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. The latitudinal dependency of POC/PON is significant between 20° N ~ 90° N but weak in low latitude areas and in the southern hemisphere. The mean values of POC/PON in the southern and northern hemispheres were 7.40 ± 3.83 and 7.80 ± 3.92, respectively. High values of POC/PON appeared between 80° N ~ 90° N (12.2 ± 7.5) and 70° N ~ 80° N (9.4 ± 6.4), while relatively low POC/PON were found from 20 ° N (6.6 ± 2.8) to 40 ° N (6.7 ± 2.7). The latitudinal variation of POC/PON in the northern hemisphere is much stronger than in the southern hemisphere due to the influence of more terrestrial organic matter. Higher POC and PON could be expected in coastal waters. POC/PON growth ranged from 6.89 ± 2.38 to 7.59 ± 4.22 in the northern hemisphere, with an increasing rate of 0.0024/km from coastal to open ocean. Variations of POC/PON in lake water also showed similar latitude-variation tendency of POC/PON with ocean water but was significantly regulated by the lakes' morphology, trophic state and climate. Small lakes and high latitude lakes prefer relatively high POC/PON, and large lakes and low latitude lakes tend to prefer low POC/PON. 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 implications of these values on 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. Thus they 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 CH_4, 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 waters could increase 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 received carbon in inland waters from terrestrial ecosystems can reach to 5.7 PgC/yr (Le Quéré et al., 2015). The carbon stored in the sediment and discharged into oceans could increase to 2.6 PgC/yr by subtracting 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 at 0.9 PgC/yr (Tranvik et al., 2009), or higher (Raymond et al., 2013 and Le Quéré et al., 2015). The absorption of atmospheric CO_2 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, water environment (Thornton and McManus, 1994; Gruber and Galloway, 2008) and human activities (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 is 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, Sterner et al., 2008). 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), 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., 2005; Martiny et al., 2013a; 2013b; DeVries and Deutsch, 2014). The factors influencing variations in C/N are complex due to the loss and product rates of POC and PON. Nitrogen, light limitation and phytoplankton can only explain approximately 20% of the variation in C/N on a global scale (Martiny et al., 2013b). Temperature, composition of organic matter and dynamic characteristics of water significantly determine the loss rates of POC and PON 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 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 POC, 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 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 still needs to be

complemented and perfected (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 40,482 samples to 80° N ~ 78° S with 63,184 samples, to re-examine variations in POC, PON and POC/PON on a global scale. Values for POC, PON and

80 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

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

85 were acquired (detailed information is 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 similar methods, where C and N were analyzed on a C/N elemental analyzer after water samples were filtered

90 through pre-weighed, pre-combusted (450°C for 4 hours) GF/F filters and acidified. The units of POC and PON in all data (µg/L, µmol/L) were unified to µmol/L via molecular-weight of C and N.

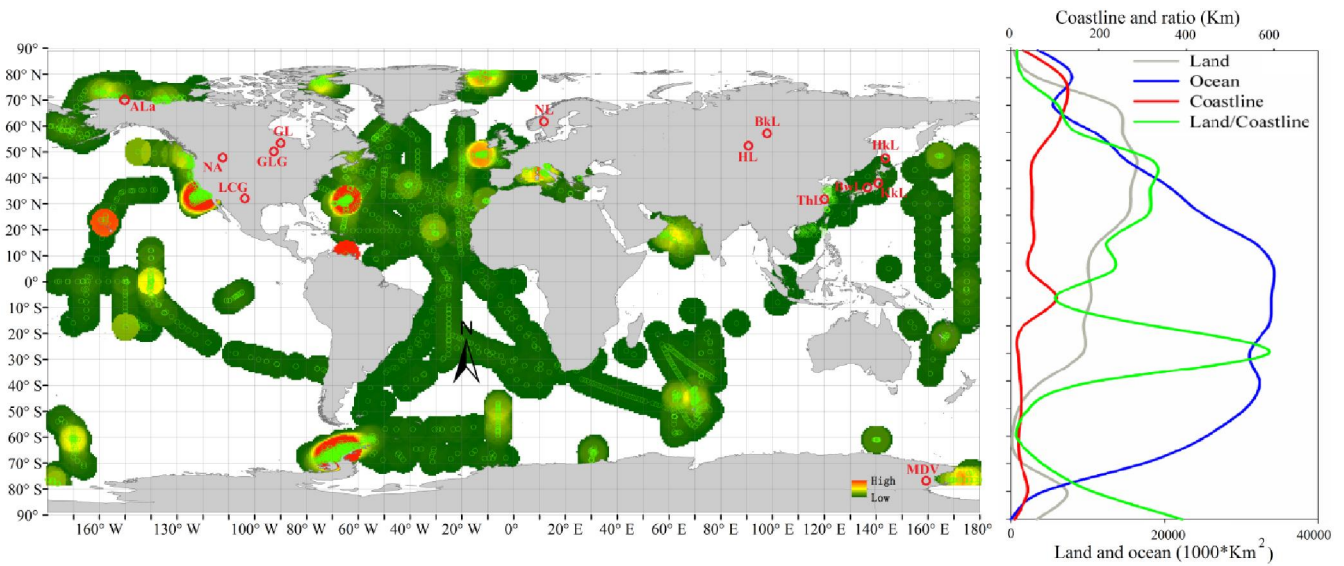
Geographical land and ocean distribution data and soil organic carbon data (harmonized world soil database, http://daac.ornl.gov/SOILS/guides/HWSD.html) were also used to analyze the factors influencing variations in POC, PON and POC/PON.

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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/.

100   2.2 Data category and analyses methods

Samples with extremely low POC (< 0.01 μmol/L) and PON (< 0.001 μmol/L) values were removed due to the limit of detection for the analysis. The collection of ocean data from previous studies and web-sharing databases contained variable ranges of POC and PON with latitude, time, depth and temperature. To reveal the pattern of POC and PON, the remaining data were classified into four types relating to latitude, depth, offshore distance and

105   temperature to aid data analysis: 1) Oceanic samples, taken from 80° N to 78° S, were divided into 17 ranges with 10° latitudinal intervals (Table S2). The data in each latitudinal range includes all ranges of temperature, time and depth for samples. 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 S3 and Figure S1). The distribution of samples in each depth covers most ranges of latitude, time and temperature for POC and PON. 3)

110   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 the buffer 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 the same category for each offshore distance range. The samples in

different ranges of buffers (different distances offshore) can show the variation of POC, PON and POC/PON from coastal areas to open sea (Figure S2).

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

The number of samples is 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 soil organic carbon, were regressed to explore the effect of each influencing factor on 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 on the variation of oceanic POC, PON and POC/PON.

3. Results and discussion

3.1 Spatial variation of POC, PON and POC/PON in the ocean

3.1.1 Latitudinal variation of POC, PON and POC/PON

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). Compared with the strongly latitudinal-dependent relationship in the elemental ratios (Martiny et al., 2013a), both POC and PON barely show a global latitudinal pattern, but latitudinal variations in POC and PON in the southern hemisphere are much weaker than in the northern hemisphere (Figure 2A, B). The latitudinal dependency of POC/PON in the northern hemisphere is stronger than in the southern hemisphere, especially between 40N and 90N, which shows an attenuation trend with a decrease of latitude (Figure 2C). Different from 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, 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 mean value of POC/PON in the northern hemisphere (7.50 ± 4.65) is slightly lower than in the southern hemisphere (7.81 ± 3.79) and close to the global mean value of POC/PON (7.54 ± 3.82). The variation for POC/PON in the northern hemisphere is bigger than in the southern hemisphere (Table S2). This could indicate that biogeochemical processes and the circulation of carbon and nitrogen in the northern hemisphere are much more complex than in the southern hemisphere.

PON and POC co-vary, resulting in a strongly coupled relationship (Figure 3A-3D). Linear functions (including and excluding intercepts) and power functions can be used to express the relationship between carbon and nitrogen for each latitudinal range (Table S2). However, the optimal function is different for each latitudinal range. The regression functions for POC and PON and the best regression results (highest R^2) noted with an asterisk are listed in Table S2. The linear function used to describe the relationship between POC and PON globally is POC = 6.17 × PON + 1.24 (R^2 = 0.916). The linear function between POC and PON for southern and northern hemispheres are POC = 5.974 × PON + 1.528 (R^2 = 0.913) and POC = 7.062 × PON - 0.624 (R^2 = 0.899), respectively. The slopes of the linear regressions in northern and southern hemispheres (5.97 and 7.06) are very

close to the Redfield ratio of 6.63 and almost cover the range of POC/PON 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 linear slope between POC and PON (6.17) is

165 slightly lower than the Redfield ratio of 6.63.
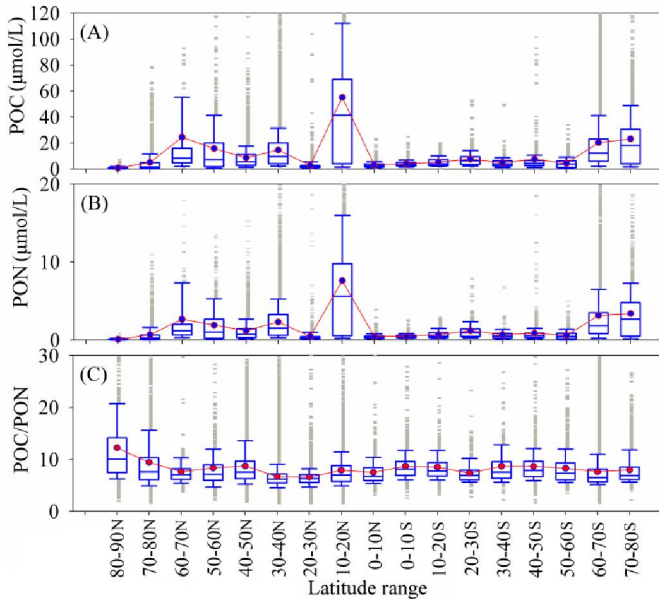
Figure 2 Latitudinal variation of POC (chart A), PON (chart B) and the POC/PON (chart C) ratio from the compiled statistical results of depth-integrated data for all ocean data. The box plots show the median and 25th and 75th percentiles, with whiskers covering most of the data. The red line with green boxes shows the mean value for each
170 latitudinal range.
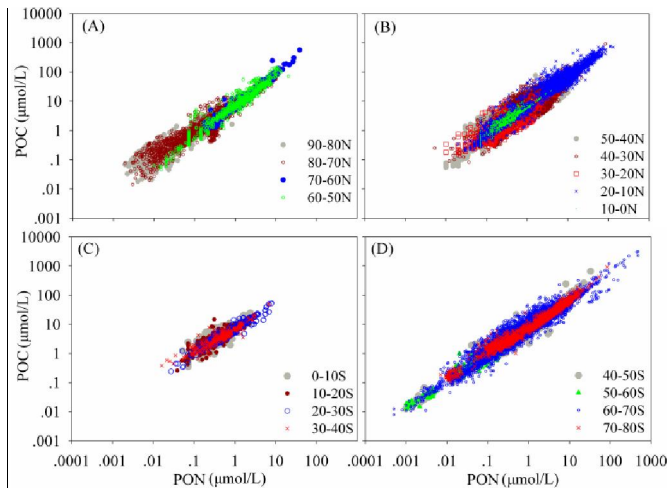
Figure 3 charts A and B are scatter plot of POC and PON for each latitudinal range of northern hemisphere. Charts A and B are scatter plot of POC and PON for each latitudinal range of southern hemisphere. The relationships between POC and PON are listed in Table S2.

175

3.1.2 Depth variation of POC, PON and POC/PON

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). The distributions of POC and PON present that the relatively high POC and PON were distributed in the surface water (0 - 5 m) in the northern hemisphere with mean values of 17.83 ± 2.03 μmol/L (POC) and 2.72 ± 0.29 μmol/L (PON). Conversely, relatively high POC and PON in the southern hemisphere appeared in deeper water (10-20 m) with mean values of 16.79 ± 1.51 μmol/L (POC) and 2.49 ± 0.23 μmol/L (PON) (Figure 4A, B). However, the depth-dependence of POC/PON in the northern and southern hemispheres is weak (Figure 4C). 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 (Figure 4C). Increases in POC/PON with depth in the northern hemisphere occurred at rates of 5.2/km (depth < 200 m). 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 coupling relationship between POC and PON is relatively lower at other depths, such as deeper than 80 m (Figure S3B) and in surface water (Figure S3A) in the northern hemisphere. The relationship between POC and PON in the southern hemisphere is much stronger than in the northern hemisphere (Figure S3C and S3D). The regression functions of POC and PON for each depth are listed in Table S3.
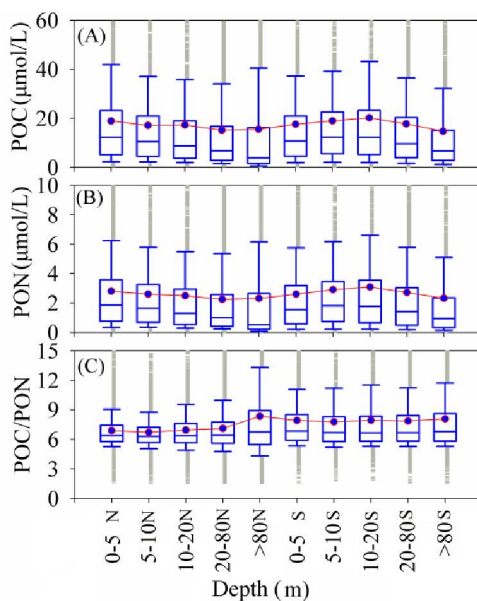
Figure 4 Depth-dependence of POC and PON in the southern hemisphere and depth-dependence of POC/PON in the northern hemisphere. The box plots show the median and 25th and 75th percentiles, with whiskers covering most of

the data. The red line with green boxes shows the mean value at each depth.

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

Previous studies indicate that a large amount of terrestrial carbon is discharged from rivers to oceans (Cole et al.,

2007), causing variations in POC, PON and POC/PON, especially in coastal regions (Martiny et al., 2013b). Most

of the terrestrial carbon will sink as sediment in estuaries or transport to open ocean, although a large amount (0.3

PgC/yr) of terrestrial carbon (0.5 PgC/yr) is emitted as CO_2 (Cai, W.J., 2011).

Variations occur in POC and PON levels when taking into account the distance from shore, showing that there is

a significant separation zone (50 km), dividing POC and PON levels into two regions in the northern hemisphere

(Figure 5A, B). POC levels close to land (0 - 50 km) (region close to shore, 21.90 ± 11.01 μmol/L) are nearly two

times larger than in regions more than 50 km from land (offshore region, 11.65 ± 3.58 μmol/L) due to terrestrial

influences. The distribution of PON is similar, as PON levels are higher close to shore (0 - 50 km, 3.19 ± 1.46

μmol/L) compared to offshore (>50 km, 1.67 ± 0.44 μmol/L). Conversely, POC/PON increases from 6.89 ± 2.38

to 7.59 ± 4.22 with distance from shore to open sea in the northern hemisphere (Figure 5C). Terrestrial impacts

on POC and PON levels in the southern hemisphere are relatively weak (POC, 20.14 ± 5.51 μmol/L; PON 3.12 ±

0.87 μmol/L) (Figure 5D, E). In addition, there is little change in POC/PON with distance from coastal (7.59 ±

3.77) to offshore regions (7.90 ± 3.99) in the southern hemispheres (Figure 5F).

Coastal water with relatively high POC and PON levels has a low POC/PON within 75 km of the coast in the

northern hemisphere (Table S4, northern hemisphere). This is inconsistent with previous studies that show that

coastal water has a higher POC/PON than offshore water (Sterner et al., 2008; Kaiser et al., 2014) due to the

discharge of terrestrial organic matter with high POC/PON (Hilton et al., 2015; Cai, Y.H. et al., 2015). A 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).

The over-consumption of carbon could reduce the POC/PON ratio in the coastal waters. Zooplankton,

phytoplankton and high nutrient levels also reduce POC/PON in coastal waters (Koeve, 2006; Martiny et al.,

2013b; 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 distance is very significant in the northern hemisphere, with an increasing rate of 0.0024/km (POC/PON=0.0024 × D+7.1764, R^2=0.519), especially within 75 km of the coast (POC/PON = 0.0262 × D + 6.421, R^2=0.855), but insignificant in the southern hemisphere, with a rate of 0.0004/km (POC/PON=0.0004 × D + 7.7346, R^2=0.118) (Figure 6).
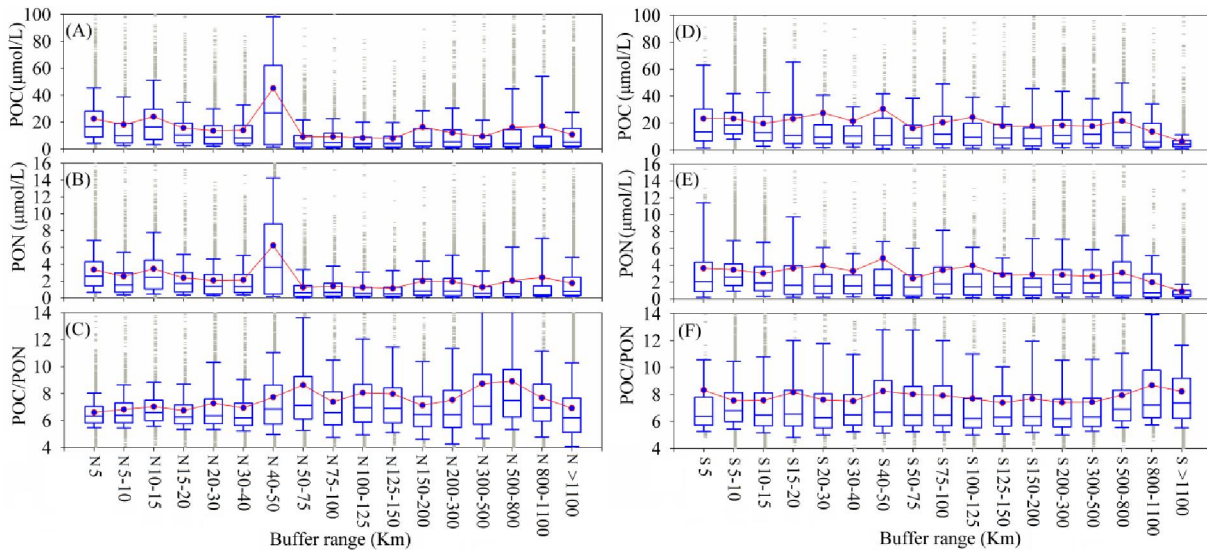
Figure 5 Variation of POC, PON and POC/PON with distance from shore. The number of samples for each buffer is listed in Table S4. The box plots show the median and 25th and 75th percentiles. The red line with green boxes shows the mean value for each range.
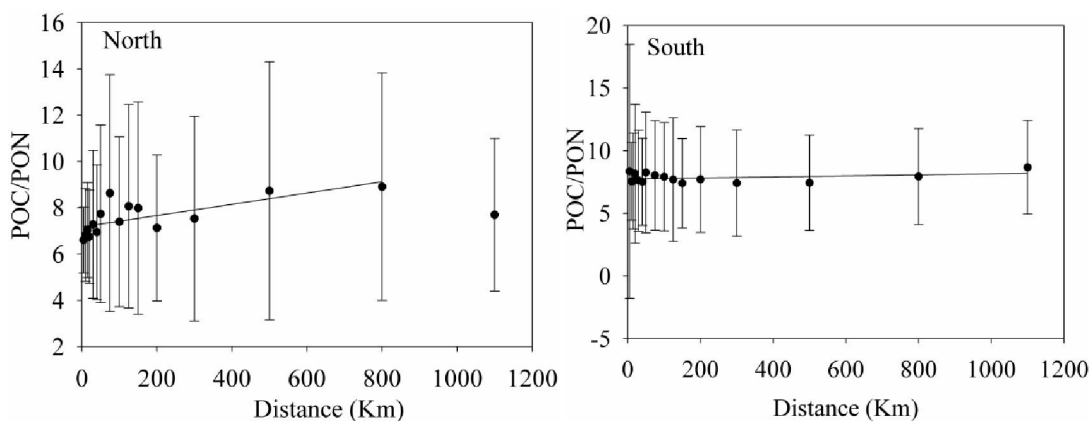
Figure 6 The variation of POC/PON with distance from the shore to open sea. The relationships between POC/PON and distance are POC/PON=0.0024*D+7.1764 (R^2=0.519, northern hemisphere) and POC/PON=0.0004*D+7.7346 (R^2=0.118, southern hemisphere).

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

3.2.1 Lake water

Inland waters play an important role in the global carbon cycle, linking the terrestrial, atmospheric, and oceanic carbon pools. The lakes investigated in this study were sorted by latitude, according to geographical position. POC and PON in lake waters exhibit a similar latitudinal variation trend with the ocean of the northern hemisphere, where POC and PON decreased with latitude, but had greater variability than in oceans due to the strong dual influences of terrestrial and aquatic organic matter (Figure 7) (Wilkinson et al., 2013). In contrast to the latitudinal variation trend of POC and PON, The POC/PON in lake waters increased with latitude. However, the lake's morphology, trophic state, climate and other influencing factors also could regulate the latitude variation of POC/PON in lake waters. The investigated data from 8,300 lakes indicate that the average carbon/nitrogen stoichiometry in different types of lakes are approximately 10.6 at the global scale, 9.5 for small lakes, 8.5 for large lakes, 8.16 for shallow lakes, 5.67 for deep lakes, 11.46 for frigid northern lakes and 10.37 for temperate lakes (Chen et al., 2015; Sterner et al., 2008). For example, Kasumigaura Lake is an extremely eutrophic lake, with a mean (from 1977 to 2013) chlorophyll-a concentration of 67 ± 44 µg/L and relatively high POC and PON (POC, 332.76 µmol/L and PON, 47.94 µmol/L). The trophic state of Lake Taihu 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 ± 3.96) is much smaller than in Kasumigaura Lake (7.1 ± 1.5). This could be caused by the over-mineralization of organic carbon reducing the POC/PON in large shallow lakes (e.g., Lake Taihu) and emitting much more CO_2 than the smaller lakes (e.g., Kasumigaura Lake) (Xiao et al., 2014; Hotchkiss et al., 2015). The large and deep lakes, including the Great Lakes, also show a relatively low POC/PON ratio (5.07). Lakes located in cold-dry climatic zones (McMurdo 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 7). This agrees with previous studies 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). Meanwhile, the coupling relationship between POC and PON for each lake was also regulated by these influencing factors (Table S5 and Figure S5). The relationships between PON and POC for each lake are listed in
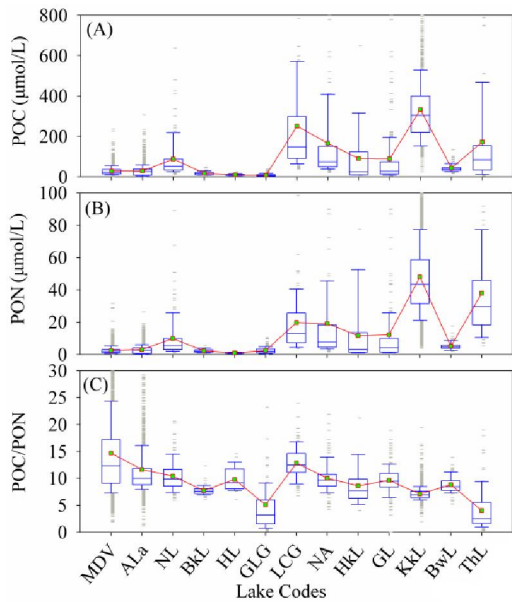
Table S5.

Figure 7 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 are listed in the Table S7.

3.2.2 River water

Rivers not only bridge the carbon and nitrogen elemental cycles in the land and ocean through the transmission of organic matter, but they 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 in oceans and lakes, especially in large and highly turbid rivers (such as Yanagtze River, Amazon River in Figure 8A and B). The POC and PON in Yanagtze River (the highest POC and PON river, 4154.6 ± 3109.6 µmol/L and 290.7 ± 180.5µmol/L) are proximately 100- and 80-fold bigger than in Fraser River (the lowest POC and PON river in this study, 39.7 ± 54.9 µmol/L, 3.7 ± 4.3 µmol/L), indicating huge spatial variation of POC and PON in the river system. It also could be that big rivers with high POC and PON discharge much more POC and PON into the ocean (global annual flux of POC is 216 Tg, Voss, 2009), accompanied by high runoff. Previous studies also proposed that the temporal variation of POC and PON in rivers is significant (Verity, 2002; Ward et al., 2012). However, the

variation of POC/PON (variable coefficient, 0.47) in river waters is much smaller than POC (variable coefficient, 2.03) and PON (variable coefficient, 1.81). The value and variation of POC/PON (12.5 ± 5.8 with variable coefficient of 0.47) in this study is much bigger than in previous studies (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 8C). 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 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), which is closer to the 5.67 ratio for deep lakes (Chen et al., 2015). The latitude dependence of POC, PON and POC/PON were not evaluated because the samples of each river did not follow the latitude-distribution. The relationships between PON and POC for each river are listed in Table S6 (Figure S6).
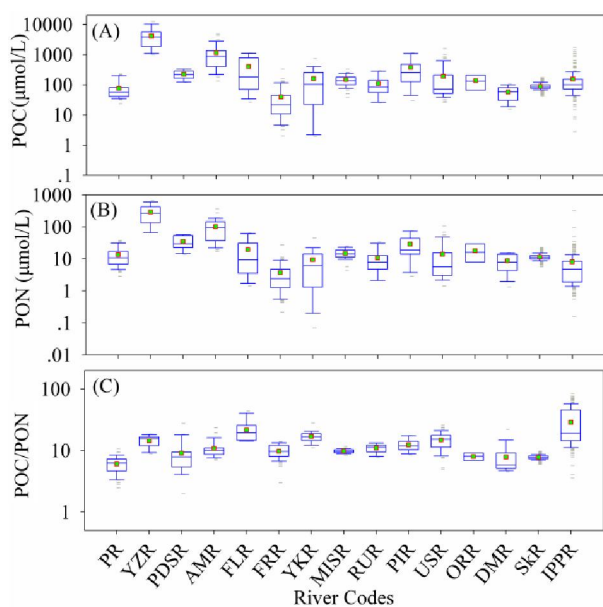
Figure 8 Variation of PON, POC and POC/PON in river waters. PR is Pearl River (China), YZR is Yanagtze River (China), PDSR is paraiba do sul River (Brazil), AMR is Amazon River (Brazil), FLR is Fly River (Papua New Guinea), FRR is Fraser River (Canada), YKR isYukon River (USA), MISR is Mississippi River (USA), RUR is Russian rivers (Russia), 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 the 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 has a high positive correlation to POC and PON levels in oceans (Figure 9A, 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 40 °N ~ 50 °N and 80 °N ~ 90 °N (marked with an ellipse in Figure 9A, 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 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 9C).
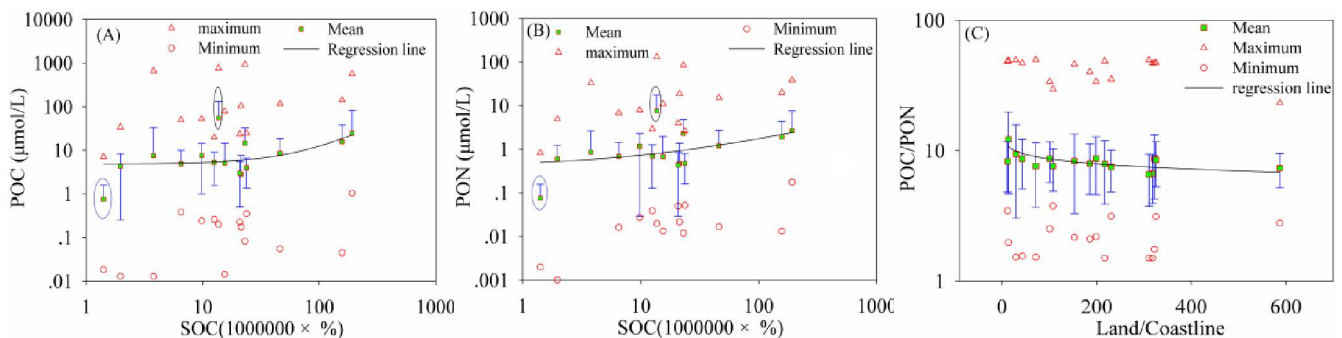
Figure 9 (A) and (B) Relationship between POC, PON and soil organic carbon. (C) The relationship between POC/PON and the ratio of land area to coastal linear length. The red boxes with green shading are the mean values of POC, PON and POC/PON in each latitudinal range, the blue line is the standard deviation, and the red triangles and circles 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 show a high positive correlation 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 10A, 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 showed a high negative correlation 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 10C). 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; Crawford et al., 2015; Talmy et al., 2016).
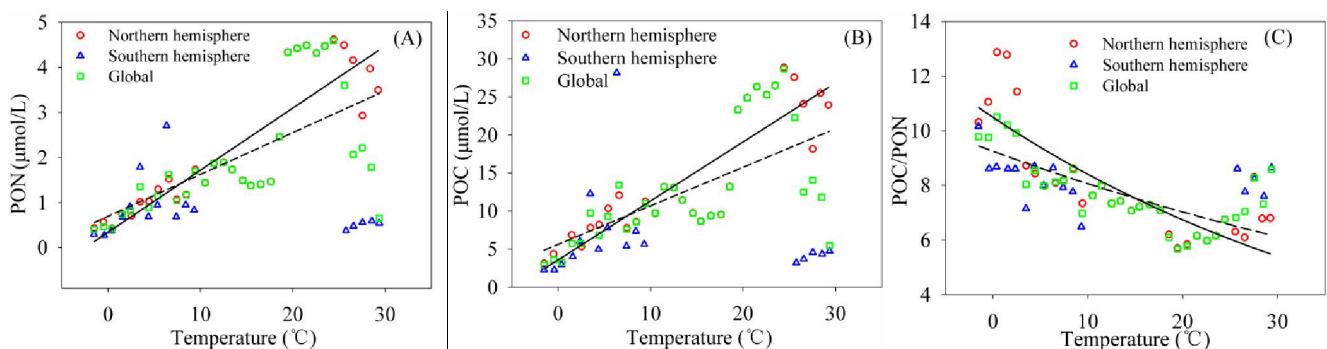
Figure 10 Relationships between POC, PON, and POC/PON and temperature (T). POC, PON and POC/PON are highly correlated to temperature in the northern hemisphere (solid line), with relationships of PON=0.142*T+0.260 (R^2=0.74), POC=0.788*T+3.340 (R^2=0.74) and POC/PON=11.88*T$^{-0.190}$ (R^2=0.81), respectively. 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 (dashed line) 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

355   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 show a high positive correlation to C_{Chl-a} for oceans, lakes, eutrophic lakes, rivers and coastal waters (Figure 11A). The best-fit function for the relationship between POC and C_{Chl-a} varies with water

360   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

365   (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; in lakes, following a linear function, it is higher than in coastal waters.

370   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 11B) is very similar to studies that show that POC has a high, positive correlation with to suspended particulate matter (Ni et al., 2008; Cetinić et al., 2012; Woźniak et al.,

375   2016; Yang et al., 2016). 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.
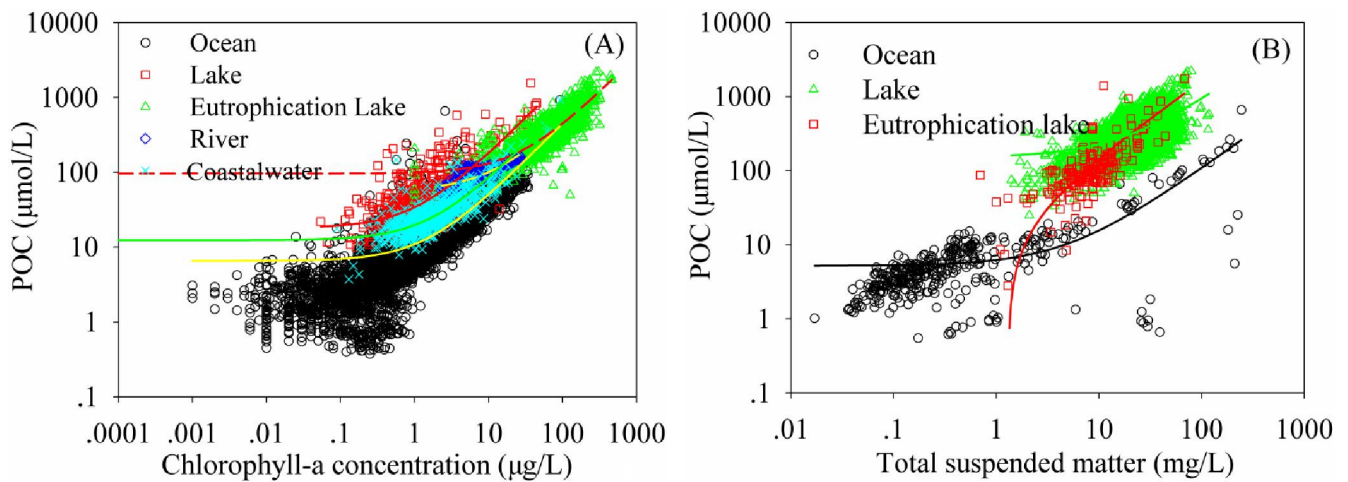
Figure 11 (A) Comparison of the relationships between POC and chlorophyll-a concentration (C_{Chl-a}) for oceans, lakes, eutrophic lakes, rivers and coastal waters. (B) Comparison of the relationship between POC and total suspended matter concentration (C_{TSM}) for oceans, lakes and eutrophic lakes. The relationships between POC and C_{Chl-a} are POC=4.429*C_{Chl-a}+6.531 (R^2=0.51, N=5462, yellow solid line); POC=16.420*C_{Chl-a}+17.855 (R^2=0.64, N=984, red solid line); POC=3.513*C_{Chl-a}+96.528 (R^2=0.72, N=4656, red dashed line); POC=4.458*C_{Chl-a}+55.931 (R^2=0.77, N=936, yellow dashed line); and POC=7.357*C_{Chl-a}+12.349 (R^2=0.82, N=692, green solid line) 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, black solid line); POC=15.932*C_{TSM}-25.645 (R^2=0.67, N=191, green solid line); and POC=7.984*C_{TSM}+149.950 (R^2=0.27, N=4683, red solid line) 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 11A and Figure 12A), 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 shows a strong positive correlation 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 12A) 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 12B). Thus, inland water holds much more DOC, which may result in the high emission of

CO_2 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 combined data of lakes, oceans and coastal waters. The

regression function (black line in the Figure 12C) between POC and DOC is DOC = 0.315 * POC + 64.88

(R^2=0.58 n=570), not including river data. High DOC/POC (1.48 ± 0.75 for Coastal water, 7.57 ± 6.83 for river,

1.18 ± 0.77 for lakes and 4.02 ± 2.13 for ocean) 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, in addition to the interaction with the inorganic carbon and nitrogen (such as CO_2, nutrients, N_2

and NO_x).
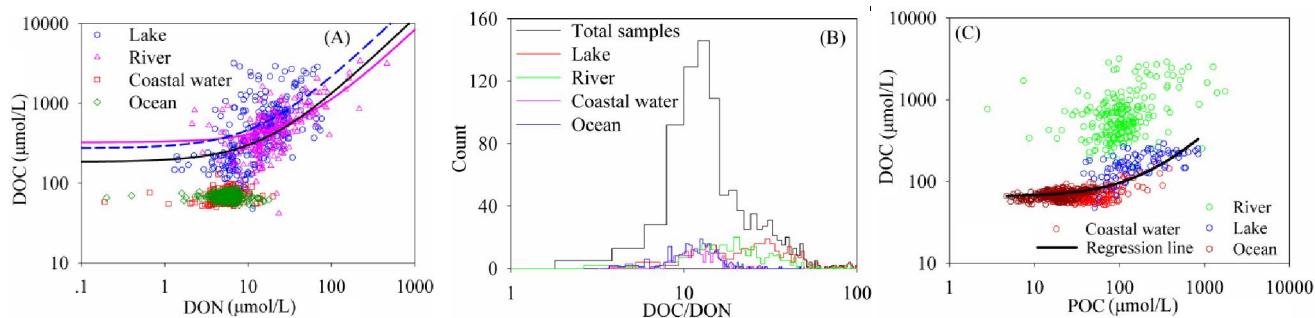
Figure 12 (A) Comparison of the relationships between DOC and DON for oceans, lakes, rivers, and coastal waters. The relationships between DOC and DON are DOC = 11.738*DON + 165.41 (R^2=0.35, n=995, black solid line); DOC = 19.037*DON + 273.59 (R^2=0.20, 288, blue dashed line); and DOC = 11.932*DON + 234.36 (R^2=0.61, n=255, pink solid line) for all samples, in 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 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 combined data of lakes, oceans and coastal waters. The regression function (black line in the figure) between POC and DOC is DOC = 0.315 * POC + 64.88 (R^2=0.58, n=570), not

including river data.

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 have biogeochemical implications. 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 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; 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 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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