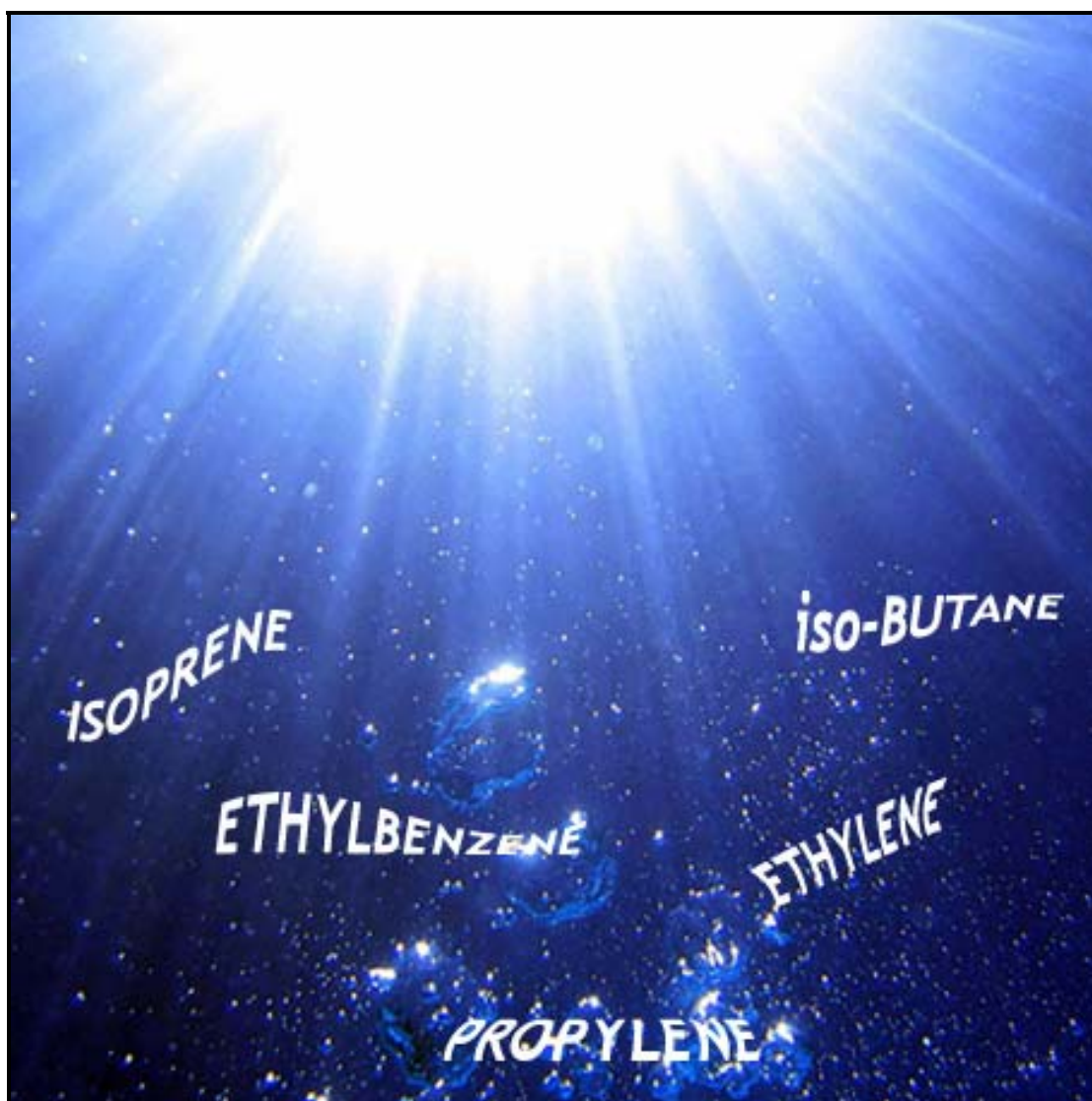


Coastal Marine Institute

Determination of Net Flux of Reactive Volatile Organic Compounds at the Air-Water Interface in the Gulf of Mexico



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ABOUT THE COVER

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ABSTRACT

The downwind transport of primary pollutants leading to excessive secondary pollutant production has been gaining acceptance since the early 1990's work of the Southern Oxidant Study (<http://www.ncsu.edu/sos/pubs.html>). Initial Southern Oxidant Study research suggested that transport of ozone and ozone precursors could have significant negative impacts on ozone and haze in downwind urban areas. Hence, the possibility that air quality problems in coastal urban centers, namely Texas and Louisiana, derive to some extent from downwind transport of natural volatile organic compounds (VOCs) and, in particular, the reactive volatile organic compounds (RVOCs) emitted in the gulf must be considered. Thus, the transfer of reactive volatile organic compounds from the sea surface to the atmosphere in the Northern GOM region may represent an environmentally significant source with respect to air quality problems in urbanized areas on the Gulf Coast.

Currently, the impact of natural RVOC emissions on the Gulf Coast environment, especially in comparison with production related emissions, remains an open question. Because the emission areas are large and the emission time frame is long, it is critical to have a reasonably accurate characterization of specific RVOCs from natural emissions and the material flux from the sea surface to the atmosphere in order to estimate the effect these sources have on nearby (or not so nearby) land areas. Estimates based on generalized emission factors are useful starting points, but the use of unvalidated factors can lead to large, unknown errors in actual environmental impact. The specific contribution of RVOCs to ozone formation potential depends not only on the amount of RVOCs in the air mass but also on the specific RVOCs present due to the fact that photochemical activity for individual RVOCs varies widely. Thus, a speciated characterization of RVOC flux, including identification of RVOCs is necessary for creating an accurate estimate of the expected impact of natural GOM emissions on coastal urban centers.

This study directly examined analytical methodology that can be used to study the net flux of reactive volatile organic compounds (RVOC) from the sea surface to the atmosphere in the Gulf of Mexico in order to provide a better understanding of factors specific to the Gulf of Mexico region that affect the RVOC load from non-production sources. This project also provides quantitative information that will allow more accurate estimates of RVOC load contributed by natural processes. The goal of the project is to provide technology for estimating the specific net flux data in terms of composition and quantity for selected exemplar areas that can then be used to estimate flux for a more encompassing area of the GOM. Two area types were examined: (1) areas near-shore to the GOM with optimum wind conditions (e.g. winds out of the south, southeast, or southwest); and, (2) one offshore transect in the Green Canyon, GOM.

Air sampling and analysis procedures were developed and validated for two different analytical instrument systems, the microFAST GC and a lab based gas chromatograph-time-of-flight mass spectrometer system using thermal desorption tube samples. Four field validation sampling trips were made to near-shore locations, and to one deep sea location in the Green Canyon area of the Northern GOM. The goal of the field validation trips was to establish sampling and analysis methodologies that could identify individual RVOCs in a large number of air samples and in water samples. The OCS RVOC data could then be used to establish whether or not RVOCs emitted from natural sources in the GOM represents potential air quality problems if transported

to an environment containing high levels of NO_x (e.g. a nearby urban environment), an active ingredient necessary in the formation of atmospheric ozone.

The OCS RVOC information from water and air samples can also be used to infer sea-air flux of RVOCs from the Green Canyon area (a well known natural seep) of the Northern GOM. In the very limited data set from this study, atmospheric RVOC concentrations may not be explained only by the flux from naturally-occurring biogenic sources (e.g. marine organisms, algae, and oil seeps) within the seawaters of sampled area in the northern Gulf of Mexico. Therefore, the concentrations of RVOCs in the marine atmosphere may be affected by anthropogenic sources (e.g. marine transport) and subsequent long-range transport of RVOC compounds.

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1.0 INTRODUCTION

The downwind transport of primary pollutants leading to excessive secondary pollutant production has been gaining acceptance since the early 1990's work of the Southern Oxidant Study (SOS) (<http://www.ncsu.edu/sos/pubs.html>; Chameides and Cowling 1995). Initial SOS research suggested that transport of ozone and ozone precursors could have significant negative impacts on ozone and haze in downwind urban areas. Hence, the possibility that air quality problems in coastal urban centers, namely Texas and Louisiana, derive to some extent from downwind transport of natural volatile organic compounds (VOCs) and, in particular, the reactive volatile organic compounds (RVOCs) emitted in the gulf must be considered. The quantitation and characterization of RVOC emissions in the Gulf of Mexico (GOM) is an item of interest to Bureau of Ocean Energy Management, Regulation and Enforcement (BOEMRE) because BOEMRE is responsible for air quality management of potential ozone formation issues in the GOM that may affect adjacent urban areas. Therefore, information regarding the ozone formation potential contributed by the GOM is important for understanding and managing haze and ozone formation in the areas under BOEMRE responsibility and for use by planning agencies in downwind areas as well.

The most visible potential sources of ozone formation precursor compounds in the Gulf of Mexico are production and transportation related. These emissions are being assessed with programs such as the Gulf Wide Emissions Inventory. In contrast, natural sources like natural oil seeps are easily overlooked. Some of the largest and best known natural seeps of petroleum and natural gas are found in the GOM, as well as, off the coast of Southern California. Currently, the impact on the Gulf Coast environment of these natural related emissions, especially in comparison with production related emissions, remains an open question. A number of natural factors (e.g. insolation, algae/plankton density, biological productivity, sea state, oil and gas seeps) may contribute to sea-air RVOC emissions. However, the precise correlation of these features with respect to RVOC emissions is less clear. It is important to eventually obtain rates and composition of RVOC emissions from these identifiable features in order to fully estimate future impacts of natural sources on ambient air quality.

Offshore RVOCs can be produced from petroleum as well as biogenic activity. The most important RVOC compounds from petroleum are the alkyl benzene homologs with 1 to 3 alkyl groups on the benzene ring. These compounds generally have atmospheric lifetimes measured in hours, where as the saturated hydrocarbons from petroleum have lifetimes measured in days. Biogenic hydrocarbons, include the C₂ to C₆ olefins and isoprene (2-methyl-1, 3-butadiene), have atmospheric lifetimes measured in hours. Accordingly, RVOC compounds with significant tropospheric ozone formation potential in off-shore areas of the Gulf of Mexico include the alkyl benzenes from petroleum and the biogenic olefins and isoprene.

Natural sources of ozone precursors never come into port, nor do they have visible man-made structures associated with them. RVOCs associated with natural sources may be emitted over very large areas so even a relatively small flux of material can represent a considerable atmospheric load. Natural sources such as seeps also continue to emit material more or less continually 7 days a week, 365 days a year. As a result, the transfer of RVOCs from the sea surface to the atmosphere in the Northern GOM region may represent an environmentally significant source with respect to air quality problems in urbanized areas on the Gulf Coast. In

order to estimate the effect of these sources on nearby (or not so nearby) land areas, it is important to have a reasonably accurate characterization (qualitative and quantitative) of the material flux from the sea surface to the atmosphere.

The total surface area of the Gulf of Mexico is 1.5 million km². Even a restricted area of interest encompassing only the Northern Gulf easily concerns over 100,000 km² of water surface. Using emission factors based on coastal California oil seeps, a 15,000 km² area of the Northern GOM was estimated to be the source of, on the order of 6,300 tons per year of VOC (Marse and Tsofilas 2001). Globally, natural non-methane hydrocarbon (NMHC) emissions from the sea surface have been estimated at $2 - 50 \times 10^{15}$ g/year (Shaw et al. 2003). This global total, however, obscures variations between locations and some areas will have higher emission levels than others. The GOM, having a high concentration of natural hydrocarbon seeps and high biological productivity, would likely be on the upper end of the emissions curve. Estimates based on generalized emission factors are useful starting points, but the use of unvalidated factors can lead to large, unknown errors in actual environmental impact. Additionally, estimates to date have been generally for total RVOCs. Any estimates of RVOC emissions from GOM waters based on currently available RVOC flux data would be suspect because of uncertainties in the ultimate sources of a large fraction of the total RVOC load and the absence of GOM specific flux information. RVOC emission rates specific to the GOM would greatly improve the accuracy and reliability of air impact estimates for natural reactive volatile organics.

The specific contribution of VOCs to ozone formation depends not only on the amount of VOCs in the air mass but also on the specific compounds present because the photochemical activity for individual VOCs varies widely. Emissions from the sea surface of biogenic RVOCs, such as isoprene and ethene, have been demonstrated by Fall et al. (2001). Reasonable extrapolation of the literature results suggests that isoprene emissions alone could be as high as 100 kg/hour during daylight hours over the GOM region. Further, isoprene emissions may be only a fraction of the total reactive hydrocarbons introduced to the atmosphere by natural processes. Ethene and propene have been identified as principle RVOC species in seawater both at the surface and at depth (Bonsang 2000). As much as 40% of total NMHC (C₂-C₅) may be comprised of ethene (Plass-Duelmer et al. 1995). Studies of alkane and alkene emissions from the sea surface have not been convincingly correlated with insolation or chlorophyll content, suggesting photosynthetic or photochemical processes are not primary factors determining the concentration of alkanes and alkenes in seawater. Previous work on light hydrocarbons in near surface soil gas (Carney et al. 1996; Jones and Burtell 1996; Jones et al. 2000; Molecke et al. 1996) also showed the predominance of ethane and ethene in microseeps above oil and gas reservoirs. Given these results and the uncertainty with respect to the source of ethane and ethene at the sea-air interface, it is plausible that a significant fraction of ethane/ethene transported from the sea to the atmosphere may ultimately be derived from deep-sea hydrocarbon seeps as well as biogenic metabolism of dissolved organic matter (DOM).

Hydrocarbon seeps (macroseeps) on the sea floor in the Gulf of Mexico represent a significant potential source of atmospheric RVOCs as the seep material rises to the sea surface and volatilizes. Of these geogenic RVOCs, a significant number (the alkyl benzenes) are highly reactive in the context of atmospheric photochemistry and may contribute significantly to ozone formation. These compounds may reach the surface in three ways. First, they may rise to the

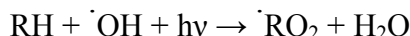
surface in gas bubbles. Methane is released in many seeps and as the methane gas rises to the surface, the bubbles may include not only ethane and other “gaseous” constituents, but also volatilized heavier RVOCs. Second, the volatile compounds may be dissolved in the liquid phase oil from the seeps as it rises to the surface. The concentrations of these dissolved volatile compounds, primarily ethylene, are usually supersaturated compared to air concentrations (Bonsang et al. 1988). Finally, the compounds may be dissolved in the water column. Many of the most photochemically reactive compounds are also among the most water-soluble constituents of the oil. Some anthropogenic RVOCs can be transported from coastal areas after dissolution in water columns via ocean currents (Nutmagul and Cronn 1985). Volatilization of dissolved anthropogenic RVOCs over open waters has been suggested by Greenberg and Zimmerman (1984) to be a significant source of these compounds in the atmosphere. All of these mechanisms are likely to be occurring simultaneously as the oil/gas mixture works its way to the water surface.

The partitioning of RVOCs among three phases (i.e. water, oil, and gas) will change as pressure and temperature changes with depth. Each mechanism will have its own characteristics with respect to transferring RVOCs to the atmosphere. Compounds entrained in gas bubbles will be very effectively transferred to the atmosphere. The rate of transport from depth will be relatively rapid and vertical, and, as the bubble erupts at the water surface, the RVOCs will be almost completely released to the atmosphere. Compounds dissolved in the liquid oil will not rise so quickly and at the surface they will more slowly volatilize from the resulting oil slick. Finally, the constituents that dissolve in water may take very long times to reach the surface as the principle transport mode to the surface for dissolved organics will be upwelling and diffusion. A substantial fraction of the dissolved components may never reach the surface, being biodegraded or otherwise removed from the water column before reaching the surface. The result of these various transport mechanisms is that a natural seep at the sea floor can be expected to produce multiple VOC emission microenvironments. The gas and liquid oil transport will produce the expected oil slick with possible gas bubbles erupting somewhere in the vicinity. VOCs dissolved in the water as the oil approaches the surface will produce a “halo” region around the oil slick exhibiting high volatilization rates of VOCs relative to background areas. Dissolved VOCs may only appear at areas of upwelling, far removed from both the actual seep location and its visible surface manifestation.

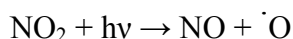
The ozone formation potential associated with natural RVOC emissions in the GOM is NO_x limited. RVOCs emitted from the sea surface typically are not directly photolyzed by solar radiation in the lower troposphere and usually NO_x levels in remote marine environments are lower than their urban counterparts and more than likely will not lead to significant tropospheric ozone creation (Greenberg and Zimmerman 1984). However, all combustion activities offshore produce NO_x . Therefore, production, exploration and transportation activities along the Northern Gulf region can be considered as sources of NO_x that will eventually affect RVOC concentrations downwind. The RVOCs emitted represent a potential to form low-level ozone that is fully realized when they are transported to an environment containing higher levels of NO_x , such as an urban environment with industrial and automotive combustion sources.

NO_x and RVOCs are two primary precursors in the formation of low level ozone (Dawson et al. 2007; Manahan 1994; Sillman 1999). Nitrogen oxides in the atmosphere participate in the

formation of ozone through a series of complex reactions that often involve RVOCs. This reaction sequence, simplified in the following reactions, is initiated by the presence of reactive hydrocarbons and hydroxyl radical formed from the reaction of atmospheric water and sunlight.



This reaction is then followed by the reaction of RO_2 with NO. NO is a product of the reaction of NO_2 and sunlight energy.



The formation of tropospheric ozone occurs through the reaction of atomic oxygen created during the photolysis of NO_2 and molecular oxygen present in the atmosphere. M in the following equation is an energy-absorbing third body and can be particles, trace gases, or even surfaces. M is the heat sink for the heat generated in production of ozone.




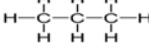
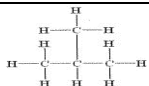
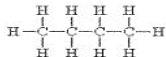
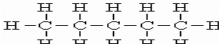
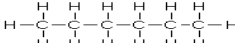

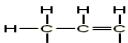


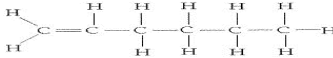
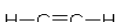
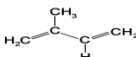



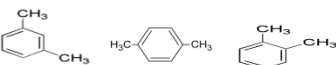
Furthermore, when RVOCs like propane, propylene butenes, and pentenes are oxidized in the presence of NO_x peroxyacetyl nitrate (PAN) is formed. PAN is a secondary air pollutant and a major cause of photochemical smog (Whalley et al. 2004). A simplified equation for this reaction would be:



PAN can then decompose to form peroxyacetyl radical and NO_2 which can subsequently form ozone (Dawson et al. 2007; Manahan 1994) and the reaction cycle can repeat.

The principal factor of interest with respect to air quality is the ozone formation potential that marine RVOC emissions represent. The photochemical reactivity of the various RVOCs that one may find in the marine air varies considerably. With respect to geogenic sources, some components (e.g. saturated hydrocarbons) may produce only a minimal effect, unless present in large amounts. Others, (e.g. alkyl benzenes and low molecular weight olefins) may result in significant additional ozone formation potential at very low concentrations. Consequently, the ultimate impact on nearby urban areas is a function of not only the quantity of RVOCs emitted into the atmosphere, but also by their composition. It is anticipated that highly reactive analytes of interest will include the various alkyl benzenes especially toluene, xylenes and trimethylbenzenes. The saturated volatile components of crude oil will be of some interest because they may be present in high concentrations. Further, one would expect to find olefins such as ethylene, propylene, isoprene and possibly the butene and pentene isomers. A list of RVOCs of interest is given in Table 1 along with RVOC formulae, structure, and possible sources (anthropogenic, biogenic, or petrogenic).

Table 1
RVOC Analytes of Interest List

<u>Alkanes:</u>	<u>Formula:</u>	<u>Structure:</u>	<u>Possible Sources:</u>
Ethane	C ₂ H ₆		Petrogenic; Anthropogenic
Propane	C ₃ H ₈		Petrogenic; Anthropogenic
iso-Butane	iC ₄ H ₁₀		Petrogenic
n-Butane	C ₄ H ₁₀		Petrogenic; Anthropogenic
n-Pentane	C ₅ H ₁₂		Petrogenic; Anthropogenic
n-Hexane	C ₆ H ₁₄		Petrogenic
<u>Alkenes:</u>	<u>Formula:</u>	<u>Structure:</u>	<u>Source:</u>
Ethylene	C ₂ H ₄		Biogenic
Propylene	C ₃ H ₆		Biogenic
1-Butene	C ₄ H ₈		Biogenic
1-Pentene	C ₅ H ₁₀		Biogenic
1-Hexene	C ₆ H ₁₂		Biogenic
<u>Other:</u>	<u>Formula:</u>	<u>Structure:</u>	<u>Source:</u>
Acetylene	C ₂ H ₂		Anthropogenic
Isoprene	C ₅ H ₈		Biogenic
Benzene	C ₆ H ₆		Petrogenic; Anthropogenic
Toluene	C ₆ H ₅ CH ₃		Petrogenic; Anthropogenic
Ethylbenzene	C ₈ H ₁₀		Petrogenic; Anthropogenic
Xylenes (m, o, p)	C ₆ H ₄ C ₂ H ₆		Petrogenic; Anthropogenic

1.1 RESEARCH OBJECTIVES

This project is designed to be a pilot study of a methodology that may yield better estimates of geogenic and biogenic sources of RVOCs to the atmosphere. The project involves lab studies for the development of RVOC sampling and analysis methods, and field evaluation of the lab generated methodologies. Additional objectives of this project are to preliminarily examine the concentration of RVOCs at the sea surface-atmosphere interface in the Northern Gulf of Mexico, and, to provide a quantitative methodology for more accurate estimates of RVOC loads contributed by natural sources and/or processes. The objectives are based on providing a better understanding of factors specific to the GOM region that affect the RVOC load from non-production sources.

1.2 RELEVANCE

This project complements ongoing BOEMRE programs to inventory emissions related to production activities. In conjunction with these other BOEMRE programs, this project will start to enable a comprehensive judgment regarding the relative impacts of natural and production related processes on coastal air quality issues. A further benefit of this project will be the development of a methodology that can be used to establish the relationship, if any, between "background" emissions of compounds such as ethane and ethene with natural oil and gas seeps. The source of these compounds is currently not well established and it is possible that their widespread presence at low levels may be a manifestation of organic input by natural seeps.

2.0 METHODOLOGY

Prior to any field validation, the analytical methodology was developed and optimized. After installation of the instruments, the sampling and analysis methods were evaluated and modified to obtain reliable and reproducible results for the targeted analytes in low parts per billion by volume (ppbv) concentrations. The validation of methodology encompassed the entire analytical process, including sampling, storage, and instrumental techniques of analysis for the laboratory as well as field analyses techniques.

Samples were collected and analyzed by two different techniques and instrument systems. The microFAST GC (a dual column/dual flame ionization detector gas chromatograph) collected and analyzed ambient air samples on-site. Alternatively, sorbent trap samples were collected concurrently on-site but these samples had to be transported back to the laboratory for analysis. The sorbent trap samples were cleaned and capped with their own screw caps in the lab prior to sample collection. They were then stored in sealed jars in an ice chest with cold packs during transport into the field and during transportation back to the lab. One sorbent tube was always used as a trip blank. Once at the lab, the samples were transferred into a freezer and analyzed the next day by a gas chromatograph-time-of-flight-mass spectrometer instrument system (GC-TOFMS) with a thermal desorption injection system. The instrumentation methodology was evaluated and modified as necessary after initial field-testing to accomplish the goals of speciating and quantifying RVOC concentrations. Modifications were made to the chemical analysis procedure, the sampling procedure, sample distribution or sampling location based the previous field trips. Any changes made maintained the comparability between data from the various sampling trips and between the different sampling area types.

Over the course of this project, a total of 353 on-site microFAST GC air samples were analyzed and 108 sorbent tube/GC-TOFMS samples were collected and analyzed from five different locations at different times of the year. Water samples were collected during the off-shore sampling trip to Green Canyon, GOM due to the fact that this was the only off-shore sampling trip that accommodated itself to water sampling for determining net flux. Ten total water samples (duplicate samples at 5 locations) were collected along a sampling transect onto sorbent tubes for GC-TOFMS analysis at LSU. Water sampling was limited by the number of sorbent tube traps available during the trip since the majority of the tube traps were used for air sampling and two of the ten water sample sorbent tubes were analyzed for semivolatile organic compounds. Method development work required an additional 200-300 microFAST GC and GC-TOFMS runs in preparation for the field work.

2.1 AIR SAMPLING

A two-fold analytical procedure was used for detecting reactive volatile organic compounds (RVOC) in air samples at the low ppbv level. First, some samples were collected on dual bed sorbent tube traps and the traps returned to the laboratory for conventional thermal desorption GC-TOFMS analysis of the samples. Second, other air samples were collected concurrently and analyzed in the field with a portable GC instrument, the microFAST GC. The lab based GC-TOFMS system provided higher resolution and lower detection limits than the microFAST GC

system, which was utilized as an on-site screening tool. Minimum detection limits for each analytical system were 0.10 ppbv and 1.0ppbv, respectively.

It is important to point out that conventional environmental analyses use what is termed targeted compound analyses. These analytical methods determine the concentrations of a list of compounds, the target list, in environmental samples, and they in general only detect compounds that are on the list. This project has used environmental analytical methods that are designed to detect a wide range of organic compounds of air quality interest in the sample (i.e. highly volatile and reactive compounds like the C₂, C₃, C₄ and C₅ alkanes and olefins that are known to be ozone precursors) and is not limited to those analytes on EPA TO-17 target list.

2.2 MICROFAST GC

The portable microFAST GC instrument, shown in Figure 1, was used to collect and analyze air samples on-site at each sample location. The deployment of the microFAST GC allowed operators to make on-site decisions regarding sample locations and other important operational parameters based on near real-time analysis of ambient air samples. More importantly, due to this instrumentation's fast cycle times, new samples could be analyzed every ten minutes and this allowed a relatively large number of analyses to be performed at each sampling location. The microFAST GC is shown in Figure 1 with a Portapack that supplied the power (24VDC) and the gases (hydrogen and air) needed to run the instrument in the field. Data acquisition and instrument control were achieved through use of software that runs on a laptop computer.



Figure 1. The microFAST GC setup.

The microFAST GC was equipped with a combination of columns and trap packing material to detect the very light hydrocarbon compounds from ethane to the BTEX (benzene, toluene, ethylbenzene and the xylenes) aromatic compounds associated with petroleum. These compounds, particularly the olefins and alkyl benzenes, are important ozone precursors. They were analyzed by the microFAST GC in the field with a detection limit of 1.0 ppbv. The separation columns used in the field were unable to distinguish between hexane and isoprene and these two compounds co-eluted for this instrument system. Isoprene is a much more reactive ozone precursor than hexane as far as ozone reactivity is concerned, and this is an unfortunate limitation to these field analyses. Isoprene is believed to be naturally produced by algal growths/blooms in marine areas during the daylight hours and is usually not a derivative of petroleum. Thus, isoprene is not associated with natural petroleum seeps or petroleum exploration and production activities.

The microFAST GC uses an internal microtrap to collect and concentrate air samples, and the analytes are then thermally desorbed onto dual high resolution GC columns for on-site chromatographic separations. Samples were introduced into the microFAST GC through a Teflon sampling valve. This valve replaced an electronic solenoid valve, which was susceptible to contamination with semivolatile compounds during sampling. Typically, this Teflon sampling valve was opened for four minutes, enabling approximately 100 mL of an air sample to be pulled into the microFAST GC and through the internal microtrap. The microtrap was a dual bed micro trap filled with 80/100 mesh Tenax GR followed by Carboxen. After sampling, the trap was flushed and inerted with carrier gas and then blastically heated from 40°C to 280°C. Organic compounds that were trapped from the sample were then backed flushed from the heated trap into the two capillary columns for GC separations and FID detections. In this project, the columns were a Gas Pro gas solid phase GC column (2 meters long, 320 microns ID), used for detection of the very light hydrocarbons (C_2 to C_7), and a DB-5 gas liquid phase GC column (2 meters long, 320 microns ID) used for detection of the C_7 to C_{17} range hydrocarbon compounds. After injection, the trap was automatically cleaned by back flushing to vent for 60 seconds while held at 280°C. Chromatographic separations were obtained using an isothermal initial hold time of 22 seconds at 40°C; a temperature program from 40°C to 280°C at 5°C/s; and a final hold at the upper temperature for 30 seconds. This gave a total chromatographic separation time of 100 seconds. After chromatographic separations were completed, the GC system was returned to all initial temperatures in preparation for the next analysis. The total cycle time from one run to the next was typically 10 minutes. A diagram of the flow paths for the microFAST GC is shown in Figure 2, which also includes a picture of the Teflon sampling valve that was used to let air samples into the portable GC instrumentation.

Two microFAST GC instruments were deployed on the aft deck of a 65-foot vessel in the Green Canyon sampling area of the Northern GOM for sampling and analysis of RVOCs at the low ppbv (>1.0 ppbv) concentrations. The vessel was positioned such that the 10-15 mph wind was blowing over its port side and the instruments were situated near the port side free of obstructions upwind. The boat's diesel generator exhaust was vented on the starboard side, well downwind from the analytical instruments. At least one blank analysis was performed at each sampling location to ensure that there was no diesel contamination.

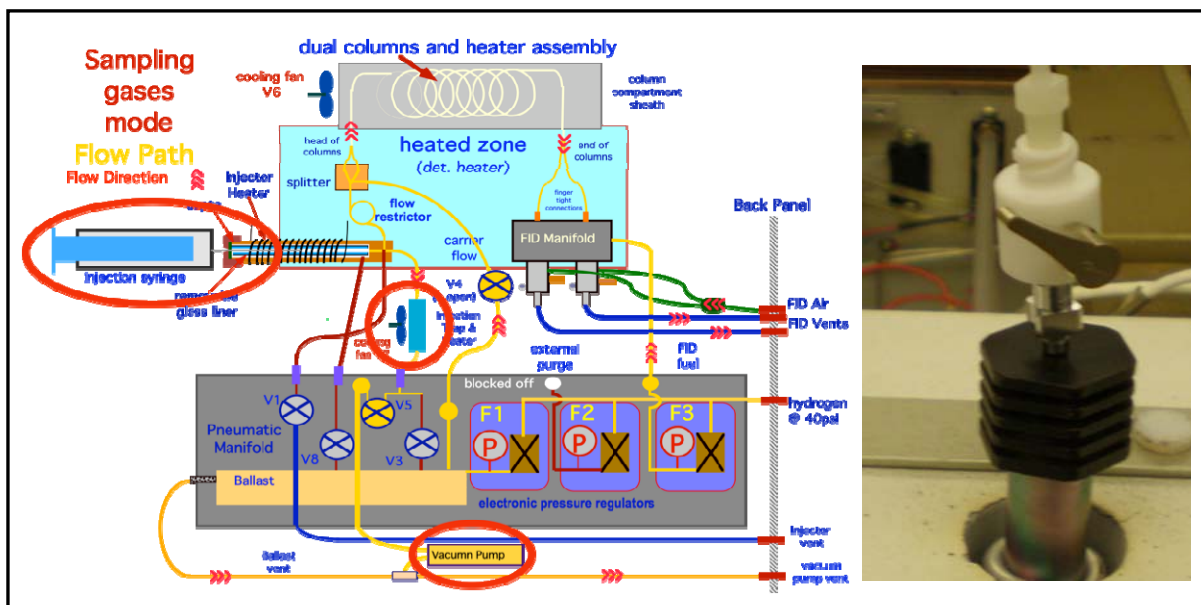


Figure 2. Flow schematic of the microFAST GC (left) and air sampling valve (right).

2.3 SORBENT TUBE TRAP/GC-TOFMS

The sorbent tube collection process utilized a multitube flowmeter system with three 150-mm direct-reading flowtubes calibrated for air and Teflon tubing. The system was setup with a common exhaust with parallel inlets configuration. The flow rates were verified and adjusted using a battery powered digital flow meter. The flow was set at approximately 200-mL per minute and sampled for 10 minutes for all near-shore sampling trips and 20 minutes for the deep sea sampling trip to Green Canyon. These flow rates allowed for the collection of 2 - 4 L of air over a ten to twenty minute time frame. The vacuum for collecting the air samples was obtained using a 12-VDC Air Cadet vacuum/pressure pump rated at 22.6 L/minute. The air sampling pump apparatus that was used for collection of samples on the sorbent tube traps is shown in Figure 3.

The samples were pulled through ambient temperature traps at the site of sample collection with the vacuum pump. The traps were immediately sealed after the targeted sample volume was achieved and were then refrigerated and transported to the laboratory for thermal desorption and GC-TOFMS analysis within a 24 hour time period. Prior to each field sampling trip, randomly selected sorbent tube traps were spiked with known concentrations of a RVOC analyte standard (AirGas, Inc., Baton Rouge, Louisiana) for standardization and calibration purposes.

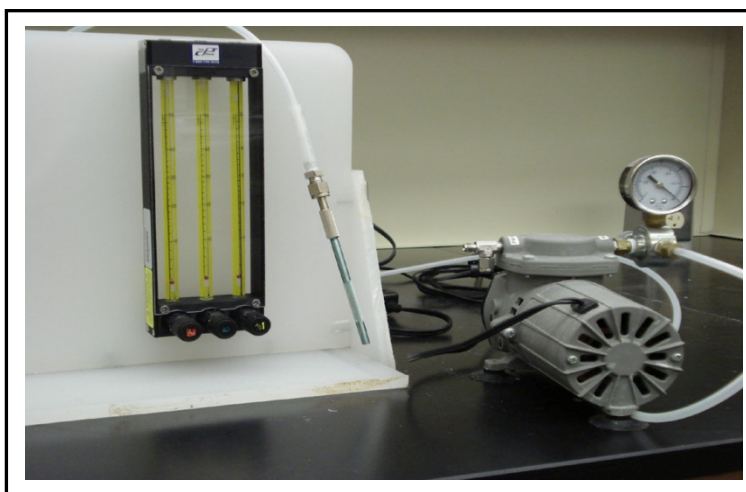


Figure 3. Sorbent tube trap air sampling apparatus.

The sorbent tubes were purchased from Scientific Instrument Services, Inc. (SIS) of Ringoes, NJ and thermally desorbed using an SIS TD-5 short path Thermal Desorption System instrument interfaced to an Agilent 6890N gas chromatograph/ LECO Pegasus III time of flight mass spectrometer (GC-TOFMS). A schematic diagram of the thermal desorption GC/MS analyzer and a picture of the sorbent tube trap is given in Figure 4. The TD-5 was purged with inert carrier gas and rapidly heated to 300°C. During this heating, the trap was swept with carrier gas onto the head of the GC separation column. Immediately after desorption, the GC column was temperature programmed from 35°C to 280°C at 5°C/minute while eluting compounds were detected with the TOFMS detector. The GC-TOFMS used a 60 m, 320 micron ID Gas Pro gas-solid separation column that allowed separation of the very volatile ozone precursors such as ethane and ethylene up to compounds as large as benzene, toluene and the xylenes. These compounds are known as “highly reactive” VOCs or RVOCs as far as their ability to react with other pollutants, especially NO_x, are concerned, and this secondary reaction can result in the formation of tropospheric ozone through the series of reactions described earlier in the introduction.

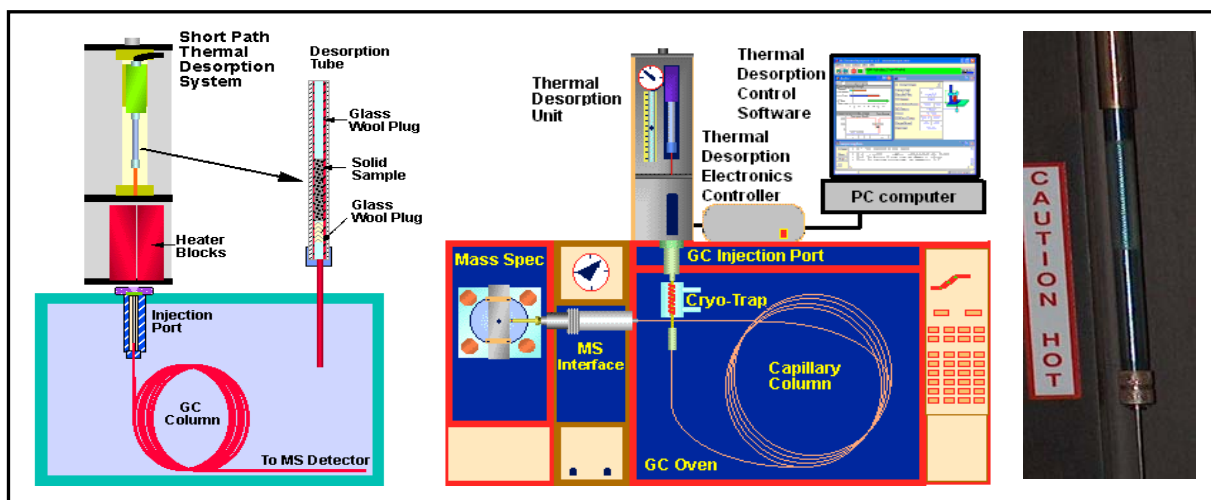


Figure 4. Schematic diagram of the thermal desorption methodology and a photo of the actual desorption tube (far right).

Thermal desorption GC/MS analysis of air samples provides a method for detection of unknown and/or unexpected compounds in air samples as well as target RVOC analytes, given in Table 1. It also serves as a significant quality assurance source for the on-site GC analyses, since detection is based on both retention time separations and mass spectral compound identification. No on-site sampling decisions could be made from the sorbent tube sampling. Any modifications in the sorbent tube sampling methodology were made after the tubes were returned to the lab and analyzed.

A few randomly selected air samples from the off-shore sampling trip to Green Canyon, GOM were qualitatively analyzed on an Agilent 7890A GC/5975C quadrupole MS (GC/MS). The quadrupole GC/MS used a 30 m, 320 micron gas/liquid GC separation column coated with 0.4 microns DB-5 liquid phase. This column allowed separation of compounds that have molecular sizes larger than the RVOC compounds meaning the semivolatile organic compounds (SVOCs). The SVOCs were not included in the analytes of interest listed in Table 1 solely because they are not considered to be very reactive. Therefore, the analysis for the SVOCs was done to determine if there were any other possible analytes of interest that may need to be included in future air monitoring projects. Analyzing a few of the air samples collected on the sorbent tube traps for both the RVOCs and SVOCs allowed for a very broad range of possible compounds at a detection limit of 0.1 ppbv.

2.4 WATER SAMPLING

Water samples were taken at a depth of five meters and were then placed in a pre-cleaned headspace free 1-gallon amber borosilicate jar with a Teflon-lined metal lid and purged (Figure 5). The sample jars were pre-cleaned in the lab prior to the sampling trip. They were washed in hot soapy water, rinsed with deionized water, rinsed with methanol, and dried in a 105°C oven overnight. Air was purged through the water sample and collected on the same type of sorbent tube traps that were used for the air sampling.

Collection of RVOCs from the water samples utilized the exhaust from a vacuum pump that was routed thru Teflon tubing into a hydrocarbon gas purification cartridge. The air exited the cartridge through another Teflon tube into an air sparging apparatus enclosed in another 1-gallon amber borosilicate jar with a Teflon-lined metal lid. The purged air entered the jar through a 1/8" stainless steel compression bulkhead fitting (top of jar, on the right in Figure 5) and then through a 1/8" Teflon tube into a 1/2" stainless steel spherical microbubbler. The purged air exited the jar via a secondary 1/8" stainless steel threaded bulkhead fitting (top of jar, on the left in Figure 5) screwed to a threaded desorption tube traps. Flow rates were verified and adjusted with a battery powered digital flow meter. Flow was adjusted using a Teflon-lined three-way valve positioned ahead of the hydrocarbon gas purification cartridge to a flow of 200 mL/minute for ten minutes. The sorbent tube traps from the purged water samples were then sealed and stored in a cool ice chest during the remainder of the 1-day sampling trip and during transportation back to the lab. Once at the lab, the sorbent tubes, in the sealed container, were transferred to a freezer until GC-TOFMS analysis. Keeping the sorbent tube traps cool prevented any speciation from occurring during transit and holding time prior to analysis. The GC-TOFMS methodology was the same methodology employed to analyze the ambient air

sorbent tube samples. All sorbent trap tubes were analyzed within two days (48 hours) after collection.



Figure 5. Water sampling apparatus.

2.5 FIELD VALIDATION

After the initial setup and validation period, sampling trips near and into the Gulf of Mexico were made. The sampling trips and dates are summarized in Table 2. At each sample location, air samples were collected with active sampling onto the sorbent tube traps and the microFAST GC was also used for rapid on-site analysis of air samples. Meteorological conditions (e.g. relative humidity, temperature, wind directions, etc.) were recorded for all field validation trips and throughout the course of the sampling period.

Our initial field validation plan called for deployment of the sorbent tube traps and the microFAST GC instrumentation in near shore areas of the Gulf using a 21-foot center console boat (out to approximately 10 miles offshore) in calm weather conditions, and the use of a chartered 65-foot vessel for deep sea air and water sampling. After the hurricane season of 2005, turbulent near-shore sea states dominated the 2006 and 2007 summer sampling seasons which prohibited the use of the 21-foot boat for near-shore sampling. Furthermore, chartering the 65-foot vessel was difficult and the cost had increased three fold which limited the deep sea sampling to one trip to the Green Canyon area. As a result, it was decided to do near-shore sampling from unobstructed areas along the beaches at Grand Isle, Port Fourchon, and near Cameron, Louisiana, during times when the wind was of blowing out of the south, southeast or southwest directions (e.g. from offshore GOM areas). These on-shore instrument deployment locations provided some degree of protection of the analytical instrumentation while still allowing detection of RVOC compounds that originated from near-shore areas of the Northern GOM.

Table 2
Summary of Field Validation Trips

Trip #:	Date:	Location:	Coordinates:	Average Sampling Time:
1	August 20-23, 2007	Grand Isle, LA	29°15'37.66"N, 89°57'03.54"W 29°15'37.68"N, 89°57'03.112"W	2 hrs 10 min
2	September 5-6, 2007	Cameron, LA	29°46'30.70"N, 93°18'05.34"W	2 hrs 23 min
3	September 17, 2007	Port Fourchon, LA	29°06'49.80"N, 90°11'04.20"W	6 hrs 15 min
4	October 1-4, 2007	Port Fourchon, LA	29°06'49.48"N, 90°11'03.54"W	8 hrs 19 min
5	June 9-10, 2008	Green Canyon, GOM	27°48'28.56"N, 90°39'42.68"W – 27°57'02.45"N, 90°51'35.35"W	6 hrs 30 min

The first trip was to Grand Isle, Louisiana, and occurred after the initial instrumentation qualification and method validation was completed in the laboratory setting. The trip focused on near-shore monitoring for three days and at least 4 hours of sampling each day. The secondary focus of this trip was to test sampling flow rates outside of the laboratory setting for the sorbent tubes so that the best rate, one that minimized breakthrough, was used for future trap sampling trips. The methodology for both instrumentation techniques was verified prior to this trip by establishing linearity of each analyte of interest with 5-point calibration curves.

The second trip took place in early September near Cameron, Louisiana. In the interim, the data from the first trip was evaluated and adjustments in the sampling plan were tested and implemented. The majority of the adjustments made to the air sampling methodologies, Table 3, were first tested in the lab using known concentrations of the RVOC standard and then field tested to ensure that the adjustments were suited for field use and that comparable results could be obtained. The focus of the second trip was near-shore monitoring for RVOCs and to assess the final lab-based adjustments to the air sampling methodologies.

The third and fourth trips were to Port Fourchon, Louisiana. The goal for these two trips was to implement the finalized methodologies while performing near-shore monitoring for RVOCs. By trip four, the sampling and analysis protocols were firmly established and no modifications in procedures were required. These trips were done in mid-September and early October. The September trip was a day trip and the October trip lasted for four days.

The final trip was to Green Canyon, approximately 80 miles south of Port Fourchon, and was made in early June 2008. A chartered boat departed from Port Fourchon around noon in order to arrive at the targeted sampling location around 4 pm. The vessel was situated such that the 5-10 mph south wind was blowing over the port side of the vessel and this orientation was maintained for the entire sampling session. The instrumentation was set up such that there was an unobstructed and uncontaminated path from the south wind for the duration of on-site operations. The route of the trip was planned so that the bulk of the available sampling time was spent at the primary target area, a transect near the natural seeps that occur in the area. The sampling route was carefully coordinated to avoid other ship traffic and local fishing activity, both of which are

anthropogenic sources of RVOCs. Once more, surface meteorological conditions were monitored during the sampling period. Air samples were collected in the same manner as the near-shore sampling trips with active sampling onto sorbent tube traps above the water surface and the microFAST GC provided on-site analysis. Water samples were also collected, as previously described, using a subsurface water sampler, at a depth of 5 meters (approximately 16 feet) below the water surface and the water sparging device.

Table 3
Air Sampling Methodology Adjustments

microFAST GC Adjustments:	Initial:	Final:
Column Temperature Ramp	30°C - 280°C @ 5°C/sec	40°C - 280°C @ 5°C/sec
Isothermal Hold Time	30 sec	22 sec
Sample Time	45 sec	4 min
Trap Desorption Temperature Ramp	40°C - 250°C	40°C - 280°C
Sorbent Tube Trap Adjustments:	Initial:	Final:
Sample Time and Vacuum Pump Flow Rate	10 min @ 100mL/min 20 min @ 100mL/min	10 min @ 200mL/min 20 min @ 200mL/min

2.6 ESTIMATING NET FLUX OF RVOCs

Mass flux of RVOCs to and from marine surface waters can be appropriately estimated using the boundary layer model outlined by Sauer (1980). This model simply predicts the flux of RVOCs across the air-water interface as a function of concentration gradient and molecular diffusion. Fluxes are determined on the assumption that there is no previous contribution of RVOC from the atmosphere. If components are present, flux from the seawater will be reduced due to the decrease in concentration difference or gradient. The RVOC flux (F in $\text{mol m}^{-2}\text{s}^{-1}$) can be calculated by using the following equation:

$$F = k_L (C_w - K_H P_{\text{cmpd}}),$$

where k_L (ms^{-1}) represents the liquid phase transfer velocity, C_w is the seawater concentration, K_H ($\text{mol kg}^{-1} \text{atm}^{-1}$) is the components Henry's Law constant, and P_{cmpd} is the partial pressure of that specific compound. The liquid phase transfer velocity, k_L , is determined by using the following equation:

$$k_L = 2.778 \times 10^{-6} (0.31 U^2 (\text{Sc}/660)^{-1/2}),$$

where U (ms^{-1}) represents wind velocity and Sc (dimensionless) is the Schmidt number. The Schmidt number (ν/D) is expressed as the ratio of the transfer coefficient for momentum (kinematic viscosity) and mass (molecular diffusivity).

The diffusion coefficient, D , can be calculated by using a revised Othmer-Thakar equation. The diffusion coefficient of sparingly soluble gases, such as NMHCs, from the subsurface seawater can be estimated using the expression:

$$D_{cmvd} = (13.26 \times 10^{-5}) \mu^{-1.4} V_m^{-0.589},$$

where μ (cP) represents seawater viscosity and V_m ($\text{cm}^3\text{mol}^{-1}$) is the molar volume of the individual compound. The diffusion coefficient for the individual compounds were calculated using an estimated molar volume in conjunction with expressions (Hayduk and Laudie, 1974) relating solution viscosity and molar volume.

The seawater viscosity (μ , cP) and kinematic viscosity (V_m , cm^2s^{-1}) were set at 0.894 and 8.5×10^{-3} , respectively, for all net flux calculations. The average wind speed (U) was recorded at 2.24 ms^{-1} during the Green Canyon field study.

It is important to point out that accurate flux estimates are extremely difficult to calculate due to the large number of variables associated with sources and other contributions to the lifetime of reactive compounds in the air shed over marine areas. In fact, one of the primary goals of this project was the development of analytical methods that would allow collection of a large number of data points for accurate flux measurements. Variability caused by numerous geogenic and biogenic sources of RVOCs, as well as sources of NO_x, in the Northern GOM can be overcome with enough RVOC concentration data points.

3.0 DATA AND RESULTS

3.1 TRIP #1: GRAND ISLE, LOUISIANA, AUGUST 2007

A total of 36 microFAST GC samples and 25 sorbent tube trap samples were analyzed for the initial field validation trip to the beach at Grand Isle, Louisiana. Table 4 gives the sampling information for Trip #1 and Figure 6 displays the average RVOC concentrations for the microFAST GC over the course of the sampling trip. Detailed microFAST GC analytical results from this sampling trip are given in Appendix A.

Table 4

Sampling Information for Trip #1: Grand Isle, Louisiana

Average Temperature: 91°F		
Average Humidity: 73%		
Average Wind Speed: 5 mph, S-SE		
Date & Time Start	Hours Sampled	# of Samples
08/20/2007, 15:56	3.50	7 microFAST 5 sorbent tube trap
08/21/2007, 10:53	1.25	17 microFAST 5 sorbent tube trap
08/22/2007, 10:20	1.75	12 microFAST 9 sorbent tube trap
08/23/2007, 10:26	1.00	6 sorbent tube trap

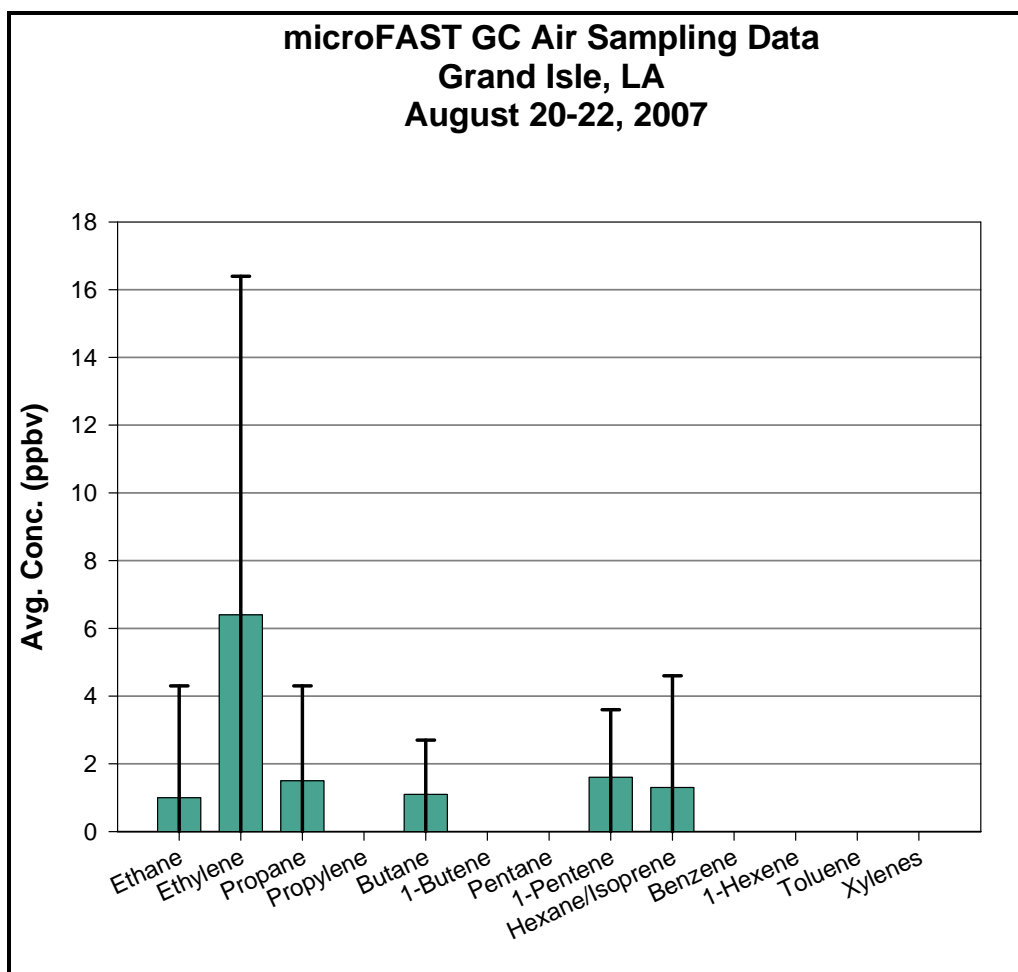


Figure 6. Average RVOC concentrations for on-site microFAST GC air samples, Grand Isle, Louisiana, August 2007. (n=36)

As shown in the graph, the predominant RVOCs (analytes with a 3-day average at or over the 1.0 ppbv detection limit) detected by the microFAST GC during the sampling trip to Grand Isle were ethane (1.0 ppbv); ethylene (6.4 ppbv); propane (1.5 ppbv); butane (1.1 ppbv); 1-pentene (1.6 ppbv); and, hexane/isoprene (1.3 ppbv). Hexene was not detected on any of the three days and the following were below the detection limit (BDL) of 1.0 ppbv: propylene; 1-butene; pentane; benzene; toluene; and the xylenes.

Figures 7 display the average sorbent tube trap/GC-TOFMS concentrations for each of the four days of this first near-shore monitoring trip to Grand Isle. Sampling sessions were the same as the microFAST GC sessions previously mentioned except that sorbent tubes were collected one additional day, August 23rd, than the microFAST GC due to testing of sample flow rates for the sorbent tubes. Detailed sorbent tube trap/GC-TOFMS analytical results for this sampling trip are given in Appendix B.

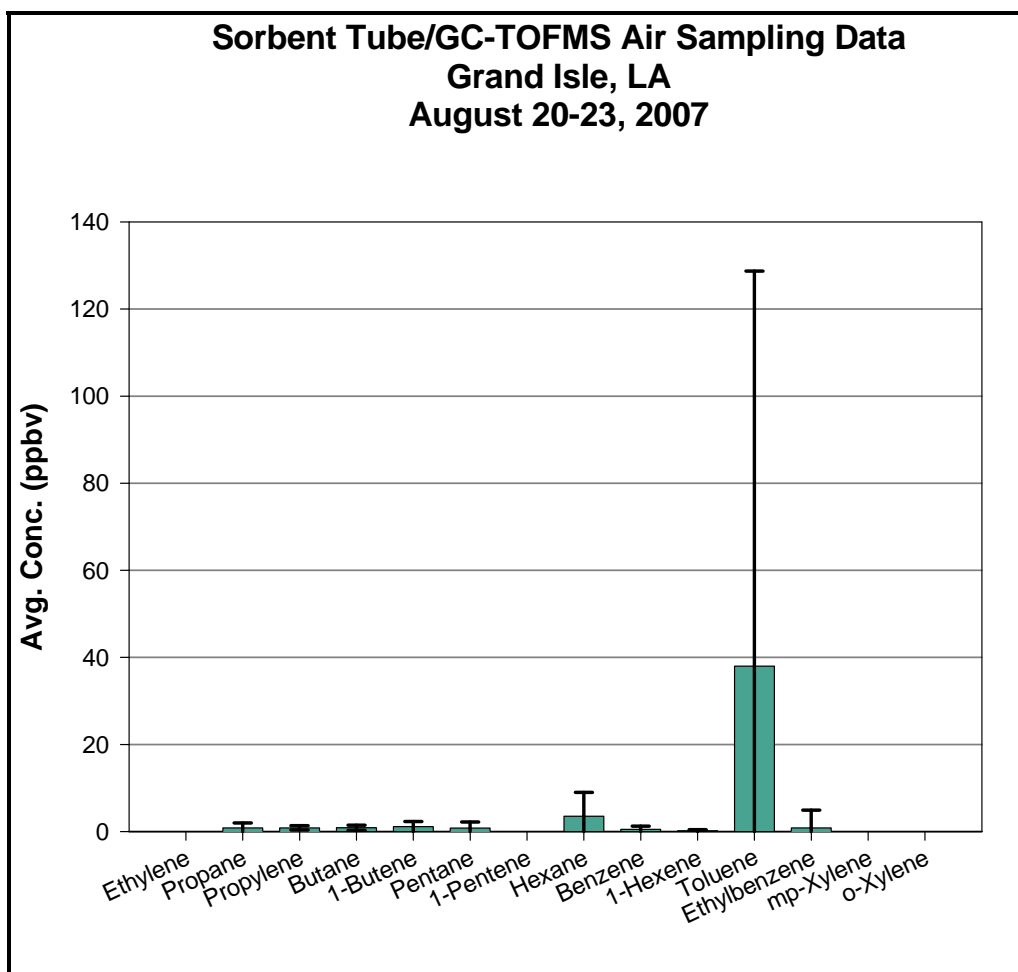


Figure 7. Average RVOC concentrations for sorbent tube/GC-TOFMS air samples, Grand Isle, Louisiana, August 2007. (n=25)

The predominant RVOCs, analytes with a 4-day average over the 0.1 ppbv detection limit, collected on the sorbent tube traps and detected by GC-TOFMS during the sampling trip to Grand Isle were propane (0.83 ppbv); propylene (0.84 ppbv); butane (0.85 ppbv); 1-butene (1.1 ppbv); pentane (0.78 ppbv); hexane (3.5 ppbv); benzene (0.52 ppbv); 1-hexene (0.14 ppbv); toluene (38 ppbv); and ethylbenzene (0.82 ppbv). Ethylene and 1-pentene were not detected over the course of 4 days and the xylenes were below detection limits.

Large variations in RVOC concentrations are very apparent after this first near-shore monitoring trip. The reason for this variation is not known but may be due to the fact that there are periodic releases of RVOCs from natural oil seeps into the water column and then into the air. Furthermore, concentrations of RVOCs are not homogeneous in the water column and therefore, will not be homogeneous in the air resulting in “spikes” of RVOCs over the course of a day. Spikes of RVOCs were detected throughout the sampling period and since the concentrations presented in this report are averaged based on the number of samples, the length of the sampling period will affect the number of samples. If the number of samples with no RVOCs increases, the RVOC spikes in some of the samples are offset and appear less significant. This variation was evident in all the field validation trips.

3.2 TRIP #2: CAMERON, LOUISIANA, SEPTEMBER 2007

A total of 29 microFAST GC samples and 20 sorbent tube samples were analyzed for field validation trip #2 to Cameron, Louisiana. Table 5 gives the sampling information for Trip #2 and Figure 8 presents the 2-day averaged microFAST GC concentrations of RVOCs for the sampling trip to Cameron, Louisiana. Detailed analytical results for the microFAST GC from this trip are given in Appendix A.

Table 5

Sampling Information for Trip #2: Near Cameron, Louisiana

Average Temperature: 91°F		
Average Humidity: 75%		
Average Wind Speed: 3 mph, S-SE		
Date & Time Start	Hours Sampled	# of Samples
09/05/2007, 13:46	3.75	12 microFAST 20 sorbent tube trap
09/06/2007, 15:04	1.00	17 microFAST

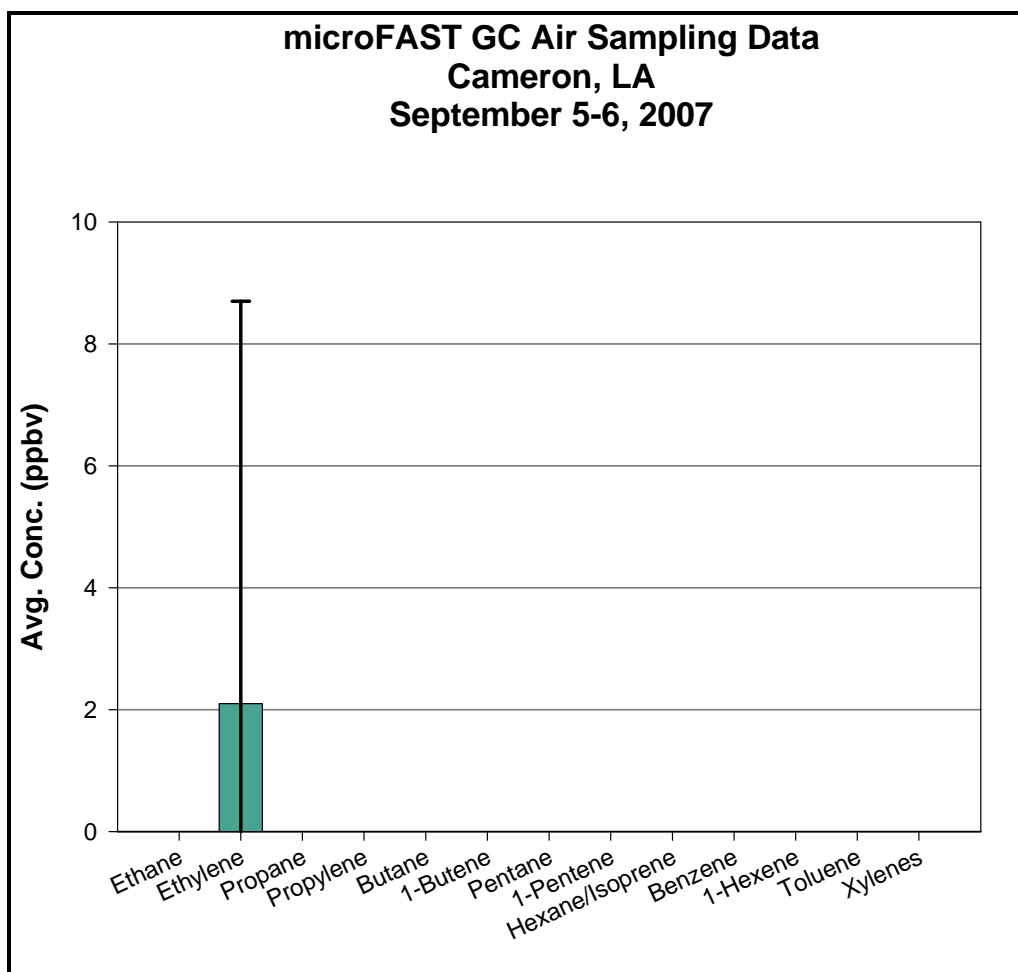


Figure 8. Average RVOC concentrations for on-site microFAST GC air samples, Cameron, Louisiana, September 2007. (n=29)

The microFAST GC detected only one RVOC with a 2-day average over 1.0 ppbv at the Cameron, Louisiana, sampling site and that was ethylene (2.1 ppbv). Compounds not detected were 1-butene, pentane, and 1-hexene. All the other compounds were under the 1.0 ppbv detection limit.

Figure 9 illustrates the average sorbent tube trap/GC-TOFMS RVOC concentrations for the air samples collected in Cameron, Louisiana. Sampling sessions were the same as the microFAST GC sessions previously mentioned except that sorbent tubes were collected on only one of the two days for this field validation trip. Detailed analytical results for the sorbent tube trap/GC-TOFMS for Cameron, Louisiana, are given in Appendix B.

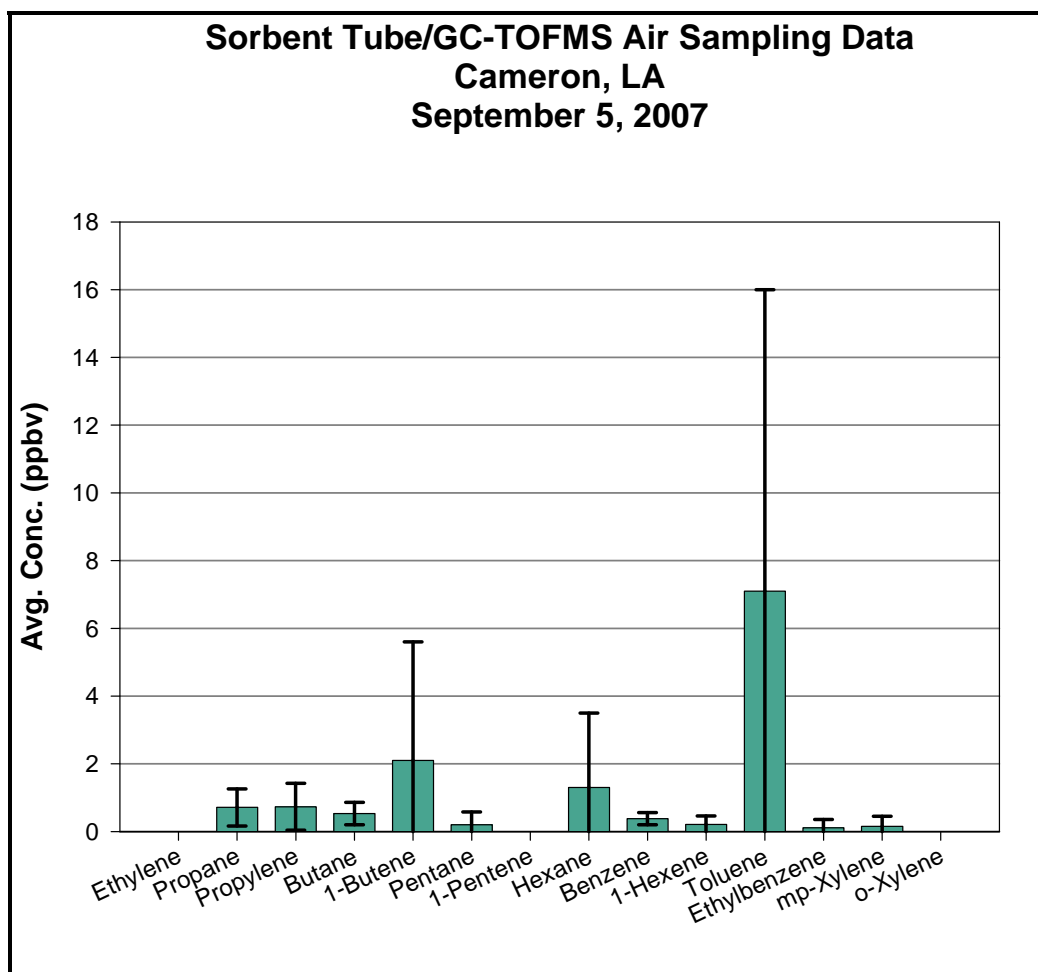


Figure 9. Average RVOC concentrations for sorbent tube/GC-TOFMS air samples, Cameron, Louisiana, September 2007. (n=20)

The average concentrations of RVOCs detected at Cameron by sorbent tube trap/GC-TOFMS air sampling methodology were propane (0.71 ppbv); propylene (0.73 ppbv); butane (0.53 ppbv); 1-butene (2.1 ppbv); pentane (0.20 ppbv); hexane (1.3 ppbv); benzene (0.38 ppbv); 1-hexene (0.21 ppbv); toluene (7.1 ppbv); ethylbenzene (0.11 ppbv); and m+p-xylene (0.15 ppbv). O-xylene was below the 0.1 ppbv detection limit; and, ethylene and 1-pentene were not detected in the samples collected on September 5th.

3.3 TRIP #3: PORT FOURCHON, LOUISIANA, SEPTEMBER 2007

A total of 7 microFAST GC samples and 24 sorbent tube samples were analyzed for field validation of trip #3 to Port Fourchon, Louisiana. Trip #3 to Port Fourchon was a day trip designed to test the finalized methodologies for the sorbent tubes and the microFAST GC. A multiday trip back to Port Fourchon would follow this initial day trip. Table 6 gives the sampling information for Trip #3 and Figure 10 displays the average RVOC concentrations in the ambient air detected with the on-site microFAST GC. Unfortunately, on this sampling trip, the microFAST GC had a malfunction that could not be resolved in the field and had to be returned to lab for troubleshooting and correction. As a result, only seven microFAST GC

samples were collected. Again, detailed microFAST GC analytical results for this trip are given in Appendix A.

Table 6
Sampling Information for Trip #3: Port Fourchon, Louisiana

Average Temperature: 83°F		
Average Humidity: 72%		
Average Wind Speed: 6 mph, SE		
Date & Time Start	Hours Sampled	# of Samples
09/17/2009, 10:58	6.25	7 microFAST 24 sorbent tube

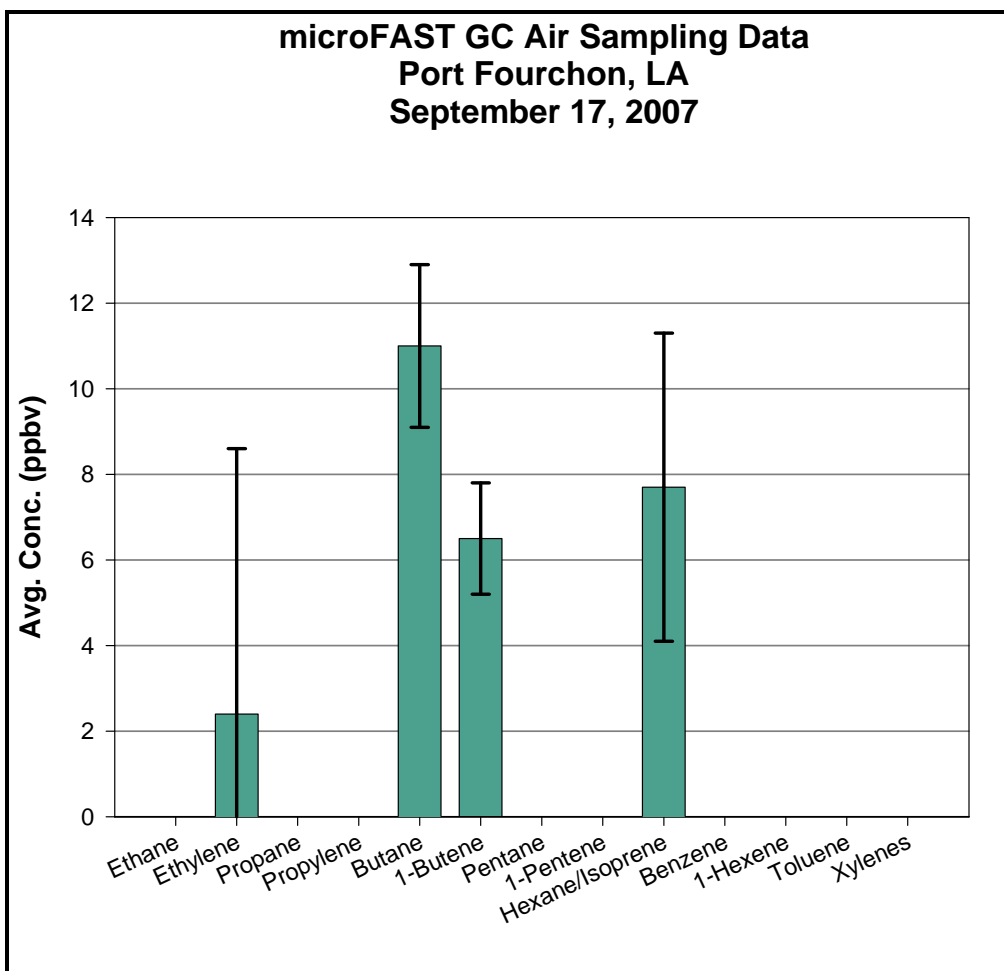


Figure 10. Average RVOC concentrations for on-site microFAST GC air samples, Port Fourchon, Louisiana, September 2007. (n=7)

The following RVOCs detected at Port Fourchon by the microFAST GC had averages over the 1.0 ppbv detection limit: ethylene (2.4 ppbv); butane (11 ppbv); 1-butene (6.5 ppbv); and, hexane/isoprene (7.7 ppbv). Ethane, propane, propylene, benzene, toluene, and the xylenes were below the detection limit; and, pentane, 1-pentene, and 1-hexene were not detected during the course of the sampling period.

Figure 11 illustrates the average sorbent tube trap/GC-TOFMS RVOC concentrations for the air samples collected during the day trip to Port Fourchon. Detailed sorbent tube trap/GC-TOFMS analytical results are given in Appendix B.

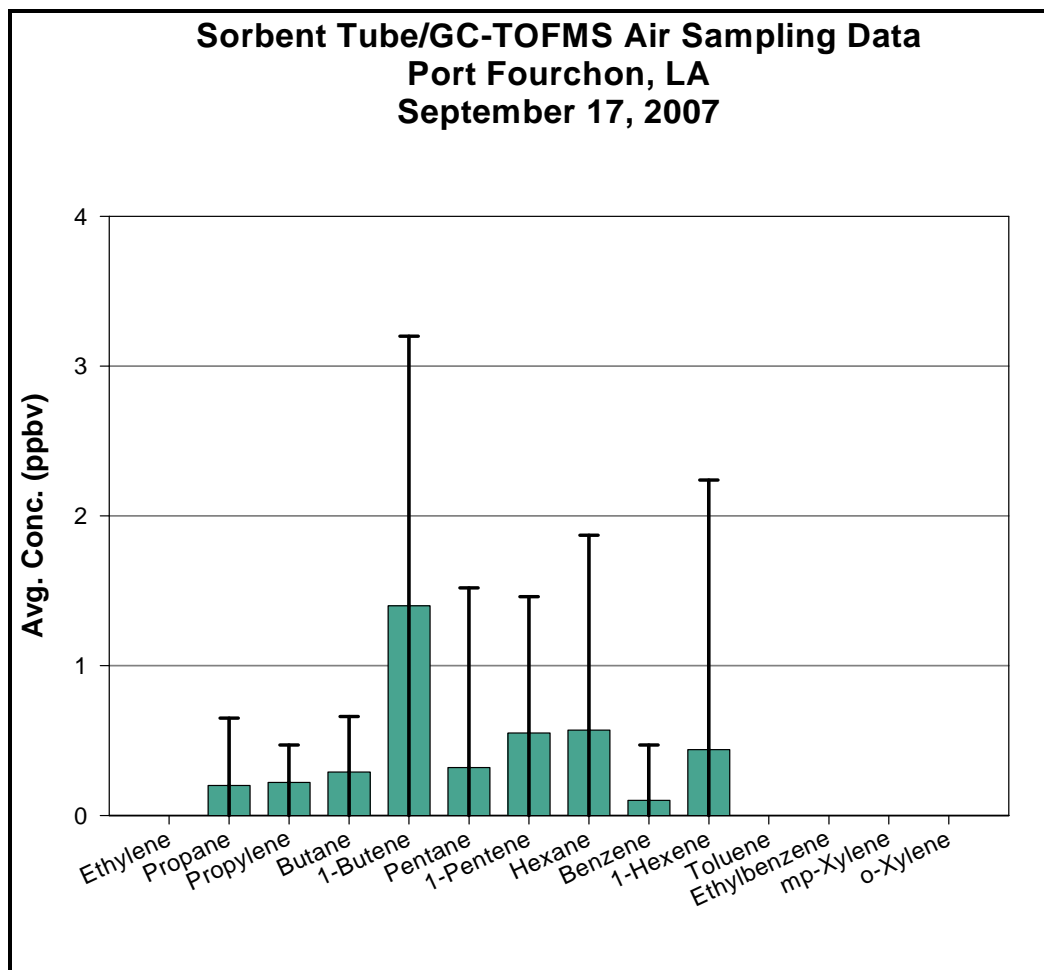


Figure 11. Average RVOC concentrations for sorbent tube/GC-TOFMS air samples, Port Fourchon, Louisiana, September 2007. (n=24)

Average RVOC concentrations detected at or above the 0.1 ppbv detection limit of the GC-TOFMS were: propane (0.20 ppbv); propylene (0.22 ppbv); butane (0.29 ppbv); 1-butene (1.4 ppbv); pentane (0.32 ppbv); 1-pentene (0.55 ppbv); hexane (0.57 ppbv); benzene (0.10 ppbv); and, 1-hexene (0.44 ppbv). Toluene was below the detection limits; and ethylene, ethylbenzene, and the xylenes were not detected during this sampling trip.

3.4 TRIP #4: PORT FOURCHON, LOUISIANA, OCTOBER 2007

A total of 112 microFAST GC samples were analyzed for field validation trip #4 to Port Fourchon, Louisiana. Sorbent tube trap samples were not performed on this sampling trip because the tubes were being reconditioned from the previous sampling trip to Port Fourchon on September 17th. This repeat trip to Port Fourchon was in addition to the day trip to Port Fourchon. By this point in the project, the sampling and analysis protocols were firmly established and no modifications in procedures were required. Table 7 gives the sampling information for Trip #4 and Figure 12 shows the 4-day averaged RVOC concentrations detected by the on-site microFAST GC. Detailed microFAST GC analytical results for this 4-day sampling trip are given in Appendix A.

Table 7

Sampling Information for Trip #4: Port Fourchon, Louisiana

Average Temperature: 81°F		
Average Humidity: 73%		
Average Wind Speed: 9 mph, S-SE		
Date & Time Start	Hours Sampled	# of Samples
10/01/2007, 10:18	10.25	38 microFAST
10/02/2007, 09:00	8.00	25 microFAST
10/03/2007, 11:00	12.75	41 microFAST
10/04/2007, 07:45	2.25	8 microFAST

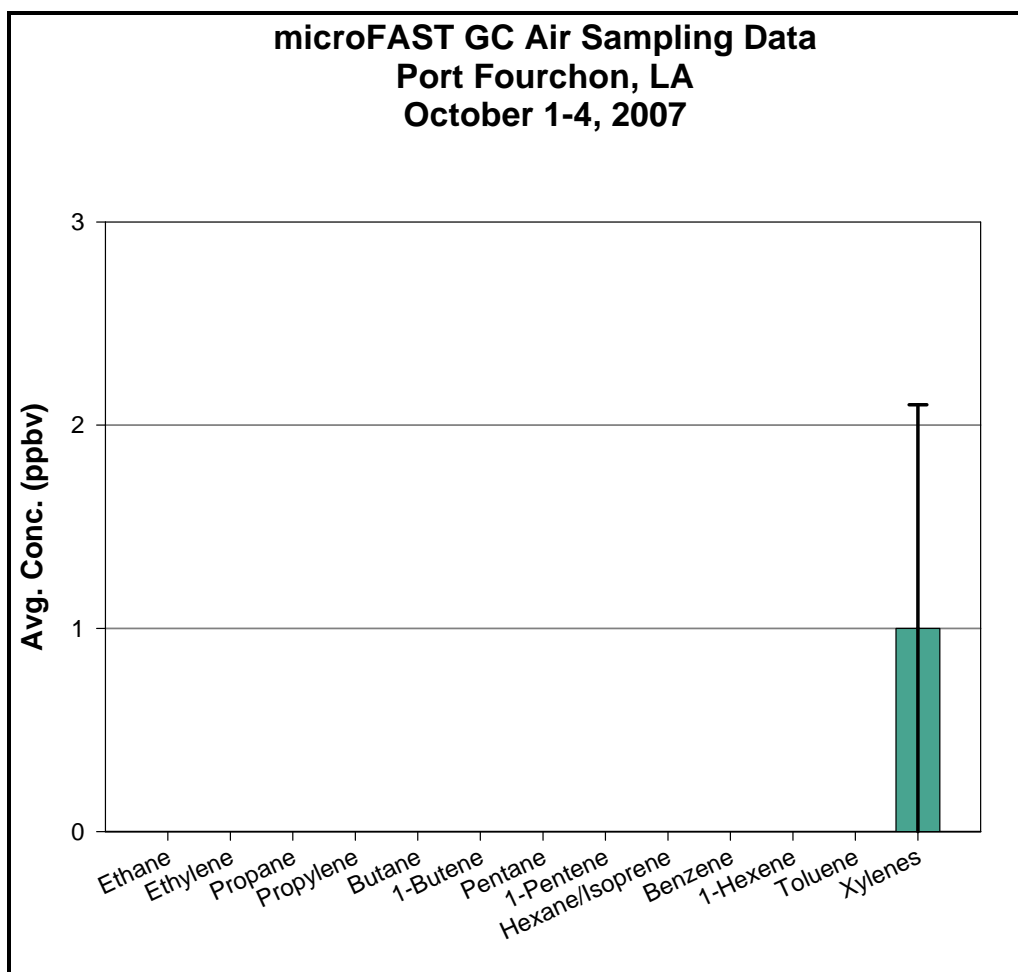


Figure 12. Average RVOC concentrations for on-site microFAST GC air samples, Port Fourchon, Louisiana, October 2007. (n=112)

The xylenes were the only RVOCs with 4-day average concentrations over 1.0 ppbv. Analytes below the detection limit include ethane, ethylene, propane, propylene, butane, 1-butene, pentane, 1-pentene, hexane/isoprene, benzene, and toluene. Over the course of four days at Port Fourchon, 1-hexene was not detected.

3.5 TRIP #5: GREEN CANYON, GOM, JUNE 2008

A total of 23 microFAST GC samples and 28 sorbent tube trap samples (22 air and 6 water) were analyzed for field validation trip #5 to Green Canyon, about 80 miles south of Port Fourchon in the Northern GOM. Table 8 gives the sampling information for trip #5 and Figure 13 illustrates the average microFAST GC RVOC concentrations for the one day sampling trip to Green Canyon. Detailed microFAST GC analytical results are given in Appendix A.

Table 8

Sampling Information for Trip #5: Green Canyon, GOM

Average Temperature: 88°F		
Average Humidity: 75%		
Average Wind Speed: 5 mph, S		
Date & Time Start	Hours Sampled	# of Samples
06/09/2008, 18:23	6.5	23 microFAST 32 sorbent tube trap: 22 air 6 water 4 SVOC

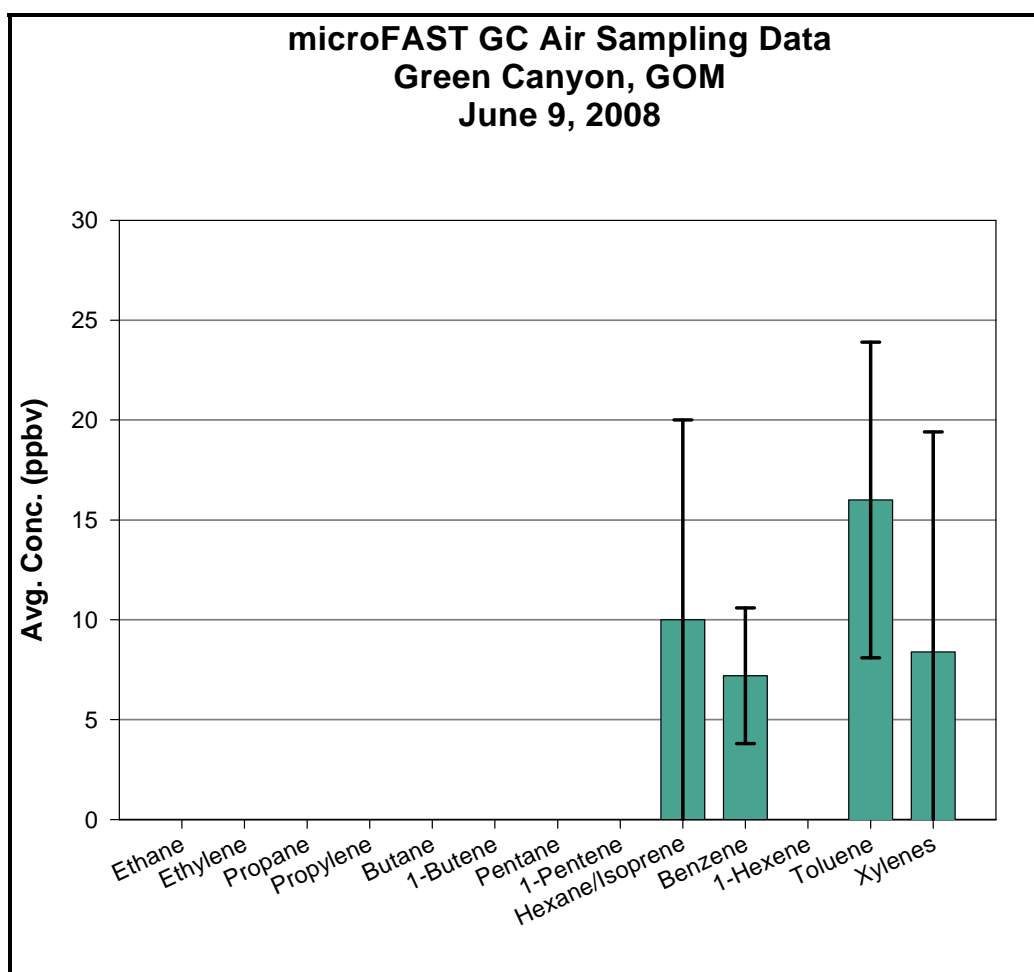


Figure 13. Average RVOC concentrations for on-site microFAST GC air samples, Green Canyon, GOM, June 2008. (n=23)

The RVOCs detected by the microFAST GC were hexane/isoprene (10 ppbv average), benzene (7.2 ppbv average), toluene (16 ppbv average), and the xylenes (8.4 ppbv average). All the other RVOCs were not detected by the microFAST GC during the course of the sampling period.

Figure 14 displays the average RVOC concentrations in air collected on the sorbent tube traps and analyzed by GC-TOFMS from Green Canyon. Air samples were collected from 18:23 to 00:55 for the Green Canyon sampling trip.

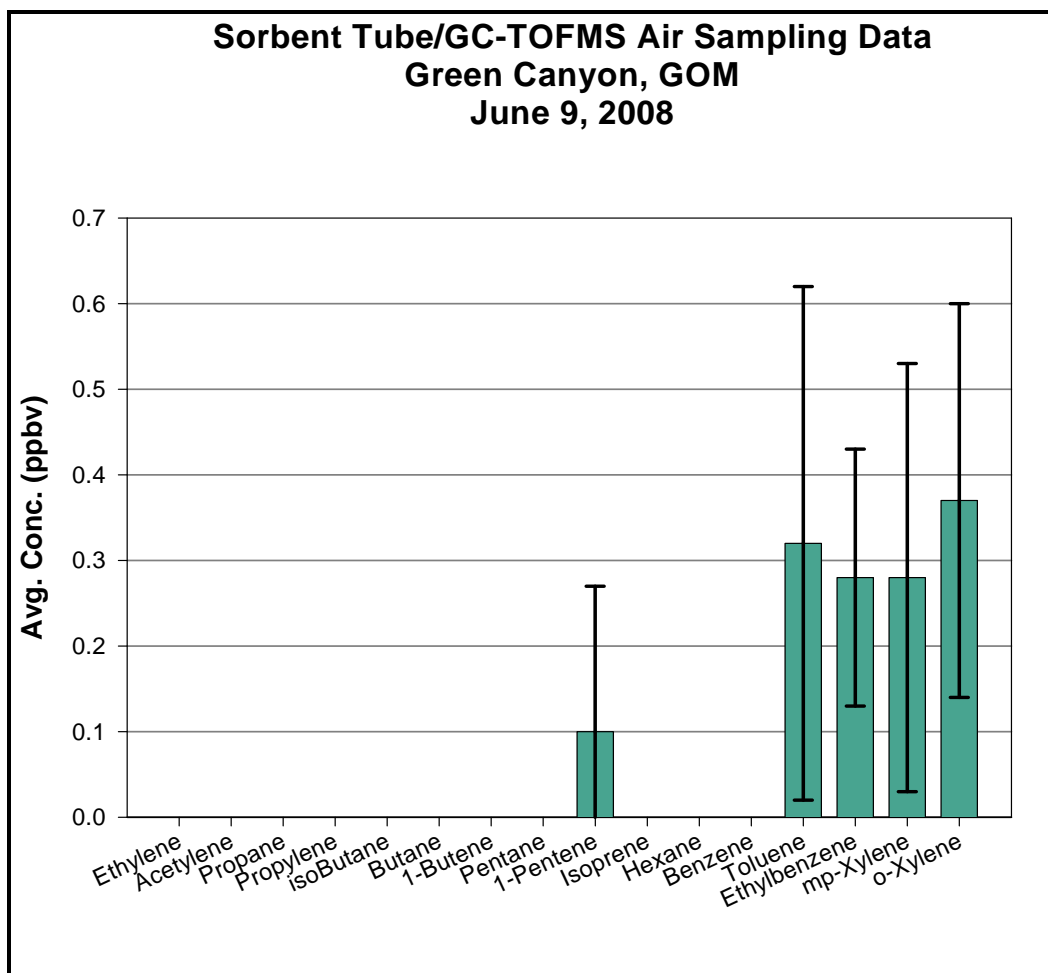


Figure 14. Average RVOC concentrations for sorbent tube/GC-TOFMS air samples, Green Canyon, GOM, June 2008. (n=22)

RVOCs detected in the sorbent tube trap/GC-TOFMS air samples were: 1-pentene (0.10 ppbv average); toluene (0.32 ppbv average); ethylbenzene (0.28 ppbv average); m+p-xylenes (0.28 ppbv average); and, o-xylene (0.37 ppbv average). RVOCs under the 0.1 ppbv detection limit were ethylene, acetylene, propane, propylene, iso-butane, butane, 1-butene, and benzene. Pentane, isoprene, and hexane were not detected in any of the air samples collected during this sampling trip.

Figure 15 shows the average RVOC concentrations, pmol/L, in the purged water samples collected on the sorbent tube traps and analyzed by GC-TOFMS from Green Canyon. Water

samples were collected at 18:23, 20:55, 21:45, and 23:01. The concentrations of RVOCs over the course of this sampling trip in the water samples are given in Appendix C.

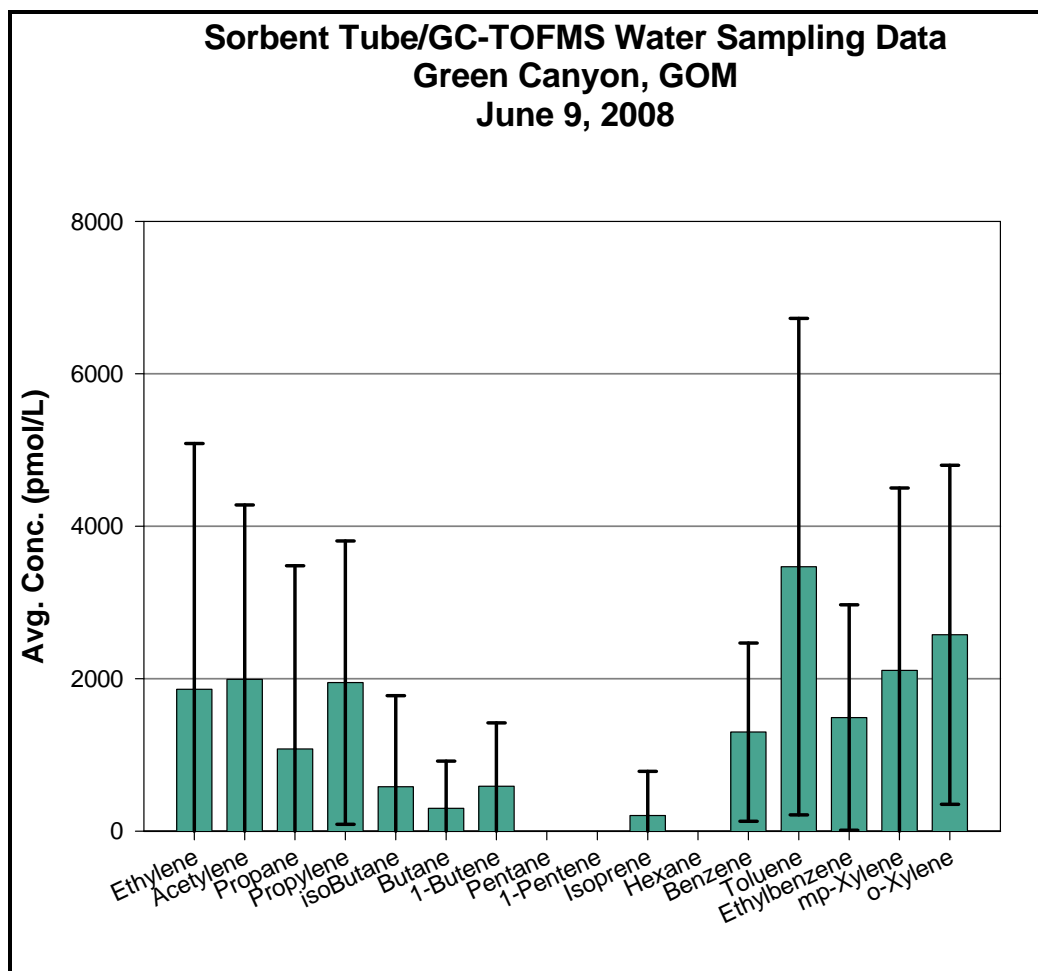


Figure 15. Average RVOC concentrations for sorbent tube/GC-TOFMS water samples, Green Canyon, GOM, June 2008. (n=8)

The majority of the target RVOCs were detected in the purged water samples using the sorbent tube trap/GC-TOFMS methodology. Hexane was detected in one of the sorbent tubes, but the average hexane concentration was below the detection limit of 100 pmol/L. Pentane and 1-pentene were not detected in the water samples throughout the course of this sampling trip. Differences between the number of analytes detected in the air versus (5 out of 16 RVOCs) the water (12 out of 16 RVOCs) can be attributed to slight changes in wind velocities or directions. The air concentration of 1-pentene is right at the detection limits of the sorbent tube/GC-TOFMS detection limit and has a high standard deviation which may explain why 1-pentene was not detected in the water. Many of the RVOCs detected in the water samples were detected in the air samples but the air concentrations when averaged were below the detection limit.

It should be noted that the analyte list for the GC-TOFMS methodology is slightly different than all the previous field validation trips. This is a result of a new standard mixture that was ordered prior to this sampling trip to Green Canyon. The new standard was a premixed “ozone

precursors” gas mixture prepared by the vendor. None of the target analytes were excluded from the standard; but, the standard did include a few additional air quality analytes like acetylene, iso-butane, and isoprene. A new standard was necessary due to the lapse in time between the last field validation trip in October of 2007 and the trip to Green Canyon in June of 2008.

As previously stated in the methodology section, four sorbent tubes were qualitatively analyzed for semivolatile organic compounds (SVOCs). Two water samples and two air samples were randomly selected and analyzed using thermal desorption and GC/MS scanning methodology with library confirmation to get an idea of what other compounds were in each matrix sampled. These analyses were purely lagniappe. Some of the SVOCs present in the samples are listed in Table 9, in no particular order, for the air and water samples.

Table 9
SVOC Qualitative Results for Select Air and Water
Sorbent Tube Trap Samples from Green Canyon

SVOCs RESULTS	
Air Samples: (Tube S/N#: A4595 & A4570)	Water Samples: (Tube S/N#: A4614 & A5574)
Hexanal	Nonanal
Octanal	Decanal
Nonanal	Hexadecane
Decanal	Heptadecane
	Butylated Hydroxytoluene
	1-Chloroundecane
	1-Chlorododecane

3.6 NET FLUX OF RVOCs AT AIR-WATER INTERFACE

Net flux estimations of the target RVOCs were determined for air and water samples collected during the Green Canyon, GOM field validation trip on June 9, 2008. Net flux estimations generated from data having large standard error typically produces results which are generalized and not site specific. Table 10 presents an estimation of concentrations of the project target analytes in marine air and seawater in the Green Canyon area of the Northern GOM. As previously stated in the field validation section of this report (2.5), water samples were only collected during the one off-shore field validation trip to Green Canyon. Concentrations of atmospheric RVOCs ranged from an average of 0.10 to 0.34 ppbv \pm 0.13. Several of the RVOC compounds were not detected. The average seawater concentrations ranged from non-detect to 3500 pmol/L.

The calculated average fluxes for samples taken in the Northern Gulf of Mexico are displayed in Table 11. The flux ranged from 20 nmol m⁻² day⁻¹ for isobutene to 1000 nmol m⁻² day⁻¹ for o-xylene, assuming the concentration of the individual components in the marine atmosphere were zero.

Table 10

RVOC Concentrations in Marine Air and Seawater from Green Canyon, Northern GOM

Compound	MW (g mol ⁻¹)	Henry's Law Constant, K _H (mol kg ⁻¹ atm ⁻¹)	Air (ppbv)	Seawater (pmol l ⁻¹)
Ethylene	28	2.28E-01	bdl	1900
Acetylene	26	4.00E-02	bdl	2000
Propane	44	1.40E-03	bdl	1100
Propylene	42	4.80E-03	bdl	2000
isoButane	58	8.40E-04	bdl	580
Butane	58	1.10E-03	bdl	300
1-Butene	56	4.00E-04	bdl	590
Pentane	72	7.80E-04	nd	nd
1-Pentene	70	2.50E-03	0.10	nd
Isoprene	68	2.70E-02	nd	210
Hexane	86	7.60E-04	nd	bdl
Benzene	78	1.80E-01	bdl	1300
Toluene	92	1.60E-01	0.32	3500
Ethylbenzene	106	1.20E-01	0.28	1500
m+p-Xylene	106	1.50E-01	0.28	2100
o-Xylene	106	1.90E-01	0.37	2600

bdl = below detection limit nd = non-detect

Table 11

Estimation of RVOC Flux from Green Canyon, Northern GOM

Compound	Molar Volume, V _m (cm ³ mol ⁻¹)	Diffusion Coefficient, D (cm ² s ⁻¹)	Schmidt Number, Sc (dimensionless)	Liquid Phase Transfer Velocity, k _L (m s ⁻¹)	Flux (nmol m ⁻² day ⁻¹)
Ethylene	41	1.7E-05	4.9E+02	5.0E-06	-
Acetylene	41	1.7E-05	4.9E+02	5.0E-06	-
Propane	66	1.3E-05	6.4E+02	4.4E-06	-
Propylene	62	1.4E-05	6.2E+02	4.5E-06	-
isoButane	86	1.1E-05	7.6E+02	4.0E-06	-
Butane	86	1.1E-05	7.6E+02	4.0E-06	-
1-Butene	82	1.2E-05	7.3E+02	4.1E-06	-
Pentane	107	9.9E-06	8.6E+02	3.8E-06	-
1-Pentene	103	1.0E-05	8.4E+02	3.8E-06	-
Isoprene	99	1.0E-05	8.2E+02	3.9E-06	90
Hexane	127	8.9E-06	9.5E+02	3.6E-06	-
Benzene	91	1.1E-05	7.8E+02	4.0E-06	-
Toluene	111	9.7E-06	8.8E+02	3.7E-06	1100
Ethylbenzene	132	8.8E-06	9.7E+02	3.6E-06	450
m+p-Xylene	132	8.8E-06	9.7E+02	3.6E-06	640
o-Xylene	132	8.8E-06	9.7E+02	3.6E-06	770

Values that were looked up for the flux calculations include the molecular weight of the analytes and the Henry's Law constants (K_H). The air and seawater concentrations were taken from the Green Canyon sampling trip data. The Schmidt number, liquid phase transfer velocity and flux were calculated using the molar volume and diffusion coefficient values given in Hayduk and Laudi (1974).

4.0 DISCUSSION

The main goal of this project was to develop and evaluate analytical methodology that could be used to estimate geogenic and biogenic sources of RVOCs coming from OCS areas of the Northern Gulf of Mexico. The process of accurately estimating OCS flux is extremely difficult since the water area is so large, and the possible natural sources are so variable (seeps, algal blooms, geogenic emissions, etc). Our secondary object focused on developing quantitative analytical capability to collect and analyze a large number of air and water samples across typical GOM areas during a variety of meteorological conditions. In order for this to be feasible, we also wanted to use readily accessible sampling platforms such as small fishing vessels rather than the large and expensive offshore research vessels. Therefore, much of the project focused on a twofold approach of using on-site analytical instrumentation for analysis of the primary RVOCs backed up with collection of concurrent samples in absorbent traps followed by GC-TOFMS analysis done in a conventional laboratory setting.

The microFAST GC data from five field validation trips shows that ethylene and hexane/isoprene dominated the RVOC profile due to the fact that these RVOCs were detected at three out of five field validation trips. Furthermore, the majority of the targeted RVOCs were detected above the detection limits at least one time out of five field validation sampling trips. The exceptions were propylene, pentane, and 1-hexene; these RVOCs were not detected above the detection limit at any of the five sampling locations. Butane was detected at two of the five validation trips; and, ethane, propane, 1-butene, 1-pentene, benzene, toluene, and the xylenes were detected at one of the five sampling locations. Ambient air samples taken by the on-site microFAST GC during the off-shore sampling trip to Green Canyon was dominated by hexane/isoprene and the alkyl benzenes.

The sorbent tube trap/GC-TOFMS data from four field validation trips also shows that almost all the targeted RVOCs were detected, above detection limits, at each sampling event. Propane, propylene, butane, 1-butene, pentane, hexane, benzene, 1-hexene, toluene, and ethylbenzene were detected at three out of four sampling events. 1-pentene and m+p-xylenes were detected at two of four sampling events, and o-xylene was detected during one sampling event. Ambient air samples collected on the sorbent tube traps during the off-shore sampling trip to Green Canyon were also dominated by the alkyl benzenes. The purged water samples contained all the targeted RVOCs except pentane and 1-pentene. The average hexane concentrations in the purged water sample were below the detection limits of 100 pmol/L. Of the targeted RVOCs for the off-shore sampling trip to Green Canyon, the ambient air and water samples were mutually dominated by alkyl benzenes.

The alkyl benzenes (benzene, toluene, ethylbenzene, m+p-xylenes, and o-xylenes, or BTEX) were detected at two of the five sampling trips by the on-site microFAST GC and four of the four sorbent tube sampling trips. BTEX can be indicative of fossil fuel combustion exhaust and other anthropogenic sources. On the other hand, BTEX compounds can be indicative of petrogenic sources and since they were detected in the air and in the water 80 miles offshore in the Green Canyon area of the Gulf, a well known seep area (Beukelaer et al. 2003; Kennicutt et al. 1988; MacDonald et al. 2002; Mitchell et al. 1999) they may have originated from natural petroleum or gas seeps.

Ethylene (ethene) and isoprene are two of the RVOCs detected by either the microFAST GC or the sorbent tube traps that have biogenic sources. Ethylene and isoprene are two of the more reactive RVOCs studied in this project. Ethylene is a metabolic product of microorganisms; plays a role in plant growth and development; and can be produced by plants under stress (Riemer et al 2000; Broadgate et al. 2004). Ethylene could also be formed from anaerobic reductions of petrogenic ethane by microorganisms. Ethylene is not a compound found in oil; however, detection of ethylene gas can indicate the presence of petroleum near fault lines (Carney et al. 1996; Jones and Burtell 1996; Jones et al. 2000). Isoprene stems from photosynthetic organisms in the ocean such as phytoplankton and several species of seaweed (Broadgate et al. 2004; Buzcu and Fraser 2006; Derwent 1999). Isoprene is species, temperature, and light dependent (Broadgate et al. 2004; Hagerman et al. 1997). The Green Canyon field validation cruise was performed in the evening (sampling started at 6:30 pm) so that the contribution of biogenic RVOCs (e.g. isoprene) would be lower than RVOCs that were emanating from the natural seeps in the area. Isoprene was detected with the sorbent tubes and the microFAST GC; however, the concentration decreased as the evening progressed.

It is important to point out that the microFAST GC was configured to be more sensitive for the detection of the very light RVOC compounds, like ethane and ethylene, and was less sensitive to the larger RVOC compounds like BTEX. Hexane and isoprene co-eluted in the microFAST GC system as did the xylenes. Conversely, the sorbent tube/GC-TOFMS system could resolve hexane and isoprene and the xylenes into the m+p-xylene and o-xylene. The sorbent tube/GC-TOFMS system could not detect ethane most likely due to ethane breakthrough when collecting the air samples on the sorbent tubes.

The primary focus for the on-site and sorbent tube trap analyses was the detection of RVOCs. However, two sorbent tube traps from air sampling and two sorbent tube traps from the purging of water samples in the Green Canyon sampling area were analyzed for SVOCs (semi-volatile) in addition to the RVOC (volatile) targets. These analyses were done in scan mode (qualitative) on a GC/MS system to check for unexpected compounds that could have an impact on air quality or that could be used to determine the source of possible volatile organic compounds (such as petroleum contamination). Both water samples contained very low levels of a number of compounds that appeared to be of biogenic origin or from very low level contamination with food additive/skin care products (in spite of extreme efforts to prevent contamination from the handling of water samples during collection and sparging). There was no evidence in the two water samples of any of the semivolatile components commonly found in petroleum. Likewise, the two air samples analyzed for semivolatile compounds contained a number of straight chain aldehydes from C₇ to C₁₀ at very low concentrations. There was no evidence of any petroleum compounds in these two air samples.

The variability in the analytical results of this study is related to two things: a non-homogeneous mixture of RVOCs moving through the water column and into the air; and, the reactivity of the target RVOC compounds with hydroxyl radicals, NO_x, and ozone. The fact that some RVOCs were detected in spikes at some point during each sampling trip indicates that the instrumentation was working correctly and that the variation was a naturally occurring event. This may be attributed to the fact that RVOCs are not homogeneously dispersed in the water column which

results in a non-homogenous mixture in the air, or “patchiness”. Patches of RVOCs were detected at different times throughout the sampling periods but these patches were often averaged out especially if a large number of samples were collected for that day, resulting in averages that were below the detection limit. RVOCs such as ethylene, propylene, and isoprene are short-lived because they are more reactive compounds. Their concentrations may be low; however, due to their reactivities these compounds are very important in terms of the production of low-level ozone (Bonsang and Lambert 1985; Bonsang et al. 1988; Bonsang and Boissard 1999; Derwent 1999; Sillman 1999). This is not to say that the other target analytes of this study are not important; they just have lower reaction potentials. Saturated alkanes (e.g. ethane, propane) are generally detected at higher concentrations compared to alkenes due to lower reaction potentials (Carter 1994). The light alkanes are associated with geogenic sources of petroleum. Higher saturated alkane concentrations can translate into air quality problems when they reach NO_x rich urban environments. The longer-lived RVOCs emitted from the sea surface typically are not directly photolyzed by solar radiation in the lower troposphere often due to the fact that NO_x concentrations are limited in remote areas compared to urban NO_x concentrations. Ozone increases with increasing RVOC concentrations in a NO_x saturated environment; therefore, RVOCs with lower reaction potentials represent a tropospheric ozone forming potential that can be realized when they are transported to an environment containing higher levels of NO_x (Sillman 1999).

The data from this project is comparable to the numerous other research projects cited in this report and is evidence of the importance of RVOCs from marine environments. This project, along with similarly related projects, shows that the ultimate impact on nearby urban areas is likely a function of not only the quantity of RVOCs emitted into the atmosphere, but also by their composition. The detection of the various alkyl benzenes, especially toluene and the xylenes, and the highly reactive olefins, ethylene, propylene, and isoprene, was anticipated prior to project method development. As a result, the analytical methodologies and instrumentation was optimized for a full range of RVOCs. All of these RVOCs were detected at one point or another during the field validation trips. Since the majority of the field validation trips were near-shore monitoring, it is tricky to deduce marine source RVOCs from anthropogenic and continental sources of RVOCs. Every effort was made to make sure wind directions were optimum for detecting RVOCs coming from the GOM; however, wind directions and speeds can briefly change which could result in plumes from sources other than the GOM.

If RVOCs are assumed to be in equilibrium between the seawater and the air boundary layer above it, their concentration in the seawater should be equivalent to the product of Henry’s Law constant (Table 10) and the partial pressure of the specific compound in the atmosphere. The average products ($P_{\text{compd}} \times K_H$) for the individual RVOCs within the seawater exceeded the equilibrium product concentrations, indicating a net flux of RVOCs from the seawater into the atmosphere. Results from the Green Canyon sampling trip in the Northern GOM indicate the flux between the seawater and air boundary layers are comparable to those of previous studies (Marse and Tsoflis 2001, Milne et al. 1995, and Sauer 1980). The aromatic RVOCs (e.g. BTEX range) were 2-3 times higher than anticipated, but may have been influenced by elevated levels of observed vessel traffic near the sampling transect. Atmospheric RVOC concentrations cannot be fully explained by the flux from naturally-occurring biogenic sources (e.g. marine organisms and oil seeps) within the seawaters of the Northern Gulf of Mexico. Therefore, the

concentrations of RVOCs in the marine atmosphere are more than likely affected by anthropogenic sources (e.g. marine transport) and subsequent long-range transport of RVOC compounds.

Analytical results of the air and water samples from the Green Canyon sampling trip indicated a large standard deviation among the individual gas components. The large standard deviation implies a wide, naturally occurring RVOC distribution throughout the sampling area, but actual analyses indicate localization of some individual components within the Northern GOM. Given both biogenic and anthropogenic source contributions for the individual compounds and the patchiness of detectable quantities, extrapolation of these few flux rates to give estimates of Northern GOM marine RVOC inputs to the atmosphere requires further investigation.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Information regarding the impact of marine RVOCs has benefited over the last several years from an increase in field and laboratory research and air quality databases. However, even with an increase in research regarding marine RVOCs, it is still difficult to concisely estimate their impact. In general, this project proved to be much more difficult than originally anticipated, and was much more expensive to implement. On the other hand, this project demonstrates the ability to detect low part per billion levels of RVOCs, from compounds as volatile as ethane and ethylene to the less volatile BTEX compounds, with a relatively large number of both on-site analyses as well as conventional laboratory-based analyses. Furthermore, it demonstrates the capacity of analyzing a relatively large number of air and water samples that are needed to accurately estimate flux from the OCS area. The results of this study show that the day-to-day variations in RVOC concentrations are quite large, which emphasizes the importance of non-homogeneous mixtures of RVOCs being released from the surface waters resulting in localized plumes of RVOCs from the GOM in addition to the individual reactivity of each RVOC species.

In conclusion, this project has established three overall concepts:

- 1.) The analytical methodology used for this project produced comparable data to other similar research cited in this report. The analytical methodologies and instrumentation used for this project are relatively cost-effective in comparison to using more complex sampling strategies (e.g. collection of air samples by airplane). This project demonstrates the ability to readily go into the field with sophisticated quantitative analytical equipment and perform on-site analyses of RVOCs at low part per billion levels. The on-site analyses were confirmed by conventional laboratory-based analytical methods and in general, there was good agreement between field analytical results and those produced in the laboratory. An important lesson learned in the process of doing field analyses was the need to have a suitable sampling platform that adequately protects the field equipment from salt water and the other offshore elements. For the offshore sampling expeditions (e.g. Green Canyon), the sampling platform must be stable and protective enough for both the staff and equipment, as well as being free of contamination from engine exhaust. Perhaps the use of suitable offshore production platforms as stable sampling locations should be considered in future analytical efforts.
- 2.) There is a need for standardized, cost-effective air and water monitoring for RVOCs from the GOM. This would require a multi-agency and industry effort to accomplish a true estimation of RVOC inputs from the GOM. As always, the cost of such a large effort is problematic. The literature has numerous examples of research cruises that use on-board laboratories for detecting organic compounds in vast ocean areas around the world. However, these cruises are very expensive and, in general, result in collection of a relatively small number of samples and resulting data points. This sparse data is then extrapolated over entire ocean areas. While this process may work to give a global overview of inputs of naturally produced RVOCs, it is difficult

to directly correlate this information for estimating regional impact of OCS activities on urban ozone formation in Texas and Louisiana. Furthermore, many different detection techniques are utilized in the literature making it hard to determine which methodology is the best for the cost. The monitoring approach of this project is very cost effective relative to the use of a large research vessel collecting a relatively few samples at a very expensive total expedition cost. In an effort to truly characterize RVOC flux from the GOM, consideration should be given to the use of strategically placed monitoring instrumentation on fixed offshore structures such as oil platforms and the use of field analytical instrumentation in small movable sampling vessels for monitoring known oil and natural gas seeps in the GOM. The same field analytical instrumentation could be used for near-shore monitoring to determine what RVOCs are reaching land from the GOM to correlate the platform monitoring and small vessel monitoring to air quality problems in urban coastal areas. A multi-agency effort and industry cooperation would greatly enhance confidence in the analytical results, decrease assumptions and large uncertainties inherent in RVOC modeling efforts, and would allow for an extensive monitoring network.

- 3.) Estimating RVOC flux from the GOM requires a very large number of air and water samples and instrumentation with very low detection limits. RVOC flux was calculated for only six water samples which clearly is not enough samples for the size of the GOM. However, the dual instrument sampling strategy of this project could easily result in a sufficient sample number for estimating flux. This project uses a field gas chromatograph, the microFAST GC, equipped with dual columns and dual flame ionization detector as the primary analytical device for on-site RVOC analyses in conjunction with concurrent, conformational samples that are trapped on sorbent tubes and returned to the laboratory for GC-TOFMS analyses. The microFAST GC has detection limits in the low part per billion levels but was subject to instrumental drift near the limits of detection. This drift was further complicated by operation in a field environment that is not controlled in terms of temperature, humidity, power, and operational utilities. Optimum control conditions are only available in laboratory settings. The GC-TOFMS has RVOC detection limits in the low part per trillion levels; however, loss of some of the RVOCs during the time after collection up to GC-TOFMS analysis occurs regardless of proper sample handling and storage requirements. In general, estimating RVOC flux is very complex, not only in terms of low RVOC detection limits and a large sample size, but in terms of determining the effect of water column mixing and upwells on RVOCs from the GOM.

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APPENDIX A:
MICROFAST GC
AIR SAMPLE DATA TABLES

Grand Isle, Louisiana
August 20-22, 2007

ANALYTES:													
8/20/2007 Sample ID:	Ethane ppbv	Ethylene ppbv	Propane ppbv	Propylene ppbv	Butane ppbv	1-Butene ppbv	Pentane ppbv	1-Pentene ppbv	Hexane/ Isoprene ppbv	Benzene ppbv	1-Hexene ppbv	Toluene ppbv	Xylenes ppbv
070820-004	nd	33	12	4.6	4.0	nd	nd	nd	nd	bdl	nd	bdl	bdl
070820-005	nd	nd	7.9	bdl	2.2	3.3	4.4	nd	nd	bdl	nd	bdl	bdl
070820-006	9.6	34	5.4	3.1	4.7	4.8	nd	nd	11	bdl	nd	bdl	bdl
070820-007	nd	nd	4.5	1.4	3.1	nd	nd	nd	9.5	bdl	nd	bdl	bdl
070820-008	nd	22	3.4	bdl	3.5	nd	nd	nd	6.1	bdl	nd	bdl	bdl
070820-009	nd	36	6.6	2.4	4.3	nd	4.6	nd	7.5	bdl	nd	bdl	bdl
070820-010	nd	nd	2.8	bdl	2.9	nd	nd	nd	12	bdl	nd	bdl	bdl
8/21/2007 Sample ID:	Ethane ppbv	Ethylene ppbv	Propane ppbv	Propylene ppbv	Butane ppbv	1-Butene ppbv	Pentane ppbv	1-Pentene ppbv	Hexane/ Isoprene ppbv	Benzene ppbv	1-Hexene ppbv	Toluene ppbv	Xylenes ppbv
070821-004	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070821-005	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070821-006	nd	nd	1.7	nd	3.4	nd	nd	3.6	nd	bdl	nd	bdl	bdl
070821-007	nd	9.9	1.1	nd	1.9	nd	nd	nd	nd	bdl	nd	bdl	bdl
070821-008	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070821-009	nd	nd	nd	nd	nd	nd	nd	3.8	nd	bdl	nd	bdl	bdl
070821-010	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070821-011	nd	nd	1.3	nd	nd	nd	nd	4.7	nd	bdl	nd	bdl	bdl
070821-012	nd	nd	nd	nd	nd	nd	nd	5.0	nd	bdl	nd	bdl	bdl
070821-013	nd	13	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070821-014	nd	12	nd	bdl	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070821-015	2.1	9.6	nd	nd	nd	nd	nd	3.7	nd	bdl	nd	bdl	bdl
070821-016	5.6	nd	2.4	nd	2.7	nd	nd	nd	nd	bdl	nd	bdl	bdl
070821-017	nd	nd	nd	nd	nd	nd	nd	4.1	nd	bdl	nd	bdl	bdl
070821-022	nd	nd	nd	nd	nd	nd	nd	3.8	nd	bdl	nd	bdl	bdl
070821-023	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	nd
070821-024	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	nd
8/22/2007 Sample ID:	Ethane ppbv	Ethylene ppbv	Propane ppbv	Propylene ppbv	Butane ppbv	1-Butene ppbv	Pentane ppbv	1-Pentene ppbv	Hexane/ Isoprene ppbv	Benzene ppbv	1-Hexene ppbv	Toluene ppbv	Xylenes ppbv
070822-006	nd	nd	nd	nd	nd	nd	nd	4.0	nd	bdl	nd	bdl	bdl
070822-007	nd	8.9	nd	nd	nd	nd	nd	4.1	nd	bdl	nd	bdl	bdl
070822-008	1.6	8.9	nd	nd	3.1	nd	nd	4.1	nd	bdl	nd	bdl	bdl
070822-009	17	16	4.0	nd	3.1	nd	nd	nd	nd	bdl	nd	bdl	bdl
070822-010	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070822-011	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070822-012	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070822-013	nd	nd	nd	nd	nd	nd	nd	3.5	nd	bdl	nd	bdl	nd
070822-014	nd	13	nd	nd	nd	nd	nd	3.9	nd	bdl	nd	bdl	nd
070822-015	nd	nd	nd	nd	nd	nd	nd	3.9	nd	bdl	nd	bdl	bdl
070822-019	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	nd
070822-020	nd	14	nd	nd	nd	nd	nd	3.9	nd	bdl	nd	bdl	nd
TOTAL =	36	230	53	13	39	8.1	9.0	56	46	6.6	nd	4.5	3.9
AVERAGE =	1.0	6.4	1.5	bdl	1.1	bdl	bdl	1.6	1.3	bdl	nd	bdl	bdl
STDEV =	3.3	10	2.8	bdl	1.6	bdl	bdl	2.0	3.3	bdl	nd	bdl	bdl

bdl = below detection limits

nd = non-detect

Cameron, Louisiana
September 5-6, 2007

ANALYTES:													
9/5/2007 Sample ID:	Ethane ppbv	Ethylene ppbv	Propane ppbv	Propylene ppbv	Butane ppbv	1-Butene ppbv	Pentane ppbv	1-Pentene ppbv	Hexane/ Isoprene ppbv	Benzene ppbv	1-Hexene ppbv	Toluene ppbv	Xylenes ppbv
070905-005	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070905-006	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070905-007	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070905-008	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070905-009	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070905-010	nd	nd	nd	nd	nd	nd	nd	3.8	nd	bdl	nd	bdl	bdl
070905-011	nd	nd	nd	nd	2.8	nd	nd	nd	nd	bdl	nd	bdl	bdl
070905-012	nd	nd	4.9	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070905-018	13	nd	4.8	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070905-019	14	34	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070905-020	nd	nd	nd	nd	2.7	nd	nd	4.1	nd	bdl	nd	bdl	bdl
070905-021	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
9/6/2007 Sample ID:	Ethane ppbv	Ethylene ppbv	Propane ppbv	Propylene ppbv	Butane ppbv	1-Butene ppbv	Pentane ppbv	1-Pentene ppbv	Hexane/ Isoprene ppbv	Benzene ppbv	1-Hexene ppbv	Toluene ppbv	Xylenes ppbv
070906-003	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070906-004	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070906-005	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	nd	bdl
070906-006	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	nd	bdl
070906-007	nd	nd	nd	nd	nd	nd	nd	3.9	nd	bdl	nd	bdl	bdl
070906-008	nd	nd	nd	nd	nd	nd	nd	4.1	nd	bdl	nd	bdl	bdl
070906-009	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070906-010	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl	nd	bdl	bdl
070906-011	nd	nd	nd	nd	1.9	nd	nd	3.9	nd	bdl	nd	bdl	bdl
070906-012	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070906-013	nd	8.6	nd	nd	nd	nd	nd	nd	2.8	bdl	nd	bdl	nd
070906-014	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	nd
070906-015	nd	8.9	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070906-016	nd	8.9	nd	1.6	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
070906-017	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	nd
070906-018	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	nd
070906-020	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
TOTAL =	27	60	10	1.6	7.3	nd	nd	20	3.3	4.3	nd	1.9	2.6
AVERAGE =	bdl	2.1	bdl	bdl	bdl	nd	nd	bdl	bdl	bdl	nd	bdl	bdl
STDEV =	bdl	6.6	bdl	bdl	bdl	nd	nd	bdl	bdl	bdl	nd	bdl	bdl

bdl = below detection limits

nd = non-detect

Port Fourchon, Louisiana
September 17, 2007

ANALYTES:													
9/17/2007	Ethane	Ethylene	Propane	Propylene	Butane	1-Butene	Pentane	1-Pentene	Hexane/ Isoprene	Benzene	1-Hexene	Toluene	Xylenes
Sample ID:	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>
070917-012	nd	nd	nd	1.6	14	8.9	nd	nd	9.5	bdl	nd	nd	bdl
070917-013	nd	nd	nd	nd	11	5.4	nd	nd	8.0	bdl	nd	bdl	bdl
070917-014	nd	nd	nd	nd	8.0	4.9	nd	nd	9.3	nd	nd	bdl	nd
070917-015	nd	nd	nd	bdl	10	6.5	nd	nd	6.8	bdl	nd	nd	bdl
070917-016	5.0	16	1.5	nd	11	7.1	nd	nd	10	bdl	nd	bdl	bdl
070917-017	nd	nd	nd	nd	9.7	7.1	nd	nd	10	bdl	nd	bdl	nd
070917-018	nd	nd	nd	bdl	9.6	5.6	nd	nd	nd	bdl	nd	nd	nd
TOTAL =	5.0	16	1.5	2.7	74	45	nd	nd	54	bdl	nd	bdl	bdl
SITE AVG =	bdl	2.4	bdl	bdl	11	6.5	nd	nd	7.7	bdl	nd	bdl	bdl
STDEV =	bdl	6.2	bdl	bdl	1.9	1.3	nd	nd	3.6	bdl	nd	bdl	bdl

bdl = below detection limits

nd = non-detect

Port Fourchon, Louisiana

October 1, 2007

10/1/2007 Sample ID:	ANALYTES:												
	Ethane ppbv	Ethylene ppbv	Propane ppbv	Propylene ppbv	Butane ppbv	1-Butene ppbv	Pentane ppbv	1-Pentene ppbv	Hexane/ Isoprene ppbv	Benzene ppbv	1-Hexene ppbv	Toluene ppbv	Xylenes ppbv
071001-011	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	3.3
071001-012	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl	nd	bdl	3.1
071001-013	nd	nd	nd	nd	nd	nd	nd	nd	nd	3.6	nd	1.8	3.0
071001-014	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.6
071001-015	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.4	nd	bdl	2.4
071001-016	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.5	nd	bdl	2.5
071001-017	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.1	nd	bdl	2.3
071001-018	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.6	nd	1.1	2.2
071001-019	nd	nd	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1.8	nd	1.1	2.3
071001-021	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.0	nd	1.0	2.0
071001-022	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.2	nd	1.2	2.0
071001-023	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.3	nd	1.0	1.9
071001-024	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.0	nd	1.1	1.8
071001-025	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.0	nd	1.1	1.7
071001-026	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.2	nd	1.1	1.8
071001-027	nd	nd	nd	nd	nd	nd	nd	bdl	nd	2.9	nd	1.6	1.8
071001-028	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.6	nd	1.3	1.7
071001-029	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.2	nd	1.1	1.5
071001-034	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	3.6	9.0
071001-035	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.6	nd	1.7	1.6
071001-036	nd	nd	nd	nd	nd	nd	nd	bdl	nd	2.3	nd	1.6	1.5
071001-037	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.1	nd	1.8	1.6
071001-038	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.9	nd	1.8	1.6
071001-039	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.6	nd	1.6	1.5
071001-040	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.9	nd	1.8	1.5
071001-041	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.6	nd	1.6	1.4
071001-042	nd	nd	nd	nd	nd	nd	nd	bdl	nd	2.0	nd	1.7	1.4
071001-043	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.6	nd	1.7	1.2
071001-044	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.6	nd	1.6	1.3
071001-047	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.2	nd	2.0	1.1
071001-048	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.6	nd	1.8	1.0
071001-049	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.9	nd	1.9	1.2
071001-050	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.6	nd	1.6	1.0
071001-051	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.6	nd	1.7	1.0
071001-052	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.8	nd	1.8	bdl
071001-053	nd	nd	nd	nd	nd	nd	nd	bdl	nd	2.0	nd	2.0	bdl
071001-054	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.8	nd	1.9	bdl
071001-055	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.9	nd	2.0	bdl

Port Fourchon, LA (continued)

October 2, 2007

10/2/2007	Ethane	Ethylene	Propane	Propylene	Butane	1-Butene	Pentane	1-Pentene	Hexane/ Isoprene	Benzene	1-Hexene	Toluene	Xylenes
Sample ID:	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>
071002-018	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	6.1	4.1
071002-019	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	3.6	2.4
071002-020	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.4	bdl
071002-021	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.0	bdl
071002-022	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.2	bdl
071002-023	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.1	bdl
071002-024	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.2	bdl
071002-025	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071002-026	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.1	bdl
071002-027	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071002-028	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071002-029	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071002-030	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071002-031	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071002-032	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.0	bdl
071002-033	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071002-034	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.3	bdl
071002-035	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071002-037	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.7	bdl
071002-038	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.6	bdl
071002-040	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.3	bdl
071002-041	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.2	bdl
071002-042	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.1	bdl
071002-043	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.0	bdl
071002-044	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.1	bdl

Port Fourchon, LA (continued)

October 3 & 4, 2007

10/3/2007 Sample ID:	Ethane ppbv	Ethylene ppbv	Propane ppbv	Propylene ppbv	Butane ppbv	1-Butene ppbv	Pentane ppbv	1-Pentene ppbv	Hexane/ Isoprene ppbv	Benzene ppbv	1-Hexene ppbv	Toluene ppbv	Xylenes ppbv
071003-007	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.2
071003-008	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	1.6
071003-009	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.0
071003-010	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071003-011	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	1.3
071003-012	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	nd	nd	1.0
071003-013	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl
071003-014	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl
071003-015	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl
071003-016	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl
071003-017	nd	nd	nd	nd	nd	nd	bdl	nd	nd	nd	nd	bdl	1.2
071003-020	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	1.0
071003-021	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl
071003-022	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	nd	bdl	bdl
071003-023	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl
071003-024	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl
071003-025	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.9	nd	bdl	bdl
071003-026	nd	nd	nd	nd	nd	nd	nd	bdl	nd	nd	nd	nd	bdl
071003-027	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl
071003-028	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.4	nd	bdl	bdl
071003-029	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.1	nd	bdl	bdl
071003-030	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.1	nd	1.1	1.5
071003-031	nd	nd	nd	nd	nd	nd	nd	bdl	nd	nd	nd	bdl	bdl
071003-032	nd	nd	nd	nd	nd	nd	nd	bdl	nd	nd	nd	nd	bdl
071003-033	nd	nd	nd	nd	nd	nd	nd	bdl	nd	nd	nd	nd	bdl
071003-034	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071003-035	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl
071003-036	nd	nd	nd	nd	nd	nd	nd	bdl	nd	nd	nd	nd	bdl
071003-037	nd	nd	nd	nd	nd	nd	nd	bdl	nd	1.3	nd	bdl	bdl
071003-038	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl
071003-039	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	nd	nd	bdl
071003-042	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071003-043	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.1	nd	bdl	bdl
071003-044	nd	nd	nd	nd	nd	nd	nd	bdl	nd	nd	nd	nd	bdl
071003-045	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	bdl
071003-046	nd	nd	nd	nd	bdl	nd	nd	bdl	nd	nd	nd	bdl	bdl
071003-047	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071003-048	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	bdl
071003-049	nd	nd	nd	nd	nd	nd	nd	bdl	nd	bdl	nd	nd	bdl
071003-050	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	nd
071003-051	nd	nd	nd	nd	bdl	nd	nd	nd	nd	bdl	nd	bdl	bdl
10/4/2007 Sample ID:	Ethane ppbv	Ethylene ppbv	Propane ppbv	Propylene ppbv	Butane ppbv	1-Butene ppbv	Pentane ppbv	1-Pentene ppbv	Hexane/ Isoprene ppbv	Benzene ppbv	1-Hexene ppbv	Toluene ppbv	Xylenes ppbv
071004-006	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.4	nd	bdl	bdl
071004-007	nd	nd	nd	nd	nd	nd	nd	nd	bdl	2.8	nd	1.4	bdl
071004-008	bdl	nd	nd	nd	nd	nd	nd	nd	bdl	2.8	nd	1.2	bdl
071004-010	bdl	nd	nd	nd	nd	nd	nd	nd	nd	1.8	nd	1.1	nd
071004-011	1.2	bdl	nd	nd	nd	nd	nd	nd	nd	2.1	nd	1.8	bdl
071004-012	bdl	bdl	nd	nd	nd	nd	nd	nd	nd	1.7	nd	1.1	nd
071004-013	bdl	nd	nd	nd	nd	nd	nd	nd	nd	2.4	nd	1.1	nd
071004-014	bdl	nd	nd	nd	nd	nd	nd	nd	nd	1.5	nd	bdl	nd
TOTAL =	4.7	1.0	0.1	0.1	nd	0.1	0.4	3.2	1.7	88	nd	106	116
AVERAGE =	bdl	bdl	bdl	bdl	nd	bdl	bdl	bdl	bdl	bdl	nd	bdl	1.0
STDEV =	bdl	bdl	bdl	bdl	nd	bdl	bdl	bdl	bdl	bdl	nd	bdl	1.1

bdl = below detection limits

nd = non-detect

Green Canyon, GOM

June 9, 2008

ANALYTES:													
6/9/2008 Sample ID:	Ethane ppbv	Ethylene ppbv	Propane ppbv	Propylene ppbv	Butane ppbv	1-Butene ppbv	Pentane ppbv	1-Pentene ppbv	Hexane/ Isoprene ppbv	Benzene ppbv	1-Hexene ppbv	Toluene ppbv	Xylenes ppbv
080609-007	nd	nd	nd	nd	nd	nd	nd	nd	52	20	nd	18	58
080609-008	nd	nd	nd	nd	nd	nd	nd	nd	17	9.0	nd	38	12
080609-009	nd	nd	nd	nd	nd	nd	nd	nd	13	12	nd	32	7.0
080609-011	nd	nd	nd	nd	nd	nd	nd	nd	20	8.0	nd	19	7.0
080609-017	nd	nd	nd	nd	nd	nd	nd	nd	13	8.0	nd	16	6.0
080609-018	nd	nd	nd	nd	nd	nd	nd	nd	12	6.0	nd	21	6.0
080609-019	nd	nd	nd	nd	nd	nd	nd	nd	11	8.0	nd	22	5.0
080609-020	nd	nd	nd	nd	nd	nd	nd	nd	7.0	5.0	nd	20	4.0
080609-021	nd	nd	nd	nd	nd	nd	nd	nd	10	5.0	nd	12	3.0
080609-022	nd	nd	nd	nd	nd	nd	nd	nd	5.0	4.0	nd	11	3.0
080609-023	nd	nd	nd	nd	nd	nd	nd	nd	5.0	4.0	nd	13	5.0
080609-024	nd	nd	nd	nd	nd	nd	nd	nd	10	6.0	nd	21	7.0
080609-032	nd	nd	nd	nd	nd	nd	nd	nd	7.0	10	nd	8.0	14
080609-034	nd	nd	nd	nd	nd	nd	nd	nd	6.0	5.0	nd	10	6.0
080609-035	nd	nd	nd	nd	nd	nd	nd	nd	5.0	4.0	nd	8.0	3.0
080609-036	nd	nd	nd	nd	nd	nd	nd	nd	6.0	7.0	nd	8.0	3.0
080609-037	nd	nd	nd	nd	nd	nd	nd	nd	6.0	7.0	nd	13	5.0
080609-038	nd	nd	nd	nd	nd	nd	nd	nd	5.0	6.0	nd	16	6.0
080609-039	nd	nd	nd	nd	nd	nd	nd	nd	6.0	6.0	nd	18	11
080609-041	nd	nd	nd	nd	nd	nd	nd	nd	6.0	6.0	nd	8.0	5.0
080609-042	nd	nd	nd	nd	nd	nd	nd	nd	5.0	7.0	nd	11	6.0
080609-043	nd	nd	nd	nd	nd	nd	nd	nd	5.0	7.0	nd	9.0	6.0
080609-044	nd	nd	nd	nd	nd	nd	nd	nd	6.0	6.0	nd	6.0	6.0
TOTAL =	nd	nd	nd	nd	nd	nd	nd	nd	238	166	nd	358	194
AVERAGE =	nd	nd	nd	nd	nd	nd	nd	nd	10	7.2	nd	16	8.4
STDEV =	nd	nd	nd	nd	nd	nd	nd	nd	10	3.4	nd	7.9	11

bdl = below detection limits

nd = non-detect

APPENDIX B:
SORBENT TUBE TRAP/GC-TOFMS
AIR SAMPLE DATA TABLES

Grand Isle, Louisiana
August 20-23, 2007

	ANALYTES:													
08/20/2007:	Ethylene	Propane	Propylene	Butane	1-Butene	Pentane	1-Pentene	Hexane	Benzene	1-Hexene	Toluene	Ethylbenzene	mp-Xylene	o-Xylene
Tube #:	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>
A5372	nd	0.47	0.51	0.79	0.35	nd	nd	nd	0.20	nd	0.60	nd	nd	nd
A5380	nd	1.2	1.8	1.2	0.91	nd	nd	1.9	0.48	nd	6.3	nd	nd	nd
A4836	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
A4751	nd	0.99	0.54	0.72	0.63	nd	nd	1.7	0.38	nd	4.1	nd	nd	nd
A5567	nd	0.58	0.49	1.1	4.0	nd	nd	nd	0.19	0.40	0.71	nd	nd	nd
08/21/2007:	Ethylene	Propane	Propylene	Butane	1-Butene	Pentane	1-Pentene	Hexane	Benzene	1-Hexene	Toluene	Ethylbenzene	mp-Xylene	o-Xylene
Tube #:	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>
A5438	nd	0.15	0.42	1.9	0.55	nd	nd	nd	0.31	nd	1.7	nd	nd	nd
A4572	nd	0.65	0.75	0.76	1.5	nd	nd	1.5	0.27	nd	16	nd	nd	nd
A4531	nd	0.73	1.3	0.94	2.9	nd	nd	0.70	0.21	0.40	34	nd	0.33	nd
A4618	nd	1.4	1.4	0.82	0.48	1.4	nd	4.6	0.82	0.20	2.8	nd	nd	nd
A5272	nd	0.46	0.91	0.93	2.0	nd	nd	nd	0.42	0.42	81	nd	nd	nd
08/22/2007:	Ethylene	Propane	Propylene	Butane	1-Butene	Pentane	1-Pentene	Hexane	Benzene	1-Hexene	Toluene	Ethylbenzene	mp-Xylene	o-Xylene
Tube #:	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>
A5121	nd	0.69	0.54	0.42	0.40	nd	nd	1.4	0.32	nd	1.3	nd	nd	nd
A4581	nd	1.8	1.9	0.73	0.60	1.3	nd	2.1	0.26	nd	2.1	nd	nd	nd
A5444	nd	nd	1.4	0.64	0.51	1.6	nd	13	0.73	nd	2.1	nd	nd	nd
A5574	nd	0.71	0.68	0.37	0.39	nd	nd	nd	0.20	nd	0.87	nd	nd	nd
A5458	nd	0.45	0.39	1.2	0.70	nd	nd	0.75	0.28	nd	20	nd	nd	nd
A4622	nd	0.79	1.6	0.64	3.5	0.81	nd	4.6	0.38	0.37	14	nd	nd	nd
A5363	nd	nd	0.51	0.56	0.28	2.8	nd	18	3.6	0.35	nd	21	nd	0.29
A5347	nd	0.50	0.54	0.84	0.46	nd	nd	1.8	0.32	nd	3.3	nd	nd	nd
A5246	nd	nd	0.67	0.60	0.51	1.1	nd	2.9	0.69	nd	2.1	nd	nd	nd
08/23/2007:	Ethylene	Propane	Propylene	Butane	1-Butene	Pentane	1-Pentene	Hexane	Benzene	1-Hexene	Toluene	Ethylbenzene	mp-Xylene	o-Xylene
Tube #:	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>	<u>ppbv</u>
A5399	nd	nd	0.49	0.34	0.23	nd	nd	1.5	0.20	nd	15	nd	nd	nd
A5356	nd	0.68	0.40	0.48	0.40	nd	nd	nd	nd	nd	2.1	nd	nd	nd
A5691	nd	4.6	1.3	2.6	3.5	5.7	nd	15	1.2	1.1	337	nd	0.25	nd
A5357	nd	0.56	0.57	0.65	0.41	1.5	nd	2.0	0.25	nd	38	nd	nd	nd
A5431	nd	nd	0.63	nd	0.43	nd	nd	nd	0.17	nd	44	nd	nd	nd
A5537	nd	3.5	1.4	2.0	2.5	3.4	nd	16	1.1	0.29	329	nd	nd	nd
TOTAL =	nd	21	21	21	28	20	nd	88	13	3.5	958	21	0.6	0.3
AVERAGE =	nd	0.83	0.84	0.85	1.1	0.78	nd	3.5	0.52	0.14	38	0.82	bdl	bdl
STDEV =	nd	1.1	0.50	0.59	1.2	1.4	nd	5.5	0.71	0.25	91	4.1	bdl	bdl

bdl = below detection limits

nd = non-detect

Cameron, Louisiana
September 5, 2007

09/05/2007: Tube #:	ANALYTES:													
	Ethylene ppbv	Propane ppbv	Propylene ppbv	Butane ppbv	1-Butene ppbv	Pentane ppbv	1-Pentene ppbv	Hexane ppbv	Benzene ppbv	1-Hexene ppbv	Toluene ppbv	Ethylbenzene ppbv	mp-Xylene ppbv	o-Xylene ppbv
A5458	nd	0.32	0.44	nd	0.22	nd	nd	nd	0.29	0.23	2.6	nd	nd	nd
A5246	nd	0.26	nd	nd	0.46	nd	nd	nd	0.39	nd	1.5	nd	nd	nd
A5444	nd	0.28	0.42	0.39	nd	nd	nd	nd	0.34	nd	4.2	nd	nd	nd
A4618	nd	0.41	0.23	0.22	0.19	nd	nd	nd	0.10	nd	0.93	nd	nd	nd
A5091	nd	0.74	0.59	0.45	0.41	nd	nd	1.3	0.57	nd	5.8	nd	nd	nd
A5272	nd	1.0	1.6	0.81	4.8	1.2	nd	4.0	0.60	0.38	35	0.36	0.56	nd
A4531	nd	0.64	1.9	1.1	8.6	nd	nd	3.2	0.44	0.47	8.5	0.49	0.97	0.73
A4581	nd	1.2	0.73	0.55	0.50	0.65	nd	nd	0.46	0.29	4.7	nd	nd	nd
A5431	nd	0.69	2.1	0.86	12	0.46	nd	2.7	0.52	0.57	24	0.40	0.64	0.41
A5510	nd	0.82	0.43	0.28	0.65	nd	nd	1.6	0.64	nd	6.2	nd	nd	nd
A5121	nd	1.2	2.4	0.92	9.1	nd	nd	2.3	0.47	0.67	16	nd	0.70	nd
A4572	nd	1.1	0.58	0.53	0.69	nd	nd	nd	0.44	0.35	1.7	nd	nd	nd
A3742	nd	0.31	0.60	0.31	0.87	nd	nd	nd	0.39	nd	2.9	nd	nd	nd
A5347	nd	0.96	0.43	0.37	0.32	nd	nd	nd	0.29	0.15	4.3	nd	nd	nd
A4836	nd	0.60	0.43	0.79	0.72	nd	nd	nd	0.30	nd	3.8	nd	nd	nd
A5363	nd	nd	0.20	0.32	0.26	nd	nd	nd	0.22	nd	1.2	nd	nd	nd
A4966	nd	nd	nd	0.45	0.36	0.57	nd	8.6	nd	0.20	0.18	0.93	nd	nd
A5438	nd	nd	0.38	0.31	nd	nd	nd	nd	0.15	nd	2.5	nd	nd	nd
A5372	nd	1.7	0.37	0.80	0.59	nd	nd	nd	0.39	0.81	1.3	nd	nd	nd
A5574	nd	1.9	0.81	1.0	0.99	1.1	nd	1.8	0.67	0.14	14	nd	0.20	nd
TOTAL =	nd	14	15	11	42	3.9	nd	26	7.7	4.3	142	2.2	3.1	1.1
AVERAGE =	nd	0.71	0.73	0.53	2.1	0.20	nd	1.3	0.38	0.21	7.1	0.11	0.15	bdl
STDEV =	nd	0.55	0.69	0.33	3.5	0.38	nd	2.2	0.18	0.25	8.9	0.25	0.30	bdl

bdl = below detection limits

nd = non-detect

Port Fourchon, Louisiana

September 17, 2007

ANALYTES:														
09/17/2007: Tube #:	Ethylene ppbv	Propane ppbv	Propylene ppbv	Butane ppbv	1-Butene ppbv	Pentane ppbv	1-Pentene ppbv	Hexane ppbv	Benzene ppbv	1-Hexene ppbv	Toluene ppbv	Ethylbenzene ppbv	mp-Xylene ppbv	o-Xylene ppbv
A4966	nd	1.1	0.86	1.7	0.17	nd	nd	1.6	0.43	8.6	bdl	nd	nd	nd
A5246	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
A4611	nd	nd	0.12	nd	1.7	nd	nd	nd	nd	nd	nd	nd	nd	nd
A4652	nd	nd	0.17	0.43	3.2	nd	0.43	nd	nd	nd	nd	nd	nd	nd
A5363	nd	nd	nd	0.14	3.5	nd	nd	nd	nd	nd	nd	nd	nd	nd
A4531	nd	nd	nd	nd	5.3	nd	nd	4.5	nd	nd	0.40	nd	nd	nd
A5438	nd	nd	0.18	0.25	6.3	nd	0.68	nd	nd	nd	nd	nd	nd	nd
A5510	nd	nd	0.26	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
A5361	nd	1.0	nd	0.16	nd	nd	1.1	1.6	nd	nd	nd	nd	nd	nd
A4575	nd	nd	0.21	0.43	nd	nd	1.2	nd	nd	nd	bdl	nd	nd	nd
A4756	nd	nd	0.25	0.81	nd	nd	nd	nd	0.07	nd	nd	nd	nd	nd
A5417	nd	nd	0.17	nd	nd	nd	0.71	nd	nd	0.23	nd	nd	nd	nd
A5177	nd	nd	0.08	0.26	nd	nd	0.87	nd	nd	nd	nd	nd	nd	nd
A4561	nd	nd	0.36	0.83	nd	nd	4.1	4.4	nd	1.2	nd	nd	nd	nd
A4738	nd	0.27	0.99	nd	nd	2.5	nd	nd	1.8	nd	nd	nd	nd	nd
A4910	nd	nd	0.24	0.35	3.9	nd	0.52	nd	nd	nd	0.15	nd	nd	nd
A5243	nd	nd	0.20	0.29	3.7	nd	nd	nd	nd	nd	nd	nd	nd	nd
A5347	nd	0.73	0.33	0.41	3.8	nd	1.6	1.7	nd	nd	0.19	nd	nd	nd
A4893	nd	nd	0.36	0.20	2.1	nd	0.95	nd	nd	nd	nd	nd	nd	nd
A4696	nd	nd	0.14	0.31	3.2	nd	0.97	nd	nd	0.56	nd	nd	nd	nd
A5537	nd	1.6	0.22	0.26	0.43	nd	nd	nd	nd	nd	nd	nd	nd	nd
A4838	nd	nd	nd	nd	0.71	nd	nd	nd	nd	nd	nd	nd	nd	nd
A5458	nd	nd	nd	nd	0.75	nd	nd	nd	nd	nd	nd	nd	nd	nd
A5356	nd	nd	0.19	0.24	1.1	nd	nd	nd	nd	nd	nd	nd	nd	nd
TOTAL =	nd	4.8	5.3	7.0	35	7.8	13	14	2.3	11	0.85	nd	nd	nd
AVERAGE =	nd	0.20	0.22	0.29	1.4	0.32	0.55	0.57	0.10	0.44	bdl	nd	nd	nd
STDEV =	nd	0.45	0.25	0.37	1.8	1.2	0.91	1.3	0.37	1.8	bdl	nd	nd	nd

bdl = below detection limits

nd = non-detect

Green Canyon, GOM

June 9, 2008

GREEN CANYON AIR SAMPLES

ANALYTES:																
06/09/2008: Tube #:	Ethylene ppbv	Acetylene ppbv	Propane ppbv	Propylene ppbv	isoButane ppbv	Butane ppbv	1-Butene ppbv	Pentane ppbv	1-Pentene ppbv	Isoprene ppbv	Hexane ppbv	Benzene ppbv	Toluene ppbv	Ethylbenzene ppbv	mp-Xylene ppbv	o-Xylene ppbv
A5399	nd	nd	nd	bdl	bdl	nd	nd	nd	nd	nd	nd	bdl	0.54	0.45	0.88	0.86
A4521	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	bdl	0.92	0.47	0.87	0.81
A4922	nd	bdl	nd	bdl	nd	bdl	nd	nd	nd	nd	nd	bdl	0.29	0.40	0.25	0.55
A5177	nd	nd	nd	nd	nd	nd	nd	nd	0.10	nd	nd	bdl	0.13	0.30	0.19	0.40
A5567	0.12	0.12	nd	0.16	nd	nd	bdl	nd	nd	nd	nd	bdl	0.18	0.38	0.24	0.54
A4966	nd	nd	nd	bdl	bdl	bdl	nd	nd	nd	nd	nd	bdl	0.59	0.30	0.53	0.51
A5121	0.17	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.10	0.16	0.10	0.23
A5361	nd	nd	nd	bdl	nd	nd	nd	nd	nd	nd	nd	nd	0.18	0.29	0.18	0.38
A4622	bdl	bdl	0.11	bdl	bdl	bdl	nd	nd	nd	nd	nd	bdl	0.48	0.51	0.34	0.33
A4751	0.12	nd	nd	nd	nd	nd	0.11	nd	nd	nd	nd	bdl	0.41	0.20	0.34	0.34
A4561	bdl	bdl	nd	nd	nd	nd	bdl	nd	nd	nd	nd	nd	0.17	0.19	0.12	0.26
A5417	bdl	nd	nd	nd	nd	nd	bdl	nd	0.40	nd	nd	bdl	0.12	nd	nd	nd
A5363	bdl	nd	0.12	bdl	bdl	bdl	nd	nd	0.15	nd	nd	nd	0.12	0.31	0.20	0.44
A5458	bdl	nd	bdl	nd	nd	nd	0.21	nd	bdl	nd	nd	nd	bdl	nd	nd	nd
A4575	bdl	nd	nd	nd	nd	nd	nd	nd	0.62	nd	nd	bdl	0.15	0.46	0.32	0.32
A4738	bdl	nd	nd	bdl	bdl	bdl	bdl	nd	nd	nd	nd	0.11	0.16	0.25	0.16	0.35
A5246	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.13	0.22	0.15	0.32
A4618	nd	nd	nd	nd	nd	nd	bdl	nd	nd	nd	nd	bdl	1.0	0.38	0.24	0.52
A5091	nd	bdl	nd	nd	nd	nd	bdl	nd	0.19	nd	nd	nd	bdl	bdl	bdl	nd
A5431	nd	nd	nd	bdl	nd	nd	nd	nd	0.37	nd	nd	nd	0.18	0.20	0.13	0.28
A5243	bdl	nd	nd	bdl	nd	nd	bdl	nd	0.28	nd	nd	bdl	0.19	0.13	bdl	0.17
TOTAL =	0.66	0.28	0.34	0.60	0.19	0.14	0.52	nd	2.2	nd	nd	0.46	6.4	6.0	6.0	7.9
AVERAGE =	bdl	bdl	bdl	bdl	bdl	bdl	bdl	nd	0.10	nd	nd	bdl	0.32	0.28	0.28	0.34
STDEV =	bdl	bdl	bdl	bdl	bdl	bdl	bdl	nd	0.17	nd	nd	bdl	0.30	0.15	0.25	0.23

bdl = below detection limits

nd = non-detect

APPENDIX C:
SORBENT TUBE TRAP/GC-TOFMS
WATER SAMPLE DATA TABLES

Green Canyon, GOM

June 9, 2008

GREEN CANYON WATER SAMPLES

ANALYTES:																
06/09/2008: Tube #:	Ethylene pmol/L	Acetylene pmol/L	Propane pmol/L	Propylene pmol/L	isoButane pmol/L	Butane pmol/L	1-Butene pmol/L	Pentane pmol/L	1-Pentene pmol/L	Isoprene pmol/L	Hexane pmol/L	Benzene pmol/L	Toluene pmol/L	Ethylbenzene pmol/L	mp-Xylene pmol/L	o-Xylene pmol/L
A4755	nd	nd	nd	1395	nd	nd	274	nd	nd	nd	nd	535	7696	2500	6332	4701
A4572	nd	2464	nd	2306	nd	664	692	nd	nd	nd	nd	581	8290	2309	4972	3801
A5390	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1718	2461	767	1569	3294
A4581	2857	nd	nd	2262	nd	nd	nd	nd	nd	1638	nd	4007	5504	3791	2429	5269
A5347	382	nd	nd	2063	351	nd	1965	nd	nd	nd	nd	766	806	nd	nd	nd
A4838	nd	3466	nd	1614	nd	nd	nd	nd	nd	nd	nd	1120	2225	2557	1564	3541
A5372	2328	4613	1816	nd	860	nd	nd	nd	nd	nd	580	1152	nd	nd	nd	nd
A5468	9312	5381	6809	5945	3441	1721	1782	nd	nd	nd	nd	512	760	nd	nd	nd
TOTAL =	14879	15924	8625	15586	4652	2385	4713	nd	nd	1638	580	10392	27742	11924	16866	20607
AVERAGE =	1860	1990	1078	1948	582	298	589	nd	nd	205	bdl	1299	3468	1490	2108	2576
STDEV =	3224	2287	2401	1860	1195	620	829	nd	nd	579	bdl	1169	3257	1479	2393	2224

bdl = below detection limits

nd = non-detect