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Research Article

Penetration of ultraviolet radiation in streams of eastern Pennsylvania: Topographic controls and the role of suspended particulates

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Abstract. Penetration of ultraviolet radiation (UVR) in stream ecosystems is determined by the concentration and optical properties of suspended sediment and dissolved organic carbon (DOC). This study documents the base-flow optical environment of 37 first- and second-order tributaries distributed throughout the Lehigh River watershed, eastern Pennsylvania, over a four year period. We measured a large range of attenuation coefficients (K_{d380}: 0.68 – 151.1 m^{-1}, K_{d320}: 0.95 – 316.2 m^{-1}) and 1 % transmission depths (2 cm – 147 cm). In addition, we quantified the significance of particulate material in UVR attenuation in streams, which generally accounted for 10–30 % of attenuation for the UV-B waveband. Our results indicated that basin morphology, particularly mean watershed slope (MWS), was highly correlated with UVR penetration (MWS:K_{d320}, $r^2 = 0.68$, $P < 0.0001$), DOC concentration (MWS:DOC, $r^2 = 0.65$, $P < 0.0001$), and DOC optical quality (MWS:Fluorescence Index, $r^2 = 0.71$, $P < 0.0001$). The fact that these relationships are robust across a variety of watersheds that differ in land use, forest coverage, and wetland coverage, indicates that the geomorphic coevolution of hillslope form and process exert a strong control on stream optical environments via the establishment of hydrologic and edaphic conditions. Agricultural land use exerts secondary, but discernable effects on DOC concentration (% Agriculture:DOC, $r^2 = 0.39$, $P = 0.012$) and optical quality (% Agriculture:Fluorescence Index, $r^2 = 0.32$, $P = 0.036$) in watersheds devoid of wetlands.

Key words. Ultraviolet radiation; dissolved organic carbon; geomorphology; land use.

Introduction

Quantifying penetration of ultraviolet radiation (UVR) in streams is the first, necessary step towards understanding organismal responses and adaptations to UVR exposure in lotic environments. Exposure to damaging ultraviolet-B radiation (UV-B; 280–320 nm) in stream ecosystems is an important concern due to recent and pervasive changes in atmospheric, climatic, and riparian zone factors that strongly influence stream optical environments (Madronich et al., 1998). Two fundamental questions in aquatic ecology that are yet to be comprehensively addressed include: a) what environmental factors control the

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UVR environment in streams at different spatial and temporal scales, and b) which of those scales are most important for understanding the ecology of those systems? For example, at the global scale, the anthropogenic changes in stratospheric ozone over the past few decades has influenced the flux of UV-B reaching Earth's surface, an effect that will likely persist for several decades with large spatial and year-to-year variability (UNEP, 2006). More proximate to streams, destruction of riparian corridors and removal of shade canopies also increase the direct exposure to and penetration of UV-B in streams (Kelly et al., 2003).

The optical environment of stream benthos is a function of water depth, incident solar radiation, stream channel morphology, and absorptive properties of dissolved and particulate material in suspension (Madronich, 1993; Hargreaves, 2003; Diamond et al., 2005). The goals of our study were to: a) measure the optical environment in 37 streams in eastern Pennsylvania, b) quantify the relative contribution of suspended particulate material to total UVR attenuation in these streams, and c) link the flux and absorptive qualities of dissolved and suspended particulate material to watershed characteristics, including natural topographic, geomorphic, hydrologic, and biologic processes as well as human-mediated land-use practices. To begin to address these questions we applied a paired catchment approach, sampling as many as 47 streams, for as long as four years (2002 – 2005), with intensive study of 15 streams, including base-flow and stormflow conditions in 2002. We selected these watersheds with the intent to cover the regional spectrum of optical environments, topography and forested to agricultural land use. The study area was selected for the fact that it spans a broad range of watersheds, covering four physiographic provinces, in a relatively small area. The compact, but diverse, nature of the Lehigh watershed made it logistically possible to study a large range of streams that are generally representative of moderately humid, low relief landscapes.

Land use effects on stream optical environment

Land use can have both direct and indirect impacts on the optical conditions in streams. Indirect impacts are mediated by upland changes in the flux of dissolved organic carbon (DOC) and sediment, both of which have been shown to control UVR transparency in aquatic ecosystems (Morris et al., 1995; Laurion et al., 2000; Findlay and Sinsabaugh, 2003). Land use can also change the concentration and/or optical quality of dissolved organic carbon (DOC) transported from the watershed (Frost et al., 2005). Conversion of forest to agricultural or urban land use, for example, can change the quantity and grain size distribution of sediment contributed to the stream (Kondolf et al., 2002), which has implications for stream channel morphology (Leopold et al., 1964; Pizzuto et al., 2000; Galster et al., 2006). For example, transition to a wider, shallower channel increases UVR exposure on the benthos. Loss of riparian vegetation can have the direct effect of causing an instantaneous, localized increase in UVR flux reaching the stream (DeNicola et al., 1992; Kelly et al., 2003; Brown et al., 1994) or indirectly increase benthic exposure to UVR through bank destabilization (Hession et al., 2003), which could also lead to channel widening and shallowing (Galster et al., 2006). Current lack of understanding of how upland hillslope form and geomorphic process influence many of the environmental parameters that influence UVR transparency is a critical limitation on the development of broadly applicable, predictive models of UVR penetration in streams.

The role of DOC in attenuation of UVR

Studies of lakes demonstrate that UVR attenuation is strongly controlled by the concentration (Morris et al., 1995; Laurion et al., 2000) and optical quality (De Lange, 2000; Morris and Hargreaves, 1997) of DOC. In one of the few surveys of streams, Frost et al. (2006a) demonstrated that among-stream differences in UV-B penetration could be accounted for by DOC concentration and canopy cover in several streams in northern Michigan. Wetlands exert control over DOC concentrations in some stream and lake systems (Gorham et al., 1998; Mulholland, 2003), but the relationship between DOC production and topography has not been thoroughly explored for landscapes containing little or no wetland cover.

The prevailing paradigm of DOC transport in rivers holds that most DOC in small (1–3 order) streams is derived from leaf litter and soil organic matter (SOM: McDowell and Likens, 1988; Rasmussen et al. 1989; Xenopoulos et al., 2003; Nelson et al., 1993; see Findlay and Sinsabaugh, 2003 for extensive discussion of SOM production, interaction, solubility and relation to DOC). Currently, our understanding of controls on patterns of SOM is insufficient for proper development of widely-applicable, predictive models of organic carbon storage and transport, which limits our ability to determine how aquatic ecosystems will be affected by changes in land use and climate change. Fundamentally, SOM content is controlled by numerous soil forming and environmental factors (Jenny, 1941; Birkeland, 1999; Aitkenhead-Peterson et al., 2005).

Yoo and Amundson (2005) demonstrated that soil thickness and hillslope curvature exert primary control on SOM storage. Soil thickness is determined by the balance of soil production and hillslope gradient-dependant erosional losses (Gilbert, 1909; Heimsath et al., 1997; Heimsath et al., 1999). In soil-mantled landscapes, a typical hillslope cross-section from valley floor to ridge top consists of a concave-up lower portion near the valley floor and convex-up portion near the ridge. Storage of C is higher on concave hillslopes and decreases with increasing convexity (Yoo and Amundson, 2005). Therefore, SOM production and storage capacity are highly dependant on the geomorphic processes that establish hillslope form. Vegetation type, soil texture and climate also strongly influence the amount and vertical distribution of SOM (Jobbagy and Jackson, 2000), with a strong autocorrelation to local geomorphic process.

The range of organic compounds found in a landscape is set primarily by the biota. During transport from terrestrial to aquatic ecosystems, organic carbon compounds can be fractionated, altered, and lost from the system (see Findlay and Sinsabaugh, 2003 for complete review). Fractionation can occur as a result of hydrologic flow paths (Schindler and Krabbenhoft (1998), and preferential adsorption to soil particles (Kaiser et al. 2001). Microbial processing (Amon and Benner, 1996; Cole et al. 1984) and photochemical degradation (Hargreaves, 2003) can also substantially alter the molecular weight, functional groups, and optical properties of DOC in transport (Osburn et al. 2001). Once the SOM has been leached from its substrate, the resulting DOC can be lost through microbial uptake or mineralization (Yano et al. 2000).

Current ecological research has not sufficiently linked DOC quality and concentration in aquatic systems to the SOM pool with consideration for the geomorphic processes that underpin the relationships we observe. In particular, factors influencing molar absorptivity of different DOC types are poorly understood and the relationship between the optical environment and changes in catchment hydrology and land use are poorly documented.

The role of suspended particulates in attenuation of UVR

Attenuation of UVR can be enhanced by both particle absorption and scattering. The role of particulate material in UVR attenuation is generally small in lakes, but can be significant in very low DOC systems (Laurion et al., 2000; Belzile et al., 2002). For stream systems, which often contain relatively high suspended loads of mineral origin, the influence of particulate material in UVR attenuation is virtually unstudied. Furthermore, the influence of watershed characteristics and land use on the optical quality of particulate material has not been explored, and might be expected to vary due to the diversity of sediment sources at the watershed scale.

Study area and methods

Study area and sampling site selection

We sampled small basins distributed throughout the Lehigh River watershed (40.5N, 75.4W), eastern Pennsylvania, between June 5, 2002 and July 20, 2005 (Fig. 1). The Lehigh watershed is approximately 3500 km^2, with elevations ranging from 48 to 684 meters above sea level. The northern Lehigh River watershed is underlain by Late Devonian Catskill Formation and Mississippian Pocono and Mauch Chunk formations, generally consisting of quartz-rich sandstone, shale and conglomerate. The southern portion of the Lehigh watershed is underlain by Martinsburg Formation shale and slate, Cambro-Ordovician carbonates, and Precambrian crystalline rocks of South Mountain that define the watershed's southern boundary (Berg et al., 1980).

The Lehigh watershed spans four physiographic provinces, including the Ridge and Valley and Pocono Plateau in the northern part, and the Great Valley and South Mountain in the southern part. The northern portion of the watershed is covered in a non-uniform mantle of glacial drift, a remnant of several advances and retreats of the Laurentide ice sheet over the past ~2 Myr. The most recent advance reached its maximum extent approximately 18,000 years ago near, but not south of Blue Mountain, a prominent ridge that separates the northern and southern parts of the Lehigh River watershed (Berg et al., 1980). As a result, the northern part of the watershed has a poorly-integrated drainage network and supports extensive, humic wetlands, historically rendering the land impractical for agriculture. Most of the northern Lehigh watershed has been logged in the past, but currently supports large tracts of intact secondary-growth (50+ years) beech/maple deciduous forest.

In contrast, the southern part of the Lehigh watershed supports extensive corn and soy agriculture, with patches of secondary-growth hardwood forest as well as several large urban and suburban areas. Riparian buffers are generally lacking in many of the primarily agricultural watersheds in the lower Lehigh, but no-till farming practices are used in some of the basins sampled. In stark contrast to the basins

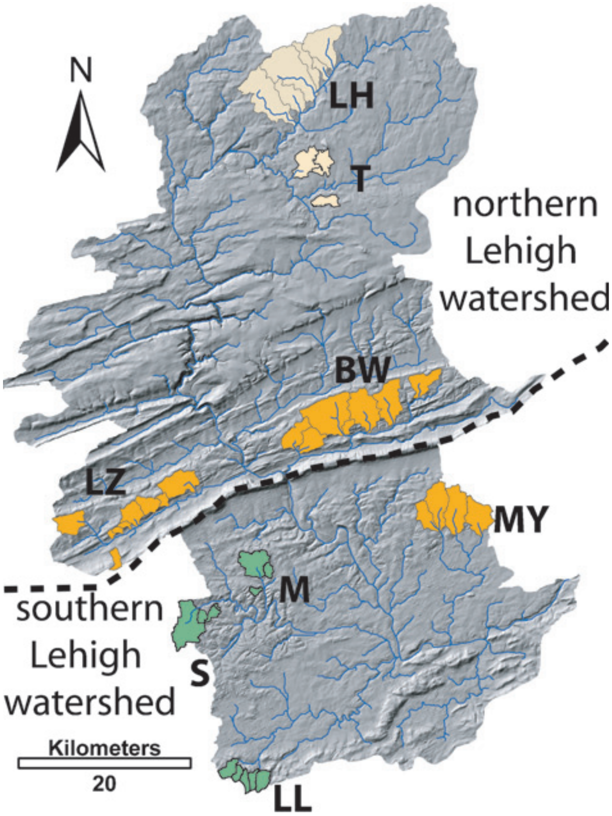

Figure 1. Sampling locations in the Lehigh River watershed with Blue Mountain dividing the northern and southern portions. Samples were collected from the mouths of each of the watersheds as they are delineated here. Initials indicate the Lehigh River tributaries to which each of the sampled streams contribute. BW = Buckwha Creek tributaries; LH = Lehigh River headwater tributaries; LL = Little Lehigh Creek tributaries; LZ = Lizard Creek tributaries; M = Mill Creek tributaries; MY = Monocacy Creek tributaries; S = Switzer Creek tributaries; T = Tobyhanna Creek tributaries.

selected for sampling in the upper Lehigh watershed, the lower Lehigh basins are nearly devoid of wetlands.

We limited our sampling locations to first and second order streams to avoid complications introduced by in-stream production and processing of organic matter in larger streams. We selected sampling locations in three stages. During 2002, we sampled several streams within the Little Lehigh (LL1 – LL5), Switzer Creek (S1, S2, S4) and Mill Creek (M1 – M3) watersheds. In 2003, we expanded into the northern Lehigh watershed, sampling several of the Lehigh River headwater tributaries (LH1 – LH5) as well as several small tributaries to the Tobyhanna River (T1 – T3), in addition to all 2002 sites. In 2004 and 2005, we expanded our study area to additionally include several Buckwha Creek tributaries (BW1 – BW7) and several Lizard Creek tributaries (LZ1 – LZ9) in the northern Lehigh River watershed as well as four tributaries to Monocacy Creek (MY1 – MY4), part of the southern Lehigh River watershed (Fig. 1).

Field methods

We measured water temperature, pH, conductivity, dissolved oxygen and turbidity using a Quanta G hydroprobe (Hydrolab-Hach Company, Loveland, CO) in 2002 (June – October) and 2003 (June – August) and using a YSI Data Sonde 6600 EDS-M (YSI Incorporated, Yellow Springs, OH) in 2004 (August) and 2005 (June – July). Depth-integrated samples were collected in one liter, acid-washed Nalgene bottles and kept on ice and in the dark for transport to the laboratory.

Geomorphic channel width and depth were estimated once as reach averages and channel bed sediment grain size was qualitatively observed as sand or gravel. Water depth was measured at a single reference point at each stream, each time a water sample was collected.

Laboratory methods

Samples were filtered through Whatman glass fiber filters (GF/F: nominal pore size 0.7 μm) within 24 hours of collection and the filtrate was refrigerated until analysis. Total suspended solids (TSS) concentration was determined by measuring the mass of material retained after filtering a known volume of water through a pre-ashed, pre-weighed GF/F filter after drying the filter at 65°C to a constant weight. Percent particulate organic carbon (POC) was determined as 47 % of the mass lost after combusting the filters at 450°C for 3 h (Sutherland, 1998). DOC was measured on a Shimadzu TOC 5000 (Columbia, Maryland) after acidification to pH below 2.0 and sparging of CO_2 (Sharp et al., 1993).

Fluorescence was measured on a Shimadzu RF-551 fluorometer. Emission intensity was measured for the entire visible spectrum (400–700 nm) using constant excitation of 370 nm. A blank was subtracted from the spectrum and ten-point averages centered on 450 and 500 nm were used to calculate the Fluorescence Index (FI, see McKnight et al., 2001).

Measurements of dissolved absorption (a_d) were made on filtrate from rinsed Whatman GF/F filters using a Shimadzu UV-VIS 1601 dual beam spectrophotometer (200 – 800 nm) in a 10 cm or 1 cm quartz Supersil cuvette referenced to air (Belmont et al., 2007). Particulate absorption (a_p) was measured using an adapted quantitative filter pad technique calibrated for fluvial sediments by Belmont et al., (2007; see also Mitchell et al., 1990; Roesler, 1998; Lohrenz, 2000). Essentially, suspended particulate material from a measured volume of water was concentrated on a pre-rinsed Whatman GF/F filter. A Shimadzu

UV-VIS 1601 dual beam spectrophotometer was then used to measure the spectral optical density (280 – 800 nm) of the GF/F filter plus particulate material against a wet, Whatman GF/A reference filter (1.6 μm minimum retention size). Corrections are applied to account for pathlength and multiple scattering as the light passes through the filter. All samples were kept in a 4°C refrigerator and scanned within 48 hours, which is the minimum time over which the spectral signal has been shown to be stable. The diffuse attenuation coefficient ($K_d(\lambda)$) was calculated using Equation 1:

$$K_d(\lambda) = \frac{a_t(\lambda)}{\mu(\lambda)} \quad (1)$$

where $a_t(\lambda)$ is the total absorption coefficient (the sum of a_d, a_p and absorption of pure water (a_w)) and $\mu(\lambda)$ is a correction factor that accounts for the angular distribution of natural light (see Belmont et al., 2007; Kirk, 1994). Here we apply, for all sites, the same μ values derived in Belmont et al., 2007, which calibrated this method for the Lehigh River. We calculated 1 % transmission depths (the depth at which only 1 % of incident radiation remains) using Equation 2:

$$UVB_{z1\%} = \frac{Ln(100) - Ln(1)}{K_d(\lambda)} \quad (2)$$

GIS Methods

A digital elevation model (DEM) of the entire Lehigh River watershed was assembled from 10-meter Shuttle Radar Topography Mission data obtained from the U.S. Geological Survey (http://ned.usgs.gov/). ArcGIS 9.1 was used to rectify and delineate all watersheds. Basin-mean watershed slope (MWS) was calculated using the ArcGIS Spatial Analyst extension, which computes the slope of steepest descent ($\frac{rise}{run} \times 100$) between each 10 x 10 m pixel of the DEM. MWS is calculated as the mean slope of all pixels throughout the basin. Land use was quantified (agriculture, forest, urban) using a coverage digitized by the Lehigh Earth Observatory (www.leo.lehigh.edu) from 1993 air photos. Wetland cover (U.S. FWS, 2005) and bedrock geology (Berg et al., 1980) was quantified using the 2001 coverage from PASDA Geospatial Data Clearinghouse (www.pasda.psu.edu). The ultimate base level for the Lehigh River is set by the elevation of the confluence of the Lehigh with the Delaware River. Distance to base level was measured as the river distance between each sampling point and the confluence of the Lehigh and Delaware Rivers.

Statistical methods

We analyzed data from base-flow samples and storm event samples separately, to best represent the optical environment for these two distinct flow conditions. Base-flow is defined here as that resulting from no measurable rainfall in the basin within the previous 24 hours and less than 10 mm within previous 72 hours. The small streams in our study respond rapidly to hydrological changes and return to base-flow conditions within that time frame.

We found the averages of most analyzed parameters during 2002 (a drought year) to be within one standard deviation of the averages from 2003, 2004 and 2005 (average precipitation years). We combined all four years to calculate interannual averages, which we used to examine the relationships between optical parameters and environmental variables (land use/cover and MWS). We used simple regression analysis in Sigmaplot 10.0 (Systat Software Inc., Richmond, CA) to evaluate the relationships between K_{d320} and DOC as well as the relationships between environmental variables (land use/cover, MWS) and optical parameters.

Results

Climate data

Over the four study years, we observed generally consistent air temperature and precipitation during the sampling season except for 2002, which was considerably drier (Table 1). The warmest and wettest year overall was 2005, though summer precipitation was similar for 2003, 2004 and 2005. A drought ensued throughout 2002, with most of the precipitation deficit accounted for by an exceptionally dry summer, during which less than half the normal amount of rain was recorded.

Basin and channel geomorphology

Stream size and channel morphology varied substantially among sites. Most stream channels in agricultural catchments had relatively low width to depth ratios (typically between 1–5), while channels in forested catchments were generally wider and shallower (w/d typically > 10). Channel beds were covered by a relatively thin mantle of alluvium with grain sizes ranging from fine sand to small boulders. M and S streams were the exception, with a narrower grain size distribution dominated by sand and gravel. Water depth during base-flow conditions ranged between 10 cm and 30 cm among different streams at the sampling sites, though the step-pool and pool-riffle morphologies of these stream channels makes for substantial within-stream variability. Discharge varied

Table 1. Eastern Pennsylvania climate data

	2002	2003	2004	2005
Annual Average Air Temperature (°C)	11.8	11.1	11.9	13.9
June – Sept. Average Air Temperature (°C)	21.9	20.8	21.4	22.6
Annual Precipitation (cm)	75.5	116.1[a]	126	168.5
June – Sept. Precipitation (cm)	16.9	55.7[a]	50.1	51.9

[a]Six weeks of summer precipitation data supplemented from NE Philadelphia Airport (PNE) record. All other data obtained from Lehigh Valley International Airport (ABE) record (http://climate.met.psu.edu/ida/).

Table 2. Geographic characteristics of watershed sampling locations.

Site[a]	Northing[b]	Easting[b]	Area (km^2)	Mean Watershed Slope (%)	Canopy Cover at Sample Location (%)[c]	# Samples
BW1	4524758	463845	6.7	11.5	NA	3
BW2	4521691	460830	11.5	13.3	NA	3
BW3	4520558	457718	13.1	12.4	NA	3
BW4	4520300	455318	1.7	15.0	NA	3
BW5	4520327	454936	19.2	13.6	NA	3
BW6	4518367	449793	6.2	14.5	NA	2
BW7	4518692	449388	6.7	13.9	NA	3
LH1	4562885	453793	14.3	4.4	NA	6
LH2	4561727	453076	2.6	3.6	NA	6
LH2A	4560725	452095	5.3	4.2	NA	3
LH4	4558049	449915	7.9	3.7	NA	5
LH5	4556657	449436	20.5	3.6	NA	5
LL1	4482077	442487	3.1	7.1	72	24
LL2	4482149	442911	1.5	9.1	91	24
LL3	4481906	448595	1.8	6.6	90	24
LL4	4481520	445124	1.8	6.4	29	24
LL5	4481347	445267	3.3	8.1	0	24
LZ1	4510178	424944	7.1	11.0	NA	3
LZ2	4508937	426227	2.3	12.3	NA	3
LZ4	4508351	428235	0.8	11.6	NA	3
LZ5	4508851	429218	1.0	10.4	NA	3
LZ6	4509397	430380	5.4	10.6	NA	3
LZ8	4511262	433011	1.6	11.5	NA	3
LZ9	4512085	434688	10.3	10.5	NA	3
M1	4503891	445351	8.3	7.1	82	24
M2	4503972	446202	1.5	5.1	0	23
M3	4502545	445685	1.0	11.8	26	16
MY1	4509258	466127	5.2	9.0	NA	2
MY2	4509253	466204	10.0	8.1	NA	2
MY3	4508636	468165	11.6	7.9	NA	2
MY4	4508560	471149	9.6	8.3	NA	2
S1	4500221	438329	13.4	5.9	0	25
S2	4500267	438429	1.4	7.0	96	25
S4	4500526	440010	1.6	7.1	92	23
T1	4551083	452889	4.7	2.2	NA	6
T2	4547522	451233	3.3	1.9	NA	6
T3	4550503	449149	7.2	1.4	NA	4

[a]See figure 1 for geographic locations and clarification of abbreviations. Number order within each major watershed indicates relative distance from confluence with the Lehigh River with lowest numbers indicating furthest distance.
[b]UTM Coordinates in zone 18, NAD 27 datum
[c]Average of 3 measurements using a spherical densiometer at sampling location only.

up to 100-fold between summer low-flow and peak storm-flow conditions. Sampling location, watershed size, canopy coverage at the sampling location, and total number of base-flow samples obtained from each of the basins during the four year study is shown in Table 2. Table 3 lists the watershed land use/land cover statistics.

Stream Chemistry and Optical Properties

Over the entire period of study, we found an exceptionally large range of UV-A and UV-B attenuation coefficients (K_{d380}: 0.68 – 151.1 m^{-1}, K_{d320}: 0.95 – 316.2 m^{-1}) compared to other studies in lentic (Morris et al., 1995: ranges $K_{dUVA} = 0.2–55.7$ m^{-1}, $K_{dUVB} = 0.4–133$ m^{-1}; De Lange, 2000: ranges $K_{dUVA} = 3.7–31.1$ m^{-1}, $K_{dUVB} = 9.1–70.7$ m^{-1});) and lotic (Frost et al., 2005:

ranges $K_{dUVA} = 4.5-77.6\ m^{-1}$, $K_{dUVB} = 10.3-225\ m^{-1}$) environments (all measurements for all dates included in supplementary appendix). Attenuation coefficients during base-flow conditions (K_{d305}, K_{d320}, K_{d340}, K_{d380}) were all significantly correlated to DOC concentration. Figure 2 shows the relationship between K_{d320} and DOC concentration for all base-flow samples over the four year study (n = 391).

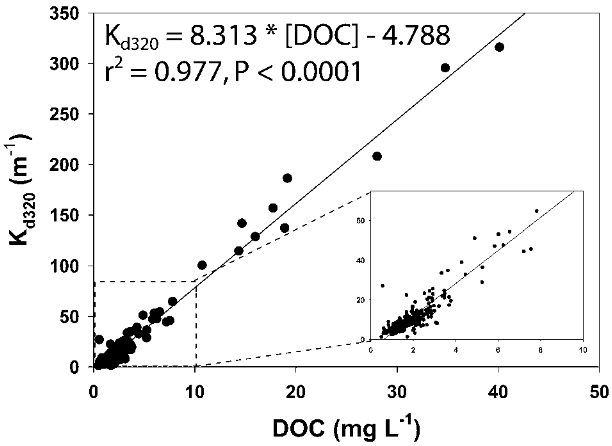

Figure 2. Regression analysis of DOC concentration and K_{d320} with each data point representing an individual sample collected from one of our sampling streams in the Lehigh River watershed, 2002–2005 (n=391, $P < 0.0001$).

The interannual (all years on record) averages of the proportion of K_{d320} that is attributable to particulate absorption (a_{p320}/a_{t320}) are shown in figure 3. The mean values for a_{p320}/a_{t320} range between 0.05 and 0.69, with an average coefficient of variation of 31 %. Figure 3b shows the mean theoretical UVB 1 % transmission depths ($UVBz_{1\%}$), which is the depth at which only 1 % of incident radiation remains (calculated using Eq. 2). The ranges are relatively consistent within each region, but vary between 2 and 147 cm across the spectrum of watersheds sampled. The average coefficient of variation among streams is 15 %, but ranges between 2–41 % for each individual stream.

Percent agricultural cover did not correlate strongly with interannual DOC concentration or any index of DOC optical quality (% agriculture vs UV-B spectral slope $r^2 = 0.003$, $P = 0.77$ and % agriculture vs FI $r^2 = 0.03$, $P = 0.41$) when considering all basins sampled. However, considering only the wetland-devoid basins in the southern Lehigh watershed (LL, S, M and MY), a moderate correlation existed (% agriculture in southern LR watershed only vs [DOC] $r^2 = 0.39$, $P = 0.012$ and % agriculture in southern LR watersheds only vs FI $r^2 = 0.32$, $P = 0.036$). Neither percent agricultural cover nor MWS correlated to [TSS] or normalized suspended sediment absorption (a_{p320}/[TSS]), but MWS did correlate to the proportion of total absorption accounted for by particles (a_{p320}/a_{t320}; $r^2 = 0.21$, $P = 0.0048$).

In contrast, K_d values covaried strongly with watershed topographic metrics (Fig. 4) with an approximately exponential decay relationship between interannual average K_{d320} and MWS. MWS also strongly correlated to the average DOC concentration measured in the streams over the entire study period, but the relationship is slightly weaker than that observed between MWS and K_{d320} ($[DOC] = 55^{(-0.6621*(MWS))}$; $r^2 = 0.65$, $P < 0.0001$; data not shown). In addition, MWS correlated with the Fluorescence Index (FI), the ratio of fluorescence at 450 to 500 nm with 370 nm excitation light, (Fig. 5; $FI = 0.0367(MWS) + 1.291$, $r^2 = 0.71$, $P < 0.0001$).

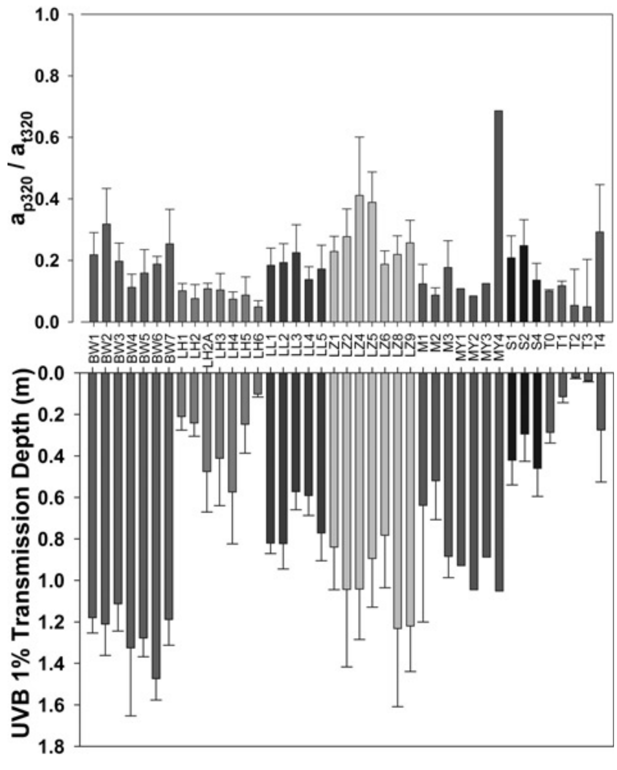

Figure 3. a) The ratio of the particulate absorption coefficient to the total absorption coefficient, which serves as a proxy for the proportion of K_{d320} that is accounted for by particulate material. b) The depth at which only 1 % of the incident flux of 320 nm light remains (Eq. 2). Most 1 % transmission depths exceed the actual depth of the streams sampled (10–30 cm) indicating >1 % of incident radiation reaches the benthos. Error bars represent one standard deviation and illustrate the variability during base-flow conditions for all years sampled.

Stream optical environments during altered hydrological conditions

The summer drought in 2002 allowed us to examine the influence of precipitation on water chemistry and

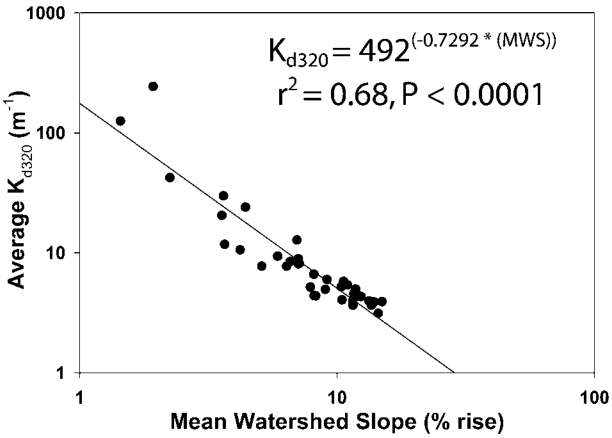

Figure 4. Interannual average of K_{d320} regressed against mean watershed slope for each of the sites sampled.

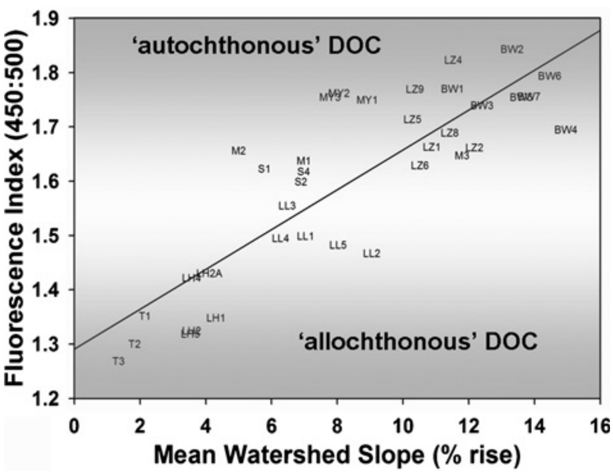

Figure 5. Mean watershed slope correlated to DOC source, as indicated by the FI. An FI value of ~ 1.4 indicates primarily terrestrial (allochthonous) origin of DOC derived from high-lignin material and a value of 1.8 indicates low-lignin (autochthonous) DOC of microbial or algal origin.

absorptive properties. In basins that were sampled throughout all four years (LL1 – LL5, M1, M2, S1, S2, S4), the 2003, 2004 and 2005 values for any given parameter generally did not fall outside one standard deviation of the values measured in 2002, our most intense year of study. However, several consistent trends were observed. Most notably, DOC concentration was somewhat lower in 2002, compared to the combined average of 2003, 2004 and 2005 with the exception of S1 and S2 (see digital supplement appendix). Particulate absorption and dissolved absorption were consistently higher in agricultural catchments, but lower in forested catchments during 2002. The proportion of total absorption that can be attributed to particulate absorption (a_{p320}/a_{t320}) was lower during 2002 for most of the sites sampled.

The few samples obtained in 2002 during stormflow conditions indicated substantially altered chemistry and optical properties (data available in supplementary appendix). During storm events, DOC concentrations increased two to three fold. Total suspended solids concentration increased variably and changed dramatically throughout storm hydrographs, usually rising quickly and then rapidly decreasing before peak discharge. Due to the high variability, both among storms and within a given storm hydrograph, the methods used to sample storm events in this study render the data useful only for qualitative analysis.

Discussion

Our experimental design was tailored to investigate variability in UVR transparency within- and among-streams and constrain the environmental variables that influence UVR attenuation. The large ranges of attenuation coefficients (K_{d380}: 0.68 – 151.1 m^{-1}, K_{d320}: 0.95 – 316.2 m^{-1}) and 1 % transmission depths (2 cm – 147 cm) indicate substantial among-stream variability in optical environments of small tributaries distributed throughout the Lehigh River watershed during base-flow conditions. In contrast, much smaller within-stream variability in attenuation coefficients and 1 % transmission depths observed over the entire study period indicates that the optical environment within any given stream water column is relatively stable (coefficient of variation of K_{d320}, K_{d380} and $UVBz_{1\%}$ average for all sites was 15 %, range = 2–41 %) during base-flow conditions. We have documented the role of particulate absorption, which differs substantially among streams, but generally accounts for approximately 10–30 % of attenuation in the UV-B waveband. Furthermore, we have documented strong topographic control of UVR attenuation, DOC concentration and DOC optical quality.

UVR attenuation at the regional and local scale.

We used a quantitative filterpad technique (QFT) to measure particulate absorption, independent of dissolved absorption, in a laboratory-based spectrophotometer (Belmont et al., 2007). The QFT approach facilitates precise estimates of attenuation in shallow and/or rapidly flowing streams where attenuation often can not be measured in situ with a profiling radiometer. Profiling radiometers are sensitive to sun angle and must be used within a few hours of solar noon, precluding nearly instantaneous attenuation estimates over a large geographic region that can be obtained from single-day sampling campaigns, as we have done here. In situ measurements are also sensitive to canopy cover and sky conditions, which may bias an individual measurement. The primary drawback of the laboratory-based method is that the estimated K_d values are generally insensitive to the micro-scale environmental conditions discussed above, which have potential to be of ecological significance. For the purposes of a regional survey, the laboratory-based technique is preferable. However, depending on the nature of the hypotheses being tested and considering the general paucity of attenuation data for lotic environments, both approaches are valuable and continued application of each is highly desirable.

The large range of attenuation coefficients observed in this study is a consequence of the diverse study area that spans four physiographic provinces underlain by diverse geology and soils. Ultimately, the differences observed are an integrated effect of the geology and climate which fundamentally establish the template upon which the ecologic, hydrologic and geomorphic processes function, to directly influence water transparency. Despite the drastically different sources and environmental characteristics of each of the watersheds, the relationship between bulk concentration of DOC and K_{d320} is stronger than has been observed in previous studies, which were constrained by smaller ranges in both DOC and K_{d320} (Frost et al., 2005; Morris. et al., 1995; Peterson et al., 2002). This indicates that at the regional scale, DOC optical quality is relatively consistent and therefore, DOC concentration can be used as an independent variable to estimate attenuation regionally. However, considering the most transparent systems ($K_{d320} < 30\ m^{-1}$), where UV-B stress is most likely to be important, the variability in the Kd-DOC relationship is substantial (see scatter of data points in bottom-left corner of figure 2). Therefore, although DOC dominates attenuation at the regional scale, measurements of dissolved and particulate absorption are necessary to more accurately estimate UVR attenuation in transparent systems.

The ecological relevance of 1% transmission depths ($UVBz_{1\%}$) is not well documented, but because resilience to UV-B varies substantially on a species-to-species basis, $UVBz_{1\%}$ is a useful metric to convey penetration. The $UVBz_{1\%}$ observed throughout the Lehigh watershed vary substantially and many of the $UVBz_{1\%}$ reported here are substantially deeper than those recently reported for streams in northern Michigan (Frost et al., 2005). On average, within-stream variability (1 standard deviation) of $UVBz_{1\%}$ was 15% above/below the mean value for any given stream. Notably, the mean $UVBz_{1\%}$ values reported here are generally far in excess of the actual water depth at the sampling sites (10–30 cm), meaning that the benthic environments of all but the T and LH streams are receiving much greater than 1% of incident radiation. Typical water depths for riffle sections in our streams were 10–20 cm and many pools were < 50 cm.

Tree canopy cover is an important consideration for putting 1% transmission depths into context. Full canopy cover can reduce radiation flux by more than 90% (Grant et al., 2002). In the main stem of the Lehigh River, canopy only extends over a small fraction of the water surface, which is typically greater than 50 m in width. In the main stem however, water depth (typically > 100 cm) is likely sufficient to reduce UV-B flux to negligible levels. In contrast, for the first- and second-order tributaries studied here, water depth in transparent systems is insufficient to reduce the UV-B flux substantially, which enhances the importance of canopy cover to reduce the UV-B flux to the stream benthos. Many of the sampled streams in the heavily agricultural southern Lehigh River watershed have patchy, longitudinally discontinuous canopy cover (Table 2), where riparian vegetation has typically either been entirely removed or left entirely intact, resulting in a step function of UV-B exposure as organisms move up or downstream.

The role of suspended particulates in UVR attenuation

Using the QFT, we are among the first to quantify the proportion of UV-B attenuation in streams that is accounted for by particulate material (a_{p320}/a_{t320}). Although DOC concentration dominates UV-B attenuation, suspended particles do account for a significant fraction of total attenuation in most of the streams studied (Fig. 3a). Both the concentration and optical properties of suspended solids contribute to the particulate absorption signal. The fact that no significant relationship was observed between land use and POC is likely an artifact of our limited POC dataset (only in LL, M and S streams for 2002 sampling season) and the limited POC range observed (8.0–12.5%). We would expect land use and POC to be related if land use/cover has altered the carbon content, hydrology or C mobility significantly, all of which appear to have occurred. The a_{p320}/a_{t320} ratio is a more sensitive metric than [TSS] or the procedurally-related POC measurement and the weak, but significant relationship between MWS and a_{p320}/a_{t320} supports the notion that study focused more specifically on this parameter may reveal a relationship between land use and POC that is not apparent at the scale of our study.

Table 3. Watershed land cover/land use

Site	Forest (%)	Agriculture (%)	Urban (%)	Other (%)	Wetland (%)[a]
BW1	45	47	0	7	1
BW2	32	55	0	13	0
BW3	36	49	0	15	0
BW4	26	22	0	52	0
BW5	47	38	4	11	0
BW6	57	27	7	9	0
BW7	58	21	3	18	0
LH1	95	2	0	0	9
LH2	90	7	0	0	5
LH2A	98	0	0	0	31
LH4	97		0	0	5
LH5	98	1	1	0	8
LL1	75	19	0	6	0
LL2	74	13	0	12	1
LL3	39	50	0	11	0
LL4	67	21	0	11	0
LL5	76	16	0	7	0
LZ1	41	45	0	14	0
LZ2	89	3	0	8	0
LZ4	64	28	6	2	0
LZ5	24	67	7	2	0
LZ6	50	42	0	8	0
LZ8	60	36	0	4	0
LZ9	34	61	0	5	0
M1	27	69	3	0	0
M2	4	96	0	0	0
M3	46	54	0	0	0
MY1	10	84	0	5	1
MY2	63	20	0	15	2
MY3	14	71	5	10	0
MY4	19	52	3	26	0
S1	15	83	1	1	1
S2	21	77	0	2	0
S4	12	87	0	0	1
T1	84	4	0	0	40
T2	83	0	0	0	25
T3	92	3	0	0	44

[a]Forest and wooded wetland were not treated as mutually exclusive categories, so percent land cover/use may exceed 100 %.

Linking stream optical environment to watershed topography and geomorphology

Watershed topography, rather than land use or wetlands cover (Gorham et al., 1998) appears to exert the strongest control over stream optical environment in our study. The relationship between wetland cover and DOC has been previously documented (Gorham et al., 1998; Frost et al., 2006b) and since wetlands typically are distributed on very gently sloping topography, a topographic control in this case should be obvious. In the watersheds studied here however, wetlands are nearly absent where slopes are greater than 5 % (Table 2). The fact that the relationships are robust even for these more steeply sloping watersheds demonstrates that the coevolution of hillslope form and process, which results in extant topography, ultimately regulates generation, processing and transport of DOC and sediment from the hillslopes to the stream.

The metric we used to examine the relationship between topography and stream optical environment was basin-averaged hillslope gradient, expressed as mean watershed slope (MWS). MWS is a relevant metric because it integrates a complex combination of factors that regulate the generation, storage and transport of sediment and soil carbon on the hillslopes. In general, higher MWS increases sediment transport and decreases the concentration and optical quality of carbon contributed from the watershed across our entire study area.

Hillslope morphology is controlled by several exogenic factors over landscape evolution timescales (10^3–10^6 yrs). Bedrock geology exerts a primary control on hillslope morphology and soil texture (Jenny, 1941). Similarly, climate shapes hillslopes not only with the amount, but also the intensity, of rainfall (Etheridge et al., 2004). Vegetation and other biological activity are limited by geology and climate, but in turn dominate the local conversion of rock to soil. The long-term vertical incision rate of rivers between opposing hillslopes defines the local base level conditions to which the overall hillslope gradient adjusts over soil-forming time scales.

In transport-limited (soil mantled) landscapes, hillslopes generally develop concavo-convex morphology (Gilbert, 1909). The convex-up portion near the ridge is an erosional surface with generally coarser-grained soil and low carbon generation and storage capacity. The concave-up portion that constitutes the lower hillslope and valley bottom is a depositional surface with generally more moist, deeper, finer-grained soils that have higher carbon generation and storage capacity. Increased MWS is indicative of enhanced erosional surface, which results in higher contribution of sediment, but lower potential for soil organic carbon generation and transport.

MWS is maximized where the underlying rocks are hard and resistant to the forces of erosion, the soil mantle is thin, and/or where the local base level rate of lowering is rapid, as is the case for rapidly incising streams. Conversely, MWS is minimized where the underlying rocks are soft, the soil mantle is thick, and/or the local base level rate of lowering is slow, as is the case for slowly incising streams. The base level for our watersheds is set by the elevation and vertical incision rates of the Lehigh and Delaware rivers. The long-term rate of incision for these streams is known to be slow at ~ 20–30 m/Myr (Pazzaglia and Gardner, 1994); however, knickpoints, local increases in river channel gradient, attest to unsteady waves of incision that initiate down stream and travel upstream through the trunk channels and into the tributaries, including the watersheds in our study. Base level is relatively stable upstream of these knickpoints consistent with gentle, graded hillslopes, but below the knickpoints base level has been lowered, prompting tributary incision and hillslope steepening.

The Lehigh River longitudinal profile shows a knickpoint that has propagated up to, and is continually forming, the Lehigh River Gorge (Fig. 1). As a result, the knickpoint has imparted a base level fall for the lower part of the watershed (below the Lehigh Gorge; Fig. 1). In response, tributary streams and their constituent hillslopes are steepening. Those watersheds that have most recently begun to experience the base level fall and are underlain by harder rocks are steeper (Fig. 6, Group B) compared to hillslopes of the lower Lehigh watershed, which are developed on softer rocks and experienced passage of the knickpoint millions of years before present (Fig. 6, Group A). Far upstream from the knickpoint location are tributaries that have yet to experience the base level fall and as a result, watershed slopes here are relatively gentle (Fig. 6, Group C). In this way, the upstream progression of the knickpoint in the Lehigh River watershed has partitioned the landscape into three broad regions, each in a different stage of evolution. The long-term evolution of this landscape therefore establishes a framework for understanding regional stream optical environments.

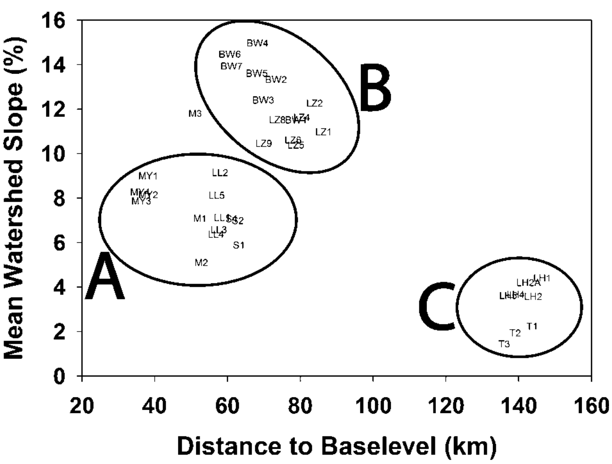

Figure 6. The relationship of mean watershed slope and distance to base level (the Lehigh River mouth) indicates that the southern (A), mid (B) and northern (C) tributary basins are currently in three distinct phases with respect to base level fall on the Lehigh River.

Hillslope gradient, soil texture, and soil thickness, collectively establish the C storage capacity and provide an explanation for the MWS-DOC covariance (Berhe et al., 2008). Gentle hillslopes, such as those atop the Pocono Plateau upland, have a large SOM pool in thick, organic-rich soils, a condition fostered by insulation from base level fall, gently-dipping sedimentary strata, and poorly-drained glacial parent materials. Similarly, gentle hillslopes in the southern Lehigh watershed have thick soils developed from soft, clay-rich rocks that have long since adjusted to the base level fall. In both cases, but for different reasons, both the Pocono Plateau and southern watershed soils are poorly-drained which leads to shallow, lateral flow through organic rich A and O horizons where the soil water becomes enriched in DOC en route to the stream channel.

Steep hillslopes, in contrast, support thinner, but texturally more coarse, and compositionally more quartz-rich, well drained soils. Dense forest cover and the well drained conditions render these soils particularly acidic as vertically infiltrated soil water leaches DOC from the A and/or O horizons that is rapidly consumed by hydrolysis of siliciclastic material in the subsurface horizons. E-horizons are common in these soils as hydrolysis and the acidic vadose waters leach all available sesquioxides. As a result, the soil water that remains to recharge the ground water table and stream channels generally lacks DOC.

The relationship between hillslope gradient and DOC optical quality is more difficult to reconcile mechanistically. Vegetation type most certainly plays a role in determining carbon quality exported across the entire range of watersheds we investigated. However, differences in vegetation can not explain the differences observed among the LZ, BW streams and LL, S and M streams, which all contain similar plant communities. The range of the Fluorescence Index (1.25 – 1.85) measured here is larger than has been observed in other river systems (~1.3 – 1.6, McKnight et al., 2001; Hood et al., 2006). The FI characterizes DOC based on the presence of lignin, which is produced by terrestrial plants and contains a significant proportion of aromatic carbon (FI = ~ 1.4), compared to algal or microbe-derived, autochthonous DOC, which contains less aromatic carbon (FI = ~ 1.8). It is important to note however, that in figure 5, the watersheds naturally group by geographic proximity. The LH and T streams, which contain extensive wetlands, group near the high-lignin, terrestrially-derived end of the spectrum, the LZ and BW streams group near the low-lignin end of the spectrum and the LL, S and M streams group together, intermediate between the other two groups. Anomalously low lignin-derived DOC in LZ and BW streams may be an artifact of preferential storage of aromatic carbon compounds or enhanced soil microbe processing of SOM in these relatively young, well-drained soils.

Agricultural land use appears to only have a significant impact on DOC concentration and quality in the southern Lehigh tributary streams. This is most likely due to the fact that agriculture in the southern

Lehigh watershed is more extensive and has been practiced historically for much longer. Also, agriculture in the LZ and BW watersheds is patchy and often spatially disconnected from the stream, whereas agricultural practices in the S, M and MY basins, and to a lesser extent, the LL basins, often have displaced the riparian buffer and cultivated fields occasionally extend through the riparian zone to the edge of the stream channel. Also, the relationships between land use and DOC are reversed in the northern Lehigh watersheds. The extensive wetlands in the LH and T watersheds dominate DOC contributions in the northern watersheds. In contrast, the agricultural catchments contribute more DOC compared to forested catchments in the southern Lehigh watershed, presumably because of frequent disruption to the A_p soil horizon and more rapid biomass turnover.

Conclusions

We have documented the UVR environment in 37 small tributaries distributed throughout the Lehigh River watershed, eastern Pennsylvania, and explored the ecological and geomorphic processes that determine stream optical conditions. The wide ranges of attenuation coefficients (K_{d380}: 0.68 – 151.1 m^{-1}, K_{d320}: 0.95 – 316.2 m^{-1}) and 1 % transmission depths (2 cm – 147 cm) are closely related to watershed topography, specifically mean watershed slope. Notably, the theoretical 1 % transmission depths were typically far in excess of the actual stream water depth (10–30 cm), indicating that much more than 1 % of incident radiation typically reaches the stream benthos. The proportion of attenuation that is attributable to suspended particulate material is 10–30 % on average.

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