

Article

# Characteristics of Sedimentary Organic Matter and Phosphorus in Minor Rivers Discharging into Zhejiang Coast, China

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**Abstract:** In this study, the spatial distribution of lignin-derived phenols, bulk elemental composition and different phosphorus (P) species in surface sediments along six rivers discharging into Zhejiang coast, Southeast China, were investigated to improve the understanding of the carbon and P dynamics in these small river systems. The Shuang, Jiao, Ximen, Feiyun and Ao Rivers have total organic carbon (TOC) ranging from 0.29% to 2.77% and  $\Lambda$  (total lignin in mg/100 mg TOC) ranging from 0.24 to 4.24; Qiantang River has the lowest  $\Lambda$  (0.08–0.19) but the highest TOC (1.05%–6.46%). Jiao, Ximen, Feiyun and Ao Rivers have mean the total P (TP) and bioavailable P (BAP) of 34 to 124 mg/kg and 29 to 89 mg P/kg, and mean OC/OP molar ratio of 397–917. Qiantang River has the lowest mean TP and BAP of 13 mg P/kg and 7 mg P/kg, and highest OC/OP of 18,753; whereas Shuang River has the highest mean TP and BAP of 645 mg P/kg and 559 mg P/kg, and lowest mean OC/OP of 90. The lowest  $\Lambda$ , TP and BAP, but highest OC/OP, in the Qiantang River could be due to tidal bore causing rapid cycling of carbon and P. Trends of slight decrease in abundance of OC,  $\Lambda$ , TP and BAP, but increasing ratios of vanillic acid to vanillin [(Ad/Al)v], syringic acid to syringaldehyde [(Ad/Al)s] and OC/OP farther downstream of the rivers indicate a continuous decomposition of organic matter during transport along the rivers.

Keywords: minor rivers; terrestrial organic matter; sedimentary P species; bioavailable P

# 1. Introduction

Rivers are home to various organisms, animals and plant species, providing livelihood to human and serving as a regulator of carbon and nutrient [1,2]. However, many of the world's rivers have become 'sick rivers' because of human activities such as deforestation, river engineering, overfishing and pollution [3–5]. The presence of dams [6] and extreme weather affect the chemical and biological compositions of river systems. As a consequence, many plant and animal species are facing extinction. Loss of buffering capacities of rivers has increased pollution in coastal zones [1]. Many studies have been carried out for larger rivers [7–10], while small rivers were given less priorities though they undergo severe degradation in recent decades and they will likely disappear first compared to large rivers.

Various studies on bulk elemental composition, stable carbon isotope and biomarkers in sediments and particulate organic matter (POM) have improved the understanding on the biogeochemistry of sedimentary organic matter in lakes [11,12], coastal zones and oceans [13–15], as well as river systems [9,10]. Studies have found phytoplankton to be the major source of POM downstream of the Mississippi, Colorado, Rio Grande and Columbia Rivers [16]. On the other hand, detection of



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older POM in the Hudson-Mohawk river systems was due to the contribution of older soil organic matter [17]. The mainstream of a small mountainous river, Lanyang Hsi, has POM characteristics of soil and rock materials, but its tributaries showed signal of plant materials [18]. Elsewhere, deforestation has resulted in the presence of highly degraded lignin materials in the Rio Tapajos [19]. Downstream Kapuas River has high sedimentary organic carbon (OC), but not corresponding high lignin content, indicating contribution of OC from anthropogenic sources [9]. The sediments along the Yangtze River have organic matter of plant and soil origins and showed effects from local inputs [10].

Sedimentary phosphorus (P) species have also been studied extensively in rivers [20,21] as only certain P forms are associated with P pollution in the aquatic environments [22,23]. Extremely polluted rivers are loaded with high sedimentary TP, NaOH-P (or Fe/Al-P, the P fraction which composed the loosely bound P and P bound to hydrated oxides of Al and non-reducible Fe), and organic P (OP) fractions [24]. Another study found a significant correlation between P release rate and NaOH-P fraction, indicating the importance of the iron-bound P contributing to the P in the water. This bioavailable Fe-P pool was released from sediments during hypoxia and caused an increase in primary production in coastal zone [25].

In this study, surface sediments from six rivers discharging into the Zhejiang coast were determined for lignin-derived phenols, bulk elemental composition and different P species. Lignins are complex molecules present only in vascular plant tissues, and thus, lignins are used as biomarkers for land-derived or terrestrial organic matter. Some lignin monomers produced upon CuO oxidation can be indicative of vegetation types and lignin decomposition stage. For example, the ratios of syringyl/vanilyl (S/V) and cinnamyl/vanillyl (C/V) phenols are indicators of angiosperm versus gymnosperm, and non-woody versus woody tissues; the vanillic acid/vanillin and syringic acid/syringaldehyde ratios, abbreviated as (Ad/Al)v and (Ad/Al)s, are indicators of decomposition stage of lignin materials [26]. Likewise, TOC/TN molar ratio is also used as an indicator of organic matter sources, as terrestrial organic matter has relatively higher TOC/TN (> 23) than marine organic matter (5–12) [27]. The sedimentary P species elucidated in this study include the NaOH-P, HCl-P or apatite P, inorganic P (IP), OP and TP. The NaOH-P fraction is composed of the loosely adsorbed, exchangeable and water soluble P, as well as the Fe-P, which is pH- and redox-sensitive, and is a source of internal P loading during anoxic conditions. OP is released during aerobic decomposition of organic matter and HCl-P is the most stable P form [28,29]. Thus, understanding the sources, distribution and chemical stability of sedimentary organic matter and P will improve our knowledge on the carbon and P dynamics in these small river systems.

# 2. Materials and Methods

# 2.1. Study Areas and Sampling

Surface sediments were collected from along six rivers that discharge into the Zhejiang coast: Qiantang River in Hangzhou, Shuang River in Ningbo, Jiao River in Taizhou and Ximen, Feiyun and Ao Rivers in Wenzhou. The Qingshan Bay off the Shuang River mouth and some locations at the Leqing Bay off Ximen Island were also sampled. The sampling information and locations are given in Appendix A (Table A1) and Figure 1. The distance between two sampling locations was 0.15–11.31 km but mostly 1–2 km. The sampling locations along the middle part of the rivers were accessed by boat and the surface sediments were collected using a grab sampler. The sediments were stored frozen at -20 °C, freeze dried and homogenised using a mortar and pestle.



**Figure 1.** ① Map showing the sampling locations: Qiantang River (Q), Shang River (S), Jiao River (J), Ximen Island (X), Feiyun River (F), Ao River (A); Maps showing the sampling locations along each river magnified: ② Qiantang River, ③ Shuang River, ④ Jiao River, ⑤ Ximen Island, ⑥ Feiyun River and ⑦ Ao River.

# 2.2. Analytical Methods

# 2.2.1. Bulk Elemental and Lignin Analysis

Dry sediment was added to an excess of 1 N HCl and let to stand overnight to remove the inorganic carbon. The residues were dried in oven at 50 °C for two days, homogenised using a mortar and pestle. They were weighed precisely into tin foil and crimped into pellets, and determined for TOC and TN using a LECO-CHN 932 elemental analyser (Elementar, Germany). BCSS-1 and NIST-1 were used as the standard reference materials. The precision for TOC and TN was <5%.

Lignin analysis was carried out based on the CuO oxidation method. Precisely 0.5 g dry sediment and 1.0 g CuO powder were weighed into a 25 mL polytetrafluoroethylene (PTFE) vessel. Precisely 10 mL of 2 M aqueous NaOH in a test tube was bubbled with  $N_2$  for 3 min. The PTFE vessels, test tubes and their contents were purged with  $N_2$  for a few minutes in a glove bag, the NaOH solution was then poured into the contents of the PTFE vessel, and the vessel was capped. The vessels were then heated from room temperature to 170 °C for 3 h and manually shaken every hour. After 3 h, the vessels were allowed to cool. The contents of the vessel were washed three times with 20 mL of 1 M NaOH and centrifuged. The supernatants were combined, acidified to pH 1 with 6 M HCl and extracted three times with 20 mL ethyl acetate. The extracts were then dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered through Whatman filter paper, and spiked with 100  $\mu$ L ethyl vanillin as the internal standard. This was concentrated to 1–2 mL and N<sub>2</sub> blown down. The oxidation product was dissolved in equal amounts of pyridine and bis-(trimethylsilyl) trifluoroacetamide with 10% trimethylchlorosilane and derivatised at 90 °C for 10 min. The solution was ready to be analysed by gas chromatography HP5880A (Agilent Technologies, USA) with flame ionisation detection. The column temperature increased from 100 °C to 300 °C at 4 °C min<sup>-1</sup>.

# 2.2.2. Sedimentary P Species

Determination of different sedimentary P species was carried out based on the 'Standards, Measurements and Testing (SMT)' method by Ruban et al. [30,31] to elucidate different sedimentary P fractions such as NaOH-P, HCl-P, OP and IP. Precisely 200 mg of sediment was added with 20 mL of 1 M NaOH, shaken for 16 h and then centrifuged at 2000 g for 15 min and the supernatant was determined for NaOH-P or Fe/Al-P. The sediment residue was washed with 12 mL of 1 M NaCl, stirred for 5 min and centrifuged at 2500 rpm for 15 min. The supernatant from this step was discarded. After that, the residue was added with 1 M HCl, shaken for 16 h, centrifuged and the supernatant was measured for HCl-P.

Another set of dry sediment was weight to 200 mg and added with 10 mL of 1 M HCl. This was extracted by shaking for 16 h, centrifuged and the supernatant was determined for IP. The residue was washed twice with distilled water and centrifuged. The residue was then combusted at 500 °C for 6 h, added with 20 mL of 1 M HCl and extracted by shaking for 16 h. The following day, this was centrifuged and the supernatant was determined for OP. Total P was the sum of IP and OP. P was determined using the molybdate blue method at a wavelength of 885 nm. P concentration was determined based on the absorbance of the sample extract and calculated as follows: C = SV, where C = concentration of P in mg P/kg, S = concentration of sample obtained from the calibration curve (mg/kg) and V = volume of solvent used [30,31]. All solutions were stored in plastic containers as a precautionary measure. We presume there will be no silicate interference throughout the process, as the tartrate in the working reagent could also prevent reaction between silicate and ammonium molybdate [32].

#### 3. Results

#### 3.1. Sedimentary Organic Matter

The complete results of lignin parameters, TOC and TOC/TN molar ratios are given in Appendix A (Table A2). The Qiantang River has the highest %TOC (ranged from 1.05% to 6.46%) compared to the other five rivers (0.29%–2.77%). Similarly, the percentage of TN was also the highest in Qiantang River (0.21%–1.36%), followed by Shuang River (0.09%–0.44%) and Ao River (0.09%–0.20%). Jiao, Ximen and Feiyun Rivers had a low TN content of 0.06%–0.14%. The overall TOC/TN molar ratios varied at 5.0–11 in all the rivers.

Total lignin ( $\Lambda$ , mg/100 mg TOC) ranged from 0.075 to 4.236. Locations along Qiantang River had the lowest  $\Lambda$  values of 0.075–0.186. Ao and Shuang Rivers had  $\Lambda$  values of 0.244–1.706 and 0.329–1.909, respectively. Jiao, Ximen and Feiyun River had higher  $\Lambda$  values of 0.325–4.236. Similar to  $\Lambda$  and TOC, the S/V ratios (0.72–12.33, excluding the highest values of 21 and 37) and C/V ratios (0.486–8.000) in Qiantang River were higher than the S/V (0.250–3.500) and C/V ratios (0.02–0.692) in other five rivers. The rivers in this study had a wide range of (Ad/Al)v values of 0.045–1.842 and (Ad/Al)s values of 0.088–2.540. The extremely high S/V, C/V, TOC, but rather low  $\Lambda$ , in Qiantang River compared to the other five rivers is further illustrated in Figure 2. Correlation results among lignin parameters and bulk

elemental composition showed no relationship, except for the significant positive correlation between TOC and TN (Appendix A, Table A3).



**Figure 2.** Mean values of lignin parameters in the study areas. The study locations include Qiantang (Q), Jiao (J), Feiyun (F), Shuang (S), Ximen (X) and Ao (A) Rivers.

# 3.2. Sedimentary P Species

The results of sedimentary P fractions are given in Appendix A (Table A4). Percentages of each P fraction and bioavailable P to TP, and OC/OP molar ratios are then calculated. Table 1 shows the ranges and mean values of these parameters. The mean TP concentrations for these rivers are in the following order: Shuang ( $645 \pm 29 \text{ mg P/kg}$ ) > Ao ( $124 \pm 45 \text{ mg P/kg}$ ) > Jiao ( $81 \pm 16 \text{ mg P/kg}$ ) > Feiyun ( $79 \pm 7 \text{ mg P/kg}$ ) > Ximen ( $34 \pm 5 \text{ mg P/kg}$ ) > Qiantang ( $13 \pm 4 \text{ mg P/kg}$ ). Similar to TP, all P fractions were highest at Shuang River and lowest at Qiantang River. The extremely high concentrations of all P fractions of Shuang River sediments compared to the other five rivers are further illustrated in Figure 3. Bioavailable P (BAP) is the sum of NaOH-P and OP. The mean concentrations of bioavailable P are in this order: Shuang (559 mg P/kg) > Ao (89 mg P/kg) > Jiao (42 mg P/kg) > Feiyun (39 mg P/kg) > Ximen (29 mg P/kg) > Qiantang (559 mg P/kg). The percentages of bioavailable P to TP are in the following order: Shuang (87%) > Ximen (84%) > Ao (69%) > Qiantang (53%) > Jiao (50%) > Feiyun (49%). The Shuang River has the highest concentration of BAP, which was about 6 to more than 100 times higher than the other five rivers.

Table 1. Ranges, mean and percentages P fractions.

Locs		Concentration	Ranges and M	Iean (in Brack	ets) (mg P/kg)		P	Percenta	iges to T	ГР (%)	
Lots	NaOH-P	AP	IP	OP	ТР	BAP	NaOH-P	AP	IP	OP	BAP
Q	1.08–7.16 (2.57)	1.54–15.15 (4.16)	2.39–14.45 (9.03)	3.44–6.63 (4.44)	6.49–19.98 (13.47)	4.74–12.69 (7.01)	19.08	30.88	67.04	32.96	52.04
S	175.60–442.12 (283.74)	303.34–378.91 (345.45)	338.37–395.93 (370.23)	244.55–311.60 (275.19)	600.23–686.60 (645.42)	445.81–703.97 (558.93)	43.96	53.52	57.36	42.64	86.60
J	4.48–35.23 (12.81)	23.07–43.48 (35.48)	39.09–66.50 (51.18)	6.68–55.81 (29.41)	52.51–106.54 (80.59)	14.35–76.10 (42.22)	15.90	44.03	63.51	36.49	52.39
x	2.29–10.03 (5.03)	10.40–17.41 (14.38)	5.26–18.47 (10.03)	12.20–31.04 (23.72)	26.20–39.91 (33.75)	14.63–40.16 (28.75)	14.90	42.61	29.72	70.28	85.19
F	4.16–13.20 (8.36)	21.51–34.40 (27.89)	27.66–62.95 (48.36)	17.52–50.40 (30.61)	70.96–92.95 (78.97)	23.09–60.12 (38.97)	10.59	35.32	61.24	38.76	49.35
А	5.95–48.77 (17.88)	26.55–52.87 (44.30)	48.38–61.31 (52.90)	35.64–168.97 (71.04)	84.91–221.09 (123.94)	46.26–187.61 (88.92)	14.43	35.74	42.68	57.32	71.74



Figure 3. Concentrations of all P fractions among the rivers.

The mean OC/OP molar ratios are in the following order: Qiantang (18,754) > Jiao (917) > Ximen (729) > Feiyun (635) > Ao (397) > Shuang (90). Very high OC/OP ratio at Qiantang River was attributable to the highest TOC (ranged between 1.05% and 6.46%) and lowest OP (ranged from 3 to 7 mg/kg) in the Qiantang River compared to the other five rivers (TOC ranged from 0.29% to 2.77%; OP ranged from 26 to 687 mg/kg). As OP is preferentially utilized relative to OC during aerobic organic matter decomposition, higher TOC and higher OC/OP ratios indicate the presence of labile materials where the P was easily degradable [33]. Most of the sedimentary P species have significant positive correlation among one another (Appendix A, Table A5).

# 4. Discussion

# 4.1. Sources of Sedimentary Organic Matter

As angiosperms are composed of syringyl (S) and vanillyl (V) phenols, and gymnosperms contain vanillyl phenol, higher S/V ratios indicate the presence of more angiosperm compared to gymnosperm tissues. Higher C/V ratios indicate non-woody tissues as cinnamyl (C) phenols are found in non-woody tissues but not in woody tissues. Studies have demonstrated that S/V > 0.4 indicates the presence of angiosperm tissues and C/V > 0.2 indicates non-woody tissues [34,35]. The S/V and C/V ratios in the Shuang, Jiao, Ximen, Feiyun and Ao Rivers ranged from 0.250 to 3.500 and from 0.020 to 0.692, respectively, which showed predominance of non-woody angiosperms in these rivers, except for a few locations in Shuang and Jiao Rivers which have demonstrated the presence of some woody signal as represented by some rather low C/V ratios. The S/V and C/V compositional plot showed that most ratios fall within the range for non-woody angiosperm tissues (Figure 4). These results are inconsistent with other locations in this region such as Changjiang Estuary [10] and salt marsh at the southwest of Hangzhou Bay [36] which had shown predominance of non-woody angiosperm tissues.

Higher TOC/TN ratios could be due to preferential loss of N components that are protein-rich, lower TOC/TN could be due to conversion of plant materials to microbial biomass [37]. Low C/N ratios have also been demonstrated for organic matter from meta-sedimentary rocks [18]. Thus, the rather low TOC/TN molar ratios (which ranged from 5 to 11) in the rivers in this study (including Qiantang River) indicate decomposed organic matter, as also supported by the elevated (Ad/Al)v and (Ad/Al)s values in these rivers, which indicate more degraded lignin materials.



**Figure 4.** Plots of S/V and C/V ratio in sediments from sampling areas (**a**) including Q region, and (**b**) without Q region.

## 4.2. P Pollution

The Shuang River TP was slightly higher than the other rivers. The high NaOH-P, as well as all P contents, at the Shuang River most likely indicates P pollution from anthropogenic activities, as higher content of loosely bound-P has been associated with wastewater discharge [38]. The TP levels in rivers investigated in this study were slightly lower compared to some other locations in China such as the Min River Estuary marsh sediments which have TP ranging from 338 mg P/kg to 932 mg P/kg [39]; rivers discharging into the Bohai Sea such as Liao and Yongdingxin have TP of 219 mg P/kg and 913 mg P/kg [24]; TP in the Yellow River delta sediments was 542 mg P/kg [40]; and studies of ten major basins in China found that the average TP in sediments was around 733 mg P/kg [41].

The rivers in this study have high proportion of BAP in their sediments because of their high OP contents which constitute of 34% to 69% of TP. The percentage of NaOH-P to TP ranged from 11% to 44%, indicating that a portion of this fraction, which includes the loosely bound P and Fe-P, can be released to the aquatic environments. The BAP in these rivers were higher in comparison to some locations such as the east coast of Hainan Island (20% to 54% of BAP) [42] and the Jiazhou Bay (40%–53% BAP) [38]; rivers discharging into the Bohai Sea that were polluted with fertilizer and sewage have high abundances of NaOH-P and OP of 223 mg/kg NaOH-P (24% of TP) and 125 mg/kg OP (14% of TP), respectively [24]. These results suggest that sediments in these rivers are prone to release P to the overlying water column.

#### 4.3. Dynamics of Sedimentary Organic Matter and P

Our results revealed slight decrease of  $\Lambda$  values along the rivers, followed by drastic increases in  $\Lambda$  values at some locations, especially at the river mouths. There were mixed trends of (Ad/Al)v and (Ad/Al)s values, with the locations at the river mouths usually have higher ratios (Figure 5). TOC and TN showed slight increase along the rivers, then decrease at the river mouths, as supported by the significant negative correlation between  $\Lambda$  with TOC and TN (p < 0.05), indicative of contribution from anthropogenic carbon and nitrogen besides terrestrial materials farther downstream. The P forms gradually increased, followed by decreasing trend along Qiantang and Jiao Rivers; and gradual decrease along the rivers at Feiyun, Shuang and Ximen; but gradual increase along Ao Rivers (Figure 6).





Figure 5. Cont.

← TOC (%) …O… TN (%)

7

6

5





3.0

2.5

2.0

(b) C (filled) and TN (transparent) along Qiantang, Shuang, Jiao, Ximen, Feiyun and Ao Rivers.

Figure 5. Cont.



(c) TOC/TN molar ratio along Qiantang, Shuang, Jiao, Ximen, Feiyun and Ao Rivers.

Figure 5. Cont.



(d) (Ad/Al)v (square) and (Ad/Al)s (round) ratios along Qiantang, Shuang, Jiao, Ximen, Feiyun and Ao Rivers.

**Figure 5.** Spatial distribution of (a)  $\Lambda$ , (b) TOC, TN, (c) TOC/TN molar ratio, (d) (Ad/Al)v and (Ad/Al)s ratios.

Decreasing abundance of terrestrial organic matter and P was most probably attributed to decomposition of terrestrial organic matter along the rivers. There was increased accumulation and further decomposition of terrestrial organic matter at the river mouths. Both continuous decomposition of terrestrial organic matter along the rivers and at the river mouths also indicate that these rivers most probably serve as carbon source. This is consistent with other studies which have found that rivers are carbon sources due to decomposition of fresher [43] terrestrial organic matter [44].

Increasing trends of TOC/TN ratios along the Qiantang, Shuang, Jiao, Ximen and Feiyun Rivers further supported increased organic matter decomposition farther downstream. The gradual increases of TOC/OP along the rivers indicate accumulation of terrestrial organic matter farther downstream and increased decomposition downstream. There were drastic decreases of TOC/TN ratios at the Ximen and Feiyun river mouths, this could indicate more decomposed materials, as supported by the very

high (Ad/Al)v and (Ad/Al)s values here. The Qiantang River is well-known for the occurrence of tidal bore [45]. Thus, the lowest  $\Lambda$  values and P in the Qiantang River could be attributable to the rapid organic matter decomposition due to physical disturbances of the tidal bore facilitated mixing and resuspension, thus, further facilitated decomposition of sedimentary organic matter.



(a) Sedimentary P species including the NaOH-P, HCl-P, IP, OP, BAP and TP

Figure 6. Cont.





(**b**) TOC/TP molar ratios along the length of the rivers

**Figure 6.** Spatial distribution of (**a**) sedimentary P species and (**b**) TOC/OP molar ratios along the Qiantang (Q), Shuang (S), Jiao (J), Ximen (X), Feiyun (F) and Ao (A) Rivers.

# 5. Conclusions

The S/V and C/V ratios in sediments of small rivers along the Zhejiang Coast of SE China indicate predominance of non-woody angiosperm tissues and the large ranges of (Ad/Al)v and (Ad/Al)s values indicate the presence of fresh to degraded lignin materials. The ranges of TOC in Shuang, Jiao, Ximen, Feiyun and Ao Rivers were 0.29%–2.77%; Qiantang River has the highest TOC of 1.05%–6.46%. Total lignin,  $\Lambda$ , in Shuang, Jiao, Ximen, Feiyun and Ao Rivers ranged from 0.24 to 4.24; Qiantang River has the lowest  $\Lambda$  of 0.08 to 0.19. TP was the highest in Shuang (645 mg P/kg), followed by the other four

rivers (34–124 mg P/kg) and the lowest in Qiantang River (13 mg P/kg). On the other hand, Qiantang River has the highest OC/OP molar ratio (18,753), followed by the other four rivers (397–917) and Shuang River (90). High TOC in Qiantang River could be due to anthropogenic input. High OC/OP but low TP and  $\Lambda$  in Qiantang River indicates rapid recycling of organic matter and P. The high TP and low OC/OP in Shuang River could be due to the relatively higher P pollution in this river in comparison to the other rivers. Our results indicate rapid cycling of sedimentary organic matter and P along these rivers, resulting in highly degraded materials at the river mouths and low P pollution in the sediments.

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Conflicts of Interest: The authors declare no conflict of interest.

# Appendix A

Date	Station	Longitude (°)	Latitude (°)	Date	Station	Longitude (°)	Latitude (°)
2014.10.16	A1	120.6009	27.5884	2014.10.18	J1	121.4632	28.6900
	A2	120.5952	27.5901		J2	121.4511	28.6930
	A3	120.5827	27.5873	-	J3	121.4421	28.6958
Ao River	A4	120.5725	27.5803	-	J4	121.4265	28.6992
nonwei	A5	120.5620	27.5793	- Iiao River	J5	121.4206	28.6991
	A6	120.5546	27.5864	Juo tuver	J6	121.4115	28.7001
	A7	120.5562	27.5879	-	J7	121.3905	28.7028
2014.10.17	F1	120.6456	27.7355	-	J8	121.3928	28.7014
	F2	120.6371	27.7426	_	J9	121.3675	28.7036
	F4	120.6242	27.7604	-	J10	121.3522	28.7058
	F5	120.6200	27.7664	2014.10.19	S1	121.5572	29.2164
	F6	120.6170	27.7734		S2	121.5702	29.1933
Feiyun River	F7	120.6193	27.7807	_	S3	121.5905	29.1744
	F8	120.6170	27.7877	-	S4	121.6085	29.1631
	F9	120.6130	27.7924	- Shuang River	S5	121.6238	29.1669
	F10	120.6282	27.7703		S6	121.6252	29.1808
	F11	120.6455	27.7341	-	S7	121.6253	29.1883
	F12	120.6526	27.7275	-	S8	121.6073	29.1961
2014.10.18	X1	121.2078	28.3264	_	S9	121.6217	29.1997
	X2	121.2127	28.3306	2014.10.20	Q4	120.4421	30.3903
	X3	121.2166	28.3261		Q5	120.4533	30.3921
	X4	121.2144	28.3194	_	Q7	120.4224	30.3635
	X5	121.2121	28.3118	-	Q8	120.4176	30.3520
Ximen Island	X6	121.2085	28.3193	-	Q9	120.4128	30.3405
	X7	121.2103	28.3082	<ul> <li>Qiantang River</li> </ul>	Q10	120.4067	30.3266
				-	Q11	120.4019	30.3133
	No	101 0110	00 0005		Q12	120.4185	30.3074
	X8	121.2112	28.3035		Q13	120.4244	30.3185
					Q14	120.4292	30.3308

#### Table A1. Locations information.

					( <b>a</b> ) Qiar	itang River (Q)						
Qiantang	S (mg/g)	V (mg/g)	C (mg/g)	Total (mg/g)	S/V	C/V	(Ad/Al)v	(Ad/Al)s	TOC (%)	TN (%)	C/N	Λ (mg/100 mg TOC)
Q11	0.007	0.004	0.009	0.020	1.750	2.250	0.188	0.757	2.66	0.53	5.9	0.075
Q12	0.006	0.002	0.005	0.013	3.000	2.500	1.060	0.403	1.74	0.35	5.8	0.075
Q10	0.042	0.002	0.005	0.049	21.000	2.500	0.343	0.206	2.63	0.52	5.9	0.186
Q13	0.005	0.004	0.004	0.013	1.250	1.000	0.432	2.709	1.05	0.21	5.8	0.124
Q9	0.074	0.002	0.016	0.092	37.000	8.000	0.619	0.283	6.46	1.36	5.5	0.142
Q14	0.022	0.002	0.003	0.027	11.000	1.500	0.235	0.088	1.81	0.33	6.3	0.149
Q8	0.037	0.003	0.002	0.042	12.333	0.667	0.414	0.209	4.06	0.83	5.7	0.103
Q7	0.037	0.004	0.002	0.043	9.250	0.500	0.091	0.216	3.49	0.40	10.3	0.123
Q4	0.047	0.037	0.018	0.102	1.270	0.486	0.955	0.765				
Q5	0.006	0.008	0.011	0.025	0.750	1.375	0.178	1.016	2.04	0.38	6.3	0.123
Mean	0.028	0.007	0.008	0.043	9.860	2.078	0.451	0.665	2.88	0.55	6.4	0.122
					( <b>b</b> ) Shu	ang River (S)						
Shuang	S (mg/g)	V (mg/g)	C (mg/g)	Total (mg/g)	S/V	C/V	(Ad/Al)v	(Ad/Al)s	TOC (%)	TN (%)	C/N	Λ (mg/100 mg TOC)
	0.018	0.033	0.006	0.057	0.545	0.182	0.164	0.504	0.97	0.20	5.6	0.588
<b>S</b> 9	0.043	0.042	0.012	0.097	1.008	0.284	0.375	0.357	0.67	0.14	5.6	1.454
<b>S</b> 7	0.037	0.052	0.006	0.095	0.712	0.115	0.377	0.503	1.17	0.14	9.5	0.812
<b>S6</b>	0.027	0.048	0.009	0.084	0.563	0.188	0.147	0.459	0.44	0.10	5.3	1.909
S5	0.018	0.035	0.003	0.056	0.514	0.086	0.242	0.485	0.46	0.09	6.0	1.217
S4	0.019	0.038	0.004	0.061	0.500	0.105	0.378	0.668	0.84	0.19	5.0	0.726
S3	0.024	0.035	0.004	0.063	0.686	0.114	0.319	0.594	0.90	0.14	7.5	0.700
S2	0.043	0.049	0.001	0.093	0.878	0.020	1.344	1.070	0.90	0.09	11.0	1.033
<b>S1</b>	0.043	0.042	0.006	0.091	1.024	0.143	0.275	0.570	2.77	0.44	7.3	0.329
Mean	0.030	0.042	0.006	0.077	0.714	0.137	0.402	0.579	1.01	0.17	7.0	0.974
					( <b>c</b> ) Ji	ao River (J)						
Jiao	S (mg/g)	V (mg/g)	C (mg/g)	Total (mg/g)	S/V	C/V	(Ad/Al)v	(Ad/Al)s	TOC (%)	TN (%)	C/N	Λ (mg/100 mg TOC)
J10	0.008	0.018	0.006	0.032	0.444	0.333	0.842	0.616	0.62	0.10	7.1	0.516
J9	0.026	0.019	0.004	0.049	1.368	0.211	1.217	0.136	0.65	0.11	7.1	0.754
17	0.019	0.030	0.005	0.054	0.633	0.167	0.058	0.547	0.63	0.11	7.0	0.857
J8	0.028	0.008	0.003	0.039	3.500	0.375	0.110	0.143	0.67	0.11	7.3	0.582
J6	0.080	0.090	0.008	0.178	0.889	0.089	0.353	0.491	0.65	0.11	7.2	2.738
J4	0.090	0.141	0.037	0.268	0.638	0.262	1.837	0.158	0.68	0.11	7.4	3.941
J3	0.052	0.050	0.011	0.113	1.040	0.220	0.342	0.319	0.58	0.08	8.0	1.948
J2	0.055	0.066	0.009	0.13	0.833	0.136	0.101	0.161	0.64	0.09	8.1	2.031
J1	0.021	0.019	0.008	0.048	1.105	0.421	0.045	0.346	0.62	0.09	8.0	0.774
Mean	0.042	0.049	0.010	0.101	1.161	0.246	0.545	0.324	0.64	0.10	7.5	1.571

**Table A2.** Lignin parameters, TOC, TN and C/N ratios along (a) Qiantang River (Q), (b) Shuang River (S), (c) Jiao River (J), (d) Ximen Island (X), (e) Feiyun River (F), (f) Ao River (A).

					( <b>d</b> ) Xin	nen Island (X)						
Ximen	S (mg/g)	V (mg/g)	C (mg/g)	Total (mg/g)	S/V	C/V	(Ad/Al)v	(Ad/Al)s	TOC (%)	TN (%)	C/N	Λ (mg/100 mg TOC)
X2	0.041	0.051	0.007	0.099	0.804	0.137	0.249	0.249	0.55	0.11	6.0	1.800
X1	0.036	0.038	0.015	0.089	0.947	0.395	0.170	0.316	0.48	0.09	6.0	1.854
X3	0.043	0.062	0.021	0.126	0.694	0.339	0.391	0.892	0.74	0.14	6.3	1.703
X6	0.011	0.013	0.005	0.029	0.846	0.385	0.706	2.540	0.81	0.14	6.9	0.358
X4	0.033	0.043	0.008	0.084	0.767	0.186	0.478	0.722	0.64	0.11	6.7	1.313
X5	0.033	0.056	0.016	0.105	0.589	0.286	0.282	0.603	0.77	0.13	6.8	1.364
X7	0.032	0.036	0.008	0.076	0.889	0.222	0.481	1.203	0.63	0.10	7.2	1.206
X8	0.040	0.041	0.009	0.090	0.976	0.220	0.275	0.973	0.29	0.06	5.4	3.103
Mean	0.034	0.043	0.011	0.087	0.814	0.271	0.379	0.937	0.61	0.11	6.4	1.588
					( <b>e</b> ) Fei	yun River (F)						
Feiyun	S (mg/g)	V (mg/g)	C (mg/g)	Total (mg/g)	S/V	C/V	(Ad/Al)v	(Ad/Al)s	TOC (%)	TN (%)	C/N	Λ (mg/100 mg TOC)
F9	$0.053 \pm 0.0065$	$0.067 \pm 0.0113$	$0.016 \pm 0.0062$	0.137	$0.798 \pm 0.0497$	$0.244 \pm 0.0749$	$0.269 \pm 0.1485$	$0.232 \pm 0.0842$	0.60	0.09	8.1	2.294
F8	0.013	0.028	0.008	0.049	0.464	0.286	0.348	0.553	0.64	0.09	8.7	0.766
F7	0.031	0.034	0.011	0.076	0.912	0.324	0.088	0.169	0.65	0.09	8.6	1.169
F6	0.053	0.061	0.009	0.123	0.869	0.148	0.530	0.888	0.68	0.09	8.8	1.809
F5	0.010	0.008	0.008	0.026	1.250	1.000	0.061	0.597	0.80	0.10	9.5	0.325
F10	0.030	0.054	0.006	0.090	0.556	0.111	0.602	0.652	0.67	0.10	8.1	1.343
F4	0.016	0.027	0.004	0.047	0.593	0.148	0.121	0.417	0.67	0.09	8.7	0.701
F2	0.030	0.043	0.008	0.081	0.698	0.186	0.269	0.331	0.71	0.10	8.6	1.141
F1	0.067	0.067	0.024	0.158	1.000	0.358	0.076	0.113	0.76	0.10	9.3	2.079
F11	0.108	0.109	0.016	0.233	0.991	0.147	0.295	0.239	0.55	0.08	7.7	4.236
F12	0.007	0.028	0.003	0.038	0.250	0.107	0.981	1.107	0.68	0.10	7.8	0.559
Mean	0.038	0.048	0.010	0.096	0.762	0.278	0.331	0.482	0.67	0.09	8.5	1.493
					(f) A	o River (A)						
Ao	S (mg/g)	V (mg/g)	C (mg/g)	Total (mg/g)	S/V	C/V	(Ad/Al)v	(Ad/Al)s	TOC (%)	TN (%)	C/N	Λ (mg/100 mg TOC)
A6	0.042	0.054	0.020	0.116	0.778	0.370	0.160	0.143	0.68	0.09	8.6	1.706
A7	0.036	0.035	0.008	0.079	1.029	0.229	0.285	0.460	0.60	0.09	8.0	1.317
A5	0.039	0.045	0.011	0.095	0.867	0.244	0.274	0.225	0.68	0.09	8.7	1.397
A4	0.045	0.067	0.015	0.127	0.672	0.224	0.267	0.165	1.03	0.15	7.8	1.233
A3	0.011	0.013	0.009	0.033	0.846	0.692	0.152	0.201	1.35	0.20	8.0	0.244
A2	0.018	0.013	0.009	0.040	1.385	0.692	0.321	0.240	0.98	0.19	6.0	0.408
A1	0.041	0.050	0.010	0.101	0.820	0.200	0.377	0.258	0.64	0.09	8.1	1.578
Mean	0.033	0.040	0.012	0.084	0.914	0.379	0.262	0.242	0.85	0.13	7.9	1.126

# Table A2. Cont.

**Table A3.** Correlation among the lignin parameters. (a) Qiantang River (Q): N = 10, (b) Shuang River (S): N = 9, (c) Jiao River (J): N = 9, (d) Ximen Island (X): N = 8, (e) Feiyun River (F): N = 11, (f) Ao River (A): N = 7.

			( <b>a</b> ) Qia	antang River	(Q): N = 10			
Q	S/V	C/V	(Ad/Al)V	(Ad/Al)S	Λ	TOC	TN	C/N
S/V	1	0.692 *	-0.031	-0.669 *	0.501	0.861 **	0.871 **	0.124
C/V		1	0.261	-0.171	0.009	0.661	0.764 *	-0.393
(Ad/Al)V			1	0.344	-0.387	0.058	0.199	-0.468
(Ad/Al)S				1	-0.490	-0.545	-0.439	-0.287
Λ					1	0.127	0.112	0.054
TOC						1	0.954 **	0.037
TN							1	-0.262
C/N			(1) (1)		(2) 3.7			1
			(b) S	huang River	(S): $N = 9$			
S	S/V	C/V	(Ad/Al)V	(Ad/Al)S	Λ	тос	TN	C/N
S/V	1	-0.209	0.464	0.446	-0.396	0.779 *	0.572	0.664
C/V		1	-0.723 *	-0.656	0.144	0.006	0.227	-0.683 *
(Ad/Al)V			1	0.967 **	-0.026	-0.024	-0.225	0.778 *
(Ad/AI)S				1	-0.112	0.020	-0.152	0.646
					1	-0.704 *	-0.681 *	-0.212
TOC						1	0.939 *	0.243
							1	-0.094
ÇN			(.)	T' D' /I				1
			(C)	jiao kiver (j	): N = 9			
J	S/V	C/V	(Ad/Al)V	(Ad/AI)S	Λ	TOC	TN	C/N
S/V	1	0.265	-0.203	-0.367	-0.260	0.454	0.351	-0.166
C/V		1	0.040	0.312	-0.460	-0.024	-0.127	0.108
(Ad/Al)V			1	0.110	0.514	0.429	0.374	-0.336
(Ad/Al)S				1	-0.362	-0.306	-0.106	-0.255
					1	0.382	0.140	0.110
TOC						1	0.796 *	-0.423
							1	-0.865 **
			(d) Y	imon Island	$(\mathbf{X}) \cdot \mathbf{N} = 8$			1
<b>v</b>	s/W	CN			$\frac{(X) \cdot I = 0}{\Lambda}$	тос	TN	C/N
	3/ V	0.056		(Au/Al)5	<u> </u>	0.047	0.4(2	
5/V	1	-0.056	0.457	0.544	0.263	-0.347	-0.462	-0.031
		1	0.076	0.394	-0.241	0.288	0.299	0.070
(Ad/Al)v			1	0.645	-0.655	0.002	0.303	0.002
(Ad/Al)5				1	-0.319	0.300	0.521	0.391
					1	-0.645	0.700	-0.031
TN						1	0.901	0.600
C/N							1	1
			(e) F	eivun River (	F): N = 11			-
F	S/V	C/V	(Ad/Al)V	(Ad/Al)S	Λ	тос	TN	C/N
S/V	-, ·	0.590	-0.490	-0.376	0.396	0.207	-0.258	0.433
C/V	1	1	-0.523	-0.158	-0.335	0.639 *	0.290	0.710 *
(Ad/Al)V			1	0.798 **	-0.070	-0.183	0.204	-0.603 *
(Ad/Al)S				1	-0.497	0.220	0.416	-0.168
Λ				-	1	-0.632 *	-0.655 *	-0.455
тос					-	1	0.810 **	0.806 **
TN						-	1	0.378
C/N								1

(f) Ao River (A): N = 7										
Α	S/V	C/V	(Ad/Al)V	(Ad/Al)S	Λ	TOC	TN	C/N		
S/V	1	-0.221	0.560	0.193	0.157	-0.628	-0.341	-0.364		
C/V		1	-0.397	0.485	-0.888 **	0.742	0.844 *	-0.574		
(Ad/Al)V			1	-0.001	0.176	-0.449	-0.242	-0.365		
(Ad/Al)S				1	-0.636	0.226	0.377	-0.376		
Λ					1	-0.825 *	-0.931 **	-0.666		
TOC						1	0.931 **	-0.360		
TN							1	-0.688		
C/N								1		

Table A3. Cont.

\* represents significance to 0.05; \*\* represents significance to 0.01.

**Table A4.** Sedimentary P fractions in the rivers. (a) Qiantang River (Q), (b) Shuang Creek (S), (c) Jiao River (J), (d) Ximen Island, (e) Feiyun River (F), (f) Ao River (A).

			(a	) Qiantang River	(Q)			
		Co	ncentration of F	fraction (mg/kg	<u>z</u> )			OC/OP molar
Locs	NaOH-P	HC1-P	IP	ОР	ТР	BAP	- OC (%)	ratio
Q11	2.55	2.85	9.37	3.48	12.85	6.03	2.66	19741
Q12	4.30	1.54	9.28	3.44	12.72	7.74	1.74	13050
Q10	1.12	2.21	6.77	4.01	10.78	5.13	2.63	16921
Q13	2.53	2.15	10.71	5.41	16.12	7.94	1.05	5005
Q9	1.73	2.14	9.26	3.70	12.96	5.43	6.46	45130
Q14	2.03	5.41	11.79	6.63	18.42	8.66	1.81	7050
Q8	1.08	1.90	7.93	3.66	11.59	4.74	4.06	28621
Q7	$1.78 \pm 0.24$	$2.74 \pm 1.29$	$8.35 \pm 0.14$	$4.42 \pm 0.59$	12.77	6.20	3.49	20410
Q4	7.16	15.1480	14.45	5.53	19.98	12.69		
Q5	1.40	5.5449	2.39	4.10	6.49	5.50	2.04	12853
Mean	2.57	4.16	9.03	4.44	13.47	7.01	2.88	18753
stdev	± 1.87	± 4.11	± 3.18	$\pm 1.07$	± 3.87	± 2.39	± 1.63	$\pm 12214$
			(1	<b>b</b> ) Shuang Creek	(S)			
Law		Co	ncentration of I	fraction (mg/kg	<u>;</u> )			OC/OP molar
Locs	NaOH-P	HCl-P	IP	OP	ТР	BAP	00(1/6)	ratio
<b>S</b> 8	379.14	315.42	375.00	311.60	686.60	690.74	0.97	80
<b>S</b> 9	$442.12 \pm 17.41$	$303.34 \pm 2.39$	$338.37 \pm 2.80$	$261.85 \pm 8.87$	600.22	703.97	0.67	66
<b>S</b> 7	349.51	313.79	354.98	275.26	630.24	624.77	0.71	66
<b>S</b> 6	288.74	378.91	339.34	278.53	617.87	567.27	0.44	41
<b>S</b> 5	175.60	352.34	395.93	270.21	666.14	445.81	0.46	44
S4	231.12	339.26	370.65	303.27	673.92	534.39	0.84	72
<b>S</b> 3	229.94	373.42	395.53	271.49	667.02	501.43	0.73	70
S2	213.81	374.51	393.66	244.55	638.21	458.36	0.90	95
S1	243.64	358.08	368.59	259.95	628.54	503.59	2.77	275
Mean	283.74	345.45	370.23	275.19	645.42	558.93	0.94	90
Stdev	$\pm 88.31$	± 28.87	± 22.57	± 20.95	$\pm 29.10$	± 95.33	$\pm 0.71$	± 71
				(c) Jiao River (J	)			
Locs		Co	ncentration of F	fraction (mg/kg	<u>ç</u> )		- 00 (%)	OC/OP molar
LOCS	NaOH-P	HCl-P	IP	OP	ТР	BAP	00 (78)	ratio
J10	4.48	24.12	66.50	9.87	76.37	14.35	0.62	1629
J9	8.11	23.07	45.83	6.68	52.51	14.79	0.65	2507
J8	8.11	43.48	49.54	12.25	61.79	20.36	0.67	1406
J7	8.06	39.97	50.42	28.06	78.48	36.12	0.63	579
J6	$35.22 \pm 10.85$	$34.43 \pm 5.74$	$43.56 \pm 6.54$	$40.87\pm5.06$	84.43	76.09	0.65	411
J4	9.05	38.56	39.09	41.37	80.46	50.42	0.68	422
J3	17.81	38.50	50.73	55.81	106.54	73.62	0.58	268
J2	13.79	42.85	48.59	45.83	94.42	59.62	0.64	360
J1	10.62	34.38	66.35	23.98	90.33	34.6	0.62	672
Mean	12.81	35.48	51.18	29.41	80.59	42.22	0.64	917
stdev	± 9.24	$\pm 7.44$	± 9.41	$\pm 17.55$	$\pm 16.35$	± 23.99	$\pm 0.03$	± 765

				(d) Ximen Island	l			
_		Со	ncentration of P	fraction (mg/kg	)			OC/OP molar
Locs	NaOH-P	HC1-P	IP	ОР	ТР	BAP	- OC (%)	ratio
X2	4.40	13.34	7.07	31.04	38.11	35.44	0.55	453
X1	10.03	15.77	9.78	30.13	39.91	40.16	0.48	412
X3	3.12	17.41	6.85	28.76	35.61	31.88	0.75	651
X6	2.29	10.40	5.26	20.94	26.2	23.23	0.81	997
X4	3.76	13.48	8.84	30.65	39.49	34.41	0.64	537
X5	$4.49 \pm 0.45$	$15.69 \pm 0.59$	$11.32 \pm 0.41$	$20.43 \pm 1.13$	31.75	24.92	0.77	969
X7	2.43	15.18	18.47	12.20	30.67	14.63	0.63	1337
X8	9.75	13.78	12.65	15.57	28.22	25.32	0.29	475
Mean	5.03	14.38	10.03	23.72	33.75	28.75	0.62	729
stdev	± 3.11	± 2.12	± 4.19	± 7.42	± 5.27	± 8.22	$\pm 0.17$	± 335
			(	e) Feiyun River (	F)			
Lan		Со	ncentration of P	fraction (mg/kg)	)		$OC(\theta')$	OC/OP molar
LOCS	NaOH-P	HCl-P	IP	OP	TP	BAP	- UC (%)	ratios
F9	12.01	34.40	48.43	35.81	84.24	47.82	0.60	430
F8	5.57	21.51	60.38	17.52	77.9	23.09	0.64	943
F7	$13.20 \pm 0.25$	$24.09 \pm 0.67$	$51.47 \pm 0.47$	$23.80 \pm 2.82$	75.27	37	0.65	707
F6	6.05	21.83	49.89	24.59	74.48	30.64	0.68	716
F5	4.16	27.49	58.80	23.61	82.41	27.77	0.80	870
F10	8.75	28.22	34.47	47.43	81.9	56.18	0.67	365
F4	6.41	28.01	45.28	36.19	81.47	42.6	0.67	475
F2	11.89	34.30	62.95	30.00	92.95	41.89	0.71	607
F1	9.84	32.86	49.52	21.44	70.96	31.28	0.76	914
F11	9.72	27.97	27.66	50.40	78.06	60.12	0.55	284
F12	4.34	26.11	43.13	25.90	69.03	30.24	0.68	679
Mean	8.36	27.89	48.36	30.61	78.97	38.97	0.67	635
Stdev	± 3.23	± 4.51	± 10.67	± 10.69	± 6.70	± 11.96	$\pm 0.07$	± 225
				(f) Ao River (A)				
Locs		Co	ncentration of P	fraction (mg/kg)	)		- 00 (%)	OC/OP molar
Locs	NaOH-P	HCl-P	IP	OP	ТР	BAP	00 (70)	ratio
A6	14.60	40.79	54.79	52.08	106.87	66.68	0.68	338
A7	10.62	38.74	49.27	35.64	84.91	46.26	0.60	435
A5	48.77	49.05	61.31	62.68	123.99	111.45	0.68	279
A4	18.73	50.68	48.38	57.13	105.51	75.86	1.03	465
A3	$7.87 \pm 0.84$	$51.42 \pm 1.83$	$54.91 \pm 6.17$	$40.99 \pm 2.62$	95.9	48.86	1.35	851
A2	5.95	52.87	49.51	79.79	129.3	85.74	0.98	317
A1	18.64	26.55	52.12	168.97	221.09	187.61	0.64	97
Mean	17.88	44.30	52.90	71.04	123.94	88.92	0.85	397
stdev	$\pm 14.50$	$\pm 9.54$	$\pm 4.55$	$\pm 45.54$	$\pm 45.47$	$\pm 48.90$	$\pm 0.28$	± 233

Table A4. Cont.

 Table A5. Correlation analyses among the P species and some lignin and elemental parameters.

	HCl-P	IP	ОР	ТР	BAP	OC	TOC/OP
NaOH-P	0.919	0.923	0.925	0.932	0.983	-0.0964	-0.208
	1.232E-022	2.977E-023	1.895E-023	1.270E-024	3.586E-040	0.492	0.135
	54	54	54	54	54	53	53
HCl-P		0.992	0.963	0.989	0.958	-0.122	-0.258
		1.765E-048	2.291E-031	1.522E-044	8.198E-030	0.385	0.0618
		54	54	54	54	53	53
IP			0.963	0.993	0.960	-0.133	-0.266
			2.722E-031	3.153E-050	1.951E-030	0.342	0.0543
			54	54	54	53	53
OP				0.988	0.978	-0.160	-0.293
				9.743E-044	2.619E-037	0.254	0.0335
				54	54	53	53
TP					0.977	-0.146	-0.280
					1.698E-036	0.298	0.0424
					54	53	53
BAP						-0.128	-0.252
						0.360	0.0683
						53	53
OC							0.945
							2.270E-026
							53

	LIGNIN	TN	TOC/TN	(Ad/Al)v	(Ad/Al)s	
NaOH-P	-0.0422	-0.0665	-0.127	-0.0376	-0.0152	
	0.764	0.636	0.366	0.787	0.913	
	53	53	53	54	54	
HC1-P	-0.0435	-0.105	-0.0565	-0.00136	-0.00302	
	0.757	0.455	0.688	0.992	0.983	
	53	53	53	54	54	
IP	-0.0691	-0.117	-0.0172	-0.00292	-0.0157	
	0.623	0.405	0.903	0.983	0.910	
	53	53	53	54	54	
OP	0.00593	-0.135	-0.0818	-0.0404	-0.0384	
	0.966	0.336	0.560	0.772	0.783	
	53	53	53	54	54	
TP	-0.0373	-0.126	-0.0453	-0.0192	-0.0257	
	0.791	0.370	0.747	0.891	0.854	
	53	53	53	54	54	
BAP	-0.0201	-0.100	-0.108	-0.0397	-0.0266	
	0.887	0.475	0.443	0.776	0.849	
	53	53	53	54	54	
OC	-0.473	0.977	-0.204	0.0123	-0.0990	
	0.000352	1.103E-035	0.142	0.930	0.481	
	53	53	53	53	53	
TOC/OP	-0.421	0.950	-0.268	0.0472	-0.0729	
	0.00170	1.752E-027	0.0528	0.737	0.604	
	53	53	53	53	53	
LIGNIN		-0.450	0.0934	0.126	-0.207	
		0.000717	0.506	0.367	0.138	
		53	53	53	53	
TN			-0.345	0.0338	-0.0762	
			0.0114	0.810	0.587	
			53	53	53	
TOC/TN				0.0185	-0.142	
				0.895	0.310	
				53	53	
(Ad/Al)v					0.198	
-					0.151	
					54	
(Ad/Al)s						

Table A5. Cont.

The pair(s) of variables with positive correlation coefficients and p values below 0.050 tend to increase together. For the pairs with negative correlation coefficients and p values below 0.050, one variable tends to decrease while the other increases. For pairs with p values greater than 0.050, there is no significant relationship between the two variables. Pearson Product Moment Correlation; Data source: Data 13 in Notebook1; Cell Contents: Correlation Coefficient; p Value; Number of Samples.

#### References

- 1. Wohl, E. A World of Rivers. Environmental Change on Ten of the World's Great Rivers; University of Chicago Press: Chicago, IL, USA, 2013; p. 359.
- 2. Kandasamy, S.; Nagender Nath, B. Perspective on the terrestrial organic matter transport and burial along the land-deep sea continuum: Caveats in our understanding of biogeochemical processes and future needs. *Front. Mar. Sci.* **2016**, *3*, 259. [CrossRef]
- 3. Blaas, H.; Krosze, C. Excessive nitrogen and phosphorus in European rivers: 2000–2050. *Ecol. Indic.* 2016, 67, 328–337. [CrossRef]
- Mandaric, L.; Diamantini, E.; Stella, E.; Cano-Paoli, K.; Valle-Sistac, J.; Molins-Delgado, D.; Bellin, A.; Chiogna, G.; Majone, B.; Diaz-Cruz, M.S.; et al. Contamination sources and distribution patterns of pharmaceuticals and personal care products in Alpine rivers strongly affected by tourism. *Sci. Total Environ.* 2017, 590, 484–494. [CrossRef]
- Peng, F.J.; Pan, C.G.; Zhang, M.; Zhang, N.S.; Windfield, R.; Salvito, D.; Selck, H.; Van den Brink, P.J.; Ying, G.G. Occurrence and ecological risk assessment of emerging organic chemicals in urban rivers: Guangzhou as a case study in China. *Sci. Total Environ.* 2017, *589*, 46–55. [CrossRef] [PubMed]

- 6. Syvitski, J.P.M.; Vörösmarty, C.J.; Kettner, A.J.; Green, P. Impact of humans on the flux of terrestrial sediment to the global coastal ocean. *Science* **2015**, *308*, 376–380. [CrossRef] [PubMed]
- Aufdenkampe, A.K.; Mayorga, E.; Hedges, J.I.; Llerena, C.; Quay, P.D.; Gudeman, J.; Krusche, A.V.; Richey, J.E. Organic matter in the Peruvian headwaters of the Amazon: Compositional evolution from the Andes to the lowland Amazon mainstem. *Org. Geochem.* 2007, *38*, 337–364. [CrossRef]
- 8. Alin, S.R.; Aalto, R.; Goñi, M.A.; Richey, J.E.; Dietrich, W.E. Biogeochemical characterization of carbon sources in the Strickland and Fly rivers, Papua New Guinea. *J. Geophys. Res.* **2007**, *113*, F01S05. [CrossRef]
- Loh, P.S.; Chen, C.T.A.; Anshari, G.Z.; Wang, J.T.; Lou, J.Y.; Wang, S.L. A comprehensive survey of lignin geochemistry in the sedimentary organic matter along the Kapuas River (West Kalimantan, Indonesia). *J. Asian Earth Sci.* 2012, 43, 118–129. [CrossRef]
- Li, Z.; Peterse, F.; Wu, Y.; Bao, H.; Eglinton, T.I.; Zhang, J. Sources of organic matter in Changjiang (Yangtze River) bed sediments: Preliminary insights from organic geochemical proxies. *Org. Geochem.* 2015, *85*, 11–21. [CrossRef]
- Ishiwatari, R.; Fujino, N.; Brincat, D.; Yamamoro, S.; Takahara, H.; Shichi, K.; Krivonogov, S.K. A 35 kyr record of organic matter composition and δ<sup>13</sup>C of n-alkanes in bog sediments close to Lake Baikal: Implications for paleoenvironmental studies. *Org. Geochem.* 2009, 40, 51–60. [CrossRef]
- 12. Tareq, S.M.; Kitagawa, H.; Ohta, K. Lignin biomarker and isotopic records of paleovegetation and climate changes from Lake Erhai, southwest China, since 18.5 ka BP. *Quarter. Inter.* **2011**, *229*, 47–56. [CrossRef]
- Wu, Y.; Dittmar, T.; Ludwichowski, K.U.; Kattner, G.; Zhang, J.; Zhu, Z.Y.; Koch, B.P. Tracing suspended organic nitrogen from the Yangtze River catchment into the East China Sea. *Mar. Chem.* 2007, 107, 367–377. [CrossRef]
- Goñi, M.A.; Aceves, H.; Benitez-Nelson, B.; Tappa, E.; Thunnell, R.; Black, D.E.; Muller-Karger, F.; Astor, Y.; Varela, R. Oceanographic and climatologic controls on the compositions and fluxes of biogenic materials in the water column and sediments of the Cariaco Basin over the Late Holocene. *Deep-Sea Res. I* 2009, 56, 614–640. [CrossRef]
- Yao, P.; Yu, G.; Bianchi, T.S.; Guo, Z.; Zhao, M.; Knappy, C.S.; Keely, B.J.; Zhao, B.; Zhang, T.; Pan, H.; et al. A multiproxy analysis of sedimentary organic carbon in the Changjiang Estuary and adjacent shelf. *J. Geophys. Res. Biogeo.* 2015, 120, 1407–1429. [CrossRef]
- 16. Kendall, C.; Silva, S.R.; Kelly, V.J. Carbon and nitrogen isotopic compositions of particulate organic matter in four large river systems across the United States. *Hydrol. Proces.* **2001**, *15*, 1301–1346. [CrossRef]
- Longworth, B.E.; Petsch, S.T.; Raymond, R.A.; Bauer, J.E. Linking lithology and land use to sources of dissolved and particulate organic matter in headwaters of a temperate, passive-margin river system. *Geochim. Cosmochim. Acta* 2007, *71*, 4233–4250. [CrossRef]
- 18. Kao, S.J.; Liu, K.K. Stable carbon and nitrogen isotope systematic in a human-disturbed watershed (Lanyang-Hsi) in Taiwan and the estimation of biogenic particulate organic carbon and nitrogen fluxes. *Global Biogeochem. Cycles* **2000**, *14*, 189–198. [CrossRef]
- 19. Farella, N.; Lucotte, M.; Louchouarn, P.; Roulet, M. Deforestation modifying terrestrial organic transport in the Rio Tapajós, Brazilian Amazon. *Org. Geochem.* **2001**, *32*, 1443–1458. [CrossRef]
- Tian, J.R.; Zhou, P.J. Phosphorus fractions of floodplain sediments and phosphorus exchange on the sediment-water interface in the lower reaches of the Han River in China. *Ecol. Eng.* 2007, 30, 264–270. [CrossRef]
- 21. Sun, S.J.; Huang, S.L.; Sun, X.M.; Wen, W. Phosphorus fractions and its release in the sediments of Haihe River, China. *J. Environ. Sci.* **2009**, *21*, 291–295. [CrossRef]
- 22. Nürnberg, G.K. Prediction of phosphorus release rates from total and reductant-soluble phosphorus in anoxic lake sediments. *Can. J. Fish. Aqua. Sci.* **1988**, *45*, 453–462. [CrossRef]
- 23. Loh, P.S.; Molot, L.A.; Nürnberg, G.K.; Watson, S.B.; Ginn, B. Evaluating relationships between sediment chemistry and anoxic phosphorus and iron release across three different water bodies. *Inland Waters* **2013**, *3*, 105–118. [CrossRef]
- 24. Shan, B.; Li, J.; Zhang, W.; Di, Z.; Jin, X. Characteristics of phosphorus components in the sediments of main rivers into the Bohai Sea. *Ecol. Eng.* **2016**, *97*, 426–433. [CrossRef]
- 25. Adhikari, P.L.; White, J.R.; Maiti, K.; Nguyen, N. Phosphorus speciation and sedimentary phosphorus release from the Gulf of Mexico sediments: Implication for hypoxia. *Estuar. Coast. Shelf Sci.* **2015**, *164*, 77–85. [CrossRef]

- 26. Ertel, J.R.; Hedges, J.I. The lignin component of humic substances: Distribution among soil and sedimentary humic, fulvic, and base-insoluble fractions. *Geochim. Cosmochim. Acta* **1984**, *48*, 2065–2074. [CrossRef]
- 27. Meyers, P.A. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.* **1994**, *114*, 289–302. [CrossRef]
- 28. Kopáček, J.; Borovec, J.; Hejzlar, J.; Ulrich, K.-U.; Norton, S.A.; Amirbahman, A. Aluminum control of phosphorus sorption by lake sediments. *Environ. Sci. Technol.* **2005**, *39*, 8784–8789. [CrossRef] [PubMed]
- 29. Hiriart-Baer, V.P.; Milne, J.E.; Marvin, C.H. Temporal trends in phosphorus and lacustrine productivity in Lake Simcoe inferred from lake sediment. *J. Great Lakes Res.* **2011**, *37*, 764–771. [CrossRef]
- Ruban, V.; Lópezsánchez, J.F.; Pardo, P.; Rauret, G.; Muntau, H.; Quevauviller, P. Selection and evaluation of sequential extraction procedures for the determination of phosphorus forms in lake sediment. *J. Environ. Monit.* 1999, 1, 51–56. [CrossRef]
- Ruban, V.; Lópezsánchez, J.F.; Pardo, P.; Rauret, G.; Muntau, H.; Quevauviller, P. Development of a harmonised phosphorus extraction procedure and certification of a sediment reference material. *J. Environ. Monit.* 2001, *3*, 121–125. [CrossRef]
- 32. Galhardo, C.X.; Masini, J.C. Spectrophotometric determination of phosphate and silicate by sequential injection using molybdenum blue chemistry. *Anal. Chim. Acta* 2000, 417, 191–200. [CrossRef]
- 33. Ni, J.; Lin, P.; Zhen, Y.; Yao, X.; Guo, L. Distribution, source and chemical speciation of phosphorus in surface sediments of the central Pacific Ocean. *Deep. Sea Res. Part I: Oceanogr. Res. Pap.* **2015**, *105*, 74–82. [CrossRef]
- 34. Goñi, M.A.; Yunker, M.B.; Macdonald, R.W.; Eglinton, T.I. Distribution and Sources of Organic Biomarkers in Arctic Sediments from the Mackenzie River and Beaufort Shelf. *Mar. Chem.* **2000**, *71*, 23–51. [CrossRef]
- 35. Miltner, A.; Emeis, K.-C. Origin and transport of terrestrial organic matter from the Oder lagoon to the Arkona Basin, Southern Baltic Sea. *Org. Geochem.* **2000**, *31*, 57–66. [CrossRef]
- Yuan, H.W.; Chen, J.F.; Ye, Y.; Lou, Z.H.; Jin, A.M.; Chen, X.G.; Jiang, Z.P.; Lin, Y.S.; Chen, C.T.A.; Loh, P.S. Sources and distribution of sedimentary organic matter along the Andong salt marsh, Hangzhou Bay. *J. Mar. Syst.* 2017, 174, 78–88. [CrossRef]
- Selvaraj, K.; Lee, T.Y.; Yang, J.Y.T.; Canuel, E.A.; Huang, J.C.; Dai, M.; Liu, J.T.; Kao, S.J. Stable isotopic and biomarker evidence of terrigeneous organic matter export to the deep sea during tropical storm. *Mar. Geol.* 2015, 364, 32–42. [CrossRef]
- Kang, X.M.; Song, J.M.; Yuan, H.M.; Shi, X.; Wang, W.F.; Li, X.G.; Li, N.; Duan, L.Q. Phosphorus speciation and its bioavailability in sediments of the Jiaozhou Bay. *Estuar. Coast. Shelf Sci.* 2017, 188, 127–136. [CrossRef]
- Zhang, W.L.; Zeng, C.S.; Tong, C.; Zhai, S.J.; Lin, X. Spatial distribution of phosphorus speciation in marsh sediments along a hydrologic gradient in a subtropical estuarine wetland, China. *Estuar. Coast. Shelf Sci.* 2015, 154, 30–38. [CrossRef]
- 40. Cui, Y.; Xiao, R.; Xie, Y.; Zhang, M. Phosphorus fraction and phosphate sorption-release characteristics of the wetland sediments in the Yangtze River Delta. *Phys. Chem. Earth* **2018**, *103*, 19–27. [CrossRef]
- 41. Yang, Y.; Gao, B.; Hao, H.; Zhou, H.; Lu, J. Nitrogen and phosphorus in sediments in China: A national-scale assessment and review. *Sci. Total Environ.* **2017**, *576*, 840–849. [CrossRef]
- 42. Yang, B.; Liu, S.-M.; Wu, Y.; Zhang, J. Phosphorus speciation and availability in sediments off the eastern coast of Hainan Island, South China Sea. *Conti. Shelf Res.* **2016**, *118*, 111–127. [CrossRef]
- Mayorga, E.; Aufdenkampe, A.K.; Masiello, C.A.; Kruscge, A.V.; Hedges, J.I.; Quay, P.D.; Richey, J.E.; Brown, T.A. Young organic matter as a source of carbon dioxide outgassing from Amazonian rivers. *Nature* 2005, 436, 538–541. [CrossRef] [PubMed]
- Chen, C.T.A.; Zhai, W.; Dai, M. Riverine input and air-sea CO<sub>2</sub> exchanges near the Changjiang (Yangtze River) Estuary: Status quo and implication on possible future changes in metabolic status. *Conti. Shelf Res.* 2008, 28, 1476–1482. [CrossRef]
- 45. Li, Y.; Pan, D.Z.; Chanson, H.; Pan, C.H. Real-time characteristics of tidal bore propagation in the Qiantang River Estuary, China, recorded by marine radar. *Conti. Shelf Res.* **2019**, *180*, 48–58. [CrossRef]



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