

# Anthropogenic Activities Have Contributed Moderately to Increased Inputs of Organic Materials in Marginal Seas off China

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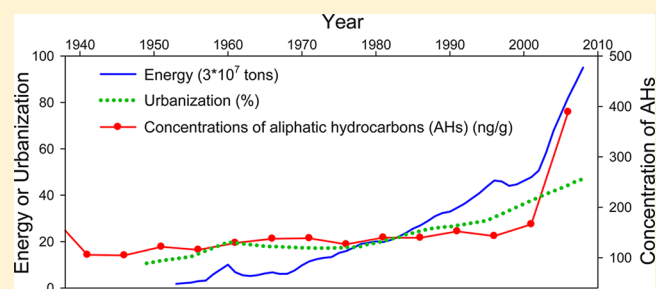
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## Supporting Information

**ABSTRACT:** Sediment has been recognized as a gigantic sink of organic materials and therefore can record temporal input trends. To examine the impact of anthropogenic activities on the marginal seas off China, sediment cores were collected from the Yellow Sea, the inner shelf of the East China Sea (ECS), and the South China Sea (SCS) to investigate the sources and spatial and temporal variations of organic materials, i.e., total organic carbon (TOC) and aliphatic hydrocarbons. The concentration ranges of TOC were 0.5–1.29, 0.63–0.83, and 0.33–0.85%, while those of  $\Sigma n\text{-C}_{14-35}$  (sum of *n*-alkanes with carbon numbers of 14–35) were 0.08–1.5, 0.13–1.97, and 0.35–0.96  $\mu\text{g/g}$  dry weight in sediment cores from the Yellow Sea, ECS inner shelf, and the SCS, respectively. Terrestrial higher plants were an important source of aliphatic hydrocarbons in marine sediments off China. The spatial distribution of  $\Sigma n\text{-C}_{14-35}$  concentrations and source diagnostic ratios suggested a greater load of terrestrial organic materials in the Yellow Sea than in the ECS and SCS. Temporally, TOC and  $\Sigma n\text{-C}_{14-35}$  concentrations increased with time and peaked at either the surface or immediate subsurface layers. This increase was probably reflective of elevated inputs of organic materials to marginal seas off China in recent years, and attributed partly to the impacts of intensified anthropogenic activities in mainland China. Source diagnostics also suggested that aliphatic hydrocarbons were mainly derived from biogenic sources, with a minority in surface sediment layers from petroleum sources, consistent with the above-mentioned postulation.



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## INTRODUCTION

Riverine runoff and atmospheric deposition play important roles in the geochemical cycling of organic matter and accumulation of terrestrial organic materials in coastal marine systems.<sup>1,2</sup> Therefore, coastal marine sediments are important sinks for these materials.<sup>3,4</sup> Environmental changes caused by anthropogenic activities are often recorded in residues of chemicals buried with sediment, making study of such valuable in assessing such changes.<sup>5–7</sup> For example, the evolution of anthropogenic activities in mainland China was reconstructed through characterization of polycyclic aromatic hydrocarbons (PAHs) in sediment cores from the Yellow Sea and the South China Sea (SCS).<sup>7</sup> This information should be useful for the management community to implement appropriate control measures for protecting coastal ecosystems through thorough understanding of the pollution histories.

Aliphatic hydrocarbons (AHs) have three main sources: biogenic (e.g., terrestrial higher plants and phytoplankton),

diagenesis from biogenic materials, and petroleum residues. Each is characterized by specific profiles. Aliphatic hydrocarbons of both terrestrial higher plants and emergent plants predominately have *n*-C<sub>29</sub> (*n*-C<sub>*a*</sub>, straight-chain alkanes with “*a*” as the carbon number) and/or *n*-C<sub>31</sub> isomers.<sup>8</sup> Those from floating plants peak at *n*-C<sub>23</sub> and/or *n*-C<sub>25</sub>, while those from planktonic algae mainly consist of low molecular weight *n*-C<sub>15</sub> to *n*-C<sub>20</sub>, especially *n*-C<sub>17</sub>.<sup>8</sup> As such, AHs have been used as molecular markers to distinguish between biogenic and anthropogenic sources of organic materials;<sup>9,10</sup> to investigate the relative contributions of autochthonous and allochthonous hydrocarbons;<sup>11</sup> to assess the sedimentary environment in aquatic systems;<sup>12</sup> and to reveal historical changes of lake

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productivities.<sup>13</sup> Geolipids (e.g., *n*-alkanes) recorded in sediments of Lakes Ontario and Erie track historical changes in the watershed, such as increases in lake productivity from increased input of soil nutrients.<sup>13</sup> Therefore, AHs could be used as an indicator to track the influence of terrestrially anthropogenic activities. Various studies separately investigated historical inputs of organic materials by reconstructing sedimentary records of AHs in the Bohai Sea,<sup>14</sup> Yellow Sea,<sup>15</sup> East China Sea (ECS),<sup>16</sup> and South China Sea (SCS).<sup>12,17</sup> These studies were carried out during different historical periods with varying means of data interpretation (Supporting Information (SI) Table S1), making it difficult to have a consistent and unified view of factors controlling inputs of organic materials to China's marginal seas over space and time.

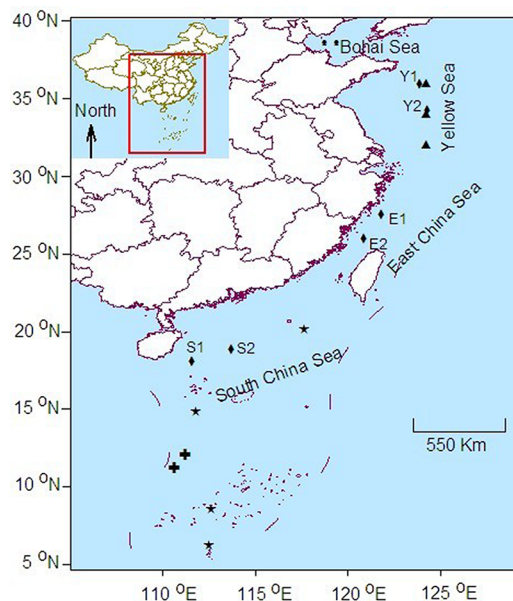
Our previous studies demonstrated the importance of coastal marine sediments off China as the sink of PAHs<sup>18</sup> and AHs.<sup>4</sup> The marine systems along the eastern coast of China, the Yellow Sea, ECS, and SCS are much closer to mainland China than to any other regions. Due to such geographical locality, sediments in these marine systems presumably record terrestrial materials mainly from northern, central, and southern China, respectively. Regional differences in environmental factors and anthropogenic activities could possibly lead to divergences in sedimentary records of organic chemicals. This has indeed been shown for PAHs, which have a decreasing trend alongshore the Chinese coast.<sup>18</sup> However, it is not yet clear what the extent of terrestrial inputs of organic matter in general are to the sediments of China's marginal seas, compared to atmospheric deposition,<sup>2</sup> as well as other processes, e.g., sediment resuspension, transport, and mixing. To our knowledge, no study has been conducted to investigate not only individual temporal variations in AHs and overall organic matter (expressed as total organic carbon, TOC), but also spatial trends among the above-mentioned coastal marine systems off China. The present study was intended to address this knowledge gap, by analyzing the sources and spatial-temporal variability of AHs and TOC among the marginal seas off China. This analysis allowed us to reconstruct the historical inputs of terrestrial organic materials to this region and to investigate the possible influence of evolving anthropogenic activities on the sediment quality.

## EXPERIMENTAL SECTION

**Sample Collection and Preparation.** A mud area (deposition zone) forms in the central area of the Yellow Sea due to upwelling.<sup>19</sup> Sediments discharged from the Yangtze River mainly deposit in the Yangtze River Estuary and the coastal mud off Zhejiang and Fujian Provinces, and are sinks for organic chemicals associated with fine-grained sediments.<sup>20</sup> Due to monsoon winds, circulation in the SCS is cyclonic in winter and anticyclonic in summer.<sup>21</sup>

Two sediment cores from the Yellow Sea mud area (Y1 and Y2), the ECS inner shelf (E1 and E2), and the SCS (S1 and S2) were collected, respectively, with a box corer over August to September 2007 during the South China Sea Open Cruise of *R/V SHIYAN III* and the Open Research Cruise Offshore China of *R/V KEXUE I* (Figure 1). Sediment cores were transported to the laboratory and frozen at  $-20\text{ }^{\circ}\text{C}$  until analysis.

Detailed sample preparation procedures are described elsewhere.<sup>7,18</sup> Briefly, sediment cores were manually sliced with a stainless steel saw, which was cleaned after each slice. The sliced sections were packed into prebaked aluminum foil



**Figure 1.** Map showing the locality for sampling sites in the marginal seas off China. The “◆” symbols (Y1, Y2, E1, E2, S1, and S2) represent sampling sites in the present study, while other symbols refer to those in previous studies: circles in the Bohai Sea,<sup>14</sup> triangles in the Yellow Sea,<sup>15</sup> crosses in the Nansha Sea,<sup>12</sup> and stars in the South China Sea.<sup>17</sup> The water depths of sampling site Y1, Y2, E1, E2, S1, and S2 were 72.3, 80.4, 49.3, 59.2, 131, and 1302 m, respectively. YRE is the acronym for the Yangtze River Estuary.

and freeze-dried, after which samples were ground and large particulates removed by a 0.18 mm mesh stainless steel sieve. Homogenized samples were weighed onto precleaned filter papers. After addition of the surrogate standard *n*-C<sub>24</sub>-d<sub>50</sub> (*n*-C<sub>a</sub>-d<sub>b</sub>; the subscript “*b*” refers to the number of deuterium atoms) and copper sheets to remove elemental sulfur, each sample was Soxhlet-extracted with 200 mL of a hexane/acetone mixture (1:1 by volume) for 48 h. The extract was reduced in volume with a Zymark TurboVap 500 (Hopkinton, MA) and fractionated on a glass column containing 3% water deactivated silica/alumina. This column was eluted first with 5 mL of hexane (discarded) and then another 20 mL of hexane to collect *n*-alkanes.<sup>4</sup> This *n*-alkane fraction was concentrated under gentle nitrogen flow to 0.5 mL and spiked with the internal standard *n*-C<sub>30</sub>-d<sub>62</sub> prior to instrumental analysis.

**Total Organic Carbon Measurement.** An aliquot of each sliced sediment sample was acidified with 10% HCl (to remove inorganic carbon), washed with distilled water, dried to constant weight, and homogenized. Contents of TOC were determined using an elemental analyzer (Vario EL III Elementar, Germany).<sup>22</sup> Triplicate acetanilide standards were analyzed with each set of 20 field samples. Field sample analysis was done only if the relative deviations of measured C values in the acetanilide standards from the certified value (71.09%) were less than 5%.

**Instrumental Analysis.** Detailed information about instrumental analysis conditions are described elsewhere.<sup>4</sup> Briefly, *n*-alkanes were quantified with a Shimadzu Model 2010 gas chromatograph–mass spectrometer (Shimadzu, Japan) on a 30 m × 0.25 mm-i.d. × 0.25- $\mu\text{m}$  film thickness DB-5 column (J&W Scientific, Folsom, CA). Quantification of each *n*-alkane compound was based on characteristic ions at *m/z* 85 and 71.

**Table 1. Ranges (Means in Parentheses) of Diagnostic Indices for Aliphatic Hydrocarbons and Bulk Materials in Sediment Cores Collected from the Marginal Seas off China**

parameter <sup>a</sup>	Y1 (37) <sup>b</sup>	Y2 (39)	E1 (29)	E2 (35)	S1 (36)	S2 (21)
CPI <sub>15-20</sub>	1.2–3.9	0.9–1.9	1.1–2.0	1.4–2.1	0.9–1.2	0.8–1.6
ACL	29.3–29.8	29.3–30	28.4–29.9	28.4–29.6	29.1–30	29.3–29.9
<i>n</i> -C <sub>17</sub> /Pr	0.57–2.7	0.38–1.09	0.59–1.39	0.38–0.47	0.75–1.05	0.78–1.02
<i>n</i> -C <sub>18</sub> /Ph	0.22–3.57	0.26–1.15	0.72–1.96	0.78–2.22	0.60–1.20	0.73–2.70
%waxCn	31.0–86.6 (55.4)	18.6–54.7 (46.0)	21.0–44.6 (35.7)	18.9–35.3 (29.6)	22.9–33.3 (26.7)	17.4–28.1 (21.4)
OEP	6.0–32.7 (14.7)	5.1–11.2 (9.3)	3.6–9.6 (7.5)	3.8–7.9 (7.0)	5.9–7.5 (6.6)	5.6–6.8 (6.2)
Pr/Ph	0.18–8.64 (2.08)	0.84–1.56 (1.32)	1.21–6.63 (3.89)	2.6–7.52 (5.42)	0.97–1.48 (1.18)	0.73–3.12 (1.53)
<i>n</i> -C <sub>29</sub> / <i>n</i> -C <sub>17</sub>	3.4–31.0 (9.5)	4.3–16.3 (11.4)	2.8–8.2 (4.4)	2.5–4.6 (3.3)	1.1–3.1 (2.0)	2.4–6.5 (3.4)
TAR	4.9–20 (10)	5.7–17 (13)	3.7–8.4 (5.0)	2.0–4.1 (3.0)	2.5–6.1 (3.4)	1.5–3.6 (2.3)
TOC (%)	0.8–1.29 (1.02)	0.5–0.73 (0.63)	0.63–0.72 (0.68)	0.65–0.83 (0.72)	0.33–0.67 (0.49)	0.61–0.85 (0.74)
CPI <sub>1</sub>	2.12–6.04 (3.9)	1.42–3.84 (3.1)	1.62–3.06 (2.5)	1.64–2.51 (2.2)	1.60–1.91 (1.7)	1.67–2.23 (1.9)
CPI <sub>24-34</sub>	2.3–8.6 (5.7) <sup>c</sup>	1.6–4.4 (3.8)	1.8–3.7 (2.9)	1.6–3.0 (2.6)	2.1–2.8 (2.5)	2.1–2.6 (2.3)
UCM (μg/g)	ND–9.6	ND–8.6	4.3–16.8	3.1–11.1	2.7–11.3	1.8–15.6

<sup>a</sup>Abbreviations: ND = not detected, CPI = carbon preference index, ACL = average chain length, Pr = pristane, Ph = phytane, %waxCn = plant wax *n*-alkanes, OEP = odd–even carbon number preference, TAR = terrigenous to aquatic ratio, TOC = total organic carbon, and UCM = unresolved complex mixture. <sup>b</sup>Numbers in parentheses after site names indicate the number of sediment slices in each core. Total number of slices is 197. <sup>c</sup>An abnormally high value was not included here.

**Quality Assurance and Quality Control (QA/AC).** One procedural blank, one spiked blank, and one matrix spiked sample were processed along with each batch of 15 field samples. The recoveries (mean ± standard deviation) of *n*-alkane surrogate standard *n*-C<sub>24</sub>-d<sub>50</sub> were 85 ± 15% and 87 ± 19% for field samples and QA/QC samples, respectively. Blank levels of *n*-alkane compounds varied among different sample processing periods, ranging from below to approximately 3 times higher than the lowest calibration level. The blank-corrected concentration level for each congener in field samples was 5 to 200 times above its lowest calibration level, depending on *n*-alkane compounds and sediment core slices. The lowest calibration level (50 ng/mL) was corrected with the final extract volume (0.5 mL) and divided by the average sample weight (23 g) to derive the reporting limit, which was 1.1 ng/g in the present study.

**Sediment Dating.** Sedimentation rates were obtained through the calculation of excess unsupported <sup>210</sup>Pb activity measured in 2011. The α-radioactivity of <sup>210</sup>Po, a decay product of <sup>210</sup>Pb, was extracted, purified, and analyzed with a multichannel α-spectrometer (BH12240-Spectrometry) interfaced with gold–silicon surface barrier detectors to obtain <sup>210</sup>Pb activity indirectly.<sup>6</sup> A constant initial <sup>210</sup>Pb concentration model<sup>23</sup> was applied to determine the sedimentation rates, which were 0.3 cm/y for core Y2,<sup>7</sup> 0.76 cm/y for core E2, and 0.2 cm/y for core S1.<sup>7</sup> The other three cores were not dated.

**Data Analysis.** The quantification of odd-carbon compounds, for which corresponding standard materials were unavailable, followed a previously described method.<sup>4</sup> Concentrations of *n*-alkanes were blank corrected but not surrogate recovery corrected, and are presented on a dry sample weight basis. The quantitation of an unresolved complex mixture (UCM) followed previously described methods.<sup>4,11</sup> The calculation of carbon preference index (CPI) was performed on a molar basis, while those for other source diagnostic indexes on a weight basis. The indices employed in the present study are CPI,<sup>24</sup> terrigenous to aquatic ratio (TAR),<sup>13</sup> odd–even carbon number preference (OEP),<sup>25</sup> plant wax *n*-alkanes (%waxCn),<sup>26</sup> and average chain length (ACL):<sup>27</sup>

$$CPI_{15-20} = \frac{n-C_{15} + n-C_{17} + n-C_{19}}{n-C_{16} + n-C_{18} + n-C_{20}} \quad (1)$$

$$CPI_1 = \frac{\sum_{o=15}^{34} n-C_o}{\sum_{e=15}^{34} n-C_e} \quad (2)$$

where subscripts “o” and “e” refer to odd and even numbers.

$$CPI_{24-34} = \frac{1}{2} \left( \frac{\sum_{o=25}^{33} n-C_o}{\sum_{e=24}^{32} n-C_e} + \frac{\sum_{o=25}^{33} n-C_o}{\sum_{e=26}^{34} n-C_e} \right) \quad (3)$$

$$TAR = \frac{n-C_{27} + n-C_{29} + n-C_{31}}{n-C_{15} + n-C_{17} + n-C_{19}} \quad (4)$$

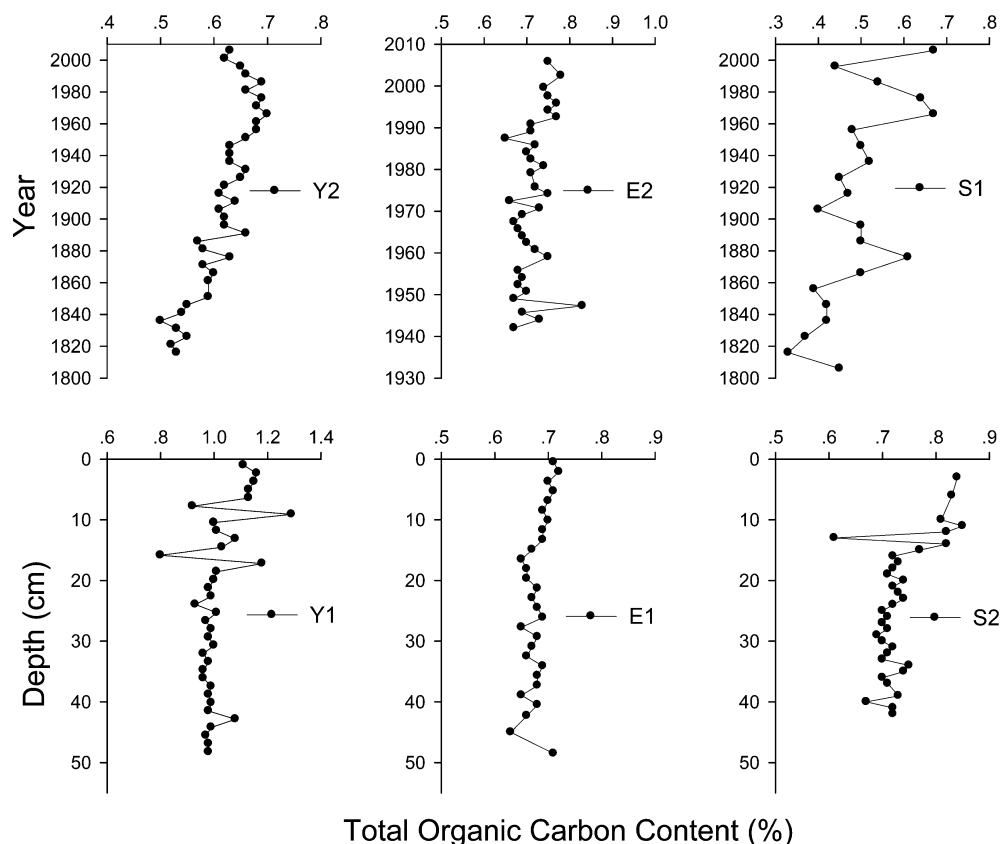
$$OEP = \frac{n-C_{25} + 6 \times n-C_{27} + n-C_{29}}{4(n-C_{26} + n-C_{28})} \quad (5)$$

$$\%waxCn = \frac{\sum \left[ n-C_a - \frac{1}{2}(n-C_{a-1} + n-C_{a+1}) \right]}{\sum n-C_{15-34}} \quad (6)$$

$$ACL = (25 \times n-C_{25} + 27 \times n-C_{27} + 29 \times n-C_{29} + 31 \times n-C_{31} + 33 \times n-C_{33}) \times (n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31} + n-C_{33})^{-1} \quad (7)$$

## RESULTS AND DISCUSSION

**Total Organic Carbon.** The average TOC content in the sediment cores of the marginal seas off China, from north to south, were 1.02%, 0.63%, 0.68%, 0.72%, 0.74%, and 0.49%, respectively (Table 1). These TOC contents were much greater than those from the subtropical Atlantic Ocean (0.2%–0.32%).<sup>28</sup> They were also slightly higher than or comparable to those from the Nansha Sea (0.7% and 0.53%),<sup>12</sup> and those in seven short sediment cores from the southern Okinawa Trough (0.55%, 0.68%, 0.38%, 0.61%, 0.61%, 0.72%, and 0.63%).<sup>16</sup> However, they were much lower than those from inland lakes, e.g., Lakes Ontario and Erie (1.5%–5%)<sup>13</sup> which have both



**Figure 2.** Vertical profiles of total organic carbon content in sediment cores collected from the marginal seas off China. Sedimentation rates in cores Y2, E2, and S1 but not in cores Y1, E1, and S2 were determined. Therefore, the top plots are marked with dates and the bottom plots marked with sediment depths.

much higher aquatic productivity than the ocean sites mentioned and more inputs of soil from runoff.<sup>13</sup>

Although TOC content did not vary much with sediment core depth, a general decreasing trend with depth (Figure 2) was observed. Similar trends in TOC content were found in sediment cores from Lakes Ontario and Erie<sup>13,29</sup> and in marine sediment cores from the Antarctic Ocean,<sup>30</sup> Nansha Sea,<sup>12</sup> and the San Pedro Shelf of California, U.S.<sup>31</sup> These trends may have resulted from biodegradation of sediment organic matter over time.<sup>12</sup> Very large changes in TOC content over depth, from 1.5–2% in deep-water sediments to 4–5% in surficial sediments,<sup>13</sup> observed in Lake Ontario sediment cores, were caused by the increase in lake productivity from the emergence of agriculture in the watershed beginning in the early 1800s.<sup>13</sup> The low and narrow ranges of TOC content in the present study (Figure 2) suggest that no such marked changes in the ecosystems of the neighboring areas had occurred, or that such changes did not reach as far offshore as the locations of our sediment cores.

#### Sources Diagnostics of Aliphatic Hydrocarbons.

Aliphatic hydrocarbons in sediments are originated from diverse sources, divided into two major categories: anthropogenic and natural sources.<sup>1</sup> Sources of anthropogenic AHs include petroleum use and fossil fuel,<sup>32</sup> while natural sources include terrestrial higher plants, aquatic macrophytes, plankton, and bacteria. The presence of UCM and absence of odd–even preference with CPI values close to unity<sup>33</sup> suggest petroleum-derived hydrocarbons and/or aged and degraded hydrocarbon mixtures. Hydrocarbons derived from terrestrial higher plants

lack UCM and are dominated by high molecular weight odd carbon fractions (e.g.,  $n$ -C<sub>27</sub>,  $n$ -C<sub>29</sub>, and  $n$ -C<sub>31</sub>).<sup>34</sup>

The CPI<sub>24–34</sub> values (1.6–8.6 in all cores; Table 1) were greater than one but lower than those of typical higher plants (5–10),<sup>31</sup> suggesting the accumulation of hydrocarbons derived from terrestrial higher plants with minor amounts from other sources, possibly from petroleum residues. The presence of UCM was observed in the surficial layer of Yellow Sea sediment cores and in almost every section of the cores from the ECS inner shelf and SCS. However, the occurrence of UCM (absence to 16.8  $\mu$ g/g; Table 1) may not necessarily suggest petroleum contamination, as 10  $\mu$ g/g of UCM was commonly found in uncontaminated sediments.<sup>34</sup>

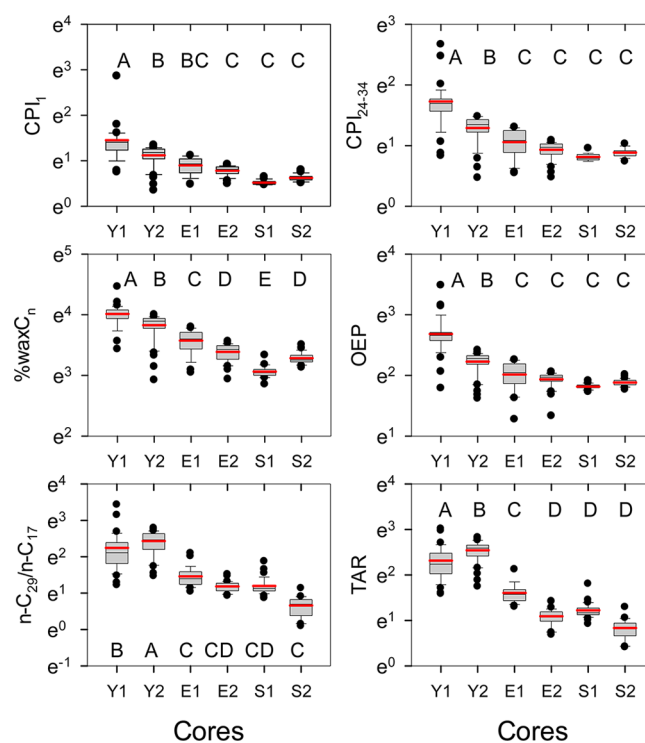
Besides UCM and CPI, other indices such as  $n$ -C<sub>17</sub>/Pr,  $n$ -C<sub>18</sub>/Ph, and pristane/phytane (Pr/Ph) can also be used to identify hydrocarbons of petroleum origin. Low  $n$ -C<sub>17</sub>/Pr and  $n$ -C<sub>18</sub>/Ph values (<1) are characteristic of degraded petroleum because the isoprenoids, pristane and phytane, are more recalcitrant to biodegradation compared to  $n$ -alkanes.<sup>33</sup> The  $n$ -C<sub>17</sub>/Pr values were lower than or close to unity in all sediment cores with the exception of YS1 (maximum 2.7). In contrast, the  $n$ -C<sub>18</sub>/Ph values were generally greater than one. This inconsistency may have resulted from the uncertainties in using  $n$ -C<sub>17</sub>/Pr and  $n$ -C<sub>18</sub>/Ph ratios to indicate petroleum sources because large amounts of pristane could be produced by zooplankton.<sup>35</sup> Pr/Ph values close to unity suggest petroleum sources, while the dominance of a single isoprenoid (pristane) indicates a biogenic origin.<sup>33</sup> The Pr/Ph values in the present study were generally greater than unity (0.18–8.64 in all cores; Table 1), possibly suggesting biogenic hydrocarbons were

predominant. Therefore, no clear evidence for petroleum contamination across all of the cores was observed, based on these three indices. However, some more specific trends can be ascertained from these ratios. When compared with other studies, the Pr/Ph values in the present study (Table 1) were greater than those from the Nansha Sea (0.44–0.87, with an average of 0.62),<sup>12</sup> and lower than those from the Antarctic Ocean ( $\geq 3$ ).<sup>36</sup> Low Pr/Ph values in sediment cores from the Nansha Sea<sup>12</sup> was mainly caused by microbial activity, while high Pr/Ph values in Antarctic marine sediments<sup>36</sup> was ascribed to inputs from marine phytoplankton. Spatially, the highest Pr/Ph values (1.21–6.63 and 2.6–7.52 with means of 3.89 and 5.42 in E1 and E2, respectively) and lowest  $n\text{-C}_{17}/\text{Pr}$  values (0.59–1.39 and 0.38–0.47 in E1 and E2, respectively) were observed in cores from the ECS inner shelf (Table 1), most probably suggesting biogenic sources (i.e., phytoplankton) rather than petroleum contamination there.

Average chain length was suggested as an additional source indicator for petrogenic hydrocarbons.<sup>27</sup> Generally, the ACL values (Table 1) in cores collected from the ECS inner shelf exhibited relatively wider ranges (28.4–29.9) than those in the Yellow Sea (29.3–30) and SCS (29.1–30). The ACL values in cores from the ECS inner shelf were comparable to those in marine sediments, with petroleum input, off southwestern Taiwan (28.4–29.3),<sup>27</sup> while those in cores from the Yellow Sea and SCS were comparable to those in river sediments (with major biogenic sources) of southwestern Taiwan (29.2–30.5).<sup>27</sup> The wider ranges of ACL values in cores from the ECS inner shelf may be attributed to the addition of various fractions of petroleum to biogenic hydrocarbons.<sup>27</sup> However, taking the above discussion into account, the wider ranges of ACL values were most probably attributed to the mixture of a variety of plant species.

Further evidence for sedimentary AHs being biogenically dominant in our study area is suggested by other indices. The CPI values of  $n$ -alkanes from anthropogenic sources such as vehicular emissions are close to unity,<sup>37</sup> while those from terrestrial higher plant waxes are greater than one.<sup>31</sup> All CPI<sub>1</sub> values were greater than one (Table 1), consistent with previous observations of biogenic sources as the major contributors of  $n$ -alkanes to the present study area.<sup>4</sup> Furthermore, AHs in the present study were characterized with an apparent odd-to-even carbon number preference, i.e., OEP in the range of 3.8–32.7 in all cores (Table 1), and a high relative abundance of  $n\text{-C}_{31}$ , evidence for the input of terrestrial higher plant waxes.

The fraction of  $n$ -alkanes from plant wax could be estimated by %waxCn (Table 1).<sup>26</sup> Spatially, the values of CPI<sub>1</sub>, CPI<sub>24–34</sub>, OEP, and %waxCn (Table 1) in Yellow Sea sediment cores (1.42–6.04, 1.6–8.6, 5.1–32.7, and 18.6–86.6 for CPI<sub>1</sub>, CPI<sub>24–34</sub>, OEP, and %waxCn, respectively) were generally statistically greater (ANOVA,  $p < 0.01$ , Figure 3) than those in the ECS inner shelf (1.62–3.06, 1.6–3.7, 3.6–9.6, and 18.9–44.6) and the SCS (1.60–2.23, 2.1–2.8, 5.6–7.5, and 17.4–33.3). This spatial pattern might suggest higher fraction of terrestrial higher plant sources of AHs in Yellow Sea sediments.<sup>4</sup> The CPI values, and means in parentheses, of  $n$ -alkanes in sediments from near-shore coastal areas of China, from north to south, were 0.9–2.0 (1.3) in Jiaozhou Bay, Qingdao,<sup>10</sup> 1.1–4.8 (3.4) in the Yangtze River Estuary,<sup>38</sup> and 1.45–4.98 in the Pearl River Estuary and northern SCS.<sup>39</sup> The spatial pattern of CPI values of  $n$ -alkanes in sediments from the above-mentioned near-shore coastal areas of China was not as

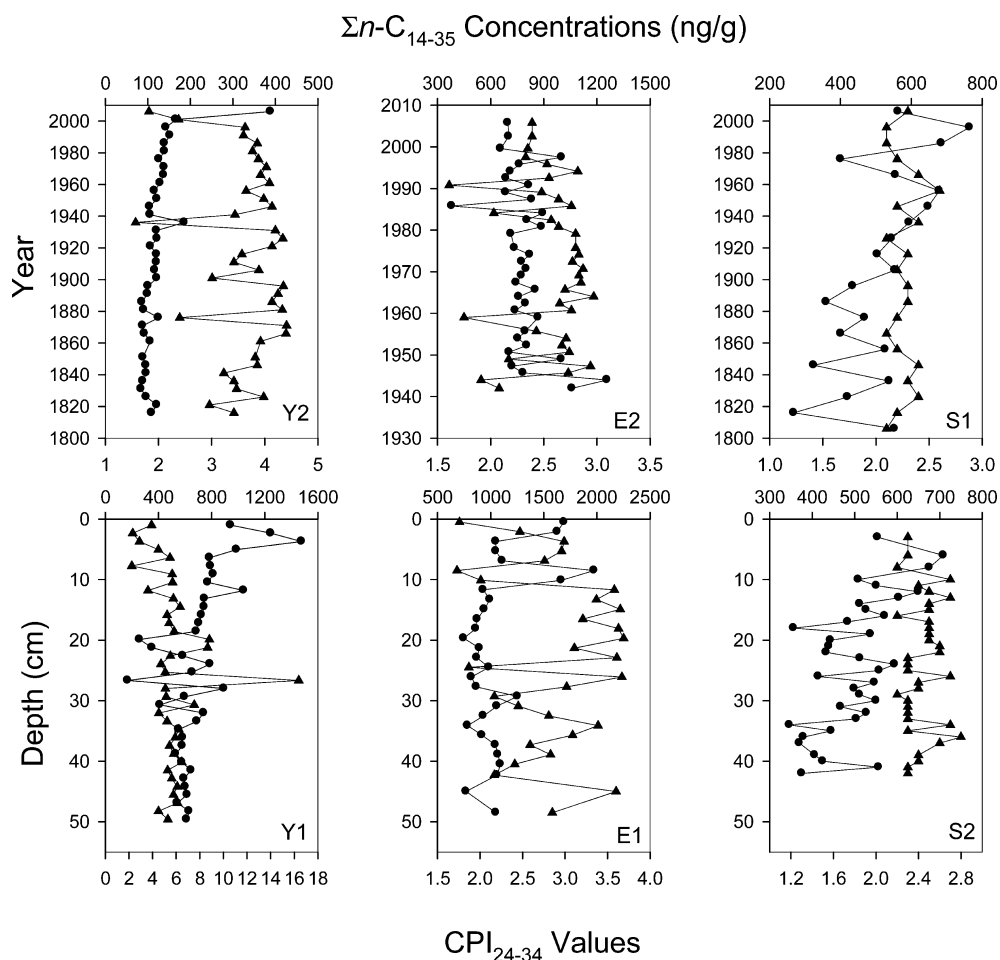


**Figure 3.** Values of CPI<sub>1</sub>, CPI<sub>24–34</sub>, OEP, %waxCn, TAR, and  $n\text{-C}_{29}/n\text{-C}_{17}$  in sediment cores collected from the Yellow Sea (Y1 and Y2), inner shelf of the East China Sea (E1 and E2), and the South China Sea (S1 and S2). Ratios with different letters are significantly different ( $p < 0.01$ ). The definitions of acronyms CPI<sub>1</sub>, CPI<sub>24–34</sub>, OEP, %waxCn, TAR, and  $n\text{-C}_{29}/n\text{-C}_{17}$  can be found in the main text. Sampling sites were depicted in Figure 1. Box plots represent median (line through middle of box), 25th and 75th percentiles (bottom and top of box, respectively), 10th and 90th percentiles (ends of whiskers), and outliers (outlier points). Red lines inside the boxes are mean values.

clear as that in sediment from the marginal seas investigated in the present study. Near-shore sediments may have received large amounts of hydrocarbons from various sources via different input mechanisms, whereas terrestrial  $n$ -alkanes in coastal marine sediments off China were believed to stem primarily from atmospheric deposition.<sup>4</sup>

Besides terrestrial higher plant waxes, plankton and bacteria also contributed to biogenic  $n$ -alkanes. Aliphatic hydrocarbons of planktonic origin are characterized by an odd–even carbon number preference with CPI values greater than one,<sup>40</sup> while those from bacterial sources are dominated by even carbon  $n$ -alkanes.<sup>41</sup> The CPI<sub>15–20</sub> values in cores from Yellow Sea and the inner shelf of ECS were generally greater than one, while those in cores from the SCS were close to unity (Table 1). These observations suggested that bacterial sources somewhat contributed to the organic matter in sediments of the SCS.

In summary, the weight of evidence by the various AH indices suggests that these compounds in marine systems off China arose mainly from biogenic rather than petrogenic sources. Accordingly, there is little evidence that anthropogenic activities in China impact these waters as much compared to the significant impact evidenced closer ashore,<sup>10,42</sup> at least for AHs. Black carbon may provide additional information on sources of anthropogenically derived organic materials.<sup>20</sup> However, analysis of black carbon was beyond the scope of the present study.



**Figure 4.** Time and depth profiles of  $\Sigma n\text{-C}_{14-35}$  concentrations (black circles using top  $x$ -axis scale) and  $\text{CPI}_{24-34}$  values (black triangles using bottom  $x$ -axis scale) in sediment cores collected from the coastal marine systems off China. Sedimentation rates in cores Y2, E2, and S1 but not in cores Y1, E1, and S2 were determined. Therefore, the top plots use date and the bottom plots use depth.

**Contributions of Various Hydrocarbons.** Due to the predominance of  $n\text{-C}_{29}$  and  $n\text{-C}_{17}$  in terrestrial higher plant waxes and nonsiliceous species of plankton, respectively, the ratio of  $n\text{-C}_{29}/n\text{-C}_{17}$  is taken as an indicator of the relative importance of allochthonous versus autochthonous inputs of organic matter.<sup>11</sup> Another ratio, TAR<sup>29</sup> is also employed to assess the relative contributions of terrestrial over aquatic inputs of hydrocarbons.<sup>11</sup> Higher values of these two ratios suggested increased contribution from terrestrial inputs. Differences among sites of TAR and  $n\text{-C}_{29}/n\text{-C}_{17}$  values were observed, with statistically greater values (see site-by-site ANOVA results in Figure 3) found in cores from the Yellow Sea than those from the ECS and SCS. This observation may suggest greater contributions from terrestrially derived hydrocarbons in the Yellow Sea than in the other seas, in agreement with the results gained from the surficial sediments.<sup>4</sup> Regional differences were also observed for sedimentary PAHs (both in concentrations and compositions) at the same sampling areas.<sup>18</sup> This spatial distribution may have resulted from many factors, such as depositional environments, regional sources (intensity and profile), and input mechanisms, among others.<sup>18</sup> Temporally, TAR and  $n\text{-C}_{29}/n\text{-C}_{17}$  values within each sediment core had no clear trends with depth (SI Figure S1). Presumably, TAR and  $n\text{-C}_{29}/n\text{-C}_{17}$  values decreased with depth since low molecular weight  $n$ -alkanes are generally more amenable to biodegradation.<sup>5</sup> The absence of clear

temporal trends of TAR and  $n\text{-C}_{29}/n\text{-C}_{17}$  values in the present study may suggest that AHs suffered little selective postdepositional degradation (from the 1800s to 2007 for Y2 and E1 and from the 1940s to 2007 for E2).

**Spatial-Temporal Variation of  $n$ -Alkane Concentrations and Implication for Anthropogenic Impacts.**

Spatially, the highest concentrations of  $\Sigma n\text{-C}_{14-35}$  (Figure 4) were found in cores from the ECS inner shelf. Also,  $\Sigma n\text{-C}_{14-35}$  concentrations (0.08–1.5  $\mu\text{g/g}$ ) in cores from the Yellow Sea were lower than those (0.7–15.8  $\mu\text{g/g}$ ) reported in a previous study conducted there.<sup>15</sup> The  $\Sigma n\text{-C}_{14-35}$  concentrations in cores from the inner shelf of ECS (0.13–1.97  $\mu\text{g/g}$ ) were considerably lower than those of southern Okinawa Trough ( $\Sigma n\text{-C}_{15-35}$ , 1.2–4.19  $\mu\text{g/g}$ ).<sup>16</sup> Terrigenous  $n$ -alkanes in cores from the SCS were previously investigated, with  $n\text{-C}_{29}$  concentrations being 15–250 ng/g,<sup>17</sup> comparable to the  $n\text{-C}_{29}$  concentrations in cores from the SCS (23–66 ng/g) in the present study. It should be pointed out that only preliminary conclusions can be drawn for the spatial distribution of AHs in such a large coastal marine system due to the limited number of sampling sites in the present study.

Generally, the temporal  $\Sigma n\text{-C}_{14-35}$  concentrations in each sediment core from coastal marine systems off China exhibited narrow ranges, extending within 1 order of magnitude (Figure 4). In terms of historical trends of  $n$ -alkane concentrations, only those data in dated sediment cores (Y2, E2, and S1) will be

discussed in detail. Concentrations of PAHs recorded in the same sediment cores were suggested to have closely followed the historical socioeconomic development patterns in China.<sup>7</sup> Although similar increasing trends toward the sediment surface were observed for *n*-alkanes, historical concentration trends did not track the historical anthropogenic events as closely as PAHs did (SI Figure S2),<sup>7</sup> suggesting different sources and/or input pathways of *n*-alkanes and PAHs. This observation allowed us to study the impacts of terrestrial inputs on coastal marine systems from a different angle. The  $\Sigma n\text{-C}_{14-35}$  concentrations increased with time in cores Y2 and S1 but not E2 (Figure 4 and Table 2), i.e., they began to increase around the 1880s and

**Table 2. Pearson Correlations of  $\Sigma n\text{-C}_{14-35}$  (or Unresolved Complex Mixture; UCM) Concentrations with Time and Carbon Preference Index (CPI<sub>24-34</sub>). Historical (1953–2008) Energy Consumption Data were Compiled from a Chinese Governmental Source<sup>44</sup>**

$\Sigma n\text{-C}_{14-35}$ concentrations	year	correlation ( <i>r</i> , <i>p</i> )	
		CPI <sub>24-34</sub>	energy
Y1		−0.748 <sup>a</sup> , 0.000	
Y2	0.568 <sup>a</sup> , 0.000	−0.629 <sup>a</sup> , 0.000	0.839 <sup>a</sup> , 0.001, 11 <sup>b</sup>
Y2 (UCM)			0.967 <sup>a</sup> , 0.002, 6 <sup>c</sup>
E1		−0.774 <sup>a</sup> , 0.000	
E2	−0.402, 0.017	−0.519 <sup>a</sup> , 0.000	
S1	0.621 <sup>a</sup> , 0.003	−0.062, 0.788	
S2		−0.452 <sup>a</sup> , 0.006	

<sup>a</sup>Correlation is significant at the 0.01 level (2-tailed). <sup>b</sup>Concentrations of AHs in upper 11 sediment slices after year 1953 were correlated with historical energy consumption. <sup>c</sup>Concentrations of UCM in upper six sediment slices after 1980 were correlated with historical energy consumption.

continued to rise till the sampling time for Y2 and the 1990s for S1 (Figure 4 and SI Figure S2). The moderate increase of TOC content (Figure 2) and *n*-alkane concentrations (Figure 4 and SI Figure S2) may have been caused by increasing inputs of terrestrial organic materials with time, and/or by selective degradation of organic matter in lower layers of sediment.

Opposite temporal trends of  $\Sigma n\text{-C}_{14-35}$  concentrations and CPI<sub>24-34</sub> values were observed in all cores but S1 (Figure 4 and Table 2). This was similar to that found in New York City's Central Park Lake,<sup>43</sup> which was ascribed to increasing use of petroleum since the mid-1930s around that area. In the present study, the presence of UCM (SI Figures S3 and S4) in the surface layers of Yellow Sea sediment cores, as previously noted, indicated that the increase in *n*-alkane concentrations may be partially due to the input of petroleum hydrocarbons. In core S1, uniform CPI<sub>24-34</sub> values with time were observed instead (Figure 4), similar to the results of a previous study in the SCS.<sup>17</sup> The low and rather stable CPI<sub>24-34</sub> values in core S1 probably suggested steady depositional environment,<sup>17</sup> or that the *n*-alkane concentration increase in the SCS cores was mainly caused by increasing input of terrestrial higher plant waxes rather than petroleum.

Selective degradation in deeper layers of sediment is another possible reason for increasing *n*-alkane concentrations with time. For example, settling particles and surficial sediments together with sediment traps collected in the Río de la Plata Estuary, Argentina had a 20-fold reduction of *n*-alkane concentrations in settling particles compared to surficial

sediments and a 2-fold reduction of *n*-alkane concentrations in sediment core with depth.<sup>5</sup> The absence of any obvious decreasing trend of *n*-C<sub>29</sub>/*n*-C<sub>17</sub> and TAR values (SI Figure S1) with depth contrasts the aforementioned results.<sup>5</sup> This contrast might suggest that AHs accumulated in marginal sea sediments in the present study experienced considerable degradation before depositing to sediments, and/or very little in situ alteration after deposition within the dated time period. Therefore, the increase of *n*-alkane concentrations with time was most probably ascribed to increased inputs rather than depletion of hydrocarbons due to degradation in lower layers. Different from PAHs, the historical profiles of AH concentrations did not closely follow historical socioeconomic development patterns in China (SI Figure S2), which merits further assessment on whether anthropogenic activities have accounted for the increased inputs of terrestrial organic materials.

During the past several decades, China has experienced rapid urbanization, as characterized by the ratio of urban to total populations, which has accelerated in recent years (SI Figure S5).<sup>44</sup> Increased delivery of nutrients to Lake Ontario due to the urbanization of the watershed after 1940 accounted for the historical increase of organic materials in Canada.<sup>29</sup> Urbanization of mainland China probably has contributed to the increasing inputs of organic materials in marginal seas off China as well. Also, atmospheric transport was suggested as an important input mechanism of AHs accumulated in coastal sediments off China.<sup>4</sup> For atmospheric input, transport of AHs in association with particulate matter is an important mode, while emission of particulate matter is presumably related to energy consumption.<sup>45</sup> Excellent correlations (*r* = 0.84 and 0.97) between  $\Sigma n\text{-C}_{14-35}$  (and UCM) concentrations (in Y2) and historical energy consumption were found in the present study (Table 2 and SI Figure S6), suggesting that at least some of the UCM observed came from anthropogenic inputs. Apparently, temporal patterns of anthropogenic activities, such as urbanization and energy consumption,<sup>44</sup> have partially contributed to the increasing inputs of organic materials in marginal seas off China, especially in the Yellow Sea.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Additional figures containing information from data analyses not presented in the main text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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