The Major Driving Force on Net Ecosystem Production in the North Estuary, China

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Abstract. This study aims to understand the major driving force on net ecosystem production (NEP) in estuaries. Season variation in NEP was investigated over two years in the North estuary China, along with physical (water temperature, river discharge, turbidity, salinity), chemical (nutrients, chemical oxygen demand), and biological (chlorophyll a) properties. NEP varied from -5.79 mgO₂L⁻¹d⁻¹ to 7.29 mgO₂L⁻¹d⁻¹ with a relatively low annual average of -1.13 mgO₂L⁻¹d⁻¹ during our monitoring period from 2010 to 2011. NEP was significantly positively correlated with chlorophyll a, dissolved oxygen, and solar radiation, but significantly negatively correlated with turbidity, river discharge, and chemical oxygen demand. The stepwise multiple linear regression models showed that dissolved oxygen, river discharge and solar radiation were particularly important factors that influenced the variation in NEP. NEP was the lowest during peak discharge period in autumn and increased in summer. The autotrophic state prevailed on most days in summer, whereas the heterotrophic state occurred in spring and autumn. Hydrologic alteration and seasonal variation simultaneously affected the estuarine NEP. High turbidity lowered NEP much further in autumn.

1. Introduction
Estuaries are among the most productive environments on the Earth [1]. Higher productivity is attributed to enhanced nutrient input through natural and anthropogenic sources [2, 3]. Ecosystem functions, which describe interactions between abiotic and biotic components, are sensitive indicators of responses to perturbations because they integrate responses to multiple stressors across levels of ecological organization [4]. Net ecosystem production (NEP; analogous to net ecosystem metabolism) is the balance between gross primary production and ecosystem respiration, integrates responses by autotrophic and heterotrophic organisms and is a direct measure of production and energy flow through food webs [5, 6]. Therefore, NEP may be a good indicator of perturbations associated with global environmental change [7], such as changes in hydrology [8]. It is also important to clarify the response mechanism of NEP on environmental variability for understanding the major driving force on NEP.
Advances in sensor technology and data collection have made it possible to generate data sets of daily productivity for analysing the major driving force of NEP [9-12]. Major factors influencing NEP include river exports of nutrient availability and organic carbon conditions [2, 13, 14], season variation of water temperature, solar radiation, and river discharge [8-10], salinity [10], and biotic factors [15]. However, the major driving factors of NEP in different estuaries are not the same. In addition, the relationship between NEP and the major driving factor is inconsistent. For example, river discharge and water temperature were considered as two of the most important factors affecting the aquatic metabolism [2, 6]. River discharge can cause water column more heterotrophic due to more suspended particulate matter and high turbidity [16], or more autotrophic due to more nutrients availability and water transparency in different estuaries [12]. Simultaneously, the water temperature was higher, and the metabolism rate was faster. The gross primary production and ecosystem respiration rates were usually highest in summer [12]. However, higher water temperature can cause water column more heterotrophic [9] or more autotrophic [8] in different estuaries.

In fact, the controlling mechanisms of NEP remain poorly understood in the estuaries. The goal of our study was to use statistical analysis of field monitoring data to determine the major driving force on NEP in the Yellow River estuary, China. The results may improve our understanding of the response mechanism of NEP and estuarine carbon cycle to the variable environment in estuaries.

2. Methods

2.1. Monitoring sites and field data

The study area, Yellow River estuary, is located in the eastern part of Shandong Province (Fig. 1). The Yellow River estuary is shallow, with a water depth ranging from 1.3 to 5.5 m and mean tidal range from 0.73 to 1.77 m. It is characterized by a high sediment concentration in the water column caused by the large sediment loads produced by erosion in the middle reaches of the Yellow River. The average annual rainfall ranges from 530 to 630 mm, and rainfall tends to be higher in summer (70% of the annual total). Average annual runoff is $31.3 \times 10^9$ m$^3$; the highest and lowest annual runoffs were $97.3 \times 10^9$ m$^3$ and $1.9 \times 10^9$ m$^3$, which occurred in 1964 and 1997, respectively [8].

Four sampling sites (A to D) were chosen at locations with open water and without canopy cover (Fig. 1). Sites A, B and C were located in the channel of the estuary and site D was located coastline. The distance between each two neighboring sites was ~10 km. The salinity gradient of sampling sites was: site A low salinity (always < 1‰), B and C variable salinity, D marine salinity (always > 18‰). Salinity increased when there was salt water in spring and winter at sites B and C. Salinity decreased when the runoff increased. The monitoring periods in our study included spring (April 2010 and April
2011), summer (May 2010 and June 2011), and autumn (September 2010 and October 2011). The mean water depth was approximately 2 m at all of our monitoring sites.

To reduce the variability resulting from weather-related effects, we avoided data collection on rainy or cloudy days. At each sampling site, we measured the water depth, water temperature ($T$), salinity, pH and chlorophyll a (Chla), dissolved oxygen (DO), and DO saturation percentage (DO%) at 15-min intervals over a 24-h period, using Hydrolab series DS5X sondes (Hydrolab DS5X, Hach, Loveland, CO, U.S.). Each site was continued monitoring one or three days in each sampling period and these were used to represent the status of water column at that period. Turbidity ($\pm 2\%$) was measured three times per monitoring day using a Hach 2100P turbidimeter (Hach, Loveland, CO, U.S.). WatchDog 2000 series weather station (Spectrum Technologies, Inc. Aurora, U.S.) was used to measure wind velocity (m s$^{-1}$) and daily solar radiation (w m$^{-2}$), which located 10 km from the estuarine channel. Daily discharge was collected from the Lijin hydrologic station, which is the last hydrologic station of the Yellow River.

Water samples were collected three times per monitoring day at each sampling site and immediately transferred to the laboratory for analysis of nutrients and chemical oxygen demand (COD; mg L$^{-1}$). Water samples were filtered through 0.45-μm cellulose acetate membranes in laboratory. Dissolved inorganic nitrogen (DIN; N-NH$_3^+$ + N-NO$_3^-$ + N-NO$_2^-$, mg L$^{-1}$) in the water column, was measured with the salicylate–hypochlorite colorimetric method (N-NH$_3^+$, detection limit: 0.02–2.50 mg L$^{-1}$), cadmium reduction method (N-NO$_3^-$, detection limit: 0.002–0.3 mg L$^{-1}$) and diazo coupling-spectrophotometry method (N-NO$_2^-$, detection limit: 0.3–30 mg L$^{-1}$), respectively. The dissolved inorganic phosphate (DIP; PO$_4^{3-}$, mg L$^{-1}$) was measured with a Mo-Sb anti-spectrophotometer (detection limit: 0.02–2.5 mg L$^{-1}$). All analyses were used Hach prefabricated reagents (Hach, Loveland, CO, U.S.). The mean of the three measurements was used in data analysis.

2.2. Estimating NEP

Daily NEP was calculated using the single-station open-water method, which uses diel changes in oxygen concentrations over a 24-h period to estimate NEP in the estuary using the following equation [6, 8, 17]. Because the time interval during our monitoring was 15 min, we divided $K$ by 4 to obtain a 15-min rate:

$$\text{NEP} (\text{d}t) = \left[ (C_t - C_{t-1})/\text{d}t \right] \cdot Z - KD/4$$

(1)

where $t$ (s) is time and $\text{d}t$ is the time interval between measurements. $C_t$ (mg L$^{-1}$) is the concentration of O$_2$ measured at time $t$. $Z$ is the monitoring water depth (1m in our study). The KD represents the rate of oxygen exchange across the air-water interface, which increases or decreases DO concentrations in the water column. $K$ (gO$_2$ m$^{-2}$s$^{-1}$), re-aeration coefficient at 0% saturation, was determined based on water temperature ($T$) and wind velocity [17]. The resulting equation was as follows:

$$K = 0.2v \cdot T_{10} \cdot \exp (T - 20)$$

(2)

where $v$ (m s$^{-1}$) is the wind velocity at 10 m above the water surface. $T_{10}$ = 1.024, which is a temperature correction factor. $D$ is the oxygen deficit ($D = 1 - (S_t + S_{t-1})/200$). It represents the difference between the measured DO concentration and the concentration for water that is fully saturated with oxygen; $S_t$ is the DO saturation (%) measured at time $t$. The 15-min wind and water temperature-diffusion-corrected rates of DO change were then summed over a 24-h period to calculate daily NEP (gO$_2$ m$^{-2}$d$^{-1}$ or mgO$_2$ L$^{-1}$d$^{-1}$).

2.3. Data Analysis

The arithmetic means of the hydrologic and nutrient variables were calculated for each diurnal dataset. ANOVA and Duncan’s multiple comparisons at a 0.05 confidence level for environmental factors and NEP were used to test the differences among different seasons. To explore the potential driving factors of NEP, correlation analysis and stepwise line regression analysis were performed to identify the relationships between the NEP and environment factors. Differences were considered significant when
Thirty two analyses were carried out using SPSS 22.0 for Windows (SPSS for Windows, IBM, Armonk, U.S.).

3. Results

3.1. Variation of Environment Properties and NEP.

The total descriptive statistics of environment factors and NEP during our sampling period in the Yellow River are showed in Table 1. Monthly variations in environment factors and NEP are compared (Fig. 2). The results showed that water temperature varied from 7.13 °C to 25.98 °C. It significantly increased from spring to summer and decreased in autumn (Fig. 2A). The pH significantly decreased in autumn (Fig. 2B). Chlorophyll a varied from 0.84 \( \mu g \) L\(^{-1}\) to 15.28 \( \mu g \) L\(^{-1}\) and it significantly decreased in autumn (Fig. 2C). DO% significantly increased in summer and decreased in autumn, whereas DO (mg L\(^{-1}\)) did not vary significantly (Fig. 2D, E).

Table 1. Descriptive statistics of environment factors and net ecosystem production during our sampling from 2010 to 2011 in the Yellow River estuary, values are reported as minimum, maximum, mean and standard deviation (N= 24, "N" representative days).

| Parameter Value (Abbreviation, units) | Minimum | Maximum | Mean | Std. Deviation |
|--------------------------------------|---------|---------|------|----------------|
| Water temperature (T, °C)            | 7.13    | 25.98   | 18.21| 4.79           |
| pH                                   | 7.86    | 9.42    | 8.50 | 0.40           |
| Salinity (Sal, %)                    | 0.29    | 33.15   | 7.95 | 12.53          |
| Chlorophyll a (Chla, \( \mu g \) L\(^{-1}\)) | 0.84   | 15.28   | 6.04 | 3.74           |
| DO (%) saturation                    | 75.76   | 148.69  | 93.55| 16.46          |
| Dissolved oxygen (DO, mg L\(^{-1}\)) | 6.13   | 13.84   | 8.48 | 1.71           |
| Turbidity (Turb, NTU)                | 8.18    | 1000.00 | 338.17| 399.32         |
| Water discharge (Q, m\(^{3}\) s\(^{-1}\)) | 59.75 | 1870.00 | 524.90| 595.51         |
| Solar radiation (Rs, w m\(^{-2}\))   | 48.72   | 331.54  | 192.67| 76.71          |
| Dissolved inorganic nitrogen (DIN, mg L\(^{-1}\)) | 0.02   | 0.75    | 0.22 | 0.19           |
| Dissolved inorganic phosphorus (DIP, mg L\(^{-1}\)) | 0.80   | 4.81    | 3.00 | 1.19           |
| Chemical oxygen demand (COD, mg L\(^{-1}\)) | 5.00  | 110.00  | 35.00| 33.92          |
| Net ecosystem production (NEP, mg O\(_2\) L\(^{-1}\)d\(^{-1}\)) | -5.79  | 7.29    | -1.13| 2.96           |

Turbidity varied from 8.18 NTU to 1000 NTU, and it significantly increased in autumn (>1000 NTU) (Fig. 2F). Daily river discharge varied from 59.75 m\(^{3}\) s\(^{-1}\) to 1870.00 m\(^{3}\) s\(^{-1}\), and it significantly increased in autumn at Lijin gauge (Fig. 2G). Solar radiation varied from 48.72 w m\(^{-2}\) to 331.54 w m\(^{-2}\) and it significantly decreased in autumn (Fig. 2H). DIN and DIP did not vary significantly (Fig. 2I, J). COD significantly increased in autumn (Fig. 2K). NEP varied from -5.79 mgO\(_2\)L\(^{-1}\)d\(^{-1}\) to 7.29 mgO\(_2\)L\(^{-1}\)d\(^{-1}\) with a relatively low annual average of -1.13 mgO\(_2\)L\(^{-1}\)d\(^{-1}\) (Table 1), and it significantly decreased in autumn. The autotrophic state prevailed on most days in summer, whereas the heterotrophic state occurred in spring and autumn (Fig. 2L).
Figure 2. Season variations in environment factors and net ecosystem production during our sampling period at four sampling sites in the Yellow River estuary. a, b, c Different letters indicate significant differences of environment properties and metabolism among different seasons in the estuary.

3.2. The main driving factors of NEP

We calculated the correlations between NEP and environmental factors to clarify the relative strengths of the drivers of NEP in the Yellow River estuary. NEP was significantly positively correlated with chlorophyll a, DO%, DO, and solar radiation, but significantly negatively correlated with turbidity, freshwater discharge, and COD (Table 2). River discharge was significantly positively correlated with turbidity and COD, but negatively correlated with pH, chlorophyll a, solar radiation. In addition, both nutrients (DIP and DIN) and turbidity were significantly negatively correlated with salinity.

Table 2. Pearson correlation coefficients for the net ecosystem production (NEP) and environmental factors in the Yellow River estuary (N=24). Environmental factors: water temperature (T), pH, salinity (Sa), chlorophyll a (Chla), DO (% saturation), dissolved oxygen (DO, mg L⁻¹), turbidity (Tur), freshwater discharge (Dis), solar radiation (Rs), dissolved inorganic phosphorus (DIP), dissolved inorganic nitrogen (DIN), chemical oxygen demand (COD), and net ecosystem production (NEP).

| Factors | T  | pH | Sa  | Chla | DO% | DO  | Tur | Dis | Rs  | DIP | DIN | COD | NEP |
|---------|----|----|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| T       |    | .115 | -.278 | .168 | .262 | -.165 | .280 | .172 | -.037 | .000 | .033 | .349 | .016 |
| pH      | .115 |    | -.128 | .335 | -.060 | -.264 | -.350 | .412** | .397 | -.073 | .280 | -.336 | .082 |
| Sa      | -.278 | -.128 |    | -1.194 | .121 | .103 | -.513** | -.096 | .176 | -.483** | -.885** | -.026 | .178 |
The stepwise multiple linear regression models of NEP as a function of environmental factors showed that DO% and river discharge were two particularly important factors that influenced the variation in NEP (Table 3, model 1-2). In addition, when we excluded DO% and DO, the stepwise multiple linear regression models of NEP showed that solar radiation was the most important factor that influenced the variation in metabolism (Table 3, model 3). The regression equation was that: NEP = 0.029Rs-6.635. The coefficients of the constant and solar radiation is 0.000. It means that river discharge and seasonal variation simultaneously affected the estuarine NEP. The effects of river discharge on estuarine NEP was more than that of the seasonal variation in the Yellow River estuary.

Table 3. Stepwise multiple linear regression models of NEP as a function of water temperature, pH, salinity, dissolved oxygen (excluded in model 3), freshwater discharge (Dis), turbidity, dissolved inorganic nitrogen, dissolved inorganic phosphorus, COD, and solar radiation (Rs). Only parameters that fulfilled the required significance level of $P < 0.05$ are shown ($N$= 24).

| Dependent variable | Model | Overall | $R^2$ | F value | Coefficient | Sta. Error | $P$ value |
|--------------------|-------|---------|-------|---------|-------------|------------|-----------|
| NEP                | Model 1 | constant | 0.706 | 52.762 | -15.255     | 1.973      | 0.000     |
|                    |        | DO%     |       |         | 0.151       | 0.021      | 0.000     |
| NEP                | Model 2 | constant | 0.874 | 72.880 | -13.270     | 1.373      | 0.000     |
|                    |        | DO%     |       |         | 0.141       | 0.014      | 0.000     |
|                    |        | Dis     |       |         | -0.002      | 0.000      | 0.000     |
| NEP                | Model 3 | constant | 0.549 | 26.747 | -6.635      | 1.142      | 0.000     |
|                    |        | Rs      |       |         | 0.029       | 0.006      | 0.000     |

4. Discussions

Productivity is one of fundamental and functional indicators of aquatic ecosystem. River discharge modifies physical and biogeochemical processes in the estuary through changes in salinity, stratification, suspended load, organic carbon, and nutrient input [15]. Significant modification of physic-chemical properties by river discharge led to changes in phytoplankton composition and dead organic matter concentrations that alters biomass, abundance, and composition of zooplankton[18], and thus alters the productivity in estuaries.

In our study, the stepwise multiple linear regression models showed that DO%, river discharge, and solar radiation were particularly important factors that influenced the variation in NEP. NEP was significantly positively correlated with chlorophyll a, dissolved oxygen, and solar radiation, but significantly negatively correlated with turbidity, river discharge, and COD. Simultaneously, river discharge was significantly positively correlated with turbidity and COD, but negatively correlated with pH, Chla, and solar radiation. It suggests that higher river discharge caused higher turbidity and COD, but lower pH and Chla in autumn.
NEP significantly decreased and heterotrophic conditions dominated the water column in autumn. Light availability decreased because of high turbidity and low solar radiation due to higher river discharge, which can cause lower NEP in autumn. High COD may stimulate high respiration and lower chlorophyll a may limit the gross primary production, both of the two lead to lower NEP and heterotrophic state occurred in autumn.

5. Conclusion
NEP varied from -5.79 mgO$_2$L$^{-1}$d$^{-1}$ to 7.29 mgO$_2$L$^{-1}$d$^{-1}$ with a relatively low annual average of -1.13 mgO$_2$L$^{-1}$d$^{-1}$ during our monitoring period from 2010 to 2011 in the Yellow River estuary. NEP was significantly positively correlated with chlorophyll a, dissolved oxygen, and solar radiation, but significantly negatively correlated with turbidity, river discharge, and chemical oxygen demand. The stepwise multiple linear regression models showed that dissolved oxygen, river discharge, and solar radiation were particularly important factors that influenced the variation in NEP. The autotrophic state prevailed on most days in summer, whereas the heterotrophic state occurred in spring and autumn. Hydrologic alteration and seasonal variation simultaneously affected the estuarine NEP. High turbidity lowered NEP much further in autumn.

Acknowledgments
This work was supported by the National Key R&D Program of China (2017YFC0404506), the National Natural science foundation of China (41701027), and the Research start-up funds of DGUT (GC300501-06).

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