Marine Pollution Bulletin 90 (2015) 121–128

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Three decadal inputs of total organic carbon from four major coastal river basins to the summer hypoxic zone of the Northern Gulf of Mexico

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ARTICLE INFO

Article history:
Available online 1 December 2014

Keywords:
Total organic carbon
Riverine input
Coastal water quality
Louisiana
Gulf of Mexico

ABSTRACT

This study investigated long-term (1980–2009) yields and variability of total organic carbon (TOC) from four major coastal rivers in Louisiana entering the Northern Gulf of Mexico where a large-area summer hypoxic zone has been occurring since the middle 1980s. Two of these rivers drain agriculture-intensive (>40%) watersheds, while the other two rivers drain forest-pasture dominated (>50%) watersheds. The study found that these rivers discharged a total of 13.0×10^4 t TOC annually, fluctuating from 5.9×10^4 to 22.8×10^4 t. Seasonally, the rivers showed high TOC yield during the winter and early spring months, corresponding to the seasonal trend of river discharge. While river hydrology controlled TOC yields, land use has played an important role in fluxes, seasonal variations, and characteristics of TOC. The findings fill in a critical information gap of quantity and quality of organic carbon transport from coastal watersheds to one of the world's largest summer hypoxic zones.

1. Introduction

A hypoxic zone with dissolved oxygen (DO) concentrations <2 mg L^{-1} has been observed each summer since the mid-1980s off Louisiana's coast in the Northern Gulf of Mexico (Rabalais et al., 2007, 2010; Turner et al., 2008). A recent study (Obenour et al., 2013) also found that the thickness of the hypoxic zone has increased over the past 30 yrs. The hypoxic area has large reaching effects, ecologically and economically, including massive fish kill and economic consequence from lost fisheries and food processing incomes (O'Connor and Whitall, 2007; Diaz and Rosenberg, 2011). Researchers have attributed this "dead zone" to the enrichment of nitrogen and phosphorus (Turner and Rabalais, 1991, 1994) as high annual inputs of the nutrients have been found from the Mississippi–Atchafalaya River System (MARS) (Goolsby et al., 2001; Turner et al., 2012; Xu, 2013).

Nutrient availability, especially nitrogen, can be affected by organic carbon levels in water bodies (Newcomer et al., 2012; Xing et al., 2013). For instance, denitrification bed, which uses organic carbon as substrates, is a cost-effective technology for removing nitrate from point source discharge (Cameron and Schipper, 2010). In order to manage nitrogen and phosphorus, it is important to manage the amount and availability of organic carbon. Therefore, riverine transport of organic carbon to the oceans plays a significant role in the global carbon, nitrogen, and phosphorus cycling. At the same time, the input of organic carbon to the oceans provides crucial sources in food web of estuarine ecosystems.

As the largest river system in North America, MARS has been investigated intensively. Fluxes of nutrients and organic carbon from MARS to the Northern Gulf of Mexico (NGOM) have been estimated for the past several decades (e.g. Bianchi et al., 2007; Turner et al., 2007; Xu, 2006 and 2013). A high organic carbon input to NGOM has been quantified from the Mississippi River main stem (403.0×10^4 t yr^{-1}, Bianchi et al., 2007) and from its tributary, the Atchafalaya River (113.9×10^4 t yr^{-1}, Xu, 2013), providing critical information on the sources for the hypoxic dead zone. However, little is known about fluxes of nutrients and organic carbon from the major coastal rivers of Louisiana that discharge a considerable amount of freshwater and sediment to NGOM (Rosen and Xu, 2011).

While MARS has deeper off-shore effects due to its large discharge volume and power, coastal rivers entering NGOM may have strong seasonal effects on near-shore water quality and nutrient availability in the region's estuaries. The objectives of this study are (1) to quantify fluxes of total organic carbon (TOC) from four major coastal rivers in Louisiana to the Northern Gulf of Mexico, and (2) to determine seasonal, interannual, and decadal trends of TOC yield in the rivers. We also estimated fluxes of nitrogen and phosphorus that are detailed in another manuscript to assess nutritional condition of the four river's waters to NGOM.

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http://dx.doi.org/10.1016/j.marpolbul.2014.11.010
0025-326X/

2. Methods

2.1. Study area

The four coastal rivers investigated in this study include the Sabine, Calcasieu, Mermentau, and Vermilion Rivers that enter the Gulf of Mexico (GOM) in southwest Louisiana, USA (Fig. 1). These rivers flow throw the Chenier Plain comprising an area of approximately 5000 km^2 with a west–east coastline of about 200 km (Gammill, 2002), stretching geographically from approximately 29.5°N to 33.2°N and from 91.3°W to 94.0°W. The Sabine River has a drainage area of 25,267 km^2 with a total length of 893 km bordering Texas and Louisiana and draining into Sabine Lake before the GOM (Phillips, 2003). The Calcasieu River drainage basin is 9780 km^2 and the river is 322 km long and discharges into Calcasieu Lake before the GOM (Nichol et al., 1992). The Mermentau River drains a land area of 16,997 km^2 with a length of 115 km discharging into Grand Lake before reaching the Gulf of Mexico (USACE, 2014). The Vermilion River is 116 km long with a basin area of 4470 km^2 draining into Vermilion Bay (US EPA Region 6, 2001; USACE, 2004).

Climate of this region can be characterized by hot, humid summers and generally mild winters. Land use conditions are different among the four river basins. The Mermentau and Vermilion River Basins are much more dominated by agricultural land use (67% and 40%, respectively) when compared with the Sabine and Calcasieu River Basins (14% and 26%) (Rosen and Xu, 2011). The latter two river basins have a much higher forest-pasture land use (54% and 51%) than the first two do (7% and 22%). The difference in land use dominance may have profound effects on carbon yield from the river basins.

2.2. Data collection

To estimate total organic carbon yields for each of the four coastal rivers, long-term (1980–2009) daily discharge at the lower Sabine, Calcasieu, Mermentau, and Vermilion Rivers were collected from the U.S. Geological Survey (USGS). The gauge stations were chosen based on their proximity to the mouth of the river for optimal drainage representation and minimal tidal influence. Specifically, the locations with their USGS gauge station numbers were Sabine River near Ruliff, TX (08030500), Calcasieu River near Kinder, LA (08015500), Mermentau River at Mermentau, LA (08012150), and Vermilion River at Perry, LA (07386980).

Long-term monthly water quality data were obtained from the Louisiana Department of Environmental Quality (LDEQ) for the following stations (station#): Sabine River northeast of Orange, TX (LA110301_00), Calcasieu River near Kinder, LA (LA030103_00), Mermentau River at Mermentau, LA (LA050401_00), and Vermilion River at Perry (LA060802_00) (Fig. 1). Table 1 summarized the station identification numbers and data coverage of the four rivers. Water quality data included monthly measurements on a series of chemical and physical parameters, of which concentrations of TOC, total Kjeldahl nitrogen (TKN, which is the sum of organic nitrogen and ammonia nitrogen), and nitrate plus nitrite nitrogen ($NO_2 + NO_3$), and total phosphorus (TP) were used in this study. Details on field sampling and laboratory analysis methods can be found in LDEQ's Quality Assurance Project Plan for the Ambient Water Quality Monitoring Network (LDEQ, 2013).

2.3. TOC yield and flux calculation

TOC yield of a river is essentially a product of river discharge and TOC concentration. In this study we estimated daily TOC yield using a rating curve that can be generally described in a natural logarithm as below (Xu, 2013):

$$\ln(S(t)) = b_0 + b_1 \ln(Q_{day}(t)) + \varepsilon(t) \quad (1)$$

where Q_{day} represents daily discharge in liters, $S(t)$ is daily TOC yield in grams, and $\varepsilon(t)$ is an error term assumed to be normally distributed.

To reduce possible long-term change effects, we developed three rating curves for each of the four rivers to represent the periods of the 1980s, 1990s, and 2000s. The regression (i.e. Eq. (1)) was performed using the SAS Statistical Software package (SAS Institute Inc., Cary, NC). The fitted parameters and the statistical measures of fitness are summarized in Table 2. The residual analysis of Eq. (1) is presented in Fig. 2.

The mass yields estimated from the regression equation were summed up over time to provide monthly, annual and decadal TOC yields for the period from 1980 to 2009. TOC fluxes (mass per unit area per unit time) were calculated for each river basin

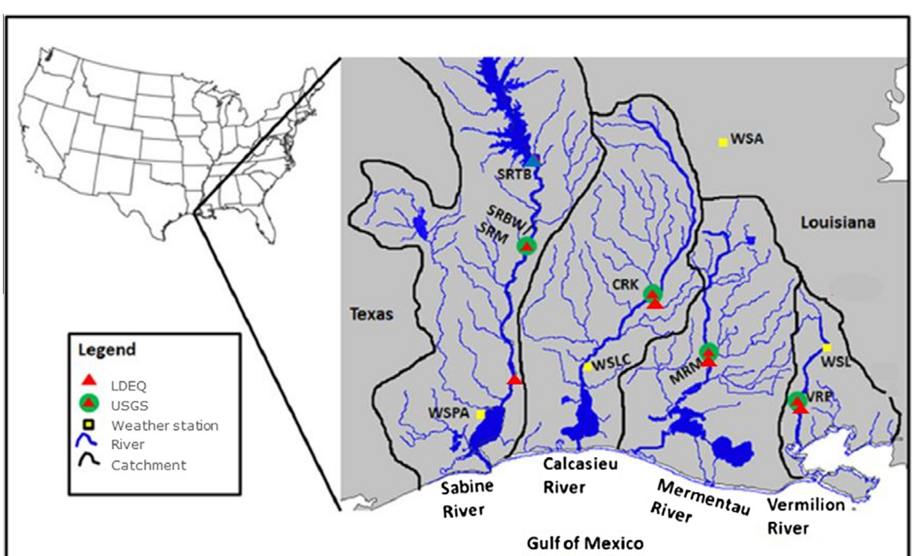

Fig. 1. Geographical location of the Sabine, Calcasieu, Mermentau, and Vermilion Rivers entering the Northern Gulf of Mexico, and the locations of USGS river gauging stations and LDEQ water quality sampling sites.