Variability in the Composition and Amount of DOC in Surface Waters: Implications for UV Radiation Penetration.

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PROJECT SUMMARY

Dissolved organic carbon (DOC) provides a major control on the penetration of UV radiation in surface water with higher DOC concentrations reducing the depth to which radiation penetrates. The absorbance of radiation by DOC is due primarily to the highly photoreactive structural compounds found in the fulvic acid fraction of these dissolved organic compounds. In general, algal-derived DOC is low in photoreactive fulvic acids while terrestrially derived DOC is high. In aquatic environments where the annual hydrologic cycle is dominated by snowmelt (such as those found in Rocky Mountain National Park), there is a pronounced natural cycle in DOC concentrations. Snowmelt flushes soils of accumulated DOC each spring resulting in high DOC concentrations, with high photoreactivity, while autochthonous production increases the proportion of algal-derived, low photoreactive DOC later in year. Within this annual cycle, landscape position results in significant variability in the amount and composition of DOC both through the strength of hydrologic connections to surface water and through the availability of carbon and nutrients from different soil and vegetation types.

INTRODUCTION

Observed declines in amphibian populations have raised concerns that large-scale environmental perturbations (e.g. climate change, acid deposition, increased UV radiation) may be damaging protected ecosystems. However, it has been difficult to ascribe these observed declines to any single cause. For example, recent studies designed to evaluate the effects of UV radiation on amphibian populations have ranged from reports of no deleterious effects to complete mortality. While the explanations for this wide range of findings can, and are, argued, enough information exists indicating that UV-B radiation is a significant stressor to amphibians. Consequently, recent research has been devoted to the question: *What are the controls on UV exposure to amphibians in natural systems?*

Within the atmosphere, ozone is the major control on the amount of UV radiation reaching the surface of the earth. Once UV has reached the surface of a water body the primary control on how deep it penetrates is the amount and composition of dissolved organic carbon (DOC). Concern over the composition of DOC arises because the photoreactivity/ absorbtivity is largely determined by the chemical structure of the diverse compounds that comprise natural dissolved organic matter. The majority of UV protection is thought to be due to the operationally defined “hydrophobic” DOC fraction, composed primarily of fulvic acids. In general, DOC derived from terrestrial sources is higher in hydrophobic, photoreactive compounds than aquatic-derived DOC. Therefore, controls on the delivery of terrestrial DOC to aquatic systems may have significant effects on UV-B penetration in surface water, and the question becomes; *What are the controls on the amount of photoreactive, terrestrial-derived DOC in surface water?*

The amount and composition of DOC are controlled by a number of processes including; 1)transport of allochthonuos DOC into the systems from neighboring environments, 2) authochnous production of DOC, 3) heterotrophic consumption within the water column, 4) photochemical degradation, and 5) export out of the system. Physical transport (processes 1&5) is controlled by the hydrology of the site, while biogeochemical modifications (processes 2,3&4) are controlled by a variety of factors including vegetation, geology, temperature, nutrients, insolation, pH. In these snowmelt dominated systems, however, transport processes often exert the greatest control on amount of DOC in surface water. Specifically, a snowmelt pulse of DOC from soil to water each spring provides an episodic input of carbon that may vary between sites (based largely on vegetation structure and soil development) and between years (based largely on climate variability, especially snowfall). Consequently, interannual variability in climate may have a significant impact on the UV exposure animals in the same pond/ environment from year to year.

We hypothesized, that just as variability in atmospheric ozone is an important control on UV dose at the surface of the earth, spatial and temporal variability in the amount of this photoreactive DOC will have a large effect on the UV dose experienced by organisms within the water column.

RESEARCH GOALS

1) To quantify the total amount of DOC and the percentage of hydrophobic, potentially photoreactive fulvic acids in DOC in four parks in the Western U.S.

2) To evaluate the importance of the hydrophobic component of DOC to the extinction of UV radiation *in situ*, and

3) To assess the temporal variability in amount and composition of DOC in amphibian habitats,

5) To evaluate interannual variability in the amount and composition of DOC.

RESULTS: VARIABILITY IN DOC COMPOSITION AND AMOUNT

Sequoia/ Kings Canyon

Surface water in Sequoia/ Kings Canyon had the lowest DOC of all sites. Little vegetation and poor soil development result in low levels of DOC available to be exported during melt. Increases in total and hydrophobic DOC in late summer are probably due to rare summer thunderstorms providing a secondary flush of DOC that accumulated in soil over the summer.

Glacier

Surface water in Glacier exhibited a wide range of DOC concentrations, composition and seasonal patterns. For example, increases in total DOC combined with a decrease in hydrophobic DOC are indicative of high levels of autochthonous primary production. In contrast, decreases in concentrations over time at other sites indicate heterotrophic depletion of a limited labile carbon pool.

Rocky Mountain

Rocky Mountain has the widest range of DOC concentrations in surface water ranging from ~1 to >50 mg C L^{-1}. It is the only park with two years of data, and as such provides some evidence of the interannual variability in the processes that control of DOC in these systems. For example, DOC concentrations in Glacier Basin were similar in 1999 and 2000, but the amount of hydrophobic DOC was much lower (0.9 to 1.4 mg/L) in 1999 than in 2000 (2.0 to 3.5 mg/L). The precipitous decrease in DOC while the hydrophobic content increased in 1999 is indicative of heterotrophic consumption of labile carbon. Sharp increases in both amount and hydrophobicity in early September are indicative of an autumn flush of soil DOC with a rain event. Gradual increases in DOC while hydrophobic content declines can be seen in late summer at several sites and is indicative of aquatic primary production. A gradual decline in both total and hydrophobic DOC at Timber Creek in 1999 is indicative of the slow decay of DOC transported to the site during snowmelt.

Olympic

Difficult access limited the number of samples from Olympic, but one site indicates relatively low DOC concentrations. Similar to one of the sites in Glacier, the increase in total DOC with a decrease in hydrophobic content indicates that primary production is a significant source of DOC in this pond.

INFORMATION TRANSFER

SUMMARY

Variability in climate, primarily precipitation, coupled with local hydrologic flowpaths and landscape position exert a significant control on UV exposure in the aquatic environment. This control is mediated through the amount and composition of DOC transported from the terrestrial environment to the aquatic ecosystem. Future work should focus on quantifying both the spatial and temporal variability in the DOC mediated UV exposure to these, and other aquatic ecosystems characterized by episodic hydrological inputs of terrestrial DOC to surface water.

APPENDIX 1. MANUSCRIPT IN REVIEW

Climate-mediated DOC concentrations control amphibian exposure to UV-B.

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The amount of dissolved organic carbon (DOC) in surface water controls the exposure of aquatic organism to UV-B radiation [(1,2)], yet only a portion of the total DOC pool is capable of absorbing UV radiation. This research was designed to identify spatial and temporal variability in this photoreactive component of DOC at protected sites in Rocky Mountain National Park (RMNP) with a history of

amphibian decline. Water samples collected in 1999 and 2000 demonstrate that the fulvic acid DOC fraction is responsible for controlling the depth to which UV-B radiation penetrates. This fraction of the total DOC pool originates primarily in surrounding soils and is transported to surface water by precipitation events. Consequently, the amount of photoreactive fulvic acid in the surface water environment is highly variable and related to variability in precipitation [3, 4, 5, 6]. This suggests that droughts may result in one to several year periods where concentrations of photoreactive fulvic acids are low and consequently, UV-B exposure to aquatic organisms is high. This additional stressor is consistent with previously observed, but unexplained declines in amphibian populations.

Widespread reports of amphibian decline in protected ecosystems have been considered an early warning of large-scale environmental degradation [7,8,9,10]. Postulated causes include introduced disease, acid deposition, increased UV radiation, and climate change [11, 12, 13,14]. While UV radiation has received considerable research interest as a mechanism for observed declines, studies designed to evaluate the effects of UV radiation on amphibian populations have ranged from reports of no deleterious effects [15] to significant mortality [16,17,18]. Recently, two papers have suggested that episodic droughts may result in high UV exposure by decreasing the depth of water in which amphibians breed [19, 20]. However, a concerted effort to describe the *in situ* variability in UV penetration in surface water environments, which is controlled by dissolved organic compounds, has been absent from most studies. The chemical structures capable of absorbing UV radiation (chromophores) are found primarily in the aromatic fulvic acid fraction of DOC [21, 22], most of which originate in the soil environment [23]. In fact, variations in the fulvic acid composition can be used as markers for the influence of the terrestrial environment on aquatic carbon cycling [22, 23]. Amphibian habitats in mountain environments often are closely linked to terrestrial ecosystems, i.e. shallow water environments, ponds, wetlands, etc. with relatively short hydrologic residence times. Consequently, biogeochemical controls (e.g. temperature, moisture, vegetation, soil charcteristics) on the amount of terrestrial DOC, together with hydrologic controls on DOC transport will affect the fulvic acid composition in surface water and consequently

UV-B extinction/ exposure in the aquatic environment. The objective of this research was to identify the controls on the UV exposure to aquatic organisms within the range of aquatic, hydrological, and chemical processes that supply photoreactive dissolved organic compounds in natural systems.

Total DOC and hydrophobic fulvic acid content were measured approximately weekly at three sites, chosen to represent high, moderate, and low DOC environments, in RMNP during 1999 and 2000. During one to three of these visits the extinction of UV radiation was measured *in situ* using a hand held Advanced Photonics radiometer. Water samples were collected in ashed amber glass bottles and immediately filtered through ashed glass fiber filters and transported to the laboratory on ice. The fulvic acid fraction was isolated by column chromatography using XAD-8 resins to produce hydrophobic/ fulvic acid and hydrophilic fractions [24]. Total DOC, hydrophobic/ fulvic acid, and hydrophilic acids subsequently were analyzed on a Shimadzu TOC analyzer.

Similar to other reports [1,2] there is a negative exponential relationship between *in situ* measurements of UV radiation and total DOC concentrations in samples collected on the same date (Fig. 1a). It is clear however, that the extinction of UV radiation is due primarily to the fulvic acid DOC fraction (Fig. 1b). In contrast, a weak relationship between the hydrophilic DOC fraction and UV extinction (Fig. 1c) is explained by the fact that the extinction data were collected in the field with each data point is associated with both hydrophilic and hydrophobic DOC fractions. Furthermore, the relationship between the fulvic acid DOC fraction and UV extinction remains strong at low DOC concentrations while the relationship with hydrophilic DOC decreases drastically.

Because UV extinction is controlled by structures in the fulvic acid, primarily terrestrially-derived DOC fraction, the size of this DOC pool is more important than the total amount of DOC for assessing UV exposure to aquatic organisms. This is especially important in low DOC waters where small changes in the amount of photoreactive fulvic acids, with or without changes in the total amount of DOC may have a large effect on UV exposure. Therefore, understanding the controls on the delivery of terrestrial DOC to surface water is a key to evaluating the importance of UV exposure to amphibian decline in past data or predicting populations at risk from future exposure.

In these aquatic ecosystems the annual hydrologic cycle is dominated by an extended period of snow accumulation followed by a relatively short snowmelt period that accounts for 65% to 85% of annual discharge. Snowmelt flushes soil of accumulated DOC resulting in peak annual DOC concentrations in spring and early summer [5,6,25]. This general pattern of high total and fulvic acid DOC during early summer is seen in the three intensively monitored sites in 1999 (Fig 2). Exceptions to this general pattern include; 1) episodic rainstorms that result in short duration increases in both total and fulvic acid DOC (Fig 2a,b), and 2) increases in total DOC while the fulvic acid fraction continues to decrease (Fig 2c) due to autochthonous algal primary production. While increases in total and fulvic acid DOC associated with rain events were observed in 2000 (Fig 3a), the early season peak in DOC followed by a slow decline was not as pronounced at these sites in 2000 (Fig 3). The difference between the two years is explained by lower precipitation, and consequently lower amounts of terrestrial DOC transported to surface water in 2000. For example, total precipitation at the Loch Vale National Atmospheric Deposition Program (NADP) site within the park was 1080 mm in 1999, but only 780 mm in 2000 (data may be found at http://nadp.sws.uiuc.edu/nadpdata/siteinfo.asp?id=CO19&net=NADP).

The lower precipitation amounts in 2000 resulted in a 20% to 52% reduction in total DOC, and a 27% to 59% decrease in fulvic acid DOC during the first week in July (Fig 4). The result of this reduction in fulvic acid DOC on UV extinction was relatively small at the moderate and high DOC sites, but results in an approximate doubling of the 90% extinction depth (from 8 cm to 17 cm) at the low DOC Glacier Basin site. Because the majority of surface waters in RMNP, as well as other mountain catchments, are characterized by total DOC concentrations below 5 mg/L, natural variability in precipitation may result in large increases in UV exposure during relatively dry years. While there are no long-term records of DOC composition and amount in RMNP that can be used to test this relationship between precipitation and DOC concentrations, there are hydrochemical data from other Colorado catchments with a similar range of physical and vegetative characteristics. Long-term data from Deer Creek and the upper Snake River catchments, approximately 90 km South of RMNP, reveal a significant, positive relationship between precipitation and DOC (Fig. 5) with DOC concentrations higher during years with high winter/spring precipitation. This relationship holds in both catchments even though they are characterized by different bedrock geology and soil chemistry[3]. Consequently, natural variability in precipitation has a large effect on the amount of terrestrially derived, fulvic acid DOC transported from soil to surface water, suggesting that aquatic organisms may experience higher UV stress during low precipitation years.

While several recent studies have linked the extinction of UV radiation to variability in DOC chemistry [26, 27], most studies addressing amphibian decline have not reported total DOC or more importantly, the photoreactive DOC fraction. However, because the photoreactive DOC fraction is associated with precipitation, climate data can be used to predict relative trends in photoreactive DOC during previous amphibian surveys. For example, surveys conducted in RMNP during an extended dry period (48% to 82% of the 1980 to 1999 average at the Loch Vale NADP site in the park) indicated that at least one amphibian species disappeared from 9 of 16 sites surveyed during 1988, 1989, and 1990[28]. In contrast, only one site had a new species recorded during this same period. Furthermore, by the third year of this drought there was a 16% reduction in the number of sites where successful breeding was observed.

It appears likely that climate-induced variability in the production and transport of DOC to surface water results in higher UV exposure to amphibians during drought years. This is similar to reports that boreal toads in Oregon deposit eggs in shallower water in drought years, possibly resulting in greater exposure to UV and consequently, higher mortality due to infection by the water mold *Saprolegnia ferax*[1]. However, this explanation is true only if the total amount of photoreactive DOC in the water column above the eggs also is lower during drought years. The results from this paper suggest that is indeed the case and, together with the research from Oregon could explain observations of declines in amphibian populations following periods of lower than normal precipitation [12, 14, 19, 29], as well as some of the widely disparate results obtained in field exposures of amphibians to UV radiation. It is unclear whether the episodic stress of increased levels of UV radiation every few years contributes to amphibian decline directly, acts in conjunction with other known stressors such as acidification or fungal infection, or is ameliorated by changes in amphibian behavior. These issues should be systematically examined with the context of climate induced variability in UV.

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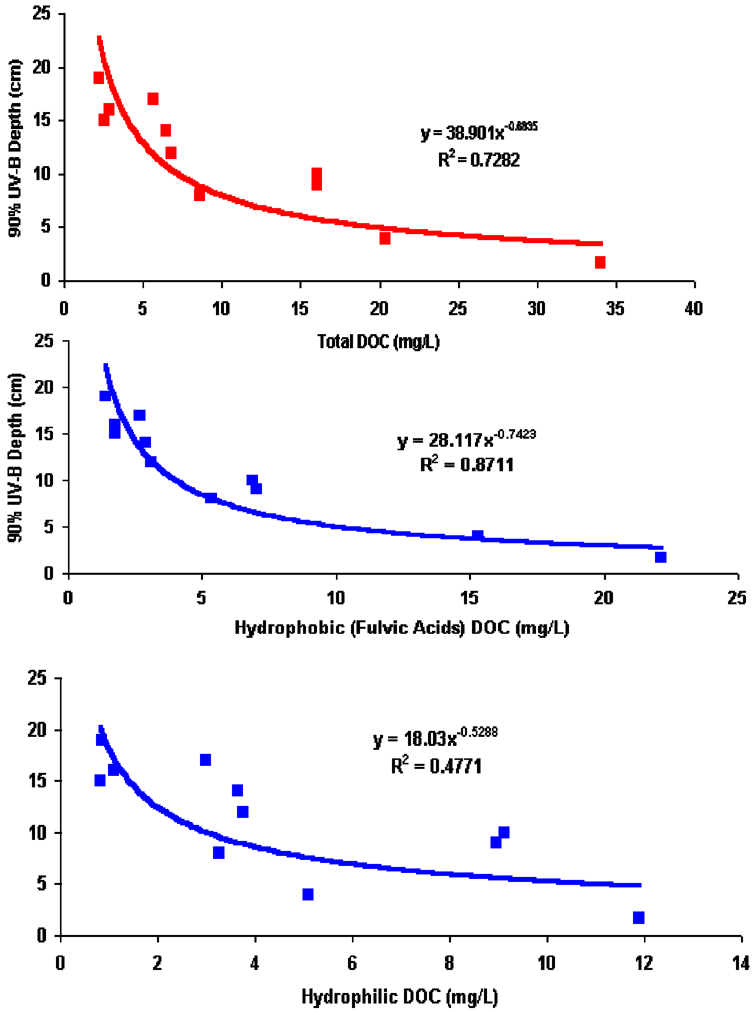
Figure 1. The relationship between UV-B extinction measured in the field and total DOC concentration (top), hydrophobic fulvic acid DOC concentration (middle), and hydrophilic DOC (bottom) demonstrates that the fulvic acid DOC fraction is primarily responsible for UV attenuation in surface waters.

Figure 2. DOC concentrations and hydrophobic content at three sites in Rocky Mountain National Park during the summer of 1999.

Figure 3. DOC concentrations and hydrophobic content at three sites in Rocky Mountain National Park during the summer of 2000.

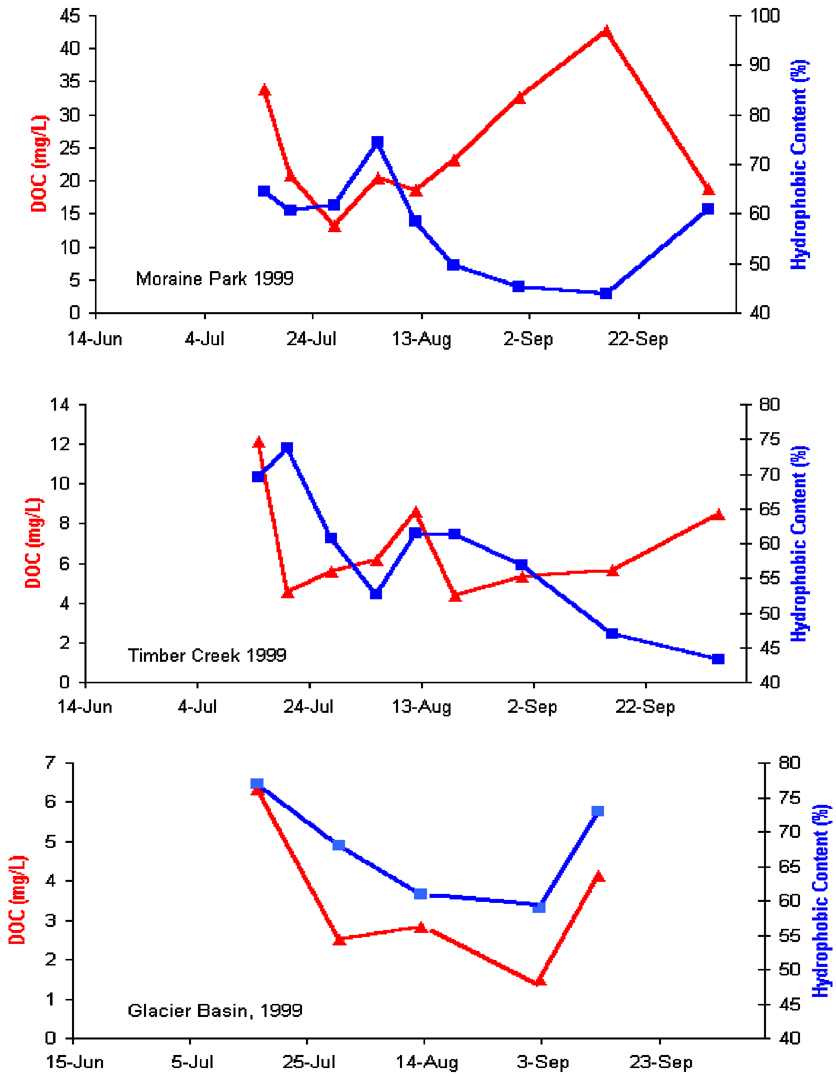
Figure 4. Difference in total DOC (top) and hydrophobic/ fulvic acid DOC amounts (bottom) in the three sites between 1999, a wet year and 2000 a dry year.

Figure 5. Relationship between surface water DOC concentrations and water yield for two catchments with different geology and soils demonstrate that increased precipitation/ runoff results in higher total DOC amounts.

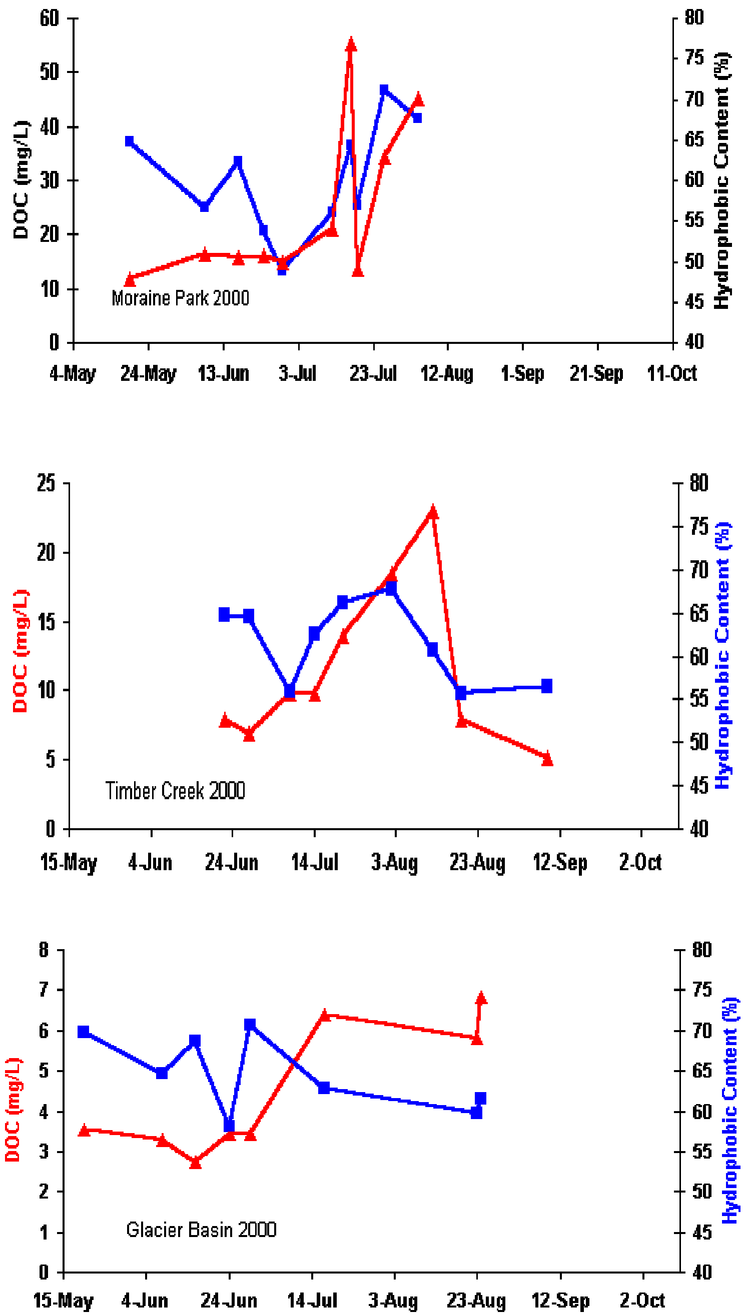


25
20
15
10
5
0
90% UV-B Depth (cm)
y = 38.901x
R2 = 0.7282
0
5
10
15
20
25
30
35
40
Total DOC (mg/L)
25
20
15
10
5
0
90% UV-B Depth (cm)
y = 28.117x-0.7423
R2 = 0.8711
0
5
10
15
20
25
Hydrophobic (Fulvic Acids) DOC (mg/L)
25
20
15
10
5
0
y = 18.03x-0.5288
R2 = 0.4771
0
2
4
6
8
10
12
14
Hydrophilic DOC (mg/L)

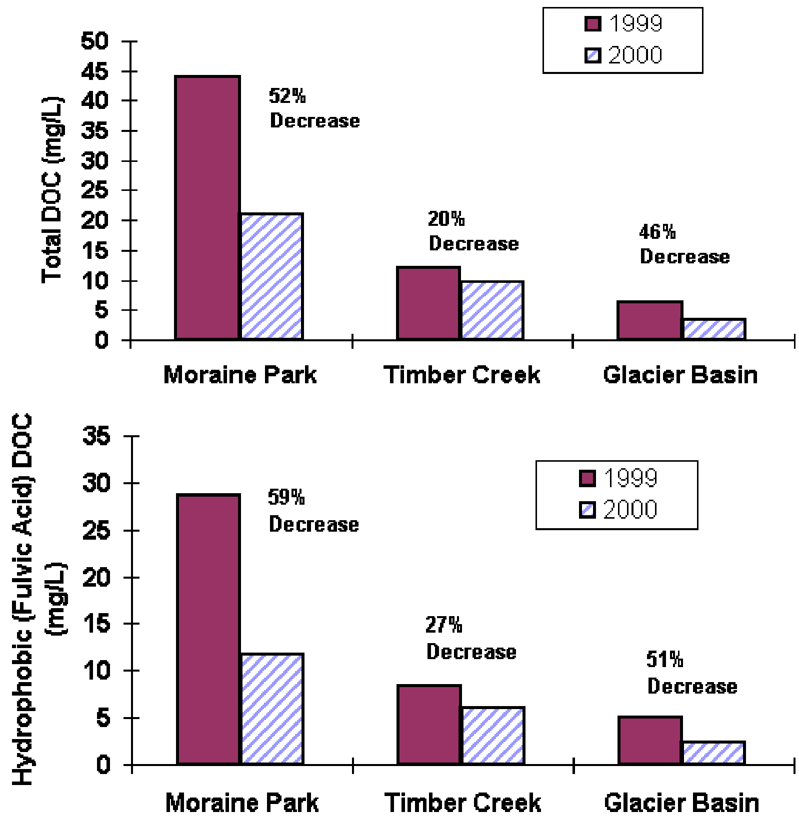
Brooks_fig1


DOC (mg/L)
Hydrophobic Content (%)
Moraine Park 1999
14-Jun
4-Jul
24-Jul
13-Aug
2-Sep
22-Sep
Timber Creek 1999
Glacier Basin, 1999
15-Jun
5-Jul
25-Jul
14-Aug
3-Sep
23-Sep

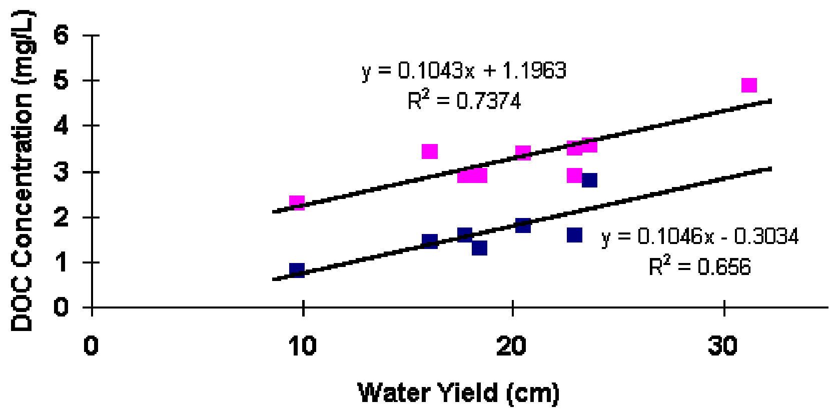
Brooks_fig2


Moraine Park 2000
DOC (mg/L)
Hydrophobic Content (%)
0
10
20
30
40
50
60
40
45
50
55
60
65
70
75
80
4-May
24-May
13-Jun
3-Jul
23-Jul
12-Aug
1-Sep
21-Sep
11-Oct
Timber Creek 2000
DOC (mg/L)
Hydrophobic Content (%)
0
5
10
15
20
25
40
45
50
55
60
65
70
75
80
15-May
4-Jun
24-Jun
14-Jul
3-Aug
23-Aug
12-Sep
2-Oct
Glacier Basin 2000
DOC (mg/L)
Hydrophobic Content (%)
0
1
2
3
4
5
6
7
8
40
45
50
55
60
65
70
75
80
15-May
4-Jun
24-Jun
14-Jul
3-Aug
23-Aug
12-Sep
2-Oct

Brooks_fig3


1999
2000
Total DOC (mg/L)
50
45
40
35
30
25
20
15
10
5
0
52% Decrease
20% Decrease
46% Decrease
Moraine Park
Timber Creek
Glacier Basin
1999
2000
Hydrophobic (Fulvic Acid) DOC (mg/L)
35
30
25
20
15
10
5
0
59% Decrease
27% Decrease
51% Decrease
Moraine Park
Timber Creek
Glacier Basin

Brooks_fig4


DOC Concentration (mg/L)
6
5
4
3
2
1
0
0
10
20
30
Water Yield (cm)
y = 0.1043x + 1.1963
R2 = 0.7374
y = 0.1046x - 0.3034
R2 = 0.656

Brooks_fig5

APPENDIX 2. PAPERS PRESENTED

Brooks, P.D K. Tonnessen, S. Diamond, K. Czarnowski, C. Ronca. (2001) Variability in the amount and composition of DOC: Implications for UV-B attenuation and observed patterns of amphibian decline. Ecological Society of America Annual Meeting, Madison, WI, August.

Brooks, P.D. and K.A. Tonnessen. (2000) Variability in the Amount and Composition of DOC in Rocky Mountain, Glacier, Olympic, and Sequoia/ Kings Canyon National Parks: Implications for UV-B Attenuation and Observed Patterns of Amphibian Decline**.** American Geophysical Union fall meeting, San Francisco, CA. December.

APPENDIX 3. DATA