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Multiple proxy estimates of source and spatial variation in organic matter in surface sediments from the southern Yellow Sea

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ABSTRACT

Marginal seas play an important role in the global carbon cycle as organic matter (OM) buried in shelf seas accounts for ca. 80% of marine sedimentary OM. The Yellow Sea (YS) is a significant sink for both terrestrial OM (TOM) and marine OM (MOM), so the source and spatial variation of sedimentary OM in the southern YS were investigated by analyzing several parameters for 54 surface sediment samples. Spatial ranges were 5.4–12.8 for total organic carbon/total organic nitrogen (TOC/TON), −22.8‰ to −19.9‰ for TOC $\delta^{13}C$, 421–4515 ng/g TOC for $\sum(C_{27}+C_{29}+C_{31})$ *n*-alkanes, 33–152 ng/g TOC for branched glycerol dialkyl glycerol tetraethers, 316–8550 ng/g TOC for total marine biomarkers. TOC/TON displayed no distinct spatial pattern, but the BIT (branched isoprenoid tetratether index) proxy, TMBR [terrestrial and marine biom arker ratio: $(C_{27}+C_{29}+C_{31}$ *n*-alkanes)/$(C_{27}+C_{29}+C_{31})$ *n*-alka nes + (brassicasterol + dinosterol + alkenones)] and $\delta^{13}C$ values revealed similar spatial distribution patterns, indicating higher TOM near coastal regions and especially near the old Huanghe Estuary. Quantitative estimates using a binary model revealed higher %TOM (avg. 34%) from TMBR than from $\delta^{13}C$ (avg. 26%) and BIT (avg. 12%). TMBR is a proxy incorporating both soil OM (OM_{soil}) and plant OM (OM_{plant}) while BIT is a proxy for OM_{soil}, so quantitative estimates using a three end member model indicated higher OM_{plant} and OM_{soil} values near the old Huanghe Estuary, but $\%OM_{plant}$ (avg. 23%) was higher than $\%OM_{soil}$ (avg. 13%). Our study suggests that these proxies can be used to study the spatial and temporal variation and delivery mechanisms for both OM_{soil} and OM_{plant} in marginal seas.

1. Introduction

Organic matter (OM) buried in shelf seas and deltas accounts for ca. 80% of marine sedimentary OM (Berner, 1982; Hedges and Keil, 1995), due to the combined effects of high terrestrial OM (TOM) input, enhanced production of marine OM (MOM) and high sedimentation rate, which all enhance OM preservation and burial. Since sedimentary OM is a long term carbon sink, it is necessary to distinguish and estimate the relative contributions of TOM and MOM as they play different roles as long term carbon sinks and in global climate change (Pearson et al., 2001).

Global carbon budgets predicted that the input of riverine particulate organic carbon (POC) was adequate for providing all the OC buried in marine sediments. However, molecular and isotope studies suggested that only a small fraction of TOM was buried in marine sediments (Hedges et al., 1997). The contradiction could be caused either by a remarkable degradation rate for TOM (Hedges et al., 1997) or an underestimate of TOM preservation in marine sediments using traditional proxies (Gordon and Goñi, 2003; Smith et al., 2010). Marine sedimentary OM sources have been determined using both bulk parameters and biomarkers. TOM usually has higher C/N and lighter $\delta^{13}C$ values than MOM (Hedges et al., 1997), so these two parameters have been used to determine the relative proportions of TOM and MOM in marine sediments.

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However, the application of these TOC-based proxies has some limitations for marginal sea sediments (Xing et al., 2011b), where $\delta^{13}C$ values are influenced by plant type (Goñi et al., 1998; Zhang et al., 2003), microbial OM contribution (Ruttenberg and Goñi, 1997) and diagenesis (Hopmans et al., 2004). Particle absorption could also affect C/N (Hedges and Oades, 1997; Schubert and Calvert, 2001).

Biomarkers have been demonstrated to offer great potential in estimating the TOM contribution to marginal sea sediments (Smith et al., 2012 and references therein) because of their more specific origins. The branched isoprenoid tetraether (BIT) index (Hopmans et al., 2004) has been applied to estimate both TOM and soil OM (OM_{soil}) contribution to marine sediments (Weijers et al., 2009). More specific sources, such as soil, plant and marine, can be assigned via a multi-proxy approach by combing the BIT index, C/N and $\delta^{13}C$ (Smith et al., 2010; Weijers et al., 2009). However, multi-proxies could also yield conflicting results for different environments (Kim et al., 2006; Walsh et al., 2008; Smith et al., 2010, 2012). For example, BIT values correlated well with both TOC $\delta^{13}C$ values and C/N, but these three proxies were all weakly correlated with lignin content for surface sediment samples from a fjord of New Zealand's South Island (Smith et al., 2010). On the other hand, the BIT index correlated well with TOC $\delta^{13}C$ but had no significant correlation with C/N for soil, river and marine sediment samples from the NW Mediterranean (Gulf of Lions; Kim et al., 2006). The BIT index did not correlate with both lignin content and $\delta^{13}C$ for Vancouver Island fjords and the Vancouver-Washington Margin (Walsh et al., 2008). Smith et al. (2012) recently observed that the variation in the BIT Index was dominated by changes in the delivery of MOM to sediments, which resulted in a non-linear mixing line between MOM and TOM end members. An alternative approach was proposed by using branched glycerol dialkyl glycerol tetraether (brGDGT) yield as an OM_{soil} proxy, which reduced estimates of $\%OM_{soil}$ in the Gulf of Mexico. Therefore, the application of multi-proxies and the selection of suitable proxies are critical for accurately estimating the relative contributions of TOM and MOM to marginal sea sediments.

The Yellow Sea (YS), between China and the Korean Peninsula, is an important marginal sea ecosystem (Tang, 2009). Sediments in the YS have complex sources, but most of the terrestrial material is from the modern Huanghe River and old Huanghe deposition. The Huanghe River discharged about 1.1×10^9 t/yr sediments to the sea during the past millennium (Milliman et al., 1987; Milliman and Meade, 1983). But sediment load dramatically declined after the 1980s (Wang et al., 2007), with an amount of 1.51×10^8 t/year from 2000 to 2005 (Peng et al., 2010). Sediment transport from the old Huanghe delta to the YS is about 0.5×10^9 t/yr (Lim et al., 2007). Terrestrial material in the delta along the eastern coast of the Shandong Peninsula (Fig. 1) is derived from the modern Huanghe River (Cai et al., 2003; Lan et al., 2005); in contrast, sediments buried near the old Huanghe Estuary were derived mainly from eroded old Huanghe material (Chen et al., 1999; Lan et al., 2007; Song et al., 2008; Yin et al., 2007). Terrestrial material in the middle of the southern YS (SYS) is derived from both the old Huanghe and the modern Huanghe (Lan et al., 2007; Lee and Chough, 1989), whereas sediments in the eastern region of the YS are from the Korean Peninsula (Wang et al., 2001; Yang and Youn, 2007).

These terrestrial inputs mean that the YS is also an important sink for TOM (Chen and Borges, 2009) and a few studies have focused on the distribution and origins of sedimentary OM. High TOC content in the muddy sediments of the western YS (Yang and Youn, 2007) suggested a significant TOM contribution from the modern Huanghe River. More negative TOC $\delta^{13}C$ values indicated high TOM burial in the delta off the Shandong Peninsula and the Jiangsu coast (Cai et al., 2003). Polynuclear aromatic hydrocarbon (PAH) distributions in YS sediments indicated a seaward decreasing trend of TOM contribution (Cai et al., 2003). Sediment core records suggested that *n*-alkanes were transported mainly to the YS via river discharge, while anthropogenic PAHs produced mainly by fossil burning were transported mainly by aerosol deposition (Wu et al., 2001). Biomarkers in surface sediments indicated higher TOM contribution nearshore and higher MOM contribution in the central basin (Xing et al., 2011a). However, most of these studies used one proxy for qualitative estimates of the distribution and origin of sedimentary OM in the YS, each with some limitations.

In this study, multi-proxies employing C/N, $\delta^{13}C$, BIT and TMBR (Xing et al., 2011b) for surface sediment samples of the southern YS (Fig. 1) were used to distinguish, and to quantitatively and comparatively estimate, the source and spatial variation in sedimentary OM. It was hoped that evaluation of these proxies would support their application for reconstructing both TOM and MOM records and to study the Holocene carbon cycle in the YS and other marginal seas.

2. Material and methods

2.1. Material

The SYS (Fig. 1) is a semi-enclosed shallow shelf sea bordered with the northern YS and the East China Sea, with a mean water depth of 44 m and a maximum depth of 140 m (Feng et al., 2004). The surface circulation of the SYS consists of the Yellow Sea Warm Current (YSWC, a branch of the Kuroshio) and the Yellow Sea Coastal current (YSCC) and the Korean Coastal Current (KCC) (Fig. 1). The northward flow of the YSWC and the southward flow of the Yellow Sea Coastal Current (YSCC) along the coast form a counterclockwise (cyclonic) gyre in the western SYS.

Surface sediments from 54 sites (Supplement Table 1) covering the SYS were collected using a box corer (0–5 cm) during the China and Korea joint cruise in August of 2008 (Fig. 1, ▲) and a grab sampler (0–10 cm) during a cruise by the Qingdao Institute of Marine Geology in December of 2008 (Fig. 1, •). All samples were stored at −20 °C.

2.2. Methods

2.2.1. TOC, C/N and $\delta^{13}C$ of TOC

For TOC and TN analysis, the samples were acidified with 4 N HCl. After rinsing with deionized water several times and drying in an oven at 55 °C, the carbonate-free samples were measured for TOC and TN in duplicate using a Thermo Flash 2000 Elemental Analyzer, with a standard deviation of 0.02 wt% ($n = 6$) and 0.002 wt% ($n = 6$) respectively. TOC $\delta^{13}C$ values were determined using a Thermo Delta V mass spectrometer (continuous flow mode), with a standard deviation of 0.2‰ ($n = 6$; Xing et al., 2011b).

2.2.2. Phytoplankton biomarker and n-alkane analysis

Detailed methods for biomarker analysis are given by Xing et al. (2011b). Briefly, freeze-dried samples were extracted (4×) with dichloromethane (DCM)/MeOH (3:1, v/v) using sonication, after addition C_{19} *n*-alkanol and *n*-$C_{24}D_{50}$ as internal standards. Each extract was hydrolyzed in KOH/MeOH and separated into fractions using silica gel chromatography. The non-polar fraction eluted by hexane containing *n*-alkanes was dried under a N_2 stream for instrumental analysis. The neutral fraction, eluted with DCM/MeOH (95:5, by volume) and containing marine phytoplankton biomarkers (brassicasterol, dinosterol and C_{37} alkenones) was