Characterization of Surface-Water Quality Based on Real-Time Monitoring and Regression Analysis, Quivira National Wildlife Refuge, South-Central Kansas, December 1998 Through June 2001

U.S. Department of the Interior
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Lawrence, Kansas
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CONVERSION FACTORS, ABBREVIATIONS, AND DEFINITIONS

Multiply	By	To obtain
acre	4,047	square meter
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
inch (in.)	2.54	centimeter
microgram per liter (μg/L)	0.00539	pound per day
mile (mi)	1.609	kilometer
milligram per liter (mg/L)	5.39	pound per day
milliliter (mL)	0.0338	ounce, fluid
pound (lb)	453.6	gram
pound per acre (lb/acre)	1.121	kilogram per hectare
pound per acre per year [(lb/acre)/yr]	1.121	kilogram per hectare per year
pound per day (lb/d)	453.6	gram per day
pound per year (lb/yr)	453.6	gram per year
square mile (mi^2)	2.590	square kilometer
ton (short)	0.9072	megagram

Temperature can be converted to degrees Celsius (^{o}C) or degrees Fahrenheit (^{o}F) by the equations:

$$^oC = 5/9 \, (^oF - 32)$$
$$^oF = 9/5 \, (^oC) + 32.$$

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By Victoria G. Christensen

Abstract

Because of the considerable wildlife benefits offered by the Quivira National Wildlife Refuge in south-central Kansas, there is a desire to ensure suitable water quality. To assess the quality of water flowing from Rattlesnake Creek into the refuge, the U.S. Geological Survey collected periodic water samples from December 1998 through June 2001 and analyzed the samples for physical properties, dissolved solids, total suspended solids, suspended sediment, major ions, nutrients, metals, pesticides, and indicator bacteria. Concentrations of 10 of the 125 chemicals analyzed did not meet water-quality criteria to protect aquatic life and drinking water in a least one sample. These were pH, turbidity, dissolved oxygen, dissolved solids, sodium, chloride, phosphorus, total coliform bacteria, E. coli bacteria, and fecal coliform bacteria. No metal or pesticide concentrations exceeded water-quality criteria. Twenty-two of the 43 metals analyzed were not detected, and 36 of the 46 pesticides analyzed were not detected.

Because dissolved solids, sodium, chloride, fecal coliform bacteria, and other chemicals that are a concern for the health and habitat of fish and wildlife at the refuge cannot be measured continuously, regression equations were developed from a comparison of the analytical results of periodic samples and in-stream monitor measurements of specific conductance, pH, water temperature, turbidity, and dissolved oxygen. A continuous record of estimated chemical concentrations was developed from continuously recorded in-stream measurements.

Annual variation in water quality was evaluated by comparing 1999 and 2000 sample data—the 2 years for which complete data sets were available. Median concentrations of alkalinity, fluoride, nitrate, and fecal coliform bacteria were smaller or did not change from 1999 to 2000. Dissolved solids, total suspended solids, sodium, chloride, sulfate, total organic nitrogen, and total phosphorus had increases in median concentrations from 1999 to 2000. Increases in the median concentrations of the major ions were expected due to decreased rainfall in 2000 and very low streamflow late in the year. Increases for solids and nutrients may have been due to the unusually high streamflow in the early spring of 2000. This was the time of year when fields were tilled, exposing solids and nutrients that were transported with runoff to Rattlesnake Creek.

Load estimates indicate the chemical mass transported into the refuge and can be used in the development of total maximum daily loads (as specified by the U.S. Environmental Protection Agency) for water-quality contaminants in Rattlesnake Creek. Load estimates also were used to evaluate seasonal variation in water quality. Seasonal variation was most pronounced in the estimates of nutrient loads, and most of the nutrient load transported to the refuge occurred during just

a few periods of surface runoff in the spring and summer. This information may be used by resource managers to determine when water-diversion strategies would be most beneficial. Load estimates also were used to calculate yields, which are useful for site comparisons.

The continuous and real-time nature of the record of estimated concentrations, loads, and yields may be important for resource managers, recreationalists, or others for evaluating water-diversion strategies, making water-use decisions, or assessing the environmental effects of chemicals in time to prevent adverse effects on fish or other aquatic life at the refuge.

INTRODUCTION

The Quivira National Wildlife Refuge is a natural wetlands area located in the Rattlesnake Creek Basin of south-central Kansas (fig. 1) and is managed by the U.S. Fish and Wildlife Service (USFWS). The funding for the initial acquisition of the refuge was obtained in 1955; the refuge applied for a water permit in 1957 and development began. The area provides food, water, cover, and protection for many species of birds, fish, and other wildlife. Several types of waterfowl take advantage of the refuge in their annual migration including the endangered whooping crane. Since the initial acquisition, the refuge has been enhanced and includes more than 30 marshes and ponds covering more than 22,000 acres in Stafford, Reno, and Rice Counties.
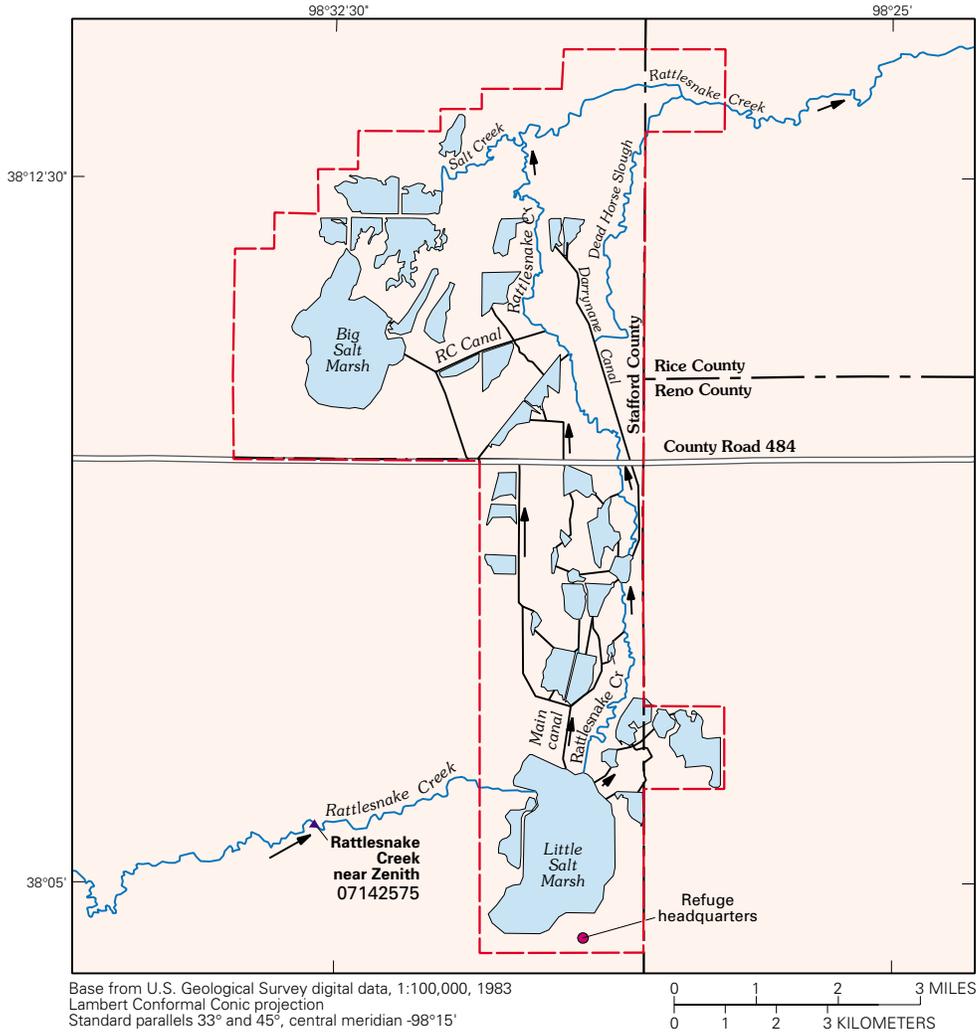
The importance of maintaining an adequate water supply to preserve valuable wildlife habitat was recognized early on. A channel was constructed by local duck clubs in the late 1920s or early 1930s to permit Rattlesnake Creek to flow directly into the Little Salt Marsh (fig. 1), one of two large saline marshes on the refuge. Additional canals and ponds have been constructed since, providing the entire area with a more dependable surface-water supply. However, in the late summer of dry years, an adequate water supply is still a problem as upstream water demands reduce the flow from Rattlesnake Creek to the Quivira National Wildlife Refuge. The U.S. Geological Survey (USGS) developed a computer-based, water-budget model (Jian, 1998) to assist the USFWS in determining the outcome of possible management options with respect to water supply.

Not only is there a desire to ensure a dependable water supply to Quivira National Wildlife Refuge, there also is a strong desire to ensure suitable water quality. In response to the Federal Clean Water Act of 1972, the Kansas Department of Health and Environment (1998) listed segments of Rattlesnake Creek and Little and Big Salt Marshes as water-quality impaired. A water body is designated "water-quality impaired" if it does not meet water-quality criteria established to protect the water body's designated uses.

Rattlesnake Creek is listed as being impaired by chloride and sulfate. The Little and Big Salt Marshes are identified as being eutrophic (abundance of nutrients and seasonal deficiency of oxygen) and impaired for specific uses by pH. The Little Salt Marsh is impaired by fecal coliform bacteria. The Federal Clean Water Act requires that the State of Kansas establish total maximum daily loads (TMDLs) to meet established water-quality criteria and to ensure protection of the creek's and marshes' designated beneficial uses. A TMDL is a calculation and allocation among sources of the maximum amount of a contaminant that a water body can receive and still meet water-quality criteria (U.S. Environmental Protection Agency, 1999).

A proposal for a large hog-processing plant near Great Bend, Kansas (Suber, 1998), was anticipated to lead to significant changes in land use in the Rattlesnake Creek Basin. Great Bend is located north of Rattlesnake Creek Basin (fig. 1), and the construction of a hog-processing plant would lead to substantial increases in the production of feed grains for hogs and in hog farming in the Rattlesnake Creek Basin. These changes in land use could have substantial effects on water quality such as an increase in the use of fertilizers and potential transport of hog wastes to streams that, in turn, may affect the aquatic ecosystem at the refuge.

The presence of chemicals that do not meet water-quality criteria and the lack of a substantial water-quality database for Quivira National Wildlife Refuge have led to the need for further evaluation. Furthermore, the lack of chemical data makes it difficult to calculate loads for the evaluation of TMDLs. With increased regulatory emphasis on TMDLs related to nonpoint-source pollution, refuge managers in the future may need to quantify loads of nutrients, bacteria, and other chemicals entering the refuge. Thus, a study was conducted by the USGS in cooperation with the USFWS to (1) quantify concentrations and

Figure 1. Location of Rattlesnake Creek Basin and marshes, ponds, and canals at Quivira National Wildlife Refuge, south-central Kansas.

temporal variation in selected water-quality chemicals and properties and to (2) estimate chemical concentrations, loads, and yields transported into the Quivira National Wildlife Refuge during a wide range of flow conditions.

Purpose and Scope

This report characterizes the surface-water quality of Rattlesnake Creek immediately upstream from the Quivira National Wildlife Refuge. Data were collected at the USGS streamflow-gaging station on Rattlesnake Creek near Zenith, Kansas (station 07142575, fig. 1). Concentrations of selected water-quality constituents were identified through the manual collection and subsequent analysis of water samples from December 1998 through June 2001. These water samples were collected throughout a range of streamflow conditions so as to reflect conditions that may affect the variability of chemical concentrations and loads. Annual variation was evaluated by comparing 1999 and 2000 data—the 2 years for which complete data sets were available. However, because of the limited number of samples that were collected, seasonal variability was better evaluated using continuous water-quality data and regression-based estimates, as described in the following paragraphs.

Chemical concentrations and loads transported into the Quivira National Wildlife Refuge were estimated for alkalinity, dissolved solids, total suspended solids, sediment, sodium, chloride, fluoride, sulfate, nitrate, total organic nitrogen, total phosphorus, and fecal coliform bacteria. Because these chemicals cannot be measured continuously, regression equations were developed between in-stream (in situ) measurements of physical properties (specific conductance, pH, water temperature, turbidity, and dissolved oxygen) and the chemicals of concern to the refuge (alkalinity, dissolved solids, total suspended solids, sediment, sodium, chloride, fluoride, sulfate, nitrate, total organic nitrogen, total phosphorus, and fecal coliform bacteria). Regression equations were developed using all available in-stream and collected data sets (December 1998 through June 2001). Concentration and load estimates are available in real time to refuge managers and others on the World Wide Web at URL http://ks.water.usgs.gov/Kansas/rtqw/.

This study shows how chemical loads may be estimated using continuous data and that real-time application of regression equations can be used by resource managers to protect wildlife. The methods used in this study could be used at other sites in Kansas and the Nation to estimate chemical loads, providing input data for the development of TMDLs. Results also may contribute toward improved understanding of factors such as land use that could affect water quality at the refuge.

Description of Study Area

The Quivira National Wildlife Refuge is near the downstream end of the Rattlesnake Creek Basin. Rattlesnake Creek drains about 1,047 mi^2 before entering the refuge. Nearly one-half of the drainage area is considered noncontributing (Putnam and others, 2001). Water supply to the refuge includes diversions from Rattlesnake Creek into the Little Salt Marsh located in the southern part of the refuge (fig. 1). Additionally, substantial quantities of water are supplied by natural ground-water seepage in the northern part of the refuge near Big Salt Marsh (Sophocleous and Perkins, 1992). The Rattlesnake Creek Basin occurs in an area of high salinity ground water (Buchanan, 1984), and naturally occurring intrusion of this highly mineralized ground water affects Rattlesnake Creek, Big Salt Marsh, and Little Salt Marsh. The outflow from the refuge re-enters Rattlesnake Creek to the north near its confluence with the Arkansas River.

Oil and gas are produced in the basin, and numerous oil-production facilities are located at or near the refuge (Allen, 1991); however, land use is dominated by agriculture, which includes production of livestock and crops. Agricultural chemicals applied to crops in the basin include fertilizers and pesticides. These chemicals can be transported through surface or ground water and suspended sediment and may have detrimental effects on the aquatic ecosystem at the refuge. Nutrient enrichment, intensified by fertilizer use, can lead to eutrophication of the water bodies at the refuge, which can lead to loss of habitat and food sources for migratory waterfowl.

The dominance of agriculture in the basin and a semiarid climate have led to widespread use of irrigation in the area. Not only is irrigation a concern in relation to water supply at the refuge, but also it is a water-quality concern. Irrigation return flows to Rattlesnake Creek may contain increased concentrations of certain chemicals (selenium, for example) that may cause adverse health effects and bioaccumulate in aquatic organisms and birds at the refuge.

METHODS

Data Collection and Analysis

A continuously recording (15-minute to 60-minute intervals) water-quality monitor (fig. 2) was installed at the USGS stream-flow-gaging station on Rattlesnake Creek near Zenith, Kansas, on October 28, 1998 (station 07142575, fig. 1). This gaging station is located approximately 2.5 stream mi upstream from the inlet to the wildlife refuge. Water-quality properties measured with the monitor from Decem-ber 1998 through June 2001 included specific conductance, pH, water temperature, turbidity, and dissolved oxygen. Measurements were transmitted every 4 hours via satellite to the USGS office in Lawrence, Kansas, and were made available in real time on the World Wide Web at URL http://ks.water.usgs.gov/Kansas/rtqw/. The water-quality monitor was inspected onsite by USGS personnel approximately every 2 weeks to maintain calibration. Guidelines and standard procedures for maintaining the sites and reporting the data are described in Wagner and others (2000).

Each sensor on the water-quality monitor has a certain range of operation. Specific conductance, pH, water temperature, and dissolved oxygen sensors have very wide ranges of operation that were not exceeded during the study and are not likely to be exceeded in any Kansas stream. The turbidity sensor at this site has a maximum reading of approximately 1,750 nephelometric turbidity units (NTU). Although a limit of 1,750 NTU could be problematic for Kansas streams, the Rattlesnake Creek turbidity did not reach this limit in 1999 and 2000.

In addition to the data collected with the in-stream water-quality monitor, the USGS manually collected water-quality samples using depth- and width-integrating techniques (Edwards and Glysson, 1988). Four quarterly (base-flow) samples, five event (base-flow plus runoff) samples, and one quality-assurance sample were collected each year and analyzed for physical properties, solids, sediment, major ions, nutrients, and bacteria. The event-related samples also were analyzed for metals and pesticides.
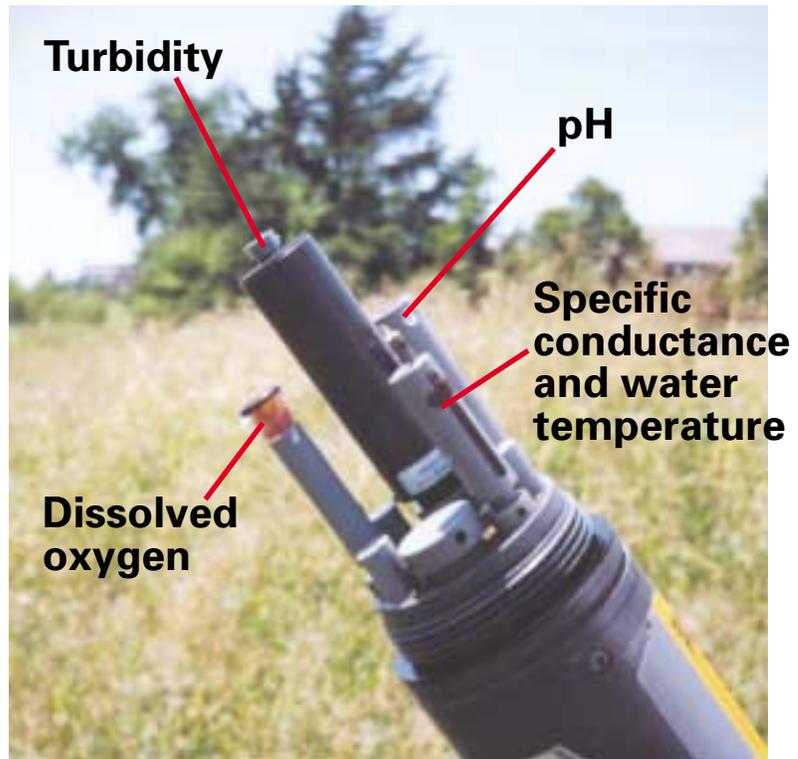
Figure 2. In-stream water-quality monitor used to continuously measure and record specific conductance, pH, water temperature, turbidity, and dissolved oxygen.

The USGS National Water-Quality Laboratory in Denver, Colorado, provided the analytical services for most chemicals, with the exception of triazine herbicides and bacteria analyses. The water samples were analyzed for triazine herbicides at the USGS Organic Geochemistry Research Laboratory in Lawrence, Kansas, according to methods presented in Thurman and others (1990) and Zimmerman and Thurman (1999), and water samples were analyzed for total coliform, E. coli, enterococci, fecal coliform, and fecal strepto-cocci bacteria at the USGS office in Wichita, Kansas, according to methods presented in Myers and Sylvester (1997). Individual data values for all samples collected are on file at the USGS office in Lawrence, Kansas.

Water samples may be collected from a single point in the stream section, along a vertical line between the surface and the streambed (depth-integrated), or at several vertical lines across the entire stream section (depth- and width-integrated). A sample collected using depth- and width-integrating techniques is considered more representative of the entire cross-sectional streamflow than a sample collected at a single point in the stream (Wilde and others, 1999).

Samples were collected using depth- and width-integrating techniques whereas the continuous water-quality monitor probes the water at a single point in the stream. Therefore, part of the difference between measurements in collected water samples and measurements using the water-quality monitor was due to different sampling techniques. No adjustments were applied to the regression equations to correct for these small differences.

Development of Regression Equations

It is possible to express one chemical in terms of another chemical or property (often called a surrogate) using simple linear regression equations (Helsel and Hirsch, 1992). Therefore, data from the water-quality samples and the water-quality monitor were used to develop regression equations used in estimating daily and annual mass loads of chemicals of concern at the refuge. The simplest regression equation can be expressed as:

$$y_i = mx_i + b + e_i \quad i = 1, 2, ..., n, \tag{1}$$

where

y_i is the i th observation of the response (dependent) variable;

m is the slope;

x_i is the i th observation of the explanatory (independent) variable;

b is the intercept;

e_i is the random error for the i th observation; and

n is the number of samples.

The parameters m and b must be estimated from the data set. The most common estimation technique is called least squares estimation (Helsel and Hirsch, 1992). The error term, e_i, is assumed to be normally distributed with a mean equal to zero and a constant variance, s^2.

The first step in choosing a regression equation was to plot each possible explanatory variable against the response variable and to look for patterns in the data. Next, to determine which explanatory variable or variables to include in the regression equation for each chemical of concern, both a step-wise procedure (Ott, 1993, p. 656) and an overall method (Helsel and Hirsch, 1992, p. 312–314) were used. In the step-wise procedure, each explanatory variable was added to the regression equation one at a time to determine if there was a statistically significant correlation. The possible

explanatory variables included each of the sensor measurements of the water-quality monitor (specific conductance, pH, water temperature, turbidity, and dissolved oxygen), streamflow, and time. Explanatory variables were considered significant if the p-value (probability value) was less than 0.05. The overall method evaluated all possible regression equations. If there were several acceptable equations, the one with the lowest PRESS statistic was chosen. PRESS (acronym for "PRediction Error Sum of Squares") is one of the best measures of the goodness of fit of a regression equation (Helsel and Hirsch, 1992, p. 248). Additionally, explanatory variables were included in an equation only if there was a physical basis or explanation for their inclusion. When more than one explanatory variable is used to express the response variable, it is called multiple regression.

In addition to the PRESS, four common diagnostic statistics were used to evaluate regression equations. These are the mean square error *(MSE)*, the coefficient of determination (R^2), the relative mean absolute error *(RMAE)*, and relative percentage difference *(RPD)*.

MSE is calculated as follows:

$$MSE = \sqrt{\frac{\sum_{i=1}^{n} [y_i - E(y_i)]^2}{n-2}}, \tag{2}$$

where y_i represents the value of y at the i th data point, $E(y_i)$ is the estimated value of y at the i th data point (where $E(y_i) = mx_i + b$), and n is the number of samples. The *MSE* is determined for each equation to assess the variance between estimated and measured values.

MSE is a dimensional measure. Dimensionless measures often are required in practice for the purpose of comparing chemicals or properties with different dimensions (units of measure). A dimensionless measure of fitting y on x is the R^2, or the fraction of the variance explained by the regression:

$$R^2 = 1.0 - (SSE/SSy). \tag{3}$$

SSE and *SSy* are calculated as follows:

$$SSE = \sum_{i=1}^{n} [y_i - E(y_i)]^2, \text{ and} \tag{4}$$

$$SSy = \sum_{i=1}^{n} (y_i - \bar{y})^2, \tag{5}$$

in which $\bar{y}$ is the mean of y. The R^2 ranges from 0 to 1 and often is called the multiple coefficient of determination in multiple linear regression.

The *RMAE*, expressed as a percentage, is calculated as follows:

$$RMAE = \frac{\frac{1}{n}\sum_{i=1}^{n}|A - B|}{M_B} \times 100, \qquad (6)$$

where A is the estimated concentration, B is the measured concentration, and M_B is the mean (average) of all the measured concentrations.

Relative percentage differences (*RPD*s) between measured and estimated chemical concentrations were calculated for each simultaneous data set using the following equation:

$$RPD = [\;|B - A|/(A)\;] \times 100, \qquad (7)$$

where

> RPD is the relative percentage difference;
> A is the measured chemical concentration; and
> B is the estimated chemical concentration.

The *RPD* also was used to evaluate the differences in replicate data sets (quality-assurance samples).

Graphical plots were constructed to examine the linearity of the relation between explanatory and response variables. Certain explanatory variables and response variables were transformed to convert all equations presented herein to linear equations. Transformations (for example, base-10 logarithmic or power) of variables can eliminate curvature and simplify analysis of the data (Ott, 1993, p. 454).

Outliers were identified graphically and investigated to determine their validity. No outliers were eliminated from the data used to develop the equations contained in this report. One sample (collected on December 7, 1999) had total organic nitrogen and total phosphorus concentrations that were less than the analytical detection limit (0.10 mg/L for total organic nitrogen and 0.05 mg/L for total phosphorus). Values of one-half the detection limits were used for this sample in developing the total organic nitrogen and total phosphorus regression equations. Nitrate concentrations were calculated by subtracting nitrite concentration from the nitrite plus nitrate as nitrogen concentrations reported by the USGS National Water-Quality Laboratory.

Some of the response variables in the regression equations for estimating water quality at the Rattlesnake Creek gaging station (07142575, fig. 1) were transformed to eliminate curvature and achieve a simpler linear equation; therefore, retransformation of regression-estimated concentrations was necessary. However, retransformation can cause an underestimation of chemical loads when adding individual load estimates over a long period of time. Applying Duan's bias correction factor (Duan, 1983) to the annual load calculation presented in this report allowed correction for this underestimation. The bias correction factors for estimates in this report were between 1.01 and 1.33. Cohn and others (1989), Gilroy and others (1990), and Hirsch and others (1993) provide additional information on interpreting the results of regression-based load estimates.

Calculation of Measured and Estimated Chemical Loads and Yields

Measured and estimated instantaneous chemical loads, expressed in units of pounds per day, were calculated by multiplying instantaneous chemical concentrations (in milligrams per liter) by instantaneous streamflow (in cubic feet per second) and an appropriate conversion factor (5.39). Instantaneous concentration and instantaneous streamflow correspond to a single moment in time as opposed to an average or sum. Annual loads were calculated by multiplying the instantaneous loads (expressed as daily load) by 365. Measured and estimated instantaneous yields (in pounds per acre) were calculated by dividing the instantaneous chemical load by the contributing drainage area (1,047 mi^2) in acres (670,080 acres).

CHEMICAL CONCENTRATIONS, LOADS, YIELDS, AND VARIABILITY

Measured Concentrations

From December 1998 through March 2001, water-quality samples were collected and analyzed for 125 physical properties and chemicals (table 1). These samples were collected throughout a range of streamflow conditions, and analytical results showed seasonal and hydrologic variability for many chemicals. Two quality-assurance (replicate) samples (one in 1999 and one in 2000) also were collected and analyzed. These two samples indicated a mean

Table 1. Statistical summary of water-quality data collected from Rattlesnake Creek near Zenith, Kansas, December 1998 through June 2001

[ft³/s, cubic feet per second; μS/cm, microsiemens per centimeter at 25 degrees Celsius; NTU, nephelometric turbidity units; mg/L, milligrams per liter; CaCO₃, calcium carbonate; *, mean and median values were estimated using a log-probability regression to predict values of data less than the detection limit; col/100 mL, colonies per 100 milliliters of water; --, not calculated or not applicable; μg/L, micrograms per liter; AL, State of Kansas aquatic life support criteria; VI, USEPA recommended criteria for Ecoregion VI; SDWR, Secondary Drinking Water Regulation; MCL, Maximum Contaminant Level; DWEL, Drinking Water Equivalent Level; <, less than; HAL, Health Advisory Level; MCLG, Maximum Contaminant Level Goal; EPA CRC, U.S. Environmental Protection Agency Contact Recreational Criteria; KS CRC, State of Kansas Contact Recreational Criteria]

Water-quality chemical or property (unit of measurement)	Number of samples	Concentration			Water-quality criteria
		Range	Mean	Median	
Physical properties, solids, and sediment					
Instantaneous streamflow (ft³/s)	25	3.6–840	130	53	--
Specific conductance (μS/cm)	29	453–9,930	3,560	3,040	--
pH (standard units)	27	7.3–8.8	8.1	8.2	6.5–8.5 (AL)
Water temperature (degrees Celsius)	30	3.4–34.0	19.4	21.2	--
Turbidity (NTU)	24	5.0–480	124	83	9.9 (VI)
Oxygen, dissolved (mg/L)	24	3.1–12.8	9.5	10	5 (AL)
Alkalinity (mg/L as CaCO₃)	18	91–224	180	190	--
Total organic carbon (mg/L)	10	2.4–17	11	11	--
Total suspended solids (mg/L)	18	14–270	106	80	--
Dissolved solids (mg/L)	18	264–5,460	1,870	1,640	500 (SDWR)
Suspended sediment (mg/L)	10	14–1,820	418	325	--
Major ions					
Calcium, dissolved (mg/L)	18	21–100	73	79	--
Calcium, total (mg/L)	17	22–100	78	83	--
Magnesium, dissolved (mg/L)	18	3.1–35	15	14	--
Magnesium, total (mg/L)	17	3.6–37	16	16	--
Potassium, dissolved (mg/L)	18	3.5–9.3	5.7	5.4	--
Potassium, total (mg/L)	17	4.4–11	6.4	6.1	--
Sodium, dissolved (mg/L)	18	50–1,880	585	466	20 (DWEL)
Sodium, total (mg/L)	17	49–1,940	576	453	--
Chloride, dissolved (mg/L)	18	67–3,000	927	757	860 (AL)
Fluoride, dissolved (mg/L)	18	0.2–0.6	.4	.5	4.0 (MCL)
Silica, dissolved (mg/L)	18	5.1–21	15	15	--
Sulfate, dissolved (mg/L)	18	11–269	104	95	352 (AL)
Bromide, dissolved (mg/L)	7	<0.01–0.36	.12*	.04*	--
Nutrients					
Ammonia plus organic nitrogen (mg/L)	20	0.19–1.1	.50	.50	--
Nitrogen, total organic (mg/L)	20	0.10–2.5	1.2	1.1	2.18 (VI)
Ammonia nitrogen (mg/L)	20	<0.02–0.19	.03*	.01 *	--
Nitrite plus nitrate, dissolved (mg/L)	20	<0.05–2.1	.77*	.74*	--
Nitrite nitrogen (mg/L)	20	<0.01–0.05	.02*	.01*	--
Phosphorus, dissolved (mg/L)	20	<0.05–0.23	.09*	.06*	--
Ortho phosphorus (mg/L)	20	<0.01–0.21	.07*	.03*	--
Phosphorus, total (mg/L)	20	<0.05–0.76	.27*	.22*	.076 (VI)

Table 1. Statistical summary of water-quality data collected from Rattlesnake Creek near Zenith, Kansas, December 1998 through June 2001—Continued

Water-quality chemical or property (unit of measurement)	Number of samples	Concentration			Water-quality criteria
		Range	Mean	Median	
Metals					
Aluminum, dissolved (μg/L)	10	not detected	--	--	50 (SDWR)
Aluminum, total (μg/L)	10	188–5,890	2,060	1,730	--
Antimony, dissolved (μg/L)	10	not detected	--	--	6.0 (MCL)
Antimony, total (μg/L)	10	not detected	--	--	--
Arsenic, dissolved (μg/L)	10	1.2–3.7	2.4	2.3	10 (MCL)
Arsenic, total (μg/L)	10	1–5	3	3	--
Barium, dissolved (μg/L)	10	51–205	135	144	2,000 (MCL)
Barium, total (μg/L)	10	<100–253	173*	173*	--
Beryllium, dissolved (μg/L)	10	not detected	--	--	4.0 (MCL)
Beryllium, total (μg/L)	10	<20–68	--	--	--
Cadmium, dissolved (μg/L)	10	not detected	--	--	--
Cadmium, total (μg/L)	10	not detected	--	--	--
Chromium, dissolved (μg/L)	10	not detected	--	--	--
Chromium, total (μg/L)	10	<4–4	2*	2*	--
Cobalt, dissolved (μg/L)	10	not detected	--	--	--
Cobalt, total (μg/L)	10	<2–3	2*	2*	--
Copper, dissolved (μg/L)	10	not detected	--	--	--
Copper, total (μg/L)	10	<1–7	3*	3*	--
Cyanide, dissolved (mg/L)	10	<0.01–0.15	--	--	--
Cyanide, total (mg/L)	10	not detected	--	--	--
Iron, dissolved (μg/L)	18	<50–80	16*	9.8*	300 (SDWR)
Iron, total (μg/L)	18	<155–4,670	1,920*	1,630*	--
Lead, dissolved (μg/L)	10	not detected	--	--	15 (MCL)
Lead, total (μg/L)	10	<4–6	3*	3*	--
Lithium, dissolved (μg/L)	10	5.8–75	27	22	--
Lithium, total (μg/L)	10	7.2–63	30	29	--
Manganese, dissolved (μg/L)	18	<20–120	16*	9*	50 (SDWR)
Manganese, total (μg/L)	18	30–238	114	94	--
Mercury, dissolved (μg/L)	10	not detected	--	--	2.0 (MCL)
Mercury, total (μg/L)	10	not detected	--	--	--
Molybdenum, dissolved (μg/L)	10	not detected	--	--	--
Molybdenum, total (μg/L)	10	1–5	3	3	--
Nickel, dissolved (μg/L)	10	not detected	--	--	--
Nickel, total (μg/L)	10	<1–7	3*	3*	--
Selenium, dissolved (μg/L)	10	not detected	--	--	50 (MCL)
Selenium, total (μg/L)	10	not detected	--	--	--
Silver, dissolved (μg/L)	10	not detected	--	--	100 (MCL)
Silver, total (μg/L)	10	not detected	--	--	--
Strontium, dissolved (μg/L)	10	133–1,140	521	465	--

Table 1. Statistical summary of water-quality data collected from Rattlesnake Creek near Zenith, Kansas, December 1998 through June 2001—Continued

Water-quality chemical or property (unit of measurement)	Number of samples	Concentration			Water-quality criteria
		Range	Mean	Median	
Metals—Continued					
Strontium, total (µg/L)	10	140–1,150	580	589	--
Vanadium, dissolved (µg/L)	10	not detected	--	--	--
Zinc, dissolved (µg/L)	10	not detected	--	--	--
Zinc, total (µg/L)	10	not detected	--	--	--
Pesticides (dissolved)					
2,6-Diethylaniline (µg/L)	9	not detected	--	--	--
Acetochlor (µg/L)	9	<0.008–0.005	--	--	--
Alachlor (µg/L)	9	<0.01–0.12	--	--	2.0 (MCL)
Atrazine (µg/L)	9	0.01–1.5	.37	.15	3.0 (MCL)
Benfluralin (µg/L)	9	not detected	--	--	--
Butylate (µg/L)	9	not detected	--	--	350 (HAL)
Carbaryl (µg/L)	9	not detected	--	--	700 (HAL)
Carbofuran (µg/L)	9	not detected	--	--	40 (MCL)
Chlorpyrifos (µg/L)	9	not detected	--	--	--
Cyanazine (µg/L)	9	not detected	--	--	1.0 (HAL)
Deethylatrazine (µg/L)	9	0.01–0.13	.06	.03	--
Diazinon (µg/L)	9	not detected	--	--	.600 (HAL)
Dieldrin (µg/L)	9	not detected	--	--	--
Disulfoton (µg/L)	9	not detected	--	--	--
EPTC (µg/L)	9	not detected	--	--	--
Ethalfluralin (µg/L)	9	not detected	--	--	--
Ethoprop (µg/L)	9	not detected	--	--	--
Fonofox (µg/L)	9	not detected	--	--	--
Lindane (µg/L)	9	not detected	--	--	--
Linuron (µg/L)	9	not detected	--	--	--
Malathion (µg/L)	9	<0.005–0.009	--	--	--
Methyl azinphos (µg/L)	9	not detected	--	--	--
Methyl parathion (µg/L)	9	not detected	--	--	--
Metolachlor (µg/L)	9	<0.01–0.87	.12*	.02*	70 (HAL)
Metribuzin (µg/L)	9	<0.004–0.150	--	--	100 (HAL)
Molinate (µg/L)	9	not detected	--	--	--
Napropamide (µg/L)	9	not detected	--	--	--
p,p'DDE (µg/L)	9	not detected	--	--	--
Parathion (µg/L)	9	not detected	--	--	--
Pebulate (µg/L)	9	not detected	--	--	--
Pendimethalin (µg/L)	9	not detected	--	--	--
Permethrin (µg/L)	9	not detected	--	--	--
Phorate (µg/L)	9	not detected	--	--	--
Prometon (µg/L)	9	<0.02–1.3	--	--	100 (HAL)

Table 1. Statistical summary of water-quality data collected from Rattlesnake Creek near Zenith, Kansas, December 1998 through June 2001—Continued

Water-quality chemical or property (unit of measurement)	Number of samples	Concentration			Water-quality criteria
		Range	Mean	Median	
Pesticides—Continued					
Pronamide (µg/L)	9	not detected	--	--	--
Propachlor (µg/L)	9	not detected	--	--	90 (HAL)
Propanil (µg/L)	9	not detected	--	--	--
Propargite (µg/L)	9	not detected	--	--	--
Simazine (µg/L)	9	<0.005–0.009	--	--	4.0 (MCL)
Tebuthiuron (µg/L)	9	not detected	--	--	500 (HAL)
Terbacil (µg/L)	9	not detected	--	--	90 (HAL)
Terbufos (µg/L)	9	not detected	--	--	--
Thiobencarb (µg/L)	9	not detected	--	--	--
Triallate (µg/L)	9	not detected	--	--	--
Triazine (µg/L)	18	<0.1–2.0	0.6*	0.3*	--
Trifluralin (µg/L)	9	not detected	--	--	5.0 (HAL)
Bacteria					
Total coliform bacteria (col/100 mL)	4	105–43,900	--	--	0 (MCLG)
E. coli bacteria (col/100 mL)	17	13–1,830	360	162	256 (EPA CRC)
Enterococci bacteria (col/100 mL)	3	62–1,550	--	--	--
Fecal coliform bacteria (col/100 mL)	23	7–20,000	1,400	500	200 (KS CRC)
Fecal streptococci bacteria (col/100 mL)	20	<2–4,600	410	170	--

RPD of about 2 percent for all properties and chemicals analyzed.

Ten of the 125 properties and chemicals (39 of which have established or proposed criteria) did not meet water-quality criteria at some time during the study. These were pH, turbidity, dissolved oxygen, dissolved solids, sodium, chloride, phosphorus, total coliform bacteria, E. coli bacteria, and fecal coliform bacteria. Although water-quality criteria represent goals to support designated uses of a water body, for some chemicals enforceable standards for the designated use do not exist. Therefore, water-quality conditions may be compared to proposed criteria or criteria for an alternate use (drinking water, for example).

pH levels below 6.5 or above 8.5 have caused both the Little and Big Salt Marshes to be listed as pH impaired (Kansas Department of Health and Environment, 2001). The pH range for water from Rattlesnake Creek near Zenith during the period of manual data collection was 7.3 to 8.8 standard units (table 1). Turbidity ranged from 5.0 to 480 NTU. The recommended USEPA guideline for turbidity is 9.9 NTU (U.S. Environmental Protection Agency, 2000a) for rivers and streams. Dissolved oxygen is necessary for the survival of fish and other aquatic life, and therefore, the Kansas Department of Health and Environment (KDHE) has established an aquatic life (minimum) criteria of 5.0 mg/L. One sample, with a dissolved oxygen concentration of 3.1 mg/L, did not meet this minimum criteria. Dissolved solids ranged from 264 to 5,460 mg/L. The Secondary Drinking Water Regulation (SDWR) for dissolved solids is 500 mg/L (U.S. Environmental Protection Agency, 2000b). The USEPA has established a Drinking-Water Equivalent Level (DWEL) for sodium of 20 mg/L, which was exceeded in all 18 samples from Rattlesnake Creek near Zenith with a range of 50 to 1,880 mg/L. Chloride concentrations ranged from 67 to 3,000 mg/L; 15 of the 18 samples exceeded the USEPA's SDWR of 250 mg/L (U.S. Environmental Protection Agency, 2000b), and 6 of the 18 samples exceeded KDHE's acute aquatic life criteria of 860 mg/L (Kansas Department of Health and Environment, 2000).

Because States and Tribes consistently identify excessive levels of nutrients as a major reason why surface water does not meet water-quality criteria, the USEPA has recommended new water-quality criteria for nutrients (U.S. Environmental Protection Agency, 2000a). In the new recommended criteria, the United States is divided into 14 nutrient ecoregions, according to procedures described in the "Nutrient Criteria Technical Guidance Manual—Rivers and Streams" (U.S. Environmental Protection Agency, 2000c). Kansas is divided among four of the 14 ecoregions. The northeast part of the State is in Ecoregion VI (Corn Belt and Northern Great Plains). The Quivira National Wildlife Refuge is in Ecoregion V (South-Central Cultivated Great Plains); however, recommended criteria for Ecoregion VI are used as a reference in table 1 as nutrient recommendations have not been established yet (June 2001) for Ecoregion V. Total phosphorus concentrations ranged from less than 0.05 to 0.76 mg/L in Rattlesnake Creek, exceeding the Ecoregion VI proposed criteria of 0.076 mg/L.

No metal or pesticide concentrations exceeded water-quality criteria. In fact, 22 of the 43 metals analyzed were not detected, and 36 of the 46 pesticides analyzed were not detected.

Total coliform bacteria densities ranged from 105 to 43,900 col/100 mL (colonies per 100 milliliters of water). The USEPA has established a Maximum Contaminant Level Goal (MCLG) of 0 col/100 mL for drinking water. E. coli bacteria ranged from 13 to 1,830 col/100 mL. Five of 17 samples exceeded the USEPA Contact Recreational Criteria of 256 col/100 mL. Fecal coliform bacteria densities ranged from 7 to 20,000 col/100 mL. The segment of Rattlesnake Creek upstream from the refuge is designated for contact recreation by KDHE. Primary contact recreation means recreational activity whereby the body is immersed in the water to the extent that some inadvertent ingestion of water is probable (swimming, for example) (Kansas Department of Health and Environment, 1997). Because of public-health concerns associated with fecal contamination, KDHE established water-quality criteria of 2,000 col/100 mL for secondary contact recreation (fishing, for example) and 200 col/100 mL (from April 1 through October 31) for primary contact recreation on the basis of a geometric mean (Kansas Department of Health and Environment, 2001). Nine percent of the water samples had fecal coliform bacteria densities greater than the secondary contact criteria, and 70

percent of the water samples had densities greater than the primary contact criteria.

Hydrologic conditions within the Rattlesnake Creek Basin differed slightly between 1999 to 2000 (fig. 3A) especially during September and October. The 1999 and 2000 mean monthly streamflows differed in comparison to long-term (October 1973–December 2000) mean monthly streamflow (fig. 3B). Mean monthly precipitation was 2.2 in. in 1999 compared to 1.5 in. in 2000; differences between the 2 years for individual months were generally large (fig. 4). Precipitation contributes to runoff, which may result in increased concentrations of sediment, bacteria, and other chemicals reaching the stream. Seasonal variation in water quality was difficult to evaluate for many chemicals because of the limited number of samples collected (one to two per season). However, differences between 1999 and 2000 were evaluated by comparing annual median concentrations for selected chemicals (fig. 5). Percentage change was calculated by dividing the difference between 1999 and 2000 median concentrations (1999 concentration minus 2000 concentration) by the 1999 median concentration and multiplying by 100.

Chemicals that had a decrease or essentially no change in median concentration between 1999 and 2000 included alkalinity, fluoride, nitrate, and fecal coliform bacteria. Chemicals that had an increase in median concentration between 1999 and 2000 included dissolved solids, total suspended solids, sodium, chloride, sulfate, total organic nitrogen, and total phosphorus.

Increases in the median concentrations of the major ions (sodium, chloride, and sulfate) in 2000 were reasonable considering the decreased rainfall (fig. 4) and the very low streamflow in September and October (fig. 3). Low streamflow corresponds to an increase in that part of streamflow coming from ground water (base flow), which has naturally high concentrations of sodium, chloride, and sulfate in the study area (Kansas Department of Health and Environment, 2001).

Increases in dissolved solids, total suspended solids, total organic nitrogen, and total phosphorus were not as readily explained. However, unusually high streamflow occurred in early spring of 2000 (fig. 3A), which corresponded to the time of year when fields were tilled, exposing the solids and sediment that are eventually transported to Rattlesnake Creek. Fertilizer applied to the agricultural fields also may be a major
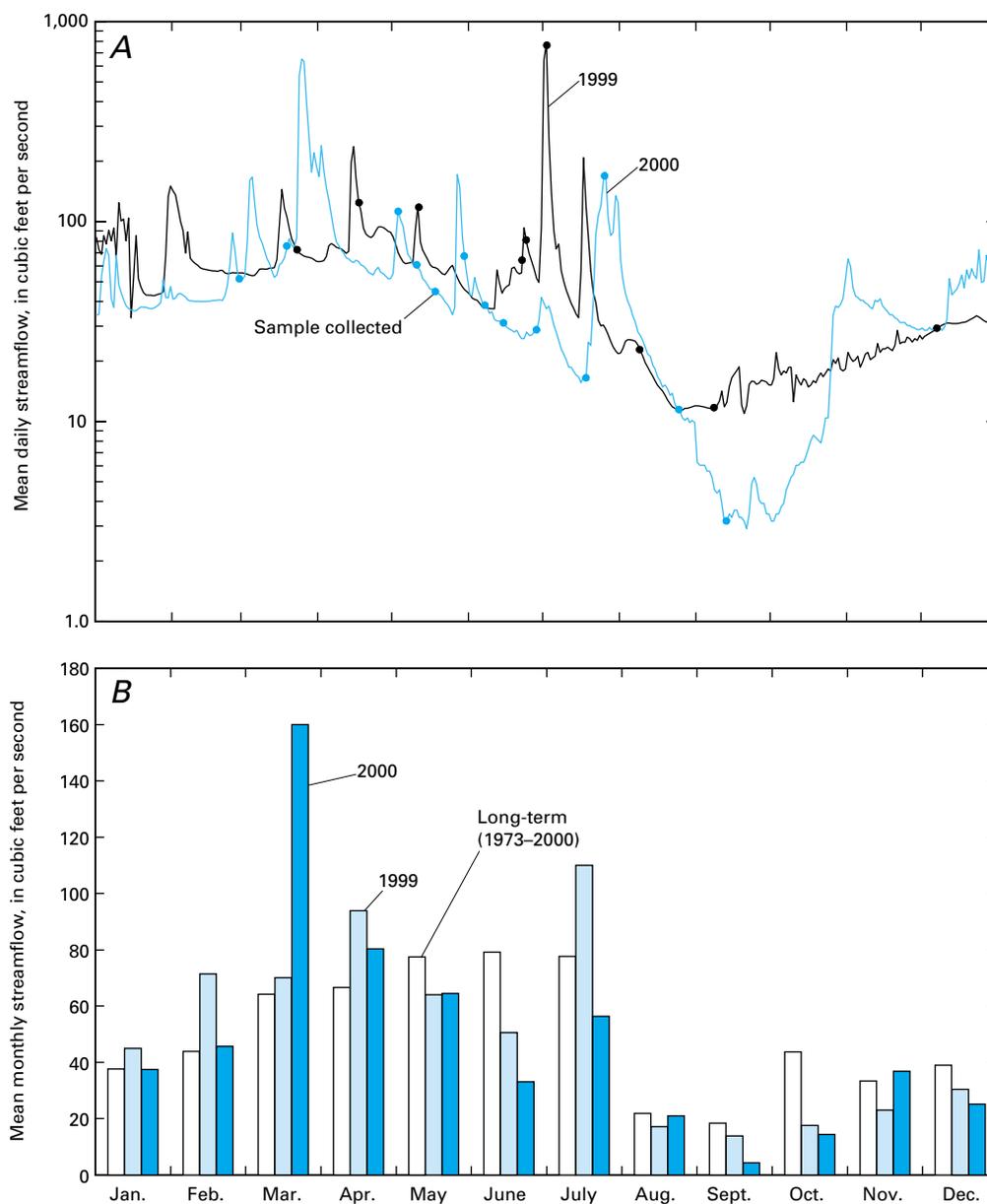
Figure 3. Comparison of (A) mean daily streamflow and (B) long-term mean monthly streamflow (1973–2000) for Rattlesnake Creek near Zenith.

level of uncertainty exists due to the large gaps in time between collection of samples. The availability of continuous data (and regression-based estimates) would reduce this uncertainty, as would the collection of additional samples.

Regression-Estimated Concentrations Using Real-Time Water-Quality Monitoring

Whereas pH and turbidity can be measured directly by the in-stream water-quality monitor, concentrations of most chemicals of concern needed to be estimated on the basis of in-stream, water-quality monitor measurements and regression analysis. In addition to those measured chemicals that sometimes that do not meet water-quality criteria (dissolved solids, sodium, chloride, and fecal coliform bacteria), other chemicals also were a concern for the health and habitat of fish and wildlife at the

source of the nitrogen and phosphorus in Rattlesnake Creek, and concentrations of these nutrients in runoff can be several times greater during high flows in the spring than during low flow. In 1998, it was estimated that 42,104 tons of fertilizer were bought and potentially used in the basin (Kansas Department of Health and Environment, 2001).

The changes in median concentrations between 1999 and 2000 may be due in part to the times of the year when samples were collected. Because only nine samples were collected per year for most chemicals, a

Quivira National Wildlife Refuge. A discussion of each chemical of concern and the associated regression equation (table 2) follows.

Through the least-squares process, certain explanatory variables were selected that have a significant relation (p-value less than 0.05) to the response variable. However, an explanatory variable was included in the regression equation only if there was a physical basis or explanation for its inclusion. Of the equations presented in table 2, each is site specific and applies only to Rattlesnake Creek near Zenith, Kansas. Addi-
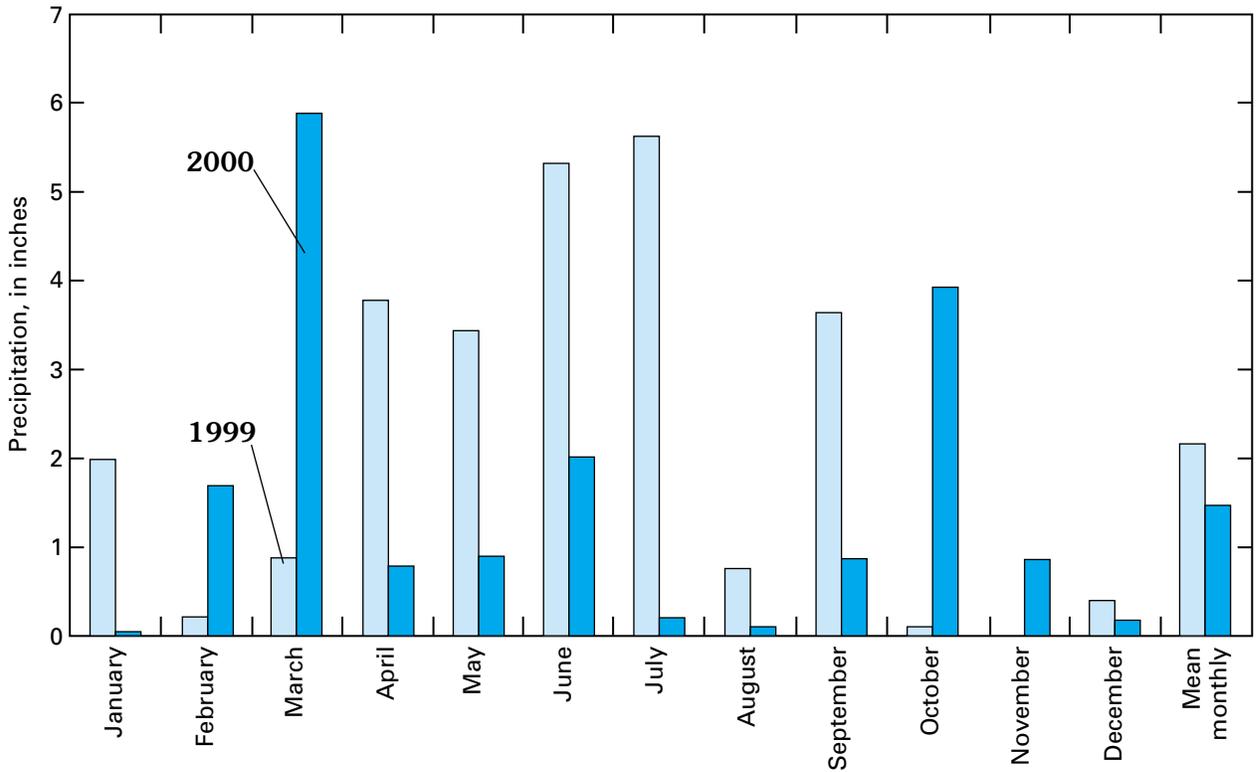
Figure 4. Comparison of 1999 and 2000 monthly precipitation at Rattlesnake Creek near Zenith gaging station (07142575, fig. 1).
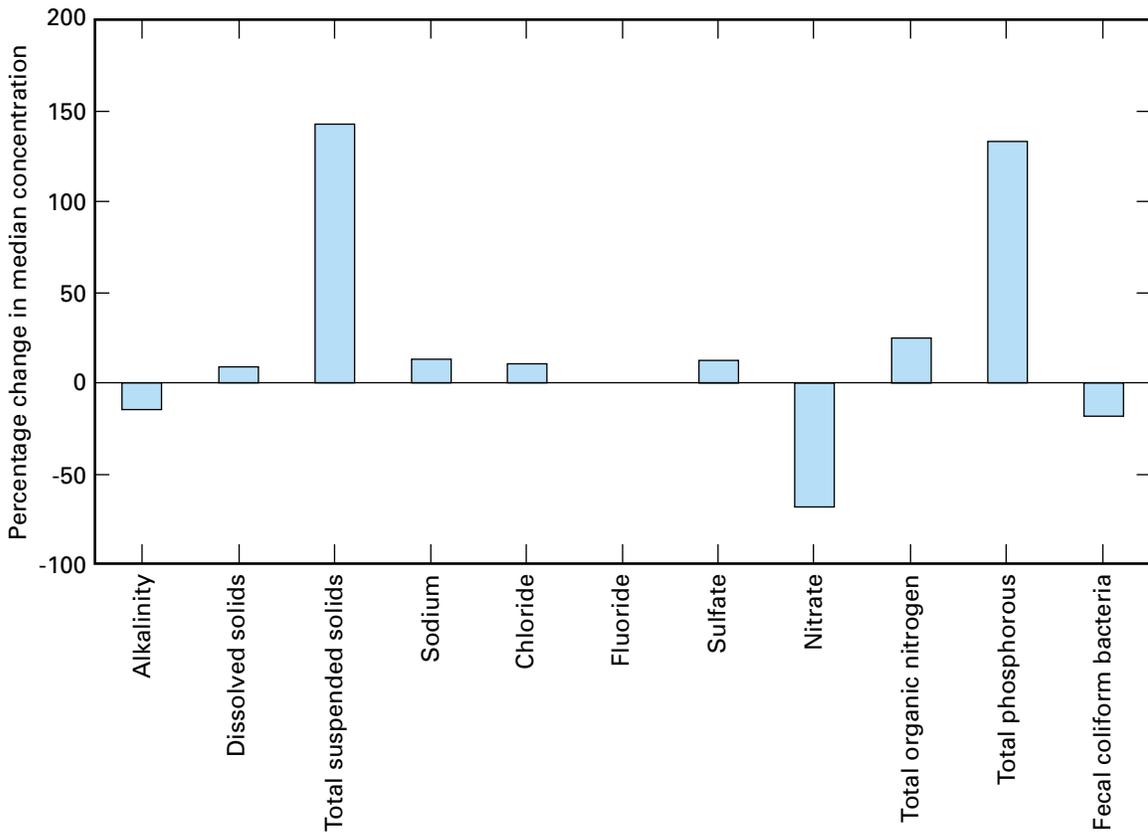

Figure 5. Percentage change in median concentrations of selected water-quality chemicals between 1999 and 2000 (1999 concentration minus 2000 concentration, divided by 1999 concentration) for Rattlesnake Creek near Zenith.

Table 2. Linear regression equations for estimation of physical properties, solids, sediment, major ions, nutrients, and bacteria in Rattlesnake Creek near Zenith, Kansas, December 1998 through June 2001

[n, number of samples; MSE, mean square error; R^2, coefficient of determination; RMAE, relative mean absolute error; RPD, relative percentage difference; $\log_{10}$, base-10 logarithm; ALK, alkalinity, in milligrams per liter; *WT*, water temperature, in degrees Celsius (°C); *Q*, streamflow, in cubic feet per second; *DS*, dissolved solids, in milligrams per liter; *SC*, specific conductance, in microsiemens per centimeter at 25 °C; *TSS*, total suspended solids, in milligrams per liter; *NTU*, turbidity, in nephelometric turbidity units; *SSC*, suspended sediment concentration, in milligrams per liter; *Na*, sodium, in milligrams per liter; *Cl*, chloride, in milligrams per liter; *F*, fluoride, in milligrams per liter; SO_4, sulfate, in milligrams per liter; NO_3, nitrate, in milligrams per liter; *TN*, total organic nitrogen, in milligrams per liter; *TP*, total phosphorus, in milligrams per liter; *FCB*, fecal coliform bacteria density, in colonies per 100 milliliters of water; --, not applicable]

Water-quality chemical or property	Regression equation	n	Concentration range[1]	p-value	MSE	R^2	RMAE	Median RPD
Physical properties, solids, and sediment								
Alkalinity	$\text{Log}_{10}ALK = -0.000368Q - 0.000148WT^2 + 2.36$	18	*ALK* 91–224	--	0.00454	0.710	10.2	7.77
			Q 3.6–840	<0.001	--	--	--	--
			WT 3.4–31.5	.015	--	--	--	--
Dissolved solids	$DS = 0.549SC + 14.3$	18	*DS* 264–5,460	--	707	.999	1.00	1.20
			SC 453–9,930	<.001				
Total suspended solids	$\text{Log}_{10}TSS = 0.818\log_{10}NTU + 0.348$	18	*TSS* 14–270	--	.0241	.825	27.3	20.1
			NTU 5–270	<.001	--	--	--	--
Suspended sediment	$\text{Log}_{10}SSC = 0.926\log_{10}NTU + 0.438$	9	*SSC* 14.3–1,820	--	.0991	.926	37.5	11.1
			NTU 5–480	<.001	--	--	--	--
Major ions								
Sodium	$Na = 0.203SC + 0.0938Q - 117$	18	*Na* 50–1,880	--	597	.998	2.93	2.53
			SC 453–9,930	<.001	--	--	--	--
			Q 3.6–840	.006	--	--	--	--
Chloride	$Cl = 0.319SC + 0.113Q - 172$	18	*Cl* 67–3,000	--	654	.999	1.85	2.33
			SC 453–9,930	<.001	--	--	--	--
			Q 3.6–840	.002	--	--	--	--
Fluoride	$\log_{10}F = -0.000255Q + 0.162\log_{10}SC - 0.892$	18	*F* 0.2–0.6	--	.00317	.826	11.3	10.2
			Q 3.6–840	.018	--	--	--	--
			SC 453–9,930	.022	--	--	--	--
Sulfate	$SO_4 = 0.0268SC + 13.17$	18	SO_4 12–269	--	75.3	.983	6.86	4.76
			SC 453–9,930	<.001	--	--	--	--
Nutrients								
Nitrate	$\text{Log}_{10}NO_3 = -0.000442SC + 2.60\log_{10}SC - 0.000998WT^2 - 7.37$	20	NO_3 0.014–2.13	--	.0942	.829	37.3	40.0
			SC 453–9,930	<.001	--	--	--	--
			WT 3.4–31.5	.002	--	--	--	--
Total organic nitrogen	$TN = 0.00317NTU + 0.0234WT - 0.0000655SC + 0.469$	20	*TN* 0.050–2.5	--	.0798	.806	16.2	14.8
			NTU 5–480	<.001	--	--	--	--
			WT 3.4–31.5	.008	--	--	--	--
			SC 453–9,930	.050	--	--	--	--

Table 2. Linear regression equations for estimation of physical properties, solids, sediment, major ions, nutrients, and bacteria in Rattlesnake Creek near Zenith, Kansas, December 1998 through June 2001—Continued

Water-quality chemical or property	Regression equation	n	Concentration range[1]	p-value	MSE	R^2	RMAE	Median RPD
Nutrients—Continued								
Total phosphorus	$TP = 0.00103NTU - 0.227\log_{10}SC + 0.00570WT + 0.776$	20	TP 0.025–0.755	--	0.00179	0.960	11.2	12.9
			NTU 5–480	<0.001	--	--	--	--
			SC 453–9,930	<.001	--	--	--	--
			WT 3.4–31.5	<.001	--	--	--	--
Bacteria								
Fecal coliform bacteria[2]	$\log_{10}FCB = -3.40\log_{10}WT + 0.432\log_{10}NTU + 6.53$	18	FCB 90–20,000	--	.124	.661	43.4	50.0
			WT 9.3–32.2	<.001	--	--	--	--
			NTU 5–480	.036	--	--	--	--

[1]Concentration ranges and sample sizes are not always the same as those presented in table 1 because these data represent a subset of table 1.

[2]Equation developed only for samples during the recreation period from April 1 through October 31.

tionally, the equations presented in table 2 are valid only for the concentration ranges given in table 2.

Physical Properties, Solids, and Sediment

The physical properties, solids, and sediment discussed in this report are alkalinity, dissolved solids, total suspended solids (*TSS*), and suspended sediment concentration (*SSC*). A comparison of the measured and regression-estimated concentrations is shown in figure 6.

It is important to consider these properties and chemicals in water because they can be indicators of stream health. Streams with a low alkalinity have a low buffering capacity, which may pose a risk to aquatic life. Excessively large concentrations of dissolved solids are objectionable in drinking water because of possible physiological effects (U.S. Environmental Protection Agency, 1986). *TSS* and *SSC* can cause problems for fish by clogging gills and for aquatic plants by reducing light penetration and thus limiting growth. In addition, solids and sediment provide a medium for accumulation and transport of other chemicals such as phosphorus and bacteria. For these reasons, it is important to monitor alkalinity, dissolved solids, *TSS*, and *SSC* not only because of the effect on fish, but also on waterfowl that depend on fish for their survival.

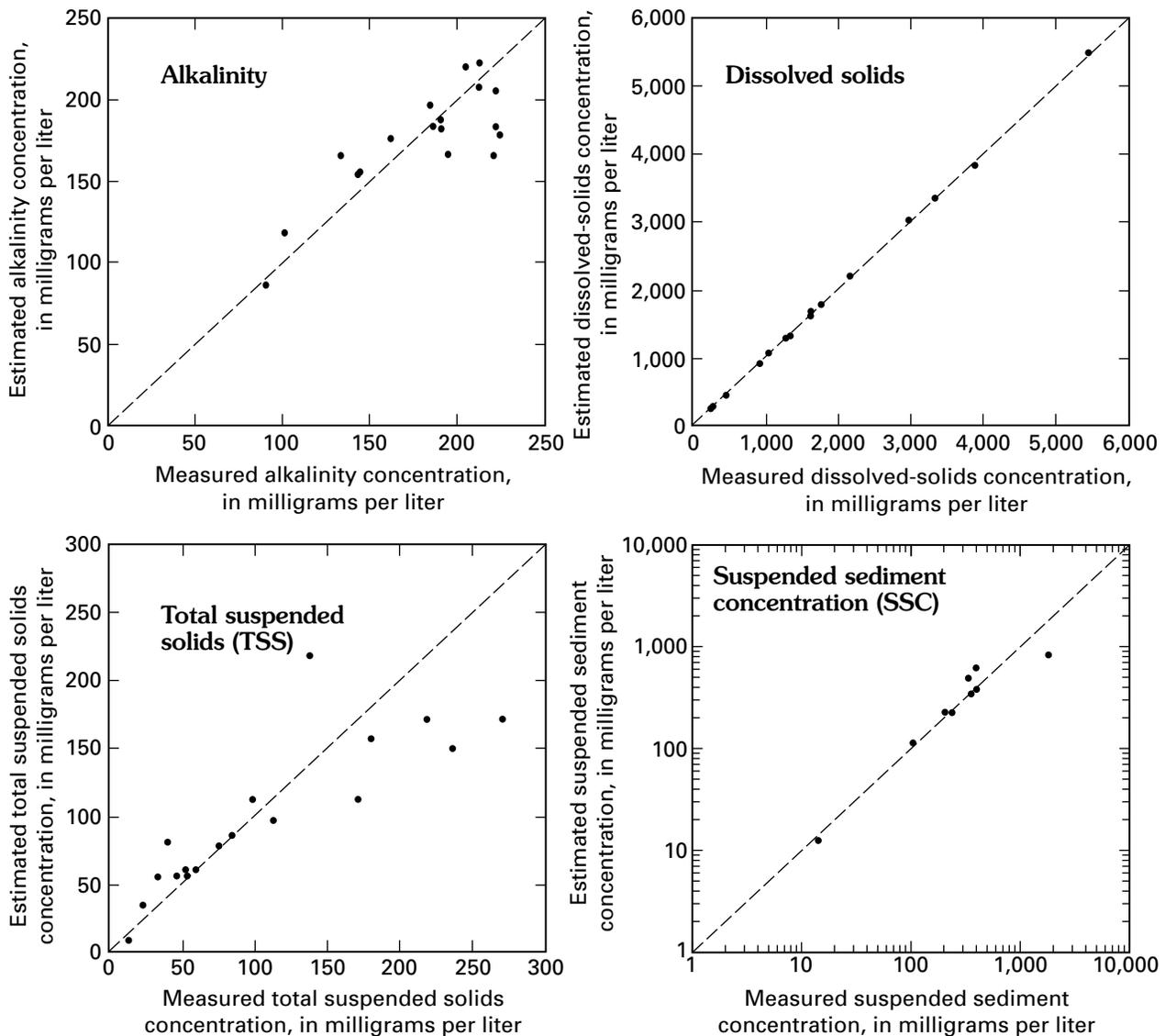The alkalinity of water may be defined as the capacity for solutes in the water to react with and neu-

Figure 6. Comparison of measured and regression-estimated alkalinity, dissolved solids, total suspended solids, and suspended sediment concentrations in water from Rattlesnake Creek near Zenith, December 1998 through June 2001.

tralize acid. Alkalinity is important in determining a stream's ability to neutralize acidic pollution from rainfall or wastewater. Streams with low alkalinity are not well buffered and often are affected adversely by acid inputs. The pH levels in low-alkalinity streams can decrease to a point that eliminates acid-intolerant forms of aquatic life. Fish are particularly affected by low pH water. Explanatory variables for the estimation of alkalinity in water from Rattlesnake Creek near Zenith were streamflow and water temperature. Shallow ground water beneath irrigated cropland and petroleum-production land in south-central Kansas was shown to have significantly larger concentrations of alkalinity (Helgesen and others, 1994) than water beneath undeveloped rangeland. This ground water may then become base flow to streams. Values of streamflow and alkalinity are correlated because of the dilution effect of runoff. In addition, Hem (1992, p. 107) notes that temperature has an effect on the percentage of dissolved carbon dioxide species, and in most natural water, alkalinity is produced by the dissolved carbon dioxide species, bicarbonate and carbonate.

Dissolved solids include both organic and inorganic material dissolved in a sample of water (Bates and Jackson, 1984). Dissolved solids may be the result of natural dissolution of rocks and minerals or of discharges from municipal sources (Christensen and Pope, 1997). Large dissolved-solids concentrations, like those in Rattlesnake Creek, may be expected in areas underlain by ancient marine sediment containing large salt deposits (Bevans, 1989; Gillespie and Hargadine, 1994). Ground water may dissolve these salts and eventually may discharge into Rattlesnake Creek. This process may be augmented by the use of ground water for irrigation, some of which may become "return flows." Helgesen and others (1994) also showed that dissolved-solids concentrations were significantly larger in ground water beneath petroleum-production land (much of the land immediately upstream from the Rattlesnake Creek streamflow-gaging station is in this category) than in water beneath undeveloped rangeland. This ground water could become base flow to streams or be used for irrigation. Because of widespread use of ground water for irrigation in Rattlesnake Creek Basin, it may be important to monitor the dissolved solids entering the refuge. Dissolved solids in water at the Rattlesnake Creek streamflow-gaging station were highly correlated with specific conductance.

TSS and *SSC* represent suspended solid-phase material in a water sample. *SSC* differs from *TSS* in that *SSC* data are produced by measuring the dry weight of all the sediment of a known volume of water-sediment mixture (unlike *TSS* in which the data are produced from a subsample of the original) (Gray and others, 2000). Certain solute-sediment interactions (between sediment and organic compounds, for example) make *TSS* and *SSC* important water-quality factors. Both *TSS* and *SSC* were highly correlated with turbidity. The turbidity ranges for *TSS* and *SSC* are different because analysis of *SSC* did not begin until March 2000. Turbidity is an indicator of sediment and other solid material transported in a stream and, therefore, has a relation to *TSS* and *SSC*.

Major Ions

Major ions discussed in this report are sodium, chloride, fluoride, and sulfate. A comparison of measured and regression-estimated concentrations is shown in figure 7. The sources of sodium, chloride, fluoride, and sulfate in south-central Kansas are, in part, geologic (dissolution of natural deposits by ground water) (Buchanan, 1984; Bevans, 1989; Gillespie and Hargadine, 1994). Sodium and chloride concentrations varied seasonally in Rattlesnake Creek and were larger in the winter when most of the streamflow was from ground-water discharge. Although some organisms can adapt to saline conditions, excessively large concentrations of ions can be toxic to other organisms and plants (Mitsch and Gosselink, 1993).

Sodium and chloride concentrations in water from the Rattlesnake Creek Basin are naturally high due to dissolution of natural salt deposits. In addition, increased chloride concentrations in the basin may be due in part to oil-and-gas production. The production of oil and gas results in a brine (water with a high content of dissolved salt) that often is disposed of through injection wells or disposal ponds. Helgesen and others (1994) showed that there were significantly larger concentrations of sodium and chloride in shallow ground water beneath petroleum-production land than in water beneath undeveloped rangeland. Numerous oil-production facilities are located at and near the refuge (Allen, 1991).

Sodium and chloride are charged ionic species that make water conductive. As sodium and chloride concentrations increase, the conductivity of a solution increases (Hem, 1992), and because sodium and chlo-
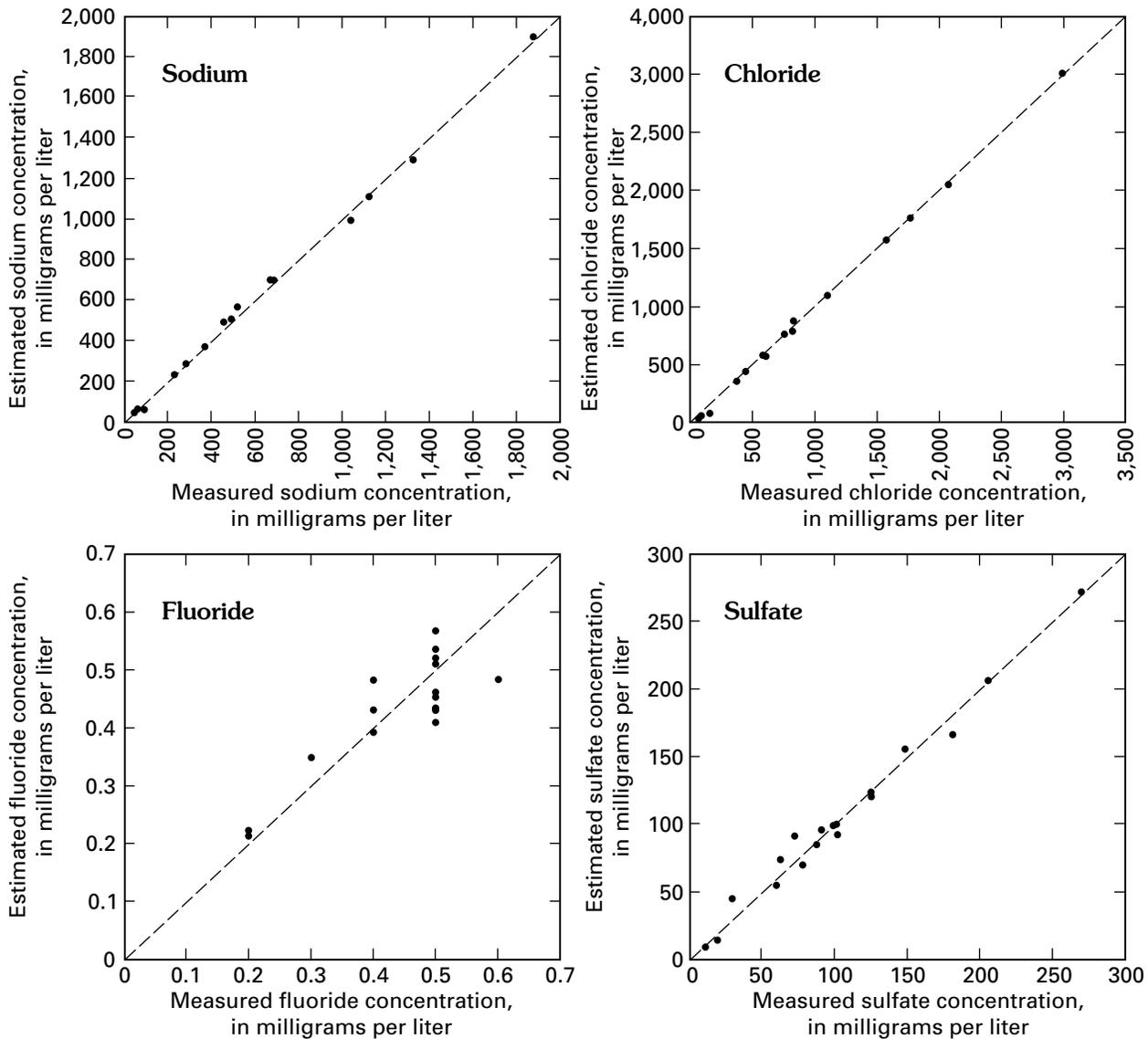
Figure 7. Comparison of measured and regression-estimated major ion concentrations in water from Rattlesnake Creek near Zenith, December 1998 through June 2001.

ride are the most abundant charged ions in Rattlesnake Creek, specific conductance is directly related to both sodium and chloride. The multiple linear regression equations for both sodium and chloride included specific conductance and streamflow.

Concentrations of fluoride present in water from Rattlesnake Creek were small (a median concentration of 0.5 mg/L during the study period) as it is in most natural water (Hem, 1992). The explanatory variables used in the regression equation for fluoride were specific conductance and streamflow. Because the source of fluoride is geologic, higher concentrations of fluoride were present during base flow when specific con-

ductance also was high. During higher streamflow, the base flow was diluted, and fluoride concentrations decreased.

Specific conductance was used for estimating sulfate concentrations in water from Rattlesnake Creek. Sulfate, like sodium, chloride, and fluoride, is a charged ionic species, and specific conductance is correlated with sulfate concentration. Sulfate in water with saline base flow (such as in Rattlesnake Creek) can have well-defined relations with specific conductance (Hem, 1992), except during high flows when the mineralized ground water is diluted.

Nutrients

Nutrients included in this report are nitrate, total organic nitrogen, and total phosphorus. A comparison of measured and regression-estimated nutrient concentrations is shown in figure 8. Nitrogen occurs in water in several forms including elemental nitrogen, ammonia, nitrite, and nitrate. Phosphorus also occurs in several forms including elemental phosphorus and dissolved orthophosphorus. Although nutrients are vital to growth and reproduction in an ecosystem, in excess amounts they can interfere with these functions (Mueller and Helsel, 1996; Sharpley and Rekolainen, 1997). Accelerated growth of algae can lead to eutrophication of a water body. Phosphorus in its elemental form may be toxic to aquatic organisms and may bioaccumulate in much the same manner as mercury (U.S. Environmental Protection Agency, 1986).

Major sources of nutrients include agricultural activities, such as the pasturing and confined feeding of livestock, and the use of synthetic fertilizers. Another source for nutrients is wastewater discharges from communities within a basin. In the Rattlesnake Creek Basin, the town of Saint John is the only permitted wastewater treatment facility and seems to have minimal effect on the basin (Kansas Department of Health and Environment, 2001). Geologic formations contain small amounts of phosphorus (as much as 0.5 percent of total weight) and may contribute to phosphorus load (Kansas Department of Health and Environment, 2001).

The explanatory variables for the estimation of nitrate in water from Rattlesnake Creek near Zenith were specific conductance and water temperature. The explanatory variables for the estimation of total organic nitrogen were turbidity, water temperature, and specific conductance. Figure 8 shows that larger measured and estimated nitrate concentrations are more widely scattered than those at the lower left of the graph. In fact, the nitrate regression is not as good (on the basis of RPD and R^2) as the regressions for the other nutrients, indicating that the best surrogate for nitrate concentrations has not been found.

Specific conductance and water temperature varied seasonally and can be used to describe the seasonal variation in concentrations of nitrate and total organic nitrogen in Rattlesnake Creek, which in turn may reflect the seasonality of agricultural activities such as fertilizer application. Turbidity varied directly with total organic nitrogen concentration.
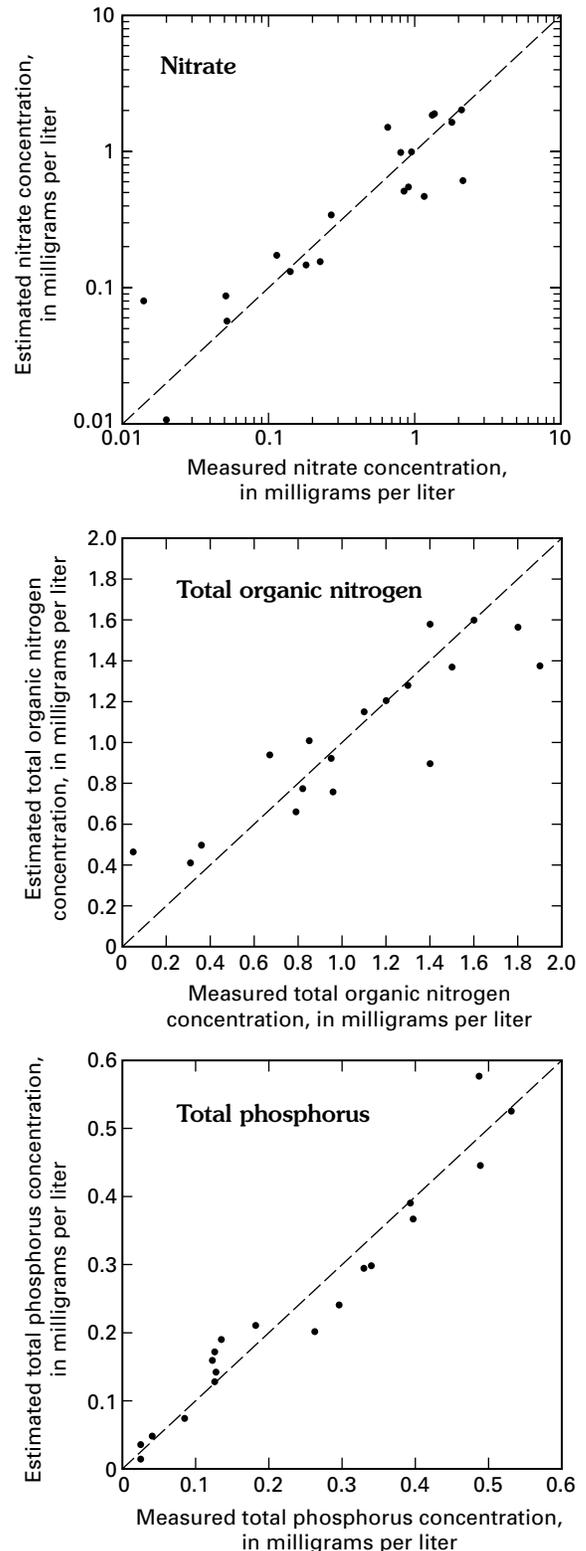

Figure 8. Comparison of measured and regression-estimated nutrient concentrations in water from Rattlesnake Creek near Zenith, December 1998 through June 2001.

The explanatory variables used for the estimation of total phosphorus were turbidity, specific conductance, and water temperature. Total phosphorus includes the dissolved (for example, organic phosphate) and particulate forms. Because turbidity is a measure of the amount of particulate matter in water and because phosphorus in water is mostly present in the particulate form, the two variables are related. Specific conductance, which was high during low flow (because of the larger contribution from ground water), may have had a secondary indirect relation with total phosphorus, which tended to be higher during high flow. Alternatively, water with high specific conductance values may affect the precipitation and adsorption of phosphorus in the sample after collection, which in turn may affect the total phosphorus concentration. Organic phosphate species, which are synthesized by plants and animals, constitute a fraction of total phosphorus (Hem, 1992). The distribution of dissolved phosphate species is pH and temperature dependent (Hem, 1992), and therefore, total phosphorus concentration shows a relation to water temperature. Alternatively, specific conductance and water temperature may be surrogates for time (season); however, neither day of year nor the sine or cosine of time (to represent seasonal cycles) were correlated with total phosphorus for this data set.

Fecal Coliform Bacteria

A comparison of measured and regression-estimated bacteria densities is shown in figure 9. The presence of fecal coliform bacteria in surface water indicates fecal contamination and possibly the presence of other organisms that could cause disease. Fecal coliform bacteria analyses were chosen for regression analysis because current (2001) State of Kansas water-quality criteria (2,000 col/100 mL for secondary contact recreation and 200 col/100 mL for primary contact recreation, on the basis of a geometric mean) are based on fecal coliform bacteria densities (Kansas Department of Health and Environment, 2000). The primary contact recreational criterion is valid from April 1 through October 31.

Because runoff from a basin may transport fecal coliform bacteria to streams, it is expected that bacteria densities would vary with streamflow and, additionally, with time of year (as runoff characteristics vary seasonally). Previously developed fecal coliform bacteria regression equations for south-central Kansas sites used time (either day of year or month of year) as
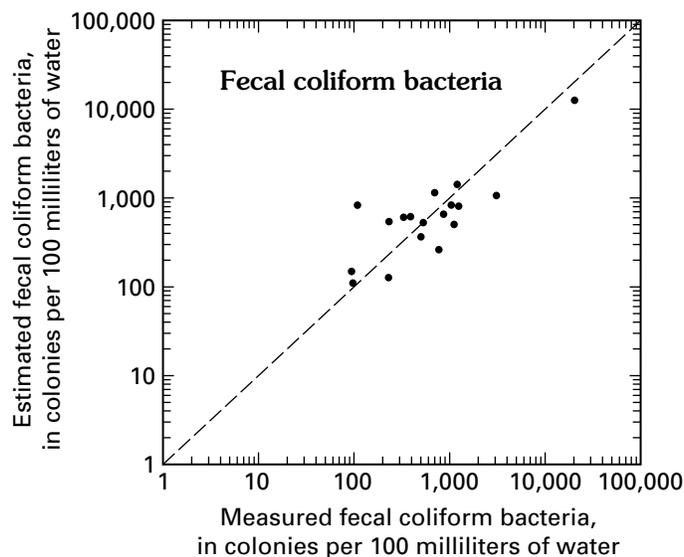

Figure 9. Comparison of measured and regression-estimated fecal coliform bacteria densities in water from Rattlesnake Creek near Zenith, December 1998 through June 2001.

the explanatory variable (Christensen and others, 2000, 2001). However, no acceptable equation was found for the 23 samples collected between December 1998 and June 2001. This may be due in part to the number of samples (5 of the 23) for which plate counts were outside the ideal count range (Myers and Wilde, 1999), primarily those samples with either very low or very high reported densities.

Because concern over bacteria densities is greatest during the summer months when recreational users may be exposed to the bacteria in surface water, the regression equation for fecal coliform was developed using only the 18 samples collected between April 1 and October 31. This equation used water temperature and turbidity as explanatory variables and is not valid for estimating bacteria densities from November through March.

The relatively low R^2 (0.661) and relatively high median RPD (50.0 percent) for the fecal coliform bacteria equation (table 2) indicate that the equation has a higher degree of uncertainty compared with the equations for other chemicals. It is noted, however, that a large part of the uncertainty may be due to lack of precision in the analytical method rather than to lack of fit of the regression. Analytical error for the determination of fecal coliform bacteria can be as high as 50 percent (American Public Health Association and others, 1992); in addition 3 of 18 water samples from the April 1 to October 31 data set were not in the ideal colony count range for fecal coliform bacteria.
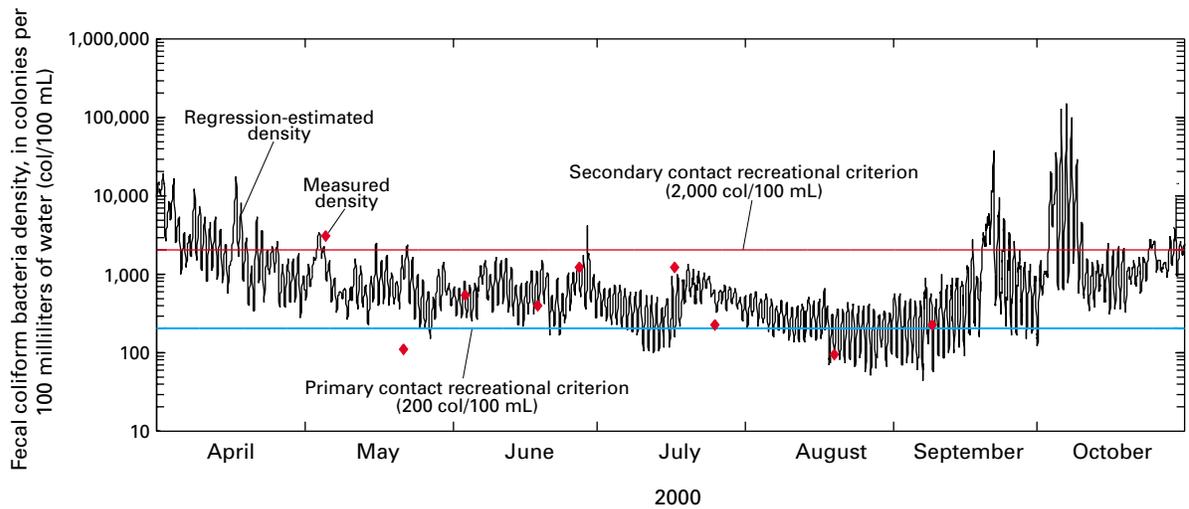
Figure 10. Comparison of measured and regression-estimated fecal coliform bacteria densities in water from Rattlesnake Creek near Zenith, April 1 through October 31, 2000. Recreational water-quality criteria established by Kansas Department of Health and Environment (2000).

Despite the uncertainty, the usefulness of the regression-estimated concentrations to recreationalists and resource managers is evident (fig. 10). The regression equation was applied to continuously (hourly) collected water temperature and turbidity data in 2000 to show when regression-estimated concentrations of fecal coliform bacteria in Rattlesnake Creek exceeded primary contact and secondary contact recreation criteria. During 2000, primary contact criterion for fecal coliform bacteria was exceeded many times. In July, a popular month for recreational activities, the 30-day mean estimated density was 480 col/100 mL (on the basis of about 700 hourly measurements), exceeding the geometric mean criterion of 200 col/100 mL (requiring at least five individual measurements during a 30-day period). However, with a contaminant such as fecal coliform bacteria, it is the density at the time of contact with the water that is important, not a monthly mean. When regression-estimated densities are available in real time (currently available at http://ks.water.usgs.gov/Kansas/rtqw/), immediate action may be taken to avoid contact with the water until water-quality conditions improve or to make other water-use decisions.

Estimated Loads, Yields, and Variability

Although concentrations are useful for evaluating Rattlesnake Creek with respect to current water-quality criteria, load estimates are useful for regulatory authorities and resource managers. A chemical load is the chemical concentration multiplied by streamflow and an appropriate conversion factor, and gives an indication of the mass of that chemical transported past a given site during a given time. Regulatory authorities may use load estimates in the development of TMDLs. Estimates of chemical loads for Rattlesnake Creek are particularly important to resource managers because those loads are transported into Quivira National Wildlife Refuge and could have a harmful effect on aquatic life or threatened and endangered species. Chemical loads also may be used to evaluate trends, which can be compared to land use and other factors affecting water quality.

Regression-estimated loads and yields of each chemical were calculated for 1999 and 2000 (table 3) on the basis of approximately 8,760 measurements (hourly measurements for 1 year) made by the continuously recording in-stream water-quality monitor. If data from the water-quality monitor were not available, annual load estimates would have to be based on the nine samples collected in 1999 and the nine samples collected in 2000. There are several computer programs available to help estimate loads by interpolating chemical concentrations between samples and (or) by using only discharge as a surrogate (commonly used because it is the only surrogate available continuously at most USGS streamflow-gaging stations). Loads for most chemicals, especially those that are not significantly related to discharge, could not be estimated as accurately using these programs.

Table 3. Estimated loads and yields of selected chemicals in water from Rattlesnake Creek near Zenith, Kansas, 1999 and 2000

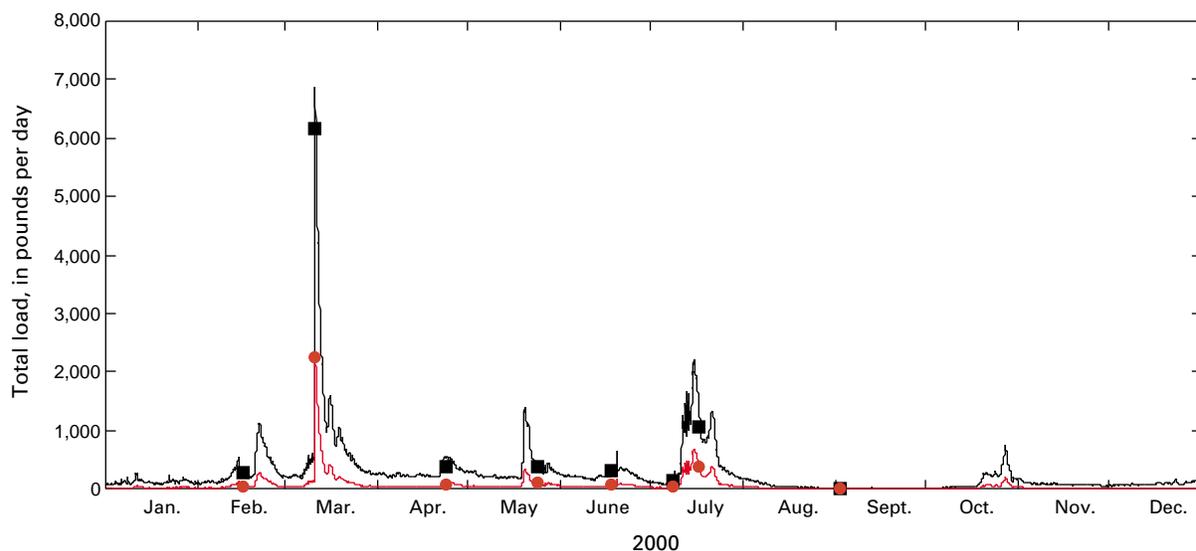[All loads are expressed in pounds per year, and all yields are expressed in pounds per acre per year]

Chemical	Estimated load		Estimated yield	
	1999	2000	1999	2000
Physical properties, solids, and sediment				
Alkalinity	20,200,000	19,000,000	30.1	28.3
Dissolved solids	170,000,000	151,000,000	254	225
Total suspended solids *(TSS)*	8,660,000	10,000,000	12.9	15.0
Suspended sediment *(SSC)*	17,500,000	21,300,000	26.1	31.8
Major ions				
Sodium	51,200,000	45,000,000	76.4	67.1
Chloride	82,000,000	71,500,000	122	107
Fluoride	47,400	42,900	.071	.0640
Sulfate	9,650,000	8,580,000	14.4	12.8
Nutrients				
Nitrate	166,000	130,000	.248	.194
Total organic nitrogen	93,100	92,000	.139	.137
Total phosphorus	17,900	19,300	.0267	.0289

Evaluating the differences in loads can be valuable for evaluating methods. For example, *TSS* load is about one-half the *SSC* load (table 3). *TSS* and *SSC* are both used to quantify concentrations of suspended solid-phase material in surface water (Gray and others, 2000) and theoretically should be the same. However, the uncertainty (*RPD*, table 2) of the *TSS* equation was substantially larger than the uncertainty for the *SSC* equation, possible due to a less reliable analytical method.

Loads of major ions can be compared from year to year to evaluate the effects of ground-water discharge and irrigation return flows on water quality. Annual nutrient loads can be evaluated with respect to annual variability in algal booms, which may be a sign of eutrophication problems in ponds at the refuge. Seasonal variation in nutrients are substantial, and most of the total organic nitrogen and total phosphorus loads (fig. 11) are transported to the refuge during just a few periods of surface runoff. This information may be used by the resource managers to determine when water-diversion strategies would be most beneficial. Fecal coliform bacteria loads may be compared from year to year to evaluate effective wastewater-treatment strategies or the effects that changes in land use (such as cattle production) or wildlife may have on a water body. Estimated annual fecal coliform bacteria loads were not included in table 3 because the equation for fecal coliform (table 2) was not developed with data from, nor is valid for, the entire year.

Yield estimates also are useful to resource managers. A yield is an area normalized load, or in other words, the chemical load divided by the drainage area. Yields thus enable comparison of sites with different drainage areas. The differences in estimated nutrient yields also may help assess and prioritize land-management practices within or among basins. Rattlesnake Creek 1999 and 2000 estimated nitrate yields (0.248 and 0.194 lb/acre/yr, respectively) were comparable to a median annual basin yield (0.232 lb/acre/yr or 26 kg/km^2/yr for 1990–95) for 85 relatively undeveloped basins across the United States (Clark and others, 2000). On the other hand, 1999 and 2000 total phosphorus yields for Rattlesnake Creek (0.0267 and 0.0289 lb/acre/yr, respectively) were less than a median annual basin yield (0.0758 lb/acre/yr or 8.5 kg/km^2/yr for 1990–95) for those same 85 basins. Yields were calculated using total drainage area for Rattlesnake Creek Basin and the 85 undeveloped basins (G.M. Clark, USGS, written commun., November 6, 2001). However, nearly one-half of the Rattlesnake Creek Basin is considered noncontributing, and if yield calculations only used contributing drainage area, phosphorus yields in Rattlesnake Creek Basin would approach the median annual basin yield for the undeveloped basins.

Estimated alkalinity and dissolved-solids loads and yields were smaller in 2000 compared to 1999, whereas estimated total suspended solids and suspended sediment loads and yields were larger in 2000 compared to 1999. Estimated loads and yields for all

Figure 11. Comparison of measured and regression-estimated total organic nitrogen and total phosphorus loads in water from Rattlesnake Creek near Zenith, 2000.

the major ions were smaller in 2000 compared to 1999. Estimated nitrate and total organic nitrogen loads and yields were slightly smaller, whereas estimated total phosphorus loads and yields were slightly larger in 2000 compared to 1999 (table 3).

Uncertainty Associated with Regression-Based Estimates

It would not be prudent to consider the estimates presented herein without understanding the uncertainty involved. The R^2, MSE, $RMAE$, and RPD (table 2) all give an indication of uncertainty. The nitrate and bacteria equations have a higher degree of uncertainty than do those of the other chemicals. The high RPD for bacteria not only includes the uncertainty due to regression but also includes analytical uncertainty, which can be as high as 50 percent for bacteria analysis. In addition, the water-quality monitors have an upper limit of measurement with respect to turbidity (1,750 NTU). This upper limit can cause an underestimation of concentrations and may have a

substantial effect on load and yield estimates for 5 of the 12 chemicals of concern that use turbidity as a surrogate. However, turbidity values did not approach this upper limit during the study period. Another limitation was the small number of samples (about 18 samples for most chemicals) available for the development of the regression equations.

SUMMARY

The Quivira National Wildlife Refuge is a natural wetlands area located in the Rattlesnake Creek Basin of south-central Kansas. To improve the water supply and preserve valuable wildlife habitat, canals and ponds have been constructed throughout the refuge since the early part of the 20th century. The refuge now contains more than 30 ponds and marshes and provides food, water, cover, and protection for many species of birds, fish, and other wildlife.

Not only is there a desire to ensure a dependable water supply to Quivira National Wildlife Refuge, there also is a strong desire to ensure suitable water

quality. In response to the Federal Clean Water Act of 1972, the Kansas Department of Health and Environment listed segments of Rattlesnake Creek as water-quality impaired. Little and Big Salt Marshes are identified as being eutrophic and impaired for specific uses by pH, and the Little Salt Marsh is impaired by fecal coliform bacteria. Rattlesnake Creek is listed as being impaired by chloride and sulfate. The Federal Clean Water Act requires that the State of Kansas establish TMDLs to meet established water-quality criteria and to ensure protection of the creek's and marshes' designated beneficial uses.

There are several factors that affect the water quality at the refuge. Substantial quantities of water are supplied by highly mineralized ground-water seepage near Big Salt Marsh. The water quality in the refuge also may be affected by oil-and-gas production and agriculture. The dominance of agriculture in the basin and a semiarid climate have lead to the widespread use of irrigation in the area. Irrigation return flows may contain increased concentrations of certain chemicals that may cause adverse health effects in aquatic organisms and birds at the refuge.

In response to the need for additional chemical data, concentrations of selected water-quality chemicals were identified through the collection and analysis of water samples from December 1998 through June 2001 at the USGS streamflow-gaging station on Rattlesnake Creek near the inlet to the refuge. Samples were collected throughout a range of streamflow conditions and analyzed for physical properties, solids, sediment, major ions, nutrients, and indicator bacteria. Event-related (base-flow plus runoff) samples also were analyzed for metals and pesticides. Ten of the 125 chemicals analyzed did not meet established or proposed water-quality criteria to protect aquatic life and drinking water in at least one sample. These were pH, turbidity, dissolved oxygen, dissolved solids, sodium, chloride, phosphorus, total coliform bacteria, E. coli bacteria, and fecal coliform bacteria. No metal or pesticide concentrations exceeded water-quality criteria. Twenty-two of the 43 metals analyzed were not detected, and 36 of the 46 pesticides analyzed were not detected.

Annual variation in water quality was evaluated by comparing median concentrations for selected chemicals between 1999 and 2000. Median concentrations of alkalinity, fluoride, nitrate, and fecal coliform bacteria were either smaller in 2000 compared with 1999 or did not change. Chemicals with larger median

concentrations in 2000 compared to 1999 included dissolved solids, total suspended solids, sodium, chloride, sulfate, total organic nitrogen, and total phosphorus. Increases in the median concentrations of the major ions (sodium, chloride, and sulfate) in 2000 were somewhat expected due to the decreased rainfall in 2000 and very low streamflow late in the year. Low streamflow corresponds to an increase in that part of streamflow coming from ground water, which has naturally high concentrations of sodium, chloride, and sulfate. Increases in dissolved solids, total suspended solids, total organic nitrogen, and total phosphorus concentrations were not as readily explained. However, unusually high streamflow occurred in early spring of 2000, which corresponded to the time of year when fields were tilled, exposing the solids, sediment, and associated nutrients that were eventually transported to Rattlesnake Creek. Fertilizer applied to these agricultural fields also may be a major source of the nitrogen and phosphorus (components of fertilizer) in Rattlesnake Creek. Periodic samples collected from December 1998 through June 2001 may not represent a typical range in hydrologic and environmental conditions. Below-average streamflow and precipitation occurred in 1999, and 2000 was unusually dry for Rattlesnake Creek Basin. In addition, the changes in median concentrations between 1999 and 2000 may be due in part to the times of the year when samples were collected. Because only nine samples were collected per year for most chemicals, uncertainty exists due to the large gaps in time between collection of periodic samples. The availability of continuous data would reduce this uncertainty as would the collection of additional samples.

To meet the need for continuous data, a continuously recording water-quality monitor was installed at the USGS streamflow-gaging station on Rattlesnake Creek near Zenith on October 28, 1998. Water-quality chemicals measured with the monitor from December 1998 through June 2001 were specific conductance, pH, water temperature, turbidity, and dissolved oxygen.

Regression equations were developed between real-time measurements (specific conductance, pH, water temperature, turbidity, and dissolved oxygen) and the chemicals of concern to the refuge (alkalinity, dissolved solids, total suspended solids, sediment, sodium, chloride, fluoride, sulfate, nitrate, total organic nitrogen, total phosphorus, and fecal coliform bacteria). Although pesticides are a concern to

wildlife, there were very few detections for any of the pesticides analyzed as part of this study, and regression equations for these chemicals were not developed.

From the regression equations, loads and yields also were calculated. Estimated alkalinity and dissolved-solids loads and yields were smaller in 2000 compared to 1999, whereas estimated total suspended solids and suspended sediment loads and yields were larger in 2000 compared to 1999. Estimated loads and yields for all the major ions were smaller in 2000 compared to 1999. Estimated nitrate and total organic nitrogen loads and yields were slightly smaller, whereas estimated total phosphorus loads and yields were slightly larger in 2000 compared to 1999. When Rattlesnake Creek nutrient yields were compared to 85 relatively undeveloped basins across the United States, nitrate yields were similar, whereas total phosphorus yields were smaller in the Rattlesnake Creek Basin.

Continuous data collection with the water-quality monitor allowed for an evaluation of variation in seasonal loading. The seasonal cycle in total organic nitrogen and total phosphorus loads was pronounced, and most of the nutrient load transported into the refuge occurred during just a few periods of surface runoff. This information may be used by the resource managers to determine when water-diversion strategies would be most beneficial.

The development of regression equations using in-stream water-quality measurements and chemical concentrations from samples collected periodically enables a more accurate representation of daily loads. The regression-estimated loads may be more reflective of actual loads because they are based on continuous (hourly) data for the explanatory variables. On the other hand, loads calculated from collected samples are based on a limited number of discrete samples collected throughout the year, and fluctuations in concentration are often missed.

The innovative approach used in this study to estimate chemical concentrations, loads, yields, and variability of water flowing into the Quivira National Wildlife Refuge will allow resource managers to protect wildlife by reacting quickly to changes in water quality and allow recreationalists to make water-use decisions. The increasing public interest in TMDLs and the concern for threatened and endangered species make this study of regional, as well as national, importance because it shows how chemical loads may be estimated using continuous data and that real-time application of regression equations can be used by resource managers to protect wildlife. The methods used in this study may be used for other sites in Kansas and the Nation to estimate chemical loads and in providing input data for the development of TMDLs.

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