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Baseline

Origins of suspended particulate matter based on sterol distribution in low salinity water mass observed in the offshore East China Sea

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ABSTRACT

The molecular composition and distribution of sterols were investigated in the East China Sea to identify the origins of suspended particulate matter (SPM) in offshore waters influenced by Changjiang River Diluted Water (CRDW). Total sterol concentrations ranged from 3200 to 31,900 pg L^{-1} and 663 to 5690 pg L^{-1} in the particulate and dissolved phases, respectively. Marine sterols dominated representing 71% and 66% in the particulate and dissolved phases, respectively. Typical sewage markers, such as coprostanol, were usually absent at ~250 km offshore. However, sterols from allochthonous terrestrial plants were still detected at these sites. A negative relationship was observed between salinity and concentrations of terrestrial sterols in SPM, suggesting that significant amounts of terrestrial particulate matter traveled long distance offshore in the East China Sea, and the Changjiang River Diluted Water (CRDW) was an effective carrier of land-derived particulate organic matter to the offshore East China Sea.

Particulate organic matter (POM) is the primary carrier transporting surface organic carbon to the deep sea environment (Laureillard and Saliot, 1993). Therefore, it is essential to identify the sources of POM that contribute to the downward flux of organic matter to better understand the biogeochemical cycle of carbon in the ocean (Hedges et al., 2000; Benner, 2002; Lee et al., 2004; Loh et al., 2008; Christodoulou et al., 2009). However, most organic matter in ocean water remains uncharacterized at the molecular level.

Low molecular weight organic compounds such as fatty acids and sterols in water can function as molecular markers that aid in detecting and tracing the sources and transport of organic matter (Takada and Eganhouse, 1998; Zimmerman and Canuel, 2001; Foster and Walls, 2003). Sterols with various biological origins are relatively stable in the aquatic environment and known to be useful in identifying the sources of organic matter input (Heftmann, 1971; Volkman, 1986; Wakeham and Lee, 1989; Saliot et al., 1991; Benfenati et al., 1994; McCallister et al., 2006). Sterols can differentiate allochthonous, autochthonous, and anthropogenic lipid carbon sources in the aquatic environments (Hudson et al., 2001; Mudge and Duce, 2005). The terrestrial ecosystem contains mainly C_{29} sterols such as ergosterol, stigmasterol, β-sitosterol, lanosterol, and stigmastanol that form the main elements of terrestrial vascular plants and fungi (Laureillard and Saliot, 1993; Li et al., 1995). Sterols excreted by marine phytoplankton and zooplankton are mostly C_{28} type such as desmosterol, brassicasterol and cholesterol (Volkman, 1986; Saliot et al., 1991). Coprostanol (5β-cholestan-3β-ol) is produced when cholesterol is decomposed by bacteria in the small intestine of animals (Walker et al., 1982; Writer et al., 1995) and has long been used as a fecal sewage indicator (Hatcher and McGillivary, 1979; Brown and Wade, 1983; Writer et al., 1995).

Many studies on the occurrence and origins of sterols in the marine environment have mostly focused on the nearshore areas, such as sewage tracing in urbanized coasts (e.g., Chan et al., 1998; Carreira et al., 2004; Peng et al., 2005) and tracing the source of organic matter in the coastal and/or estuarine environment (e.g., Mudge and Norris, 1997; Canuel and Zimmerman, 1999; Countway et al., 2007). Some studies measured distribution of sterols in offshore or open ocean waters, but the reported sterols were mostly of marine or planktonic origins, with a minor contribution from terrestrial sources, such as terrestrial vascular plants (e.g., Méheust et al., 2013; Tolosa et al., 2013). Additionally, these sterols do not provide unambiguous evidence for terrigenous organic matter, as some sterols of terrestrial plants may also be synthesized by marine phytoplankton (Volkman, 1986). Although some studies detected clear terrestrial signatures of sterol composition in offshore seawater, they were usually measured in enclosed seas, such as the Mediterranean and the Black seas (e.g., Maldonado et al., 1999; Tolosa et al., 2003).

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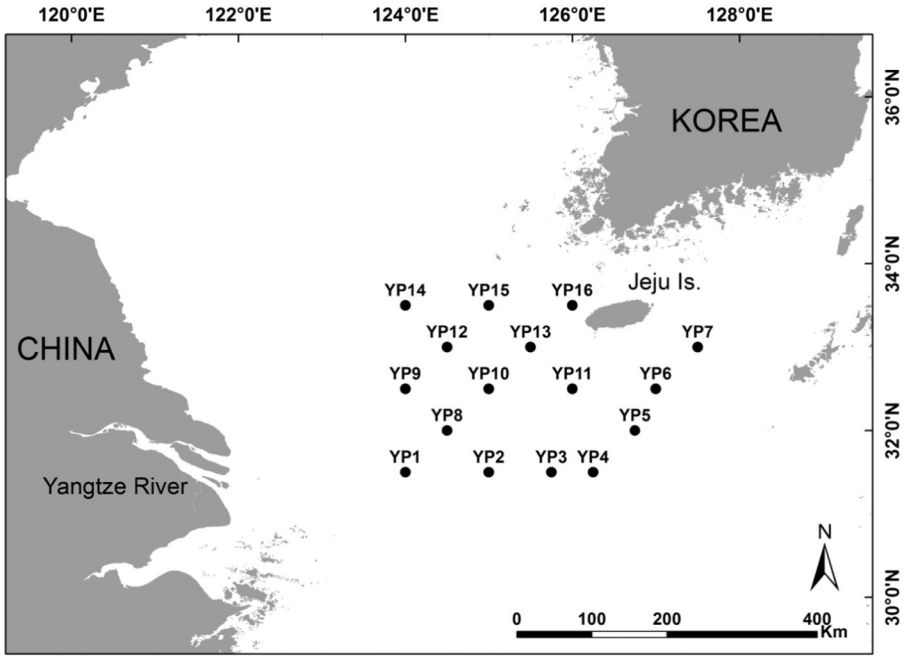

Fig. 1. Map showing the sampling locations in the East China Sea.

The offshore East China Sea can be considered as pristine because it is remote from major terrigenous sources. Although the East China Sea receives large amounts of terrestrial materials from large rivers, such as the Yangtze (also known as Changjiang), Huanghe, and Huaihe Rivers in China and the Han River in Korea, most terrestrial materials are deposited at the mouth of these rivers (Tian et al., 1992). However, the isolated low salinity water mass from the Changjiang River (Changjiang River Diluted Water; CRDW) is observed frequently in the East China Sea, and may be an effective carrier of terrigenous materials to the offshore East China Sea. Considering these factors, the geographical distribution of terrigenous sterols in surface water can provide information on transport of terrigenous organic matter to the East China Sea.

Previous studies on sterols in sediment and suspended particulate matter in the East China Sea have mostly focused on the Yangtze Estuary and adjacent nearshore areas of the East China Sea (e.g., Tian et al., 1992; Sicre et al., 1994; Jeng and Huh, 2004; Zhu et al., 2012; Yan et al., 2015). This study reports, for the first time, the presence of significant amounts of terrigenous sterols in the offshore East China Sea (~250 km from the Yangtze River mouth) that were likely transported by the Changjiang River Diluted Water mass. This study describes the horizontal distribution of sterols and their compositions in the East China Sea between the Yangtze River mouth and Jeju Island (Fig. 1).

Seawater was collected during sampling cruises in July 2007. Sixteen surface water samples (YP1–YP16) were collected using a high-volume water sampling system consisting of a stainless steel drum, a filtering train, a Teflon hose, and a Teflon-lined submerged water pump. Immediately after collection, the seawater (~100 L) was placed in the precleaned stainless steel drum. It was then filtered through glass fiber filters (GF/F 150 mm Ø, Whatman) at less than 1 L min^{-1} on a research vessel to obtain suspended particulate matter (SPM). Sterols in the dissolved fraction were captured using a XAD-resin adsorbent column placed after the filter in a flow-through system. Immediately after the filtration, the filters and XAD resins were stored at −20 °C until analysis. Regular seawater parameters, including salinity and water temperature, were measured with a conductivity–temperature–depth sensor (CTD; SBE 911 plus, SeaBird Inc., Bellevue, USA).

Sterols in the particulate (SPM) and dissolved (DP) phases were analyzed according to the methods described in Li et al. (2007) and Lee et al. (2011). SPM in the filters was dehydrated with activated anhydrous sodium sulfate and Soxhlet extracted using dichloromethane (DCM) for 16 h. A surrogate internal standard (5α-androstan-3β-ol) was added before extraction to validate extraction efficiency. XAD-2 resins were extracted twice with sequential addition of 200 mL of methanol, DCM, and hexane, and the solvents were pooled for further processing. The extracts were concentrated to less than 0.2 mL using a rotary evaporator and a micro concentration device with a gentle flow of dry nitrogen and brought to a final volume of 1 mL in acetone. After addition of approximately 100 μL of BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide) for silyl derivatization, the extracts were concentrated to below 0.5 mL and purified using activated florisil (1 g). The target derivatives were eluted with 7 mL of hexane. The eluents were concentrated to approximately 0.3 mL with a gentle flow of nitrogen gas. After an addition of 200 ng of GC internal standard (pyrene-d_{10}) to the derivatized samples, the final volume was brought to 1 mL.

Sterols were analyzed using a gas chromatograph (Shimadzu GC-2010) coupled with a mass spectrometer (Shimadzu MS QP-2010). Helium was used as a carrier gas, with a column flow rate of 1 mL min^{-1}. Sterols were separated using a 30 m × 0.32 mm (i.d.),

Table 1
Solid–water distribution coefficients, log (C_s/C_w), of sterol compounds in the study area.

Sterols[a]	Mean log (C_s/C_w)[b]	n[c]	SD[d]
Coprostanone	5.74	2	0.81
Cholesterol	5.47	11	0.22
Cholestanol	5.52	11	0.26
Desmosterol	5.47	11	0.17
Brassicasterol	5.36	11	0.30
Cholestenone	6.21	3	1.23
Fucosterol	5.13	11	0.45
Stigmasterol	5.36	11	0.32
β-Sitosterol	5.30	11	0.28
Stigmastanol	5.78	11	0.38

[a] See Table S1 for acronyms and chemical names.
[b] C_s and C_w are the concentrations in the particulate (pg/kg-dry wt) and dissolved (pg/L) phases, respectively.
[c] n = sample number.
[d] SD = standard deviation.