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Assessment of a sinkhole filter for removing agricultural contaminants

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Abstract: The impact on water quality by agricultural activity in karst terrain is an important consideration for resource management within the Appalachian Region. Three USDA Natural Resource Conservation Service–designed sinkhole filters for removing contaminants from manure-impacted infiltrating water were assessed for removal efficiency of indicator bacteria and nitrate. Geometric mean fecal coliform bacteria concentrations decreased 85% to 96%. Mean nitrate concentrations increased 130% at two of the filter locations. The sinkhole filters probably filtered out sediment and associated contaminants, such as fecal coliform bacteria, but had no filtering effect on solutes like nitrate. Nitrate concentrations might have increased because of nitrification in the filter media between runoff events. The sinkhole filter appears to be an effective management tool in order to reduce inputs of pathogens to karst groundwater aquifers.

Key words: fecal coliforms-filtration-karst-nitrate-sinkhole management

Karst is a major land resource area of the Appalachian region that accounts for a large portion of the region's agricultural production (Pasquarell and Boyer 1995). Appalachian karst is characterized by extensive cave and conduit systems, sinkholes, and sinking streams. Soils range in depth from 0 to 10 m (0 to 32.8 ft) (Jones 1997). Interrupted surface drainage and conduit flow in mature karst terrain results in a rapid and direct connection between surface and ground water (Gerhart 1986; Hallberg 1986; Quinlan and Alexander 1987). Water entering the karst aquifers through sinkholes and as sinking streams undergoes little natural filtration and quickly reappears in springs. Every sinkhole is a potential injection well for transmitting contaminants to the aquifer (Jones 1997). Sources of contamination may be detected miles from their origins within very short travel times of hours to a few days. Tracer tests in the area show a mean travel time of 0.64 km d⁻¹ (0.4 mi day⁻¹) (Jones 1997). Large variations in groundwater quality can occur over short periods of minutes to hours (Boyer and Pasquarell 1996; Boyer and Kuczynska 2003).

The karst springs of southeastern West Virginia have been reported to be contaminated with nitrate (Boyer and Pasquarell 1995), herbicides (Pasquarell and Boyer 1996), fecal coliform bacteria (Boyer and Kuczynska 2003; Pasquarell and Boyer 1995), and *Cryptosporidium parvum* (Boyer and Kuczynska 2003). The linkage between grazing agriculture and karst aquifer contamination by nitrates and fecal coliforms has been shown (Boyer and Pasquarell 1996; Boyer and Pasquarell 1999). Direct relationships between percentage of karst watershed area in agriculture and nitrates and fecal bacteria have been demonstrated (Boyer and Pasquarell 1995; Kastrinos and White 1986; Pasquarell and Boyer 1995).

Boyer (2005) collected and analyzed water quality data from several karst locations in southeastern West Virginia and found a lack of consistent improvements in water quality, at the watershed scale, following several years of voluntary government assistance programs. However, there was improvement at the sinkhole scale leading to the conclusion that best management practices might need to be targeted in order to realize water quality improvement goals at watershed scales. Sinkhole filters could be one practice for realizing significant reductions in contaminants in targeted sinkholes. Farmers generally understand that runoff into sinkholes can pose a water quality problem and have expressed interest in best management practices that would reduce runoff contamination in sinkholes (Huber 1990). Several best management practices have been proposed and implemented in karst areas, but the complicated hydrology of such areas can make it difficult to conduct in-situ tests of their effectiveness for water quality improvement (Urich 2002). Petersen and Vondracek (2006) found vegetative filter strips to be an effective practice to protect sinkholes. An effective sinkhole filter used in conjunction with vegetative filter strips would add extra protection in sinkholes where concentrated flow or sinkhole flooding occurs.

Best management practices used on grazing lands in the central Appalachian karst are concentrated on controlling nutrients and animal wastes. Practices include nutrient management planning and application, distributed animal watering systems, rotational grazing, manure containment systems, animal exclusions, stream bank protection, and sinkhole fencing. The USDA Natural Resources Conservation Service (NRCS) in West Virginia proposed a sinkhole filter (figure 1) as a structural best management practice to filter contaminants from water before it enters the karst aquifer. Similar filters have been used to filter highway runoff in Indiana (Keith 1996) and Tennessee (Zhou et al. 2003). The Tennessee filter also used peat to filter out dissolved contaminants. A sinkhole filter with peat was not considered feasible for agricultural runoff because of the expense of periodically replacing the peat.

The purpose of this study was to assess the effectiveness of the West Virginia USDA NRCS sinkhole filter for reducing contaminants such as nitrate and fecal coliform bacteria concentrations. Since the filter was designed to not significantly alter sinkhole hydrology it was hypothesized that the filter would not effectively remove dissolved nitrate. It was hypothesized that sediment and sediment-bound contaminants such as fecal coliform bacteria concentrations would be effectively reduced before entering the karst aquifer.

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Figure 1



Idealized schematic (adapted from the original USDA NRCS design drawing) sinkhole filter design.

Materials and Methods

The basic sinkhole filter design (figure 1) consists of a thick, concrete plug over the sinkhole throat. A 15-cm (6-in) diameter perforated PVC pipe through the concrete plug allows filtered water to flow into the aquifer. The perforated section of PVC pipe is wrapped in filter fabric. A gradation of crushed rock is layered around the perforated PVC pipe. Approximately 20 cm (8 in) of topsoil and grass cover over the entire sinkhole filter completes the structure. Filter fabric is sandwiched between the coarse and fine crushed rock layers. A transect of suction lysimeters were installed down to the top of the bedrock for study purposes only (figure 1). No two sinkholes are exactly alike so each sinkhole filter requires some modification to fit the specific sinkhole.

Three sinkhole filters were installed in the Greenbrier Hydrologic Unit in Greenbrier County, West Virginia. The Greenbrier Hydrologic Unit, described by Boyer (2005), is underlain by Mississippian carbonate bedrock dominated by the Greenbrier Limestone. The soil series are Caneyville (fine loamy, mixed, active, mesic, Typic Hapludalfs) in sinkhole floors and Frederick (clayey, mixed, active, mesic, Typic Paleudult) on side slopes. Most of the aquifer recharge is autogenic in the study area, which is dominated by a sinkhole plain that includes thousands of karst features like sinkholes and blind valleys that funnel surface water into the karst aquifer. Some allogenic

recharge occurs as sinking streams flowing off of the older Maccrady shale along the eastern border of the limestone and off of the sandstones and shales of the younger Mauch Chunk Formation to the west.

The first sinkhole was located in a pasture intermittently grazed by dairy cattle downslope from a dairy milk house and barnvard. The sinkhole was located in a narrow valley bottom between north and south hillsides. The slope to the milk house area was about 16% and the opposite slope was pasture with a slope of about 8%. The sinkhole often received surface flow from the pasture and the milk house area. A narrow cornfield on the slope between the sinkhole filter and the milk house provided little vegetative filtering of cattle waste products flowing away from the barnyard during storms. The sinkhole contained a natural, solutionally-enlarged basin in the limestone bedrock beneath the sinkhole filter. The natural, solutionally-enlarged basin held water and contaminants until storms caused the basin to overflow into a fracture open to the aquifer. Sinkhole number one's filter was installed September 1994. Water samples were collected from the basin several months prior to filter installation (June 1993 to September 1994) as well as several months following the installation (December 1994 through October 1996).

The second sinkhole filter was placed in beef cattle pasture grazed continuously (stocking density about 3 head ha⁻¹ [1.2 head ac⁻¹]) during the growing season and intermittently in winter. The sinkhole was located at the lowest point of the pasture (near the center) and often received flow from the sloped edges of the pasture. The pasture bottom was an ellipsoid of about 190×76 m (625 × 250 ft). The slopes above the pasture bottom were about 12% on the long sides and 24% on the short sides. Like sinkhole number one, sinkhole number two stored water in a natural basin just below the surface. Water samples were taken from the natural basin via access through the 15cm (6-in) diameter PVC pipe. This sinkhole occasionally flooded to 1 or 2 m (3.3 to 6.6 ft) above the top of the sinkhole filter. The sinkhole filter in sinkhole two was installed in August 1995, and water samples were taken from September 1995 through March 2005.

The third sinkhole filter was constructed September 2002 in a large sinkhole in a pasture rotationally grazed by beef cattle (stocking density about 3.5 head ha⁻¹ [1.4 head ac⁻¹]) on a stocker beef operation (Boyer and Alloush 2001). Sinkhole three was circular with a diameter of 59 m (194 ft) and depth of 6 m (20 ft). Side slopes were about 20%. This sinkhole did not have a natural water collection basin below the surface so a 50 L (13.2 gal.) polypropylene reservoir was positioned below the filter's drainage pipe. The reservoir was perforated by a vertical line of 6-mm (1/4-in) diameter holes spaced 50 mm (2 in) apart so it could empty between storms. A pressure transducer placed in the sampling reservoir and connected to a data logger signaled when storm flow was occurring through the filter's drainage pipe. The data logger triggered an automatic sampler that collected 24 one-liter (0.26-gal) samples at 10-min intervals. Samples were removed soon after storm completion and were transported on ice back to the laboratory for analyses. A PVC passive stormflow collector situated in the throat of the sinkhole was used to collect storm samples prior to sinkhole filter installation. Prefilter water samples were taken from May 1998 through August 2002, and filtered water samples were obtained from September 2002 through November 2004. An adjacent, but smaller and unfiltered, sinkhole in the same grazing paddock was instrumented with a PVC passive stormflow collector in the sinkhole throat. Samples were collected from the adjacent sinkhole prior to and after sinkhole Figure 2

filter installation in sinkhole number three.

The suction lysimeters were maintained at a constant vacuum of 50 kPa (-7.25 psi) and sampled following each storm. All water samples were analyzed for fecal coliform bacteria by membrane filtration (0.45 μ m [0.000018 in]) using mFC agar nutrient media and incubated at 44.5°C (112°F) (APHA 1995). Nitrate N concentrations were determined by suppressed ion chromatography on filtered (0.45 μ m [0.000018 in]) water samples (APHA 1995).

Statistical analyses were performed with the Statistical Analysis System (SAS Institute Inc. 2004). Geometric means of the fecal coliform data were computed by calculating the mean of log-transformed values and then transforming the mean of the logs back to real numbers. The Wilcoxon (also known as Mann-Whitney) rank sum test was used to test for differences in locations of the sample populations of prefilter and postfilter data. The Wilcoxon rank sum test is nonparametric and does not assume normality (Mosteller and Rourke 1973). The Wilcoxon rank sum tests were run in SAS as the NPAR1WAY procedure (SAS 2004).

Results and Discussion

Distributions of the prefilter and postfilter data at each of the sinkholes are graphically represented by box plots in figure 2. Sinkhole one geometric mean fecal coliform concentrations in prefilter and filter water were 238 CFU 100 mL⁻¹ and 35 CFU 100 mL⁻¹, respectively. Mean NO₃-N concentrations increased from 2.0 mg L⁻¹ (2.0 ppm) to 4.6 mg L⁻¹. All concentration differences were statistically significant (p < 0.05) according to the Wilcoxon rank sum test.

Prefilter sampling was not performed at sinkhole two. All sample analysis results are from data collected after installation of the sinkhole filter. Geometric mean fecal coliform concentration was 190 CFU 100 mL⁻¹. Mean NO₃-N concentrations were 2.3 mg L⁻¹.

In sinkhole three, geometric mean fecal coliform concentrations in prefilter and filter water were 3,783 CFU 100 mL⁻¹ and 160 CFU 100 mL⁻¹, respectively. Mean NO₃-N concentrations increased from 5.5 mg L⁻¹ to 12.9 mg L⁻¹. All concentration differences were statistically significant (p < 0.05 NO₃-N) (p < 0.1 for the fecal coliforms) according to the Wilcoxon rank sum test.

Distributions of prefilter and postfilter (a) fecal coliform and (b) NO₂-N data at each sinkhole.



Notes: The boxes represent the median, 25th percentile, and the 75th percentile. The whiskers represent 10th and 90th percentiles, and the filled circles represent maximum and minimum values. The maximum postfilter NO_3 -N value for sinkhole three (not shown) is 108.6 mg L⁻¹.

Since the sinkhole filters were designed to allow water to pass through quickly in order to avoid sinkhole flooding, it is no surprise that a solute such as nitrate was not controlled by the filters. The filters were expected to effectively block out particulates such as microorganisms and ions attached to soil particles. The results appear to show effective filtering of fecal coliform bacteria. A sinkhole adjacent to sinkhole three, in the

Figure 3 Results of sampling in sinkhole three during an 8-mm storm on June 11, 2004.





same pasture, had runoff water to its drain hole sampled three times after the filter was installed in sinkhole three. Fecal coliform concentrations during those three storms were 137,000, 100, and 16,400 CFU 100 ml⁻¹ in that sinkhole. Geometric mean fecal coliform concentrations in the filtered water of sinkhole three were 162, 17, and 5,841 CFU 100 ml⁻¹ for the same three storms, respectively. Prior to installation of the filter in sinkhole three, geometric mean fecal coliform concentrations of four storms were 2,022,000, 250,000, 31,600, and 173,000 CFU 100 ml⁻¹ in sinkhole three, and fecal coliform concentrations were 17,300, 65,000, 166,000, and 44,000 CFU 100 ml⁻¹



Note: The sampling interval was 10 min, the line is water depth in the sample collection basin, and solid circles are fecal coliform concentrations.

in the adjacent sinkhole. Geometric mean fecal coliform concentrations in sinkhole three stormwater were 4 to 120 times greater, in three out of four storms in sinkhole three, than the fecal coliform concentrations in the adjacent sinkhole prior to sinkhole filter installation. Following installation of the sinkhole filter, fecal coliform concentrations were 3 to 800 times greater in the adjacent sinkhole's stormwater than the geometric mean fecal coliform concentrations of sinkhole three.

Peak fecal bacteria concentrations have been shown to coincide with peak flow and peak sediment load in karst springs (Boyer and Kuczynska 2003), indicating that soil attachment is an important mode of transport. The 85% and 96% reductions in geometric mean fecal coliform concentrations in sinkholes one and three, respectively, show that the filters were effective for reducing fecal coliforms. The filters might also be effective for controlling other contaminants that are known to attach to soil particles. Pesticides and phosphorus are known to be transported with soil particles as sorbed chemicals (Ghadiri and Rose 1991). Cryptosporidium transport has also been associated with suspended particles (Searcy et al. 2005).

Individual storm data analyses of sinkhole three showed that maximum fecal coliform concentrations occurred in the initial stormwater flush through the sinkhole filter drainage pipe (figures 3 to 5). Fecal coliform concentrations then declined throughout the storm period. Figure 3 shows fecal coliform concentrations during a June 11, 2004, storm of 8 mm (0.3 in) precipitation. The initial fecal coliform concentration was nearly 33,000 CFU 100 ml⁻¹ and decreased to less than 13,000 CFU 100 ml-1. In a 16-mm (0.6 in) storm on May 2, 2004, fecal coliforms rapidly increased to a concentration of 150,000 CFU 100 ml-1 and decreased to 30,000 CFU 100 ml⁻¹ (figure 5). Figure 4 shows a large storm (precipitation = 49 mm [1.9 in]) on June 4, 2004. Fecal coliforms started out at 8,500 CFU 100 ml⁻¹ and decreased to 1,800 CFU 100 ml⁻¹. The fecal coliform concentrations in the May 2 and July 11 stormflows appear to be high, at first glance, but are actually low when compared to the stormwater fecal coliform concentrations previously reported for the four prefilter storms (173,000 to 2,022,000 CFU 100 ml-1). Although the fecal coliform concentrations appear to be high, especially

Figure 5 Results of sampling in sinkhole three during a 16-mm storm on May 2, 2004.





at the onset of the storms, the overall reduction of fecal coliforms was significant. The filters can serve as an effective tool for reducing fecal coliform concentrations entering the sinkholes.

The sinkhole filters appear to be effective for reducing fecal coliform bacteria concentrations. The 85% to 96% reduction in geometric mean concentrations is probably a result of sediment entrapment within the filters. Fecal coliform bacteria are often attached to sediment and become trapped along with the sediment. However, high concentrations of fecal coliform bacteria during some storms following sinkhole filter installation indicates that bacteria attached to very fine sediments and colloidal materials and unattached fecal coliform bacteria were able to move through the filters. Other sediment-related contaminants like phosphorus and some pesticides also might be effectively trapped by the sinkhole filter, but further studies will be necessary in order to make those determinations.

Initially high NO₃-N concentrations in sinkhole three after filter installation may have been caused by fertilization to ensure a good grass cover on the filter. When the first three observations after filter installation at sinkhole three were excluded from analysis, the changes were still statistically significant (mean NO₃-N concentration increased from 5.5 mg L^{-1} to 7.8 mg L^{-1}).

Since fertilization only occurred during

filter construction and no follow up applications of N fertilizer were made, NO₂-N concentrations would be expected to decrease over time. Initial fertilization was conducted by the contractors, and rates and type of fertilizer were unknown. Regression analyses were done on the NO₂-N data after installation of the filters. Sinkhole filter one showed no significant trend in NO₂-N concentrations after installation. However, NO₂-N concentrations in sinkholes two and three showed significant decreases over time indicating a decreasing effect of the fertilizer. NO₃-N concentrations decreased 1.9 × $10^{-4} \text{ mg } L^{-1} d^{-1}$ and $1.6 \times 10^{-2} \text{ mg } L^{-1} d^{-1}$ at sinkholes two and three, respectively. The first three samples after filter installation in sinkhole three had high NO₂-N concentrations (96 to 109 mg L⁻¹) and were left out of the regression analysis.

 NO_3 -N concentrations in the suction lysimeters remained high throughout the study. Mean lysimeter NO_3 -N concentrations following sinkhole filter installations were 12.7, 14.1, and 20.4 mg L⁻¹ in the sinkholes one, two and three lysimeters, respectively. The mean NO_3 -N concentration in the shallow soil suction lysimeters was 6.2 mg L⁻¹ before installation of sinkhole filter three. Spikes in lysimeter NO_3 -N concentrations immediately following filter installation in sinkholes two and three were probably a result of fertilization to establish a grass cover on the filters. Exclusion of the

first six lysimeter NO₂-N values after filter two installation resulted in a mean lysimeter NO₂-N concentration of 9.2 mg L⁻¹. Exclusion of the first two lysimeter NO₂-N values after filter three installation resulted in a mean lysimeter NO₃-N concentration of 12.6 mg L⁻¹. In all three sinkhole filters, the lysimeter NO₃-N concentrations were higher than the NO₃-N concentrations of the water that had passed through the filters. Small sets of surface runoff samples at sinkholes one and three showed mean NO₂-N concentrations of 1.09 mg L⁻¹ and 0.85 mg L-1, respectively. The elevated NO₃-N concentrations in the lysimeters were probably a result of nitrification within the unsaturated filter gravels between storms.

Summary and Conclusions

The sinkhole filters were not effective for reducing nitrate concentrations. Nitrate is a solute and is not subject to physical filtration. Increases of about 130% in nitrate concentrations indicate that nitrification might have been occurring within the filters between storms. Inorganic nitrogen fertilizer applied to the filters for grass establishment also contributed to increased nitrate concentrations. However, the spike in fertilizer nitrate concentration was temporary. Since the sinkhole filters were not effective for reducing nitrate, a nutrient management practice accounting for animal waste inputs in the sinkhole areas might be a more effective means for reducing soluble nutrient concentrations as well as for further reduction of fecal coliform concentrations.

The sinkhole filter appears to be an effective management tool, along with responsible land management, in order to reduce inputs of pathogens to karst groundwater aquifers. Effective protection of groundwater from nonpoint source pollution often requires a suite of practices tailored to conditions of the nonpoint source area. The sinkhole filter is an addition to our suite of practices for protecting groundwater quality, especially in situations of concentrated flow or flooding sinkholes. The use of a sinkhole filter in conjunction with a vegetative filter strip could be a highly effective barrier to contaminant delivery to karst aquifers.

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References

- APHA (American Public Health Association). 1995. Standard Methods for the Examination of Water and Wastewater, 19th edition. Washington, DC: American Public Health Association.
- Boyer, D.G. 2005. Water quality improvement program effectiveness for carbonate aquifers in grazed land watersheds. Journal of the American Water Resources Association 41(2):291-300.
- Boyer, D.G., and G.C. Pasquarell. 1995. Nitrate concentrations in karst springs in an extensively grazed area. Water Resources Bulletin 31(4):729-736.
- Boyer, D.G., and G.C. Pasquarell. 1996. Agricultural land use effects on nitrate concentrations in a mature karst aquifer. Water Resources Bulletin 32(3):565-573.
- Boyer, D.G., and G.C. Pasquarell. 1999. Agricultural land use impacts on bacterial water quality in a karst groundwater aquifer. Journal of the American Water Resources Association 35(2):291–300.
- Boyer, D.G., and G.A. Alloush. 2001. Spatial distribution of nitrogen on grazed karst landscapes. TheScientificWorld 1:5.
- Boyer, D.G., and E. Kuczynska. 2003. Storm and seasonal distributions of fecal coliforms and *Cryptosporidium* in a spring. Journal of the American Water Resources Association 39(6):1449-1456.
- Gerhart, J.M. 1986. Ground-water recharge and its effects on nitrate concentration beneath a manured field site in Pennsylvania. Ground Water 24(4):483-489.
- Ghadiri, H., and C.W. Rose. 1991. Sorbed chemical transport in overland flow. I. A nutrient and pesticide enrichment mechanism. Journal of Environmental Ouality 20(3):628–633.
- Hallberg, G.R. 1986. From hoes to herbicides: Agriculture and groundwater quality. Journal of Soil and Water Conservation 41(6):357-364.
- Huber, G. 1990. Landowner perceptions of sinkholes and groundwater contamination. Journal of Soil and Water Conservation 45(2):323–327.
- Jones, W.K. 1997. Karst Hydrology Atlas of West Virginia. Charles Town, WV: Karst Waters Institute.
- Kastrinos, J.R., and W.B. White. 1986. Seasonal, hydrogeologic, and land-use controls on nitrate concentration of carbonate ground waters. *In* Proceedings of Environmental Problems in Karst Terranes and Their Solutions Conference, 88-114. Dublin, OH; Bowling Green, KY: National Water Well Association.
- Keith, J.H. 1996. Runoff treatment systems reduce highway-related impacts in the Indiana karst. Land and Water 40(3):12-16.
- Mosteller, F., and R.E.K. Rourke. 1973. Sturdy Statistics: Nonparametrics and Order Statistics. Reading, MA: Addison-Wesley Publishing.
- Pasquarell, G.C., and D.G. Boyer. 1995. Agricultural impacts on bacterial water quality in karst groundwater. Journal of Environmental Quality 24(5):959–969.

- Pasquarell, G.C., and D.G. Boyer. 1996. Herbicides in karst groundwater in southeast West Virginia. Journal of Environmental Quality 25(4):755-765.
- Petersen, A., and B. Vondracek. 2006. Water quality in relation to vegetative buffers around sinkholes in karst terrain. Journal of Soil and Water Conservation 61(6):380-390.
- Quinlan, J.E., and E.C. Alexander. 1987. How often should samples be taken at relevant locations for reliable monitoring of pollutants from an agricultural, waste disposal, or spill site in a karst terrane? A first approximation, *In* Proceedings of the 2nd Multidisciplinary Conference on Sinkholes and the Environmental Impacts of Karst, Orlando, FL, ed. B. Beck, 277–286.
- SAS Institute Inc. 2004. SAS/STAT 9.1 User's Guide. Cary, NC: SAS Institute Inc.
- Searcy, K.E., A.I. Packman, E.R. Atwill, and T. Harter. 2005. Association of *Cryptosporidium parvum* with suspended particles: Impact on oocyst sedimentation. Applied and Environmental Microbiology 71(2):1072-1078.
- Urich, P.B. 2002. Land use in karst terrain: Review of impacts of primary activities on temperate karst ecosystems. Wellington, New Zealand: New Zealand Department of Conservation.
- Zhou, W., B.F. Beck, and T.S. Green. 2003. Evaluation of a peat filtration system for treating highway runoff in a karst setting. Environmental Geology 44(2):187-202.