

QUALITY OF STORM-WATER RUNOFF IN THREE WATERSHEDS IN ELIZABETHTOWN, KENTUCKY

By Rene Garcia

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To obtain
acre	4,047	square meter
	0.4047	hectare
	0.004047	square kilometer
cubic foot (ft ³)	0.02832	cubic meter
foot (ft)	0.3048	meter
foot per second (ft/s)	0.3048	meter per second
gallon (gal)	3.785	liter
inch (in.)	2.54	centimeter
mile (mi)	1.609	kilometer
mile per day (mi/d)	1.609	kilometer per day
square mile (mi ²)	2.590	square kilometer

Degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) by use of the following equation: $^{\circ}\text{F} = (9/5)(^{\circ}\text{C}) + 32$.

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929--a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviated water-quality units used in this report: Chemical concentrations and water temperature are given in metric units. Chemical concentration is given in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million.

Bacteria densities are expressed as number of colonies per 100 milliliters of water (col/100 mL).

Other abbreviations used in this report:

mL	milliliters
2,4-D	2,4-Dichlorophenoxy-acetic acid
2,4-DP	2,4-Dichlorophenoxy-propionic acid
BTX	benzene, toluene, and xylenes
MCL	Maximum Contaminant Level
PGC	portable gas chromatograph
SMCL	Secondary Maximum Contaminant Level
VOC	volatile organic compounds

The use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

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By Rene Garcia

ABSTRACT

The quality of storm-water runoff and its potential effect on the quality of ground water were investigated in three small watersheds in the mature karst terrane of Elizabethtown, Ky. The watersheds are tributaries to Valley Creek, a losing stream. Previous dye-trace studies have determined that specific improved and unimproved sinkholes, Valley Creek, and municipal supply wells and springs are hydraulically connected.

The study results indicate that densities of fecal-coliform bacteria in storm-water runoff from the watersheds are high and are a potential source of contamination for the receiving streams and for ground water. Densities of fecal-coliform bacteria ranged from more than 500 to more than 60,000 colonies per 100 milliliters of sample water.

Herbicide transport from the study area is another potential source of contamination. Herbicides such as Dicamba, Prometon, and others were reported in runoff samples from one or more of the watersheds. Concentrations of herbicides ranged from less than 0.1 to 7.2 micrograms per liter and were largest in runoff samples from the suburban watershed.

Loads of selected constituents were estimated on the basis of water-quality analysis of storm-water runoff samples collected from the watersheds during the period May 1990 through July 1991. Loads indicate that storm-water runoff from watersheds A and B, which have a greater housing density than watershed C, transported the largest amounts of major ions, nitrogen, and metals; however, yields (loads per square mile) reveal that roadside deposition does not seem to be a significant source of metals in storm-water runoff from the three watersheds.

The concentration of tetrachloroethylene (6.3 micrograms per liter) in a first-flush, storm-water runoff sample from a watershed with mixed land uses exceeded the maximum contaminant level (MCL) for finished drinking water of 5.0 micrograms per liter established by the U.S. Environmental Protection Agency. Concentrations of inorganic constituents in the composite runoff samples, however, did not exceed MCL's. The range of concentrations of selected major ions, nutrients, metals, volatile organic compounds, and herbicides measured in the runoff samples were, in general, comparable to the ranges reported for spring and well samples collected in the study area as part of previous investigations. The range of concentrations for residue of dissolved solids was considerably lower in runoff composite samples when compared to the range reported for water samples from springs and wells.

INTRODUCTION

Approximately 50 percent of the terrane of Kentucky and Tennessee is karst. Karst is a type of topography formed in limestone, gypsum and other soluble rocks, and is characterized by sinkholes, caves, and underground drainage. In many karst areas, it is a common practice to construct drainage wells or to modify sinkholes for drainage of storm water. Modification of sinkholes can enhance the transport of water from the land surface to the natural subsurface conduit system. The U.S. Environmental Protection Agency (USEPA) has classified "improved" or modified sinkholes and drainage wells as Class V injection wells regulated under the Safe Drinking Water Act (U.S. Environmental Protection Agency, 1990a). Because of the rapid and direct infiltration of surface runoff, storm-water runoff from watersheds having various land uses has the potential to adversely affect ground-water quality in karst terrane. Approximately 65 percent of the water used by the city of Elizabethtown, Ky. for public supply is obtained from wells and springs in karst terrane. Karst terrane in the study area has, in addition to the above mentioned characteristics, sinking streams, and well-integrated subsurface conduit systems. Results from dye-trace studies have demonstrated connections between surface water and ground water used for public water supply in the Elizabethtown area. Knowledge of the physical, chemical, and bacteriological quality of storm-water runoff is needed to evaluate the quality of surface and ground waters in karst terrane. To meet these needs, the U.S. Geological Survey (USGS) designed and conducted this study in cooperation with the USEPA.

Purpose and Scope

The report describes selected physical, chemical, and bacteriological characteristics of storm-water runoff in Elizabethtown, Ky. Three urban watersheds within the drainage basin of Valley Creek, a losing stream, were selected for this investigation. Hydrologic data were collected to characterize and quantify runoff from three watersheds during selected storm events for the period May 1990 through July 1991. Loads and yields were computed and used to determine if storm-water runoff from primarily residential watersheds have the potential to affect ground-water quality.

Acknowledgments

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DESCRIPTION OF STUDY AREA AND WATERSHED LAND USES

The watersheds investigated during this study are within the drainage basin of Valley Creek, a tributary of the Nolin River, near Elizabethtown, Hardin County, in north-central Kentucky (fig. 1). The study area lies within the Interior Low Plateau physiographic province (Fenneman, 1938), which is characterized as a broad, gently rolling karst plain that slopes to the southwest. This mature karst terrane includes numerous sinkholes that contribute water directly to an underlying, well-developed, conduit-flow aquifer system. This aquifer system drains to numerous springs and provides base flow in the gaining reaches of Valley Creek and other streams in the area. In places, Valley Creek has losing reaches that redirect water back to the karst aquifer system. Hydrologic connections between specific improved and unimproved sinkholes, Valley Creek, and the springs and wells used for public water supply by Elizabethtown were identified by Mull and Lyverse (1984). The results of spring-discharge measurements indicate that ground-water flow in the study area can reach velocities of 23 mi/d (1.4 ft/s). Such rapid ground-water velocities are achieved due to the large component of conduit flow through secondary openings in the limestone. In general, the southwesterly ground-water flow coincides with the slope of the land surface, and, with few exceptions, the chemical quality of the ground water was found acceptable for domestic purposes (Plebuch and others, 1985).

Sites for ground-water sampling were not selected because ground-water discharge to the intermittent drainages is negligible. The potentiometric surface of the carbonate aquifer lies 20 to 60 feet below land surface in most areas, as indicated by water-level mapping (Lambert, 1979; Mull and others, 1988). Discharge from the aquifer is controlled by the elevations of the main stem and tributaries of Valley Creek, a base-level stream draining the area. There is no evidence of a laterally continuous perched water table in the area, although wet-weather season perched springs do occur.

Human activities can be a major threat to the quality of the water resources in Elizabethtown, which has become a center of commercial and industrial growth. Economic indicators, such as the number of businesses and employment figures, reflect the local growth. For example, for the period 1979-87, the number of businesses increased from 753 to 1369--an 82-percent increase. During the same period, employment increased by 52 percent (Booker Associates, 1988). Population is expected to increase by 37,000 over the next three decades, and the resultant increase in water demand could be satisfied by a combination of surface-water reservoirs and the karst aquifer system (Lambert, 1979). Accompanying the urban growth will be increased land disturbance and development, which will change the character of storm-water runoff as previously undeveloped land becomes urbanized.

The Valley Creek drainage basin in the Elizabethtown area includes numerous small watersheds, each representing a variety and mixture of land uses. Study objectives required that the selected watersheds be generally uniform in land use. Land use was determined from a digital data base (U.S. Geological Survey, 1986), which was updated with information from city planners and information collected during the field reconnaissance surveys. A description of the land use in each watershed is presented in table 1.

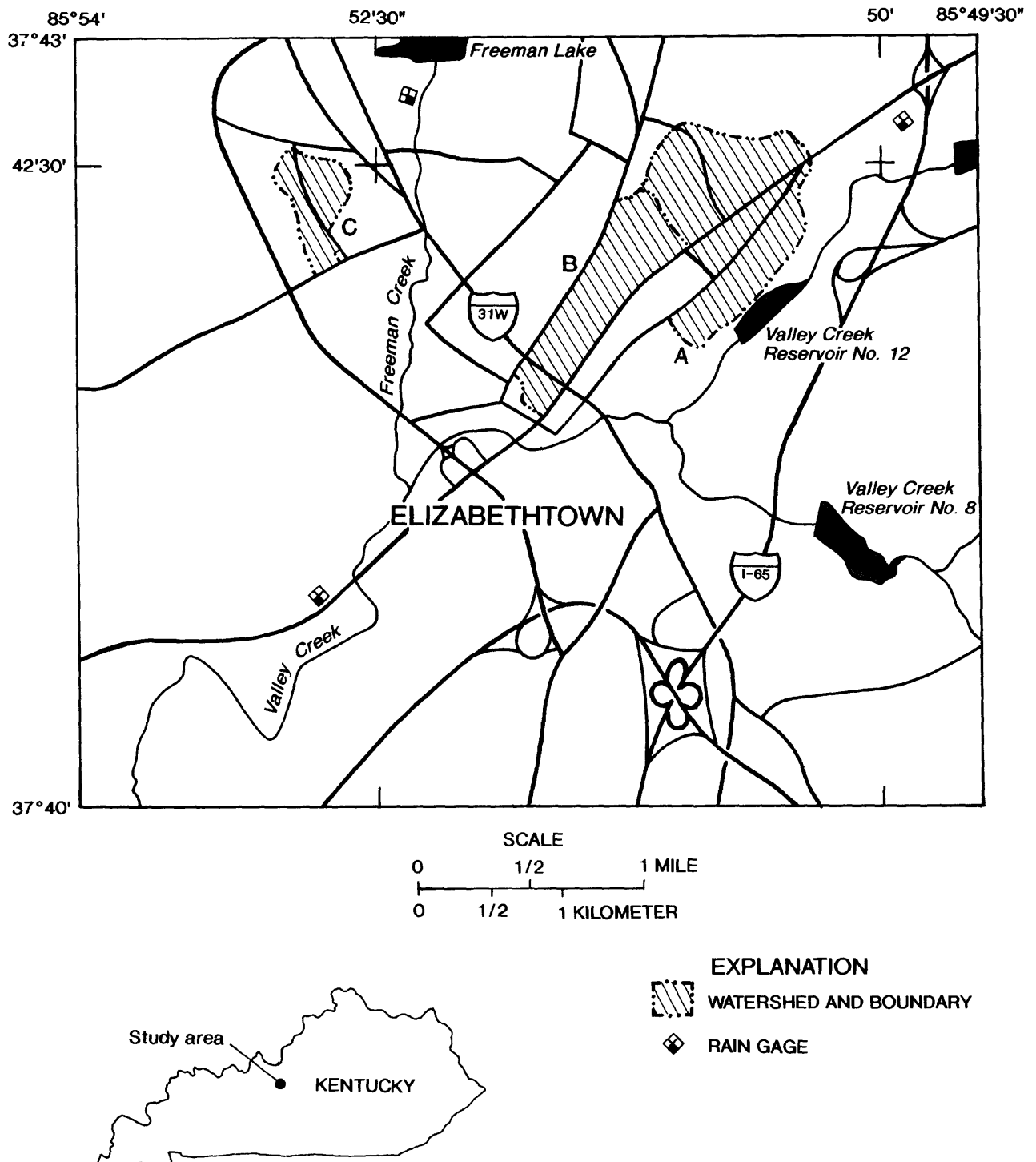


Figure 1.--Location of study area, watersheds, and rain gauges in Elizabethtown, Kentucky.

Table 1.--Types of land use at three watersheds, Elizabethtown, Kentucky
1990-91

[--, land use not in watershed; <, less than]

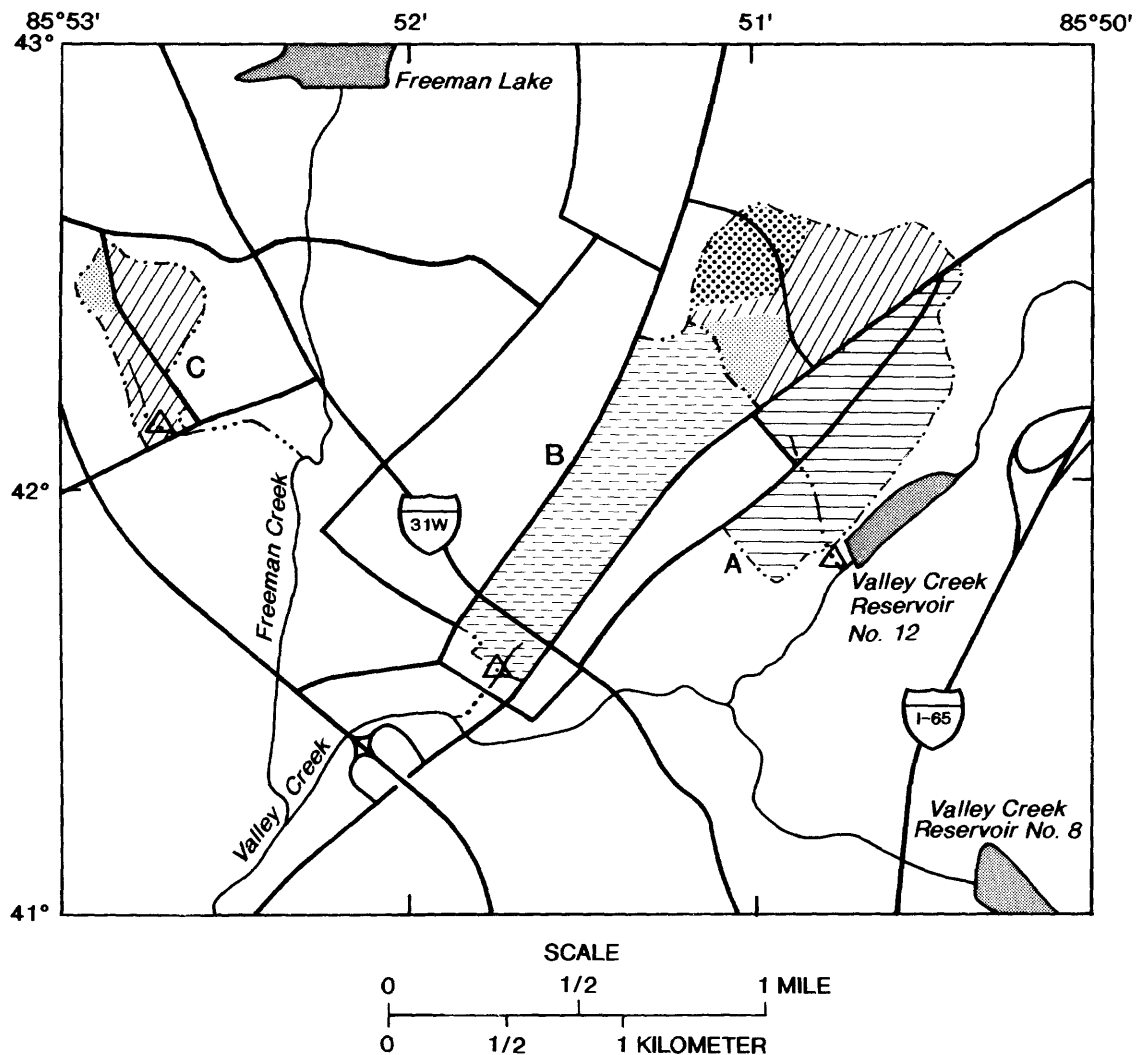
Watershed characteristic	Watershed		
	A	B	C
<u>Land use, in percent</u>			
Residential	78	79	90
Open space	5	17	10
Park	12	--	--
Commercial	<5	<4	--
Watershed area, in square miles	4.36	2.52	0.09
Impermeable area, in percent	10	14	24

Commercial areas, which consist mainly of small businesses that are converted residencies along major streets, constitute less than 5 percent of watersheds A and B, and they are not represented in watershed C. Because they are so small, commercial land-use areas are not shown on figure 2.

Land use in watershed A is primarily residential with some park and open space. Nearly 80 percent of the watershed contains two categories of single-family, low-density housing (2 and 3 units per acre). Approximately two-thirds of watershed A is represented by a housing density of 3 units per acre, and the other one-third is represented by a housing density of 2 units per acre. The contaminant contribution of this watershed is expected to be intermediate, relative to the other two watersheds.

Eighty percent of watershed B consists of single-family, medium-density housing, comprised mostly of 4-5 units per acre with limited areas of 2-3 units per acre. Watershed B contains the highest population density, has the greatest volume of vehicular traffic, and generally includes older homes than the other two watersheds. Watershed B is expected to contribute the greatest amount of contaminants to storm-water runoff.

Land use for watershed C is primarily residential with some open space. Ninety percent of this watershed consists of single-family, low-density housing of 2 units per acre. Though watersheds A and C are similar because of



EXPLANATION

- //// 2 HOUSING UNITS PER ACRE
- ==== 3 HOUSING UNITS PER ACRE
- ~~~~ 2-5 HOUSING UNITS PER ACRE
- PARK
- OPEN SPACE
- WATERSHED BOUNDARY
- △ SAMPLING SITE

Figure 2.--Location of sampling sites and land uses in watersheds in Elizabethtown, Kentucky.

low-density housing, they are different with respect to the average lot size. The average lot size in watershed C (20,000 square feet) is twice the size of the average lot in approximately two-thirds of the residential area in watershed A. Low-density housing areas generally have a low population density and light vehicular traffic volume; consequently, watershed C should contribute less contaminants to storm-water runoff than the other two watersheds.

METHODS OF INVESTIGATION

The study design for the determination of the water quality of storm-water runoff in the three watersheds called for the measurement of instantaneous discharge, the collection of multiple discrete samples and related physical data, the field screening of selected discrete samples, the preparation of flow-weighted composite samples, and the analysis of the composite and selected discrete samples by the USGS National Water-Quality Laboratory in Arvada, Colo. The analytical results, as well as computed loads and yields, were evaluated within and among the watersheds.

Selection of Study Watersheds and Sampling Sites

The selection of potential study watersheds was based on an evaluation of land-use patterns and hydrography within the study area. Information provided by Elizabethtown Planning and Development Commission personnel, digital data (U.S. Geological Survey, 1986), and the Elizabethtown and Cecilia topographic maps were used in this evaluation. Specific criteria used for selecting watersheds for the study included (1) relatively homogeneous land use, (2) location within the recharge area of public water-supply wells and springs of Elizabethtown, and (3) location within the Valley Creek basin, upstream from the public water supply of Elizabethtown. Within each watershed, a primary site was selected for the measurement of runoff discharge and collection of water-chemistry samples that best represented the watershed characteristics. Alternative stream sites also were identified within each watershed.

Sample Collection and Field Measurements

Certain conditions were required for a "runoff event"--that is, a period when field crews were sent to the sites to collect discharge data and water-chemistry samples. A period of at least 72 hours must have preceded the forecasted storm, during which the average daily rainfall was less than 0.1 inch. (Daily rainfall data from the rain gages shown in figure 1 were used to verify that this requirement was met.) In addition, the weather forecast must have predicted that the storm would be of sufficient intensity to produce measurable runoff in the study area and have an anticipated duration sufficient to maintain runoff for at least 3 hours. Finally, adequate lead time was required to enable the field crews to arrive at a sampling site in advance of measurable rainfall and subsequent runoff to collect a first-flush sample during the first 30 minutes of the runoff event.

On August 13, 1990, and April 4, 1991, the intensity and duration of rainfall were sufficient to meet the conditions of the study design. During these runoff events, selected water-quality and hydrologic data were collected at approximately 30-minute intervals including water temperature, pH, and specific conductance as well as measurements of instantaneous discharge and stage (gage height). At each sampling interval, discrete samples were collected for (1) preparation of flow-weighted composite samples and (2) screening and quantitative analysis of volatile organic compounds (VOC's) and herbicides. In addition, a discrete sample was collected during the first-flush for the analysis of fecal-coliform and fecal-streptococci bacteria by the membrane-filter method (Britton and Greeson, 1988). The study design called for only one discrete runoff sample from each site to be analyzed for herbicides.

Sample Screening by Use of a Portable Gas Chromatograph

For this investigation, an HNU Systems Model 311 portable gas chromatograph (PGC) was used to screen water samples for the presence of VOC's. The instrument is equipped with an isothermal oven, a photoionization detector, and a packed column designed for analysis of VOC's. Relative retention-time standards were prepared from benzene, toluene, and xylenes (BTX). Preset volumes of standards, deionized water, and air blanks were analyzed during sample-screening procedures to check syringes and column and instrument response and to ensure correct retention times for the standards according to the guidelines outlined by Brock (1990).

Of the five 40-mL septum vials collected for VOC analysis, two were used for screening. If screening indicated that VOC's were present in the sample, the remaining three vials were submitted to the laboratory for VOC analysis. If all screening results were negative, three of the remaining vials from only those samples collected during the first flush were shipped to the laboratory for analysis. Quantitative VOC analysis was done by gas chromatography according to procedures outlined in the USEPA method 524.2 (D.L. Rose, U.S. Geological Survey, oral commun., 1992).

Sample Screening by Use of Immunoassays

Discrete storm-water runoff samples were tested for the presence of triazine and 2,4-Dichlorophenoxy-acetic acid (2,4-D) by use of immunoassay RES-I-MUNE Kits (ImmunoSystems, Inc.). An aliquot from each chilled sample was allowed to reach room temperature before testing for each herbicide according to the manufacturer's instructions. The test reaction was analyzed visually by comparing the intensity of the blue color in the sample tube to that of the control tube. First-flush samples testing positive were submitted for quantitative herbicide analysis by gas chromatography (Wershaw and others, 1987).

Sample Compositing

Preparation of a flow-proportional composite sample of storm-water runoff based on the series of discrete samples collected at a site required development of a rating curve based on the discharge measurements made during the runoff event. A hydrograph of discharge as a function of time was then drawn for each storm on the basis of the rating curve and the stages recorded during the event. Each hydrograph was divided into sections representing the integrated volume for each of the sampling intervals for the storm (fig. 3). The midpoint for each section was the sampling time for each discrete sample set, and the boundaries of each section were drawn at half the time between sequential samples. The volume represented by each section was determined, and these were totaled to provide the volume of the storm represented by the samples collected. The aliquot needed from each discrete sample to prepare the composite sample was derived by multiplying the composite volume needed by the ratio of the corresponding section block count to total blocks of storm, as sampled.

An example of the steps for compositing a runoff sample is shown below (also refer to fig. 3).

Composite volume needed is 6,000 mL

Total blocks for storm as sampled is 455
 $30 + 65 + 125 + 115 + 75 + 45 = 455$

Aliquot per section = $6,000 \text{ mL} \times (\text{section blocks} / \text{total blocks})$
 $6,000 \text{ mL} \times (30 / 455) = 396 \text{ mL}$

Sample composite is the total of the aliquots
 $396 + 857 + 1,648 + 1,516 + 989 + 593 = 5,999 \text{ mL}$

The composite sample was prepared and mixed in a clean polyethylene churn. Samples for the analysis of dissolved constituents were obtained by filtering the composite water through a 0.45-micrometer (nominal pore size) membrane filter by means of a peristaltic pump. The samples were preserved and chilled, as required (Ward and Harr, 1990), and were shipped to the laboratory for analysis.

QUALITY OF STORM-WATER RUNOFF

The following sections contain the discussion of the physical data, inorganic and organic constituent concentrations, bacteria counts, and the computed loads and yields of selected constituents for the three watersheds investigated. Physical data are discussed with respect to the impermeable and catchment areas of the respective watersheds. The analytical results for inorganic and organic constituents are compared to ground-water data and are evaluated on the basis of land use within each watershed. Watershed characteristics, also, are used in comparisons of computed loads and yields of selected constituents within and among the watersheds.

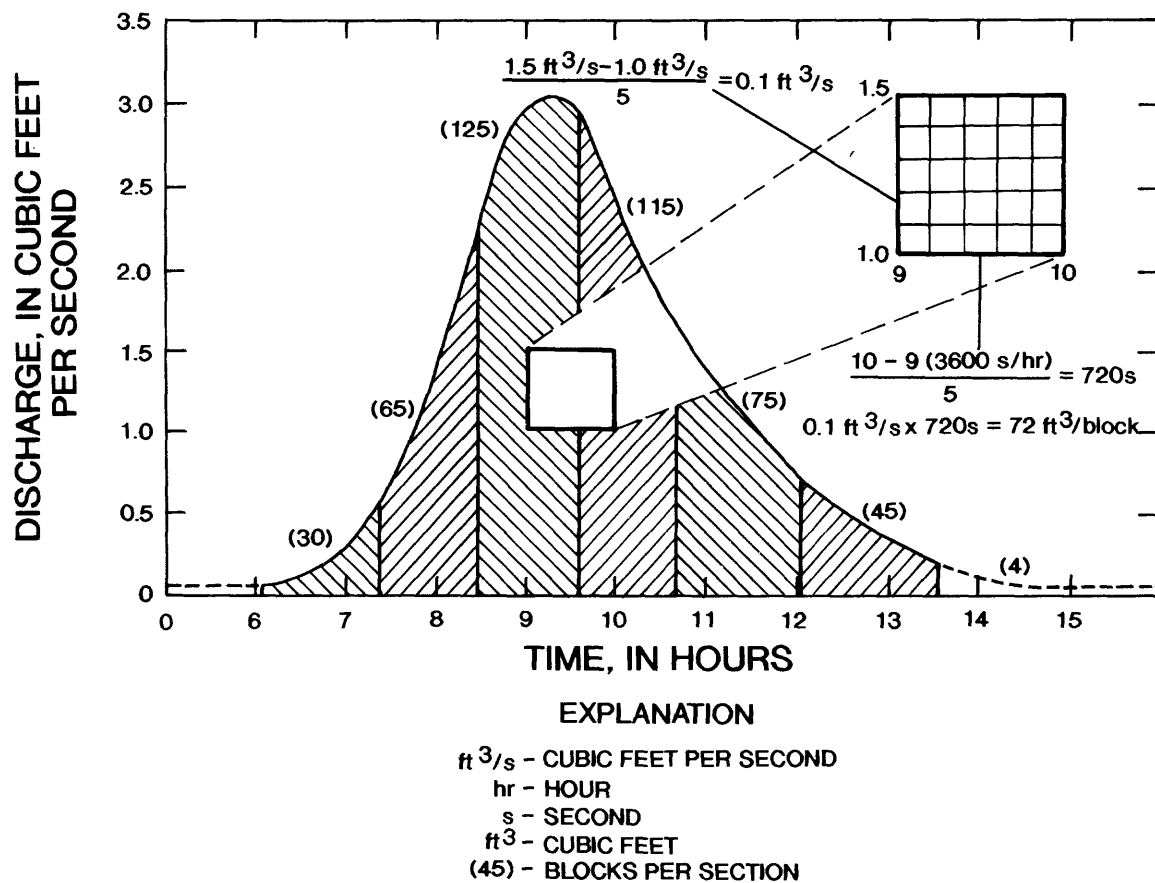


Figure 3.--Hydrograph for deriving sample interval and total volumes for a hypothetical storm.

Physical Properties

The relation of discharge and specific conductance as a function of time for the two storms, as shown in figure 4, indicates the presence of two transport patterns among the three watersheds. The graph for site C demonstrates a pulse effect in the transport of dissolved constituents in the watershed during both storms. A reduced rainfall retention time, due in part to the larger impermeable area of watershed C compared to the other two watersheds, is a possible explanation for the pulse that effectively "flushes" dissolved constituents that have accumulated in the watershed since the previous runoff event. Before the storm of August 13, 1990, 7 days had passed since 0.1 in. or more of rainfall was recorded in the study area, and 12 days had passed before the storm of April 4, 1991. The dilution effect shown in the graphs for sites A and B is due, in part, to the smaller relative impermeable area (10 and 14 percent, respectively) and larger catchment of their respective watersheds. Together, these factors allow for longer "flush" times and greater discharges to dilute dissolved constituents before they reach the sampling site.

An evaluation of the physical data for all watersheds (table 2) did not indicate a discernable pattern for pH or temperature with respect to discharge. Values for pH ranged from 6.32 to 8.15 and were smallest at watershed C for the storm of August 13, 1990. Temperatures ranged from 13.0 to 23.0 degrees Celsius. The difference in temperature values between storms at watershed C is seasonal. A summary of the discharge data is presented in table 3.

Major Ions, Nutrients, and Metals

Concentrations of major ions and dissolved solids were generally larger in composite samples from sites A and C than for site B (table 4). Small concentrations of barium, iron, manganese, mercury, strontium, and zinc were detected at all sites. The concentrations for beryllium, cadmium, chromium, lead, lithium, molybdenum, nickel, selenium, silver, and zinc were at or below detection level in all composite samples. Of the metals associated with roadside deposition (cadmium, lead, nickel, and zinc), due to vehicular traffic (Van Hassel and others, 1990), only zinc was detected in storm-water runoff composite samples from all three sites. Concentrations of zinc ranged from 9 to 20 $\mu\text{g/L}$ and was largest at site B. The concentrations for detected inorganic constituents were below Maximum Contaminant Level (MCL's) and Secondary Maximum Contaminant Level (SMCL's) established by the U.S. Environmental Protection Agency (1990b, 1990c, 1990d, and 1991) for finished drinking water.

The ranges of concentrations for selected major ions, nutrients, and metals in the composite samples are listed in table 5. The concentrations of these constituents in composite runoff samples are comparable to the ranges reported for water samples from 28 springs and wells in the Elizabethtown area (Mull and Lyverse, 1984) and those determined in 4 samples from the two water-supply springs serving Elizabethtown (samples collected by the USGS in 1991 as part of another investigation). The range of concentrations in composite-runoff samples for barium, calcium, fluoride, magnesium, sodium, and silica are slightly lower than those reported for water samples from springs and

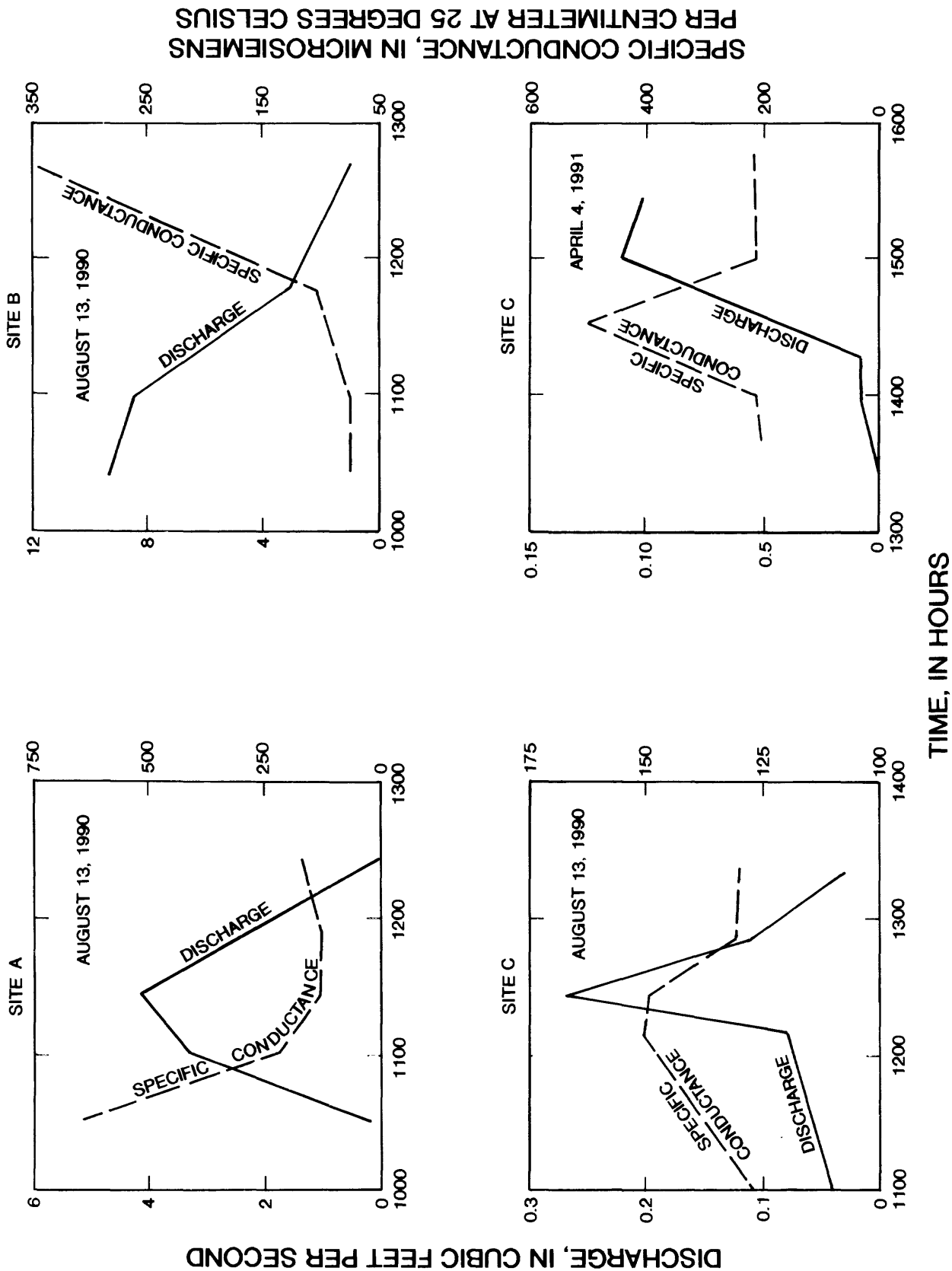


Figure 4.--Discharge and specific conductance over time at the three watersheds.

Table 2.--Physical data for storms at three watersheds,
Elizabethtown, Kentucky

[ft³/s, cubic feet per second; μ S/cm, microsiemens per
centimeter at 25 degrees Celsius: deg C,
degrees Celsius]

Physical characteristic	Data at indicated sampling time				
<u>Watershed A - August 13, 1990</u>					
Time, 24-hour	1030	1055	1125	1155	1225
Streamflow, ft ³ /s	0.5	3.3	4.1	2.2	0.3
Specific conductance, μ S/cm	634	219	132	129	171
pH	7.01	7.33	7.42	7.34	7.22
Temperature, water, deg C	19.0	21.5	22.0	22.0	22.0
<u>Watershed B - August 13, 1990</u>					
Time, 24-hour	1025	1100	1145	1240	
Streamflow, ft ³ /s	9.6	8.4	3.3	1.1	
Specific conductance, μ S/cm	78	77	106	345	
pH	8.15	8.05	7.55	7.30	
Temperature, water, deg C	22.5	22.5	23.0	21.5	
<u>Watershed C - August 13, 1990</u>					
Time, 24-hour	1100	1210	1225	1250	1320
Streamflow, ft ³ /s	0.04	0.08	0.27	0.11	0.03
Specific conductance, μ S/cm	126	152	150	132	130
pH	6.32	6.59	6.74	6.85	6.93
Temperature, water, deg C	22.3	21.9	22.0	21.9	22.2
<u>Watershed C - April 4, 1991</u>					
Time, 24-hour	1340	1400	1430	1500	1545
Streamflow, ft ³ /s	<0.01	0.01	0.01	0.11	0.10
Specific conductance, μ S/cm	210	219	512	215	228
pH	7.75	7.80	7.65	7.65	7.75
Temperature, water, deg C	13.0	13.2	13.3	13.2	13.1

Table 3.--Summary of discharge measurements for storms at three watersheds, Elizabethtown, Kentucky

[ft³, cubic feet; ft³/s, cubic feet per second]

Measurement	<u>August 13, 1990</u>			<u>April 4, 1991</u>
	Site A	Site B	Site C	Site C
Duration, hours and minutes	2:25	3:45	3:35	3:30
Volume, ft ³	20,325	49,755	1,300	581
Mean discharge, ft ³ /s	2.33	3.68	.10	.046

wells. The range of concentrations for residue of dissolved solids in composite-runoff samples is considerably lower than the reported range for water samples from springs and wells.

Volatile Organic Compounds

Screening for the presence VOC's by use of a PGC indicated that detectable levels of BTX were not present in the 19 discrete samples from both storms. Nevertheless, all samples collected during the first-flush period were shipped to the laboratory for VOC analysis; the results are presented in table 6. Tetrachloroethylene, detected at a concentration of 6.3 µg/L in the first-flush sample collected at site A on August 13, 1990, exceeded the MCL of 5.0 µg/L (U.S. Environmental Protection Agency, 1991).

The range of values for VOC's for first-flush runoff samples for the three watersheds and for four samples from two water-supply springs serving Elizabethtown (U.S. Geological Survey, unpublished 1991 data) are presented in table 7. Except for tetrachloroethylene from watershed A and 1,1,1-trichloroethane from one of the spring samples, all concentrations were below detection level.

Herbicides

The results from the immunoassay screening tests for triazines with a control of 0.1 µg/L were negative for each of the 14 discrete samples collected at the three sites during the runoff event of August 13, 1990. Of the 14 samples screened for 2,4-D, with a control of 1.0 µg/L, only the first-flush sample from site C tested positive. Nevertheless, all the samples collected during the first-flush period of the runoff were shipped to the

Table 4.--Dissolved inorganic constituents in composite runoff samples,
Elizabethtown, Kentucky

[MCL, maximum contaminant level, U.S. Environmental Protection Agency, 1991, 1990b, and 1990c; SMCL, Secondary maximum contaminant level, U.S. Environmental Protection Agency, 1990d; -, no established regulation; <, less than; N, nitrogen; N/A, not analyzed; deg C, degrees Celsius]

	<u>August 13, 1990</u>			<u>April 4, 1991</u>		
Constituent	Site 1	Site 2	Site 3	Site 3	MCL	SMCL
Concentration, in milligrams per liter						
Calcium	31	13	15	30	-	-
Chloride	5.5	2.6	6.5	11	-	250
Fluoride	.20	<.10	<.10	.10	4	2
Magnesium	2.6	1.2	2.8	4.2	-	-
Nitrite as N	.03	.03	.03	N/A	1	-
Nitrite plus nitrate, as N	.50	.50	.50	N/A	10	-
Silica	2.4	1.2	4.3	3.2	-	-
Sodium	2.9	1.6	2.4	8.0	-	-
Solids, residue, at 105 deg C	123	62	102	122	-	500
Sulfate	21	8.5	16	15	-	250
Concentration, in micrograms per liter						
Arsenic	1	<1	1	<1	50	-
Barium	19	11	17	21	1,000	-
Beryllium	<.5	<.5	<.5	<.5	-	-
Cadmium	<1.0	<1.0	<1.0	1.0	5	-
Chromium	<5	<5	<5	<5	100	-
Cobalt	<3	<3	<3	<3	-	-
Copper	<10	20	<10	<10	-	1,000
Iron	27	35	62	25	-	300
Lead	<10	<10	<10	<10	50	-
Lithium	<4	<4	<4	<4	-	-
Manganese	20	14	12	8	-	50
Mercury	.4	.4	.2	<.1	2	-
Molybdenum	<10	<10	<10	<10	-	-
Nickel	<10	<10	<10	10	-	-
Selenium	<1	<1	<1	<1	50	-
Silver	<1.0	<1.0	<1.0	<1.0	50	100
Strontium	150	78	96	130	-	-
Vanadium	<6	<6	<6	<6	-	-
Zinc	11	20	9	12	-	5,000

Table 5.--Ranges in concentrations of selected major ions, nutrients, and metals for composite runoff, springs, and wells, Elizabethtown, Kentucky

[n, number of samples; <, less than; N, Nitrogen;
deg C, degrees Celsius]

Constituents	Composite storm- runoff samples (n = 4)	Discrete samples from springs and wells ¹ (Mull and Lyverse, 1984) (n = 32)
<u>Dissolved major ions and nutrients</u>	Ranges of concentrations, in milligrams per liter	
Calcium	13-31	41-92
Chloride	2.6-11	.8-120
Fluoride	<.1-.2	.1-1.6
Magnesium	1.2-4.2	2.6-30
Nitrite as N	.03	<.01-.25
Nitrite plus nitrate, as N	.5	.1-10
Silica	1.2-4.3	8-13
Sodium	1.6-8.0	1.8-64
Solids, residue, at 105 deg C	62-123	258-270
Sulfate	8.5-21	1.7-110
<u>Dissolved metals</u>	Ranges of concentrations, in micrograms per liter	
Arsenic	<1-1	<1
Barium	11-21	23-220
Beryllium	<.5	<.5-1
Cadmium	<1-1	<1-3
Chromium	<5	<5-20
Cobalt	<3	<3-3
Copper	<10-20	<10-10
Iron	27-62	3-71
Lead	<10	<10-20
Lithium	<4	<4-18
Manganese	12-20	1-320
Mercury	<.1-.4	<.1
Molybdenum	<10	<10-30
Nickel	<10-10	<10
Selenium	<1	<1
Silver	<1	<1-1
Strontium	78-150	58-25,000
Vanadium	<6	<6-6
Zinc	9-20	<3-2,200

¹Includes unpublished U.S. Geological Survey data for four spring samples collected in 1991.

Table 6.--Concentrations of tetrachloroethylene and selected herbicides in first-flush runoff samples from three watersheds, Elizabethtown, Kentucky

[MCL, maximum contaminant level, U.S. Environmental Protection Agency, 1991; <, less than; --, no sample collected; -, no established regulation; concentrations reported in micrograms per liter]

Constituent, total recoverable	August 13, 1990			April 4, 1991	
	Site A	Site B	Site C	Site C	MCL
Tetrachloroethylene	6.3	<3.0	<3.0	<3.0	5.0
Prometon	.2	.1	<.1	--	-
Dicamba	<.1	<.1	.9	--	-
2,4-Dichlorophenoxy-acetic acid (2,4-D)	<.1	.3	7.2	--	70
2,4-Dichlorophenoxy-propionic acid (2,4-DP)	<.1	.4	<.1	--	-

laboratory for analysis of herbicides. Concentrations, presented in table 6, ranged from less than 0.1 to 7.2 $\mu\text{g/L}$ and are largest in runoff samples from site C.

Concentrations of the broadleaf weed-control herbicide Prometon, detected at sites A and B (0.2 and 0.1 $\mu\text{g/L}$, respectively), are considerably lower than the Lifetime Health Advisory concentration in drinking water of 100 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 1989). The USEPA concludes that, as a guideline, drinking water containing Prometon at or below this level does not pose a health effect (it is not carcinogenic) over the course of a person's lifetime.

Many herbicides commonly used for the control of broadleaf weeds during the postemergence cycle of crops, such as corn, soybeans, and small grains, contain Dicamba and 2,4-D (Martin and Green, 1988). Dicamba and 2,4-D are also used to control weeds in noncropland areas such as lawns, fence rows, and roadways. Sales figures for Dicamba and 2,4-D in Hardin County were 380 and 438,215 pounds, respectively, in 1990 (Ernest Collins, Kentucky Department of

Table 7.--Ranges in concentrations of selected volatile organic compounds in first-flush runoff samples from three watersheds and in spring samples, Elizabethtown, Kentucky

[n, number of samples; <, less than; range of concentrations in micrograms per liter]

Volatile organics, total recoverable	Watershed samples (n = 4)	Spring samples ¹ (n = 4)
Benzene	<3	<3
Bromoform	<3	<3
Carbon tetrachloride	<3	<3
Chlorobenzene	<3	<3
Chlorodibromomethane	<3	<3
Chloroethane	<3	<3
Chloroform	<3	<3
Dichlorobromomethane	<3	<3
Dichlorodifluoromethane	<3	<3
Ethylbenzene	<3	<3
Methyl bromide	<3	<3
Methyl chloride	<3	<3
Methylene chloride	<3	<3
Styrene	<3	<3
Tetrachloroethylene	<3-6.3	<3
Toluene	<3	<3
Trichloroethylene	<3	<3
Trichlorofluoromethane	<3	<3
Vinyl chloride	<1	<1
Xylene	<3	<3
1,1-Dichloroethane	<3	<3
1,1-Dichloroethylene	<3	<3
1,1,1-Trichloroethane	<3	<3-3.9
1,1,2-Trichloroethane	<3	<3
1,1,2,2-Tetrachloroethane	<3	<3
1,2-Dibromoethane	<3	<3
1,2-Dichlorobenzene	<3	<3
1,2-Dichloroethane	<3	<3
1,2-Dichloropropane	<3	<3
1,2-trans-Dichloroethene	<3	<3
1,3-Dichloropropene	<3	<3
1,3-Dichlorobenzene	<3	<3
1,4-Dichlorobenzene	<3	<3
2-Chloroethyl vinyl ether	<3	<3
cis-1,3-Dichloropropene	<3	<3
trans-1,3-Dichloropropene	<3	<3

¹Unpublished U.S. Geological Survey data for four spring samples collected in 1991.

Agriculture, written commun., 1991). On the basis of these sales figures, Hardin County is ranked third statewide in the purchase of Dicamba and 2,4-D. Concentrations of Dicamba, 2,4-D, and 2,4-Dichlorophenoxy-propionic acid (2,4-DP) were small in discrete samples from sites B and C (table 6). The reported concentrations for 2,4-D are well below the MCL of 70 $\mu\text{g/L}$ for finished drinking water (U.S. Environmental Protection Agency, 1991).

Except for Prometon, Dicamba, 2,4-D, and 2,4-DP, herbicide concentrations in the first-flush samples for the storm of August 13, 1990 and in four samples from two water-supply springs serving Elizabethtown (table 8), collected by the USGS in 1991 as part of another investigation, were below the detection level of the method.

Fecal-Coliform Bacteria

Densities of fecal-coliform and fecal-streptococci bacteria in runoff samples collected during the first-flush interval of the runoff events are presented in table 9. Fecal-coliform and fecal-streptococci bacteria are used as an indirect measure of a recent or ongoing contamination problem. They are an indirect measure because these organisms can survive in soil as well as in animal or human feces. Densities of fecal-coliform bacteria ranged from more than 500 to more than 60,000 col/100 mL of water sample. Densities of fecal-streptococci bacteria ranged from more than 200 to more than 40,000 col/100 mL. The Commonwealth of Kentucky has established a monthly geometric-mean water-quality criteria for fecal-coliform bacteria of 2,000 col/100 mL for domestic water supply (Kentucky Natural Resources and Environmental Protection Cabinet, 1990). The coliform densities reported at the sites were high but comparable to the densities found at urban storm-water sampling sites in the Louisville, Ky., metropolitan area (R.D. Evaldi, U.S. Geological Survey, oral commun. 1992). Sewage treatment plant effluent is not a component of the discharge at these urban storm-water sampling sites.

Loads and Yields of Selected Constituents

Computation of the constituent load for a particular stream reach or watershed is useful in determining the quantity of a particular constituent being contributed to the environment by the area upgradient from the sampling point. It is computed by multiplying the concentration of the constituent by the discharge. In general, loads are directly related to the drainage area of the stream reach or watershed; that is, the larger the watershed, the higher its constituent transport capacity. The yield is derived by dividing the constituent load by the drainage area. The yield is useful in comparing constituent contributions from watersheds which differ in the size of their catchment area.

Table 8.--Ranges in total recoverable herbicide concentrations in first-flush runoff samples from three watersheds and in spring samples, Elizabethtown, Kentucky

[n, number of samples; <, less than; --, no sample collected;
range of concentrations in micrograms per liter]

Herbicide, by class	Watershed samples (n = 4)	Spring samples ¹ (n = 4)
<u>Triazines and other nitrogen-containing herbicides</u>		
Alachlor	<0.1	<0.1
Ametryne	<.1	<.1
Atrazine	<.1	<.1
Cyanazine	<.1	<.1
Metolachlor	<.1	<.1
Metribuzin	<.1	<.1
Prometon	<.1-.2	<.1
Prometryne	<.1	<.1
Propazine	<.1	<.1
Simazine	<.1	<.1
Simetryne	<.1	<.1
Trifluralin	<.1	<.1
<u>Chlorophenoxy acid herbicides</u>		
Dicamba	<0.1-0.9	--
Picloram	<.1	--
2,4-Dichlorophenoxy-acetic acid (2,4-D)	<.1-7.2	--
2,4-Dichlorophenoxy- propionic acid (2,4-DP)	<.1-.4	--
2,4,5-Trichlorophenoxy- acetic acid (2,4,5-TP)	<.1	--
2,4,5-Trichlorophenoxy- propionic acid (2,4,5-TP Silvex)	<.1	--

¹Unpublished U.S. Geological Survey data for four spring samples collected in 1991.

Table 9.--Bacteria counts in first-flush runoff samples.
Elizabethtown, Kentucky

[col/100 mL, colonies per 100 milliliter;
 >, greater than]

Measurement	<u>August 13, 1990</u>			<u>April 4, 1991</u>
	Site A	Site B	Site C	Site C
Coliform, fecal, col/100 mL	>12,000	>60,000	>60,000	540
Streptococci, fecal, col/100 mL	14,000	23,200	44,000	242

Loads and yields were computed for selected major ions, dissolved solids, nitrogen, and metals; the computations are presented in tables 10 and 11. For this study, loads were calculated by use of the equation

$$Q_s = Q_w * C_s * K,$$

where

Q_s is the load, in pounds per runoff event;

Q_w is storm volume, in cubic feet;

C_s is the constituent concentration, in mg/L; and

K is the conversion constant, 6.244E-5.

Because of the small sample set from this study, the transferability of the load and yield values to other watersheds in mature karst terrane may be limited.

The load for most constituents was greater at sites A and B than at site C. The dissolved-solids load was two orders of magnitude greater at sites A and B than at site C. One reason for the larger loads for sites A and B is the greater transport capacity of their respective watersheds as a result of having larger catchment areas than watershed C. Except for the yield of arsenic at site A, which was twice that of site C, all other constituent yields at this site were smaller than at sites B and C for the storm of August 13, 1990. The yields of nitrogen, calcium, copper, manganese, mercury, strontium, and zinc were largest at site B. The higher housing and population density and the greater volume of traffic of watershed B are possible factors for the higher loads and yields at site B compared to sites A and C.

Table 10.--Loads of selected dissolved constituents in composite storm-water samples, Elizabethtown, Kentucky

[BDL, below detection level; <, less than; N, nitrogen; N/A, not analyzed; deg C, degrees Celsius; load is reported in pounds per storm]

Constituent	<u>August 13, 1990</u>			<u>April 4, 1991</u>
	Site A	Site B	Site C	Site C
	Load			
Arsenic	0.0013	BDL	<0.00010	BDL
Barium	.024	0.034	.0014	0.00076
Cadmium	BDL	BDL	BDL	<.00010
Calcium	39	40	1.2	1.1
Chloride	7.0	8.1	.53	.40
Copper	BDL	.062	BDL	BDL
Fluoride	.25	BDL	BDL	.0036
Iron	.034	.11	.0050	.00091
Magnesium	3.3	3.7	.23	.15
Manganese	.025	.044	.00097	.00029
Mercury	.00051	.0012	<.00010	BDL
Nitrite plus nitrate, as N	.63	1.6	.041	N/A
Silica	3.0	3.7	.35	.12
Sodium	3.7	5.0	.19	.29
Sulfate	27	26	1.3	.54
Solids, residue, at 105 deg C	160	190	8.3	4.4
Strontium	.19	.24	.0078	.0047
Zinc	.014	.062	.00073	.00044

Table 11.--Yields of selected dissolved constituents in composite storm-water samples, Elizabethtown, Kentucky

[BDL, below detection level; N, nitrogen; N/A, not analyzed;
deg C, degrees Celsius; yield is reported in pounds per
storm per square mile]

Constituent	<u>August 13, 1990</u>			<u>April 4, 1991</u>
	Site A	Site B	Site C	Site C
	Yield			
Arsenic	0.00029	BDL	0.00090	BDL
Barium	.0055	0.014	.015	0.0085
Cadmium	BDL	BDL	BDL	.00040
Calcium	9.0	16	14	12
Chloride	1.6	3.2	5.9	4.4
Copper	BDL	.025	BDL	BDL
Fluoride	.058	BDL	BDL	.040
Iron	.0079	.043	.056	.010
Magnesium	.76	1.5	2.5	1.7
Manganese	.0058	.017	.011	.0032
Mercury	.00012	.00049	.00018	BDL
Nitrite plus nitrate, as N	.14	.62	.45	N/A
Silica	.70	1.5	3.9	1.3
Sodium	.84	2.0	2.2	3.2
Solids, residue, at 105 deg C	36	76	92	49
Sulfate	6.1	10	14	6.0
Strontium	.044	.096	.086	.052
Zinc	.0032	.025	.0081	.0048

SUMMARY AND CONCLUSIONS

Three watersheds in Elizabethtown, Ky., were studied to determine the quality of storm-water runoff from the watersheds and to evaluate the potential effect of storm-water runoff on the quality of ground water in the vulnerable, mature karst terrane. These watersheds drain into Valley Creek, which has been demonstrated to be hydraulically connected to the wells and springs that supply drinking water to the community. Water-quality data for storm-water runoff obtained at the watersheds during the storm events on August 13, 1990 and April 4, 1991, and calculated loads and yields of selected constituents were evaluated. The following conclusions can be made on the basis of these evaluations.

1. The densities of fecal-coliform (more than 500 to more than 60,000 col/100 mL) and fecal-streptococci (more than 200 to more than 40,000 col/100 mL) bacteria were high at the three watersheds. These densities are comparable to those from urban storm-water sites in the Louisville metropolitan area.
2. Detectable levels of the herbicides of interest were reported at one or more locations in the study area. Herbicide concentrations ranged from less than 0.1 to 7.2 $\mu\text{g/L}$ and were largest in runoff samples from site C (suburban watershed). The data indicate that storm-water runoff from watersheds B and C is transporting more herbicides than storm-water runoff from watershed A. Laboratory analysis confirmed the 2,4-D immunoassay positive test result from the first-flush sample at site C. Dicamba was also detected in first-flush samples from site C, Prometon was detected in the first-flush samples from sites A and B, and 2,4-DP was reported in the first-flush sample from site B.
3. Total recoverable tetrachloroethylene, a common degreasing and dry-cleaning solvent, was detected in one sample at a concentration of 6.3 $\mu\text{g/L}$ from site A on August 13, 1990. This concentration exceeds the MCL of 5.0 $\mu\text{g/L}$ for finished drinking water.
4. On the basis of the limited composite data, roadside deposition of metals associated with vehicular traffic (cadmium, lead, nickel, and zinc) does not appear to be a significant source of metals in storm-water runoff.
5. None of the inorganic constituents from the composite samples exceeded U.S. Environmental Protection Agency MCL's for finished drinking water.
6. The range of concentrations of selected major ions, nutrients, and metals measured in composite runoff samples were comparable to the ranges reported for water samples from 32 springs and wells collected in the study area as part of previous investigations. Only residue of dissolved solids was found to have a range of concentrations considerably lower than reported for water samples from springs and wells.

7. The largest loads of dissolved inorganic constituents were from watersheds A and B because of their relatively large catchment area.
8. The yields of nitrogen, calcium, copper, manganese, mercury, strontium, and zinc were largest at site B.
9. The relation of discharge and specific conductance as a function of time for site C demonstrates a pulse effect of dissolved constituents in the watershed because of its comparatively small basin size and large relative impermeable area.

The vulnerability of the karst aquifer system in the Elizabethtown area to potential contamination from the direct recharge of storm-water runoff through sinkholes, losing reaches of streams, and Class V injection wells, which include improved sinkholes and drainage wells, has been well documented. The results of this study reveal that storm-water runoff from the three watersheds contains fecal bacteria that have the potential to contaminate the receiving streams and ground water. The data indicate that storm-water runoff from watersheds B and C is transporting more herbicides than storm-water runoff from watershed A. The results also indicate that roadside deposition by vehicular traffic does not seem to represent a potentially significant source of metals in storm-water runoff from these three watersheds. Although the data set from this study is small, the results point to the need for further investigation to determine whether fecal-bacteria contamination and the transport of herbicides and metals are truly issues of concern with respect to the effects of land use on storm-water quality and the water resources of Elizabethtown.

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