Intensive Water Quality Monitoring in Two Karst Watersheds of Boone County, Missouri

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Abstract

Karst watersheds with significant losing streams represent a particularly vulnerable setting for ground water contamination because of the direct connection to surface water. Improvement of water quality in this type of karst setting faces many of the same management challenges as typical surface watersheds with regards to implementation of best management practices and responsible development in urbanizing areas. Because of the existing agricultural land-use and future threat of heavy urbanization, two losing stream karst basins were chosen for intensive monitoring in Boone County, Missouri: Hunters Cave and Devils Icebox Cave. Land use within both watersheds is similar with nearly equal percentages of row-crops, grasslands, and forest. Year-round monitoring was initiated in April 1999 with the objective of characterizing the water quality status of the main cave streams relative to herbicide, nutrient, and coliform bacterial contamination. Water sampling for contaminants entails grab samples at regular intervals and runoff event sampling using automated sampling equipment. In the first year, at least one herbicide or metabolite was detected in 60% of Hunters Cave samples and 72% of Devils Icebox samples. Total and inorganic nitrogen and phosphorus concentrations were generally much higher than existing Environmental Protection Agency guidelines for nutrient contamination of streams. Fecal coliform bacteria levels were generally above the whole body contact standard (200 cfu/100 ml^{-1}) in the Icebox, regardless of flow conditions. Under runoff conditions, fecal coliform levels in both caves can exceed 10,000 cfu/100 ml^{-1}. Prevailing land management has significantly degraded the water quality in both watersheds.

Materials and Methods

Cave Watersheds and Land Use

The watershed of the Devils Icebox and Hunters Caves are both located within the Bonne Femme Creek watershed located due south of Columbia, Missouri, USA. The caves were formed in the Mississippian Burlington Formation, a crinoid-rich limestone with distinct chert nodules in sub-horizontal layers (Halihan *et al.*, 1998). The upper (eastern) portions of both cave watersheds are covered by glacial and loess deposits and these glacial-derived soils coincide with the areas of most intense row cropping (Figures 1 and 2). Lower (western) portions of each watershed are characterized by residual soils (that is, aluminosilicate minerals remaining after bedrock dissolution) and associated karst features, such as sinkholes, caves, and springs.

The Devils Icebox watershed has been delineated by dye-tracing (Crunkilton and Whitley, 1983; St. Ivany, 1988), and other hydrologic studies have proven the link between the main cave stream and Bonne Femme Creek, as well as the hydrologic connection to the Pierpont sinkhole plain (Wicks, 1997) (Figure 1). The Devils Icebox watershed is approximately 12.5 square miles, and it icomprises two distinctive hydrologic areas: (1) surface drained upper watershed corresponding to Bonne Femme Creek; and (2) internally drained lower watershed encompassing the Pierpont sinkhole plain. Bonne Femme Creek is the primary source of water to the main cave stream (Wicks, 1997). Land-use/land cover data

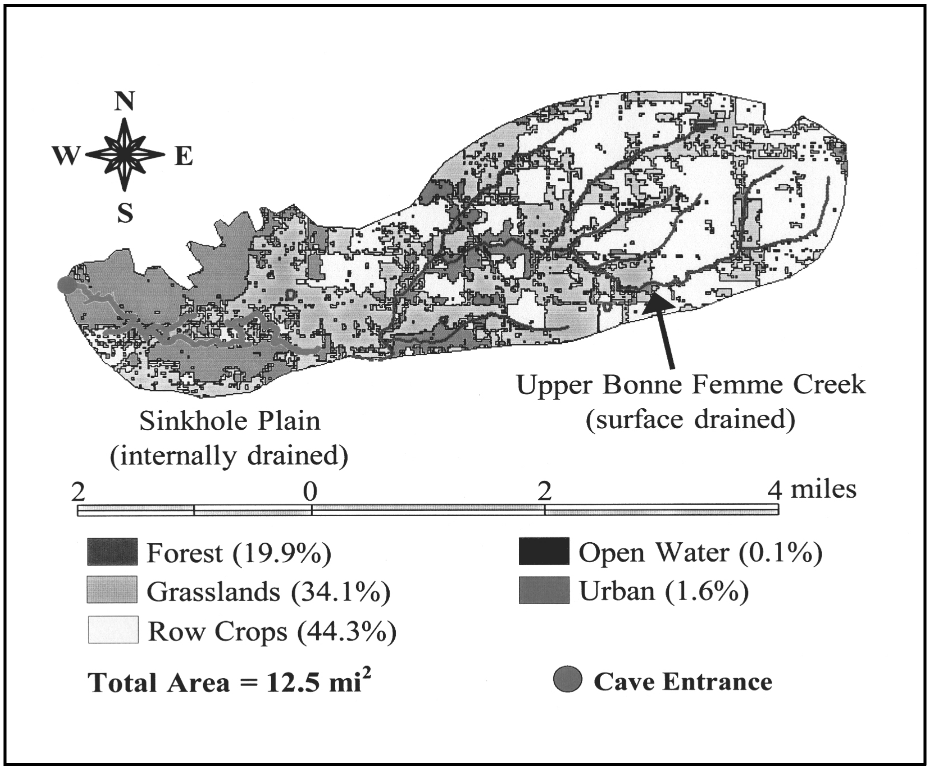

Figure 1. *Land use/land cover data for Devils Icebox recharge area based on 30-meter LANDSAT data from 1999.*

were determined using ArcView GIS (version 3.2) and 1999 LANDSAT data with 30 meters resolution (Figures 1 and 2). This recent land-use data is a major improvement in resolution and in distinction between different land-use categories, most notably the distinction between row-crop and grassland areas. Predominant land uses within the Devils Icebox watershed are row-crops (44.3%), grasslands (34.1%), forest (19.9%), and limited urban (1.6%) areas along U.S. Highway 63. Row crops are mainly corn and soybeans.

Approximately 40% of the grasslands

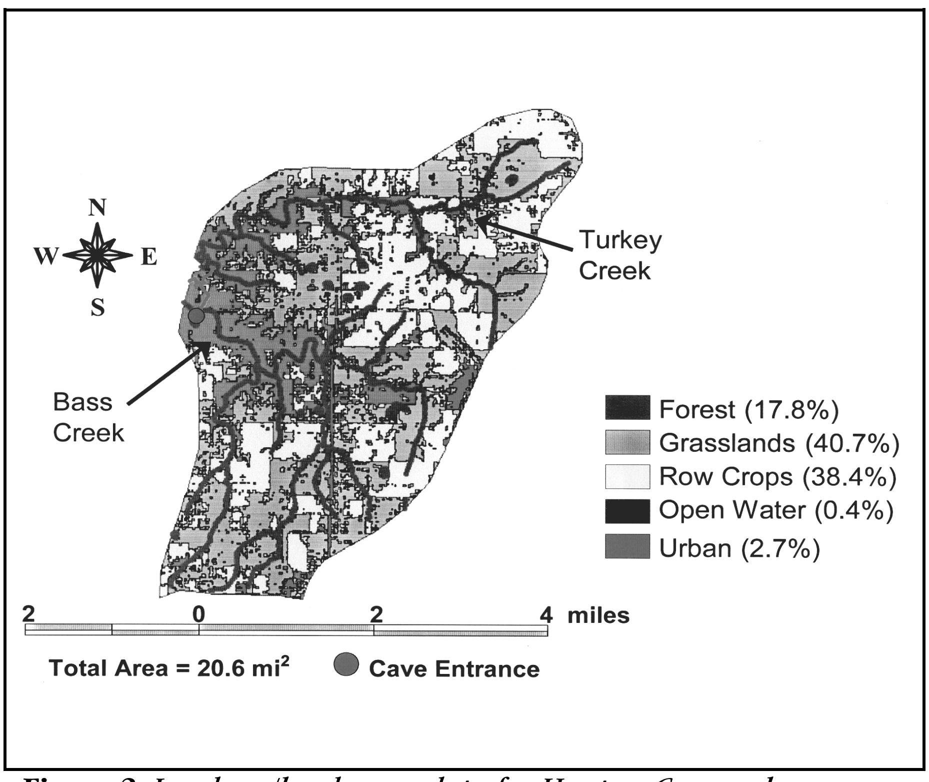

Figure 2. *Land use/land cover data for Hunters Cave recharge area based on 30-meter LANDSAT data from 1999.*

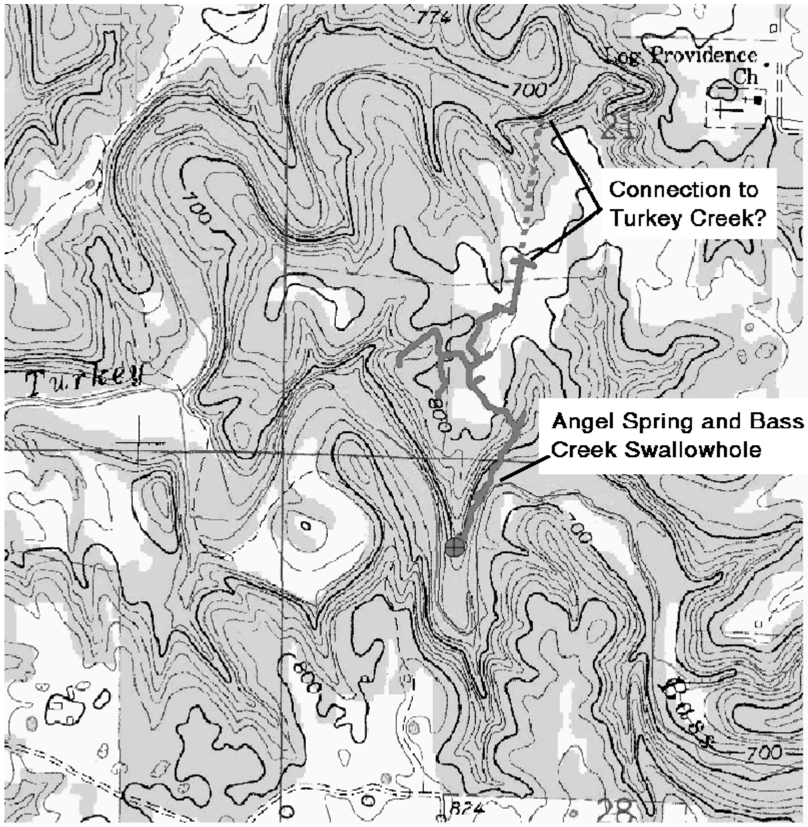

Figure 3. *Overlay of the 1958 Hunters Cave survey on the Ashland topographic map.*

are rangeland, with cattle and horses the predominant livestock. The remainder of the grasslands represent forage production for hay. Forested areas mostly lie within Rock Bridge Memorial State Park and they are mainly oak-hickory forests typical of the Ozarks region.

Hunters Cave watershed has not been delineated with dye-tracing. However, existing evidence, based on overlaying a line plot from the 1958 survey on the topographic map of the area, strongly suggests that both Turkey and Bass Creeks contribute to the Hunters Cave stream (Figure 3). From this overlay, it can be seen that Bass Creek comes in very close proximity to the cave passage. The estimated distance of this near intersection corresponds to the location of Angel Spring, suggesting a swallow hole and/or significant losing reach of Bass Creek upstream from this point. In addition, the un-mapped portion of the cave stream beyond the Big Room will almost assuredly place the cave in close proximity to Turkey Creek (Figure 2). Members of Chouteau Grotto are currently re-mapping Hunters Cave in order to produce a complete map. Contaminant transport data also support this delineation (data not shown). The estimated watershed of Hunters Cave is 20.6 square miles, an area 1.6 times greater than that of the Devils Icebox.

Using this tentative delineation for the Hunters Cave watershed, land-use/land-cover data showed that the area comprises grasslands (40.7%), row-crops (38.4%), forest (17.8%), and urban (2.7%), with the former two land-uses accounting for nearly 80% of the watershed (Figure 2). The Hunters Cave watershed has more grassland and urban areas but less row crops than the Devils Icebox watershed. Urban areas are composed of commercial development along U.S. Highway 63, the Columbia Regional Airport in the eastern portion of the watershed and residential development in Ashland, Missouri. Of particular interest to water quality in the cave stream is the distribution of row-crop areas within Turkey and Bass Creeks. Within the Turkey Creek watershed there is a distinct concentration of row-crop area in the eastern portion of the watershed extending into the northern portion of Bass Creek as well. In general, row-cropping intensity appears to be lower and more randomly distributed within the Bass Creek watershed, but some of the row-crop areas are in closer proximity to the cave than those within the Turkey Creek watershed.

Water Quality Monitoring Protocols

Year-round monitoring was initiated in April 1999 at the stream resurgence of each cave. Stream discharge is monitored at five-minute intervals using pressure transducers to measure the height of the water column. At the Devils Icebox, a rating curve was developed for the site (Halihan, 1998; Vandike, unpublished) so that stream height can be related to discharge. Hunters Cave cannot be accessed during high flow periods because of dangerously high flow in Bass Creek, so a reliable rating curve covering the upper range of observed stream heights could not be developed. Therefore, the flow velocity has been estimated with Manning's equation,

$$V = \frac{1.49}{n} \times R^{2/3} \times S^{1/2}$$

where V = velocity (ft/s), n = roughness coefficient, R = hydraulic radius [R = A/P, where A = cross sectional area of the channel and P = wetting parameter, with P = w+2d (w = channel width and d = channel depth or stream height)], and S = channel slope. Since we have measured the channel slope, width, and stream height (or channel depth), the only unknown variable is the roughness coefficient, n. Typically, one assumes a constant n, but direct measurements of flow velocity versus stream height, indicated n was not a constant for the range of stream heights observed. Therefore, a variable n was used as a function of stream height. By combining stream height data, channel geometry, and flow velocity (based on Manning's equation), the discharge can be estimated.

Geochemical parameters are continuously monitored at both caves using a YSI 6920 probe. Data are collected at 15 minute intervals for dissolved O_2, specific conductance, pH, temperature, and turbidity. For nutrient and herbicide analyses, grab samples are collected at regular intervals: (a) weekly from April through June and (b) twice monthly from July through March. Storm runoff events are monitored using Sigma 900 automatic samplers (autosamplers). Autosamplers are programmed to take samples with decreasing frequency through the course of an event. Sampling intervals range from five minutes to four hours, and the program was designed to collect samples at approximately equal proportions relative to the average time for runoff events at each site (24 hours at Hunters Cave; 36 hours at Devils Icebox). Samples collected for bacterial coliform analyses were collected on a quarterly basis from June 1999 to September 2000 at seven sites within Devils Icebox and five sites within Hunters Cave. Sites within the Devils Icebox included three locations along the main cave stream plus four significant tributaries. Sample sites within Hunters Cave included three sites along the main cave stream and two significant tributaries. Data are presented as the average of all sites for the quarter sampled.

Contaminant Analyses

Samples analyzed for nutrients, herbicides, and bacteria were transported to the laboratory on ice and refrigerated (2° to 4°C). Herbicide and dissolved nutrient samples were filtered through 0.45 m nylon filters within 48 to 72 hours of collection. Nutrient analyses included total and dissolved nitrogen and phosphorus species. Total nitrogen and phosphorus were determined on thoroughly mixed, unfiltered 60 millileter samples by autoclave digestion with potassium persulfate (Nydahl, 1978). For total nitrogen and phosphorus determination, persulfate digestion quantitatively converts all nitrogen forms to nitrate (NO_3^-) and all phosphorus forms to orthophosphate (PO_4^{3-}) which are then determined colorimetrically by a Lachat flow injection system (Lachat Instruments, Milwaukee, Wisconsin) as described below. Dissolved nitrogen and phosphorus were also determined by Lachat flow injection. For nitrate+nitrite-nitrogen, nitrate is quantitatively reduced to nitrite using a copperized Cd column. Nitrite is then determined by diazotizing with sulfanilamide followed by complexation with nitrogen-(1-napthyl)ethylenediamine dihydrochloride. The resulting magenta color is then read at 520 nm (Lachat Instruments, QuikChem Method 10-107-04-1-A). Since nitrite would not be expected to be significant in these samples, the nitrate+nitrite-nitrogen will be subsequently referred to as nitrate-nitrogen (NO_3-nitrogen). Ammonium-nitrogen (NH_4-nitrogen) was determined by heating with salicylate and hypochlorite in an alkaline phosphate buffer to produce an emerald green color. The color is subsequently enhanced by complexation with sodium nitroferricyanide and the color is read at 660 nm (Lachat Instruments QuikChem Method 10-107-06-2-C). Orthophosphate-phosphorus (PO_4-phosphorus) was determined by reaction with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. The complex is then reduced with ascorbic acid to produce a blue color which is read at 880nm

(Lachat Instruments QuikChem Method 10-115-01-1-A).

Herbicide analyses were conducted for several of the commonly used soil-applied corn and soybean herbicides: atrazine, alachlor, acetochlor, metolachlor, and metribuzin (Lerch *et al.*, 1995; Blanchard and Lerch, 2000). The stable atrazine metabolites deethylatrazine, deisopropylatrazine, and hydroxyatrazine were also analyzed. For all herbicides and metabolites, analyses were conducted by passing 200 ml samples through C_{18} solid-phase extraction (SPE) cartridges. A sequential elution SPE procedure was used in which 2.4 ml of ethyl acetate is the first eluant followed by 3.4 ml of 9:1 methanol: 0.05M KH_2PO_4, pH.7.5. All herbicides and metabolites, except hydroxyatrazine (HA), are eluted in the ethyl acetate fraction, and HA is eluted in the methanol/phosphate buffer fraction. For all herbicides and metabolites, except HA, the herbicides were quantitated using gas chromatography/mass spectrometry. HA was quantitated by high performance liquid chromatography with ultraviolet detection. Method detection limits were (in ng/L or ppt): atrazine, 8.00; alachlor, 3.00; acetochlor, 6.00; metolachlor, 2.00; metribuzin , 8.00; deethylatrazine (DEA), 4.00; deisopropylatrazine (DIA), 8.00; and HA, 25.0. More detailed descriptions of the herbicide analyses were provided by Lerch and Donald (1994), Lerch *et al.* (1995), Donald *et al.* (1998), and Lerch *et al.* (1998).

All bacterial analyses were conducted within 24 hours of collection. Fecal coliform analyses were determined by membrane filtration and incubation using specific growth media (Greenberg *et al.*, 1992; Procedure 9222 D). For samples with high coliform densities, dilutions were made as necessary to facilitate accurate counting of colonies. All bacterial densities are expressed as colony forming units (cfu) per 100 ml of sample.

Results and Discussion

Hydrology

Estimated discharge for Years 1 and 2 showed very different seasonal distributions (Figure 4) because of the large differences in total precipitation and rainfall distribution during the first two years of the study. Year 1 showed typical seasonal trends of significant discharge through the spring and winter months, with this period including the major rainfall and runoff events for Year 1. However, discharge for the five months from July through November 1999 was extremely low in both caves because of prevailing drought conditions. Total discharge for Year 1 was approximately 52,000,000 cubic feet for Devils Icebox and 23,000,000 cubic feet for Hunters Cave. Thus, Devils Icebox had about 2.3 times more discharge than Hunters Cave. Average monthly flow rates were 0.7 cubic feet per second at Hunters Cave and 1.7 cubic feet per second at Devils Icebox. Total precipitation for Year 1 was about 28 inches in each watershed. The greater average flow rate of the Icebox reflected its much greater peak discharge during runoff events, and its consis-

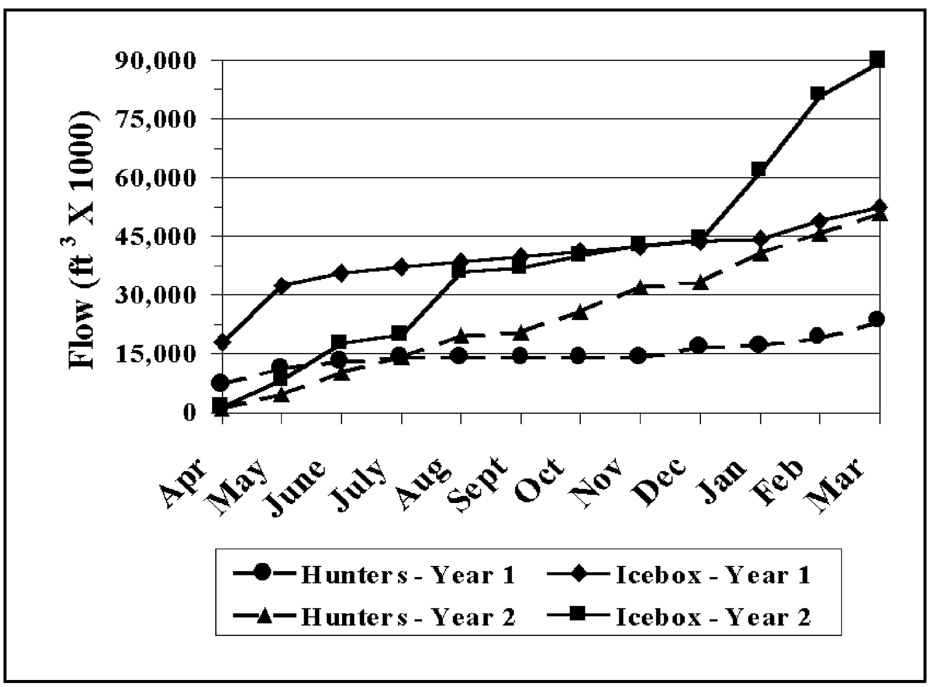

Figure 4. *Cumulative monthly discharge at Devils Icebox and Hunters Cave. Year 1 = April 1999 to March 2000. Year 2 = April 2000 to March 2001*

tently greater discharge during the drought period. Apparently, the Devils Icebox watershed has a much larger storage capacity than that of Hunters Cave.

In Year 2, discharge was very low during April and early May 2000. For example, discharge estimates for Hunters Cave were just under 7,000,000 cubic feet in April 1999 but only 1,100,000 cubic feet in April 2000. The differences were even more extreme for Devils Icebox with an estimated discharge of 18,000,000 cubic feet in April 1999 compared to just 1,400,000 cubic feet in April 2000. However, unlike most years, the summer of 2000 was characterized by frequent and intense rainfall, resulting in steady increases in cumulative discharge through the period. In fact, Hunters Cave showed an almost linear increase in cumulative discharge throughout Year 2. The largest event of Year 2, and so far in the study, occurred from August 7 through 9, 2000. Estimated discharge for this event was just over 7,000,000 cubic feet at Devils Icebox, with a peak flow rate of about 200 cubic feet per second, and 1,700,000 cubic feet at Hunters Cave, with a peak flow rate of 55 cubic feet per second. From the hydrograph and in-cave observations at Hunters, it appeared that Bass Creek flowed into the cave for about an hour, leaving deposits of organic matter-rich surface sediments about 200 feet into the cave. Another interesting feature of Year 2 hydrology was the number of significant runoff events during January through March 2001. At least six significant runoff events occurred during this period at each site, with corresponding increases in discharge. During February 2001, the Devils Icebox had 19,300,000 cubic feet, the highest monthly discharge to date. Total discharge for Year 2 was about 90,000,000 cubic feet at Devils Icebox and 51,000,000 cubic feet at Hunters Cave, indicating that the Icebox had about 1.8 times as much discharge as Hunters in Year 2. Average monthly flow rates were 2.7 cubic feet per second at Devils Icebox and 1.6 cubic feet per second at Hunters Cave. Total precipitation for Year 2 was about 42 inches in each watershed. As in Year 1, the greater average discharge at Devils Icebox resulted from the much greater peak runoff flow rates and greater duration of runoff events. However, Hunters Cave can exhibit monthly average discharge equal to or greater than that of the Devils Icebox stream. For example, Hunters had consistently greater average and total discharge from October through December 2000 apparently due to slightly greater rainfall and more intense precipitation events.

Contaminant Transport – Nutrients

Concentrations of total nitrogen and phosphorus were consistently higher in Devils Icebox compared to Hunters Cave from April 1999 to March 2000 (Figure 5). Presently, land use within the Hunters Cave drainage basin is not resulting in significantly elevated levels of these nutrients except under high flow conditions in winter and spring. Total nitrogen and phosphorus levels in Devils Icebox indicate a more significant and negative impact of land management on water quality within this watershed. Median and peak nutrient concentrations in Devils Icebox were consistently higher than Hunters indicating higher nutrient inputs to the watershed as a result of prevailing farm practices and possibly greater impact of on-site

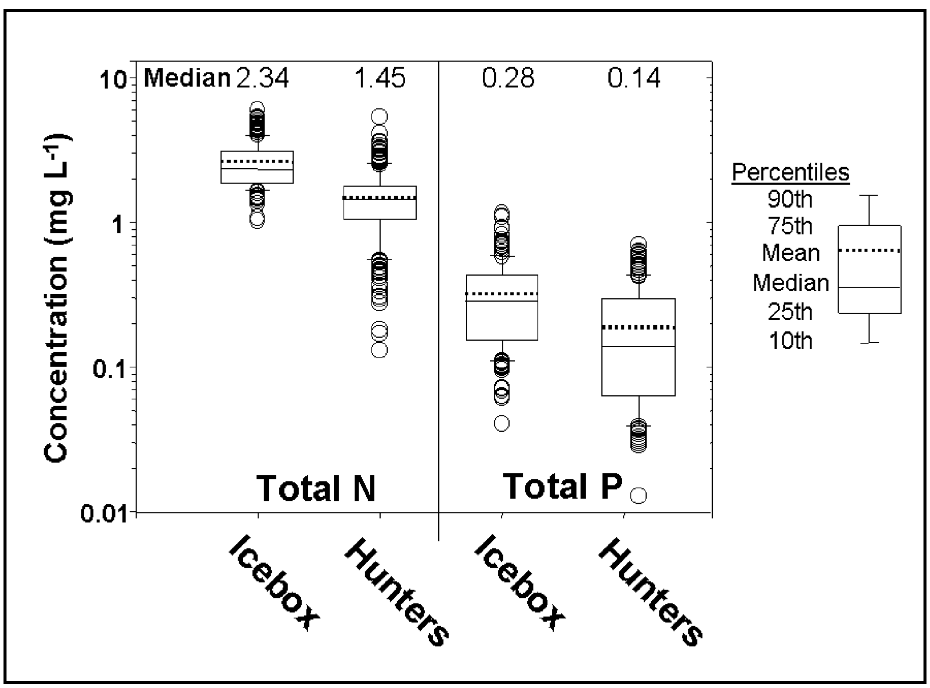

Figure 5. *Total nitrogen and phosphorus concentrations in Devils Icebox and Hunters Cave, April 1999 to March 2000.*

sewer systems. A previous unpublished study at Devils Icebox from 1982 to 1984 showed average nitrate (total nitrogen was not determined) of 2.1 ppm and average total phosphorus of 0.1 ppm. In the current study, nitrate has accounted for about 60% of the total nitrogen in samples collecting during Year 1. Assuming this same proportion for the 1982 to 1984 study, estimated average total nitrogen would have been 3.5 ppm. Thus, average total nitrogen at Devils Icebox has decreased 25% since 1982 to 1984. While total nitrogen levels have decreased over the last 17 to 19 years, total phosphorus levels have increased by about three fold over this same time period (Figure 5).

In the first year of the study, high nutrient concentrations were always associated with runoff events. Maximum total nitrogen concentrations were 6.0 ppm at Devils Icebox and 5.4 ppm at Hunters Cave, and maximum total phosphorus concentrations were 1.1 ppm at Devils Icebox and 0.7 ppm at Hunters Cave. Total nitrogen and phosphorus often closely correspond with each other and are directly related to stream flow and sediment transport. A major portion of the total nitrogen and phosphorus is transported in organic form bound to sediment particles. Partitioning of the total nutrient loads into inorganic and organic components indicates that 40 to 50% of the total nitrogen is in organic form with the remainder as nitrate. The fraction of the total nitrogen as nitrate has been consistently higher at Devils Icebox than Hunters Cave, providing further indication of greater inorganic nitrogen inputs in the Devils Icebox watershed. Ammonium-nitrogen accounted for 2% or less of the total nitrogen at either site. Partitioning of total phosphorus showed that both sites had about 60% organic phosphorus and 40% inorganic phosphorus.

Herbicides

Herbicides were frequently detected at both sites (Figure 6). Overall, 94.5% of Hunters Cave samples and 99.6% of Devils Icebox samples collected from April 1999 to March 2000 had a detection of at least one herbicide or metabolite compound. At the Icebox, atrazine was the most commonly detected herbicide with atrazine present in 96% of all samples. Because of the frequent detections of atrazine, its stable metabolites were also commonly detected. Atrazine metabolites were detected in 50% to

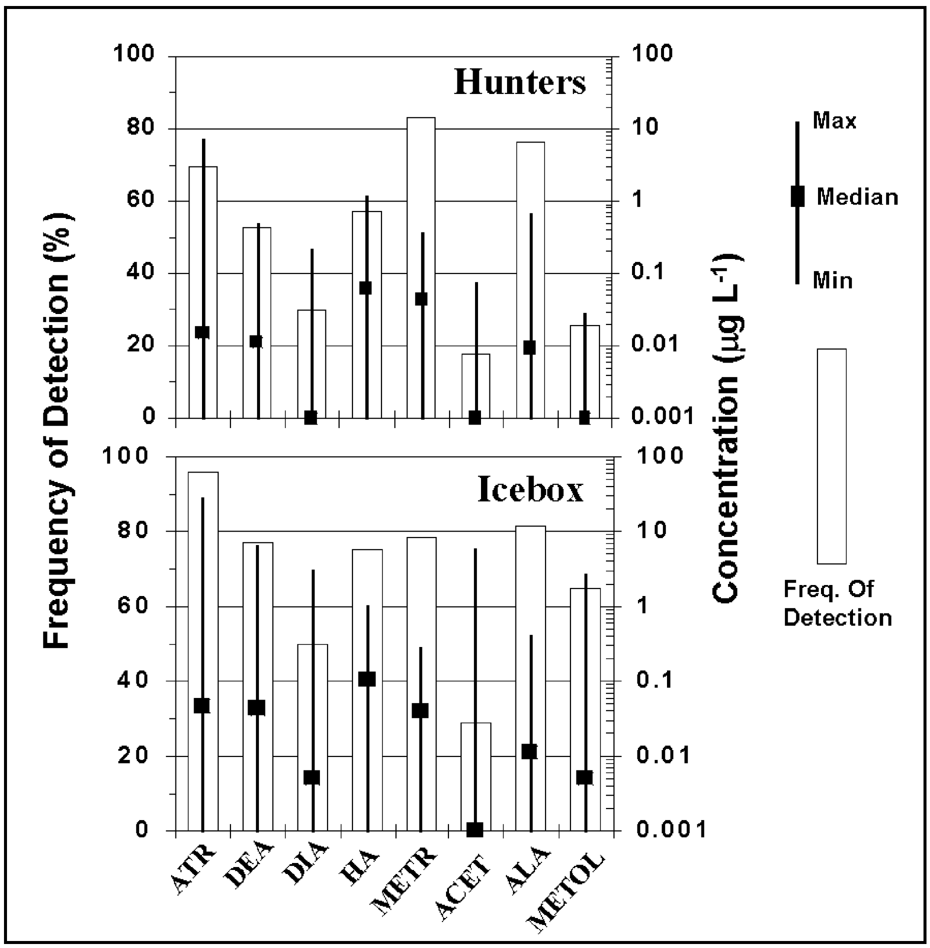

Figure 6. *Frequency of detection (bars) and concentration ranges (lines) of herbicides and atrazine metabolites in Devils Icebox and Hunters Cave from April 1999 to March 2000.*
ATR = atrazine, DEA = deethylatrazine, DIA = deisopropylatrazine, HA = hydroxyatarzine, METR = metribuzin, ACET = acetochlor, ALA = alachlor, METOL = metolachlor

77% of all samples. Alachlor was the next most frequently detected herbicide (81%) followed by metribuzin (79%) and metolachlor (65%). These results were typical for Missouri and midwestern streams, with atrazine, alachlor, and metolachlor all frequently present in Devils Icebox stream (Thurman *et al*., 1991; Blanchard and Lerch, 2000). However, the high frequency of detection for metribuzin was greater than previously reported. The lower detection limits of the method employed in the present study represents a five- to ten-fold improvement over the earlier studies, and this is likely the primary reason for the higher detection frequency observed for metribuzin. In addition, the frequent detections of metribuzin may reflect greater usage than is typical for most watersheds within Missouri or the Midwest.

At Hunters Cave, metribuzin was the herbicide most often detected. Metribuzin was detected in 83% of the samples followed by alachlor (76%) and atrazine (69%). Acetochlor and metolachlor were detected much less frequently in Hunters Cave compared to Devils Icebox. The lower detection frequency of atrazine in Hunters Cave led to a commensurate decrease in detection of its metabolites. Atrazine metabolites were detected in only 30% to 57% of samples collected. The high detection frequency of metribuzin was unusual for northern Missouri streams. While improved analytical methods can partially explain the increase in metribuzin detections, higher than normal metribuzin input to the Hunters Cave recharge area appears likely. This further implies that soybean acreage is the dominant row-crop within the recharge area, which is also supported by the lower detection frequency of corn herbicides, atrazine and acetochlor, compared to the Devils Icebox and other northern Missouri streams (Blanchard and Lerch, 2000).

Although herbicides were frequently detected in both cave streams, the median concentrations for the first year (April 1999 to March 2000) of the study were rather low except in the spring (Figure 6). Median concentrations at both sites were at or below 0.1 ppb for all compounds studied. At both sites the persistent atrazine metabolite, hydroxyatrazine, had the highest median concentrations.

At the Devils Icebox, median concentrations were in the order: hydroxyatrazine > atrazine metribuzin > DEA > alachlor > DIA ≈ metolachlor > acetochlor. At Hunters Cave, median concentrations were in the order: hydroxyatrazine > metribuzin > atrazine > DEA > alachlor > DIA ≈ metolachlor ≈ acetochlor. With the exception of metribuzin, maximum and median concentrations of all herbicides and metabolites were greater at Devils Icebox than Hunters Cave. This indicated that prevailing row crop production practices were having a greater impact on Devils Icebox than Hunters Cave. In addition, the Devils Icebox recharge area apparently has proportionally more corn production than Hunters Cave as indicated by the greater concentrations and detection frequencies of the corn herbicides atrazine, atrazine metabolites, acetochlor, and metolachlor. The higher median metribuzin concentrations at Hunters Cave compared to Devils Icebox was a further indicator of its greater usage within the Hunters recharge area.

Maximum herbicide and metabolite concentrations were observed during the "spring-flush" period from late April through June. This period represents the most vulnerable time for herbicide transport to surface water and consequently to losing streams. Several factors contribute to the spring-flush: (1) application of herbicides generally occurs in April and May; (2) intense thunderstorms are most common during this period; (3) mitigating processes of sorption and degradation have not had sufficient time to significantly reduce the mass of herbicides available for transport; and (4) degradation that does occur during this period results in the formation of mobile metabolites susceptible to surface transport. At both sites, high parent compound levels were observed in only one or two spring runoff events. Other than atrazine and its metabolites, the levels tend to quickly return to low levels (ppb) because of the relatively short half-life of most of these compounds. Atrazine may persist in soils for 30 to 60 days and thus it will maintain higher levels for a longer period of time than the other parent compounds. In addition, atrazine metabolite levels may remain high (0.1 ppb) until late summer or even into the fall in the case of hydroxyatrazine, the most persistent of the compounds analyzed in this study. Although not measured in this study, stable metabolites of alachlor, acetochlor, and metolachlor were likely present at significant levels from late May through early fall given the high levels (1 ppb) of the parent compounds observed during the spring-flush. Alachlor, acetochlor, and metolachlor represent the most commonly used compounds in a class of herbicides known as acetanilides. The acetanilides all degrade via common pathways to their respective oxanilic acid and ethane sulfonic acid metabolites in soils. These metabolites are then quite mobile in soil, and their presence has been reported in ground and surface waters

(Kalkhoff *et al*., 1998). Median annual herbicide concentrations reported for this study were lower than levels reported for samples collected at pre-plant (February to early April) in several other studies (Thurman *et al*., 1991; Donald *et al*., 1998; Blanchard and Lerch, 2000). Donald *et al*. (1998) reported average annual atrazine levels in Goodwater Creek, a stream located about 30 miles to the north of the sites reported here, of 3.88 ppb in 1993 and 2.6 ppb in 1994. These levels are about two to three times greater than the average annual atrazine concentrations at Devils Icebox and 20 to 30 times higher than average annual atrazine levels at Hunters Cave.

Fecal Coliform Bacteria

Levels of fecal coliform bacteria exceeded the U.S. Environmental Protection Agency whole body contact standard (126 cfu/100ml) in four of six quarters at Devils Icebox and two of six quarters at Hunters Cave (Figure 7). Fecal coliform concentrations varied from 60 to 21,920 cfu/100 ml at Devils Icebox, and the highest levels were observed during the second quarter of 1999 and 2000. At Hunters Cave, fecal coliform concentrations varied from 17 to 11,750 cfu/100 ml, with the highest observed levels occurring in the second and third quarters of 2000. In general, fecal coliform levels were similar between sites, but Devils Icebox was higher in four of the six quarters. Furthermore, both cave streams are vulnerable to periodic pulses of high fecal coliform concentrations that may endanger human health because of recreational caving. The large difference in fecal coliform levels observed for the second quarter 1999 sampling were due to differences in flow conditions at the time of sampling. Hunters Cave samples were collected on June 23, 1999, under very low flow conditions; the average daily flow was 0.09 cubic feet per second. Subsequently, there was a runoff event that prevented access to Devils Icebox until June 29, 1999, and this sample set was collected at the tail end of the event when the average daily discharge was 0.96 cubic feet per second. Although the event only reached peak discharge of 5.4 cubic feet per second, the change from baseflow to runoff conditions at this time of year was sufficient to cause the large differences in observed fecal coliform concentrations. The seasonal variations observed at both sites are similar to those reported by Edwards *et al*. (1997) for several small streams in northwest Arkansas in which the highest fecal coliform levels occurred in spring and summer. The range of fecal coliform concentrations reported in this study were within the ranges reported for other studies in similar karst settings in West Virginia (Boyer and Pasquarell, 1999) and Kentucky (Howell *et al*., 1995). In the study by Boyer and Pasquarell (1999), highest fecal coliform concentrations in The Hole Basin Cave System were associated with a tributary known to be directly impacted by dairy cattle production. Median fecal coliform levels in the dairy-impacted tributary, and a site immediately downstream, were the highest in the cave system. However, Edwards *et al*. (1997) reported high fecal coliform (10^2 to 10^6 cfu/100 ml) and streptococcus levels in runoff from grazed or ungrazed fields in northwest Arkansas.

In general, variation in fecal coliform levels was related to stream discharge and water tem-

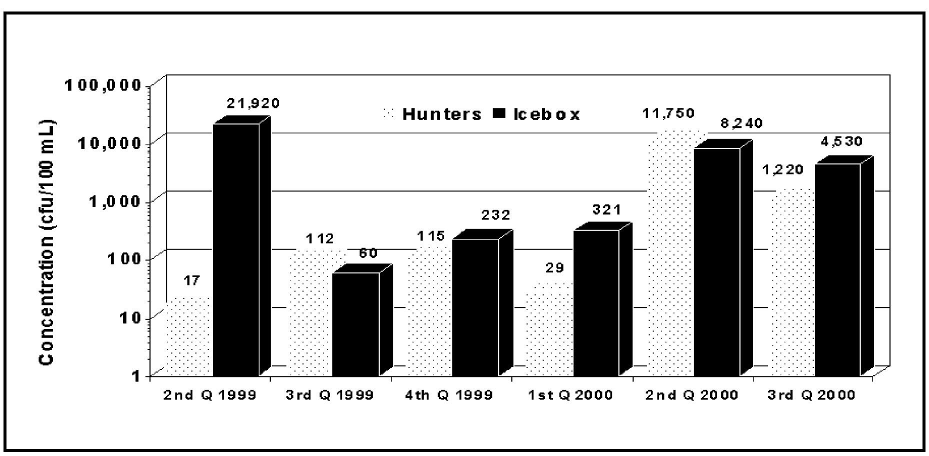

Figure 7. *Quarterly fecal coliform concentrations in Devils Icebox and Hunters Cave from June 1999 to September 2000. Data represents average of seven sites in Devils Icebox and five sites in Hunters Cave. EPA whole body contact standard is 126 cfu/100 ml.*

perature. The highest observed levels occurred under moderate to high flow conditions during warm months, when the stream water temperatures were at or near their annual maxima. There is a strong interaction between these variables. A given amount of discharge results in different levels ofbacteria transported, depending upon the time of year. For instance at Devils Icebox, the second quarter 1999 sample set resulted in 21,920 cfu/100 ml when average daily discharge was 0.96 cubic feet second. Thus, the average fecal coliform density per unit discharge was 22,830 cfu/100ml/cubic feet second, or stated another way, a 1 cubic feet second discharge rate would resulted in an average fecal coliform density of 22,830 cfu/100ml for the second quarter of 1999.For the first quarter 2000 sample set collected on March 21, 2000, the average daily discharge was 1.7 cubic feet second and the fecal coliform density was 321 cfu/100 ml, giving an average bacterial density per unit discharge of 189 cfu/100ml/cubic feet second. Hence, a given unit of discharge transports varying amounts of bacteria based on the season of the year. Since the input sources of fecal coliforms do not vary significantly by season in these watersheds, the interaction between flow and stream water temperature on fecal coliform concentrations must reflect differences in coliform survival in the soil and water. It is important to note that the data presented here do not provide any direct indication ofbacterial sources. However, the two watersheds collectively have a population of approximately 38,000 people, based on the 2000 census, and the majority of the residences have on-site sewage systems. It is therefore reasonable to assume that a significant proportion of the fecal coliforms are derived from humans. Other significant sources include livestock, particularly cattle and horses, and wildlife.

Summary and Conclusions

The combination of greater flow and consistently greater contaminant concentrations within the Devils Icebox watershed results in considerably greater annual transport of contaminants compared to Hunters Cave watershed. As a crude estimate, the median concentrations of total nitrogen and phosphorus, atrazine, and acetanilide herbicides were multiplied by the total annual flow in order to compute contaminant mass transport through each cave on an annual basis (Figure 8). The Devils Icebox has about four times as much nitrogen, phosphorus, and acetanilide herbicides and seven times as much atrazine transported through its cave stream compared to Hunters Cave on an annual basis. Computation

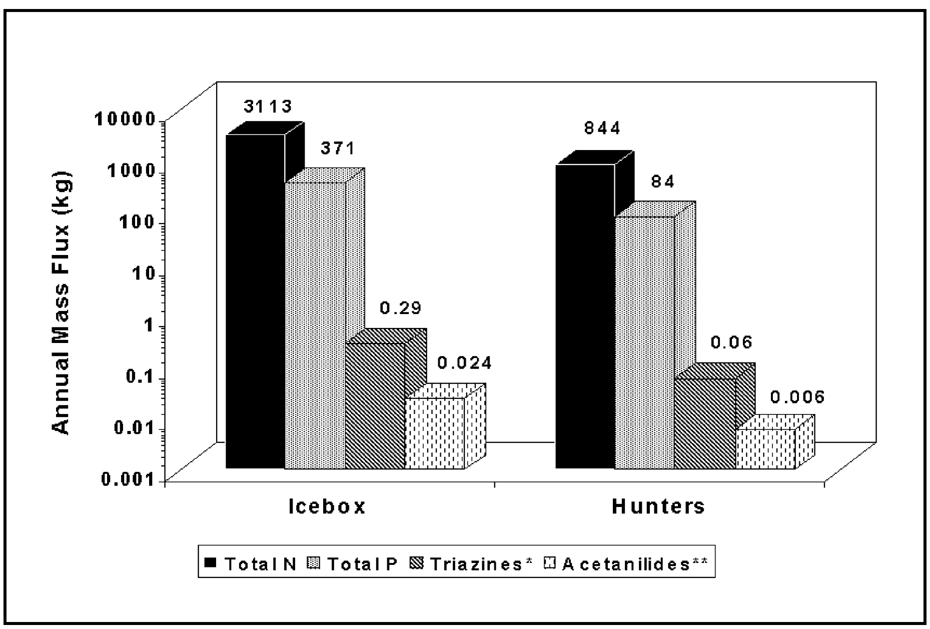

Figure 8. *Estimated annual mass flux of nutrients in Devils Icebox and Hunters Cave for year one (April 1999 to March 2000). *Sum of atrazine plus metabolites. **Sum of alachlor, acetochlor, and metolachlor.*

of mass flux is also useful for providing perspective to the relative mass transport of nutrients compared to herbicides. Nutrient transport in either watershed is three to five orders of magnitude greater than herbicide transport. Given the similarity in land-use and land cover in the two watersheds, it is apparent that prevailing agricultural and land-use practices are resulting in consistently greater water quality degradation in the Devils Icebox watershed. Furthermore, targeting and implementation of best management practices needs to be more strenuously pursued in the Devils Icebox watershed, but Hunters Cave watershed will require continued vigilance to prevent further water quality degradation. The first full year of nutrient and herbicide data indicates that, overall, contamination is generally as low or lower than most of the agricultural watersheds of northern Missouri, particularly with respect to herbicide contamination. However, the observed levels are still a cause for concern given the greater sensitivity of cave-adapted aquatic species that are impacted by the contamination.

To date, the contaminant of greatest concern to water quality in both watersheds is fecal bacteria. Existing data clearly show that excessively high fecal bacteria levels occur in both cave streams and these high levels are associated with runoff events during warm weather when bacterial survival is apparently greater. Because of the recreational uses of the caves, the levels of bacteria present potential human health threats. Likely sources of fecal bacteria are livestock, improperly functioning on-site sewer systems, and wildlife. The data presented in this report do not provide bacterial source-tracking information.

From a management and education perspective, there are several implications that stem from this work. First and foremost, it needs to be made clear to land managers, politicians, farmers, and homeowners that caves in losing stream basins are directly affected by surface land-use activities. The notion that caves are isolated systems protected from surface activities must be dispelled in order to manage losing stream basins in a manner that preserves the cave ecosystem and protects human health. This research adds to a growing body of literature regarding the impact of surface land-use activities on water quality in karst basins. In this study, the current land-use activities that are having the most negative impact on the cave streams are agricultural production and on-site sewer systems. Current management efforts should focus on implementing agricultural best management practices that reduce contaminant transport from row-cropped fields and minimize negative impacts of livestock on streams. Improved maintenance and design of on-site sewers also needs to be vigorously pursued to mitigate fecal bacteria inputs to these basins.

Future management considerations for these basins should focus on impending urbanization. Since 1990, the greater Bonne Femme watershed, which encompasses both of the karst basins reported in this study, has experienced a 40% increase in population, and future growth from the cities of Columbia and Ashland, Missouri, are anticipated to heavily impact these basins. Urban land-use management planning should include the following components: (1) local governments need to adopt policies and procedures for new development that provide special protections for karst basins; (2) developers, builders, and homeowners need to implement best management practices (for example: erosion control during construction, storm water control strategies, minimizing impervious surface, environmentally friendly lawn care, and the like.); and (3) technical and financial assistance should be provided to developers and homeowners to further encourage adoption of best management practices. These basic objectives were incorporated into a Section 319 grant submitted by the Boone County Commission for the purpose of comprehensive land-use planning to protect water quality in the Bonne Femme watershed.

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