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Relating nutrient and herbicide fate with landscape features and characteristics of 15 subwatersheds in the Choptank River watershed

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ABSTRACT

Excess nutrients and agrochemicals from non-point sources contribute to water quality impairment in the Chesapeake Bay watershed and their loading rates are related to land use, agricultural practices, hydrology, and pollutant fate and transport processes. In this study, monthly baseflow stream samples from 15 agricultural subwatersheds of the Choptank River in Maryland USA (2005 to 2007) were characterized for nutrients, herbicides, and herbicide transformation products. High-resolution digital maps of land use and forested wetlands were derived from remote sensing imagery. Examination of landscape metrics and water quality data, partitioned according to hydrogeomorphic class, provided insight into the fate, delivery, and transport mechanisms associated with agricultural pollutants. Mean Nitrate-N concentrations (4.9 mg/L) were correlated positively with percent agriculture ($R^2 = 0.56$) and negatively with percent forest ($R^2 = 0.60$). Concentrations were greater ($p = 0.0001$) in the well-drained upland (WDU) hydrogeomorphic region than in poorly drained upland (PDU), reflecting increased denitrification and reduced agricultural land use intensity in the PDU landscape due to the prevalence of hydric soils. Atrazine and metolachlor concentrations (mean 0.29 μg/L and 0.19 μg/L) were also greater ($p = 0.0001$) in WDU subwatersheds than in PDU subwatersheds. Springtime herbicide concentrations exhibited a strong, positive correlation ($R^2 = 0.90$) with percent forest in the WDU subwatersheds but not in the PDU subwatersheds. In addition, forested riparian stream buffers in the WDU were more prevalent than in the PDU where forested patches are typically not located near streams, suggesting an alternative delivery mechanism whereby volatilized herbicides are captured by the riparian forest canopy and subsequently washed off during rainfall. Orthophosphate, CIAT (6-chloro-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine), CEAT (6-chloro-*N*-ethyl-1,3,5-triazine-2,4-diamine), and MESA (2-[(2-ethyl-6-methylphenyl) (2-methoxy-1-methylethyl)amino]-2-oxoethanesulfonic acid) were also analyzed. These findings will assist efforts in targeting implementation of conservation practices to the most environmentally-critical areas within watersheds to achieve water quality improvements in a cost-effective manner.

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1. Introduction

The Chesapeake Bay is the largest estuary in the United States. Located in the Mid-Atlantic region, its watershed spans 167,000 km^2 and is home to approximately 16 million people. Water quality and overall ecosystem health in the Chesapeake Bay have declined significantly since the 1960s, primarily as a result of nutrient enrichment leading to the depletion of O_2 in bottom waters during the summer (Kemp et al., 2005). Most notable has been the severe decline in populations of the native oyster species *Crassostrea virginica* and the disappearance of large areas of submerged aquatic vegetation (SAV) (Orth et al., 2006). Both oysters and SAV act as filters for sediments (Ulanowicz and Tuttle, 1992; Newell, 1988) and SAV serve as habitat for many diverse species including the blue crab *Callinectes sapidus*.

The State of Maryland, the Commonwealths of Virginia and Pennsylvania, and the District of Columbia signed an agreement in 2000 with goals designed to restore the health of the Chesapeake Bay

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(MDDNR, 2000). Agreement signees committed to a 40% reduction in controllable nutrient loads by 2010 and to a reduction of chemical contaminants to levels that result in no toxic or bioaccumulative impact on living resources. A watershed-based approach was recommended at that time for implementation of tributary strategies to protect water quality. Those goals were not achieved, and in 2010, to address United States Environmental Protection Agency (US EPA) Total Mean Daily Load (TMDL) limits for Chesapeake Bay tributaries, the state governments initiated a two-year milestone program for attaining water quality objectives. This followed the Presidential Executive Order 13508 of May 12, 2009 (Executive Order, 2009) which prioritized federal agency involvement in Chesapeake Bay restoration and recovery. To increase the effectiveness of watershed conservation efforts, a detailed analysis of site-specific landscape factors that contribute to non-point source pollution of local surface waters is needed.

Nutrient losses from agricultural land have been identified as a significant contributor to water quality impairment in the Chesapeake Bay with urban and suburban wastewater treatment and various land use practices contributing substantial loads of nitrogen (N) and phosphorus (P) (Fisher et al., 1998, 2006; Sprague et al., 2000). In addition, exposure to pesticide residues can negatively affect sensitive species of plants or animals already under stress from habitat degradation or poor water quality conditions (Preston, 2001). Achieving restoration goals in the Chesapeake Bay will require significant effort and innovation by the agricultural and urban communities as well as consideration of the effect of site-specific biophysical processes on pollutant transport and fate. In Maryland, agricultural conservation practices are promoted and cost-shared by state and federal programs, and some farmers are succeeding in reducing the loss of nutrient, pesticides, and sediment from their farms by improving nutrient management, planting cover crops, reducing tillage, improving infrastructure, and focusing on more sustainable crop management strategies. However, management of high-input cropping systems remains a considerable challenge to farmers who are interested in reducing the environmental impacts of farming. Effective resource-conserving agricultural practices must be identified and promoted on a large scale to reduce off-farm losses of nutrients and pesticides significantly. Successful modern farms will manage cropping systems in a way that is profitable, sustainable, and comfortable for both the farmer and the environment.

The Choptank River flows into the Chesapeake Bay from the Eastern Shore, draining a portion of the Delmarva Peninsula. Located within the Mid-Atlantic Coastal Plain physiographic region of the United States, it is an area with a long cultural and agricultural history (Fig. 1). The mouth of the river is an estuarine tidal embayment; 311 km^2 (15%) of the 2057 km^2 Choptank River basin is open water and home to crabs, oysters, and local watermen. The upland non-tidal reaches split into the Tuckahoe Creek to the west and the Upper Choptank to the east, draining a landscape comprised of forests and forested wetlands interspersed with productive farmland, with an ever-increasing degree of residential development. Since 1998, various segments of the Choptank River have been classified as "impaired waters" under the Federal Clean Water Act (MDE, 2004) due to fecal coliform, nutrients, and sediments. It also received low scores on the biotic integrity surveys conducted during the 2000–2002 Maryland Biological Stream Survey (MDDNR, 2008) and has recently exhibited a decline in the extent of submerged aquatic vegetation within the estuary.

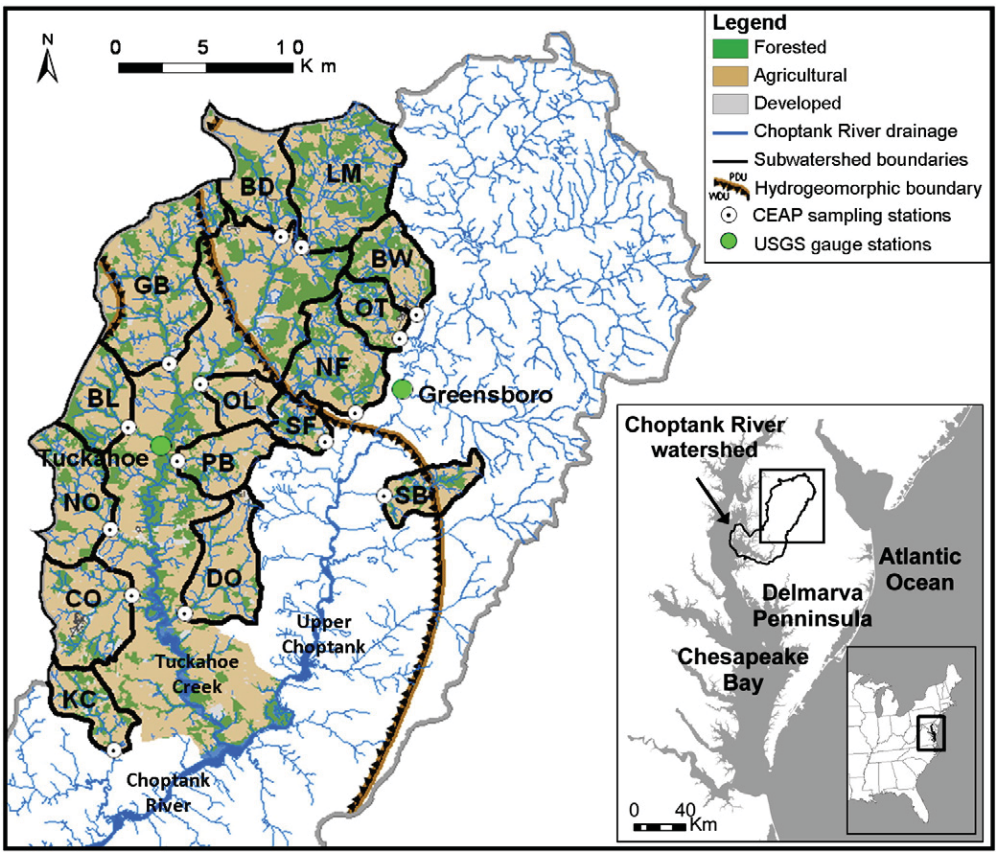

Fig. 1. Map of the Choptank River watershed and the 15 subwatershed sampling locations with associated landscape features. Hydrogeomorphic regions: PDU = poorly drained uplands; WDU = well-drained uplands. Subwatersheds: BD = Beaverdam; BL = Blockston; BW = Broadway; CO = Cordova; DO = Downes; GB = German; KC = Kittys Corner; LM = Long Marsh; NF = North Forge; NO = Norwich; PB = Piney; OL = Oakland; OT = Oldtown; SB = Spring; SF = South Forge. See Table 1 for more information on subwatershed characteristics.

The lower Choptank is impaired due to low dissolved oxygen and high nutrient levels, and since 1997 the mouth of the Choptank River has undergone an 85% decrease in SAV area (Orth et al., 1998). Prior to 1995, the river showed a long-term trend toward increasing nitrate concentrations (Fisher et al., 2006), after which agricultural loading of nitrogen in the Upper Choptank declined somewhat during the 1990s (Sprague et al., 2000). However, the upward trends for total N, total P, and nitrate continued after 2000 (Fisher et al., 2010). In the German Branch subwatershed of the Tuckahoe River, nitrogen concentrations have remained stable while baseflow orthophosphate concentrations have decreased by 28% following local targeted implementation of agricultural conservation practices (Sutton et al., 2010). A recent study of surface water quality in the Choptank estuary identified agriculture as the main source of N, while waste water treatment plants were implicated in P loading (Whitall et al., 2010). A seasonal spike in herbicide concentrations was also observed in the Choptank estuary following the springtime planting season.

Approximately 60% of land use in the Choptank River watershed is agricultural, with large acreages of corn (*Zea mays*), soybean (*Glycine max*), wheat (*Triticum aestivum*), and barley (*Hordeum vulgare*). Much of the grain production supports small- and medium-sized animal feeding operations (mostly poultry with some dairy and horse husbandry; USDA-NASS, 2006). Manure from poultry houses is routinely recycled as a fertilizer on agricultural production fields along with chemical fertilizer application. Soil phosphorus levels can be excessive in fields receiving long-term manure applications (Brock et al., 2007), and local soil nitrate concentrations routinely exceed 10 mg/L in shallow groundwater below agricultural fields (Staver and Brinsfield, 1998). Nitrogen loss from farmlands in the watershed tends to occur via leaching to groundwater during hydrologically active periods, particularly during the springtime planting season when summer row crops have not achieved full root development, and again during the cool fall and winter seasons when wet soil conditions promote leaching of residual soil nitrogen following the summer cropping season (Böhlke, 2002). Excess soil N accumulates as inorganic nitrogen (ammonium and nitrate) in the absence of significant crop uptake, and the nitrate is then subject to leaching (Staver and Brinsfield, 1998; Böhlke and Denver, 1995). Phosphorus, in contrast, adheres to soils and tends to move primarily via surface runoff and soil erosion, but also through vadose-zone preferential flow pathways in soils with excessive phosphorus content (Kleinman et al., 2009). Non-agricultural sources of pesticides and nutrients to the Choptank (Fisher et al., 2006; Sprague et al., 2000; Staver et al., 1996) include residential areas and waste water treatment plants.

The upper reaches of the Choptank River watershed can be partitioned between two hydrogeomorphic units: the well-drained uplands (WDU), characterized by narrow incised stream valleys and oxic groundwaters, and the poorly drained uplands (PDU), characterized by minimal stream incision and prevalence of hydric soils (Phillips et al., 1993; Shedlock et al., 1999). While there is local variability in depth of the surficial aquifer and location of confining units, the overall differences between WDU and PDU and associated extent of hydric soils are largely attributable to the degree of stream incision. The largely-non-dissected PDU occupies the central portion of the Delmarva Peninsula (Phillips et al., 1993), including the headwaters of the Upper Choptank and Tuckahoe Creek, and the more incised WDU occupies the gradual slopes between the central peninsula and the Chesapeake Bay. Studies of regional groundwater have identified differences in nutrient and pesticide concentrations based on hydrogeological setting, where the PDU exhibited decreased groundwater oxygen concentrations along with decreased concentrations of nitrate and pesticides, while greater pollutant concentrations were observed in oxic groundwater within WDU (Böhlke et al., 2007; Denver et al., 2010; Phillips et al., 1993) and below well-drained agricultural fields. Agricultural ditch drainage is prevalent, particularly in the non-dissected uplands, contributing to increased water yield (Koskelo, 2008).

Numerous studies have investigated nutrient or pesticide movement in river basins of the Midwest United States (e.g., Capel et al., 2001). Some authors have characterized various aspects of nutrient and/or pesticide movement in groundwater or surface waters in coastal areas of the Chesapeake Bay (Ator et al., 2004; Böhlke et al., 2007; Debrewer et al., 2008; Denver et al., 2004, 2010; Jordan et al., 1997a, 1997b; Phillips et al., 1993; Sprague et al., 2000), but only a few have included simultaneous measurement of nutrients and pesticides in streams draining multiple agricultural subwatersheds under baseflow conditions, when groundwater is the dominant contributor to stream flow (Ator et al., 2004; Fisher et al., 2006; Staver et al., 1996). A recent interpretation of river monitoring data has identified a pronounced increase in Choptank River nitrogen loading under baseflow conditions (Hirsch et al., 2010). This report presents the results of two years of monthly baseflow sampling of streams draining 15 subwatersheds located within the non-tidal upper portion of the Choptank River watershed (Fig. 1). Nine subwatersheds are located within the Tuckahoe Creek sub-basin, five within the Upper Choptank River sub-basin, and one below the Upper Choptank-Tuckahoe confluence. Spatial and temporal changes in nutrient and herbicide concentrations at baseflow were examined as a function of landscape metrics and related to the predominant source and transport processes. This information will be used to develop assessment tools to evaluate agricultural conservation practice effectiveness as required in the 2002 Farm Bill and in TMDL development. The results will also assist land managers in identifying areas where targeted changes in management practices will yield the most benefit.

2. Materials and methods

2.1. Site description—hydrologic and morphological characteristics

The Choptank River watershed is a site of focused long-term environmental research associated with the USDA Conservation Effects Assessment Project (McCarty et al., 2008; USDA-NRCS-CEAP, 2010). The Tuckahoe Creek and Upper Choptank River sub-basins (Fig. 1) are located on Mid-Atlantic Coastal Plain soils (Ator et al., 2005) with parent materials defined by the superposition of upper-delta-plain sands and gravel on marine-inner-shelf sands and a surficial unconfined aquifer ranging in depth from 8 to more than 30 m (Phillips et al., 1993). Local soil types under cropland production include the Othello series (fine-silty, mixed, active, mesic typic endoaquults) which are poorly drained with moderately-low permeability, and the Mattapex series (fine-silty, mixed, active, mesic aquic hapludults) which are moderately well drained with moderate or moderately-low permeability (Soil Survey Staff, 2010).

Sampling sites were established at the outlets of 15 non-tidal upland subwatersheds of the Choptank River drained by third and fourth order streams (Fig. 1). Seven subwatersheds fell within the WDU hydrogeomorphic region, five within the PDU, and three included mixed portions of PDU and WDU (Table 1). Together, the 15 subwatersheds drain 317 km^2 of upland, making up 16% of the Choptank River basin.

2.2. Sample collection, processing, and analysis

Sample collection occurred on an approximately monthly basis from June 2005 to June 2007 (21 sampling dates, 315 total samples). Sampling occurred at least two days after any significant (greater than 10 mm) rainfall-runoff event and with observed stream flows below 5 m^3/s at the two local USGS monitoring stations (USGS 01491000:

Table 1
Area, mean baseflow, landuse, and hydrologic characteristics in the 15 subwatersheds in the Choptank River watershed shown in Fig. 1; CREP = Conservation Reserve Enhancement Program; WDU = well-drained uplands; PDU = poorly drained uplands; percent forested wetlands included in percent forest.

Hydrogeomorphic regions			Area	Mean baseflow	Crop and pasture	Forest	CREP	Developed	Forested wetlands	Hydric soils	Chicken barns
			km^2	L/s	%	%	%	%	%	%	#
WDU: well-drained upland											
		mean	19	290	68	22	3	6	11	29	8
		median	17	270	69	21	2	6	12	28	9
		stdev	7	210	8	8	4	2	6	9	3
WDU/PDU: mixed WDU and PDU											
		mean	24	560	61	29	4	5	10	41	10
		median	12	96	61	28	3	6	12	42	7
		stdev	24	810	6	5	1	2	4	8	9
PDU: poorly drained upland											
		mean	23	450	55	35	4	5	13	60	5
		median	23	380	52	38	5	3	12	60	5
		stdev	11	310	9	8	2	2	1	5	3
Subwatersheds											
WDU:	CO	Cordova	26	310	69	21	2	8	12	20	11
	NO	Norwich	25	180	62	27	5	4	16	41	9
	DO	Downes	23	630	74	15	2	8	5	22	10
	BL	Blockston	17	95	60	26	11	2	16	40	7
	PB	Piney	15	52	74	20	1	5	5	28	4
	KC	Kittys Corner	14	460	59	35	1	6	18	31	12
	OL	Oakland	10	270	78	11	2	9	3	19	4
WDU/PDU:	GB	German	51	1500	61	28	5	6	14	49	20
	SB	Spring	12	87	67	25	3	4	6	32	7
	SF	South Forge	8	96	55	35	3	6	12	42	2
PDU:	LM	Long Marsh	41	380	50	42	5	3	15	64	7
	NF	North Forge	25	950	57	34	6	3	11	53	5
	BD	Beaverdam	23	500	70	22	5	3	12	66	4
	BW	Broadway	16	260	52	38	0	5	12	58	8
	OT	Oldtown	12	140	47	41	4	9	13	60	0

38.99719, −75.78581; USGS 01491500: 38.96681, −75.94606) (Figs. 1, 2). Hydrograph separation (Lim et al., 2005) was applied to the USGS gauging stations to confirm that sampling occurred under baseflow conditions. Precipitation data records were obtained from the University of Maryland Wye Research and Education Center in Queenstown, MD.

Water temperature and conductivity were measured *in situ* using a YSI 556 multiparameter field meter (Geotech Environmental Equipment, Inc., Denver, CO). Samples were collected from the center of flow with a stainless steel pail, stored in glass (nutrient analysis) or stainless steel containers (pesticide analysis) on ice, and transported to the laboratory for processing within 24 h. Subsamples for nutrient analysis were filtered through a 45 mm filter and Ortho-P (molybdate reactive orthophosphate PO_4^{3-}–P, Quickchem Method 10-115-01-1-A) as well as Nitrate-N (nitrate + nitrite NO_3^-–N + NO_2^-–N, Quickchem Method 12-107-01-1-B) concentrations were determined colorimetrically with a Quickchem automatic flow injection ion analyzer (Lachat Instruments, Milwaukee, WI).

Additional subsamples were filtered to 0.7 μm prior to processing and analysis for pesticides and pesticide degradation products using

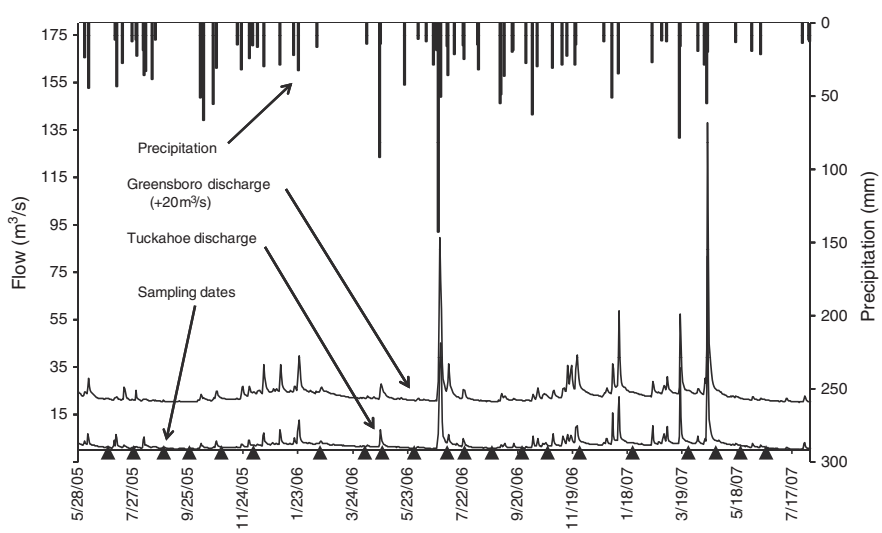

Fig. 2. Sampling dates, precipitation events from Wye Research and Education Center, Queenstown, Maryland, and discharge from two USGS gauging stations. Flow data from the Greensboro station have been displaced by +20 m^3/s for clarity. Location of gauging stations is depicted in Fig. 1.

procedures published previously (McConnell et al., 2007). Briefly, MESA {2-[(2-ethyl-6-methylphenyl) (2-methoxy-1-methylethyl) amino]-2-oxoethanesulfonic acid} extraction was conducted using a solid phase extraction (SPE) cartridge (Oasis HLB, Waters Corp., Milford, MA) using triphenylphosphate (Supelco Inc., Bellefonte, PA) as an extraction surrogate. Atrazine [6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine], CIAT [6-chloro-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine], CEAT [6-chloro-*N*-ethyl-1,3,5-triazine-2,4-diamine], and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] were extracted using an SPE cartridge (ENV+, Biotage Products, Inc., Charlottesville, VA); diazinon-diethyl-d_{10} {*O*,*O*-[^{2}H]diethyl *O*-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate} (Cambridge Isotope Laboratories Inc., Andover, MA) was the extraction surrogate. Cartridges were eluted and the extract concentrated under high purity nitrogen, transferred to a 2-mL amber glass vial, and stored at −20 °C until analysis. [^{13}C]2,4-Dichlorophenoxyacetic acid (100 μg/mL) and atrazine-ethylamine-d_5 (47.0 μg/mL) (both obtained from Cambridge Isotope Laboratories) were added as internal standards for MESA analyses and for all other pesticide compounds, respectively. Except for MESA concentrations, which were measured by high performance liquid chromatography/triple quadrupole mass spectrometry (HPLC/MS-MS), all pesticide and pesticide degradation products were measured using gas chromatography–mass spectrometry (GC–MS).

2.3. Land use data development

A high-resolution geospatial coverage of watershed land use was developed through on-screen digitizing in ArcMap 9.1 (Esri, Redlands, CA) using the 1998 National Agricultural Imagery Program digital orthophoto quad imagery (1:12,000 scale) as a base map (USDA-FSA-APFO, 2010). Identified land use categories included: agriculture (grain, forage, vegetable, nursery crops); forest (deciduous and evergreen); Conservation Reserve Enhancement Program (CREP; as identified on Farm Service Administration farm enrollment documents); water (ponds, streams, drainage ditches); and developed areas (residential development, urban areas, industrial operations). Occurrence was summarized as total area (m^2) and as percent of subwatershed area (Table 1). Land use categories were created for chicken houses, barnyards (e.g., dairy barns and operational headquarters for grain and vegetable production), and horse tracks (pervious oval structures) which were summarized by count rather than areal extent. Several additional geospatial data layers were developed for landscape analysis (Table 1) including hydric soils (soil classes C and D from the Soil Survey Geographic (SSURGO) coverage; USDA-NRCS, 2008) and forested wetlands (using C-band radar analysis; Lang et al., 2008).

2.4. Statistical analysis

Means and medians were calculated using individual, unweighted values for each sample within a group. Single variable linear regression was used to assess the relationship (R^2) between observed analyte concentrations and subwatershed land use parameters (described above) using SigmaPlot® 10.0 (Systat Software, Inc., Chicago, IL) or Microsoft® Excel 2007 software (http://office.microsoft.com). Box-plot analyses to assess temporal and spatial variability in analyte concentrations were conducted using GraphPad Prism® (GraphPad Software, La Jolla, CA); to test for differences among hydrogeomorphic regions, one-way analysis of variance were calculated using a Kruskal–Wallis test (a nonparametric test that does not assume Gaussian distribution).

The link between land use and observed nutrient concentrations was investigated using multivariate linear regression and analysis of variance (ANOVA) within the R statistical package version 2.11.1 (http://www.r-project.org). Multivariate regression models were constructed using either forest or agriculture, but not both simultaneously because percent forest and percent agriculture were inversely related and comprised the great majority (86% to 94%) of land use. Initially, a full multivariate linear model that included a response variable (analyte concentration) and all reasonable predictor variables (land use parameters, Table 1) was run. In subsequent runs, all non-significant predictor variables, along with predictor variables that exhibited negligible contribution to total explained sum of squares, were sequentially removed from the model, arriving at an the optimum multivariate linear model associated with each observed analyte.

3. Results

3.1. Land use and characteristics

Land use and soil characteristics in the subwatersheds are related to hydrogeomorphic setting. The WDU subwatersheds are characterized by well-drained agricultural areas on topographic highs and poorly drained forested floodplains located along narrow riparian corridors associated with highly incised streams. In contrast, PDU streams are smaller and slower running with shallow incision, low gradients, higher water tables in the surrounding uplands, and a high prevalence of agricultural ditch drainage associated with hydric soil classes. Sampled subwatersheds ranged in size from 8 to 51 km^2 (Fig. 1, Table 1). Although mean percent forest cover (35%) is greater in the PDU subwatersheds (Table 1) than in the WDU (22%), riparian forest buffers are much less prevalent. Forested patches within the PDU are generally not associated with stream channels and instead contain many seasonally-inundated wetland depressions and flats. The PDU subwatersheds have slightly greater abundance of forested wetlands (13%; Table 1) compared to the WDU (11%), and have a much greater abundance of hydric soils (60% versus 29%, respectively). The abundance of hydric soils led historically to construction of extensive drainage ditch networks to convert poorly drained areas into agricultural production. Small depressional wetlands (Delmarva bays) that were drained and converted to agricultural land use have been shown to retain some of their denitrification function even when under agricultural cultivation (Lang et al., 2008).

The dominant land use in the WDU subwatersheds (Table 1) is agriculture, i.e., crop and pasture land, (59–78%; mean 68%) followed by forest (11–35%; mean 22%), whereas the PDU subwatersheds are characterized by somewhat less agriculture (47–70%; mean 55%) and slightly more forest (22–42%; mean 35%). Occurrence of chicken barns ranged from 0 to 20 per subwatershed (less than 0.7 per km^2) with a greater concentration in the WDU (mean of 8.1) than in the PDU (mean of 4.8). CREP is a voluntary riparian buffer restoration program (USDA-FSA, 2010) and represented 0.2–10.8% of subwatershed land use (Table 1) with the greatest occurrence in subwatersheds with the least residential and urban development (German, Beaverdam, Long Marsh, Norwich, North Forge, and Blockston), although these were not necessarily the subwatersheds with the greatest percentage of agricultural land. Percent of developed lands in all the subwatersheds ranged from 2 to 9%.

3.2. Nutrients

Nitrate-N was detected in all samples, with concentrations ranging from 0.56 to 11 mg/L and mean and median concentrations of 4.9 mg/L and 4.4 mg/L, respectively (Table 2A). Nitrite and ammonia concentrations were comparatively low and are not reported here. Although little seasonal variability was observed in Nitrate-N concentrations (Fig. 3), consistent variation was seen among subwatersheds on any given date (Fig. 4). Significant differences in Nitrate-N concentrations were observed between the hydrogeomorphic regions (Table 3), with the highest mean concentrations

Table 2A
Mean and median for analytes, temperature, and conductivity for each subwatershed. Subwatersheds are arranged largest to smallest within each hydrogeomorphic group.

			Nitrate-N		Ortho-P		Conductivity		Temperature	
			Mean	Median	Mean[a]	Median[a]	Mean	Median	Mean	Median
			mg/L		mg/L		mS/cm		°C	
All samples			4.9	4.4	0.033	0.022	0.20	0.17	17.0	18.7
Hydrogeomorphic region subwatersheds										
WDU:	CO	Cordova	6.8	6.4	0.060	0.058	0.39	0.34	16.4	18.5
	NO	Norwich	3.0	3.2	0.041	0.041	0.23	0.24	16.7	18.7
	DO	Downes	8.1	8.0	0.022	0.022	0.18	0.18	17.1	18.5
	BL	Blockston	6.8	7.2	0.025	0.020	0.21	0.22	16.2	18.4
	PB	Piney	8.7	8.9	0.048	0.035	0.34	0.32	16.1	17.9
	KC	Kittys Corner	3.1	3.4	0.035	0.028	0.21	0.21	16.3	17.8
	OL	Oakland	8.9	9.3	0.057	0.042	0.19	0.19	16.3	17.2
WDU/PDU:	GB	German	4.7	4.8	0.090	0.071	0.21	0.21	16.5	18.4
	SB	Spring	5.4	5.2	0.023	0.014	0.12	0.11	16.4	18.2
	SF	South Forge	5.2	5.1	0.018	0.016	0.15	0.15	17.5	18.8
PDU:	LM	Long Marsh	2.3	2.3	0.016	0.014	0.16	0.16	18.1	19.9
	NF	North Forge	2.7	2.7	0.011	0.009	0.14	0.14	17.3	18.9
	BD	Beaverdam	4.1	4.3	0.019	0.014	0.16	0.16	17.3	19.3
	BW	Broadway	1.4	1.2	0.013	0.010	0.15	0.15	18.5	21.2
	OT	Oldtown	2.9	2.7	0.011	0.009	0.15	0.14	17.9	19.5

[a] Includes all samples.

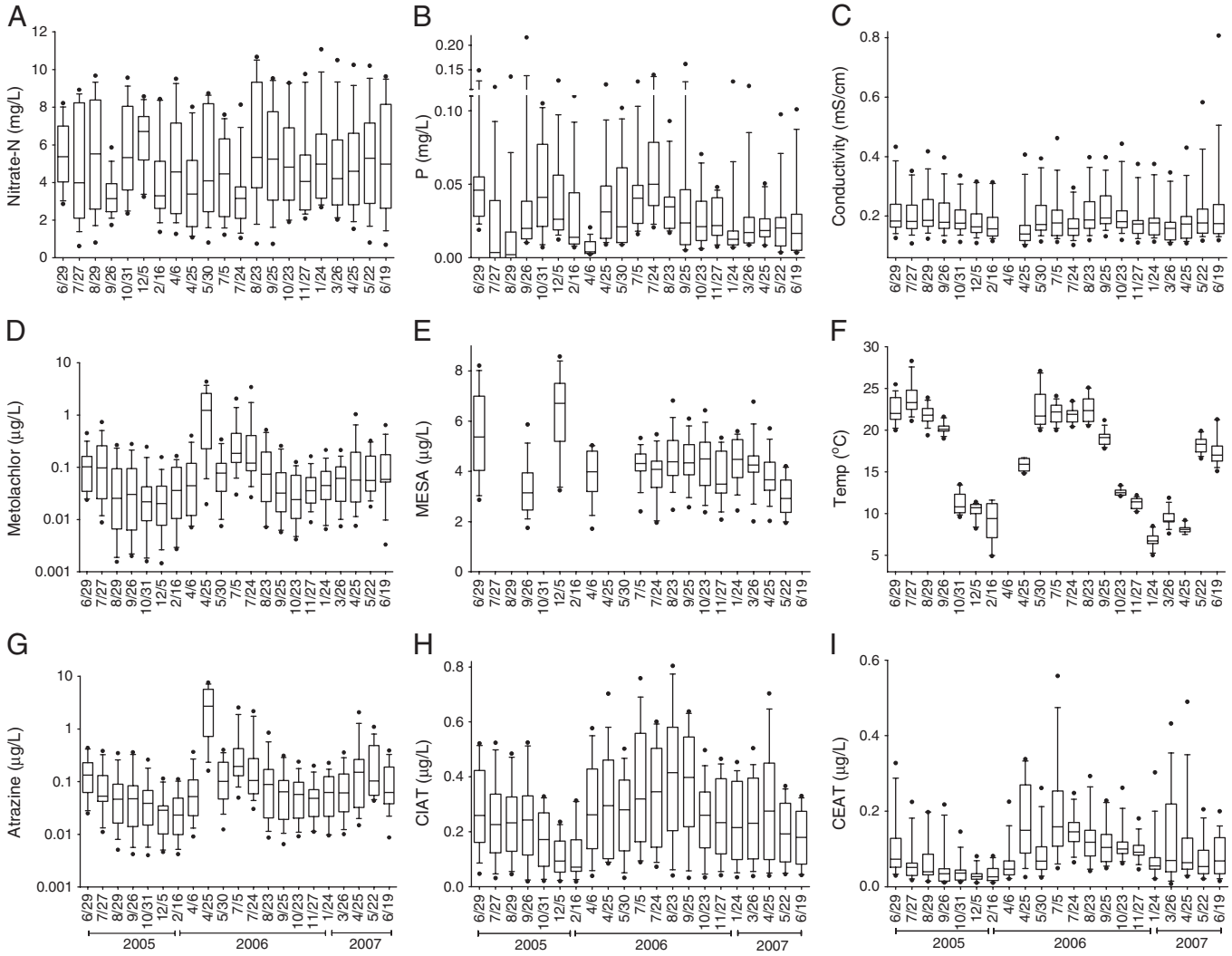

Fig. 3. Box plots summarizing analyte concentrations and water quality parameters for all sampled subwatersheds in the Choptank River watershed as a function of sampling date. Points denote minimum and maximum values, bars the 10% and 90% percentile and median, and boxes the interquartile range.

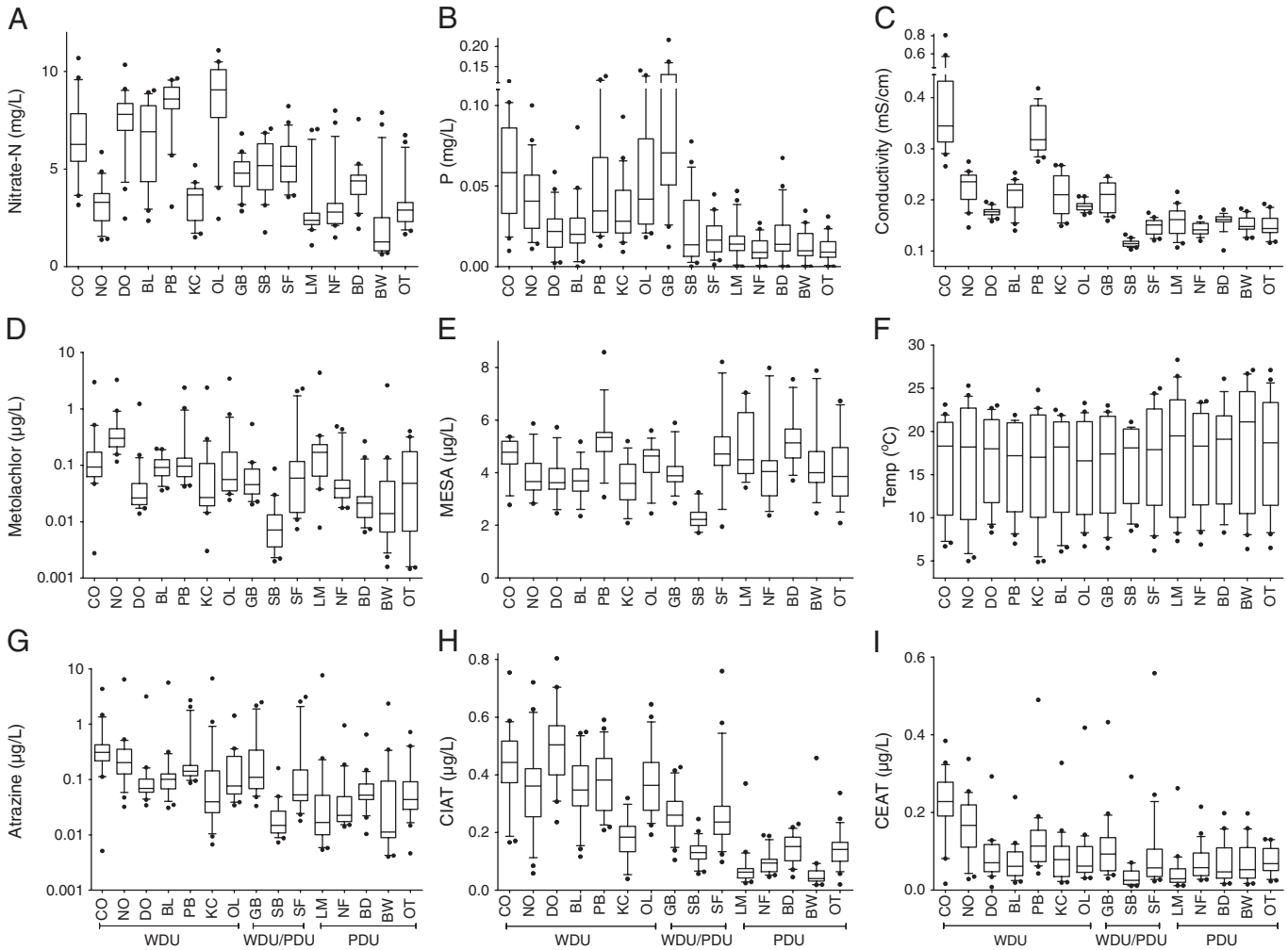

Fig. 4. Box plots summarizing analyte concentrations and water quality parameters observed over the two-year period as a function of subwatershed. Subwatersheds are arranged largest to smallest within each hydrogeomorphic group. Points denote minimum and maximum values, bars the 10% and 90% percentile and median, boxes the interquartile range.

Table 2B
Mean and median for pesticides and pesticide degradation products for each subwatershed. Subwatersheds are arranged largest to smallest within each hydrogeomorphic group.

			Atrazine		Atrazine (non-planting season)		CIAT		CEAT		Metolachlor		Metolachlor (non-planting season)		MESA	
			Mean	Median	Mean	Median	Mean	Median	Mean	Median	Mean	Median	Mean	Median	Mean	Median
			µg/L		µg/L		µg/L		µg/L		µg/L		µg/L		µg/L	
All samples			0.19	0.06	0.13	0.06	0.25	0.22	0.09	0.07	0.29	0.07	0.12	0.05	4.2	4.1
Hydrogeomorphic region subwatersheds																
WDU:	CO	Cordova	0.56	0.31	0.36	0.26	0.44	0.13	0.22	0.23	0.28	0.09	0.14	0.08	4.6	4.8
	NO	Norwich	0.53	0.20	0.21	0.20	0.36	0.36	0.16	0.15	0.50	0.30	0.35	0.25	3.9	3.7
	DO	Downes	0.23	0.07	0.07	0.06	0.50	0.50	0.09	0.07	0.09	0.03	0.04	0.02	3.8	3.6
	BL	Blockston	0.37	0.10	0.09	0.09	0.36	0.35	0.07	0.05	0.10	0.09	0.10	0.09	3.7	3.7
	PB	Piney	0.38	0.14	0.17	0.13	0.38	0.38	0.14	0.13	0.28	0.10	0.14	0.09	5.3	5.3
	KC	Kittys Corner	0.43	0.04	0.05	0.03	0.18	0.19	0.08	0.07	0.17	0.03	0.05	0.03	3.6	3.5
	OL	Oakland	0.19	0.08	0.19	0.07	0.38	0.36	0.09	0.07	0.29	0.06	0.32	0.05	4.4	4.6
WDU/PDU:	GB	German	0.38	0.11	0.25	0.10	0.27	0.26	0.09	0.09	0.08	0.05	0.05	0.04	4.0	3.9
	SB	Spring	0.03	0.01	0.02	0.01	0.13	0.13	0.03	0.02	0.01	0.01	0.01	0.01	2.3	2.2
	SF	South Forge	0.34	0.05	0.21	0.05	0.27	0.24	0.10	0.06	0.27	0.06	0.19	0.06	4.9	4.7
PDU:	LM	Long Marsh	0.42	0.02	0.024	0.014	0.08	0.06	0.05	0.03	0.37	0.17	0.14	0.14	4.9	4.5
	NF	North Forge	0.08	0.02	0.041	0.022	0.09	0.09	0.07	0.06	0.08	0.04	0.07	0.04	4.6	4.3
	BD	Beaverdam	0.09	0.05	0.060	0.052	0.15	0.15	0.05	0.05	0.04	0.02	0.05	0.02	5.3	5.1
	BW	Broadway	0.17	0.01	0.056	0.010	0.07	0.04	0.07	0.05	0.15	0.01	0.03	0.01	4.5	4.0
	OT	Oldtown	0.12	0.04	0.074	0.042	0.14	0.14	0.07	0.06	0.10	0.05	0.09	0.02	4.1	3.9

observed in Oakland followed by Piney and Downes (all WDU subwatersheds with high percentages of agriculture), and the lowest mean concentrations found in the PDU region, including Broadway, Long Marsh, and North Forge subwatersheds.

Ortho-P (dissolved P) was also detected in all samples (Table 2A); however, concentrations in 15% of the samples were below the analytical limit of quantitation (LOQ = 0.01 mg/L). Ortho-P concentrations ranged from less than 0.01 mg/L to 0.22 mg/L with a mean concentration, using all observations, of 0.03 mg/L and median of 0.02 mg/L. The highest mean Ortho-P concentrations were observed in the German followed by Cordova, Oakland, Piney, Norwich, and Kittys Corner subwatersheds; all are WDU subwatersheds except for German (WDU/PDU). The mean concentrations for the remaining subwatersheds were less than or equal to 0.025 mg/L.

3.3. Herbicide residues

Each water sample was analyzed for the herbicides atrazine and metolachlor and for the atrazine dealkylation products CIAT and CEAT. Of the 21 sampling events, only 13 were analyzed for the sulfonic acid degradation product of metolachlor (MESA). Atrazine, CIAT, CEAT, metolachlor, and MESA were detected in all analyzed samples (Table 2B). Across all subwatersheds, concentrations for atrazine and metolachlor ranged from 0.004–7.6 μg/L to 0.001–4.4 μg/L, respectively. Unlike the nutrients, parent herbicide concentrations exhibited high temporal variability, increasing by several orders of magnitude in the springtime (Figs. 3D, G, 5).

The mean and median concentrations of atrazine and metolachlor for the non-planting seasons were calculated using all the data except those samples collected during the spring planting season (April and May). As with the nutrients, significant differences in parent herbicide concentrations were observed between the WDU and the PDU subwatersheds (Table 3). Atrazine and metolachlor concentrations observed in the PDU subwatersheds were significantly lower than the WDU (Table 3). During the non-planting seasons, the mean atrazine concentrations in the WDU subwatersheds ranged from 0.05 to 0.37 μg/L with the highest values observed in Cordova (0.37 μg/L) and Norwich (0.21 μg/L); mean atrazine concentrations for the PDU subwatersheds ranged from 0.02 to 0.07 μg/L. For metolachlor during the non-planting seasons, the mean concentrations in the WDU subwatersheds ranged from 0.04 to 0.35 μg/L with the highest values in Norwich (0.35 μg/L) and Oakland (0.32 μg/L); mean metolachlor concentrations in PDU subwatersheds were less than 0.10 μg/L except for Long Marsh (0.14 μg/L).

CIAT and CEAT concentrations across all subwatersheds ranged from 0.02–0.80 μg/Lto 0.01–0.56 μg/L, respectively, with respective mean and median concentrations of 0.25 μg/L and 0.22 μg/L, and 0.09 μg/L and 0.07 μg/L (Table 2B). Some seasonal response was observed in CIAT and CEAT with the highest concentrations seen in late summer and fall (Figs. 3, 4). CIAT and CEAT concentrations were significantly greater in the WDU subwatersheds as compared to the PDU subwatersheds (Table 3). MESA concentrations ranged from 1.7 to 8.6 μg/L with a mean and median of 4.3 and 4.1 μg/L (Table 2B). Essentially no temporal or spatial trends were observed for MESA concentrations.

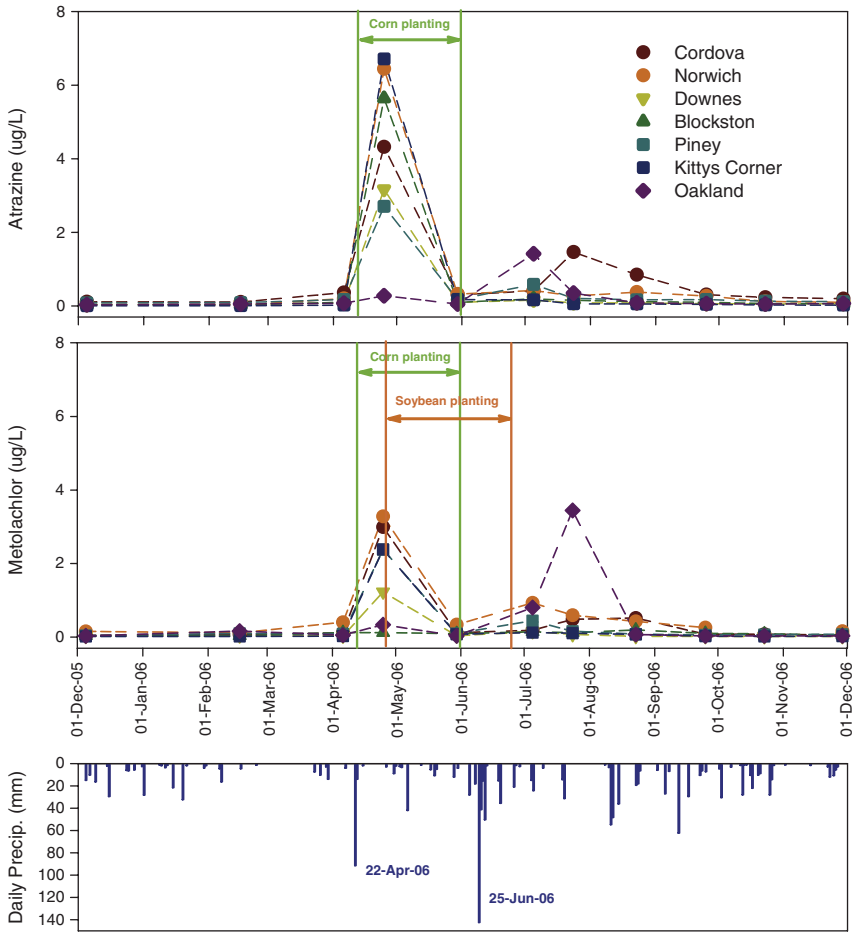

Fig. 5. Atrazine and metolachlor concentrations in water from WDU (well-drained uplands) subwatersheds (Fig. 1) of the Choptank River with corn and soybean planting dates and precipitation records.

Table 3
Comparison of mean values with standard errors for analytes, temperature, and conductivity per hydrogeomorphic regions; LOQ = Limit of Quantitation; WDU = well-drained uplands; PDU = poorly drained uplands; Kruskal-Wallis test conducted with significant differences between hydrogeomorphic regions noted (a, b, c); *** $p<0.0001$.

	Units	LOQ	Hydrogeomorphic regions			p
			WDU	WDU/PDU	PDU	
Nitrate-N	mg/L	0.01	$6.5^{a} \pm 0.2$	$5.1^{a} \pm 0.1$	$2.7^{b} \pm 0.1$	***
Ortho-P	mg/L	0.01	$0.042^{a} \pm 0.002$	$0.044^{a} \pm 0.006$	$0.016^{b} \pm 0.001$	***
Atrazine	μg/L	0.002	$0.38^{a} \pm 1.0$	$0.25^{b} \pm 0.63$	$0.17^{b} \pm 0.79$	***
Atrazine (non-planting)	μg/L	0.002	$0.16^{a} \pm 0.02$	$0.16^{a} \pm 0.06$	$0.05^{b} \pm 0.008$	***
CIAT	μg/L	0.002	$0.37^{a} \pm 0.01$	$0.22^{b} \pm 0.02$	$0.11^{c} \pm 0.01$	***
CEAT	μg/L	0.002	$0.12^{a} \pm 0.01$	$0.07^{b} \pm 0.01$	$0.06^{b} \pm 0.004$	***
Metolachlor	μg/L	0.001	$0.24^{a} \pm 0.55$	$0.12^{b} \pm 0.39$	$0.15^{b} \pm 0.50$	***
Metolachlor (non-planting)	μg/L	0.001	$0.16^{a} \pm 0.03$	$0.08^{b} \pm 0.04$	$0.07^{b} \pm 0.01$	***
MESA	μg/L	0.01	$4.2^{a,b} \pm 0.1$	$3.7^{a} \pm 0.2$	$4.6^{b} \pm 0.2$	0.008
Conductivity	mS/cm	0.01	$0.25^{a} \pm 0.008$	$0.16^{b} \pm 0.006$	$0.15^{b} \pm 0.002$	***
Temperature	°C	0.15	16.5 ± 0.5	16.8 ± 0.7	17.9 ± 0.6	0.066

4. Discussion

Distinct differences in water quality parameters were observed among subwatersheds based upon hydrogeomorphic region. In comparison to the poorly drained upland (PDU) subwatersheds, the well-drained upland (WDU) subwatersheds exhibited significantly greater conductivity and concentrations of Nitrate-N, atrazine, metolachlor, CIAT, and CEAT, while mean annual temperatures were somewhat lower in the WDU (Table 3). Landscape metrics also showed consistent variation between hydrogeomorphic regions. The PDU subwatersheds exhibited a greater prevalence of hydric soils in both agricultural and forested areas, with a corresponding decreased occurrence of crop and pasture land and an increased occurrence in forest (Table 1). Forests and forested wetland areas in the PDU tended to occur in large contiguous patches, in comparison to the WDU subwatersheds where forests and forested wetlands were largely concentrated in near-stream riparian areas (Fig. 1). Examination of landscape metrics and water quality data, partitioned according to hydrogeomorphic class, provided insight into the fate, delivery, and transport mechanisms associated with agricultural impacts on water quality parameters.

4.1. Nutrient fate

In this study, Nitrate-N concentrations were significantly greater in the subwatersheds of the WDU than those of the PDU. The WDU subwatersheds with the highest concentrations of Nitrate-N in streams also had the greatest percent agricultural production (and therefore the lowest percent forest). Similarly, the PDU subwatersheds with the lowest observed concentrations of Nitrate-N had a greater extent of forest cover and decreased occurrence of crop and pasture land.

Observed Nitrate-N concentrations exceeded 2.2 mg/L in 86% of all samples. The overall mean of 4.9 mg/L was slightly greater than the mean baseflow Nitrate-N concentrations of about 3 mg/L calculated by others for first order streams on the Delmarva Peninsula (Denver et al., 2004). Observed mean Nitrate-N concentrations (Table 3) were positively correlated with percent agriculture ($R^2 = 0.56$), and were negatively-correlated with percent forest ($R^2 = 0.60$) and percent hydric soils ($R^2 = 0.51$). Results of multivariate linear models ($R^2 = 0.72$) relating observed stream water Nitrate-N concentrations with landscape variables indicated that either percent forest or percent agriculture could serve as the primary explanatory variable (explaining 60% or 56% of observed variation, respectively). Percent CREP conservation reserve (1% of observed variation), percent developed lands (8% of observed variation), percent forested wetlands (3% of observed variation), and percent hydric soils (6% of observed variation) were also significant predictor variables (best Nitrate-N model: $[NO_3^-] = 1.5882 + 8.76 * \text{Cropland\%} + 36.05 * \text{CREP\%} + 21.84 * \text{Developed\%} + (-17.52) * \text{ForestedWetland\%} + (-6.32) * \text{HydricSoils\%}$).

Correlations of baseflow Nitrate-N with percent agriculture and percent forest have previously been observed locally (Jordan et al., 1997a, 1997b; Norton and Fisher, 2000; Fisher et al., 2010; Sutton et al., 2010) and research has documented relatively-conservative groundwater Nitrate-N transport in oxic groundwaters below well-drained areas of the Delmarva Peninsula (Bachman and Phillips, 1996). In the WDU, oxic groundwater carrying nitrogen from agricultural fields has been shown to pass underneath riparian wetlands and upwell directly to stream channels without significant denitrification. In contrast, non-riparian forested, depressional wetlands have been shown to play a role in denitrification of groundwater flowing from upland agricultural areas (Phillips et al., 1993; Böhlke and Denver, 1995), and in providing uncontaminated recharge to aquifers in areas isolated from agricultural practices. The lower concentrations of Nitrate-N and pesticides observed regionally in the PDU have been attributed to denitrification and degradation within anoxic groundwaters, especially in agricultural fields with hydric soils (prior converted wetlands), and in areas where oxic groundwater leaving well-drained agricultural fields encounters anoxic groundwaters associated with forested wetlands prior to entering the stream channel (Böhlke et al., 2007; Denver et al., 2010; Phillips et al., 1993).

The low concentrations of Ortho-P observed at all the subwatershed monitoring stations were consistent with typical phosphorus behavior under baseflow conditions. Overall, observed Ortho-P baseflow concentrations were low in comparison with concentrations found during storm events by Koskelo (2008), but were similar to concentrations observed during baseflow in the Upper Choptank River (Sprague et al., 2000). Koskelo (2008) observed that the baseflow Ortho-P concentration in Choptank River subwatersheds was significantly correlated with the number of confined animal feeding operations (CAFOs) in each subwatershed ($R^2 = 0.47$, $p<0.01$), although his definition of CAFO was not easily separable from general agricultural land use.

Results of multivariate linear models relating baseflow Ortho-P concentrations with landscape variables ($R^2 = 0.30$) indicated that the number of chicken barns per subwatershed was the primary explanatory variable, explaining 18% of observed variation, while percent agricultural or percent forested lands each explained 9% of observed variation. Percent developed lands (1%) and subwatershed area (1%) were also significant predictor variables (best Ortho-P model: $[\text{OrthoP}] = (-0.05862) + 0.08499 * \text{Cropland\%} + 0.25229 * \text{Developed\%} + 0.002145 * \#\text{ChickenBarns} + 0.0004566 * \text{WatershedAreakm2}$).

The weaker correlation between observed baseflow Ortho-P concentrations and landscape parameters is indicative of the increased reliance of phosphorus transport on event flow and in-stream, sediment-driven processes. This is in contrast to the transport of Nitrate-N, which is readily transportable through groundwater flow pathways. It must be emphasized that baseflow transport accounts for only a portion of agricultural non-point-source pollutant delivery processes, with the

bulk of Nitrate-N delivery expected under baseflow conditions, and the bulk of Ortho-P delivery expected to occur during overland flow and sediment transport associated with precipitation events.

4.2. Herbicide transport processes

Local corn planting and concomitant fertilizer and herbicide application commence in early April (USDA-NASS, 2008) and continue until the first week of June. Soybean planting begins a few weeks earlier, in late April, and continues until early July. At planting, corn fields typically receive applications of nutrients, atrazine, and metolachlor, while soybeans receive only metolachlor. Springtime planting periods were readily identified in the water quality monitoring data by sharp peaks in stream water herbicide concentrations observed at that time (Fig. 5), suggesting a need for improved herbicide management practices and reduced chemical application to maintain stream water quality. These peak concentrations exceeded the drinking water maximum contaminant level of 3 μg/L for atrazine and the level (0.5 μg/L) where reductions were observed in egg production of fathead minnow (*Pimephales promelas*) managed in flow-through systems (Tillitt et al., 2010). However, the levels were not greater than the US EPA level of concern for aquatic ecosystems (10 to 20 μg/L) (US EPA, 2006). Similar springtime spikes for parent herbicides have been observed elsewhere (Meyer et al., 2007). Atrazine concentrations in all subwatersheds during non-planting seasons rarely exceed 0.5 μg/L and were similar to monitoring results from a nearby Delmarva watershed (Ator et al., 2004).

In 2006, a large precipitation event (91 mm) occurred during the springtime planting period, three days prior to the April 25th sampling (Fig. 5). On this sampling date, baseflow separation (Lim et al., 2005) showed that the larger watersheds contributing to the Tuckahoe and Greensboro USGS stations were in a late recession or elevated baseflow stage three days after a large rainfall event with a small mix of quick flow present within the hydrograph. Baseflow separation for the 15 subwatersheds on this date showed that these smaller streams had, indeed, returned to largely baseflow conditions. However, no sharp distinction exists because a variety of quickflow pathways in the vadose-zone and within hydrologically active

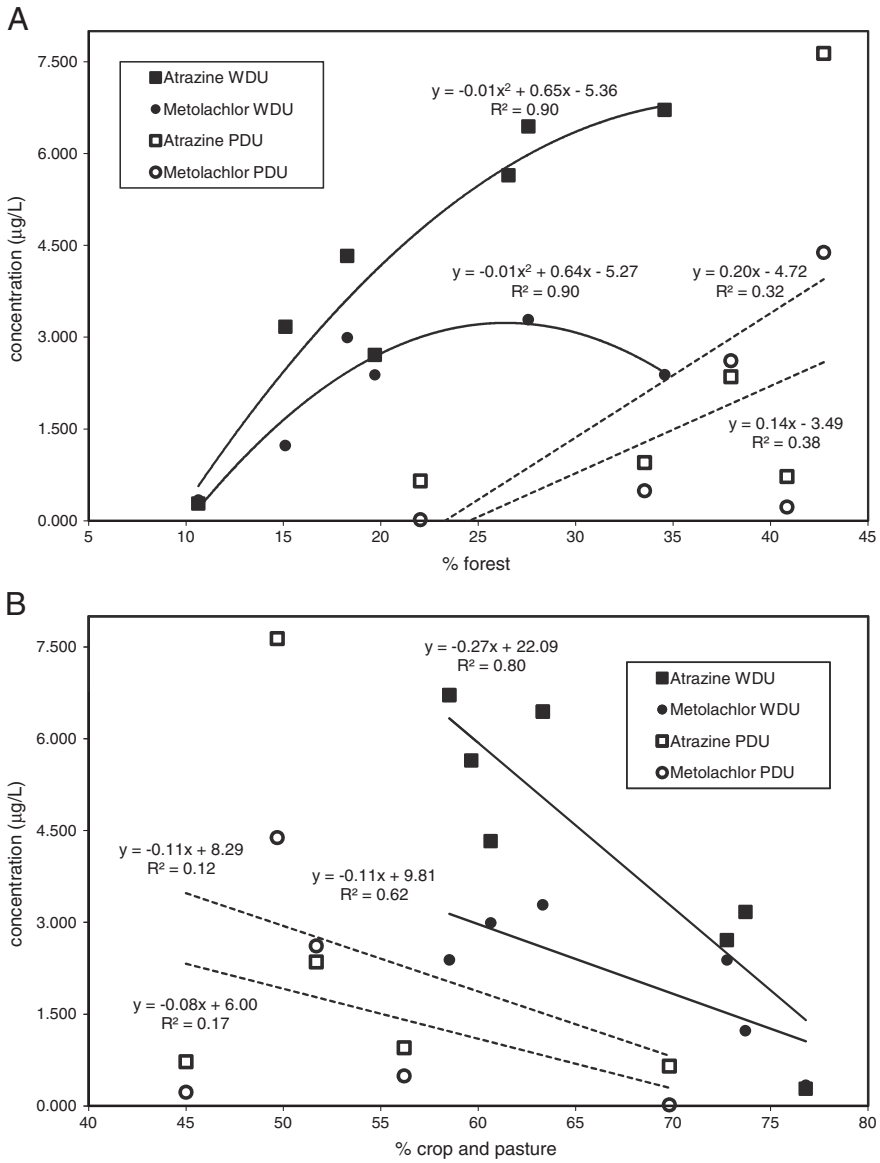

Fig. 6. Concentration of atrazine and metolachlor versus percent forest (A) and versus percent crop and pasture land (B) in samples collected on April 25, 2006 from the WDU (well-drained uplands) and PDU (poorly drained uplands) subwatersheds (Fig. 1) of the Choptank River.

wetland areas contribute to the gradual draining of the landscape once the main runoff event has passed.

Atrazine concentrations in samples taken from the seven WDU subwatersheds on April 25th were positively correlated ($R^2 = 0.90$; curvilinear fit, Fig. 6A) to the percent forest within each subwatershed, and were negatively-correlated ($R^2 = 0.80$; linear fit, Fig. 6B) to the percent crop and pasture land. Herbicide concentrations tended to increase with increasing forest cover, but then leveled off as the amount of forest cover reached 25–30%, suggesting the prevalence of forest edge effects in herbicide transport processes. In 2007, smaller and less frequent precipitation events occurred during the springtime planting period, resulting in much lower seasonal concentration peaks and a minimal positive correlation between atrazine concentration and percent forest ($R^2 = 0.50$) for the May 22nd sampling, when the highest concentrations were observed that year. Observed metolachlor concentrations on April 25, 2006 were also positively correlated ($R^2 = 0.90$; curvilinear fit, Fig. 6) to the percent forest within each subwatershed of the WDU, with a lesser degree of correlation observed on May 22, 2007 ($R^2 = 0.59$). Blockston was not included with the other six WDU subwatersheds because metolachlor concentrations at this site were very low and showed little seasonal change over the course of the study (mean = 0.10 ± 0.05 μg/L); this may reflect that little agricultural metolachlor application occurred in this subwatershed.

The appearance of elevated baseflow concentrations of atrazine and metolachlor during the planting season might be caused in part by residual overland flow and shallow subsurface flow processes following the pulse of herbicide loading that would be expected during springtime storm events. While groundwater movement is expected to be limited due to the high reactivity of the parent compounds with soil carbon (Puckett and Hughes, 2005), herbicide volatilization can be significant for several days following application especially under humid conditions and/or when soils are moist (Gish et al., 2009), Thus, the strong positive correlation between the observed parent herbicide concentrations on April 25, 2006 and percent forest in the WDU subwatersheds (Fig. 6: atrazine $R^2 = 0.90$; metolachlor $R^2 = 0.90$) suggests involvement of an alternative delivery mechanism whereby herbicide drift and volatilized residues are captured by the riparian forest canopy and are subsequently washed off during rainfall to the riparian stream channels.

This phenomenon has been observed elsewhere in Maryland (Rice et al., 2008); where narrow riparian forests have been postulated to concentrate wash-off of aerially-deposited herbicides from the tree canopy and to deposit the residues in the near-stream wetland area (Angier et al., 2002, 2004). Forested buffer strips have been shown to capture the majority of herbicide drift within 6–7 m of the field edge (Lazarro et al., 2008). This canopy capture and subsequent wash-off mechanism would be expected to be more prominent in the WDU subwatersheds, due to the greater occurrence of narrow forest buffers near the streams, than in the PDU where large forest patches are more dominant and the majority of agricultural lands are heavily ditched with grass rather than forest buffers. The slightly greater mean stream temperatures observed in the PDU subwatersheds (17.9 °C versus 16.5 °C for WDU; Table 3) is consistent with a warming effect (Rutheford et al., 2004) on waters running through the grass-buffered drainage ditches prevalent in the PDU, compared to streams with riparian forest buffers in the WDU. As predicted, the springtime herbicide concentrations in the PDU showed little correlation with percent forest cover (atrazine 2006–$R^2 = 0.32$, 2007–$R^2 = 0.10$; metolachlor 2006–$R^2 = 0.38$, 2007–$R^2 = 0.46$) (Fig. 6).

Although the positive correlation of parent herbicide concentrations with percent forest and negative correlation with percent crop and pasture land (Fig. 6) is counterintuitive, the relative magnitude of land use change (the independent variable) is different. In the WDU, crop and pasture land varied from 59% to 78% among subwatersheds, a relative increase of only 32% in an already strong agricultural signal. In contrast, the percent forest in the WDU subwatersheds increased from 11% to 35%, which is a 218% relative increase in forest occurrence. Increasing the occurrence of cropland would be expected to increase the amount of land to which herbicides are applied; however, this might not result in increased herbicide concentration in stream water if airborne residues are transported off-field and deposited on soil areas where they are subject to degradation. In contrast, the 218% relative increase in forested areas could significantly increase capture of airborne residues, resulting in increased residue concentrations in stream water following precipitation events.

4.3. Herbicide degradation processes

Microbial dealkylation of atrazine in all the subwatersheds afforded CIAT over CEAT by about a 3:1 ratio which is similar to previous observations in the Midwest (Shipitalo and Owens, 2003). Atrazine (non-planting seasons), CIAT, CEAT, and metolachlor (non-planting seasons) concentrations exhibited a similar behavior pattern to Nitrate-N, with significantly lower concentrations found in the PDU subwatersheds than in WDU, perhaps due to increased degradation in the PDU hydric soil areas and perhaps also due to a reduced agricultural land use intensity in the PDU (Tables 1 and 3). The atrazine degradation products CIAT and CEAT showed a summertime peak in observed concentration approximately 2–3 months after the springtime application period for the parent compound (Fig. 3). Observed concentrations of MESA were relatively consistent among subwatersheds, sampling dates, and hydrogeomorphic regions (Figs. 3,4) as is expected for a compound which does not readily degrade (McConnell et al., 2007). The increased variability in MESA concentrations observed within the PDU streams (Fig. 4) might be attributed to the diversity and distribution of agricultural land use practices, groundwater flow paths, and landscape features among the subwatersheds.

5. Conclusions

Complex interactions between land use patterns, geomorphology, hydrologic setting, agricultural intensity, and connectivity of agricultural lands to landscape flow pathways combine to influence nutrient and herbicide concentrations in agricultural streams. Streams draining the 15 agricultural subwatersheds of the Choptank River generally showed lower pollutant concentrations in the poorly drained subwatersheds (PDU) than in the well-drained subwatersheds (WDU), although concentrations within individual subwatersheds were quite variable. The greater extent of hydric soils within the poorly drained uplands (PDU) appeared to be associated with increased denitrification and herbicide degradation, leading to better water quality. Managers might consider promoting strategies to restore hydrologic function to previously hydric field areas, such as construction of controlled drainage structures to regulate the outflow from agricultural drainage ditches (McCarty et al., 2008; Fisher et al., 2010). There were also significant unexplained differences in observed water quality parameters among the 15 subwatersheds that can be attributed to local variability in a variety of important factors such as hydrogeomorphology and farm management. Future studies might benefit by mapping such factors, and incorporating them as covariates in the analysis of stream water quality data. Elevated concentrations of stream water, along with springtime peaks in herbicide concentrations, indicate the need for continued implementation of agricultural best management practices and the promotion of resource-conserving farming strategies.

Riparian forests and farm hedgerows provide numerous important landscape benefits including nutrient capture, soil retention, carbon sequestration, agroecological benefits, habitat diversity, stream water cooling, and other ecosystem services. However, this study provided evidence that the amount and pattern of forest patches influences delivery of herbicide parent compounds to streams. The extent of narrow forested buffers along streams appeared to be linked to a mechanism of atmospheric deposition followed by wash-off from the canopy, although herbicide delivery through short vadose-zone flow

pathways could not be excluded (Böhlke et al., 2007). Managers might wish to consider the width and structure of riparian buffers not only in relation to groundwater hydrology, but to capture of volatilized herbicide residues. Riparian buffers, or hedgerows, located at least 7 m from the edge of streams and wetlands widths, or hedgerow placement, should minimize delivery of captured volatilized residues to nearby streams. An even better solution would be to develop technology and farming systems to avoid pesticide usage and to minimize spray drift and volatilization.

Pollutant concentrations measured in streams under baseflow conditions can provide important information on the distribution and function of watershed pollutant transport processes, although this information must be coupled with storm-flow analysis and site-specific observation of management practice outcomes. However, the separation of multiple source factors is made difficult by the high degree of both human and biophysical variability affecting land management in the study watersheds. Effective evaluation of water quality conservation practices will require a better understanding of complex landscape interactions between land use, agricultural management, and hydrogeomorphology. To estimate the effectiveness of conservation practices at the watershed scale accurately, high-resolution mapping of important landscape variables, along with water quality models that recognize both linear and nonlinear interactions among multiple parameters, will be required. Development of these tools will also assist efforts to target implementation of conservation practices to the most environmentally-critical areas within watersheds with the objective of obtaining water quality improvements in a cost-effective manner.

Abbreviations used

CIAT	6-chloro-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine
CEAT	6-chloro-*N*-ethyl-1,3,5-triazine-2,4-diamine
CREP	Conservation Reserve Enhancement Program
CEAP	Conservation Effects Assessment Project
GC	gas chromatography
HPLC	high performance liquid chromatography
LOQ	limit of quantitation
MESA	2-[(2-ethyl-6-methylphenyl) (2-methoxy-1-methylethyl) amino]-2-oxoethanesulfonic acid
MS	mass spectrometry
PDU	Poorly Drained Uplands hydrogeomorphic region
SAV	submerged aquatic vegetation
SPE	solid phase extraction
SSURGO	Soil Survey Geographic
TMDL	total maximum daily load
USDA	United States Department of Agriculture
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WDU	Well-Drained Uplands hydrogeomorphic region

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