Variation pattern of particulate organic carbon and nitrogen in oceans and inland waters

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Abstract: We examined the relationship between, and variations in, particulate organic carbon (POC) and particulate organic nitrogen (PON) based on previously acquired ocean and inland water data. Some new points were found beside the traditional latitude, depth and temperature dependence of POC, PON and POC/PON. The global average value of POC/PON (7.54 ± 3.82, mean value ± standard deviation) is higher than the Redfield ratio (6.63). The mean values of POC/PON in south and north hemisphere are 7.40±3.83 and 7.80±3.92, respectively. The high values of POC/PON appeared between 80° N ~ 90° N (12.2 ± 7.5) and 70° N ~ 80° N (9.4 ± 6.4), and relatively low POC/PON were found from 20 °N (6.6 ± 2.8) to 40 °N (6.7 ± 2.7). The latitudinal dependency of POC/PON in the northern hemisphere is much stronger than in the southern hemisphere. Variations of POC/PON in lake water also showed similar latitude-dependency of POC/PON in ocean water, but significantly regulated by lake's morphology, trophic state and climate, etc. factors. Higher POC and PON could

be expected in the river and coastal waters, while POC/PON significantly increased from 6.89 ± 2.38 to 7.59 ±

4.22 in north hemisphere with the increasing rate of 0.0024/km from coastal to open ocean. The coupling

relationship between POC and PON in oceans is much stronger than in inland waters. Variations in POC, PON

and POC/PON in inland waters should receive more attention due to the importance of these values to global

carbon and nitrogen cycles and the indeterminacy of the relationship between POC and PON.

1. Introduction

Inland waters and oceans transport, transform and contain large amounts of organic carbon and thus play an important

role in global carbon, nitrogen and nutrient cycles (Cole et al., 2007). Inland waters receive carbon from terrestrial

ecosystems at a rate of 2.9 PgC/yr. Of this carbon, 21% (0.6 PgC/yr) is stored in sediment, 48% (1.4 PgC/yr) is emitted

to the atmosphere as CO_2, and 31% (0.9 PgC/yr) is discharged into oceans via rivers (Tranvik et al., 2009). Recent

studies suggest that the emission of CO_2 in inland water could increased to 2.1 PgC/yr (Raymond et al., 2013) from

past estimates of 0.8 (Cole et al., 2007) and 1.4 PgC/yr (Tranvik et al., 2009). The receive carbon in inland water from

terrestrial ecosystems can reach to 5.7 PgC/yr in recent study (Le Quéré et al., 2015). The stored in the sediment and

discharged into ocean carbon could increased to 2.8 PgC/yr by subject 2.1 PgC/yr from 5.7 PgC/yr according to

Raymond et al., (2013) and Le Quéré et al., (2015). The ocean is an important carbon sink due to the flux of riverine

carbon (0.9 PgC/yr, Tranvik et al., 2009, maybe more than 0.9 PgC/yr according to Raymond et al., 2013 and Le Quéré

et al., 2015) and the absorption of atmospheric CO_2, which is fixed by phytoplankton at a rate of 2.3±0.7 PgC/yr (IPCC,

2013).

There is a strong relationship between nitrogen and carbon cycles in natural aquatic ecosystems. The input of nitrogen into aquatic ecosystems as nutrients from the land and atmosphere stimulates additional uptake of carbon (Hyvönen et al., 2007), and fixed carbon and nitrogen are released as gas and ions (CO_2, CH_4 and NOx, etc.) when organisms are mineralized (Galloway, et al., 2004; Flückiger et al., 2004). This relationship is made stronger by the life processes of organisms, but it is weakened by variations in the sequestration and mineralization rates of carbon and nitrogen (Gruber and Galloway, 2008). The relationship between carbon and nitrogen is relatively stable in natural aquatic ecosystems, although carbon and nitrogen levels vary depending on autotrophic biotypes and water environment (Thornton and McManus, 1994; Gruber and Galloway, 2008). This relationship is also affected by human activity (Gruber and Galloway, 2008; Galloway et al., 2008; Perga et al., 2016).

The elemental composition of organic matter affects the global biogeochemical cycle and varies depending on its sources (DeVries and Detsch, 2014). The carbon to nitrogen (C/N) ratio affected by the life processes of organisms and is a good measure of the relationship between carbon and nitrogen cycles (Sterner and Elser, 2002; Schneider et al., 2003; Meisel and Struck, 2011; Babbin et al., 2014). Organic nitrogen originates from plant proteins and nucleic acids and, to a lesser extent, from lignin and cellulose. The C/N ratio in terrestrial plants is much higher than in autotrophic phytoplankton due to their high lignin and cellulose content (Kendall et al., 2001; Mcgroddy et al., 2004; Watanabe and Kuwae, 2015). This leads to a C/N ratio that is higher and much more variable in inland waters than in offshore oceans; there is also a sharp contrast in nutrient levels and water residence times between the two (Hall et al., 2007,

60   Sterner et al., 2008; Watanabe and Kuwae, 2015). Several studies suggest that the currently observed C/N ratio, and

variations in it, are difficult to reconcile with the value estimated by Redfield (6.63-7.7), which was based on data

taken from ocean-surface plankton and deep, dissolved nutrients from 1898 to 1933 (Kokrtzinger et al., 2001;

Schneider et al., 2004; Koeve, 2006; Sterner et al., 2008; Martiny et al., 2013a; 2013b; DeVries and Deutsch, 2014;

Watanabe and Kuwae, 2015). The factors influencing variations in C/N are complex due to the loss and product rate of

65   POC and PON. Nitrogen and light limitation and phytoplankton can only explain approximately 20% of the variation

in C/N on a global scale (Martiny et al., 2013b). The temperature, composition of organic matter, dynamic

characteristics of water will significantly conduct the loss rates of OC and ON in the water (Stief 2007; Gälman et al.,

2008; Gudasz et al., 2010; Sobek et al., 2014; Cardoso et al., 2014). Other factors that regulate C/N on a regional scale

include microzooplankton (Talmy et al., 2016), heterotrophic microbes (Crawford et al., 2015) and terrestrial

70   organisms (Jiang, 2013). This variation in C/N increases the uncertainty of global carbon and nitrogen estimation

(Babbin, 2014). Consequently, understanding temporal and spatial variation in particulate organic carbon (POC),

particulate organic nitrogen (PON) and the POC/PON ratio, as well as the processes that govern POC/PON, is critical

to better explain the global biogeochemical cycles of carbon and nitrogen.

Recently, global oceanic studies have proposed that the median global value of C/N in oceans is close to the Redfield

75   value, but there is significant regional variation (Martiny et al., 2013b). Meanwhile, POC/PON exhibits a strong

latitudinal pattern, with lower values in the cold ocean waters of the higher latitudes (Martiny et al., 2013a). In contrast

to the study of oceanic POC/PON, the elemental stoichiometry research of C/N in inland waters is still need to be

complement and perfection (Sterner et al., 2008). In this study, we extend the study area and dataset of previous studies (Martiny et al., 2013b; 2014; Kim et al., 2015), from 60° N ~ 78° S with 40482 samples to 80° N ~ 78° S with 63184

80   samples, to re-examine variations in POC, PON and POC/PON on a global scale. Values for POC, PON and POC/PON

in inland waters were combined to further reveal the relationship between POC and PON and deviations in POC/PON

from the classical Redfield value.

2. Data and Methods

2.1 Data collection

85   To achieve this study's objective, datasets from previously published studies and publicly available online data

were acquired (detailed information was listed in the supporting material Table S1). This compiled dataset

contained 63,184 paired POC and PON samples (northern hemisphere, 40,809 samples; southern hemisphere,

22,448 samples) from offshore and coastal oceans and 23,996 samples from inland waters (rivers and lakes). The

spatial distribution of samples is shown in Figure 1. Measurements of particulate elements were carried out by

90   standard methods, which C and N were analyzed on C/N elemental analyzer after water samples filtered through

preweighed, precombusted (450°C for 4 hours) GF/F filters and acidified treatment. The units of POC and PON

in all data (μg/L, μm/L) were unified to μm/L via molecular-weight of C and N.

Geographical land and ocean distribution data and soil organic carbon data (harmonized world soil database, http://daac.ornl.gov/SOILS/guides/HWSD.html) were also used to analyze the factors influencing variations in

95 POC, PON and POC/PON.
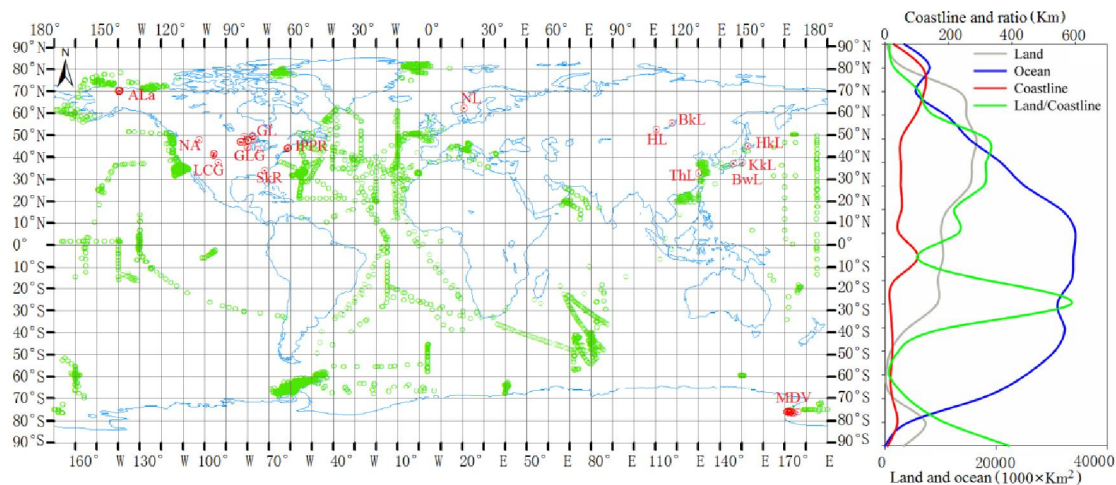
Figure 1 Global distribution of paired samples of POC and PON. Green circles are oceanic samples and red circles are inland samples. Land and ocean area, coastline length and the ratio of land area to coastline are also shown. The original map data of world vector downloaded from http://www.naturalearthdata.com/.

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2.2 Data category and analyses methods

Samples with extremely low POC (< 0.01 μm/L) and PON (< 0.001 μm/L) values were removed due to the limit

of detection for the analysis. The collection data of ocean from previous studies and web-sharing database

contained variable ranges of POC and PON with latitude, time, depth and temperature. In order to reveal the

105 pattern of POC and PON, the remaining data were classified into groups relating to latitude, depth, offshore

distance and temperature to aid data analysis: 1) Oceanic POC and PON data, taken from 80° N to 78° S, were

divided into 17 ranges with 10° latitudinal intervals (Table S2). The data in each latitudinal range include all

ranges of temperature, time and depth for POC and PON. 2) Ocean POC and PON samples were separated into

0-5m, 5-10m, 10-20m, 20-80m and >80m depth ranges according to the distribution of samples' number (Table

110 S3 and Figure S1). The distribution of samples in each depth covers most ranges of latitude, time and temperature

for POC and PON. 3) POC and PON samples were divided into temperature ranges with an interval of approximately 1 degree centigrade. 4) Offshore distance ranges (5, 10, 15, 20, 25, 50, 75, 100, 125, 150, 200, 300, 500, 800 and 1100 km) were created via buffers establishment module in Arcgis 10 (Esri), and the samples located in each range were separated and statistically analyzed (Table S4). All ranges of POC and PON with different depth, time and latitude in each buffer were treated as same category for each offshore distance range. The samples located on different ranges of buffers (different distance from offshore) can show the variation of POC, PON and POC/PON from coastal to open sea (Figure S2).

The lake collection data of POC and PON was analyzed for individual lakes. Some measurements of POC and PON are multiple observations in many small lakes. These observational data were processed as lake groups, such as Great Lakes Group, Lacustrine Central Group, Alaskan Lakes and so on (Table S7).

The number of samples was listed in the tables of supporting material (Table S2 – S6). Statistical values (mean, maximum, minimum and standard deviation) were calculated for POC, PON and POC/PON for all groups. The relationships between PON and POC for all categories (ocean and lakes) were also regressed and listed in the supporting material. The relationships between particulate organic matter (PON and POC) and water properties (temperature, DOM, chlorophyll and total suspended sediment), as well as the soil organic carbon, were regressed to explore the effect of each influencing factors to the variation pattern of POC and PON.

The soil organic carbon data from harmonized world soil database was also divided into 17 ranges with 10° latitudinal intervals according to the process of oceanic POC and PON data. The soil organic carbon and oceanic

POC, PON and POC/PON in the same latitudinal range were statistically compared with mean, maximum, and minimum value, respectively. The relationships between soil organic carbon and POC, PON and POC/PON reveal the potential impact of terrestrial organic matter to the variation of oceanic POC, PON and POC/PON.

3. Results and discussion

3.1 Latitude- and depth-dependent POC, PON and POC/PON variation in the ocean

The spatial distributions of POC, PON and POC/PON significantly affect marine carbon and nitrogen flux estimation as well as the air-ocean exchange of CO_2 via the global ocean carbon cycle model (Schneider et al., 2004). Studies have proposed that the elemental ratio (POC/PON) of particulate organic matter in marine environments is characterized by a strong latitudinal pattern (for 60° N ~ 60° S) due to the influence of nutrients, temperature and respiration (Martiny et al., 2013a; Devries and Deutsch, 2014). Microzooplankton and algae production also regulate POC/PON in the ocean (Tamelander et al., 2013; Crawford et al., 2015; Talmy et al., 2016). PON and POC co-vary, resulting in a strongly coupled relationship. Both POC and PON show a latitudinal pattern globally, but variations in POC and PON in the northern hemisphere are much more variable than in the southern hemisphere (Figure 2A, B); the latitudinal dependency of POC/PON in the northern hemisphere is much stronger than in the southern hemisphere (Figure 2C). In contrast to a previous study (Crawford et al., 2015), which observed that a low POC/PON ratio (2.1 to 5.6) existed in the middle-high latitudes (80° N ~ 50° N) due to the presence of heterotrophic microbes in summer time, we found high values for POC/PON, 12.2 ± 7.5 and

9.4±6.4 between 80° N ~ 90° N and 70° N ~ 80° N, respectively. Relatively low POC/PON ratios were found

from 20 °N (6.6 ± 2.8) to 40 °N (6.7 ± 2.7). Consistent with earlier studies, the low POC/PON ratios were very

close to the Redfield value (6.625). The determined coefficient (R^2) of the relationship between POC and PON in

the southern hemisphere is slightly higher than in the northern hemisphere (Table S2). The mean value of

150   POC/PON in northern hemisphere (7.50 ± 4.65) is slight lower than in southern hemisphere (7.81 ± 3.79). These

indicate that geobiochemical processes and the circulation of carbon and nitrogen in the northern hemisphere are

much more complex than in the southern hemisphere. The variation for POC/PON in the northern hemisphere is

bigger than in the southern hemisphere (Table S2).

Linear functions (including and excluding intercepts) and power functions can be used to express the relationship

155   between carbon and nitrogen for each latitudinal range (Table S2). However, the optimal function is different for

each latitudinal range. The best regression results with the highest R^2 are noted with an asterisk in Table S2. A

power function is used to describe the relationship between carbon and nitrogen globally (POC = (6.998±0.645) ×

$PON^{(0.901±0.081)}$, R^2 = 0.905 ± 0.052). A linear function (including and excluding intercepts) also describes the

relationship between carbon and nitrogen well (POC = (7.545±2.498) × PON + (0.302±2.658), R^2 = 0.891 ±

160   0.047; POC = (7.666±2.169) × PON, R^2 = 0.882 ± 0.048). The regression functions for POC and PON are listed in

Table S2. The slopes of the linear regressions in this study are bigger than in previous regional studies (e.g., 5.89,

5.06 and 4.63, Caperon, 1976; 6.43, Verity, 2002; 5.8, Lara et al., 2010; 5.53 and 5.38, Crawford et al., 2015; 6.62,

Cai, P.H. et al., 2015; 6.75, Kim et al., 2015). However, the global mean value of POC/PON (7.54 ± 3.82) is

higher than the Redfield ratio of 6.63, as well as some recent studies (6.62, Cai, P.H. et al., 2015; 6.75, Kim et al.,

165   2015).

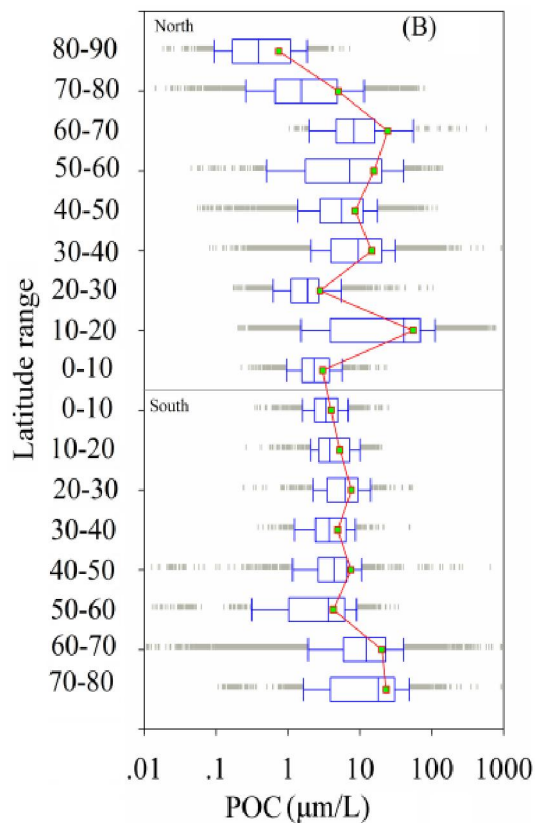
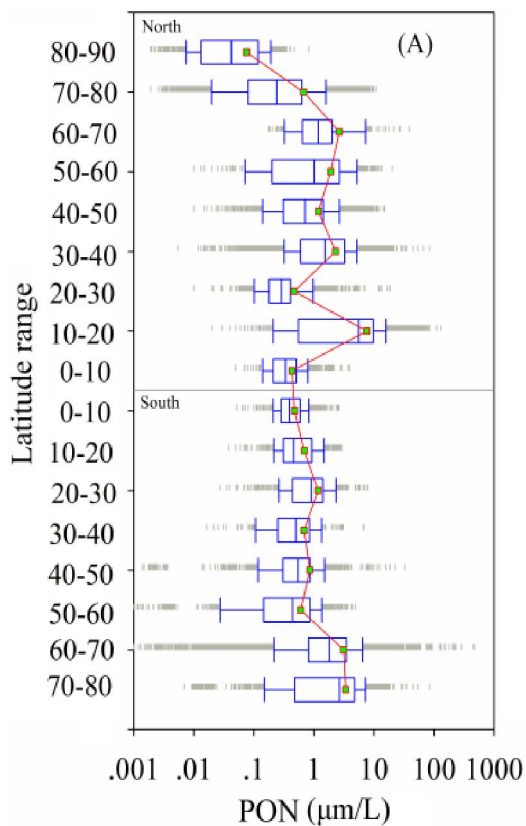
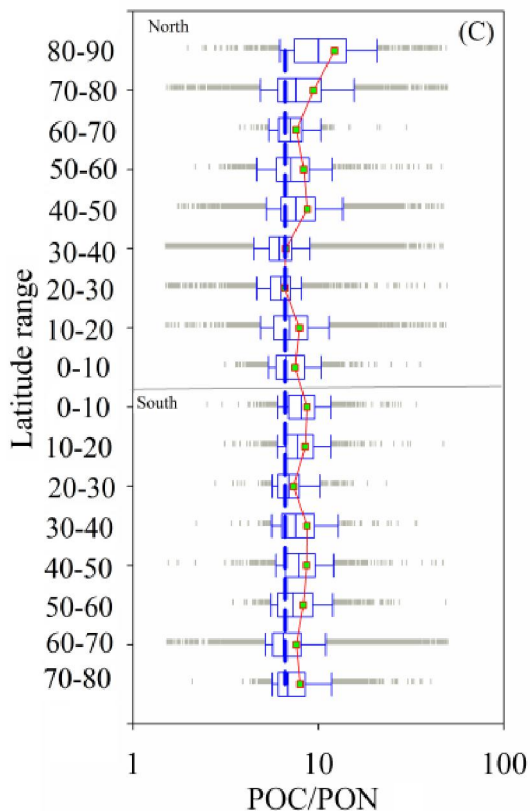



Figure 2 Latitudinal variation of PON, POC and the POC/PON ratio from the compiled statistical results of depth-integrated data for all ocean data. The box plots show the median and 25th and 75th percentiles, with whiskers covering most of the data. The red line with green boxes shows the mean value for each latitudinal range. The bold blue dashed line in (C) is the Redfield value (6.625).

The vertical distributions of POC and PON, and the resulting variations in POC/PON, have a critical impact on

carbon and nitrogen cycles in oceans and should be considered in models of the biogeochemical cycle (Schneider

et al., 2003; 2004; 2005; Babbin et al., 2014). These distributions also indicate that the depth-dependence of POC

and PON in the southern hemisphere (POC: 17.83 ± 2.03 μmol/L ,PON: 2.72 ± 0.29 μmol/L) is stronger than in

the northern hemisphere (POC: 16.79 ± 1.51 μmol/L, PON: 2.49 ± 0.23 μmol/L) (Figure 3A, B). However, the

depth-dependence of POC/PON in the southern hemisphere is weaker than that in the northern hemisphere

(Figure 3C). POC/PON increased significantly, from 6.88±2.3 (0 - 5 m) to 8.36 ± 6.5 (> 80 m), in the northern hemisphere but was nearly constant (7.92 ± 0.10) in the southern hemisphere (Table S3). Increases in POC/PON with depth in the northern and southern hemispheres occurred at rates of 5.2/km and 2.5/km (depth < 200 m), respectively. These increasing rates are much higher than the 0.2 ± 0.1/km (0 - >5000 m) rate proposed by Schneider (2004). This may be due to the predominance of nitrogen remineralization in shallow ocean water (Babbin et al., 2014). The linear slope of POC and PON in the northern hemisphere (7.11 ± 0.36) is larger than in the southern hemisphere (6.12±0.72) (Table S3) with a global mean value of 6.341±0.856.

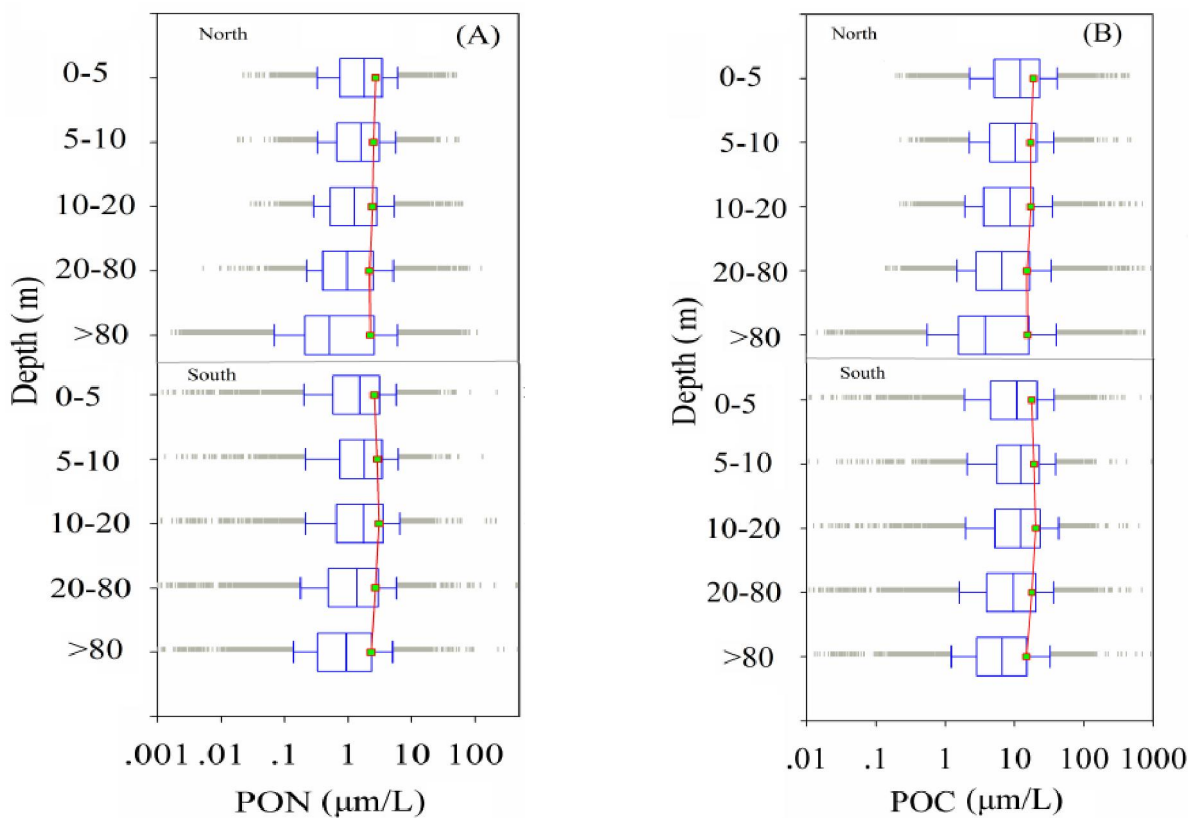
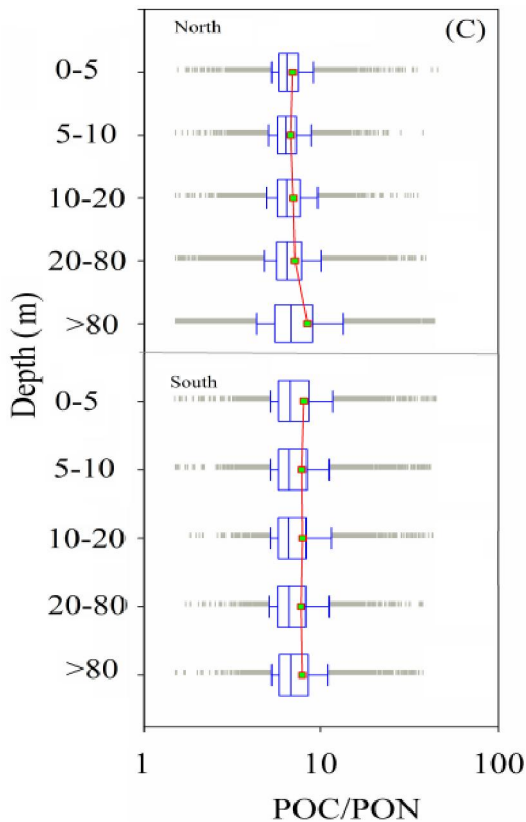



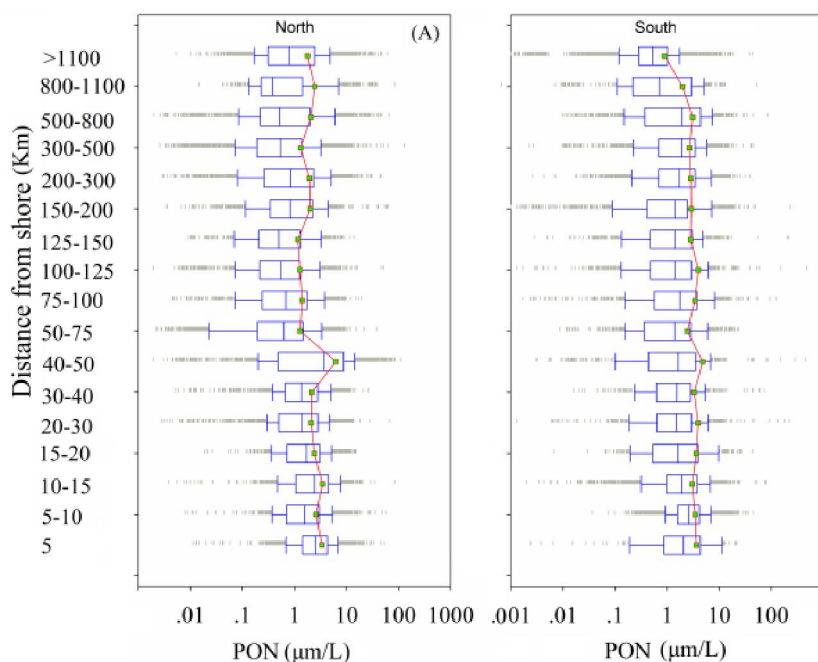
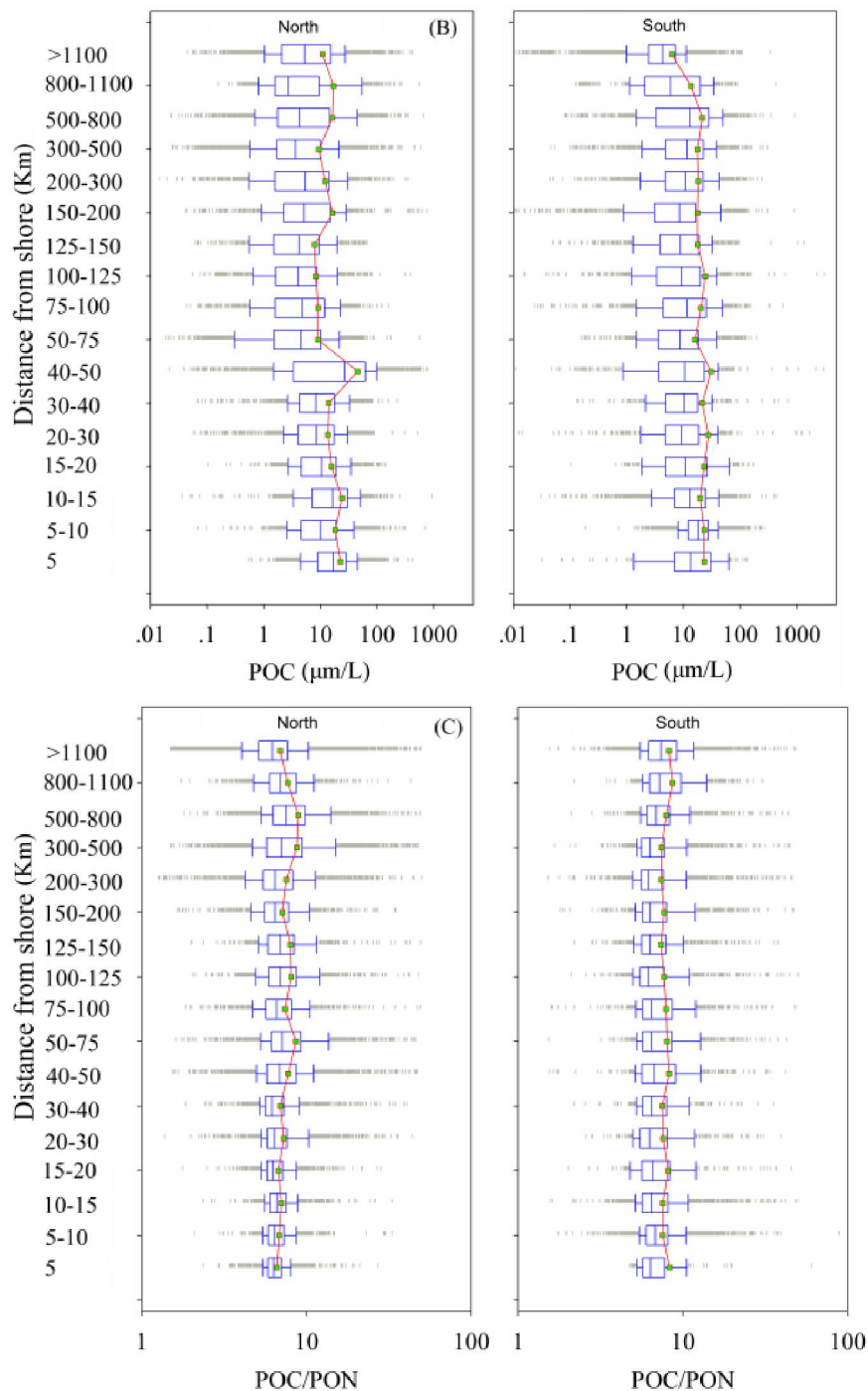
Figure 3 Depth-dependence of POC and PON in the southern hemisphere and depth-dependence of POC/PON in the northern hemisphere. The box plots show the median and 25th and 75th percentiles, with whiskers covering most of the data. The red line with green boxes shows the mean value at each depth. The number of samples for each depth is listed in Table S3.

3.2 Variations in POC, PON and POC/PON with offshore distance

Previous studies indicate that about 0.9 PgC/yr of carbon are discharged from rivers to oceans (Cole et al., 2007); approximately 50% of terrestrial carbon exists in organic form (0.3 PgC/yr of DOC and 0.2 PgC/yr of POC) (Cole et al., 2007; Bianchi, 2011). The enriched terrestrial carbon delivered from rivers causes variations in POC, PON and POC/PON, especially in coastal regions (Martiny et al., 2013b), although a large amount (0.3 PgC/yr) of terrestrial carbon (0.5 PgC/yr) is emitted as CO_2 (Cai, W.J., 2011) and most of the remaining terrestrial carbon

sinks as sediment in estuaries.

Variations in POC and PON levels with distance from shore show that there is a significant separation zone (50 km) dividing POC and PON levels into two regions in the northern hemisphere (Figure 4A, B). POC levels close to land (0 - 50 km) (region of close to shore, 21.90±11.01 μm/L) are nearly two times larger than in regions more than 50 km from land (region of offshore, 11.65±3.58 μm/L) due to terrestrial influences. The distribution of PON is similar; PON levels are higher close to shore (3.19±1.46 μm/L, 0 - 50 km) compared to offshore (1.67±0.44 μm/L, >50 km). Terrestrial impacts on POC and PON levels in the southern hemisphere are relatively weak (POC, 20.14 ± 5.51 μm/L; PON 3.12 ± 0.87 μm/L) for all distances from shore (Figure 4A, B). In addition, variation in POC/PON with distance from shore is insignificant in both the northern (7.5 ± 4.6) and southern (7.8 ± 3.8) hemispheres. The POC/PON ratio close to shore (6.89 ± 2.38 in north and 7.59 ± 3.77 in south) is smaller than in offshore regions (7.59 ± 4.22 in north and 7.90 ± 3.99 in south). Coastal water with relatively high POC and PON levels has a low POC/PON ratio in the northern and south hemisphere (Table S4). This is inconsistent with previous studies that show coastal water has a higher POC/PON ratio than offshore water (Sterner et al., 2008; Kaiser et al., 2014; Watanabe and Kuwae, 2015) due to the discharge of terrestrial organic matter (Hilton et al., 2015; Cai, Y.H. et al., 2015). The over-consumption of carbon in coastal waters reduces the POC/PON ratio of terrestrial organic matter. Previous study proposed that more than 0.2 PgC/yr of CO_2 is emitted from coastal waters due to the microbial decomposition of terrestrial organic matter (Cai, W.J. et al., 2011) as well as the priming effect (Bianchi, 2011). Zooplankton, phytoplankton and high nutrient levels also reduce POC/PON in

coastal waters (Koeve, 2006; Martiny et al., 2013b; Watanabe and Kuwae, 2015; Talmy et al., 2016). The relatively high POC/PON ratio in offshore water is primary caused by small phytoplankton, which is the dominant contributor to POC levels at the ocean surface and has a high POC/PON ratio (Richardson and Jackson, 2007; Puigcorbé et al., 2015). The increase of POC/PON with the distance is very significant in the North hemisphere with the increasing rate of 0.0024/km (POC/PON=0.0024*D+7.1764, R^2=0.519), but insignificant in South hemisphere with rate of 0.0004/km (POC/PON=0.0004*D+7.7346, R^2=0.118) (Figure S3).

225   Figure 4 Variation of POC, PON and POC/PON with distance from shore. The number of samples for each buffer is listed in Table S4. The box plots show the median and 25th and 75th percentiles, with whiskers covering most of the data. The red line with green boxes shows the mean value for each range.

3.3 Variability of POC, PON and POC/PON in inland waters

 3.3.1 Lake water

Inland waters play an important role in the global carbon cycle, linking the terrestrial, atmospheric, and oceanic

carbon pools. The lakes was sorted by the latitude according to the position. POC and PON in lake waters exhibit

a similar trend with that in ocean of north hemisphere, which POC and PON decreased with the latitude, but

greater variability than in oceans due to the strongly dual influences of terrestrial and aquatic organic matter

235 (Figure 5) (Wilkinson et al., 2013). The POC/PON in lake waters decreased with the latitude. However, the lake's

morphology, trophic state, climate and other influencing factors also cloud regulate latitude-dependent of

POC/PON in lake waters. For example, Kasumigaura Lake is an extremely eutrophic lake, with a mean (from

1977 to 2013) chlorophyll-a concentration of 67 ± 44 µg/L. High productivity in Kasumigaura Lake leads to

relatively high POC and PON levels (POC, 332.76 µm/L and PON, 47.94 µm/L). The trophic state of Lake Taihu

240 is similar to Kasumigaura Lake (Huang et al., 2015), and the POC and PON levels in Lake Taihu are very close to

those in Kasumigaura Lake. However, the POC/PON ratio in Lake Taihu (4.04) is much smaller than in

Kasumigaura Lake due to over-consumption of organic carbon; large areal lakes, (e.g., Lake Taihu) emit much

more CO_2 than small lakes (e.g., Kasumigaura Lake) (Xiao et al., 2014; Hotchkiss et al., 2015). The Great Lakes

(large areal lakes) also have a low POC/PON ratio (5.07). Lakes located in cold-dry climatic zones (McMurdo

245 Dry Valleys Lakes, Alaskan Lakes, Norwegian Lakes, Lake Baikal, and Hovsgol Lake) tend to have low POC and

PON levels but a high POC/PON ratio (Figure 5). This agrees with previous studies that show that inland waters

maintain high POC/PON ratios due to the strong impact of terrestrial organic matter (Guo et al., 2003; Cai, Y.H. et al., 2008). The data indicate that the average POC/PON ratios in lakes are approximately 10.6 at the global scale, 5.67 for deep lakes, 8.16 for shallow lakes, 11.46 for frigid northern lakes and 10.37 for temperate lakes (Chen et al., 2015). The relationships of PON and POC for each lake were listed in Table S5.

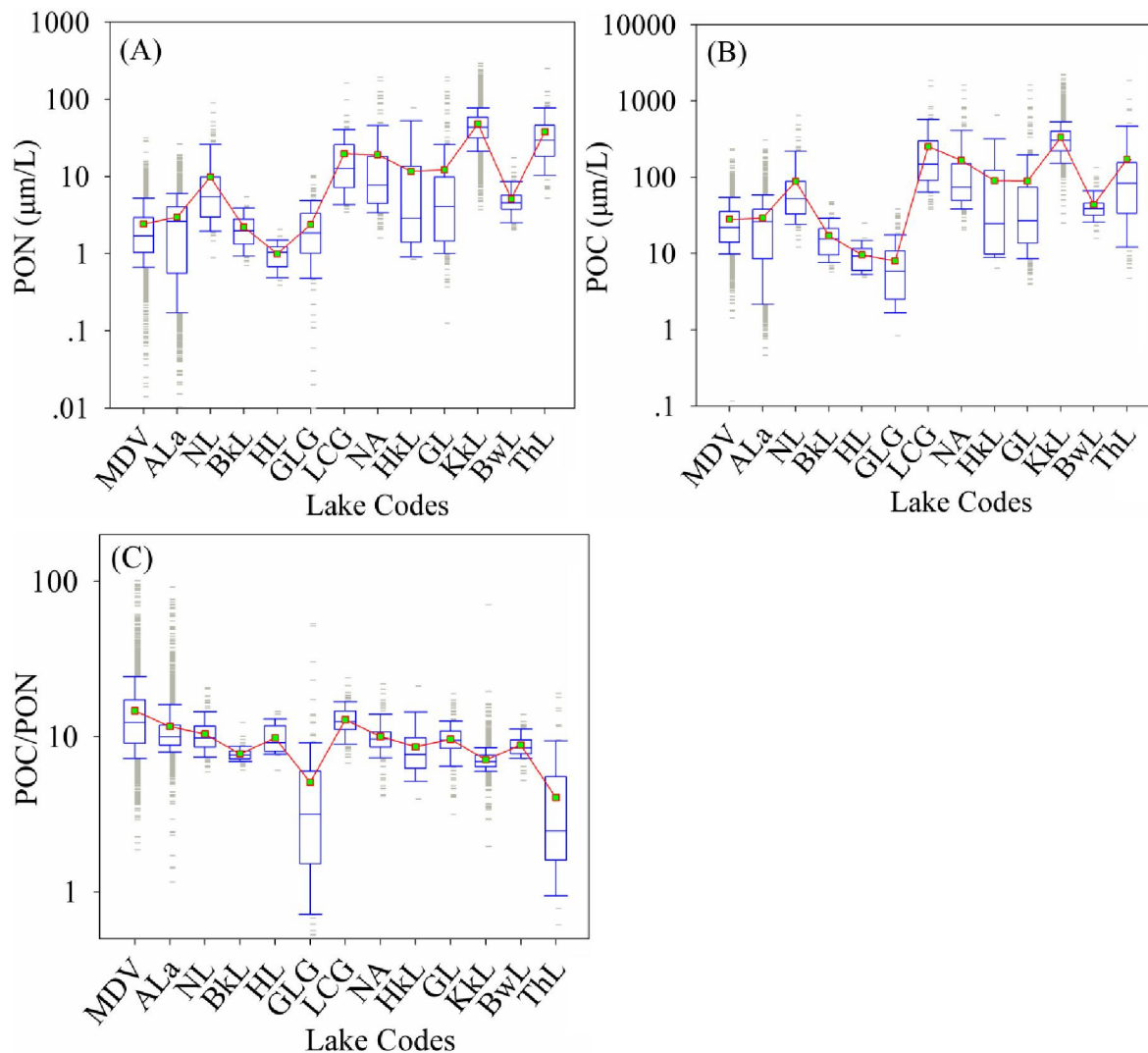



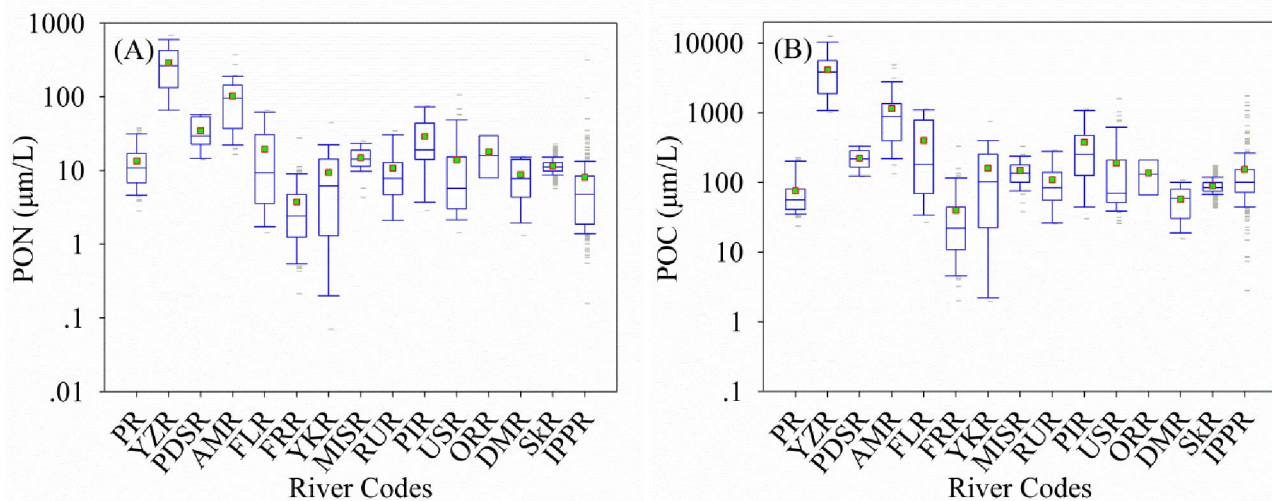
Figure 5 Variation of PON, POC and POC/PON in lake waters. The lakes are mainly located in the northern hemisphere. Eutrophic, small, large, and shallow lakes are included in the dataset. MDV is McMurdo Dry Valleys

Lakes (Antarctica), ALa is Alaskan Lakes(USA), NL is Norwegian Lakes (Norway), NA is Northern American Lakes (USA), HkL is Hokkaido Lakes (Japan), LCG is Lacustrine Central Group (USA), KkL is Lake Kasumigaura (Japan), BwL is Lake Biwa (Japan), HL is Lake Hovsgol (Mongolia), BkL is Lake Baikal (Russia), GL is Green Lake (Canada), ThL is Lake Taihu (China), GLG is Great Lakes Group (USA), The box plots show the median and 25th and 75th percentiles, with whiskers covering most of the data. The red line with green boxes shows the mean value of each range. The lake names and their abbreviations were listed in the Table S7.

3.3.2 River water

Rivers not only bridge the carbon and nitrogen elemental cycles in the land and ocean through the transmission of organic matters, but also conduct the emission of CO_2 in the inland water (Raymond et al., 2013; Ward et al., 2017; Sawakuchi et al., 2017). The POC and PON in the river are relatively higher than that in the ocean and lake, especially in the big and high turbid rivers (such as Yanagtze River, Amazon River in figure 6). The POC and PON in Yanagtze River (the highest POC and PON river, 4154.6 ± 3109.6 μm/L and 290.7 ± 180.5μm/L) are proximate 100- and 80-fold bigger than in Fraser River (the lowest POC and PON river in this study, 39.7 ± 54.9 μm/L, 3.7 ± 4.3 μm/L), indicating the hugely spatial variation of POC and PON in river system. It also could manifest that big rivers with high POC and PON may discharge much more POC and PON into ocean (globally annual fluxe of POC is 216 Tg, Voss, 2009) accompanied by high runoff. Previous studies also proposed that that the temporal variation of POC and PON in river is significant (Verity, 2002; Ward et al., 2012). However, the variation of POC/PON (variable coefficient, 0.47) in river waters is much small than POC (variable coefficient, 2.03) and PON (variable coefficient, 1.81) in river water. The value and variation of POC/PON (12.5 ± 5.8 with variable coefficient of 0.47) in this study is much bigger than that in previous study (10.6 ± 2.3 with variable coefficient of 0.21, Meybeck, 1982). The highest POC/PON ratio appeared in the Ipswich and Parker rivers (IPPR,

28.73 in figure 6C). This value is higher than in previous studies on the Mississippi River (9.74 ± 0.70, this study; 9.7 Trefry et al., 1994; 14.4, Cai Y.H. et al., 2015), the USA central river (11.22 ± 1.86, Onstad et al., 2000) and

280   the Amazon River (10.8 ± 3.3, this study; 11.6, Moreira-Turcq et al., 2013), but it is still lower than in northern rivers such as the Chena River (32 ± 12, Guo et al., 2003; 34.33 (Cai, Y.H. et al., 2008). The lowest POC/PON ratio appeared in the Pearl River (PR, 6.02 ± 1.91), closing to the 5.67 for deep lakes (Chen et al., 2015). The latitude-dependent of POC, PON and POC/PON were not evaluated due to that the samples of each river were not follow the latitude-distribution. The relationships of PON and POC for each river were listed in Table S6.

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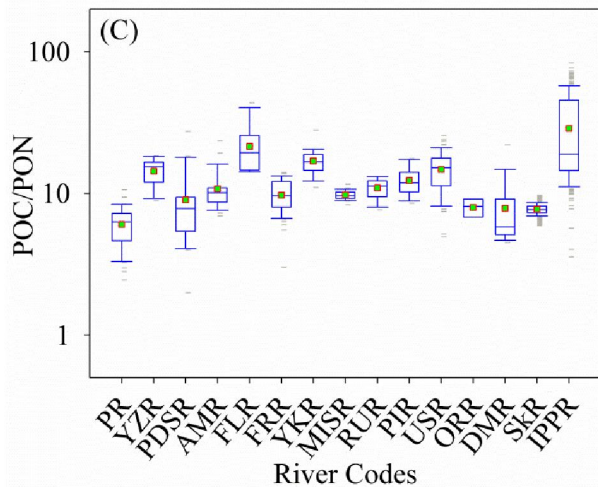


Figure 6 Variation of PON, POC and POC/PON in river waters. PR is Pearl River (China), YZR is Yanagtze River (China), PDSR is paraiba do sul River (Brazil), AMR is Amazon River (Brazil), FLR is Fly River (Papua New Guinea), FRR is Fraser River (Canada), YKR isYukon River (USA), MISR is Mississippi River (USA), RUR is Russian rivers (Russian), PIR is Ping River (Thailand), USR is Union and Skokomish River (USA), ORR is Orinoco river(Venezuela), DMR is Mandovi river (India), SkR is Skidaway River (USA), IPPR is Ipswich and Parker rivers (USA).

3.4 Drivers of POC, PON and POC/PON variation

3.4.1 Terrestrial organic carbon

Land is a huge organic carbon pool and delivers a large amount of POC into oceans via rivers (IPCC, 2013). Global studies of riverine export of POC have proposed that POC export from land to the oceans is mostly caused by physical erosion (Galy et al., 2015). The storage and distribution of soil organic carbon (Köchy et al., 2015) in the global terrestrial sphere is highly positively correlated to POC and PON levels in the oceans (Figure 6A, B). The linear functions POC = 0.0961*SOC + 3.4355 (R^2=0.86) and PON = 0.0103*SOC + 0.5132 (R^2=0.83) express the relationship between PON, POC and SOC well, except between of 40 °N ~ 50 °N and 80 °N ~ 90 °N (marked with an ellipse in Figure 7A, B). PON and POC levels between 40 °N ~ 50 °N are underestimated by the

relationship between PON, POC and SOC due to excess organic matter from phytoplankton (satellite estimation result chlorophyll-a in ocean color products, http://oceancolor.gsfc.nasa.gov/cgi/l3). Overestimated PON and POC levels for 80 °N ~ 90 °N are primarily caused by ice on the land and ocean. POC/PON is negatively

305   correlated to the ratio of land area to coastline length (land/coastline): POC/PON =11.938*(land/coastline)$^{-0.078}$

(R^2=0.41) (Figure 7C).

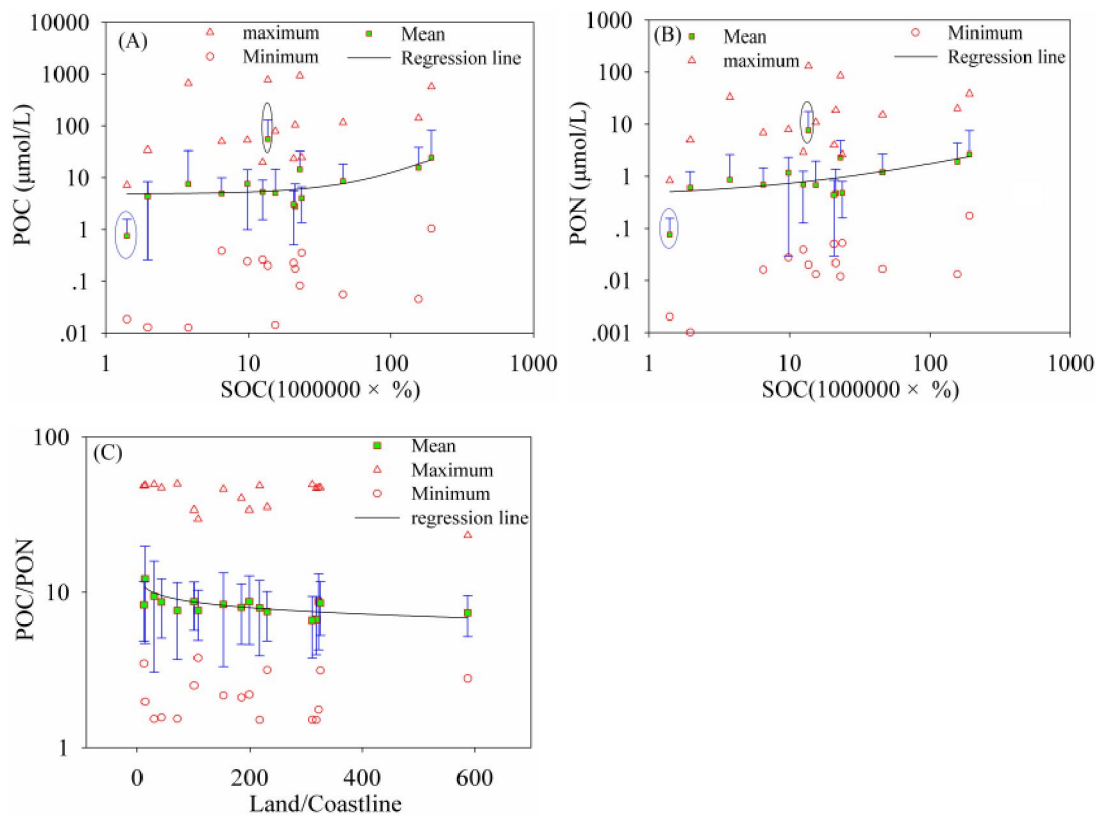



Figure 7 (A) and (B) Relationship between POC, PON and soil organic carbon. (C) The relationship between
310   POC/PON and the ratio of land area to coastal linear length. The red boxes with green shading are the mean values of POC, PON and POC/PON in each latitudinal range, the blue line is the standard deviation, and the red triangle and roundness are the maximum and minimum values of POC, PON and POC/PON in each latitudinal range.

3.4.2 Temperature

The temperature dependence of organic carbon production (e.g., primary production, released from permafrost and soil erosion) and consumption (e.g., mineralization, respiration and methane emission) increases the influence of temperature on aquatic ecosystems and reflects the importance of temperature in the carbon cycle (Gudasz et al., 2010; Padfield et al., 2015; Yvon-Durocher et al., 2011a; 2011b; 2012; 2014; 2015a; 2015b; Zona et al., 2016). POC and PON levels are highly positively correlated to temperature in the northern hemisphere with the relationships PON=0.142*T+0.260 (R^2=0.74) and POC=0.788*T+3.340 (R^2=0.74). However, the effect of temperature on POC and PON levels in the southern hemisphere is not very significant, with correlation coefficients (r) of -0.11 and -0.08, respectively. The influence of temperature on POC and PON levels at a global scale is not homogeneous (Figure 8A, B). The increased sensitivity of POC and PON to temperature in the northern hemisphere may be caused by relatively large amounts of nutrients and a large land area when compared to the southern hemisphere. POC/PON is highly negatively correlated to temperature in the northern hemisphere, with the relationship POC/PON=11.88*$T^{-0.190}$ (R^2=0.81) (not including samples with subzero temperature). Phytoplankton and microzooplankton growing in low temperatures (subzero) may regulate POC/PON, keeping the value low (Crawford et al., 2015; Talmy et al., 2016), and nitrogen (NO_3^- and NH_4^+) uptake and light may also play a role (Yun et al., 2012). The impact of temperature on POC/PON in the southern hemisphere (r=-0.31) is relatively low when compared to the northern hemisphere (Figure 8C). This may indicate that the mineralization of organic carbon occurs at a much higher rate than organic nitrogen with increasing temperature or that terrestrial organic carbon, which has a high POC/PON ratio, is more efficiently kept than phytoplankton- and

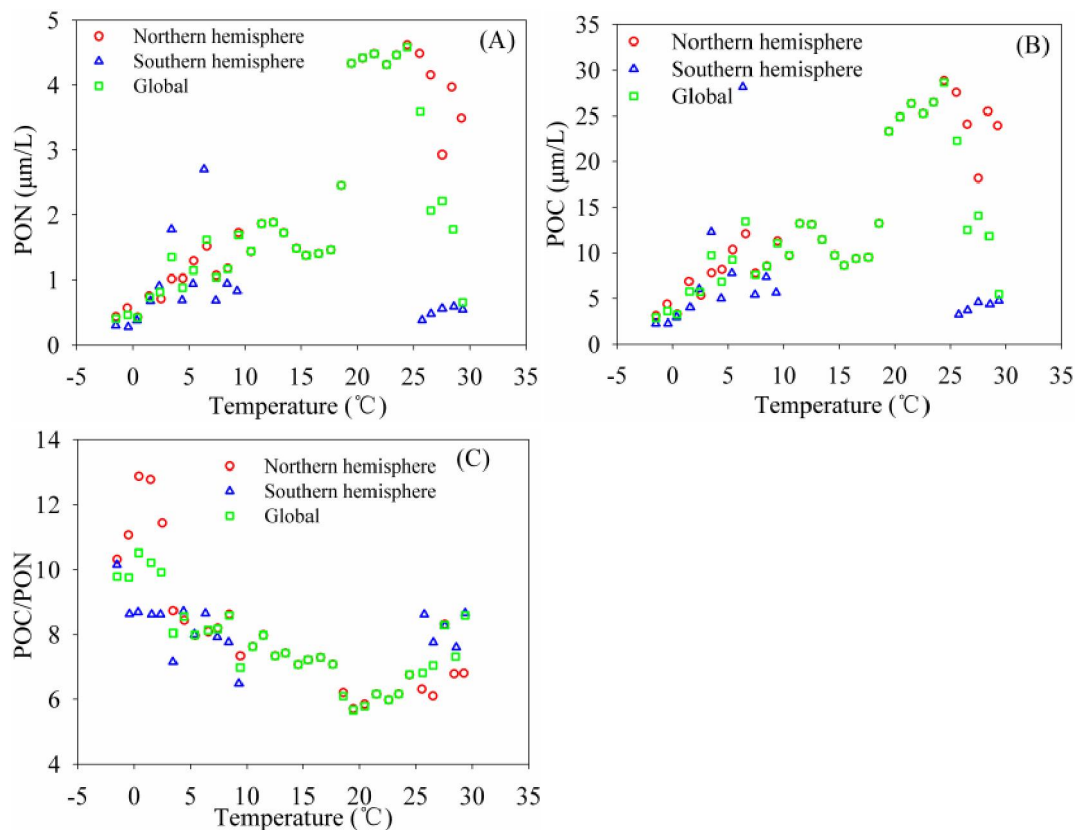
microzooplankton-derived organic carbon, which has a low POC/PON ratio, with increasing temperature (Sharma, et al., 2015; Porcal et al., 2015; Watanabe and Kuwae, 2015; Crawford et al., 2015; Talmy et al., 2016).

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Figure 8 Relationships between POC, PON, and POC/PON and temperature (T). POC, PON and POC/PON are highly correlated to temperature in the northern hemisphere, with relationships of PON=0.142*T+0.260 (R^2=0.74), POC=0.788*T+3.340 (R^2=0.74) and POC/PON=11.88*T$^{-0.190}$ (R^2=0.81), respectively. There is almost no correlation in the southern hemisphere, with correlation coefficients of -0.11, -0.08 and -0.31 for PON, POC and POC/PON, respectively. The relationships between POC, PON, and POC/PON and T at a global scale are PON=0.093*T+0.697 (R^2=0.42), POC=0.507*T+5.630 (R^2=0.41) and POC/PON=10.02*T$^{-0.122}$ (R^2=0.57).

3.4.3 Productivity and migration

Phytoplankton is an agent of the biological pump, which sequesters carbon from the atmosphere to the deep sea (Koeve, 2006); thus, it influences the global carbon cycle and the climate system (Lam et al., 2011). Studies have

proposed general relationships between POC and chlorophyll-a concentration (C_{Chl-a}) to describe the dominant effect of phytoplankton on the POC reservoir (Peña et al., 1991; Legendre and Michaud, 1999; Lefevre et al., 2003; Wang et al., 2011; Wang et al., 2013). However, the relationship between POC and C_{Chl-a} can't accurately explain POC variation at the global scale due to high variation in POC/C_{Chl-a} (Arrigo et al., 2003; Sathyendranath et al., 2009). POC levels are highly positively correlated to C_{Chl-a} for oceans, lakes, eutrophic lakes, rivers and coastal waters (Figure 9A). The best fit function for the relationship between POC and C_{Chl-a} varies with water type. A linear function is best for lakes (R^2=0.64) and coastal waters (R^2=0.82), and a power function is best for oceans (R^2=0.68) and eutrophic lakes (R^2=0.77). Both linear and power functions can be used in rivers (linear, R^2=0.77; power, R^2=0.77). This is partly consistent with previous studies on ocean water, where POC co-varied with C_{Chl-a} via a power function (Sathyendranath et al., 2009; Wang et al., 2011). However, the power exponent for the global ocean (0.581) is slightly higher than that of Wang (0.5402, 2011). The highest power exponent (0.645) is for eutrophic lakes, and the lowest (0.434) is for rivers. The slope of the linear fit function in lakes is much higher than in coastal waters. The best-fit power function for POC and C_{Chl-a} in oceans, eutrophic lakes and rivers demonstrates that phytoplankton carbon sequestration efficiency reduces with increasing chlorophyll-a in these water types. Consequently, carbon sequestration efficiency in eutrophic lakes, following a power function, is much higher than in oceans and rivers, and in lakes, following a linear function, it is higher than in coastal waters. Thus, the regulation of lake water requires more attention, as it significantly affects the global carbon cycle.

Total suspended particulate matter transported from the continental biosphere significantly affects POC levels in the water body, in addition to producing phytoplankton (Galy et al., 2015). The relationship between POC and

suspended particulate matter concentration (C_{TSM}) (Figure 9B) is very similar to studies that show that POC is highly

positively correlated to suspended particulate matter (Ni et al., 2008; Cetinić et al., 2012; Woźniak et al., 2016; Yang et al., 2016). The linear relationship between POC (μm/L) and C_{TSM} (mg/L) is shown in Figure 7B. The

power relationship between POC (mg/L) and C_{TSM} (mg/L) at the global scale (POC=0.2641*$C_{TSM}^{0.8466}$, R^2=0.81,

n= 5306) is close to the same relationships in the Baltic Sea (POC = 0.317*$C_{TSM}^{0.969}$, R^2=0.86, Woźniak et al., 2016)

and surface water in the US (POC = 0.2992*$C_{TSM}^{0.3321}$, R^2=0.593, Yang et al., 2016). However, this relationship

differs slightly from the one presented by Galy (2015, Figure 1–3), in which the global flux of terrestrial POC to

oceans is composed of biospheric (80%) and petrogenic (20%) POC, with the relationship POC_{exp} =

0.0524*$C_{sed}^{0.665}$. This indicates that suspended particulate matter includes large amounts of organic carbon in

addition to terrestrial organic carbon due to primary productivity and the subsequent zooplankton in the food

chain.

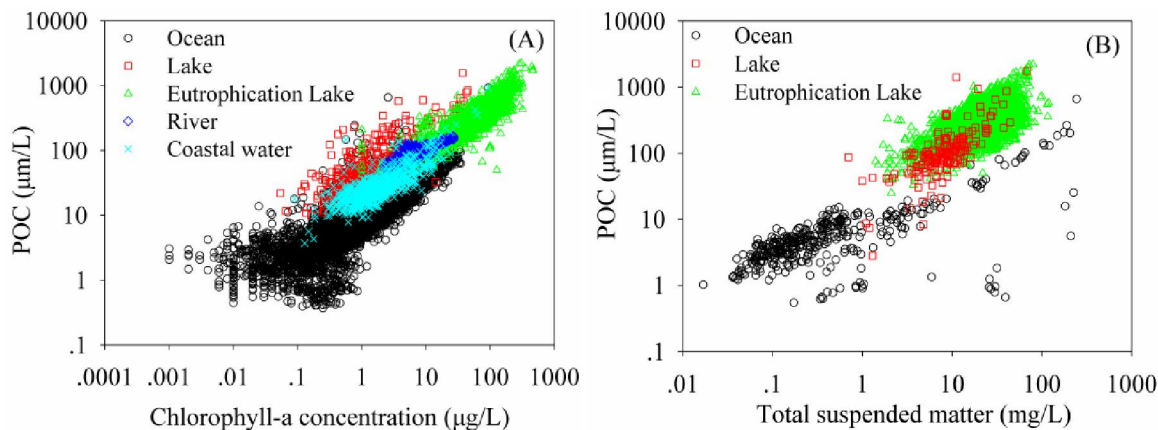



Figure 9 (A) Comparison of the relationships between POC and chlorophyll-a concentration (C_{Chl-a}) for oceans, lakes, eutrophic lakes, rivers and coastal waters. (B) Comparison of the relationship between POC and total suspended matter concentration (C_{TSM}) for oceans, lakes and eutrophic lakes. The relationships between POC and C_{Chl-a} are POC=4.429*C_{Chl-a}+6.531   (R^2=0.51,   N=5462);   POC=16.420*C_{Chl-a}+17.855   (R^2=0.64,   N=984); POC=3.513*C_{Chl-a}+96.528   (R^2=0.72,   N=4656);   POC=4.458*C_{Chl-a}+55.931   (R^2=0.77,   N=936);   and POC=7.357*C_{Chl-a}+12.349 (R^2=0.82, N=692) for oceans, lakes, eutrophic lakes, rivers, and coastal waters, respectively. The relationships between POC and C_{TSM} are POC=1.045*C_{TSM}+5.198 (R^2=0.53, N=432); POC=15.932 *C_{TSM}-25.645 (R^2=0.67, N=191); and POC=7.984*C_{TSM}+149.950 (R^2=0.27, N=4683) for oceans, lakes, and eutrophic lakes, respectively.

3.4.4 Dissolved organic carbon and nitrogen

DOC, which is present in much higher concentrations than POC (Figure 9A and Figure 10A), quantitatively represents the most important carbon pool (Emerson and Hedges, 2008). DOC is a complex mix of organic compounds from both autochthonous and allochthonous sources that primarily originate from aquatic organisms and runoff, respectively (Doval et al., 2016; Kuliński et al., 2016). DON is highly positively correlated to DOC, with a best-fit function of DOC=17.825*$DON^{1.019}$ (R^2=0.58, n=995) at the global scale. The linear regression model (Figure 10A) shows that the slope of the linear function is smaller than in previous regional studies (13.3 ± 0.8, Doval et al., 1999; 20.5 ± 3, Aminot and Kérouel, 2004) and is also smaller than DOC sequestered in the deep sea (17.38) via the microbial carbon pump (Jiao et al., 2010). The DOC/DON ratio in lakes (40.43 ± 34.56) and rivers (29.35 ± 34.93) is much higher than in oceans (12.86 ± 4.88) and coastal waters (13.15 ± 4.95) (Figure 10B); thus, inland water holds much more DOC, which may result in the high emission of CO2 in inland waters (Raymond et al., 2013; Hotchkiss et al., 2015). The correlation between POC and DOC is weak for individual water types, but is strong for the whole data of lake, ocean and coastal water. The regression function (gray line in the

400   Figure 9 C) between POC and DOC is DOC = 0.315 * POC + 64.88 (R^2=0.58 n=570), except the data of river.

High DOC/POC and DOC/DON ratios indicate that organic carbon is mostly stored in dissolved form. DOC and

DON regulate the organic carbon and nitrogen equilibrium system with the POC and PON, besides the interaction

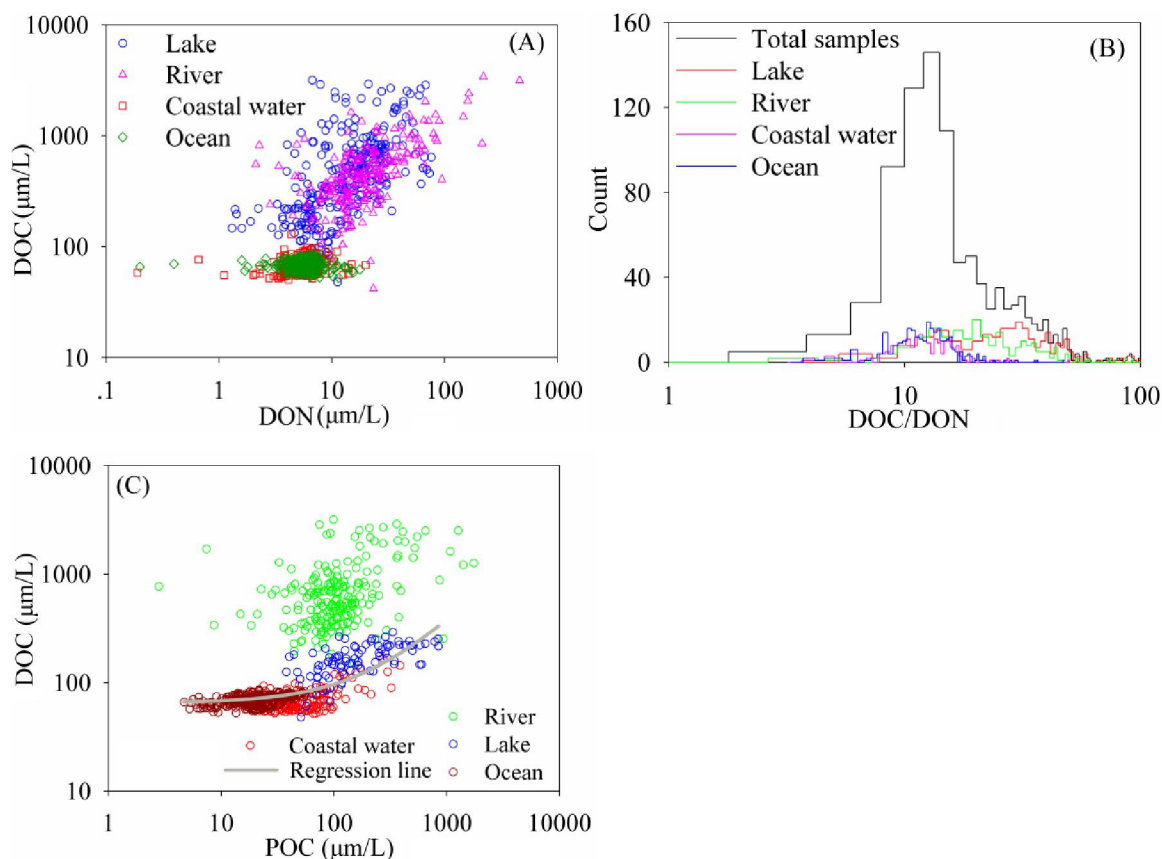
with the inorganic carbon and nitrogen (such as $CO2$, nutrients, N_2 and NO_x).

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Figure 10 (A) Comparison of the relationships between DOC and DON for oceans, lakes, rivers, and coastal waters. The relationships between DOC and DON are DOC = 11.738*DON + 165.41 (R^2=0.35, n=995); DOC = 19.037*DON + 273.59 (R^2=0.20, 288); and DOC = 11.932*DON + 234.36 (R^2=0.61, n=255) for all samples, lakes and rivers, respectively. The correlation coefficients for DOC and DON are r=0.44, 0.78, 0.15 and -0.15 for lakes, rivers, coastal
410   waters and oceans, respectively. (B) DOC/DON for oceans, lakes, rivers and coastal waters. The DOC/DON ratios are 24.10 ± 24.57, 40.43 ± 34.56, 29.35 ± 34.93, 13.15 ± 4.95 and 12.86 ± 4.88 for all samples, lakes, rivers, coastal waters and oceans, respectively. The corresponding POC/PON ratios are 9.65 ± 16.73, 7.71 ±0.61, 7.07 ± 2.44 and 6.24 ± 1.20 for lakes, rivers, coastal waters and oceans, respectively. (C) Relationships of POC and DOC for different

water types. The correlation between POC and DOC is weak for individual water types, but is strong for the whole data of lake, ocean and coastal water. The regression function (gray line in the figure) between POC and DOC is DOC = 0.315 * POC + 64.88 (R^2=0.58, n=570), except the data of river.

Analysis of global temporal and spatial variation in POC, PON and POC/PON and the analysis of drivers that influence POC, PON and POC/PON distribution is the basis of biogeochemical implication. The simple mean value of POC/PON at the global scale (7.54±3.82) is higher than the Redfield ratio (6.63), but the linear regression slope (including intercept, 6.17; excluding intercept, 6.23) for all ocean data is much lower than the simple mean value of POC/PON and the Redfield ratio. The linear regression slopes between POC and PON in the northern hemisphere (including intercept, 7.06 and excluding intercept, 7.00) are much higher than in the southern hemisphere (including intercept, 5.97; excluding intercept, 6.03). Variations in POC, PON and POC/PON in inland waters requires further attention due to the importance of inland waters in global carbon and nitrogen cycles and the indeterminacy of the relationship between carbon and nitrogen. Land and soil organic carbon distribution and offshore distance were appeared to be controlled factors to the variation of POC, PON and POC/PON at a global scale besides the temperature and productivity.

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