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Plankton Community Respiration and Productivity for the  
Louisiana Offshore Ecosystem, July 2007 Results

by

Brandon Michael Boyd  
Department of Oceanography and Coastal Sciences  
LSU

Undergraduate honors thesis under the direction of

Dr. Brian Fry  
Department of Oceanography and Coastal Sciences

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### Abstract

The offshore estuarine ecosystem affected by the Mississippi River is large and extends over most of the Louisiana continental shelf. The Louisiana continental shelf experiences summer hypoxic episodes as a result of the nutrient loading and fresh water input of the Mississippi River. Productivity and the related oxygen dynamics are an important piece of understanding overall controls and effects of hypoxia. Phytoplankton production (P) and community respiration (R) were studied during a summer 2007 cruise west of the mouth of the Mississippi River. To document offshore spatial patterns of P and R, we collected water samples for oxygen concentration and isotope measurements and conducted 24 hour dark respiration experiments. The respiration measurements showed a strong river influence, with highest R inshore and near the river. P estimates were obtained using a new method proposed by Fry and Boyd (in press) for calculating minimum P/R ratios from oxygen isotope measurements. Combination of P/R and R estimates yielded conservative (minimum) estimates of P across the shelf system, with P showing strong river forcing. Average R in surface waters was  $19 \pm 2 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ , average P/R in surface waters was  $1.06 \pm 0.02$ , average gross P was  $20 \pm 2 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$  and average net P in surface waters was  $1.1 \pm 0.7 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ . In the central shelf, imported productivity seemed to play an important role in bottom hypoxia while in other areas net P in surface waters may have been sufficient to fuel hypoxia in underlying bottom water.

### Introduction

The Louisiana offshore shelf ecosystem is relatively well studied in relation to hypoxia (low dissolved oxygen,  $<2 \text{ mg l}^{-1}$  or  $64 \text{ mmol O}_2 \text{ m}^{-3}$ ) that regularly occurs in bottom waters during warmer months of the year (Dagg et al. 2007, Rabalais et al. 2007). The areal extent of hypoxia has fluctuated, largely in response to river discharge (Justić et al. 2007), with smaller-scale hypoxia present on the shelf prior to 1900 (Osterman et al. 2007). The extent of this hypoxia has been mapped annually since 1985 during cruises conducted from the mouth of the Mississippi River to the Louisiana-Texas border (Rabalais et al. 2000). A recent study of Atlantic croaker has demonstrated that hypoxia can cause severe reproductive impairment in fish and possible long term impacts on abundance of living resources (Thomas and Rahman 2009). The economic benefit of recreational and commercial fishing alone in this region is \$4.2 billion and the support of 46,000 jobs (Southwick Associates 2005).

Loading of both freshwater and nutrients are important controls of hypoxia, with the Mississippi River providing abundant supplies of both (Bierman et al. 1994, Justic et al. 2007, Green et al. 2008). The Mississippi River drains 41% of the continental United States, and the large freshwater loading creates persistent stratification of offshore waters in summer months, stratification that prevents reaeration of low-oxygen bottom waters by the atmosphere. The Mississippi River is also the source of nutrients that fertilize the Louisiana shelf system, with fisheries productivity historically showing a spatial pattern consistent with river forcing (Moore et al. 1970). However, increased nutrient loading in the last half century has led to stronger algal growth in shelf waters (Turner et al. 1998, 2007), with more algal fuel for decomposition in bottom waters and large-scale summer hypoxia.

While river discharge of nutrients and freshwater are widely accepted as the main factors controlling the development and extent of hypoxia, research continues to investigate other possible causes and amplifiers of hypoxia in the Gulf of Mexico (Dagg et al. 2007). Regardless of the ultimate controls leading to the ecosystem-level spread of hypoxia, occurrence of summer-time hypoxia is dependent on two cardinal factors: a large fresh-water flux to and decomposition of organic matter in the benthos (Rabalais et al. 2002). Primary production is the source for the particulate organic matter (POM) whose decomposition leads to hypoxic episodes (Rabalais et al. 2002, Green et al. 2008). One large counterpart to production is respiration dynamics.

The most common method of measuring respiration is to monitor changes in dissolved oxygen concentrations in dark bottles over several hours (Hopkinson & Smith 2005). This approach measures community metabolism, the combined respiration that results mostly from algae and bacteria (Hopkinson & Smith 2005). Other methods of measuring community metabolism are less direct, estimating respiration as a derivative function of primary production (Flynn 2005) or via near-instantaneous metabolic assays (Dortch et al. 1992, 1994). Unfortunately, these latter techniques involved several assumptions and are less satisfactory than directly measuring oxygen changes (Hernández-León & Ikeda 2005).

However, the oxygen concentration measurements provide only an estimate of the balance of production (P) and respiration (R). Stable isotopes have long been used to better understand the biochemical relationship of organisms and their habitat (Peterson & Fry 1984, Fry 2006). More specifically, many studies have used  $\delta^{18}\text{O}$  measurements to better understand photosynthetic production and community metabolism (Hama et al. 1983, Guy et al. 1993,

Thompson 1994, Rau et al. 1996, Luz et al. 2002, Quinones-Rivera et al. 2007). The benefit of adding stable isotopes in oxygen modeling is that this allows estimates of gross or total fluxes, whereas concentrations alone allow calculation only of net fluxes (Fry 2006).

The P rates are difficult to measure directly, but Bender and Grande (1987) proposed a novel oxygen isotope-based technique for estimating P/R ratios that allows calculation of P when R is measured or known (Bender & Grande 1987). The appeal of this approach is that only ambient water samples need be collected and analyzed for these P/R estimates, without need for phytoplankton productivity incubations and the many possible artifacts associated with incubations and increased sample handling.

However, the Bender and Grande (1987) approach is a modeling approach that has assumptions about fractionation during respiration and gas exchange and in fact the model failed to fit the published field data in the initial calibrations. A more recent application of a modified form of this continuous bloom model showed better success, with a consistent spatial productivity pattern extracted by the P/R modeling for the Louisiana shelf (Quinones et al. 2007). Boyd and Fry (in press) also investigated the strengths and weakness of the P/R approach with oxygen isotopes. Modeling exercises and experimental work showed the importance of atmospheric exchange, cycling and mixing in addition to P and R. Based on their findings, Fry and Boyd (in press) developed a conservative (minimum) P/R estimate using oxygen isotopes.

This study investigated two research hypotheses: 1) community R and P in surface waters follows river-related gradients, i.e. stronger R and P near the river, inshore and for surface waters and weaker R and P away from the river, offshore, and in bottom waters and 2) areas of strong bottom water hypoxia have strong net P in overlying waters.

### Site Map

The study site was the Louisiana continental shelf where a series of sample stations established by Dr. Nancy Rabalais were used as sample sites in this study (Fig. 1). The study area is a shallow (<60 m) and heavily influenced by the Mississippi river. The Mississippi river watershed is drained by the Mississippi and Atchafalaya rivers on the Louisiana coast (Fig. 2).

## Methods

Approximately 400 water samples and 200 POM samples were collected from July 21 to July 27, 2007. Surface samples were taken within 1m of the water surface and bottom water samples were obtained within 2 m of the seafloor. Oxygen samples generally were collected, prepared and analyzed following the methods of Quinones Rivera et al. (2007). Both freshwater and saltwater standards were prepared and used to make salinity based corrections to the  $\delta^{18}\text{O}$  data (Wissel et al. 2008) using isotope ratio mass spectrometry (Fig. 3).

We used classic dark incubation techniques to measure respiration rates (Turner et al. 1998). Water samples were collected in glass BOD bottles from both surface and bottom waters following Quinones-Rivera et al (2007). Initial water samples were poisoned immediately with 1ml 6N HCl. Incubations of a second bottle were done over 24hr ( $\pm 3$ hr) at ambient seawater temperature, then also poisoned with 1 ml 6N HCl. Experimentation using 3-5 time points showed that oxygen uptake during respiration was fairly linear and 2 time points was sufficient for measurement of R values (data not shown).

Modeling of P/R uses the methods proposed by Fry and Boyd (in press) which are based on Quinones-Rivera et al. (2007) and the original Bender and Grande (1987) model. The minimum or conservative P/R was calculated from  $\delta^{18}\text{O}$  of the water and the  $\delta^{18}\text{O}$  of the dissolved  $\text{O}_2$  as:

$$\text{Minimum P/R} = [69.173 \cdot \exp(0.2768 \cdot \delta^{18}\text{O}_{\text{water}})] \cdot [\delta^{18}\text{O}_{\text{DO}} \cdot \exp(-0.0777 \cdot \delta^{18}\text{O}_{\text{water}} - 1.3592)].$$

Salinity and chlorophyll a were measured using CTD and Hydrolab® equipment maintained by the crew of the R/V Pelican of LUMCON.

## Results

Chlorophyll showed a strong linear correlation with salinity (Fig. 4). Spatial distribution of P/R across the shelf showed a band of  $\text{P/R} > 1$  near the shore and most of the offshore shelf having a minimum  $\text{P/R} < 1$  (Fig. 5). Highest P/R values were found near the river inputs with the exception of a large area of  $\text{P/R} > 1$  near the Louisiana-Texas border. The average minimum P/R of the shelf was  $1.06 \pm 0.02$  (SE,  $n=84$ ). Daily R averaged  $19 \pm 2 \text{ mmol O}_2 \text{ m}^{-3}$  across the Louisiana continental shelf. Daily net P averaged  $1.1 \pm 0.7 \text{ mmol O}_2 \text{ m}^{-3}$  across the shelf. These and further results are summarized in Table 1. There was no significant correlation between

surface R and bottom R. Correlation of salinity with daily gross P shows highest P values at moderate salinities ( $n = 84$ ,  $r^2 = 0.54$ ; Fig. 6).

Respiration in the bottom water and fractionation during respiration was also calculated. The average rate of respiration in the bottom water ranged from 2 – 23  $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$  and averaged  $8.9 \pm 0.6 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$  ( $n=78$ ). Fractionation during respiration, calculated using the  $\Delta$  method (see Fry 2006), averaged  $21.2 \pm 0.6 \text{ ‰}$  ( $n=84$ ) and  $21.6 \pm 0.6 \text{ ‰}$  ( $n=78$ ) for the surface and bottom waters, respectively. Fractionation during respiration ranged from 8 – 37 ‰ in bottom waters and from 10 – 36 ‰ in surface waters. Fractionation factors were not significantly related to respiration rates ( $P>0.05$ ) and there was no discernable geographic pattern in these respiratory fractionation factors for surface or bottom waters.

Salinity of the river was used to track the forcing of the Mississippi River (Fig. 7). Salinity increased along three gradients across the shelf: 1) from east to west across the shelf, 2) inshore to offshore and 3) surface to bottom. Spatial distribution of R showed a similar east/west, inshore/offshore and surface/bottom gradient (Fig. 8). P values also followed the east/west pattern and mirrored salinity (Fig. 9). Gross P showed a strong correlation with salinity but there was no relationship with net P or salinity (Fig. 10). P over hypoxic waters was on average lower ( $0\text{--}10 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ ) than net P found elsewhere on the shelf (Fig. 11).

## Discussion

The Mississippi River had a large influence on community R along several gradients (inshore-offshore, east-west, and surface-bottom) for the Louisiana shelf, with higher R generally occurring in river-influenced waters. Highest P was observed at intermediate salinities is in agreement with past studies (Chin-Leo and Benner 1992). The spatial distribution of P, R and P/R showed the Mississippi River system to be a major factor influencing biological activity on the shelf. Production was expected to be linked to chlorophyll concentration and correlative results support this expectation. A comparison of inshore/offshore P values from this summer 2007 study with satellite chlorophyll data from a summer 2001 study showed a similar spatial pattern (Fig. 12, Walker and Rabalais 2006), indicating ecosystem similarity across years.

There was some coupling between surface P and bottom R in waters on the western shelf, but not on the eastern shelf. For the western and eastern zones of hypoxia, high productivity did occur over hypoxic bottom waters in some areas. Thus, organic matter could be produced over

and directly sink into hypoxic waters contributing to hypoxia. However, during this shelfwide, the Louisiana coastal waters were not experiencing high productivity (minimum  $P/R=1.06$ ) confirming the idea that hypoxia setups up earlier in the late spring through nutrient loading and is sustained through summer by stratification water inputs until winter fronts mix the water column (Rabalais et al. 2002b).

Respiration rates calculated during this study were similar to those found in this system by previous investigators (Table 2). Respiration rates for the Louisiana shelf fall in the 0 to 45  $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$  range with higher rates in surface waters and intermediate salinities. Further investigation is needed to determine how R varies on a seasonal and year-to-year scale and see if seasonality explains the differences in the rates found on this shelf.

Our pattern of summer respiration is very similar to that documented by Dortch et al. (1994). That study used electron transport system (ETS) measurements to indirectly estimate oxygen consumption, and showed that activity decreased from inshore to offshore in most summer months. We observed the same inshore/offshore pattern, both in the surface and bottom water. Also, Dortch et al. (1994) found an east to west gradient with surface ETS activity highest near the mouth of the Mississippi River and decreasing westward. We observed this same pattern on a smaller scale, from the Atchafalaya River westward towards the Louisiana-Texas border, although the east-west pattern for bottom respiration was not as distinct as the surface pattern. Lastly, Dortch et al. (1994) showed bottom water with high ETS activity at shallow stations (< 6m); we found similar results for bottom respiration.

Other studies have observed a positive correlation between depth and respiration. The log:log relationship between depth and respiration, demonstrated in the open ocean by Suess (1980) and by Turner et al. (1998) on the Louisiana continental shelf. For 5 separate occasions, Turner et al. (1998) found a significant relationship between the slope of the  $\log_{10}(R)-\log_{10}(\text{depth})$  regression and corresponding Si:DIN atomic ratio of the Mississippi River. This study also observed decreasing R with increasing distance and depth offshore.

### Conclusion

Using a combination of oxygen concentration measurements, oxygen isotope determinations and respiration experiments allowed estimates of both community-level P and R during our shelfwide 2007 study. Regular P and R patterns were documented and seemed similar



to those seen in previous studies in this area where measurements were made at smaller spatial scales. For hypoxic zones, there was some coupling between surface P and bottom R in waters on the easternmost and western shelf, but not on the central shelf. More study of productive nearshore areas may be useful in determining the sources of imported phytoplankton that is sustaining bottom water hypoxia.

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**Table 1. Surface Production (P) and Respiration (R) rates from the 2007 July shelfwide. P calculations were made from  $\delta^{18}\text{O}$  measurements and R calculations were made from dark bottle incubation experiments.**

	<b>Hourly R</b>	<b>Daily R</b>	<b>Hourly Gross P</b>	<b>Daily Gross P</b>	<b>Daily Net P</b>
<b>Minimum</b>	0.1	2.4	0.2	2.5	-11.9 (heterotrophic)
<b>Maximum</b>	3.1	74.9	8.8	105.9	31.1
<b>Average</b>	$0.80 \pm 0.07$	$19 \pm 2$	$1.7 \pm 0.2$	$20 \pm 2$	$1.1 \pm 0.7$

Values in  $\text{mmol O}_2 \text{ m}^{-3}$  and error in SEM(n=84)

Table 2. Daily respiration rates ( $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ ) from previous studies on the Louisiana continental shelf. ETS was used to calculate respiration rates in Dortch et al. 1992 and Dortch et al. 1994. Turner and Allen (1982) used concentrated water samples (10-50x).

Turner and Allen 1982	Turner et al 1998	Dortch et al 1992,1994	Chin-Leo and Benner 1992	This Study
Bottom water  $1.5 \pm 0.2$ (n=14)	Bottom Water	Bottom water (1992)  24	R range  3-39	Bottom Water  $8.9 \pm 0.6$ (n=78)
	1992 Average  $10 \pm 3$ (n=18)	Surface water (C transect) (1992)  33		
	1994 Average  $23 \pm 5$ (n=22)	Bottom water (C transect) (1992)  17		Surface Water  $20 \pm 2$ (n=84)
	1998 Average  $19 \pm 6$ (n=3)	20m isobath, surface and bottom (F3,G3,H3,I3,J3,K4) (1994)  0-20		

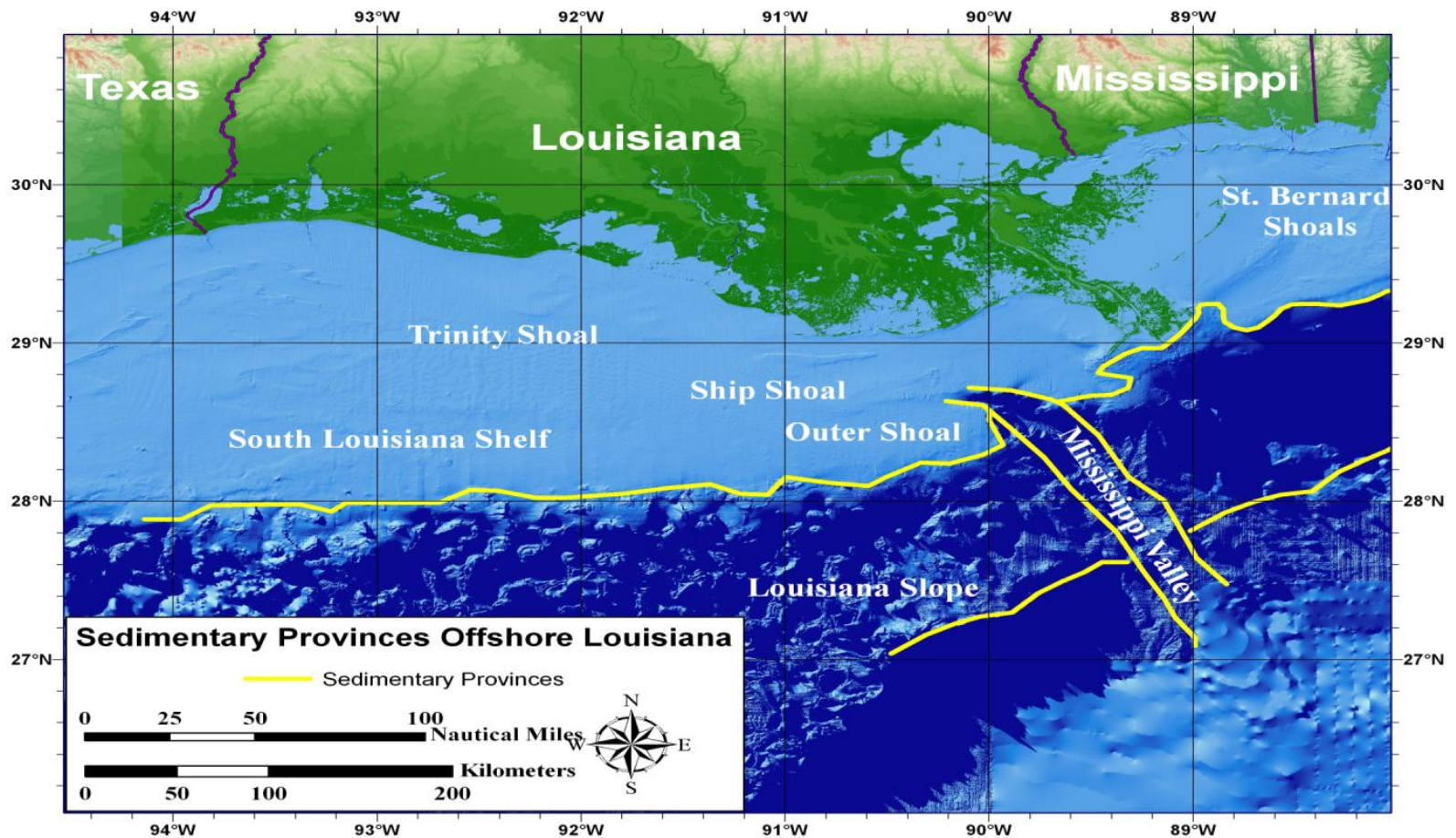


Figure 1. Louisiana continental shelf. Study area spans longitudinally from 89.3W to the LA-TX border. (source credit: USGS,2006)

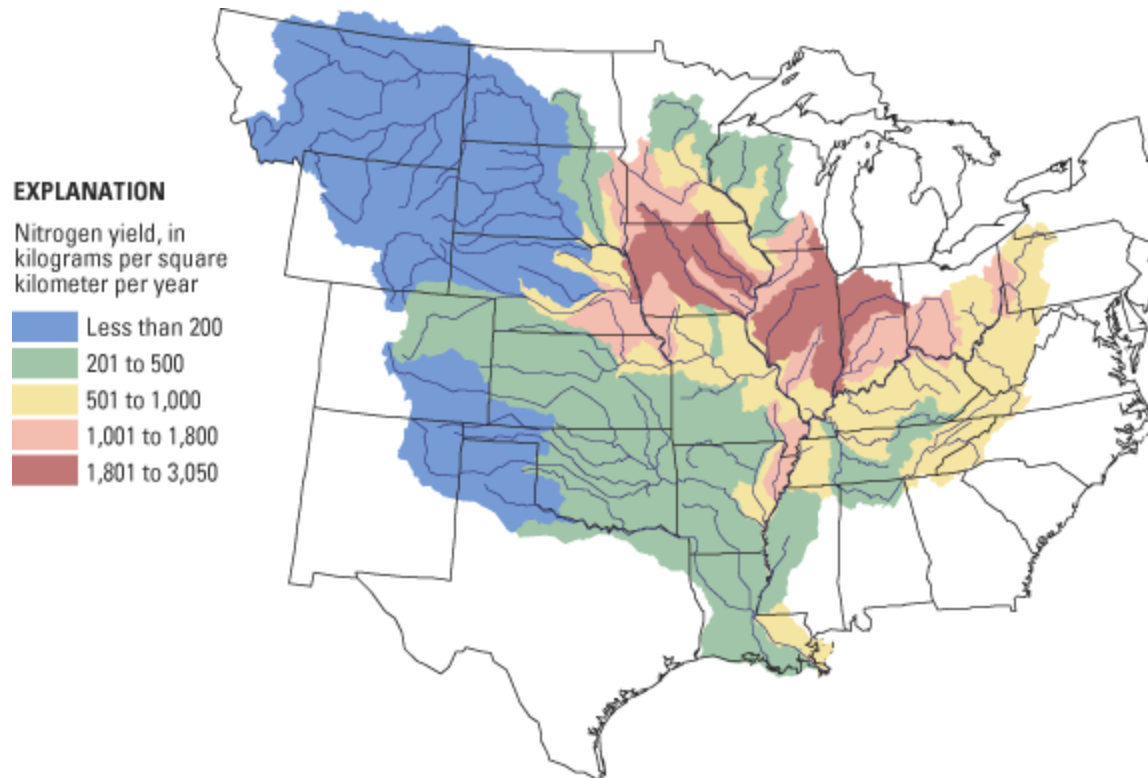


Figure 2: Nitrogen yield of Mississippi water shed. Used here to depict the drainage basin of the Mississippi River and corresponding nitrogen load, a major forcing of the Gulf of Mexico Hypoxia.

(USGS, <http://pubs.usgs.gov/fs/fs-076-02/images/nitrogenyield.gif>)



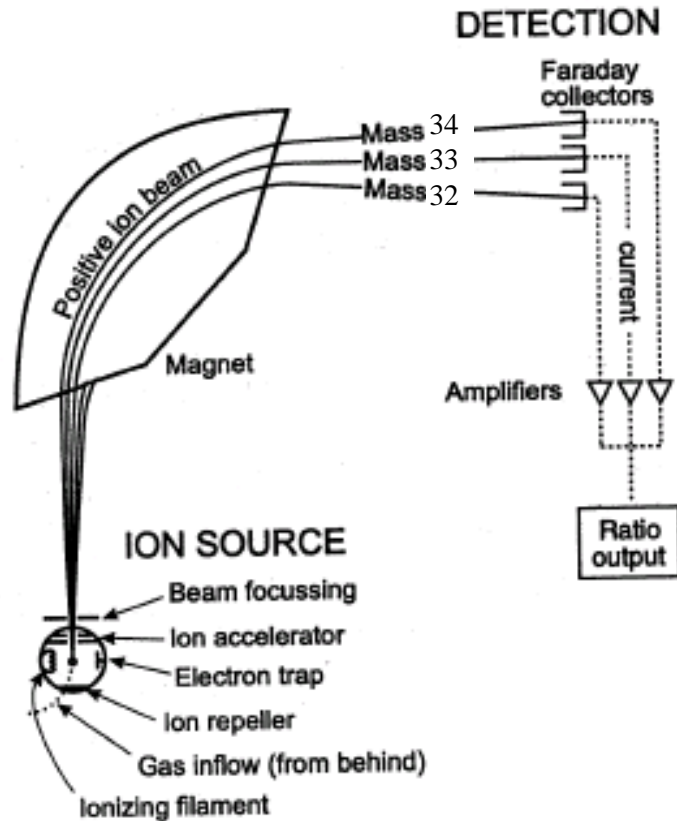


Figure 3. Isotope Ratio Mass Spectrometer Instrument, used to measure abundance of oxygen and oxygen isotopes. Inertia of larger mass atoms or molecules results in the wider path through the magnet, separating molecules of different mass. Source: [http://upload.wikimedia.org/wikipedia/commons/b/b8/Mass\\_spectrometer\\_schematics.png](http://upload.wikimedia.org/wikipedia/commons/b/b8/Mass_spectrometer_schematics.png)

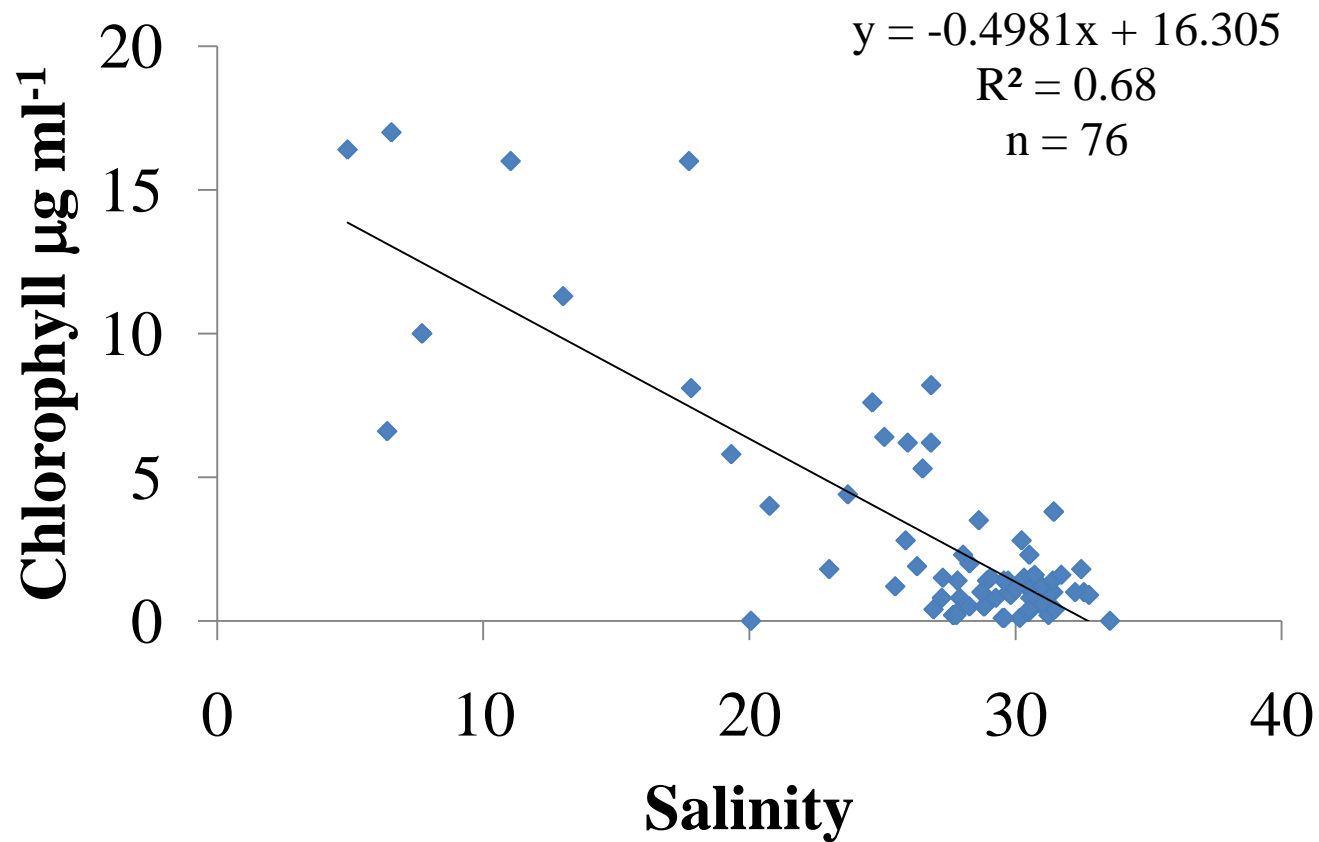


Figure 4. Salinity versus surface chlorophyll a concentration. Chlorophyll measured shipboard using a Hydrolab® outfitted with a fluorometer.

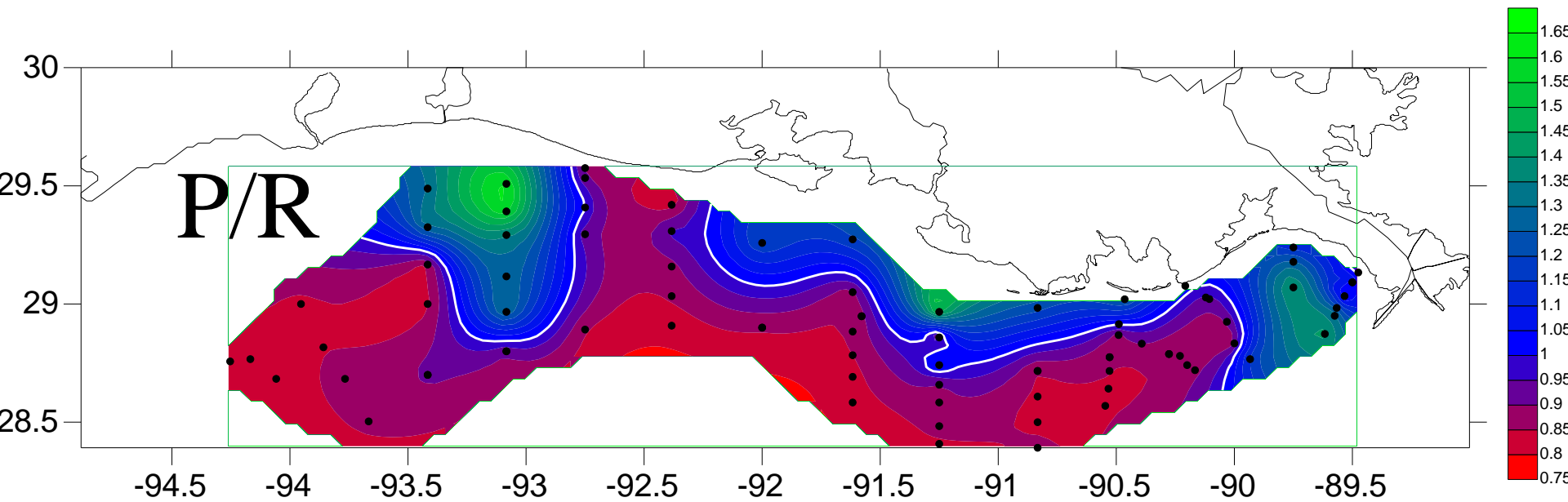


Figure 5. The spatial distribution of minimum P/R calculated using the Fry and Boyd approach. Black dots represent sample stations. The white contour line represents a P/R of 1.

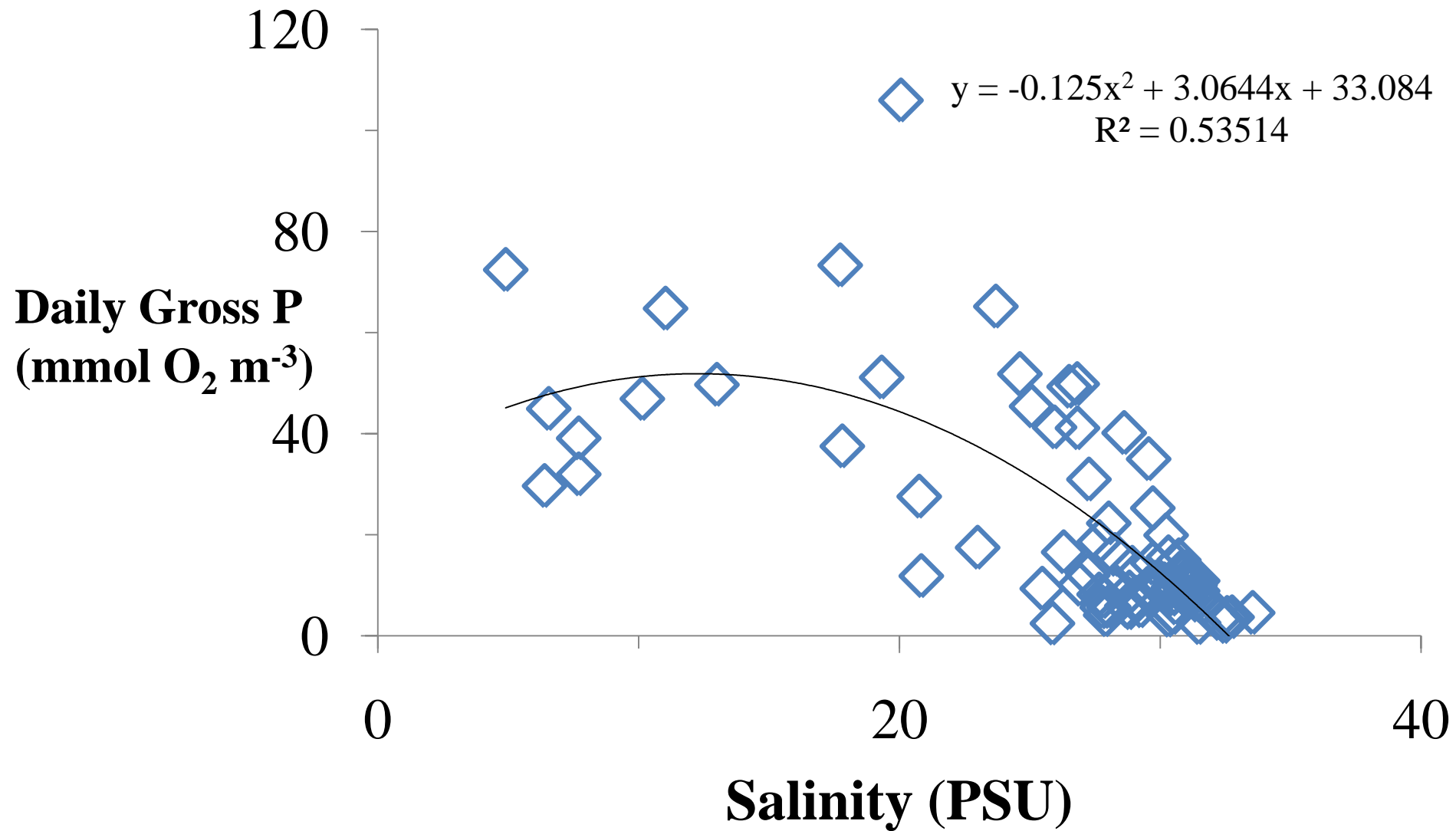


Figure 6. Salinity versus daily gross P, with a 2<sup>nd</sup> order fitted polynomial showing highest productivity at mid salinities.

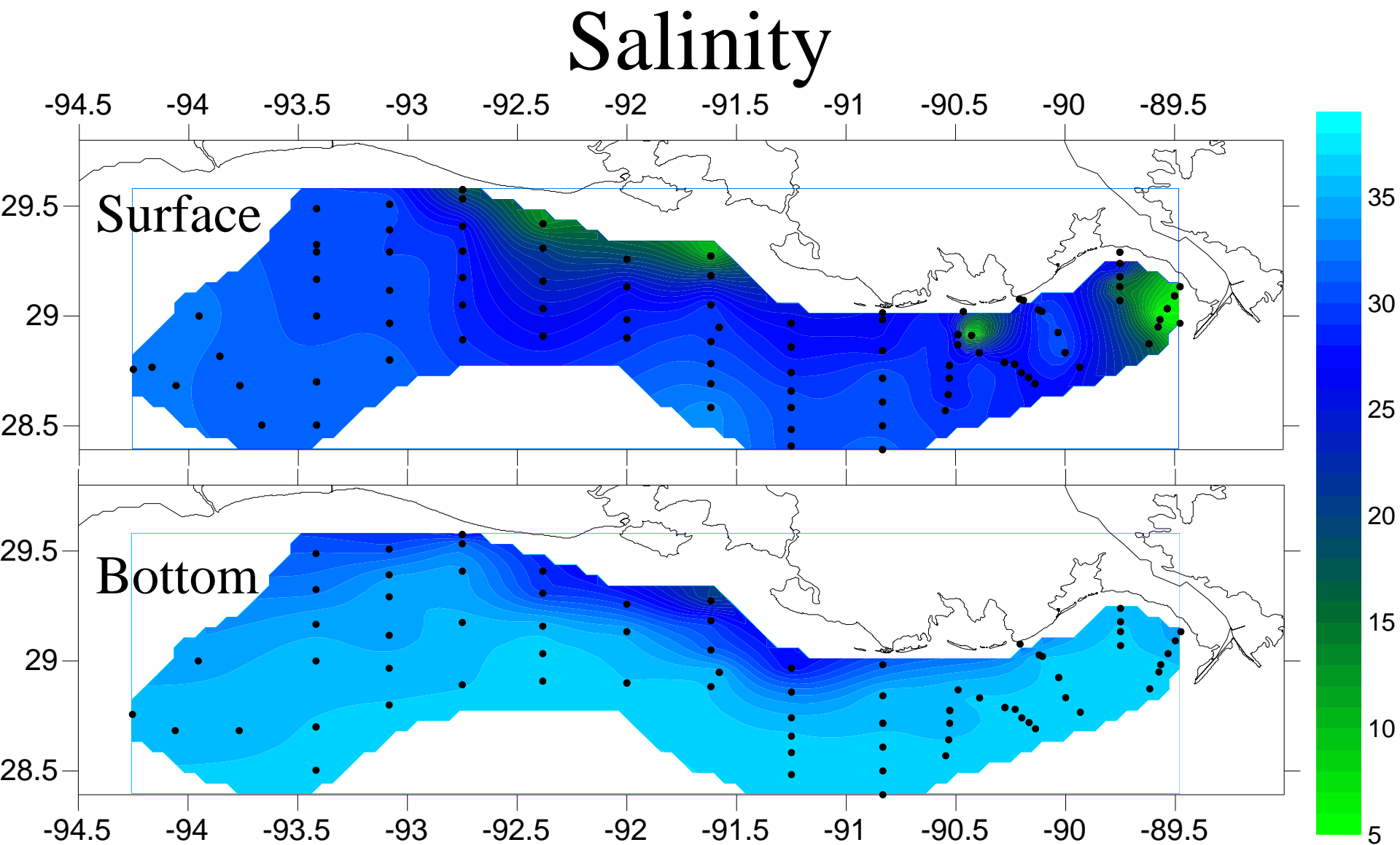


Figure 7. Salinity distributions for the surface and bottom waters during the July 2007 shelfwide. Louisiana Gulf coast is shown to the north of the sample area. Black dots represent sample stations.

# Respiration (mmol O<sub>2</sub> m<sup>-3</sup> d<sup>-1</sup>)

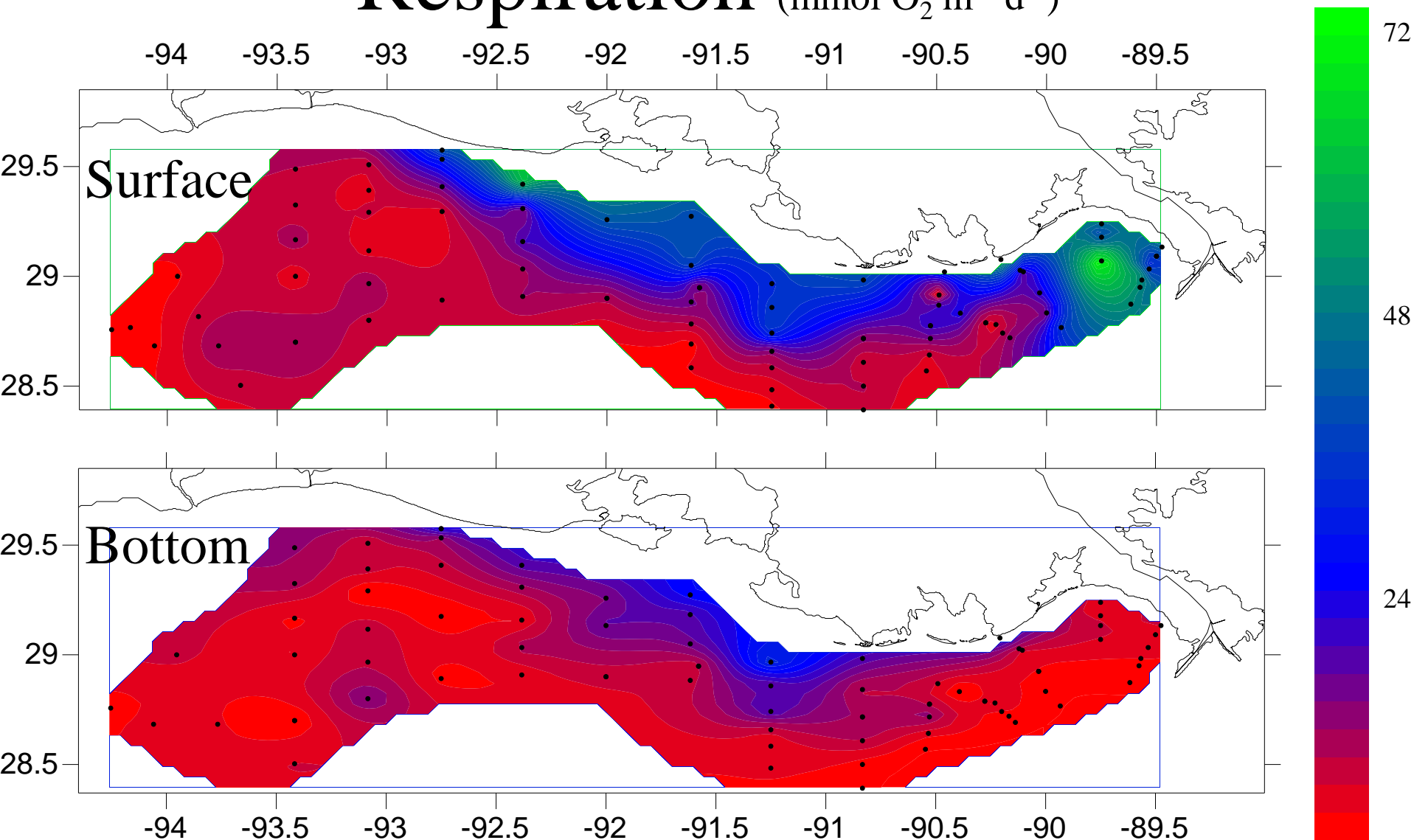


Figure 8. Respiration distributions for the surface and bottom waters during the July 2007 shelfwide. Black dots represent sample stations.

# Daily Net P

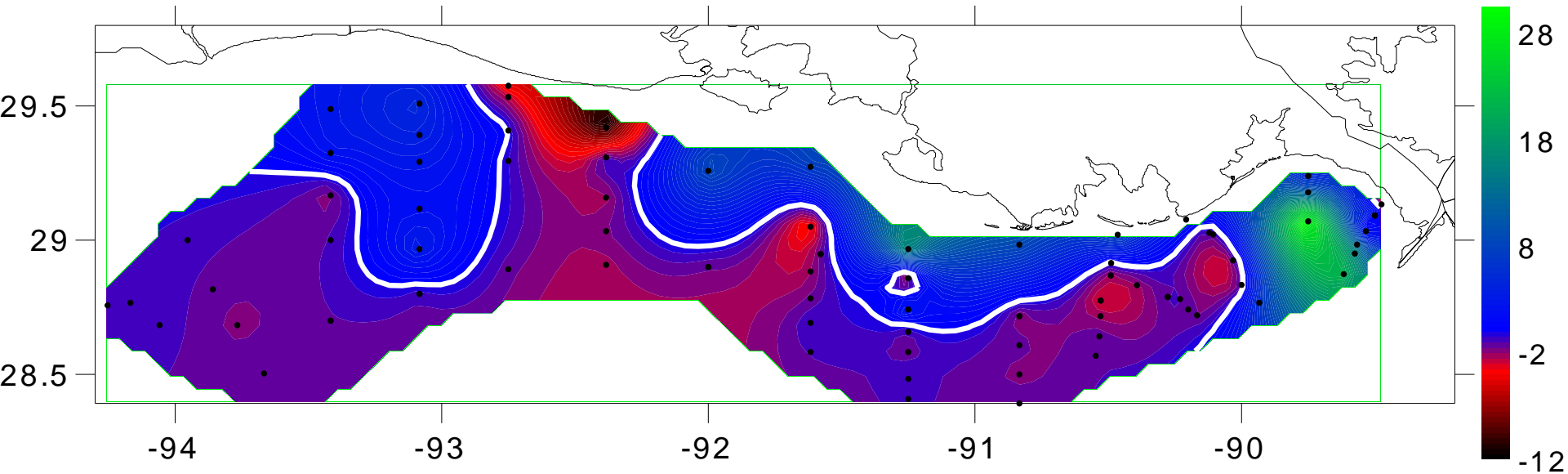


Figure 9. Spatial distribution of Daily Net P for the July 2007 shelfwide. White line represents the Net P = 0 isoline. Black dots represent sample stations.

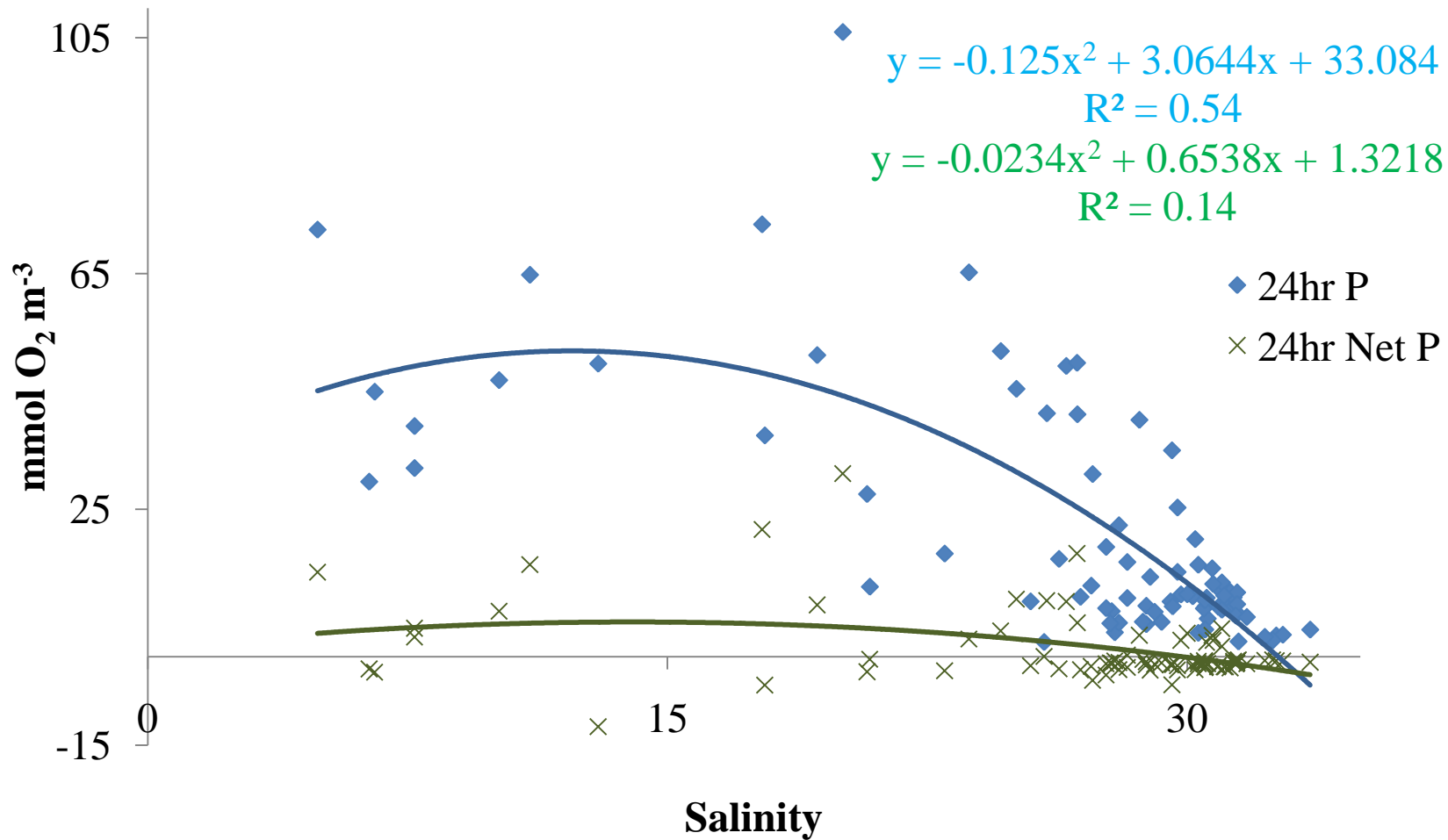


Figure 10. Salinity versus daily gross P (blue diamonds) and daily net P (green crosses).



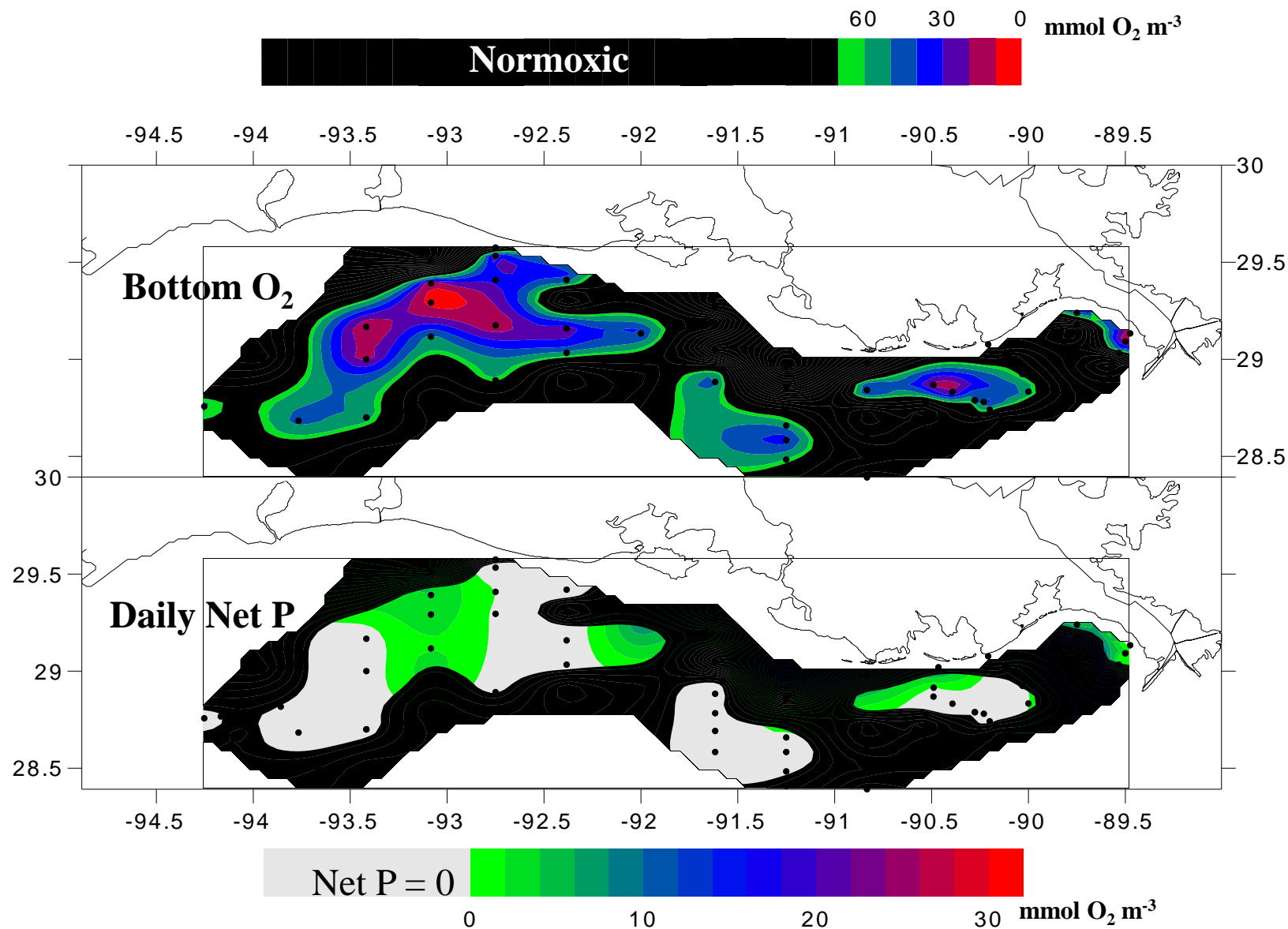


Figure 11. Spatial distribution of bottom  $O_2$  concentrations (top) and surface daily net P (bottom). Black areas represent areas where bottom waters were not hypoxic during the July 2007 shelfwide ( $>64\ mmol\ O_2\ m^{-3}$ ).

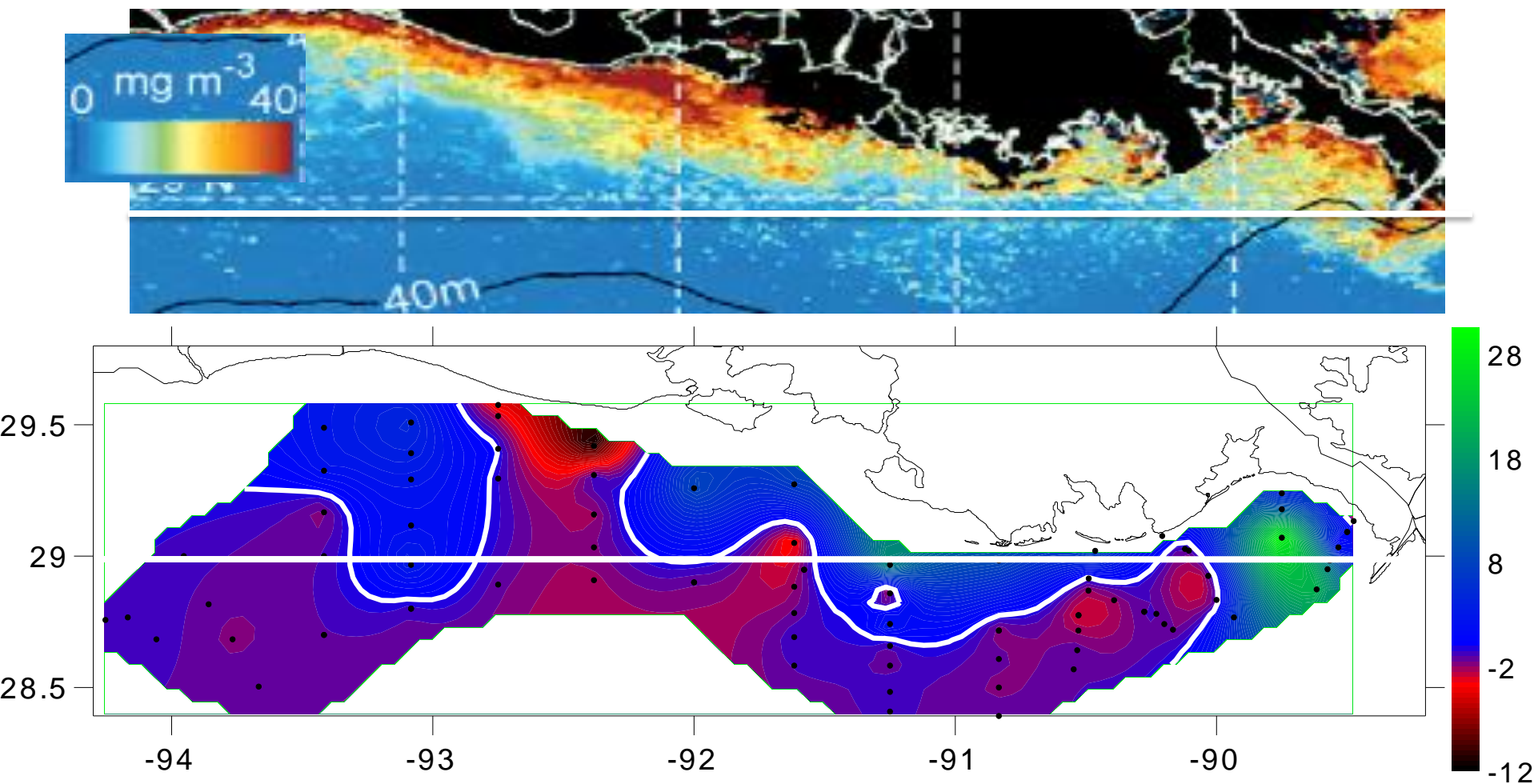


Figure 12. Comparison of June 2001 satellite chlorophyll data (top, Walker and Rabalais 2006) with Net P estimates (bottom, July 2007). White line in both images provides a common reference latitude at  $\sim 29^\circ\text{N}$ .