Water Quality of Hunters and Devils Icebox Caves

Year 2 Annual Report, February 2000-March 2001

Since inception of the project through March 2001, nutrient and herbicide analyses have been completed on 271 samples from Hunters Cave and 224 from Devils Icebox. This report details some key findings and progress made during the second year of the project, as well as plans for the third, and final, year of the project.

Changes to Runoff Event Sampling Protocol

In August 2000, a new Sigma 900 autosampler was installed at the Devils Icebox. With the deployment of this new autosampler, both locations now had comparable instruments with greater capabilities in regards to runoff sampling protocols. Up to this point in the study, runoff samples were collected at 30 minute intervals for 12 hours, giving a total of 24 samples over the 12 hour period. With the information acquired over the first 1.5 years of monitoring it was evident that runoff events generally occur over a much longer period than 12 hours, resulting in no samples at the “tail-end” of runoff events. At Hunters Cave, most runoff events last from 18-30 hours and at the Icebox from 24-48 hours. Therefore, a variable time interval sampling protocol was initiated to improve sampling of runoff events. The new sampling protocols were designed to sample over 24 hours at Hunters Cave and 36 hours at the Icebox. In addition, the program was designed to take samples very frequently early in an event, when contaminant concentrations change most rapidly, with increasing interval length as the event progresses. Sampling intervals vary from 5 minutes to 4 hours. The sampling intervals were chosen to cover the same percentage of the events to ensure comparable sampling representation at each site (Fig. 1).

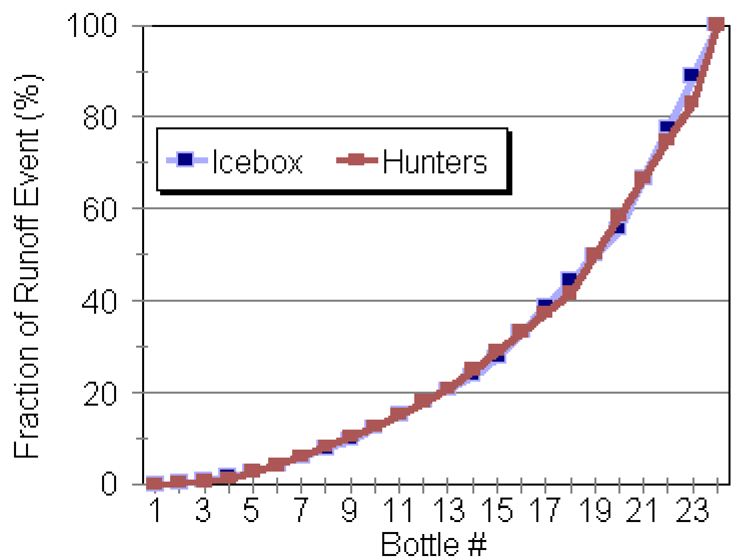


Figure 1. Variable time interval runoff sampling initiated in August, 2000.

Key Findings

Hydrology

Flow estimates are based on the stream height data (measured at 5 min. intervals) which is calibrated to a section of the cave stream with known channel width. For Hunters Cave, flow velocity continues to be estimated with Manning's equation (Eqn. 1),

$$(1) \qquad V = (1.49/n)*R^{2/3}*S^{1/2}$$

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. 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 flow can be estimated (Fig. 2). Flow estimates for the Icebox were based on a previously developed rating curve in which stream height was correlated directly to flow. The intent for Year 2 was to also develop a rating curve for Hunters Cave, but this has

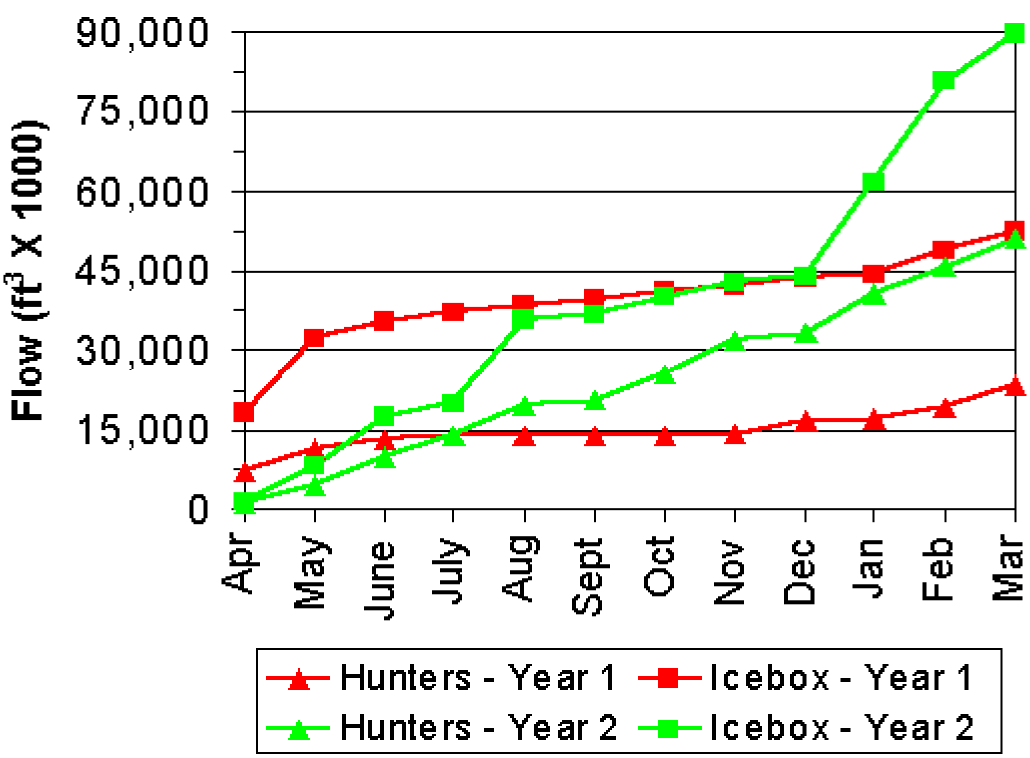


Figure 2. Cumulative monthly flow from Devils Icebox and Hunters Cave. Year 1 - April 1999 to March 2000; Year 2 - April 2000 to March 2001.

proven to be impossible. The primary obstacle to development of a rating curve is that during periods of high flow the cave is inaccessible because of dangerously high flow in Bass Creek. Therefore, I will continue to estimate flow using Manning's equation combined with the stream height and channel geometry for the duration of the study.

Estimated flow for Years 1 and 2 showed very different seasonal distributions (Fig. 2) 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 flow through the spring and winter months, with this period including the major rainfall and runoff events for Year 1. However, flow for the 5 months from July-November 1999 was extremely low in both caves because of the prevailing drought conditions. Total flow for Year 1 was approximately 52,000,000 ft^3 for the Icebox and 23,000,000 ft^3 for Hunters. Thus, the Icebox had about 2.3 times more flow than Hunters. Average monthly flow rates were 0.7 cfs at Hunters and 1.7 cfs at the Icebox. Total precipitation for Year 1 was about 28 in. in each watershed. The greater average flow of the Icebox reflected its much greater peak flow during runoff events, and its consistently greater flow during the drought period. Apparently, the Icebox watershed has a much larger storage capacity than that of Hunters.

In Year 2, flow was very low during April and early May 2000. For example, flow estimates for Hunters Cave were just under 7,000,000 ft^3 in April 1999 but only 1,100,000 ft^3 in April 2000. The differences were even more extreme for the Icebox with an estimated flow of 18,000,000 ft^3 in April 1999 compared to just 1,400,000 ft^3 in April 2000. However, unlike most years, the summer of 2000 was characterized by frequent and intense rainfall, resulting in steady increases in cumulative flow through the period. In fact, Hunters showed an almost linear increase in cumulative flow throughout Year 2. The largest event of Year 2, and so far in the study, occurred from August 7-9, 2000. Estimated flow for this event was just over 7,000,000 ft^3 at the Icebox, with a peak flow rate of about 200 cfs (cubic feet per second), and 1,700,000 ft^3 at Hunters Cave, with a peak flow rate of 55 cfs. 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' into the cave. Another interesting feature of Year 2 hydrology was the number of significant runoff events during January through March 2001. At least 6 significant runoff events occurred during this period at each site, with corresponding increases in flow. During February 2001, the Icebox had 19,300,000 ft^3, the highest monthly flow to date. Total flow for Year 2 was about 90,000,000 ft^3 at the Icebox and 51,000,000 ft^3 at Hunters, indicating that the Icebox had about 1.8 times as much flow as Hunters in Year 2. Average monthly flow rates were 2.7 cfs at the Icebox and 1.6 cfs at Hunters. Total precipitation for Year 2 was about 42 in. in each watershed. As in Year 1, the greater average flow of the Icebox resulted from the much greater total peak runoff flow rates and greater duration of runoff events. However, Hunters Cave can exhibit monthly average flow equal to or greater than that of the Icebox. For example, Hunters had consistently greater average and total flow from October through December 2000 apparently due to slightly greater rainfall and more intense runoff events.

Cave Watersheds and Land-Use

Hunters Cave watershed has not been rigorously 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 (Fig. 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

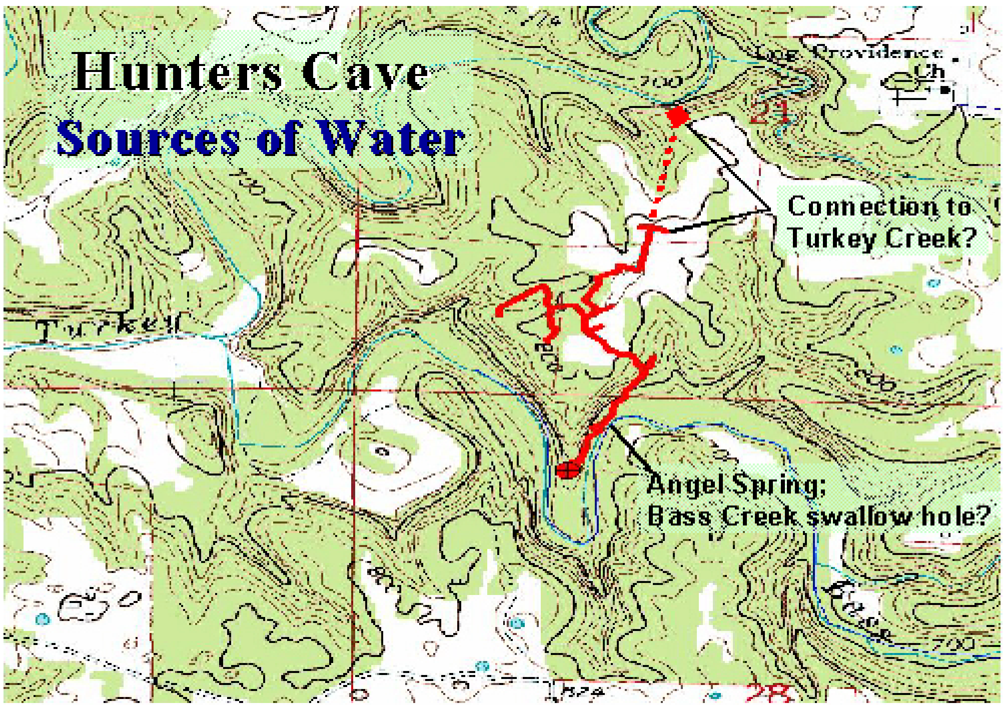


Figure 3. Hunters Cave line plot from the 1958 survey overlaid on the topographic map (Ashland Quad).

assuredly place the cave in close proximity to Turkey Creek (Fig. 3). From this delineation, the estimated drainage area of Hunters Cave is 20.6 mi^2, an area 1.6 times greater than that of the Devils Icebox watershed. Given the flow data (Fig. 2), Hunters Cave stream captures a much smaller proportion of Turkey and Bass Creeks compared to the proportion of Bonne Femme Creek captured by the Icebox cave stream.

Using this tentative delineation for Hunters Cave watershed, land-use/land cover data were determined using ArcView GIS (version 3.2) and recently available 30 m LANDSAT data from 1991-1993 (Fig. 4). 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. From the ArcView analysis, Hunters Cave watershed is comprised primarily of grassland, row-crops, and forest (Fig. 4), with the former two land-uses accounting for 80% of the area within the watershed. 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

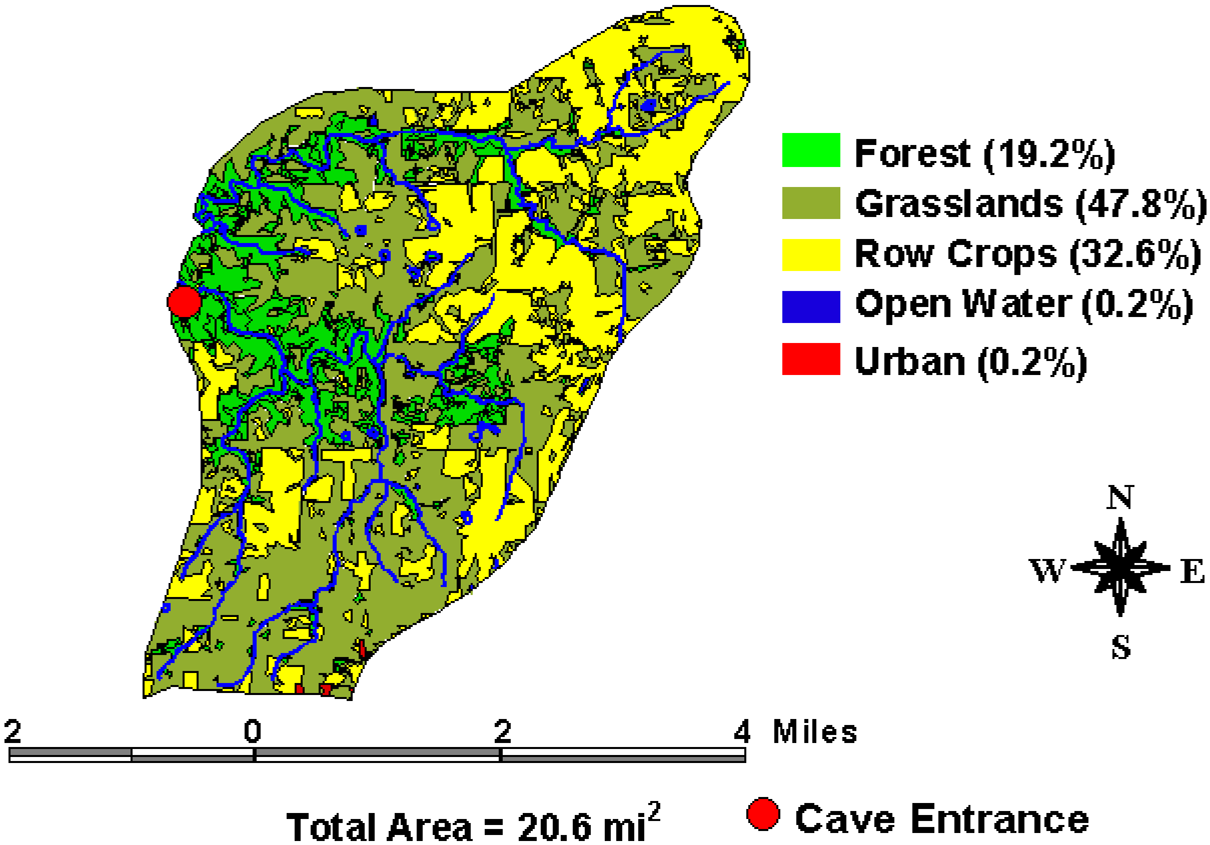


Figure 4. Land-use/land cover for Hunters Cave watershed based on 30 m LANDSAT data from 1991-1993.

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.

The Devils Icebox watershed has been more rigorously delineated by dye-tracing and other hydrologic studies that have proven the link between the main cave stream and Bonne Femme Creek, as well as the hydrologic connection to the Pierpont sinkhole plain (Vineyard, 1983; St. Ivany, 1988; Wicks, 1997) (Fig. 5). The Icebox watershed is approximately 12.5 mi^2 and is comprised of 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 (Vandike, 1983; Wicks, 1997). Land-use/land cover data for the Icebox watershed shows a nearly identical distribution of grassland, row-crop, and forest areas to that of the Hunters watershed. Given the similarities in land-use between the two watersheds, differences in stream water contamination can be attributed to management choices by landowners such as crop type, fertilizer and pesticide input levels, timing of chemical application, type and frequency of tillage, intensity of livestock grazing (cattle appear to be the only significant type of livestock within either of the watersheds), and implementation (or the lack) of conservation practices.

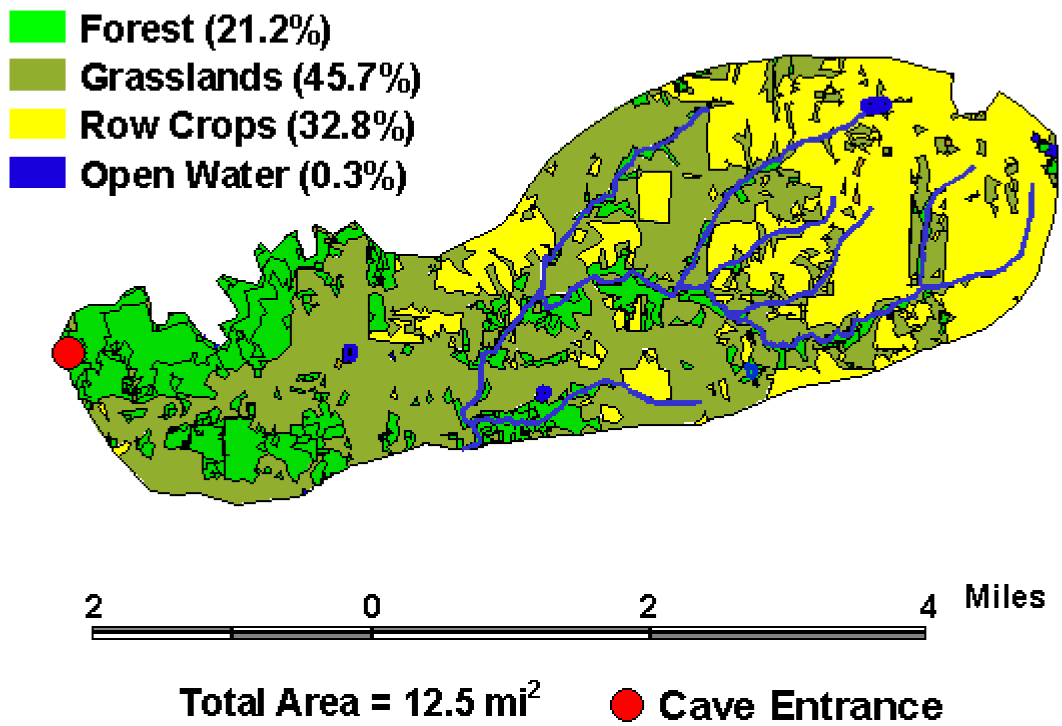


Figure 5. Land-use/land cover for Devils Icebox watershed based on 30 m LANDSAT data from 1991-1993.

Contaminant Levels

Nutrients

Concentrations of total nitrogen (N) and phosphorus (P) were consistently higher in the Icebox compared to Hunters Cave from April 1999 to March 2000 (Fig. 6). Presently, land-use within the Hunters drainage basin is not resulting in significantly elevated levels of these nutrients except under high flow conditions in winter and early spring. Total N and P levels in the Icebox indicate a more significant and negative impact of land management on water quality within this watershed. Median and peak nutrient concentrations in the Icebox are 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 sewer systems. A previous study at the Icebox from 1982-84 showed average nitrate (total N was not determined) of 2.1 ppm and average total P of 0.1 ppm. The median and average total N at the Icebox in this study suggest that N levels have decreased somewhat since nitrate accounted for about 60% of the total N in samples from Year 1 of this study. Assuming this same proportion for the 1982-84 study, estimated total N would have been 3.5 ppm. While total N levels have likely decreased over the last 17-19 years, total P levels have increased by about 3 fold over this same time period (Fig. 6).

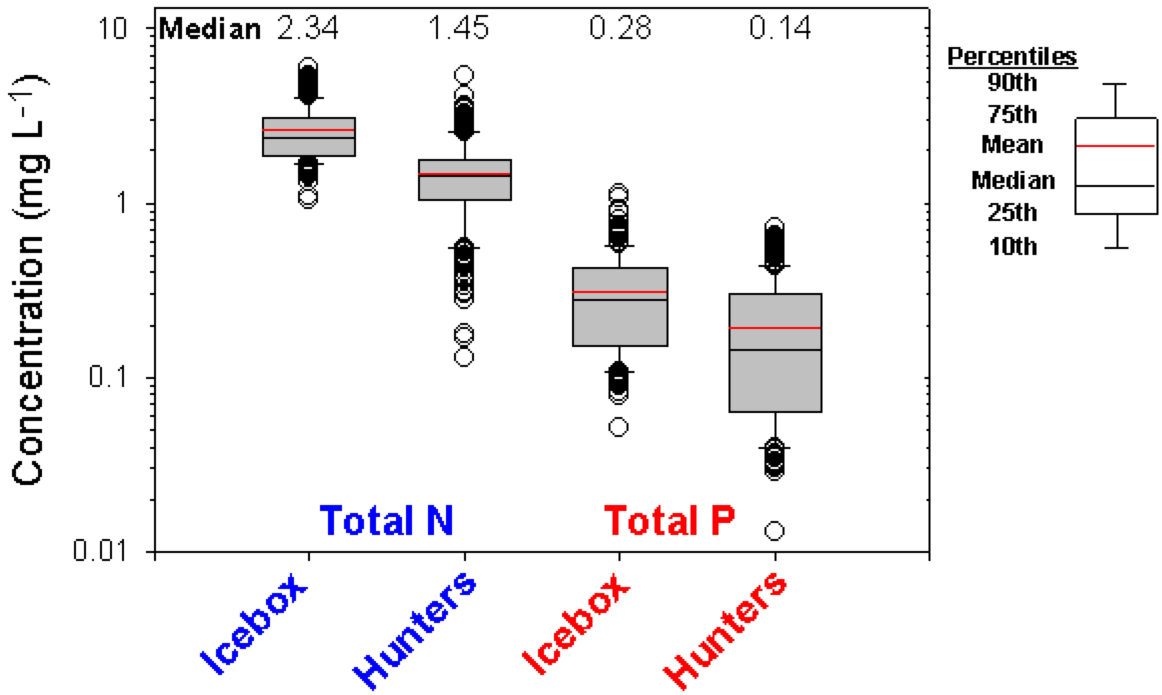


Figure 6. Total nitrogen and phosphorus levels in Devils Icebox and Hunters Caves from April 1999 to March 2000.

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

Herbicides

Herbicide levels were generally very low in both cave streams during Year 1 with the exception of several samples collected during May 1999 (Fig. 7). At Hunters Cave, several of the commonly used soybean and corn herbicides were often detected, with metribuzin, alachlor, atrazine, and two atrazine metabolites (deethylatrazine and hydroxyatrazine) detected in more than 50% of the samples. Maximum herbicide levels only exceeded 1 ppb for atrazine (6 ppb) and hydroxyatrazine (1.1 ppb), and median herbicide concentrations were all less than 0.1 ppb. At the Icebox, herbicides were detected more frequently with atrazine, deethylatrazine, hydroxyatrazine, metribuzin,

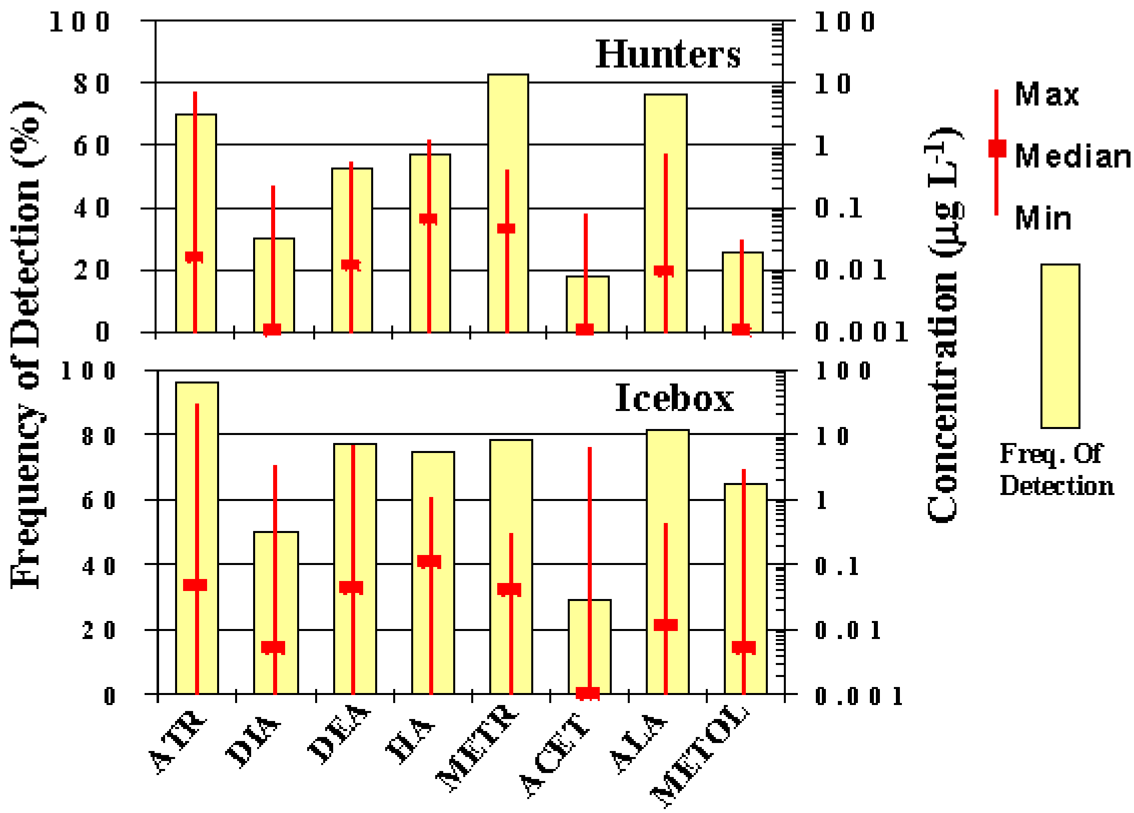
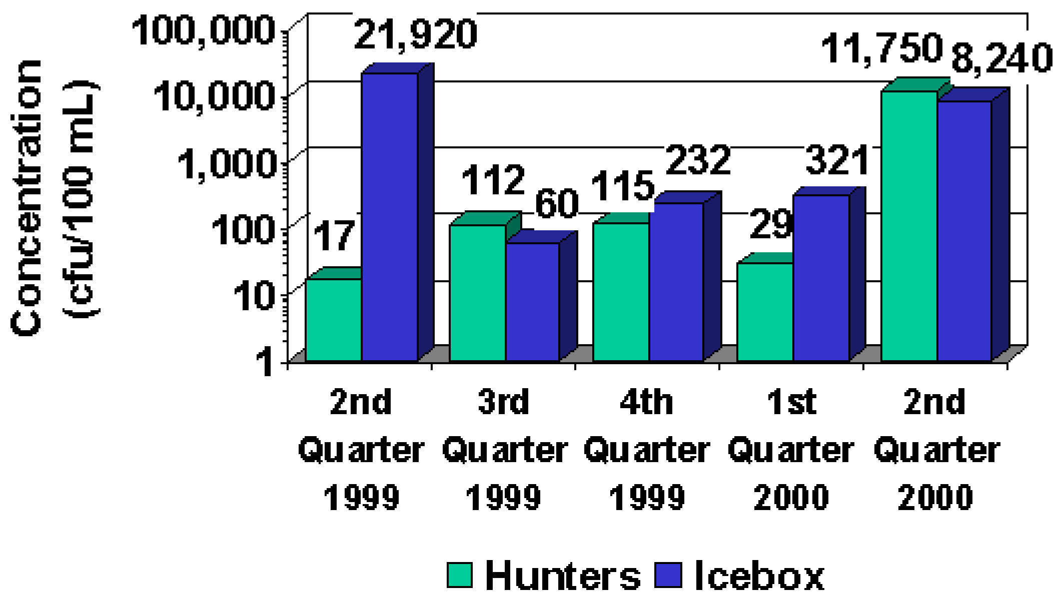


Figure 7. Herbicide frequency of detection and concentrations for Year 1 (April 1999 - March 2000). ATR = atrazine; DIA = deisopropylatrazine; DEA = deethylatrazine; HA = hydroxyatrazine; METR = metribuzin; ACET = acetochlor; ALA = alachlor; METOL = metolachlor.

alachlor, and metolachlor detected in 60% or more of the samples. Maximum concentrations were also higher at the Icebox: atrazine, 28 ppb; deisopropylatrazine, 2.9 ppb; deethylatrazine, 6.2 ppb; hydroxyatrazine, 0.99 ppb; acetochlor, 5.8 ppb; and metolachlor, 2.6 ppb. Although the maximum herbicide concentrations in the Icebox were greater, indicating higher inputs, median levels of all herbicides and metabolites were 0.1 ppb or less for Year 1. Maximum concentrations at both sites were associated with runoff events following herbicide application in May 1999, and concentrations quickly decreased to low levels by June 1999. The frequent but low levels of herbicides and metabolites in both caves suggests long-term herbicide usage but limited mass input in both watersheds. Because of the relatively small watershed areas, the applied mass of herbicides is fairly small resulting in the brief period of high concentrations followed by a rapid decline in levels. Another important consideration in small watersheds will be the possible “crop rotation” effect on herbicide concentrations. Since corn-soybean rotations are the most commonly employed, it is possible that the 1999 growing season represented a year in which soybeans were the predominant row-crop, and the 2000 growing season will have greatly increased corn acreage, with resulting increases in stream water concentrations of the commonly used corn herbicides (atrazine, acetochlor, and metolachlor).

Fecal Coliform Bacteria

From June 1999 to June 2000, five sets of quarterly samples were collected at various locations within each cave. At Hunters Cave, samples were collected at 5 sites: entrance; Angel Spring; Watercrawl, Iron Dome, and Big Room. At the Icebox, samples were collected at 7 sites: entrance, Polly's Pot, Rollercoaster, 1810R, cave stream below 2210L; 2210L; and cave stream above 2210L. Fecal coliform concentrations are reported as the average of these sites for each quarterly sample set (Fig. 8). Fecal coliform levels for the first four sets of samples showed low levels at Hunters Cave, but all four sample sets were collected under low flow conditions (<0.5 cfs), except the 1st quarter 2000 samples in which flow at the entrance was about 2 cfs. However, very high fecal coliform levels were observed for the 2nd quarter 2000 samples which were collected under high flow conditions (4 cfs). At the Icebox, the high levels of fecal coliforms observed for the 2nd quarter 1999 and 2000 sets coincided with moderate flow conditions (1-2 cfs) following runoff events the day before sampling. The 3rd and 4th quarter 1999 and 1st quarter 2000 samples were taken under low flow conditions (0.6 cfs), and much lower levels of fecal coliform were observed. However, only the 3rd



EPA Standard for Whole Body Contact is 126 cfu 100 mL^{-1}

Figure 8. Fecal coliform levels in Devils Icebox and Hunters Caves from June 1999 to June 2000.

quarter 1999 sample set was under the whole body contact standard. The main conclusions from this data were: 1) both caves can have extremely high fecal coliform levels during high flow, warm weather conditions; 2) the Icebox had consistently greater fecal coliform levels compared to Hunters Cave; 3) the Icebox generally exceeded the whole body contact standard regardless of flow conditions or time of year; and 4) low flow, cold weather conditions result in lowest observed fecal coliform levels.

The data in Figure 8 provided the impetus to expand the fecal bacteria monitoring to the major streams in the Bonne Femme and Little Bonne Femme watersheds, as well as to increase the frequency of sampling. Key questions left unanswered by the quarterly sampling data were: 1) Are fecal bacteria levels high under cold weather, high flow conditions?; 2) Is the problem widespread in the streams that contribute to the caves as well as others within adjacent watersheds?; 3) How do fecal bacterial levels change during the course of a runoff event?; and 4) How much does the Pierpont sinkhole plain contribute to bacterial levels in the Icebox? The new monitoring plan calls for bi-weekly (i.e., twice weekly) sampling one month out of each quarter at 8 locations: Hunters cave stream, Icebox cave stream, Clear Creek, Gans Creek, Bonne Femme Creek at US 63, Turkey Creek, Bass Creek, and Bonne Femme Creek at Nashville Church Rd. (downstream of the confluence of Turkey, Bass, and upper Bonne Femme Creeks). Bacterial analyses include quantitation of fecal coliforms for all sample sets and quantitation of total coliforms and *E. Coli* on half of the sample sets (i.e, once per week). Monitoring was initiated in January-February 2001.

Results of the first sample set show a very strong positive correlation between stream flow and *E. Coli* levels in all streams (Fig. 9). Two major rainfall events provided ideal conditions for contrasting the impact of flow on fecal bacterial levels during the sampling period. The strong relationship between stream flow and fecal bacteria has two important implications for fate and transport of fecal bacteria: 1) the observed high levels during winter runoff events implies a continuous source of bacteria given that survival in or on the soil would be expected to be only a few days during cold weather;

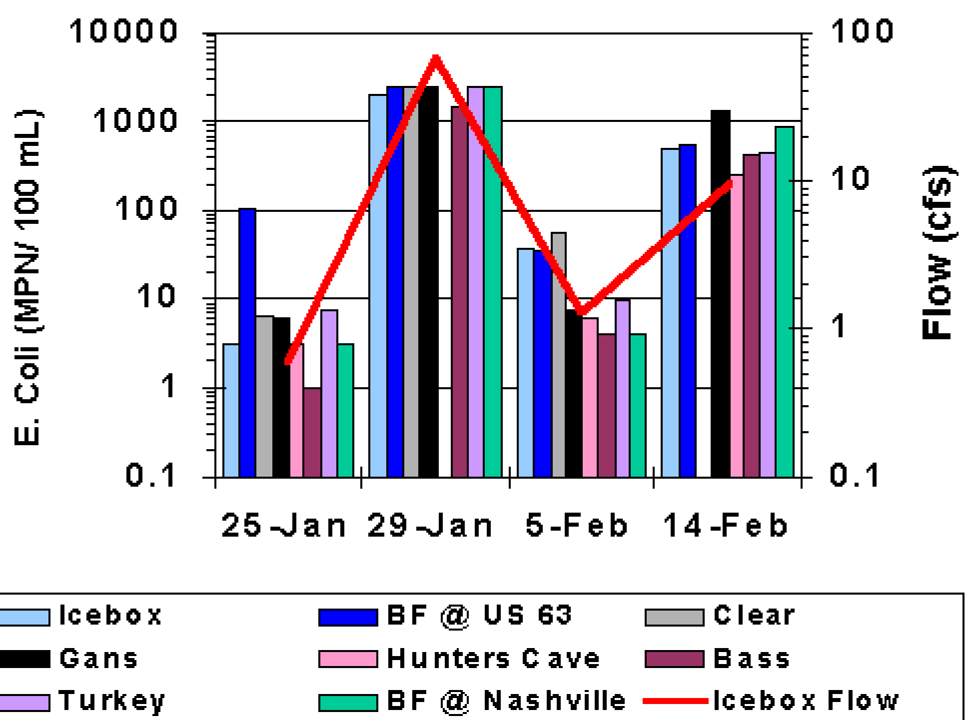


Figure 9. *E. Coli* levels of eight southern Boone County streams in January and February 2001. Daily average flow at the Devils Icebox is shown by the red line as a relative indicator of flow conditions at sampling.

and 2) the observed bacterial levels are consistent with transport of contaminants that are strongly bound to soils (and therefore are subject to transport via surface runoff), and the source(s) are broadly distributed throughout all watersheds monitored. Since the losing surface streams of the Bonne Femme watershed are the primary sources of water to the caves, the cave streams merely reflect the contamination of the surface streams. Even with the relatively long flow path of the Icebox cave stream (over 4 miles), the residence time of water within the cave during runoff events is insufficient to cause a significant die-off of bacteria. This is supported by the fact the bacterial levels under runoff conditions in Bonne Femme Creek at US 63 were essentially the same as levels observed at the entrance to the Icebox. Another important finding was the *E. Coli* levels in Bonne Femme Creek at US 63 were equal to or greater than the Icebox cave stream under low flow conditions (January 25 and February 5, 2001 samples). If contamination originated from the Pierpont sinkhole plain, then bacterial levels should have increased along the flow path from Bonne Femme at US 63 to the cave entrance since the only significant source of water between these points would be the sinkhole plain.

Summary

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 N and P and atrazine were multiplied by the total annual flow in order to compute contaminant mass transport through each cave on an annual basis (Fig. 10). A more detailed determination of annual mass flux will be made based on individual sample concentrations and flow measurements. The Icebox has about 4 times as much N and P and 7 times as much atrazine transported

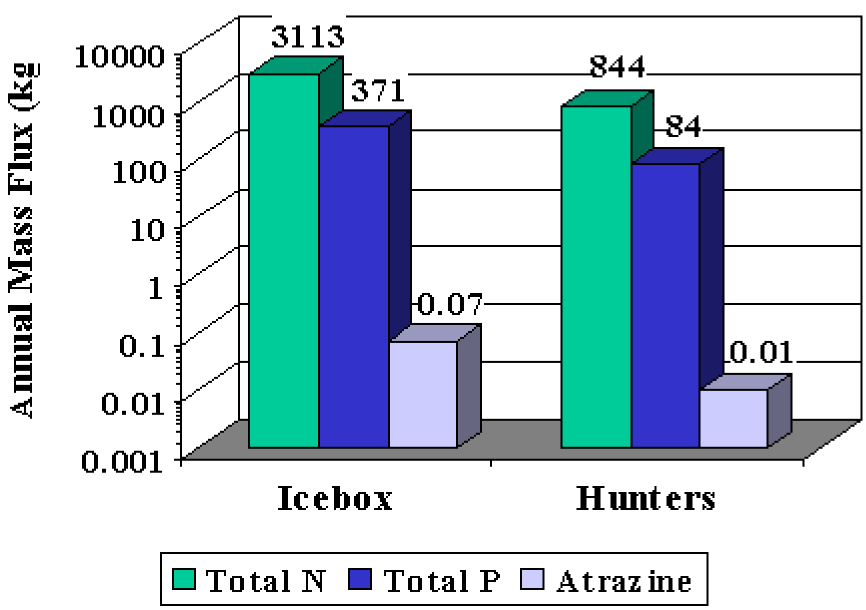


Figure 10. Estimated annual mass flux of nitrogen, phosphorus, and atrazine for Devils Icebox and Hunters Caves. Year 1 - April 1999 to March 2000.

through its cave stream compared to Hunters Cave on an annual basis. Computation 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 atrazine transport. Given the similarity in land-use/land cover in the two watersheds, it is apparent that prevailing agricultural practices are resulting in consistently greater water quality degradation in the Icebox watershed. It is further apparent that targeting and implementation of best management practices needs to be more strenuously pursued in the 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 (Donald et al, 1998; Blanchard and Lerch, 2000). 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 significant year-round inputs of fecal bacteria lead to excessively high fecal bacteria levels under runoff conditions. Because of the recreational uses of these streams, the levels of bacteria present potential human health threats during periods of high flow, even several days after peak flow rates. Likely sources of fecal bacteria are livestock, improperly functioning on-site sewer systems, and wildlife. The data presented in this report provide no information about bacterial sources. As Outstanding State Resources, Bonne Femme, Bass, and Turkey Creeks are, in theory, afforded protection from land-use activities that will result in water quality degradation. Obviously, detrimental land-use activities are currently in practice within all three watersheds, and they are resulting in water quality degradation.

Year 3 Plans

No significant changes are planned for the third, and final, year of the study with respect to hydrologic and contaminant monitoring. Collection, analysis, and interpretation of hydrologic and contaminant data will remain the primary focus of the study. Preparation of peer-reviewed manuscripts will begin in earnest during this last year of data collection. Additional fundamental hydrologic work to be accomplished includes: 1) dye-tracing to definitively establish the hydrologic link between Turkey and Bass Creeks to the Hunters Cave stream; 2) qualitative analysis for the presence optical brighteners which would establish hydrologic links to anthropogenic sources of water, such as on-site sewers; and 3) completion of the survey of the main stream passage in Hunters Cave to determine the proximity of the cave stream to Turkey Creek.

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