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

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SPONSORING OCS REGION: Gulf of Mexico

APPLICABLE PLANNING AREA: Northern

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KEY WORDS: RVOC; reactive volatile organic compound; VOC; volatile organic compound; low-level ozone; air quality; hydrocarbons; microFAST GC; sorbent tube; thermal desorption; GC-TOFMS; gas chromatography; time of flight mass spectrometry; northern Gulf of Mexico; flux; net flux

BACKGROUND: 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). 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 (VOC's) and, in particular, the reactive volatile organic compounds (RVOC's) emitted in the gulf must be considered.

OBJECTIVES: This project is designed to be a pilot study of a methodology that may yield better estimates of geogenic and biogenic sources of RVOC's 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 RVOC's 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.

DESCRIPTION: 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 and 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. 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) offshore in the Green Canyon area.

Currently, the impact on the Gulf Coast environment of these natural emissions, 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 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 RVOC's to ozone formation potential depends not only on the amount of RVOC's in the air mass but also on the specific RVOC's present due to the fact that photochemical activity varies widely for individual RVOC's. Thus, a speciated characterization of RVOC's, including identification of highly reactive volatile organic compounds (HRVOC's) is necessary for creating an accurate estimate of the expected impact of natural GOM emissions on coastal urban centers.

Air sampling and analysis procedures were developed and validated for two different analytical instrument systems, the on-site microFAST GC and a lab based time-of-flight gas chromatograph 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 Northern GOM. The goal of the field validation trips was to establish sampling methodologies that could identify individual RVOC's in a large number of air samples and in water samples. The data can 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.

SIGNIFICANT CONCLUSIONS: This project demonstrates the ability to detect low part per billion levels of RVOC's, 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 potential capacity of analyzing a relatively large number of air and water samples that are needed to accurately estimate flux from the OCS area.

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 quantitative analytical equipment and perform on-site analyses of RVOC's.

STUDY RESULTS: Overall detection of RVOC's was highly variable from site to site and day to day for both instrument systems. The variability in the analytical results of this study is related to two things: a non-homogeneous mixture of RVOC's 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 microFAST GC data from five field validation trips shows that ethylene and hexane/isoprene dominated the RVOC profile due to the fact that these RVOC's were detected at three out of five field validation trips. Furthermore, the majority of the targeted RVOC's 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 RVOC's 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 was 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 RVOC's for the off-shore sampling trip to Green Canyon, the ambient air and water samples were mutually dominated by alkyl benzenes.

The data from this project is comparable to the numerous other research projects cited in this report and is evidence of the importance of RVOC's 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 RVOC's 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 RVOC's. All of these RVOC's were detected at one point or another during the field validation trips.

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 (Milne 1994 and Sauer 1980). If RVOC's are assumed to be in equilibrium between the seawater and air boundary layer above it, their concentration in the seawater should be equivalent to the product of Henry's Law constant and the partial pressure of the specific compound in the atmosphere. The average products (P_{cmpd} x K_H) for the individual RVOC's within the seawater exceeded the equilibrium product concentrations, indicating a net flux of RVOC's from the seawater into the atmosphere. 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.

STUDY PRODUCT: Overton, E.B; M.S. Miles; Ashton, B.M; and R.L. Wong. 2010. Determination of net flux of reactive volatile organic compounds at the air-water interface in the Gulf of Mexico. U.S. Dept. of the Interior, Bureau of Ocean Energy Management, Regulation and Enforcement, Gulf of Mexico OCS Region, New Orleans, LA. OCS Study BOEMRE 2010-043. 65 pp.

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