# Variations of DOC and Phenolics in Pore-water of Peatlands

**Kang, Hojeong***, **Chris Freeman**[1] **and Seon-Young Kim**

(*Department of Environmental Science and Engineering, Ewha Womans University, Seoul, Korea*
[1]*School of Biological Sciences, University of Wales, Bangor, LL57 2UW, UK*)

**The amount and composition of dissolved organic carbon in wetlands are of great importance for their influence in secondary productivity, various biogeochemical processes, and aquatic ecosystem functions. In the present study, we measured variations of DOC and phenolics concentrations in pore-water of three northern peatlands (bog, fen, and swamp) over a 1-year period. General microbial activity (soil respirometry) and phenol oxidase enzyme activity were determined in the same peatlands to elucidate mechanisms underlying the differences in DOC and phenolics contents. The concentrations of DOC varied 25.5-45.4 (bog), 29.2-71.4 (fen), and 13.5-87.6 (swamp) mg/L, while phenolic concentrations ranged 13.3-48.1 (bog), 7.6-29.5 (fen), and 4.9-30.8 (swamp) mg/L. The seasonal variations of DOC and phenolics in the swamp suggest that litterfall may be one of the most important factors for the DOC dynamics in such systems. The lowest microbial activity and phenol oxidase activity were found in the bog, which appears to induce high percentage of phonolic contents in pore-water from bogs. It is also suggested that not only the DOC concentrations but also composition of DOC is of great importance in wetland biogeochemistry.**

**Key words : enzymes, recalcitrant, carbon cycle, dissolved organic carbon, peatland**

## INTRODUCTION

Wetlands are transitional zones between terrestrial and aquatic ecosystems, mediating important biogeochemical processes (Mitsch and Gosselink, 1993). One of those is the production of dissolved organic carbon (DOC), which is the dominant form of organic carbon in many aquatic ecosystems (Wetzel, 1983). The main significance of DOC in wetlands is related to the followings. First, DOC is an important component of organic energy pathways in ecosystems (Middelboe and Sondergaard, 1993), and hence the amount and the composition of DOC affect substrate availability for heterotrophic bacterial growth (Mann and Wetzel, 1995). Although many complicating factors have been reported due to other physicochemical or biological influences such as temperature, UV radiation, nutrient, or grazing (Findlay *et al*., 1991), a correlation between bacterial production and DOC has been widely acknowledged in the field conditions (Cole *et al*., 1992). Further, several studies have shown that DOC in wetlands would affect various microbial-mediated processes such as trace gas flux (Bianchi *et al*., 1996) and extracellular enzyme activities (Freeman *et al*., 1998). Secondly, wetlands may represent a substantial source of dissolved organic carbon (DOC) for freshwater streams (Schiff *et al*., 1998). Many studies have shown that wetlands play a role in the functional processes of the recipient waters by affecting the amounts and types of DOC present (Wetzel, 1992). From a global perspective, for example, Lugo *et al*. (1989) have estimated that wetlands contribute 20% of

* Corresponding Author: Tel: 02) 3277-3916, Fax: 02) 3277-3275, E-mail: hjkang@ewha.ac.kr

DOC exports from continent to the oceans. Finally, it has been reported that DOC influences bio-availability and toxicity of various toxins such as trace metals and organic contaminant by sorption (Santschi *et al*., 1997).

Even though DOC has widely been studied as a readily-utilizable carbon pool in many ecosystems, such pool may be much smaller than DOC data simply imply. The reason is that large fraction of DOC originated from terrestrial ecosystems is recalcitrant such as lignin or phenolics, and hence such DOC is not metabolised by microbes quickly. Among the various types of wetlands, we have collected samples from a bog, a fen, and a swamp for this study.

The specific aims of this study were 1) to compare the monthly variations of quantity and quality of DOC in three different types of wetlands by monthly analysis of DOC and phenolics content in pore-water of three different wetlands, and 2) to elucidate the underlying mechanisms for the differences among the wetlands by determining microbial activities in the peat.

## MATERIALS AND METHODS

### Site description

The study sites were an acidic bog in Migneint (UK grid reference SH 805 458), a calcareous fen in Gors Goch (UK grid reference SH 497 826), and a forested swamp in Cwm-y-Glo (UK grid reference SH 554 626), north Wales, UK. Detailed characteristics and locations of the sites were previously reported (Kang and Freeman, 1999). The bog site is near Ffestiniog in north Wales and covered with several *Sphagnum* spp. The fen site is located on Anglesey island, north Wales, and dominated by *Juncus* spp., *Festuca* spp., *Cladium* spp., and *Carex* spp. The swamp site is *Alnus* spp. and *Salix* spp. dominated area, which is adjacent to Afon Rhythallt stream.

### Water sampling

We conducted a monthly-based sampling in 1997. Using syringe and water sampler placed at 10 cm depth, *ca*. 10 ml of water samples were withdrawn. The water sampler is composed of a tube (3 mm in diamter) connected to the tip of a 10 ml syringe packed with glass wool. Water samples were filtered with 0.2 μm filter on the day of the sampling, and maintained at 2°C until chemical analysis. Five replicates were collected at each sampling occasion. Dissolved organic carbon (DOC) was determined by the difference between total carbon (TC) and inorganic carbon (IC) in the samples. TC and IC were measured with a TOC meter (Simadzu TOC-500), by injecting 10 μl samples separately. Standard curves were prepared using 0-40 ppm of potassium hydrogen phthalate solution (for TC) or 0-40 ppm of sodium hydrogen carbonate / sodium carbonate solution (for IC). Phenolic contents were assayed using Folin-Ciocalteau phenol reagent (Box, 1983). One ml of sample was added with 1.5 ml of $Na_2CO_3$ solution (50 g/L). Then 0.5 ml of Folin-Ciocalteau solution (1/4 diluted with deionised water; 0.5 N) was added, and the mixture was maintained for 2 hours at room temperature. A standard curve was prepared by applying the same chemicals to 0-2 mg/L phenol solution. The change of colour of the reactants was measured by a spectrophotometer at 750 nm. When the samples were out of the range of the phenol standard solution, the samples were diluted with deionised water and the procedure was repeated. In general, samples from the bog and the fen required 3-5 folds dilution, while no dilution was needed for the swamp samples.

### Microbial activity

To assess general microbial activity, respiration of microbes was determined in July. In addition, phenol oxidase activity was measured in July to assess degradation rates of recalcitrant organic carbon in the study sites. Peat samples (0-10 cm depth) were collected from each wetland and activities were measured as follows. The measurement of respiration involved a noting of $CO_2$ accumulation in a McCartney bottle placed with 1 ml of peat for 1 hour under 10°C. Phenol oxidase (EC 1.10.3.2) activity was determined using 10 mM L-DOPA (dihydroxy phenylalanine) solution as a substrate according to Pind *et al*. (1994).

## RESULTS

The monthly variations of DOC and phenolics are presented in Fig. 1. The DOC concentrations varied 25.5-45.4 (bog), 29.2-71.4 (fen), and 13.5-87.6 (swamp) mg/L. In the bog, the variation was minimal with a slight decrease in early spring

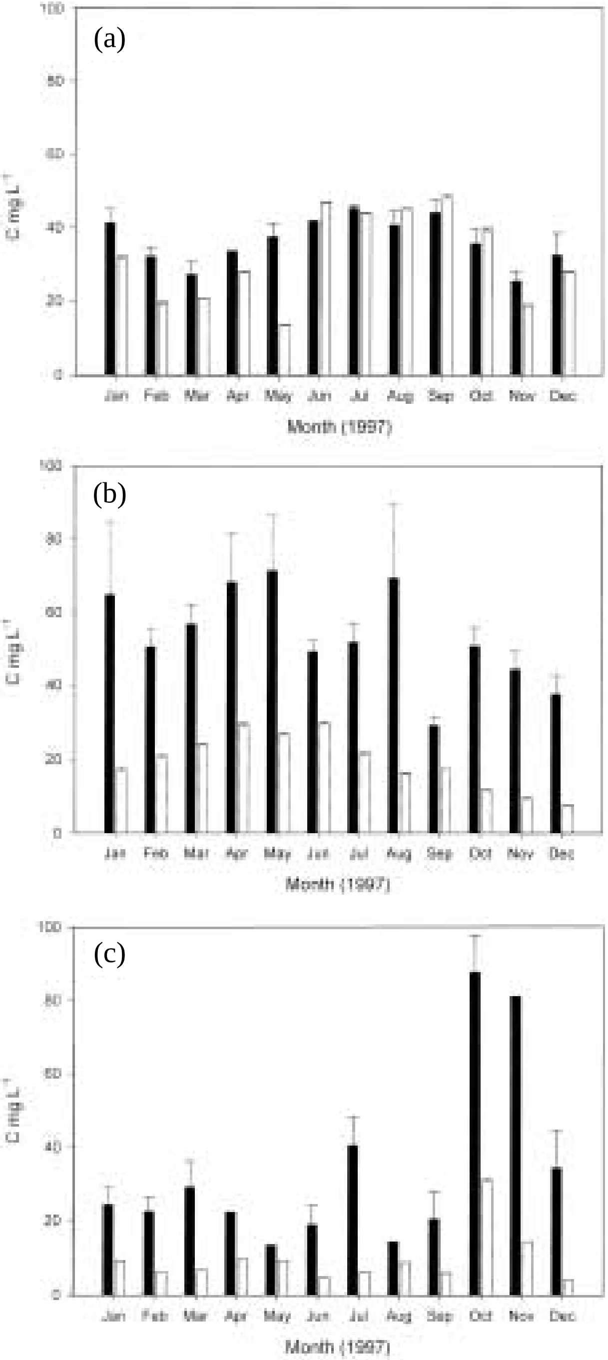


**Fig. 1.** Monthly variations of DOC and phenolics in three wetlands in 1997 in north Wales, UK.

(March) followed by an increase over summer season (Fig. 1-(a)). In contrast, DOC concentrations were relatively high in early months and the lowest concentration was found in September in the fen (Fig. 1-(b)). The seasonal variation was most distinctive in the swamp, where the concentration was high in October and November (Fig. 1-(c)). The ratios between the highest concentrations and the lowest ones of DOC were 1.8, 2.4, and 6.5 for the bog, the fen, and the swamp, respectively.

The phenolics concentrations were 13.3-48.1 (bog), 7.6-29.5 (fen), and 4.9-30.8 (swamp) mg/L. The concentration increased in summer (July-October) in the bog site while the lowest concentration was found in May (Fig. 1-(a)). In the fen site, phenolic concentrations increased gradually from January to June followed by a gradual decrease toward the end of the year (Fig. 1-(b)). In contrast, the phenolic concentrations followed a similar pattern as DOC in the swamp in such a way that relatively high concentrations of phenolics were found in October and November (Fig. 1-(c)). In average, phenolics comprise of 87% of DOC in the bog, while the percentages were 36% and 28% for the fen and the swamp, respectively.

Respiration rate was the highest in the swamp (157.5 $\mu g\ g^{-1}\ h^{-1}$), followed by the fen (123.2 $\mu g\ g^{-1}\ h^{-1}$) and the bog (94.3 $\mu g\ g^{-1}\ h^{-1}$) (Table 1). However, the difference between the bog and fen was not statistically significant. In contrast, phenol oxidase in the bog (15.2 $\mu M$ diqc $g^{-1}\ min^{-1}$) was significantly lower than the other two sites, and no differences were found between the fen and the swamp (Table 1).

**Table 1.** Respiration rates and phenol oxidase activity in the wetland sediments in July, 1996. The values are mean with the standard error in the parenthesis (n = 4). Values with different letters in the same columns are significantly different at $P < 0.05$ (Tukey's test).

| | Respiration ($CO_2\ \mu g\ g^{-1}\ h^{-1}$) | Phenol oxidase ($\mu M$ diqc $g^{-1}\ min^{-1}$) |
|---|---|---|
| Bog | 94.3 (11.8)$^a$ | 15.2 (2.2)$^a$ |
| Fen | 123.2 (16.6)$^a$ | 44.5 (0.5)$^b$ |
| Swamp | 157.5 (15.4)$^b$ | 58.6 (5.7)$^b$ |

## DISCUSSION

The composition and availability of dissolved organic carbon (DOC) have been studied extensively in aquatic ecosystems (Münster, 1991) and wetlands (Dalva and Moore, 1991). Those studies have indicated that wetlands export substantial amount of DOC and hence have a strong influence on the chemistry of surface waters such as pH or iron concentrations. It is also pointed out that DOC plays a key role in secondary production and other biogeochemical reactions such as trace gas flux (Mann and Wetzel, 1995). However, DOC concentrations alone have often been reported in many studies, which could be problematic. For example, our results exhibited that DOC concentration in the bog was comparable to the fen or the swamp. However, most of the DOC in the bog was composed of recalcitrant phenolics and microbial activity was the lowest as shown in the respiration rates (Table 1). This indicates the importance of chemical composition of DOC rather than DOC concentration *per se* in systems with high phenolic contents. In each site, a significant correlation between DOC and phenolics was found (Fig. 2). The slope of this regression line (the ratio of phenolics/DOC) may represent the quality of carbon supply in the site, because phenolics represent a recalcitrant and inhibitory component in the DOC metabolism (Freeman and Lock, 1995). The slope was highest in the bog, and similar in magnitude in the fen and the swamp (Fig. 2). The differences in the slopes are likely to be related to differences in chemical composition of vegetation (e.g., high phenolic content of *Sphagnum* in the bog), and lower microbial activity, especially phenol-degrading enzyme activity in the bog (Table 1). This finding also suggests that information on chemical composition (e.g., ratio of phenolic content and DOC) would be of a valuable index to represent organic

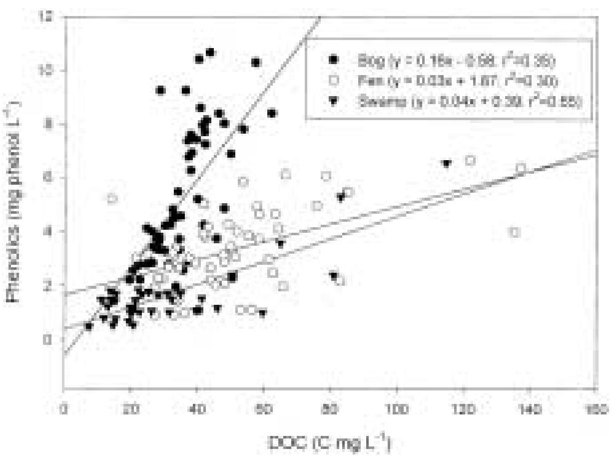


**Fig. 2.** Relationship between DOC and phenolics in the wetlands. All correlation coefficients are significant at $P < 0.01$ (n = 60 for each wetland).

matter decomposition potential and hence carbon availability to heterotrophic microbes in peatlands.

Freeman *et al.* (2001a) have reported that inhibition of phonol oxidase may impede other hydrolase activities in wetlands and hence induce accumulation of organic matter. Our results suggest that the lower phenol oxidase activity in the bog was one of the mechanisms for the lower decomposition rates in bogs.

A recent study has suggested that elevated temperature by global warming could induce higher carbon decomposition in peatlands and hence higher DOC input to aquatic ecosystems in UK (Freeman *et al.*, 2001b). The present study implies that this might be the case in bogs where most of the soil is organic matter with extremely low primary productivity. Indeed, we observed a positive correlation between temperature and DOC concentration in the bog ($r = 0.671$, $P < 0.05$, $n = 12$). However, peatlands with relatively high inorganic material and deciduous vegetation may respond in a different way. In the present study, neither DOC nor phenolics exhibited significant correlations with temperature in the fen or the swamp. The results of our study suggest that the seasonal variability of DOC concentrations is closely related to litter fall production in the swamp (Fig. 1-(c)). As such, not only the temperature but also other factors affecting primary productivity such as nutrient availability, water level, or $CO_2$ concentrations in the atmosphere would be important controlling variables for DOC dynamics in swamps under the conditions that are predicted by global climatic change models.

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<국문적요>

# 이탄습지 공극수내 용존유기탄소와 페놀계열 물질의 변화도

강 호 정* · Chris Freeman[1] · 김 선 영

(이화여자대학교 환경학과, [1]School of Biological Sciences, University of Wales, Bangor LL57 2UW, UK)

습지내의 용존유기탄소의 함량과 구성은 이차생산, 다양한 생지화학적 반응, 그리고 수생태계의 기능에 중요한 영향을 미친다. 본 연구에서는 북구이탄습지 (bog, fen, swamp) 의 공극수내의 용존유기탄소와 페놀계열 물질의 농도를 1997년도에 1년에 걸쳐 조사하였다. 일반적인 미생물의 활성 (토양 호흡도)와 페놀산화효소의 활성도 측정하여, 용존유기탄소와 페놀계열 물질의 변화에 대한 기작을 밝히고자 했다. 용존유기탄소 농도는 25.5-45.4 (bog), 29.2-71.4 (fen), 13.5-87.6 (swamp) mg/L를 보였고, 페놀계열 물질의 경우에는 13.3-45.4 (bog), 7.6-29.5 (fen), 4.9-30.8 (swamp) mg/L의 변화정도를 보였다. Swamp에서의 계절적인 변화양상을 살펴보면, 낙엽생산이 용존유기탄소의 변화에 많은 영향을 미침을 알 수 있었다. Bog에서의 미생물활성도와 페놀산화효소의 활성이 가장 낮게 나타났는데 이것이 bog 내의 높은 페놀계열물질의 농도를 야기시킨 것으로 사료된다. 본 연구의 결과는 습지내 용존유기탄소의 양 뿐만 아니라 그 화학적인 구성이 습지 생지화학에서 중요함을 보여주었다.