Geogenic Inputs to the Northern Gulf of Mexico Airshed

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ABSTRACT

Correlation between natural oil and gas seeps at the sea surface, and potential subsurface hydrocarbon reservoirs has driven interest in quantifying the frequency and abundance of hydrocarbon seeps. The subsequent discovery of abundant continental margin fluid seeps realized impacts to both oceanography and the atmospheric sciences. Emissions of volatile organic compounds (VOCs) generated by these unusual sources may be significant in the determination of ozone formation, as well as other air quality factors. The Minerals Mangement Service (MMS), an Interior Department agency, is currently conducting an emission inventory of the northern Gulf of Mexico (NGOM). The inventory will include the effects of geogenic inputs on the air quality of the surrounding airshed, with emphasis on the coastal counties. Methodology assumptions are discussed, including the results of field studies of fluid seep rates from around the globe. Calculated VOC emissions range from 987089 to 8478539 tons annually, averaging 26,000 tons per year for the study area.

INTRODUCTION

The Environmental Protection Agency (EPA) recently promulgated new, more stringent ambient air quality standards for ozone and is drafting regulations concerning regional haze. These regulations will require State agencies to perform modeling for ozone and regional haze for use in their State Implementation Plans. The new regulations require that the Gulf Coast States have air quality information for the year 2000 regarding Outer Continental Shelf (OCS) activities in the western Gulf of Mexico (west of 87º 30' West longitude) for input into their ozone and regional haze models. Toward this requirement, the MMS Gulf of Mexico (GOM) OCS Region has issued NTL No. 99-G15, directing lessees and operators of each affected OCS lease in the NGOM in to collect and report facility and equipment activity data during the period January 1, 2000, to December 31, 2000. The "Gulf-wide Offshore Activities Database System" (GOADS) uses a Microsoft Access© database designed to inventory all OCS emission-producing activities occurring in the study area during the designated time frame. Supplemental to the GOADS effort, other non-MMS regulated emissions source activity data such as tanker traffic, and commercial and recreational fishing vessel activities will be compiled. Natural VOC emissions from oil and gas seeps found prevalently along the NGOM continental slope will also be estimated. The activity data will be analyzed with other emissions information to provide a database capable of meeting the EPA ozone modeling requirements.

METHODOLOGY

Terminology

The following definitions will apply in this article:

- Volatile organic compounds have been defined by the EPA as "any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric chemical reactions" (40 CFR 51.100, February 3, 1992). Many organic compounds have been found to have "negligible photochemical reactivity," and with regard to ozone formation potential, are exempt from the strict definition of VOC. Included in this exemption category are methane, ethane, methylene chloride, methyl chloroform, and several classes of chlorofluorocarbons and perflurocarbons (AWMA, 1998).

- Total organic compounds (TOC) include all VOCs and all exempted organic compounds listed above, along with toxics, hazardous air pollutants (HAPs), aldehydes and semi-volatile compounds (AWMA, 1998).

- Reactive organic gases (ROG) are defined in this paper as precursors in forming ozone.

Geological Background

The geology of the continental slope is extremely diverse topographically and sedimentologically. The NGOM continental slope covers an area of approximately 500,000 km^2. The most complex area is the 120,000-km^2 Louisiana-Texas slope. Large volume influx of sediments during lowered sea level in the Tertiary (recent time to 65 million years ago) caused the deformation of the underlying Jurassic-age (145-200 million years ago) salt bodies (Coleman *et al*., 1989). Salt movement results in stresses and rapid sedimentation rates create compaction. These processes create the complex faulting patterns in the NGOM (Coleman *et al*., 1989). The faults act as conduits of fluid migration from the subsurface to the seafloor.

Different features on the seafloor characterize the flux of hydrocarbons. Mud volcanoes, mud mounds, gas hydrates, and chemosynthetic communities have all been associated with hydrocarbon seeps (Roberts, 1996 and Kennicutt *et al*., 1989). Gas hydrates are ice-like solids composed of water and methane gas. These structures are stable in regions of high pressure and low temperature, such as the deepwater Gulf of Mexico. Gas bubble streams have been observed in the vicinity of gas hydrates indicating that hydrates are both decomposing and forming in NGOM waters (Kennicutt *et al.,* 1989). Chemosynthetic species contain bacterial symbionts that utilize methane and hydrogen sulfide as their energy sources. Numerous chemosynthetic communities have been documented in areas of hydrocarbon seepage on the seafloor (Sassen *et al*., and Roberts *et al*., 1998).

As figure 1 illustrates, the deepwater (> 200m depth) NGOM has extensive areas of gas hydrates and chemosynthetic communities that are indicative of gas and liquid hydrocarbon flux to the seafloor. The fate of seep-source hydrocarbons is determined largely by the environmental conditions at the exit point. Seep hydrocarbons can be trapped as gas hydrates, biodegraded, or dissolved in the water column. Released hydrocarbons can also be transported to the sea surface, where the gas phase can volatilize into the atmosphere, and liquid hydrocarbons appear as slicks on the water surface.

Activity Data Estimation Methods

In general, highly variable spatial and temporal discharge rates characterize natural seep activity. Therefore, several assumptions are required to form practical estimates of their emissions. Activity data are estimated from measurements of a few individual seeps, which are extrapolated to encompass the entire study area.

Oil

The total volume contained in naturally occurring oil slicks can be assessed by employing a variety of methods, the most economical of which exploit hydrophobic phenomena and the differing refractive properties of oil and water. Visual observation has proven to be a reliable method of locating oil slick presence and extent. The greater surface tension of oil creates an area of glass-like smoothness in contrast to wind-rippled water. The use of modern remote sensing technology such as satellite imagery has made it possible to observe the global-scale presence of both natural and man-made oil slicks in real-time. MacDonald and others (1993 and 1998) have employed photography from NASA's space shuttle *Atlantis*, and thematic mapper images from the *Landsat* orbiter to track several large slicks in the Green Canyon area of the NGOM with successful results.

Gas

In shallow water (less than 200-meter depth), seep gases, consisting of methane, ethane, propane, butane, and longer chain hydrocarbons, can be directly measured as they rise through the water column as bubble streams and enter into the atmosphere at the sea surface. The Institute for Computational Earth System Science (ICESS) based at the University of California is currently using sonar surveys to map and quantify reactive organic gas (ROG) emission rates at Coal Oil Point in the Santa Barbara Channel, California. The ICESS findings have suggested that seep ROG emissions may be comparable to the total mobile source ROG emissions in Santa Barbara County (Washburn and Clark, 1998).

At this time, activity estimates for deepwater seeps have not been attempted. However, assuming a constant equilibrium concentration of dissolved gases in a large water parcel such as the NGOM, the total input of ROG from gas seeps into the water column must be equal to the total flux out of the system assumed to escape into the atmosphere. Transport aided by thermal mixing, continental upwellings, and loop and eddy currents, moves seep fluids to the air/sea interface, where evaporation of volatile gases into the atmosphere may occur. Vertical and horizontal currents, which are altered by several factors including bottom topography and thermal and saline stratification, can lengthen the residence time of ROG in the water column substantially (Current, 2001). Partial and total oxidation of ROG components may then occur via biological and chemical transformation, yielding relatively inert carbon dioxide.

Emission Factor Estimation Methods

Emission factors for total organic gases (TOGs) from seep oil and gas were based on the emission factors used in the "EIR/EIS Proposed ARCO Coal Oil Point Project Volume 1, Appendix 4 - Air Quality," 1986. The emission factors for liquid crude oil and unprocessed natural gas are 105 pounds per barrel and 48,648.65 pounds per million cubic feet, respectively. In reality, seep emission factors would vary among individual seeps, with an uncalculated standard deviation, but are assumed to be less than a factor of ten. To date, emission factors specific to NGOM seeps have not been developed. However, site-specific data are currently available, and a more rigorous analysis is under consideration by the MMS.

RESULTS

Emission Estimates

Oil

MacDonald *et al's* 1993 satellite imagery analysis of sea-surface slicks considered a 15,000 km^2 area of the NGOM, centered at 91.5° W, 27.5° N. The analysis estimated that approximately 120,000 barrels of oil (i.e. 5 million gallons or 19.1 million liters) found its way to the sea-surface annually. Employing the California Air Resources Board (CARB) emission factor of 105 pounds per barrel of oil results in annual emissions of approximately 6300 tons TOG for this small yet active area of the NGOM (Table 1).

Considering the entire GOM, estimates of total oil seepage rates have been calculated at 625 to 1,875 barrels per day, which translates into 2.5 to 6.9 x 10^5 barrels per year, or 9.6 to 28.7 million gallons annually (Mitchell *et al*, 2000). These values may appear staggering, especially considering the National Research Council's estimate of 150,000 tons, based on MacDonald *et al's* most recent work (NAS, 2001). Table 1 presents several estimates of NGOM and global seepage rates recently published by various investigators.

Gas

Rates of natural gas seepage have not been estimated for the NGOM, but may be substantial particularly from shallower seeps (< 200 meters). Based on ICESS's Coal Oil Point study, seepage estimates for an area the size of the NGOM continental slope range from x to y. Hornafius *et al* used sonar data to evaluate the same seep field in 1999, and estimated TOG emissions as 1.7 $\pm$ 0.3 x 105 m^3 per day, and non-methane hydrocarbons (NMHC) at 35 $\pm$ 7 tons per day.

CONCLUSIONS

Relevance to Air Quality Programs

Coincidentally, McDonald *et al's* study area of 15,000 km^2, about 6.7% of the area of the NGOM, emits approximately 6% of the MMS OCS VOC emission projection for the year 2009 (Ref.). Although the value of 6300 tons TOG cannot be extrapolated to the entire NGOM, the comparison does provide insight to the relevance of natural VOC emissions when addressing remote areas such as the offshore environment.

Geogenic ROG emissions are known ozone precursors. Tropospheric ozone is a modern environmental challenge in many areas of the developed world. The Gulf Coast currently has three ozone non-attainment areas: LaFourche Parish, Louisiana, the Beaumont-Port Arthur area (Jefferson County), and the Houston-Galveston-Brazoria area (Brazoria, Chambers, Fort Bend, and Galveston Counties) in Texas. In order to develop accurate ozone formation and dispersion modeling, accurate estimates of natural and anthropogenic VOC emissions are required.

Certain TOCs that are relatively inert as ozone precursors are nevertheless potent greenhouse gases. Methane (CH_4) has been implicated as a major contributor to global climate change. Positive feedback loops can increase the rate at which TOCs are released from the oceans into the atmosphere (Harvey, 1998).

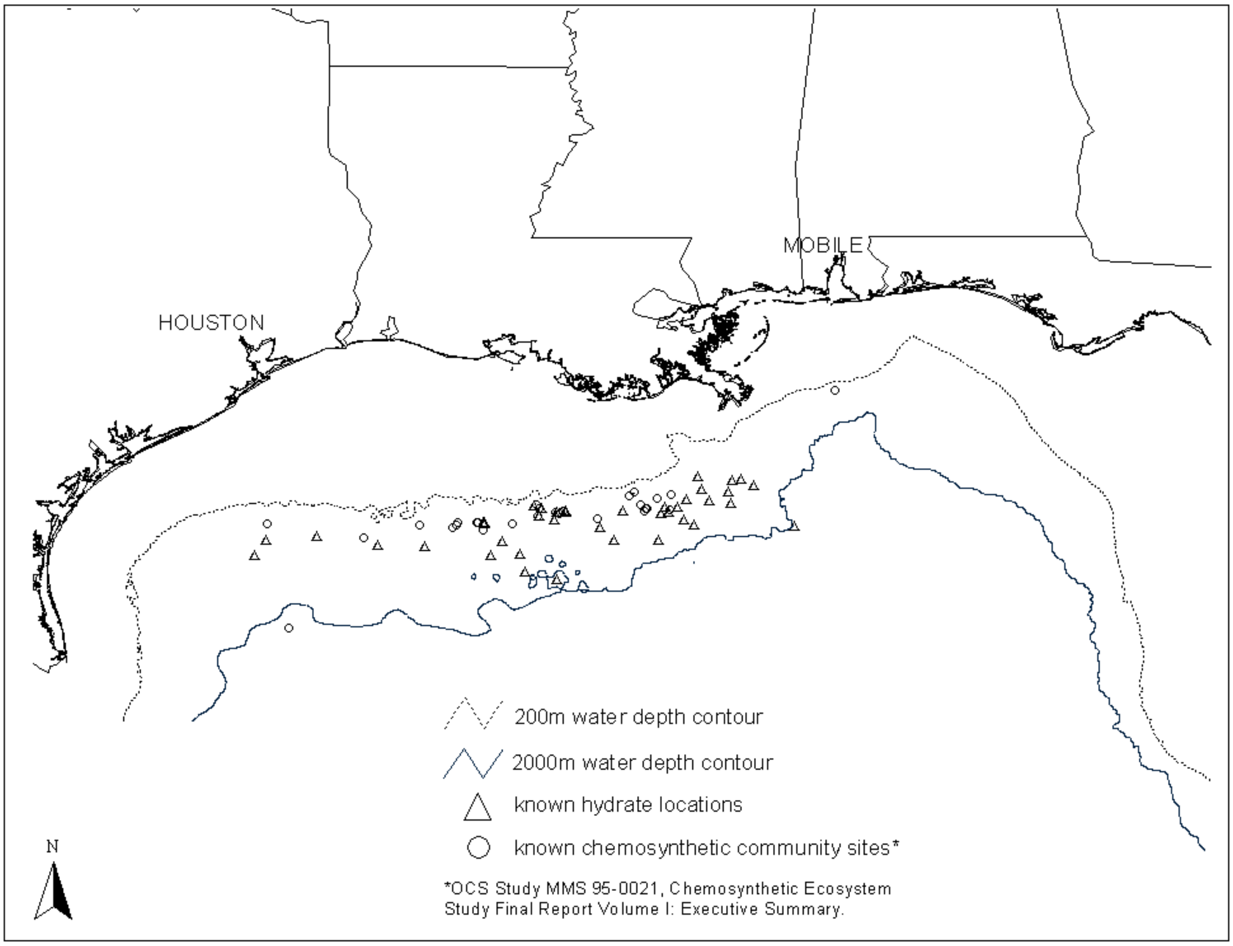

Figure 1: Location of known hydrate formations and chemosynthetic communities in the NGOM.

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KEY WORDS

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