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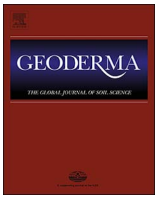

Topographic and physicochemical controls on soil denitrification in prior converted croplands located on the Delmarva Peninsula, USA

Xia Li[a], Gregory W. McCarty[b,*], Megan Lang[c], Thomas Ducey[d], Patrick Hunt[d], Jarrod Miller[d]

[a] *Department of Geographical Sciences, University of Maryland, College Park, MD 20742, USA*
[b] *USDA ARS, Hydrology & Remote Sensing Laboratory, Beltsville, MD 20705, USA*
[c] *Fish and Wildlife Service, Falls Church, VA 22041, USA*
[d] *USDA ARS, Coastal Plains Soil, Water, and Plant Research Center, Florence, SC 29501, USA*

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ABSTRACT

Topographic and soil physiochemical characteristics exert substantial controls on denitrification, and the effect of these controls is especially evident in fertilized agricultural lands. To depict these controls at a landscape scale for decision support applications, metrics (i.e., proxies) must be developed based on commonly available geospatial data. In this study, we carried out an observational study on denitrification potential (DP) and capacity (DC) in three actively farmed crop fields that were converted from forested wetlands (i.e., prior converted croplands). The combined effects of ten topographic and physiochemical factors, including three topographic attributes (relief, topographic wetness index, and positive openness), two soil texture indices (sand and clay), and five soil properties (soil moisture, pH, electrical conductivity, soil organic carbon and total nitrogen), on DP and DC were analyzed. The three topographic attributes were developed using a digital elevation model (DEM) derived from light detection and ranging (LiDAR) data. Nitrate and carbon addition led to a doubling in DP compared to DC without soil amendment. Topography explained the greatest amount of variation in DP across the three sites. The relationship between topography and DP may partly be explained through the relatively robust relationships between topography and soil moisture, texture, and carbon content. Soil electrical conductivity (EC) exhibited the highest correlation with DC (r^2 = 35%). DP and DC were higher under drought conditions with low soil moisture, relative to average conditions with relatively higher soil moisture, which may be related to the substantial increase in soil EC under drought conditions. However, DP and DC were less responsive to soil EC at sandy sites that tended to have low soil moisture. Results of this study suggest that the spatial-temporal variations in denitrification at these croplands were primarily caused by complex interactions between soil properties and landscape position. Topographic metrics derived from LiDAR data have the potential to improve understanding of denitrification variability at the landscape scale.

1. Introduction

Denitrification is the primary process supporting nitrate removal from terrestrial ecosystems (Knowles, 1982; Hunter et al., 2009). Under anaerobic conditions, nitrate (NO_3^-) is typically reduced to molecular nitrogen (N_2) and nitrous oxide (N_2O), which are subsequently emitted to the atmosphere. Denitrification is affected by three controlling factors, including oxygen, NO_3^-, and organic carbon (C) levels (Seitzinger et al., 2006; Palta et al., 2013). Usually, denitrification occurs when O_2 concentrations are $< 0.2\ \mathrm{mg\ L^{-1}}$ and N_2 is the primary end product (Seitzinger et al., 2006). However, N_2O production relative to N_2 increases during denitrification if soil NO_3^- is elevated because NO_3^- is a preferred electron acceptor over N_2O. The denitrification process is also closely related to other parameters, such as soil C:N ratio, pH, and soil moisture (Ullah et al., 2005; Ruser et al., 2006; Morse et al., 2012; Hunt et al., 2014).

Wetlands have demonstrated high efficiency in removing nutrients, especially nitrate-nitrogen, from waters (Lowrance et al., 1997; Mayer et al., 2007; Ducey et al., 2015). In the United States (U.S.), about 53% of wetlands have been converted to other land use types over the past 100 years (Dahl, 1990). Large areas of wetlands have been drained and used as arable lands for crop cultivation (Johnston, 1994). Conversion of wetland to agricultural land substantially changes soil moisture conditions through fill, surface or sub-surface drainage (i.e., open ditches or tile drains), and/or high water consumption by agricultural plants (Blann et al., 2009; Murray et al., 2009; Li et al., 2016a; Li et al.,

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[*] Corresponding author.
E-mail address: greg.mccarty@ars.usda.gov (G.W. McCarty).

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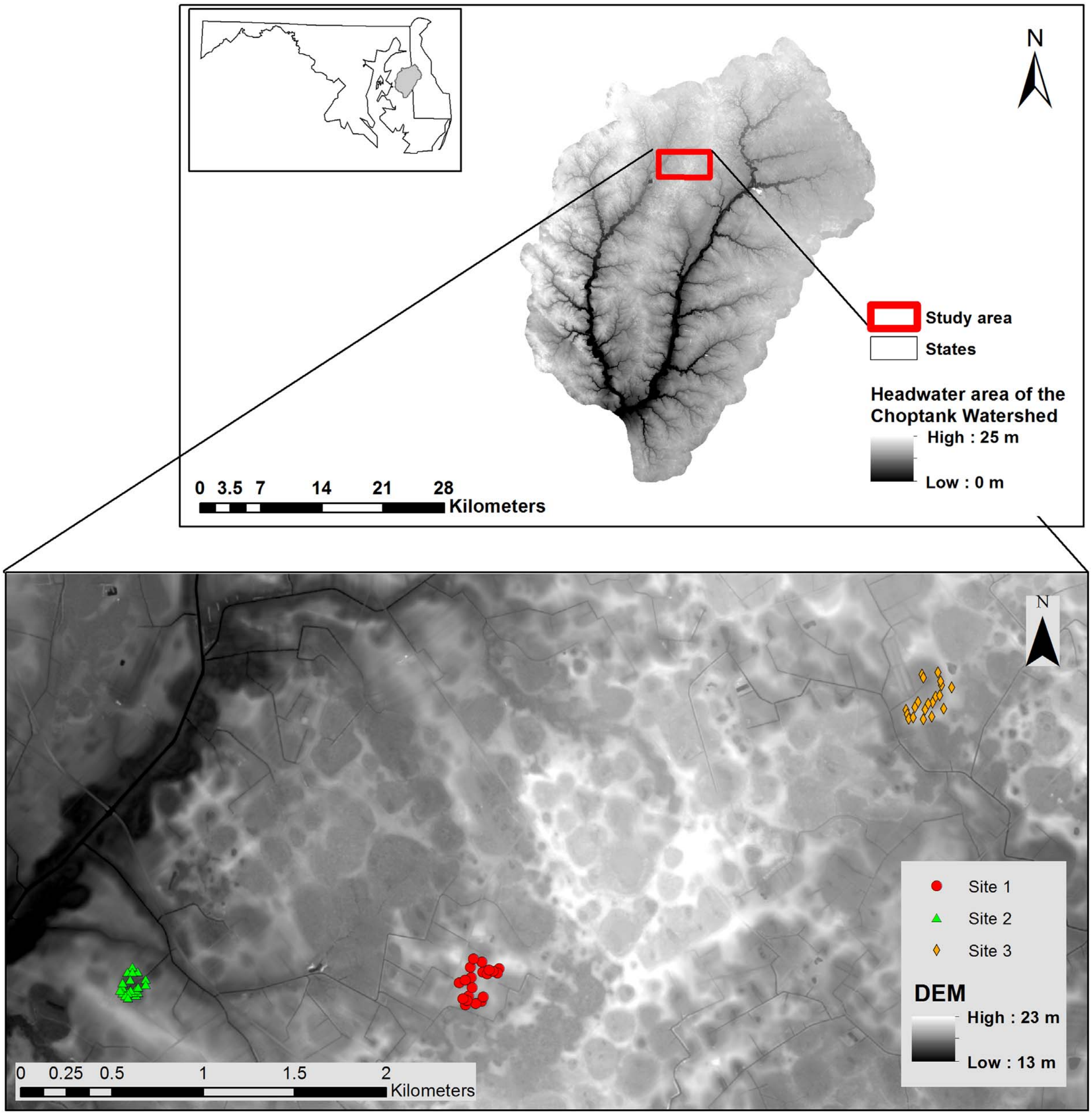

Fig. 1. Location of the study areas.

2017). Unlike hydric soils in wetlands that are usually in a state of low oxygen content (Mitsch and Gosselink, 2015), top soils in most agricultural lands are under aerobic conditions (Blann et al., 2009; Munch and Velthof, 2006). Extent of anaerobic conditions in agricultural land depends on multiple factors, including precipitation, irrigation, and soil texture, which influence soil volumetric water content (Munch and Velthof, 2006). Denitrification rates tend to be site- and time-specific due to variations in hydrologic conditions (Dobbie et al., 1999; Ruser et al., 2006).

In addition to soil properties, such as soil organic matter and soil moisture, the effect of topography on denitrification has received increasing attention because it may affect denitrification by controlling soil water saturation, texture, and biogeochemistry (Shaftel et al., 2012; Duncan et al., 2013; Anderson et al., 2014, 2015). Topography is often depicted using digital elevation models (DEMs), which can be generated using multiple data sources. One relatively new and rapidly developing data source is Light Detection and Ranging (LiDAR). Compared to traditional, non-LiDAR derived DEMs, data from LiDAR often provide more detailed and more accurate topographic information (Coren and Sterzai, 2006; Glenn et al., 2006).

Topographic metrics derived from DEMs have been developed to understand spatial-dependent processes in response to landscape morphology. Several studies have employed either topographic position or topographic wetness index (TWI) to investigate spatial variation in denitrification (Hunt et al., 2007; Duncan et al., 2013; Anderson et al., 2014, 2015). However, a single topographic attribute is not enough to obtain a robust understanding of topographic effects on denitrification (Florinsky et al., 2004). Based on the spatial scope of variables, there are three main groups of topographic attributes, including local topographic characteristics (surface geometry of a studied point), non-local topographic variables (relative position of a studied point on the surface), and combined topographic characteristics (local and nonlocal variables) (Florinsky, 1998). Topographic openness is a non-local topographic index which presents an angular surface measure and represents the topographic dominance or enclosure of any location in an irregular surface (Yokoyama et al., 2002; Smith and Clark, 2005;

Doneus, 2013). It has rarely been used in denitrification investigations. However, its high efficiency in revealing depressions (Doneus, 2013) makes openness a good candidate parameter to explain spatial variability of denitrification in a landscape that is characterized by depressional features (Fenstermacher et al., 2014). Topographic relief is a widely used non-local topographic index, and has been found to help characterize denitrification patterns by depicting the distribution of soil organic matter and soil water content (Luizão et al., 2004; Lang et al., 2013). TWI as a combined topographic metric, considers both slope and upslope area that may contribute to runoff generation, and thus has been used to characterize soil wetness. This index has been found to explain up to 68% of variation in NO_3^- reduction in forested watersheds (Ogawa et al., 2006).

Delmarva Peninsula is located within the Mid-Atlantic coastal plain of United States and depressions are prominent features of the Delmarva landscape. However, this region was extremely ditched and a significantly portion of depressions have been converted to croplands or drained for agriculture (Fenstermacher et al., 2014). In this study, we employed both field observations and map interpretations to quantify the effects of soil physicochemical characteristics and topographic metrics on denitrification in three agricultural production fields containing prior converted croplands on the Delmarva Peninsula. Three indices including openness, relief, and TWI were used as representative topographic metrics for the three sites. The prior converted cropland term refers to wetlands that were converted to commodity croplands through drainage, vegetation clearing or other manipulation prior to 1986 (Johnson, 1993). It is reported that about 60% of soil carbon was loss after wetland conversion to cropland in the Mid-Atlantic region (Fenstermacher et al., 2016). Decreased soil carbon content may become the most important factor influencing denitrification processes in the prior converted croplands. Therefore, in this study, we hypothesized that: 1) soil property, especially soil carbon content, is the most influential effect controlling denitrification processes in the three prior converted croplands; 2) denitrification processes would vary with topography in croplands containing a high density of drained depressional wetlands. The objectives of this observational study were: 1) to investigate spatial and temporal variations in denitrification; 2) to explore the relationships between selected variables and denitrification; and 3) to characterize underlying mechanisms regulating denitrification in the study area.

2. Materials and methods

2.1. Site description

The three prior converted croplands are located within the headwater region of the Choptank River Watershed (Fig. 1). The Choptank River is a major tributary of the Chesapeake Bay, originating in Kent County, Delmarva. The Choptank River watershed is located on the Delmarva Peninsula within the Coastal Plain Physiographic Province, with an area of 1756 km^2. This area has a humid temperate climate with mean annual precipitation of 120 cm (Ator et al., 2005). Low relief and suitability of soils for ditch drainage combined with increasing human activities in this area have resulted in intensive conversions of primary forest and forested wetlands to agricultural lands (Benitez and Fisher, 2004). It was estimated that 70% of Delmarva bay wetlands have been converted to or impacted by agriculture (Fenstermacher et al., 2014). Currently, cropland is the dominant land use type and covers about 60% of the Choptank River watershed (McCarty et al., 2008). Many historical wetlands have been converted to row crops of *Zea mays* and *Glycine* max (Yepsen et al., 2014).

2.2. Field sampling

Field data were collected at the study sites on April 14, 2011 and April 11, 2012. According to the National Oceanic and Atmospheric Administration (NOAA) Palmer Z index (NOAA National Climate Data Center, http://www.ncdc.noaa.gov/) over a 3-month period (February–April), the selected periods represented two climate conditions – an average condition (2011; Palmer Z index = −0.37) and a moderate drought condition (2012, Palmer Z index = −1.93). The location of sampling points was randomly assigned using ArcGIS 10.2.2 (ESRI, Redlands, CA) to characterize both upland and depressional areas within each field with the depressional areas that were wetlands having been later drained to produce arable land (i.e. prior converted croplands). For each production field, we collected soil at 20 sampling points. Geographic coordinate information of sampling points was recorded using a Trimble GeoXT global positioning system (GPS). Three soil samples were randomly collected within a 0.5 m radius of each sampling point. All of the samples were from the upper 10 cm of soil and were mixed together to get a composite sample. The samples were kept in a cooler with ice packs while in transit to the lab for denitrification and soil chemical analyses. In total, 120 composite soil samples (20 samples per site × 3 sites × 2 years) was collected for the study. Soil temperature and electrical conductivity (EC) were measured in the field using an ECTestr11 + meter (Spectrum Technologies, East Plainfield, IL) and soil moisture was measured using a Delta-T HH2 Moisture meter (Dynamax, Houston, TX).

2.3. Topographic metrics

A LiDAR derived DEM was used to develop topographic metrics. The LiDAR data were collected by an Optech Airborne Laser Terrain Mapper (ALTM) 3100 sensor with a wavelength of 1064 nm. The validation of geolocation accuracy was conducted using over 100 points that were precisely located by the Trimble GPS/base station combination at sites of stable elevation (e.g. road intersections) and a survey benchmake provided by the Maryland State Highway Administration. LiDAR data on March 27, 2007 were used in this study with a pulse frequency of 100,000 Hz and a scan rate of 50 Hz at a scan angle of ± 20° at a height of 610 m above the Earth's surface. Raw data were converted to LAS files that contain x, y, z information. The data had a vertical accuracy of ≤ 0.15 m and an average point density of ~ 2.5 pts. m^{-2} (0.40 m post spacing). More detailed description of the dataset has been provided by Lang et al. (2013).

Inverse distance weighted (IDW) interpolation was used to produce a 3 m gridded DEM. Then topographic metrics, including topographic relief, topographic wetness index (TWI), and positive openness were quantified based on the 3 m DEM. The topographic relief map was generated using ArcGIS software according to the method of Lang et al. (2013). Following this method, two datasets were created using the 3 m DEM; one was a continuous surface of maximum elevation per 100 m radius, and the other one was a filtered 3 m DEM that was created by filtering twice using a 3 kernel low pass filter. After that a topographic relief map was produced by subtracting the filtered 3 m DEM from the maximum elevation dataset.

The TWI index is a function of local slope and upslope contributing area (Eq. (1); Beven and Kirkby, 1979).

$$\mathrm{TWI} = \ln\left({}^{A_S}\!/_{\tan\beta}\right) \tag{1}$$

in which A_s is upslope contributing area per unit contour length (m). β is local topographic gradient. During the estimation, β is usually estimated using the same procedure, while A_s can be generated with different flow routing algorithms. In this study, the FD8 flow routing algorithm was used to calculate A_s. It directs water to all eight neighboring pixels according to slope, such that steeper slopes route more water than shallower slopes (Freeman, 1991). The TWI map based on the FD8 flow routing algorithm was created using the System for Automated Geoscientific Analysis (SAGA) v. 2.2.5. To reduce noise due to local variation, the 3 m DEM was iteratively filtered with kernel sizes of 3 and 9 low pass filters. The filtered 3 m DEM was then used as an

Table 1
Average and standard deviation (in parentheses) of topographic properties and soil textures for the three sites ($n = 20$ for each site).

Sites				Texture		
	Relief	TWI	P_Op	Sand (%)	Clay (%)	Silt (%)
Site 1	1.1 (0.2) ab[†]	10.8 (0.4) ab	0.81(0.04)ab	67.7 (2.8)a	13.0 (1.4)a	19.3 (1.9)b
Site 2	1.6 (0.1)a	11.9 (0.3) a	0.72(0.03)b	58.5 (2.4)b	15.0 (1.2)a	26.5 (1.7)a
Site 3	1.0 (0.1)b	11.2 (0.3) b	0.90(0.04)a	59.8 (4.3)b	14.9 (2.2)a	25.3 (2.5)a

TWI is topographic wetness index. P_OP is positive openness.

[†] Letters estimate based on Duncan's multiple range tests. There are no significant ($p < 0.05$) differences for a parameter with the same letter.

input to the SAGA Wetness Index module in SAGA to generate the TWI map for the study sites.

The topographic openness index is a metric that measures the viewshed of a point on a landscape surface (e.g., the amount of observable sky). Positive openness generally shows high values at convex locations on a surface, as example ridges, whereas negative openness exhibits high values at locations with a concave character (e.g., depressions; Yokoyama et al., 2002). Before producing the topographic openness product, we first increased vertical distance of the 3 m unfiltered DEM by a factor of 100 to enhance the distinguishability of openness due to the study sites' relatively flat surface (elevation ranges from 15 m to 21 m). After filtering twice through low pass filters, the exaggerated and smoothed DEM was imported to the SAGA topographic openness module to create positive openness.

2.4. Laboratory analysis

Soil organic C (SOC) and total N (TN) were measured using a TruSpec CN analyzer (Leco Corp, St Joseph, MI). Soil pH was measured using a 1:1 mixture of soil and water. Denitrification was assessed by denitrification enzyme activity (DEA) that was estimated using the acetylene inhibition method (Tiedje, 1994; Hunt et al., 2014). Specifically, about 10 to 15 g of soil was placed in a 60-mL serum bottle with 5 mL solution of chloramphenicol (0.1 mg mL^{-1}) to suppress protein synthesis. Six bottles were used for each soil samples to allow triplicates for two treatments. The two treatments were used to investigate variations in the baseline DEA level and non-limited DEA and were as follows for measurement of denitrification capacity (DC) (i) and potential (DP) (ii):

i. Denitrification capacity measurement: 15×10^{-3} L acetylene was used to block denitrification at the N_2O phase, leading to an increase of N_2O percentage in final gas emission.
ii. Denitrification potential measurement: 15×10^{-3} L acetylene and 5 mL of amendment (200 mg L^{-1} NO_3–N and 600 mg L^{-1} glucose-C) were added to measure the maximal enzyme activity rate with blockage of N_2O reduction.

2.5. Statistical analysis

Duncan's multiple range tests ($p \leq 0.05$) were used to detect statistical differences of topographic and soil physiochemical variables within the three sites in 2011 and 2012. Correlations between topographic metrics and soil physiochemical variables and their controls on denitrification at different sites and in different years were analyzed using the Pearson's correlations. We log-transformed the variables of relief, TWI, clay, pH, EC, and TN to meet the normal distribution before the correlations. Models of DP and DC were developed by stepwise linear regression. DP and DC was log-transformed to ensure the models obey the assumptions of the normality of target variables (tested by Shapiro-Wilk tests), normality of residuals (tested by quartile-quartile plots and Shapiro-Wilk tests) and homoscedasticity (tested by residual-fitted value plots and White tests). We used leave-one-site-out (LOSO) cross-validation with Akaike Information Criterion with a correction (AICc) to obtain the best fitted models. The LOSO cross-validation criterion allows one to omit a single field from the training set and use data from the remaining fields to predict them. After identifying the optimal variables by AICc, we developed models using the chosen variables and selected the best performing models based on the LOSO cross-validation criterion. Variables left for model development are significant at 15% level. Adjusted R squared (R_{adj}^2) was estimated to present the explanatory power of regression models. Ten variables including TWI, Relief, P_Openness, sand, clay, SOC, TN, pH, EC, and soil moisture were used as input data for model selection. To better investigate the relationships between different parameters and denitrification, the parameters were first divided into three groups –topography (relief, TWI, and P_Openness), soil textures (sand and clay), and soil properties (SOC, TN, pH, EC, and soil moisture). LOSO cross-validation with AICc was used to identify the combination of variables in each group that best simulated DEA variations. Then, the selected variables for the three sub-models were combined together to produce a final model. Multicollinearity among predictors was detected by variable inflation factor (VIF). In this study, all independent variables selected in the models had VIFs lower than the threshold of 10, which means there was no considerable collinearity between predictors (Klemettilä et al., 2017). All data analyses were carried out using SAS v. 9.2 (SAS Institute).

3. Results

3.1. Soil properties and topographic indexes

All study sites had low relief (≤ 1.6 m) with soils containing high sand content ($> 58\%$; Table 1). Mean sand percentage ranged from 58.5 ± 2.4% to 67.7 ± 2.8%, and mean clay was between 13.0 ± 1.4% and 15.0 ± 1.2%. The highest sand content was observed at site 1. All topographic indices varied significantly between different sites (Table 1, Duncan's multiple range tests, $p < 0.05$). Relief and TWI at site 2 were significantly higher than the other two sites. In contrast, positive openness was the lowest at site 2 among the three sites.

The study sites had high spatial and temporal variations in soil moisture and pH as suggested by Duncan's multiple range tests (Table 2, $p < 0.05$). Soil moistures were higher in 2011 than they were in 2012 due to a relative drought condition in 2012. The highest soil moisture

Table 2
Average and standard deviation (in parentheses) of soil physiochemical characteristics for three prior converted croplands in 2011 and 2012 ($n = 20$ in 2011, $n = 20$ in 2012 for each site).

	Sites	Moisture (%)	pH	EC (μS cm^{-1})	SOC (%)	TN (%)
2011	Site 1	17.0 (1.4)ab[†]	5.0 (0.1) e	59.5 (10.0)c	1.3 (0.1) a	0.17 (0.01) ab
	Site 2	15.6 (0.7)ab	5.3 (0.1) d	64.4 (7.5)c	1.2 (0.1) a	0.18 (0.00) a
	Site 3	19.7 (1.5)a	5.5 (0.1) d	65.5 (10.9)c	1.6 (0.2) a	0.19 (0.01) a
2012	Site 1	12.9 (1.7)bc	6.5 (0.1) a	241.0 (17.6)a	1.4 (0.1) a	0.13 (0.01) c
	Site 2	10.6 (1.6)c	6.2 (0.1) b	201.8 (9.4)b	1.4 (0.1) a	0.14 (0.01) bc
	Site 3	13.0 (1.4)bc	5.8 (0.1) c	52.5 (9.5)c	1.5 (0.2) a	0.13 (0.02) c

EC is electrical conductivity. SOC and TN are soil organic carbon and total nitrogen, respectively.

[†] Letters estimate based on Duncan's multiple range tests. There are no significant ($p < 0.05$) differences for a parameter with the same letter.

Table 3
Pearson's correlation between topographic metrics and soil physicochemical conditions in three converted croplands (n = 120).

	Relief	TWI	P_Op	Sand	Clay	SM	pH	EC	SOC	TN
Relief	1.00									
TWI	**0.78*****	1.00								
POP	**− 0.67*****	**− 0.64*****	1.00							
Sand	− 0.56***	− 0.56***	0.54***	1.00						
Clay	0.56***	**0.61*****	**− 0.65*****	**− 0.78*****	1.00					
SM	0.39***	0.48***	− 0.44***	**− 0.61*****	0.50***	1.00				
pH	–	–	–	–	–	− 0.35***	1.00			
EC	0.36***	0.32**	− 0.44***	− 0.36***	0.34**	–	0.55***	1.00		
SOC	0.54***	**0.66*****	**− 0.61*****	**− 0.75*****	**0.72*****	**0.74*****	–	0.36***	1.00	
TN	0.42***	0.47***	− 0.49***	− 0.56***	0.47***	**0.68*****	− 0.46***	–	**0.62*****	1.00

TWI is topographic wetness index. P_OP is positive openness. EC is electrical conductivity. SM is soil moisture. SOC and TN are soil organic carbon and total nitrogen, respectively. The value in bold is correlation coefficient > 0.6.

** $p < 0.05$.

*** $p < 0.0001$.

was observed at site 3 in 2011 and 2012. Higher pH occurred in 2012 relative to 2011. The study sites were slightly acidic, with pH ranging from 5.0 to 5.5 in 2011, but were more neutral with a range of 5.8 to 6.5 in 2012. EC did not present statistically significant spatial variation in 2011 (Duncan's multiple range tests, $p > 0.05$), but varied significantly in 2012 (Duncan's multiple range tests, $p < 0.05$). EC was more than four times higher at the highest site (site 1) than at the lowest site (site 3) in 2012. For temporal variation, averaged EC was 2.6 times higher in 2012 than in 2011. Soil TN also differed significantly among sites and between periods (Duncan's multiple range tests, $p < 0.05$). TN contents at three croplands were lower in 2012 than in 2011. SOC content showed insignificant variations with time and space (Duncan's multiple range tests, $p > 0.05$). Soil samples collected from site 3 had the highest SOC content.

Correlation coefficients larger than 0.6 were highlighted (values in bold type) in Table 3 to show the correlations between topographic metrics and soil physiochemical variables in the three croplands. As introduced in the methods section, the variables were divided into topography, soil texture, and soil property groups. Variables within each group showed high correlations, especially in the topography and soil texture groups. Relief was highly positively correlated with TWI and negatively correlated with positive openness with correlation coefficients of 0.78 and − 0.67, respectively. The variable that had the highest correlation with clay was sand with an r of − 0.78. Variability in clay content was also strongly controlled by topographic variables such as TWI (r = 0.61) and positive openness (r = − 0.65). For the soil property group, the highest correlation coefficient of 0.74 was observed between SOC content and soil moisture. In addition, SOC content was highly influenced by variables in the other two groups with $|r|$ values larger than 0.6, including TWI, positive openness, and soil textures of sand and clay. Soil moisture was strongly regulated by soil texture and the correlation coefficient was about − 0.61 for sand.

3.2. Denitrification enzyme activity

The addition of nitrate and glucose (DP) more than doubled DEA rates compared to the treatment rely on in-situ nitrate and soluble C (DC) (Table 4; Fig. 2). DC ranged from 5 μg N_2O-N kg^{-1} soil h^{-1} to 105 μg N_2O-N kg^{-1} soil h^{-1} and DP ranged from 120 μg N_2O-N kg^{-1} soil h^{-1} to 264 μg N_2O-N kg^{-1} soil h^{-1} (Table 4). The highest average DEA rates were observed at site 2, followed by site 3 and the lowest rates occurred at site 1 for both measurements (Fig. 2). In terms of temporal variation, averaged DEA rates showed higher values in 2012 than in 2011. Especially for DC, the rate in 2012 was about four times higher than in 2011.

Table 4
Average and standard deviation (in parentheses) of denitrification potential (DP) and capacity (DC) (μg N_2O-N kg^{-1} soil h^{-1}) in three prior converted croplands in 2011 and 2012 (n = 20 in 2011, n = 20 in 2012 for each site).

Sites	DP		DC	
	2011	2012	2011	2012
Site 1	158.9 (57.0)	168.5 (49.8)	5.0 (1.6)	50.6 (16.9)
Site 2	120.0 (20.4)	263.7(58.5)	6.6 (0.7)	104.8 (32.0)
Site 3	178.3 (64.7)	152.6 (46.6)	11.6 (7.9)	45.6 (25.4)

3.3. Controlling factors for denitrification

To determine the controlling factors at different sites and under different drought conditions, DP and DC were grouped and analyzed using Pearson's correlation analysis (Table 5). Generally, all factors had stronger effects on DP than DC. Relief, TWI, clay, EC, moisture, SOC, and TN were significantly positively related to denitrification rates under both measurement conditions and sand and positive openness showed significant negative correlations with DEA variability (Table 5). Correlation coefficient p-values for pH were larger than 0.05 at all study sites, which indicated that pH was likely not an efficient controller affecting denitrification variability over the selected sites. At site 1, soil physiochemical characteristics were the most correlated with denitrification. Soil moisture (r = 0.71) had the highest correlation coefficient with DP, and electrical conductivity (r = 0.59) had the highest value with DC. Unlike site 1, soil moisture had a weaker effect (r = 0.36) on DP at site 2. The highest correlation coefficients were soil organic carbon for both treatments. Sand also showed a high correlation coefficient (r = − 0.76) with DP at this site. For site 3, topographic metrics had the most influential impacts on DEA with nitrate and carbon addition. Relief showed the highest correlation coefficient (r = 0.77) with DP, followed by TWI (r = 0.76); whereas SOC was the most important factor (r = 0.73) and showed a significantly positive correlation with DC.

Although soil moisture was lower in 2012 than that in 2011, the dominant factors that influence DP were the same during both years (Table 5). Relief exhibited the highest correlations with DP during both years. In terms of DEA without soil amendment, soil organic carbon (r = 0.50) and sand (r = − 0.50) had the highest correlation coefficients in 2011, while EC (r = 0.63) and TN (r = 0.63) had the highest correlations with DC in 2012.

The model with the best performance including relief, SOC and EC, explained 58% of variation in DP (Table 6). Consistent with correlation analyses, relief explained the greatest amount of variability for DEA under the non-nitrate and carbon limiting treatment with an r^2 of 51%. SOC content had the second largest explanatory power. It was

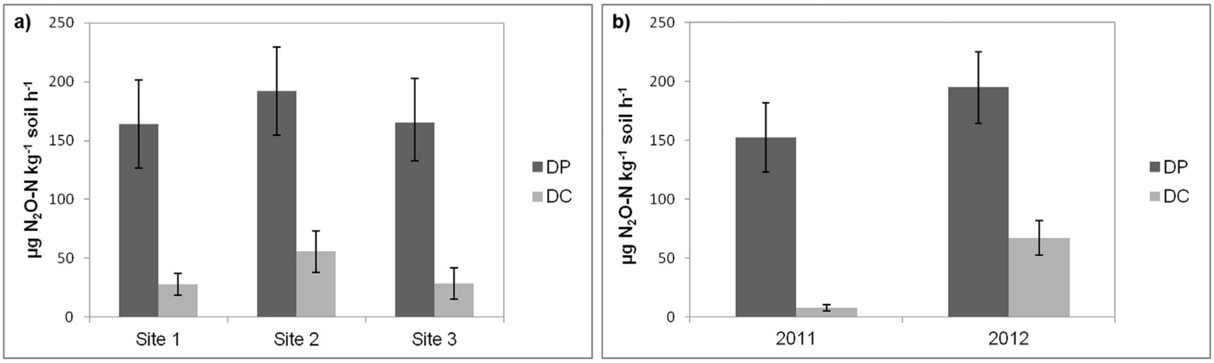

Fig. 2. Comparison of denitrification potential (DP) and capacity (DC) a) at three sites and b) in two years.

Table 5
Pearson's correlation between soil physicochemical conditions and denitrification potential (DP) and capacity (DC) in three converted croplands.

		Relief	TWI	P_Op	Sand	Clay	SM	pH	EC	SOC	TN
Site	Site 1 ($n = 20 \times 2$ years)										
	DP	0.59***	0.56***	− 0.67***	− 0.69***	0.60***	0.71***	–	0.33*	0.69***	0.42**
	DC	0.31*	0.29*	− 0.42*	− 0.36*	0.36*	0.34*	–	0.59***	0.47**	–
	Site 2 ($n = 20 \times 2$ years)										
	DP	0.71***	0.72***	− 0.58***	− 0.76***	0.63***	0.36*	–	–	0.85***	0.55**
	DC	0.37*	0.38*	–	− 0.50**	0.36*	–	–	0.50**	0.65***	–
	Site 3 ($n = 20 \times 2$ years)										
	DP	0.77***	0.76***	− 0.66***	− 0.48**	0.69***	0.73***	–	0.64***	0.73***	0.51**
	DC	0.54*	0.53**	− 0.54**	− 0.59***	0.63***	0.62***	–	0.60***	0.73***	0.64***
Time	2011 ($n = 20 \times 3$ sites)										
	DP	0.80***	0.75***	− 0.72***	− 0.56***	0.73***	0.71***	− 0.27*	0.61***	0.74***	0.66***
	DC	0.44***	0.41**	− 0.45**	− 0.50**	0.45**	0.42**	–	0.42**	0.50**	0.45**
	2012 ($n = 20 \times 3$ sites)										
	DP	0.67***	0.62***	− 0.62***	− 0.45**	0.60***	0.58***	–	0.42**	0.63***	0.57***
	DC	0.58***	0.48***	− 0.60***	− 0.45**	0.54***	0.41**	–	0.63***	0.57***	0.63***

TWI is topographic wetness index. P_OP is positive openness. EC is electrical conductivity. SM is soil moisture. SOC and TN are soil organic carbon and total nitrogen, respectively.

* $p < 0.05$.

** $p < 0.05$.

*** $p < 0.0001$.

significantly correlated with DP and explained 46% of its variation. Similar to the combined model, both the topographic effect and soil property effect sub-models had robust adjusted coefficient of determination (R_{adj}^2) values (Table 6). Each sub-model explained about 50% variation in DP; while the soil texture sub-model only explained 37% of the variation. For DC, soil property was the most influential group accounting for 49% of the variation. EC in this group exhibited the highest correlations with DC and explained 35% of its variation. SOC content was also a significant variable for DC with an r^2 of 28% (Table 6). Another important factor referred to the sub-model of topographic effect, which explained 25% of the capacity's variation. The final DC model combined soil property and topographic effects with an explanatory power of 50%.

4. Discussion

4.1. Influence of soil properties on denitrification

The soil property effect sub-models suggested that our results partially agreed with our first hypothesis that soil property was the most influential factor controlling denitrification processes. The soil property effect showed the highest or close to the highest explanatory powers in

Table 6
Stepwise regression results for denitrification potential (DP) ($\mu g\ N_2O\text{-}N\ kg^{-1}\ soil\ h^{-1}$) and capacity (DC) ($\mu g\ N_2O\text{-}N\ kg^{-1}\ soil\ h^{-1}$) (log 10 transformation) correlated to site physiochemical and topographic effects in three converted croplands ($n = 20 \times 3$ sites $\times$ 2 years).

		Models	N	AICc	R_{adj}^2	Rejected variables
DP model	All effects	0.359 + 0.499Relief + 0.465SOC + 0.001EC[a]	3	− 36.839	0.58	
	Sub-models					
	Topographic effect	0.672 + 0.316Relief + 0.140TWI–1.099P_Openness	3	− 22.000	0.53	
	Soil texture effect	0.796 + 0.067Clay	1	9.002	0.37	Sand
	Soil property effect	0.433 + 0.794SOC + 0.002EC	2	− 15.318	0.49	pH, Moisture, TN
DC model	All effects	0.267 + 0.004EC + 0.422SOC–0.697P_Openness	3	− 3.163	0.50	
	Sub-models					
	Topographic effect	2.622–2.300P_Openness	2	43.374	0.25	Relief, TWI
	Soil texture effect	− 0.025 + 0.055Clay	1	47.046	0.22	Sand
	Soil property effect	− 0.488 + 0.004EC + 0.534SOC	2	− 1.981	0.49	pH, Moisture, TN

TWI is topographic wetness index. P_OP is positive openness. EC is electrical conductivity. SOC and TN are soil organic carbon and total nitrogen, respectively. N is the number of variables in the model.

[a] The order of variables is based on the stepwise selection steps.

DC and DP simulations. However, EC instead of SOC was the most influential factor and showed the highest correlation with DC in this effect group ($r^2 = 0.35$; $p < 0.0001$). Values of EC are usually high in prior converted croplands due to fertilizer use for crop production (Rhoades, 1993; Adviento-Borbe et al., 2006; Hunt et al., 2014). This can reduce soil microbial activity due to increased osmotic stress on soil microbial communities (Rietz and Haynes, 2003). However, denitrifiers have a generally greater tolerance and are more competitive than other microbes, such as nitrifiers and decomposers, and can quickly adapt to high salt stress (Adviento-Borbe et al., 2006). Highly positive correlations were observed between EC and DEA rates under both measurement conditions. The results agree with the study of Adviento-Borbe et al. (2006), which found increased total denitrification with increased EC during laboratory incubations. One possible explanation is that alternate electron donors, such as H_2S and FeS, may exist during denitrification at high EC conditions (Reddy et al., 1982; Weston et al., 2011; Marton et al., 2012). Moreover, it is reported that higher EC can be correlated with NO_3^-, which is a prerequisite for denitrification processes, and thus promotes N_2O production (Patriquin et al., 1993; Adviento-Borbe et al., 2006; Reddy and Crohn, 2014).

Soil C was found to be the primary soil properties linked with denitrification (Table 5; Seitzinger et al., 2006; Palta et al., 2013). Soil organic C acts as an electron donor and would significantly influence NO_3^- reduction during denitrification (Burford and Bremner, 1975; Reddy et al., 1982; Weier et al., 1993). Under anaerobic conditions, higher rates of anaerobic carbon mineralization are the prerequisite for higher denitrification rates because organic carbon decomposition consumes larger amounts of NO_3^- than O_2 and converts NO_3^- to N_2O or N_2 (McCarty and Bremner, 1992; Kim, 2014). In prior converted croplands, SOC is usually lower compared to natural wetlands due to increases in oxidative decomposition (Hunt et al., 2014; Fenstermacher et al., 2016; Li et al., 2016b). Low carbon content and high N input from fertilization in prior converted croplands probably leads to C limitation during denitrification (Ju et al., 2009). Therefore, a higher positive relationship was observed between SOC content and DC ($r^2 = 0.28$, $p < 0.0001$) compared to correlation between TN content and DC ($r^2 = 0.15$, $p < 0.0001$), and the addition of glucose-C and NO_3^- stimulated decomposition processes, resulting in a doubling of DEA rates compared to the treatment without additions of soluble C or N.

Increased denitrification activity in response to increased soil moisture was often reported from laboratory and field investigations (Linn and Doran, 1984; Ullah et al., 2005; Ruser et al., 2006; Vilain et al., 2010). Soil water content in the three prior converted croplands ranged from 10.6 ± 1.6% to 19.7 ± 1.5%, which were lower than those in natural wetlands on the Delmarva Peninsula (Hunt et al., 2014; Ducey et al., 2015). High water content in soil leads to low air-filled porosity and, thereby, creates an anaerobic condition that provides a suitable environment for denitrification. The significant positive relationship between soil moisture and DP ($r^2 = 0.33$, $p < 0.0001$) in the study supports this explanation. However, a relatively low r^2 was found between soil moisture and DC ($r^2 = 0.09$, $p = 0.001$). This suggests that other factors were more important drivers of DEA without additions of soluble C or N. Similar results can be found in the study of Ruser et al. (2006), which suggested that denitrification processes would be more related to organic matter than soil moisture under relatively high water content conditions.

4.2. Influence of topographic factors on denitrification

Results of this study suggest that topography strongly influenced DP and DC at our study sites, which supports our second hypothesis. Anderson et al. (2015) found a greater denitrification activity in foot slope positions of a mixed land-use headwater catchment compared with denitrification in depressions and shoulder areas, and concluded that the variability in denitrification was because topographic positions were strongly related to soil moisture. However, our study indicated that the reason for the strong influence of topographic effects on denitrification was complex. Relief was the most important variable of DP, which was not limited by N or C, explaining 51% of variation. Although relief was significantly correlated with soil moisture, the correlation coefficient was only 0.39. Relief had higher correlation coefficients with soil texture indices (Table 3, Sand: $r = -0.56$, $p < 0.0001$; Clay: $r = 0.56$, $p < 0.0001$), as well as with soil organic matter (Table 3, SOC: $r = 0.54$, $p < 0.0001$; TN: $r = 0.42$, $p < 0.0001$). The high correlations above suggest that besides soil moisture, redistribution of organic matter and inorganic sediment via water or wind was probably also controlled in part by topography, contributing to variation in denitrification (Florinsky et al., 2004; Ogawa et al., 2006; Chan et al., 2007; Hunt et al., 2014).

TWI is a widely used index in hydrological models since it quantifies the effect of topography on surface runoff and reflects the soil moisture conditions. It was proven to be an effective indicator of denitrification in previous studies (Ogawa et al., 2006; Anderson et al., 2014). However, our investigation indicates that this index had less ability to capture the variability in denitrification (DP: $r^2 = 0.44$, $p < 0.0001$; DC: $r^2 = 0.17$, $p < 0.0001$) compared to relief (DP: $r^2 = 0.51$, $p < 0.0001$; DC: $r^2 = 0.24$, $p < 0.0001$). One possible reason for the inconsistency is that TWI may not capture the movement of water flow well at low relief sites (Hjerdt, 2004). The assumption of TWI is that the local drainage can only be affected by upslope areas. However, water movement is more divergent in low relief areas and is the balance between upslope contributing areas and downslope areas that control the water from any location (Speight, 1980; Crave and Gascuel-Odoux, 1997). The above reasons may reduce TWI control on the distribution of soil moisture and soil organic matter, and therefore decrease the influence of TWI on denitrification processes. Furthermore, TWI was better at representing wetness distribution in wet periods compared to dry periods because it depicts the potential for lateral surface movement of water (Grayson et al., 1997; Lang et al., 2013). Therefore, relief was shown to be a more efficiency variable in simulating denitrification than TWI during average and drought conditions at the study area.

Openness is a less frequently used topographic index that was also shown to be significantly related to denitrification at the study sites. Positive openness represents convexity of the surface. It was negatively related to DEA rates at our sites, suggesting that denitrification was higher in concave landforms with low positive openness values when compared with convex landforms with high positive openness values. This finding is consistent with observations that depressions often hold the highest water content, and thus are more likely to provide suitable anaerobic environments for denitrification (Vilain et al., 2010; Anderson et al., 2015). Depressions also represent locations of Delmarva Bays that were drained for crop production (i.e., prior converted croplands) (Fenstermacher et al., 2014).

4.3. Influence of soil texture on denitrification

Although soil texture did not have the highest correlation with denitrification in this study, it still explained 37% of the variation in DP and 22% of the variation in DC (Table 6). This result is consistent with the study of Weier et al. (1993), which reported that total N loss increased with decreasing sand and increasing clay content. Finer soil texture may enhance soil water retention, and therefore increase the likelihood of anaerobic conditions that facilitate denitrification (Groffman and Tiedje, 1989; Pihlatie et al., 2004). The significant correlations between soil texture and soil moisture (Table 3, Sand: $r = -0.61$, $p < 0.0001$; Clay: $r = 0.50$, $p < 0.0001$) within our study further support this assertion. Another reason that could possibly explain the control of soil texture on denitrification was the increase in SOC when soil clay increased (Table 3, $r = 0.72$, $p < 0.0001$). Soil clay can physically protect SOC through the formation of aggregates, which lead to a higher availability of SOC for denitrification in soils with higher clay content (Hassink, 1997; Six et al., 2002). Moreover, due to higher leaching rates at sandy sites, soil organic carbon may be mobilized by surface and subsurface runoff, and thus can result in lower denitrification rates (Luizão et al., 2004). This mechanism could partly explain the strong negative relationship between sand and SOC (Table 3, $r = -0.75$, $p < 0.0001$) in this study.

4.4. Temporal and spatial controls on denitrification

DP and DC measured from all study sites during a drought condition (2012) were higher than those during an average weather condition (2011), which is inconsistent with previous studies that suggested that denitrification would be enhanced under higher water content conditions. The high temporal variability may partly be due to variation in EC between the two years. In a dry period when precipitation was low, high concentrations of salts can accumulate at the soil surface through capillary movement, leading to high soil EC values (Corwin and Lesch, 2003; Pan et al., 2013). As discussed in previous section, denitrifiers are more competitive than nitrifiers at high EC conditions and increased EC may stimulate the denitrification process. The fact that EC explained the greatest amount of variability in DC in 2012 appears to highlight the important influence of EC on denitrification (Table 5). Similar results were observed by Marton et al. (2012), which found increased denitrification rates with elevated EC, but no significant relationships between denitrification and soil moisture. Moreover, due to an increase in surface and subsurface runoff during an averaged period, more soluble carbon may be leached from top soils than a drought period (Lepistö et al., 2008). The higher SOC in 2012 (1.43%) than in 2011 (1.38%) may also be an explanation for the higher DC in the drought period. DP did not significantly vary with time in this study (Fig. 2). Spatial control was the main effect on denitrification when electron acceptor (NO_3^-) and donor (SOC) were not limiting factors due to nitrate and carbon addition and relief was the dominant variable with the highest correlation coefficients in both years.

The DEA rates varied with study sites, and the highest two-year averaged values were observed at site 2 for both measurements (Fig. 2a). High values of EC could be one of the factors leading to high nitrate reduction because DEA rates increased greatly at sites 1 and 2 when EC largely increased during 2012. However, it was not the only potential explanation since average EC at site 1 was higher than that at site 2, but the DEA increase rates were lower at site 1. The results may be caused by differences in soil texture. Sand percentage at site 1 was 15% more than sand at site 2 (Table 1), leading to stronger responses of denitrification to moisture in soils with higher sand content (Table 5; Pihlatie et al., 2004). Therefore, stimulation of denitrification because of elevated EC at site 1 in 2012 may partly be offset by decreased soil moisture, causing less increase in N_2O production compared with N_2O variation at site 2.

5. Conclusions

This study demonstrated how topographic and physicochemical conditions jointly affected denitrification in three crop production fields containing prior converted croplands. Generally, selected indices were well correlated with DEA rates, and the predication models explained 58% and 50% of variations in DP and DC, respectively. The topographic attributes including relief, TWI and positive openness explained the most variability in DP. Besides topographic effect, soil parameters, such as SOC and EC, were also strongly correlated with DP. For DC, soil EC was the most important variable, followed by SOC and positive openness. DP and DC also varied with time and space and the variations may largely be due to increased EC. However, further field investigations must be conducted to better explore potential mechanisms for the high correlations between denitrification and EC.

Topographic effect is a relatively new factor considered in denitrification studies with now commonly available high resolution DEMs derived from LiDAR. The strong correlations with DEA rates indicate that the topographic parameters derived from LiDAR data could be a simple and flexible tool to reconstruct spatial variability of denitrification at a landscape scale. Several factors, such as soil moisture, SOC, and soil texture, varied significantly with topographic metrics and could be a cause for the strong topographic controls on denitrification. However, the dependence of soil physiochemistry on topography is demonstrated to rely on several topographic metrics instead of a particular one (Florinsky et al., 2004). Further study is needed to develop a representative set of topographic variables for investigating and predicting denitrification to gain a better insight in "topography – soil biogeochemistry" interactions.

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