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Review

Global Increases in Dissolved Organic Carbon in Rivers and Their Implications

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DOC (Dissolved Organic Carbon) is an operational terminology for organic carbon molecules dissolved in natural waters. DOC has been studied by ecologists extensively, because it plays a key role in various ecological functions such as substrates for secondary production and the carbon cycle. DOC also represents a substrate for microbial growth within potable water distribution systems, and can react with disinfectants (e.g., chloride) to form harmful disinfection by-products. In addition, residual DOC may carry with it organically bound toxic heavy metals. DOC in aquatic ecosystems may ultimately be transported to the oceans, or released back to the atmosphere by heterotrophic respiration, which can accelerate global climate change. There is evidence that DOC concentrations in aquatic ecosystems are increasing in many regions of the world including Europe, North America, and even in Korea. Land use changes, elevated temperature, elevated CO_2, recovery from acidification, and nitrogen deposition have been proposed as mechanisms for the trend. However, the key driving mechanism is yet to be conclusively determined. We propose that more extensive and longer-term observations, research of chemical properties of DOC, impacts of elevated DOC on environmental issues and interdisciplinary approaches are warranted as future studies to fill the gaps in our knowledge about DOC dynamics.

Key words : Dissolved Organic Carbon (DOC), carbon cycle, climate change

TERMINOLOGY

DOC (Dissolved Organic Carbon) is an operational terminology for organic carbon molecules dissolved in natural waters, which pass a known size of filter (typically 0.45 μm). Conventionally organic carbon in water has been reported as BOD (Biochemical Oxygen Demand) or COD (Chemical Oxygen Demand) in environmental engineering. BOD represents portion of organic matter that can be metabolized by microorganism, while COD is determined by noting oxygen changes by oxidation of organic matter by catalysts such as Mn or Cr. In comparison, DOC is typically determined by complete oxidation of organic carbon in water using heat and catalyst and measuring CO_2 released by an IR sensor. Other terminology includes NOM (Natural Organic Matter). NOM focuses on organic matter from natural sources while DOC does not discriminate its sources. Persistent organic pollutants (POPs) are toxic chemicals that adversely affect human health and the environment around the world (US-EPA). ROM (Refractory Organic matter) represents organic carbon in any media that resist decomposition and hence remain in the system without undergoing biochemical transformation.

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The sources of DOC in natural streams and rivers may include root exudates, products of litter decomposition, soil organic matter, and primary production of algae in water (Leenheer, 1994). Decomposability (lability) of DOC is substantially different depending on its sources. For example, DOC originated from old soil organic matter is rich in humic and fulvic acids, which are highly recalcitrant. In contrast, recent root exudates or algal biomass are relatively easily metabolized by microorganism. In addition to natural sources, DOC is also composed of synthetic materials from anthropogenic sources such as textile, paper mills, pharmaceuticals, and food industry. Some of such compounds are highly resistant to decomposition in aquatic ecosystems.

IMPORTANCE OF DOC

DOC has been studied by ecologists extensively, because it plays a key role in various ecological functions such as substrates for secondary production and carbon cycle. Organic matter in aquatic ecosystems is used as a carbon source for microorganism and small animals. POC (Particular Organic Carbon) needs to be degraded to a small size to be metabolized by microorganism. High correlations between DOC concentrations and microbial activities have been widely reported in aquatic ecosystems (McKnight and Aiken, 1998). In addition to natural scientific interests, DOC has drawn much attention from environmental scientists for following reasons;

1) DOC can be a part of energy input into stream food web (Allan and Castillo, 2007). Carbon is generally considered as limiting factor in stream secondary production, and hence DOC is key C sources for heterotrophic microorganisms.
2) DOC represents a substrate for microbial growth within water distribution systems as well and is a substrate for fouling on water treatment systems. As such, high concentrations of DOC in water distribution system cause lower water quality and production of biofilm in pipes and other systems. In addition, blockage or lower performance of membrane systems can be induced.
3) DOC can react with disinfectants (e.g., chloride) to form disinfection by-products such as trihalomethanes (THMs; $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$), haloacetic acids (HAA) or haloacetonitriles (HAN), all of which are now recognized to adversely affect human health (Bull *et al.*, 1995). Those by-products can be produced by reactions between phenolic residue in fulvic acids and chloride in water (Leenheer *et al.*, 2001).
4) DOC may also carry with it organically bound toxic heavy metals and also potentially toxic organic pollutants such as pesticides, pharmaceuticals, hormones, perfluorinated compounds and polyaromatic hydrocarbons (Baldauf, 2006; Katsoyiannis *et al.*, 2007). For example, several studies reported associations between DOC dynamics and Hg, Pb transport in aquatic ecosystems (McKnight *et al.*, 1992; Kögel-Knabner and Totsche, 1998).
5) DOC in aquatic ecosystems may ultimately be transported to the oceans, or released back to the atmosphere by heterotrophic respiration, which can accelerate global climate change. Products of photosynthesis of terrestrial plants that are not fully decomposed but rather transported through rivers to the oceans become an important component of the global carbon cycle (Raymond and Bauer, 2001). It has been reported that *ca.* 20% of DOC input to the oceans originated from inland wetlands with high primary production or low decomposition of organic matter. Approximately 0.4×10^{15} g of carbon is transported to the oceans through rivers, which is around 1/8 of annual increase in atmospheric CO_2.

CHANGES IN DOC CONCENTRATIONS IN GLOBAL RIVERS AND STREAMS

There is evidence that DOC concentrations in aquatic ecosystems are increasing in many regions of the world including Europe and North America (Freeman *et al.*, 2001; Evans *et al.*, 2005). Particularly, increases in DOC concentrations of streams of peat-dominated watershed are well documented (Freeman *et al.*, 2001; Worrall *et al.*, 2004; Evans *et al.*, 2005; Skjelkvåle *et al.*, 2005). For example, DOC concentrations in UK upland waters have increased by an average of 91% during the last 15 years, i.e. an average annual increase of 6%. Over the past two decades the concentration of DOC in some of these source waters has more than doubled and continues to rise. There is a strong relationship with the amount of organic matter (predominantly peat) in catchment soils (Hope *et al.*, 1997), and DOC increases are greatest in peat-dominated catchments. Not only peat-dominated watersheds but also other temperate regions such as North America, Japan and Korea exhibit similar increases in DOC concentrations in rivers and lakes. Long-term data on DOC are absent in Korea, but data of BOD and COD can be used as surrogate for DOC. For example, BOD in Paldang Lake in 2007 was 1.2 mg L^{-1}, which is of 'good' grade (Ib) of water regulation in Korea. However, COD in the same lake was 3.9 mg L^{-1}, which is in 'fair' grade (II). BOD concentrations have actually decreased substantially in recent decades due to successful construction and operation of wastewater treatment plants in the watershed, although COD concentrations have continued to increase (Fig. 1). This suggests that recalcitrant DOC may contribute a large proportion of the organic carbon in the system. In North America, many rivers have exhibited rapid increase in DOC concentrations of 0.1 mg L^{-1} yr^{-1} between 1990 and 2004 (Monteith *et al.*, 2007).

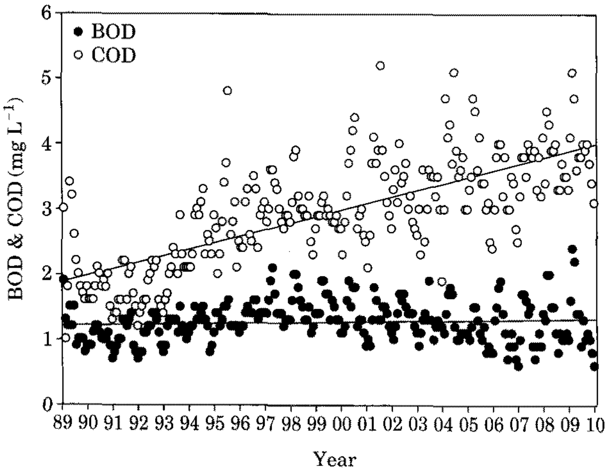

Fig. 1. BOD and COD concentrations in Paldang Lake (Data form groundwater quality monitoring stations (Water Information System).

MECHANISM FOR DOC INCREASES

There is increasing evidence to suggest that the process is being driven by regional or global-scale environmental changes, although the key driving mechanisms have yet to be conclusively identified. Proposed drivers for increasing DOC include factors related to climate change, atmospheric deposition, and land-use patterns, of which the hypotheses and literature sources are summarized in Table 1.

Several hypotheses have been proposed to explain the increases in DOC concentrations in global streams and rivers, which are explained in turn;

1) Land use changes such as expansion of agricultural lands and urban areas can increase DOC input to streams (Garnett, 2000). This could partly explain DOC variations in Korea where land use changes have been extensive, but cannot explain changes in DOC in natural watersheds in European countries.
2) Elevated temperature by climate change can accelerate decomposition rates in soil organic matter and litter resulting in increases in DOC leaching to aquatic ecosystems (Freeman *et al.*, 2001). However, it is argued that temperature change in recent decades is not sufficient to explain current large DOC increases.
3) Climate change also accompanies higher frequencies of drought and heavy rain fall, which can increase DOC leaching from upland to aquatic ecosystems (Tranvik and Jansson, 2002). During the long period drought, organic matter can accumulate as decomposition products, which then, would be flushed out by heavy rainfall. However, time series analysis of long-term data suggest that raining pattern is not necessarily associated with DOC increases.
4) Elevated CO_2 was found to increase porewater DOC in peatland by releasing root exduates from enhanced primary production (Freeman *et al.*, 2004). However, this hypothesis is only

Table 1. Proposed mechanism for higher DOC in aquatic ecosystems.

Key drivers proposed	Regions studied	Sources
Land use changes	Europe	Garnett, 2000
Temperature rise	Europe	Freeman *et al.*, 2001
Higher frequencies of drought and flooding	Europe	Tranvik and Jansson, 2002
Elevated CO_2 in the atmosphere	Europe	Freeman *et al.*, 2004
Recovery from acidifications of watersheds	Europe, N. America	Monteith *et al.*, 2007
Increases in nitrogen deposition	N. America	Findlay, 2005

applicable to peat-dominated watersheds.

5) Reduction in acid rains and recovery of acidified watershed were found to be associated with DOC increases in North America and Europe (Monteith *et al.*, 2007). However, regions with high acid deposition still exhibit increases in DOC concentrations in streams and rivers, suggesting limitation of this hypothesis.
6) Nitrogen deposition has been proposed as another mechanism for higher DOC, because N addition was found to enhance the production of humic materials by microorganism (Findlay, 2005). However, this explanation was not confirmed in the field condition, but only applicable local scale. A similar response has been found in peatlands (Bragazza *et al.*, 2006).
7) Concentrated precipitation accompanying increases in suspended solids could be another mechanism (Ludwig and Probst, 1996). Particularly, this could be a substantial source of DOC in Korea where heavy rains in monsoon season can increase soil erosion and turbidity in streams in very short time.

No single hypothesis can explain observations made all over the world, because different regions have dissimilar watershed characteristics, intensity of human intervention, and impact of atmospheric deposition. Probably, mechanism may function regionally with two or three factors function interactively.

Worrall *et al.* (2005) have shown that inclusion of kinetically-limited DOC production, proportional to the severity of summer drought, greatly improves the modelling of DOC fluxes and solves the problem of poor fit between DOC flux records and linearly trending drivers such as air temperature or atmospheric CO_2 increase. There are step changes in DOC flux from several UK catchments that coincide with the aftermath of the most severe droughts during the periods of available DOC flux records (Worrall and Burt, 2007). These are proposed to be related to opening of an enzymic latch mechanism; Freeman *et al.* (2001) have proposed hydrolase enzymes, the primary agents of decomposition, become active as the water table falls during the drought because inhibitory phenolic materials are removed by extracellular phenol oxidase. These hydrolases are not repressed again after the water table recovers until phenolics re-accumulate and so trigger indirect additional production.

FUTURE STUDIES

Although there is increasing evidence to suggest that increases in DOC concentrations are being driven by regional or global-scale environmental changes as discussed above, the key driving mechanisms have yet to be conclusively identified. We would like to suggest following topics for future studies in relation to DOC increases to fill the gaps in our knowledge.

First, more extensive and longer-term observation of DOC fluxes in rivers and streams are needed. Geographically, previous studies have focused on European countries and North America, while other types of watersheds have not fully assessed yet. For example, tropical rivers are important ecosystems considering their magnitude of DOC transport, but little information is available. As such, global networks of field observation of DOC are highly desirable. Secondly, chemical properties of DOC should be thoroughly characterized by employing various techniques. Sources of DOC can be determined by stable isotope analysis (Raymond and Bauer, 2001), which will provide valuable information for key mechanism for DOC increases. Chemical fractionation also provides valuable information (Leenheer, 1994), because DOC composition and decomposability would determine its long-term fate and hence role in the carbon cycle at the global scale. Thirdly, impacts of elevated DOC on human health via environmental issues such as disinfection by-product formation, fouling of membranes, and other such public health issues. There have been many studies indicating that DOC concentrations are associated with formation of disinfection by-products, but few studies have yet integrated such information from natural dynamics of DOC to dynamic health impacts in human populations. Thirdly, diverse scales and approaches should be employed simultaneously to better understand the mechanism driving DOC increases. For example, ecosystem-level manipulation experiments, watershed or regional scale modeling, new tools for chemical and microbiological analyses of DOC characteristics, and diverse statistical analyses including advanced time series analysis should be applied and their results integrated across scales and between disciplines. The case for assembling multidisciplinary teams to address these issues is becoming ever more compelling. Finally, not only climate changes but also direct human impacts should be addressed in terms of DOC increases. For example, 'Grand River Project' in Korea may modify the structure and functions of rivers substantially, of which consequences on DOC dynamics should be monitored and addressed.

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