events, the activity record was examined to estimate the frequency of the events and whether spikes were common following the events. Admittedly, the record is too short to be conclusive, however, the analysis may be useful.

Uploading and cleaning of barges-

This activity was very common and was in the record in June (17th, 21-23rd,27-30th), July 9th-10th, August 2-3rd, September 2nd, 3rd, 6th, 15th, 18th, 19th, 22th), October (5th, 6th, 7th, 12th, 19th, 20-23rd, 28th). On each of these dates barges were being offloaded or cleaned at the Bourg facility. Since the frequency of the activity was much higher than the observed spikes, it is unlikely that this activity is solely responsible for the observed spikes. In particular, a flurry of activity at the dock was concentrated around September and October. As observed previously, one of the large benzene spikes (9/30/98) could have resulted from the barge activity although unloading of wastes occurred on many other weeks around the period of the spike and none was observed then.

Working the stockpile

This activity was also common in the record occurring in June (1st and 15th), July (23rd), August (5th and 12th), October (10th), January (13th, 14th, 19th, 20th, 21st, 27th), February 2nd, 4th-11th, 15th and 19th-24th). The high frequency of the stockpile activity in January and February also allows the air record to be examined for elevations during this period. None were observed.

Watering and dewatering of cells

This activity is very common, occurring on average several times per week, too frequent to list here. Since the frequency of spikes is much lower, it is impossible to ascribe the activity as the cause of the increase in air concentration.

The examination of the air record and the activity log is a useful exercise. It allows for high frequency activities such as the stockpile work that occurred during January and February of 1999 to be evaluated with respect to increases in air concentrations of target contaminants. Clearly, numerous factors contribute to the development of spikes of BTEX concentration at the fenceline. One could hypothesize that these would develop as a complex series of circumstances including the waste composition, the meteorological conditions (particularly wind speed and direction), and the activity at the site. Of course, off-site activities such as vehicle traffic and other sources of hydrocarbons may play an important role as well. Results indicate that while spikes do occur, no activity appears to be inherently responsible. For example, mixing and “working” the stockpile does not inherently cause a BTEX excursion at the fenceline.

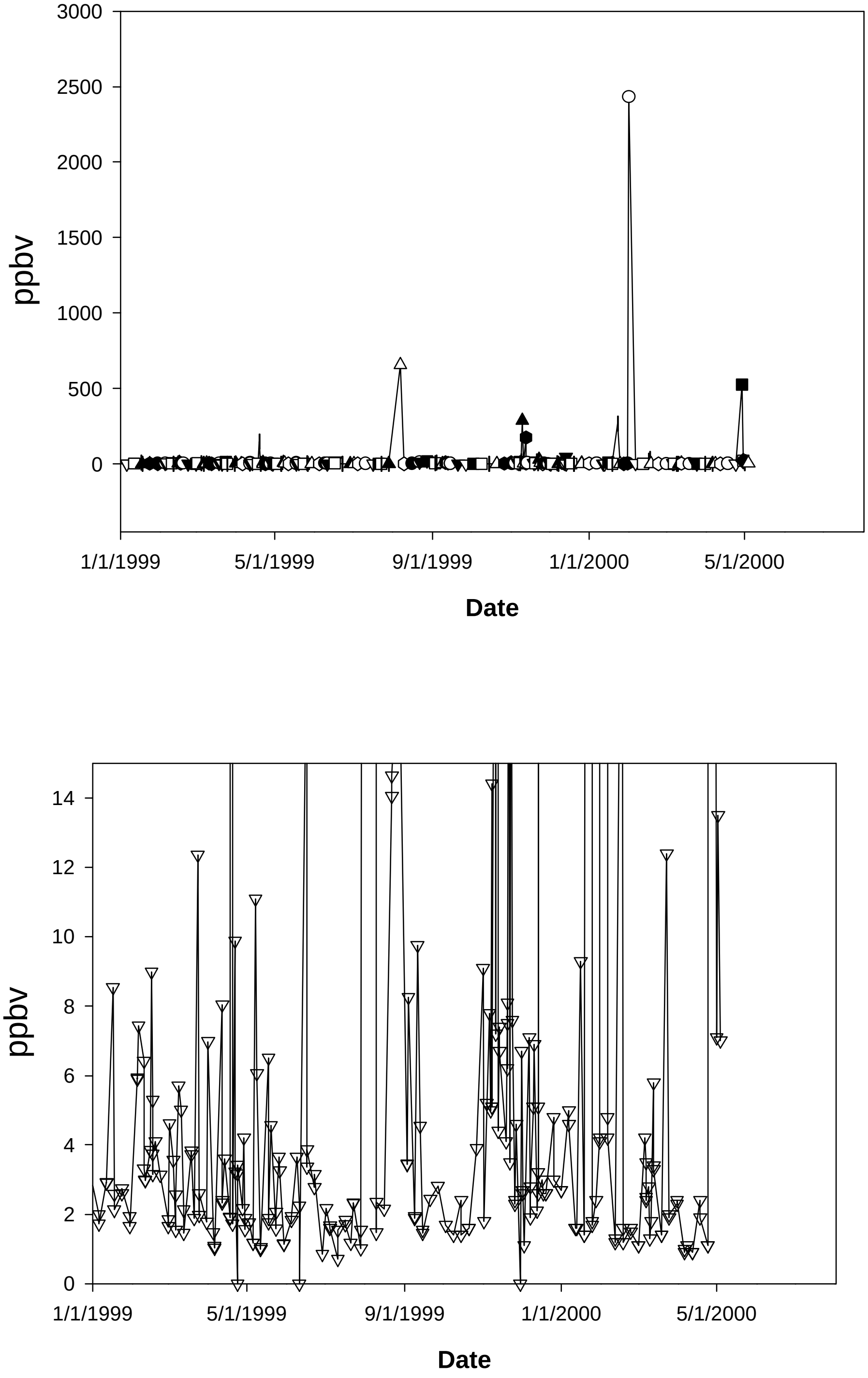
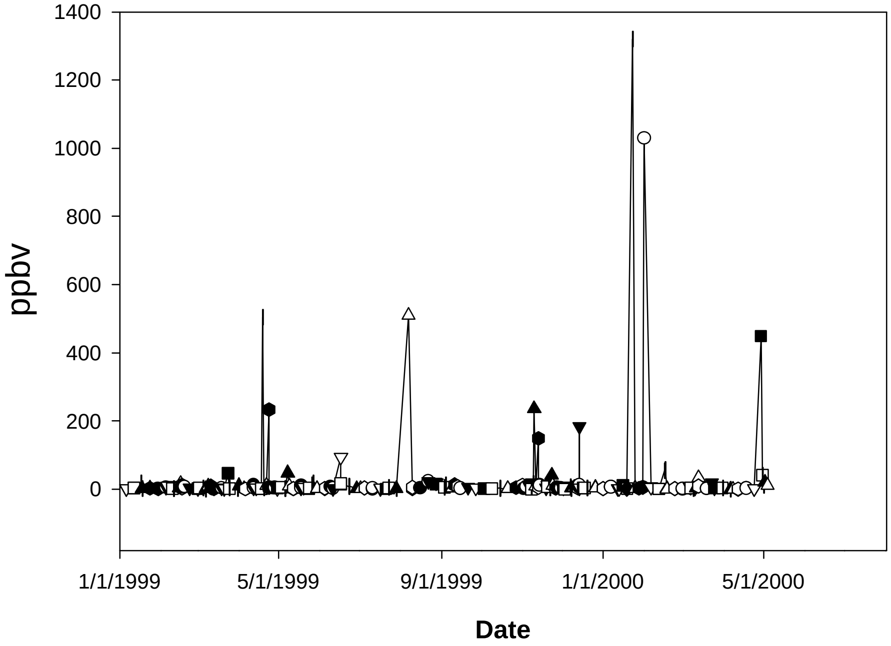


Figure 5-1. Measured benzene concentrations at the Bourg, LA US Liquids fenceline



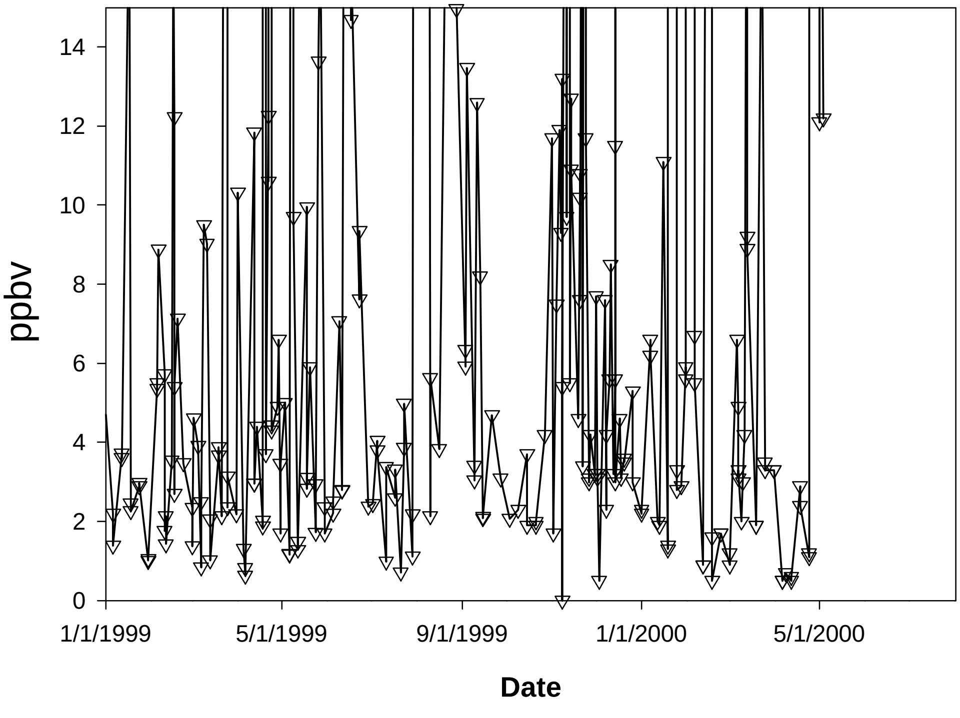


Figure 5-2. Measured toluene concentrations at the Bourg, LA US Liquids fenceline

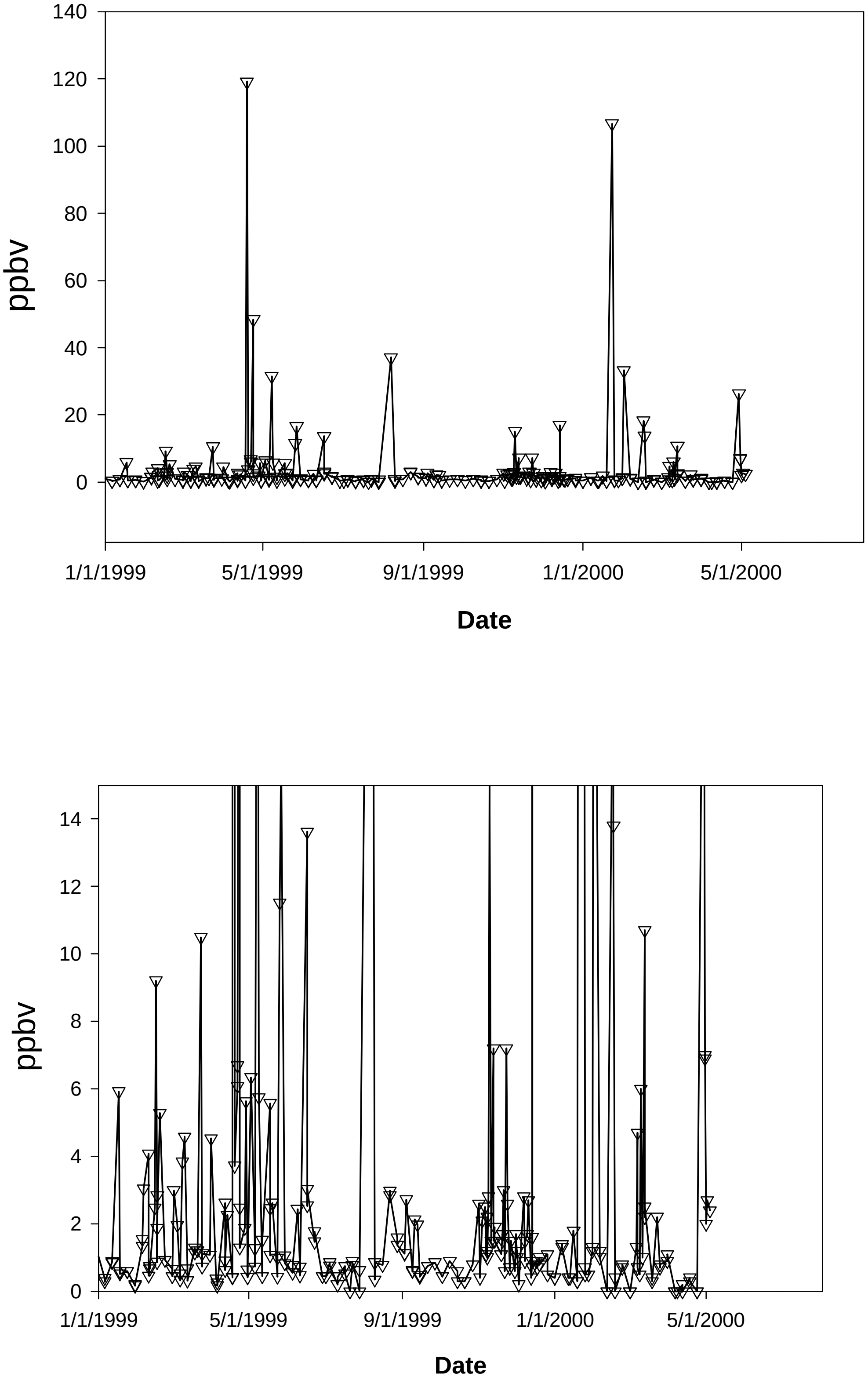
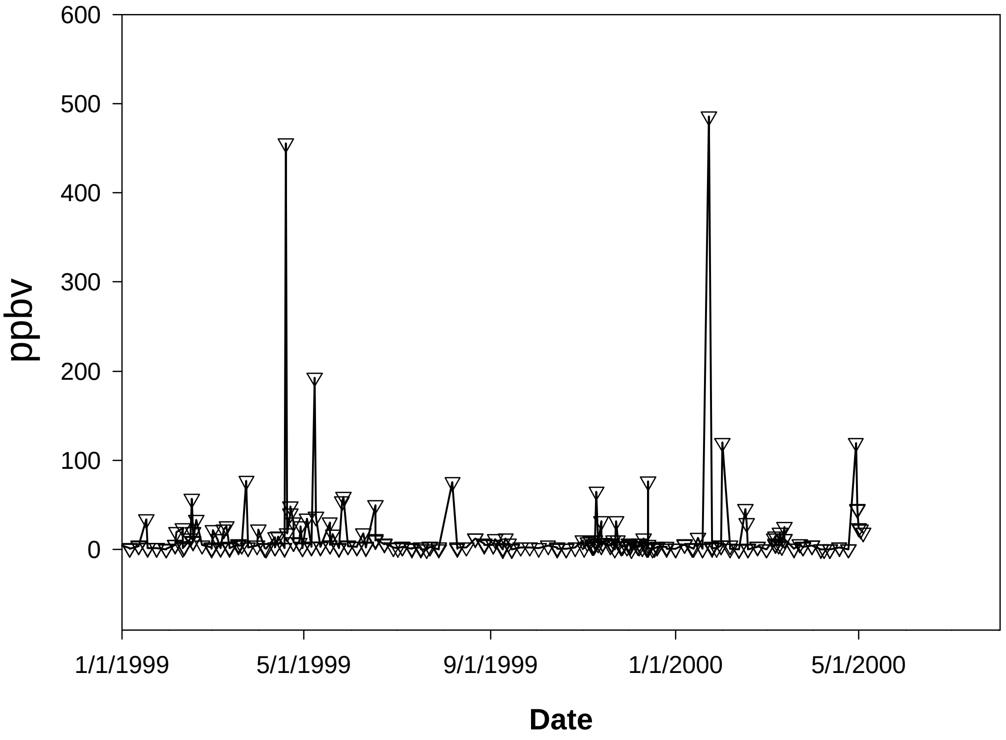


Figure 5-3. Measured ethylbenzene concentrations at the Bourg, LA US Liquids fenceline



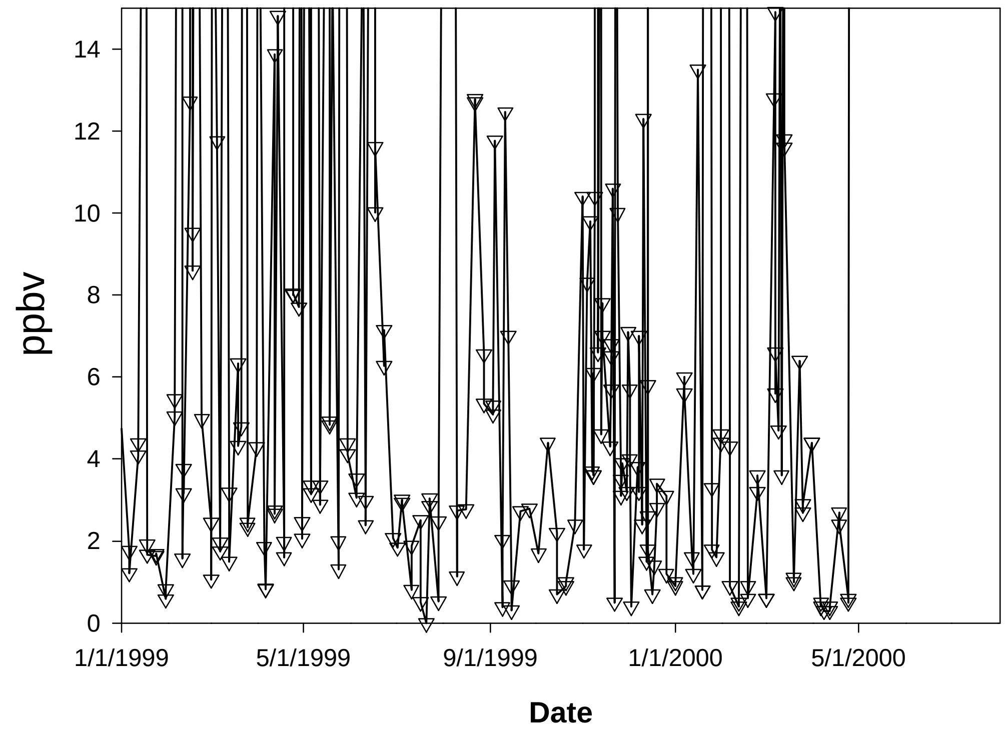
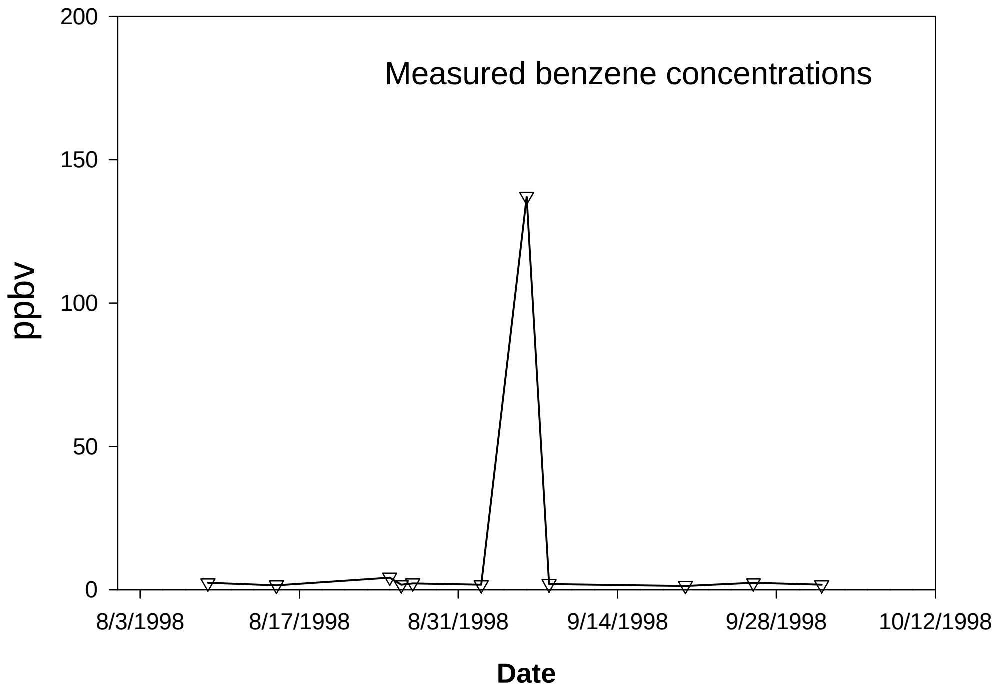


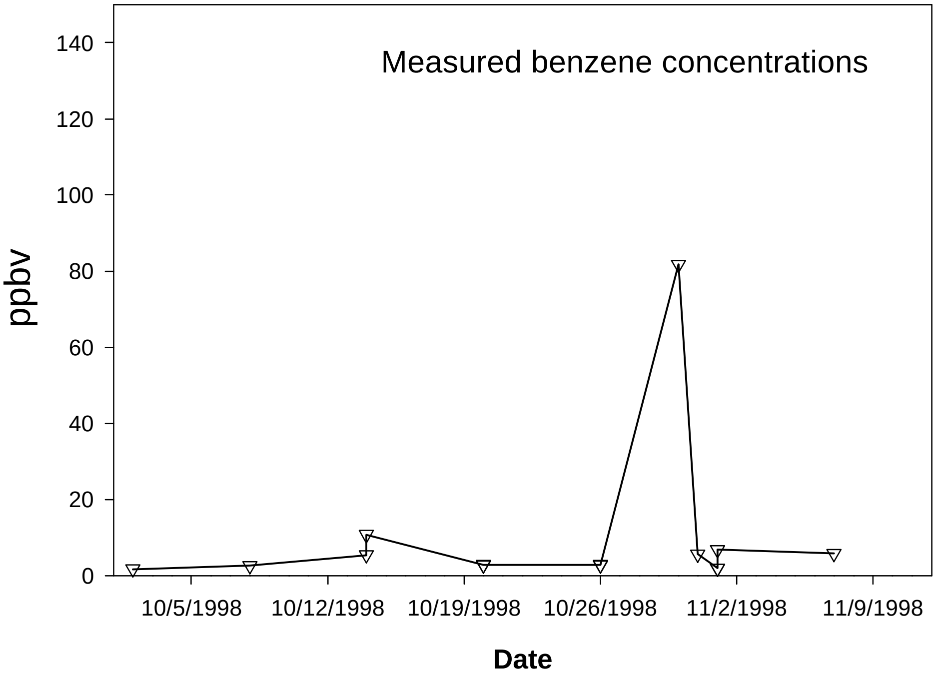
Figure 5-4. Measured xylene concentrations at the Bourg, LA US Liquids fenceline



Activities Log

02-Sep-98	L/F	N/A	0800-1030	dig drainage in yard
	002, stock pile	backhoe	1030-1200	set up pumps
	dock	N/A	1300-1800	wash barges
	wash rack	N/A	0800-1030	clean wash rack
	002, stock pile	N/A	1030-1200	set up pumps
	dock	super-sucker truck	1300-1800	wash Marshland 124
03-Sep-98	shop	Yutani, cherry picker	0600-1500	work with mechanic
	L/F, cells 5, 10	backhoe	1500-1800	set up and start pumps on 5, 10
	office, wells	N/A	1800-1945	receive trucks, change filters
	dock	N/A	0600-1200	wash barges
	dock	N/A	1300-1800	wash barges
04-Sep-98	dock, cells 5, 10, 15, 18	backhoe	0600-0930	set up pumps, close flange on 18/ open 15 and flood, dewater 5, 10
	cell 1	Yutani	0600-1200	row 1
	L/F	Yutani	1300-1800	work L/F, dock pumps
05-Sep-98	wash rack	Yutani	0600-1230	work with mechanic
	L/F	N/A	1300-1800	set up pumps, run L/F
06-Sep-98	dock	super-sucker truck	0730-1100	work with Houma oil treater
	L/F	N/A	1300-1800	set up pumps

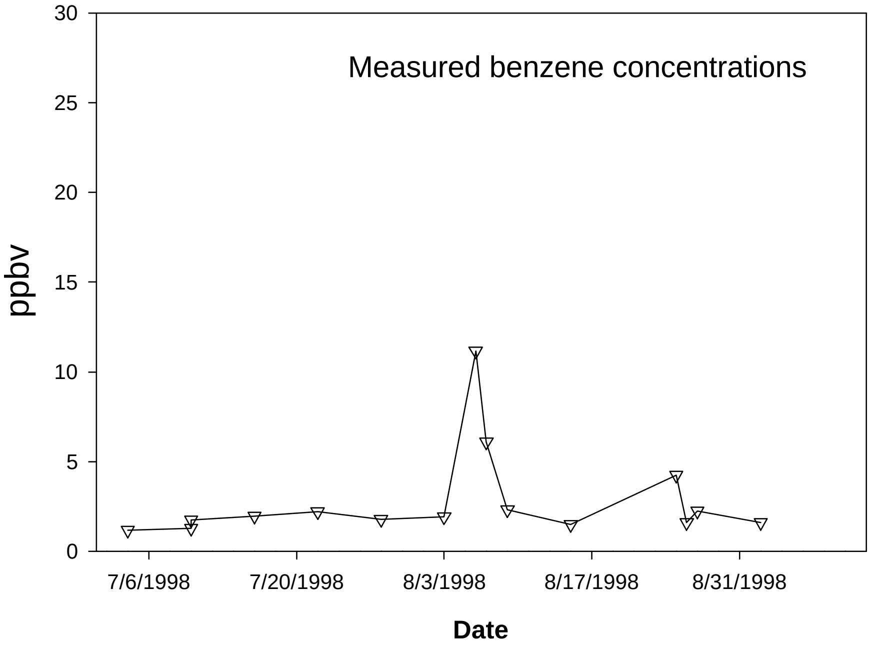
Figure 5-5. Benzene concentrations and activity log for 9/2/98 to 9/6/98



Activity Log

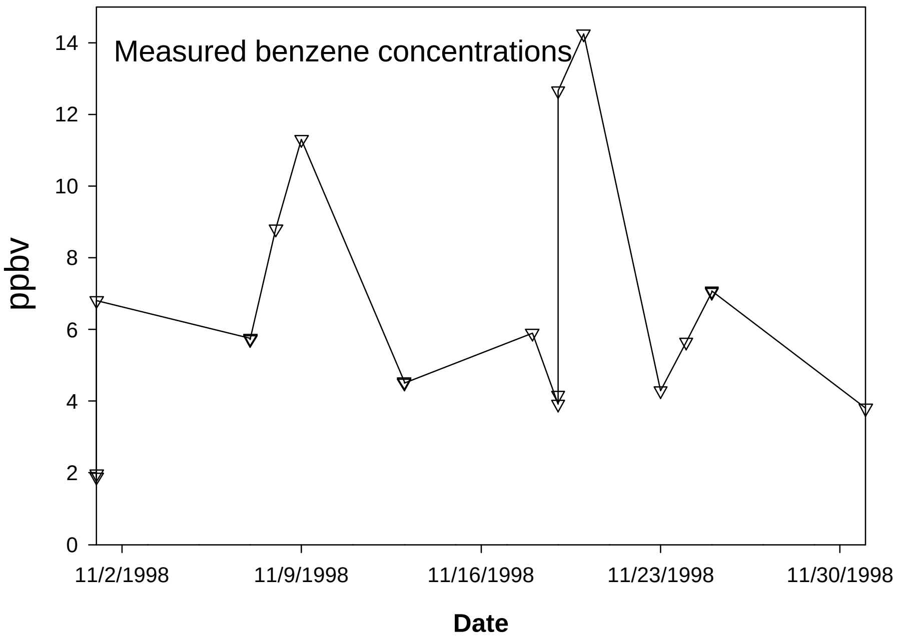
24-Oct-98	L/F, cells 6 A, 18	backhoe	0600-1200	move pumps to 6 A, 18
	L/F, cells 6 A, 14, 15 18	backhoe	1300-1800	dewater 6 A, 18, and uniditch of 14, 15
25-Oct-98	L/F, cells 6 A, 14, 15 18	backhoe	0600-1200	dewater 6 A, 18, and uniditch of 14, 15
	L/F, cells 6 A, 14, 15 18	backhoe	1300-1800	dewater 6 A, 18, and uniditch of 14, 15
26-Oct-98	shop	little red truck	0600-1200	change fuel pump, work on truck
	shop	little red truck	1300-1800	change fuel pump, work on truck
27-Oct-98	stock pile	CAT.320-dock machine	0700-1000	scrap up dirt from levee
	shop	little red truck	1000-1200	work on red truck
	shop	N/A	1200-1400	parts for red truck
	shop	little red truck	1400-1600	work on red truck
	stock pile	CAT.320-dock machine	1600-1800	load dirt for levee
28-Oct-98	dock	CAT.320-dock machine	0600-1200	off load DE 48
	dock	CAT.320-dock machine	1300-1800	off load DE 48
29-Oct-98	dock	super-sucker truck	0600-1200	wash barge DE 48
	dock	super-sucker truck	1300-1700	wash barge DE 48
	wash rack	super-sucker truck	1700-1800	wash out truck
	cell 17	Yutani	0600-1200	row 17
	cell 6	little dozer	1300-1800	work on ramp B
30-Oct-98	cells 6A, 10, 18	backhoe	0600-1200	set up and move pumps
	L/F	backhoe	1300-1800	work/clean land farm

Figure 5-6. Benzene concentrations and activity log for 10/24/98 to 10/30/98



02-Aug-98	wells	super-sucker truck	0600-0900	pump sump, clean SIAB at wells
	L/F	backhoe	0900-1200	run pumps
	office	N/A	1300-1500	receive trucks
	dock	CAT.320-dock machine	1500-1845	off load barge Marshland 131
03-Aug-98	dock	CAT.320, super-sucker	0600-1630	clean Marshland 131
	office	N/A	1630-1800	receive trucks
04-Aug-98	L/F	CAT.320-dock machine	0600-0800	service machine and cross highway
	stock pile	CAT.320-dock machine	0800-1200	clean out road between stock piles
	stock pile	CAT.320-dock machine	1300-1830	clean out road between stock piles
	cell 6	CAT.325-dock machine	0600-1200	work levee
	cell 6	CAT.325-dock machine	1300-1800	work levee
05-Aug-98	stock pile	CAT.320-dock machine	0600-1800	clean out road between stock piles
	cell 6	CAT.325-long arm	0600-1200	work new ramp
	cell 6, stock pile	CAT.325-long arm	1300-1800	work new ramp on 6, work stock pile 3
06-Aug-98	office	N/A	0600-0730	rig battery on phone
	dock	backhoe	0730-0830	work on Toyo pump
	wells	N/A	0830-0930	clean filters
	dock	backhoe	0930-1200	switch Toyo pumps
	dock	CAT.325-long arm	1300-1630	work on back dock
	wells	N/A	1630-1800	clean and change filters
09-Aug-98	cell 18	CAT.325-long arm	0630-1100	work and clean out ramp
	cell 18	CAT.320-dock machine	1300-1500	work 18, clean out ramp

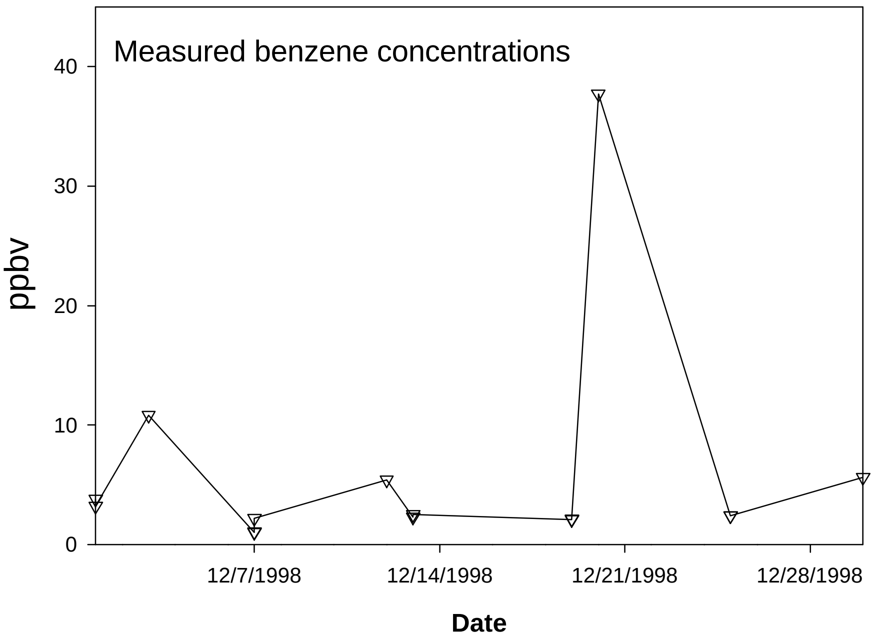
Figure 5-7. Benzene concentrations and activity log for 8/2/98 to 8/9/98



Activity Log

13-Nov-98	dock	N/A	0600-0800	wash TS 7
	dock	super-sucker truck	0600-0800	wash TS 7
	cell 10	Yutani	1300-1800	row 10
	dock	jet pump	1300-1600	work on pump
	L/F	N/A	1600-1700	make rounds for pumps
14-Nov-98	cells 2, 6	backhoe	0600-1000	move and set up pumps
	cell 6B, road	backhoe, dump truck	1000-1200	lay rock for ramp B
	cell 6, L/F	CAT.320, dump truck	1300-1800	move dirt at 6, set up pumps
15-Nov-98	wash rack	backhoe	0600-0900	dig wash rack 2
	wash rack	CAT.320-dock machine	0900-1100	dig wash rack 1
	wells, 002, cells 2, 18	N/A	1300-1800	remove water
16-Nov-98	wells	N/A	0600-1000	clean and wash filters
	wells	N/A	1300-1530	wash filters, fill up oilers
18-Nov-98	lab	N/A	0600-1200	work on rec trucks
	L/F	backhoe	1300-1400	move 3" pump from 6B to tank battery ring levee
	dock, lab	N/A	1400-1800	work on jet pump, received trucks
19-Nov-98	L/F, cells 2, 5, 6B, 10	backhoe	0600-1000	run pumps on 2, 5, 6B, 10
	lab	N/A	1000-1200	work in lab
	cell 17	CAT.320-dock machine	1300-1800	row 17
20-Nov-98	lab	N/A	0600-1200	work in lab
	L/F, 002, cells 2, 5, 6B	N/A	1300-1800	run pumps on 2, 5, 6B, 002

Figure 5-8. Benzene concentrations and activity log for 11/13/98 to 11/20/98



Activity Log

Date	Activity	Equipment	Time	Purpose
13-Dec-98	cell 17	CAT.320-dock machine	0600-1800	work on 17
14-Dec-98	cell 17	CAT.320-dock machine	0600-1200	work on 17
	wash rack	little dozer	1600-1800	wash little dozer
15-Dec-98	cell 17	little dozer, CAT.320	0600-1800	work on 17
	cell 18	Yutani	0600-1800	relay material to back
16-Dec-98	cell 17	little dozer, CAT.320	0600-1600	work on 17
	cell 18	Yutani	0730-1700	relay material to back
17-Dec-98	cell 6	CAT.320-dock machine	0700-1100	set up 6 for LSU
	cell 17	CAT.320-dock machine	1100-1500	work on 17
	cell 6	CAT.320-dock machine	1500-1600	work with LSU
	cel 17	CAT.320-dock machine	1600-1730	work on 17
19-Dec-98	L/F, cells 6B, 18	backhoe	0600-0830	fuel pumps, start 6B, 18
	wells	N/A	1000-1100	change and rinse 20 filters
	shop	dump trucks	1300-1700	work on machines
	cell 6A	CAT.325-long arm	1700-1800	relay material away from ramp
20-Dec-98	shop	N/A	0700-1930	attend classes
21-Dec-98	shop	dump trucks	0700-1000	work with welder
	wash rack	backhoe, dump truck	1000-1100	dig new wash rack
	wash rack	dump truck	1100-1400	wash out truck bed
	wash rack	backhoe	1400-1500	clean off old wash rack
	wells	N/A	1500-1600	wash filters
	dock	jet pump	1600-1700	work on pump
	office	N/A	1700-1830	receive trucks

Figure 5-9. Benzene concentrations and activity log for 12/13/98 to 12/21/98

6.0 Conclusions and recommendations

Emission flux measurements were conducted at landfarm cells containing exploration and production (E&P) wastes at the U.S. Liquids facilities in Bourg and Bateman Island, Louisiana. Flux measurements were conducted using dynamic emission flux chambers with a special design for the consistency of these wastes. Measurements were targeted at BTEX VOCs (benzene, toluene, ethylbenzene and xylene) and sulfides. The primary objectives of the study were to identify and quantify emissions of hydrocarbons and H_2S from the landfarm process at US Liquids facilities and to identify operational activities associated with these emissions. In addition, am objective was to determine whether the magnitude and extent of these emissions pose a threat to human health and the environment.

Fluxes of BTEX were measurable and ranged from 2 to 200 mg/m^2/day. The relative magnitude of the fluxes was consistent with toluene>*o*-xylene>*m*-, *p*-xylene>ethylbenzene>benzene. Flux measurements were used to predict the overlying air concentrations using a simple impoundment model using some relatively conservative assumptions for wind speed. In all cases, the impoundment model well-predicted the concentrations of benzene in the air above the cells (~1 ppb). The measurements demonstrated that while BTEX emissions were measurable from the landfarm cells, they did not produce concentrations that exceeded OSHA or Louisiana ambient air standards. Since the Bourg facility was receiving reduced volumes of E&P wastes at the time of these measurements it was decided to move the study to the Bateman Island facility, a location that was receiving more typical loadings of a commercial facility.

Fluxes ranged from a low of non-detectable for a benzene measurement to 327 mg/m^2/day for a measured toluene flux. Again the relative magnitude of the fluxes was consistent with toluene>*o*-xylene>*m*-, *p*-xylene>ethylbenzene>benzene. Although one measurement produced BTEX fluxes that were higher than the Bourg facility, the bulk of the flux measurements were of similar magnitude, indicating limited risk. There was a strong relationship between cell age and the magnitude of the flux. After the cells were closed to further waste loadings, emissions of BTEX dropped considerably. Again, the simple impoundment model was effective at predicting air concentrations of benzene, which were also around 1 ppbv.

Measured fluxes at the Bourg facility varied over one several orders of magnitude from 0.02 to ~6 mg of S/m^2-hr. At Bateman Island, measured sulfide fluxes were much less variable and ranged from 0.01-0.16 mg/m^2-hr. These fluxes are comparable to the natural fluxes observed from salt marshes. Again, the simple impoundment model predicted the ambient sulfide air concentrations that were below 80 ppbv, which is the restrictive Texas ambient air standard. The only concern with regard to sulfide was the results of a walking tour of the Bourg, LA facility with the sulfide meter. While ambient levels of sulfide were below the Texas standard of 80 ppb, air concentrations directly over a sump indicated ppmv concentrations, suggesting that the sumps are a major source of sulfide emission at these facilities.

The facility log-book at Bourg was analyzed to determine a time sequence of activities for 1998-1999. The Louisiana Department of Environmental Quality conducted a time-series of air concentrations for hazardous air pollutants during this period at the fenceline of the Bourg facility. These data were characterized by periods of static concentrations interspersed with peaks. A series of peaks were analyzed and compared with logbook records for the activities occurring at the time. In reverse fashion, a set of activities documented by the logbook was examined and the concentrations of benzene that developed from these activities were documented. No direct correlation could be made with the observed peaks and any activities suggesting that concentrations of benzene at the fenceline may be the result of a complex suite of activities including onsite activities not documented in the logbook (loading of the cells by truck haulers) and offsite activities (automobile traffic).

Based on these results several recommendations can be made.

1. At a minimum, maintain loading of wastes at rates observed during the study period. These loading rates did not produce fluxes of concern.

2. Further evaluate sulfide emissions from the sump system. This is the only source of sulfides detected at the facility and the control of sulfide emissions from these point sources is straightforward.

3. A scientifically based cell management approach that would maintain benzene levels below levels of concern is possible based on the simple emission models calibrated during this study. An approach that manages the cells based on benzene concentrations of waste loads is straightforward based on the study results but would require significantly more effort to implement. However, measured emission rates and long-term records of air concentrations near the facilities suggest that this is not necessary at present.

In conclusion, fluxes of BTEX and sulfide were measurable at the US Liquids facilities and were predictable from simple impoundment models and more complex mass transfer models. These measurements provide a scientific basis for establishing a “loading factor” procedure for managing these facilities based on the expected benzene concentration of each waste type. However, existing loading of wastes at the Bourg and Bateman Island facility did not produce fluxes of BTEX and sulfide of concern. This gives several regulatory options for reducing the risk of the emissions of these waste components.

7.0 References

Adams, D.F., S.O. Farwell, E. Robinson, M.R. Pack, and W.L. Bamesberger. 1981. Biogenic sulfur source strengths. *Environ. Sci. Technol*. 15:1493-1498.

Adams, D.F., S.O. Farwell, M.R. Pack and E. Robinson. 1981. Biogenic sulfur gas emission from soils in Eastern and Southeastern U.S. J. Air Pollut. Control Assoc. 31:1083-1089.

Berresheim, H. 1993. Distribution of atmospheric sulfur species over various wetland regions in the southeastern U.S.A. *Atmos. Environment* 27:211-221

Carroll, M.A., L.E. Heidt, R.J. Cicerone and R.G. Prinn. 1986. OCS, H_2S and CS_2 fluxes from a salt water marsh*. J. Atm. Chem*. 4:375-395.

Castro, M.S. and F.E. Dierberg. 1987. Biogenic sulfide emissions from selected Florida wetlands. *Water, Air and Soil Pollut*. 33:1-13.

Cooper, D.J., W.Z. Demello, W.J. Cooper, R.G. Zika, E.S. Saltzman, J.M. Prospero, and D.L. Savoie. 1987. Short-term variability in biogenic sulfur emission from a Florida Spartina alterniflora marsh. *Atmos. Environ*. 21:7-12.

Cooper, D.J., W.J. Cooper, W.Z. Demello, , E.S. Saltzman and R.G. Zika.. 1987. Variability in biogenic sulfide emissions from Florida wetlands. In, Biogenic sulfur in the Environment (Edited by E.S. Salzman and W.J. Cooper) pp:31-43. American Chemical Society, Washington, D.C.

Dacey, J.W.H., G.M. King, and S.G. Wakeman. 1987. Factors controlling emission of dimethylsulfide from salt marshes. Nature 330:643.

DeMello, W.Z., D.J. Cooper, W.J. Cooper, E.S. Salzman, R.G. Zika, D.L. Savoie, and J.M. Prospero. 1987. Spatial and diel variability in the emissions of some biogenic sulfur compounds from a Florida *Spartina alterniflora* coastal zone. *Atmos. Environ*. 21:987-990.

Denmead, O.T., M.R. Raupach. 1993. In, *Agricultural Ecosystem Effects on Trace Gases and Global Climate Change*, Special Publication No. 55; Soil Science Society of America, Madison, WI, pp. 19-43.

Gao, F., S.R. Yates, M.V. Yates, J. Gan, and F.F. Ernst. 1997. Design, fabrication, and application of a dynamic chamber for measuring gas emissions from soil. *Environ. Sci. Technol.* 31:148-153.

Giblin, A.E. and R.K. Wieder. 1992. Sulphur cycling in marine and freshwater wetlands. In *Sulphur Cycling on the Continents: Wetlands, Terrestrial Ecosystems and Associated*

Water Bodies. (Edited by R.W. Howarth, J.W.B. Stewart, and M.V. Ivanov) pp: 85-117. John Wiley, New York.

Goldberg, A.B., P.J. Maroulis, L.A. Wilner, and A. Bandy. 1981. Study of H_2S emission from a salt water marsh *Atmos. Environ* 15:11-18.

Hansen, M.H., K. Ingvorsen, and B.B. Jørgensen. 1978. Mechanisms of hydrogen sulfide release from coastal marine sediments to the atmosphere. *Limnol. Oceanogr*. 23:68-76.

Jørgensen, B.B. and B. Okholm-Hansen, B. 1985. Emissions of biogenic sulfur gases from a Danish estuary. *Atmospheric Environment* 19:1737-1749.

Kanda, K., Tsuruta, H. and K. Minami. 1992. Emission of dimethyl sulfide, carbonyl sulfide, and carbon disulfide from paddy fields. *Soil Sci. Plant Nut.* 38:709-716.

Majewski, M.S., Glotfelty, D.E., U, K.T.P; Seiber, J.N. 1990. *Environmental Science & Technol*. 24:1490-1497.

Morrison, M.C. and M.E. Hines. 1990. The variability of biogenic sulfide flux from a temperate salt marsh on short time and space scales. *Atmos. Environment* 24:1771-1779.

Rolston, D.F. 1986. In, *Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods*, 2nd edition; Klute, A., ed., American Society of Agronomy: Madison, WI, pp. 1103-1119.

Steudler, P.A. and B.J. Peterson. 1984. Contribution of gaseous sulfur from salt marshes to the global sulfur cycle. *Nature* 311:455-457.

Steudler, P.A. and B.J. Peterson. 1985. Annual cycle of gaseous sulfur emissions from a New England *Spartina alterniflora* marsh. *Atmos. Environ.* 19:1411-1416.

Tarver, G.A. and P.K. Dasgupta. 1997. Oil field hydrogen sulfide in Texas: emission estimates and fate. *Environ. Sci. Technol*. 31:3669-3676.

Wesley, M.L., Lenschow, D.H., Denmead, O.T. 1989. In, *Global Tropospheric Chemistry: Chemical Fluxes in the Global Atmosphere*; Lenschow, D.H., Jicks, B.B. (ed.), National Center for Atmospheric Research: Boulder, CO, pp. 31-46.