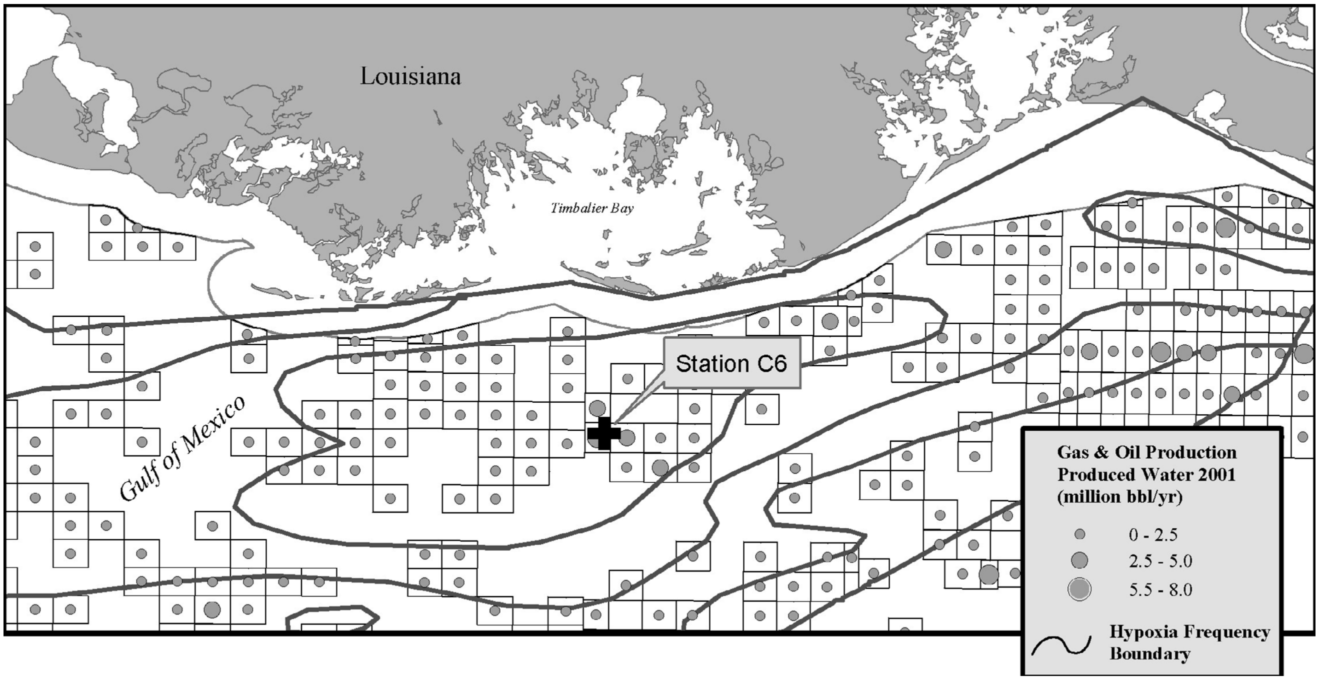
OCS Study
MMS 2005-044

Relative Contribution of Produced Water Discharge in the Development of Hypoxia



U.S. Department of the Interior
Minerals Management Service
Gulf of Mexico OCS Region

OCS Study
MMS 2005 – 0044

Gulf of Mexico OCS Region

Relative Contribution of Produced Water Discharge in the Development of Hypoxia

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ABOUT THE COVER

The inner continental shelf of central Louisiana with OCS blocks, total produced water volume for 2001, and contours of frequency of mid-summer, bottom-water hypoxia for the period 1985-2002. Contours from station C6 to the southeast represent the presence of hypoxia at greater than 75 percent, greater than 50 percent, greater than 25 percent, and less than 25 percent of the sampling events.

EXECUTIVE SUMMARY

The northern Gulf of Mexico is the site of the world's second largest zone of anthropogenic coastal hypoxia (water with dissolved oxygen less than 2 mg l^{-1}, ppm). It is also an area of extensive oil and gas exploration and production activity. The distribution, severity and temporal variability in hypoxia and its historic worsening is most closely related to the flux of nitrate-nitrogen from the Mississippi River system and its increase over the last half of the 20th century. The discharge of the Mississippi River, which directly influences the formation and dynamics of hypoxia, has made it difficult to isolate the influences of the river from those related to offshore production activities. Examination of these relationships has mostly focused on river-coastal ecosystem interactions and their influence on benthic communities that are also exposed to contaminants from oil and gas production activities. More recently, questions have been raised regarding the relative contribution of riverine organic carbon and nitrogen loads to those from produced water discharge in the formation of continental shelf hypoxia.

Management options are being considered for implementation within the Mississippi River watershed to reduce the nutrient inputs to the Gulf of Mexico in order to reduce the size, severity and duration of hypoxia. If produced water discharges were to contribute substantially, either directly or indirectly, to the respiratory consumption of dissolved oxygen, then a case could be made under the U.S. Environmental Protection Agency ocean discharge criteria to impose effluent limitations on offshore produced water discharges to prevent unreasonable degradation of the marine environment.

The objective of this analysis is to evaluate the relative contribution of produced water organic and nutrient compounds in relation to those of the Mississippi and Atchafalaya discharges in the context of hypoxia formation on the continental shelf. Relevant information includes:

(1) geographic extent, severity and duration of the hypoxic zone;

(2) causes of hypoxia;

(3) produced water constituents, volumes, and geographic location;

(4) relative inputs of organic matter and nitrogen from produced water and river discharge;

(5) oxygen utilization as a result of chemical constituents of produced water; and

(6) potential for nutrient-enhanced production related to produced water nutrients.

Produced water generated during the production of oil and gas is a mixture of hypersaline water with volatile, water soluble and more recalcitrant hydrocarbons, reduced metals, radionuclides, occasional pipe scale particulates, and sulfur and nitrogen compounds. The organic content of produced waters has the potential to be degraded by aerobic microbes, the activity of which may reduce dissolved oxygen in the ambient water. The nitrogen, mostly in the form of ammonium, has the potential to stimulate phytoplankton production, some of which may flux to the lower water column to be decomposed and contribute to the respiratory demand in the bottom waters.

The relative amounts of organic carbon and ammonium in produced water discharges were compared to those delivered by the Mississippi and Atchafalaya Rivers to the adjacent continental shelf. Estimates were made both across the large area where hypoxia occurs and in the area of South Timbalier Blocks 52 and 53 where more detailed data on oxygen and carbon dynamics are available for composite station C6* in 20-m water depth in the core of the hypoxic zone. The inputs from the Mississippi River are well characterized and modeled as to their effects on the continental shelf, including the formation of hypoxia on fine temporal scales at composite station C6* and over a broad spatial scale from the Mississippi River to the upper Texas coast.

This project required the comparison of a minimal amount of produced water constituent load data to more thoroughly characterized Mississippi River data. The relationships between multiple forms of

organic carbon measurement to each other and to oil and grease measurements have not been established. Additionally, the concentration of nitrogen compounds in produced water from differing locations or hydrocarbon extraction activities is not known. Therefore, numerous assumptions were made and the first order estimations presented lean towards worst-case scenarios for both the produced water carbon and nitrogen inputs. However, the expected dilutions and dispersions correspond to available models.

The oil and grease loadings do not track well with total organic carbon content of produced water nor do they distinguish among the hydrocarbon compounds that vary with regard to volatility, solubility, photo-oxidation, likelihood of adhering to sedimenting particles and susceptibility to microbial degradation. All hydrocarbons included in the oil and grease content and loadings were included in calculations of organic carbon that would reach the lower water column and sediments and contribute to respiratory reduction of dissolved oxygen. This, of course, is not the case. Estimates of produced water ammonium were compared to river ammonium, nitrate and nitrite (dissolved inorganic nitrogen) and total nitrogen that includes both dissolved and particulate organic nitrogen, because all can stimulate phytoplankton production. The role of dissolved inorganic nitrogen in the dynamics of hypoxia is better understood than the organic fraction of total nitrogen.

The first order estimations of the contribution of carbon and nitrogen in produced water discharges are minimal compared to those of the river. The produced water ammonium discharged within the area subject to hypoxia is estimated to be 0.013 percent of the total nitrogen delivered by the Mississippi River system, 0.008 percent of the total dissolved inorganic nitrogen, and 0.002 percent of the total ammonium.

Up to 4 percent of the organic carbon delivered to the Gulf of Mexico, which includes terrestrial material along with oil and grease from nonpoint source runoff, is estimated to contribute to respiratory demand in water below the pycnocline in the area of hypoxia. The produced water oil and grease load for the Gulf of Mexico is 10.9 percent of the oil and grease load from the Mississippi River that might contribute to hypoxia. Ideally, there would be TOC, DOC, and POC data for direct comparison of produced water and riverine discharges. With the data currently available it would be inappropriate to compare produced water oil and grease loads to riverine TOC data. However, considering that the Gulf produced water oil and grease load is a relatively small percent of the Mississippi River load that might contribute to hypoxia, it is reasonable to expect that this small percentage would also be overwhelmed by the nutrient-enhanced surface *in situ* production offshore. The *in situ* production is estimated to be 96 percent of the organic matter loading that drives the oxygen and carbon budgets of the continental shelf where hypoxia occurs, compared with the up to 4 percent riverine organic loading that might contribute. The produced water contribution of organic carbon in the total loading of organic carbon within the hypoxic area appears to be insignificant given the present body of information.

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ABBREVIATIONS, ACRONYMS, AND SYMBOLS

ADCP	acoustic Doppler current profiler
AEC	acid-extractable compounds
CTD	conductivity, temperature, and depth
C6*	combination of stations in South Timbalier Blocks 52 and 53
bbl	barrel (1 bbl = 42 gallon)
B/N	base/neutral fraction
BOD	biochemical oxygen demand
BOD_5	biochemical oxygen demand (5 day)
BOD_{21}	biochemical oxygen demand (21 day)
BSi	biologically bound silica
BTEX	benzene, toluene, ethyl benzene, xylene
CENR	Committee on Environment and Natural Resources
DOC	dissolved organic carbon
DOI	Department of the Interior
GOOMEX	Gulf of Mexico Offshore Operations Monitoring Experiment
HC	hydrocarbon
µM	micromoles
mg	milligram
MMS	Minerals Management Service
N	nitrogen
organic nitrogen	(organic nitrogen = TKN - NH_4^+)
inorganic nitrogen	(inorganic nitrogen = NO_3^- + NO_2^- + NH_4^+)
NH_4^+	ammonium
NO_3^-	nitrate nitrogen
NO_2^-	nitrite nitrogen
NPDES	National Pollutant Discharge Elimination System
NRC	National Research Council
O_2	oxygen
OC	organic carbon
OCS	Outer Continental Shelf
OOC	Offshore Operators Committee
POC	particulate organic carbon
P	phosphorus
PAH	polycyclic aromatic hydrocarbon
ppm	parts per million
ppt	parts per thousand
psu	practical salinity units
Ra	radium
SBF	synthetic-based fluid
Si	silicon
ST	South Timbalier
TKN	total Kjeldahl nitrogen (TKN = organic nitrogen + ammonium nitrogen)
TOC	total organic carbon
USEPA	United States Environmental Protection Agency
VFA	volatile fraction (all)
WD	West Delta

BACKGROUND

The northern Gulf of Mexico is the site of the world's second largest zone of anthropogenic coastal hypoxia (water with dissolved oxygen less than 2 mg l^{-1}, ppm). The northern Gulf of Mexico is also an area of extensive oil and gas exploration and production activity. The United States Environmental Protection Agency (USEPA) is tasked with protecting the nation's water quality while the Department of the Interior, Minerals Management Service (DOI, MMS) is tasked with managing the development of hydrocarbon resources while protecting the environment. In this overlapping area of concern on the Gulf of Mexico Outer Continental Shelf (OCS) is the large area of hypoxia off the Louisiana and Texas coasts that occurs each spring through summer. Many studies of the cause and effects of the hypoxic zone have been published. Similarly, many studies have documented the impacts of OCS produced water discharges on sediment, water, and biota. The discharge of the Mississippi River, which directly influences the formation and dynamics of hypoxia, has made it difficult to isolate the influences of the river from those related to offshore production activities (Bedinger 1981; Rabalais et al. 1993; Kennicutt 1995).

Produced water is a waste product generated during the production of oil and gas. It is also called formation water or brine. It is a mixture of hypersaline water with varying volatile, water soluble and more recalcitrant hydrocarbons, reduced metals, radionuclides, occasional pipe scale particulates, and sulfur and nitrogen compounds, as well as residual chemicals added to assist in production or to treat the produced water prior to discharge.

The USEPA *Best Available Treatment Technology Economically Achievable* for the National Pollutant Discharge Elimination System (NPDES) permit restricts the concentration of oil and grease in produced water destined for ocean disposal to a monthly average of 29 mg l^{-1} (USEPA 1993). The produced water also must meet an acceptable toxicity level. The majority of research efforts on produced waters have focused on the directly toxic or persistent, bioaccumulative constituents in produced water, such as the volatile hydrocarbons, polycyclic aromatic hydrocarbons, and heavy metals.

A toxic endpoint resulting from oxygen depletion has not been a part of prior MMS studies or USEPA NPDES regulations. The potential for produced water constituents to contribute to the biochemical oxygen demand (BOD) in offshore waters has not been studied. The BOD of produced waters may be a feature of concern where seasonal hypoxic waters form yearly on the northwestern Gulf of Mexico continental shelf. The nitrogen in produced water, primarily ammonium, may also be a concern in as far as it contributes to enhanced primary production in surface waters or BOD in bottom waters. There are no known analyses of phosphorus (either total or speciated) in produced water, published or otherwise (J. P. Smith, ExxonMobil Upstream Research Company, pers. comm.).

The upper limit for a consistent definition of hypoxic waters in the northern Gulf of Mexico is 2 mg l^{-1} (Rabalais et al. 2002a). Below this level, the catch of demersal fish and crustaceans in bottom trawls is minimal or zero (Renaud 1986; Pavela et al. 1983). Some fauna, such as sharks, may be affected at levels of low oxygen at or below 3 mg l^{-1}, whereas some benthic infauna may be resistant to extremely low levels of dissolved oxygen, approximately 0.5 mg l^{-1} (Rabalais et al. 2001). The loss of essential fish and crustacean habitat for extended periods in spring and summer, disruption of demersal organism migratory patterns, loss of infaunal prey organisms, increase in susceptibility to predation, decrease in reproductive and growth indicators, and direct mortality are concerns for managers and fishers of the abundant living marine resources in the Gulf of Mexico.

The USEPA published (October 2004) the Notice of Final NPDES General Permit for New and Existing Sources and New Discharges in the Offshore Subcategory of the Oil and Gas Extraction Category for the Western Portion of the Outer Continental Shelf of the Gulf of Mexico (GMG290000). The Ocean Discharge Criteria prevent unreasonable degradation of the marine environment and authorize the imposition of effluent limitations, including prohibition of discharge, if necessary to ensure this goal. Unreasonable degradation is defined under the Clean Water Act Section 403(c) as "(1) significant adverse changes in the ecosystem diversity, productivity, and stability of the biological community within the area of discharge and surrounding biological communities, (2) threats to human health through direct exposure to pollutants or consumption of exposed aquatic organisms, or (3) loss of esthetic, recreational, scientific, or economic values which are unreasonable in relation to the benefits derived from the discharge." For produced water, the permit requires that the operator must meet technology standards so that the best available treatment technology is used to reduce oil and grease and toxicity before discharge. Although MMS and USEPA have funded studies, which assist them in their respective responsibilities, and the National Oceanic and Atmospheric Administration through the Coastal Ocean Program has funded competitive research programs on the influence of the Mississippi River on the adjacent continental shelf, including the dynamics of hypoxia, none have researched the contribution of produced water discharge, if any, to the hypoxic zone. Relevant information exists in many studies to be summarized and synthesized to address this question.

OBJECTIVES

The objective of this analysis is to extract and utilize data from existing studies in order to describe the relationship of produced water discharges to the hypoxic zone. Relevant information includes:

(1) geographic extent, severity and duration of the hypoxic zone;

(2) causes of hypoxia;

(3) produced water constituents, volumes, and geographic location;

(4) relative inputs of organic matter and nitrogen from produced water and river discharge;

(5) oxygen utilization as a result of chemical constituents of produced water; and

(6) potential for nutrient-enhanced production related to produced water nutrients.

Rather than collect new data, this report summarizes published information, unpublished data relevant to the question at hand, and existing summaries of industry or MMS data. These data allow insight into (1) the dynamics of hypoxia, (2) the characterization of produced waters and their discharge into the northwestern Gulf of Mexico, and (3) the relative contribution of oxygen demanding materials and nutrients from produced waters compared with those of the Mississippi River and *in situ* marine phytoplankton production.

A summary of the knowledge of hypoxia in the Gulf of Mexico was presented in the findings of the Committee on Environment and Natural Resources (CENR) Integrated Assessment of Hypoxia in the Northern Gulf of Mexico (CENR 2000) and the six technical reports on which it was based (Rabalais et al. 1999; Diaz and Solow 1999; Goolsby et al. 1999; Brezonik et al. 1999; Mitsch et al. 1999; Doering et al. 1999). Portions of these reports and additional papers have since been published that complement or refine these syntheses.

The available produced water data were used to assess relationships among variables such as change in produced water through time versus change in hypoxic area through time. First-order calculations were made with regard to the amount of nitrogen and organic carbon in produced water discharges compared to similar discharges from the Mississippi River, the Mississippi River nutrient-enhanced *in situ* production of carbon on the shelf, and ambient nutrient conditions offshore during the period of hypoxia formation.

HYPOXIA IN THE NORTHWESTERN GULF OF MEXICO

DISTRIBUTION AND DYNAMICS

A zone of hypoxia forms each spring and summer on the Louisiana-Texas shelf beneath a well-defined density stratification. The hypoxic zone increased from an average size of 8,300 km^2 in 1985-1992 to over 16,000 km^2 in 1993-1997 (Rabalais et al. 1999, 2002a), and reached a record 22,000 km^2 in 2002 (Figure 1). The size of the hypoxic zone is directly correlated with the flux of nitrogen from the Mississippi River and river discharge (Scavia et al. 2003; Turner et al. 2005). The bottom area size relationship is strongest when the integrated nitrate-N flux over 75 days prior to the mapping cruise is the independent variable (R^2= 0.61, $P < 0.001$, $n = 16$); Justić et al. unpubl. data). The oceanographic conditions and weather prior to and during the time of the mid-summer cruise also dictate the configuration. For example, the predicted size of the hypoxic area in 2003 was 20,000 km^2, but the measured size was less than half that, because a series of tropical storms and hurricanes in the two weeks preceding the mapping mixed and re-aerated the water column.

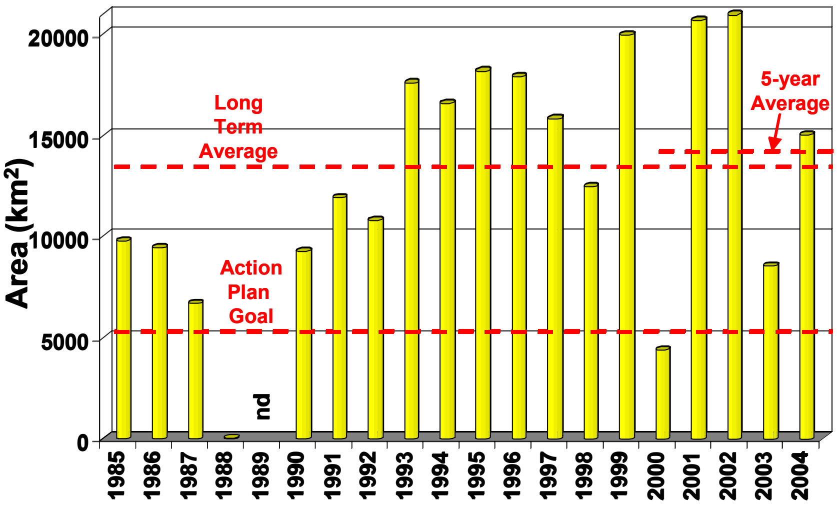


Figure 1. Estimated size of the bottom area encompassed by dissolved oxygen values less than 2 mg l^{-1} during a 5- to 6-day mapping cruise in mid-summer (nd=no data) (modified from Rabalais et al. 2002a). The Action Plan Goal of 5,000 km^2 running average by 2015 is denoted along with the 1985-2004 average size and the 5-yr running average.

Hypoxic waters are distributed from shallow depths near shore (4 to 5 m) and reach to 60 m water depth. They more typically occur between 5 and 35 m. They can impinge onto the barrier islands when upwelling-favorable conditions drive hypoxic waters towards shore. Hypoxia occurs mostly in the lower water column but encompasses as much as the lower half to two-thirds of the water column. The summertime frequency distribution of bottom water hypoxia is shown in Figure 2, and qualitatively depicts the relative, integrated down-current effects of Mississippi and Atchafalaya discharges.

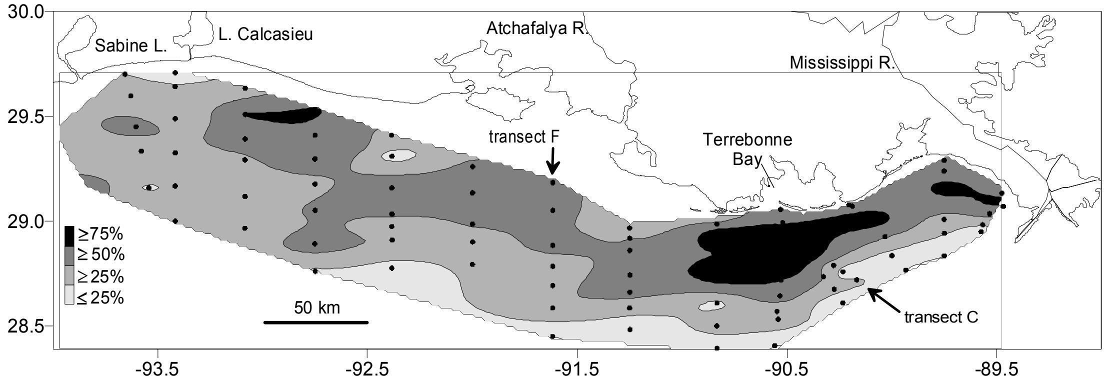


Figure 2. Frequency of occurrence of mid-summer, bottom-water hypoxia in the Gulf of Mexico from 1985-2002 (modified from Rabalais et al. 2002a).

Data collection along transect C, off Terrebonne Bay, began in 1985 and has continued fairly consistently since 1989. Initially, two production platforms, a non-production platform and an open shelf 'control'—all within the persistent summertime hypoxic zone on the southeastern Louisiana shelf—were investigated to determine the response of benthic infauna to hydrocarbon contaminants in the context of natural, temporal variability as caused by hypoxic bottom waters (Rabalais et al. 1993). A platform in West Delta Block 32 (20,000 bbl d^{-1} produced water discharge) and an open water site in the same block were characterized by silty sediments and intermittent summertime hypoxia. A production platform in South Timbalier Block 53 with a 5,500 bbl d^{-1} discharge [station C6 of Rabalais et al. (1999) hypoxia studies] and a non-discharging platform in the same block [station C6A of Rabalais et al. (1999)] were characterized by primarily silty sands and low dissolved oxygen levels for prolonged periods. After the non-discharging platform at C6A was dismantled and removed, another non-discharging platform in that block [station C6B] was used for hydrographic profiles and instrument moorings in subsequent hypoxia studies (Rabalais et al. 1995, 1999). Eventually the instrument mooring was moved to South Timbalier Block 52A [station C6C] where it is currently in operation in collaboration with Louisiana State University WAVCIS (http://wavcis.csi.lsu.edu/, select station CSI-6). The production platform in this block South Timbalier 52C (20,000 bbl d^{-1}) was under consideration for the initial study by Rabalais et al. (1993), but was eliminated due to the extensive shell pad and the limitations to box coring due to the numerous pipelines that feed the platform.

The location of station C6 moved several times in the past decade in response to changes in platform activity. When the data has been composited, the station location is referred to as composite station C6*. Composite station C6* denotes a combination of sampling stations in South Timbalier Blocks 52 and 53 in 20-m depth (C6, C6A, C6B and C6C).

Data collected from transect C indicate that hypoxic conditions begin in early to mid-spring but are most prevalent and widespread from late spring through late summer (Figure 3).

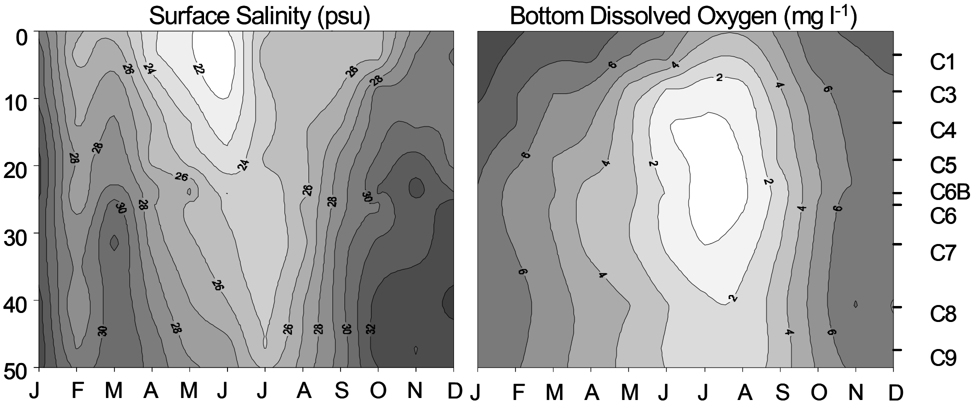


Figure 3. Seasonal changes in average surface water salinity (psu) and average bottom water dissolved oxygen (mg l^{-1}) along transect C by month January through December 1985-2002 (modified from Rabalais et al. 2002c). Y axis is distance from shore (km). Station C1 is in 5 m, C6* in 20 m and C9 in 30 m.

The seasonal progression of lower surface water salinity from winter through summer (as shown for transect C in Figure 3) is dictated by higher river discharge in March-May (long-term average) when persistent winds from the southeast and Coriolis effect move most of the water from the Mississippi River birdfoot delta to the west along the inner to mid continental shelf. In summer, winds more often from the south and southwest hold the river water (lower in volume) on the shelf for a continued stratified system. Water from the Atchafalaya River in summer often moves eastward to the area of transect C and contributes to lowered surface salinity and strengthened stratification.

The average bottom waters along transect C are well oxygenated from October through March (Figure 3). The nearshore waters are more likely to be oxygenated through the year because of the shallow depth and influence of wind-induced mixing, but hypoxia will occur there. The offshore waters are less likely to be hypoxic compared to the stations in 10 to 25 m depth because they are affected by the advection of deeper oxygenated waters from offshore and stratification intensity is less. The majority of the transect is depleted in oxygen for most of June through August.

There is a seasonal peak in dissolved inorganic nitrogen (DIN) (DIN = $NO_3^- + NO_2^- + NH_4^+$) in the spring followed by an increase in surface water chlorophyll biomass (an indicator of phytoplankton production) (Figure 4). The concentration of bottom water phaeopigments (the degradation products of chlorophyll in organic matter that fluxes from the surface waters) parallels the generation of phytoplankton biomass in the spring and is intensified under strong stratification in the summer (Rabalais et al. 2002b).

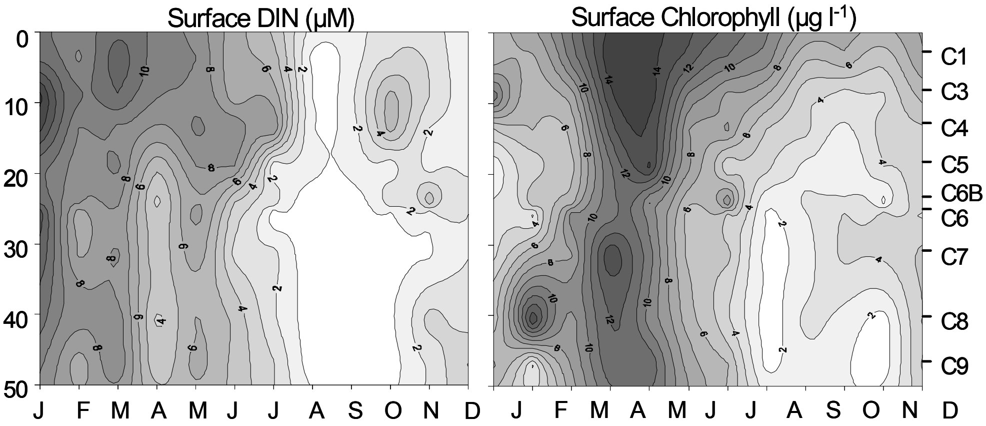


Figure 4. Seasonal changes in average surface water dissolved inorganic nitrogen ($NO_3^- + NO_2^- + NH_4^+$ in µM) and average surface water chlorophyll biomass (µg l^{-1}) along transect C by month January through December 1985-2002 (modified from Rabalais et al. 2002c). Y axis is distance from shore (km). Station C1 is in 5 m, C6* in 20 m and C9 in 30 m.

The mid-summer mapping and monthly transect data are supplemented by continuous data from a series of oxygen meters deployed at composite station C6* since 1989. As noted above, composite station C6* denotes a combination of four sampling stations in South Timbalier Blocks 52 and 53 in 20-m depth (C6, C6A, C6B and C6C). While spatially limited, these data provide the time series of coupled physical and biological processes that affect the concentration of oxygen. An example of bottom water dissolved oxygen is illustrated in Figure 5. The features in this time series include: (1) A gradual decline of bottom oxygen concentrations through the spring. Respiration during decomposition of organic matter in bottom waters occurs at a rate faster than dissolved oxygen can diffuse from surface waters across a strong pycnocline. (2) Reoxygenation of bottom water from mixing events. As stratification reforms, oxygen consumption rates in the lower water column begin to outpace resupply of oxygen from the surface layer and hypoxia reforms. (3) Persistent hypoxia and often anoxia for extended periods in May-September. (4) A mixing event in mid-summer that reaerates the water column followed by a decline in oxygen similar to that seen in the spring. This event resulted from a tropical storm that crossed the Gulf of Campeche and generated 3- to 4-m waves at the instrument deployment site. (4) An intrusion of more saline, higher oxygen content water from deeper offshore during an upwelling regime in September followed by a downwelling regime and movement of the low oxygen water mass back offshore. (5) Cold fronts in October and November that continue to mix the water column sufficiently to prevent prolonged instances of hypoxic conditions (Rabalais and Turner 2001).

The deployed instruments provide the detail often missed by monthly sampling cruises. The bottom oxygen conditions fall below 2 mg l^{-1} in October-November and February-March (not shown), but these events are unlikely to be captured in a one-day cruise. Hypoxia during these months, however, seldom persists due to the high frequency of mixing events. Hypoxia has not been recorded in the months of December-January.

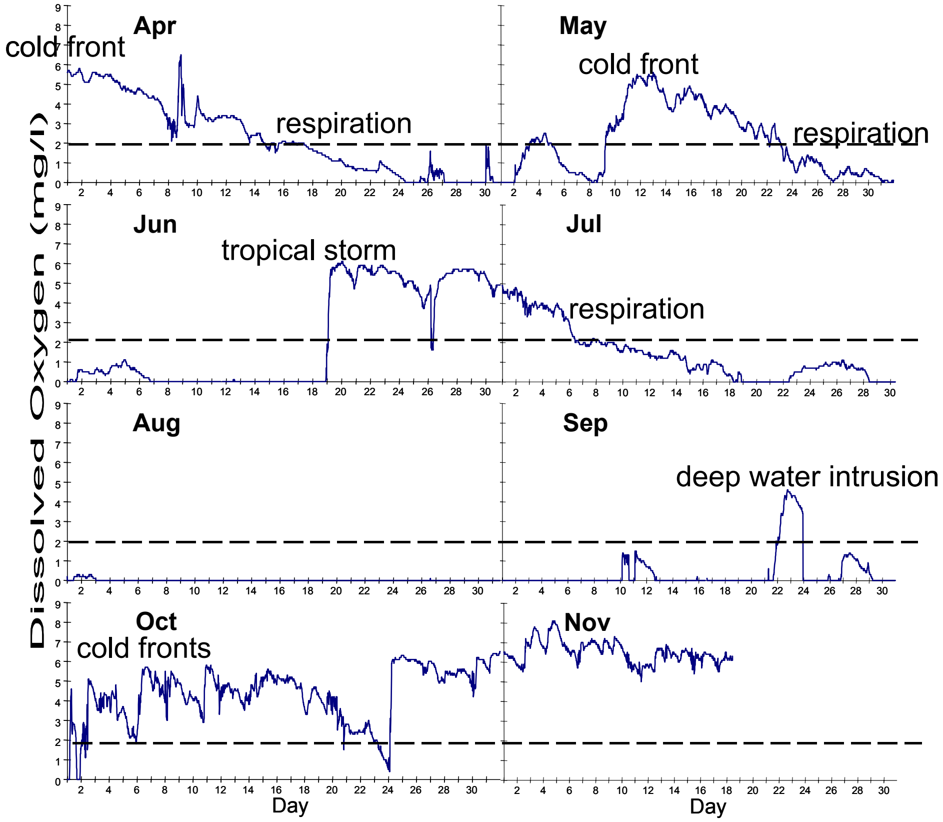


Figure 5. Bottom water dissolved oxygen concentration (mg l^{-1}) within 1 m of the bottom in 20 m depth at station C6B, from April through November 1993 (modified from Rabalais and Turner 2001). The dashed line defines hypoxia as 2 mg l^{-1} (~20% oxygen saturation).

CAUSES OF HYPOXIA

The currently accepted paradigm supported by peer-reviewed literature is that nutrients and fresh water from the Mississippi River, coupled with physical stratification of Gulf of Mexico coastal waters, are the principal complementary causes of hypoxia (Rabalais et al. 1999, 2002b; CENR 2000). This paradigm is also supported by numerous studies from other coastal hypoxic areas worldwide (Boesch 2002). The relative influence of the physical features of the system and the progression of biological processes vary spatially and over an annual cycle, are complexly inter-related, and are directly linked with the dynamics of the Mississippi and Atchafalaya discharges.

Acoustic Doppler current profiler (ADCP) data from 14 March through 12 November 2002 at station C6B, midway between the Mississippi River birdfoot delta and the Atchafalaya River delta illustrate the anticipated strong dominance of the alongshore currents (Figure 6) (Wiseman et al. 2004). The flow is strongly sheared in the alongshore direction with weak lower layer flow and a weak indication of reversal. The cross-shore flow is consistent with a wind-driven downwelling regime as would be expected under the predominantly southeasterly winds affecting the region. More surprising is the highly variable structure of the flow. Periods of strong vertical shear (e.g., hours 3200-3500) are interspersed with long periods of very weakly sheared flow (e.g., hours 4800-5000). Long periods of flow contrary to the expected westward flow regime were also observed (e.g., hours 2700-3100).

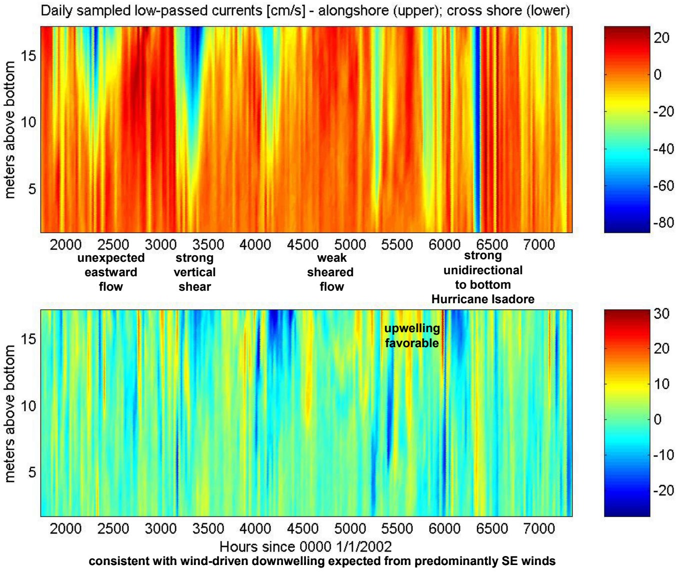


Figure 6. Contoured daily samples of low-pass filtered currents (cm s^{-1}) after rotation into alongshore (top) and cross-shore (bottom) directions (from Wiseman et al. 2004). Bins are 0.5 m thick and begin 1.71 m above bottom.

Two-layered flows or flow confined to the upper layer were anticipated from both theory and prior isolated observations, particularly during the highly stratified summer season. Yet an empirical orthogonal functions analysis of the ADCP data in Figure 6 (Wiseman et al. 2004) indicated that 82 percent of the variance in the low-passed currents was accounted for by the first mode, which describes nearly unidirectional, vertically-sheared flow (Figure 7). The second mode accounted for only 13 percent of the variance and describes a two-layered flow field. The latter condition was most prevalent in spring and summer, when bottom currents were weakest, the lower water column was more stagnant, and hypoxia was more likely to form.

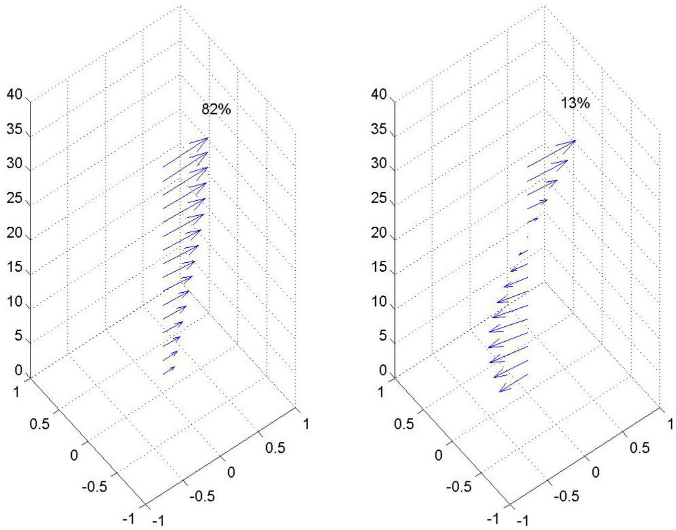
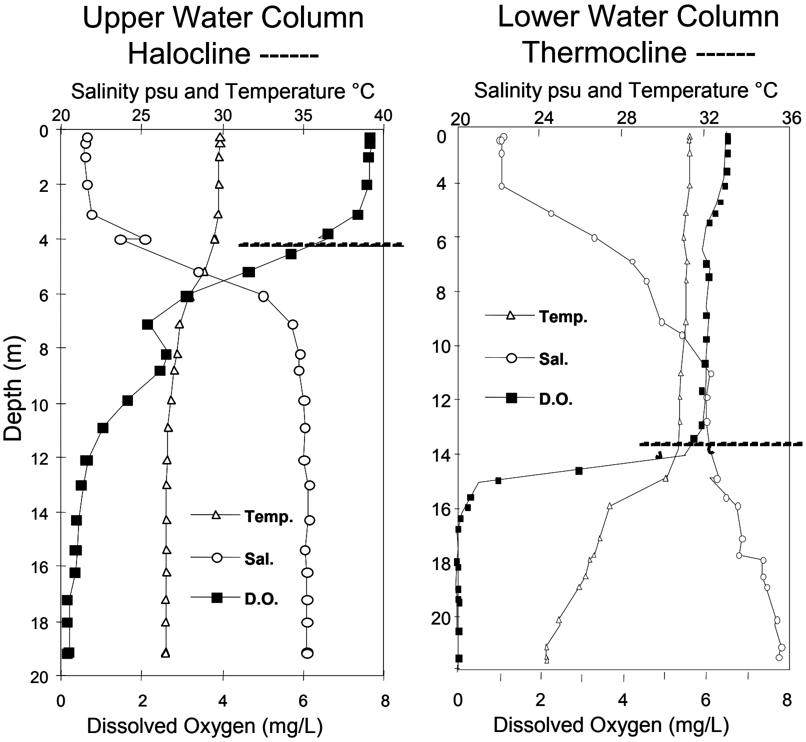


Figure 7. First (left) and second (right) empirical orthogonal functions from the acoustic Doppler current profiler (ADCP) data (from Wiseman et al. 2004). Values associated with every second ADCP bin are plotted.

Hypoxia is most evident when the water column is stratified as a result of high fresh water runoff, warmed surface waters, and calm winds. The physical structure of the water column is defined by water masses that differ in temperature, salinity, or both. Fresh water from rivers and seasonally warmed surface waters reside above the saltier, cooler, and denser water near the bottom. The existence of a strong near-surface pycnocline, usually controlled by salinity differences, is a necessary condition for the occurrence of hypoxia, while a weaker, seasonal pycnocline, influenced by temperature differences, often guides the morphology of the bottom water hypoxia (Wiseman et al. 1997) (Figure 8).


Upper Water Column
Halocline ------

Lower Water Column
Thermocline ------

Figure 8. Examples of pycnoclines and oxyclines at station C6B (from Rabalais and Turner in press). Left panel: example of upper water column halocline and oxycline. Right panel: example of upper water column halocline and lower water column thermocline and oxycline.

The concentrations and total loads of nitrogen, phosphorus, and silica delivered to the coastal ocean influence the productivity of the phytoplankton community, the types of phytoplankton that are most likely to grow, and the flux of phytoplankton-derived organic matter (Rabalais et al. 1996; Turner et al. 1998; Dortch et al. 2001). Phytoplankton not incorporated into the food web, and fecal material generated via the food web, sink into bottom waters where they are decomposed by aerobic bacteria, which consume oxygen in the process. The source of the organic matter for this respiratory activity is mostly from phytoplankton growth stimulated by river-delivered nutrients, and not from the carbon in the Mississippi River (Eadie et al. 1994), although the relative amount of allochthonous carbon and the lability of both has been questioned (see Other Factors).

Primary production in shelf waters near the delta and to some distance from it is significantly correlated with nitrate and nitrite concentrations and loads (Lohrenz et al. 1997; Justić et al. 1993, 1997, 2002). The relationship with dissolved orthophosphate is linear but not significant (Lohrenz et al. 1997). There is a pattern of localized maxima of phytoplankton biomass and production in salinities of 15 to 25 psu where water clarity improves in the presence of relatively high nutrient levels (Lohrenz et al. 1997; Rabalais et al. 2002b), similar to other major rivers including the Amazon (DeMaster et al. 1986; Smith and DeMaster 1996), Huanghe (Turner et al. 1990) and Changjiang (Xiuren et al. 1988).

The distribution of low dissolved oxygen in bottom waters is related to high surface net production, but this relationship is lagged in time (Justić et al. 1993; Rabalais et al. 1994). Phytoplankton and fecal pellets in surface waters fall into the bottom layers quickly, perhaps in a day or less, but surface and bottom currents are not traveling in the same direction or at the same speed (Figures 6 and 7). Most of the organic matter reaching the bottom is not consumed in hours, but many days (and probably weeks). The depletion of oxygen is cumulative, and depends also on the re-aeration rate (Justić et al. 1996). There is a downstream transition away from the discharges of the Mississippi and Atchafalaya Rivers from lower to higher salinities, higher to lower nutrients, shifts in nitrogen compounds, higher to lower surface chlorophyll *a* concentrations and accumulation of phaeopigments in the lower water column. This results in a consistent transition away from the river discharges in production of carbon, flux of organic material, respiration rates, and incidence of bottom water hypoxia.

The vertical export of particulate organic carbon (POC) should be high, given the high rates of primary production, and should be roughly proportional to the quantity of carbon fixed in the surface waters, as predicted by Suess (1980). The net production rates for the upper water column, represented by composite station C6* (Justić et al. 1997) showed a well-defined seasonal cycle with a minimum of -0.2 g C m^2 d^{-1} in December and a maximum of 1.2 g C m^2 d^{-1} in April. The high particulate organic carbon flux to a 15-m moored trap at station C6B in spring was sufficient to fuel hypoxia in the bottom waters below the seasonal pycnocline (Qureshi 1995; Justić et al. 1996). The flux of organic matter in summer, while it sustained hypoxia, was incremental to the majority flux of carbon in the spring (Qureshi 1995).

Despite the high nutrient inputs to the shelf, nutrients are depleted to low, and sometimes undetectable, concentrations within a short distance of the river mouth (Lohrenz et al. 1990, 1997, 1999; Bode and Dortch 1996; Dortch and Whitledge 1992; Nelson and Dortch 1996; Rabalais et al. 1996, 2002b). Patterns of nutrient depletion provide evidence that riverine inputs of nutrients and their pattern of regeneration ultimately limit the extent of river-enhanced production and biomass. Ambient nutrient concentrations and ratios, bioassay experiments, and other indicators of nutrient limitation (Rabalais et al. 1999, 2002b) suggest that nitrogen (N), phosphorus (P), silicon (Si) or combinations of these may be limiting at some times and places in the outflow of the Mississippi River, the details of which are not completely known. Although limitation by both Si and P does occur, N limitation extends over a larger area. Consequently, the rate of N loading is considered to be a critical factor in regulating the overall production of phytoplankton over the broad region influenced by the river and affected by bottom water hypoxia.

HISTORICAL CHANGES

Given the high volume of fresh water and nutrients delivered by the Mississippi River to this stratified coastal system, one might expect a propensity for the ecosystem to develop hypoxia naturally and that hypoxia has always been a natural feature of this system. While average river discharge over the last 150 years has not changed, nutrient flux has. The annual flux of nitrate nitrogen from the Mississippi basin to the Gulf almost tripled between the periods 1955-1970 and 1980-1996 from 0.33 to 1.6 million metric tons per year. Nitrate inputs to the basin are primarily from nonpoint sources (90 percent) of which 74 percent are agricultural in origin; 56 percent of the nitrate enters the Mississippi River system north of the Ohio River. Organic nitrogen measurements were not regularly made before 1973 but show no trend since then. Both stream flow and nitrate flux have become much more variable in the last 25 years (Goolsby et al. 1999).

Because relevant offshore water column data do not exist before 1972 and systematic hydrographic data collection did not start until 1985, the sediment record was examined for palaeoindicators of long-term transitions related to eutrophication and oxygen conditions beneath the Mississippi River plume (summarized in Rabalais et al. 2002a). These records reflect conditions at the time the sediment was deposited and thus provide clues to temporal changes in biogeochemical conditions.

Sediment core analyses (Eadie et al. 1994, Turner and Rabalais 1994) document increased recent eutrophication and increased organic sedimentation in bottom waters, with the changes being more apparent in areas of chronic hypoxia and coincident with the increasing nitrogen loads beginning in the 1950s. The evidence is increased accumulation of diatom remains (biologically bound silica, BSi) and marine-origin carbon accumulation in the sediments. Because there have been no significant increases in either the riverine organic carbon or silica loads, it is reasonable to infer that these increases in the sediment record since the 1950s are due to *in situ* production of marine algae.

A series of indicators serve as surrogates for oxygen conditions: glauconite abundance (a clay mineral formed under reducing conditions), benthic foraminiferans, and ostracods (Nelsen et al. 1994; Blackwelder et al. 1996; Rabalais et al. 1996; Sen Gupta et al. 1996). These surrogates for oxygen conditions indicate an overall increase in continental shelf oxygen stress (in intensity or duration) in the last 100 years that has accelerated since the 1950s. These indicators of worsening oxygen conditions parallel the increase in indicators of surface water primary production that accumulate in the sediments, i.e., diatom remains and accumulated carbon. Examination of specific foraminiferans indicates that a hypoxia-tolerant species has increased markedly in recent decades and now dominates the present-day population within areas of chronic seasonal hypoxia. A hypoxia-intolerant foraminiferan was a conspicuous member of the fauna from 1700 to 1900 but is no longer present, indicating that oxygen stress was not a problem prior to 1900.

Hypoxia is not a natural feature of this continental shelf but has worsened consistent with landscape changes and increased nitrogen load from the Mississippi River (Rabalais et al. 2002a; Turner and Rabalais 2003). Hindcasting by models based on measured conditions beginning in the 1980s indicate that hypoxia, as a widespread phenomenon or as a frequently occurring condition, was not present before the early to mid-1970s (Justić et al. 2002, Scavia et al. 2003, Turner et al. 2005).

OTHER FACTORS

While literature supports that only increased nitrogen loads from the Mississippi River system can account for the changes in hypoxia since the 1950s, other factors may contribute to its formation, dynamics and historical change. These are not competing hypotheses, but rather a set of potential contributing factors that were considered as to their relative importance by CENR (2000) and Rabalais et al. (2002a).

With the release of a USEPA Region 4 paper (USEPA 2004), the importance of phosphorus in contributing to hypoxia in the northern Gulf of Mexico has resurfaced since the CENR (2000) assessment. The new focus calls for a consideration of phosphorus management along with that of nitrogen. With regard to the issue of produced water and hypoxia, there are no known analyses of phosphorus in produced water (see Background).

Earlier researchers (cited in Turner and Allen 1982) proposed that intrusion of a low-oxygen layer from deeper, offshore waters onto the continental shelf was the source of shelf bottom water hypoxia. This low-oxygen layer at 400-700 m was first documented in the Gulf of Mexico in the mid-1930s (Conseil Permanent International pour l'Exploration de la Mer 1936). There were no oxygen values in that data set, however, that were less than 4.3 mg l^{-1}. Low oxygen conditions reported from the Gulf in the 1930s, therefore, are clearly references to the oxygen minimum layer in deeper waters that are not connected to the continental shelf hypoxia that has been measured beginning in the 1970s (Pokryfki and Randall 1987, Rabalais et al. 1991a).

Organic carbon supplied by the Mississippi River could contribute to the oxygen demanding materials in the hypoxic zone (Carey et al. 1999). Because the suspended sediment load has declined by about half since the 1950s, the particulate organic load that could settle on the shelf has likely decreased as well. Terrestrially derived carbon is deposited close to the birdfoot delta (Turner and Rabalais 1994). Stable carbon isotope data indicate that 80 percent of the carbon accumulated in the Mississippi River bight hypoxic zone is of marine, not terrestrial, origin (Eadie et al. 1994). The distances to which particulate organic carbon would need to be transported to affect the large area of hypoxia are too great to provide a significant load. A maximum deposition of labile carbon from the Mississippi River into the bottom layer of the hypoxic zone was estimated by Boesch (1999) to be 11 percent of the total oxygen demanding carbon load (Figure 9). This calculation was based on respiration rates, annual organic carbon consumption, and proportion of labile carbon (Dortch et al. 1994; Trefry et al. 1994; Ittekkot 1988; respectively). If less than 35 percent of this organic matter is actually oxidizable within the time frame in which hypoxia develops, the contribution of terrigenous organic sources to hypoxia must be a small part of the carbon respired in hypoxic waters (negligible up to 4 percent of the total terrestrial organic flux). On the other hand, the production of plankton carbon in the surface waters overlying hypoxic waters (CENR 2000) is 9 to 32 times greater than the maximum amount of riverine labile carbon reaching hypoxic zones, depending on assumptions about the lability of the terrestrial carbon. About 44 percent of the surface carbon production in the form of phytoplankton eventually reaches the seafloor, either as senescent cells, in fecal pellets, or in aggregates.

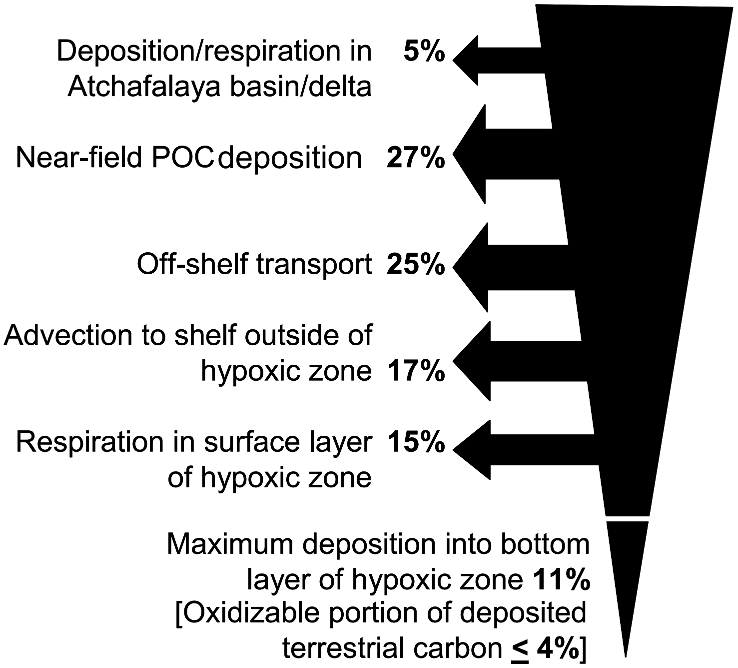


Figure 9. Potential contribution of labile allochthonous carbon to the continental shelf from the Mississippi River (modified from Boesch 1999).

Decreased over-bank flooding in the Mississippi delta and Louisiana wetland loss are not considered to be relevant factors in the formation and historical change of hypoxia. Leveeing of the river, completed in 1927 to reduce flooding, occurred well before the significant increase in nitrate loads and indicators of hypoxia began in the 1950s. Mass flux calculations of organic matter from wetland loss clearly indicate this is a relatively small source of organic carbon, and stable carbon isotope analyses indicate that wetland organic carbon accumulation is confined to a narrow band next to shore. However, restoration of wetlands and river flood plains within the basin would contribute to an overall reduction in nutrients reaching the river terminus (Mitsch et al. 2001).

The Mississippi and Atchafalaya Rivers contribute, by far, the major sources of nutrients to the northern Gulf of Mexico (Dunn 1996). Direct atmospheric deposition to the offshore surface waters is a small amount of the total nitrogen budget (1 - 2 percent, Goolsby et al. 1999). Upwelled nutrients from deeper waters may be important at the shelf edge (100 m), but there are limited transport mechanisms for this source to enhance continental shelf processes. Groundwater discharges to the Gulf are unlikely to be important because of the lack of shallow aquifers along the Louisiana coast. The best current knowledge is that the outflows of the two rivers dominate the nutrient loads to the continental shelf where hypoxia is likely to develop.

River discharge, nitrate concentration, and sediment core data provide over 100 years of record for this system. On that time scale, there is no indication that climate factors override the impacts of human activities in the basin. The long-term river discharge (150 years), while variable, shows no long-term statistical trend. Average annual flow in the Mississippi River increased 30 percent between 1955 -1970 and 1980-1996 (Bratkovich et al. 1994) compared to the 300 percent increase in nitrate flux over this period (Goolsby et al. 1999). Using two different approaches, Donner et al. (2002) and Justić et al. (2003) agreed that 20-25 percent of the increased nitrate flux between the mid-1960s to the mid-1990s was attributable to greater runoff and river discharge, with the rest (75-80 percent) due to increased nitrogen loading on the landscape.

Stow et al. (2004) analyzed summer data from 1982 to 2002 and found that the degree of stratification needed to induce hypoxia has decreased. Within their summertime data set, surface water temperature increased and subsequently oxygen saturation decreased. Their results imply a long-term factor for summer conditions that transcends flow-induced stratification differences. One explanation would be the increase in nutrient loads in summer during their period of record, i.e., the nutrient load increase has led to more hypoxia regardless of the stratification. An alternative explanation might be that surface water temperatures have increased due to climate change (at least for the period of record of these data). There is, however, no literature for the northern Gulf that identifies a long-term warming of surface waters.

HYDROCARBONS IN THE GULF OF MEXICO

HISTORY OF THE OFFSHORE PETROLEUM INDUSTRY IN THE GULF OF MEXICO

The first oil well drilled in the open Gulf in 1938 was the Creole field about 2.4 km from the Louisiana coastline (Bedinger 1981). Significant development to explore the offshore did not commence until 1947 when the Ship Shoal Block 32 field was found 19 km from the coastline. Once the ownership and jurisdiction of the OCS was defined by the Submerged Lands Act and the Outer Continental Shelf Lands Act, leasing and development activities in the Gulf of Mexico accelerated. In 1955, there were 400 wells drilled, increasing to 5,702 wells in 1966, and 16,169 wells drilled in 1978. The proportion of the total U.S. production coming from the Gulf of Mexico increased over the same time period to a peak in 1972 of 389 million barrels of oil and gas condensate, which was 10.7 percent of the nation's domestic production. Production has decreased since then, but is being supplemented from new fields in deeper Gulf waters (>300 m). A new forecast from the Department of the Interior, Minerals Management Service, indicates that oil production in the Gulf may start to decline within the next six years (Holden 2004). In the 'ultradeep' waters (>1500 m) and areas that are more than 9 km beneath the shallow sea floor, production will temporarily surge. But that surge will be short-lived and Gulf production is likely to decline after 2011.

HYDROCARBON INPUTS TO THE GULF OF MEXICO

Several sources of materials are released to the water column from exploration, drilling, and production of oil and gas. These releases are intentional and permitted, or accidental. They include permitted deck runoff of rainfall which may contain some oil and grease, permitted treated sewage and domestic waste disposal, permitted drilling and produced water discharges, occasional accidental releases of product, diesel fuels or chemicals associated with production, and sloughing of organic matter from biofouling organisms on surfaces of the platform (Neff et al. 1987). It should be noted that oil seeps are a major source of hydrocarbon input to the Gulf of Mexico and outweigh the sum of all inputs related to human activities. The following discussion focuses on sources related to human activities rather than naturally occurring sources.

Drilling discharges consist of formation solids that are separated from the circulating mud stream and bulk mud discharges (Ayers 1983). Over the time it takes to drill a well (3 - 6 mo), 1000 m^3 (2000 tons) of material (dry weight basis) will be discharged for water-based muds. Mud additives, which are mostly inert, account for roughly half of this amount, and formation solids, the other half. The muds are either discharged beneath the surface through a large diameter (25 cm) shunt pipe or allowed to freefall from the rig to the ocean surface. The main plume sinks rapidly leaving only 5 -7 percent of the materials in the surface plume. Unlike the North Sea, where they were allowed until 1997, the discharge of oil-based drilling fluids or of cuttings drilled with these fluids is not permitted in the U.S. OCS and thus do not contribute to organic loading in the vicinity of the platform or subsequent, localized depletion of oxygen.

Synthetic-based drill fluids (SBF) are increasingly used in difficult or deep-water drilling. The discharge of SBFs is not permitted. However, drill cuttings that are wetted with SBF may be discharged following treatment to remove the SBF. The residual SBFs that adhere to the cuttings are biodegradable and thus contribute to the organic loading in the vicinity of the platform. At sites where SBF-wetted cuttings had been discharged, studies noted an increase in organic enrichment and suboxic conditions in sediment samples (CSA 2004; Trefry et al., 2005). The concentrations of SBF decline over time in both laboratory and field studies and degradation rates may take from months to several years (Roberts, in preparation; CSA, 2004). The primary mechanism for the degradation of SBF is sulfate reduction (Nguyen, 2005).

During the production of crude oil, condensates or natural gas, water that is trapped within permeable sedimentary rock may also be brought to the surface. This water is called formation water, produced water or oil field brine. The water must be removed from the oil, condensate, or gas as completely as possible in order to transport and use the product. The separated produced water may be reinjected down a well, either for disposal or to enhance recovery of hydrocarbons, or as is the case of the vast majority of production from the Federal waters of the northwestern Gulf of Mexico region, it is discharged into the sea. Produced waters generally have concentrations of dissolved salts much higher than sea water (Rittenhouse et al. 1969). In addition, produced waters may contain various inorganic and organic substances and radionuclides. The constituents in produced water may contribute to biological oxygen demand either directly, through organic matter decomposition, or indirectly through the flux of carbon from nutrient-enriched phytoplankton production, or chemical oxygen demand in bottom waters.

Petroleum hydrocarbons enter the marine environment from a number of sources including produced water. The most recent *Oil in the Sea III* (NRC 2003) report updated estimates of these sources for North American and global marine waters for natural seeps, and for petroleum extraction, transportation and consumption. The estimates for produced water in the United States are given in Table 1. Of the total petroleum sources to the marine environment in North America and the combined central and western Gulf of Mexico, produced water discharges comprise a little more than 1 percent and 2.5 percent of the total petroleum, respectively.

Table 1

Estimates of Oil Discharges to the Marine Environment from Produced Water Discharges
(taken from NRC 2003)

Area	Produced Water (1,000 bbl y^{-1})	Oil & Grease Content (mg l^{-1}) (min-max estimates)	Oil & Grease Discharge (tonne y^{-1}) (min-max estimates)
Total U.S.	745,000	20	2,500 (2,000-3,600)
Gulf of Mexico OCS	473,000	20 (15-29)	1,700 (1,300-2,500)
Louisiana Territorial Seas	186,000	20 (15-29)	600 (450-860)
Texas Territorial Seas	4,300	6.6	4.5
Total U.S. Gulf of Mexico	663,300	~6.6-29	2,305
Mexico	15,200	~60 (29-100)	140 (66-230)

Estimates of petroleum inputs to the marine environment attributable to the consumption of hydrocarbons, through river and urban runoff, oil spills from cargo ships, operational discharges from commercial vessels and recreational craft and atmospheric deposition are high (NRC 2003; Rabalais 2003). Diffuse sources of petroleum on land contribute to runoff and rivers polluted with petroleum. Although individual releases may be very small, the cumulative load from all land-based sources accounts for about half the total annual load of petroleum to the marine environment from human-related activities. Thus, in terms of volume, these sources far exceed the contribution of activities associated with the extraction and transportation of petroleum, combined. Based on the average annual flow of major rivers for which oil and grease concentration data were available, the Mississippi River contributes 70 percent of the riverborne hydrocarbons to the northwestern Gulf of Mexico yearly (Table 2) (see also Oxygen and Carbon Budgets).

Table 2

Estimates of Land-Based Contributions of Hydrocarbons and Polycyclic Aromatic Hydrocarbons (PAH) to Marine Waters in the Northwestern Gulf of Mexico (taken from NRC 2003)

Coastal Zone Description	OC Flux (tonne y^{-1})	Oil & Grease (tonne y^{-1})	Hydrocarbon (tonne y^{-1})	PAH (tonne y^{-1})
Coastal Sources		85,345	1,416	14
Gulf Coast Refineries		2,005	43	0
Brazos River		16,309	271	3
Colorado River		16,879	280	3
Mississippi River	DOC 3,477,000	525,638	7,885	79
	POC 3,209,536	(15% of DOC flux)		
	TOC 6,686,536			
Rio Grande River		49,709	825	8
Sabine River		7,896	131	1
Trinity River		26,736	444	4
Total		730,517	11,294	113

DOC – dissolved organic carbon
POC – particulate organic carbon
OC – organic carbon
TOC – total organic carbon
PAH – polycyclic aromatic hydrocarbon

PRODUCED WATER CONSTITUENTS

Produced waters vary in salinity from 3 to 300 psu, but are generally more concentrated in salinity than normal seawater (Rittenhouse et al. 1969). Produced waters may contain various inorganics (ammonium, sulfide and elemental sulfur) and elevated levels of several metals—barium, beryllium, cadmium, copper, iron, lead, nickel, silver, zinc, and mercury (Neff et al. 1989). Radionuclides also occur at elevated levels in produced water, primarily as ^{226}Ra and ^{228}Ra (Reid 1983). Produced waters also contain high concentrations of organic compounds, primarily petroleum hydrocarbons but also partially oxidized organics. The petroleum hydrocarbon fraction has been thoroughly analyzed (Neff et al. 1987, 1989; Boesch and Rabalais 1989a, b; Rabalais et al. 1991b, Ray and Engelhardt 1992).

The OCS-generated produced waters sampled by Rabalais et al. (1991b) ranged between 43 and 192 ppt salinity. There was little variation in the salinity through time for effluents sampled two to four times. The Offshore Operators Committee (OOC) (2004) reports mean salinity of produced water as 113 ppt (median 95 ppt). Sulfide concentrations were high (113 to 134 µg as S l^{-1}) in one discharge, elevated in several others (3.6 to 48 µg as S l^{-1}), while the remaining discharges contained trace or nondetectable sulfide (Rabalais et al. 1991b). Where elevated levels were detected, the analyses were consistent across time for those discharges sampled more than once.

The nature of the hydrocarbons in produced water differs depending on the product type, oil, condensate or gas (Melancon, Minerals Management Service, pers. comm., August 2004). Wells in the eastern portion of the Central Planning Area of the Gulf of Mexico tend to produce more oil while those in the western Gulf produce more gas. Knowing the properties of the formation that generate the produced water may help to predict the proportion of constituents in produced water on a Gulf-wide basis.

The OCS-generated produced water discharges varied greatly in the concentrations of identified organic compounds (Rabalais et al. 1991b). The variations result from differences in treatment processes, the product being treated, and efficiency of separation. The volatile fraction contains mainly benzene with lower amounts of toluene, xylene, and ethyl benzene (BTEX). They likely contain other volatile compounds at low levels such as short chain normal alkanes, cyclic alkanes, other C_3-benzenes, C_4-benzenes and ketones. The volatiles, while acutely toxic, are highly water soluble and likely to be diluted and dispersed in the water column, thus not contributing to the BOD of the effluent.

The acid-extractable compounds (AEC) were usually the largest component of the organics measured in most OCS discharges. Although they are a small fraction of crude oil, these compounds have the highest water solubility, which favors their incorporation in produced water at higher levels than the less soluble polycyclic aromatic hydrocarbon (PAH) fraction. The AEC fraction contained high amounts of aliphatic fatty acids, aromatic acids, benzoic acid, and alkyl-substituted benzoic acids. This is the most degradable fraction of produced waters. These compounds are less likely to be deposited in sediments, but are more likely to be diluted in the water column and dispersed from the discharge point (see Produced Water Fate).

The saturated hydrocarbons were the organic compounds next highest in concentration after the AEC. This fraction is composed of normal straight-chain hydrocarbons (alkanes), isoprenoid hydrocarbons, branched-chain hydrocarbons and naphthenes (cycloalkanes). This unresolved class of petroleum components accounts for more than 50 percent of the total saturated hydrocarbons. The saturated hydrocarbons are the least toxic fraction of crude oil, and are very susceptible to microbial degradation when deposited in the environment. This component of produced waters would contribute to the BOD of the effluent.

The PAH class was the smallest organic component of the produced water discharges, consisting of naphthalene and its alkylated analogs, napththalenes, phenanthrenes, and fluorenes. This fraction is the heaviest, most toxic, and environmentally stable fraction of crude oil. The toxicity of crude oil is a reflection of its aromatic content, primarily the akyl-substituted naphthalenes and phenanthrenes (NRC 1985). The PAHs are the most likely components of produced water to be incorporated into the sediments because of low water solubilities and high sorption coefficients. The compounds are longer lasting than the AEC and less likely to contribute to the BOD of the effluent.

For purposes of calculating the carbon load from representative produced water constituents, the worst-case scenario can be based on maximal concentrations from Louisiana OCS produced water discharges (Table 3).

Table 3

Maximal Concentrations of Representative Compounds in OCS Produced Waters from Louisiana (Rabalais et al. 1991b)

Constituent	Concentration ($\mu g\ l^{-1}$)
Benzene	≤ 4,000
Toluene	≤ 1,000
Aromatic acids	≤ 18,000
Aliphatic fatty acids	≤ 120,000
Saturated HC	≤ 20,000
Total HC	≤ 150,000
PAH	≤ 500

In the absence of adequate Gulf of Mexico data for total organic carbon (TOC), data from the North Sea fields has been used. Although there are differences between the North Sea and the Gulf of Mexico, findings from the North Sea generally indicate what may be expected to occur in the Gulf of Mexico. The TOC for Gulf of Mexico produced waters averaged 340 mg l^{-1} (median of 193 mg l^{-1}) (OOC 2004). These values are similar to North Sea produced water where the TOC averaged 185 mg l^{-1} (range 45-350 mg l^{-1}) (Flynn et al. 1996). The OOC (2004) also reports BOD for produced water with a mean of 1,007 mg $O_2\ l^{-1}$ (BOD_{21}) (median of 580 mg $O_2\ l^{-1}$). The BOD reflects the degradable materials in the produced waters, i.e., oxygen consumption potential.

The ammonium-N content of produced waters from several North Sea fields ranged from 1-17 mg l^{-1} for Murchison and 0-8.9 mg l^{-1} for Hutton, compared to literature values of 10-250 mg l^{-1} for the North Sea and 10-300 mg l^{-1} for other areas (Tibbetts et al. 1992). The OOC (2004) reports average total Kjeldahl nitrogen (TKN) (ammonium + organic N) values from Gulf of Mexico produced waters as a mean of 150 mg l^{-1} (median 135 mg l^{-1}). The nitrogen in the TKN is present primarily as ammonium.

PRODUCED WATER FATE

Several studies have been conducted in the North Sea on the fate of produced waters upon release into ambient waters. Flynn et al. (1996) reviewed North Sea produced water discharges, three from oil production and one from gas condensate production. Upon release, the constituents in the produced water will volatilize, biodegrade, and disperse.

Biodegradation tests indicated that the majority of organic materials in Clyde produced water (North Sea, Flynn et al. 1996) were readily biodegradable. The ultimate BOD was reached in less than 9 days. Ninety percent of the total organic carbon (TOC) was biodegraded within 8 days and after 28 days the proportion had risen to 96 percent (Table 4). The addition of inorganic nutrients to the BOD tests made little difference, suggesting that the nutrient status of produced water is sufficient to support substantial biodegradation. Volatilization will occur rapidly for the lower molecular weight components, especially the phenols and BTEX.

Table 4

Effect of Biodegradation on Selected Organics in Produced Water Collected from North Sea Fields
(from Flynn et al. 1996)

Time (days)	TOC (mg l^{-1})	VFA (mg l^{-1})	Phenols ($\mu g\ l^{-1}$)	BTEX ($\mu g\ l^{-1}$)	Total B/N ($\mu g\ l^{-1}$) *	PAH ($\mu g\ l^{-1}$)
0	45	25	8,810	4,800	9,210	1,460
8	1.42	6	4.7	<0.5	610	99
28	0.52	4	na	<0.5	630	4.6

* – Total B/N Total Bases/Neutral Fraction, BTEX + non-volatile base neutrals
BTEX – benzene, toluene, ethyl benzene, xylene
na – not available
PAH – Polycyclic aromatic hydrocarbon
TOC – total organic carbon
VFA – volatile fraction (all)

Flynn et al. (1996) also summarized the results of a particle-tracking model applied to the dilution of a produced water plume after discharge. The model predicted that the center of the discharge plume would sink about 10 m due to the high salinity of the produced water and the initial momentum. As the plume entrains more sea water, it becomes neutrally buoyant and the center line of the plume stabilizes in the water column. During a tidal cycle the plume becomes relatively long and narrow (approx. 50 m x 4 m in cross section at 100 m (0.06 mi) from the platform) and rotates around the platform. The greatest proportion of the dilution effect is manifest in the first 100 m (0.06 mi) from the discharge. At 500 m (0.3 mi) from the platform the model predicts that the minimum dilution at any point in the plume will approach a value of 775 for a short period during the tidal cycle. The minimum dilution was predicted to reach 9,000 at 20 km (12.4 mi). The conversion to miles is included here for comparison with other calculations based on 5-, 10-, and 20-mi distances for cumulative discharge volumes. Over this distance, biodegradation would begin to have a significant impact. At 15°C the minimum dilution of 60,000 is reached at 20 km (12.4 mi) from the platform. The initial PAH concentrations in produced water discharged from four platforms on the OCS off Louisiana and Texas were much lower (37 to 578 $\mu g\ l^{-1}$) than those of the North Sea (1,460 $\mu g\ l^{-1}$) and reached background concentrations (0.058 to 0.118 $\mu g\ l^{-1}$) 2 km (1.2 mi) down-current from the discharge point, similar to ambient concentrations in the open Gulf of Mexico (Neff and Sauer 1996).

Brandsma and Smith (1996) used the OOC model to estimate concentrations of discharged produced water based on conditions applicable to the Gulf of Mexico, primarily to assess the concentrations where potential effects could occur. The information, however, proves useful to estimates of dilution from the point of discharge. They used a median flow rate for the Gulf of Mexico (728 bbl d^{-1}, 116 $m^3\ d^{-1}$), a slow current speed of 3.3 cm s^{-1}, and an intermediate density gradient to predict a maximum concentration at 100 m (0.06 mi) from the outfall in 27 m water depth of 0.04 percent. They used the maximum allowable discharge of 25,000 bbl d^{-1} (3,978 $m^3\ d^{-1}$), under the permit then in effect, with field current data within a 100-m vertical cylinder and predicted that the maximum concentration estimated at the edge of the cylinder during the 24-h period was 0.35 percent. It was noted by Scott Wilson (pers. Comm., USEPA Region 6) that the method the authors used to calculate the effluent concentration appears to overestimate dispersion. Constantly changing current conditions and the effects of volatilization, biodegradation or precipitation may act to remove produced water components at a higher rate than just simple dispersion.

The median density stratification used by Brandsma and Smith (1996) for the Gulf of Mexico was 0.15 kg m-3 m-1, but ranged from relatively weak to strong (0.04 to 0.2-0.7 kg m-3 m-1). Similar results were obtained in a recent model simulation (OOC 2004) (Figures 10 and 11), where weak density gradients led to ‘trapping’ of discharge plumes.

Density difference values for composite station C6* in the core of the hypoxic zone off Terrebonne Bay in 20 m were higher than the value used by Brandsma and Smith (1996) for most of the stratified spring and summer (0.25 to 0.55 kg m^{-3} m^{-1}) but minimal in winter (0.02 kg m^{-3} m^{-1}) (Justić et al. 1993). Station C6* is a suite of stations in 20-m water in South Timbalier Blocks 52 and 53. Strong density stratification would not affect the precipitation of particle adhered hydrocarbons to the sediments. Given that zooplankton fecal pellets sink to the bottom in less than 1 day in 20 m water depth, it would be expected that particle adhered hydrocarbons would also reach the bottom.

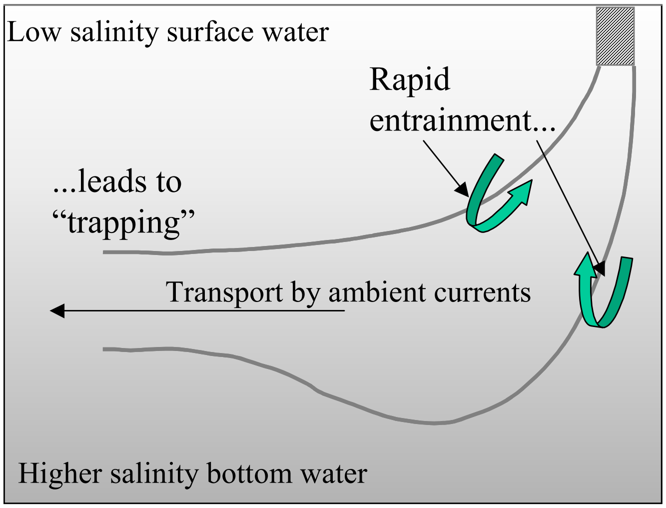


Figure 10. Conceptual model of transport in stratified receiving water (OOC 2004).

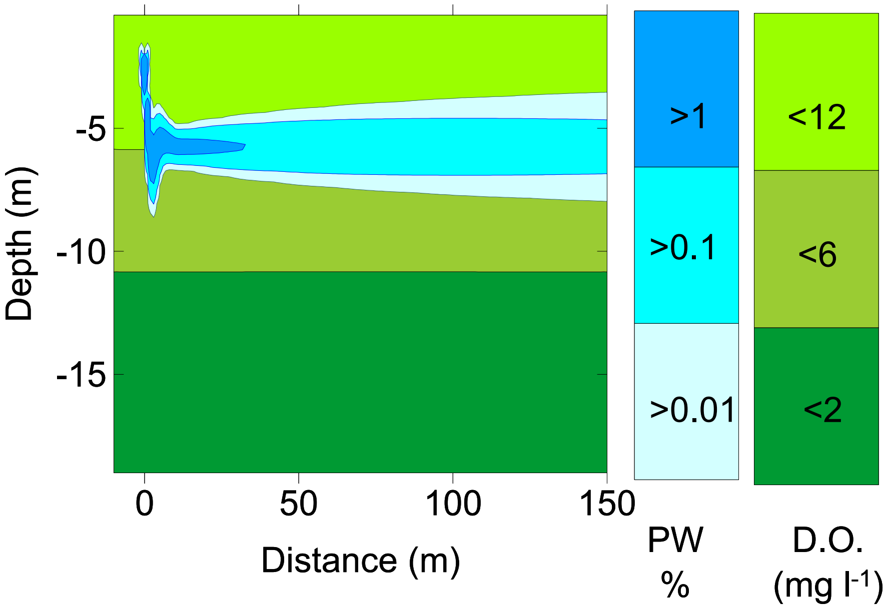


Figure 11. Model prediction of plume behavior for strong stratification, based on data for dissolved oxygen, salinity, and temperature reported in Rabalais et al. (1993) (OOC 2004).

Most of the produced water discharges are thought to be located near the surface in the Louisiana-Texas hypoxic zone (Figure 12) (OOC 2004). Therefore, the effluent would likely be entrained in the upper water column, and dispersed similar to the Brandsma and Smith (1996) model. If produced waters were discharged below a seasonal pycnocline when bottom current speeds are minimal (< 5 cm s^{-1}) (W. J. Wiseman, Jr. et al. unpubl. Data) and the plume were to contact the seabed, dispersion would be minimized and a hypersaline produced water plume at the bottom could result (see Interaction of Hypoxia and Produced Water).

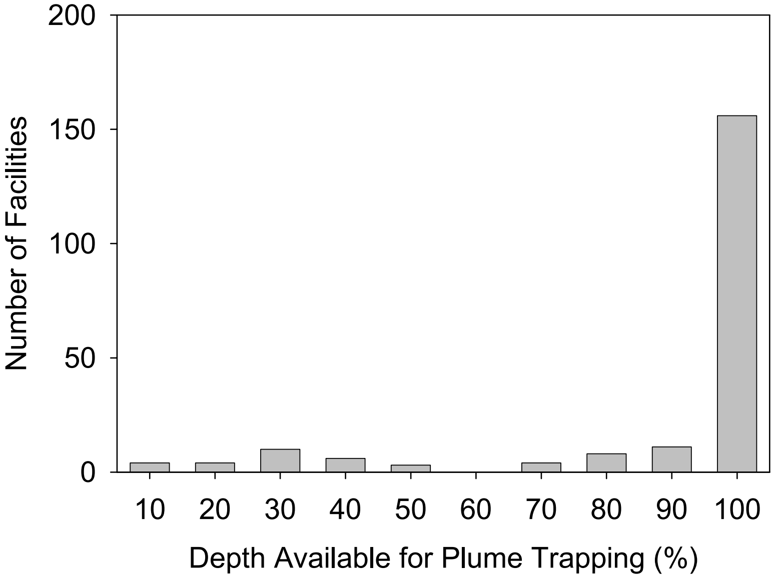
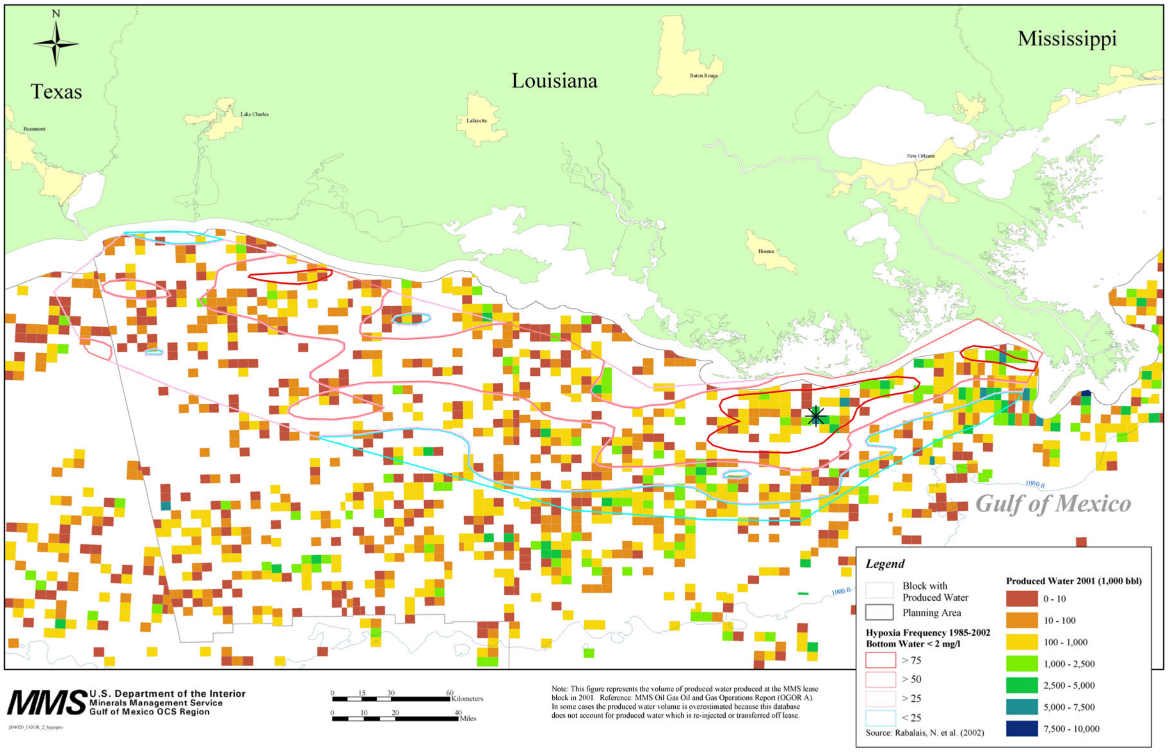


Figure 12. Histogram of fraction of water depth between discharge pipe and sea bottom for produced water discharges in the hypoxic zone. The overwhelming majority of outfalls are located within 5% of the sea surface or above the sea surface entirely [developed by OOC (2004) from data in Shannon 1992].

PRODUCED WATER DISCHARGES – VOLUME AND GEOGRAPHIC DISTRIBUTION

The discharge of produced waters into the offshore waters of Louisiana and Texas is extensive (Figure 13). Estimates of produced waters discharged into OCS waters of the northwestern Gulf were 494.4 x 10^6 bbl y^{-1} with the predominance of the discharges occurring off Louisiana (Rabalais et al. 1991b). A more recent estimate (NRC 2003) indicated 473 x 10^6 bbl y^{-1} for the OCS across the Gulf with an additional 186 x 10^6 bbl y^{-1} for Louisiana territorial waters and 4.3 x 10^6 bbl y^{-1} for Texas territorial waters for a total U.S. Gulf of Mexico of 663.3 x 10^6 bbl y^{-1} produced water effluent (Table 1). The OCS total volumes from the two estimates are quite similar. The MMS data indicate that there has been a slight decline in the volumes discharged into the hypoxia zone between 1996 and 2004 (Figure 14).



Note: This figure represents the volume of produced water produced at the MMS lease block in 2001. Reference: MMS Oil Gas Oil and Gas Operations Report (OGOR A). In some cases the produced water volume is overestimated because this database does not account for produced water which is re-injected or transferred off lease.

Figure 13. Distribution of produced water discharge volumes by OCS lease block for a portion of the Central and Western OCS superimposed on the frequency of mid-summer, bottom-water hypoxia. The asterisk (*) indicates the general location of composite station C6* in 20-m water depth, which is the location of specific carbon, nitrogen, and oxygen calculations. [Map generated by the Minerals Management Service with input from Rabalais et al. (2002) for the distribution of hypoxia frequency.]

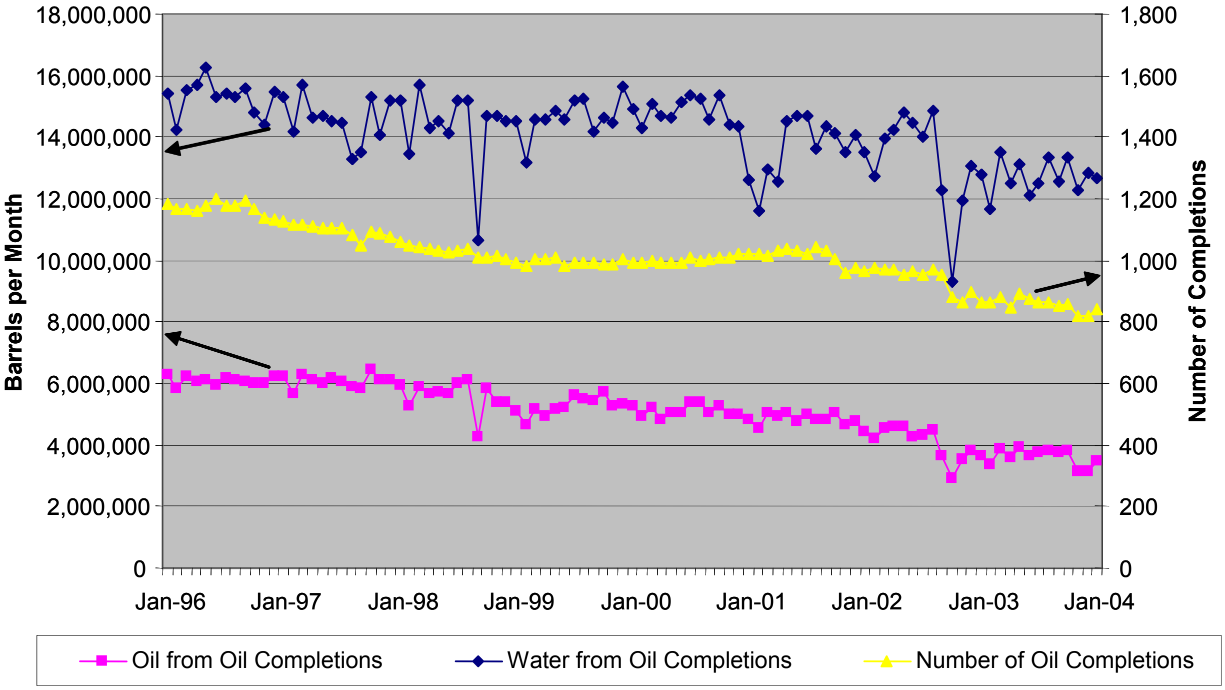


Figure 14. Number of oil completions and oil and water from oil completions within the area of hypoxia (Figure 13) for the period 1996-2003 (from Mike Melancon, Minerals Management Service, pers. Comm., August 2004).

The amount of produced water generated by any single well tends to go up as the oil or gas product is depleted from the formation, and may be as high as 95 percent of the product stream in older fields such as coastal Louisiana and Texas (Neff et al. 1987). Thus, as a field ages the produced water effluents also rise. However, once a formation is depleted, the well is taken off line and no longer generates produced water. There is a general decline in the Gulf of Mexico (Figure 14) of the number of oil completions and the amount of oil from completions from January 1996 to January 2004, with a step-wise decrease in water from oil completions during that period beginning 2001 and 2002. There has been a steady decrease in gas production from gas completions from January 1996 to January 2004, a slight decrease in gas completions during that period and no change in the produced water volume from gas depletions (M. Melancon, Minerals Management Service, pers. Comm., August 2004).

Volumes of produced water were calculated for the area surrounding composite station C6* in South Timbalier Blocks 52 and 53, within 5-, 10-, and 20-mi radius circles of station C6C, for comparison with estimated net production of carbon in surface waters. These values are illustrated in Figure 15 for 1984-2001 and provided in Appendix 2. The average produced water discharge has risen fairly consistently for this part of the Louisiana OCS where the amount of formation water may be increasing as the amount of petroleum product decreases. Changes in produced water volume were compared with changes in the size of the hypoxic zone to see if there were any empirical relationships. While the relationship between area and produced volume within 5 mi of C6* is significant ($R^2 = 0.24$, $P < 0.02$), the relationships between area and cumulative volume within 10 mi and 20 mi are not ($R^2 = 0.30$, $P < 0.1$ and $R^2 = 0.15$, $P < 0.12$, respectively). None of the relationships of hypoxic area with produced water volume are particularly strong (all $R^2 < 0.24$), thus there is little evidence to link the increase of produced water volume with changing size of the hypoxic zone. The size of the hypoxic area, however, is strongly correlated with the integrated flux of nitrate from the Mississippi River 75 days prior to the survey cruise ($R^2 = 0.61$, $P < 0.001$).

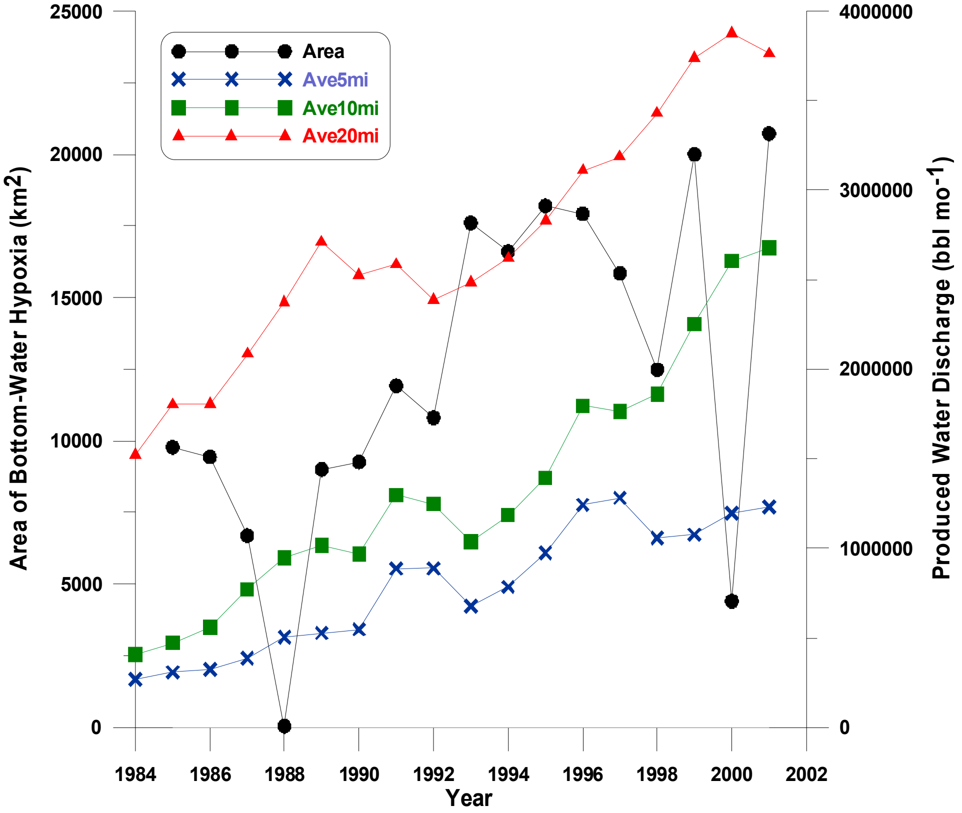


Figure 15. Time course of produced water volumes for all platforms within a 5-, 10-, and 20-mi radius of composite station C6* and size of the bottom water hypoxic area based on a 5-day mid-summer mapping cruise. Data for produced water volumes provided by the Minerals Management Service. Data for size of hypoxic zone modified from Rabalais et al. (2002) for all years except 1989, which is derived from Turner et al. (2005).

INTERACTION OF HYPOXIA AND PRODUCED WATERS

LOUISIANA SHELF

The initial reconnaissance work on the four platforms in Rabalais et al. (1993) revealed varying levels of hydrocarbon contamination with distance from the produced water discharge. For comparison, the levels of representative constituents of produced water in the sediments are presented in Table 5. In general (based on the complete data set), there were no consistent spatial or temporal trends in hydrocarbon chemistry at the platforms. Hydrocarbon concentrations, in general, were low for most, even where the sediments were silty, or were characterized as weathered petrogenic or biogenic in nature. There were stations, however, where sediment hydrocarbons were elevated and distinctly petrogenic, but there were no clear patterns or gradients. The hydrocarbon characteristics, along with some sedimentary variability, and differences in the hypoxic conditions from the West Delta area to the South Timbalier area made it difficult to discern trends in benthic community changes due to hydrocarbons in sediments. Differences in benthic communities, however, could be attributed to sediment characteristics and oxygen environments (Rabalais et al. 1993).

Table 5

Comparative Values of Produced Water Constituents in Sediments within 100 or 250 m
at Production Platforms in June 1990 (Rabalais et al. 1993).
(OCS block numbers, hypoxia station designations, and discharge volumes as indicated.)

Platform	WD32	WD32	ST53	ST53	ST52	ST52
Station			(C6)	(C6)	(C6C)	(C6C)
	(20,000 bbl day^{-1})		(5500 bbl day^{-1})		(20,000 bbl day^{-1})	
Distance (m)	100	250	100	250	100	250
Constituent						
Zn (ppm)	92.1	89.4	48.2	98.6	88.3	133.4
Pb (ppm)	17.0	0.0	6.0	11.8	0.0	1.8
Total Saturated HC (ppb)	7,659	6,052	3,197	2,183	3,257	1,3758
Alkylated PAH (ppb)	425	180	68	84	98	470
WD – West Delta ST – South Timbalier						

The Rabalais et al. (1993) study and further work in the hypoxic area off Terrebonne Bay provided many hydrographic profiles for comparing temperature, salinity, dissolved oxygen, redox and pH between discharge and non-discharge sites. Two or sometimes three of the stations [C6 (discharge), C6B (no discharge) and C6C (discharge)] were profiled in the same day within an hour's time. The comparative profiles of these data are illustrated in Appendix 1. The profiles of C6 and C6B were essentially the same for 2000-2004. There was a concerted effort to compare C6B and C6C before moving the instrument mooring to a fixed position at C6C for real-time data transmission. Ten of the 18 comparative profiles were similar, while eight profiles indicated a thin, hypersaline, lower dissolved oxygen lens very near the bottom, within 0.05 to 1 m above the sea floor; the dissimilar profiles occur primarily at C6C in 2003-2004. The near-bottom oxygen meter at C6C is positioned 1+ m above the bottom to avoid the hypersaline waters that can distort the dissolved oxygen values more representative of the broader area around the platform. Good coherence of conductivity, temperature, and depth (CTD) profiles for all three stations is illustrated in Figure 16 for 4/11/2003 and for two stations for 11/22/2004, but the bottom water lens of C6C is apparent in the 5/13/2003 and 5/5/2004 comparisons. These hypersaline waters are reduced in pH and redox; redox can fall below 0 mV. With the exception of these hypersaline plumes at C6C in

2003-2004, most profiles of dissolved oxygen and salinity near production platforms are similar to waters some distance from the platform or to platforms without a discharge.

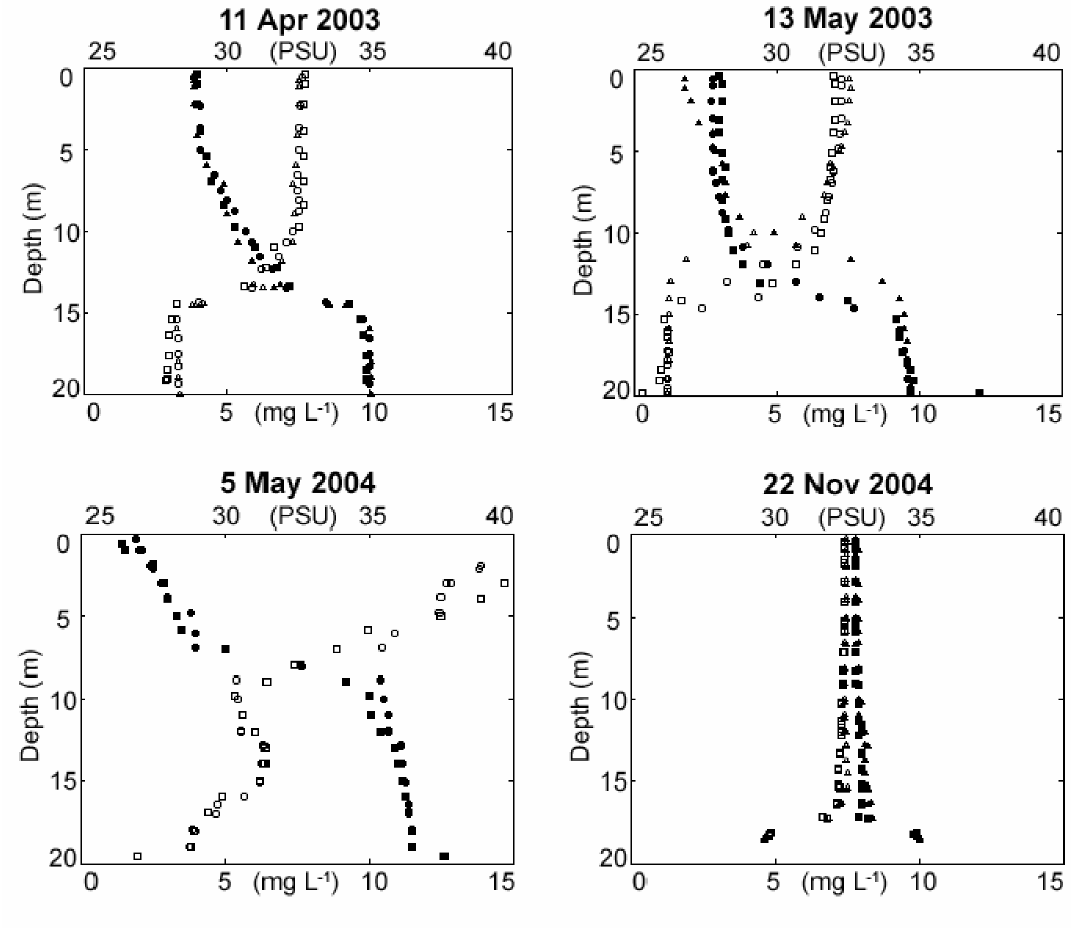


Figure 16. Dissolved oxygen (mg l^{-1}) and salinity (psu) profiles for stations C6 (triangles), C6B (circles) and C6C (squares) for dates indicated. Solid shapes are salinity and open shapes are dissolved oxygen (from Rabalais et al., unpublished data from hypoxia studies).

GULF OF MEXICO OFFSHORE OPERATIONS MONITORING EXPERIMENT (GOOMEX)

In the GOOMEX studies of drilling and produced water discharges off the Texas coast (Kennicutt 1995), the production platforms had little effect on most ambient water properties. The exception was that hypoxic or near hypoxic conditions were observed in the summer near the platforms at Matagorda Island Block (MAI)-686 (29 m depth) and Mustang Island Block MU-A85 (85 m deep) during periods of high stratification. Dissolved oxygen values determined at these two platforms during stratification (Cruises 2 and 4) were 1.76 and 0.32 mg l^{-1} for MAI-686 and 2.7 and 2.54 mg l^{-1} for MU-A85. The drilling discharges had been shunted to the bottom at MU-A85, but not at MAI-686. High dissolved nitrate, phosphate, and silicate concentrations in the bottom water during hypoxia indicated that they were being regenerated from the sediments.

Sediment texture was predominantly sand near the platforms as a result of disposal of drill cuttings. The organic carbon content decreased toward the platforms as the sand content increased. The inorganic carbon increased near the platform, most likely due to deposition of calcareous debris from platform associated fauna and the disposal of carbonate-containing cuttings. Hydrocarbon contaminants were elevated in sediments close to the MU-A85 platform (85 m, summer, near-hypoxia) but rapidly decreased over a distance of 100 to 200 m from the platform. Most hydrocarbons were degraded at MU-A85, but those of several stations at MAI-686 (29 m, summer hypoxia) were rich in n-alkanes. PAH levels in sediments were well below levels known to be associated with toxic biological effects (< 4000 ppb).

The localized bottom water hypoxia occurred only during stratified conditions. However, localized hypoxia was not observed during all episodes of stratified conditions. No clear conclusion can be drawn as to whether the localized hypoxia was a result of elevated hydrocarbons in the sediments, organic loading from produced waters, degradation of biofouling materials from the platform legs, or a combination of these.

OXYGEN AND CARBON BUDGETS

Oxygen profiles and calculations of oxygen anomalies for composite station C6* over the period 1985-1992 were used to define oxygen and carbon budgets for an area that is consistently hypoxic on a seasonal basis (station C6* in Figure 13) (Justić et al. 1996, 1997). The surface-water layer oxygen content, above the prevalent pycnocline at 10 m, is above the saturation level expected for the temperature and salinity conditions during February-July; the maximum in April and May coincides with mean peak Mississippi River flow. Oxygen content above saturation indicates that phytoplankton photosynthesis rates are high resulting in high levels of organic carbon production that can be redistributed within the system; much of this will eventually reach the lower water column and sediments. The bottom layer oxygen content, below the pycnocline to 20 m, is less than the saturation level expected for salinity and temperature conditions, meaning that respiration rates are exceeding any oxygen production rates. The oxygen content of bottom waters is lowest in July when surface-to-bottom density differences are greatest.

The integrated annual net productivity (NP) of the upper water column (0-10 m) at composite station C6* is 423 g O_2 m^{-2} (Figure 17), however, 90 percent occurs between February and June. Conversion by an oxygen-to-carbon ratio of 3.47 by weight results in total net carbon production of 122 g C m^{-2} y^{-1}. The excess of organic matter, derived from primary production, is redistributed within the system, and eventually decomposed in the lower water column and in the sediments. The integrated annual oxygen uptake rate in the lower water column at composite station C6* is 197 g O_2 m^{-2} y^{-1}, which converts to a value of 57 g C m^{-2} y^{-1} for the respiration process. Thus, on an annual basis, 47 percent of the surface net organic production at composite station C6* is decomposed in the lower water column and in the sediments (Total Respiration:Net Production, TR:NP = 0.47) (see Figure 17). This model closely replicates field measurements (Justić et al. 2002). The oxygen and carbon dynamics at composite statation C6* are strongly correlated with nitrate flux from the Mississippi River (Justić et al. 2003).

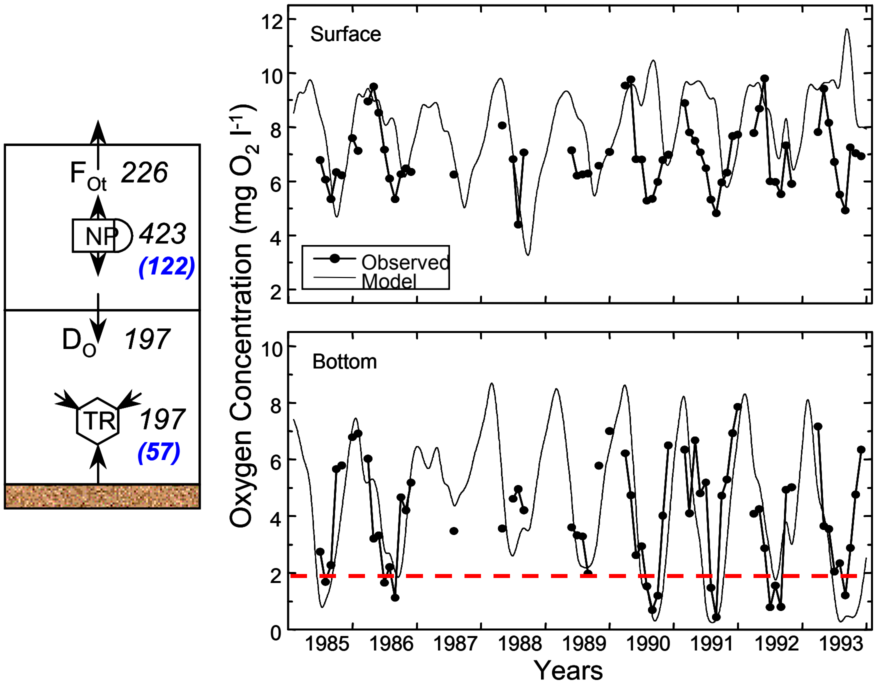


Figure 17. Coupled physical-biological model of oxygen and carbon dynamics at representative composite station C6* in the core of the hypoxic zone (from Justić et al. 1996, 1997, 2002). TR is total respiration, NP is net production, F_{Ot} is flux of oxygen across the air-water interface, D_O is diffusion of oxygen across the pycnocline, values in black are oxygen, and values in blue parentheses are oxygen converted to carbon equivalents.

RELATIVE CONTRIBUTION OF INPUTS OF PRODUCED WATER VERSUS THOSE OF THE MISSISSIPPI RIVER (DIRECT AND INDIRECT) IN THE DYNAMICS OF HYPOXIA

Nitrogen

One of the constituents of produced water, nitrogen, is an essential nutrient that supports primary production on the continental shelf. The Mississippi River delivers a large amount of nitrogen to the shelf that supports the high primary production there. The forms of nitrogen delivered by the Mississippi River are dissolved or particulate nitrogen and organic or inorganic nitrogen. The dissolved nitrate in the Mississippi River is the largest proportion of the total nitrogen (Table 6) (Goolsby et al. 1999). The average TKN in a produced water discharge is 150 mg l^{-1}, of which ammonium is the predominant nitrogen form (OOC 2004).

Table 6

Mean Annual Flux of Nutrients from the Mississippi-Atchafalaya River Basin to the Gulf of Mexico, 1980-1996 (adapted from Goolsby et al. 1999)

Nutrient	Mean Flux (metric tons)	Percent of Total
Nitrogen (N), Total	1,567,900	100
Nitrate	952,700	61
Ammonium	31,000	2
Dissolved organic N	376,000	24
Particulate organic N	204,000	13

A first order estimation of the amount of ammonium discharged onto the continental shelf area affected by hypoxia (20,000 km^2) was compared to the amount of nitrogen discharged to the continental shelf from the Mississippi and Atchafalaya rivers. This comparison assumes that the average produced water volume within a 20-mi circumference of composite station C6* (813.6 km^2) is representative of the average produced water volume over a 20,000 km^2 area. The produced water discharge and the Mississippi River discharge were estimated on an annual basis. However, the produced water discharge through the year is fairly constant (Figure 18), but the load of nitrogen from the river peaks in April and most is delivered between March and June. The conversion also assumes that the inputs of the numerous forms of nitrogen are all equivalent with regard to supporting primary production, which is not the case. Calculations of components that would be relevant are difficult because of lack of data and the uncertainty of uptake of some forms of nitrogen by different taxa of phytoplankton and bacteria. Still, the comparison provides a relative statement of inputs. Conversion of the ammonium in produced water to the area of hypoxia produces a value of 2.1 x 10^5 kg y^{-1}. The amount of total nitrogen delivered to the shelf (assuming that it affects the same area) is 1.6 x 10^9 kg y^{-1}. The produced water ammonium load is therefore estimated to be 0.013 percent of the total nitrogen delivered by the Mississippi River system, 0.008 percent of the total dissolved inorganic nitrogen and 0.002 percent of the total ammonium.

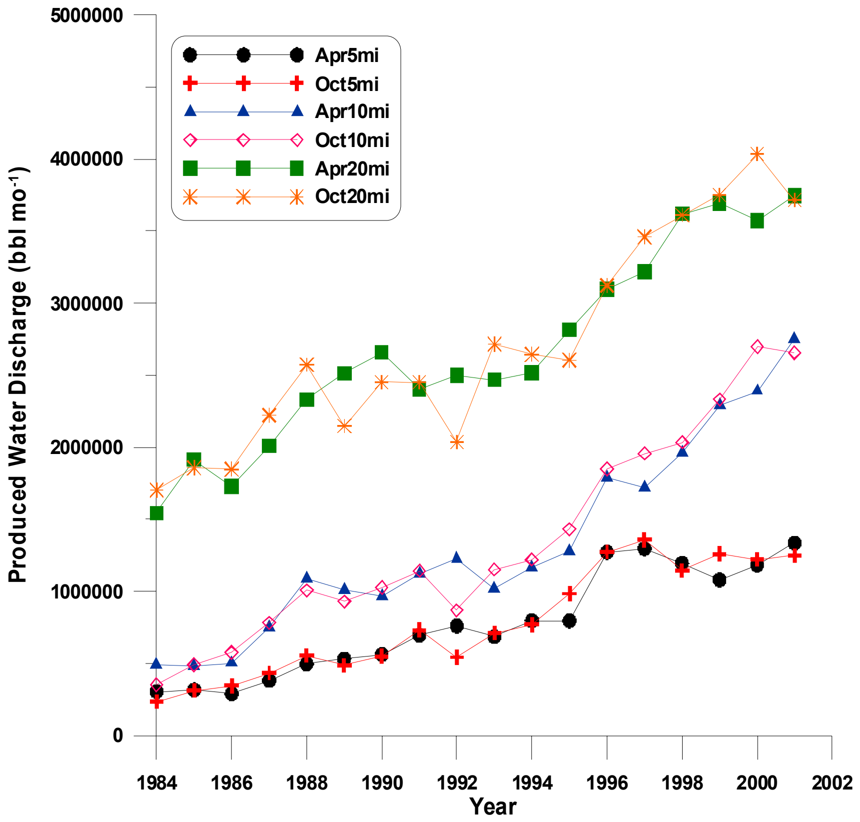


Figure 18. Produced water discharge volume in April (during high Mississippi River discharge) and October (during low Mississippi River discharge) by year for all discharging platforms in 5-mi, 10-mi, and 20-mi radius circles around composite station C6*. Data for produced water volumes provided by the Minerals Management Service.

Average concentration of dissolved inorganic nitrogen at composite station C6* over the period 1985-1998 indicate that average surface values range from 8 to 10 µM in late winter and early spring when river discharge is high and below 1 µM after the peak of chlorophyll biomass in the spring and early summer and when the river discharge is low in summer (Figure 4). Concentration of ammonium can be high in bottom waters when the oxygen level is close to anoxia, but otherwise falls mostly below 5 µM. Nitrate concentrations are mostly below 10 µM with the majority below 5 µM; highest values are in dissolved oxygen less than 2 mg l^{-1} (other than two outliers in Figure 19). A mean of 150 mg l^{-1} ammonium (equivalent to 8,333 µM $NH4^{+}$) in produced water would be discharged into ambient surface dissolved inorganic nitrogen (6 to 8 µM in spring and 1 µM in summer). If the produced water ammonium is reduced to 0.1 percent of the discharge concentration within a short distance of the plume and 0.01 percent of the discharge within 150 m [according to OOC (2004) dispersion model], the ammonium in the produced water discharge would be within the concentration of ambient dissolved inorganic nitrogen within 50 to 150 m from the discharge (see Figure 11). If a produced water were discharged below the pycnocline into the minimal currents typical of summer bottom water, the concentration of the ammonium in the discharge would be elevated in comparison to the ambient conditions for both ammonium and nitrate. However, the diffusion or recycling rates of the bottom-water nitrogen compounds are not known.

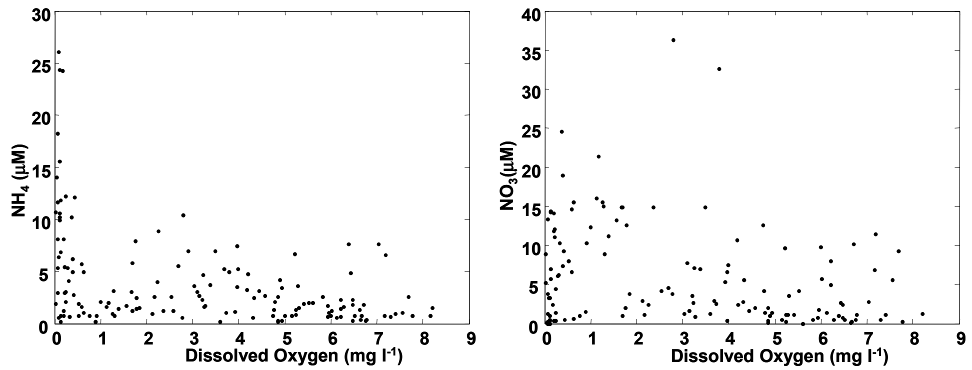


Figure 19. Bottom water concentration of NH_4^+ and NO_3^- (μM) at station C6* compared to bottom water dissolved oxygen (mg l^{-1}) for period 1985-2002 (from Rabalais et al. unpubl. data from hypoxia studies 1985-2005).

Hydrocarbons

Several assumptions and comparison of dissimilar data sets were necessary to develop first order estimates of the contribution of organic carbon from produced waters to the Mississippi River in supporting biochemical oxygen demand that leads to hypoxia. The assumptions lean to worst-case scenarios for the produced water carbon inputs, but the expected dilutions and dispersions correspond to available models. The oil and grease loadings do not distinguish among the various hydrocarbon compounds that might be in the effluent or the river. The compounds are of various categories—aromatics, medium-molecular weight PAHs, acid extractable compounds, saturated hydrocarbons and fatty acids. There is considerable variability among the many compounds with regard to volatility, solubility, photo-oxidation, the likelihood of adhering to sedimenting particles, and the susceptibility to microbial degradation. All hydrocarbons included in the oil and grease content and loadings were included in calculations of organic carbon that would reach the lower water column and sediments and contribute to respiratory reduction of dissolved oxygen. This, of course, is not the case.

The discharge of oil and grease from produced waters in U.S. Gulf of Mexico waters is 2,305 tonne y^{-1} (primarily discharged into the northwestern Gulf) and from the Mississippi River is 525,638 tonne y^{-1} (Tables 1 and 2). The riverine particulate organic carbon (POC) load is 3,209,536 tonne y^{-1}, and the dissolved organic carbon (DOC) load is 2,951,362 tonne y^{-1} (Goolsby et al. 1999). The produced water oil and grease loads are for the entire U.S. Gulf of Mexico, but discharges west of the Mississippi River delta far exceed those to the east. The majority of the discharge from the Mississippi River moves westward from the delta most of the year. If there were impacts from either source, they would most likely affect the shelf to the west of the delta. The oil and grease load in the river discharge is expected to dilute in the plume as it mixes with Gulf waters and follow the path of reduction outlined in Figure 9 for allochthonous carbon from the Mississippi River basin. If 4 percent of the oil and grease from the river were to contribute to organic loading below the pycnocline, as is expected for the TOC load, then 21,025 tonne y^{-1} of the Mississippi River oil and grease could potentially contribute to organic loading leading to hypoxia. The produced water oil and grease load for the Gulf of Mexico is 10.9 percent of the oil and grease load from the Mississippi River that might contribute to hypoxia and 0.04 percent of the total Mississippi River oil and grease load.

Without appropriate TOC, DOC and POC data for produced water discharges in the area of hypoxia, it would be inappropriate to compare produced water oil and grease loads to riverine TOC data. However, considering that the Gulf produced water oil and grease load is a relatively small percent of the Mississippi River load that might contribute to hypoxia, it is reasonable to expect that this small percentage would also be overwhelmed by the nutrient-enhanced surface *in situ* production offshore. The *in situ* production is estimated to be 96 percent of the organic matter loading that drives the oxygen and carbon budgets of the continental shelf where hypoxia occurs, compared with the up to 4 percent riverine organic loading that might contribute. The produced water contribution of organic carbon in the total loading of organic carbon within the hypoxic area appears to be insignificant given the present body of information.

IMPLICATIONS

The estimates used in this report to compare produced water inputs, either carbon or nitrogen, to similar inputs from the Mississippi River are first order calculations with numerous assumptions. Estimates were made both across the large area where hypoxia occurs and in the area of South Timbalier Blocks 52 and 53 where more detailed data on oxygen and carbon dynamics are available for a suite of stations (composite station C6*) in the core of the hypoxic zone (Figure 13). The inputs from the Mississippi River are well characterized and modeled as to their effects on the continental shelf, including the formation of hypoxia on fine temporal scale at composite station C6* and over a broad spatial scale from the Mississippi River to the upper Texas coast.

More detailed calculations of produced water carbon and nitrogen inputs to the continental shelf may be needed to resolve which compounds are relevant to the stimulation of phytoplankton production and respiration of fluxed organic matter, either directly or indirectly, and to what extent. The biochemical oxygen demand (BOD) of produced waters was not considered in this report, but may prove a useful line of investigation to actual carbon loading that leads to oxygen consumption. There may also be a need to distinguish between localized effects and regional effects. The suite of produced water discharges surrounding composite station C6* in OCS South Timbalier Blocks 52 and 53, however, appear to be an average condition when compared with the distribution geographically and by volume of discharges that occur in the hypoxic zone (Figure 13). Inputs of produced water used to calculate loads of carbon and nitrogen in this report were assumed to be at or near the surface, but some discharges occur closer to the bottom below the seasonal pycnocline. The fates of produced water effluents are likely to be different in these two discharge scenarios (Figure 12).

When considering whether or not to reduce produced water effluents that may contribute to respiratory demand in waters of the hypoxic zone, data from this report and observations currently underway should be placed within the context of what other mitigating measures might be taken within the Mississippi River watershed (CENR 2000, Mississippi River/Gulf of Mexico Watershed Nutrient Task Force 2001). The mitigating measures outlined in the Integrated Assessment and Action Plan are related primarily to the reduction of nutrients, both nitrogen and phosphorus, with a focus on nitrogen. The focus on nitrogen derives from the strong empirical relationships of oxygen decrease through time with increasing nitrogen loads from the river and the close fit of models for oxygen dynamics on the shelf linked to nitrate flux. Similar empirical relationships and modeling exercises with phosphorus are not robust. However, management of both nitrogen and phosphorus is recommended as is the case elsewhere in the U.S. and globally.

The mitigation measures include a suite of agricultural best management practices, methods to facilitate the retention of nutrients and denitrification of nitrogen within the landscape, and tertiary treatment of wastewater. There are differences among the many methods with regard to initial and long-term cost, and immediate and long-term effectiveness of nutrient removal. Not all methods are conducive to the reduction of both nitrogen and phosphorus, but instead one or the other, and do not necessarily achieve similar reductions for effort and cost expended. It is not known what potential reduction in nitrogen and organic carbon can be achieved for what cost through possible USEPA regulations on produced water discharge in the Gulf of Mexico OCS under a revised General Permit.

The loads of nitrogen and organic carbon (in the form of oil and grease in the estimates) from produced water discharges in the hypoxic zone as estimated in this analysis are minimal compared to inputs from the Mississippi River and do not likely contribute in a significant way to the dynamics of hypoxia in the OCS. Current scientific knowledge is that nutrients from the Mississippi River are the primary cause of excess primary production that leads to hypoxia. The first order estimates of contribution of produced water carbon and nitrogen appear to support the current paradigm of causes of hypoxia.

SUMMARY

Hypoxia is a seasonal, recurring feature of the Louisiana/Texas continental shelf adjacent to the Mississippi and Atchafalaya river deltas. The coupled biological/physical system is driven by the freshwater discharge and nutrient loads from a river basin that encompasses 40 percent of the lower 48 United States. The strongest evidence in the current literature is for oxygen and carbon dynamics in the hypoxic zone to be directly linked with seasonal stratification and nitrate flux from the Mississippi River. Increases in the overall productivity of the continental shelf ecosystem and the worsening of oxygen conditions below the pycnocline(s) is most closely correlated with changes in nitrate loads. The stratified structure of the water column in which hypoxia can form and be maintained is required and physics often dictates the overall distribution of hypoxia. Changes in hypoxia over time are not correlated with annual changes in produced water discharges. There are no seasonal changes in produced water discharges as there are for seasonal river discharge, nutrient flux and hypoxia.

There is some evidence of hypersaline, oxygen-depleted plumes of produced water at the seabed during summer stratified conditions (e.g., selected production platforms in GOOMEX and Rabalais et al. unpubl. data from hypoxia studies 1985-2005). The plumes are not the source of the stratification but become more defined and differentiated in stratified water columns. The dissolved oxygen content of these hypersaline plumes is below that of the water 1 to 2 m higher in the water column and the bottom water surrounding the platform. The location of the discharge within the water column may affect the presence of a bottom saline plume. The produced water plume is seldom seen at the seabed during unstratified conditions. If discharged above a pycnocline typical of summertime hypoxic conditions and into water with a slow current speed, produced water discharge volumes up to 15,000 bbl d^{-1} would be diluted to less than 1 percent within 100 m of the discharge.

There were many assumptions made and different data sets used for the first order estimates of produced water constituents that might contribute to the formation of hypoxia. These first order estimates of the contribution of carbon and nitrogen in produced water discharges compared to those of the Mississippi River indicated that the constituents from produced waters were minimal compared to those of the river.

The produced water ammonium discharged within the area subject to hypoxia is estimated to be 0.013 percent of the total nitrogen delivered by the Mississippi River system, 0.008 percent of the total dissolved inorganic nitrogen and 0.002 percent of the total ammonium. The ammonium in the produced water discharge would reach the concentration of ambient dissolved inorganic nitrogen within 50 to 150 m from the discharge. If discharged below the pycnocline in minimal currents typical of summer bottom water, the concentration of the ammonium in the discharge would exceed the ambient conditions for both ammonium and nitrate.

Only up to 4 percent of the terrestrial carbon delivered to the Gulf of Mexico along with oil and grease from nonpoint source runoff are estimated to contribute to respiratory demand in water below the pycnocline in the area of hypoxia. The produced water oil and grease load for the Gulf of Mexico is 10.9 percent of the oil and grease load from the Mississippi River that might contribute to hypoxia. The remainder of the organic matter reaching the bottom and fueling respiratory consumption of dissolved oxygen comes from *in situ* phytoplankton production stimulated primarily by the nutrients from the Mississippi and Atchafalaya rivers. The produced water contribution of organic carbon in the total loading of organic carbon within the hypoxic area appears to be insignificant given the present body of information.

LITERATURE CITED

Ayers, R. C. 1983. An evaluation of effluent dispersion and fate models for OCS platforms, Vol. I: summary and recommendations. In: Proc. Workshop, 1-20 February 1983, Santa Barbara, California. Prepared for the U.S. Dept. of the Interior, Minerals Management Service, Contract No. 14-12-0001-29122 by MBC Applied Environmental Sciences, and Analytic and Computational Research, Inc.

Bedinger, C. A. Jr. (ed.). 1981. Ecological investigations of petroleum production platforms in the Central Gulf of Mexico. Report to the U.S. Dept. of the Interior, Bureau of Land Management, Contract No. AA551-CT8-17, Southwest Research Institute, San Antonio, Texas.

Blackwelder, P., T. Hood, C. Alvarez-Zarikian, T. A. Nelsen and B. McKee. 1996. Benthic foraminifera from the NECOP study area impacted by the Mississippi River plume and seasonal hypoxia. Quaternary International 31:19-36.

Bode, A. and Q. Dortch. 1996. Uptake and regeneration of inorganic nitrogen in coastal waters influenced by the Mississippi River: Spatial and seasonal variations. Journal of Plankton Research 18:2251-2268.

Boesch, D. F. 1999. The role of the Mississippi River in Gulf of Mexico hypoxia: Oversimplifications and confusion. Document submitted to the Gulf of Mexico Hypoxia Working Group, National Oceanic and Atmospheric Administration. 19 pp.

Boesch, D. F. 2002. Challenges and opportunities for science in reducing nutrient over-enrichment of coastal ecosystems. Estuaries 25:886-900.

Boesch, D. F. and N. N. Rabalais, eds. 1989a. Produced waters in sensitive coastal habitats: An analysis of impacts, Central Coastal Gulf of Mexico. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, Louisiana. OCS Study MMS 89-0031. 157 pp.

Boesch, D. F. and N. N. Rabalais, eds. 1989b. Environmental impact of produced water discharges in coastal Louisiana. Report to the Louisiana Division of the Mid-Continent Oil and Gas Association. Louisiana Universities Marine Consortium, Chauvin, Louisiana. 287 pp.

Brandsma, M. G. and J. P. Smith. 1996. Dispersion modeling perspectives on the environmental fate of produced water discharges. In: M. Reed and S. Johnsen, eds. Produced Water 2: Environmental Issues and Mitigation Technologies. 1996. Plenum Press, New York. Pp. 213-224.

Bratkovich, A., S. P. Dinnel and D. A. Goolsby. 1994. Variability and prediction of freshwater and nitrate fluxes for the Louisiana-Texas shelf: Mississippi and Atchafalaya River source functions. Estuaries 17:766-778.

Brezonik, P. L., V. J. Bierman, Jr., R. Alexander, J. Anderson, J. Barko, M. Dortch, L. Hatch, G. L. Hitchcock, D. Keeney, D. Mulla, V. Smith, C. Walker, T. Whitledge and W. J. Wiseman, Jr. 1999. Effects of reducing nutrient loads to surface waters within the Mississippi River basin and the Gulf of Mexico. Topic 4 Report for the Integrated Assessment of Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 18, NOAA Coastal Ocean Program, Silver Spring, Maryland. 130 pp.

Carey, A. C., J. R. Pennock, J. C. Hehrter, W. B. Lyons, W. W. Schroeder and J. C. Bonzongo. 1999. The role of the Mississippi River in Gulf of Mexico hypoxia. Report to the Fertilizer Institute, Environmental Institute Publ. No. 70. The University of Alabama, Tuscaloosa, Alabama, 79 pp plus Tables and Figures.

Committee on Environment and Natural Resources (CENR). 2000. Integrated assessment of hypoxia in the northern Gulf of Mexico. National Science and Technology Council, Washington, D.C. 58 pp.

Conseil Permanent International pour l'Exploration de la Mer. 1936. Bulletin hydrographique pour l'Année 1935, Series B1. Le Bureau du Conseil, Service Hydrographique, Charlottelund Slot, Danemark, 105 pp.

Continental Shelf Associates, Inc (CSA), 2004. Gulf of Mexico comprehensive synthetic based muds monitoring program, Volumes I - III. Prepared for the SBM Research Group, the U.S. Dept. of Energy and the U.S. Dept of the Interior, Minerals Management Service. 2740 pp. Internet website: http://www.gomr.mms.gov/homepg/regulate/environ/techsumm/rec_pubs.html

DeMaster, D. J., G. B. Knapp and C. A. Nittrouer. 1986. Effect of suspended sediments on geochemical processes near the mouth of the Amazon River: Examination of biogenic silica uptake and the fate of particle-reactive elements. Continental Shelf Res. 6:107-125.

Diaz, R. J. and A. Solow. 1999. Ecological and economic consequences of hypoxia. Topic 2 Report for the Integrated Assessment of Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 18, NOAA Coastal Ocean Program, Silver Spring, Maryland. 45 pp.

Doering, O. C., F. Diaz-Hermelo, C. Howard, R. Heimlich, F. Hitzhusen, R. Kazmierczak, J. Lee, L. Libby, W. Milon, T. Prato and M. Ribaudo. 1999. Evaluation of the economic costs and benefits of methods for reducing nitrate loads to the Gulf of Mexico. Topic 6 Report for the Integrated Assessment of Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 18, NOAA Coastal Ocean Program, Silver Spring, Maryland. 115 pp.

Donner, S.D., M.T. Coe, J.D. Lenters, T.E. Twine and J.A. Foley. 2002. Modeling the impact of hydrological changes on nitrate transport in the Mississippi River basin from 1955 to 1994. Global Biochemical Cycles 16(3)10.1029/2001GB001396.

Dortch, Q. and T. E. Whitledge. 1992. Does nitrogen or silicon limit phytoplankton production in the Mississippi River plume and nearby regions? Continental Shelf Research 12:1293-1309.

Dortch, Q., N. N. Rabalais, R. E. Turner and G. T. Rowe. 1994. Respiration rates and hypoxia on the Louisiana shelf. Estuaries 17:862-872.

Dortch, Q., N. N. Rabalais, R. E. Turner and N. A. Qureshi. 2001. Impacts of changing Si/N ratios and phytoplankton species composition. In: N. N. Rabalais and R. E. Turner, eds. Coastal Hypoxia: Consequences for Living Resources and Ecosystems. 2001. Coastal and Estuarine Studies 58, American Geophysical Union, Washington, D.C. Pp 37-48.

Dunn, D. D. 1996. Trends in Nutrient Inflows to the Gulf of Mexico from Streams Draining the Conterminous United States 1972 — 1993. U.S. Geological Survey, Water-Resources Investigations Report 96-4113. Prepared in cooperation with the U.S. Environmental Protection Agency, Gulf of Mexico Program, Nutrient Enrichment Issue Committee, U.S. Geological Survey, Austin, Texas, 60 pp.

Eadie, B. J., B. A. McKee, M. B. Lansing, J. A. Robbins, S. Metz and J. H. Trefry. 1994. Records of nutrient-enhanced coastal productivity in sediments from the Louisiana Continental Shelf. Estuaries 17:754-765.

Flynn, S. A., E. J. Butler and I. Vance. 1996. Produced water composition, toxicity, and fate. A review of recent BP North Sea studies. In: M. Reed and S. Johnsen, eds. Produced Water 2: Environmental Issues and Mitigation Technologies. 1996. Plenum Press, New York. Pp. 69-80.

Goolsby, D. A., W. A. Battaglin, G. B. Lawrence, R. S. Artz, B. T. Aulenbach, R. P. Hooper, D. R. Keeney and G. J. Stensland. 1999. Flux and sources of nutrients in the Mississippi-Atchafalaya River basin, Topic 3 Report for the Integrated Assessment of Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 17, NOAA Coastal Ocean Program, Silver Spring, Maryland. 130 pp.

Ittekkot. V. 1988. Global trends in the nature of organic matter in river suspensions. Nature 332:436-438.

Justić, D., N.N. Rabalais, R.E. Turner and W.J. Wiseman, Jr. 1993. Seasonal coupling between riverborne nutrients, net productivity and hypoxia. Marine Pollution Bulletin 26(4):184-189.

Justić, D., N. N. Rabalais and R. E. Turner. 1996. Effects of climate change on hypoxia in coastal waters: a doubled CO_2 scenario for the northern Gulf of Mexico. Limnology and Oceanography 41(5):992-1003.

Justić, D., N. N. Rabalais and R. E. Turner. 1997. Impacts of climate change on net productivity of coastal waters: Implications for carbon budget and hypoxia. Climate Research 8:225-237.

Justić, D., N. N. Rabalais and R. E. Turner. 2002. Modeling the impacts of decadal changes in riverine nutrient fluxes on coastal eutrophication near the Mississippi River delta. Ecological Modeling 152:33-46.

Justić, D., R. E. Turner and N. N. Rabalais. 2003. Climatic influences on riverine nitrate flux: Implications for coastal marine eutrophication and hypoxia. Estuaries 26:1-11.

Holden, C. 2004. Gulf oil decline in sight. Science 306:1469.

Kennicutt II, M.C. ed. 1995. Gulf of Mexico offshore operations monitoring experiment, Final Report. Phase I: Sublethal responses to contaminant exposure. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA. OCS Study MMS 95-0045. 709 pp.

Lohrenz, S. E., M. J. Dagg and T. E. Whitledge. 1990. Enhanced primary production at the plume/oceanic interface of the Mississippi River. Continental Shelf Research 10:639-664.

Lohrenz, S. E., G. L. Fahnenstiel, D. G. Redalje, G. A. Lang, X. Chen, and M. J. Dagg. 1997. Variations in primary production of northern Gulf of Mexico continental shelf waters linked to nutrient inputs from the Mississippi River. Marine Ecology Progress Series 155:45-54.

Mississippi River/Gulf of Mexico Watershed Nutrient Task Force. 2001. Action plan for reducing, mitigating, and controlling hypoxia in the northern Gulf of Mexico. Office of Wetlands, Oceans, and Watersheds. U.S. Environmental Protection Agency, Washington, D.C.

Mitsch, W. J., Day, Jr., J. W., J. W. Gilliam, P. M. Groffman, D. L. Hey, G. W. Randall, and N. Wang. 2001. Reducing nitrogen loading to the Gulf of Mexico from the Mississippi River basin: Strategies to counter a persistent ecological problem. BioScience 15:373-388.

Mitsch, W. J., J. W. Day, Jr., J. Wendell Gilliam, P. M. Groffman, D. L. Hey, G. W. Randall and N. Wang. 1999. Reducing nutrient loads, especially nitrate-nitrogen, to surface water, ground water, and the Gulf of Mexico. Topic 5 Report for the Integrated Assessment of Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 18, NOAA Coastal Ocean Program, Silver Spring, Maryland, 111 pp.

National Research Council (NRC). 1985. Oil in the sea: Inputs, fates, and effects. National Academy Press. Washington, D.C. 601 pp.

National Research Council (NRC). 2003. Oil in the sea III: Inputs, fates, and effects (Committee on Oil in the Sea, J. N. Coleman, J. Baker, C. Cooper, M. Fingas, G. Hunt, K. Kvenvolden, J. McDowell, J. Michel, K. Michel, J. Phinney, N. Rabalais, L. Roesner, and R. B. Spies). National Academy Press, Washington, D.C. 265 pp.

Neff, J. M. and T. C. Sauer, Jr. 1996. Aromatic hydrocarbons in produced water. Bioaccumulation and trophic transfer in marine food webs. In: M. Reed and S. Johnsen, eds. Produced Water 2: Environmental Issues and Mitigation Technologies. 1996. Plenum Press, New York. Pp. 163-175.

Neff, J. M., N. N. Rabalais and D. F. Boesch. 1987. Offshore oil and gas development activities potentially causing long-term environmental effects. In: D. F. Boesch and N. N. Rabalais, eds. Long-Term Environmental Effects of Offshore Oil and Gas Development. 1987. Elsevier Applied Science Publishers, London. Pp. 149-173.

Neff, J. M., T. C. Sauer and N. Maciolek. 1989. Fate and effects of produced water discharges in nearshore marine waters. API Publication No. 4472, American Petroleum Institute, Washington, D.C., 300 pp.

Nelsen, T. A., P. Blackwelder, T. Hood, B. McKee, N. Romer, C. Alvarez-Zarikian and S. Metz. 1994. Time-based correlation of biogenic, lithogenic and authigenic sediment components with anthropogenic inputs in the Gulf of Mexico NECOP study area. Estuaries 17:873-885.

Nelson, D. M. and Q. Dortch. 1996. Silicic acid depletion and silicon limitation in the plume of the Mississippi River: Evidence from kinetic studies in Spring and Summer. Marine Ecology Progress Series 136:163-178.

Nguyen, A. H. and D. J. Roberts. 2005. Degradation of synthetic-based drilling mud fluids by Gulf of Mexico sediments; Presented at the MMS Gulf of Mexico OCS Region's Information Transfer Meeting (ITM); January 11-13, 2005; New Orleans, LA.

Offshore Operators Committee (OOC). 2004. Hypoxia Work Group Presentation, presented by Joe Smith, ExxonMobil Upstream Research Company, Houston, Texas at "Experts' Meeting on Produced Water, Oxygen Consumption, and Contribution to Hypoxic Zone," a joint Minerals Management Service and U.S. Environmental Protection Agency Meeting, 24 August 2004, New Orleans, LA.

Pavela, J. S., J. L. Ross, and M. E. Chittenden. 1983. Sharp reductions in abundance of fishes and benthic macroinvertebrates in the Gulf of Mexico off Texas associated with hypoxia. Northeast Gulf Science 6:167-173.

Pokryfki, L. and R. E. Randall. 1987. Nearshore hypoxia in the bottom water of the northwestern Gulf of Mexico from 1981 to 1984. Marine Environmental Research 22:75-90.

Qureshi, N. A. 1995. The role of fecal pellets in the flux of carbon to the sea floor on a river-influenced continental shelf subject to hypoxia. Ph.D. Dissertation, Department of Oceanography & Coastal Sciences, Louisiana State University, Baton Rouge, LA. 255 pp.

Rabalais, N. N. 2003. Oil in the sea. Issues in science and technology 20:74-78.

Rabalais, N.N., and R.E. Turner, eds. 2001. Coastal hypoxia: Consequences for living resources and ecosystems, Coastal and Estuarine Studies No. 58, American Geophysical Union, Washington, D.C. 460 pp.

Rabalais, N. N. and R. E. Turner. in press. Oxygen Depletion in the Gulf of Mexico Adjacent to the Mississippi River. In: B. B. Jørgensen, J. W. Murray, and L. N. Neretin, eds. Past and Present Marine Water Column Anoxia. NATO Science Series: IV-Earth and Environmental Sciences.

Rabalais, N.N., R.E. Turner, W.J. Wiseman, Jr. and D.F. Boesch. 1991a. A brief summary of hypoxia on the northern Gulf of Mexico continental shelf: 1985-1988. In: R.V. Tyson and T.H. Pearson, eds. Modern and Ancient Continental Shelf Anoxia, Geological Society Special Publication No. 58, The Geological Society, London, Pp. 35-47.

Rabalais, N. N., B. A. McKee, D. J. Reed and J. C. Means. 1991b. Fate and effects of nearshore discharges of OCS produced waters. Volume II. Technical Report. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA. OCS Study MMS 91-0005. 337 pp.

Rabalais, N. N., L. E. Smith, E. B. Overton and A. L. Zoeller. 1993. Influence of hypoxia on the interpretation of effects of petroleum production activities. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA. OCS Study MMS 93-0022. 158 pp.

Rabalais, N. N., L. E. Smith, D. E. Harper, Jr. and D. Justić. 1995. The Effects of Bottom Water Hypoxia on Benthic Communities of the Southeastern Louisiana Continental Shelf. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA. OCS Study MMS 94-0054. 105 p.

Rabalais, N. N., W. J. Wiseman, Jr. and R. E. Turner. 1994. Comparison of Continuous Records of Near-bottom Dissolved Oxygen from the Hypoxia Zone along the Louisiana Coast. Estuaries 17:850-861.

Rabalais, N. N., R. E. Turner, D. Justić, Q. Dortch, W. J. Wiseman, Jr. and B. K. Sen Gupta. 1996. Nutrient Changes in the Mississippi River and System Responses on the Adjacent Continental Shelf. Estuaries 19(2B):386-407.

Rabalais, N. N., R. E. Turner, D. Justić, Q. Dortch and W. J. Wiseman, Jr. 1999. Characterization of Hypoxia: Topic 1 Report for the Integrated Assessment of Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 15. NOAA Coastal Ocean Program, Silver Spring, Maryland, 167 pp.

Rabalais, N. N., L. E. Smith, D. E. Harper, Jr. and D. Justić. 2001. Effects of seasonal hypoxia on continental shelf benthos. In: N. N. Rabalais and R. E. Turner, eds. Coastal Hypoxia: Consequences for Living Resources and Ecosystems. Coastal and Estuarine Studies 58, American Geophysical Union, Washington, D.C. Pp. 211-240.

Rabalais, N. N, R. E. Turner and D. Scavia. 2002a. Beyond science into policy: Gulf of Mexico hypoxia and the Mississippi River. BioScience 52:129-142.

Rabalais, N. N., R. E. Turner, Q. Dortch, D. Justić, V. J. Bierman, Jr. and W. J. Wiseman, Jr. 2002b. Review. Nutrient-enhanced productivity in the northern Gulf of Mexico: Past, present and future. Hydrobiologia 475/476:39-63.

Rabalais, N. N., R. E. Turner and W. J. Wiseman, Jr. 2002c. Hypoxia in the Gulf of Mexico, a.k.a. "The Dead Zone." Annual Review of Ecology and Systematics 33:235-263.

Ray, J. P. and F. R. Engelhardt, eds. 2002. Produced Water, Plenum Press, New York. 606 pp.

Reid, D. F. 1983. Radium in formation waters: how much and is it of concern? In: Proceedings, Fourth Annual Gulf of Mexico Information Transfer Meeting. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA. OCS Study MMS 84-0026. Pp. 187-191.

Renaud, M. 1986. Hypoxia in Louisiana coastal waters during 1986: Implications for fisheries. Fishery Bulletin 84:19-26.

Rittenhouse, G., R. B. Fulton III, R. J. Grabowski and J. L. Bernard. 1969. Minor elements in oil field waters. Chemical Geology 4:189-209.

Roberts, D. J. In preparation. Degradation of synthetic-based drilling mud fluids by Gulf of Mexico sediments. Prepared for the U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA.

Scavia, D., N. N. Rabalais, R. E. Turner, D. Justić, and W. J. Wiseman, Jr. 2003. Predicting the response of Gulf of Mexico hypoxia to variations in Mississippi River nitrogen load. Limnology & Oceanography 48:951-956.

Sen Gupta, B. K., R. E. Turner and N. N. Rabalais. 1996. Seasonal oxygen depletion in continental-shelf waters of Louisiana: Historical record of benthic foraminifers. Geology 24(3):227-230.

Shannon, B. 1992. OOC Produced Water Discharge Configuration Database included in a letter to Mr. Jack Ferguson, U.S. Environmental Protection Agency, Region VI, Dallas, TX. November 11, 1992.

Smith, W. O. and D. J. DeMaster. 1996. Phytoplankton biomass and productivity in the Amazon River plume: Correlation with seasonal river discharge. Continental Shelf Research 16:291-319.

Suess, E. 1980. Particulate organic carbon flux in the oceans: Surface productivity and oxygen utilization. Nature 288:260-263.

Stow, C. A., S. S. Qian and J. K. Craig. 2005. Declining threshold for hypoxia in the Gulf of Mexico. Environmental Science and Technology 39:716-723.

Tibbetts, P. J. C., I. T. Buchanan, L. J. Gawel and R. Large. 1992. A comprehensive determination of produced water composition. In: Ray, J. P. and F. R. Engelhardt, eds. Produced Water, Plenum Press, New York. Pp. 97-112.

Trefry, J. H. 2005. *Deepwater Program:* Effects of Oil and Gas Exploration and Development at Selected Continental Slope Sites in the Gulf of Mexico. Presented at the MMS Gulf of Mexico OCS Region's Information Transfer Meeting (ITM); January 11-13, 2005. New Orleans, Louisiana.

Trefry, J. H., S. Metz, T. A. Nelsen, R. P. Trocine and B. J. Eadie. 1994. Transport of particulate organic carbon by the Mississippi River and its fate in the Gulf of Mexico. Estuaries 17:839-849.

Turner, R. E. and R. L. Allen. 1982. Bottom water oxygen concentration in the Mississippi River delta bight. Contributions in Marine Science 25:161-172.

Turner, R. E. and N. N. Rabalais. 1994. Coastal eutrophication near the Mississippi River delta. Nature 368:619-621.

Turner, R. E. and N. N. Rabalais. 2003. Linking landscape and water quality in the Mississippi River basin for 200 Years. BioScience 53:563-572.

Turner, R.E., N.N. Rabalais and Z.-N. Zhang. 1990. Phytoplankton biomass, production and growth limitations on the Huanghe (Yellow River) Continental Shelf. Cont. Shelf Res. 10(6):545-571.

Turner, R. E., N. Qureshi, N. N. Rabalais, Q. Dortch, D. Justić, R. F. Shaw and J. Cope. 1998. Fluctuating silicate:nitrate ratios and coastal plankton food webs. Proceedings National Academy of Science, USA 95:13048-13051.

Turner, R. E., N. N. Rabalais, E. M. Swenson, M. Kasprzak and T. Romaire. 2005 Summer hypoxia in the northern Gulf of Mexico and its prediction from 1978 to 1995. Marine Environmental Research 59:65-77. Internet website: ScienceDirect - Marine Environmental Research : Summer hypoxia in the northern Gulf of Mexico and its prediction from 1978 to 1995.

U.S. Environmental Protection Agency. 1993. 40 CFR Part 435 [FRL-4537-1] RIN 2040-AA12 "Oil and Gas Extraction Point Source Category, Offshore Subcategory; Effluent Limitations Guidelines and New Source Performance Standards" Federal Register 58(41), March 4, 1993:12454-12512.

U.S. Environmental Protection Agency (USEPA) Region 4. 2004. Evaluation of the role of nitrogen and phosphorous [sic] in causing or contributing to hypoxia in the northern Gulf. U.S. Environmental Protection Agency, Atlanta Regional Office, Region 4, 61 Forsyth Street SW, Atlanta, Georgia. Internet website: http://initrogen.org/fileadmin/user_upload/epa_august04_hypoxia_report.pdf

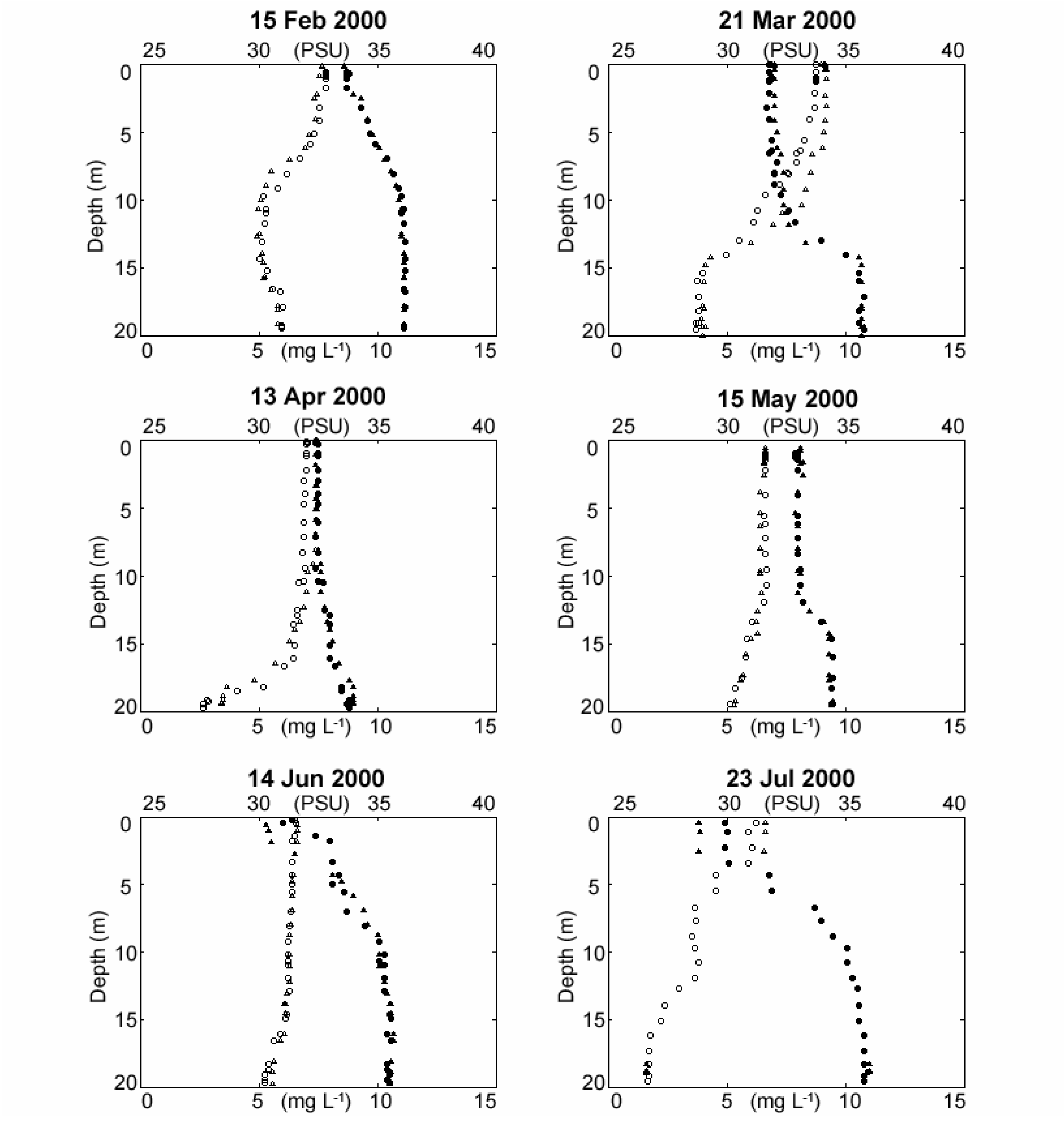
Wiseman, Jr., W. J., N. N. Rabalais, R. E. Turner, S. P. Dinnel and A. MacNaughton. 1997. Seasonal and interannual variability within the Louisiana coastal current: Stratification and hypoxia. Journal of Marine Systems 12:237-248.

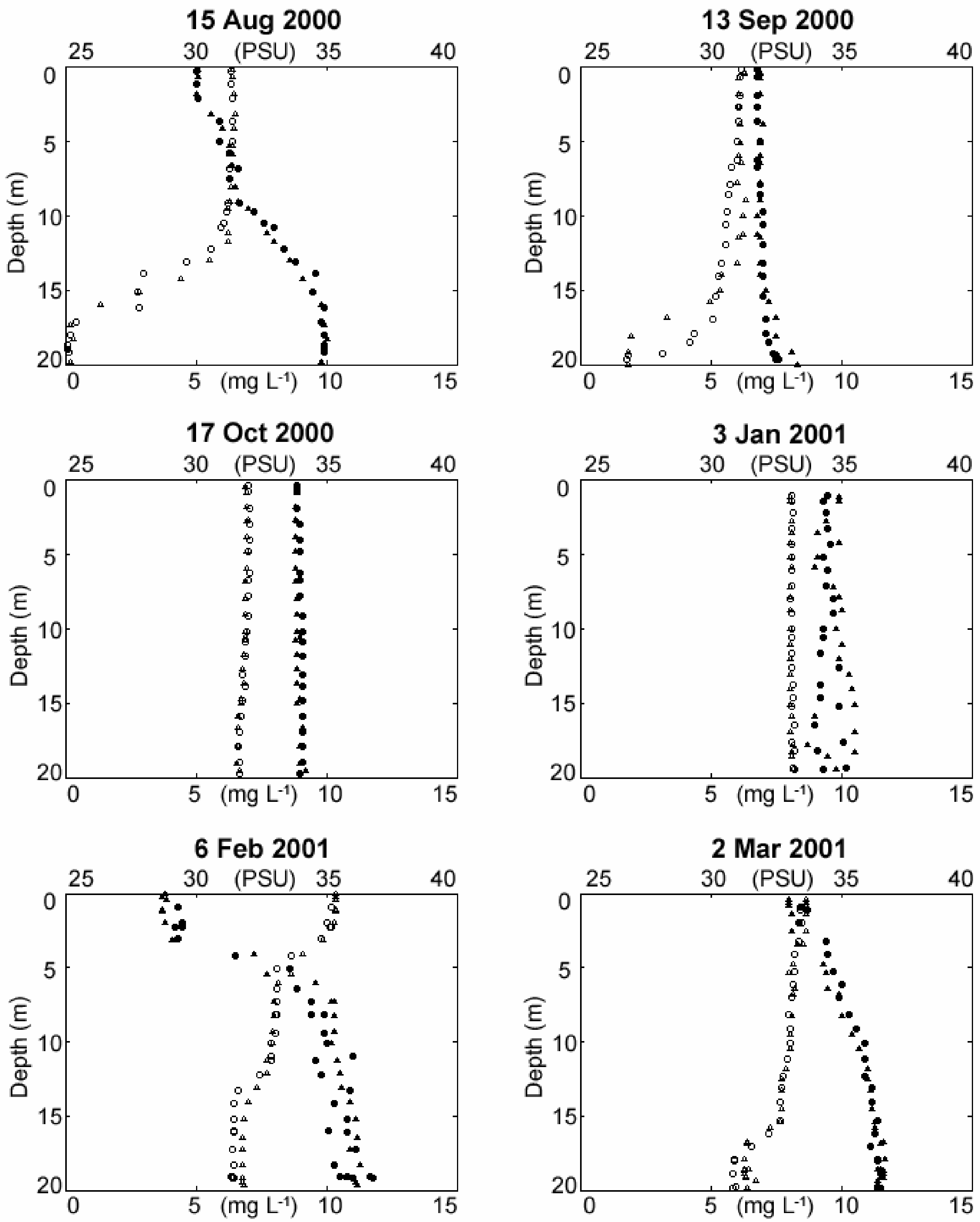
Wiseman, Jr., W. J., N. N. Rabalais, R. E. Turner and D. Justić. 2004. Hypoxia and the Physics of the Louisiana Coastal Current. 359-372 in J.C.J. Nihoul et al., “Dying and Dead Seas,” NATO Advanced Research Workshop, Liège, Belgium, NATO ASI Series, Kluwer Academic Publishers, Netherlands.

Xiuren, N., D. Vaulot, L. Zhensheng and L. Zilin. 1988. Standing Stock and Production of Phytoplankton in the Estuary of the Changjiang (Yangtze) River and the Adjacent East China Sea. Marine Ecology Progress Series 49:141-150.

APPENDIX A COMPARATIVE CTD PROFILES

Dissolved oxygen (mg l^{-1}) and salinity (psu) profiles for stations C6 (triangles), C6B (circles) and C6C (squares) for dates indicated; solid shapes are salinity and open shapes are dissolved oxygen. Data source: Rabalais et al. unpubl data from hypoxia studies 1985-2005.

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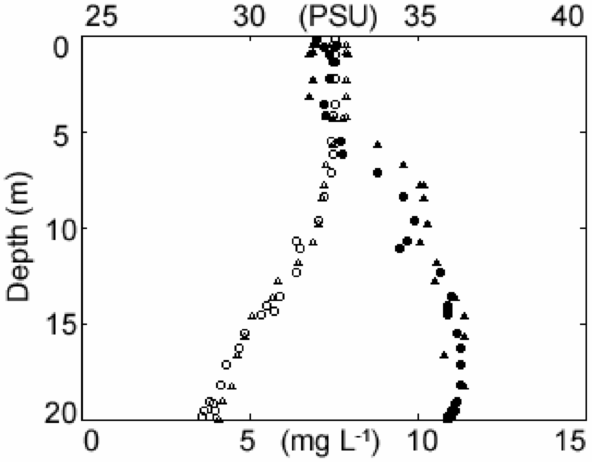

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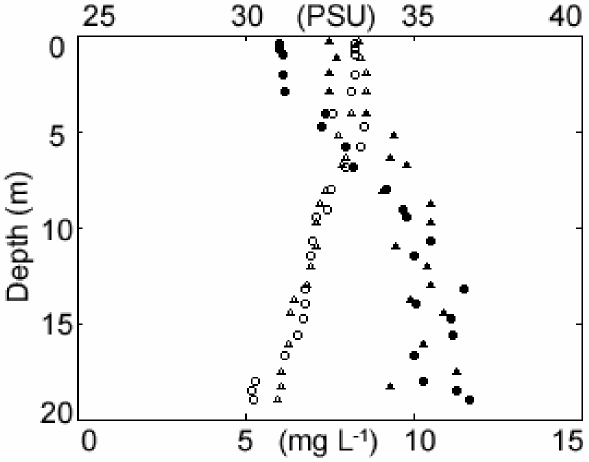

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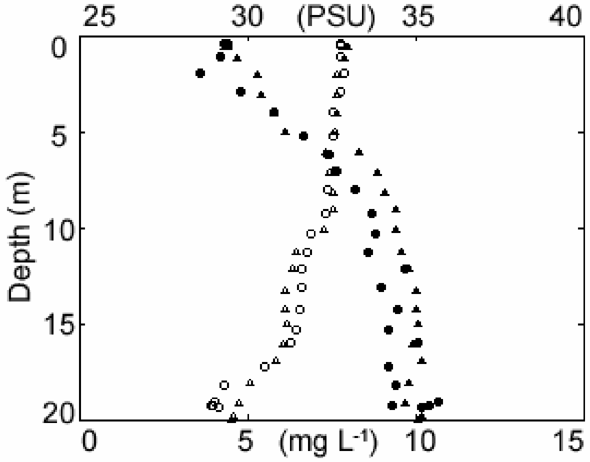

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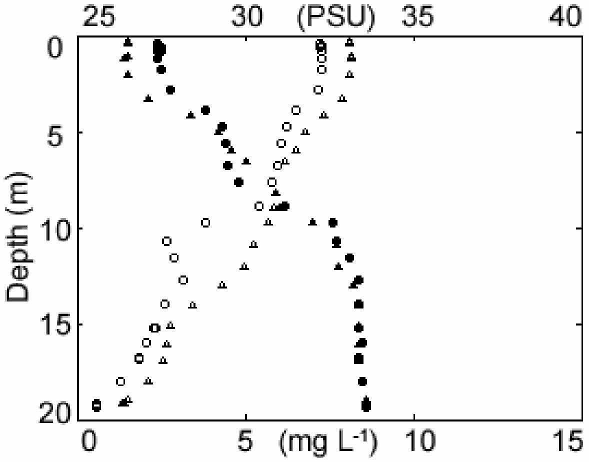

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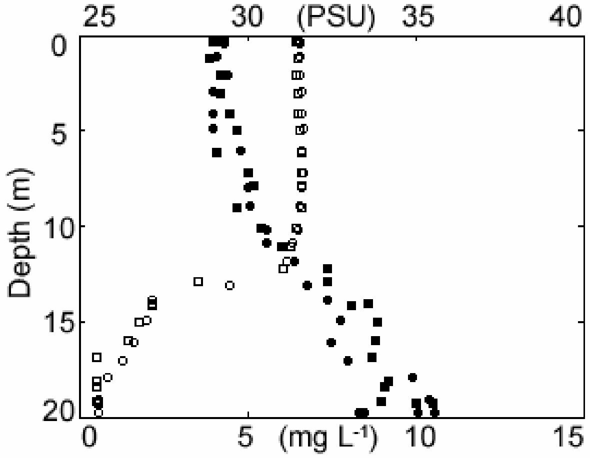

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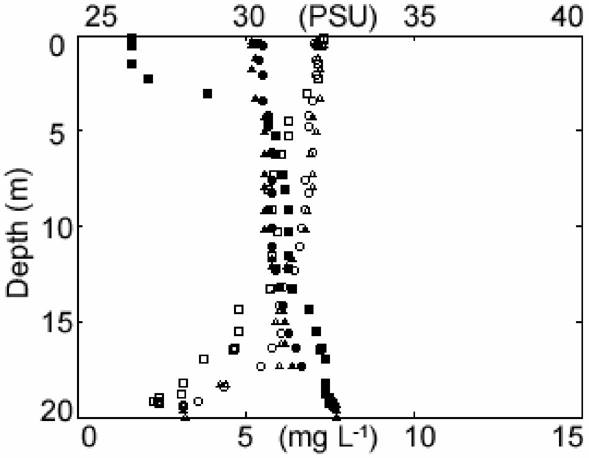

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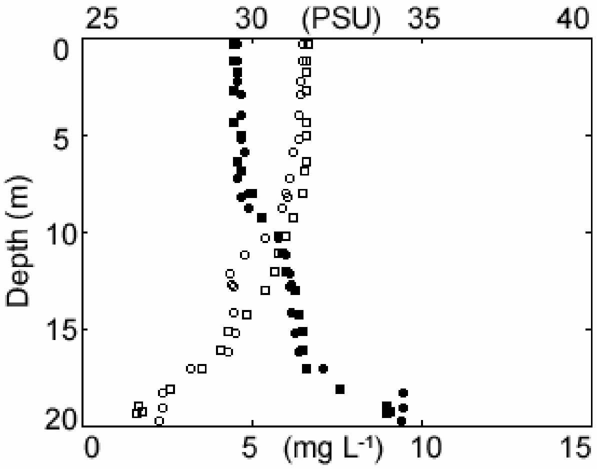

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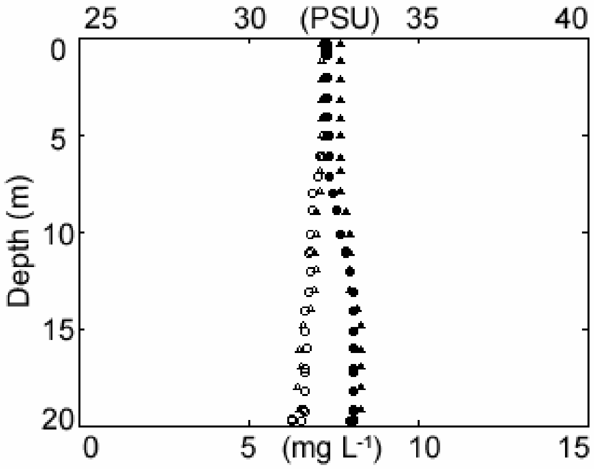

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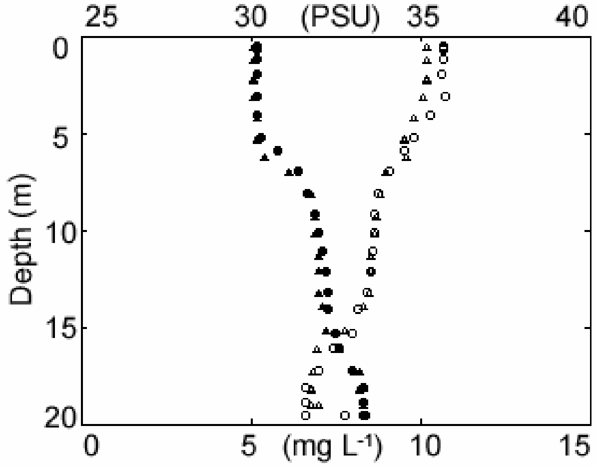

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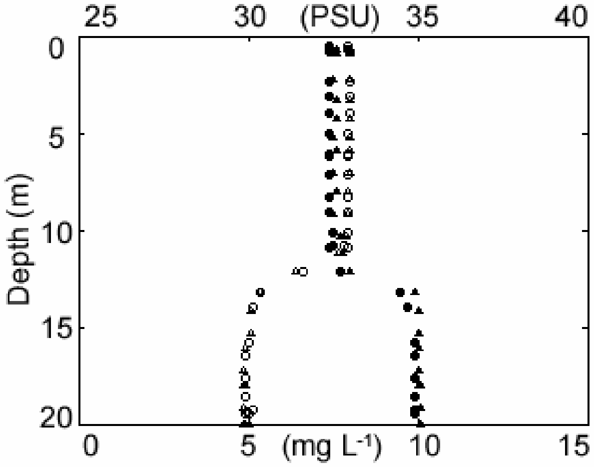

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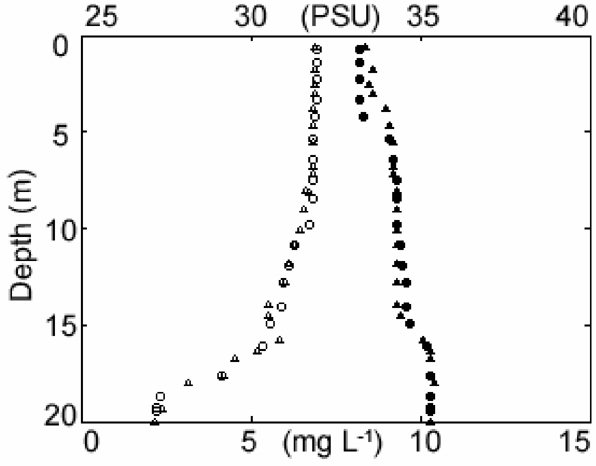

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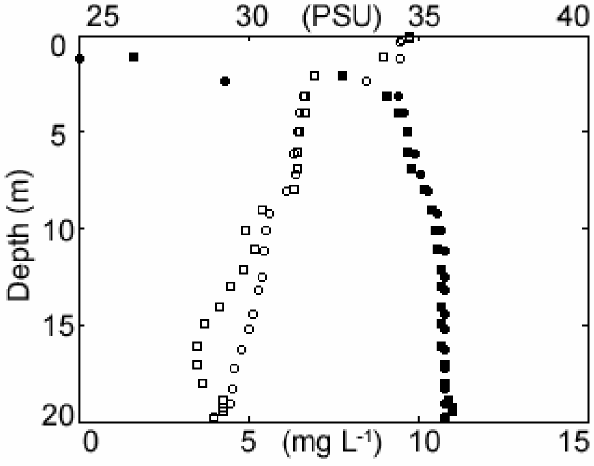

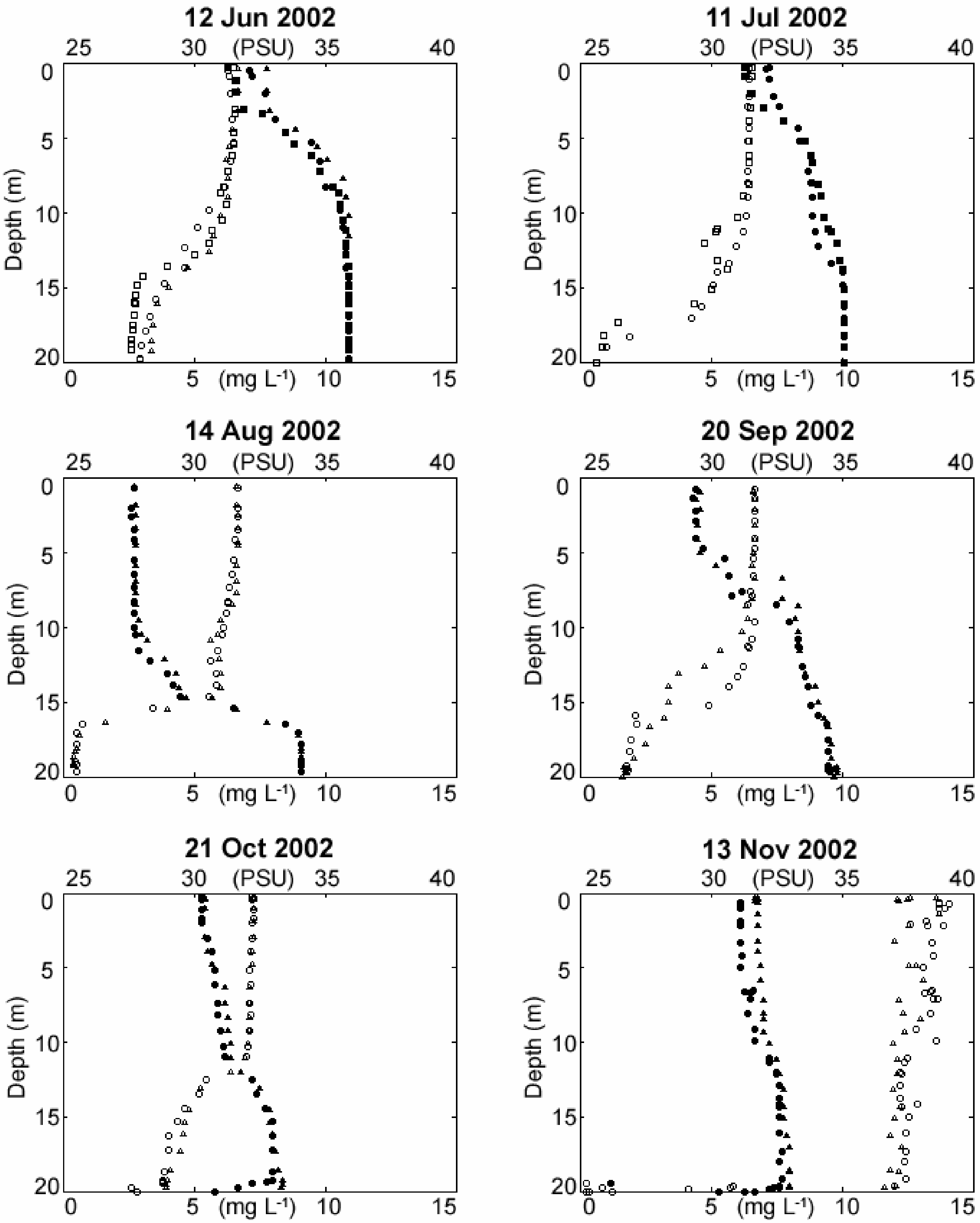
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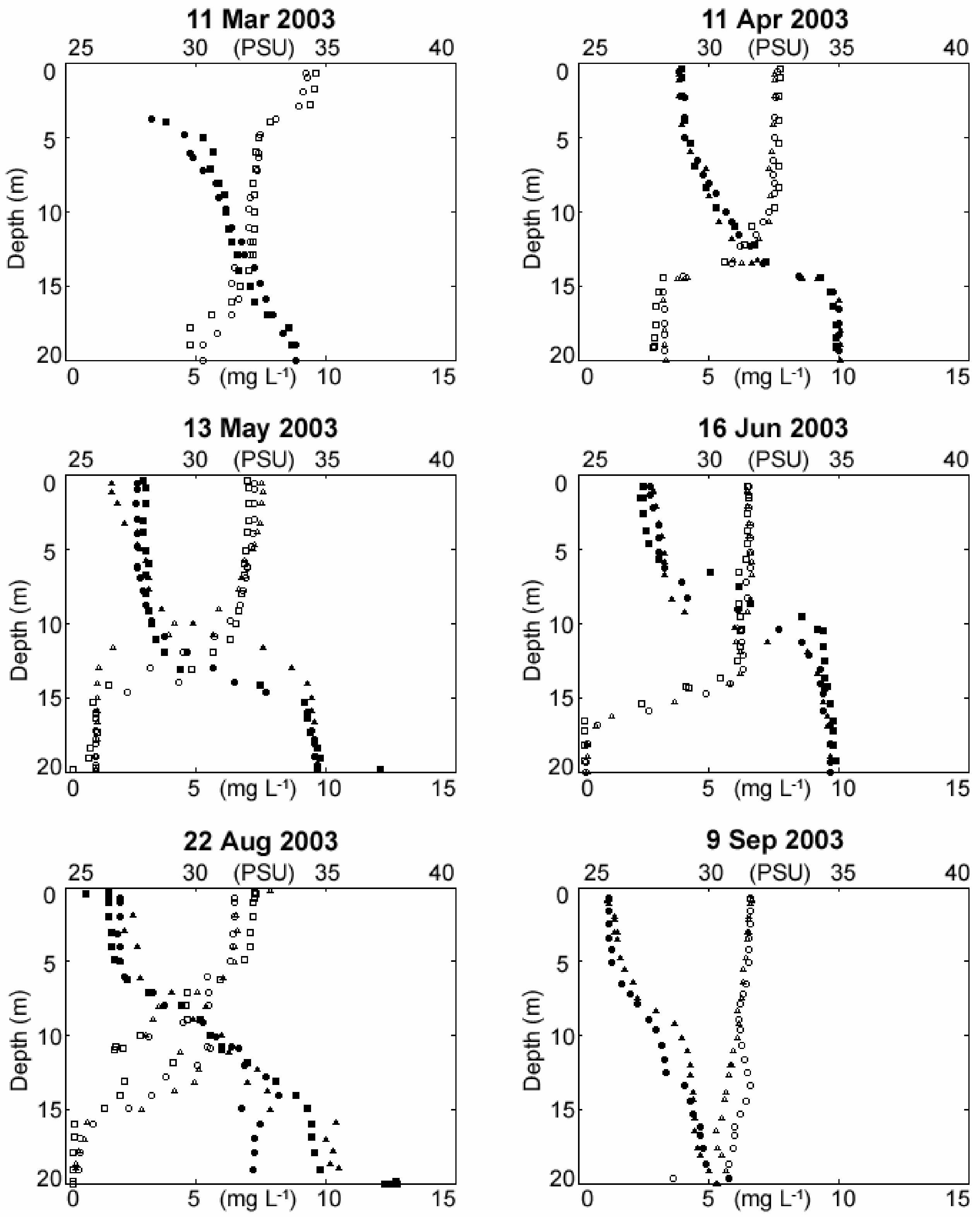
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5
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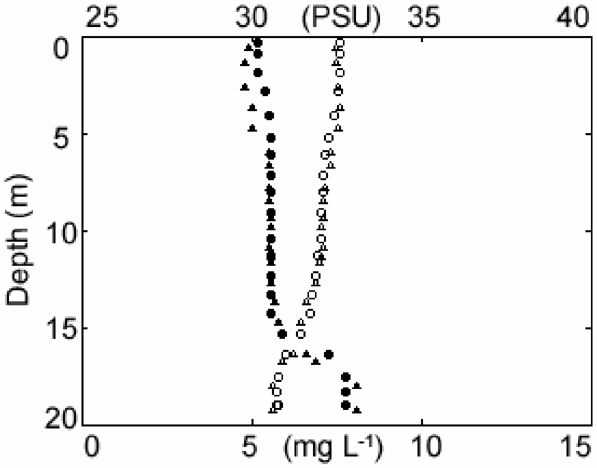
15
20
(mg L⁻¹)



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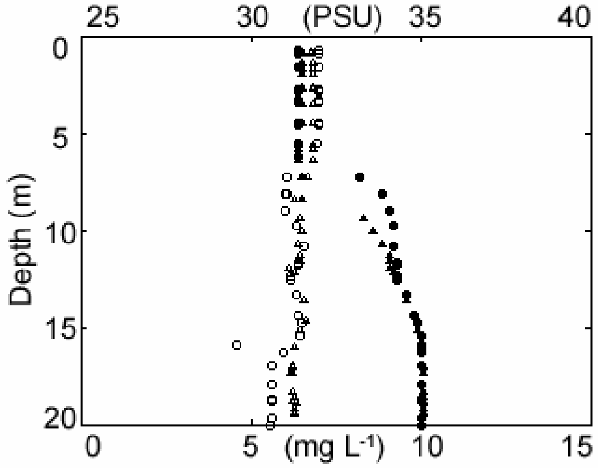

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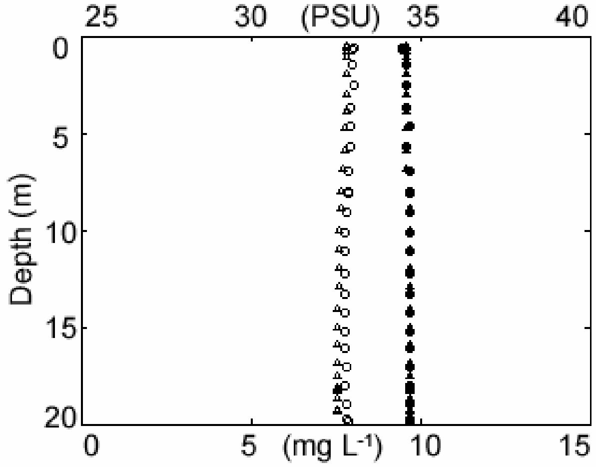

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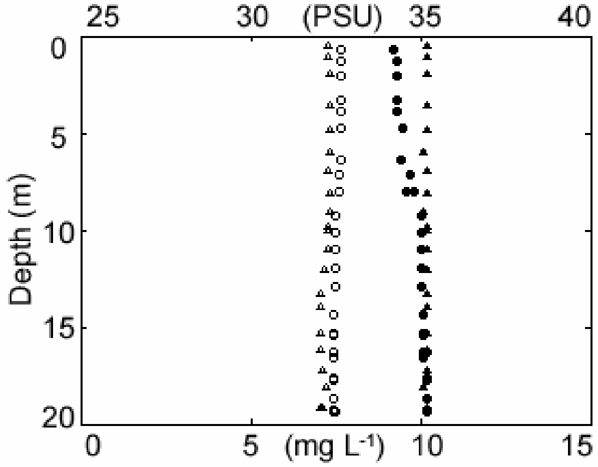

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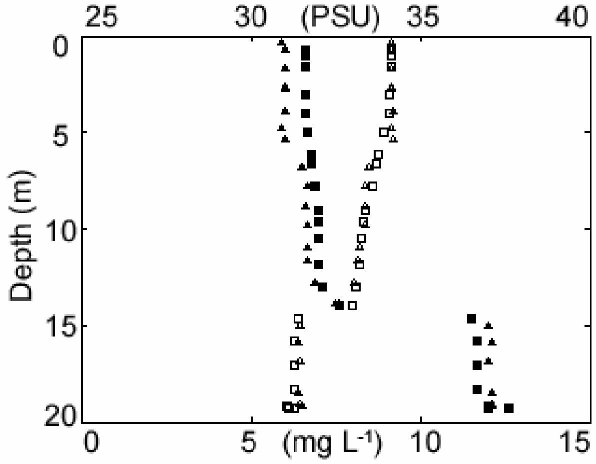

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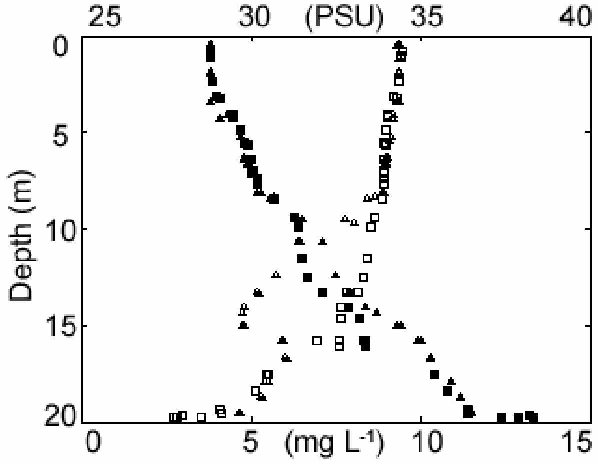

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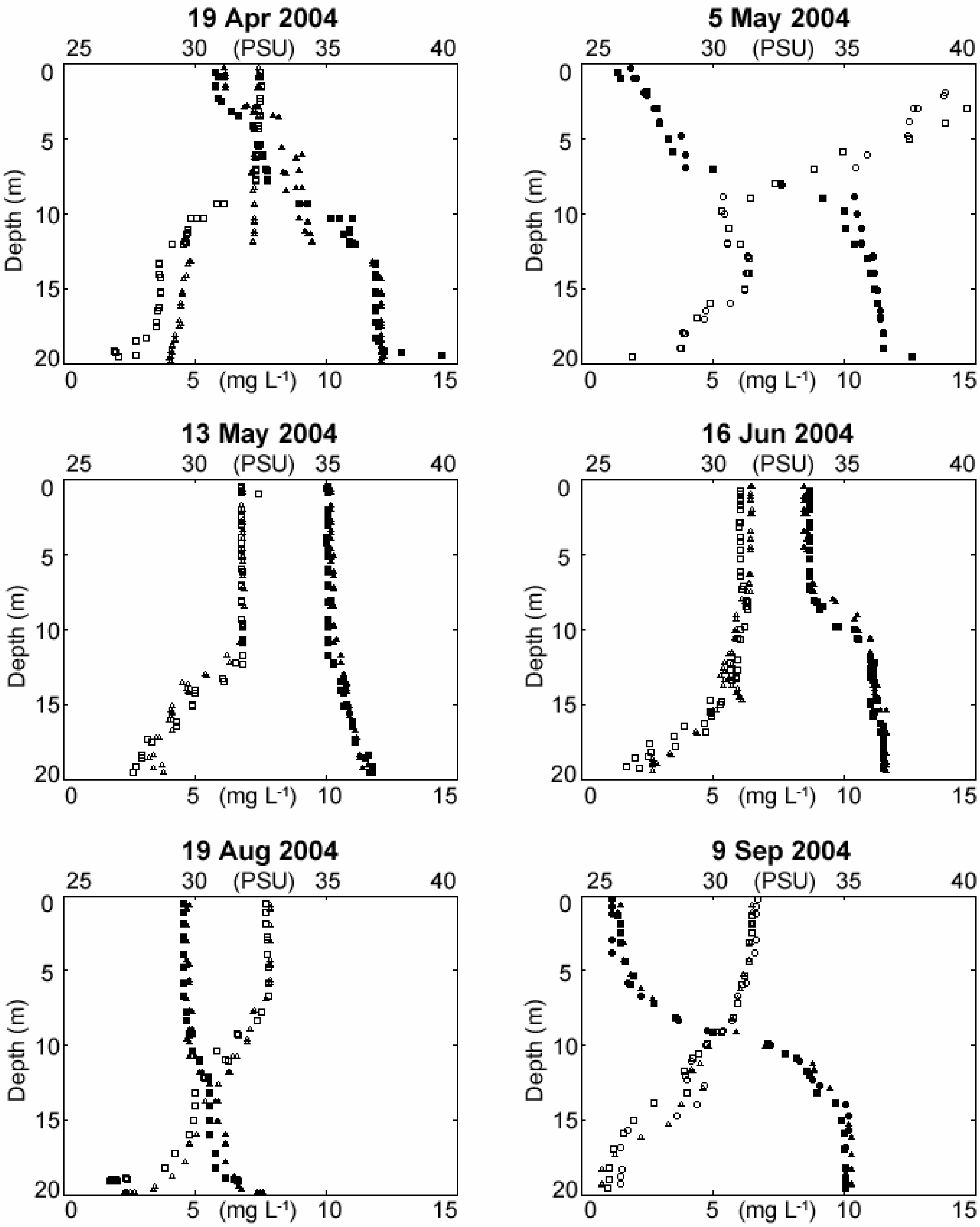
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(mg L⁻¹)
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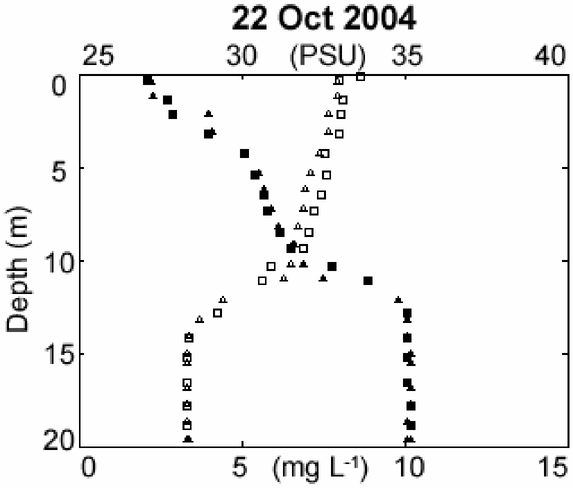
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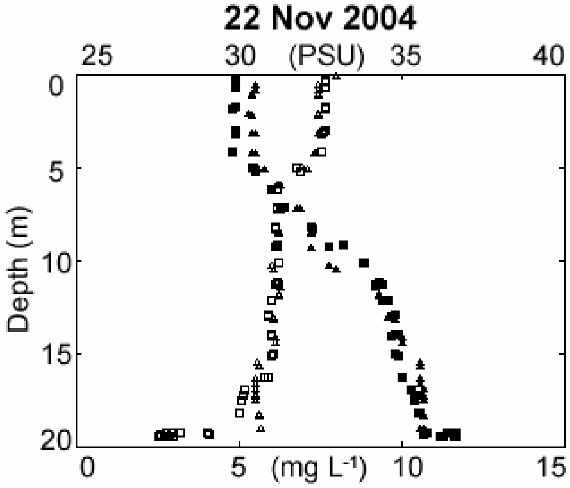
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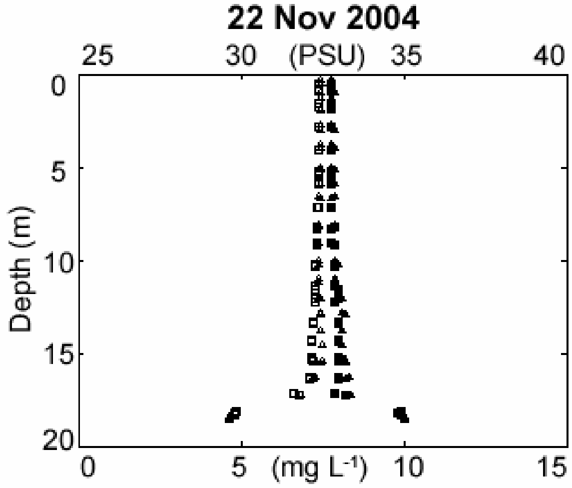
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APPENDIX B AVERAGE PRODUCED WATER VOLUME IN A 5-, 10-, AND 20-MILE RADIUS OF COMPOSITE STATION C6* (RADIUS MEASURED FROM C6C LOCATION) (BBL MO^{-1})

Year	5-Mile Radius	10-Mile Radius	20-Mile Radius
1984	269,408	405,651	1,520,797
1985	306,674	471,705	1,802,831
1986	325,443	557,275	1,806,944
1987	386,610	771,205	2,084,660
1988	503,472	945,987	2,374,878
1989	526,805	1,014,532	2,709,861
1990	547,367	968,061	2,524,706
1991	886,606	1,296,592	2,583,737
1992	887,682	1,246,444	2,384,940
1993	677,776	1,034,421	2,483,902
1994	784,031	1,185,625	2,619,488
1995	973,446	1,394,753	2,828,593
1996	1,241,297	1,796,231	3,109,922
1997	1,281,117	1,765,580	3,186,303
1998	1,057,323	1,861,618	3,428,311
1999	1,075,125	2,252,611	3,738,669
2000	1,196,975	2,603,766	3,875,918
2001	1,230,191	2,676,739	3,761,020

MARCH 3, 1849

The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

The Minerals Management Service Mission

As a bureau of the Department of the Interior, the Minerals Management Service's (MMS) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS), collect revenue from the Federal OCS and onshore Federal and Indian lands, and distribute those revenues.

Moreover, in working to meet its responsibilities, the **Offshore Minerals Management Program** administers the OCS competitive leasing program and oversees the safe and environmentally sound exploration and production of our Nation's offshore natural gas, oil and other mineral resources. The MMS **Minerals Revenue Management** meets its responsibilities by ensuring the efficient, timely and accurate collection and disbursement of revenue from mineral leasing and production due to Indian tribes and allottees, States and the U.S. Treasury.

The MMS strives to fulfill its responsibilities through the general guiding principles of: (1) being responsive to the public's concerns and interests by maintaining a dialogue with all potentially affected parties and (2) carrying out its programs with an emphasis on working to enhance the quality of life for all Americans by lending MMS assistance and expertise to economic development and environmental protection.

MMS Securing Ocean Energy &
Economic Value for America