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Sean McMillian
Tennessee State University

Ashley West
Tennessee State University

David Solomon
Tennessee State University

Roger Diehl
University of Wisconsin

Victor Roland
Tennessee State University,Univ. of Arkansas, Fayetteville

See next page for additional authors

Presenter Information
Sean McMillian, Ashley West, David Solomon, Roger Diehl, Victor Roland, Irucka Embry, and Rick Toomey

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Sean McMillan[1], Ashley West[1], David Solomon[1], Roger Diehl[2], Victor Roland[1,3], Irucka Embry[1,4], Rick Toomey, III[5], Acknowledgement - Thomas Byl[1,6]

[1] Tennessee State University
[2] University of Wisconsin
[3] Univ. of Arkansas
[4] Tenn. Tech. University
[5] Mammoth Cave International Center for Science and Learning, Mammoth Cave National Park, Western Kentucky University
[6] U.S. Geological Survey

Abstract

Studies in the 1970s found potentially toxic levels of metals entering Mammoth Cave's underground streams through storm recharge. Additional studies confirmed that stormwater from parking lots and buildings flowed rapidly into critical cave habitats. The Park's management responded to these findings by installing storm runoff filter systems on the most heavily used parking lots in 2001. The Park entered an agreement (2010-12) with Tennessee State University, the USGS, and WKU-Mammoth Cave International Center for Science and Learning to evaluate the filter systems to determine if they were removing hazardous compounds from stormwater runoff. The objective of this study was to evaluate stormwater filters before and after replacing 2-year-old ZPG cartridge filters. The study focused on the first-flush runoff waters during the storms. The filters were not effective at removing quaternary ammonia compounds (QACs), and moderately effective at removing zinc and copper. The filters were very effective at removing diesel-range aromatic ring compounds (fuels). Regression analyses were used to evaluate trends between parking lot size and filter efficiency. The efficiency of the filters to remove fuels improved with basin size. The efficiency to remove QACs decreased with basin size. Basin size did not appear to have any correlation to zinc or copper removal efficiency. Human activity, such as construction, probably played a role in the storm-water chemistry and the efficacy of the filters to remove certain contaminants.

Introduction

Mammoth Cave in Central Kentucky has unique organisms that live in the cave waters and they are dependant upon high quality water supplied through rain recharge. Barr (1976) reported elevated metals and pollutants in the cave waters and speculated sources on the surface. Meimen and others (2001) confirmed a direct hydraulic link between certain parking-lot basins and several cave streams. The Park responded to these findings by installing storm runoff filter systems in 2001. The Park entered an agreement in 2010-12 with Tennessee State University, TN USGS, and WKU-Mammoth Cave International Center for Science and Learning to evaluate the filter systems. This report focuses on the assessment of 2-year-old filters and filters less than 1 year old. The filter maintenance included cleaning leaves and detritus from the oil-grit separator, and replacing the zeolite-perlite-granulated activated carbon (ZPG) cartridges in the main filter systems.

Materials and Methodology

Storm waters were monitored using first-flush siphon samplers (Diehl, 2008). These samplers were selected because they were small, required no power, and could catch water from the rising runoff. However, if the rain was too small to produce enough rise in the water, it would pass by the sampler. A minimum of three samples representing 3 different storms were used for interpretations. A list of chemicals, analytical methods and detection ranges are listed in Table 1.

Results and Discussion

The goal of this project was to determine if the filters were adequately removing contaminants that could harm the indigenous organisms in the cave. The initial test in 2008, on 7-year old filters, found they were ineffective at removing anything (West, et al., 2010). In this round of sampling, we evaluated the ZPG filters after being in place for 2 years; the suggested life of the filters, and within 8 months of replacing the filters. There were over 2,500 chemical data points generated over the 2011-12 study. This report is limited and summarizes results for aromatic fuel compounds, QACs, zinc and copper. These four chemicals represent water soluble chemicals that are known to be toxic to aquatic organisms.

Table 1: Chemical constituents analyzed in the first flush of the storm water.

Anaylsis included:	Method	Dectection range
Quaternary ammonia compounds (CTAB)	Hach 8337	0.2-5.0 mg/L
Chemical oxygen demand	Hach 8000	1-150 mg/L
Aromatic compounds (diesel range)	Turner Design	10-038R 0.01-10 mg/L
Ammonia (Nessler's)	Hach 8075	0.1-70 mg/L
Zinc	Hach 8009	0.02 - 3.00 mg/L
Copper (Porphyrin Method)	Hach 8143	5 - 210.0 ug/L
Nitrate	Hach 8171	0.2 - 5.0 mg/L
Phosphate (reactive, PO4^3-)	Hach 8048	0.05 - 2.50 mg/L
Sulphate (modified)	Hach 8051	0.5 - 70 mg/L
Specific conductance	YSI meters	0 - 1416 uS/cm
Hardness, Calcium (as CaCO3)	Hach titration 8204	10-4000 mg/L

Diesel-range aromatic compounds (fuel)

The ZPG filters were effective at removing dissolved aromatic compounds from the storm runoff (Figure 1a). The Woodland Cottage filter received the highest average concentration of fuel in 2010, but was able to remove over 90%. The Visitor Center (which was inaccessible during the 2011 sampling period due to the Visitor Center construction), was the only filter system ineffective at removing aromatic compounds. This was probably due to sediments carried in during construction runoff that blocked the binding sites on the activated carbon. The efficiency of the filters to remove aromatic fuel compounds increased with increasing parking lot size (Figure 1b). This apparent improvement in filter efficiency was possibly a function of the filters strong performance despite more fuel being released by the greater number of cars.

Zinc and Copper

The filters did little to remove zinc from the storm water (Figure 2a). In some cases, the average zinc concentration coming out of the filter unit was higher than the zinc concentration entering the filter. However, the average concentrations of zinc going in and coming out of all the filter systems were less than 0.5 mg/L. This is probably a safe concentration for the aquatic organisms, given the short exposure time during storm runoff and the antagonistic effect of calcium on zinc toxicity (Borgmann, et al., 2005). The efficiency of the zinc-removal

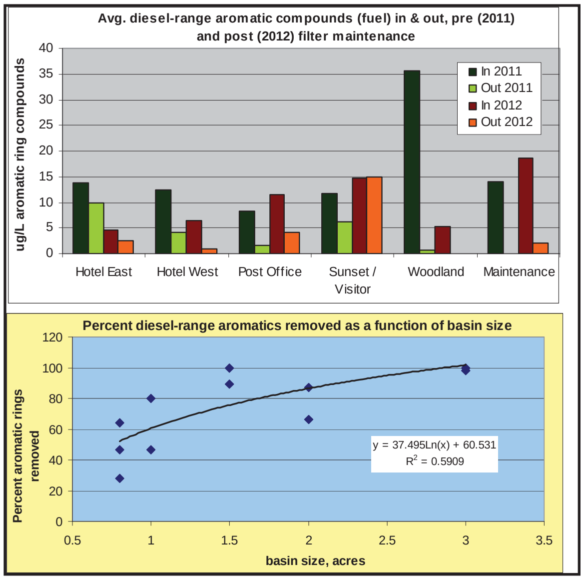

Figure 1: 1a(top graph): Average concentration of diesel range aromatic compounds dissolved in storm runoff at the filter inlets and outlets prior to and after the filters had been serviced in the late fall of 2011. [Sunset / Visitors is Sunset Lodge in 2011, and, Visitor Center in 2012; n = 3 or more] 4b (bottom graph): Regression analysis comparing the percent aromatic compounds removed by the filter as a function of parking lot size.

process was not affected by the size of the parking lot (Figure 2b). The regression shows a slight increase in efficiency with increasing lot size, but the R-square (0.08) indicates this was not a good fit with the data.

Prior to maintenance in 2011, the ability of the filters to sequester copper from the storm water was inconsistent (Figure 3a). After the filters were serviced in late 2011, the filters reliably removed greater than 50% of the copper, with the exception of the Visitor Center filter system. As noted before, the Visitor Center filter received storm runoff rich in suspended sediments after being serviced, rendering it less effective. The plot comparing filter efficiency to parking lot size illustrates there was no correlation between copper removing ability and parking lot size (Figure 3b)

Quaternary ammonia compounds

The storm filters appear to do very little to reduce QACs in the storm runoff, with the exception of the Post Office filter prior to servicing it (Figure 4a). QACs are known to adsorb to particles, especially organic particles. The cartridges and holding tank were rich in organic particles from leaf detritus prior to being serviced. The new ZPG filters were not designed to remove emulsifying compounds like QAC. The filters do tend to lower the QAC concentration, but they let approximately 50% pass through in the first flush.

When all the data were plotted comparing filter efficiency with parking lot size, there appears to be no correlation (Figure 4b).

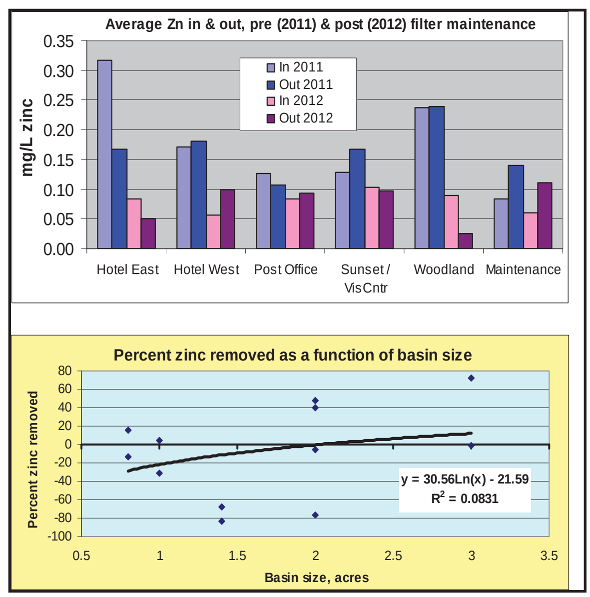

Figure 2: 2a (top graph): Average concentration of zinc (Zn^{2+}) dissolved in storm runoff at the filter inlets and outlets prior to and after the filters had been serviced in the late fall of 2011. [Sunset / Visitor bars are for Sunset Lodge in 2011, and, Visitors Center in 2012; n = 3 or more]. 2b (bottom graph): Regression analysis comparing the percent zinc removed by the filter as a function of parking lot size.

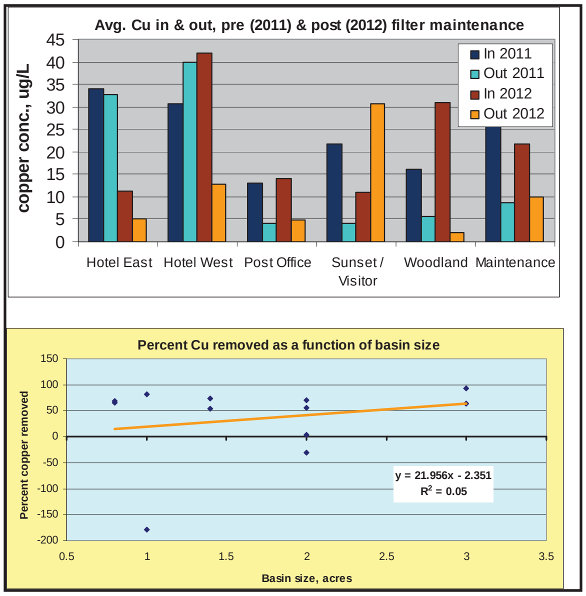

Figure 3: 3a (top graph): Average concentration of copper (Cu^{2+}) dissolved in storm runoff at the filter inlets and outlets prior to and after the filters had been serviced in the late fall of 2011. [Sunset / Visitor bars are for Sunset Lodge in 2011, and, Visitors Center in 2012; n = 3 or more]. 3b (bottom graph): Regression analysis comparing the percent copper removed by the filter as a function of parking lot size.

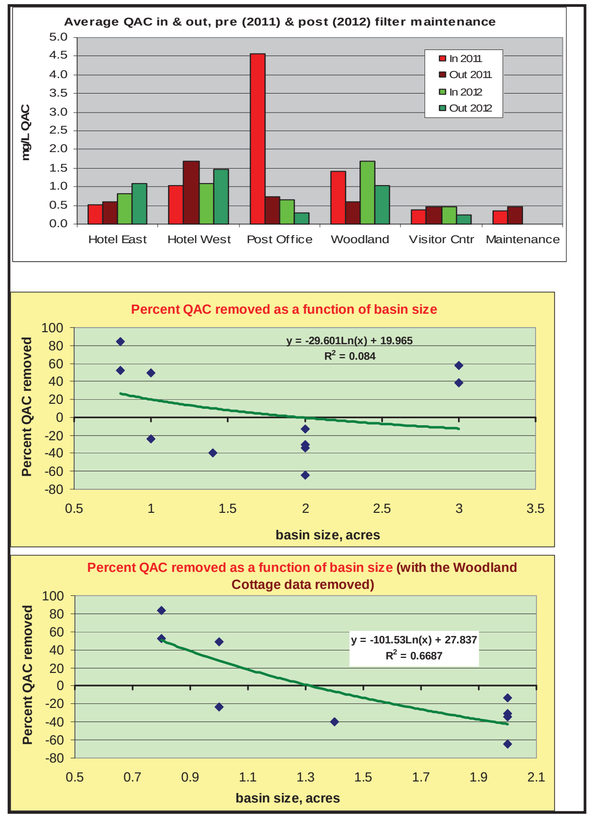

Figure 4: 4a (top graph): Average concentration of quaternary ammonia compounds dissolved in storm runoff at the filter inlets and outlets prior to and after the filters had been serviced in the late fall of 2011. [Sunset / Visitor bars are for Sunset Lodge in 2011, and, Visitors Center in 2012; n = 3 or more]. 4b (middle graph): Regression analysis using the data from all the parking lots comparing the percent QAC removed by the filter as a function of parking lot size. 4c (bottom graph): Regression analysis dropping the data from the largest parking lot, Woodland Cottage, comparing the percent QAC removed by the filter as a function of parking lot size.

However, if we remove the largest parking lot (Woodland Cottage) from the plot (Figure 4c), we get a good correlation. This correlation reveals that the larger the parking lot, the less efficient the filter systems are at removing QACs from storm runoff. This may be due to the shorter residence time in filters receiving waters from larger lots. Ho demonstrates in lab sorption experiments that sorption of QAC by the ZPG filters is dependent on time (2013, these proceedings).

Summary

This project evaluated the efficiency of the parking lot storm filters to remove various chemicals. The filters did an excellent job removing fuel compounds. They did a moderate job removing copper from the runoff, but were inconsistent at removing zinc and QACs from storm water.

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