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Metolachlor metabolite (MESA) reveals agricultural nitrate-N fate and transport in Choptank River watershed☆

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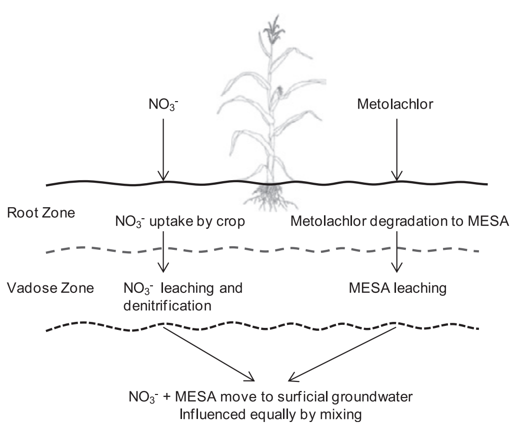
HIGHLIGHTS

- A metabolite of commonly used herbicide can trace the fate of agricultural nitrate-N.
- Streams preferentially drained croplands in heavily ditched watersheds.
- A stable tracer demonstrates nitrate-N to be highly conserved in the Choptank estuary.
- The drainage status of cropland soils is an important control on watershed N export.

GRAPHICAL ABSTRACT



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ABSTRACT

Over 50% of streams in the Chesapeake Bay watershed have been rated as poor or very poor based on the index of biological integrity. The Choptank River estuary, a Bay tributary on the eastern shore, is one such waterway, where corn and soybean production in upland areas of the watershed contribute significant loads of nutrients and sediment to streams. We adopted a novel approach utilizing the relationship between the concentration of nitrate-N and the stable, water-soluble herbicide degradation product MESA {2-[2-ethyl-*N*-(1-methoxypropan-2-yl)-6-methylanilino]-2-oxoethanesulfonic acid} to distinguish between dilution and denitrification effects on the stream concentration of nitrate-N in agricultural subwatersheds. The ratio of mean nitrate-N concentration/(mean MESA concentration * 1000) for 15 subwatersheds was examined as a function of percent cropland on hydric soil. This inverse relationship ($R^2 = 0.65$, $p < 0.001$) takes into consideration not only dilution and denitrification of nitrate-N, but also the stream sampling bias of the croplands caused by

Abbreviations: APFO, Aerial Photography Field Office; ARS, Agricultural Research Service; CBP, Chesapeake Bay program; MDE, Maryland Department of the Environment; MESA, 2-[2-ethyl-*N*-(1-methoxypropan-2-yl)-6-methylanilino]-2-oxoethanesulfonic acid; NAS, National Academy of Science; NRCS, Natural Resources Conservation Service; SSURGO, Soil Survey Geographic; SWCS, Soil and Water Conservation Society; TMDL, total maximum daily load; USDA, United States Department of Agriculture; USEPA, United States Environmental Protection Agency.

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Nitrate-N
Well-drained upland
Poorly-drained upland

extensive drainage ditch networks. MESA was also used to track nitrate-N concentrations within the estuary of the Choptank River. The relationship between nitrate-N and MESA concentrations in samples collected over three years was linear ($0.95 \leq R^2 \leq 0.99$) for all eight sampling dates except one where $R^2 = 0.90$. This very strong correlation indicates that nitrate-N was conserved in much of the Choptank River estuary, that dilution alone is responsible for the changes in nitrate-N and MESA concentrations, and more importantly nitrate-N loads are not reduced in the estuary prior to entering the Chesapeake Bay. Thus, a critical need exists to minimize nutrient export from agricultural production fields and to identify specific conservation practices to address the hydrologic conditions within each subwatershed. In well drained areas, removal of residual N within the cropland is most critical, and practices such as cover crops which sequester the residual N should be strongly encouraged. In poorly drained areas where denitrification can occur, wetland restoration and controlled drained structures that minimize ditch flow should be used to maximize denitrification.

1. Introduction

According to a 2009 United States Environmental Protection Agency (USEPA) water quality assessment, 44% of streams and rivers, 64% of lakes and reservoirs, and 30% of bays and estuaries are impaired, as defined by the 1972 Clean Water Act, and agriculture nonpoint source pollution is a major contributor, especially of nitrogen (USEPA, 2009). Reducing impairment by nonpoint source pollution is a major focus of the Total Maximum Daily Load (TMDL) framework (NAS, 2001), but this effort requires decreasing uncertainties in pollutant source predictions and improving watershed loading estimates of nonpoint source pollution. This will require innovative watershed modeling strategies and measurement techniques to identify critical areas where conservation and mitigation practices are needed (NAS, 2001; SWCS, 2006).

The Chesapeake Bay is the largest estuary in the United States (US), and over 50% of streams in the watershed have been rated as poor or very poor based on the index of biological integrity (CBP, 2010; USEPA, 2010a). Land use in the Chesapeake Bay watershed consists of 23% agriculture, 68% forested, 7% urban, and 2% waterways (CBP, 2012). The Choptank River (Fig. 1) is a tributary on the eastern shore of the Chesapeake Bay, and land use in this watershed is heavily dominated by intensive corn (*Zea maize*) and soybean (*Glycine max*)

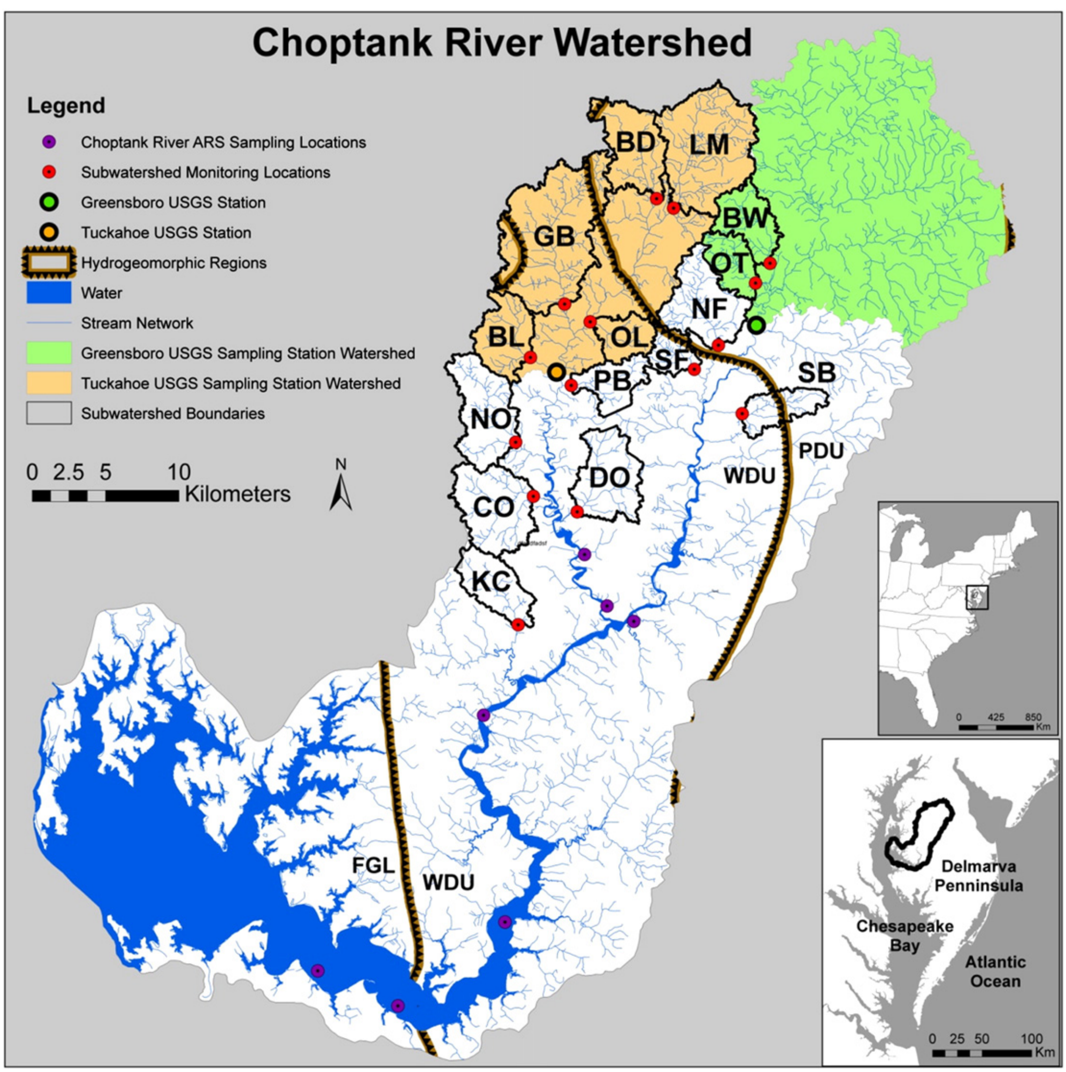

Fig. 1. Map of Choptank River Watershed with associated landscape features and the 15 subwatersheds and seven river sampling locations. Abbreviations of the subwatersheds are defined in Table 1. (WDU = well-drained upland; PDU = poorly-drained upland; FGL = finely-grained lowland).

Table 1
Conceptual model of landscape characteristics that influence transport, processing, and delivery of nitrate-N and MESA to headwater streams of the Choptank River (Ator et al., 2005; Bachman and Phillips, 1996; Denver et al., 2010, in press; Phillips and Bachman, 1996; Phillips et al., 1993).

Land use/condition	Land management	Local hydrology	Impact on water fate
Cropland on well drained soils (high permeability soils)	Low intensity ditch network and incised streams provide drainage required for crop production	Predominant movement of precipitation into shallow groundwater due to high soil permeability	Oxic groundwater flow paths to local streams through surficial aquifers; deeper flow paths to regional groundwater via high permeability sediments
Cropland with low permeability soils (prior converted wetlands)	High intensity ditch network provides drainage required for crop production	Predominant movement of precipitation by vadose zone interflow to drainage ditches; low percolation potential	Preferential ditch flow through landscape provides rapid transport to the local stream network, impacting water chemistry
Forest land with low permeability soils (forested wetlands)	Undrained with high density of naturally occurring forested wetlands	Predominant storage of precipitation in wetlands due to limited drainage networks and low permeability sediments	Preferential loss of stored water to evapotranspiration during in the growing season; anoxic groundwater flow paths to local streams through surficial aquifers

production to support poultry and some dairy production (McCarty et al., 2008). The Choptank River watershed is also a United States Department of Agriculture (USDA), Agricultural Research Service Benchmark Watershed and is part of the larger USDA Conservation Effects Assessment Project to develop a scientific basis for managing the agricultural landscape for environmental quality (NRCS, 2010). The Choptank River estuary forms at the confluence of the two upper sub-basins of the Tuckahoe Creek and Upper Choptank River. Like much of the waters in the Chesapeake Bay watershed, the Choptank River has been classified as impaired under the Clean Water Act (USEPA, 2010b).

The Choptank River watershed is located on Mid-Atlantic Coastal Plain soils (Ator et al., 2005) with parent materials defined by the superposition of Quaternary age upper-delta-plain sands and gravel deposited on Miocene and Pliocene age marine-inner-shelf sands and surficial unconfined aquifers ranging in depth from 8 to more than 30 m. The nature of these soils strongly influences the hydrology and chemistry of the Choptank River and its headwater streams (Bachman and Phillips, 1996; Phillips and Bachman, 1996; Phillips et al., 1993). The two major land uses in the watershed are cropland and forest. Forested lands are primarily located on poorly drained soils. Cropland production soils 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 moderate permeability (Table 1). Soils that are considered poorly drained generally require extensive drainage to be used in corn and soybean production.

Watershed stream flow and water quality is an assemblage of numerous ecosystem outputs resulting from highly-dynamic stream-water hydrology and chemistries. Pollutant fate and transport can vary temporally and spatially because different vadose zone and groundwater sources containing pollutants move, interact with the environmental matrix, are transformed, and respond to changing climatic conditions (Denver et al., 2010; Phillips and Bachman, 1996). Identifying an agricultural indicator can provide an essential frame of reference for analysis. This indicator should meet these criteria: (1) be highly correlated with relevant agricultural activities, (2) be conserved within the watershed, and (3) behave as a transport analog, i.e., respond similarly to ecosystem changes.

Metolachlor is a widely-used pre-emergent herbicide in corn and soybean production in the US (Thelin and Stone, 2013; Gilliom, 2007) and typically is applied to crops with nitrogen fertilizers. Glutathione conjugation is the common detoxification method for metolachlor in plants (Cole, 1994; Field and Thurman, 1996) and for its microbial degradation pathway in soil unsaturated zones (Aga and Thurman, 2001; Aga et al., 1996; Aly and Schröder, 2008; Domagalski et al., 2008). In both plant and microbial degradation, glutathione-*S*-transferase mediates glutathione nucleophilic substitution at the chlorinated carbon of metolachlor. Under aerobic conditions and through a variety of enzymatic cleavages, this conjugate gives rise to several compounds, one of which is MESA {2-[2-ethyl-*N*-(1-methoxypropan-2-yl)-6-methylanilino]-2-oxoethanesulfonic acid} (Al-Khatib et al., 2002; Feng, 1991; Field and Thurman, 1996; Graham et al., 1999).

Like nitrate-N, MESA is very soluble ($2.12*10^5$ mg/L) (Bayless et al., 2008), has a low sorption coefficient (calculated log $K_{oc} = 1.13$) (Bayless et al., 2008), and has been classified as highly mobile (Capel et al., 2008; Domagalski et al., 2008; Huntscha et al., 2008). In contrast to nitrate-N, once MESA enters ground water, it is very stable (Phillips

Table 2
Land area, use, and characteristics, and mean (standard deviation) of nitrate-N and MESA concentrations for 15 headwater subwatersheds in the Choptank River.

Subwatershed		Area (ha)	Cropland (%)	Hydric soils (%)	Cropland on hydric soils (%)	Mean nitrate-N (mg/L)	Mean MESA (μg/L)
Well drained							
German branch	GB	5662	64	65	55	4.8 (0.9)	3.8 (0.4)
Cordova	CO	2614	73	47	42	6.8 (1.9)	4.5 (0.7)
Norwich	NO	2480	61	67	58	3.2 (0.9)	3.8 (0.9)
Downes	DO	2245	79	32	26	8.1 (1.2)	3.6 (0.6)
Blockston	BL	1737	59	62	49	6.9 (1.7)	3.7 (0.6)
Kitty's Corner	KC	1587	64	58	53	3.5 (0.9)	3.5 (0.7)
Piney Branch	PB	1242	74	44	40	8.7 (1.0)	5.0 (0.7)
Oakland	OL	1035	84	29	26	9.2 (1.8)	4.4 (0.8)
South Forge	SF	808	62	54	42	5.3 (0.9)	4.4 (1.0)
Mixed drainage							
Spring Branch	SB	1143	65	41	31	5.5 (1.2)	2.2 (0.3)
Poorly drained							
Long Marsh	LM	4305	48	82	74	4.8 (0.5)	3.8 (1.0)
North Forge	NF	2404	56	70	62	2.7 (0.5)	3.8 (0.6)
Beaver Dam	BD	2259	58	84	77	4.3 (0.6)	5.1 (0.8)
Broadway	BW	1491	52	73	64	1.4 (0.7)	3.9 (0.7)
Oldtown	OT	1166	48	73	59	3.0 (1.1)	3.7 (1.1)

et al., 1999; Steele et al., 2008); MESA persists over decadal time scales (Denver et al., 2010). In surface water, the modeled half-life for all MESA processing (phototransformation, transport, etc.) within the Lake Greifensee (Switzerland) epilimnion was 100–200 days (Huntscha et al., 2008). Finally, a similar transport process was responsible for MESA and nitrate-N delivery to streams in several US agricultural watersheds (Domagalski et al., 2008). Thus, because the major metabolite of metolachlor, MESA, is exceptionally stable and soluble, has a low K_{oc}, and is formed in the unsaturated zone where nitrate-N is transported, it is an ideal transport analog for assessing the fate of agricultural nitrate-N.

Here, we consider additional data concerning MESA fate relative to nitrate-N in a small research catchment in the Chesapeake Bay watershed (Angier et al., 2002, 2005; Gish et al., 2005). We then investigated its potential use as a transport analog of agricultural nitrate-N from the Choptank River headwaters to the estuary. Previously, we reported results in studies tracking nitrate-N and MESA concentrations over several years at seven stations in the Choptank River estuary (Whitall et al., 2010) and at the stream outlets of 15 headwater subwatersheds (Fig. 1) (Hively et al., 2011). The hydrogeomorphology, land use (e.g., croplands, forest, developed, wetlands), and soil properties of the subwatersheds have been characterized and previously reported (Hively et al., 2011); some of these data are shown in Table 2 and Fig. 1. Using these datasets, we examined the relationship of MESA with nitrate-N: 1) to discern nitrate-N fate in and its sources to the estuary, 2) to reveal critical areas where enhancing nitrate-N uptake and reduction in the subwatersheds would be beneficial to meet TMDL requirements (MDE, 2012), and using this information, 3) to identify the most appropriate conservation practices for each area.

2. Materials and methods

2.1. Small research catchment in the coastal plain within the Chesapeake Bay

Groundwater samples were collected from piezometers installed a small, well-characterized, 70-ha research catchment located on the western shore of the Chesapeake Bay in the Maryland inner coastal plain (Angier et al., 2002, 2005; Gish et al., 2005). Two sets of nested piezometers at different sites within the riparian area of this catchment were sampled at various times during the year. The first set contained two piezometers which were sampled three times (September and November 2003, and January 2004); the second set contained three piezometers which were sampled twice (April and August 2001). Samples were collected as described previously (Gish et al., 2005). Briefly, piezometers were pumped at least one full water volume and allowed to fully recover; 20-mL samples were collected for nitrate-N analysis, whereas 1-L samples were needed for MESA analysis which often required hours to obtain. The samples were processed (within 24 h) and analyzed as described below.

2.2. Sampling of subwatersheds and river stations

All Choptank watershed sampling occurred at or near base flow conditions in the watershed tributaries, at least two days after any significant (greater than 10 mm) rainfall event and when flow was less than 5 m^3/s at the two local USGS stream gauge stations: Upper Choptank near Greensboro, MD (01491000) and Tuckahoe Creek near Ruthsburg, MD (01491500) (Figs. 1, 2). Using a small research vessel, estuarine

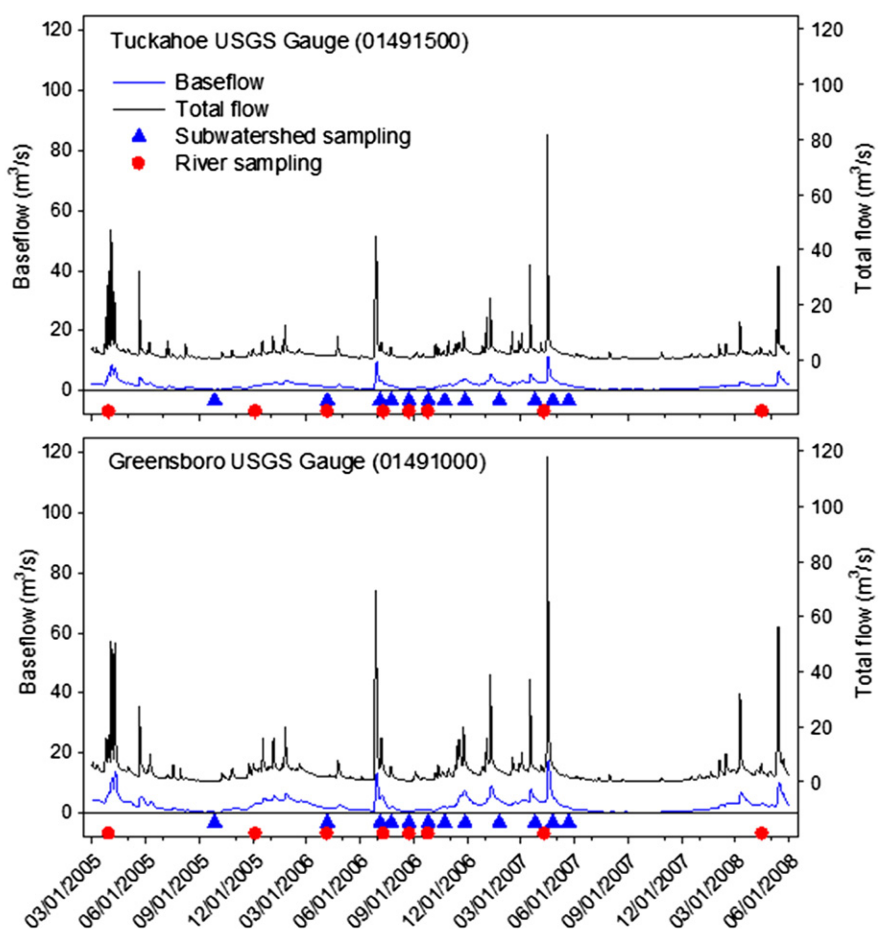

Fig. 2. Hydrograph separated flow for Tuckahoe Creek and Upper Choptank River (Greensboro gauge) with river and subwatershed sampling dates. Hydrograph separation was performed using digital filter models as described by (Lim et al., 2005).

water samples were collected between March 2005 and April 2008 just below the water surface (0.1 m) from a transect running the length of the navigable and tidal portion of the Choptank River (Fig. 1, Table 3) (Whitall et al., 2010). Subwatershed samples were collected at the outlets of 15 non-tidal upland subwatersheds of the Choptank River that were drained by third and fourth order streams (Fig. 1) (Hively et al., 2011). Nine watersheds fell mostly within the well drained hydrogeomorphic region, five within the poorly drained region, and one included mixed portions of both well and poorly drained regions (Table 2). Collection occurred on a monthly or bimonthly basis from September 2005 to May 2007; samples were taken from the center of the stream.

Salinity was measured in situ using an YSI 556 multi-parameter field meter (Geotech Environmental Equipment, Inc., Denver, CO) or an YSI 6600 multi-parameter Sonde (YSI, Yellow Springs, Ohio), except for December 5, 2005. The limit of quantitation for salinity was 0.01. Water samples were collected with a stainless steel pail, stored in glass (nutrient analysis) or stainless steel containers (MESA analysis) on ice, and transported to the laboratory for processing within 24 h. Only sampling events where both nitrate-N and MESA concentration data were available (river sampling events $n = 8$; subwatershed sampling events $n = 12$) were included in this analysis.

2.3. Sample processing and analysis

Nitrate-N (Quickchem Method 12-107-01-1-B) concentrations were determined colorimetrically with a Quickchem automatic flow injection ion analyzer (Lachat Instruments, Milwaukee, WI). The limit of quantitation for nitrate-N was 0.01 mg N/L. MESA was analyzed using procedures published previously (McConnell et al., 2007). Briefly, samples were filtered through 0.7 μm GF/F filter paper (Whatman, Inc., Florham Park, NJ) prior to processing. MESA extraction was conducted using a solid phase extraction cartridge (Oasis HLB, Waters Corp., Milford, MA) and triphenylphosphate (Supelco Inc., Bellefonte, PA) as an extraction surrogate. Concentrations were measured by high performance liquid chromatography/triple quadrupole mass spectrometry using [^{13}C]2,4-Dichlorophenoxyacetic acid (100 μg/mL) (Cambridge Isotope Laboratories, Andover, MA) as an internal standard. The limit of quantitation for MESA was 0.01 μg/L. Single variable linear regression (R^2) was used to assess the correlations using SigmaPlot® 12.3 (Systat Software, Inc., Chicago, IL) or Microsoft® Excel 2007 software (http://office.microsoft.com). Confidence values (p) were determined using SigmaPlot® 12.3.

2.4. Land use data development

A high-resolution geospatial coverage of watershed land cover was developed through on-screen digitizing in ArcMap 9.3 (ESRI, Redlands, CA) using the 1998 National Agricultural Imagery Program digital orthophoto quad imagery (1:12,000 scale) as a base map (APFO, 2010). Identified land use categories included: cropland (i.e., grain, forage, vegetable, and nursery crops); forest (deciduous and evergreen); developed areas (i.e., residential development, urban areas, industrial operations); and water (i.e., ponds, streams, drainage ditches). Land cover was prepared as total area and percent of subwatershed area (Table 2) (Hively et al., 2011). Additional geospatial data layers were developed for landscape analysis (Table 2) including hydric soils (soil classes C and D) from the Soil Survey Geographic (SSURGO) soils coverage (NRCS, 2008); and cropland on hydric soils through comparison of the previously mentioned land cover and hydric soils maps.

Table 3
Sampling station locations, water depths, and salinity with standard deviation.

Station	Latitude (north)	Longitude (west)	Water depth (m)	Salinity
1	38.60267	76.11892	10	10.5 ± 1.8
2	38.57791	76.06641	7	9.4 ± 1.8
3	38.75618	75.99879	4	6.3 ± 2.1
4	38.63382	75.98284	12	1.9 ± 1.6
5	38.81958	75.88142	5	0.5 ± 0.6
6	38.82539	75.90348	2	0.4 ± 0.5
7	38.85670	75.92215	6	0.2 ± 0.1

The 2009 and 2010 USDA-National Agricultural Statistics Service, National Cropland Data Layer were used to examine the cropland management gradient across the 15 subwatersheds (Boryan et al., 2011). Specifically, the percentage of cropland devoted to each of the three dominant summer crops (corn, soybean, double crop winter grain/soybean) were analyzed. From 2009 to 2010, the acreage of corn and full season soybean increased on all subwatersheds, while double crop small grain/soybean decreased, likely due to changes in market drivers. The occurrence of corn increased slightly more in the well drained subwatersheds (44% and 51% in 2009 and 2010, respectively), relative to the poorly drained watersheds (37% and 40%) with corresponding decreases in the occurrence of full season soybean.

3. Results and discussion

3.1. MESA and nitrate-N fate in an anaerobic environment

Previous studies have shown that no relationship exists between ground water age and MESA concentration, i.e., the MESA is stable in ground water (Steele et al., 2008). We have also examined the fate of MESA relative to nitrate-N as part of a larger study to assess the effectiveness of riparian areas in mitigating agricultural nitrate-N. This well-characterized small catchment of 70 ha consisted of a small first order stream within a riparian wetland that received ground water from the 20 ha of catchment cropland that were under continuous corn production (Angier et al., 2002, 2005; Gish et al., 2005). Metolachlor and various forms of agricultural nitrogen were applied annually (Gish et al., 2005). The hydrology of this catchment has been well characterized; most notably, oxic groundwater from the sand aquifer below the riparian wetland exfiltrated through vertical flow paths (Angier et al., 2002; Gish et al., 2005). Two sets of nested piezometers within the riparian wetland were analyzed for nitrate-N and MESA over several months (Fig. 3). Sequential consumption of oxygen and then nitrate-N was observed (Angier et al., 2005; Gish et al., 2005), and concomitantly, MESA concentrations remained stable (Fig. 3). In addition, the resulting stream water attenuated nitrate-N concentration relative to the groundwater without evidence for MESA diminishment (data not shown). These observations in conjunction with previous studies (Denver et al., 2010; Phillips et al., 1999; Steele et al., 2008; McConnell et al., 2007) indicate that 1) MESA is stable even in anaerobic

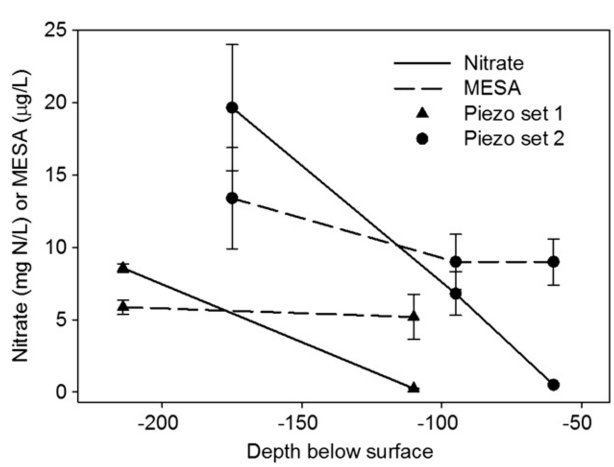

Fig. 3. Relationship between nitrate-N and MESA concentrations along flow paths of exfiltrating groundwater at two upwelling sites in a riparian wetland. The first set contained two piezometers and were sampled three times (September and November 2003, and January 2004); the second set contained three piezometers and were sampled twice (April and August 2001). Error bars indicate standard error amongst sampling dates of each piezometer.

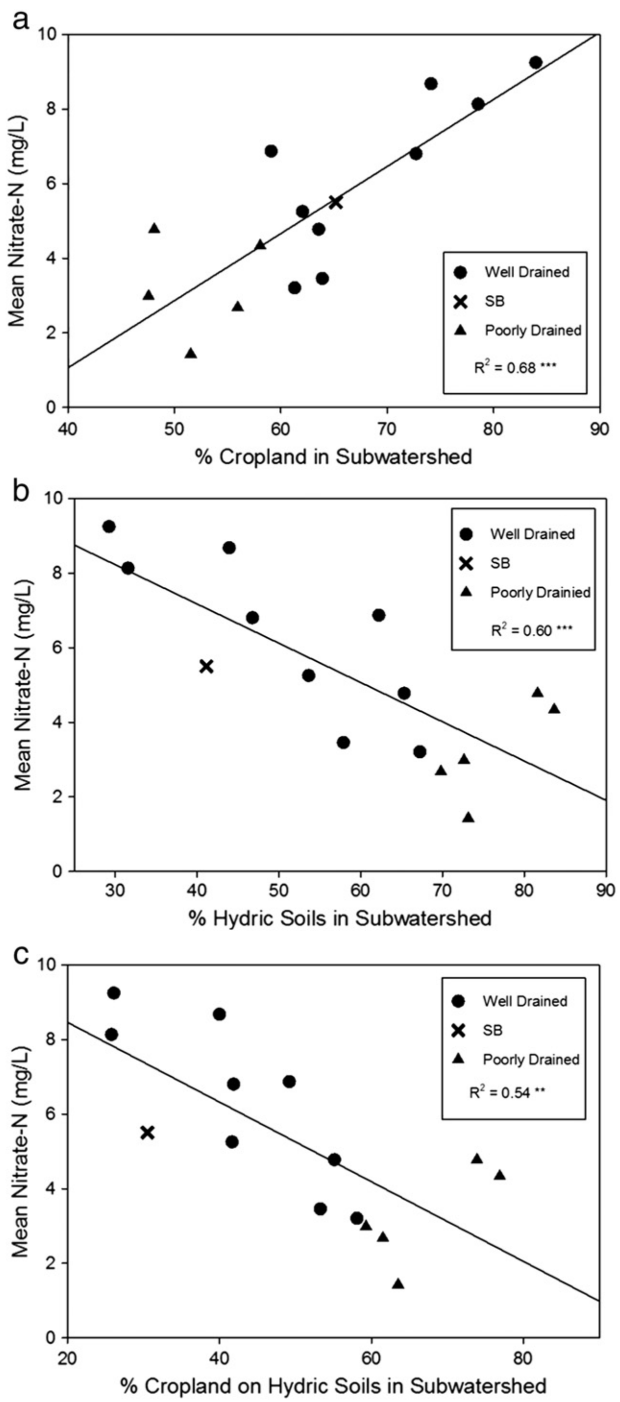

Fig. 4. Regression models for nitrate-N as a function of land use and land characteristics in 15 subwatersheds of the Choptank River ($n = 12$ sampling events): a) Mean nitrate-N concentration versus percent cropland; b) mean nitrate-N concentration versus percent hydric soils; c) mean nitrate-N concentration versus percent cropland on hydric soils. (PDU = poorly-drained upland; WDU = well-drained upland; SB = south branch, a mixed drainage subwatershed).

environments and 2) MESA can serve as an effective transport analog for nitrate-N.

3.2. MESA and nitrate-N concentrations in the subwatersheds

Baseflow water samples were collected from the outlets of 15 subwatersheds within the Choptank River watershed, five draining into the Upper Choptank River sub-basin, nine draining into Tuckahoe Creek sub-basin, and one draining near the Upper Choptank–Tuckahoe confluence (Figs. 1, 2) (Hively et al., 2011). The mean nitrate-N and MESA concentrations are shown in Table 2. Previous results indicated significant differences in nitrate-N concentrations between the well drained and poorly drained subwatersheds, however, no such trend was observed with MESA concentrations (Hively et al., 2011). Furthermore, seasonal trends of nitrate-N and MESA concentrations were essentially non-existent (Hively et al., 2011). Nitrate-N concentrations were positively correlated with percent cropland area, whereas MESA concentrations were surprisingly unrelated to percent cropland area (Hively et al., 2011), which suggests that additional factors, such as differences in drainage and geomorphology, may be influencing the delivery of agricultural waters to the sampling sites. Multivariate analyses of these data (Hively et al., 2011) along with prior regional studies (Bachman and Phillips, 1996; Böhlke and Denver, 1995; Denver et al., 2010; Phillips et al., 1993) have suggested that multiple factors influence nitrate-N concentrations in the stream waters. Agricultural drainage, percentages of agricultural, forested, developed and conservation reserve lands, and percentages of hydric soils and forested wetlands were examined, but in these previous analyses, no definitive causal relationships were discernible among these factors.

3.3. Simple models to assess the influence of cropland and hydric soils on nitrate-N in headwater streams

Comparative subwatershed studies can be a powerful tool for assessing the influence of landscape parameters on water quality. In an obvious simple model, the amount of nitrate-N exported by a subwatershed stream can be correlated to the amount of fertilizer-N applied and may therefore be strongly correlated with the amount of cropland in the subwatershed. Such a conclusion may be supported by strong correlation between the nitrate-N concentration and percent cropland in the 15 subwatersheds (Fig. 4a; $R^2 = 0.68$, $p < 0.001$). This model however, does not take into account loss processes, such as denitrification of the residual agricultural N, nitrate-N not utilized by the crop. Metrics related to landscape biogeochemistry, such as the extent of hydric soils where denitrification is favored due, could also be important predictors of stream water nitrate-N concentration. Hydric soils are frequently anaerobic due to saturation and/or ponding, but can become less anaerobic if artificially drained (NRCS, 2012). In the Choptank River subwatersheds, nitrate-N is inversely correlated to percent hydric soils, although not as strongly as agricultural land percent (Fig. 4b; $R^2 = 0.60$, $p < 0.001$).

Collinearity between landscape metrics can, however, confound interpretation of regression models and inhibit assessment of the causal

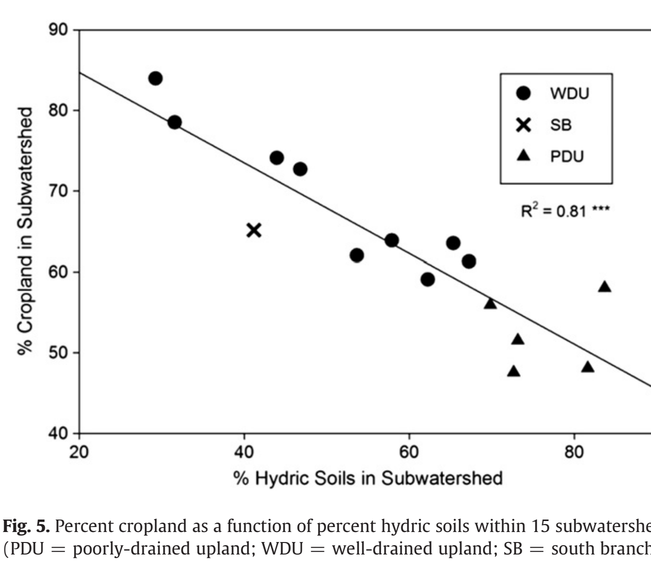

Fig. 5. Percent cropland as a function of percent hydric soils within 15 subwatersheds (PDU = poorly-drained upland; WDU = well-drained upland; SB = south branch, a mixed drainage subwatershed).

factors that affect water quality. An evaluation of the percent area of subwatershed cropland areas with respect to overall percent area of hydric soils within each subwatershed revealed a strong inverse relationship (Fig. 5; $R^2 = 0.81$, $p < 0.001$). This strong collinearity, therefore, inhibits efforts to separate the parameter effects on nitrate-N content in streams using simple regression models.

Prior to the 1600's, the Choptank River watershed contained extensive wetland complexes (Benitez and Fisher, 2004). Estimates are that approximately half of these wetlands have been lost (Lang et al., 2008), mainly due to drainage and subsequent agricultural conversion. Thus, a large portion of croplands in this region are on hydric soils. The landscape metric of percent area of hydric soils includes not only cropland but also hydric soil complexes in non-cropland areas with presumably less interaction with agricultural nitrate. A metric gauging the amount of cropland on hydric soils should be a more sensitive indicator of the biogeochemical potential for denitrification of agricultural N than percent hydric soils, because of the strong root zone and vadose zone interactions as nitrate-N moves into groundwater under the croplands (Denver et al., in press). However, this parameter lacks any consistent measure of agricultural intensity in the subwatersheds, and only a moderate inverse relationship was observed between nitrate-N and cropland on hydric soil (Fig. 4c; $R^2 = 0.54$, $p < 0.01$). This simple model lacks information concerning the transport of agricultural waters from the croplands to the stream headwaters and concomitantly the effects of dilution on nitrate-N concentration.

3.4. A conceptual model for connection of croplands to headwater streams

The analysis of upstream water quality as a function of landscape parameters often involves the implicit assumption that the cumulative stream discharge represents an unbiased integration of contributions from all the various landscape elements. These analyses are typically based on the amount of land surface area; however, they do not generally consider the proportion of surficial groundwater contribution to headwater streams relative to delivery to deeper regional groundwater.

Flow generation in the headwater streams of the Choptank River watershed is generally dominated by contributions from the surficial aquifer, which is an unconsolidated sand and gravel deposit of the Quaternary period (Trapp and Horn, 1997). In the cropland areas, the surficial aquifer is under heavy influence from agrochemical application to fields (Graphical Abstract, Table 1) (Bachman and Phillips, 1996; Denver et al., 2010, in press; Phillips and Bachman, 1996; Phillips et al., 1993). Cropland areas with well drained soils contribute more to deeper regional groundwater resources than cropland areas on poorly drained soils, and thus the proportion of surficial groundwater contribution from cropland will be less in well drained areas than in poorly drained areas (Table 2). These factors may lead to cropland contributions to stream flow that are lower than expected based on land use. In the well drained areas, non-agricultural and non-ditched portions of the subwatersheds will also contribute to the deeper regional groundwater.

Greater ditching exists in the poorly drained land areas as compared to the well drained areas (Hively et al., 2011). Ditch and tile drainage, which by design will cause preferential water movement to the streams, reduces surficial groundwater movement to deeper groundwater aquifers. As a result, cropland contributions to stream flow will be greater and not proportional to land surface area, and concomitantly, drainage from other unditched land uses in the subwatershed will be less represented in the stream flow. This interaction between ditch drainage and hydrogeomorphological classes of the subwatersheds results in differing amounts of cropland contribution to the headwater stream flow. We surmise then that an inherent bias in landscape sampling is generated by landscape position and ditch drainage; streams in poorly drained areas over-sample croplands, and streams in well drained areas under-sample croplands. Non-ditched areas in poorly drained subwatersheds are generally forested and often result in increased wetland extent and storage of surface water (Table 1) (Hively et al., 2011).

3.5. Utilizing MESA as an indicator of agricultural water and dilution in the subwatersheds

MESA is formed in the root zone where residual agricultural nitrogen is released to the surficial waters and can be used to indicate transport and dilution effects on nitrate-N versus reduction (Graphical Abstract, Table 1). The ratio of mean nitrate-N concentration/(mean MESA concentration *1000) for each subwatershed was examined as a function of percent cropland on hydric soil. This inverse relationship (Fig. 6a; $R^2 = 0.65$, $p < 0.001$) takes into consideration not only dilution and denitrification of nitrate-N, but also the stream sampling bias of the croplands caused by drainage ditch networks. Based on this new model, we hypothesize that smaller nitrate-N concentrations from poorly drained subwatersheds are due to greater nitrate-N reduction within the subwatershed and not simply due to less cropland and therefore less nitrate-N application. Furthermore, for the well drained subwatersheds, larger nitrate-N concentrations are not only a response to larger percents of cropland in each subwatershed and therefore more nitrate-N application, but also the result of less nitrate-N reduction.

The collinearity of hydric soils and croplands (Fig. 5) provides an explanation for the apparent unpredictability of MESA concentrations in the subwatersheds when using percent land use (Fig. 7a–c; $R^2 = 0.04$, 0.01, and 0.04 for percent cropland, hydric, and cropland

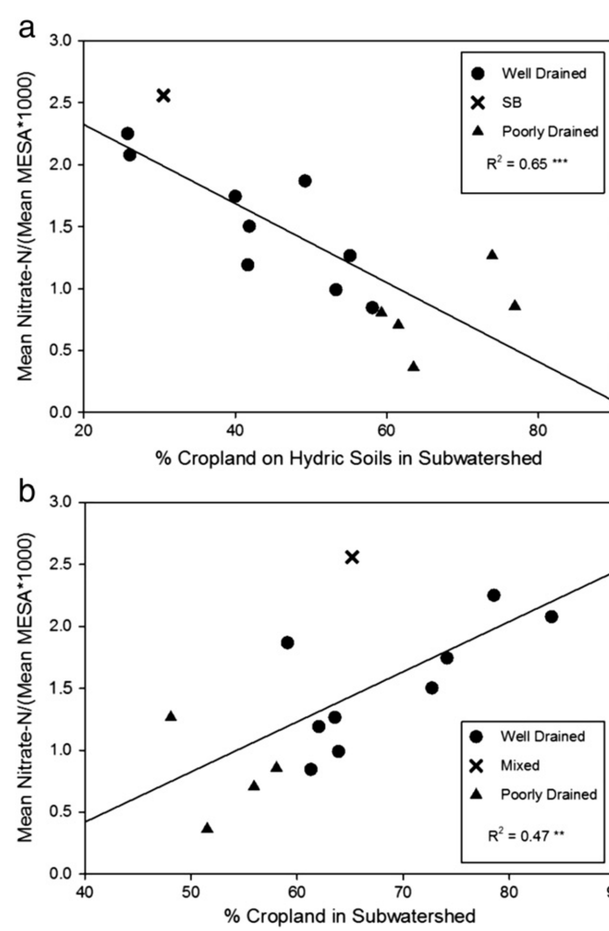

Fig. 6. Regression models for nitrate-N as a function of land use and land characteristics in 15 subwatersheds of the Choptank River ($n = 12$ sampling events): a) Mean nitrate-N concentration/(mean MESA concentration * 1000) versus percent cropland on hydric soils; b) mean nitrate-N concentration/(mean MESA concentration * 1000) versus percent cropland. (PDU = poorly drained upland; WDU = well drained upland; SB = south branch, a mixed drainage subwatershed).

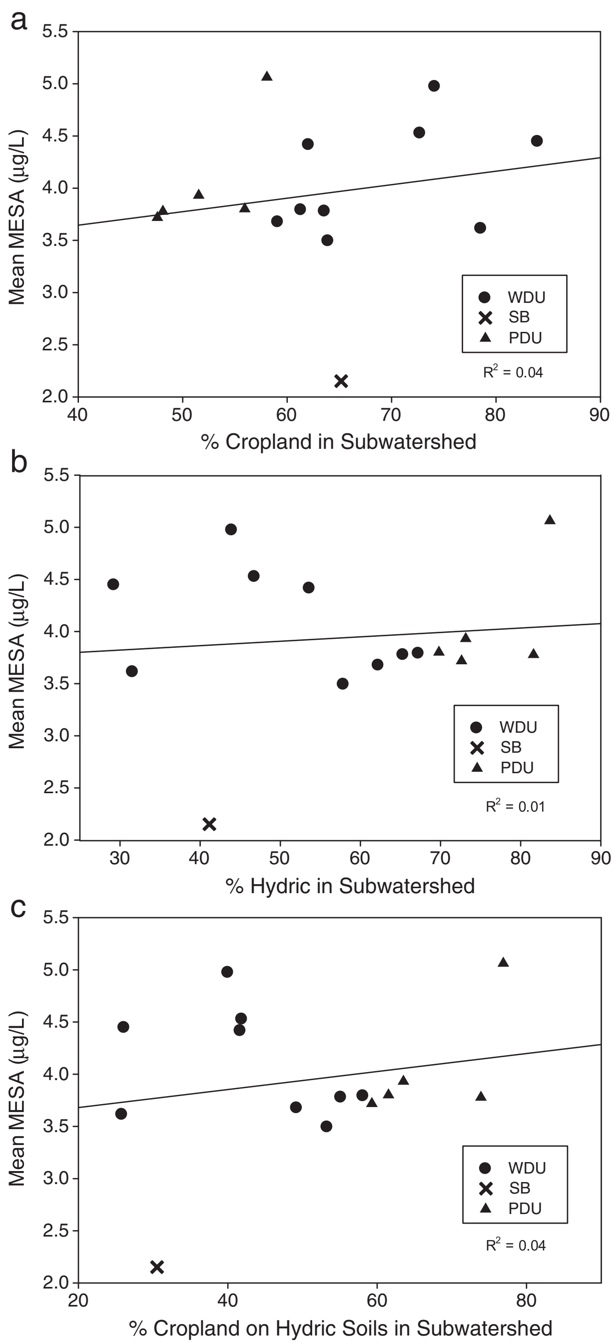

Fig. 7. MESA concentration as a function of land use and land characteristics: a) Mean MESA concentration versus percent cropland; b) mean MESA concentration versus percent hydric soils; c) mean MESA concentration versus percent cropland on hydric soils (PDU = poorly-drained upland; WDU = well-drained upland; SB = south branch, a mixed drainage subwatershed).

on hydric soils, respectively). Subwatersheds with a larger percent of hydric soils have a lower percent of cropland, but also have more efficient delivery of agricultural waters to streams via ditching, and therefore increased the sampling of croplands. Conversely, subwatersheds with a larger percent cropland area and lower percent of hydric soils have less ditching, and therefore less sampling of cropland and subsequent influence on the agrochemical magnitude in the headwater streams. The seemingly random values of MESA concentration actually afford information about the interaction between drainage and percent cropland and provide an unambiguous method to measure the sampling bias of headwater streams (Fig. 6a; B, $R^2 = 0.47$, $p < 0.01$). MESA provides a method to disentangle the complex landscape interactions that affect nitrate-N concentrations in stream water.

Finally, the mean MESA concentration for the mixed drainage subwatershed, Spring Branch (SB), is significantly less than the mean MESA concentration of all the other observations ($[\text{MESA}]_{\text{SB}} = 2.2 \pm 0.3$ µg/L; $[\text{MESA}]_{\text{Allothers}} = 4.1 \pm 0.9$ µg/L). Relative to the other subwatersheds, SB has a moderate amount of cropland and a very low percentage of hydric soils and cropland on hydric soil; most of the cropland in SB is in the well drained area. These observations are consistent with our model. The combination of a moderate amount of cropland and low percent of cropland on hydric soil (less connection to streams) leads to lower MESA in stream water, yet at the same time due to the very low amount of hydric soils leads to higher nitrate-N concentration values.

3.6. Nitrate-N in the Choptank River estuary

Tracking the fate of agricultural nitrogen in tidal estuaries is frequently confounded by tidal mixing and dilution of upland dissolved constituents. A typical approach to account for dilution in such settings is the use of saline gradient measurements obtained from estuarine transects with application of a two endmember mixing model. A linear fit to the model is indicative of conservative behavior for a dissolved constituent, whereas a nonlinear curve indicates non-conservative dynamic, i.e., the constituent is transformed or leaves the dissolved phase (Officer and Lynch, 1981).

Samples were collected at seven monitoring stations (Fig. 1) within the estuarine portion of the Choptank River on eight sampling dates (March 2005–April 2008) along a transect from near the mouth of the Choptank River main stem, beyond the confluence of the Tuckahoe Creek and the Upper Choptank River, to their northern most navigable portions; all stations were tidal (salinity range = 0.06–12) (Whitall et al., 2010). For each date, nitrate-N concentrations were examined as a function of salinity. As reported previously, a curvilinear relationship was observed for nitrate-N in the summer months, suggesting a biological processing during transport. However, the Choptank River is fed by two major upland sources, the Upper Choptank River (655 km^2 watershed) and Tuckahoe Creek (395 km^2 watershed) (Fig. 1); regional groundwater also contributes to the river estuary (Lindsey et al., 2003). Thus, a more appropriate mixing model for this complex estuary requires at least a three end-member model without a unique solution, and conclusions based on the two end-member model may be misleading.

3.7. MESA as an indicator of agricultural water in the estuary

As shown above and elsewhere (Denver et al., 2010; McConnell et al., 2007; Phillips et al., 1999; Steele et al., 2008), MESA is a stable, soluble indicator for agricultural waters and has a long half-life in surface waters (Huntscha et al., 2008). The residence time of waters in the Choptank River estuary has been estimated to be 19 days (Bricker et al., 2007). Thus, MESA provided a more accurate assessment of nitrate-N fate in the estuary than commonly-used salinity mixing curves. Nitrate-N concentrations relative to MESA concentrations along the estuary transect were linear for all eight sampling dates ($0.95 \le R^2 \le 0.99$ for all sampling dates except 25-Sep-2006 where $R^2 = 0.90$; $0.0001 > p > 0.044$; Fig. 8). This strong correlation indicates that nitrate-N was conserved in much of the Choptank River estuary on all sampling dates and that dilution is responsible for the changes in nitrate-N and MESA concentrations. An alternative, yet highly improbable, explanation is that the rates for nitrate-N loss and MESA degradation in the river are exactly the same.

Although somewhat unusual, nitrate conservation in estuaries has occurred elsewhere, for example, the Conwy estuary and Waterford Harbor in Ireland (Raine and LeB Williams, 2000) and the Delaware Bay (Fisher et al., 1988). The lack of nitrate-N reduction in the estuarine

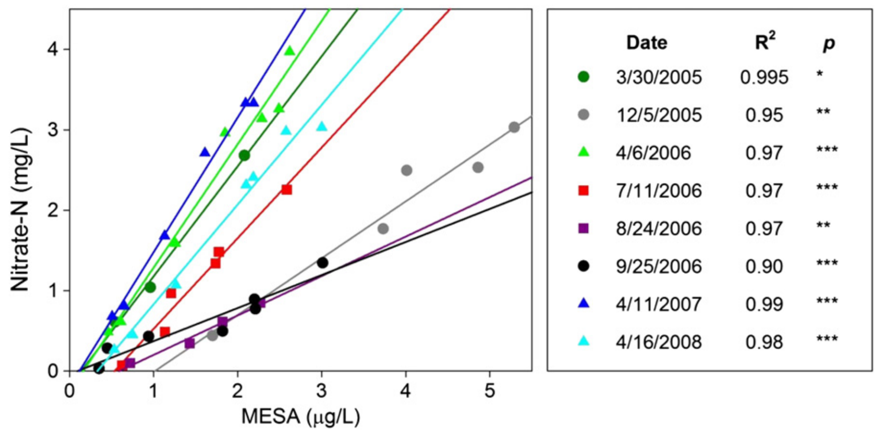

Fig. 8. Linear relationships observed between estuary nitrate-N and MESA concentrations at seven sampling stations on the Choptank River estuary ($n = 8$ sampling events).

portion of the Choptank River raises some concern because nitrate-N will drain into the Chesapeake Bay where its negative effects have been amply documented (CBP, 2010; Fisher et al., 1988; USEPA, 2010b). Newly developed TMDLs for the Chesapeake Bay and its tributaries indicate that by 2017, the state of Maryland will be required to reduce nitrogen loads to the Bay from the croplands by 23% from 7700 to 5900 metric tons per year (MDE, 2012).

4. Conclusion

Our new findings suggest that effective agricultural non-point management strategies should include methods to curb nitrate-N losses prior to release of nutrients into the Choptank River estuary, where nitrate-N transport is conservative. Agricultural conservation efforts should focus on reducing nutrient loading and enhancing denitrification further upstream, in the cropland areas of the headwater subwatersheds. Using MESA as an indicator of agricultural drainage water and dilution processes in the subwatersheds, when combined with information on land use and hydrogeomorphology, may lead to more effective implementation of conservation practices targeted to reduce nitrogen leaching in critical areas of the landscape.

The results here indicate that in well drained areas, the removal of residual N needs to be accomplished prior to entering surficial groundwaters. For example, winter cover crops can be used to reduce the loss of residual nitrogen from well drained agricultural areas. (Hively et al., 2009). In the poorly drained areas where denitrification is prevalent, wetland restoration and use of controlled drained structures that minimize ditch flow should be quite useful in maximizing denitrification and minimizing the amount of nitrate-N reaching the stream outlets (Denver et al., in press; Fisher et al., 2010; Lang et al., 2012).

Extrapolation of this method to other Chesapeake Bay tributaries may provide a means to compare nitrate-N processing in watersheds across this important and complex landscape. The specific ratio of nitrate-N and MESA leaving cropland is expected to vary regionally according to local patterns of agricultural management and should be characterized within watersheds of interest. The demonstrated relationship between agricultural nitrate-N and MESA could also be used to observe nitrate-N processing in or the in-flux of downstream N sources to other riverine ecosystems and estuaries dominated by local corn and soybean production.

Conflict of interest

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