Environmental Science Processes & Impacts

Accepted Manuscript

Dissolved carbon is an important component of the carbon cycle, and links terrestrial and aquatic ecosystems. Permafrost soils act as large sinks of organic carbon but are highly sensitive to interference such as changes in land use, which can greatly influence dissolved carbon loads in steams. The long-term land reclamation in the northeast China led to remarkable change in the total flux and exporting coefficient of the dissolved carbons, companied with the alteration in the chemical characteristics and the origin of the DOC released from the whole reaches. The alteration will have great impacts on the carbon cycling and associated environmental processes in linked aquatic and marine systems, such as the Amur River downstream.

Effects of long-term land use change on dissolved carbon characteristics in the permafrost streams of northeast China

Yuedong Guo[a], Changchun Song[a,*], Zhongmei Wan[b], Wenwen Tan[a], Yongzheng Lu[a], Tianhua Qiao [a]

[a] *Key Laboratory of Wetland Ecology and Environment, Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, Changchun 130012,China*

[b] *College of Earth Science, Jilin University, Changchun 130061, China*

E-mail: Songcc@neige.ac.cn; guoyuedong@neige.ac.cn

Abstract

Permafrost soils act as large sinks of organic carbon but are highly sensitive to interference such as changes in land use, which can greatly influence dissolved carbon loads in steams. This study examines the effects of long-term land reclamation on seasonal concentrations of dissolved carbons in the upper reaches of the Nenjiang River, northeast China. Comparison of streams in natural and agricultural systems shows that dissolved organic carbon (DOC) concentration is much lower in the agricultural stream (AG) than in the two natural streams (WAF, wetland dominated; FR, forest dominated), suggesting that land use change is associated with reduced DOC exporting capacity. Moreover, the fluorescence indexes and the ratio of dissolved carbon to nitrogen also differ greatly between the natural and agricultural streams, indicating that the chemical characteristics and the origin of the DOC released from the whole reaches are also altered to some extent. Importantly, the exporting concentration of dissolved inorganic carbon (DIC) and its proportion of total dissolved carbon (TDC) substantially increase following land reclamation, which would largely alter the carbon cycling processes in the downstream fluvial system. Although the strong association between stream discharge and DOC concentration was unchanged, the reduction in total soil organic carbon following land reclamation led to remarkable decline of the total flux and exporting coefficient of the dissolved carbons. The results suggest that dissolved carbons in permafrost streams have been greatly affected by changes in land use since the 1970s, and the changes in the concentration and chemical characteristics of dissolved carbons will be last until the alteration in both the traditional agriculture pattern and the persistent reclamation activities.

Keywords: land use change, dissolved carbon, fluorescence indexes, hydrological processes

Introduction

Dissolved carbon is an important component of the carbon cycle, and links terrestrial and aquatic ecosystems.[1,2] Globally, it is conservatively estimated that inland waters annually receives about 1.9 Pg C from the terrestrial landscape,[3] and the dissolved carbons exported from permafrost areas form an important part of this total.[4-6] Permafrost ecosystems hold 25–33% of the world's soil organic carbon,[7] which far exceeds the total amount of surficial biomass carbon in those systems, and is highly sensitive to human intervention and climatic changes.[8,9] With increasing influence of human activities in the permafrost region facilitated by climate warming, alteration in the transportation of dissolved carbons will have unpredictable impacts on linked aquatic and marine systems.

During the past decade, changes in the concentration and flux of DOC in streams have been widely reported in boreal permafrost regions.[10-12] Land use change, which represents the most powerful alteration of the terrestrial ecosystem in the past 300 years, is an important driving factor.[13] Land use change, usually associated with substantial alterations in soil temperature and hydrology, greatly affects DOC production and release within the soils of natural ecosystems.[14-16] The conversion of natural ecosystems for agriculture leads to increased surface soil temperature, which accelerates the decomposition of organic matter by stimulating microbial activities, thereby reducing soil organic carbon stock and DOC production potential.[17] However, DOC concentration in streams depends not only on the soil carbon pool, but also on the hydrological connection with the organic soil layer. Hydrological conditions can affect both the surface soil moisture and the runoff processes, which directly controls DOC production capacity in soil layers and exporting concentrations in streams.[18,19] Changes in discharge appear to strongly affect DOC concentrations in agricultural watersheds[14,20]. Basically, two kinds of driving processes of DOC exporting can be summarized: “source-limited” and “transport-limited”. In transport limited river DOC concentration increases with discharge and in source limited river DOC decreases with discharge. However, the relationship may be variable due to farming pattern alteration and drainage canal construction. Findings of “no relationship” are also reported in some study areas[21]. In summary, there is a complex interaction between DOC concentration and altered hydrological processes resulting from land use change. To date, however, it is still hard to accurately forecast the long-term effects of land use change on DOC concentration and flux in streams, especially in permafrost region where few study has demonstrated the effect of land use change.

Some studies have focused on the relationship between land use change and the chemical characteristics of DOC.[20,22,23] Modifications in soil features following land use change from natural ecosystems may result in transformation of soil organic matter characteristics over decadal time scales.[16,24] Changes in soil temperature and moisture, as well as microbial communities, can greatly alter the turnover speed of the liable organic carbon pool by microbes and even excite the activation of the stable pool with high degree of humification in permafrost region.[25,26] As a result, DOC chemical characteristics, such as humification degree and stoichiometric ratio, may become unstable in streams following land conversion. In addition, human activities in agricultural watersheds have notable effects on the chemical characteristics of riverine DOC by fertilization and crop rotation.[27,28] Hence, these consequences must be considered when evaluating the impacts on DOC dynamics by land use change and in predicting the resulting environmental responses.

Dissolved inorganic carbon (DIC) represents the main component of the total carbon flux in many large rivers of the world.[29] Globally, DIC concentration in riverine runoff to the oceans ranges from less than 2 mg l^{-1} to more than 20 mg l^{-1}, and the total flux of DIC to the Arctic Ocean is estimated at 36×10^6 t a^{-1}, which is 1.4 times the total flux of DOC.[30] However, DIC is often neglected in research involving carbon pool processes and land use change in boreal environments. As DIC is closely related to natural weathering and to a variety of anthropogenic processes on basin-wide scales, DIC concentration in river systems is influenced by a variety of environmental factors such as precipitation, chemical weathering and human activities in both temporal and spatial perspectives.[31-34] Nevertheless, there is limited literature on whether land use changes could significantly influence DIC in river systems in boreal permafrost regions.

The northern parts of the Great Xing'an Mountains in northeast China form the southern margin of the discontinuous permafrost zone in Eurasia. The soil organic carbon (SOC) stored in the cold temperate forests and wetlands in this area is estimated at more than 5473×10^4 t.[35] Driven by a marked temperature increase of up to 1.5°C during the last 50 years, the southern boundary of the permafrost has migrated northward by approximately 100 km since the 1970s, and the active layer thickness has increased by 20–40 cm from the 1970s to 2000.[36] Temperature increase associated with permafrost degradation has led to extensive reclamation of the natural forest and wetland ecosystems for agriculture since the 1970s. The agricultural area accounted for 20–30% of the total area by 2010, and the rate of expansion has gradually increased in recent years. However, to date, few studies have focused on land use change and its influences in this region, and there is a lack of preliminary knowledge about many important questions on regional carbon fluxes. This work addresses the following questions: (1) What are the concentrations and fluxes of dissolved carbon in the streams in the region? (2) How does land use change affect the concentration and chemical characteristics of DOC in the streams? (3) Has land use change led any alteration in the relationship between dissolved carbon concentration and discharge? (4) What is the possible trend of DOC and DIC concentration in the streams in the future? By addressing these questions, we hope to establish a basis for predicting future DOC export from this region, and for evaluating future environmental impacts.

Material and methods

Site description

This study focuses on the upper reaches of Nenjiang River, which is a tributary of the Amur River on the northern slopes of the Great Xing'an Mountains (Fig. 1). The study site covers an area of 29725 km^2 and is located in the discontinuous permafrost zones with an annual mean temperature ranging from -1.5°C in the north part to -0.4°C in the south part. Average annual precipitation is 435 mm and mainly occurs during June and July in the summer season (1970-2006). The growing season lasts from May to early October. The natural ecosystems are *Larix gmelinii* forest and wetland, composed mainly of *Cyperaceae* family. Soya bean and wheat have been the two dominant crops in the agricultural areas, which distribute mainly on the river plain and account for 24.7% of the total area at present. Forest covers almost 42.4% of the total area and wetland occupies 29.2%. The forests mainly distribute in mountainous areas, on slopes steeper than 15°, and the wetlands extend alongside the numerous linked streams.

Fig. 1 Sketch map of the upper reaches of Nenjiang River and the three sub-catchments.

Sampling designs and field monitoring

During the 2011 growing season, water samples were collected from the outlet of the upper reaches of the Nenjiang River (OUT), and from three sub-catchment streams (Fig. 1). The three sub-catchments represent different land use types: natural wetland and forest landscape (WAF); mainly forest landscape and small area of wetland (FR); and mostly agricultural farmland with a few degraded wetland patches

(AG). The maximum active layer depth in the WAF and FR sub-catchments varied between 1.2 m and 1.5 m in the late summer, while in the agricultural land in the south of the watershed in our study area, the depth usually exceeded 3.5 m. The mean temperature of the surface soil (0-50 cm) in the major landscape of the WAF, FR and AG season are 5.59, 7.00 and 13.26 ℃ respectively during the growing. More detailed information on the three sub-catchments is listed in Table 1. Sampling in OUT aimed to obtain basic information on the dissolved carbons released from the entire studied reaches under the current pattern of land use. Sampling in the three sub-catchments aimed to determine the effects of land use change from natural to agricultural landscapes by comparing the quantity and chemical features of the dissolved carbons, as well as their relationship with discharge processes, under different land uses.

Table 1 Detailed land use and soil physical-chemical features of the three sub-catchments in the study area.

During the study period, water samples were usually collected every 5 days, and the sampling frequency was moderately intensified during high flow periods. When sampling, three duplicates of 300 ml stream water were collected at three depths in the stream cross profiles, and it is guaranteed that no air is sealed in the sampling bottles. Then the samples were filtered using a 0.45-μm glass-fibre membrane, and refrigerated at 4°C for less than three days before conducting chemical analysis. In the outlets of the three sub-catchments, stream discharges were monitored by automatically measuring water level (Odyssey, New Zealand) and discharge velocity (Argonaut-ADV, USA) on the outlet profiles. Discharge data for OUT in 2011 were obtained from the Water Authority of Nenjiang County. Daily temperature in the WAF and FR sub-catchments is automatically monitored by meteorological observation systems (Compbell series, USA), and that in the AG is collected from the Meteorology Authority of Nenjiang County.

Chemical analysis

The stored water samples were analysed using a DOC analyser (C-VCPH, Shimadzu, Japan). Firstly, the total dissolved carbon (TDC) was measured by high-temperature combustion. Then, dissolved inorganic carbon (DIC) was measured after the sample was acidified with 25% H_3PO_4 and 2 mol l^{-1} HCL, and the DIC in the sample was transformed into CO_2. The DOC content was obtained by subtracting the DIC from the TDC. Meanwhile, total dissolved nitrogen (TDN) was determined by persulfate digestion and second-derivative spectroscopy for nitrate determination.[37] The concentrations of the organic formation of nitrogen (DON), ammonia (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-) were also measured with a continuous flow analyser (Skalar San++, Holland). DON was calculated as TDN minus the sum of NH_4^+, NO_3^-, and NO_2^-.

Fluorescence analysis

Three-dimensional excitation-emission matrix (EEM) fluorescence of the organic matter was measured using a Hitachi F-7000 fluorescence spectrometer (Hitachi High Technologies, Tokyo, Japan) with a 700-W xenon lamp at room temperature. The spectrofluorometer was set to collect the signal using a 5 nm bandpass on the excitation as well as emission monochromators with a scanning speed of 1600 nm min^{-1}. The EEMs were recorded at 2 nm intervals for excitation spectra between 220 and 450 nm and emission spectra between 250 and 550 nm. Water Raman scatter peaks were eliminated by subtracting a Milli-Q water blank of the EEM. The spectra were corrected for instrumental response according to the procedure recommended by Hitachi (Hitachi F-7000 Instruction Manual). Excitation was calibrated with rhodamine B as standard (quantum counter) and a single-side frosted red filter in the excitation scan mode. The emission was then calibrated with a diffuser in the synchronous scan mode. To eliminate the inner-filter effect, the EEMs were corrected for absorbance by multiplying each value in the EEMs by a correction factor based on the premise that the average path length for the absorption of the excitation and emission light rays was half the cuvette length.[38] Then, the EEMs were normalised to the area under the Raman scatter peak (excitation wavelength of 350 nm) of a Milli-Q water sample run the same day according to the method of Stedmon et al.[39]

The typical EEMs of organic matter for the WAR, FR and AG was shown in Fig. 2.[40] Three spectral indexes were calculated using the EEMs to describe the chemical characteristics of DOC: humification index (HIX), fluorescence index (FI), and biological index (BIX). The HIX is used to quantify the complexity and aromaticity of dissolved organic matter whose molecular structures undergo gradual alteration during microbial processes. The FI was used to distinguish the source of dissolved organic matter containing humic substances in an aquatic environment. The BIX is a complementary index for assessing the relative contribution of microbially derived organic matter in waters. More details on these indexes, including the calculation method, ecological meaning, and main references are presented in Table 2.[41-43]

Fig. 2 Typical EEMs of the dissolved organic matter for the WAR (a), FR (b) and AG (c) in the growing season. T indicates tryptophan-like fluorescence peak; C and A are fulvic-like and humic-like fluorescence peak respectively.[40] (The three samples are all collected in the base flow period of discharge in the summer 2011)

Table 2 Spectral indexes calculated from the excitation-emission matrices (EEMs): humification index (HIX), fluorescence index (FI), and biological index (BIX).

Statistical analysis

The mean and standard deviation of dissolved carbons in discharge, fluorescence strength, and the three fluorescence indexes were analysed via SPSS software (version 16.0). The difference in dissolved carbon concentrations among the four sites was tested by One-Way ANOVA analysis with a significance level of 0.05. The relationships between discharge and dissolved carbon concentrations, and the fluorescence indexes were examined via two-tailed Pearson correlation and regression analysis; a p-value of 0.05 was regarded as significant.

Results

Concentration of dissolved carbons

The concentrations of DOC and DIC at the four sites exhibit pronounced fluctuation during the growing season, as shown in Fig. 3. The mean concentration of DOC in the AG is 5.25 mg l^{-1}, which is somewhat lower than that in the OUT (5.70 mg l^{-1}) while much smaller than those in the WAF and FR (8.79 and 6.67 mg l^{-1} respectively) (see Table 3). In the WAF and FR, maximum DOC concentrations exceeded 20.00 mg l^{-1} during the flood period in June, while the minimum DOC values of less than 3.50 mg l^{-1} were observed during autumn. By contrast, DOC in the AG and OUT showed much smaller variation during the growing season. For DIC, the mean values of 6.33 ± 1.19 and 6.96 ± 2.28 mg l^{-1} in the AG and OUT are significantly higher than those in the WAF and FR ($P<0.05$). Among the four sites, the maximum mean TDC value of 13.05 ± 4.42 mg l^{-1} occurs in the WAF, while the minimum value 10.69 ± 3.37 mg l^{-1} occurs in the FR. Clearly, DOC is the predominant component for TDC in the WAF and FR, whereas DIC predominates in the AG and OUT. In the WAF and FR, the DOC: DIC ratios are 2.06 and 1.66 respectively, whereas those in the AG and OUT are only 0.83 and 0.82. For OUT, the mean concentrations of DOC are in the middle of the group, whereas the DIC value is the highest of the four sites.

Fig. 3 Seasonal variation in discharge (Q) and concentration of dissolved carbons during the growing season.

Table 3 Concentrations of dissolved carbons in relation to discharge at the three sub-catchments and the whole reaches.

Relationship between dissolved carbons, discharge, and temperature

The concentrations of dissolved carbons at the four sites show significant variation with stream discharge (Fig. 1). Regression analysis indicates significant positive correlations between DOC concentration and the logarithms of discharge in both the sub-catchments and the whole reaches (Table 3). However, no significant relationship was found between DIC and discharge, except at AG (R^2=0.23, P=0.01). Note that the slopes of the linear equations of DOC in the WAF and FR are very similar (4.49 and 4.98 respectively), which are much greater than that in the AG (2.82). The slope for the OUT is between that for AG and those of the two natural ecosystems. Among the three sub-catchments, only WAF shows a significant positive relationship between air temperature and DOC concentration ($P<0.05$), and none of the sites showed a significant relationship for DIC.

Flux and exporting coefficients of the dissolved carbons

The fluxes of the DOC and TDC in the WAF and FR are clearly higher than that in the AG (Table 4). The total flux of the TDC reaches 461.62 t during the growing season, in which DIC accounts for 55.01%. The exporting coefficient indicates the average release capacity of dissolved carbons from the catchments under the synthetic influences of hydrology, temperature, and human activities. In the WAF and FR, the exporting coefficients of DOC are much higher than those in the AG, which indicates the same trend for the total fluxes. In the OUT, the coefficients (6.99 kg km^{-2} d^{-1}) are also somewhat higher than AG. At all sites, the exporting coefficients for DIC are similar, ranging between 6.70 and 8.69 kg km^{-2} d^{-1}.

Table 4 Fluxes and exporting coefficients of dissolved carbons from the three sub-catchments and outlet of the whole reaches during the growing season.

Fluorescence characteristics of DOC

The variation in the fluorescence indexes throughout the growing season is shown in Table 5. For HIX, there is a certain degree of difference in the four sites: the highest mean value occurs in the FR (0.87 ± 0.05), which is similar to that in the WAF and is significantly higher than that in the AG. The mean HIX value in the OUT is 0.83 ± 0.04, which is significantly smaller than that in the WAF and FR. For all the sites, the maximum value of HIX during the whole growing season reaches 0.92 in the WAR on 8/5/2011 while the minimum is 0.65 in the AG on 6/1/2011. Conversely, the indexes of FI and BIX exhibit the opposite trend among the sites: the mean values of FI and BIX in the AG and OUT are significantly larger than those in the WAF and FR ($P<0.05$). Note that the fluctuation of the three fluorescence indexes is closely related to discharge at all of the sites. There are almost unanimous significant correlations between the three indexes and logarithms of discharge at all the sites, except that FI is not significantly related to discharge at the OUT site (Fig. 4). There is a clear positive correlation between HIX and discharge, whereas the FI and BIX both exhibit significant negative correlation with discharge ($P<0.05$). HIX is significantly positively correlated with air temperature during the whole growing season at WAF, whereas there is no significant relationship between temperature and the other two indexes at any of the sites.

Fig. 4 Seasonal variation in logarithms of discharge (log10Q) and humification index (HIX), fluorescence index (FI), and biological index (BIX) at the four sites during the growing season.

Table 5 Fluorescence indexes in relation to discharge at the three sub-catchments and the outlet for the whole reaches.

Ratio of dissolved carbon to nitrogen

The stoichiometric ratio is an important chemical feature of dissolved carbon molecule. Among the four sites, the ratios of DOC: DON range between 8.52 (for AG) and 14.51 (for WAF) (Table 6). In the OUT, the DOC: DON ratio is close to that in the AG while much smaller than the WAF and FR. As to TDC: TDN ratio, there is very similar trend among the four sites, and there is generally higher than the ratio of DOC: DON. In total, the AG site shows the lowest ratio of dissolved carbon to nitrogen while the WAR and FR show much higher value.

Table 6 Values and ratios of dissolved carbon to nitrogen in the three sub-catchments and the outlet of the whole reaches.

Discussion

Influence of land use on DOC exportation

In most ecosystems around the world, DOC originates from decomposing organic soils or vegetation. Globally, climatic differences can account for much variation between regions, but within regions the land use patterns within watersheds generally act as stronger controllers of DOC.[44] In regions unaltered by human activities, the proportion of wetland landscape has consistently been the best predictor of DOC concentrations in streams.[16] This is supported by the present finding that the maximum DOC concentration occurs in the WAF sub-catchment, which contains the highest proportion of wetland. Once converted to agricultural land, wetland soil can release tremendous quantities of dissolved carbons over an extended period, accompanied by the decline in organic matter content itself. Zhang et al. reported that reclaimed wetland soil in northeast China showed rapid decline of organic matter content, which subsequently stabilised 10–15 years after reclamation.[45] In our study area, a survey by Zhang found that the average carbon densities of natural forest and wetland were 17.26 and 28.80 kg m^{-3} respectively, while that of farmland reclaimed from the natural ecosystems was about 4.80 kg m^{-3} twenty years after reclamation.[46]

Some research indicates that reclamation of wetland may initially increase DOC concentration in subsequent years.[47,48] However, once reaching a relatively stable status with lower carbon content, the release capacity of DOC from the reclaimed soil is greatly reduced. In our study area, most of the agricultural land was reclaimed between the 1970s and 1990s; therefore, the organic carbon content ought to have reached a new relatively stable but much decreased density. Hence, the contribution of DOC from the agricultural land throughout the watershed scale is deemed to be relatively stable at present. According to our dataset, the AG sub-catchment shows distinctly lower DOC concentration and exporting coefficient than the two natural sub-catchments, suggesting that long-term reclamation for agriculture has led to the remarkable decline in the export concentration of DOC from the whole reaches. In the OUT, the finding that the mean concentration of DOC is very close to the AG while differs from the two natural sub-catchments is just the powerful proof to the suggestion.

Influence of land use on DIC and TDC

In our study, DIC exhibits the opposite trends to those of DOC: the DIC concentration and the DIC:TDC ratio in both the AG and OUT are significantly higher than those of the other two natural sub-catchments, which indicates that conversion from natural ecosystems to agricultural land has led to remarkable increase in DIC concentration in the streams. Song et al. reported similar findings in the Sanjiang

Plain of northeast China, where agricultural fields showed much higher concentration of DIC than that of natural wetlands after long-term reclamation.[47] DIC concentration in riverine systems is sensitive to soil and rock weathering, and carbonate and silicate weathering are identified as the dominant sources of DIC.[49] It has been reported that even a little distribution of carbonate can still be the major contributor to the riverine DIC.[50,51] Conversion to agricultural plantation increases soil temperature, which inevitably accelerates the weathering process of original soil minerals and organic matter. In our study area, the surface temperature (0–0.5 m depth) of agricultural land reclaimed from natural wetland is as much as 7.68 ℃ warmer than that of natural wetland during the growing season (Table 1). The remarkable elevation in the soil temperature will obviously accelerate the weathering process of original soil minerals. On the other hand, agricultural activities such as irrigation and pesticide application also increase DIC concentration by altering chemical weathering in surface soils and accelerating the mineralisation of DOC.[52] This conclusion is also supported by Kelly,[53] who found that DIC concentrations could be increased by irrigation practices associated with the addition of redox-sensitive nitrate fertilisers. Hence, the increasing tendency of DIC at the OUT site will likely persist if the conversion of natural ecosystems continues in the watershed. The increased DIC concentration and DIC: TDC ratio in the streams is a notable phenomenon that will alter the holistic distribution pattern of carbon forms throughout the entire fluvial ecosystem of the Amur River. Further research is required on the source, dynamics and ecosystem functions of DIC in waters, and comparison with DOC, especially with respect to the effects of agricultural activities in the catchment.

Alteration in chemical characteristics and origin of DOC

Fluorescence indexes provide a powerful tool to determine the integrated chemical features and origin of organic matter. The finding that the HIX, FI, and BIX of the water samples from all the sites fluctuated obviously during the growing season indicates remarkable variations in the chemical characteristics of the DOC. The significant positive relation between HIX and discharge means the humification degree and complexity of the DOC molecule increase during the flood peak period of the discharge while return to the low level in the base flow period. The fact that the close relationship shows in all the sites indicates that the land use change has not changed the transport processes of DOC in the permafrost region by discharge. However, the higher HIX at WAF and FR compared with the AG site confirm that the humification degree of DOC in the natural ecosystems is higher than that in the agriculture system. The similarity of the mean HIX in the OUT and AG sites demonstrates that the conversion to farmland has led to the decline of the humification degree of the DOC exported from the watershed. FI and BIX are indicators of terrestrial vs. microbial source and recent microbial production respectively. Opposite to HIX, FI and BIX, for the most part, are in the low level in the flood peak periods while amount in the base flow. The findings hint that the discharge process can lead to relative alterations in the DOC origin during the growing season, and there is a relatively constant source of DOC linked to recent microbial production that becomes more dominant a low flows.[42,43] The appearance of the tryptophan-like fluorescence peak (Peak T) in EEMs verifies the autochthonous microbial production in the stream (Fig. 2). Therefore, the significant differences between the WAR, FR and the AG, OUT in the mean values of FI and BIX suggest the conversion from natural to farm land has altered the main origin of the DOC exported from the watershed in a certain degree.

The ratios of dissolved carbon to nitrogen, as an agent of the stoichiometric features of the dissolved organic matter, can provide indirect information on the relative contents of the chemical elements in the molecule. The global model calculations by Harrison et al. indicate that regions with extensive areas of intensive agriculture or high population density exhibit elevated DON yields in comparison to DOC.[54] Mattsson et al. confirmed that the DOC:DON ratio was significantly negatively correlated with population density and the proportion of agricultural land and urban areas in the catchment, and was positively correlated with the proportion of wetlands in the catchment.[55] Our datasets also verify that the DOC:DON ratio would be reduced due to conversion from natural systems to agricultural use, as the DOC:DON ratio for the AG site is clearly lower than that for the WAF and FR. The sustained input of crop fertilisers after reclamation is likely the primary cause of the greatly altered content and cycling period of soil nitrogen. Hence, in the long-term, land reclamation has also altered the synthetic chemical stoichiometric characteristics of the riverine DOC in the permafrost streams.

Hydrological processes

It is worth noting that there are close relationships between stream discharge and DOC concentration as well as the fluorescence indexes, whereas there is no consistent relationship between seasonal air temperature and riverine DOC concentration. Hence, the variation in DOC during the growing season is predominantly introduced by the discharge processes associated with rainfall. Most importantly, our results highlight the stability of the processes that drive discharge throughout the growing season in all the three sub-catchments, as well as the whole reaches. Hence, land use change did not alter the role of discharge processes as the main driver of DOC dynamics in our study area. The proportion of wetland within a watershed has been broadly identified as the major predictor of DOC concentration in streams, for the poorly drained soils and high hydrological connectivity of wetland landscapes.[56,57] Permafrost can efficiently prevent the infiltration of water into deeper soil layers, and lead to the full interaction between the organic soil and the interflows forming the discharge in streams. In our study, the presence of permafrost is the probable cause of the close relationship between DOC concentration and discharge observed in all the landscapes. However, judged by the correlation between DOC and the logarithms of Q (Table 3), the evidently reduced slope for the AG compared to WAF and FR indicates that the exporting capacity of DOC by discharge is reduced following the conversion of land for agriculture. However, further research is required to determine whether this reduction results from the loss of soil organic carbon itself or, additionally, from changes in the hydrological paths.

Land use change as a predictor for DOC in streams

Many previous studies have reported that the conversion of natural land to agriculture causes substantial loss of organic carbon stored in soils, and have attributed this to the lowering of the water table, and to increased erosion and decomposition rates associated with physical disruption and aeration by tilling.[58,59] SOC losses following agricultural conversion often continue for decades, but the period of initial mobilisation of DOC from mineral soil appears to be shorter, lasting anywhere from < 2 to 10 years.[17,60] Hence, the net effect of land reclamation is to form a smaller terrestrial carbon pool compared to native conditions, meaning that the potential supply of organic carbon delivered to streams is reduced in the long term.

However, investigating this seemingly simple association reveals a diverse array of processes that may cause increases, decreases or no net change in stream DOC loads.[20,28,61] Agricultural practices would likely be the key process controlling the final relationship between land use and stream DOC as Stanly et al. concluded.[27] Modern changes in farming practices, such as reduced ploughing depth or no-till agriculture, have been adopted to slow or even reverse soil and SOC losses.[62,63] Amendments of crop residues, organic fertilisers, and manure disposal also add to the SOC pool. As these additions are not fully integrated into the soil structure, they may be easily mobilised and cause both short-term and more sustained increases in stream

DOC concentrations.[64,65] Thus, cases in which land-use conversion appears to produce no detectable changes in aquatic DOC may simply reflect a balance between losing one carbon source (wetlands or SOC) but gaining another (agricultural amendments). However, in our study area, the limited agricultural technology has never aimed to retain the soil organic carbon pool but only to increase crop yields since the land reclamation programmes of the 1960s. The fertilisers mainly comprise compounds of inorganic nitrogen, and no crop residues are returned to farmland because the surface plants provide the main winter fuel throughout the entire northeast region of China. Hence, the traditional agricultural pattern has led to the sustained decline of soil organic carbon pool in agricultural lands. Given the history of land reclamation from the 1960s to the present day, the trend of declining organic carbon concentration in reclaimed farmlands is evident from comparing the natural sub-catchments (WAF and FR) and the agriculture-dominated sub-catchment (AG). The trend of gradual loss of soil organic carbon in reclaimed farmland leads to the gradual decline of riverine DOC exported from the entire catchment, and will continue until agricultural practices are revised. Hence, in the absence of dramatic climatic or precipitation patterns in the future, the identified effects of traditional forms of agriculture mean that land use change is a good predictor of riverine DOC concentrations in our study area.

Conclusions

We examined the seasonal variation in dissolved carbons within the streams of three sub-catchments in a permafrost region, comprising one agricultural and two natural catchments and the entire reaches. Comparison of the DOC concentration between the natural and agricultural sites suggests that land use change has led to the reduction of DOC exporting capacity. Moreover, the chemical characteristics and the origin of the DOC exported from the entire reach were also altered to some extent. Importantly, the exported concentration of DIC and its proportion of TDC are obviously promoted due to land reclamation, which would greatly alter the carbon cycling processes in the downstream fluvial system. The results of this study suggest that dissolved carbons in permafrost streams have been greatly affected by land use change since the 1970s. The trend of decreased DOC and increased DIC concentration will persist until the stop of the reclamation activities of natural ecosystems and changes in the traditional agricultural practices.

Acknowledgements

The work was supported by Strategic Priority Research Program — Climate Change: Carbon Budget and Related Issue of the Chinese Academy of Sciences, Grant No. XDA05020508, National Natural Science Foundation of China (41273085, 41125001), National Key Basic Research and Development Projects (2012CB956103).

References

1 K. E. Frey and L. C. Smith, J. Geophysi. Res. Lett., 2005, 2: doi:1029/2004GL022025.

2 A. D. McGuire, F. G. Anderson, T. R. Christensen, S. Dallimore, L. Guo, D. J. Hayes, M. Heimann, T. D. Lorenson, R. W. Macdonald and N. Roulet, Ecol. Monogr., 2009, 79, 523–555.

3 J.J. Cole, Y.T. Prairie, N.F. Caraco, W.H. McDowell, L.J. Tranvik, R.G. Striegl, C.M. Duarte, P.Kortelainen, J.A. Downing, J.J. Middelburg and J. Melack. Ecosystems, 2007, 10:171-184.

4 S. Opsahl, R. Benner and R. M. W. Amon, Limnol. Oceanogr., 1999, 44, 2017–2023.

5 J. Lobbes, H. P. Fitznar and G. Kattner, Geochim. Cosmochim. Ac., 2000, 64(17), 2973–2983.

6 P. A. Raymond, J. W. McClelland, R. M. Holmes, A. V. Zhulidov, K. Mull, B. J. Peterson, R. G. Stregl, B. J. Aiken and T.Y. Gurtovaya, Global Biogeochem. Cy., 2007, 21: GB4011, doi:10.1029/2007GB002934.

7 S. E. Hobbie, J. P. Schimel, S. E. Trumbore and J. R. Randerson, Global Change Biol., 2000, 6,196–210.

8 E. D. Schulze and A. Freibauer, Nature, 2005, 437, 205–206.

9 A. S. Prokushkin, I. V. Gavrilenko, A. P. Abaimov, S. G. Prokushkin and A. V. Samusenko, Mitigat. Adapt. Strat. Global Change, 2006, 11, 223–240.

10 C. T. Driscoll, K. M. Driscoll, K. M. Roy and M. J. Mitchell, Environ. Sci. Technol., 2003, 37(10), 2036–2042.

11 J. Hejzlar, M. Dubrovsky, J. Buchtele and M. Ruzicka, Sci. Tot. Environ., 2003, 310, 143–152.

12 F. Worrall and T. P. Burt, J. Hydrol., 2008, 361, 262–274.

13 P. Vitousek, H. Mooney, J. Lubchenco and J. Melillo, Science, 1997, 277, 494–499.

14 C. S. Cronan, J. T. Piampiano and H. H. Patterson, J. Environ. Quality, 1999, 28, 953–961.

15 P. Vidon, L. E. Wagner and E. Soyeux, Biogeochemistry., 2008, 88, 257–270.

16 H. F. Wilson, and M. A. Xenopoulos, Ecosystems, 2008, 11(4), 555–568.

17 K. McLauchlan, Ecosystems, 2006, 9,1364–1382.

19 R. W. Skaggs, M. A. Breve and J. W. Gilliam, Crit. Rev. Environ. Sci. Technol., 1994, 24(1), 1–32.

19 H. F. Wilson and M. A. Xenopoulos, Nat. Geosci., 2009, 2, 37–41.

20 B. J. Dalzell, T. R. Filley and J. M. Harbor, Geochimica Et Cosmochimica Acta, 2007, 71(6),1448–62.

21 T. V. Royer and M. B. David, Aquat, Sci, 2005, 67(4), 465–71.

22 Y. Yamashita, L. J. Scinto, N. Maie and R. Jaffé, Ecosystems, 2010, 13, 1006–19.

23 C. J. Williams, Y. Yamashita, H. F. Wilson, R. Jaffé and M. A. Xenopoulos, Limnol. Oceanogr., 2010, 55, 1159–71.

24 S. Trumbore, Annu. Rev. Earth. Planet. Sci., 2009, 37, 47–66.

25 X.W. Wang, X.Z. Li, Y.M. Hu, J.J. Lü, J. Sun, Z.M. Li, and H.S. He, Wetlands, 2010, 30, 747–756.

26 M.P. Waldropa, J.W. Harden, M.R. Turetsky, D.G. Petersen, A.D. McGuire, M.J.I. Briones, A.C. Churchill, D.H. Doctor and L.E. Pruett, Soil Biol. Biochem., 2012, 188–198.

27 E. H. Stanley, S. M. Powers, N. R. Lottig, I, Buffam and J. T. Crawford, Freshwater Biol., 2012, 57 (Suppl. 1), 26–42.

28 Y. D. Guo, Y. Z. Lu, Y. Y. Song, Z. M. Wan and A. X. Hou, Sci. Total. Environ., 2014, 466–467,777–787.

29 J. L. Probst, P. Amiotte-Suchet and W. Ludwig, Trends Hydrol., 1994, 1, 453–468.

30 A. A. Vetrov and E. A. Romankevich, Carbon Cycle in the Russian Arctic Seas, Chapter 5: Horizontal Carbon Fluxes in the Land-Sea System. Springer Press, Berlin Heidelberg, 2004.

31 J. Chen, F. Wang, X. Xia and L. Zhang, Chem. Geol., 2002, 187, 231–255.

32 H. G. Sun, J. T. Han, S. R. Zhang and X. X. Lu, Chinese Sci. Bull., 2007, 52 (6), 805–812.

33 E. A. Atekwana and E. W. Fonyuy, J. Hydrol., 2009, 372(1–4),136–148.

34 P. R. Muduli, V. V. Kanuri, R. S.Robin, B. C. Kumar, S. Patra, A. V. Raman, R. G. Nageswara and B. R. Subramanian, India Cont. Shelf. Res., 2013, 64,75–87.

35 X. T. Liu, Wetlands in Northeastern China. Science Publisher, Beijing, 2005.

36 H. J. Jin, S. X. Li, G. D. Cheng, S. L. Wang and X. Li, Global Planet Change, 2000, 26, 387–404.

37 W. G. Crumpton, T. M. Isenhart, P. D. Mitchell, Limnol. Oceanogr., 1992, 37, 907–913.

38 S. Singh, E. D’Sa and E. M. Swenson, Sci. Total. Environ., 2010, 408, 3211–3222.

39 C. A. Stedmon, S. Markager and B. Rasmus, Mar. Chem., 2003, 82, 239–254.

40 P. G. Coble, Mar. Chem., 1996, 51, 325 – 346.

41 T. Ohno, Environ. Sci. Technol., 2002, 36,742–746.

42. R.M. Cory, M.P. Miller, D.M. McKnight, J.J. Guerard and P.L. Miller, Limnol. Oceanogr.: Methods, 2010, 8, 67–78.

43 A. Huguet, L. Vacher, S. Relexans, S. Saubusse, J. M. Froidefond, Parlanti E, Org. Geochem., 2009, 40, 706–719.

44 S. Sobek, L. J. Tranvik, Y. T. Prairie, P. Kortelainen and J. J. Cole, Limnol. Oceanogr., 2007, 52, 1208–1219.

45 J. B. Zhang, Effects of Wetland Cultivation and Land Use on Soil Carbon Fraction in the Sanjiang Plain [dissertation], Chinese Cademy of Scicence, Beijing, 2006, in Chinese

46 C. Y. Zhang, Study on soil fertility evaluation or assessment of cultivated land in Nenjiang County. [dissertation]. Chinese Academy of Agricultural Sciences, Beijing, 2011, in Chinese

47 C. C. Song, L. L. Wang, Y. D. Guo, Y. Y. Song, G. S. Yang and Y. C. Li, J. Hydrol., 2011, 398(1-2), 26-32.

48 A. Baker, S. Cumberland and N. Hudson, Area, 2008, 40 (1),117–127.

49 M. Meybeck, Am. J. Sci., 1987, 287, 401–428.

50 K. Telmer and J. Veize, Chem. Geol., 1999, 159, 61–86.

51 J. A. C. Barth, A. A. Cronin, J. Dunlop and R. M. Kalin, Chem. Geol., 2003, 200, 203–216.

52 P. Raymond, N. Oh, R. Turner and W. Broussard, Nature, 2008, 451, 449–452.

53 W. Kelly, J. Hydrol., 1997, 198,154–176.

54 J. A. Harrison, N. Caraco, S. P. Seitzinger, Global Biogeochem. Cy., 2005, 19(4), 2488-2501.

55 T. Mattsson, P. Kortelainen, A. Laubel, D. Evans, M. Pujo-Pay, A. Räike and P. Conan, Sci. Total. Environ., 2009, 407, 1967–1976.

56 S. E. Gergel, M. G. Turner and T.K. Krats, Ecol. Appl., 1999, (4), 1377–1390.

57 M. A. Xenopoulos, D..M. Lodge, J. Frentress, T. A. Kreps, S. D. Bridgham, E. Grossman and C. J. Jackson, Limnol. Oceanogr., 2003, 48(6), 2321–34.

58 L. B. Guo and R. M. Gifford, Global Change Biol., 2002, 8, 345–360.

59 M. K. Jarecki and R. Lal, Crit. Rev. Plant Sci., 2003, 22, 471–502.

60 M. H. Chantigny, Geoderma, 2003,113, 357–380.

61 T. V. Royer and M. B. David, Aquat, Sci, 2005, 67(4), 465–71.

62 P. Smith, Eur. J. Agron., 2004, 20, 229–239.

63 S. M. Ogle, F. J. Breidt and K. Paustian, Biogeochemistry, 2005, 72, 87–121.

64 E. Jardé, G. Gruau and L. Mansuy-Huault, Appl. Geochem., 2007, 22, 1814–1824.

65 J. Molinero and R. A. Burke, Hydrobiologia, 2009, 635, 289–308.

Table 1 Detailed land use and soil physical-chemical features of the three sub-catchments in the study area

Site	Area (Km^2)	Land use & area proportion	Bulk density (g cm^{-3})	SOM (g Kg^{-1})	Soil TN (g Kg^{-1})	Soil PH	Maximum depth of active layer (m)	Mean soil temperaure (□)
WAF	340	Wet: 52.5%	Wet :0.84	Wet: 32.50	Wet:10.79	Wet: 5.56	Wet: 1.20	Wet: 5.59
		For: 47.5%	For: 1.22	For:19.60	For: 2.52	For: 5.75	For: 1.30	
FR	243	For: 69.7%	For: 1.18	For: 21.30	For: 2.22	For: 5.71	For: 1.50	For: 7.00
		Wet:21.3%	Wet: 0.90	Wet: 29.40	Wet: 9.06	Wet: 5.62	Wet: 1.50	
AG	299	Farm:80.6%	Farm: 1.36	Farm: 9.02	Farm: 0.81	Farm: 6.24	Farm: 3.50	Farm: 13.26
		Wet:9.2%						

For, Wet and Farm indicate forest, wetland and agricultural landscapes, respectively; Soil features refer to 0–50 cm depth; SOM is soil organic matter content.

Table 2 Spectral indexes calculated from the excitation-emission matrices (EEMs): humification index (HIX), fluorescence index (FI), and biological index (BIX).

Index	Calculation method	Interpretation	Main references
HIX	The ratio of sum from λem = 435–480 nm to the sum from λem = 300–345 for excitation at 254 nm.	High HIX values indicate relatively highly humified organic matter derived from biomass; HIX increases with the complexity of organic matter.	(Ohno, 2002)[41]
FI	The ratio of maximum emission fluorescence intensities at 450 and 500 nm for excitation at 370 nm	The suggested range of FI for terrestrial-origin humics is 1.2, and that for materials of marine origin is 1.7.	(Cory et al., 2010)[42]
BIX	The ratio of intensities at λem 380 nm and 430 nm for excitation at 310 nm	BIX values of 1.0 or greater correspond to freshly produced DOC of microbial origin, whereas values of 0.6 and less imply little natural biological material.	(Huguet et al., 2009)[43]

Table 3 Concentrations of dissolved carbons in relation to discharge at the three sub-catchments and the whole reaches.

Site	Carbons	Mean±S.D.	Relation with $\log_{10}Q$	n	R^2	P
WAF	DOC	8.79 ± 3.74	DOC=-15.37+4.49* $\log_{10}Q$	47	0.64	0.001**
	DIC	4.26 ± 2.30	DIC=9.11-0.90* $\log_{10}Q$	47	0.11	0.07
FR	DOC	6.67 ± 3.68	DOC=-19.82+4.98* $\log_{10}Q$	32	0.61	0.001**
	DIC	4.02 ± 0.97	DIC=6.83-0.53* $\log_{10}Q$	32	0.10	0.07
AG	DOC	5.25 ± 2.54	DOC=-9.18+2.82* $\log_{10}Q$	30	0.56	0.001**
	DIC	6.33 ± 1.19	DIC=10.68-0.85* $\log_{10}Q$	30	0.23	0.01**
OUT	DOC	5.70 ± 2.36	DOC=-31.40+3.09* $\log_{10}Q$	35	0.23	0.01**
	DIC	6.96 ± 2.28	DIC=10.27-0.45* $\log_{10}Q$	35	0.01	0.70

DOC, and DIC represent total dissolved, organic, and inorganic carbon, respectively; Q is stream discharge.

Table 4 Fluxes and exporting coefficients of dissolved carbons from the three sub-catchments and outlet of the whole reaches during the growing season.

	WAF	FR	AG	OUT
Flux-TDC (t)	7.86	4.92	4.11	461.62
Flux-DOC (t)	5.29	3.07	1.86	207.68
Flux-DIC (t)	2.57	1.85	2.25	253.95
Co-TDC (kg $km^{-2}d^{-1}$)	20.51	23.11	13.71	15.53
Co-DOC (kg $km^{-2}d^{-1}$)	13.81	14.42	6.22	6.99
Co-DIC (kg $km^{-2}d^{-1}$)	6.70	8.69	7.49	8.54

Flux- and Co- are the total flux and exporting coefficients of the corresponding dissolved carbon; TDC, DOC, and DIC represent total dissolved, organic, and inorganic carbon, respectively.

Table 5 Fluorescence indexes in relation to discharge at the three sub-catchments and the outlet for the whole reaches.

Site	Indexes	Mean ± S.D.	Relation with $log_{10}Q$	n	R^2	P
WAF	HIX	0.86 ± 0.04	$HIX=0.72+0.026*log_{10}Q$	47	0.22	0.004**
	FI	1.52 ± 0.05	$FI=7.73-0.04*log_{10}Q$	47	0.28	0.001**
	BIX	0.58 ± 0.04	$BIX=0.83-0.05*log_{10}Q$	47	0.52	0.001**
FR	HIX	0.87 ± 0.05	$HIX=0.70+0.03*log_{10}Q$	32	0.35	0.001**
	FI	1.57 ± 0.06	$FI=1.86-0.06*log_{10}Q$	32	0.25	0.005**
	BIX	0.62 ± 0.06	$BIX=0.87-0.05*log_{10}Q$	32	0.20	0.01*
AG	HIX	0.79 ± 0.05	$HIX=0.62+0.03*log_{10}Q$	30	0.19	0.01**
	FI	1.64 ± 0.02	$FI=1.72-0.017*log_{10}Q$	30	0.34	0.001**
	BIX	0.79 ± 0.10	$BIX=1.04-0.05*log_{10}Q$	30	0.15	0.05*
OUT	HIX	0.83 ± 0.04	$HIX=-0.21+0.14*log_{10}Q$	35	0.49	0.001**
	FI	1.65 ± 0.03	$FI=2.04-0.053*log_{10}Q$	35	0.13	0.055
	BIX	0.72 ± 0.07	$BIX=1.97-0.17*log_{10}Q$	35	0.22	0.011*

HIX is humification index; FI, fluorescence index; BIX, biological index; Q is stream discharge.

Table 6 Values and ratios of dissolved carbon to nitrogen in the three sub-catchments and the outlet of the whole reaches.

Site	TDN (mg L^{-1})	DON (mg L^{-1})	TDC/TDN	DOC/DON
WAF	0.76	0.61	17.12	14.51
FR	0.75	0.59	14.30	11.23
AG	0.91	0.62	12.83	8.52
OUT	0.84	0.61	14.99	9.34

TDN and DON are total dissolved and organic nitrogen respectively; TDC and DOC are mean total dissolved and organic carbon respectively.

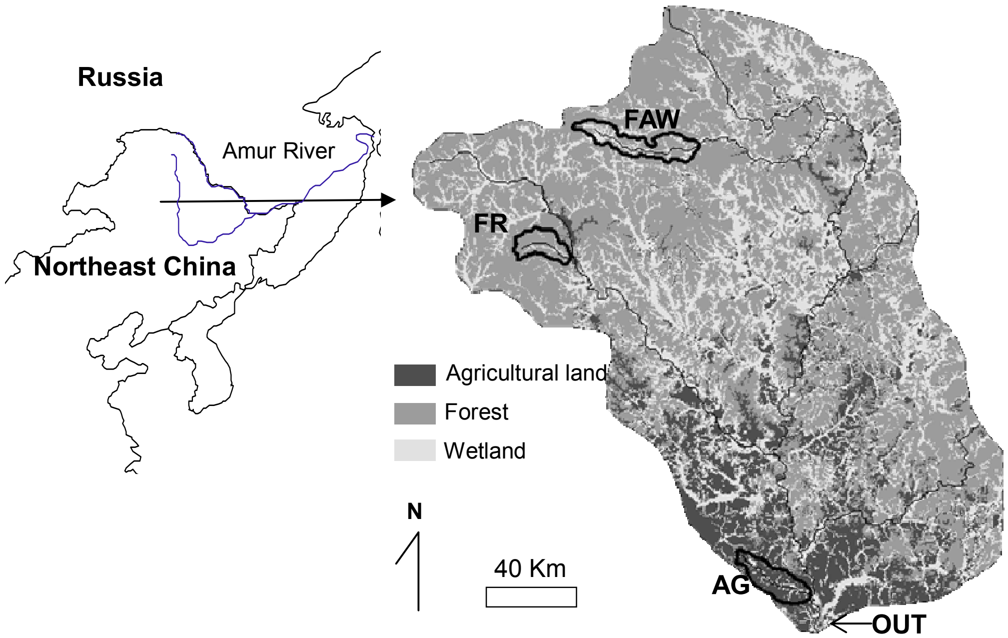

Fig. 1 Sketch map of the upper reaches of Nenjiang River and the three sub-catchments.

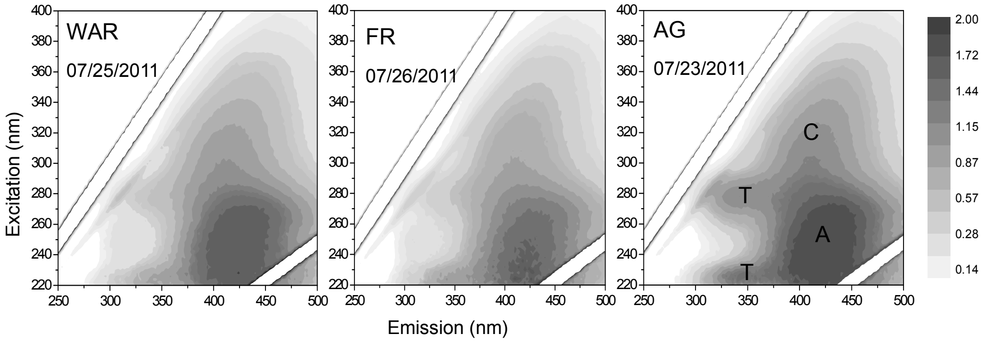

Fig. 2 Typical EEMs of the dissolved organic matter for the WAR (a), FR (b) and AG (c) in the growing season. T indicates tryptophan-like fluorescence peak; C and A are fulvic-like and humic-like fluorescence peak respectively.[40] (The three samples are all collected in the base flow period of discharge in the summer 2011)

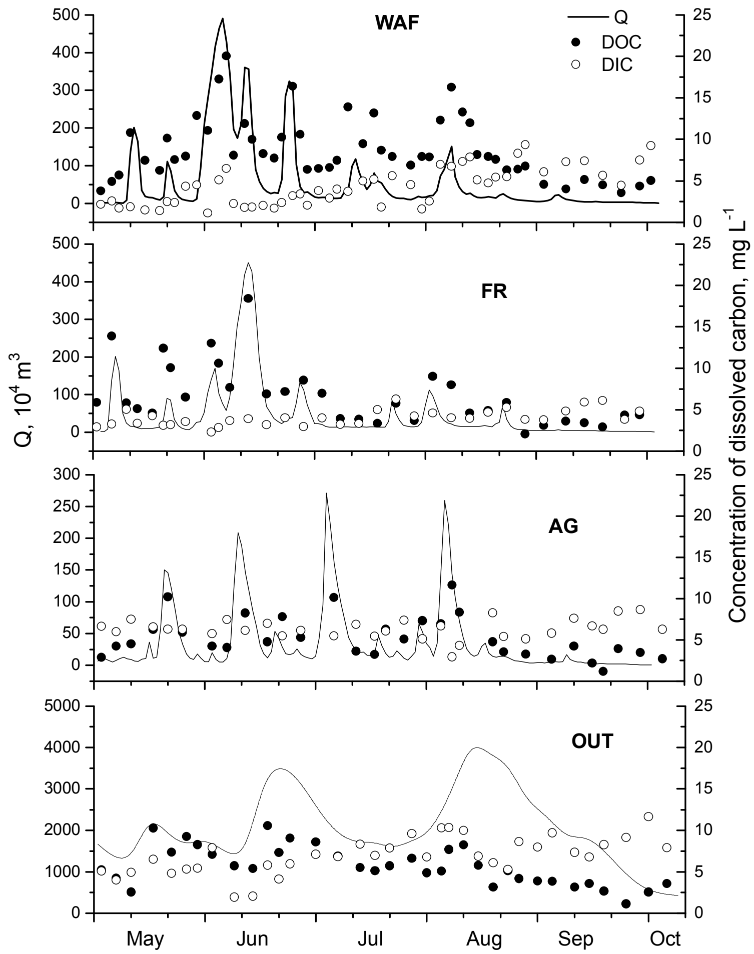

Fig. 3 Seasonal variation in stream discharge (Q) and concentration of dissolved carbons during the growing season.

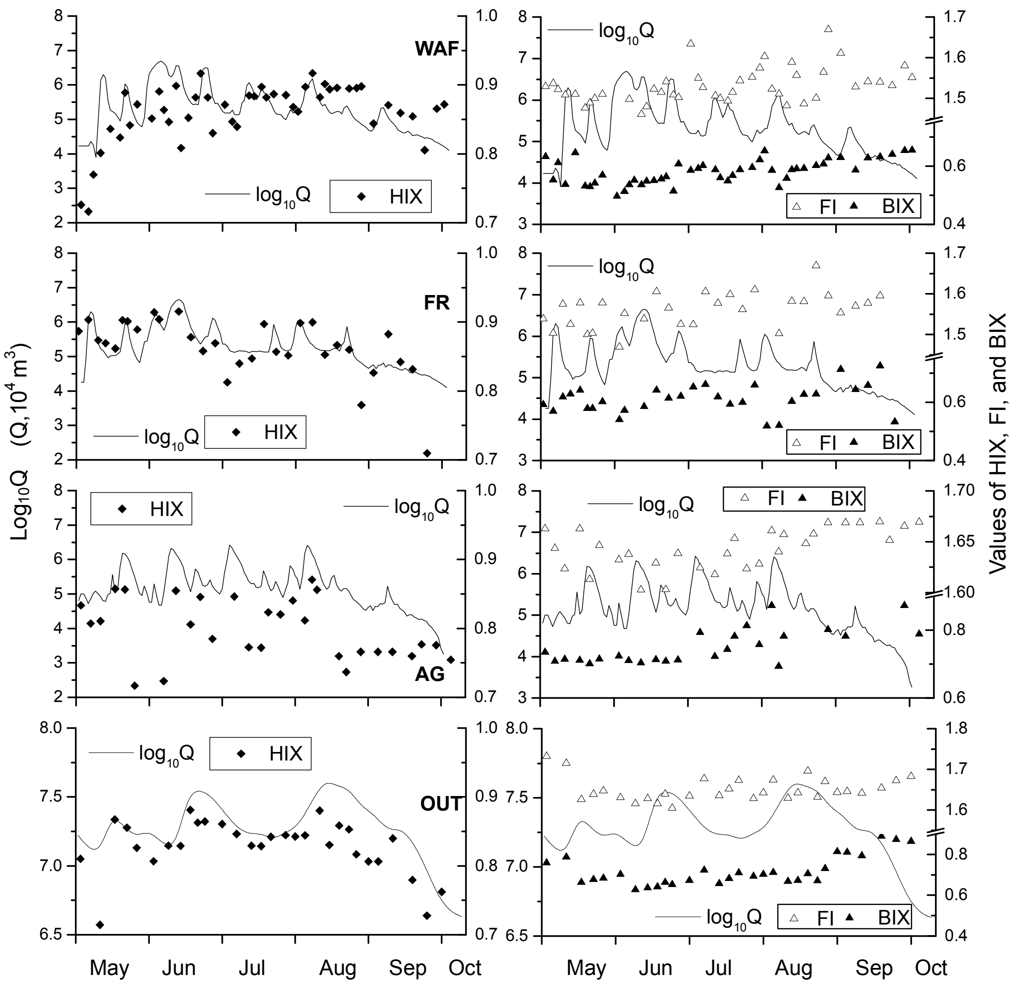

Fig. 4 Seasonal variation in logarithms of stream discharge ($\log_{10}Q$) and humification index (HIX), fluorescence index (FI), and biological index (BIX) at the four sites during the growing season.