

Groundwater Seeps: Portholes to Evaluate Groundwater's Influence on Stream Water Quality

*Michael O'Driscoll¹, David DeWalle², Charles Humphrey Jr.³, and Guy Iverson⁴

¹*Department of Coastal Studies, East Carolina University, Greenville, NC*

²*Ecosystem Science and Management, Pennsylvania State University, University Park, PA*

³*Environmental Health Sciences Program, East Carolina University, Greenville, NC*

⁴*Coastal Resources Management Program, East Carolina University, Greenville, NC*

*Corresponding Author

Abstract: Recent legal cases have suggested that contaminated seeps and/or springs that have measurable impacts on adjacent surface water quality may fall under the jurisdiction of the Clean Water Act (CWA). An improved understanding of the effects of groundwater seeps on surface water quality is needed to support the evolving legal and regulatory environment. Surface seeps or seepage zones are locations where upwelling groundwater saturates the surface. Seeps can provide groundwater that may be transported to nearby surface waters along surface and shallow subsurface flowpaths. From a water quality perspective, seeps can provide portholes to observe groundwater quality. Here we consider examples of seeps as contaminant sources or sinks across a range of watershed disturbance and synthesize the seep water quality literature to help answer the questions: Why do seeps act as contaminant sinks in some cases and contaminant sources in others? What areas of seep water quality research can help apprise the legal and policy discussion on the role of the CWA to address groundwater contamination that is conveyed to streams? Overall, the case studies and literature review indicated that seep water quality data can provide valuable insights into the effects of stream-groundwater interactions on stream water quality. Future work on seep-surface water interactions is needed to characterize seep water quality behavior across a range of hydrogeological, meteorological, and land-use conditions to better understand the locations where seeps are more likely to convey contaminants to streams and affect stream water quality.

Keywords: *stream-groundwater interactions, riparian, Clean Water Act, hydrologic connection*

The 2018 Universities Council on Water Resources (UCOWR) Annual Meeting (Pittsburgh, PA) session on "Springs and Seeps: Hydrology, Ecosystem Functions, and Management" covered a wide range of spring and seep research and management issues. The general theme was that seeps and springs are valuable windows to better understand groundwater systems and their influence on streams and groundwater-dependent ecosystems. The session called for more seep and spring research to improve understanding of the links between groundwater inputs and stream water quality/ecology. This work is needed to support the evolving legal/regulatory environment.

In the current study, a review of seep water quality literature was supplemented with select case studies of seep behavior across a range of

watershed disturbance. This approach was used to answer the question: Why do seeps act as contaminant sinks in some cases and contaminant sources in others? A review of recent legal opinions and seep literature provided a basis for the framing of scientific questions to support the legal and regulatory aspects of contaminated seeps. This work highlights areas of seep water quality and hydrological research that can apprise the legal and policy discussion on the role of the Clean Water Act (CWA) to address groundwater contamination that is conveyed to streams.

Surface seeps are locations where upwelling groundwater saturates the surface. The groundwater may be transported to nearby surface waters along surface and shallow subsurface flowpaths. Seeps are generally considered to be springs with lower

discharge magnitudes (Springer and Stevens 2009). Seeps also may be submerged. Although there is extensive literature on spring occurrence (Alfaro and Wallace 1994; Stevens and Meretsky 2008; Springer and Stevens 2009), less research has focused on seeps (Williams 2016). Seeps may differ from springs in that they often emerge over a diffuse area and generally have low flows that do not form channels. Groundwater seeps often flow diffusely through soils and vegetation (Williams 2016), therefore seep discharge may be more difficult to measure relative to larger springs. However, from a water quality perspective, diffuse seeps may receive more filtration and greater potential for biological interaction and treatment.

There is generally a flow-based continuum between seeps and springs (Springer and Stevens 2009); seeps may have a range of conditions from diffuse flow to rivulet-pipe flow (Shabaga and Hill 2010). Those conditions may vary seasonally based on the magnitude of seep discharge and evapotranspiration. Seeps may occur due to an abrupt change in topographic slope (Stein et al. 2004), also referred to as groundwater slope wetlands (Brinson 1993). Seeps may also occur due to a lateral or vertical change in subsurface sediment (Vidon and Hill 2004), soil and/or bedrock hydraulic properties, bedrock contacts, joints, fractures, and fault zones (West et al. 2001) (Figure 1).

There is limited work on groundwater seep classification systems. However, a framework exists for classifying springs based on spring hydrogeology and ecology (Springer and Stevens 2009). This spring characterization work can serve as guidance for further seep characterization efforts. Williams (2016) provided a classification of seeps into three general classes: helocrene (emerges from wetlands/marshy substrate); limnocrene (discharge into a pool); and rheocrene (flowing spring that emerges into channels) (Figure 1). Seeps and springs can also be categorized based on their magnitude of flow and flow permanence. However, since flow permanence assessment requires monitoring, many studies may not have enough data for accurate flow characterization. Williams (2016) recommended a flow characterization system for low flow: $<0.01 \text{ m}^3/\text{s}$; medium flow: $0.01\text{-}0.5 \text{ m}^3/\text{s}$; and high flow: $>0.5 \text{ m}^3/\text{s}$. Flow is

an important variable for characterizing seeps and springs because of its influence on temperature and habitat. Seep discharge can influence the local ecology due to its controls on primary productivity, food supply (leaves and detritus), and influence on spring or seep-bed substrates (Williams 2016). Seep flow magnitude and timing can influence the extent of the seep habitat, disturbances, availability of food, temperature, moisture, and water quality. The invertebrate community that lives in and around the seeps is generally adapted to the range of common flow conditions (Williams 2016).

From an ecological perspective, seeps may have less diverse fauna than springs, but there may be genera found only in seeps (seep specialists) (Williams 2016). In addition to habitat for seep and spring specialists, seeps are important to groundwater-dependent ecosystems due to the groundwater inputs they provide and their influences on temperature, water chemistry, riverine biota, and in-stream processes (Boulton and Hancock 2006). Seeps can provide a wide range of ecosystem services (Figure 2) (Griebler and Avramov 2015). Seeps can serve as a linkage between the groundwater and surface water system and during summer base flows, may provide the dominant source of streamflow in some headwater catchments (Burns et al. 1998; West et al. 2001; O'Driscoll and DeWalle 2010; Morley et al. 2011). Seeps and other groundwater inputs are important to sustaining streamflows, as groundwater is the primary source of streamflow in many catchments across the globe (Winter 2007; Santhi et al. 2008; Beck et al. 2013; Miller et al. 2016).

Seeps can bestow water quality services by contributing to food webs (Williams 2016) and by attenuation of contaminants (O'Driscoll and DeWalle 2010). However, seeps can also act as net contaminant sources (Williams et al. 2014, 2015; Humphrey et al. 2018). From a water quality perspective, seeps can provide portholes to observe groundwater quality. When groundwater flowpaths transport contaminants to seeps, the discharge water quality can provide important insights into subsurface contaminant attenuation.

Although seeps may make up a relatively small extent of a catchment, they are important components of the watershed ecosystem because of their capability to translate groundwater

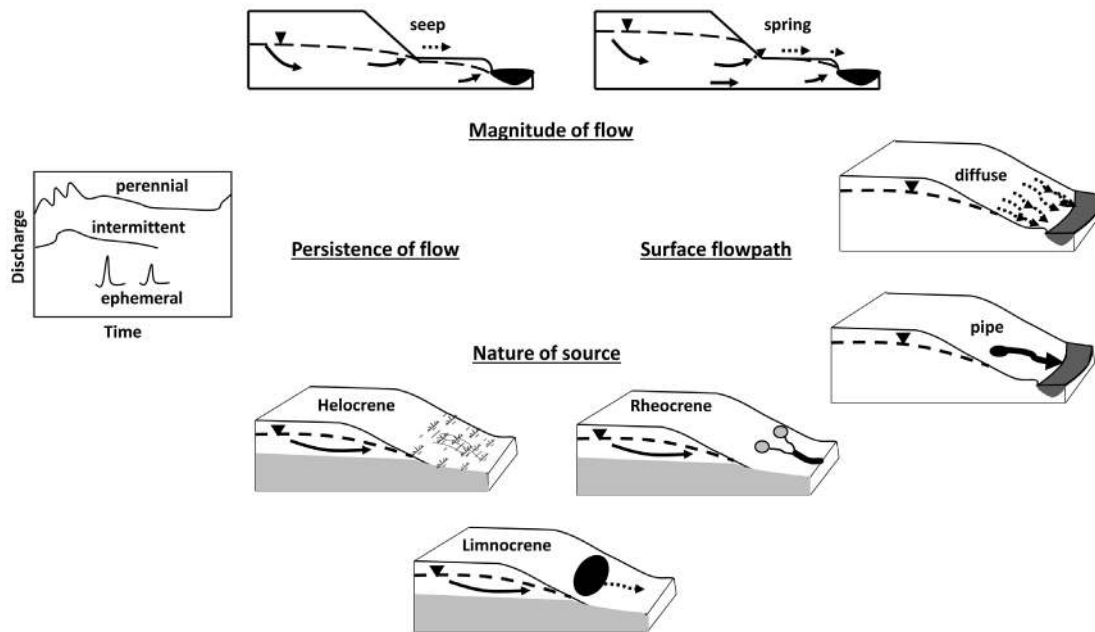


Figure 1. Variables that influence seep flow and their influence on downstream water quality (modified from Hill 1996; Shabaga and Hill 2010; Williams 2016).

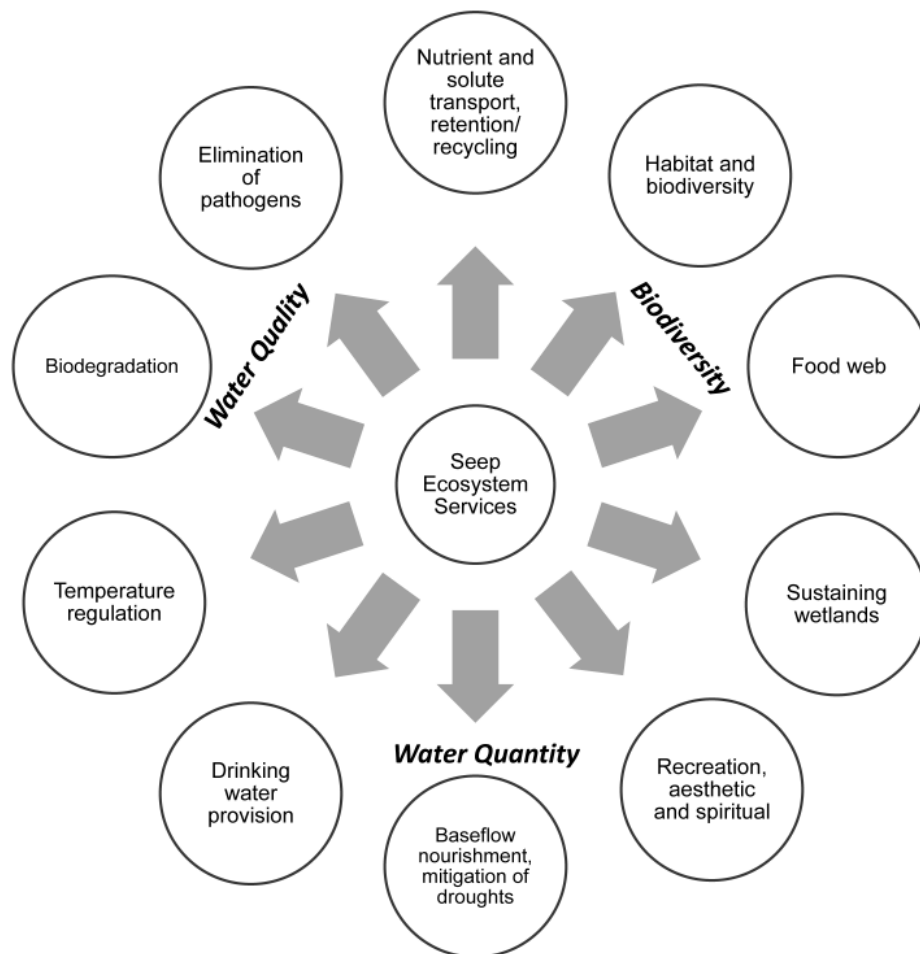


Figure 2. The variety of ecosystem services that seeps can provide including contributions to water quality, water quantity, and biodiversity (modified from Griebler and Avramov 2015).

contaminants to streams and wetlands (Williams et al. 2014; Humphrey et al. 2018) and act as nutrient cycling (McClain et al. 2003) and ecological diversity hotspots (Stevens and Meretsky 2008; Griebler and Avramov 2015; Williams 2016). Springs and seeps are key aquatic habitats because they exert a broad influence on regional ecosystem structure, function, and evolutionary processes (Stevens and Meretsky 2008). The next section will focus on seep water quality behavior across a gradient of watershed disturbance.

Seeps across a Gradient of Disturbance

In this study, examples of a range of seep water quality responses are provided from a series of seep water quality studies conducted across contrasting land-uses. The examples include a relatively undisturbed forested catchment in the Appalachian Plateau (PA), a rural Coastal Plain seep (NC), two suburban seeps in the Piedmont (NC), and an urban Coastal Plain seep (NC) (Figure 3). The seeps were sampled across several different studies, therefore the seep sampling timeframes did not overlap.

At the forested seep site at Baldwin Creek, PA, this Appalachian Plateau watershed was relatively undisturbed. Twenty-three seeps were identified and monitored monthly for a year (O'Driscoll and DeWalle 2010). Fifteen seeps flowed regularly and of these, thirteen were nitrate sinks on an annual basis (Figure 4). The results suggested that temperature (positively) and discharge (inversely) influenced the degree of seep nitrate attenuation. On an annual basis, seep nitrate concentrations declined by 31% along the seep surface flowpath (between the seep emergence point and where the seep flowed into the stream; seep flowpaths ranged from 20 - 400 m, with a median value of 150 m), suggesting that seeps generally acted as nitrate sinks. However, during winter and cooler periods, when discharge was elevated and water temperatures declined, the likelihood for seep nitrate bypass increased (O'Driscoll and DeWalle 2010) (Figure 4).

At a rural seep site in the Coastal Plain of NC (Craven County), surface seep versus subsurface flowpaths were compared for nitrogen attenuation. At this site there was a wastewater plume that was upwelling via a seep that drained to an adjacent

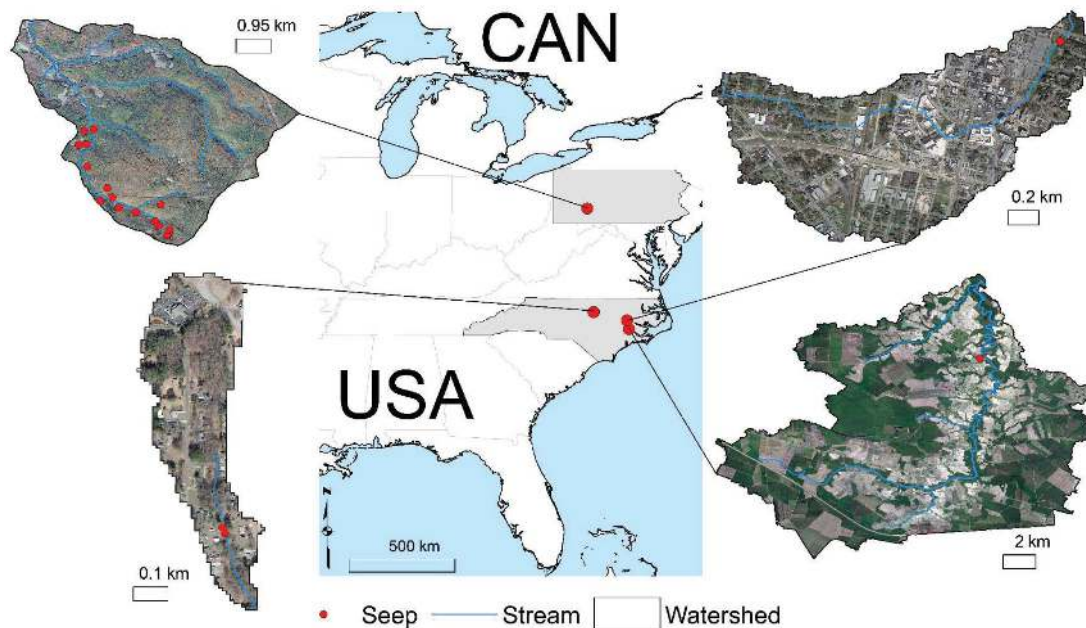


Figure 3. Maps and location information for the four seep water quality sites that occurred across a gradient of watershed disturbance. The sites include a relatively undisturbed forested catchment in the Appalachian Plateau (Baldwin Creek, PA), a rural Coastal Plain seep (Craven Co., NC), two suburban seeps in the Piedmont (Lick Creek, NC), and an urban Coastal Plain seep (Town Creek, NC).

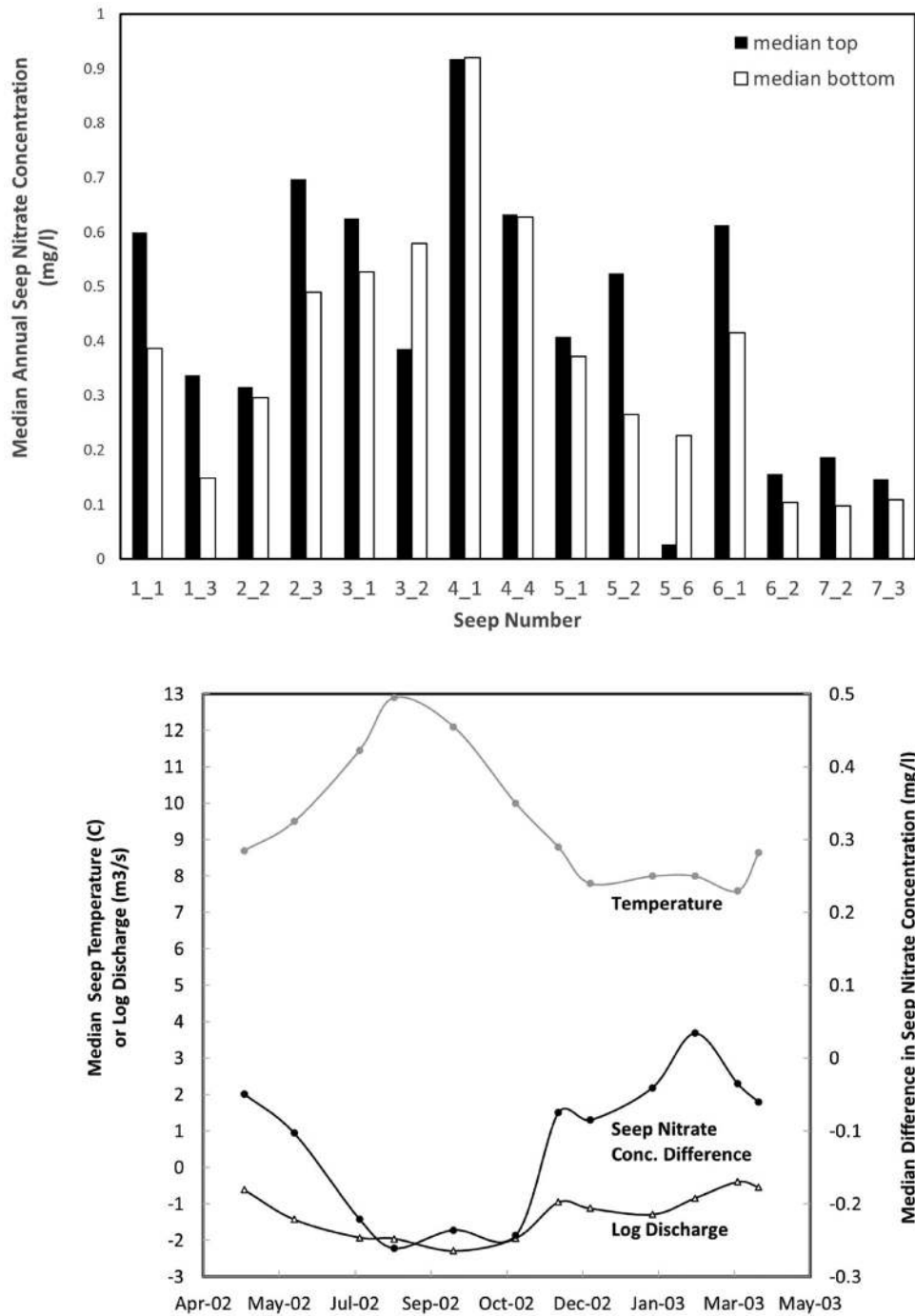


Figure 4. Seep water quality data for 15 seeps at Baldwin Creek, PA that were sampled monthly for a year. (Top) The seep nitrate concentrations typically declined from the seep emergence point to the location where the seep flowed into the stream, suggesting the seeps typically behaved as nitrate sinks. (Bottom) Water temperature and discharge data collected concurrently revealed a direct relationship between seep nitrate attenuation and temperature and an inverse relationship between seep nitrate attenuation and discharge.

stream. The wastewater plume at the site was delineated using electrical resistivity mapping, specific conductance, groundwater nitrogen concentrations, and groundwater chloride data (Humphrey et al. 2013). The seep downgradient of the plume was sampled periodically during 2012-2018 (16 seep sampling events) for comparison with groundwater quality data collected from piezometers. A comparison was made between the groundwater nutrient and chloride concentrations in the riparian buffer and the seep water. The piezometers located in the riparian buffer area had groundwater nitrogen and chloride data that indicated that the wastewater plume was upwelling in the riparian area, but at most riparian piezometers (except for piezometer 18, adjacent to the seep), the nitrogen attenuation in the surficial aquifer and

riparian zone sediments was adequate to reduce groundwater total dissolved nitrogen (TDN) concentrations to background levels. However, the groundwater that upwelled at the seep contained elevated nitrogen concentrations associated with the wastewater inputs (Figure 5). A summary of all sampling dates revealed that median TDN declined by 93% (57.3 mg/l to 3.9 mg/l) from the wastewater tank to the riparian buffer wells. However, for the portion of the wastewater plume that upwelled at the seep and flowed into the channel, the decline in groundwater TDN from the tank to the seep was 79% (57.3 mg/l to 12.3 mg/l), suggesting lower nutrient attenuation due to the groundwater flowpath upwelling prior to flowing through the forested riparian buffer. In this case the seep was behaving as a nutrient source to the stream. This

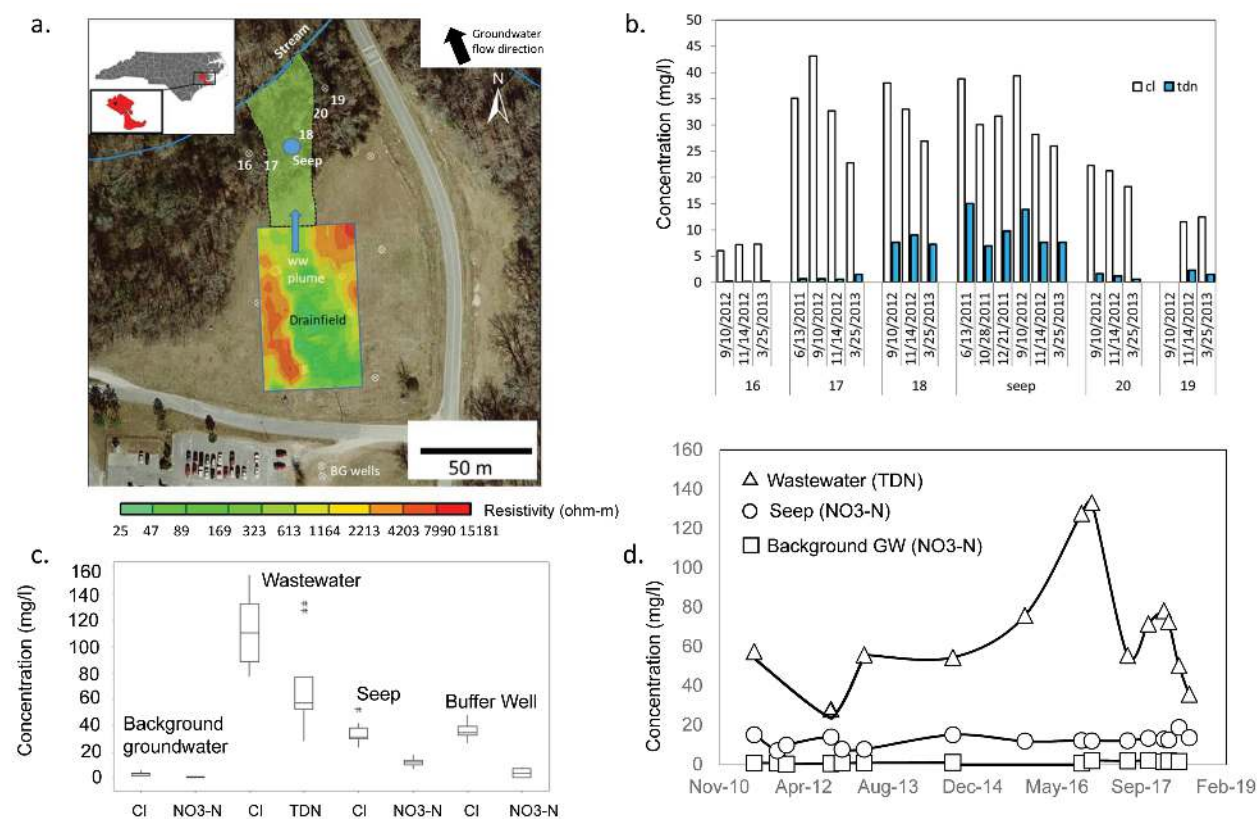


Figure 5. At an elementary school site in Craven Co., NC a seep that drained to a stream was found to be affected by a local wastewater plume. (a.) The wastewater plume at the site was delineated using electrical resistivity mapping and water quality data (Humphrey et al. 2013). (b.) Groundwater TDN and Cl concentrations in the riparian buffer and the seep water revealed that nitrogen attenuation was enhanced when groundwater flowpaths went through the riparian sediments, in contrast to the seep. (c.) Declines in nitrogen concentration between the tank, the adjacent riparian buffer well (MW-17), and the seep suggested enhanced nitrate attenuation in the riparian buffer sediments. (d.) Seep nitrate concentrations were elevated relative to background conditions, indicating wastewater-related nitrogen was being delivered to the seep.

example showed that the flowpath that groundwater takes to the stream can have a large influence on nitrogen delivery to the channel and seeps may act as nutrient (or other contaminant) sources.

At suburban seep sites in Durham County, NC, several seeps were identified at residential sites that drain to a tributary to Falls Lake. Falls Lake is a manmade reservoir that serves as a water supply for the City of Raleigh, NC. It also provides flood control and recreational opportunities. This reservoir has been classified as nutrient-sensitive since the early 1980s and was classified as eutrophic in the early 2000s. Recent nutrient management efforts have been implemented to improve water quality and use attainment (City of Durham 2012). Sampling was conducted to evaluate if the seeps were potentially transporting nutrients from onsite wastewater treatment systems to nearby creeks (Iverson et al. 2019).

Two intermittently flowing seeps were monitored from March 2017-June 2018 (seep 1, $n=8$; seep 2, $n=5$; the difference in n values occurred because seeps were not always flowing simultaneously) (Iverson et al. 2019). In an earlier study (Iverson et al. 2018) the median annual stream base flow TDN concentration was 0.97 mg/l for a nearby forested reference stream. Relative to these reference conditions, both seeps contained elevated concentrations of nutrients, but seep 1 had much greater concentrations (Figure 6). The elevated ammonium and TDN from seep 1 may be indicative

of a septic system malfunction as raw wastewater generally contains elevated TDN, mostly in the form of ammonium or organic nitrogen (US EPA 2002). Septic system malfunctions can lead to transport of ammonium and/or organic nitrogen (O'Driscoll et al. 2014). It is possible that other sources could contribute elevated TDN and ammonium (e.g., fertilizers, pet and wildlife waste); however, based on other data collected, septic systems appear to be a likely source. Median chloride concentrations in seep 1 and seep 2 were 36.1 mg/l and 28.3 mg/l, respectively. A recent study showed wastewater chloride concentrations sampled from tanks in the study area were between 43.3 mg/l and 50.7 mg/l (Humphrey et al. 2016). The seep chloride concentrations were more similar to wastewater than background stream chloride concentrations in a nearby forested watershed (9.69 mg/l). Similarly, median specific conductance measured at seep 1 and 2 was 520 μs and 242 μs , respectively, and elevated relative to median background levels in a nearby forested stream (108 μs) (Iverson et al. 2018).

$\delta^{15}\text{N}_{\text{-nitrate}}$ and $\delta^{18}\text{O}_{\text{-nitrate}}$ samples were collected from seep 1 and seep 2. For seep 2, values for $\delta^{15}\text{N}_{\text{-nitrate}}$ and $\delta^{18}\text{O}_{\text{-nitrate}}$ were 23.6‰ and 11.7‰, respectively, which falls within the manure and septic effluent range of 8 to 23‰ and 0 to 14‰ for $\delta^{15}\text{N}_{\text{-nitrate}}$ and $\delta^{18}\text{O}_{\text{-nitrate}}$, respectively (Kendall and McDonnell 1998; Silva et al. 2002). However, seep 1 values were lower at 5.5‰ and 1.9‰ for $\delta^{15}\text{N}_{\text{-nitrate}}$ and

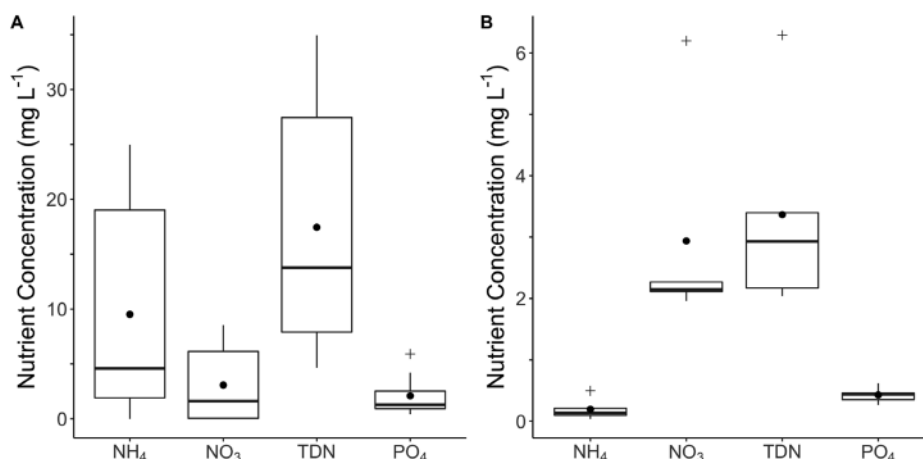


Figure 6. Nutrient concentration data for two residential seep sites along Lick Creek, Falls Lake watershed, NC. Boxplots of nitrogen [ammonium (NH₄-N), nitrate (NO₃-N), total dissolved nitrogen (TDN)] and phosphate (PO₄-P) concentrations for groundwater seep 1 (a.) and seep 2 (b.). Filled circles (•) denote mean values, while pluses (+) denote outliers.

$\delta^{18}\text{O}_{\text{-nitrate}}$, respectively, which fell slightly outside the wastewater range for $\delta^{15}\text{N}_{\text{-nitrate}}$ (Kendall and McDonnell 1998; Silva et al. 2002). That sample was collected during storm conditions and it is possible that organic, fertilizer, and/or wastewater sources of nitrate were mixed during storm events. These values are only based on one isotopic sample and more sampling would help confirm results. These watersheds contain mostly (> 90%) forest and residential land uses (Iverson et al. 2018), thus agricultural fertilizer is not a likely source of nitrogen. This example showed that seeps may act as conveyances for nutrients from wastewater, lawn fertilizer, and other anthropogenic sources in residential settings.

Seeps may also be affected by legacies

of industrial chemical disposal and leaking underground petroleum tanks. Leaking petroleum can lead to BTEX (benzene, toluene, ethylbenzene, and xylene) compound transport to streams via groundwater. At an urban Coastal Plain site, a seep was monitored that was highly impacted by two or more leaking underground storage tanks. The tanks were leaking petroleum prior to the 1980s (Blackmon 2017; Humphrey et al. 2018). Benzene was upwelling with groundwater at the seep and influencing water and soil/air quality (S&ME, Inc. 2011) along Town Creek (Greenville, NC). Soil samples collected away from the seep had lower emissions of benzene in comparison to at the seep and when compared to an unimpaired seep draining the other side of the stream. The

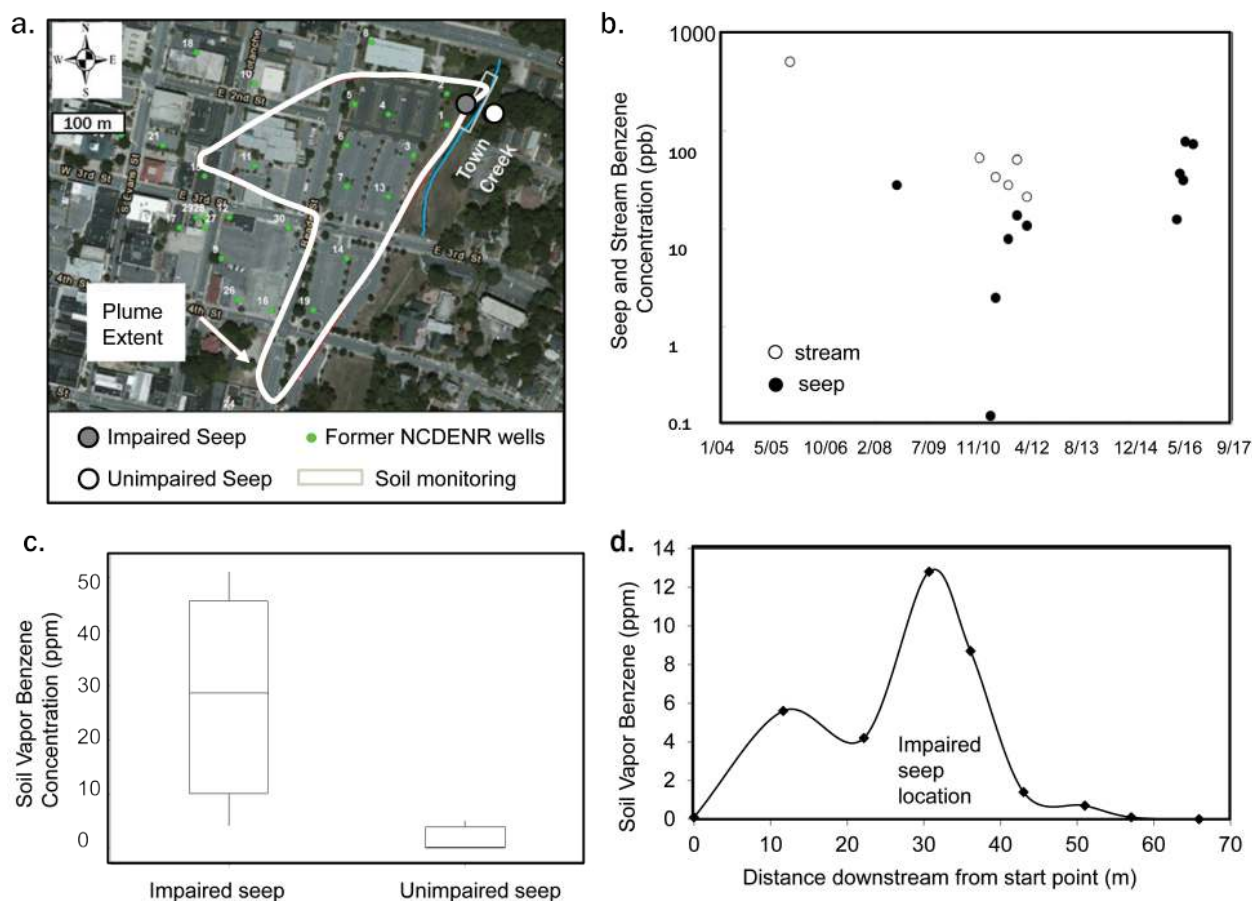


Figure 7. At an urban Coastal Plain site (Town Creek, Greenville, NC), a seep was monitored downgradient of at least two leaking underground petroleum storage tanks. (a.) the plume extent was approximated from an earlier study (NCDENR 1990). (b.) Stream and seep data from earlier studies indicated that benzene from the seep was affecting stream water quality (data source: S and ME 2011 and Humphrey et al. 2018). (c.) The impaired seep showed elevated soil benzene concentrations in contrast to a seep on the opposite side of the stream (sampled on four dates from 4/5/16 to 6/29/16, Blackmon 2017). (d.) Upstream and downstream of the impaired seep the soil benzene concentrations declined (longitudinal survey on 5/25/15).

petroleum-impaired seep was a pathway for benzene exposure via water and air (Figure 7). These data also showed that seep disturbances may originate at long distances from the actual seep, the leaking gas tanks that were the likely contaminant source were approximately 0.4 km or 0.25 miles upgradient of the seep (NCDENR 1990).

Overall, these examples showed that seeps can integrate the effects of upstream land-use disturbances and human activities on groundwater. When undisturbed and surrounded by forest canopy, seeps may be more likely to behave as contaminant sinks (particularly for nutrients), whereas when seep catchments or seeps are disturbed by a variety of human activities, seeps can serve as a conveyance to deliver a range of contaminants to the stream. The seeps that received elevated nutrient concentrations were associated with recent wastewater management activities and best management practices might reduce those inputs. In contrast, the urban seep contamination was associated with a legacy of leaking petroleum tanks; resolving that situation would require a more intensive groundwater remediation effort in the upgradient surficial aquifer. Understanding the nature of the groundwater flowpaths to seeps and associated contaminant sources can improve remedial efforts. In the peer-reviewed literature, there is a wide range of seep behavior documented. Next, the discussion will focus on previous studies on the topic of seep water quality and the factors that lead to seeps behaving as contaminant sinks or sources.

Seeps as Contaminant Sinks

Numerous studies suggest that seeps in forested catchments can act as nutrient sinks (Fisher and Acreman 2004; O'Driscoll and DeWalle 2010; Kaur et al. 2016), but seasonal variability in discharge and reduced biological activity during cooler months can lead to seeps behaving as nitrogen sources during cooler or wetter periods (O'Driscoll and DeWalle 2010; Shabaga and Hill 2010). Surface water – groundwater interactions, discharge, soil type, organic matter, moisture conditions, and vegetation all vary along seeps and their variability can influence the dominant mechanisms of nitrogen transformation and

retention along seeps. Additionally, the seasonal and event variability of runoff, temperature, and soil moisture can lead to temporal variability in nitrogen attenuation. It has also been shown that the availability of phosphorus can influence the degree of nitrogen attenuation (Gibson et al. 2015).

In two forested catchments in VT, Kaur et al. (2016) found that seeps had gross nitrification rates approximately three times higher than those for upland soils and nitrate consumption was eight times higher in seep soils vs. upland soils. Overall, their work showed that seep soils can be hotspots for nitrification and denitrification, and the balance can determine if seeps behave as nitrogen sources or sinks. In Baldwin Creek, PA (as previously mentioned), nitrate concentrations in groundwater along a series of seeps declined suggesting that the forested seeps generally acted as nitrate sinks (O'Driscoll and DeWalle 2010). In a tracer study in New Zealand, Rutherford and Nguyen (2004) injected nitrate along seeps (also referred to as riparian swales) to quantify seep nitrate attenuation. They observed a 24% decline in nitrate concentration along a 1.5 m flowpath, indicating that seeps could act as nitrate sinks. Their work suggested that significant nitrate reductions downseep could be achieved when subsurface residence times were a day or longer. However, downseep nitrate concentration bypasses (or increases) likely occur when the surface flowpath dominates the seep discharge (Rutherford and Nguyen 2004). These seep bypasses can play an important role in influencing whether a seep is a nutrient source or sink over time.

Seep bypass can be defined as an occurrence when nitrogen concentrations of upwelling seep water remain constant or increase downseep (Gold et al. 2001; Rosenblatt et al. 2001). There is a portion of seep flow, predominantly surface, that is quickly transported downgradient. This rapid surface flow may not undergo substantial biotic uptake or denitrification (Gold et al. 2001). The mechanisms that can lead to reduced nitrogen attenuation during elevated seep discharge periods include a reduction in: particle settling, sediment–water contact times, nitrogen retention in sediment and/or vegetation (Seitzinger et al. 2002; Shabaga and Hill 2010), and increased flushing of nitrate from soils (Ocampo et al. 2006).

Seeps as Contaminant Sources

A wide variety of studies have documented seeps acting as contaminant sources to rivers. Seeps and/or springs have been documented to transport nutrients (Williams et al. 2015), pesticides (Van Stempvoort et al. 2016), wastewater and pharmaceuticals (Humphrey et al. 2013; Spoelstra et al. 2017), coal combustion products (Harkness et al. 2016), petroleum-related compounds (Humphrey et al. 2018), trichloroethylene (TCE) (Chapman et al. 2007), road salts (Foos 2003), landfill leachate (Atekwana and Krishnamurthy 2004), bacteria (Fisher et al. 2000; Baker et al. 2011), *Giardia* (Rose et al. 1991), and acid mine drainage (Brake et al. 2001; Johnston et al. 2017) to nearby streams and wetlands. Generally, these elevated seep contaminant inputs are related to land-use and human activities within the seep catchment that are associated with fertilizer and manure, pesticide, coal, oil, and gas activities, waste management, wastewater, and livestock, pet, and wildlife waste. However, in some cases forested catchments have also shown elevated nutrient and solute concentrations at seeps (Likens and Buso 2006; Zimmer et al. 2013). One potential explanation is that due to lag times between groundwater recharge and seep or spring discharge, summer base flow can originate from previous dormant seasons when nitrate in recharge is generally elevated (Burns et al. 1998).

Studies revealing seeps as nutrient sources have mainly been conducted in agricultural watersheds (Shabaga and Hill 2010; Williams et al. 2014, 2015, 2016) and are associated with upgradient fertilizer and manure applications. The most detailed work on seeps as nitrogen sources in agricultural watersheds has been performed at Mahantango Creek watershed in central PA by the USDA-ARS. In this agricultural watershed, Williams et al. (2014, 2015, 2016) performed a series of seep studies focused on improving the understanding of agricultural nitrogen transport to streams. In general their work showed that seeps can provide preferential flowpaths that convey nutrients from agricultural fields to streams and can lead to elevated nutrient transport to streams (Williams et al. 2014, 2015, 2016). They recommended to prioritize seep areas for enhanced

management in agricultural catchments because they can be nutrient hotspots (Williams et al. 2014). In addition, their work indicated the importance of time-varying stream-groundwater interactions and the influence of seep presence on agricultural nutrient delivery to streams (Williams et al. 2016). In related work, a USGS study across a range of five agricultural watersheds (Tesoriero et al. 2009) looked at base flow and nutrient pathways to streams. They concluded nitrate transport has a high degree of spatiotemporal variability, and preferential flowpaths such as seeps can play a large role in nitrate transport to streams. These studies indicate the importance of detailed riparian groundwater and seep measurements to understand nitrogen delivery to streams.

The type of seep flow can also influence nutrient transport in agricultural watersheds. In Ontario, Canada, Shabaga and Hill (2010) found that the seep flow to the channel played a large role in nitrogen attenuation. They developed a conceptual model of the seep end-members of rivulet-pipe flow and diffuse surface flow. Overall, they found that nitrate removal along rivulet-pipe networks was inefficient, but when waters flowed diffusely through the riparian zone large nitrate declines could occur, particularly in the summer months.

Seeps in agricultural watersheds can also transport pesticides to streams. In a study in the Nottawasaga River Basin, ON, Canada, Van Stempvoort et al. (2016) studied glyphosate, a widely used pesticide that is expected to sorb to soil particles (Borggaard and Gimsing 2008). However, leaching may occur in settings where preferential flowpaths exist, such as groundwater seeps. They collected 153 samples of seep groundwater along the Nottawasaga River and found that 7.8% of those seep samples had detectable concentrations of glyphosate, with most detections occurring in the spring and summer. Shorter term seeps were more likely to have glyphosate since it is more likely to be transported along shorter residence time flowpaths where attenuation is minimal, and those ephemeral seeps may only be active during wetter periods. Overall, the results suggested that glyphosate could be transported from field application sites via groundwater flowpaths to seeps, and seeps that flow less regularly may drain shallower groundwater that is more likely to be

contaminated by surface activities. Tang et al. (2012) looked more broadly at general pesticide transport mechanisms from agricultural fields and found that saturation excess runoff generation mechanisms could transport pesticides from field to stream. Upwelling groundwater at seeps flowing to the stream can serve as a transport mechanism. Saturated areas related to toe slopes where seeps may occur are generally more vulnerable to pesticide loss via overland flow than the rest of the catchment because of greater runoff generation in these areas (Tang et al. 2012).

In addition to nutrients and pesticides, agricultural watersheds have also been shown to transport bacteria to seeps. Livestock agriculture can be one of the major causes of bacterial contamination of surface and ground waters (Jamieson et al. 2002). In their review of fecal bacteria transport in agricultural soils and subsurface drainage, they documented the main factors influencing fecal bacteria survival, such as: soil type and moisture conditions, temperature, pH, rate of manure inputs, nutrient status, and microbial competition. Bacterial survival and transport is enhanced in cool conditions and when macropore flows occur, since the physical filtration through micropores is the main factor controlling bacteria mobility. Their work suggests that seep transport of bacteria from livestock operations may occur if seep flow is fed through macropores. Because livestock are generally drawn to water and shade during warmer months, they can often graze in riparian areas where seeps are more common and impacts can include soil compaction/erosion, devegetation, and water quality degradation (Agouridis et al. 2005). Approaches to protect riparian seep areas include riparian fencing, off-stream water sources, stream crossings, riparian buffers, and grazing management (Agouridis et al. 2005; Swanson et al. 2015). Although relationships with riparian pasture cover and increased *E. coli* have been documented (Scott et al. 2017), limited studies have evaluated seep *E. coli* transport in pasture lands (Collins and Rutherford 2004). Collins and Rutherford (2004) developed a model to simulate *E. coli* and used field measurements to illustrate elevated *E. coli* inputs from seepage areas accessed by cattle (10^4 to 10^8 MPN) during base flow and rain events. Although there are

a range of studies on domesticated livestock impacts to riparian areas (Agouridis et al. 2005), less information is available on impacts by feral livestock. However, studies have shown impacts by feral hogs to seeps (FL) (Engeman et al. 2007) and feral horses to riparian areas (NV) (Beever and Brussard 2000).

In addition to bacteria, protozoa (*Cryptosporidium*) have been found to discharge at springs (Rose et al. 1991) and the authors suggested based on their results that upwelling groundwater that contains *Cryptosporidium* can present a risk of transmission of infections if the water is not treated. This and other studies suggest there is the possibility of spreading infections by groundwater seeps. For example, in Townsville, Australia, researchers found that groundwater seeps contained a bacterium linked to a fatal type of pneumonia (melioidosis) (Baker et al. 2011). They concluded that groundwater seeps may facilitate exposure to the bacterium and this may have contributed to the clustering of melioidosis in the area. This study revealed that seep exposure data may provide public health officials with guidance to implement management actions.

Another common source of contaminants to streams is wastewater (Humphrey et al. 2015), which can contain elevated concentrations of nutrients, bacteria, and pharmaceuticals. In rural settings where decentralized wastewater treatment results in wastewater inputs to the surficial aquifer, wastewater plumes that intersect and upwell at groundwater seeps may serve as a source of contaminants to seeps (Figures 5 and 6). Wastewater-impacted groundwater and its transport to seeps can deliver pharmaceutical and personal care products to adjacent surface waters. In a recent study in the Nottawasaga River Basin, ON, Canada, Spoelstra et al. (2017) evaluated groundwater wells and seeps along the banks of the river to evaluate if wastewater from local septic systems was discharging at the seeps or present in well water. They utilized four common artificial sweeteners as tracers and found those tracers in approximately 30% of the samples. For the seeps studied, 2 - 4.7% of the seeps had a septic effluent contribution of at least 1%. This study showed that pharmaceutical and personal care products associated with onsite wastewater effluent can be

transported to surface waters via groundwater seeps (Spoelstra et al. 2017). In a similar effort in the Puget Sound watershed in WA, James et al. (2016) sampled approximately 20 seeps draining to the sound. They sampled seeps for a suite of emerging contaminants (including caffeine, ibuprofen, sucralose, atrazine, and others) and fecal bacteria. They found that the presence of sucralose in seep water could indicate a contribution of wastewater to the seep. At sites with known or presumed impacts by septic systems they found high detection frequencies of sucralose, acetaminophen, caffeine, ensulizole, and ibuprofen and indicated that these compounds could serve as indicators of wastewater and potential bacterial contamination. It was suggested to use more than one tracer due to the variability of septic inputs (James et al. 2016).

In urban and industrial areas, a range of organic chemicals have been found to discharge from seeps, particularly petroleum-related compounds (Humphrey et al. 2018), TCE (Chapman et al. 2007), and landfill leachate (Atekwana and Krishnamurthy 2004). Leaking underground petroleum tanks have led to BTEX compounds being transported to streams via seeps (Humphrey et al. 2018) (Figure 7). In addition, industrial solvent plumes have been shown to contaminate seeps. A detailed field study of a TCE plume at a former industrial facility in CT showed that TCE was discharging to the surface via seeps. TCE at seeps and in shallow groundwater may experience volatile organic carbon mass loss to the atmosphere, a mechanism that might also contribute to plume attenuation. TCE plume attenuation was enhanced prior to discharge to the river downgradient because of groundwater discharge to a pond and smaller streams, where some attenuation could be attributed to water-air exchange (Chapman et al. 2007).

Landfills have also been shown to contribute contaminants to seeps. Atekwana and Krishnamurthy (2004) investigated groundwater seepage to a stream adjacent to a landfill in Kalamazoo, MI. They used stable carbon isotopes (^{13}C) as a tracer for landfill leachate. Groundwater from the stream bank adjacent to the landfill and groundwater seepage into the stream showed evidence of dissolved inorganic carbon that was enriched in ^{13}C , associated with landfill leachate. This study suggested that the stream

was likely affected by landfill leachate delivered via groundwater flowpaths. In another study in North Sea Harbor, NY, Gobler and Boneillo (2003) found groundwater seepage chemistry indicative of landfill leachate downgradient from an unlined municipal landfill. Groundwater seepage had elevated concentrations of ammonium, dissolved organic carbon, and low dissolved oxygen. The N-rich groundwater contributed approximately 80% of the inorganic nitrogen to the embayment. They concluded that landfill leachate upwelling at groundwater seepage areas could contribute to eutrophication (Gobler and Boneillo 2003).

Oil, gas, and coal production and use have led to seep contamination. Although naturally occurring petroleum and natural gas seeps occur in a variety of sedimentary basins (Donovan 1974; Philp and Crisp 1982; Schimmelman et al. 2018), in some cases the development activity can lead to groundwater contamination. Recent work by Woda et al. (2018) revealed that in Lycoming County, PA, leaking gas wells associated with shale gas development led to elevated methane concentrations in groundwater seeps, and they suggested that methane influx to the aquifer could lead to mobilization of groundwater contaminants such as arsenic. These and other studies suggest that greater monitoring of groundwater wells and seeps in areas of unconventional natural gas extraction may be called for (Jackson et al. 2013).

A recent study by Harkness et al. (2016) focused on evaluating the leakage from coal ash ponds in the southeastern U.S. They evaluated nine seeps adjacent to coal ash lagoons and found elevated concentrations of boron, strontium, and isotopic tracers indicative of coal combustion residuals. Overall, the seep data collected indicated that leaking coal ash ponds were impacting surface water quality. In a recent study, Brake et al. (2001) studied West Little Sugar Creek (IN) and the effects of acid mine reclamation associated with a coal mine. They found acidic seeps formed in the acid mine drainage reclamation area. The acidic effluent had low pH and several contaminants that exceeded state/or national water quality standards. They concluded that even after reclamation, the seeps and other inputs of acid mine drainage resulted in impaired aquatic ecology. Johnston et al. (2017) studied acid mine drainage from a gold

and silver mine to a headwater stream in Empire, CO. They found that pH was inversely related to seep specific conductivity. Electrical resistivity imaging helped to identify seepage areas that were contributing acid mine drainage to the stream and these approaches may help to target remediation efforts. Another study in SC showed that seeps from a reject coal pile were responsible for creating high salinity, low pH conditions in adjacent soils. The low pH and high salinity resulted in vegetation dieback and limited the revegetation of the seep area (Carlson and Carlson 1994).

Other occurrences of saline seeps have been found to be naturally occurring as a result of groundwater upwelling from buried salt deposits (e.g., Manitoba, Canada; Grasby and Londry 2007) or caused by anthropogenic activities. Anthropogenic activities that can lead to elevated salinity at seeps include oil and gas activity, agricultural irrigation in arid regions, and road salt. In a study of 37 springs and seeps in Cuyahoga Falls, OH, it was found that road salt was the primary contributor to increased total dissolved solids at the springs and seeps (Foos 2003). In arid regions, salinity can be concentrated at seeps. For example, in Australia, sandplain seeps occur where salts from groundwater discharge are concentrated at the surface due to evaporation (George 1991). The salinity can affect agricultural use and vegetation growth in seep areas and a range of reclamation efforts have been attempted to reduce associated soil salinization, including interception drains and eucalyptus trees (George 1991). Overall, a wide range of studies have shown that groundwater seeps can be contaminated by a variety of agricultural, industrial, and urban contaminant sources. Recent legal cases have focused on water quality of seeps, springs, and seepage zones along navigable rivers because of their ability to transport contaminants to navigable surface waters regulated under jurisdiction of the CWA.

Emerging Legal and Policy Issues – Seeps, Groundwater, and the Clean Water Act

Since the turn of the century, numerous court cases (Table 1) have suggested that seeps with measureable impacts on adjacent surface water

quality may fall under CWA jurisdiction if the contaminated groundwater that discharges at a spring or seep or through stream channel sediments is hydrologically connected to navigable waters. Numerous recent articles on the legal aspects of contaminated groundwater inputs to navigable streams have focused on recent case law and the applicability of the CWA to contaminated groundwater that is transported to navigable waters (Kvien 2015; Juilfs 2016; Smith 2016; William and Endres 2017). Although the CWA primarily regulates surface water quality (specifically point source contaminant inputs to navigable waters), courts have not ruled consistently on how to characterize the CWA's role in protecting water quality of groundwater and the relationship between groundwater and surface water (Kvien 2015; William and Endres 2017). There is an important legal question as to whether the CWA covers discharges of pollutants to groundwater that is hydrologically connected to navigable waters (Kvien 2015).

From the CWA perspective, the Environmental Protection Agency (EPA) defines a point source as “any discernible, confined and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling stock, concentrated animal feeding operation, or vessel or other floating craft, from which pollutants are or may be discharged” (US EPA 2018a). The distinction between point source inputs from discrete conveyances and the more diffuse subsurface transport of contaminant inputs via groundwater flowpaths becomes important in cases of contaminated groundwater seeps and springs and their function of discharging contaminants to navigable waterways.

Kvien (2015) and William and Endres (2017) provided reviews of some recent legal cases that have considered how contaminated groundwater has recently been addressed under the CWA, and the range of opinions. Notable recent cases include the Northern California River Watch v. City of Healdsburg; the Yadkin Riverkeeper v. Duke Energy Carolinas LLC, and the Hawai'i Wildlife Fund v. County of Maui (Kvien 2015; William and Endres 2017) (Table 1). These cases showed that wastewater and coal ash contaminants that were stored or injected and had hydrologic connections

Table 1. Examples of recent legal cases that considered contaminated groundwater with hydrological connections to navigable surface waters to fall under Clean Water Act (CWA) jurisdiction (modified from Kvien 2015; William and Endres 2017).

Case (Year)	Basis
Idaho Rural Council v. Bosma (2001)	Unlined wastewater ponds leached contaminants into groundwater (GW) hydrologically connected to springs that were hydrologically connected to Clover Creek.
Northern California River Watch v. City of Healdsburg (2004)	Sewage from the city was discharged into a pond which was hydrologically connected to the Russian River.
Waterkeeper Alliance, Inc. v. US EPA (2005)	Challenged that EPA's Concentrated Animal Feeding Operations (CAFO) rule was unjustified because EPA does not have jurisdiction over GW. EPA agreed it can have jurisdiction when GW connects to navigable waters.
Hernandez v. Esso Standard Oil Co. (2009)	Leaky USTs leached gasoline to GW seeps hydrologically connected to a nearby stream.
Association Concerned Over Resources and Nature, Inc. v. Tennessee Aluminum Processors, Inc.(2011)	A dump polluted GW with Al, ammonium, Cl, Pb, and Mn. Contaminated GW eventually drained to a tributary of Quality Creek.
Raritan Baykeeper, Inc. v. NL Industries, Inc. (2013)	GW discharging into the Raritan River was found to contain elevated As, Cu, Pb, Ni, and Zn.
Hawaii Wildlife Fund v. County of Maui (2014)	Wastewater injection wells were shown to be connected to coastal waters via GW transport established by tracer dye study.
Yadkin Riverkeeper, Inc. v. Duke Energy Carolinas, LLC (2015)	Coal ash storage in unlined lagoons that were hydrologically connected to the nearby Yadkin River were considered point sources under the CWA.

to the nearby surface water should be considered as point source inputs under the CWA. In these cases, when groundwater flowpaths functioned similarly to discrete conveyances of point source pollutants, numerous courts ruled that those contaminated groundwater inputs should fall under the CWA (William and Endres 2017). Although numerous recent cases have shown that the CWA can cover groundwater contaminant inputs to navigable streams (Table 1), other cases have revealed differing opinions as to CWA coverage of groundwater contaminant transport to streams (Kvien 2015; William and Endres 2017). Most recently, in February 2019 the U.S. Supreme Court agreed to hear an appeal of the Hawai'i Wildlife Fund v. County of Maui case (Savage 2019).

In the future, related cases will come forward and the US EPA (US EPA 2018b) will likely clarify their position on how groundwater-transported

pollution inputs may be subject to CWA regulation. An improved scientific understanding of seep-stream interactions can help provide guidance for legal and regulatory purposes. There are a range of hydrological questions that can help to better characterize the legal aspects of seeps and their influence on stream water quality (Kvien 2015). The questions can generally be grouped into two focus areas: the nature of the hydrologic connection between groundwater and navigable streams, and the nature of the contaminant transport and water quality effects (Figure 8).

Conclusions and Management Implications

A growing number of scientific and legal studies have focused on seep water quality and seep effects on stream water quality. In minimally

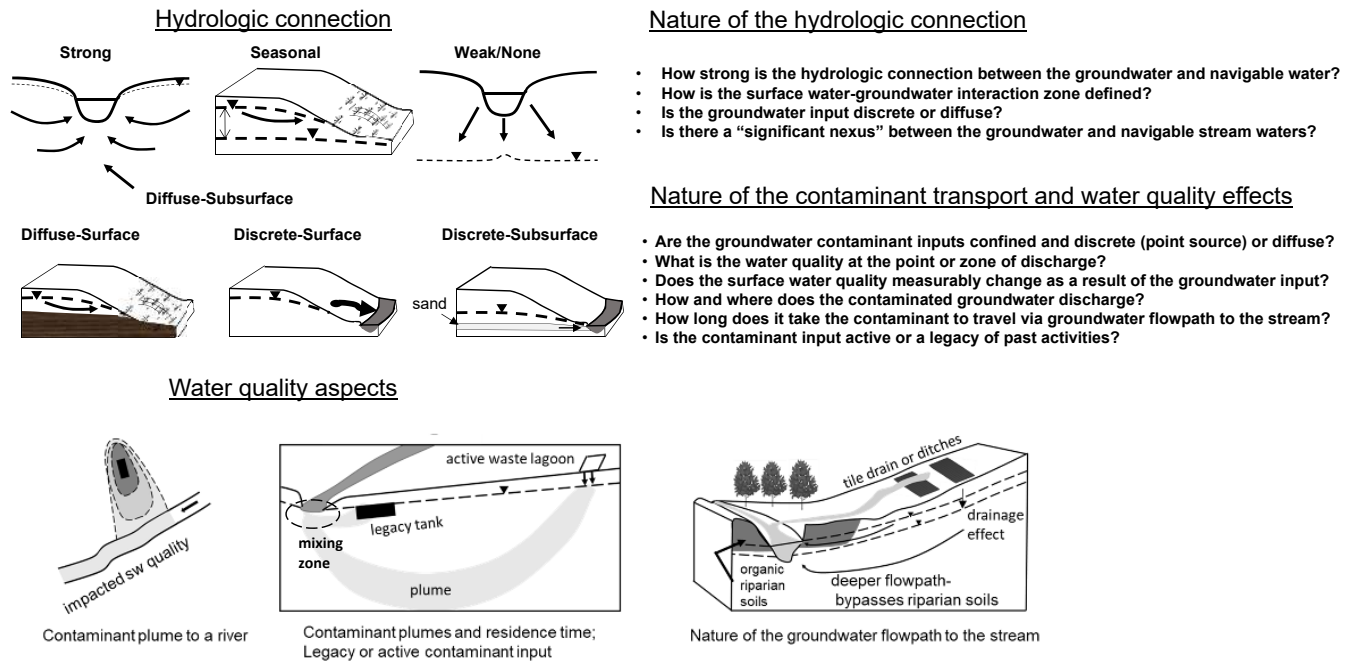


Figure 8. Hydrological questions that can help provide guidance for contaminated seeps and Clean Water Act jurisdiction. The questions can generally be grouped into two focus areas: the nature of the hydrologic connection between groundwater and navigable streams, and the nature of the contaminant transport and water quality (water quality figures modified from Heath 1983 and Puckett 2004).

disturbed forest catchments, seep attenuation of nutrients may improve downstream water quality. A wide range of studies were found that showed when human activities occur in the drainage area to the seep, seeps may act as conveyances for a number of inorganic, organic, and microbial contaminants associated with urban, wastewater, fossil fuel, and agricultural practices. In the worst-case scenarios, seeps can act as vectors for water-borne diseases and carcinogens. Although seep water quality was documented in a wide range of studies, less information was available on whether contaminated seeps measurably affected stream water quality downstream. Numerous upstream and near-seep activities may pose threats to seep flows and seep water quality including: upstream or near-seep water withdrawals, contaminant plumes, flow diversion or drainage of seep areas, and land disturbance of seep areas. Depending on the nature of groundwater flowpaths feeding the seeps, seep disturbances can be caused by land-use activities that occur far away from the immediate seep area, therefore delineating and understanding the temporal and spatial variability of the hydrological catchment area of the seep can be an important

first step towards protecting the seep. Since seeps can deliver contaminants to streams, management efforts to protect water quality should consider seep setbacks to protect the upstream area draining to seeps (seep catchments) and near-seep zones.

As it has been shown that greater contaminant attenuation can occur for diffuse flow versus rivulet-pipe flow conditions, it may be possible in some settings to reduce the seep contaminant transport to the stream by using level spreaders (Winston et al. 2011) or other approaches to reduce rivulet-pipe flow conditions and enhance diffuse flow through riparian soils and vegetation. In cases where the groundwater contamination is fairly shallow, phytoremediation (Nichols et al. 2014) and forested riparian buffers (Mayer et al. 2007) may also protect the seep area and help to reduce the contaminants surfacing at the seep and flowing to adjacent streams.

More seep focused studies are needed and it is important to collect data on some of their basic properties, including the nature of their source (helocrene, limnocrene, rheocrene); discharge magnitude; water temperature; total dissolved solids; and persistence (Springer and Stevens 2009;

Williams 2016). The frequency and duration of seep flow and the diurnal and seasonal variability of seep water temperature may help distinguish seeps that have deeper, longer-term groundwater flowpaths from ephemeral seeps fed by shorter-term groundwater flowpaths. Those with shallower flowpaths may be more sensitive to local activities and climate change. An improved understanding of the nature of groundwater flowpaths to the seep may help characterize those that are vulnerable to impairment.

Although groundwater inputs often have a large influence on base flow water quality, groundwater data are not frequently included in surface water quality studies. Groundwater seeps provide an alternate low-cost method of monitoring groundwater quality when drilling monitoring wells is not practical (e.g., in mountainous terrain or wetlands) or within the budgetary constraints of a project (Soulsby et al. 2007). Additionally, seeps can serve as valuable educational tools as these are sites where groundwater is visible. Comprehensive seep and spring location information is available in a limited number of studies (e.g., Junghans et al. 2016), but in most regions seeps are not thoroughly mapped. Without watershed seep maps and baseline seep water quality and flow data, it will be challenging to understand changing conditions. Seep inventory, discharge, and water quality projects can provide a basis to evaluate shifting water quality and flow conditions over time. Several states such as Minnesota (Minnesota Spring Inventory 2019) and Kentucky (KGDR 2019) have spring mapping programs; similar efforts for seeps (including citizen science efforts) could be fruitful. The Springs Stewardship Institute has recently begun developing an online database and Springs Online program to help users locate and document springs and seeps (<http://springstewardshipinstitute.org/>). Because many seeps occur as wetlands, in some cases they may be mapped in the National Wetlands Inventory or other databases, such as the National Hydrography Database Plus (USEPA/USGS 2005). Field mapping might be improved using recent technologies; for example, thermal imaging may help to detect seeps (Roper et al. 2014).

From a legal and regulatory perspective, there are potentially a large number of contaminated

seep sites where more research is needed to determine the hydrologic connection between the contaminated groundwater and the navigable surface water and evaluate if the groundwater inputs affect the surface water quality. These determinations can often be made with a range of field and modeling approaches including: nested piezometers, aquifer sampling and testing, water temperature and specific conductance logging, thermal imaging, geophysical surveying (ground penetrating radar, electrical resistivity, electromagnetic induction, seismic), seepage runs, nested water quality sampling, tracer studies, residence time and age dating, and surface water-groundwater modeling.

Future work on seep-stream interactions can improve understanding of the controls on: discrete vs. diffuse discharge; surface water/groundwater mixing zones; the degree of hydrologic connections; setback distances for seep protection; nature of groundwater discharge seeping into surface waters; water quality of groundwater discharge at the seep emergence point and at the point where seeps discharge to the navigable stream; magnitude and variability of groundwater residence time; seasonality of groundwater quality and discharge; influence of forested riparian buffers and hyporheic zones; and seep effects on stream water quality. Detailed seep water quality studies across a range of hydrogeological, meteorological, and land-use conditions can help improve the identification and characterization of seeps likely to convey contaminants to streams and affect stream water quality. In addition, improved understanding of seep water quality and disturbances can help in the development and testing of spring/seep ecosystem models (Springer et al. 2008; Stevens 2008; Lehosmaa et al. 2018). More work is needed to understand regional relationships between spring/seep ecological diversity and water quality (Stevens 2008).

Acknowledgments

This work was funded by the US EPA, NC Water Resources Research Institute, Pennsylvania State University, and East Carolina University. We thank Jim Watson, the ECU Environmental Research Lab, Jen Eismeier, Caitlin Skibiell, Matt Smith, Jeremy Robbins, Mark Akland, Sarah Hardison, and Jamil Blackmon for

field and water quality support. Thanks to Craven Co. and private landowners for site access to seeps. We thank Tao Wen at Pennsylvania State University for providing recent information on natural gas development and the effects on groundwater seeps.

Author Bio and Contact Information

DR. MICHAEL O'DRISCOLL (corresponding author) is a hydrologist and has been a faculty member at East Carolina University (ECU) since 2004 and an adjunct Associate Professor at Duke University since 2018. Currently he is an Associate Professor in the Department of Coastal Studies. He has earned graduate degrees in Geology, Environmental Pollution Control, and Forest Resources (Penn State University). He teaches a variety of courses in hydrology, hydrogeology, water pollution, earth and environmental sciences. His research focuses on utilizing tracers and other hydrogeological, geochemical, and geophysical techniques to develop insights into the geological controls and land-use effects on surface water-groundwater interactions and contaminant transport, particularly in nutrient-sensitive Coastal Plain and Piedmont watersheds. He may be contacted at odriscollm@ecu.edu or by mail at Department of Coastal Studies, East Carolina University, 204 Graham Building, Greenville, NC 27858.

DR. DAVID DEWALLE is a retired faculty member at Penn State University who formerly taught watershed management, snow hydrology, and forest micrometeorology courses and conducted research on a variety of environmental topics especially impacts of atmospheric deposition. He was educated in forestry and forest hydrology at the University of Missouri (BS and MS) and watershed management at Colorado State University (Ph.D.). At retirement he served as Associate Director of Penn State Institutes of the Environment and as Director of the Pennsylvania Water Resources Research Center.

DR. CHARLES HUMPHREY JR. is a NC Licensed Soil Scientist and Registered Environmental Health Specialist. He earned his BS (Ecosystems Assessment) and MS degrees (Soil Science) from North Carolina State University, and his Ph.D. (Coastal Resources Management) from East Carolina University (ECU). Dr. Humphrey is an Associate Professor of Environmental Health at ECU, where he conducts research on various water quality issues and teaches undergraduate and graduate classes on water and wastewater treatment. Prior to joining the faculty at ECU, he worked for seven years as an Environmental Agent with NC Cooperative Extension, and three years as an Environmental Health Specialist.

DR. GUY IVERSON recently completed his Ph.D. in Coastal Resources Management at East Carolina University and will begin as a faculty member in the Environmental Health Sciences Program at East Carolina University in August 2019. During his graduate studies, he has conducted research focusing on nutrient cycling in groundwater and surface water in nutrient-sensitive, water-supply watersheds in North Carolina's Coastal Plain and Piedmont.

References

- Agouridis, C., S. Workman, R. Warner, and G. Jennings. 2005. Livestock grazing management impacts on stream water quality: A review. *Journal of the American Water Resources Association* 41(3): 591-606.
- Alfaro, C. and M. Wallace. 1994. Origin and classification of springs and historical review with current applications. *Environmental Geology* 24(2): 112-124.
- Atekwana, E. and R. Krishnamurthy. 2004. Investigating landfill-impacted groundwater seepage into headwater streams using stable carbon isotopes. *Hydrological Processes* 18: 1915-1926.
- Baker, A., D. Tahani, C. Gardiner, K. Bristow, A. Greenhill, and J. Warner. 2011. Groundwater seeps facilitate exposure to Burkholderia pseudomallei. *Applied Environmental Microbiology* 77(20): 7243-7246.
- Beck, H., A. van Dijk, D. Miralles, R. de Jeu, L. Bruijnzeel, T. McVicar, and J. Schellekens. 2013. Global patterns in base flow index and recession based on streamflow observations from 3394 catchments. *Water Resources Research* 49: 7843-7863.
- Beever, E. and P. Brussard. 2000. Examining ecological consequences of feral horse grazing using exclosures. *Western North American Naturalist* 60(3): 236-254.
- Blackmon, J. 2017. An evaluation of environmental health threats associated with stream discharge from Town Creek in Greenville, North Carolina. Masters Thesis in Environmental Health, East Carolina University, Department of Health Education and Promotion, Greenville, NC. Available at: <http://thescholarship.ecu.edu/bitstream/handle/10342/6138/BLACKMON-MASTERTHESIS-2017.pdf?sequence=1&isAllowed=y>. Accessed April 19, 2019.
- Borggaard, O. and A. Gimsing. 2008. Fate of glyphosate in soil and the possibility of leaching to groundwater

- and surface waters: A review. *Pest Management Science* 64: 441-456.
- Boulton, A. and P. Hancock. 2006. Rivers as groundwater-dependent ecosystems: A review of degrees of dependency, riverine processes and management implications. *Australian Journal of Botany* 54: 133-144.
- Brake, S., K. Connors, and S. Romberger. 2001. A river runs through it: Impact of acid mine drainage on the geochemistry of West Little Sugar Creek pre- and post-reclamation at the Green Valley coal mine, Indiana, USA. *Environmental Geology* 40: 1471-1481.
- Brinson, M.M. 1993. *A Hydrogeomorphic Classification for Wetlands*. U.S. Army Corps of Engineers, Waterways Experiment Station, Vicksburg, MS, USA. Technical Report WRP-DE-4. Available at: <https://wetlands.el.erdc.dren.mil/pdfs/wrpde4.pdf#view=fit&pagemode=none>. Accessed April 19, 2019.
- Burns, D.A., P.S. Murdoch, G.B. Lawrence, and R.L. Michel. 1998. Effect of ground water springs on NO₃⁻ concentration during summer in Catskill Mountain streams. *Water Resources Research* 34: 1987-1996.
- Carlson, C.L. and C.A. Carlson. 1994. Impacts of coal pile leachate on a forested wetland in South Carolina. *Water, Air, and Soil Pollution* 72(1): 89-109.
- Chapman, S., B. Parker, J. Cherry, R. Aravena, and D. Hunkeler. 2007. Groundwater-surface water interaction and its role on TCE groundwater plume attenuation. *Journal of Contaminant Hydrology* 91(3-4): 203-232.
- City of Durham. 2012. Timeline of Water Quality Issues in Falls Lake. Available at: <https://durhamnc.gov/DocumentCenter/View/2266/Timeline-of-Falls-Lake-Nutrient-Management-Strategy-Events-PDF?bidId=>. Accessed April 19, 2019.
- Collins, R. and K. Rutherford. 2004. Modelling bacterial water quality in streams draining pastoral land. *Water Research* 38(3): 700-712.
- Donovan, T. 1974. Petroleum microseepage at Cement, Oklahoma: Evidence and mechanism. *The American Association of Petroleum Geologists Bulletin* 58(3): 429-446.
- Engeman, R., A. Stevens, J. Allen, J. Dunlap, M. Dunlap, D. Teague, and B. Constantin. 2007. Feral swine management for conservation of an imperiled wetland habitat: Florida's vanishing seepage slopes. *Biological Conservation* 134(3): 440-446.
- Fisher, D., J. Steiner, D. Endale, J. Stuedemann, H. Schomberg, A. Franzluebbbers, and S. Wilkinson. 2000. The relationship of land use practices to surface water quality in the Upper Oconee Watershed of Georgia. *Forest Ecology and Management* 128: 39-48.
- Fisher, J. and M.C. Acreman. 2004. Wetland nutrient removal: A review of the evidence. *Hydrology and Earth System Sciences* 8: 673-685.
- Foos, A. 2003. Spatial distribution of road salt contamination of natural springs and seeps, Cuyahoga Falls, Ohio, USA. *Environmental Geology* 44: 14-19.
- George, R.J. 1991. Management of sandplain seeps in the wheatbelt of western Australia. *Agricultural Water Management* 19: 85-104.
- Gibson, C., C. O'Reilly, A. Conine, and S. Lipshutz. 2015. Nutrient uptake dynamics across a gradient of nutrient concentrations and ratios at the landscape scale. *Journal of Geophysical Research-Biogeosciences* 120: 326-340.
- Gobler, C. and G. Boneillo. 2003. Impacts of anthropogenically influenced groundwater seepage on water chemistry and phytoplankton dynamics within a coastal marine system. *Marine Ecology Progress Series* 255: 101-114.
- Gold, A.J., P.M. Groffman, K. Addy, D.Q. Kellogg, M. Stolt, and A.E. Rosenblatt. 2001. Landscape attributes as controls on ground water nitrate removal capacity of riparian zones. *Journal of the American Water Resources Association* 37: 1457-1464.
- Grasby S. and K. Londry. 2007. Biogeochemistry of hypersaline springs supporting a mid-continent marine ecosystem: An analogue for martian springs? *Astrobiology* 7(4): 662-683.
- Griebler, C. and M. Avramov. 2015. Groundwater ecosystem services: A review. *Freshwater Science* 34(1): 355-367.
- Harkness, J., B. Sulkin, and A. Vengosh. 2016. Evidence for coal ash ponds leaking in the southeastern United States. *Environmental Science and Technology* 50(12): 6583-6592.
- Heath, R.C. 1983. Basic Ground-water Hydrology: U.S. Geological Survey Water-Supply Paper 2220. Available at: <https://pubs.usgs.gov/wsp/2220/report.pdf>. Accessed April 19, 2019.
- Hill, A. 1996. Nitrate removal in stream riparian zones. *Journal of Environmental Quality* 25:743-755.
- Humphrey, C., M. O'Driscoll, D. Mallinson, and S. Hardison. 2013. *Geophysical and Water Quality Characterization of On-site Wastewater Plumes*. North Carolina Water Resources Research Institute Report No. 445. Available at: <https://repository>.

- lib.ncsu.edu/bitstream/handle/1840.4/8292/NC-WRRI-445.pdf?sequence=1&isAllowed=y. Accessed April 19, 2019.
- Humphrey, C., A. Finley, M. O'Driscoll, A. Manda, and G. Iverson. 2015. Groundwater and stream *E. coli* concentrations in Coastal Plain watersheds served by onsite wastewater and a municipal sewer treatment system. *Water Science and Technology* 72(10): 1851-1860.
- Humphrey, C., J. Jernigan, G. Iverson, B. Serozi, M. O'Driscoll, S. Pradhan, and E. Bean. 2016. Field evaluation of nitrogen treatment by conventional and single-pass sand filter onsite wastewater systems in the North Carolina Piedmont. *Water, Air, and Soil Pollution* 227: 255.
- Humphrey, C., J. Blackmon, T. Kelley, M. O'Driscoll, and G. Iverson. 2018. Environmental health threats associated with drainage from a coastal urban watershed. *Environment and Natural Resources Research* 8(1): 52-60.
- Iverson, G., C. Humphrey, M. O'Driscoll, C. Sanderford, J. Jernigan, and B. Serozi. 2018. Nutrient exports from watersheds with varying septic system densities in the North Carolina Piedmont. *Journal of Environmental Management* 211: 206-217.
- Iverson, G. 2019. Nutrient contributions from septic systems in nutrient-sensitive watersheds: Quantifying nutrient inputs, reduction methods, and economic feasibility. PhD Dissertation, Coastal Resources Management, East Carolina University, Greenville, NC.
- Jackson, R., A. Gorody, B. Mayer, J. Roy, M. Ryan, and D. Van Stempvoort. 2013. Groundwater protection and unconventional gas extraction: The critical need for field-based hydrogeological research. *Ground Water* 51(4): 488-510.
- James, C., J. Miller-Schulze, S. Ultican, A. Gipe, and J. Baker. 2016. Evaluating contaminants of emerging concern as tracers of wastewater from septic systems. *Water Research* 101: 241-251.
- Jamieson, R., R. Gordon, K. Sharples, G. Stratton, and A. Madani. 2002. Movement and persistence of fecal bacteria in agricultural soils and subsurface drainage water: A review. *Canadian Biosystems Engineering* 44: 1.1-1.9.
- Johnston, A., R. Runkel, A. Navarre-Sitchler, and K. Singha. 2017. Exploration of diffuse and discrete sources of acid mine drainage to a headwater mountain stream in Colorado, USA. *Mine Water Environment* 36: 463-478.
- Juilfs, T. 2016. Muddy waters: Why polluted groundwater infiltrating navigable waters should not be excluded from National Pollutant Discharge Elimination System permitting. *Northern Illinois University Law Review* 7(2): 30-62.
- Junghans, K., A. Springer, L. Stevens, and J. Ledbetter. 2016. Springs ecosystem distribution and density for improving stewardship. *Freshwater Science* 35(4): 1330-1339.
- Kaur, A., D. Ross, J. Shanley, and A. Yatzor. 2016. Enriched groundwater seeps in two Vermont headwater catchments are hotspots of nitrate turnover. *Wetlands* 36: 237-249.
- Kendall, C. and J. McDonnell. 1998. *Isotope Tracers in Catchment Hydrology*, First edition. Elsevier Science B.V., Amsterdam, 839 pp.
- KGDR. 2019. Kentucky Groundwater Data Repository Water Well and Spring Location Map. University of Kentucky and Kentucky Geological Survey. Available at: <https://kgs.uky.edu/kgsmap/KGSWater/viewer.asp>. Accessed April 19, 2019.
- Kvien, A. 2015. Is groundwater that is hydrologically connected to navigable waters covered under the CWA?: Three theories of coverage and alternative remedies for groundwater pollution. *Minnesota Journal of Law, Science, and Technology* 16(2): 957-1010.
- Lehosmaa, K., J. Jyväsjärvi, J. Ilmonen, P. Rossi, L. Paasivirta, and T. Muotkaa. 2018. Groundwater contamination and land drainage induce divergent responses in boreal spring ecosystems. *Science of the Total Environment* 639: 100-109.
- Likens, G.E. and D.C. Buso. 2006. Variation in stream water chemistry throughout the Hubbard Brook Valley. *Biogeochemistry* 78: 1-30.
- Mayer, P., S. Reynolds, M. McCutchen, and T. Canfield. 2007. Meta-analysis of nitrogen removal in riparian buffers. *Journal of Environmental Quality* 36: 1172-1180.
- McClain, M., E. Boyer, C. Dent, et al. 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. *Ecosystems* 6(4): 301-312.
- Miller, M., S. Buto, D. Susong, and C. Rumsey. 2016. The importance of base flow in sustaining surface water flow in the Upper Colorado River Basin. *Water Resources Research* 52: 3547-3562.
- Minnesota Spring Inventory. 2019. Minnesota Department of Natural Resources. Available at: <https://www.dnr.state.mn.us/waters/groundwater/section/springs/msi.html>. Accessed April 19, 2019.
- Morley, T.R., A.S. Reeve, and A.J.K. Calhoun. 2011. The

- role of headwater wetlands in altering streamflow and chemistry in a Maine, USA catchment. *Journal of the American Water Resources Association* 47(2): 337-349.
- NCDENR. 1990. North Carolina Department of Environment and Natural Resources. A Report on the Investigation of the Town Creek Incident, Greenville, Pitt County- Incident #3212.
- Nichols, E., R. Cook, J. Landmeyer, B. Atkinson, D. Malone, G. Shaw, and L. Woods. 2014. Phytoremediation of a petroleum-hydrocarbon contaminated shallow aquifer in Elizabeth City, North Carolina, USA. *Remediation* 24(2): 29-46.
- Ocampo, C.J., C.E. Oldham, M. Sivapalan, and J.V. Turner. 2006. Hydrological versus biogeochemical controls on catchment nitrate export: A test of the flushing mechanism. *Hydrological Processes* 20: 4269-4286.
- O'Driscoll, M. and D. DeWalle. 2010. Seeps regulate stream nitrate concentration in a forested Appalachian catchment. *Journal of Environmental Quality* 39: 420-431.
- O'Driscoll, M.A., C.P. Humphrey, Jr., N.E. Deal, D.L. Lindbo, and M. Zarate-Bermudez. 2014. Meteorological influences on nitrogen dynamics of a coastal onsite wastewater treatment system. *Journal of Environmental Quality* 43: 1873-1885.
- Philp, R. and P. Crisp. 1982. Surface geochemical methods used for oil and gas prospecting: A review. *Journal of Geochemical Exploration* 17: 1-34.
- Puckett, L. 2004. Hydrogeologic controls on the transport and fate of nitrate in ground water beneath riparian buffer zones: Results from thirteen studies across the United States. *Water Science and Technology* 49(3): 47-53.
- Röper, T., J. Greskowiak, and G. Massmann. 2014. Detecting small groundwater discharge springs using handheld thermal infrared imagery. *Ground Water* 52(6): 936-942.
- Rose, J., C. Gerba, and W. Jakubowski. 1991. Survey of potable water supplies for *Cryptosporidium* and *Giardia*. *Environmental Science and Technology* 25(8): 1393-1400.
- Rosenblatt, E., A. Gold, H. Stolt, P. Groffman, and D. Kellogg. 2001. Identifying riparian sinks for watershed nitrate using soil surveys. *Journal of Environmental Quality* 30: 1596-1604.
- Rutherford, J.C. and M. Nguyen. 2004. Nitrate removal in riparian wetlands: Interactions between surface flow and soils. *Journal of Environmental Quality* 33: 1133-1143.
- Santhi, C., P. Allen, R. Muttiah, J. Arnold, and P. Tuppad. 2008. Regional estimation of base flow for the conterminous United States by hydrologic landscape regions. *Journal of Hydrology* 351: 139-153.
- Savage, D. 2019. Supreme Court to Decide if Clean Water Act Limits Hawaii's Underground Wastewater Dumping. Los Angeles Times, February 19, 2019. Available at: <https://www.latimes.com/politics/la-na-pol-court-clean-water-hawaii-20190219-story.html>. Accessed April 19, 2019.
- S&ME, Inc. 2011. Surface Water Sampling Report: Town Creek Downtown Greenville. North Carolina Department of Environment and Natural Resources.
- Schimmelmann, A., S. Ensminger, A. Drobnik, M. Mastalerz, G. Etiope, R. Jacobi, and C. Frankenberg. 2018. Natural geological seepage of hydrocarbon gas in the Appalachian Basin and Midwest USA in relation to shale tectonic fracturing and past industrial hydrocarbon production. *Science of the Total Environment* 644: 982-993.
- Scott, E., D. Mansoor, K. Leh, and B. Haggard. 2017. Spatiotemporal variation of bacterial water quality and the relationship with pasture land cover. *Journal of Water and Health* 15(6): 839-848.
- Seitzinger, S., R. Styles, E. Boyer, R. Alexander, G. Billen, R. Howarth, B. Mayer, and N. Van Breemen. 2002. Nitrogen retention in rivers: Model development and application to watersheds in the northeastern USA. *Biogeochemistry* 57: 199-237.
- Shabaga, J. and A. Hill. 2010. Groundwater-fed surface flow path hydrodynamics and nitrate removal in three riparian zones in southern Ontario, Canada. *Journal of Hydrology* 388: 52-64.
- Silva, S., P. Ging, R. Lee, J. Ebbert, A. Tesoriero, and E. Inkpen. 2002. Forensic applications of nitrogen and oxygen isotopes of nitrate in an urban environment. *Environmental Forensics* 3: 125-130.
- Smith, B. 2016. Pollution problems in paradise: Does the Clean Water Act apply to groundwater pollution in Maui? *Journal of Environmental and Sustainability Law* 22(2): 292-309.
- Soulsby, C., D. Tetzlaff, N. van den Bedem, I. Malcolm, P. Bacon, and A. Youngson. 2007. Inferring groundwater influences on surface water in montane catchments from hydrochemical surveys of springs and streamwaters. *Journal of Hydrology* 333(2-4): 199-213.
- Spoelstra, J., N. Senger, and S. Schiff. 2017. Artificial sweeteners reveal septic system effluent in rural groundwater. *Journal of Environmental Quality* 46(6): 1434-1443.

- Springer, A., L. Stevens, D. Anderson, R. Parnell, D. Kreamer, L. Levin, and S. Flora. 2008. Chapter 4: A comprehensive springs classification system: Integrating geomorphic, hydrogeochemical, and ecological criteria. In: *Aridland Springs in North America- Ecology and Conservation*, L. Stevens and V. Meretsky (Eds.). University of Arizona Press, Tucson, AZ, pp. 49-75.
- Springer, A. and L. Stevens. 2009. Spheres of discharge of springs. *Hydrogeology Journal* 17: 83-93.
- Stein, E.D., M. Mattson, A.E. Fetscher, and K.J. Halama. 2004. Influence of geologic setting on slope wetland hydrodynamics. *Wetlands* 24: 244-260.
- Stevens, L. 2008. Chapter 17: Every last drop: Future springs ecosystem ecology and management. In: *Aridland Springs in North America- Ecology and Conservation*, L. Stevens and V. Meretsky (Eds.). University of Arizona Press, Tucson, AZ, pp. 332-346.
- Stevens, L. and V. Meretsky. 2008. Chapter 1: Springs ecosystem ecology and conservation. In: *Aridland Springs in North America- Ecology and Conservation*, L. Stevens and V. Meretsky (Eds.). University of Arizona Press, Tucson, AZ, pp. 3-10.
- Swanson, S., S. Wyman, and C. Evans. 2015. Practical grazing management to maintain or restore riparian functions and values on rangelands. *Journal of Rangeland Applications* 2: 1-28.
- Tang, X., B. Zhu, and H. Katou. 2012. A review of rapid transport of pesticides from sloping farmland to surface waters: Processes and mitigation strategies. *Journal of Environmental Sciences* 24(3): 351-361.
- Tesoriero, A.J., J.H. Duff, D.M. Wolock, N.E. Spahr, and J.E. Almendinger. 2009. Identifying pathways and processes affecting nitrate and orthophosphate inputs to streams in agricultural watersheds. *Journal of Environmental Quality* 38: 1892-1900.
- US EPA and USGS. 2005. U.S. Environmental Protection Agency and the U.S. Geological Survey (USGS) National Hydrography Dataset Plus – NHDPlus 1.0. Available at: <http://www.horizon-systems.com/nhdplus>. Accessed April 19, 2019.
- US EPA. 2002. Onsite Wastewater Treatment Systems Manual. Office of Water, Office of Research Development, United States Environmental Protection Agency. EPA/625/R-00/008.
- US EPA. 2018a. Clean Water Act Section 502: General Definitions. Available at: <https://www.epa.gov/cwa-404/clean-water-act-section-502-general-definitions>. Accessed April 19, 2019.
- US EPA. 2018b. Clean Water Act Coverage of “Discharges of Pollutants” via a Direct Hydrologic Connection to Surface Water. Available at: <https://www.federalregister.gov/documents/2018/02/20/2018-03407/clean-water-act-coverage-of-discharges-of-pollutants-via-a-direct-hydrologic-connection-to-surface>. Accessed April 19, 2019.
- Van Stempvoort, D., J. Spoelstra, N. Senger, S. Brown, R. Post, and J. Strugera. 2016. Glyphosate residues in rural groundwater, Nottawasaga River Watershed, Ontario, Canada. *Pest Management Science* 72: 1862-1872.
- Vidon, P.G.F. and A.R. Hill. 2004. Landscape controls on nitrate removal in stream riparian zones. *Water Resources Research* 40(W03201): 1-14.
- West, A.J., S.E. Findlay, D.A. Burns, K.C. Weathers, and G.M. Lovett. 2001. Catchment-scale variation in the nitrate concentration of ground water seeps in the Catskill Mountains, New York, USA. *Water Air and Soil Pollution* 132: 389-400.
- William, R. and A.B. Endres. 2017. Bridging the divide: Incorporating interflow into legal discourse on surface water-groundwater interactions. *Ecology Law Currents* 44(1): 101-108.
- Williams, M., A. Buda, H. Elliott, J. Hamlett, E. Boyer, and J. Schmidt. 2014. Groundwater flow path dynamics and nitrogen transport potential in the riparian zone of an agricultural headwater catchment. *Journal of Hydrology* 511: 870-879.
- Williams, M.R., A.R. Buda, H.A. Elliott, A.S. Collick, C. Dell, and P.J.A. Kleinman. 2015. Linking nitrogen management, seep chemistry, and stream water quality in two agricultural headwater watersheds. *Journal of Environmental Quality* 44: 910-920.
- Williams, D.D. 2016. Chapter 11: Invertebrates in groundwater springs and seeps. In: *Invertebrates in Freshwater Wetlands: An International Perspective on their Ecology*, D. Batzer and D. Boix (Eds.). Springer, Switzerland, pp. 357-410.
- Williams, M.R., A.R. Buda, K. Singha, G.J. Folmar, H.A. Elliott, and J.P. Schmidt. 2016. Imaging hydrological processes in headwater riparian seeps with time-lapse electrical resistivity. *Ground Water* 55(1): 136-148.
- Winston, R., W. Hunt III, D. Osmond, W. Lord, and M. Woodward. 2011. Field evaluation of four level spreader-vegetative filter strips to improve urban storm-water quality. *Journal of Irrigation Drainage Engineering* 137(3): 170-182.
- Winter, T. 2007. The role of ground water in generating streamflow in headwater areas and in maintaining

base flow. *Journal of the American Water Resources Association* 43(1):15-25.

Woda, J., T. Wen, D. Oakley, D. Yoxtheimer, T. Engelder, M. Castrod, and S. Brantley. 2018. Detecting and explaining why aquifers occasionally become degraded near hydraulically fractured shale gas wells. *Proceedings of the National Academy of Sciences (PNAS)*: 201809013. DOI: 10.1073/pnas.1809013115. Available at: www.pnas.org/cgi/doi/10.1073/pnas.1809013115. Accessed April 19, 2019.

Zimmer, M., S. Bailey, K. McGuire, and T. Bullen. 2013. Fine scale variations of surface water chemistry in an ephemeral to perennial drainage network. *Hydrological Processes* 27: 3438-3451.