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Review

Nitrate removal uncertainty in stormwater control measures: Is the design or climate a culprit?

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ABSTRACT

Eutrophication is caused by excess nitrate and other nutrient exported via stormwater runoff to surface waters, which is projected to increase as a result of climate change. Despite recent increases in the implementation of stormwater control measures (SCM), nutrient export has not abated, indicating poor or inconsistent removal capacities of SCM for nitrate. However, the cause of the variability is unclear. We show that both design and local climate can explain nitrate removal variability by critically analyzing data reported on the international BMP database for nitrate removal by four common types of SCM: bioretention cells, grass swales, media filters, and retention ponds. The relative importance of climate or design on nitrate removal depends on the SCM type. Nitrate removal in grass swales and bioretention systems is more sensitive to local climate than design specifications, whereas nitrate removal in the retention ponds is less sensitive to climate and more sensitive to design features such as vegetation and pond volume. Media filters without amendment have the least capacity compared to other SCM types surveyed, and their removal capacity was independent of the local climate. Adding amendments made up of carbon biomass, iron-based media, or a mixture of these amendments can significantly improve nitrate removal. The type of carbon biomass is also a factor since biochar does not appear to affect nitrate removal. This analysis can help inform the selection of SCM and modification of their design based on local and projected climate to maximize nitrate removal and minimize eutrophication.

1. Introduction

Excess nutrients in stormwater from nonpoint sources cause eutrophication (Boeykens et al. 2017), resulting in significant financial losses (Deegan et al. 2012, Dodds et al. 2009). Eutrophication is projected to get worse because of climate change (Michalak et al. 2013, Sinha et al. 2017). To manage stormwater, different stormwater control measures (SCM) have been widely implemented (Bowles et al. 2018). However, the implementation of SCM on a watershed scale has often not resulted in improved water quality (Lintern et al. 2020). Among many reasons (Lintern et al. 2020), a wide variation in nitrate removal in all SCM is a primary factor (Manka et al. 2016). The cause of the wide variation is often attributed to inadequate design (Zhang et al. 2020) or local climate (Blecken et al. 2010, Kratky et al. 2017). For instance, an increase in temperature and the frequency of high-intensity rainfall events is projected to accelerate eutrophication (Ballard et al. 2019, Sinha et al. 2017). Currently, SCM is rarely designed based on local climate information or projected climate changes (Brudler et al. 2016, Kerkez et al. 2016, Zhang et al. 2019a), partly because it is not clear how nitrate removal is affected by the coupled effect of climate and design or whether any design modification could minimize the detrimental effect of changing climates on nitrate removal.

Local climate conditions and the SCM's design have been shown to affect the removal of some contaminants (Rippy 2015, Roseen et al. 2009, Valtanen et al. 2017b), so it is expected they could also affect nitrate removal (McPhillips and Walter 2015,

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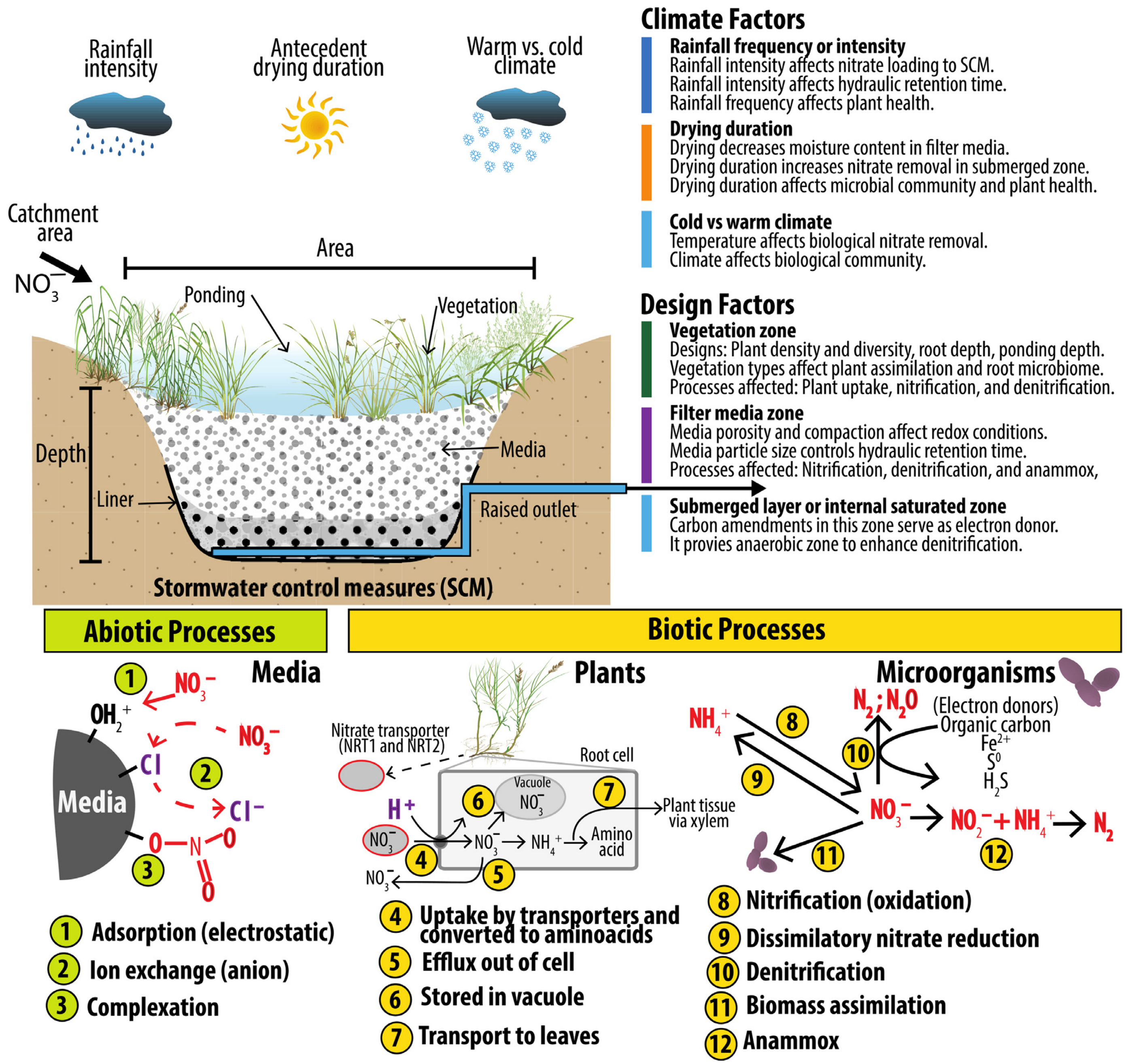

Climate Factors

Rainfall frequency or intensity
Rainfall intensity affects nitrate loading to SCM.
Rainfall intensity affects hydraulic retention time.
Rainfall frequency affects plant health.

Drying duration
Drying decreases moisture content in filter media.
Drying duration increases nitrate removal in submerged zone.
Drying duration affects microbial community and plant health.

Cold vs warm climate
Temperature affects biological nitrate removal.
Climate affects biological community.

Design Factors

Vegetation zone
Designs: Plant density and diversity, root depth, ponding depth.
Vegetation types affect plant assimilation and root microbiome.
Processes affected: Plant uptake, nitrification, and denitrification.

Filter media zone
Media porosity and compaction affect redox conditions.
Media particle size controls hydraulic retention time.
Processes affected: Nitrification, denitrification, and anammox,

Submerged layer or internal saturated zone
Carbon amendments in this zone serve as electron donor.
It provies anaerobic zone to enhance denitrification.

① Adsorption (electrostatic)
② Ion exchange (anion)
③ Complexation
④ Uptake by transporters and converted to aminoacids
⑤ Efflux out of cell
⑥ Stored in vacuole
⑦ Transport to leaves
⑧ Nitrification (oxidation)
⑨ Dissimilatory nitrate reduction
⑩ Denitrification
⑪ Biomass assimilation
⑫ Anammox

Fig. 1. Abiotic and biotic processes in stormwater treatment systems that could affect nitrate concentration in the effluent and the role of climate and design in modulating those processes. A major fraction of nitrate removal is contributed by biotic processes involving plants and soil microorganisms. Design factors such as area, depth, saturation, amendments, and plants can affect the effectiveness of chemical and biological processes. Climate such as temperature, rainfall intensity, and drying duration can affect the nitrate removal kinetics and health of microorganisms and plants that help remove nitrate from stormwater.

Payne et al. 2018, Shrestha et al. 2018). However, the relative importance of these factors on nitrate removal is unknown. In SCM, nitrate can be removed via abiotic processes such as ion exchange (Hu et al. 2020), but such process is sensitive to chloride concentration (Samatya et al. 2006). Nitrate can adsorb on filter media with net positive surface charge (Hassapak et al. 2015, Mahdy et al. 2008, Ordonez et al. 2020, Yan et al. 2016), but most media in biofilters have a net negative surface charge or become negatively charged after adsorption of organic carbon (Kaiser and Guggenberger 2003). Thus, the contribution of these abiotic processes for nitrate removal is typically low. Nitrate is typically removed in SCM via biotic processes such as denitrification (Mangum et al. 2020), dissimilatory nitrate reduction to ammonium (DNRA) (Bu et al. 2017, Burgin and Hamilton 2007), or by direct plant uptake (Morse et al. 2018) (Fig. 1). Among these processes, nitrate removal by DNRA can be temporary as oxidation of ammonium by nitrifiers can produce nitrate (Payne et al. 2014a, Payne et al. 2014b, Rahman et al. 2019). Abiotic processes are governed by amendment types and quantity and the design configuration (Grebel et al., 2013; Mohanty et al., 2018; Zhang et al., 2020). Biotic processes are governed by fluctuations in pH, dissolved oxygen, and moisture content – all factors influenced by the local climate. These factors result in soil microbial community shifts (Glassman et al. 2018) and changes in contaminant removal rates (Garfí et al. 2012). The coupled effect of climate and design modifications may act as the main cause of the high nitrate removal variability in SCM; however, to what extent climate or design factors contribute to nitrate removal uncertainty remains unclear (Gold et al. 2019, Schifman et al. 2016).

Nitrate removal in SCM fluctuates widely (Collins et al. 2010a, Lopez-Ponnada et al. 2020, Manka et al. 2016, Tian et al. 2019), and even a large-scale implementation of SCM has not lowered the nutrient loading to water bodies significantly (Lintern et al. 2020). The cause of this wide variability has been difficult to attribute at a specific site but can be attributed to several factors. First, field-scale SCM are rarely monitored long enough to accurately measure their removal potential. Even in controlled laboratory studies (Bock et al. 2015, Davis et al. 2001), nitrate removal varies widely. Second, differences in design specifications such as hydraulic retention time (McPhillips and Walter 2015), usage of amendments (Morgan et al. 2020), and configuration (Palmer et al. 2013, Wissler et al. 2020) could lead to variable nitrate removal. Third, the local climate may influence the rainfall intensity, dry periods, and temperature (Liao et al. 2018, Xie et al. 2003). Thus, a variation in local climate could cause fluctuation in nitrate removal (Berger et al. 2019, Blecken et al. 2007, Mangangka et al. 2015). However, it is unclear if the combined effects of design and climate can improve or worsen nitrate removal (Tanner and Kadlec 2013). Previous reviews have investigated specific details of SCM including the sources, cycling process, and fate and transport of nitrogen-based nutrients (Nestler et al. 2011, Reisinger et al. 2016, Yang and Lusk 2018), overall design (Collins et al. 2010b), the effect of media type and vegetation (Osman et al. 2019, Skorobogatov et al. 2020), biotic and abiotic removal mechanisms (Burgin and Hamilton 2007, Lee et al. 2009, Tang et al. 2020), and more recently the coupled effect of infiltration rate and design characteristics (Zhang et al. 2020). While many articles have recognized the lack of studies examining the effect of climate (Gold et al. 2019, Yang and Lusk 2018) and design factors (Osman et al. 2019) on the performance of SCM, previous reviews have rarely compared the importance of either factor on nitrate removal in the most common SCM.

The overall objective of this review is to evaluate the relative importance of climate and design on nitrate removal in SCM. This article compares the nitrate removal of four commonly used SCM – bioretention, grass swales, media filters, and retention ponds – based on field data reported on the BMP database from 1982 through 2018 combined with peer-reviewed articles published before June 30, 2020. By identifying the local climate of those SCM based on *Köppen-Geiger* climate classification, we link nitrate removal capacity to local climate and design configurations. We have analyzed the data against many design configurations that may affect nitrate removal in SCM, but we reported only selected configurations where sufficient data is available for statistical analysis (Table S1). The selected design configurations include the presence and depth of ponding/saturated zone, watershed area, infiltration rate, vegetation density, amendment type, length, area-to-depth ratio, and the presence of plastic linen.

2. Data collection and analysis method

To analyze the effect of different climate and design variables on nitrate removal, we used data from the BMP Database updated by June 30, 2020. The BMP Database is an open-access website initiated in cooperation between the USEPA and ASCE (Clary et al. 2011). Based on the availability of sufficient data for statistical analysis, we chose four stormwater control measures (SCM): bioretention, grass swale, media filter, and retention pond. These SCM have a unique design or configuration for the removal or release of nitrate (Table 1). Although other types of

Table 1
Summary of four common SCM, nitrate removal mechanisms, specifications of design, and project.

Properties	Stormwater Control Measures (SCM)			
	Bioretention	Grass Swale	Media Filter	Retention Pond
Design configuration	Vertical flow-through solid media with or without amendment, submerged layer, and plants	Shallow, horizontal channel with planted grass	Vertical flow-through of mixed or layered sand, peat, and/or soil	Deep and long water pool without geomedia and with surrounding vegetation
Fraction of contaminants removed	Dissolved, suspended	Suspended	Suspended	Dissolved and suspended
Main contaminants removed	Nutrients, heavy metals, suspended solids, bacteria	Heavy metals, suspended solids	Suspended solids, bacteria	Nutrients, suspended solids
Main removal mechanisms	Adsorption, plant uptake, biodegradation, filtration	Adsorption, filtration, plant uptake, sedimentation	Adsorption, filtration, direct interception, inertial impaction, and diffusion by Brownian motion	Biodegradation, sedimentation
Project area (m^2)	100 – 1,000	5 – 320	0.8 – 150	100 – 10,000
Cost ($)	100K – 300K	57K – 63K	161K – 485K	297K – 1.78M
Retention time	1 – 12 hours	1 – 3 hours	0.5 – 1.5 hours	1 – 7 days
Vegetation	Yes	Yes	No	Yes
# of sites analyzed from BMP database	10	17	15	18
# of nitrate removal data	62	217	186	247
Anoxic environment	Yes/No	Mostly No	No	Yes/No
Common locations	Rural areas, adjacent to rives	Next to roadways	Maintenance stations	Urban areas

SCM can also remove nitrate, the lack of sufficient nitrate data limited our analysis. Among types of SCM surveyed, bioretention systems are the most common, which include bioretention and infiltration basins. Media filters permit rapid infiltration of stormwater through packed sand, where pollutants can be removed by physiochemical filtration and adsorption (Sabiri et al. 2017). Media filters are mostly sand filters or sand mixed with soil to increase the hydraulic conductivity of native soil for the rapid infiltration of stormwater. Thus, they are not optimized to remove dissolved nutrients due to the low adsorption capacity of sand and low hydraulic retention time. Bioswales include both grass swales and grass strips, and they are common in the roadside environment. They do not have many design considerations other than the slope, length and depth of the depressed area. Bioretention systems can remove nitrate by filtration, adsorption, and biotransformation mechanisms (Davis et al. 2006, Kim et al. 2003, Palmer et al. 2013), whereas grass swales can treat stormwater via sedimentation and filtration (Barrett et al. 1998, Deletic and Fletcher 2006, Stagge et al. 2012). Retention ponds include wetland basins and detention basins. They are particularly useful to handle a large volume of stormwater and lower the peak flow. Thus, the design factors for retention ponds include the depth or volume of the pond and the presence or absence of plants. Retention ponds can lower nitrate concentration by dilution, photolysis, and other reactions in an aqueous medium (Chrétien et al. 2016, Krometis et al. 2009), but they can simultaneously increase nitrate concentration through nitrification and decomposition of organic matter (Bettez and Groffman 2012). In this study, we catalog all SCM data based on their design specifications such as watershed area, SCM length, volume, internal water storage (IWS) zone or submerged zone and its depth, area, depth of SCM, and hydraulic conductivity of filter media (Details in Supplementary Material).

We used *Köppen-Geiger* climate classification because it reflects the biome distribution of each region (Beck et al. 2018). *Köppen-Geiger* classifies the climate into five main groups including tropical, dry, temperate, continental, and polar, which are further divided into 30 sub-types depending on local precipitation and temperature (Peel et al. 2007). Using the global positioning system (GPS) coordinates of each SCM from the BMP database, we designated each SCM surveyed to one of the *Köppen-Geiger* climate categories.

To analyze the performance of each SCM in removing nitrate, we calculated the log removal of nitrate (LRN) as follows: $LRN_t = -\log_{10}\left(\frac{Ce_t}{Ci_t}\right)$; where C_e and C_i represent the concentration of nitrate in the effluent and influent, respectively, in a given day (t). The removal calculation assumes a steady state; that is, the influent concentration remains consistent or does not vary within the timescale of hydraulic residence time. This assumption could introduce significant error particularly if the residence time is much longer than the sampling frequency. Thus, a composite sample should be used to account for such fluctuation in influent concentration. Data without both influent and effluent for the given day was excluded from the analysis. To verify the change in performance due to design, we compared SCM located near each other and within the same climate classification. Nitrate removal was compared using Wilcoxon Test where *p-values* lower than 0.05 represent a statistical difference. To provide mechanistic insight into the link between nitrate removal and bioretention system design, results were analyzed from 29 peer-reviewed studies. These studies were collected from Web of Science based on keyword combinations of the terms “nitrate and biofilters”, “mesocosm”, or “biofiltration”. The complete dataset used in the analysis is provided in an online open-access repository, Figshare (https://doi.org/10.6084/m9.figshare.13167608.v1).

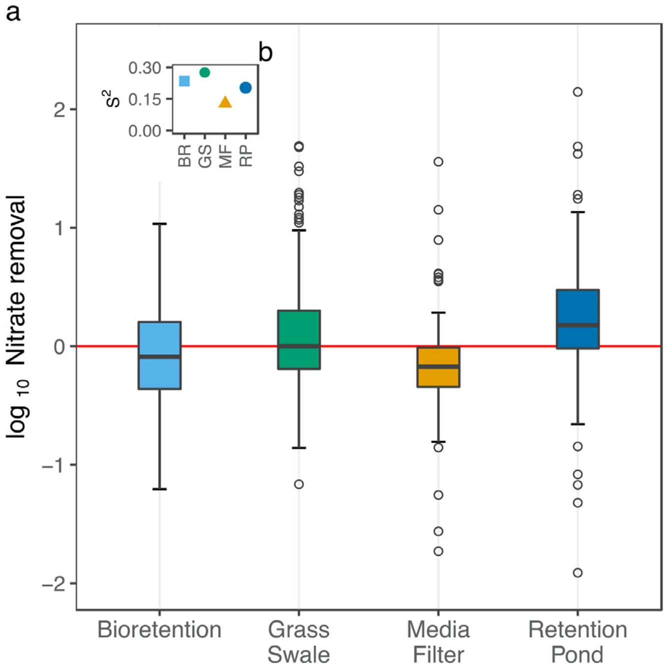

Fig. 2. (a) Log nitrate removal of four types of SCM. Log removal was calculated as the ratio between effluent and influent concentration of nitrate. The horizontal red line represents conditions where influent concentration is the same as the effluent (log removal = 0). (b) The variance (S2) of log-removal data calculated for bioretention (BR), grass swale (GS), media filter (MF), and retention pond (RP).

3. The extent of nitrate removal uncertainty in SCM

SCM are expected to have different nitrate removal capacity because of a difference in their design configurations. Our analysis reveals that, irrespective of SCM types, nitrate removal (95 percentile) varied by two orders of magnitude ranging from net positive removal to net negative removal (Fig. 2). A fluctuation in dissolved oxygen (DO) concentration diurnally could affect denitrification. However, a lack of data on the variation of DO in urban stormwater and corresponding changes in nitrate concentration prevented us from linking diurnal fluctuation in DO with denitrification. Among the four SCM types, the retention pond has a net positive median log removal of nitrate (~ 0.2). For all other SCM types, the median log removal is negative, indicating they act as a source of nitrate in most cases. The media filters perform the worst but they are also the most consistent among all SCM types. The removal performance of nitrate by media filters is similar ($p > 0.05$) to the removal performance of bioretention systems, but statistically ($p < 0.05$) different compared to the removal performance by grass swales and retention ponds.

We attribute the wide variability of the nitrate removal to a difference in design and climate. The rainfall intensity can vary widely between sampling events for the same SCM, which likely affects the nitrate loading and hydraulic retention time (Spieles and Mitsch 1999), thereby varying the nitrate removal (Berger et al. 2019). The variability of nitrate removal in grass swales could also be related to varying temperature and water salinity between seasons (Roseen et al. 2009) as salinity could lower the abundance of denitrifiers (von Ahnen et al. 2019). On the other hand, these SCM types may have different types of amendments (Kameyama et al. 2016), vegetation (Flite III et al. 2001, Shrestha et al. 2018), and size that dictate residence time (Kjellin et al. 2007). All these factors could add uncertainty to nitrate removal by these systems. We evaluate the contribution of each factor separately in the following sections.

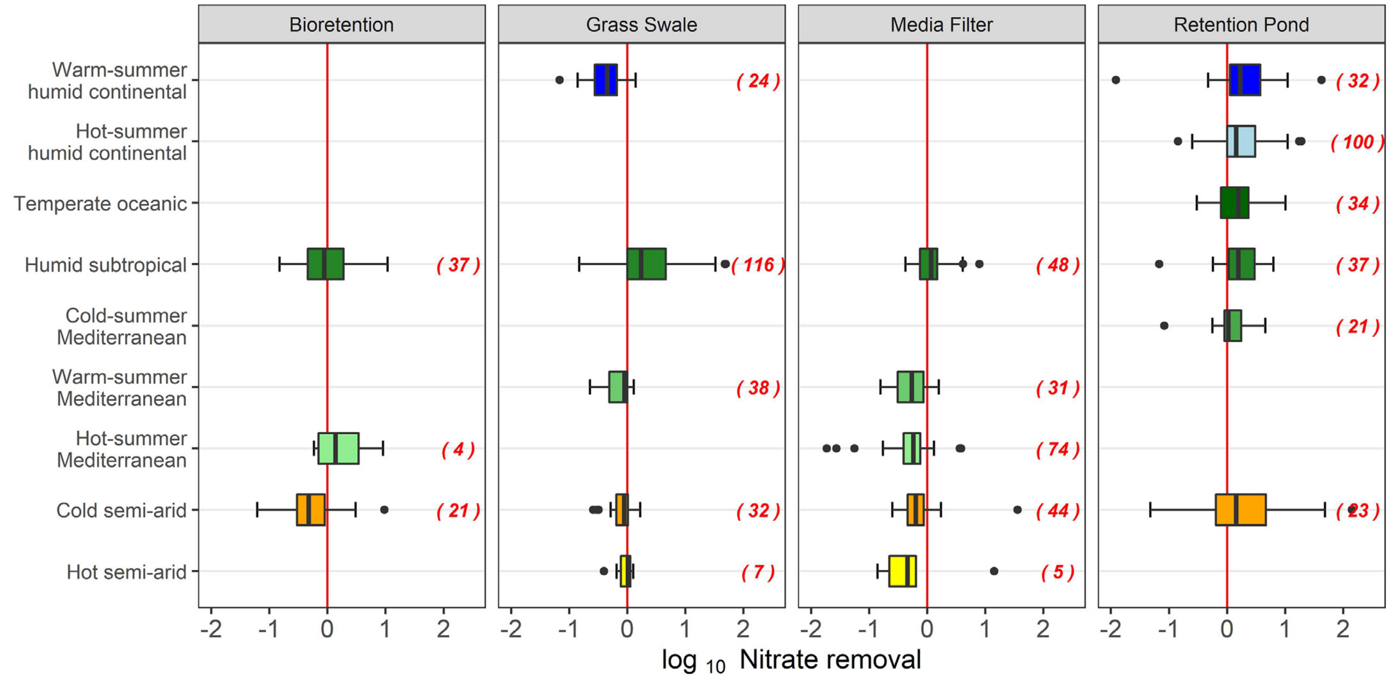

Fig. 3. Effect of climate on the performance of different green stormwater infrastructure in removing nitrate from stormwater runoff. Climate is classified based on Köppen-Geiger climate classification. The vertical red line indicates no log removal of nitrate. Numbers between parenthesis represent n-values of boxplot analysis.

4. Extent to which climate affects nitrate removal in SCM

Comparing the nitrate removal of SCM to local climate, we found that climate does not affect nitrate removal in some SCM types (Fig. 3). The result is in contrast to the results from previously published studies (Collings et al. 2020, Shrestha et al. 2018). For instance, there is no significant ($p > 0.05$) difference between nitrate removal by bioretention systems in hot-summer Mediterranean and cold-semi arid climate. In contrast, nitrate removal of grass swales in a humid tropical climate (median log removal, 0.23) is significantly ($p < 0.05$) better than the removal (– 0.35) in a warm-summer humid continental climate. In contrast to plants in other climates, native plants in tropical climates are adapted to switch nitrogen sources based on precipitation patterns and thus are more efficient at removing nitrate (Houlton et al. 2007). This probably explains why grass swales remove more nitrate in tropical climates than in any other climate condition. Irrespective of climate, media filters exhibit a negative removal of nitrate in most climates, indicating that adding media filters could potentially lead to an increase in nitrate pollution. Since media filters are typically made up of sand with aerobic features, nitrate removal via most of the biological mechanisms is not feasible. In aerobic conditions, ammonium in stormwater can be rapidly oxidized to nitrate by nitrifiers and could explain the net negative removal of nitrate. Nitrification can occur within 0.7 h (Jin et al. 2012), which is in the range of overall stormwater retention time in media filters. Thus, ammonia oxidation can make filter media a net source of nitrate.

Comparing the performance of different SCM types under the same climate classification, we found that some SCM types are more efficient than others in removing nitrate (Fig. 3). For instance, in a cold-semi arid climate, a retention pond provides a median net positive (0.16) nitrate removal while the other three SCM types exhibit net negative removal (source of nitrate). In this climate, a combination of low annual precipitation (less than 508 mm) and low mean annual temperature (Collings et al. 2020) could lead to low biological activity and explain low nitrate removal. In contrast, in humid subtropical climates, grass swales and retention ponds show a net positive median removal of 0.23 and 0.19, respectively. While warm and moist climates increase nitrate concentration due to organic matter decomposition (Bulseco et al. 2019, Joslin and Wolfe 1993, Luo et al. 1999), cold climates retard denitrification (Collings et al. 2020). Denitrification rates can vary with the season due to a difference in mean water temperature. Denitrification is typically greatest in the spring and lowest in the summer and early autumn (Zhong et al. 2010). A decrease in denitrification at low temperature can be compensated by an increase in hydraulic retention time (Wicke et al. 2015). Thus, the climate can affect the extent to which a design modification is effective for nitrate removal in SCM. The ability of SCM in removing nitrate is limited under high-intensity rainfall when most of the runoff overflows the system or infiltrates at a faster rate, thereby limiting reaction time in the SCM. In contrast, rainfall promotes the leaching of N-source from soil and favors nitrate uptake by plants (Mantelin and Touraine 2004). In addition to rainfall intensity, increasing the dry duration between rainfall events can improve the nitrate removal from trapped pore water (Berger et al. 2019, Norton et al. 2017). Consequently, a longer antecedent dry period between rainfall events partially explains why nitrate removal in hot-summer Mediterranean climates is higher than the removal in a humid subtropical climate. Collectively, these results indicate that climate can influence moisture content in SCM and affect nitrate removal by biological processes.

5. Effect of SCM design on nitrate removal

To isolate the effect of specific design factors, we selected SCM under the same climate conditions from the BMP database and compared the nitrate removal between SCM as a function of different design variables. The analysis reveals specific design parameters that could change the SCM performance from a net sink of nitrate to a net source.

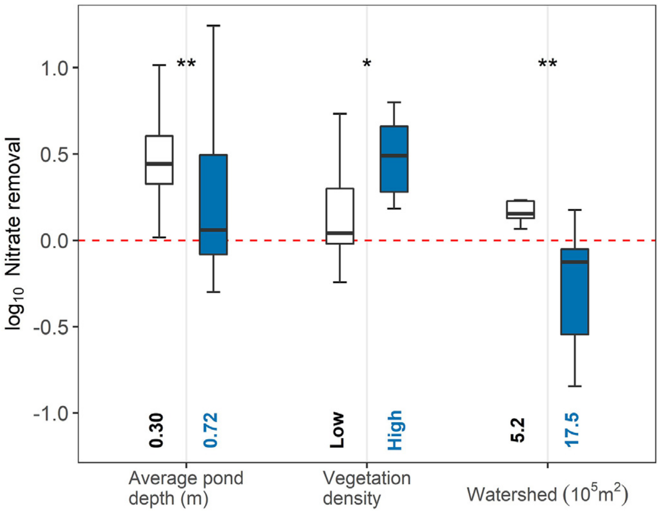

Fig. 4. Nitrate removal of retention ponds within the same climate classification is sensitive to design. Watershed area and pond depth were imported from the BMP Database summary report. The average pond depth was calculated as the ratio between permanent pool volume (m3) and the permanent pool surface area (m2). Vegetation density was evaluated using Google Earth Software. The SCM involved in the pond depth and watershed area analysis were located in a hot-summer humid continental climate and the SCM involved in the analysis of the vegetation density were located in a humid subtropical climate. Statistical analysis representation: *p-value < 0.05, **p-value < 0.01.

5.1. Which design factors affect nitrate removal in retention ponds?

To isolate the effect of designs, we compared nitrate removal between ponds within the same climate regions that differed by a single design factor. Due to the lack of available data for all climate regions, our data analysis was possible for retention ponds located in 2 climate regions: hot-summer humid continental climate and humid subtropical climate. Our analysis reveals that nitrate removal in retention ponds varies based on the pond's depth, vegetation density, and watershed area (Fig. 4). The removal decreases significantly ($p < 0.01$) when the depth of the pond increases from 0.3 m to 0.7 m. An increase in depth limits mass transfer of nitrate to the reactive zone, the interface between biofilm or sediment and water columns, thereby decreasing nitrate removal (Cubas et al. 2019). A low volume of water column per anoxic zone near sediments (Chen et al. 2019b) is critical for enhancing denitrification (Mayo 2020). This could make a shallow pond or wetland more effective in removing nitrate than deeper ponds (Chen et al. 2019a). An increase in vegetation density significantly ($p < 0.05$) increases the removal of nitrate in retention ponds, showing that plants can play a critical role in nitrate removal (Vymazal 2020). Plants boost denitrification by providing endogenous carbon through root exudates for root microbiome to get energy via denitrification (Wu et al. 2017) and increasing the hydraulic retention time (HRT) by blocking the flow in the pond (Khan et al. 2019), all of which could explain the positive effect of vegetation on nitrate removal in retention ponds. The carbon released during decomposition of plant materials provides carbon source critical for nitrogen mineralization (Hooker and Stark 2008). However, plants detritus, unless removed, can also release nitrogen into water (Knops et al. 2002). Thus, the pond should be maintained to prevent excessive accumulation of plant debris. Retention ponds located in smaller watershed areas also remove more nitrate than those located in larger watershed areas, possibly because of the increase of nutrient loading in larger watersheds (Zhang et al. 2019b). Our analysis reveals that a retention pond connected to a small watershed (5.2×10^5 m^2) removes nitrate, whereas the pond connected to a larger watershed (1.75×10^6 m^2) exports nitrate. We attribute the pond size-dependent removal capacity to the increased loading of nitrate from larger watershed due to deposition and biodegradation of plant debris (Jani et al. 2020, Krometis et al. 2009) and a faster exhaustion of pond capacity to remove nitrate. In this case, pre-treatment of influent water by an algal pond could increase the overall nitrate removal (Mayo 2020). Based on our prior analysis, the nitrate removal capacity of retention ponds is nearly similar in all climates. The design factor, rather than climate, explains the variability in the nitrate removal capacity of retention ponds.

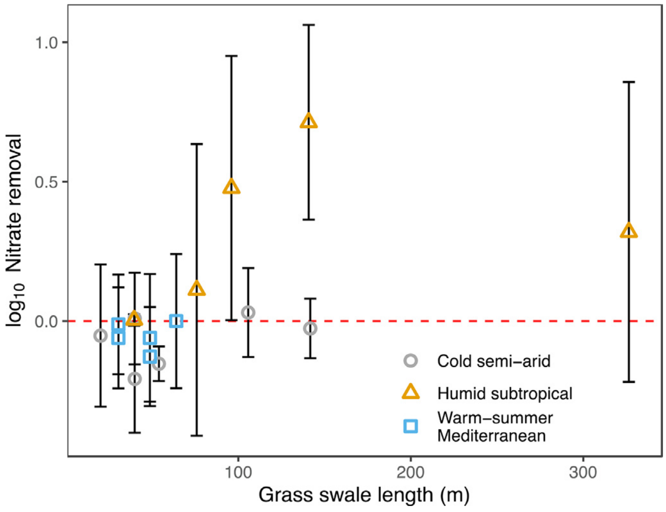

Fig. 5. Removal of nitrate by grass swale varies with the length of grass swale in a humid subtropical climate, and grass swale acts as a source (a net negative removal) in cold semi-arid or warm-summer Mediterranean climates. Sixteen (16) grass swales from the BMP database were analyzed based on average nitrate removal. The horizontal red dashed line represents no nitrate removal, whereas positive and negative values represent net-removal and net-export of nitrate, respectively.

5.2. Does grass swale length affect nitrate removal?

Our analysis shows that nitrate removal by grass swales is highly sensitive to local climate conditions (Fig. 5). Grass swales remove nitrate only in humid subtropical climates, and an increase in the length of a grass swale increases nitrate removal. In other climates, grass swales can become a source of nitrate. Although moisture is critical for plant health and may explain the nitrate removal variability, many plants are remain healthy even in low soil water environments as a result of the plant's phenotype and physiological characteristics. In humid subtropic climates, a high decomposition rate of organic debris provides carbon source essential for dentification. Moisture, carbon and nitrogen availably has been shown to increase abundance of microorganism responsible for denitrification (Attard et al., 2011, Shrewsbury et al. 2016). High moisture content or a submerged layer in the soil is needed to create local anoxic conditions (Hsieh et al. 2007), which can facilitate denitrification. Thus, we speculated that soil conditions in subtropic climate is more favorable for denitrification than other dry climate because of soil moisture, carbon and nitrogen abundance that shape the denitrifier communities in soil. High variability in nitrate removal can be attributed to the difference in a contact time as the data shows that increasing the length of a grass swale in a humid subtropical climate increased nitrate removal. However, other unexplored design parameters such as centerline slope and vegetation cover can affect how long the stormwater is detained on the grass swale, and hence their ability to remove ni-

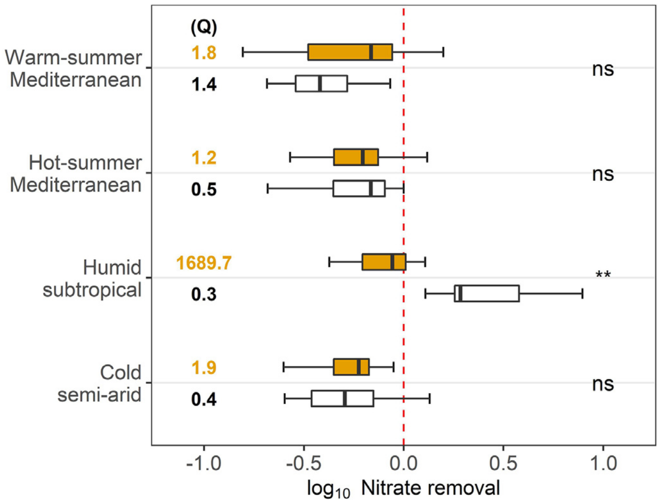

Fig. 6. Effect of peak runoff (Q, $m^3\ min^{-1}$) on nitrate removal of media filter within different climates. Vertical dashed line represents no nitrate removal, while positive and negative values represent net-removal and net-source of nitrate, respectively. Statistical analysis representation: ns = no-significance, **p-value < 0.01.

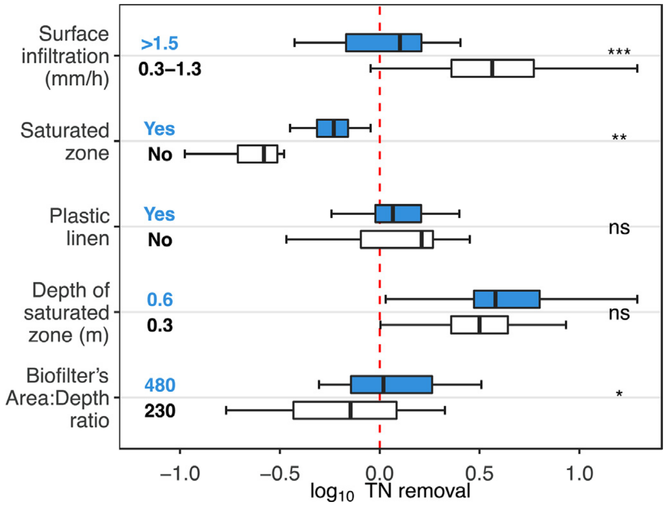

Fig. 7. Effect of various design parameters on the removal of total nitrogen (TN) in bioretention systems. Vertical red dashed line represents no removal of TN. Statistical analysis representation: ns = no-significance, *p-value < 0.05, **p-value < 0.01, ***p-value < 0.001.

trate (Wicke et al. 2015). Thus, the length of the grass swale may not be the only key factor affecting nitrate removal.

5.3. Does flow rate affect nitrate removal in the media filter?

The flow rate through media filters can depend on rainfall intensity and watershed area. An increase in these variables can lead to increases in the discharge rate or nitrogen loading to media filters. We compared the nitrate removal of paired sand filters located in the same local climate based on the Rational Method ($Q = CiA$), which permits the calculation of the peak runoff Q (Chin 2019). The precipitation (i) for the paired sand filters was assumed to be the same, and the BMP database provided the impervious area (e.g., equivalent to the runoff coefficient, C) and the watershed area (A) for each sand filter. Our analysis shows that media filters act as a net source of nitrate in all climates and flow conditions, except in a humid subtropical climate with an average flow rate of 0.33 $m^3\ min^{-1}$ (Fig. 6). In humid subtropical climates, low runoff volumes may cause a positive removal of nitrate, but heavy precipitation could reduce the removal rates (Feng et al. 2012) possibly because of a decrease in hydraulic retention time (Gottinger et al. 2011, Nakhla and Farooq 2003). As media filters mainly consist of sand, they have limited capacity to remove nitrate by adsorption or biotransformation. Furthermore, oxidation of ammonium to nitrate (Landsman and Davis 2018b) can make the filter itself a source of nitrate leaching. Therefore, filter media should not be used for nitrate removal from stormwater unless amendments are added to sand filters which can substantially increase nitrate removal (Palmer et al. 2013, Ulrich et al. 2017).

5.4. Which design factors of bioretention systems are critical for total nitrogen removal?

For bioretention systems, we analyzed total nitrogen (TN) instead of nitrate due to a lack of sufficient paired data in the BMP database that links design parameters with nitrate removal. We compared the TN removal of paired bioretention systems that were located within the same local climate but differed in only one design factor. We extracted the following data for the design parameters from published studies that analyzed the same bioretention systems reported on the BMP database: the presence of internal water storage (IWS) (Hunt et al. 2006) or plastic linen (Li et al. 2009), surface infiltration (< 0.13 or > 0.15 mm h^{-1}) and depth (0.3 or 0.6 m) of the saturated/submerged zone and surface infiltration (Brown and Hunt 2008), and biofilter area-to-depth ratio of 230 or 480 (Brown and Hunt 2012). Our analysis shows that TN removal in bioretention systems can vary based on design factors, but the presence of plastic linen and the depth of the saturated zone do not affect TN removal significantly (Fig. 7). The presence of a saturated zone slightly improved log TN removal from -0.63 to -0.24. Previous laboratory studies have demonstrated an improvement in nitrate removal by adding IWS (Alikhani et al. 2020, Lopez-Ponnada et al. 2020, Nabiul Afrooz and Boehm 2017, Zinger et al. 2013, Zinger et al. 2020). IWS typically helps maintain anoxic conditions (Ding et al. 2019) and improves nitrate removal (Palmer et al. 2013). It should be noted that in the presence of IWS, denitrification only accounts for 23% of nitrogen removal in bioretention systems (Norton et al. 2017), and DNRA may dominate nitrate removal in areas with rewetting occurrence (Friedl et al. 2018). Our analysis reveals that an increase in depth of IWS from 0.3 m to 0.6 m did not significantly improve TN removal, indicating an increase in nitrate removal is probably offset by a decrease in ammonium removal in the saturated layer. A comparison of bioretention systems with area-to-depth ratios of 230 and 480 shows that an increase in bioretention area significantly improves TN removal, possibly because the removal of particulate N occurs near the surface instead of the deep layer (Landsman and Davis 2018a).

TN removal is highly sensitive to stormwater infiltration, which is controlled by the hydraulic conductivity of filter media. An increase in retention time typically improves nitrate removal in bioretention systems (Alikhani et al. 2020, Berger et al. 2019, Ding et al. 2019, Lopez-Ponnada et al. 2020, Shrestha et al. 2018). Our analysis shows that infiltration rates exceeding 0.15 cm h^{-1} rapidly decrease TN removal from net positive to negative. Hydraulic retention time typically increases with an increase in rainfall intensity or catchment area as both factors produce a larger runoff volume and reduce TN removal (Alikhani et al. 2020). Additionally, rainfall patterns could affect the levels of dissolved organic carbon (DOC) in stormwater (Lipczynska-Kochany 2018) and the infiltration rate through SCM, which would have further implications on nitrate removal (Fidel et al. 2018). In summary, bioretention systems should be designed with a greater area, shallow submerged layer, and a relatively small catchment area, if possible.

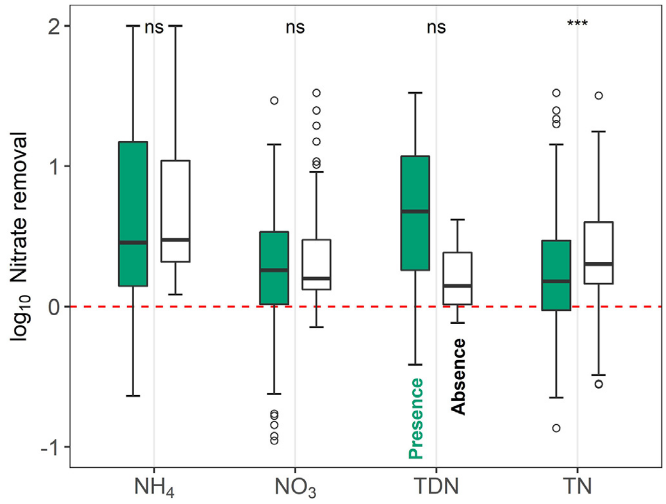

Fig. 8. Effect of presence or absence of vegetation (emergent macrophytes) on the removal of different nitrogen-based contaminants in bioretention systems. Green-filled boxplots represent bioretention systems with vegetation, while empty boxplot represents bioretention systems without vegetation. Data analysis was based on 29 peer-reviewed articles. A horizontal red dashed line represents no nitrate removal. Negative values for nitrate removal represent export or leaching of nitrate, while positive values represent net-positive removal of nitrate. Statistical analysis representation: ns = no-significance, ***p-value < 0.001.

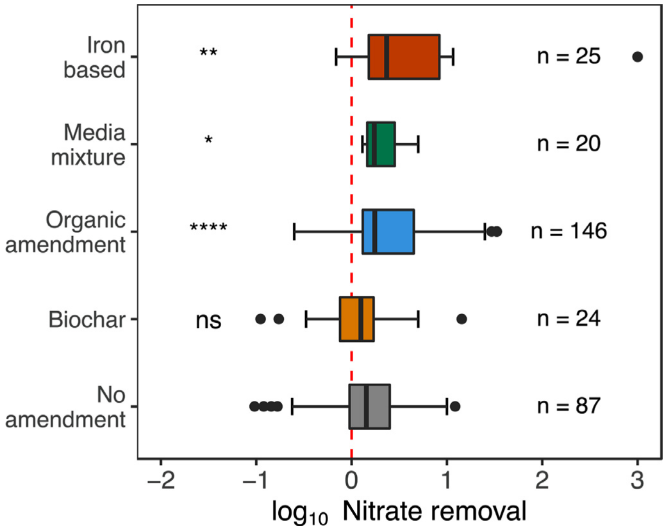

Fig. 9. Removal of nitrate in flow-through bioretention systems amended with diverse types of geomedia by analyzing the results of 24 articles. Negative values represent net export of nitrate, while positive values represent net removal. No amendment includes sand or soil. The organic amendments include compost, mulch, and other organics. Media mixture represents the mix of three or more amendments including zeolite, tire crumb, printed paper, fly ash, bark, and water treatment residuals. Statistical analysis representation: ns = no-significance, *p-value < 0.05, **p-value < 0.01, ***p-value < 0.001.

5.5. How does vegetation influence the removal of different N species?

Nearly all SCM types contains vegetation which can directly uptake dissolved nitrogen species such as nitrate and ammonium via roots (Parker and Newstead 2014, Wang et al. 2012). The presence of vegetation typically increases the removal of nitrogen by more than 75% (Barron et al. 2019, Davis et al. 2006), although some studies observed no benefits of plants (Palmer et al. 2013, Valtanen et al. 2017a). Our analysis shows that the presence of vegetation – mostly emergent macrophytes – can significantly increase TN removal (Fig. 8), but it does not affect the removal of NH_4^+, NO_3^-, and total dissolved nitrogen (TDN). The discrepancy could be attributed to the soil pH as DNRA can contribute to 18% of nitrate removal if soil pH is neutral or alkaline (Zhang et al. 2015). In addition, a lack of removal of nitrogen-based compounds could also be attributed to the leaching of different N species from the fertilizer that may have been applied to maintain the plant health and to the complexities of nitrate uptake mechanisms in plants. Compost is often added to support plant growth, which can leach nitrate (Shrestha et al. 2018). In this case, organic biomass such as woodchips, bark, mulch, wood dust, compost, or biochar can be used to improve denitrification (Greenan et al. 2009, He et al. 2019).

Nitrate uptake capacity of a plant is sensitive to the functional properties of the transporters in roots, density in the plasma membrane of root cells, the surface and architecture of the root, plants types, root depth, and leave density (Cardinale 2011, Hallin et al. 2015, Morse et al. 2018, Noguero and Lacombe 2016), because they all directly or indirectly influence nitrate assimilation pathways. The nitrate assimilation pathway in plants occurs in three steps: (1) nitrate uptake, (2) nitrate reduction, and (3) nitrate storage (Crawford and Glass 1998, Tischner 2000). First, anionic nitrate in the soil is carried toward the root systems by bulk flow and actively transported across the plasma membrane. Roots use transporters (Crawford 1995) encoded by *NRT1* (low affinity) or *NRT2* (high affinity) genes that bind to nitrate and transport them through the plasma membrane of the root cells to the root symplast. Nitrate can either be utilized into amino acids or effluxed out of the cell by loading it into the xylem and the transporter cells translocate nitrate to the leave system where it is stored in the vacuole as nitrite. Furthermore, previous studies have shown that higher biomass content in plant and microbial community diversity enhances nitrate removal rates (Deng et al. 2020, Wen et al. 2010, Zhang et al. 2016). Plant's root development depends on the presence of inorganic nitrogen (e.g. nitrate and ammonium), pH and redox potential conditions (Bloom et al. 2002), which are likely to experience seasonal variability (Fatubarin and Olojugba 2014, Fernandes et al. 2002) and affect microbial communities (Mellado-Vázquez et al. 2019). Thus, root health, plant species and their growth rate in different SCM could affect nitrate removal.

To maintain charge balance during nitrate uptake, a proton is transported into root cells. As amendments can alter pH to affect plant uptake of nitrate (Revell et al. 2012), they can indirectly affect the ability of the plant to uptake nitrate. Plants can also indirectly affect nitrate removal by altering the moisture content in the filter media via evapotranspiration and the hydraulic conductivity of the soil (Valtanen et al. 2017a) by root architecture (Wang et al. 2020). The selection of plant types should be used as a design factor to increase nitrate removal.

5.6. Which amendments have maximum removal capacity?

Nitrate removal by bioretention systems or filter media can be increased by the addition of amendments. Through literature review, we divided amendments into five categories: (1) no amendment: only sand and/or soil; (2) organic amendments: compost, mulch, bark, and woodchips; (3) media mixture: a mix of three or more amendments including zeolite, tire crumb, printed paper, fly ash, bark, and water treatment residuals; (4) biochar; (5) iron-based amendments: zero-valent iron, iron fillings, iron-oxide from water treatment residues. Our analysis shows that the median removal capacity of amendments decreases in the following order: iron-based media > media mixture > organic amendment > biochar (Fig. 9). Compared to control (no amendment), iron-based media, media mixture, and organic amendments removed significantly more nitrate ($p < 0.05$), whereas biochar offered no significant improvement in nitrate removal. These results indicate that biochar may not necessarily improve nitrate removal, although it may remove other N species such as NH_4^+ due to electrostatic adsorption based on the opposite surface charge between NH_4^+ and biochar (Hina et al. 2015, Vu et al. 2017).

Bioretention systems with organic amendments remove significantly more ($p < 0.05$) nitrate than bioretention systems without amendment. One possibility for high variability is the difference in the types of organic amendments used. Organic amendments typically provide dissolved organic carbon (an electron donor) to facilitate the reduction of nitrate (Chang et al. 2018, Pfenning and McMahon 1997); however, some organic amendments such as compost can also be a source of nitrate (Chahal et al. 2016). Thus, the amendment should be carefully selected to ensure they do not contribute nitrate to effluent. The addition of biochar to compost may decrease the leaching of nitrate from compost (Iqbal et al. 2015b), but such an alternative may not be enough to reduce the effluent nitrate concentration due to net export of nitrate (Shrestha et al. 2018).

Our analysis revealed that the benefits of biochar on nitrate removal observed in laboratory studies may not be translated to field studies. Biochar rarely removes nitrate by adsorption due to a net negative surface charge (Iqbal et al. 2015a). However, biochar can modify microbial activity and affect denitrification. Based on laboratory studies, biochar can increase total nitrogen removal by increasing the enzyme activity and reduction of ammonium nitrogen, but the extent of the enzyme activity depends on biochar feedstock and vegetation growth stage (Jing et al. 2020). Biochar addition can increase total nitrogen removal due to the higher mineralization of organic N to NH_4^+ and NO_X, which is subsequently denitrified (de Rozari et al. 2018). Similarly, the addition of biochar can slow down nitrate leaching from the biofilter and increase nitrate utilization by the denitrifying community (Berger et al. 2019). Our analysis indicates that the extent to which biochar can affect nitrate removal is limited in field conditions, and biochar alone may not be an appropriate amendment for the removal of nitrate (Poor and Mohamed 2020).

Iron-based amendment shows significant improvement compared to any other amendments for nitrate removal. Several laboratory studies confirmed the advantage of iron-based media for nitrate removal (Chen et al. 2020, Shrestha et al. 2018). The improvement can be attributed to several mechanisms including electrochemical reduction, ligand complexation, coupled microbial reduction of nitrate and iron-oxidation, and nitrate sorption onto precipitated metal oxides (Reddy et al. 2014, Scholz et al. 2016, Valencia et al. 2020, Westerhoff and James 2003). For instance, oxidation of Fe^0 to Fe^{2+} releases two electrons that could assist the electrochemical reduction of NO_3^- to NH_4^+ (Westerhoff 2003). Ligand complexation can occur when Fe^{III} binds to nitrate to form a complex (Song et al. 2017), although nitrate adsorption can be greatly reduced in the presence of other anions such as sulfate (Kalaruban et al. 2016). Some studies have shown that media mixtures (e.g., mixtures of two or more amendments such as spongy iron with pine bark, or zero-valent iron powder with activated carbon) can achieve more than 95% nitrate removal from stormwater runoff (Huang et al. 2015, Huno et al. 2018, Liu et al. 2013). Mixing iron amendments with biochar could help slow down the flow as well as increase the interactions between nitrate with iron amendment material, thereby improving overall capacity (Tian et al. 2019) even under extreme weather conditions.

6. Opportunities

Despite the challenges of variable performance, SCM are a cost-effective method to protect natural water bodies and improve water quality and quantity. Future studies should explore the effect of climate by conducting field experiments with similar variables in different climate regions. Thus, a collaboration between researchers from different institutions located in multiple climates could help design the experiments to evaluate the effect of climate. Long-term monitoring of these systems in field conditions could help determine how future climate change extremes such as prolonged drought or high-intensity storms can affect the performance of SCM.

Plants in stormwater biofilters can have a significant association with fungi that could affect nitrate utilization. The fundamental process of nitrate uptake by fungi (Garrett and Amy 1979) and plants (Crawford and Glass 1998) have been explored separately in earlier studies; however, there is a lack of fundamental studies on the coexistence of fungi and plants in SCM and their role in denitrification (Fochi et al. 2017). Beneficial interactions between biochar and fungi have been observed (Gujre et al. 2020). This is particularly important because fungi have been shown to increase plant tolerance in high salinity and drought conditions (Martínez-García et al. 2017). Fungi could facilitate nitrate uptake by actively transporting nitrate and by helping plants survive in harsh climates (Bücking and Kafle 2015). Future studies should explore whether and how the presence of fungi could increase nitrate removal in SCM and how to increase the abundance of fungi in the system.

Our analysis reveals that bioretention systems are not efficient at removing nitrate. Studies that optimize the design of bioretention systems related to media amendment, selected vegetation, and submerged layer controls would be helpful to gain further insight into these systems. Subsurface wetlands and a combination of retention ponds and bioretention systems may maximize nitrate removal due to the synergy between the removal mechanisms and added design flexibility (Saeed and Sun 2012). By actively supplying electrons or inducing reducing conditions via an external power source charged by solar panels, nitrate removal capacity may be enhanced particularly during the rainfall period (Yang et al. 2019). However, further cost-benefit analysis should be performed to evaluate the feasibility of such approach.

Although grass swales have poor performance in nitrate removal, this control measure is widely used as roadside infrastructure due to its simplicity and low maintenance requirements (Stagge et al. 2012). However, no study to date has analyzed the effect of the local climate on the performance of grass swales. Future studies should examine the specific mechanisms by which local climate can affect nitrate removal in SCM as the climate would affect the conditions and activities of plants and root microbes, which in turn could affect biological nitrate removal. In particular, future studies should examine how SCM can operate under different hydraulic conditions removes nitrate in different climate scenarios (Okaikue-Woodi et al. 2020). Furthermore, local carbon dioxide and humidity are the driving force for plant evapotranspiration and water conductance, respectively (de Boer et al. 2011, Patanè 2011). While evapotranspiration remains poorly understood in SCM (Ebrahimian et al. 2019), no study in the context of SCM has shown how plants and local CO_2 levels may affect the performance of SCM that contain plants.

Climate change is expected to alter *Köppen-Geiger* climate classification (Beck et al. 2018), which was used in this study to evaluate the effect of climate on nitrate removal capacities of SCM. In some regions, precipitation frequency or intensity is expected to increase (Tabari 2020), while other regions are expected to experience more drying duration between rainfall events (Hari et al. 2020). The resulting changes in moisture content in SCM and the loading of nitrate to SCM are expected to affect nitrate removal (Berger et al. 2019, He et al. 2020). However, SCM are rarely designed to account for changes in these variables due to climatic changes (Yazdanfar and Sharma 2015). Our analysis shows that retention ponds can be more effective in treating high nitrate loading in regions with greater rainfall events through modification of the water depth and vegetation in the ponds. The analysis also reveals that the nitrate removal capacity of bioretention systems, the most commonly used SCM, is sensitive to changing climate. The addition of specific amendments can increase their capacity in all climate conditions. The analysis also shows specific design conditions that could improve nitrate removal. Because consistent moisture is needed to improve nitrate removal, alternative innovative designs such as dual-mode stormwater-greywater biofilters could be used in a dry climate (Barron et al. 2019, Barron et al. 2020). There is also a lack of mechanistic study on how climate conditions affect the denitrifying community in SCM. Future studies should also evaluate whether climate conditions or amendments explain changes in the microbial community in SCM.

7. Conclusions

Analysis of the performance of the four most common SCM types from 60 locations listed in the BMP database reveals the following conclusions:

- Both climate and design affect the nitrate removal capacity of SCM, but the extent to which they are critical varies between SCM types.
- Low efficiency of SCM in removing nitrate could be mostly related to nitrification in oxic conditions and low efficiency of removal of nitrate in high flow conditions.
- Retention ponds provide the best nitrate removal rates partially because of the long residence time. Their removal is more sensitive to design than climate. The shallow depth and smaller catchment area improve the nitrate removal capacity of retention ponds.
- Media filter (sand filter) mostly exports nitrate irrespective of the local climate or design specifications.
- Bioretention systems are highly unreliable for the removal of nitrate. Optimizing their design by adding submerged layers and amendments, increasing the area to depth ratio, and lowering the infiltration rates could significantly improve their nitrate removal capacity and make them resilient in different climates or seasons.
- Nitrate removal capacities of filter media or bioretention systems can be improved by adding amendments including organic biomass, iron-based media, and media mixtures; however, biochar addition appears to provide no such benefits for nitrate removal.
- To alleviate the detrimental effect of changing climate on nitrate removal, retention ponds and bioretention systems with specific amendments should be implemented.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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