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Seasonal changes in photochemical properties of dissolved organic matter

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Abstract

The fate of dissolved organic matter (DOM) in lakes and streams is significantly affected by photochemical transformation of DOM. A series of laboratory photochemical experiments was conducted to describe long-term changes in photochemical properties of DOM. The stream samples used in this study originated from three different catchments on the southern-most part of the Boreal ecozone near Dorset, Ontario, Canada. A first-order kinetics equation was used to model photochemical degradation of DOM and the kinetic rate constant, K , was used as an indicator of photochemical properties of DOM. Highest K was observed in samples from the catchment dominated by coniferous forest while the lowest K was measured in the deciduous catchment. Kinetic rate constants from all three catchments showed a sinusoidal pattern during the hydrological year. K increased steadily during autumn and winter and decreased during spring and summer. The highest values were observed during spring melt events when DOM was flushed from terrestrial sources by high flows. The minimum rate constants were found in summer when discharge was lowest. DOM molecular weight and specific absorbance at 254 nm also exhibited annual cycles corresponding to the seasonal cycles of terrestrial organic matter but the relationships between these properties and K was probably affected by previous exposure to solar radiation during transit from the catchment as well as pH and iron.

1 Introduction

An increase in DOM concentrations in lake and stream waters has been observed during the last 30 yr across much of Europe and North America (Freeman et al., 2004; Worrall et al., 2004; Vuorenmaa et al., 2006) with much speculation about the reasons for the increase, e.g. changes in temperature and hydrology associated with climate change and a decrease in acidification (Porcal et al., 2009). Climate change models predict that higher temperatures are likely to occur over most of the boreal forest

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regions and these in turn are likely to lead to changes in DOM export to and DOM processing rates in lakes which will alter concentrations of DOM and its constituents (Porcal et al., 2009) with impacts felt by biological communities.

There are two major sinks of DOM in the aquatic environment – DOM is gradually degraded by microbial and photochemical processes (Stumm and Morgan, 1996) to small organic compounds, dissolved inorganic carbon (DIC) and particulate organic carbon (POC) (Wetzel, 2001) leading to loss of C to sediments and to the atmosphere. At this point, our understanding of how future changes, say, in the seasonality of DOM export will affect photochemical processing is limited.

Models of the contribution of photochemical processes in streams, rivers, and lakes to changes in DOM quality and concentrations are limited because of a lack of information on how important DOM properties vary seasonally. Seasonal changes in photochemical properties of DOM have not been reported yet but results of some studies enable us to make some observations about seasonal trends. Gennings et al. (2001) sampled headwater streams in the Dorset area from April to September 1997 and exposed them directly to solar radiation. They observed highest photodegradation rate constants in spring and decreasing rates during summer. Photodegradation rate constants of water from a stream near Dorset exposed to solar radiation decreased during summer (Molot et al., 2005). In these studies the photodegradation rate constants decrease during summer, but it is difficult to distinguish between the role of decreasing solar radiation or changing DOM properties. Brooks et al. (2007) artificially irradiated samples from several streams in Colorado that were collected during spring peak flow and summer base flow. They observed higher photodegradation in spring than in summer. Only one study known to the authors described a seasonal trend in photochemical properties. Porcal et al. (2004) exposed samples from a tributary to acidified Plešné Lake to solar radiation at 0.5 m depth during the hydrological year 2000–2001. The lowest photodegradation rate constant was observed in winter while the highest photodegradation rate constants were observed in late spring. These observations suggest

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that seasonal trends in susceptibility to photodegradation are the norm and may therefore be predictable.

Long term monitoring sites near the southern boundary of the Boreal ecozone in Ontario, Canada, where the previous photochemical studies were done (Dillon and Molot 1997a; Gennings et al., 2001; Molot et al., 2005), were selected to determine possible seasonal changes in basic photochemical properties of DOM during a hydrologic year, since the previous studies were limited only to spring and summer. Photochemically induced decrease in DOM concentration, a process combining direct photomineralization of DOM to CO₂ (Granéli et al., 1996) and possible decrease in DOM concentration due to formation of particulate organic matter (Von Wachenfeld et al., 2008; Porcal et al., 2010), was measured and modeled with first order kinetics. The relationship between calculated kinetic rate constants and DOM properties was determined during a hydrologic year in three catchments.

2 Methods

2.1 Location

Headwater streams near Dorset, Ontario, Canada were used in this study. The three study streams (Plastic Inflow #1 – PC1, Harp Inflow #4 – HP4, and Dickie Inflow #5 – DE5) are located in the districts of Muskoka and Haliburton near the southern edge of the Precambrian Shield and the boundary of the Boreal ecozone. The streams are tributaries to Plastic, Harp, and Dickie Lakes, long-term study sites of the impacts of long range atmospheric transport, climate change and recreational development on water quality in forested headwater catchments and lakes (e.g. Dillon and Molot, 1997b). Table 1 presents basic characteristics of each stream and its catchment. The catchments are in the temperate forest region of the Precambrian Shield. The Harp Lake catchment is dominated by maple and birch forest that overlies glacial till-covered bedrock of biotite, hornblende gneiss and amphibolite schist. The Plastic Lake catchment has

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thinner soils and a predominantly coniferous forest cover. The Dickie 5 catchment is underlain by metamorphic silicate bedrock and is primarily forested with conifers although wetlands are extensive throughout. The most common soils in the study catchment are brunisolic and podzolic (Molot et al., 2005). Descriptions of physiographic and meteorological features are given in Dillon et al. (1991). The ranges of ion concentrations in each stream are presented in Table 2.

2.2 Experimental design

Samples were collected from September 2007 to November 2008 at 2 to 6 week intervals. Samples were collected in 20 L PET or HDPE carboys, previously thoroughly acid-washed and rinsed with de-mineralized water. Samples were stored in the dark and transported to a refrigerator. Before each experiment samples were filtered through a series of cartridge filters with decreasing nominal pore size from 25 μm to 0.5 μm . Aliquots of each sample were exposed in 250 mL Teflon bottles to artificial solar radiation for several different time periods up to 48 h in duplicate or triplicate. Suntest XLS+ (Atlas GmbH, Germany) irradiation chambers equipped with a Xenon lamp were used. The spectral distribution of radiance was measured with an Ocean Optics USB2000 instrument deployed inside the irradiation chambers. We also measured the radiance inside Teflon bottles; they transmitted 44 % of incident UVB and 68 % of incident UVA. The intensity of irradiation was 700 W m^{-2} . It is approximately two times higher than monthly averaged midday solar insolation for the same wavelength range, on a horizontal surface in June and approximately 30 % higher than maximum outdoors irradiance under a cloudless, non-hazy sky on 21 June at our sampling location (NASA Surface meteorology and Solar Energy, <http://eosweb.larc.nasa.gov>) in July. Global horizontal radiation includes the near-infrared portion of radiation which is not measured inside the experimental irradiation chamber, hence a correction was necessary to compare global radiation to irradiation in the Suntest. Global horizontal radiation data were reduced by 50 % to eliminate the portion of near infrared radiation which ranges from 46

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to 52 % (e.g. Escobedo et al., 2011; Petty, 2006 and references therein) depending on atmospheric conditions, e.g. amount of water vapor.

The higher intensity of 700 W m^{-2} was used to reduce irradiation time and accelerate the experimental work. Previous experiments with samples from Dickie and Harp Lake catchments (DOC ranged from 4.8 to 40 mg L^{-1}) showed that photodegradation rate constants in samples irradiated under two different intensities (400 and 700 W m^{-2}) for the same amount of irradiation energy did not depend on intensity but on total amount of irradiation energy (paired t test, $p > 0.05$, $n = 4$) (Fig. 9). Samples were partly submerged in the water bath to eliminate excess heat and maintain a relatively constant sample temperature of approximately 25°C . Dark control samples, aliquots wrapped in aluminum foil and exposed for 48 h to the same temperature as irradiated samples, were used to determine the influence of microbial decomposition and temperature changes on DOM.

Concentrations of dissolved organic carbon (DOC), the absorbance spectrum, pH and molecular weight distribution were determined on all irradiated samples, in original non-irradiated samples and in dark control samples.

2.3 Analytical methods

DOC (as mg CL^{-1}) was determined by the catalytic combustion technique (Shimadzu TOC-V_{CPH}, Japan). Samples for DOC were filtered through a $0.4 \mu\text{m}$ Nylon syringe filter (Mandel, Canada) prior to analysis; filters were previously rinsed with 15 mL of demineralized water and with 15 mL of sample.

Absorbance spectrum was measured from 200 to 800 nm in a 1 cm quartz cuvette (Cary 50 UV-Vis spectrophotometer, Varian). Specific UV-A absorbance at 254 nm (SUVA_{254}) was calculated as the ratio of absorbance (A_{254} ; 1 m optical path) and DOC concentration [mg CL^{-1}].

Molecular weight distribution was determined as apparent molecular weight (Köhler et al., 2002) by high-performance size exclusion chromatography (HPSEC). The value reported as an apparent molecular weight corresponds to the observed peak which

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represents the most abundant molecular weight in a whole sample (Köhler et al., 2002). HPSEC was performed with a liquid chromatograph (Waters 600s, USA) with a photodiode array detector (Waters 996). A TSK-gel[®] column (7.8 mm × 30 cm and a particle size of 5 μm; model G2500PWXL, Tosohaas, Japan) combined with a guard column (TSK-gel[®] Guard PWxl, 6 mm × 4.0 cm, particle size 12 μm) was used for size exclusion. For each run, 100 μL of sample was injected onto the column with phosphate buffer (0.1 mol L⁻¹ NaCl, pH 6.8) as an eluent, and the buffer flow rate was set at 0.5 mL min⁻¹ (Wu et al., 2003). The column void volume and total permeation volume of the column were determined using Blue Dextran (Sigma–Aldrich) and acetone (Sigma–Aldrich), respectively. Sodium polystyrene sulfonates were used as molecular mass calibration standards (M_w 1100, 3610, 4800, 6500, 15 450, and 31 000 Da).

Discharge was measured at calibrated V-shaped or rectangular (HP4) weirs at each sampling site (Devito and Dillon, 1993).

2.4 Photodegradation rate constant

A first order kinetics equation (Eq. 1a, b) was used to describe the observed decrease in DOC concentration during irradiation experiments:

$$\frac{\partial \text{DOC}}{\partial E} = -K \cdot \text{DOC} \quad \text{and} \quad (1a)$$

$$\text{DOC} = \text{DOC}_0 \cdot e^{-KE} \quad (1b)$$

where DOC₀ is the initial DOC concentration [mg CL⁻¹], *K* is the photodegradation rate constant [m² GJ⁻¹] and *E* is the cumulative energy of irradiation [GJ m⁻²]. Non-linear regression analysis was used to fit Eq. (1) with experimental results (Brown, 2001). The minimum number of points used to fit an exponential decay curve was 4. Experiments were terminated after being irradiated for 48 h. The influence of extended irradiation time on calculated photodegradation rate constant was tested and did not

show any significant difference in modeled photodegradation rate constants. We used the calculated rate constant, K , as a photodegradation property of DOM.

The irradiation time of 48 h corresponded to approximately 11 days of average solar insolation in June at sampling locations. Potential daily percentage decrease in DOM in streams was calculated as a decrease in DOC concentration during one day of natural irradiation according to Eq. (2).

$$\Delta = \frac{(\text{DOC}_0 - \text{DOC}_1)}{\text{DOC}_0} \cdot 100 \quad (2)$$

where DOC_0 is the initial DOC concentration in stream [mgCL^{-1}] and DOC_1 is DOC concentration [mgCL^{-1}] after one day of exposure to natural solar radiation. DOC_1 was calculated according to Eq. (3),

$$\text{DOC}_1 = \text{DOC}_0 \cdot e^{-K \cdot I} \quad (3)$$

where DOC_0 is the initial DOC concentration in stream [mgCL^{-1}] at sampling, K is the calculated photodegradation rate constant, and I is the average daily insolation on horizontal surface [GJm^{-2}] for given day. The average daily insolation was calculated from monthly averaged data by linear interpolation and reduced by 50% to eliminate the portion of near-infrared radiation. Monthly averaged data of insolation on a horizontal surface for the Dorset region (22 yr average, location $45^{\circ}30' \text{N}$, $78^{\circ}30' \text{W}$) was obtained from the NASA Atmospheric Science Data Center, Surface meteorology and Solar Energy (<http://eosweb.larc.nasa.gov/sse/>).

3 Results

3.1 DOM concentration and discharge

The highest DOC concentration in all samples was 38 mgL^{-1} and was observed in July 2008 in PC1 at flow rate of 0.5 Ls^{-1} ; the lowest DOC concentration of 4.6 mgL^{-1} was

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observed in HP4 in May 2008 during the baseflow period following spring snowmelt (13 Ls⁻¹). The DOC concentration in PC1 ranged from 6.3 to 38 mgL⁻¹ (Fig. 10). The DOC concentration in HP4 was lower than in PC1 and DE5 and ranged from 4.6 to 12.1 mgL⁻¹ (Fig. 11). In DE5 the DOC concentration ranged from 6 to 23 mgL⁻¹ (Fig. 12). The discharge in all streams was low during autumn and winter 2007. Spring melt began at the end of March 2008. The magnitude of discharge was higher in HP4 than in PC1 and DE5 because of its catchment size (Table 1) but the areal runoff (discharge per unit area) was comparable between HP4 and PC1 and lower at DE5. The lower discharge in DE5 was, despite its larger catchment size, likely due to its lower catchment slope (Table 1).

3.2 Initial pH of samples

The pH in DE5 ranged from 4.2 to 5.0 with median value of 4.7. The highest pH values in DE5 occurred during summer 2008, while the lowest values were measured in autumn 2007. In PC1 the pH ranged from 4.1 to 6.0 with a median value of 4.5. The highest pH values in PC1 were observed at the end of summer 2007, the lowest values during winter months. In HP4 the pH ranged from 5.1 to 7.0 with a median value of 6.4. The highest pH values were observed in late summers of 2007 and 2008. The pH decreased during autumn and winter until spring melt and then rose again.

3.3 Irradiation results

The initial DOC concentration in all experiments decreased less than 5% in dark control samples during 48 h of dark. The DOC concentration following 48 h of irradiation decreased in all streams to as low as 22% of the initial DOC concentration (the maximum loss occurred in PC1 in winter samples). The lowest measured DOC decrease of 25% was observed in HP4 samples from late summer. The ranges in DOC decreases after 48 h of irradiation were 31 to 75%, 25 to 63%, and 31 to 78% in DE5, HP4, and PC1, respectively. The highest DOC declines during irradiation were observed in

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spring in DE5 and HP4, and in winter in PC1. The lowest decreases were observed in all streams during summer.

Photodegradation rate constants calculated according to Eq. (1b) ranged from 2.5 to 11.1 m² GJ⁻¹ in all samples. In DE5 the photodegradation rate constants ranged from 3.1 to 10 m² GJ⁻¹, with a median value of 5.7 m² GJ⁻¹ (Fig. 12). In PC1 the range of photodegradation rate constants was from 3.1 to 11.1 m² GJ⁻¹, with a median value of 7.2 m² GJ⁻¹ (Fig. 10). The photodegradation rate constants in HP4 were lower than in PC1 and DE5 (ANOVA, $F(2, 82) = 17.5, p < 0.001$), and ranged from 2.5 to 8.8 m² GJ⁻¹, with a median value of 3.7 m² GJ⁻¹ (Fig. 11).

Estimated potential daily percentage decreases in DOC (the potential decrease in DOC due to natural solar radiation) ranged from 1 to 8% (Fig. 13). Lower values are more likely in winter corresponding to the lowest intensity of solar radiation. The highest potential daily percentage decrease in DOC is possible in spring when the photodegradation rate constants are the highest. The median and maximum potential photochemical decreases in DOC in one day were 3 and 8% in both PC1 and DE5 and 2 and 7% in HP4 (Fig. 5).

3.4 Seasonal trends in photodegradation rate constants

The seasonal trends in photodegradation rate constants, K , were similar in all three streams. The photodegradation rate constants increased during autumn and were stable during winter months. In the samples collected during the first days of snowmelt the photodegradation rate constants were stable and similar to winter values (Figs. 2, 3, 4). During the continuing snow melt and following higher spring flows the photodegradation rate constants jumped to their maximum and remained high for about two weeks then sharply decreased to values lower than winter ones. The period of higher photodegradation rate constants lasted approximately one month in PC1 and HP4 and six weeks in DE5. The photodegradation rate constants continued to decrease during spring and stabilized in summer, when they reached their annual minimum. During autumn the photodegradation rate constants began to increase and reached values

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similar to the previous year. The seasonal trends observed in this study agree with earlier studies of photodegradation of DOM under natural solar radiation in North America (Molot and Dillon, 1997; Gennings et al., 2001; Molot et al., 2005) and Europe (Porcal et al., 2004) and artificial radiation in North America (Brooks et al., 2007). Only the Porcal et al. study examined a full year.

3.5 Structure of DOM: molecular weight and SUVA₂₅₄

The structure and properties of DOM were characterized by measured apparent molecular weight of DOM (Figs. 2, 3, 4). A seasonal trend was observed in all three streams. The molecular weight decreased during late summer and beginning of autumn and then began to increase consistently until the following summer when it reached its maximum in June and began to decrease to its autumn minimum. The molecular weight ranged from 1620 to 2970 Da, with a median of 2160 Da in PC1, from 1550 to 2730 with a median of 2290 Da in DE5, and from 1610 to 2810 with a median of 2160 Da in HP4. The molecular weight can be used as a proxy of freshness or age of terrestrially-derived organic matter (Cabaniss et al., 2005). The correlation between K and molecular weight in all samples was significant but not high with $r = -0.23$ ($n = 80$, $p < 0.05$).

The increase in molecular weight was accompanied by an increase in SUVA₂₅₄, a measure of the content of aromatic groups in DOM structure (Weishaar et al., 2003) although the relationship varied among the streams. SUVA₂₅₄ decreased slightly during spring snow melt and high flow and then returned to its previous level in late May – early June about a month before peak molecular weight occurred.

The relationship between photodegradation rate (K), molecular weight and aromaticity is not straightforward. In all streams (Figs. 2–4), K peaked in late April (also February in Dickie 5), followed by SUVA₂₅₄ and then molecular weight about two months after the peak in K . Whatever processes lead to higher K over winter also lead to higher SUVA₂₅₄ and molecular weight but the increases in molecular weight and SUVA₂₅₄ continued for several months after K began to decrease. The correlation between K

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and $SUVA_{254}$ in all samples was significant but weak -0.23 ($n = 85$, $p < 0.05$). In PC1 the correlation was -0.56 ($n = 31$, $p < 0.05$). No significant correlations were observed for DE5 and HP4 themselves.

The observed increase in photodegradation rate constants during autumn and winter can be attributed to formation of new previously unexposed DOM in terrestrial sources during decomposition of terrestrial biomass and its subsequent transport to streams. The formation of fresh DOM is indicated by the increase in molecular weight and aromatic content determined as $SUVA_{254}$.

4 Factors affecting seasonal trends in photoreactivity

4.1 The effect of pH

The higher pH in HP4 samples was likely the reason for observed lower photodegradation rate constants. The effect of pH on photoreactivity has been documented (e.g. Wang et al., 2000; Annesio and Granéli, 2003). Molot and Dillon (1997) determined lower photodegradation rate constants in HP4 compare to PC1 in summer 1995 under natural solar radiation. Gennings et al. (2001) measured photodegradation rate constants in PC1, HP4 and DE5 under natural solar radiation in summer 1997 and observed lower values for HP4 than in more acidic PC1 and DE5. Molot et al. (2005) exposed samples from DE5 to solar radiation and observed an increase in photodegradation rate constants with decreasing pH.

4.2 Effect of pH and Fe concentration

The major source of DOM in stream water is soil organic matter. Depending on complexing properties of soil organic matter, pH, and other conditions, soil organic matter is able to dissolve and bind metals and export them from terrestrial to aquatic systems (Mantoura et al., 1978; Vance et al., 1996). It has been shown that elevated Fe

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concentration enhances DOM photodegradation (Brickmann et al., 2003). The relation between photodegradation rate constant, pH and Fe concentration was thoroughly studied in PC1 stream and a strong regression was found (Porcal – unpublished data)

$$K = -2.38\text{pH} + 0.59\text{Fe} + 14.71; \quad R^2 = 0.78, \quad p = 0.008 \quad (4)$$

We used Eq. (4) to estimate the photodegradation rate constant at various times of the year in all three streams. Seasonal pH and Fe concentration were obtained from the Ontario Ministry of the Environment. Samples were collected at one week intervals at the same locations as our samples were taken. The predicted photodegradation rate constants showed a strong seasonal trend in all three streams but peaked several months after the measured rates peaked and at higher levels in PC1 and DE5 (Fig. 14). The correlations between predicted and measured photodegradation rate were -0.72 ($n = 29$) and -0.69 ($n = 22$) for PC1 and DE5, respectively. The correlation was weak for the whole year in HP4, however, autumn and winter samples showed strong a correlation ($r = 0.84$, $n = 14$) (Fig. 14).

The different seasonal trend in predicted photodegradation rate constants suggested that other factors affect photodegradation rate in addition to pH and Fe concentration.

4.3 Previous exposure to solar radiation

A comparison of autumn and winter to summer samples with similar DOC concentration showed that summer samples had lower photodegradation rate constants than autumn and winter samples (paired t test, $p < 0.001$). Molecular weight and SUV_{254} were higher in summer than in autumn and winter samples, but the summer photodegradation rate constant did not increase with increasing molecular weight and SUV_{254} as was observed during autumn and winter. These results show that winter and summer DOM are qualitatively different. This difference may have been caused by previous exposure to solar radiation.

To test the effect of previous exposure to solar radiation we used concentrations of DOC from samples collected upstream of our sampling site in PC1 catchment on the

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5 same days in summer. The DOC concentrations upstream were higher by 5 to 10% than our initial concentrations at the downstream site. We assumed that predicted winter photodegradation rate constants calculated according to the Eq. (4) between photodegradation rate constant and pH and Fe concentrations determined in PC1 could be used as an approximation of photodegradation rate constant for previously unexposed DOM. We calculated the necessary energy to describe the observed DOC decrease in the stream using Eq. (1b). The cumulative energy corresponding to the observed DOC reductions in the stream was in the range of 25 to 40% of the total incident solar radiation in the UV and visible range on a given day. This amount of energy would be received over a 3 to 6 h period, assuming no shading or cloud cover. Therefore, we conclude that photodegradation could be partially responsible for the observed downstream decrease in DOC. Other processes, such as dilution by lower DOC concentration ground water and/or microbially-mediated changes to the DOM pool (Mullholand and Hill, 1997), may also have affected the DOC concentration downstream.

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25 The effect of previous exposure of DOM to radiation on decreasing photoreactivity has been observed in streams, lakes and estuaries (i.e. Salonen and Vähätalo, 1994; Vähätalo et al., 2000; Twardowski and Donaghay, 2002). Porcal et al. (2010) measured photodegradation rate constants in first order streams in Maine and observed their decline along a water pathway. Similar declines in photodegradation rate constants were observed in a Swedish forested catchment where the photodegradation rate constants were higher in soil water than in streams draining the same catchment (Köhler et al., 2002). It is reasonable to assume that DOM collected from the mouth of the study streams was exposed to some solar radiation during its in-stream surface transport throughout the catchment and this previous exposure could contribute to the explanation of observed lower photodegradation rate constants in late spring and summer. The pooled K data were weakly and negatively correlated with averaged solar insolation. For better clarification of the effect of previous irradiation (insolation) on photodegradation rate constants we divided samples into three groups. In the autumn group (September, October, November and December) the correlation was -0.36 ($n = 34$, $p < 0.05$),

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in winter (January, February and March) the correlation between photodegradation rate constants and insolation was not observed because the whole catchments were covered by snow and insolation likely had a very small effect. In the spring-summer group (April–August) the correlation was -0.59 ($n = 32$, $p < 0.05$).

The effect of previous irradiation (insolation) is supported by different correlations between photodegradation rate constants and molecular weight and $SUVA_{254}$. We divided samples into two groups with regard to possible insolation. The first group of samples represented the time period when the catchments were entirely snow covered (from mid November 2007 to March 2008). Strong positive correlations between photodegradation rate constant, K , and molecular weight were observed for individual sites (PC1 $r = 0.75$, $n = 9$; HP4 $r = 0.71$, $n = 11$; DE5 $r = 0.92$, $n = 5$; $p < 0.05$ in all cases) (Fig. 15); samples collected during high flow events (Fig. 2, 3, 4) were omitted. Similar positive correlations were observed for $SUVA_{254}$ though only in HP4 was the correlation statistically significant ($r = 0.69$, $n = 10$, $p < 0.05$) (Fig. 15). The second group of samples represented the time period from mid April to October 2008 when the effect of previous irradiation (insolation) was potentially large. The correlation between K and molecular weight was negative in PC1 ($r = -0.81$, $n = 10$, $p < 0.05$) and DE5 ($r = -0.69$, $n = 10$, $p < 0.05$) (Fig. 16); a negative correlation was also observed in HP4 but was not statistically significant. Similarly, a negative correlation were observed with $SUVA_{254}$ (in PC1 $r = -0.77$, $n = 10$, $p < 0.05$, and in DE5 $r = -0.64$, $n = 10$, $p < 0.05$) (Fig. 16).

The positive correlations between winter photodegradation rate constant, K , and molecular weight and $SUVA_{254}$ support the notion that fresher DOM, having higher molecular weight and higher aromatic content ($SUVA_{254}$), easily undergoes photodegradation. The observed negative correlation despite increasing molecular weight and $SUVA_{254}$ in summer months suggests the influence of previous irradiation (insolation) and rapid photochemical changes within the catchment prior to sampling.

The increase in photodegradation rate constants during autumn and winter was likely driven by terrestrial production of fresh organic matter followed by humification as

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documented by the increase in molecular weight and SUVA₂₅₄. The spring peak in photodegradation rate constants corresponded to spring snow melt, when DOC concentrations decrease with increasing flow, a usual trend confirmed by a more than twenty years study of seasonal trends in DOC concentrations in PC1 and HP4 (Eimers et al., 2008). This seasonal pattern is typical for wetland-dominated catchments where the DOC concentrations decline during peak flow (Laudon et al., 2004). The decrease in SUVA₂₅₄ following the high discharge suggests that DOM may originate from different soil horizons in winter and summer. The decrease in photodegradation rate constants during late spring and summer may be driven by previous exposure of DOM to solar radiation during its pathway through the catchment, microbially-mediated changes to DOM while in transit and contributions of non-photoreactive DOM by aquatic primary producers to the DOM pool.

5 Importance of photochemical properties – conclusions

Molot and Dillon (1997) found that annual losses of DOM in Boreal lakes derived from short-term photodegradation experiments with in-coming stream waters could account for annual losses estimated from mass balances. Their estimates were based on photodegradation rate constants of samples collected and irradiated under natural radiation in summer and assumed that photodegradation rate constants were stable during the ice-free period. Our results found significant differences in photochemical properties during the hydrological year at all sampling locations. Significantly higher photodegradation rate constants were observed in spring than in summer, hence, Molot and Dillon's earlier annual estimates are low.

The observed seasonal cycle in photochemical properties of DOM suggests strong relationships between its terrestrial sources and hydrological processes within catchments. The significance of higher photodegradation rate constants in spring is enhanced by the fact that a large proportion of the annual DOC flux occurs at this time. In the twenty year period from 1980 to 2001 the average spring flux was 54 % of the

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annual DOC fluxes at PC1 (Eimers et al., 2008). However, the potential importance of this season on DOM cycling in lakes is tempered by spring turnover which mixes melt water into deeper water where UV penetration is limited. Residence time of new stream inflows in upper waters receiving UVB and UVA increases with the onset of stratification and the potential for DOM photodegradation will increase despite the fact that solar radiation is not high in northern latitudes in early spring. Lower photodegradation rate constants measured in summer at all sites indicates the importance of photodegradation of DOM while in transit to lakes despite the reduced solar insolation by forest canopy (Frost et al., 2005).

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Table 1. Location and basic characterization of study catchments (Dillon et al., 1991, *Kothawala et al., 2006).

Lake	Location	Tributary	Area (ha)	Average catchment grade (%)	Stream length (m)	Peat (%)
Plastic Lake	45° 11' N, 78° 50' W	PC1	23.34	5.9	790	7.0
Harp Lake	45° 23' N, 79° 08' W	HP4	119.50	5.0	2040	8.0*
Dickie Lake	45° 09' N, 79° 05' W	DE5	29.98	1.0	762	25.4

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Table 2. Median, minimum and maximum concentration of individual cations and anions in streams [mmol L^{-1}]. NH_4 and NO_3 units are $\mu\text{mol L}^{-1}$.

		Na	K	Mg	Ca	NH_4	Cl	SO_4	NO_3
PC1	min	0.02	0.002	0.01	0.02	0.53	0.00	0.00	0.26
	median	0.02	0.003	0.01	0.03	0.65	0.01	0.05	0.32
	max	0.04	0.010	0.04	0.07	2.08	0.05	0.06	0.36
HP4	min	0.03	0.006	0.02	0.04	0.12	0.01	0.04	0.26
	median	0.06	0.008	0.04	0.05	0.68	0.03	0.07	0.88
	max	0.25	0.018	0.06	0.10	2.88	0.21	0.08	1.93
DE5	min	0.02	0.001	0.01	0.02	0.30	0.01	0.01	0.22
	median	0.03	0.004	0.02	0.03	0.54	0.03	0.01	0.28
	max	0.04	0.015	0.02	0.05	1.19	0.09	0.03	0.35

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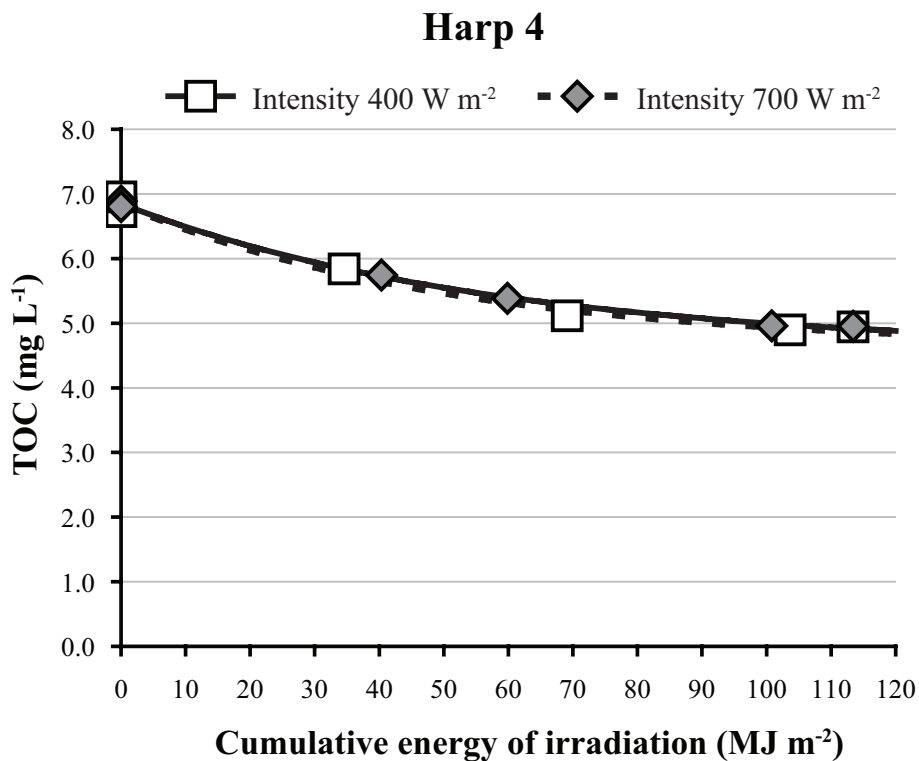


Fig. 1. The first order kinetics equation fit with measured data at different intensities of irradiation. Cumulative irradiation energy was calculated as a product of intensity and time of irradiation.

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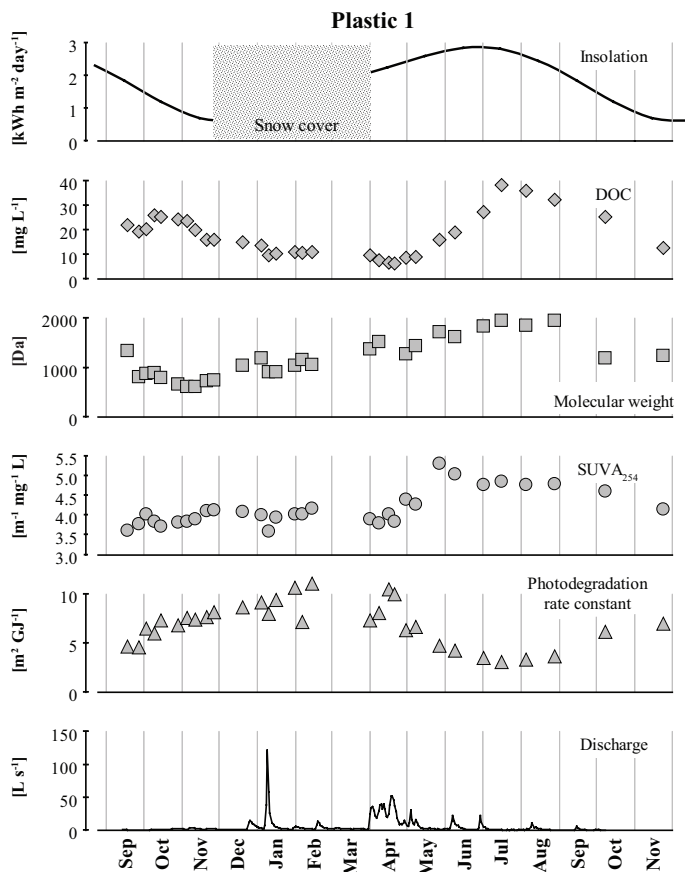


Fig. 2. Plastic 1 (PC1) tributary to Plastic Lake. Average incident insolation, DOC, apparent molecular weight, $SUVA_{254}$, photodegradation rate constant and mean daily discharge during hydrological year 2007–2008.

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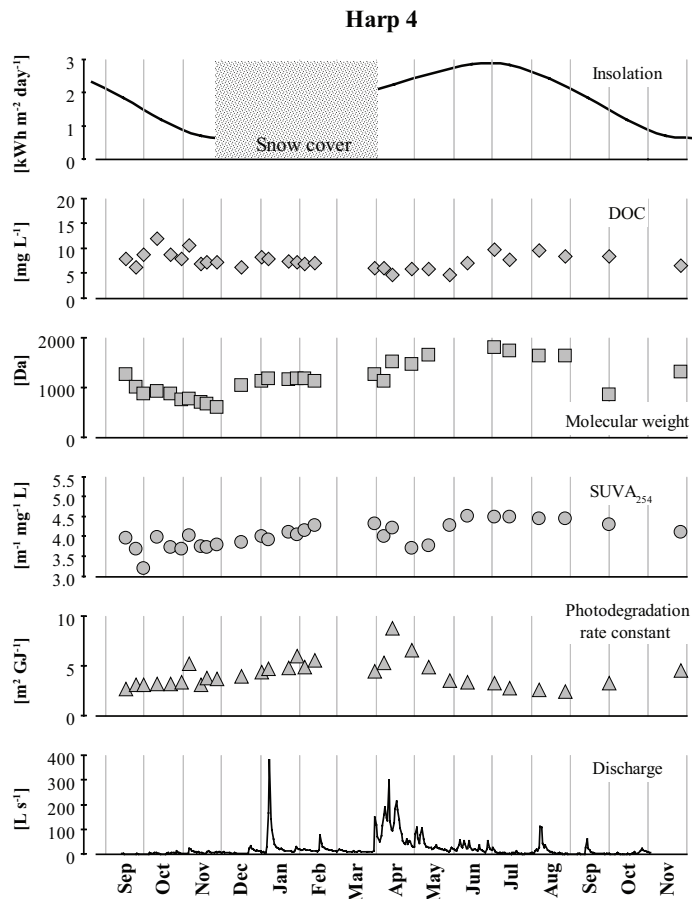


Fig. 3. Harp 4 (HP4) tributary to Harp Lake. Average incident insolation, DOC, apparent molecular weight, SUVA₂₅₄, photodegradation rate constant and mean daily discharge during hydrological year 2007–2008.

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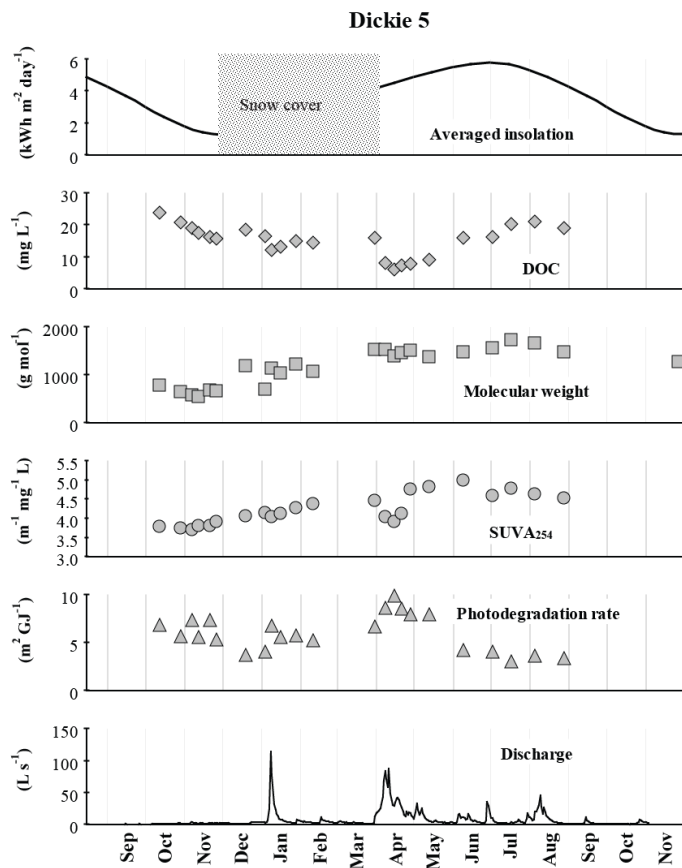


Fig. 4. Dickie 5 (DE5) tributary to Dickie Lake. Average incident insolation, DOC, apparent molecular weight, SUVA_{254} , photodegradation rate constant and mean daily discharge during hydrological year 2007–2008.

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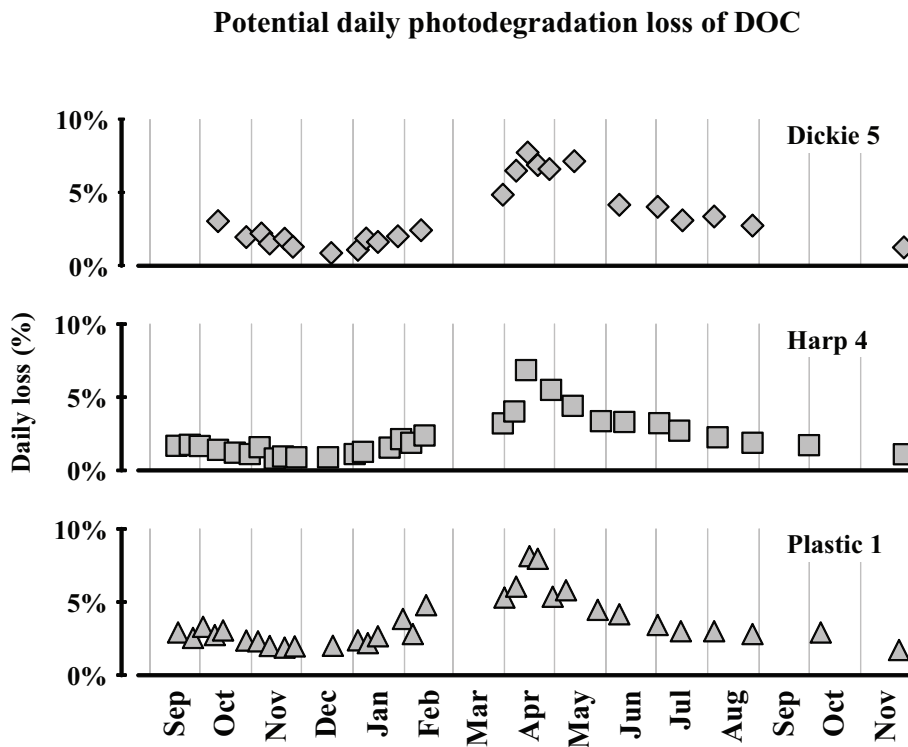


Fig. 5. Potential daily percentage decrease in DOC – calculation is based on the initial DOC concentrations, daily incident solar insolation and photodegradation rate constants determined in lab experiments (Eq. 2).

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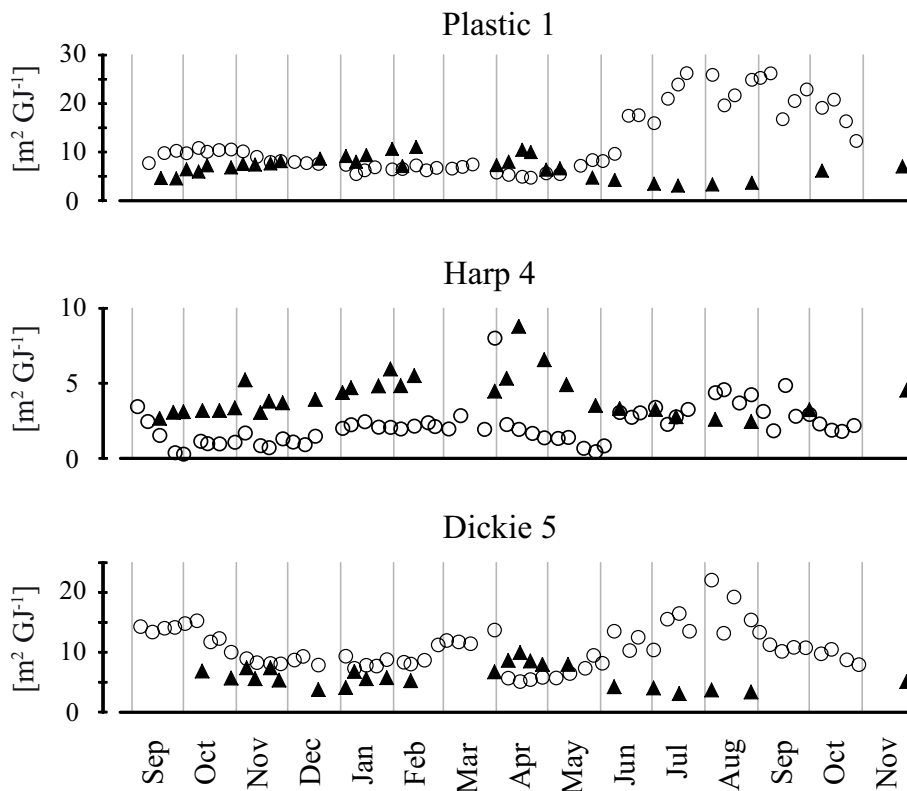


Fig. 6. Predicted (open circles) and measured (black triangles) photodegradation rate constants during hydrologic year. The estimation was based on a correlation between photodegradation rate constant, pH and Fe concentration in sample (Eq. 4) (Porcal, unpublished data).

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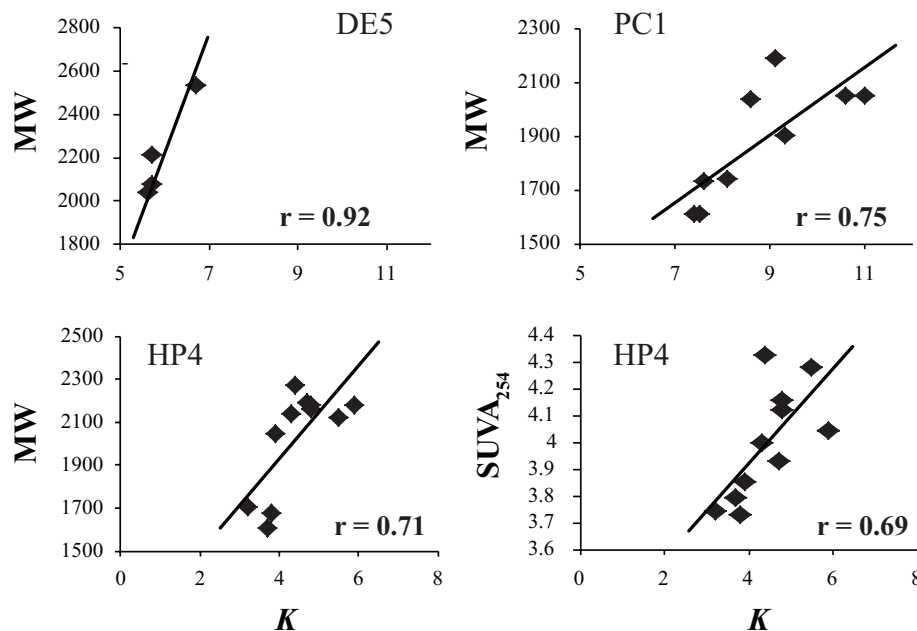


Fig. 7. Correlations between photodegradation rate constant, K [$\text{m}^2 \text{GJ}^{-1}$], molecular weight, MW [Da], and SUVA_{254} [$\text{m}^{-1} \text{mg}^{-1} \text{L}$] in DE5, PC1 and HP4 streams during winter months when the catchments were snow covered.

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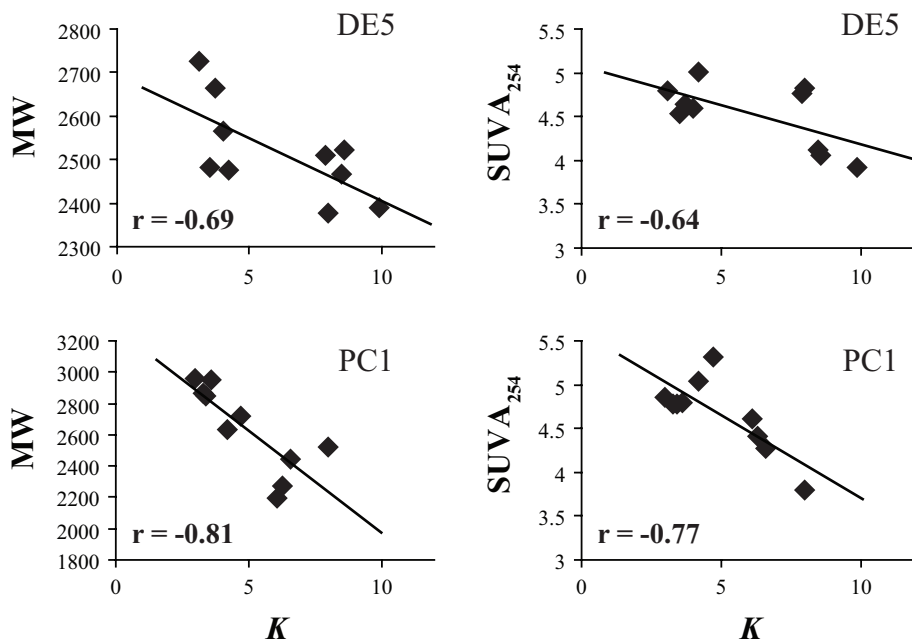


Fig. 8. Correlations between photodegradation rate constant, K [m^2GJ^{-1}], molecular weight, MW [Da], and SUVA_{254} [$\text{m}^{-1}\text{mg}^{-1}\text{L}$] in DE5 and PC1 streams during spring and summer months.

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