

## Organic matter dynamics in White Clay Creek, Pennsylvania, USA

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White Clay Creek drains agricultural and wooded land in the Piedmont Province of southeastern Pennsylvania and northern Delaware, joining the Christina River in Delaware near the Christina's discharge to the Delaware Bay. This chapter reports studies in a 725-ha watershed forming the headwaters of the East Branch. Elevations in the study watershed range from 100 m to 164 m. The stream draining the study watershed is 3rd order. The total length of stream channels (orders 1–3) is 12,900 m, and the total streambed area assessed at baseflow is 24,000 m<sup>2</sup> (Table 1).

The watershed is underlain by metamorphic crystalline rocks from the late Precambrian to early Ordovician, including gneisses, schists, quartzites, and marbles, which were subject to several episodes of folding during the Paleozoic Era (Sloto 1994). The great age of the rocks, together with the absence of quaternary glaciation account for the presence of a deep (5–15 m) regolith of weathered rock, saprolite, subsoil, and soil. Below the regolith, the bedrock is extensively fractured, providing water bearing zones to depths of >100 m (Sloto 1994). The soils are primarily typic hypludults, except in the riparian zones, where aquic fragiudults predominate (Kunkle 1959, Custer 1985). The soils are 1 to 2 m deep.

The land was settled and at least partially cleared for agriculture in the early 1700s. It is likely that it was entirely deforested in the mid 19th century to supply charcoal for local iron furnaces. Woodlots returned, however, as coal replaced charcoal, and covered 18% of the watershed in the 1950s (Kunkle 1959). Since then,

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TABLE 1. Summary descriptive data and components of the organic matter budget for White Clay Creek, southeastern Pennsylvania, U.S.A. Organic matter values (including production and respiration) are reported as ash-free-dry-mass (AFDM).

Variable	Value
<b>Physical characteristics</b>	
Latitude (°N)	40
Order	3
Catchment area (ha)	725
Streambed area at baseflow (m <sup>2</sup> )	24,000
Gradient (m/m)	0.008
Mean annual water temperature (°C)	10.6
Mean annual streamflow (L/s)	115
Mean annual precipitation (cm)	105
<b>Inputs (g m<sup>-2</sup> y<sup>-1</sup>)</b>	
Gross primary production	527
Litterfall	313
Groundwater DOM	126
<b>Standing crops (g/m<sup>2</sup>)</b>	
CBOM > 1 mm (not including wood)	118
FBOM < 1 mm	201
Wood > 1 mm	206
<b>Outputs</b>	
Total ecosystem respiration (g m <sup>-2</sup> y <sup>-1</sup> )	439
Particulate transport (kg/y)	55,600
Dissolved transport (kg/y)	27,600

hardwood forest has been reestablished in some areas, primarily riparian zones and steep slopes, so that 23% of the watershed is now in mature forest or various stages of reforestation.

Approximately 52% of watershed area is in pasture for horses and cattle, and 22% of the watershed is tilled (primarily maize and soybeans) or hayed (alfalfa). The tillage is conducted according to conservations plans developed by the US Department of Agriculture Natural Resources Conservation Service. Management practices include crop rotation in contour strips, grass waterways, and diversion berms. Most of the nutrient demands of the crops are met by manure application. The remaining land (~3%) is in residential use (approximately 60 dwellings), a commercial catering establishment, and the Stroud Water Research Center laboratory. The catering establishment discharges 42,000 L/d of treated sewage (secondary treatment) through a holding pond to a 1st-order headwater.

A 1975 survey (R. L. Vannote, unpublished

data) found that of the total low-flow streambed area of 24,000 m<sup>2</sup>, 58% was within woodland, 12% in semi-open canopy, and 30% in meadow. Approximately half of the area in "meadow" reaches had a young riparian hardwood forest, established in 1969. By 1995, the area in semi-open canopy had matured sufficiently to be categorized as woodland, and the reforested riparian zones had achieved a "semi-open" status, giving a distribution for riparian cover (by streambed area) of 70% woodland, 16% semi-open, and 14% meadow. Nearly all the area in the "meadow" category (12% of streambed area) was fenced to exclude livestock and reforested in hardwood seedlings between 1990 and 1995.

Streamflow from the 725-ha watershed averaged 115 L/s between 1975 and 1995, with annual means ranging from 66 to 156 L/s. The average annual streamwater temperature, measured in the 3rd-order reach, is 10.6°C. Annual precipitation since 1970 has averaged 1.05 m/y and is evenly distributed throughout the year. Winter precipitation frequently occurs as snow, but periods of melting prevent snowpack accumulation.

Streamwater chemistry has been monitored at weekly intervals since 1969. Median concentrations of selected constituents are: 2.9 mg/L NO<sub>3</sub>-N, <0.03 mg/L NH<sub>4</sub>-N, 0.025 mg/L soluble reactive P, 0.050 mg/L total dissolved P, 19.8 mg/L Ca, 7.5 mg/L Mg, and 15.8 mg/L SO<sub>4</sub>. The median acid neutralizing capacity is 1.1 meq/L and the median pH is 7.5.

### Inputs

Benthic GPP was estimated by the diel oxygen curve method from stream sediments placed in sealed 22-L chambers similar to those described by Bott et al. (1978). Sediments were incubated in trays embedded in the substratum for at least 1 mo prior to transfer to the chambers, which were incubated streamside at streamwater temperatures. A total of 394 24-h incubations were conducted between October 1973 and December 1975 in two 3rd-order reaches, 1 in mature woodland, and 1 in meadow. Annual estimates were obtained from monthly means. Oxygen evolution was converted to carbon production using a photosynthetic quotient of 1.35 (Vollenwieder 1969) and to organic matter production using an assumed car-

bon content of 50%. The annual average GPP for the stream was obtained as the weighted average of 286 g AFDM  $\text{m}^{-2} \text{y}^{-1}$  from the woodland reach and 1100 g AFDM  $\text{m}^{-2} \text{y}^{-1}$  from the meadow reach. For the weighting, we used the 1995 distribution of forest canopy applying the woodland value to 70% of streambed area and the meadow value to the remaining 30% of streambed area that is either in semi-open canopy or meadow. The decision to consider semi-open canopy as equivalent to meadow was based on subjective observations of light penetration and algal growth in those reaches but may result in an overestimate (by a maximum of 32%) of weighted average GPP.

Litterfall was collected in 22-L plastic pails with a 0.064- $\text{m}^2$  circular opening mounted above the stream channel on steel stakes. Collections were made weekly during the months of September through December during the years 1992 through 1994 and biweekly from May through August during 1995. We estimate roughly, from rates measured in December and May, that the absence of data from January through April may result in an underestimate of the total annual inputs by 10–15%, but the reported figures are not adjusted by this estimate. A total of 35 buckets were deployed in the 3rd-order reach, 17 in a mature woodland reach, and 18 within a semi-open reforested (1969) riparian zone. Collected materials were separated into leaves, wood, and all-other material (primarily seeds), and dried at 60°C before weighing. Dry weights were corrected for an average ash content of 7.4%. The average annual total inputs for the 2 reaches were essentially the same, at 384 g  $\text{m}^{-2} \text{y}^{-1}$  for the mature woodland and 401 g  $\text{m}^{-2} \text{y}^{-1}$  for reforested riparian zone. The 2 figures were averaged and applied to the 86% of streambed area in these 2 categories. We assumed zero inputs for the meadow reaches, yielding a streambed-area weighted average input of 313 g AFDM  $\text{m}^{-2} \text{y}^{-1}$ . Of the total litter inputs, 69% occurred as leaf litter and 10% as woody material.

Input of groundwater DOM was estimated as the product of baseflow (assumed to originate from groundwater) and groundwater concentrations obtained from monitoring wells. The mean annual baseflow of 70.5 L/s was estimated as the weekly minimum streamflows for 20 y of record (1975–1995). This simple “fixed-interval” method for separating baseflow from stormflow

can yield annual estimates of baseflow within  $\pm 5\%$  of other automated techniques and manual methods (White and Sloto 1990). A mean DOC concentration of 0.68 mg/L was obtained from 13 monitoring wells throughout the watershed, each sampled several times in 1994 and 1995. Assuming a 50% carbon content for DOC, the groundwater dissolved organic matter (DOM) input was 3024 kg/y, or 126 g  $\text{m}^{-2} \text{y}^{-1}$  on the basis of streambed area.

### Standing crops

BOM was sampled seasonally in 1976 (Minshall et al. 1983) by placing a 0.03- $\text{m}^2$  cylinder into the substratum and removing organic matter by agitation and suctioning. The collected BOM was size-fractionated through a 1-mm sieve. Estimates were based on 16–18 samples per season from the 3rd-order wooded reach. The mean annual estimates of 118 g/ $\text{m}^2$  for BOM > 1 mm and 201 g/ $\text{m}^2$  for BOM < 1 mm were applied to the entire stream, although it is likely that standing stocks in the meadow reaches were lower than this estimate. Standing stocks of woody debris were measured as dry weight in November 1991 in woodland (312 g/ $\text{m}^2$ ) and open (15 g/ $\text{m}^2$ ) reaches (Sweeney 1993). We assumed that the estimate from the woodland applied only to the 70% of streambed area within mature woodlands and used an assumed ash content of 7.4% to obtain a streambed-area weighted estimate of 206 g AFDM/ $\text{m}^2$ .

### Outputs

Total ecosystem respiration measurements were made as night-time hourly oxygen consumption in sealed chambers in conjunction with the GPP measurements discussed above. Conversion from oxygen consumption to carbon respiration assumed a respiratory quotient of 0.85, and the conversion to organic matter assumed a carbon content of 50%. The mean annual respiration was 310 g AFDM  $\text{m}^{-2} \text{y}^{-1}$  in the woodland reach and 740 g AFDM  $\text{m}^{-2} \text{y}^{-1}$  in the meadow reach. Streambed areas were weighted in the same manner as for GPP to yield an average of 439 g AFDM  $\text{m}^{-2} \text{y}^{-1}$ .

Exports of POM from the 725-ha watershed were estimated from weekly grab samples from January 1993 to November 1995 and from intensive automated sampling of 3 major storms in

1995. Samples were filtered onto pre-ashed and pre-weighed Whatman GF/F glass fiber filters, dried, and ashed to determine AFDM. Concentrations of seston, or suspended POM ( $C_s$ ), increased with stormflow but showed no apparent influence of variations in baseflow. Baseflow ( $Q_b$ ) was estimated as the weekly minimum streamflow. For samples taken at  $Q/Q_b < 1.65$ , where  $Q$  is instantaneous streamflow, the mean seston concentration was 0.66 mg/L (SD = 1.2,  $n = 131$ ) and showed no obvious seasonal variation. For samples taken at  $Q/Q_b \geq 1.65$  ( $n = 52$ ), seston varied with flow according to the regression:

$$\log(C_s) = -0.786 + 1.46 \log(Q/Q_b)$$

which accounted for 66% of the variance in log-transformed concentrations. These relationships were used as a rating curve, in combination with hourly flows from 20 y of streamflow record, to estimate hourly seston concentrations and downstream fluxes and to arrive at an estimate for mean annual seston transport of 55,600 kg/y as AFDM, or 2320 g m<sup>-2</sup> y<sup>-1</sup> on a streambed-area basis. This approach assumes that the rating curve was unaffected by long-term (e.g., year-to-year) variations in flow regime. Computed annual exports varied greatly (6280–187,000 kg/y), influenced by the frequency of large storms.

Exports of DOM were estimated from frequent measurements of DOC taken from the stream since 1976 ( $n = 1150$ ), including 10 intensively sampled storms. Samples for DOM were filtered through pre-ashed Whatman GF/F filters and analyzed for dissolved organic carbon (DOC) by uv-promoted persulfate oxidation (1976–1986) and Pt-catalyzed persulfate oxidation (1987–1995).

The variation of DOC concentration,  $C_d$ , with streamflow was described by the regression equation:

$$C_d = 1.67 + 2.82 \log(Q/Q_b)$$

which accounted for 51% of the variance in  $C_d$ . This equation was used to compute the average annual export for 20 y of streamflow record in the manner described above for export of particulate matter. Export for individual years ranged from 7070 to 25,100 kg (as carbon), with a 20-y mean of 13,800 kg. Assuming that DOM is 50% carbon, we obtained the estimated an-

nual export of 27,600 kg/y, or 1150 g m<sup>-2</sup> y<sup>-1</sup> on a streambed area basis.

Over the 20-y record, flow was less than 1.65 × baseflow 90% of the time. We used the criterion of 1.65 × baseflow to distinguish "low flow" from storm flow because within the "low flow" range there was no significant influence of streamflow on either suspended POM or DOC concentration. Of the annual water export, 33% occurred as "storm flow", which transported 66% of the DOM export and 97% of the particulate organic matter export.

### Conclusion

The total watershed exports of organic matter of 3900 g m<sup>-2</sup> y<sup>-1</sup> (on a streambed area basis) greatly exceed the total inputs of 966 g m<sup>-2</sup> y<sup>-1</sup>, suggesting that there are substantial unmeasured inputs. We did not measure lateral inputs of litter, but typical reported rates of 100–200 g/y per metre of stream channel (Webster et al. 1995) would add roughly 100–200 g m<sup>-2</sup> y<sup>-1</sup> to the streambed (average width 1.9 m), accounting for only a small fraction of the discrepancy. Also unmeasured was the litter that falls onto dry streambed within the bankfull channel area and becomes entrained during storms. The bankfull-area is unsurveyed but is probably less than 4 × the baseflow area. Thus, the dry channel might account for as much as 1000 g m<sup>-2</sup> y<sup>-1</sup> of additional inputs, still about 2000 g m<sup>-2</sup> y<sup>-1</sup> short of that needed to balance inputs with outputs. We speculate that much of the remaining discrepancy is accounted for by storm transport of both POM and DOM from ephemeral rills and overland flow and of DOM from soil-water drainage. If storm-related exports are excluded from the budget, the exports of DOM and POM reduce to 390 and 67 g m<sup>-2</sup> y<sup>-1</sup> respectively, giving a total organic matter output (including respiration) of 900 g m<sup>-2</sup> y<sup>-1</sup>, which nearly balances estimated inputs. Thus it appears that storm transport acts neither as a net exporter or net importer of organic matter, despite its dominant role in the annual organic matter budget.

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