Consolidated points and issues for discussion on the Hypoxia Advisory Panel Subgroup 1 Teleconference – 10-17-06

Hypoxia Advisory Panel Subgroup 1 - Characterization of the Causes of Hypoxia

Subgroup 1 Charge:

The development, persistence and areal extent of hypoxia is thought to result from interactions in physical, chemical and biological oceanographic processes along the northern Gulf continental shelf; and changes in the Mississippi River Basin that affect nutrient loads and fresh water flow.

A. Address the state-of-the-science and the importance of various processes in the formation of hypoxia in the Gulf of Mexico. These issues include:

i. increased volume or funneling of fresh water discharges from the Mississippi River;

ii. changes in hydrologic or geomorphic processes in the Gulf of Mexico and the Mississippi River Basin;

iii. increased nutrient loads due to coastal wetlands losses, upwelling or increased loadings from the Mississippi River Basin;

iv. increased stratification, and seasonal changes in magnitude and spatial distribution of stratification and nutrient concentrations in the Gulf;

v. temporal and spatial changes in nutrient limitation or co-limitation, for nitrogen or phosphorus, as significant factors in the development of the hypoxic zone;

vi. the implications of reduction of phosphorus or nitrogen without concomitant reduction of the other.

B. Comment on the state of the science for characterizing the onset, volume, extent and duration of the hypoxic zone.

In developing responses to assignments within the charge the Hypoxia Advisory Panel is considering the following:

Based on understanding of the current science,

- Are there summaries, conclusions, and recommendations presented in the 2000 Integrated Assessment that are not accurate or valid?
- What new findings are most relevant to this review and how do they alter our understanding of the causes of hypoxia?
- What are the strengths and limitations in scientific understanding of the issue?
- What scientific questions should be answered over the next five years?

Material Provided by Denis Gilbert and Don Wright

This material addresses but is not limited to the following parts of the charge: 1(A)(i) - the importance of increased volume or funneling of fresh water discharge from the Mississippi River, 1(A)(ii) - changes in hydrologic or geomorphic processes in the Gulf of Mexico and Mississippi Basin, and 1(A)(iv) - increased stratification, and seasonal changes in the magnitude and spatial distribution of stratification and nutrient concentrations in the Gulf.

Physical Background to Hypoxia: Some Initial Notes 2nd Draft

In the simplest of terms, hypoxic conditions arise because the consumption of oxygen exceeds the import of "new" oxygenated water. The oxygen balance in the bottom layer can be expressed at lowest order by

$$\frac{\partial O_2}{\partial t} = -u\frac{\partial O_2}{\partial x} - v\frac{\partial O_2}{\partial y} + K_z\frac{\partial^2 O_2}{\partial z^2} - \text{Respiration}$$

in which the left hand term represents the change with time, the first term on the right represents the horizontal advection by across shelf mean currents, u, the second term represents the horizontal advection by alongshore mean currents, v, the third term on the right represents vertical mixing (K_z is eddy viscosity) and the last term labeled "Respiration" is the non-conservative sink (i.e. consumption). The horizontal advection terms may reflect contributions from tides, wind stress, large-scale eddies or topographically trapped shelf waves. The last term is the one that relates most directly to organic matter mineralisation and must be understood in the context of the biogeochemical processes addressed by other sub-teams.

This sub team of subgroup 1 is focused on the physical oceanographic processes that govern the advective and vertical diffusive terms. Key physical factors that affect oxygen dynamics include buoyancy fluxes (which cause stratification that suppresses mixing), near-bed suspended sediment (which causes benthic stratification that also suppresses mixing), tidal and wind-driven currents (which are the sources of the shear that enhances mixing and are also responsible for advection) and waves (which enhance vertical mixing). A tentative outline along these lines might be the following:

1. Gradient Richardson number: (stratification/shear)
2. Buoyancy and Stratification on the Louisiana Shelf
   a) positive buoyancy in upper water column
   b) sediment-induced near-bed stratification
3. Tidal currents
4. Wind-driven circulation
5. Event-driven vertical mixing (e.g. by waves during hurricanes, internal tides, internal waves (including inertial oscillations))
6. Long-term averaged advection over the shelf

Some starter notes on these topics follow; this is not final text

1. The gradient Richardson number, Ri, expresses the ratio of turbulence suppression relative to shear production of turbulence via

$$\mathrm{Ri} = \frac{-\frac{g}{\rho}\frac{d\rho}{dz}}{\left(du/dz\right)^2} = \left(\frac{N}{\left(du/dz\right)}\right)^2 \quad .$$

When Ri > ¼, turbulence is strongly suppressed and vertical transport of oxygen from surface to bottom layers by turbulent mixing is unlikely to occur. At lowest order, scaling allows Ri to be estimated by

$$\mathrm{Ri} \approx \frac{-\frac{g}{\rho}\frac{\Delta\rho}{h}}{\left(U/h\right)^2} = \frac{\Delta\rho}{\rho}\frac{gh}{U^2}$$

where h is water depth, ρ is water density, Δρ is the density difference and U is the speed of the mean current.

2. The mouths of the Mississippi are highly stratified "salt wedge" estuaries during low and normal flows and the effluent issues onto the shelf as a discrete layer of fresh water that is spread westward in the surface layer. Total buoyancy fluxes are, of course, proportional to river discharge. This causes the turbulent-suppressing stratification of the upper water column that is strongly implicated in hypoxia. Over the Louisiana shelf, Δρ in the upper water column is large because of the fresh water discharge from the Mississippi River and U is typically small because of the low tide range and weak wind-driven circulation.

Stratification near the bed is also important on the Louisiana shelf and can also restrict the delivery of oxygen to the bed. In this case, however, Δρ is attributable to resuspended sediment and fluid mud rather than to freshwater input. To the west of the "birds foot", convergence of suspended sediment fluxes can lead to the formation of bottom layers of fluid mud on the order of 1-2 m thick that suppress vertical mixing (Wright et al., 1997; Friedrichs et al., 2000). In this case, the gradient Richardson number is determined by the gradient in suspended sediment concentration instead of salinity, i.e.

$$\mathrm{Ri} = \frac{-\frac{g}{\rho}\frac{\partial\rho}{\partial z}}{\left(\partial u/\partial z\right)^2} \cong gs\frac{(\partial c'/\partial z)}{(\partial u/\partial z)^2} \cong \frac{B}{|u|^2},$$

where c' is sediment volume concentration, s is sediment density relative to water density and B is the buoyancy anomaly within the turbid benthic layer of the thickness h' given by

$$B = gs\int_0^{h'} c'dz\ .$$

3. Tidal currents and tidal mixing over the Louisiana shelf are extremely weak because the tide range is only about 40 cm and the tides are diurnal. So the contribution of tides to the vertical exchange of oxygen is minimal (Reference on tidal mixing?).

4. The coastal physical oceanographic regime of the Louisiana shelf is presently scaled and constrained by the elongate "bird's foot" delta, which creates a barrier to east-west currents (Wiseman and Dinnel, 1988). By blocking along-isobath flow, this active delta lobe causes shelf circulation to be divided into two cells: one to the east and one to the west of the bird's foot (Smith and Jacobs, 2005). The most recent and comprehensive analysis of the shelf circulation in this region is that of Smith and Jacobs (2005) who assimilated extensive sets of current observational data with the governing dynamical shallow water equations. The Smith and Jacobs study assumes the rather simplistic situation of barotropic currents. More sophisticated models (e.g. Morey et al., 2003 and Zavala et al.,2003) take into account the baroclinic effects that typify the Louisiana shelf. The observations reported by Smith and Jacobs (2005) show that depth averaged flows to the west of bird's foot during spring and summer are weak and variable but generally set from west to east. Zavala et al. 2003 predict east to west near-coastal currents in all months but July. Stronger and more persistent flows from east to west prevail during autumn and winter.

5. There are some recent papers on hurricane induced mixing but I don't have them at my fingertips. We can get this. The paper by Sheremet and Stone (2003) shows that waves are attenuated by propagating over muddy bottom and this would presumably reduce mixing.

6. Literature search to be done.

Some References

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Material Provided by Tom Bianchi

Material addresses but is not limited to part 1(A)(iii) of the Charge: increased nutrient Loads due to coastal wetlands losses, upwelling or increased loadings from the MississippRiver Basin.

Bianchi Very Rough Outline for HAB: Linkages between Sediment Dynamics and hypoxia Events on the Louisiana Shelf

Hypoxia in northern GOM

Hypoxic-to-anoxic conditions (2-0 mg O_2 L^{-1}) occur in the bottom waters of the northern Gulf of Mexico during late spring and summer where the rate of oxygen consumption exceeds its rate of input from physical transport plus photosynthetic generation. Although consumption of oxygen in the water column via primarily oxic respiration is an important process, current data and models indicate that the loss of oxygen at and near the seafloor may be the most important sink leading to hypoxic and anoxic conditions in the overlying water in this region (Morse et al., unpublished). Rowe and Chapman (2002) have a proposed that processes related to hypoxia are different along a gradient stretching west from the delta (brown water), to green water, and finally to blue water. The presumption has been that the cause of hypoxia differs at each site: the brown water region is dominated by flocculating clay, green water is dominated by primary production enhanced by the nutrient load, and the blue water is controlled by stratification. So the driving forces here are: geochemical reactions driving hypoxia near the river mouth, biological production and respiration dominating farther from the mouth, and physical stratification controlling development of hypoxia distal to the river mouth.

The strong pycnocline that develops during the summer months on the Louisiana shelf west of the Mississippi River in the northern Gulf of Mexico (NGOM) inhibits vertical mixing and re-oxygenation of the bottom waters which results in hypoxia of bottom waters. Strong mixing from storms during the winter allows bottom water to be aerated frequently and precludes hypoxia during this time. Although these are the overarching factors driving the development and destruction of hypoxia in the NGOM, much variability in geochemical and physical processes over small temporal and spatial scales that appear to exert strong controls over the timing and location of hypoxia development. Time-series data have shown that the extent of hypoxia can vary over short timescales due to rapid changes (order of hours to days) in the position of the freshwater plume (from changes in local winds) and stratification (from the passage of atmospheric fronts) (DiMarco, et al., in press). Modeling results support these quick response times following forcing events (Hetland,in press).

Studies in the Gulf of Mexico have shown that aerobic respiration in the sediments is low during hypoxic events (Rowe et al., 2002); this suggests that anaerobic respiration, build up of reduced compounds and subsequent oxidation of these reduced species in the benthic boundary layer (BBL) and sediments may account for a large percentage of the

oxygen draw down in this area (Morse and Rowe, 1999). Unfortunately, the role of sediments in controlling hypoxia and currently not well understood.

General Background of Dynamics of RiOMars

River-dominated margins are dynamic regions that receive inputs of organic carbon (OC) derived from both terrestrial and marine sources. In these environments, the input of vascular plant-derived organic matter from land is significant (Hedges and Parker, 1976; Hedges and Ertel, 1982; Hedges, 1992), and marine primary productivity is high due to high nutrient inputs associated with riverine discharge (Turner and Rabalais, 1991; Redalje et al., 1994; Hedges and Keil, 1995). Major rivers (and associated deltaic environments) provide the dominant pathway for the input of terrestrial OC (TOC) to marine sediments and play a disproportionately important role in transporting terrestrial materials to the ocean. Approximately 60% of the total suspended matter and 66% of the total dissolved solids transported from the conterminous U.S. to the ocean is carried by the Mississippi (Presley et al. 1980), the largest river in North America. The importance of river dominated margins to global OC burial (Hedges and Kiel 1995) is indicative of the tremendous magnitude of material fluxes in these river-dominated regions (see also NSF RiOMar initiative: http://www.tulane.edu/~riomar). It has been estimated that 80% of the total OC preserved in marine sediments occurs in "terrigenous-deltaic" regions near river mouths (Romankevich, 1984; Berner, 1989). Once particulate OC (POC) is introduced by the river or fixed on the shelves, it is carried along the Louisiana shelf, decomposed, buried, or transported to deeper regions in the Gulf of Mexico. Based on coastal primary production estimates, riverine inputs and a limited number of seabed samples, earlier studies estimated that only 20-50% of the (OC) in coastal waters off the Mississippi is actually buried in Louisiana shelf sediments, and that <40% of the OC buried is of terrestrial origin Eadie et al., 1994; Trefry et al., 1994). There are two possible explanations for this observation: (1) Large amounts of TOC and marine OC (MOC) are being remineralized in shelf waters and sediments or (2) POC is transported off the shelf and buried in slope and Mississippi Canyon sediments. Understanding the transport and burial of organic matter on such a dynamic shelf is critical to in determining the benthic-pelagic linkages in hypoxia events. It is estimated that about 50% of the sediments delivered to this region are temporarily stored near the delta – with a large fraction transported along/across the shelf in the BBL [Corbett et al., 2004, 2006]. Winter fronts are most likely responsible for the resuspension and transport of sediments along- and off-shore the Louisiana coast (Allison et al., 2000; Corbett et al., 2004). More work is clearly needed to better understand the interactions between sediment transport, residence time of organic matter in surface sediments, and hypoxia events.

Like the Amazon delta, the seafloor along the LA shelf west of the Mississippi outlet is characterized by significant physical mixing (resuspension) producing a fluidized layer of sediments (mobile muds) that may have penetrated as deep as 8-9 cm in the winter season. Organic carbon of both terrestrial and marine origin, trapped within the surface mixed layer, will undergo significant biogeochemical decomposition mediated by microbial activity and fueled by additions of fresh planktonic material (co-metabolism;

Blair and Aller, 1995) prior to burial in the accumulation layer. Thus, the mixed layer works as a very efficient biogeochemical reactor and may lead to significant breakdown of organic carbon.

Biogeochemical Processes Linked with Hypoxia in Sediments

Studies in the Gulf of Mexico have shown that aerobic respiration in the sediments is low during hypoxic events (Rowe et al., 2002); this suggests that anaerobic respiration, build up of reduced compounds and subsequent oxidation of these reduced species in the BBL and sediments may account for a large percentage of the oxygen draw down in this area (Morse and Rowe, 1999). Other work found that the balance between the frequency of seabed disturbance, rate of geochemical reactions, and reactant concentrations work together to promote efficient remineralization in highly mobile muds near large river mouths (through redox cycling (McKee et al., 2004; Aller et al. ,2004; Chen et al., 2004, 2005). This frequent cycling of reduced and oxidized compounds is likely to have a profound effect on short-term oxygen consumption in the BBL, which could influence development of bottom hypoxia.

Dissolved sulfide concentrations are usually low to non-detectible near the sediment-water interface in Louisiana shelf sediments under oxic conditions as observed in this study and earlier work (e.g., Lin and Morse, 1992; Morse and Rowe, 1999). In fact, while sulfate reduction was shown to be active process in this region (14 to 16 mmol m^{-2} d^{-1}), resulting in the accumulation of substantial concentrations of total reduced inorganic sulfur (TRS), dissolved sulfide was not detectable (< 10 μM) in porewaters (Morse et al.,). This was likely the result of the high dissolved Fe^{2+} concentrations in the porewaters that limited dissolved sulfide via iron sulfide mineral formation. Low sulfide concentrations may be related to large patches of *Beggiatoa* spp. in this region (Larkin and Strohl, 1990). Filaments of the bacteria *Beggiatoa* spp. and other unidentified filamentous bacteria form on the surface of the sediments at oxygen levels as high as 1 mg l^{-1} but not higher (L. Duet, Q. Dortch, N. Rabalais, unpublished data). In fact, other work, which has detected H_2S in bottom waters, reports that the occurrence of anoxia and production of H_2S in bottom waters on this shelf are limited even though the continental shelf is seasonally hypoxic over a large area and oxygen concentrations are often below 0.5 mg l^{-1} (Rabalais and Turner 2006).

Most of the inorganic nitrogen in hypoxic bottom waters is present as nitrate, but there are sometimes significant amounts of ammonium. Denitrification rates in sediments from stations within the hypoxic zone ranged between 150 and 410 μmol N m^{-2} hr^{-1} (Childs et al. 2002, 2003). The highest rates were observed when bottom water oxygen concentrations were between 1 and 3 mg l^{-1}. Denitrification activity was significantly lower at stations where dissolved oxygen was lower than 1 mg l^{-1} or greater than 3 mg l^{-1}. Associated nutrient data indicated that the dominant form of nitrogen shifts from nitrate to ammonium as anoxia is approached (Rabalais and Turner 2006). Earlier field studies on the Louisiana shelf west of the Mississippi River (Lin and Morse, 1991; Morse and Berner, 1995; Rowe et al., 1995, 2002; Morse and Rowe, 1999; Morse unpublished data)

have been used to construct a diagenetic model for the response of sediment biogeochemistry to seasonal changes in the redox conditions of the overlying waters (e.g., Rabalais et al., 1994, 2002). The approach was to apply the diagenetic model of Eldridge and Morse (2000) largely derived from the earlier diagenetic models of Van Cappellen and Wang (1996) and Boudreau (1996). These models can be used to make better predictions of how the sediments over time will interface with hypoxia

Just an addition of some macrofaunal response info. here, I do have information on meiofaunal as well. The fish really show now well defined response at all. Despite the anoxic appearance of sediments and detection of hydrogen sulfide in overlying waters, there usually remain some surviving fauna, typically polychaetes of the genera *Magelona, Paraprionospio* or *Sigambra* or sipunculans (Rabalais et al. 2001), so that the sediments are not completely azoic. The hypoxia-affected infauna on the northern Gulf of Mexico is characterized by small, high abundance opportunistic species. *Paraprionospio pinnata* is common at all locations. *P. pinnata* is a highly fecund, multiple-spawning, ubiquitous member of the benthic macroinfauna of the northwestern Gulf of Mexico shelf (Mayfield, 1988).

I have not added anything here on the paleo-redox work since I believe Dan Conley is covering that, but I think it is still listed as my responsibility???

<u>Material Provided by Hans Paerl</u>

H. Paerl will develop a section on nutrient dynamics including nutrient limitation in various parts of the Gulf, temporal and spatial shifts between phosphorus and nitrogen limitation, and perhaps silicon, and the linkage between the period of maximum production and hypoxia. Dr. Pearl's section will address relevant parts of the charge: 1(A)(iii) - increased nutrient loads due to coastal wetlands losses, upwelling, or increased loads from the Mississippi River Basin, and 1(A)(v) - temporal and spatial changes in nutrient limitation or co-limitation, for nitrogen or phosphorus, as significant factors in the development of the hypoxic zone

Relevant questions

1. Spatially, what are the patterns of nutrient (N, P, Si) limitation in the N. GOM region affected by riverine discharge and hypoxia? Where and what is the evidence?

2. Temporally, what are the patterns of nutrient (N, P, Si) limitation in the N. GOM region affected by riverine discharge and hypoxia? Where and what is the evidence?

3. Are there seasonal shifts in these patterns, and are there documentable changes in these patterns on the multi-annual and decadal scale?

4. How does bioassay-determined nutrient limitation compare to nutrient limitation inferred from stoichiometric ratio relationships?

5. How do patterns of nutrient limitation determined by bioassays and inferred from stoichiometric relationships change in relation to riverine/wetland nutrient discharge?

6. How do episodic events (i.e. floods and droughts) impact 1-5 relative to more gradual multiannual trends?

7. How do the patterns in 1-6 relate to spatiotemporal patterns in primary production in the N. GOM?

8. Are there documentable linkages (in time and space) between trends in wetland loss, nutrient loading and limitation patterns?

9. What are the roles of upwelling compared to riverine and wetland nutrient inputs?

10. What are the impacts of nutrient limitation (and changes therein) on the composition and function of phytoplankton comprising the base of the food web?

11. What might the biogeochemical consequences of these changes be?

12. What are the potential relationships between these consequences and hypoxia dynamics in the N GOM?
13.

<u>Material Provided by Daniel Conley</u>

Last edited: 16 October 2006
Contributed by Daniel Conley

Historical changes in hypoxia and productivity in the Gulf of Mexico

There have been relatively few studies of historical changes in hypoxia and productivity in the northern Gulf of Mexico. However, all studies from dated sediment cores show consistent changes in proxies with time, although the timing and response varies depending upon the proxy studied. The pattern of change is concomitant with increased nutrient loading from the Mississippi River causing increasingly severe

hypoxia on the shelf. The published data are not sufficient to determine whether increases in the spatial extent of hypoxia has occurred with time.

Briefly, bacterial pigments characteristic of anoxygenic phototrophic sulfur bacteria have their highest concentrations between 1960 and the present (Chen et al. 2001). These bacteriopigments were not present prior to 1900. Further evidence is provided by algal pigments which show increases in the 1960s and their enhanced preservation probably also reflects enhanced preservation with hypoxia as well as nutrient-driven increases in production (Chen et al. 2001). In addition, Rabalais et al. (2004) report increases in algal pigment concentrations over time, with gradual changes from 1955 to 1970, followed by a steady increase to the late 1990s. Increases in pigment concentrations from one sediment core from west of the Atchafalya River outflow suggests that nutrient driven increases in production occurred later than in the Mississippi River Bight (Rabalais et al. 2004). There has been an increased accumulation of total organic carbon and biogenic silica in recent sediments near the mouth of the Mississippi River (Turner and Rabalais 1994; Turner et al. 2004), although the spatial and temporal variations observed between dated sediment cores are large.

Several studies have examined changes in the benthic foraminiferal community in dated sediment cores (Platon and Sen Gupta 2001; Osterman et al. 2005; Platon et al. 2005). Significant changes in the composition of the benthic foraminiferal community have occurred in the past century and several indicators, e.g. the PEB index (Osterman et al. 2005) and the A/P ratio – agglutinated to porcelaneous orders (Platon et al. 2005), indicate that increases in the intensity of hypoxic events have occurred over the past 50 years. Osterman et al. (2005) also show that several probable low oxygen events occurred in the past 180 years that are associated with high Mississippi River discharge rates, although the recent changes are more extreme than any that occurred in the past.

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Material Provided by Jim Sanders

This material addresses the following part of the charge: 1.(A)(vi) - Implications of reduction of phosphorus or nitrogen without concomitant reduction of the other)

1. Background aspects that will likely be covered by others, but need to be considered here:
   - Evidence for limitation by N, P, or Si—temporal, spatial attributes to limiting factors
   - How increases in nutrient inputs over time have affected limitation patterns
   - How changing nutrient ratios (particularly Si with N or P) affect primary production and producers

2. Other topics:
   - Discussion of the 2004 white paper, and work since that time
   - Implications of N reduction alone
   - Implications of P reduction alone
   - Feasibility of reduction plans that incorporate both
   - Science questions that remain to be answered