Dear Prof. Gerhard Herndl

First, we very appreciate the useful comments from two anonymous reviewers and these comments are very meaningful to improve the quality of this paper and our further study.

Our paper is a research paper about the stoichiometry of particulate organic carbon (POC) and particulate organic nitrogen (PON) based on expanded the global marine dataset and additional large number of inland water data. The first anonymous reviewer focuses on stoichiometry of POC and PON in the global ocean water and gave us a positive evaluation. However, the anonymous reviewer is much interesting in the review of POC, PON and carbon cycle (such as CO2 emission from inland water) in inland water and point out the data insufficient of POC and PON in inland water of our study. This is very useful and meaningful for our further study and gets an ambitious objective for global study of carbon cycle, mapped by reviewer.

Compared to the stoichiometry of POC and PON in inland water, the stoichiometry of POC and PON in the global ocean water is much stable. We also got some new findings different from previous studies based on the expanded the global marine dataset. In personal mind, we did not necessary to collect all the inland water data for the analyses of variation of POC/PON and inland water data worked as subsidiary in this study. The inland data of POC and PON includes 11875 samples in 253 lakes (small lakes in similar region were not listed separately in the supporting information). The analysis is validated if the representativeness of analyses dataset for the inland water can satisfy the variation range of such 'global synthesis'. Of course, the representativeness will be increased with much more data was utilized, and we should pay more attention to the complete collection of inland water data if we want to estimate the discharge flux to the ocean from rivers in further study.

Nonetheless, we added much more data of POC and PON in the world wide river in the revision edition and expected to improve the acknowledge of stoichiometry in the inland water according to the reviewer's comment.

We marked some major revisions in the context. the revised supporting information also was submitted.

Anonymous Referee #1

General Comments:

1) The authors have performed a review of variability in particulate organic carbon and nitrogen ratios in the world’s oceans and inland waters. While the authors include a large amount of data for the ocean that is more or less globally representative, they consider 2 small temperate rivers and 7 different lakes, all located in the Northern hemisphere. There doesn’t appear to have been any effort to incorporate data from the vast body of literature, rather data was only downloaded from websites with data readily available. For such a review to be meaningful, the authors need to spend considerable time mining the literature to collect a representative dataset. Not including large rivers in a global dataset is a massive oversight. Currently I do not see any value in this review considering the massive gaps in the data that was considered. The authors perhaps have a decent starting point with the assembled ocean datasets, but need to spend considerable time compiling the inland water data before any meaningful conclusions can be made. I have recommended some references to read through below to broaden perspectives on inland water bio-geochemical cycling that will perhaps inspire a more in depth analysis.

Response: We very appreciate the useful comments proposed by reviewer. We responded each comment carefully and did corresponding revision in the context of MS.

In fact, the purpose of this study is not review the variation of POC and PON in ocean and inland water. We compiled large of ocean (63208 samples) and inland (11875 samples, 253 lakes) data of POC and PON not only from online database but also previously studies. The lake dataset listed in the supporting information includes many lake groups. The lake group contains many lakes, not just a single lake. We can open the online link if we are interested in it. These data were used to reexamine the variation pattern and relationship of POC and PON and also compared with previous study (Martiny et al., 2013a and 2013b). We also compared the relationship of POC and PON between ocean and inland water to help us much more comprehensive understanding the variation pattern of POC and PON, although the samples in the inland water is relatively small. Some new variation pattern of POC and PON was revealed via the expanded global marine data and some inland water data.

Martiny, A.C., Pham, C.T.A., Primeau, F.W., Vrugt, J.A., Moore, J.K., Levin, S.A., Lomas, M.W., 2013a. Strong latitudinal patterns in the elemental ratios of marine plankton and organic matter. Nature geoscience 6:279-283.

Martiny, A.C., Vrugt, J.A., Primeau, F.W., Lomas, M.W., 2013b. Regional variation in the particulate organic carbon to nitrogen ratio in the surface ocean. Global Biogeochem. Cycles, 27, 723–731.

Expert (reviewer) expect a thorough study and the summarization and analyses of the global dataset of POC and PON in ocean and inland water, and broaden the POC and PON to the CO_2 in global inland water, and also proposed to separate the inland water into lake and river. This is very useful and meaningful for our further study and gets an ambitious objective, mapped by reviewer.

In personal mind, we did not necessary to collect all the inland water data for the analyses of variation of POC/PON and worked as subsidiary in this study. The analysis is validated if the representativeness of analyses dataset for the inland water can satisfy the variation range of such 'global synthesis'. Of course, the representativeness will be increased with much more data was utilized, and we should pay more attention to the complete collection of inland water data if we want to estimate the discharge flux to the ocean from rivers in further study.

Nonetheless, We added much more data of POC and PON in the world wide river in the revision edition and expected to improve the acknowledge of stoichiometry in the inland water according to the reviewer's comment.

'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 CO2 in the inland water (Raymond et al., 2013). 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 times 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 and temporal 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. 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 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 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.

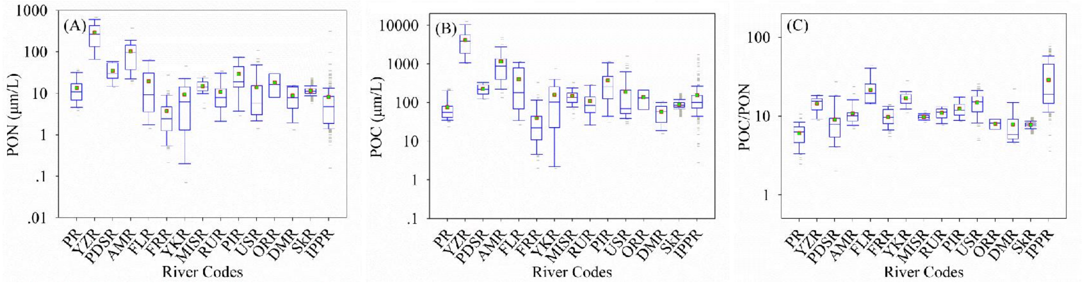


Figure 6 Variation of PON, POC and POC/PON in river waters. PR is Pearl River (China), YZR is Yanagtze River (China), PDSR is paraiba do sul River (Brazil), AMR is Amazon River (Brazil), FLR is Fly River (Papua New Guinea), FRR is Fraser River (Canada), YKR isYukon River (USA), MISR is Mississippi River (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).'

Specific Comments:

2) Line 18: It would be perhaps more interesting to first list the difference between inland waters, oceans, and estuarine C/N averages, rather than just a global average..... this comment was made before realizing how sparse the inland water dataset is.

Response: Actually, we collect large data of POC and PON from different lakes. We have more than11875 couples of POC and PON in the 253 lakes and 15 rivers. We listed the lake dataset in the supporting information, including 13 lakes' and 15 rivers' database.

We shown the variation of POC, PON and POC/PON in ocean and inland water separately primary due to facilitate comparison of our study to previous studies and reveal some new variation pattern of POC, PON and POC/PON in ocean. Meanwhile, the variation of POC, PON and POC/PON in ocean and coastal water has been studied in previous studies. The mean value of POC/PON in ocean is obviously lower than that in inland waters.

The difference of POC, PON and POC/PON in ocean and coastal water was more clearly and detailed in the section 3.2 ‘variations in POC, PON and POC/PON with offshore distance’. The box chart for different data categories (Latitude-, depth-dependent and so on), included much more statistic information than simple mean value, were used to describe the distribution and variation of POC, PON and POC/PON.

3) Line 20: C/N variability in inland waters was attributed to “lake geomorphology, trophic state,

and climate." This is a vast oversimplification, which is reflective on the manuscript in general. Rivers are not even mentioned, which are highly dynamic. For example, C/N ratios (either dissolved or particulate) can vary by several times over the course of a few hours in rivers/streams in response to rainfall. This concept is discussed in the following manuscript and the references therein and should be con-sidered for further discussion in the manuscript:

Ward, N.D., Keil, R.G., Richey, J.E. (2012) Temporal variation in river nutrient and dissolved lignin phenol concentrations and the impact of storm events on nutrient loading to Hood Canal, Washington, USA. Biogeochemistry. 111 (1-3), 629-645

The above comment was made prior to realizing the inland water dataset only included lakes and 2 rivers. Now this focus makes sense.....

Response: Yes, this description is an incomplete picture of impact factors to the variation of POC, PON and POC/PON in inland water. We knew that the POC, PON and POC/PON varied with many impact factors. Just as expert have said, the POC, PON and POC/PON can vary by several times due to the variation of streams in rivers, or the sediment resuspension in shallow lakes. However, on the one hand it is hard to get the time series data of POC and PON for worldwide rivers; on the other hand this is not our issue in this paper. Spatial variation with depth, latitude, and offshore distance is prior in our study relative to the temporal variation. Sometimes, variation trend of POC, PON and POC/PON (such variation range) in spatial scale may similar to that in temporal scale. We recognized the temporal variation in river and ocean. We cited the reference (Ward et al., 2012) and added the discussion in the revised context. The influencing factors to the variation of POC/PON are very complex (refer to the Response of comment 5). These impact factors were compacted in the abstract. We showed some detailed information in the corresponding context.

4) Line 30-35: There are much more recent syntheses of global inland water CO2 budgets that should be mentioned if this is going to be the focal point of the first paragraph. For example, see the following refs. Raymond et al. (2013) increased the outgassing component to 2.1 Pg C yr. Sawakuchi et al., (2017) noted, that a large fraction of the surface area of the world's inland waters aren't accounted for..... adding the complete surface area just of the Amazon River increases the global budget to 2.9 Pg C yr-1. This progression and factors that are still missing from global budgets were discussed in the review paper by Ward et al. (2017):

Raymond, P.A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., et al. (2013). Global carbon dioxide emissions from inland waters. Nature. 503(7476), 355-359

Sawakuchi, H.O., Neu, V., Ward, N.D., Barros, M.L.C., Valerio, A.M., Gagne-Maynard, W., Cunha, A.C., Less, D.F., Diniz, J.E., Brito, D.C., Krusche, A.V., Richey, J.E. (2017) Carbon dioxide emissions along the lower Amazon River. Frontiers in Marine Science. 4 (76) doi: 10.3389/fmars.2017.00076

Ward, N.D., Bianchi, T.S., Medeiros, P.M., Seidel, M., Richey, J.E., Keil, R.G., Sawakuchi, H.O. (2017) Where carbon goes when water flows: Carbon cycling across the aquatic continuum. Frontiers in Marine Science. 4 (7) doi: 10.3389/fmars.2017.00007.

Response: the estimation of global carbon cycle and budgets is constantly improved and perfected. Here, we want to express the important of aquatic system in the global carbon cycle.

We know the important of inland water CO_2 budget, the meaningful paper (Raymond et al., 2013) also was cited in our MS. We lose sight of the latest progress in this aspect (Sawakuchi et al., 2017; Ward et al., 2017). We should add the recent syntheses of global inland water CO_2 budgets in the introduction. Thus, we revised this part according to the reviewer's comment and added these valuable references in the corresponding context.

5) Line 50: See previous comment on Line 20. The factors controlling C/N in terrestrial environments and inland waters are grossly oversimplified. C/N in inland waters is not only a result of OM origin. Molecules are selectively leached from soils during mobilization into streams (or even the flow paths that come before this such as throughfall, stemflow, etc). Molecules are also selectively degraded and sorbed/desorbed during transport, influencing composition. The review paper mentioned above is a good place to start for honing the conceptualization and discussion of inland waters.

Response: the influencing factors to the variation of POC/PON are very complex.

Essential difference: difference accumulation rate of C and N for different plant.

The organic nitrogen presents in protein and nucleic acid of plant preferentially. Thus the organic nitrogen content in higher plants is lesser than it in lower plant (such as algae). Because of that the lignin and cellulose, which includes low organic nitrogen content, are the main component in the higher plants (Giresse, 1994). Recent study indicate that C/N ratios of higher plants can research to 30, even more than 30 (Müller, 1999). However, C/N ratios of lower plants only research to 10, commonly smaller than 10 (Tyson,1995; Kendall et al., 2001).

Environmental condition: microorganism degradation, photodegradation

The difference of mineralization rate between OC and ON also will change the ratio of carbon and nitrogen (POC/PON). The loss rates of OC and ON varied with the temperature, composition of organic matter, dynamic characteristics of water (Stief 2007; Gälman et al., 2008; Gudasz et al., 2010; Sobek et al., 2014; Cardoso et al., 2014).

We should discuss the influencing factors to the variation of POC/PON, at least should add many references for each impact factors, although they are work as supporting role in MS. We revised corresponding context in the paper.

6) Line 80: After reviewing the list of data used, it is not surprising to see the lack of inland water discussion. There is one river dataset listed as far as I can tellâ ˘A˘Tthe Ipswich and Parker rivers, 2 fairly small temperate rivers. The other inland water datasets are from 7 lakes. While the ocean dataset seems to be decently large, the attempt at a "global synthesis" of inland waters made here is non-existent. Where is the Amazon River, which makes up 20% of the freshwater flow to the ocean? How about the Congo River, the Ganges-Brahmaputra River, the Changjiang River, and all of the world's large rivers? Not to mention streams from different settings. I would recommend reading the following review from the 1980's that did a more comprehensive job than done here:

Meybeck, M. (1982). Carbon, nitrogen, and phosphorus transport by world rivers. Am. J. Sci. 282(4), 401-450

Response: in fact, our inland data includes 11875 couples of POC and PON and contains 253 lakes. The lake dataset listed in the supporting information includes many lake groups. The lake group contains many lakes, not just a single lake. We can open the online link if we are interested in it. In my mind, we did not collect all the inland water data for the analyses of variation of POC/PON and worked as contrast in this study. The analysis is validated if the representativeness of analyses dataset for the inland water can satisfy the variation range of 'global synthesis'. Of course, the representativeness will be increased with much more data was utilized, and we should pay more attention to the collection of inland water data if we want to estimate the discharge flux to the ocean from rivers. We read the reference (Meybeck 1982, is a very good paper) recommended by expert (reviewer 2), the POC/PON in Prof. Meybeck study (range from 6.9 to 13) was added. This valuable reference also was added in the context to discuss the variation of

7) For this present study to be meaningful, the authors need to include the majority of robust datasets currently available in the literature. It appears the authors only used data that could be readily downloaded from websites, rather than making a true effort to mine the literature. They have ignored the entire body of inland water literature.

Response: We can't need to assemble all the inland water data for POC, PON and POC/PON, of course, more data is necessary for more representative analyses. We use the representative inland water data includes more than 11875 couples of POC and PON in 253 lakes and 15 rivers. The different types of eutrophic, turbid small, large, and shallow lakes are included in the dataset. Thus, we think that the dataset used in this study could represent the variation of POC, PON and POC/PON in inland water, and could help us to further reveal the relationship between POC and PON and deviations in POC/PON in ocean.

Anonymous Referee #2

1) This paper expanded the global marine dataset on POC and PON, including extending the range northward a few degrees of latitude, and produced many new insights or conclusions compared to previously published studies. It's also good to see freshwater data included, and got some evidence of variability in different lake data. Such as, the finding of high C:N at high northern latitudes (ms. Fig. 2) is as far as I know novel and more or less inverts the temperature-based conclusions of Martiny et al. (who showed C:N increasing with temperature). The ms. figure 7C is quite different from what Martiny et al. (2013) showed in their figure 4. These new insights or conclusions compared to previously published studies suggest that there still are some critical things we need to know to deepen our understanding of global patterns in linkages of C and N. The authors have performed a great service in assembling these data and this is important to extend current knowledge to a wider range of geography. This paper should be published and I offer the following specific comments or suggestions on ways to improve the manuscript.

Response: Yes, as expert (reviewer 1) said, there is much knowledge of variation in POC and PON hasn't been sufficiently studied. Our study also suggest that there still are some critical things we need to know and more research on the stoichiometry is needed although our study shows some new findings.

2) Title – What is meant by “variation pattern?” Suggest a more descriptive title would be something like “Global patterns in particulate and dissolved organic carbon and nitrogen in the global ocean and inland waters.”

Response: We considered the title using ' Global patterns '. However, the inland dataset missed many data of POC and PON in inland waters, which also mentioned by expert (reviewer 2), although our data set can satisfy the variation range of “global synthesis” in inland water.

3) Figures – All of them are too small, which made it really hard to see what was going on with the data. Suggest converting each on to landscape orientation and then filling the entire page with it, or submitted each figure respectively.

Response: We will submit each figure respectively when we submit the revised edition.

4) The Abstract is adequate. but the means of (12.2±7.5) should be noted, mean value ± error or standard deviation?

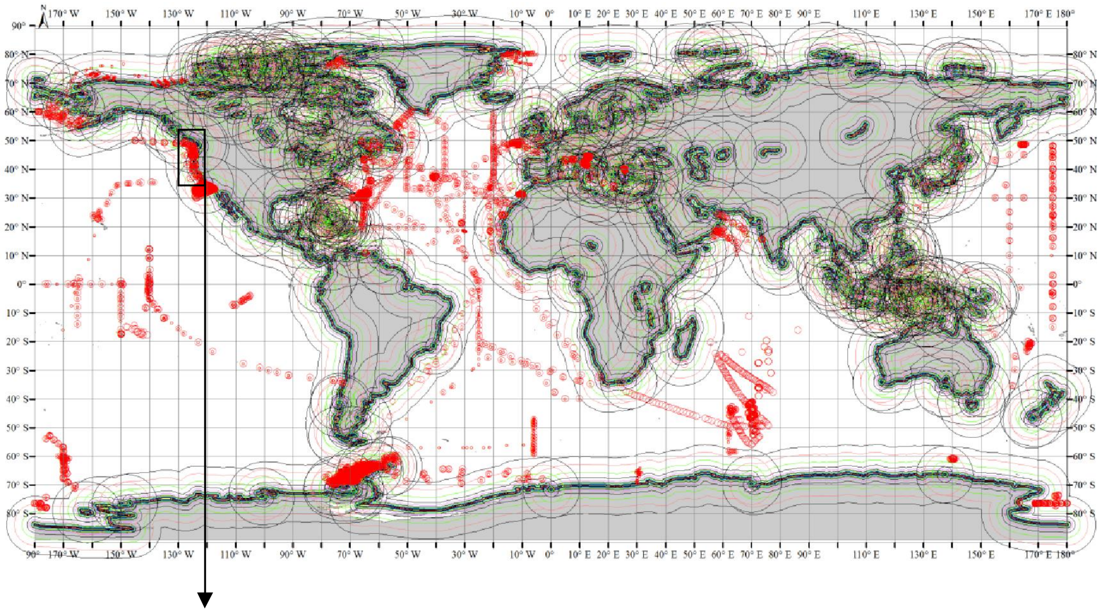
Response: It means mean value ± standard deviation, we revised it in the MS.

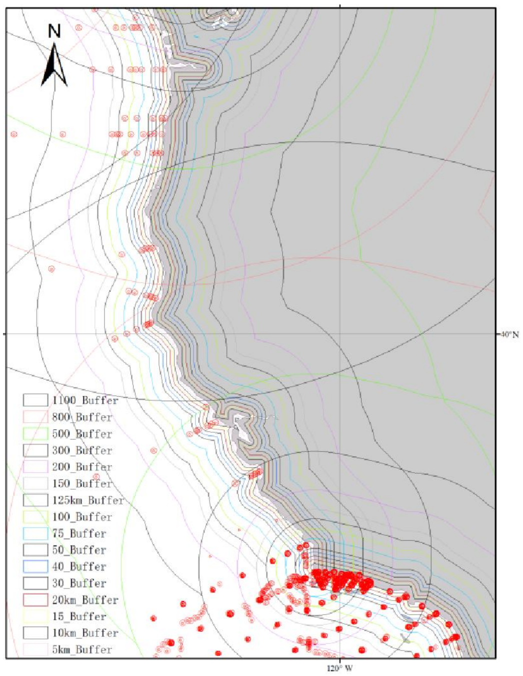
5) The Introduction is okay but not very inspiring.

Response: we revised the introduction and added some information according to the expert's (reviewer 2) suggestion.

6) I believe the analysis of distance to land (Fig. 4) is by far the most extensive one yet. The detailed analysis method should be introduced in section 2.2, although '3) Offshore distance ranges...........' was mentioned.

Response: We added the some detailed description of data process in the section of method. 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) (Following figure). The buffers overlap with continent was erased by terrestrial vector data. 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.





The establishment of buffers for different distance from offshore was implemented by Arcgis 10 (Esri). The amplification of regional part in United States West Coast (USWC) can clearly show the distribution of sampling points in each buffer.

7) The analysis concerning soil carbon and nitrogen is novel. However, there was no mention in the Methods as to where these soil data come from or how they were matched to the marine data.

Response: We added the detailed description of data process in the section of method.

8) There are some really intriguing patterns here that depart from previous work and which are based on what I believe to be the most comprehensive dataset yet assembled on these parameters although some imperfections should be polished. This dataset has some interesting patterns that will help us move stoichiometry forward.

Response: We very appreciate the helpful suggestion and comments from expert (reviewer 1). We carefully revised the MS according to the expert's comments.

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, 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 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 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 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 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

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 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 POC, PON and POC/PON.

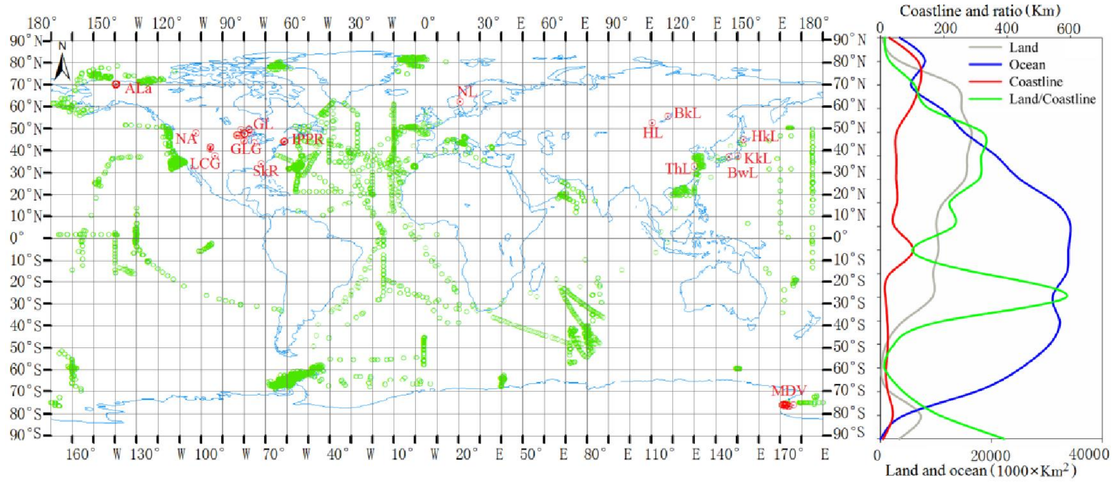


Figure 1 Global distribution of paired samples of POC and PON. Green circles are oceanic samples and red circles are inland samples. Land and ocean area, coastline length and the ratio of land area to coastline are also shown. The original map data of world vector downloaded from http://www.naturalearthdata.com/.

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 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 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 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 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 ($\mathrm{POC} = (6.998 \pm 0.645) \times \mathrm{PON}^{(0.901 \pm 0.081)}$, $R^2 = 0.905 \pm 0.052$). A linear function (including and excluding intercepts) also describes the relationship between carbon and nitrogen well ($\mathrm{POC} = (7.545 \pm 2.498) \times \mathrm{PON} + (0.302 \pm 2.658)$, $R^2 = 0.891 \pm 0.047$; $\mathrm{POC} = (7.666 \pm 2.169) \times \mathrm{PON}$, $R^2 = 0.882 \pm 0.048$). 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., 2015).

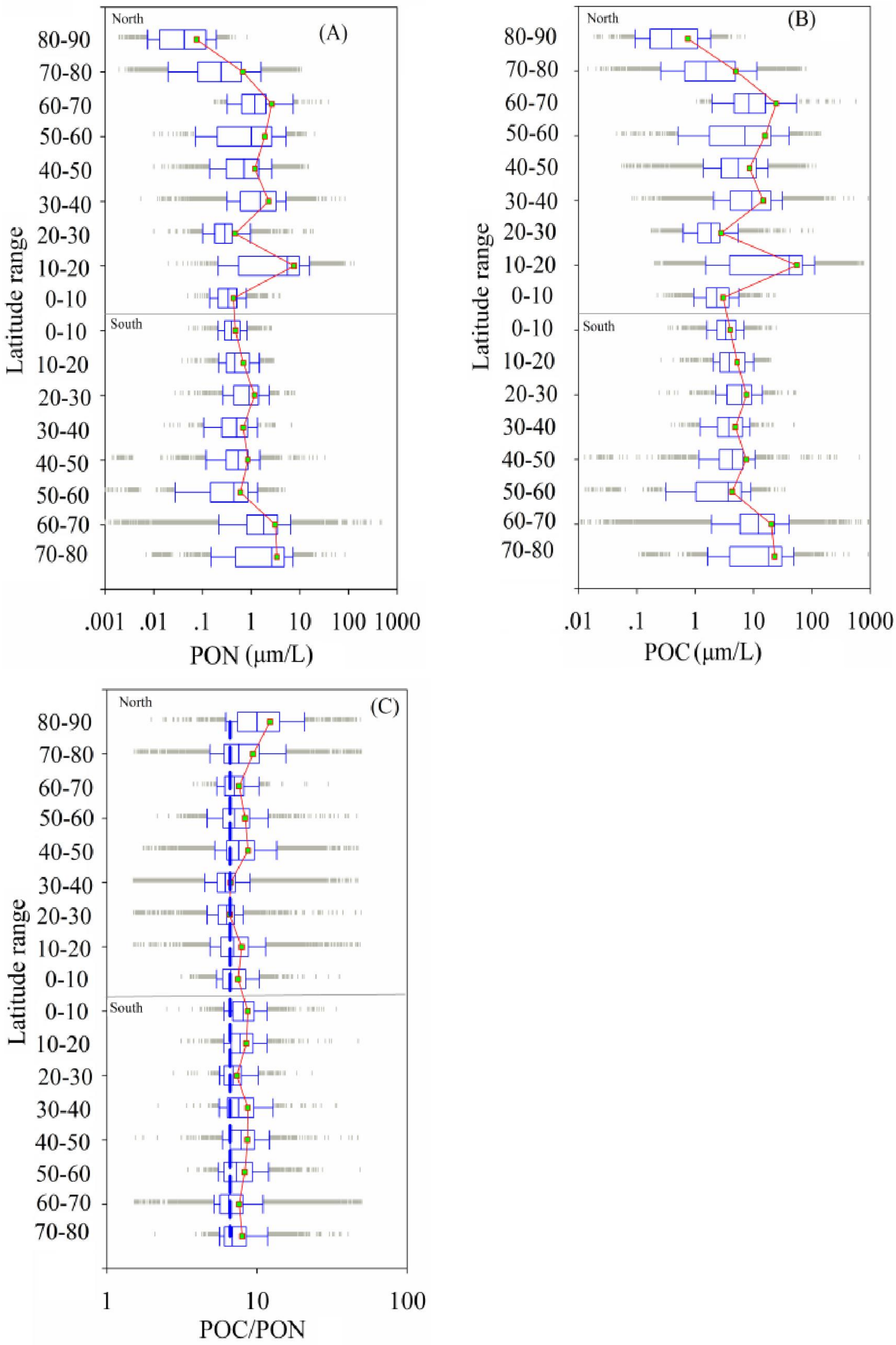


Figure 2 Latitudinal variation of PON, POC and the POC/PON ratio from the compiled statistical results of depth-integrated data for all ocean data. The box plots show the median and 25th and 75th percentiles, with whiskers covering most of the data. The red line with green boxes shows the mean value 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.

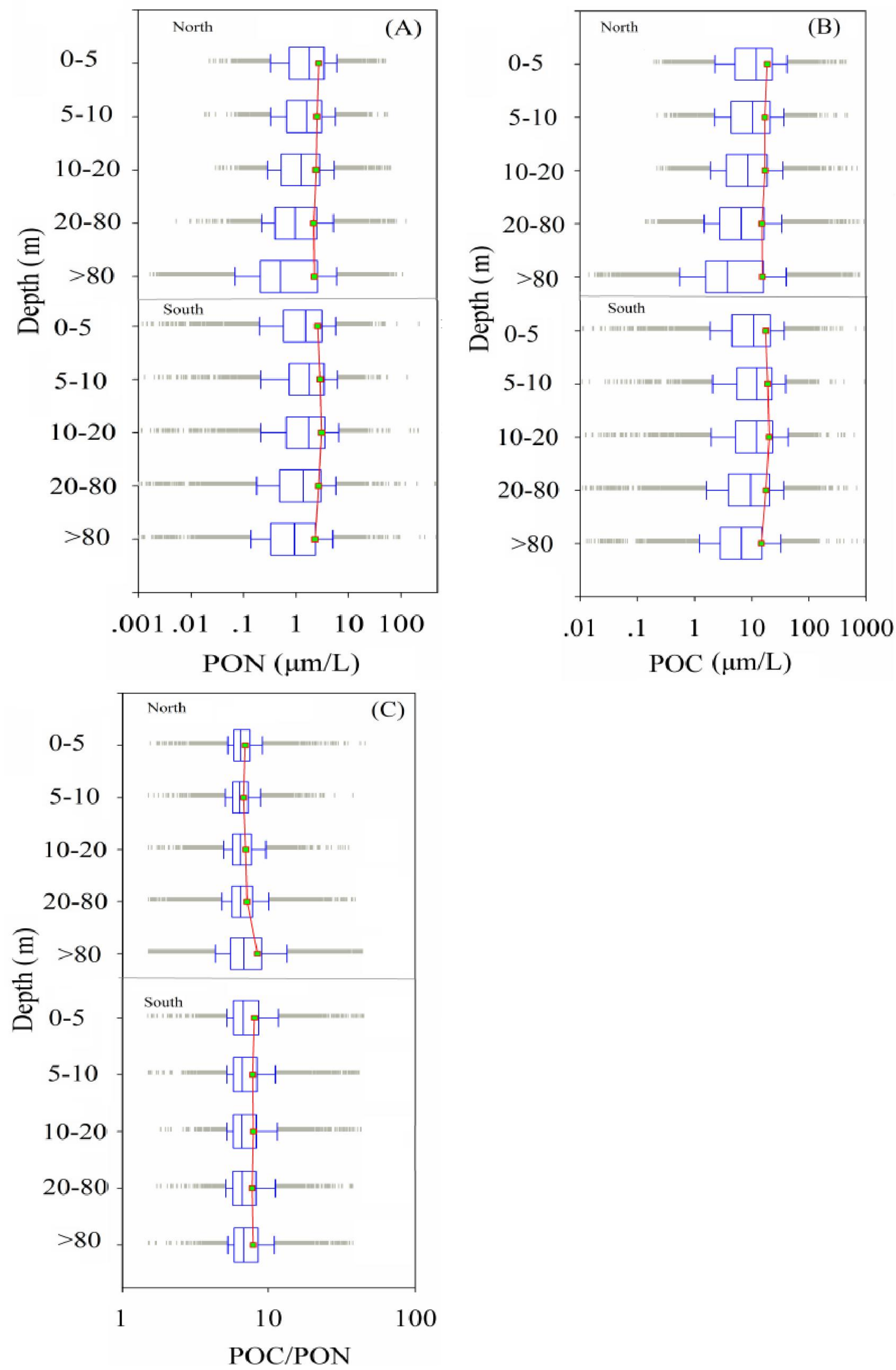


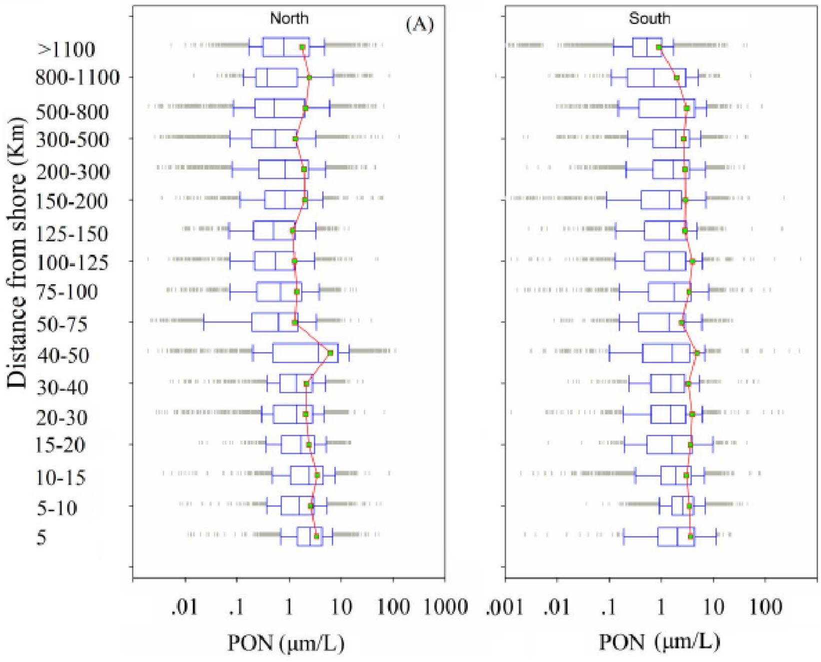
Figure 3 Depth-dependence of POC and PON in the southern hemisphere and depth-dependence of POC/PON in the northern hemisphere. The box plots show the median and 25th and 75th percentiles, with whiskers covering most of the data. The red line with green boxes shows the mean value at each depth. The number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



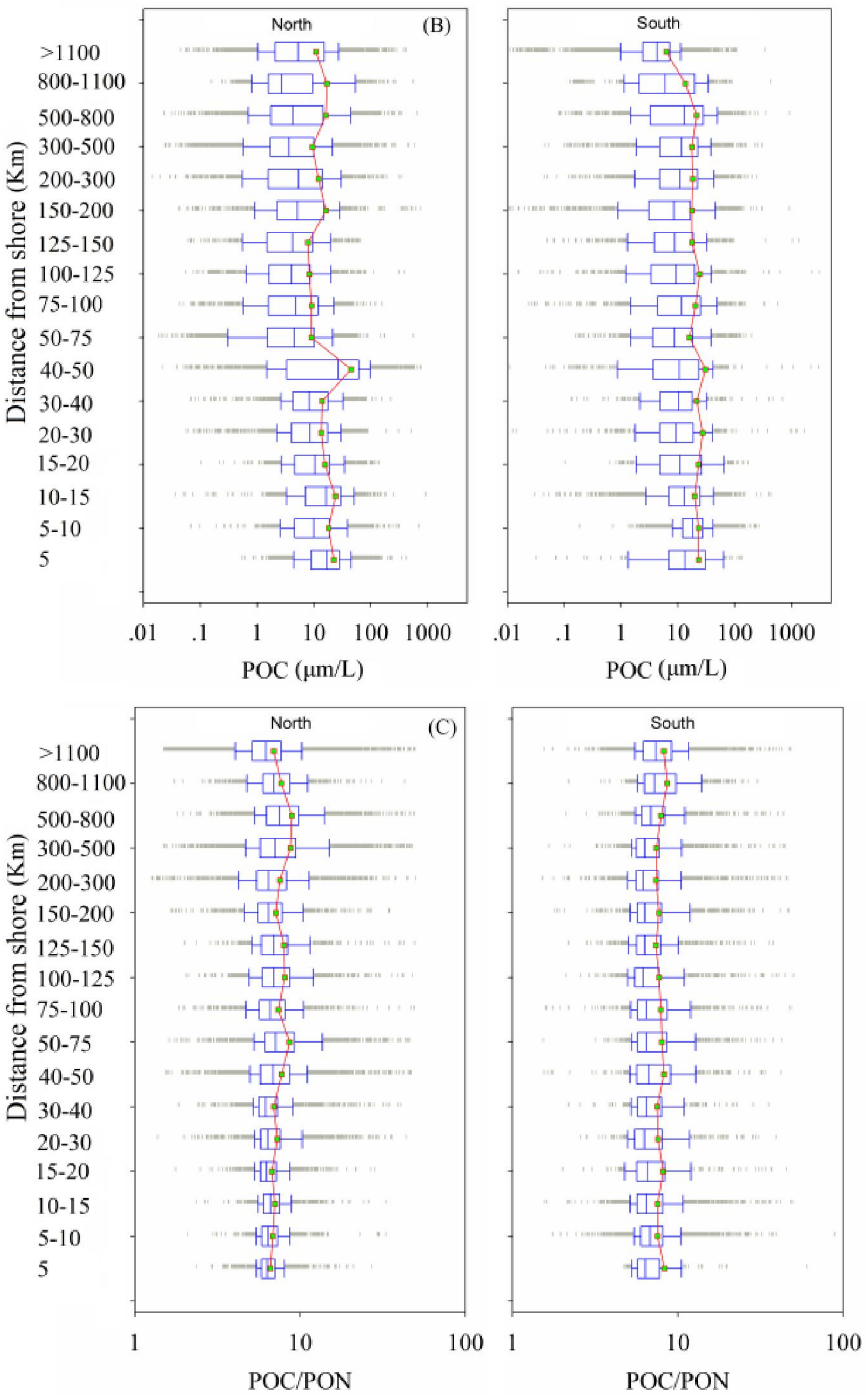


Figure 4 Variation of POC, PON and POC/PON with distance from shore. The number of samples for each buffer is listed in Table S4. The box plots show the median and 25th and 75th percentiles, with whiskers covering most of the data. The red line with green boxes shows the mean value for each range.

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 (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 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 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.

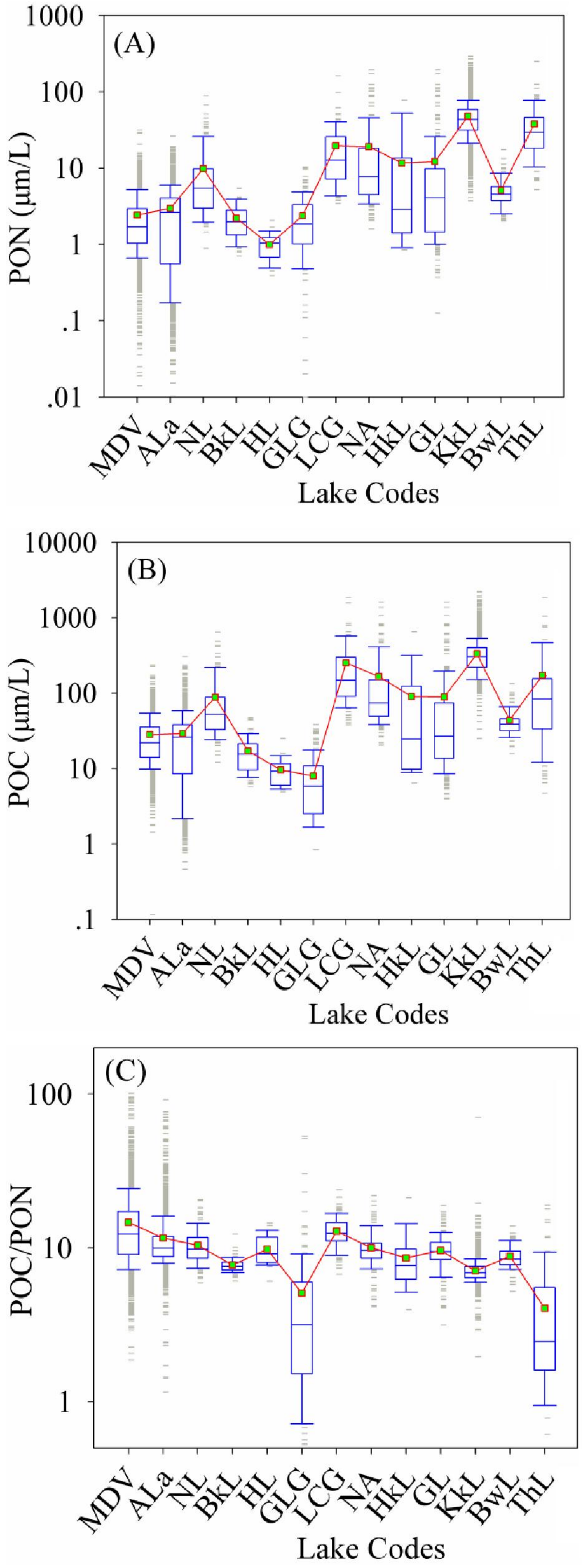
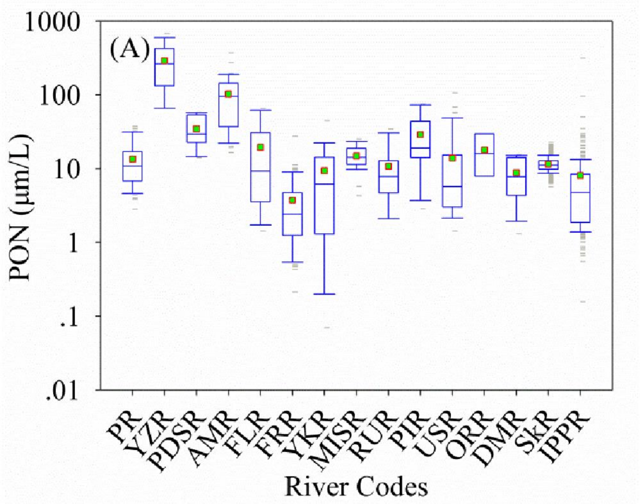


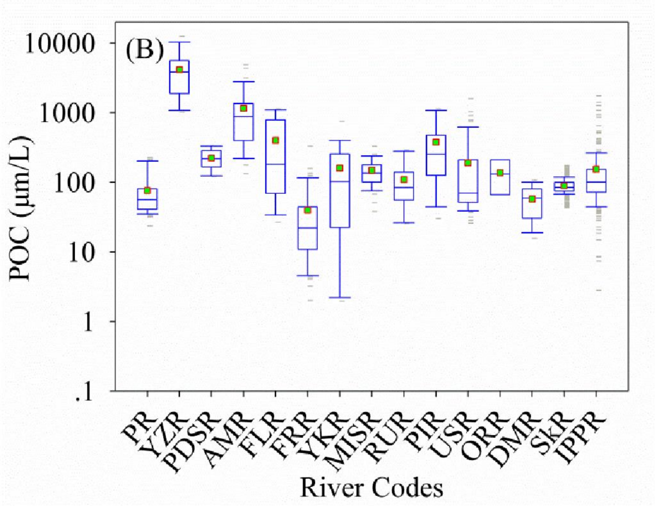
Figure 5 Variation of PON, POC and POC/PON in lake waters. The lakes are mainly located in the northern hemisphere. Eutrophic, small, large, and shallow lakes are included in the dataset. MDV

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 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.





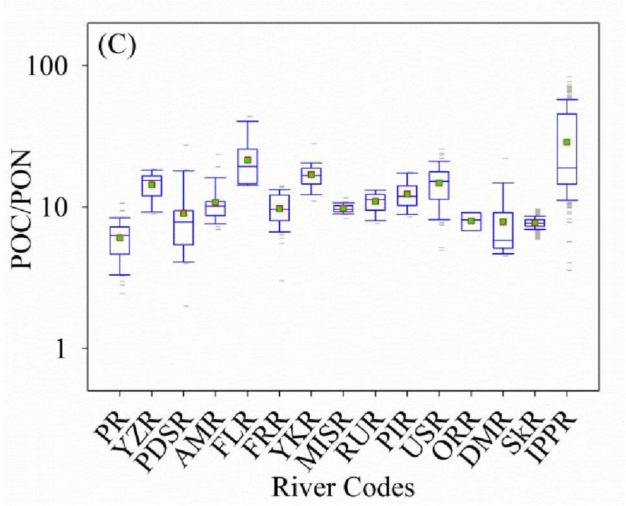


Figure 6 Variation of PON, POC and POC/PON in river waters. PR is Pearl River (China), YZR is Yanagtze River (China), PDSR is paraiba do sul River (Brazil), AMR is Amazon River (Brazil), FLR is Fly River (Papua New Guinea), FRR is Fraser River (Canada), YKR isYukon River (USA), MISR is Mississippi River (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 correlated to the ratio of land area to coastline length (land/coastline): POC/PON $=11.938*(\text{land/coastline})^{-0.078}$ (R^2=0.41) (Figure 7C).

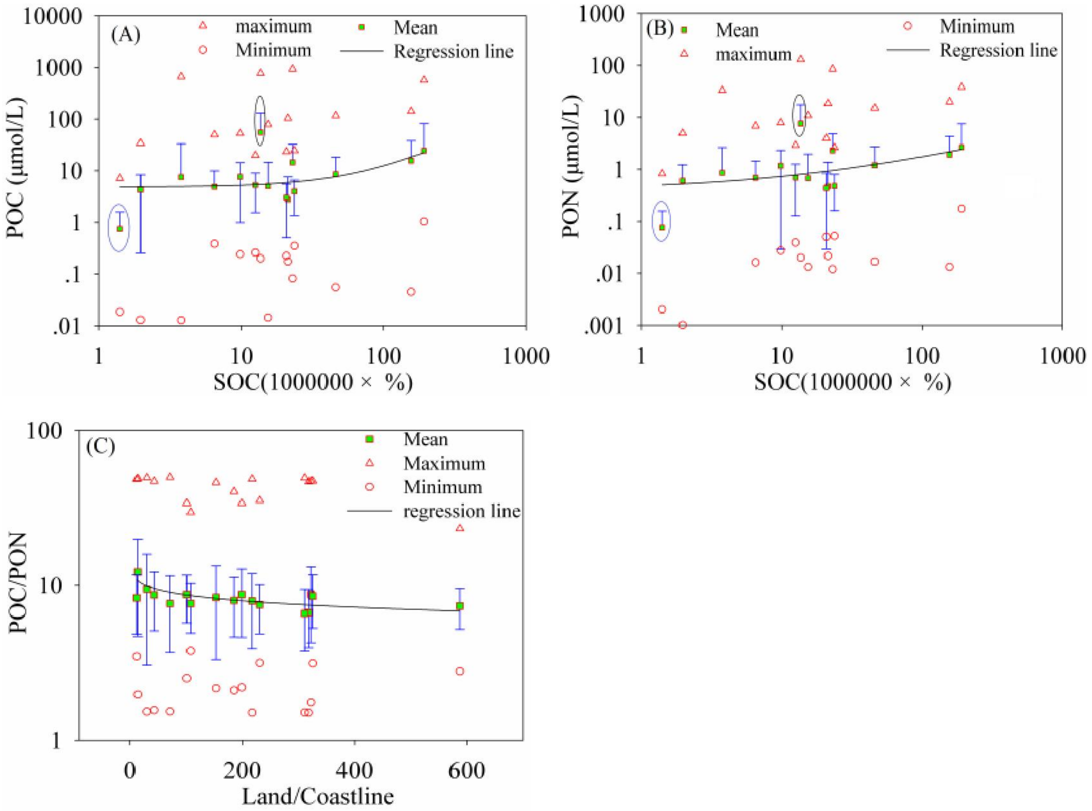


Figure 7 (A) and (B) Relationship between POC, PON and soil organic carbon. (C) The relationship between POC/PON and the ratio of land area to coastal linear length. The red boxes with green shading are the mean values of POC, PON and POC/PON in each latitudinal range, the blue line is the standard deviation,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

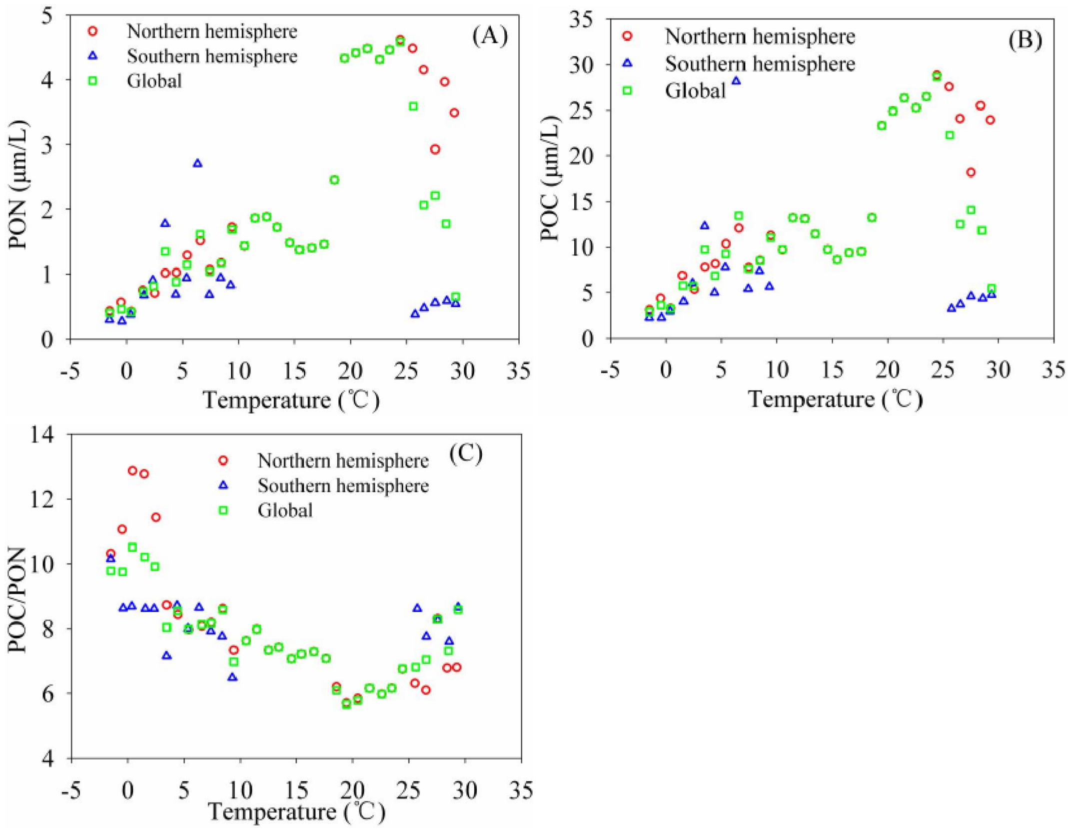


Figure 8 Relationships between POC, PON, and POC/PON and temperature (T). POC, PON and POC/PON are highly correlated to temperature in the northern hemisphere, with relationships of PON=0.142*T+0.260 (R^2=0.74), POC=0.788*T+3.340 (R^2=0.74) and POC/PON=11.88*$T^{-0.190}$ (R^2=0.81), respectively. There 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 ($C_{\text{Chl-a}}$) 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 $C_{\text{Chl-a}}$ can't accurately explain POC variation at the global scale due to high variation in POC/$C_{\text{Chl-a}}$ (Arrigo et al., 2003; Sathyendranath et al., 2009). POC levels are highly positively correlated to $C_{\text{Chl-a}}$ for oceans, lakes, eutrophic lakes, rivers and coastal waters (Figure 9A). The best fit function for the relationship between POC and $C_{\text{Chl-a}}$ 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 $C_{\text{Chl-a}}$ 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 $C_{\text{Chl-a}}$ 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 ($\mathrm{POC}=0.2641*C_{\mathrm{TSM}}^{0.8466}$, $R^2=0.81$, n= 5306) is close to the same relationships in the Baltic Sea ($\mathrm{POC} = 0.317*C_{\mathrm{TSM}}^{0.969}$, $R^2=0.86$, Woźniak et al., 2016) and surface water in the US ($\mathrm{POC} = 0.2992*C_{\mathrm{TSM}}^{0.3321}$, $R^2=0.593$, 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 $\mathrm{POC}_{\mathrm{exp}} = 0.0524*C_{\mathrm{sed}}^{0.665}$. 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.

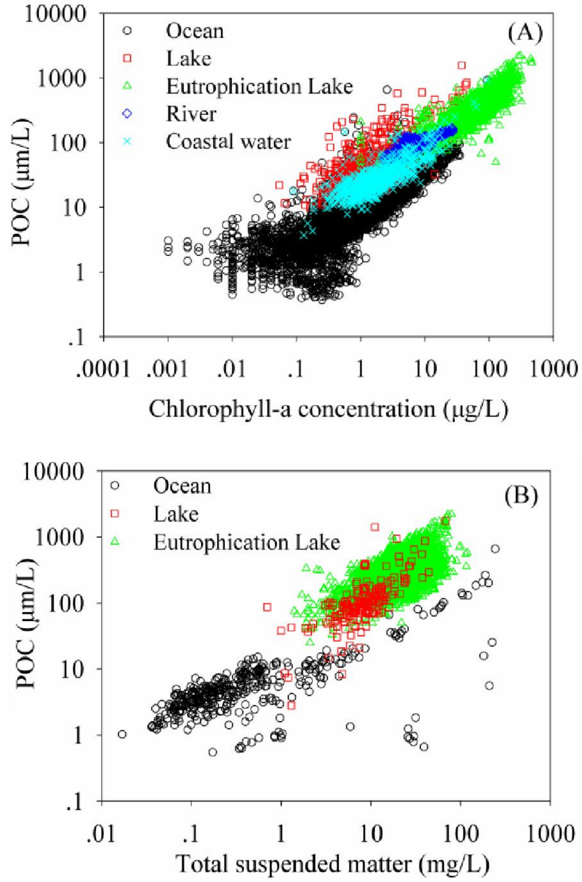


Figure 9 (A) Comparison of the relationships between POC and chlorophyll-a concentration ($C_{\mathrm{Chl\text{-}a}}$) for oceans, lakes, eutrophic lakes, rivers and coastal waters. (B) Comparison of the relationship between POC and total suspended matter concentration (C_{TSM}) for oceans, lakes and eutrophic lakes. The relationships between POC and $C_{\mathrm{Chl\text{-}a}}$ are $\mathrm{POC}=4.429*C_{\mathrm{Chl\text{-}a}}+6.531$ ($R^2=0.51$,

N=5462); POC=16.420*$C_{\mathrm{Chl\text{-}a}}$+17.855 ($R^2$=0.64, N=984); POC=3.513*$C_{\mathrm{Chl\text{-}a}}$+96.528 ($R^2$=0.72, N=4656); POC=4.458*$C_{\mathrm{Chl\text{-}a}}$+55.931 ($R^2$=0.77, N=936); and POC=7.357*$C_{\mathrm{Chl\text{-}a}}$+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 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).

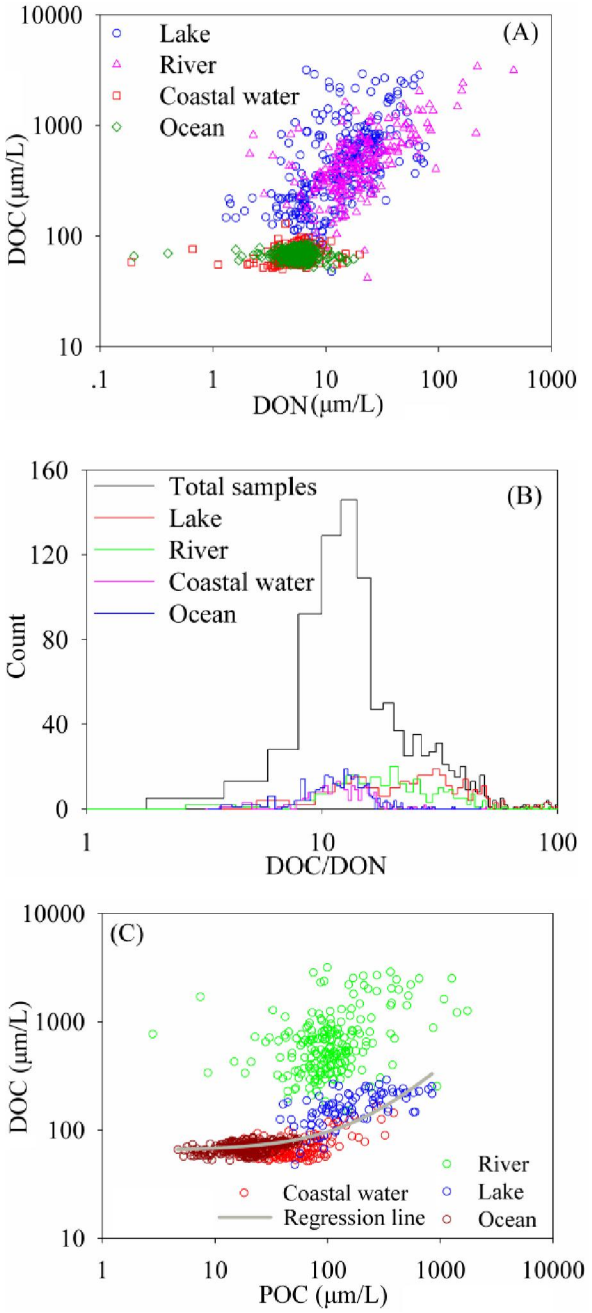


Figure 10 (A) Comparison of the relationships between DOC and DON for oceans, lakes, rivers, and coastal waters. The relationships between DOC and DON are DOC = 11.738*DON + 165.41 (R^2=0.35, n=995); DOC = 19.037*DON + 273.59 (R^2=0.20, 288); and DOC = 11.932*DON + 234.36 (R^2=0.61, n=255) for all samples, 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 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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