EFFECTS OF PRECIPITATION, AIR TEMPERATURE, AND LAND USE ON ORGANIC CARBON DISCHARGES FROM RHODE RIVER WATERSHEDS

DAVID L. CORRELL*, THOMAS E. JORDAN and DONALD E. WELLER
Smithsonian Environmental Research Center, Edgewater, MD, U.S.A.
(author for correspondence, e-mail: correll@hitter.net)*

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Abstract. We studied discharges of organic carbon from eight contiguous small watersheds on the Atlantic Coastal Plain in Maryland for up to 24 yr. Six of these watersheds were second or third order with mixed-land-use, while two were first order (one completely forested and one highly dominated by cropland). These watersheds have perched aquifers, so all groundwater discharges as well as surface runoff were measured at V-notch weirs and flumes, which included volume-integrating flow-proportional samplers. Interannual variations in annual and seasonal precipitation during this study spanned approximately the range of 160 yr weather records in the region. Annual total organic carbon (TOC) area yields from the overall Rhode River watershed varied 8-fold, correlations with precipitation were highly significant, and a power function regression explained 54% of the variance in annual TOC fluxes. TOC fluxes were higher from upland forest than mixed land use, and highest from the cropland-dominated watershed. The fluxes from first order watersheds were more variable with precipitation. In the spring, TOC fluxes were highest and most correlated with precipitation, compared to other seasons. Precipitation volume also explained much of the variance in annual and spring TOC concentrations from upland forest and cropland, with concentrations three to five times higher in very wet years than in very dry years. Variation in winter and summer air temperature was correlated with TOC concentrations from forested watersheds, and linear regressions explained 19 to 42% of the variance in TOC. A regression model was used to construct graphical and tabular summaries. Particulate organic carbon and dissolved organic carbon (DOC) concentrations and the ratio of DOC to TOC were highly correlated with water discharge for a second order, mixed land use watershed, and power function regressions explained 21 to 43% of the variance. For the first order, single-land-use watersheds the ratio of DOC to TOC was also highly correlated with discharge.

Keywords: air temperature, dissolved organic carbon, particulate organic carbon, precipitation, watershed, weather effects

1. Introduction

Increased inputs of nitrogen, phosphorus, and organic carbon have led to eutrophication of estuaries and coastal waters throughout the world (Correll, 1998; Degens *et al.*, 1991; Nixon, 1995). In the case of Chesapeake Bay, these increased inputs have brought about excessive plankton production (Boynton *et al.*, 1995; Malone *et al.*, 1986, 1988) and the increased extent and duration of hypoxic bottom waters (Taft *et al.*, 1980; Officer *et al.*, 1984). Similar eutrophication effects have also

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been observed on the Rhode River, a small tributary subestuary of the Chesapeake (Gallegos *et al*., 1992, 1997; Jordan *et al*., 1991a, b).

The organic carbon pools which control the demand for dissolved oxygen in Chesapeake Bay and other coastal waters come from three primary sources: (a) autochthonous (endogenous) primary production, (b) allochthonous inputs from the watershed, and (c) point source discharges of materials such as sewage effluents. In the Neuse River estuary in North Carolina, dissolved oxygen demand is sometimes dominated by autochthonous organic carbon sources, but at other times by allochthonous sources (Paerl *et al*., 1998). The Hudson River estuary in New York is heterotrophic and the majority of the organic carbon is allochthonous (Howarth *et al*., 1991, 1992). In Chesapeake Bay both dissolved (DOC) and particulate (POC) forms of organic carbon decline in concentration as one moves down the axis of the bay (Fisher *et al*., 1998).

Much research on organic carbon transport by major rivers has been oriented toward understanding overall land inputs to coastal waters and the oceans (e.g. Degens *et al*., 1991; Hope *et al*., 1994; Mulholland and Watts, 1982). A long history of complementary research on small watersheds, especially forested watersheds, has been more oriented to understanding sources and transport mechanisms for both POC and DOC in various parts of the world. Small watersheds are usually better understood than major river basins with respect to vegetative cover, land use, topography, soils, and climate. The Rhode River watershed falls into the small watershed category.

Quite a few studies have reported TOC fluxes for small forested watersheds, but many studies only reported DOC concentrations or fluxes (e.g. Ford and Naiman, 1989; Grip *et al*., 1994; Hedin *et al*., 1995; Newbold *et al*., 1995). Only a few studies of cropland have reported TOC fluxes (e.g. Jordan *et al*., 1997a, b) and not many even report DOC concentrations (e.g. Rutherford and Hynes, 1987), leaving an important information gap on small watersheds. The literature coverage for TOC fluxes from pasture and grazed watersheds is more comprehensive (e.g. Chichester *et al*., 1979; Jordan *et al*., 1997a, b; Nelson *et al*., 1996; Owens *et al*., 1983, 1989; Schepers and Francis, 1982; Smith *et al*., 1996).

In this study we have sampled the discharges of water and organic carbon from eight contiguous, first, second and third order subwatersheds of the Rhode River in Maryland, U.S.A., for up to 24 yr. These had different land use but similar weather, soils, geology, and hydrology. The watersheds were continuously monitored for discharge with V-notch weirs and broad-crested flumes, which included volume-integrating flow-proportional samplers. It was our objective to analyze the effects of variations in mean annual and seasonal precipitation and air temperature on discharges of total organic carbon (TOC) and the relative proportions of DOC and POC from forested, cropped, and mixed land use watersheds on the inner mid-Atlantic Coastal Plain of North America.

2. Methods

2.1. Site Description

The watersheds studied are all subwatersheds of the Rhode River (38°51′N, 76°32′W), a tidal tributary to the Chesapeake Bay in Maryland, U.S.A. The watershed is within the inner Atlantic Coastal Plain, a region which characteristically has highly erodible soils and frequent intense precipitation events, especially in the spring and summer. Watershed elevations range from 0 to 63 m. The watershed has sedimentary soils from the Pleistocene Talbot formation at low elevations on the eastern part of the watershed, Eocene Nanjemoy formation soils at low elevations further west, Miocene Calvert formation soils at intermediate elevations, and Pleistocene Sunderland formation soils at the highest elevations. The soils are fine sandy loams, and the mineralogy of the soils is fairly uniform, with a high level of montmorillonite and quartz, intermediate levels of illite and kaolinite, and low levels of gibbsite, chlorite, potassium feldspar, and plagioclase (Correll *et al.*, 1984). The soils have high moisture capacity, but relatively low infiltration rates, so that intense storms generate overland storm flows. However, about 65 to 75% of annual water discharge is via groundwater. Bedrock is about 1000 m below the surface, but the Marlboro Clay layer forms an effective aquiclude slightly above sea level throughout the watershed (Chirlin and Schaffner, 1977). Each subwatershed has a perched aquifer so that overland storm flows, interflow, and groundwater discharges all move to the channel draining each subwatershed. The overall Rhode River watershed has an area of 3332 ha, and the slopes of the watersheds average between 5 and 9% (Correll, 1977). The study subwatersheds ranged in size from 6 to 1157 ha and differed in land use (Table I). The two smallest, first order watersheds were studied because one was completely vegetated with mature hardwood forest and the other was primarily row-cropped. One second order watershed (#120) was also forested, but much of this watershed was composed of low elevation wetlands. The other watersheds were drained by second and third order streams and had mixed land use. The total area of the eight subwatersheds was 2050 ha or 62% of the total area of the Rhode River watershed. For more detailed descriptions of the site see Correll (1977, 1981) and Correll and Dixon (1980).

2.2. Sampling and Sample Analysis

Beginning in 1975, discharges from subwatersheds 101, 102, 103, 108, 109 and 110 (Table I) were measured with sharp-crested V-notch weirs, whose foundations were in contact with the Marlboro Clay aquiclude (Correll, 1977). All of these weirs were 120° notches, and each weir had an instrument building and a stilling well. Depths were measured to the nearest 0.3 mm with floats and counterweights and were recorded every 5 min for subwatersheds 101, 109 and 110 and every 15 min for subwatersheds 102, 103, and 108. Until the summer of 1996, Stevens model 61R flow meters actuated the sampling of an aliquot once every 154 m^3

of flow on the second order streams and once every 77 m^3 of flow on the first order streams. Beginning in the summer of 1996, Cambell Scientific data loggers (model CR-10) were used to control volume-integrated sampling. Samples were composited and collected weekly.

Subwatersheds 119 and 120 (Table I) were tidally influenced at the location where discharges were measured. Concrete 3.6 and 2.3 m-wide broad-crested tidal flumes (for watersheds 119 and 120, respectively) with a shallow V-shaped sill were equipped with custom tide gauges, electromagnetic current meters (Marsh-McBirney, model 711), and electronic interfaces which computed water flux and integrated it over time (Correll, 1981). The current meter sensor was mechanically held in the middle of the water column by a linkage to the tide gauge. Water samples, whose volumes were proportional to water flux, were taken every 30 min. These samples were combined to produce volume-integrated (flow-weighted) samples for one week periods as in the case of the V-notch weirs. Incoming and outgoing water samples were combined in separate containers.

The volume-integrated composite samples from the weirs and tidal flumes were collected from the beginning of 1975 through the spring of 1998. These integrated samples were preserved with sulfuric acid and were only analyzed for TOC. However, spot samples of stream water were also collected from the subwatersheds at various discharges and different times of year. We used these data to characterize the concentrations of POC and DOC as functions of discharge rate and season. Aliquots of spot samples were filtered through prewashed Millipore membrane filters (0.45 μm pore size) prior to analysis for DOC.

TOC was calculated as the difference between TOC and DOC concentrations. Organic carbon was analyzed by drying samples at 60 °C, followed by reaction with potassium dichromate in 67% sulfuric acid at 100 °C for 3 hr (Maciolek, 1962). Organic carbon was calculated from the amount of unreacted dichromate measured colorimetrically (Maciolek, 1962; Gaudy and Ramanathan, 1964).

Rainfall volume and air temperature data were obtained from the Center's weather station, located on watershed 101 (Higman and Correll, 1982 and subsequent data). All of the study area was within six km of the weather station. Rainfall volumes were measured with standard manual rainfall gauges and with a Belfort weighing gauge. Air temperatures were recorded with maximum/minimum mercury thermometers and with a Belfort recording hygrothermograph.

2.3. DATA PREPARATION

Weir discharges and rain volumes were summed, and mean daily air temperatures were averaged for watershed weeks (which normally began on Monday) and seasons, which were winter (December, January, February), spring (March, April, May), summer (June, July, August), and fall (September, October, November). Watershed years began with December. Discharge volumes were multiplied by volume-integrated concentrations to obtain weekly fluxes of organic carbon. Sea-

TABLE I

Characteristics of Rhode River subwatersheds. The Rhode River watershed is located at 38°51′N, 76°32′W

Water-shed	Stream order	Area[a] (ha)	Land use[a]				
			% Forest	% Row crops	% Pasture and hay fields	% Residential	% Old fields
101	2	226	38	10	27	6	19
102	2	192	47	18	22	6	7
103	2	253	63	2	16	5	14
108	2	150	39	24	20	3	14
109	1	16.3	36	64	0	0	0
110	1	6.3	100	0	0	0	0
119	3	1157	47	22	9	8	14
120	2	72	100	0	0	0	0

[a] Correll, 1977.

sonal and annual volume-weighted mean concentrations were calculated by summing weekly fluxes, then dividing by summed water discharges. Mean Rhode River watershed discharge data from the study watersheds (Table I) were weighted by area and are, for convenience, referred to as Rhode River discharges or overall watershed discharges.

When flow was too low to obtain an integrated sample for analysis, spot samples were analyzed. From 5 to 10% of the water discharge data for any given weir were missing due to equipment failures. When no significant precipitation occurred during the data gap, these data were estimated by interpolation of data from the same weir. When storm events occurred during the data gap, these data were estimated by correlation with discharge data from the watershed with the most similar organic carbon discharge behavior.

The mean and range of annual and seasonal precipitation observed during this study were put into perspective by comparison with a longer-term record. Higman and Correll (1982) summarized precipitation data collected from 1817 to 1977. Data for 1967 to 1977 were from our research center. Data from 1857 to 1967 were from the U.S. Naval Academy in Annapolis, MD. Data from 1817 to 1856 were from U.S. Army Fort Severn (on the Severn River near Annapolis). Gaps in the Naval Academy data were filled with data from Fort Severn. All three sites are on the upper western shore of Cheaspeake Bay within 20 km of each other. At the times of data collection all were fairly small towns, thus minimizing possible ‘heat island’ effects.

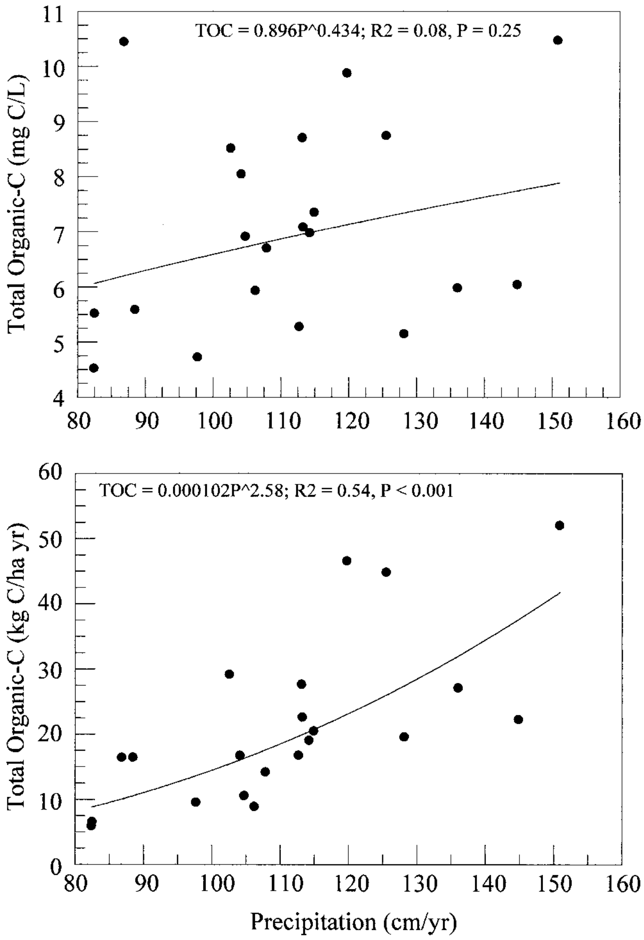

Figure 1. Variation in mean annual TOC concentration and flux with precipitation volume for the area-weighted, overall Rhode River watershed.

3. Results

3.1. Total organic carbon fluxes and concentrations

3.1.1. *Annual*

Mean annual fluxes of TOC were highest from the cropland-dominated watershed (#109), intermediate for the forest watershed (#110), and lowest for the area-weighted overall Rhode River watershed (Table II). TOC annual fluxes from the Rhode River watershed varied over 8-fold, but the range was much smaller than the ranges for the two small, single-land-use watersheds. TOC fluxes increased with precipitation volume, and the best regression fits to the data were power functions (highest R^2, Figures 1–3). Variation in precipitation explained from 54 to 66% of the variation in annual TOC fluxes and all were highly significant regressions.

TABLE II

Total organic carbon flow-weighted mean concentrations (mg C L^{-1}) and fluxes (kg C ha^{-1}) from Rhode River watershed (area-weighted mean of all watersheds shown on Table I) and subwatersheds 109 (crops) and 110 (forest). Values are means ± 1 SD. Values with a superscript 1 or 2 in common were different at $P < 0.05$, those with a superscript 3 or 4 were different at $P < 0.01$, as determined by paired *T*-tests. N is the number of years of data

Watershed	N	Concentration	Range	Flux	Range
A. Annual					
Crops	20	13.20 ± 9.48^{3}	(3.18–29.6)	35.30±34.2	(3.590–135)
Forest	20	12.60 ± 4.62^{4}	(4.72–24.5)	26.60±19.5	(1.660–73.9)
Rhode River	21	$7.08 \pm 1.83^{3,4}$	(4.53–10.5)	21.60±12.5	(5.990–52.1)
B. Winter					
Crops	22	13.20±20.3	(3.05–94.5)	9.92±9.38	(1.250–36.7)
Forest	22	8.33 ± 2.99^{3}	(3.58–14.5)	5.52±5.92	(0.107–25.9)
Rhode River	24	5.11 ± 1.26^{3}	(3.29–7.28)	5.47±2.78	(1.390–11.0)
C. Spring					
Crops	23	9.20±8.34	(2.38–38.8)	13.90±22.5	(0.650–108)
Forest	22	11.00 ± 4.10^{3}	(5.11–20.1)	12.30±9.69	(0.860–35.8)
Rhode River	24	6.25 ± 2.35^{3}	(2.31–11.9)	8.71±7.18	(1.750–29.7)
D. Summer					
Crops	21	21.80±21.9	(2.88–78.2)	9.92±21.8	(0.001–105)
Forest	21	16.60±9.70	(2.67–33.0)	5.47±9.37	(0.000–39.0)
Rhode River	22	12.80±4.24	(6.27–24.4)	4.62±4.94	(0.570–22.27)
E. Fall					
Crops	21	8.73 ± 4.39^{1}	(3.55–17.7)	1.83±2.25	(0.003–8.31)
Forest	22	$15.00 \pm 6.02^{1,3}$	(8.61–29.6)	3.58±8.67	(0.000–39.9)
Rhode River	23	9.40 ± 2.83^{3}	(4.41–17.4)	3.76±6.49	(0.230–31.0)

TOC fluxes increased more rapidly with precipitation for the small crop and upland forest watersheds (Figures 2–3).

Precipitation volume was also related to TOC concentration (Figures 1–3). This relationship was not significant for the overall Rhode River watershed but was significant and explained 38 to 45% of the variation in annual mean TOC concentrations for the small cropland and forest watersheds (Figures 2–3). In a very wet

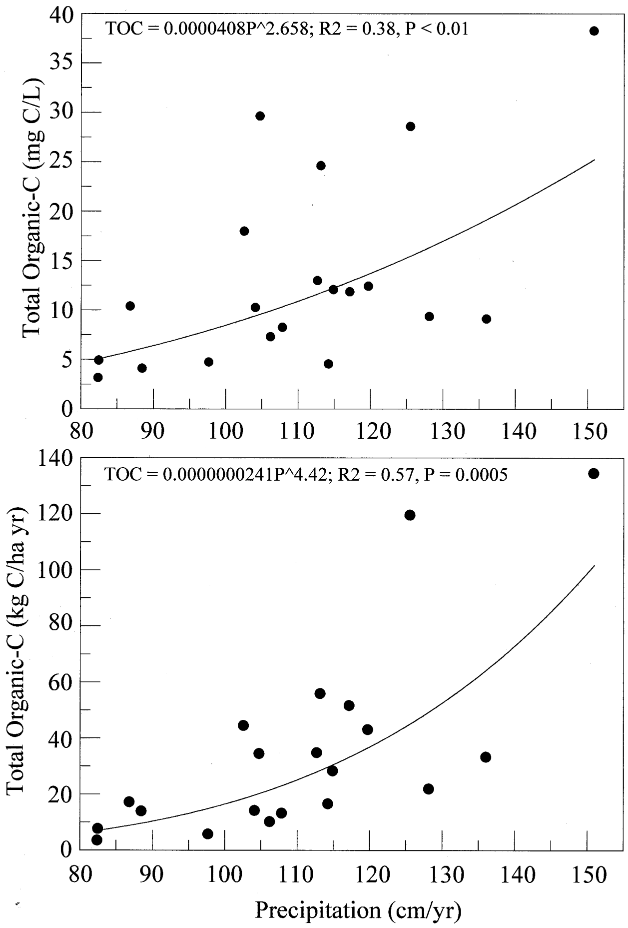

Figure 2. Variation in mean annual TOC concentration and flux with precipitation volume for the cropland watershed (#109, Table I).

year the TOC concentrations from the cropland and forest watersheds were about five and three times higher than for a very dry year, respectively. The mean annual TOC concentration for the Rhode River was about seven mg C L^{-1} (Table II), and this was significantly lower than the TOC concentrations from the cropland and forest watersheds. Although the regression of mean annual TOC concentration versus precipitation from the area-weighted mean watershed was not significant, a separate regression for the area-weighted mean of four combined second order watersheds (821 ha) was significant, and the mean annual TOC concentration from these watersheds more than doubled from a very dry to a very wet year.

The regressions of TOC flux versus precipitation (Table IV), all of which were highly significant, were used to calculate TOC fluxes for a series of precipitation scenarios for the Rhode River and the two small single-land-use watersheds

TABLE III

Annual and seasonal total organic carbon (TOC) fluxes (kg C ha^{-1} time period^{-1}) from Rhode River watersheds as a function of precipitation (P) in cm per time period. Flux values calculated from regressions in Table IV

Precipitation	Area-weighted watershed mean	Crops watershed #109	Forest watershed #110
A. Annual			
–2 SD (64.4 cm)	4.74	2.38	1.52
–1 SD (86.2 cm)	10.1	8.61	5.63
Mean (108.0 cm)	18.0	23.3	15.4
+1 SD (129.8 cm)	28.9	52.6	35.2
+2 SD (151.6 cm)	43.1	104	70.6
B. Winter			
–2 SD (10.22 cm)	1.95	2.36	0.524
–1 SD (17.41 cm)	3.40	4.32	1.52
Mean (24.6 cm)	4.87	6.38	3.04
+1 SD (31.79 cm)	6.35	8.52	5.07
+2 SD (38.98 cm)	7.85	10.7	7.63
C. Spring			
–2 SD (10.94 cm)	2.22	0.916	1.25
–1 SD (19.47 cm)	3.68	2.21	2.79
Mean (28.0 cm)	6.10	5.31	6.21
+1 SD (36.53 cm)	10.1	12.8	13.8
+2 SD (45.06 cm)	16.8	30.8	30.9
D. Summer			
–2 SD (8.40 cm)	0.606	0.137	0.0749
–1 SD (19.9 cm)	1.38	0.585	0.366
Mean (31.4 cm)	3.15	2.49	1.79
+1 SD (42.9 cm)	7.19	10.6	8.75
+2 SD (54.4 cm)	16.4	45.2	42.8
E. Fall			
–2 SD (6.64 cm)	0.163	0.0150	0.0259
–1 SD (15.57 cm)	0.398	0.0770	0.0996
Mean (24.5 cm)	0.973	0.395	0.384
+1 SD (33.43 cm)	2.38	2.02	1.48
+2 SD (42.36 cm)	5.80	10.4	5.69

TABLE IV

Regressions of total organic carbon fluxes (TOC in kg C ha^{-1} time period) and mean TOC concentrations (mg C L^{-1}) from Rhode River watersheds versus precipitation volumes (P = cm time $period^{-1}$). Crop watershed = #109, Forest watershed = #110 (Table I)

Watershed	Regression		R^2	P
A. Annual				
Area-weighted mean	TOC flux	$= 0.000102\ (P)^{2.58}$	0.54	<0.001
	TOC conc.	$= 0.896\ (P)^{0.434}$	0.08	0.25
Crop	TOC flux	$= 0.0000000241\ (P)^{4.42}$	0.57	0.0005
	TOC conc.	$= 0.0000408\ (P)^{2.66}$	0.38	<0.01
Forest	TOC flux	$= 0.0000000122\ (P)^{4.48}$	0.66	<0.00001
	TOC conc.	$= 0.0118\ (P)^{1.46}$	0.45	<0.001
B. Winter				
Area-weighted mean	TOC flux	$= 0.174\ (P)^{1.04}$	0.44	<0.001
	TOC conc.	$= 0.0150\ (P) + 4.740.01$	0.63	
Crop	TOC flux	$= 0.171\ (P)^{1.13}$	0.22	0.30
	TOC conc.	$= -0.256\ (P) + 19.90.02$	0.54	
Forest	TOC flux	$= 0.00502\ (P)^{2.00}$	0.40	0.08
	TOC conc.	$= 1.70\ (P)^{0.472}$	0.23	0.03
C. Spring				
Area-weighted mean	TOC flux	$= 1.16\ (e)^{0.0593(P)}$	0.71	<0.00001
	TOC conc.	$= 0.0748\ (P) + 4.030.10$	0.14	
Crop	TOC flux	$= 0.297\ (e)^{0.103(P)}$	0.77	<0.0005
	TOC conc.	$= 1.09\ (e)^{0.0612(P)}$	0.70	<0.00005
Forest	TOC flux	$= 0.447\ (e)^{0.0940(P)}$	0.72	<0.00001
	TOC conc.	$= 0.908\ (P)^{0.718}$	0.39	<0.01
D. Summer				
Area-weighted mean	TOC flux	$= 0.332\ (e)^{0.0717(P)}$	0.44	<0.001
	TOC conc.	$= 7.32\ (P)^{0.0151}$	0.02	0.76
Crop	TOC flux	$= 0.0477\ (e)^{0.126(P)}$	0.22	<0.005
	TOC conc.	$= 0.157\ (P)^{1.34}$	0.18	0.15
Forest	TOC flux	$= 0.0235\ (e)^{0.138(P)}$	0.42	<0.00005
	TOC conc.	$= 0.624\ (P) - 1.72$	0.41	<0.005
E. Fall				
Area-weighted mean	TOC flux	$= 0.0840\ (e)^{0.100(P)}$	0.45	<0.001
	TOC conc.	$= -0.0244\ (P) + 10.1$	0.01	0.74
Crop	TOC flux	$= 0.00446\ (e)^{0.183(P)}$	0.63	<0.0005
	TOC conc.	$= 0.162\ (P) + 4.31$	0.08	0.20
Forest	TOC flux	$= 0.00949\ (e)^{0.151(P)}$	0.50	0.002
	TOC conc.	$= 0.352\ (P) + 4.51$	0.22	<0.05

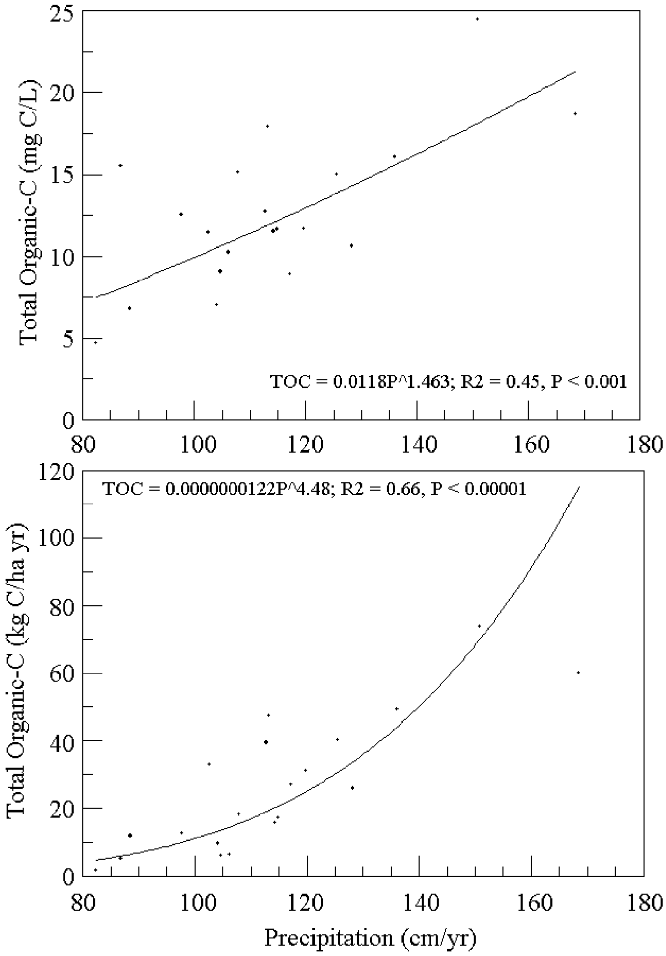

Figure 3. Variation in mean annual TOC concentration and flux with precipitation volume for the upland forest watershed (#110, Table I).

(Table III). For convenience we used the long-term (160 yr) mean precipitation depths and plus and minus one and two standard deviations from the mean. These depths correspond to very dry, dry, average, wet, and very wet years. In dry and very dry years the TOC fluxes from upland cropland and forest were below the average for the overall Rhode River watershed, while in wet and very wet years the reverse was found (Table IIIA). In wet and very wet years cropland had about 50% higher TOC fluxes than upland forest.

3.1.2. *Seasonal*

The highest TOC fluxes were observed in the spring. The highest TOC fluxes among the three watersheds in the winter, spring, and summer were from the cro-

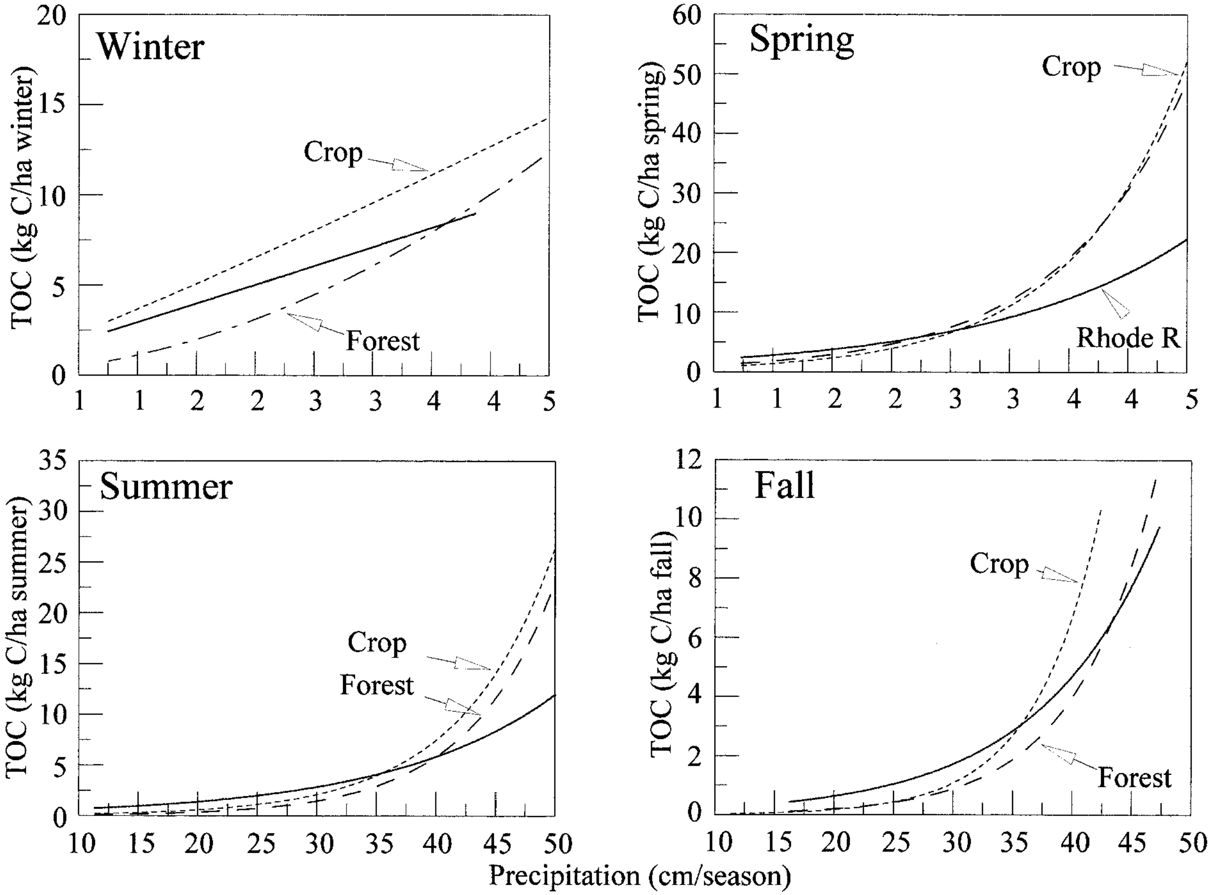

Figure 4. Seasonal TOC fluxes as functions of precipitation volume. Curves were calculated with regressions from Table IV. Solid line = area-weighted overall Rhode River watershed, dashed line = cropland watershed #109, broken line = upland forest watershed #110 (Table I).

pland (Table II). TOC fluxes from upland forest were higher than from the overall Rhode River watershed, except in the fall. The best regression fits (highest R^2) for TOC flux versus precipitation were power functions in the winter and exponential functions in the other seasons (Table IV). All regressions for spring, summer, and fall TOC fluxes were significant, but in the winter, only the regression for the area-weighted watershed was significant. These seasonal TOC flux regressions were used to visualize the effects of interannual variations in precipitation (Figure 4). In spring, summer, and fall the curves for the cropland and upland forest start out, at low precipitation levels, below the curve for the overall watershed, but cross over to higher values than those of the overall watershed at high precipitation levels (Figure 4). In the winter the pattern was different, but the regressions for the cropland and forest were not significant. The highest seasonal TOC fluxes were in very wet springs and summers (Table III). For the overall 3332 ha Rhode River watershed in a very wet spring or summer, the TOC flux to the estuary was 55.8 and 54.4 t, respectively. Fluxes of TOC from the cropland and upland forest watersheds increased with increasing precipitation (4.3- and 4.9-fold, respectively) from wet to very wet summers.

Mean TOC concentrations were significantly higher from upland forest than from the overall watershed in the winter, spring, and fall; and forest TOC concentrations were significantly higher than from cropland in the fall (Table II). Seasonal mean TOC concentrations were less variable than TOC fluxes but still exhibited a wide interannual range. In some cases, seasonal TOC concentrations did not increase significantly with precipitation (Table IV). However, TOC concentrations increased significantly with precipitation for the cropland watershed in the spring and for the upland forest in all four seasons (Table IV). Three of the four second order watersheds also had significant increases in TOC concentrations with precipitation level in the spring, but none of the large watersheds had significant changes in TOC concentrations with precipitation level in the winter, summer, or fall.

3.2. Air temperature and total organic carbon concentration

Mean annual and seasonal air temperatures varied widely during this study and might be expected to result in variations in TOC concentrations. No regressions were significant for air temperature versus mean TOC concentration for spring, fall or annual periods for any of the studied watersheds. However, for the winter and summer several regressions were significant, indicating increases in concentration with increasing temperature (Table V). The best fits were linear regressions, and the watersheds for which there were significant regressions were completely or primarily forested (Tables I and V). The extremes in winter air temperature in this study were –3.76 °C in 1977 and +6.55 °C in 1997. These winter temperatures correspond to TOC concentrations of 4.02 and 11.4 mg C L^{-1}, respectively, for watershed 110 and to 2.39 and 5.57 mg C L^{-1}, respectively, for watershed 120. The extremes in summer air temperature in this study were 20.05 °C in 1976 and

TABLE V

Regressions of mean TOC concentrations (mg C L^{-1}) from Rhode River watersheds versus mean air temperatures (T). For watershed characteristics see Table I. Only regressions significant at the 0.05 level or less are included and no TOC flux regressions were significant

Watershed number	Regression		R^2	P
A. Annual (none significant)				
B. Winter				
110	TOC conc.	= 0.714 (T) + 6.71	0.19	<0.05
120	TOC conc.	= 0.308 (T) + 3.55	0.42	0.02
C. Spring (none significant)				
D. Summer				
103	TOC conc.	= 2.870 (T) – 50.5	0.20	0.04
120	TOC conc.	= 1.820 (T) – 32.2	0.40	0.04
E. Fall (none significant)				

25.61 °C in 1996. These summer temperatures correspond to TOC concentrations of 7.04 and 23.0 mg C L^{-1}, respectively, for watershed 103 and to 4.29 and 14.4 mg C L^{-1}, respectively, for watershed 120.

3.3. Changes in DOC and POC with discharge

The concentrations and ratios of DOC and POC also changed significantly with discharge. Our analyses concentrated on the two small first order watersheds and the second order, mixed-land-use watershed 101, because many more data were taken there than for the other second and third order watersheds. In most cases power function regressions fit the data best. As discharge rate increased, DOC concentration increased, but POC concentrations increased much more rapidly, and the ratio of DOC to TOC rapidly decreased. Water discharge rates for watershed 101 explained from 21 to 43% of the variability in DOC and POC concentrations and percent TOC present as DOC, and all of these regressions were highly significant (Table VI). For the cropland watershed, water discharge explained 47% of the variability in POC, but DOC concentrations were not significantly correlated with discharge (Table VI). However, discharge was highly correlated with percentage

TABLE VI

Regressions of DOC and POC concentrations (mg C L^{-1}) and percent of TOC present as DOC from Rhode River watersheds versus instantaneous water discharge (Q = L ha^{-1} sec^{-1}). Mixed land use watershed = #101, cropland watershed = #109, forest watershed = #110 (Table I)

Watershed	Regression		N	R^2	P
Mixed use	DOC	$= 2.27Q^{0.477}$	219	0.34	<0.00001
	POC	$= 8.65Q^{0.963}$		0.43	<0.00001
	%DOC	$= 26.2Q^{-0.486}$		0.21	<0.00001
Cropland	DOC	$= 2.03Q^{0.106}$	100	0.03	0.58
	POC	$= 3.29Q^{0.982}$		0.47	<0.001
	%DOC	$= 33.3Q^{-0.674}$		0.52	<0.00001
Forest	DOC	$= 6.17Q^{0.0750}$	68	0.02	0.06
	POC	$= 3.13Q^{0.340}$		0.10	0.24
	%DOC	$= -1.55Q + 66.3$		0.16	0.0005

of TOC present as DOC from the cropland watershed (Figure 5). For the upland forest watershed, only the proportion of TOC discharged as DOC was significantly correlated with discharge, and this relationship only explained 16% of the variance. For watershed 101, when data were segregated by season, the regressions were about the same as when all data were pooled.

4. Discussion

Interest in watershed exports of organic carbon usually stems from an interest in the role of organic carbon as a substrate for microbial metabolism in receiving waters (streams, major rivers, estuaries, coastal waters, and oceans). Organic carbon is not inert. When DOC and POC are released into aquatic systems, microbial communities use these materials as an energy source. The result is a ‘spiraling’ of the carbon as it moves down stream (Newbold *et al*., 1982). Therefore, concentrations of DOC and POC often decline as water moves downstream, as in the Amazon River (Richey *et al*., 1990). In Chesapeake Bay both DOC and POC concentrations declined along the downstream axis (Fisher *et al*., 1998). The Hudson River estuary was highly heterotrophic and metabolized over 60% of the watershed TOC inputs (Howarth *et al*., 1992). At a much smaller scale, we found the same pattern for the Rhode River watershed. TOC concentrations and fluxes were much lower for the overall watershed than for the small headwater subwatersheds (Table II) except

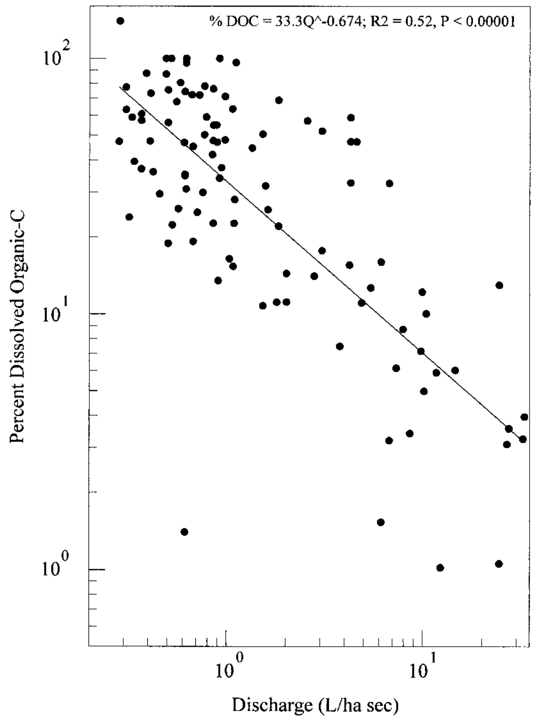

Figure 5. Percent of TOC present as DOC in spot samples from cropland watershed #109 as a function of instantaneous water discharge rate.

in dry and very dry years, when the reverse was found (Table III, Figure 4). This may have been the result of consumption of TOC in the larger stream corridors in wetter seasons and years and the release of TOC from these stream corridors in drier seasons and years. Thus, the export rates of TOC from the overall Rhode River watershed seem to be somewhat buffered from precipitation effects that occur in the headwaters subwatersheds. The lack of correlation for TOC concentrations in annual discharges from the overall watershed with precipitation seems to have been the result of offsetting behaviors for the component second and third order subwatersheds, which individually had higher correlations of TOC concentrations with precipitation.

The form in which organic carbon is exported from watersheds is also dynamic. The proportion of DOC in the TOC decreases rapidly with rate of water discharge (Table VI, Figure 5), making it difficult to measure separate fluxes of DOC and POC (Table VI, Figure 5; Martins and Probst, 1991; Richey *et al.*, 1990). The percent of organic carbon in suspended particulates also declines as discharge increases, due to the coarser, more mineral nature of particulates during larger storm events (Ittekkot and Laane, 1991).

We found the highest TOC fluxes from cropland rather than upland forest (Table II, Figure 4). This might be somewhat surprising, since the top one cm of soil in

TABLE VII

Comparisons of mean organic carbon concentrations (mg C L^{-1}) and fluxes (kg C ha^{-1} yr^{-1}) among watersheds

Watershed	TOC concentration	TOC flux	Percent DOC	Years studied	Literature source
A. Forested watersheds					
Icacos, Puerto Rico	3.9	132	65	3	McDowell *et al*., 1994
Sonadora, Puerto Rico	5.7	82	70	3	McDowell *et al*., 1994
Toronja, Puerto Rico	2.5	39	74	3	McDowell *et al*., 1994
Bear Brook, New Hampshire	–	3.85	68	1	Meyer *et al*., 1981
First Choice Creek, Quebec	–	30.7	82	1	Naiman, 1982
Beaver Creek, Quebec	–	518	93	1	Naiman, 1982
Muskrat River, Quebec	–	134	93	1	Naiman, 1982
Matamek River, Quebec	–	104	94	1	Naiman, 1982
Moisie River, Quebec	–	47.4	90	1	Naiman, 1982
Coweeta Control, North Carolina	–	21.2	71	12	Swank and Waide, 1988
Coshocton, Ohio	14.8	38.0	–	3	Owens *et al*., 1983
#301, Maryland	3.6	16.3	–	1	Jordan *et al*., 1997a
#401, Maryland	4.2	20.5	–	1	Jordan *et al*., 1997b
#110, Maryland	12.6	26.6	–	20	This study
B. Cropland watersheds (>50% crops)					
#304, Maryland	7.7	27.7	–	1	Jordan *et al*., 1997a
#305, Maryland	8.7	31.2	–	1	Jordan *et al*., 1997a
#306, Maryland	11.2	39.7	–	1	Jordan *et al*., 1997a
#310, Maryland	9.4	34.4	–	1	Jordan *et al*., 1997a
#404, Maryland	4.4	14.9	–	1	Jordan *et al*., 1997b
#408, Maryland	5.2	15.6	–	1	Jordan *et al*., 1997b
#109, Maryland	13.2	35.3	–	20	This study
C. Large complex watersheds					
Tropical rivers					
Amazon River, S.A.	4.8	85	62	3	Richey *et al*., 1990
Orinoco River, S.A.	4.6	51.5	70	2	Depetris and Paolini, 1991
Parana River, S.A.	11.4	71.9	82	2	Depetris and Paolini, 1991
Zaire River, Africa	9.6	37	89	–	Martins and Probst, 1991
Niger River, Africa	7.2	9.0	49	–	Martins and Probst, 1991
Orange River, Africa	3.2	0.40	72	–	Martins and Probst, 1991
Gambia River, Africa	3.5	4.0	69	–	Martins and Probst, 1991

TABLE VII
(continued)

Watershed	TOC concentration	TOC flux	Percent DOC	Years studied	Literature source
C. Large complex watersheds					
North temperate rivers					
Hudson River, New York	–	15.3	31	[a]	Howarth *et al*., 1991
North Dvina, Europe	–	42.2	96	10	Kempe *et al*., 1991
Rhone/Tarascon, Europe	–	50.5	67	4	Kempe *et al*., 1991
Po River, Europe	–	29.3	70	4	Kempe *et al*., 1991
St. Laurence River, N.A.	5.4	18.7	42	–	Kempe *et al*., 1991
Mississippi River, N.A.	7.1	36.1	80	–	Telang *et al*., 1991
Arctic rivers					
Mackenzie River, N.A.	7.7	31.2	42	3	Telang *et al*., 1991
Yukon River, N.A.	11.0	29.7	87	–	Telang *et al*., 1991
Lena River, Siberia	9.5	50.6	–	–	Telang *et al*., 1991
Yenisei River, Siberia	7.4	41.3	–	–	Telang *et al*., 1991
Rhode River, Maryland	7.1	21.6	–	21	This study

[a] These data derived from a watershed model.

the forest contained 4.3% organic carbon and the soil surface was covered with leaf litter, while the soil in the cropland only contained 0.87% organic carbon and the surface only had sparse litter (Correll, 1982). However, soil erosion rates from the cropland were much higher than from the forest, apparently more than compensating for the lower organic carbon content of the soils. One would also suspect that the composition of the TOC discharged from the cropland was more refractory than that discharged from the forest, since there is little surface litter on the cropland. Each watershed had its highest mean TOC flux in the spring and the lowest flux in the fall.

The highest concentrations of TOC in discharges from each of the watersheds were in the summer (Table II), and the lowest concentrations from the overall watershed and upland forest were in the winter. For the cropland watershed, the lowest TOC concentrations were in the fall. Seasonality in TOC concentrations may have resulted from two factors. First, the intensity of storms in this region is highest in the summer and lowest in the winter, and soil erosion is a function of storm intensity. Second, biological activity in the decay and fragmentation of surface litter is temperature dependent. Both of these factors favor the highest TOC concentrations in the summer and the lowest in the winter.

Variation in seasonal mean air temperature had relatively little effect on TOC discharges, except for forested watersheds (Table V). This is puzzling but may reflect the effects of major human disturbance on the other watersheds. The effects of air temperature on ecosystem processing of organic carbon may have been obscured on nonforested watersheds.

What are the characteristics of these Rhode River watersheds and how do their TOC discharges compare with other watersheds in this region and other regions? The Rhode River watershed has fairly steep slopes (Table I) and highly erodible soils characteristic of this region of the inner Coastal Plain. The native vegetation is hardwood deciduous forest, and most stream corridors are lined with riparian forest. The cropland watershed (#109) was composed of about two-thirds cropland in continuous corn production and one-third hardwood deciduous riparian forest. This forest has been shown to be effective at intercepting nutrients and sediments from lateral surface and groundwater flows (Correll and Weller, 1989; Peterjohn and Correll, 1984). The riparian forest on this watershed could also be the source of some of the TOC discharged from this watershed. The upland forest watershed (#110) was completely forested and all but an upper fringe was old growth forest. Thus, this forested watershed provides a good measure of the dynamics of the natural vegetation of this region. The only human impact on this forest in the last 50 yr has been atmospheric deposition and air pollution; the site is downwind of the Baltimore/Washington urban corridor and receives high fluxes of acids and other materials from the atmosphere (Jordan *et al.*, 1995). The organic carbon and mineral nutrient content of the soils of these two small watersheds reflect their different histories (Correll, 1982; Vaithiyanathan and Correll, 1992). We compare our results from the forested watershed (#110) with those for 13 other forested watersheds (Table VII). Our TOC fluxes fall within the range from other sites. Two other sites in Maryland and the control site at Coweeta were somewhat lower and a site in Ohio was somewhat higher. Hope *et al.*, (1994) cites the mean TOC flux for six temperate forests as 43.2 kg C ha^{-1} yr^{-1} and the range as 26.6 to 61 kg C ha^{-1} yr^{-1}. Our forested watershed had a mean TOC flux at the lower end of this range and three of the forested sites in Table VII were lower. The range of annual TOC fluxes we observed for watershed 110 was 1.7 to 74 kg C ha^{-1} yr^{-1} (Table II), indicating the difficulties of comparisons among short-term data. Much higher TOC fluxes were reported for some tropical and northern latitude forests (Table VII).

The TOC flux from cropland watershed (#109) was similar to those from four other Coastal Plain sites in Maryland with a similar proportion of row crops but higher than the TOC fluxes from two otherwise similar sites in the Maryland Piedmont (#404 and #408). This may result from the higher infiltration rates and lower erosion rates in this part of the Piedmont (Jordan *et al.*, 1997c). We found essentially no published TOC fluxes for cropland watersheds, other than our own. Perhaps this is the result of a widespread perception that croplands are a major source of mineral nutrient discharges, but not of organic carbon discharge. Our results indicate the need for more data on TOC fluxes from cropland.

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