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Application of Soil Survey to Assess Nonpoint Source of Contamination to Surface Water in Agricultural Watersheds: Heavy Metals and Alkaline Earth Elements

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Contents

List of Tables	iv
List of Figures	v
Introduction	1
The NRCS Technique	1
Estimation of Runoff Water	1
Estimation of Leaching Water	2
Soil and Water Analysis	2
Estimating Element Loss by Runoff and Leaching	3
GIS Digital Mapping	4
Application of the NRCS Technique	5
Wagon Train Watershed	5
Soil and Water Sampling	5
Soil and Water Analysis	6
Observed Inflow for Wagon Train Reservoir	6
Case Study I: Nonpoint Source of Heavy Metal Contamination to Surface Water in Wagon Train Watershed	7
Introduction	7
Materials and Methods.....	8
Results and Discussion.....	8
Runoff and Reservoir Inflow.....	8
Elements in the Soil and in the Water Phase.....	8
Elements in Stream Water	9
Element Loss by Runoff from Soils.....	12
Elements in Runoff and Loading.....	14
Case Study II: Nonpoint Source of Alkaline Earth Element Contamination to Surface Water in Wagon Train Watershed	15
Introduction	15
Materials and Methods.....	15
Removal of Calcium and Magnesium in Runoff.....	16
Results and Discussion.....	16
Elements in the Water Phase	16
Elements in the Exchangeable Phase	17
Active Forms of Elements in Soil	17
Element Loss by Runoff.....	18
Element Loading.....	19
Summary and Conclusions	21
References	23
Tables	27
Figures	37

List of Tables

Table 1.—Soil classification and selected properties for 12 major soils under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska	27
Table 2.—Predicted annual loss of water by runoff (m ³ /ha) and water present in the soil interaction zone (m ³ /ha) for 12 major soils under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska	28
Table 3.—Average (AV) and standard deviation percentage (SD%) of water-soluble elements for 12 major soils (mg/kg or µg/kg) under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska	29
Table 4.—Predicted loss of 8 elements by runoff from 12 major soils (kg/ha/yr or g/ha/yr) under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska.....	30
Table 5.—Predicted average monthly element loading by runoff water (kg) in Wagon Train Reservoir.....	31
Table 6.—Average (AV) and standard deviation (SD) of dissolved calcium, magnesium, barium, and strontium in the water phase for 12 major soils (mg/kg or µg/kg) under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska.....	32
Table 7.—Average (AV) and standard deviation (SD) of calcium and magnesium in the exchangeable phase for 12 major soils (mg/kg) under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska.....	33
Table 8.—Predicted annual loss of calcium, magnesium, barium, and strontium (kg/ha/yr or g/ha/yr) by runoff for 12 major soils under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska	34
Table 9.—Predicted average monthly element loading by runoff water (kg) into Wagon Train Reservoir, Lancaster County, Nebraska	35

List of Figures

Figure 1.—Soil and water sampling locations in Wagon Train Watershed, Lancaster County, Nebraska.....37

Figure 2.—Predicted amounts in runoff and observed monthly average concentration in stream water ($\mu\text{g/L}$) in Wagon Train Watershed for: (a) Cd, (b) Cu, (c) Ni, (d) Pb, and (e) Zn38

Figure 3.—Aluminum loss by runoff from soils (kg/ha/yr) in Wagon Train Watershed39

Figure 4.—Iron loss by runoff from soils (kg/ha/yr) in Wagon Train Watershed40

Figure 5.—Silicon loss by runoff from soils (kg/ha/yr) in Wagon Train Watershed.....41

Figure 6.—Cadmium loss by runoff from soils (kg/ha) in Wagon Train Watershed42

Figure 7.—Copper loss by runoff from soils (g/ha/yr) in Wagon Train Watershed43

Figure 8.—Nickel loss by runoff from soils (g/ha/yr) in Wagon Train Watershed44

Figure 9.—Lead loss by runoff from soils (g/ha/yr) in Wagon Train Watershed45

Figure 10.—Zinc loss by runoff from soils (g/ha/yr) in Wagon Train Watershed46

Figure 11.—Predicted calcium in runoff and observed concentration (mg/L) in stream water for Wagon Train Watershed.....47

Figure 12.—Predicted magnesium in runoff and observed concentration (mg/L) in stream water for Wagon Train Watershed.....48

Figure 13.—Predicted barium in runoff from 10- and 17-mm soil depths and observed concentration ($\mu\text{g/L}$) in stream water for Wagon Train Watershed49

Figure 14.—Predicted strontium in runoff and observed concentration ($\mu\text{g/L}$) in stream water for Wagon Train Watershed.....50

Figure 15.—Calcium loss by runoff from soils (kg/ha) in Wagon Train Watershed51

Figure 16.—Magnesium loss by runoff from soils (kg/ha) in Wagon Train Watershed52

Figure 17.—Barium loss by runoff from soils (g/ha) in Wagon Train Watershed53

Figure 18.—Strontium loss by runoff from soils (g/ha) in Wagon Train Watershed.....54

Introduction

Managing nonpoint sources of contamination from agricultural land is technically complex. Contamination sources often are located over a large geographic area and difficult to identify. Identifying hot spots within a watershed enables a more efficient use of funds to alleviate potential problems and protect water resources. Although there are models that can estimate the impact of nonpoint sources of contamination from agricultural watersheds, these models are complex and require very extensive data input.

NRCS developed a technique (Elrashidi et al., 2003, 2004, 2005a,b, 2007a,b, 2008, 2009, 2010) to estimate element loss by runoff for agricultural watersheds. The NRCS technique applies the USDA runoff model (USDA-SCS, 1991) to estimate loss of runoff water from soils. The technique assumes that dissolved inorganic chemicals are lost from a specific depth of surface soil that interacts with runoff and leaching water. These chemicals may include essential plant nutrients (e.g., nitrogen, phosphorus, copper, and zinc) and environmentally toxic elements (e.g., lead, cadmium, nickel, and arsenic). Geographical Information Systems, or GIS (ESRI, 2006) are used to present data spatially in maps of watersheds.

The technique is quick and cost-effective because it uses existing climatic, hydrologic, and soil survey information. The Soil Survey Geographic Database, or SSURGO (USDA-NRCS, 1999) is used to identify major soils, areas, and locations in the watershed. Land cover databases (NLCD, 1992) and National Agricultural Statistics Service data (NASS website) are used to identify areas of crops, pasture, forest, etc. The National Water and Climate Center (NWCC website) is used to access information on precipitation and other climate data. The United States Geological Survey (USGS, 2007) maintains stream flow gaging stations in major streams and rivers in the U.S. The water flow data along with the drainage area can be used to calculate the observed surface runoff from the watershed. This calculation can be used to validate values predicted by the runoff and percolation models.

The NRCS Technique

Estimation of Runoff Water

Rainfall is the primary source of water that runs off the surface of small agricultural watersheds. The main factors affecting the volume of rainfall that runs off are the kind of soil and the type of vegetation in the watershed (USDA-SCS, 1991). The runoff equation can be written as follows:

$$Q = (R - 0.2S)^2 \div (R + 0.8S) \quad (1)$$

Where: Q = runoff (inches), R = rainfall (inches), and S = potential maximum retention (inches) after runoff begins.

The potential maximum retention (S) can range from zero on a smooth and impervious surface to infinity in deep gravel. The S value is converted to a runoff curve number (CN), which is dependent on both the hydrologic soil group and the type of land cover, by the following equation:

$$CN = 1000 \div (10 + S) \quad (2)$$

According to Equation 2, the CN is 100 when S is zero and approaches zero as S approaches infinity. Runoff curve numbers (CNs) can be any value from 0 to 100 but

for practical applications are limited to a range of 40 to 98. Substituting Equation 2 into Equation 1 gives:

$$Q = \{R - [2(100 - CN)/CN]\}^2 \div \{R + [8(100 - CN)/CN]\} \quad (3)$$

The hydrologic groups of the identified major soils are used to determine CNs for different land covers in the watershed.

Data on the annual rainfall for the watershed was from the USDA-NRCS National Water and Climate Center (NWCC website). In Equation 3, the effective rainfall (R) is the portion of annual rainfall that could generate runoff (Gilbert et al., 1987). The hydrologic group for a given soil and related CNs for various types of land cover are published in the "USDA National Engineering Field Manual" (USDA-SCS, 1991).

For agricultural land in the watershed, the effective rainfall (R) and the runoff CNs are determined first, then the runoff equation is applied to estimate runoff water (Q) for soil under forest, pasture, and crops. The equation calculates runoff water in inches (depth of water). Values are usually converted to millimeters.

Estimation of Leaching Water

The amount of water that leaches from soil was determined by a model developed by Williams and Kissel (1991). The authors used the equation to estimate surface runoff water (Eq. 3) to develop an equation that predicts the percolation index (PI).

$$PI = (P - 0.4r)^2 / (P + 0.6r) \quad (4)$$

Where: PI = an estimate of average annual percolation in inches, P = the average annual rainfall in inches, and r = a retention parameter. The retention parameter (r) is related to a percolation curve number (PCN) by using the equation:

$$r = (1000/PCN) - 10 \quad (5)$$

The values of PCN are 28, 21, 17, and 15 for hydrologic soil groups A, B, C, and D, respectively (Williams and Kissel, 1991).

Another factor of considerable importance in estimating percolation is the seasonal rainfall distribution. Rainfall that occurs in the absence of land cover (vegetation) is much more likely to percolate than rainfall occurring during the growing season (spring and summer) because evapotranspiration is low during fall and winter. Williams and Kissel (1991) introduced the seasonal index (SI) to estimate the seasonal precipitation effects on percolation.

$$SI = (2PW/P)^{1/3} \quad (6)$$

Where: PW = the effective precipitation (rainfall occurs in the absence of land cover) and P = the annual precipitation. The effective precipitation (PW) for cropland in the watershed is computed by summing the rainfall amounts for October through May. Assuming that evapotranspiration was very low during winter, the total precipitation for December, January, and February is used to calculate PW for pastureland. For forestland, PW is calculated for fall and early spring (November through April).

The leaching index (LI) is estimated by combining Equations 4 and 6 as follows:

$$LI = (PI)(SI) \quad (7)$$

For the major soils investigated in the watershed, the amount of leaching water was calculated by using the LI for forestland, pastureland, and cropland.

Soil and Water Analysis

Soil samples are collected from major soils under various land covers in the watershed. Sampling locations are selected randomly, and the selection takes into

consideration that sites should be distributed evenly over the entire area of the watershed. At randomly selected sampling sites, three cores are taken from the 0-to-30-cm soil depth and mixed thoroughly in a stainless steel tray. The composite sample (approximately 2 kg) is placed in a plastic bag and sealed.

Soil samples are analyzed on air-dried < 2-mm soil by methods described in Soil Survey Investigations Report No. 42 (SSIR 42) (USDA-NRCS, 2004). Alphanumeric codes in parentheses next to each method represent specific standard operating procedures. Particle-size analysis is performed by sieve and pipette method (3A1). Cation-exchange capacity (CEC) is determined by NH_4OAc buffered at pH 7.0 (5A8b). Exchangeable cations (Ca, Mg, Na, and K) are determined by the NH_4OAc method (5A8c). Total carbon (C) content is determined by dry combustion (6A2f), and CaCO_3 equivalent is estimated by the electronic manometer method (6E1g). Organic C content in soil is estimated by both the total-C and the CaCO_3 -C. Soil pH is measured in a 1:1 soil/water suspension (8C1f). Bulk density (BD) is estimated from particle size analysis and organic matter content (Rawls, 1983). Liquid limit is determined by the American Society for Testing and Materials method D 4318 (ASTM, 1993).

The dissolved elements (nutrients and heavy metals) in soil are determined. Anion-exchange resin (AER) extractable-P is determined by the method described by Elrashidi et al. (2003). Soluble nitrate-N is extracted with 1.0 M KCl solution and measured by the flow injection, automated ion analyzer LACHAT Instruments (6M2a). Water-extractable elements (Al, As, B, Ba, Fe, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sr, and Zn) for soils are determined in the equilibrium water extract (EWE) according to the Kellogg Soil Survey Laboratory procedure (4D2b1) (USDA-NRCS, 2004). In this method (4D2b1), the soil:water system (20 g of soil and 100 mL of distilled water) is allowed to equilibrate at room temperature for 23 hours before the suspension is shaken for 1 hour. The supernatant is passed through a 0.45- μm filter. Elements are determined in the filtrate by the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Perkin Elmer Optima 3300 DV). Concentrations of nitrate-N, nitrite-N, sulfate-S, chloride (Cl), and fluoride (F) in the filtrate are determined by the High Pressure Ion Chromatograph (6M1c) (HPIC, Dionex Corp.). The pH in the water extract is measured with a combination electrode and digital pH/ion meter, Model 950, Fisher Scientific (8C1a) as described by USDA-NRCS (2004).

Water samples (grab) are collected in midstream by using 2-L polyethylene bottles that have been rinsed twice with stream water. These samples are taken immediately to the laboratory and refrigerated at 4 °C. Stream-water samples are filtered by using a glass syringe equipped with Whatman 25-mm GD/X disposable nylon filter media (0.45- μm pore size). Phosphorus concentration is determined by the modified phospho-molybdate/ascorbic acid method (Olsen and Sommers, 1982) or the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Perkin Elmer Optima 3300 DV). Concentrations of nitrate-N, nitrite-N, sulfate-S, chloride (Cl), and fluoride (F) in the filtrate are determined by the High Pressure Ion Chromatograph (6M1c) (HPIC, Dionex Corp.). The concentration of elements in the filtrate (Al, As, B, Ba, Fe, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sr, and Zn) are determined by the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), (Perkin Elmer Optima 3300 DV) (4I3a). The pH of the water is measured with the combination electrode and digital pH/ion meter, Model 950, Fisher Scientific (8C1a) as described by USDA-NRCS (2004).

Estimating Element Loss by Runoff and Leaching

Nutrients such as N, K, and P and other agricultural chemicals are released from a thin layer of surface soil that interacts with rainfall and runoff. In chemical transport models, the thickness of the interaction zone is determined by model calibration with experimental data, with depths ranging between 2.0 and 6.0 mm (Donigian et

al., 1977). Frere et al. (1980), however, suggested an interaction zone of 10 mm, assuming that only a fraction of the chemical present at this depth interacts with rainfall water. In previous studies, Elrashidi et al. (2003, 2004, 2005a,b, 2007a,b, 2008, 2009, 2010) successfully used a fixed soil thickness of 10 mm to estimate the loss of nutrients and heavy metals by runoff from agricultural land.

In the NRCS technique, an interaction zone of 10 mm is used to calculate the amount of element released from surface soils by runoff. Also, it is assumed that, during the runoff occurrence, water content in the surface 10-mm soil depth is at the liquid limit (the moisture content at which the soil passes from a plastic to a liquid state). Thus, during runoff occurrence, the total amount of water (where elements in the 10-mm soil depth are dissolved) is the sum of the water within the soil body (liquid limit) and the water on the soil surface (runoff water). The volume of water in the 10-mm soil depth is usually very small when compared with the runoff volume. Only elements in the runoff water are removed and lost during the runoff occurrence.

Hubbard et al. (1991) and Lowrance (1992) studied nitrate-N losses from a small watershed (0.34 ha) in southern Georgia. They found that most of the nitrate-N losses were leached from the top 30-cm soil layer when 620 mm of natural rainfall followed fertilizer application. Furthermore, in a field experiment in Wisconsin, Olsen et al. (1970) investigated the effect of spring and summer rainfall (average of 55 cm) on downward movement of N for soils under corn and determined the loss to be 336 kg NH_4NO_3 /ha. At the end of summer, they found that less than 10% of applied-N remained within the top 30 cm of the soil.

The downward movement of water (carrying dissolved elements) is the major mechanism by which dissolved elements are lost from the root zone. In their work on watersheds in southeast Nebraska, Elrashidi et al. (2004, 2005a,b, 2007a,b) found that a leaching index (LI) equivalent to the annual rainfall of 730 mm can remove dissolved elements beneath the root zone (30-cm soil depth). In this technique, the loss of elements is dependent on the predicted depth of annual water leaching through the top 30 cm of soil. A ratio of predicted leaching water depth (mm/yr) to leaching index (LI) that is equivalent to 730 (mm/yr) is used to estimate the downward movement (loss) of dissolved elements from the top 30 cm of soil. For example, a predicted leaching water depth of 73 (mm/yr) for a soil will result in downward movement of 10% ($73/730$) of elements present in the top 30 cm of soil. We used the predicted amount of leaching water (mm/yr) and predicted concentration of dissolved elements (mg/kg soil) in the surface 30 cm of soil to calculate the annual loss of elements by leaching for each soil under various land covers (crops, pasture, and forest).

GIS Digital Mapping

Digital maps for water and nutrient losses from agricultural land in the watershed are generated by Geographical Information Systems (GIS) software, namely ArcView 9.2 (ESRI, 2006). The input data required to generate the GIS map include spatial data layers (soil series and land cover) and tabular data on both runoff and leaching (amount of water and nutrient loss from soils and concentrations in both runoff and leaching waters).

The principal spatial data layer used is the Soil Survey Geographic Database (SSURGO) (USDA-NRCS, 1999). Spatial layers from both the National Land Cover (NLCD, 1992) and National Agricultural Statistics Service (NASS website) are used to identify areas of forest, pasture, and cropland within the watershed. Other types of land cover, such as urban developments, bodies of water, or marsh, are usually not mapped for the watershed. The proposed technique calculated water and nutrient losses as well as concentrations in runoff and leaching water for soils under different types of land cover (forest, pasture, and crops). Thus, GIS mapping of agricultural land in the watershed includes data layers for soils and land cover as well as water and elements.

Application of the NRCS Technique

In this report, we describe how the NRCS technique was applied to study the nonpoint source of contamination to surface water in a watershed for: 1) heavy metals and 2) alkaline earth elements. We used Wagon Train (WT) Watershed, Lancaster County, Nebraska, as the study area. Information on the watershed, major soils, and methods used for soil and water sampling as well as the description of streams and procedures used to estimate the inflow for WT Reservoir are given below.

Wagon Train Watershed

Wagon Train Watershed has a 315-acre (128-hectare) reservoir located on the Hickman Branch of Salt Creek (Platte River Basin) in Lancaster County, Nebraska (Fig. 1). The reservoir was constructed primarily as a flood-control structure by the U.S. Army Corps of Engineers in 1962. The total drainage area encompasses 9,984 acres (4,042 hectares) of agricultural land. Most of the area (70%) is cultivated with crops, specifically soybean (*glycine Willd.*), corn (*zea mays L.*), wheat (*triticum aestivum L.*), sunflower (*helianthus L.*), and alfalfa (*medicago sativa L.*). The rest of the watershed is mostly covered with grassland but includes small areas of forestland, wetland, and urban development.

The watershed topography is moderately sloping, and the soils are moderately well drained to poorly drained. The land relief consists of uplands, stream terraces, and bottom lands. There are 33 miles (53 km) of streams in the watershed and 40 ponds that range in size from 0.3 acre to 6.5 acres (0.12 hectare to 2.6 hectares). Overland flow enters the reservoir through intermittent tributaries. From the dam, the water flows into the Hickman Branch of Salt Creek, which flows west and north through Lincoln and eventually to the Platte River near Ashland, Nebraska.

We used the soil survey information from SSURGO (USDA-NRCS, 1999) to determine the major soils in the watershed. Both the National Land Cover Data (NLCD, 1992) and the National Agricultural Statistics Service data (NASS website) were used to identify different land covers. Table 1 presents the soil classification for 12 major soils under crop and grass cover in the watershed.

Soil and Water Sampling

Soils were sampled from three phases of the Wymore series (Wymore-WtB, -WtC2, and -WtD3) and two phases of the Pawnee series (Pawnee-PaC2 and -PaD2) along with seven other soil series. This approach produced a total of 12 soil map units to sample. Soil samples were collected from cropland and grassland within each map unit. Recently updated soil survey activities have split the Sharpsburg series into three soil series: Tomek, Yutan, and Aksarben. The new classifications, however, do not affect results given in this study.

Representative soil samples were collected from each of the 12 soil map units. To distribute sampling locations evenly within the agricultural area, the watershed was divided into six sections. An equal number of samples were taken at random from each section. In total, 72 soil samples from cropland and 24 from grassland were collected (Fig. 1).

At the randomly selected sampling sites, three cores were taken from the top 30-cm soil depth and mixed thoroughly in a stainless steel tray. The composite sample (approximately 2 kg) was placed in a plastic bag and sealed. Sampling was completed during April of 2003 prior to fertilizer application for the summer crop.

Many small streams receive surface water runoff from the agricultural land in the watershed. Streams located north of the reservoir eventually join in a single stream that runs southerly about 0.5 km before entering the reservoir near the north edge.

Water samples taken along the main stream were assumed to represent the surface water runoff generated from the entire watershed.

Most of the surface water runoff from the agricultural land in WT Watershed and water inflow for WT Reservoir are expected to occur during the rainy season in spring, summer, and fall (March through November). During this period, water samples were collected weekly from the main stream (Fig. 1). The analysis for major streams proved that samples taken from the main stream are representative of runoff generated from the entire watershed (Elrashidi et al., 2005a,b).

Water samples were taken from the stream under base flow conditions to ensure a clear runoff with almost no suspended particulates. Samples (grab) were collected in mid-stream using 1-L polyethylene bottles that had been rinsed twice with stream water. The water samples were taken immediately to the laboratory and refrigerated at 4°C. The water analysis was completed within a week. The soil and water sampling locations are shown in Figure 1.

Soil and Water Analysis

Soil and water samples were analyzed as described above under “The NRCS Technique” (page 1). Selected properties for soils under crop and grass cover in WT Watershed are given in Table 1.

Observed Inflow for Wagon Train Reservoir

In 1962, construction of the dam on a tributary of Salt Creek and Wagon Train Reservoir was completed. The U.S. Geological Survey, however, has monitored the water flow in Salt Creek and streams in the Platte River basin long before this (USGS, 2001). The Salt Creek gage at Roca (USGS gage # 06803000, hydrologic unit 10200203, Lancaster County, Nebraska) which had a period of record from 1951 to 2000, provided average monthly water flow rate values for a drainage area of 106,880 acres (43,286 hectares) encompassing WT Watershed (USGS, 2001). Recently, the Lower Platte South Natural Resources District (LPSNRD, 2004) used the ratio of the watershed to the Salt Creek drainage area (9.34%) to calculate the average monthly water flow rate values for WT Watershed. In our study, we used these average monthly water flow rate values to calculate the observed inflow for WT Reservoir.

Case Study I: Nonpoint Source of Heavy Metal Contamination to Surface Water in Wagon Train Watershed

Introduction

Heavy metals are present in soil in several chemical forms: water soluble, adsorbed on colloidal inorganic surfaces, complexed with organic materials, and associated with inorganic minerals (i.e., oxides, hydroxides, carbonates, and aluminosilicates) (Lindsay, 1979). At high concentrations, many of the heavy metals have toxic or detrimental effects on living organisms. The bioavailability and environmental impact are dependent upon the amount of metals dissolved in soil solution, which is controlled by soil properties (i.e., pH, redox potential, and contents of oxide/hydroxides, carbonates, clay minerals, salts, and organic matter). In this study, we investigated 8 heavy metals (Al, Fe, Si, Cd, Cu, Ni, Pb, and Zn) in 12 major soils in Wagon Train Watershed, Lancaster County, Nebraska. We were interested in understanding the role of these agricultural soils as nonpoint sources of metal contamination for surface waters.

Heavy storms may generate runoff events that remove dissolved soil chemicals from agricultural land to surface water bodies (a nonpoint source of contamination). Most heavy metals have natural input to streams, rivers, and lakes from weathering and dissolution of oxides, carbonate, and silicate minerals in soils. However, anthropogenic activities can introduce greater amounts of heavy metals to soils and natural waters. The anthropogenic inputs that can introduce heavy metals into the environment include the application of commercial fertilizers, liming materials, sewage sludge, manure, animal wastes, soil amendments, pesticides, and coal combustion by-products in addition to auto-emissions and fallout from metal-smelting industries. Losses of heavy metals by runoff from agricultural land have received little attention from agronomists and soil scientists. However, because of both the animal/human health perspective and the environmental water quality perspective, the concentrations and forms of heavy metals as well as their total quantity lost from nonpoint sources are now important concerns for both agricultural management and subsequent water use.

Chemicals and dissolved elements are released from a thin layer of surface soil that interacts with rainfall and runoff water (Sharpley, 1985). Chemicals transported by runoff water from agricultural land can pose risks to surface and ground waters (nonpoint sources of contamination). Studying nonpoint sources of contamination from agricultural land is technically complex. Contamination sources often are located over a large geographic area and difficult to identify. Identifying hot spots within a watershed enables a more efficient use of funds to alleviate potential problems and protect water resources. Although there are models that can be used to estimate the impact of nonpoint sources of contamination from agricultural watersheds, these models are too complex and expensive because they require very extensive data inputs.

USDA-NRCS developed an exploratory technique to estimate loss of elements by runoff for agricultural watersheds. This technique is quick and cost-effective because it uses existing climatic, hydrologic, and soil survey databases. Lengthy and expensive models need only be performed for certain areas of high risk. The NRCS technique was applied to estimate losses of phosphorus, nitrogen, and alkaline earth elements by runoff from agricultural land (Elrashidi et al., 2005a, 2005b, 2007). The technique applies the USDA runoff model (USDA-SCS, 1991) to estimate loss of runoff water from soils by rainfall. It assumes that water-soluble elements are lost from a specific

depth of surface soil that interacts with runoff water. A brief description of the technique is reported under “Materials and Methods” below. The objectives of this study were to apply this technique on Wagon Train Watershed to estimate: 1) losses of dissolved Al, Fe, Si, Cd, Cu, Ni, Pb, and Zn from soils by runoff water, and 2) metal loading into the reservoir.

Materials and Methods

This study was conducted on Wagon Train (WT) Watershed in Lancaster County, Nebraska. Information on the watershed, major soils, streams, and surface water bodies as well as the methods applied for soil and water sampling and analyses and for estimating heavy metal loss by runoff are given under “Application of the NRCS Technique” (page 5) .

Results and Discussion

Runoff and Reservoir Inflow

The historic record of monthly rainfall for Lancaster County (NWCC website) was applied in the runoff model (USDA-SCS, 1991) to predict the volume of runoff water. Table 2 shows the predicted annual loss of water by runoff (m^3/ha) and water present in the interaction zone (m^3/ha) for 12 major soils under crop and grass cover in WT Watershed. Generally, the annual loss of water from soil by runoff was higher for cropland than grassland. The predicted average (area-weighted) of annual runoff water was $1,122 \text{ m}^3/\text{ha}/\text{yr}$ for cropland and $942 \text{ m}^3/\text{ha}/\text{yr}$ for grassland. These results accounted for 15.4% and 12.9% of the annual rainfall for cropland and grassland, respectively. Similar values were reported for 13 U.S. soils in humid regions (rainfall $> 800 \text{ mm}/\text{yr}$); the average was 15% for cropland and 12% for grassland (Elrashidi et al., 2003).

These values, however, were relatively higher than those reported for Lancaster County, Nebraska, where WT Watershed is located (Elrashidi et al., 2004). This could be attributed to the slow water infiltration rate (hydrologic group D) of the dominant soils (Wymore, Pownee, and Mayberry) in the watershed. These soils occupy approximately 80% of the agricultural land in the watershed.

The results indicated that Wymore-WtC2 soil map unit, irrespective of the land cover, produced the highest volume of runoff water, mainly because of its abundance in the watershed. On the other hand, the Kennebec soil, which had very limited area, generated the least volume of runoff water. The total annual loss of runoff water from the 12 major soil map units was 4.15 million m^3 . The area of the 12 major soil map units (3,885 ha) incorporated about 96% of the entire watershed. When the entire watershed area (4,042 ha) was considered, the total annual runoff accounted for 4.31 million m^3 of water. The observed average annual inflow for WT Reservoir for the 50-year period between 1951 and 2000 is 4.25 million m^3 (USGS, 2001; Elrashidi et al., 2005a). The predicted annual runoff and the observed annual inflow were in good agreement.

Elements in the Soil and in the Water Phase

The average and standard deviation percentage of water soluble elements for soils (mg/kg or $\mu\text{g}/\text{kg}$) under crop and grass cover in WT Watershed are given in Table 3. For soils under crops, Al dissolved in the water phase ranged between 128 and 352 mg/kg with an area-weighted average of 239 mg/kg soil. A wider range of Al concentration (14.5 to 349 mg/kg) was observed for soils under grass. Meanwhile, the

area-weighted average for grassland (136 mg/kg soil) was lower than that for cropland. For the 12 major soils, irrespective of land cover, the average Al concentration in the water phase was 208 mg/kg soil.

For soils under crops, Fe dissolved in the water phase ranged between 72.8 and 193 mg/kg with an area-weighted average of 130 mg/kg soil. A relatively wider range of Fe concentration (8.5 to 181 mg/kg) was observed for soils under grass. However, the area-weighted average for grassland (70.9 mg/kg soil) was much lower than that for cropland. For the 12 major soils, irrespective of land cover, the average Fe concentration in the water phase was 113 mg/kg soil.

For soils under crops, Si dissolved in the water phase ranged between 184 and 668 mg/kg with an area-weighted average of 266 mg/kg soil. A wider range of Si concentration (25.8 to 568 mg/kg) was observed for soils under grass. However, the area-weighted average for grassland (173 mg/kg soil) was lower than that for cropland. For the 12 major soils, irrespective of land cover, the average Si concentration in the water phase was 238 mg/kg soil.

Compared to Al, Fe, and Si, much lower concentrations were measured for other elements (Cd, Cu, Ni, Pb, and Zn). For soils under crops, Cd dissolved in the water phase ranged between 3.52 and 6.69 $\mu\text{g}/\text{kg}$ with an area-weighted average of 4.96 $\mu\text{g}/\text{kg}$ soil. A similar range of Cd concentration (2.93 to 8.03 $\mu\text{g}/\text{kg}$) was observed for soils under grass. However, the area-weighted average for grassland (5.17 $\mu\text{g}/\text{kg}$ soil) was slightly higher than that for cropland. For the 12 major soils, irrespective of land cover, the average Cd concentration in the water phase was 5.02 $\mu\text{g}/\text{kg}$ soil.

For soils under crops, Cu dissolved in the water phase ranged between 380 and 584 $\mu\text{g}/\text{kg}$ with an area-weighted average of 433 $\mu\text{g}/\text{kg}$ soil. A similar range of Cu concentration (337 to 614 $\mu\text{g}/\text{kg}$) was observed for soils under grass. However, the area-weighted average for grassland (418 $\mu\text{g}/\text{kg}$ soil) was slightly lower than that for cropland. For the 12 major soils, irrespective of land cover, the average Cu concentration in the water phase was 429 $\mu\text{g}/\text{kg}$ soil.

For soils under crops, Ni dissolved in the water phase ranged between 135 and 244 $\mu\text{g}/\text{kg}$ with an area-weighted average of 187 $\mu\text{g}/\text{kg}$ soil. A wider range of Ni concentration (70.6 to 268 $\mu\text{g}/\text{kg}$) was observed for soils under grass. However, the area-weighted average for grassland (147 $\mu\text{g}/\text{kg}$ soil) was lower than that for cropland. For the 12 major soils, irrespective of land cover, the average Ni concentration in the water phase was 175 $\mu\text{g}/\text{kg}$ soil.

For soils under crops, Pb dissolved in the water phase ranged between 6.84 and 14.5 $\mu\text{g}/\text{kg}$ with an area-weighted average of 11.5 $\mu\text{g}/\text{kg}$ soil. A slightly wider range of Pb concentration (5.30 to 18.5 $\mu\text{g}/\text{kg}$) was observed for soils under grass. However, the area-weighted average for grassland (11.6 $\mu\text{g}/\text{kg}$ soil) was similar to that for cropland. For the 12 major soils, irrespective of land cover, the average Pb concentration in the water phase was 11.5 $\mu\text{g}/\text{kg}$ soil.

For soils under crops, Zn dissolved in the water phase ranged between 215 and 496 $\mu\text{g}/\text{kg}$ with an area-weighted average of 346 $\mu\text{g}/\text{kg}$ soil. A wider range of Zn concentration (8.55 to 600 $\mu\text{g}/\text{kg}$) was observed for soils under grass. However, the area-weighted average for grassland (229 $\mu\text{g}/\text{kg}$ soil) was smaller than that for cropland. For the 12 major soils, irrespective of land cover, the average Zn concentration in the water phase was 311 $\mu\text{g}/\text{kg}$ soil.

Elements in Stream Water

During the rainy season (March through November), the concentration of elements was measured in surface water samples collected weekly from the main stream in WT Watershed. In this study, we refer to the average element concentration in stream for the March through November rainy season as an annual average. Elrashidi et al. (2005a,b) found that water samples collected from the main stream in WT Watershed are representative of runoff generated from the entire watershed.

Both Al and Fe are abundant in soils, and their solubility is heavily dependent on pH (Lindsay, 1979). Therefore, both elements rarely occur in high concentrations in fresh waters with a neutral or alkaline pH (Hem, 1989). In this study, the annual average pH in water samples collected from the main stream in WT Watershed was 8.39. Expectedly, the observed Al and Fe concentrations were very low (where Al ranged between 1.80 and 33.1 $\mu\text{g/L}$) with an annual average of 11.1 $\mu\text{g/L}$. Crain (2001) reported a wide range of Al concentrations in 44 Kentucky stream stations—between 0.5 and 49,000 $\mu\text{g/L}$ with a median of 467 $\mu\text{g/L}$. The concentration of Fe in WT Watershed water ranged from 6.60 to 16.1 $\mu\text{g/L}$ and averaged 8.61 $\mu\text{g/L}$ annually. In a study on 4 creeks in northeastern Kansas, Schmidt (2004) found similar Fe concentrations, ranging from 5 to 30 $\mu\text{g/L}$ and averaging 6 $\mu\text{g/L}$. Higher Fe concentrations, ranging between 50 and 80 $\mu\text{g/L}$ and averaging 16 $\mu\text{g/L}$, were measured for Rattle Snake Creek in south-central Kansas (Christensen, 2001). Also, Apodaca and Bails (1999) found relatively high Fe concentrations in Frazer River (Colorado), ranging from 20 and 450 $\mu\text{g/L}$ and averaging 180 $\mu\text{g/L}$.

In contrast to Al and Fe, relatively higher concentrations were measured for Si in stream-water samples collected from WT Watershed. Si concentrations ranged from 120 to 1,032 $\mu\text{g/L}$ with an annual average of 531 $\mu\text{g/L}$. Fuhrer et al. (1996) conducted a study on the water quality in the Columbia River basin and collected water samples at 10 sites. They found that the dissolved Si concentration in water ranged between 2,337 and 9,817 $\mu\text{g/L}$ and averaged 4,160 $\mu\text{g/L}$.

USEPA (2002) recommended two criteria to determine the quality of fresh water: 1) the criterion maximum concentration (CMC), which is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect; and 2) the criterion continuous concentration (CCC), which is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect. USEPA (2002) recommended an Al concentration of 750 $\mu\text{g/L}$ for CMC and 87 $\mu\text{g/L}$ for CCC. Large amounts of Fe are undesirable in water because they can affect taste and can form a red oxy-hydroxide precipitate that stains laundry and plumbing fixtures (Hem, 1992). USEPA (2002) recommended a Fe concentration of 1,000 $\mu\text{g/L}$ for CCC while no concentration was recommended for CMC. USEPA (2002) recommended a drinking-water standard of 300 $\mu\text{g/L}$ for Fe while no regulation was established for either Al or Si. Accordingly, the concentrations of Al, Fe, and Si observed in the stream-water samples collected from WT Watershed appear to be too low to cause any ecological or human health concerns.

The observed monthly average Cd concentrations in the stream water ranged from 0.20 to 1.13 $\mu\text{g/L}$ with an annual average of 0.45 $\mu\text{g/L}$ (Fig. 2a). Apodaca and Bails (1999) reported similar values for Cd in waters of the Frazer River Watershed (Colorado), ranging from < 0.25 to 3.0 $\mu\text{g/L}$ and averaging 0.25 $\mu\text{g/L}$. Also, He et al. (2004) found similar Cd concentrations for surface runoff generated from vegetable farms and citrus groves (0.0 to 2.8 $\mu\text{g/L}$) and forestland (0.0 to 0.47 $\mu\text{g/L}$) in Florida. USEPA (2002) recommended a Cd concentration of 2.0 $\mu\text{g/L}$ for CMC and 0.25 $\mu\text{g/L}$ for CCC. The U.S. drinking-water standard for Cd is 5.0 $\mu\text{g/L}$ (USEPA, 2003). With respect to Cd, these regulations indicate that the stream water in WT Watershed does not pose any risk for human consumption. However, the indefinite exposure of the aquatic community to Cd concentration in WT Watershed stream water should be a concern since this concentration exceeds the EPA recommended CCC (0.25 $\mu\text{g/L}$).

In water samples collected from WT Watershed, values determined for concentrations of Cu were relatively higher than those for Cd. The observed monthly average Cu concentration ranged between 50.4 and 85.9 $\mu\text{g/L}$ and averaged 66.1 $\mu\text{g/L}$ annually (Fig. 2b). Similar values were reported by Crain (2001) for 44 stream stations in Kentucky, where Cu concentrations ranged between 0.5 and 82 $\mu\text{g/L}$. Lower

Cu concentrations were found for waters in the Frazer River Watershed in Colorado, ranging from < 4 to 6 µg/L and averaging 4 µg/L (Apodaca and Bails, 1999), and for waters in the Lower Columbia River basin, ranging from < 1 to 3 µg/L and averaging 1 µg/L (Fuhrer et al., 1996). Copper is an essential element for plants and animals. The toxicity of Cu to aquatic organisms is dependent on the alkalinity of the water. Copper is much more toxic to the organisms living in waters with low alkalinity than to those in waters with high alkalinity (USEPA, 1976). USEPA (2002) recommended a Cu concentration of 13 µg/L for CMC and 9.0 µg/L for CCC. The recommended Cu concentration for drinking water is 1,300 µg/L (USEPA, 2003). The fact that Cu concentrations in the stream water exceed the recommended EPA values for CMC and CCC should raise some concern for the negative effects on aquatic life in WT Watershed.

The observed monthly average Ni concentration in the stream water ranged from 5.25 to 9.27 µg/L with an annual average of 6.31 µg/L (Fig. 2c). He et al. (2004) investigated 1,277 surface runoff samples from 11 sites at vegetable farms and citrus groves in Florida. They found Ni concentrations that ranged between 0.0 and 39.3 µg/L. The authors also investigated runoff generated from forestland in South Florida, where Ni concentrations ranged from 0.0 to 13.3 µg/L and averaged 1.72 µg/L. Nickel is toxic to most plants and fungi, and the carcinogenic actions of Ni and its salts have been observed in numerous animal experiments (Berman, 1980). USEPA (2002) recommended a Ni concentration of 970 µg/L for CMC and 52 µg/L for CCC. The acceptable Ni level for drinking water in the U.S. has been established at 610 µg/L (USEPA, 2002). According to these regulations, no Ni-related environmental problems are expected in WT Watershed for aquatic organisms and human health.

Extremely low concentrations of Pb were measured in water samples taken from the main stream. The observed monthly average Pb concentration ranged between 1.06 and 1.80 µg/L with an annual average of 1.34 µg/L (Fig. 2d). Crain (2001) studied Pb concentrations in water samples collected at 44 stream stations in Kentucky and found that concentrations ranged between 0.3 and 4.5 µg/L. Similar Pb concentrations (ranging from 1 to 7 µg/L and averaging 5 µg/L) were reported for water samples collected from the Frazer River Watershed in Colorado (Apodaca and Bails, 1999). Generally, the concentration of Pb in water depends on the solubility of its minerals, which is controlled by pH (Lindsay, 1979). The high pH (8.39) measured in the water samples might explain these very low Pb concentrations. Lead enters natural waters from the atmosphere, runoff, or wastewater discharge. It may enter the environment during mining, refining, recycling, and coal combustion for fuel (USEPA, 1999). Surface waters in the United States, except when subject to contamination, seldom contain Pb in excess of 50 µg/L (Adriano, 1986). USEPA (2002) recommended a Pb concentration of 65 µg/L for CMC and 2.5 µg/L for CCC. In the U.S., the maximum contaminant level (MCL) of Pb for drinking water is 15.0 µg/L (USEPA, 2003). According to this regulation, no Pb-related environmental problems are expected in WT Watershed for aquatic organisms and human health.

In comparison to Pb, relatively higher Zn concentrations were measured in the stream water. The observed monthly average Zn concentration ranged from 1.41 to 20.0 µg/L with an annual average of 11.9 µg/L (Fig. 2e). Relatively lower Zn concentrations (ranging from < 1 to 14 µg/L and averaging 1 µg/L) were found by Fuhrer et al. (1996) in their work on water samples collected at 10 sites in the Lower Columbia River basin. Apodaca and Bails (1999), in their study on water samples from the Frazer River Watershed in Colorado, reported Zn concentrations ranging between < 8 and 100 µg/L and averaging 8 µg/L. On the other hand, Crain (2001) found a wider range and much higher Zn concentrations (0.5 to 1,650 µg/L) for water samples collected at 44 stream stations in Kentucky. Although zinc is an essential element for plant, animal, and human nutrition, a high Zn concentration in water can be harmful to aquatic life and pose a risk to human health (Berman, 1980). USEPA (2003)

recommended a Zn concentration of 120 µg/L for both CMC and CCC and established a limit of 7.4 mg/L of Zn for drinking-water supplies. According to these regulations, no Zn-related problems are expected for aquatic organisms in WT Watershed nor for human consumption of the water.

Element Loss by Runoff from Soils

Predicted losses of 8 elements by runoff from 12 major soils (kg/ha/yr or g/ha/yr) under crop and grass cover in WT Watershed are given in Table 4. As mentioned above, the measured loss of an element by runoff water (from the 10-mm interactive zone) should include all element forms dissolved in soil solution. For soils under crops in the watershed, the predicted Al loss ranged between 15.7 and 42.8 kg/ha/yr with an area-weighted average of 29.1 kg/ha/yr. A relatively wider range of Al loss (1.71 to 42.2 kg/ha/yr) was estimated for soils under grass. However, the area-weighted average for grassland (16.4 kg/ha/yr) was smaller than that for cropland. Crain (2001) reported relatively lower Al losses by runoff (ranging from 0.04 to 10.9 kg/ha/yr) from Kentucky soils. Figure 3 shows Al loss by runoff (kg/ha/yr) from soils in relation to their area and location in the watershed. Dark areas in figure 3 reflect high Al losses (≥ 30 kg/ha/yr), mainly from Wymore-WTD3 and Pawnee-PaD2 soils. For the 12 major soils, irrespective of land cover, the average Al loss by runoff was 25.3 kg/ha/yr. These data calculate an annual Al loss of 98.3 Mg from the 12 major soils in the watershed.

For soils under crops, Fe loss by runoff from soils ranged between 8.3 and 23.5 kg/ha/yr with an area-weighted average of 15.9 kg/ha/yr. A relatively wider range of Fe loss (1.01 to 21.9 kg/ha/yr) was calculated for soils under grass. However, the area-weighted average for grassland (8.54 kg/ha/yr) was smaller than that for cropland. Crain (2001) reported similar losses for Fe by runoff (0.35 to 14 kg/ha/yr) from Kentucky soils. On the other hand, He et al. (2004), in their study on Florida's acidic sandy soils, reported lower Fe losses by runoff (ranging from 0.004 to 2.42 kg/ha/yr). Figure 4 shows Fe loss by runoff (kg/ha/yr) from soils in relation to their area and location in the watershed. Dark areas in figure 4 reflect high Fe losses (≥ 17 kg/ha/yr), mainly from Wymore-WTD3 and Pawnee-PaD2 soils. For the 12 major soils, irrespective of land cover, the average Fe loss by runoff was 13.7 kg/ha/yr. These results indicate an annual Fe loss of 53.2 Mg from the 12 major soils in WT Watershed.

For soils under crops, Si loss ranged between 22.4 and 81.3 kg/ha/yr with an area-weighted average of 32.3 kg/ha/yr. A relatively wider range of Si loss (3.04 to 85.4 kg/ha/yr) was predicted for soils under grass. However, the area-weighted average for grassland (20.9 kg/ha/yr) was smaller than that for cropland. Figure 5 shows Si loss by runoff (kg/ha/yr) from soils in relation to their area and location in the watershed. Dark areas in figure 5 reflect high Si losses (≥ 45 kg/ha/yr), mainly from Wymore-WTD3, Pawnee-PaD2, Kennebec, and Burchard soils. For the 12 major soils, irrespective of land cover, the average Si loss by runoff was 28.9 kg/ha/yr. These data indicate an annual Si loss of 112.3 Mg from the 12 major soils in the watershed.

In comparison to Al, Fe, and Si, much smaller losses were predicted for other elements investigated (Cd, Cu, Ni, Pb, and Zn). For soils under crops, Cd loss ranged between 0.43 and 0.82 g/ha/yr with an area-weighted average of 0.60 g/ha/yr. A relatively wider range of Cd loss (0.35 to 0.97 g/ha/yr) was predicted for soils under grass. However, the area-weighted average for grassland (0.62 g/ha/yr) was similar to that for cropland. In a study on Kentucky soils, the average Cd loss by runoff was < 35 g/ha/yr (Crain, 2001). He et al. (2004) reported Cd losses by runoff that were extremely low (< 0.33 g/ha/yr) for vegetable farms and citrus groves in Florida. Figure 6 shows Cd loss by runoff (g/ha/yr) from soils in relation to their area and location in the watershed. Dark areas in figure 6 reflect high Cd losses (≥ 0.7 g/ha/yr), mainly from Wymore-WTD3 soil. For the 12 major soils, irrespective of land cover, the

average Cd loss by runoff was 0.61 g/ha/yr. These data indicate an annual Cd loss of 2.37 kg from the 12 major soils in the watershed.

Compared with Cd, greater losses by runoff from soils were estimated for Cu. For soils under crops, the Cu loss ranged between 46.6 and 71.3 g/ha/yr with an area-weighted average of 52.7 g/ha/yr. A similar range of Cu loss (41.1 to 74.2 g/ha/yr) was predicted for soils under grass. Therefore, the area-weighted average for grassland (50.4 g/ha/yr) was similar to that for cropland. In a study conducted on Kentucky soils, the average Cu loss by runoff was < 35 g/ha/yr (Crain, 2001). In their 2-year study on Florida soils, He et al. (2004) reported that Cu losses by runoff had a wide range (3.45 to 657 g/ha/yr) in the first year (2001) and ranged from 5.33 to 336 g/ha/yr in 2002. The higher Cu losses by runoff from soils were attributed to high applications of Cu-containing pesticides and fungicides (e.g., copper hydroxides). Figure 7 shows Cu loss by runoff (g/ha/yr) from soils in relation to their area and location in the watershed. Dark areas in figure 7 reflect high Cu losses (≥ 64 g/ha/yr), mainly from Wymore-WTD3, Kennbec, and Pawnee-PaD2 soils. For the 12 major soils, irrespective of land cover, the average Cu loss by runoff was 52.0 g/ha/yr. These data indicate an annual Cu loss of 202 kg from the 12 major soils in the watershed.

For soils under crops, the predicted Ni loss ranged between 16.6 and 29.7 g/ha/yr with an area-weighted average of 22.8 g/ha/yr. A relatively wider range of Ni loss (8.33 to 32.4 g/ha/yr) was predicted for soils under grass. However, the area-weighted average for grassland (17.8 g/ha/yr) was smaller than that for cropland. In their study on vegetable farms and citrus groves in Florida, He et al. (2004) reported that Ni losses by runoff were low, ranging from 0 to 8.71 g/ha/yr. Figure 8 shows the predicted Ni loss by runoff (g/ha/yr) from soils in relation to their area and location in the watershed. Dark areas in figure 8 reflect high Ni losses (≥ 22 g/ha/yr), derived mainly from Wymore-WTD3 and Pawnee-PaD2 soils. For the 12 major soils, irrespective of land cover, the average Ni loss by runoff was 21.3 g/ha/yr. These data indicate an annual Ni loss of 82.7 kg from the 12 major soils in the watershed.

In comparison to both Cu and Ni, much smaller losses were predicted for Pb. For soils under crops, the predicted Pb loss ranged between 0.83 and 1.77 g/ha/yr with an area-weighted average of 1.40 g/ha/yr. A relatively wider range of Pb loss (0.63 to 2.23 g/ha/yr) was predicted for soils under grass. However, the area-weighted average for grassland (1.40 g/ha/yr) was identical to that for cropland. He et al. (2004), in their work on Florida soils, reported similar Pb losses, ranging from 0 to 2.67 g/ha/yr. In another study, conducted on Kentucky soils, the Pb loss by runoff was relatively high and had a wide range between 0 and 35 g/ha/yr (Crain, 2001). Figure 9 shows the predicted Pb loss by runoff (g/ha/yr) from soils in relation to their area and location in the watershed. Dark areas in figure 9 reflect high Pb losses (≥ 1.6 g/ha/yr), derived mainly from Wymore-WtB and Nodaway soils. For the 12 major soils, irrespective of land cover, the average Pb loss by runoff was 1.40 g/ha/yr. These data predict an annual Pb loss of 5.44 kg from the 12 major soils in the watershed.

For soils under crops, Zn loss ranged between 26.4 and 60.4 g/ha/yr with an area-weighted average of 42.1 g/ha/yr. A relatively wider range of Zn loss (1.01 to 72.5 g/ha/yr) was observed for soils under grass. However, the area-weighted average for grassland (27.6 g/ha/yr) was smaller than that for cropland. In their 2-year study on Florida soils, He et al. (2004) reported that Zn losses by runoff had a wide range (12.9 to 249 g/ha/yr) in the first year (2001) and ranged from 1.46 to 74.3 g/ha/yr in 2002. The higher Zn losses by runoff from soils were attributed to high applications of Zn-containing pesticides and fungicides (He et al., 2004). In another study, conducted on Kentucky soils, the Zn loss by runoff was relatively high, having a wide range between < 35 and 175 g/ha/yr (Crain, 2001). Figure 10 shows the predicted Zn loss by runoff (g/ha/yr) from soils in relation to their area and location in the watershed. Dark areas in figure 10 reflect high Zn losses (≥ 40 g/ha/yr), derived mainly from Wymore-WTD3 and Pawnee-PaD2 soils. For the 12 major soils, irrespective of land cover, the

average Zn loss by runoff was 37.7 g/ha/yr. These data indicate an annual Zn loss of 147 kg from the 12 major soils in the watershed.

Elements in Runoff and Loading

In this study, losses predicted for runoff water (Table 2) and element losses from soils by runoff (Table 4) were used to estimate element concentrations in runoff water. The predicted average Al, Fe, and Si concentrations in runoff from soils were 23.7, 12.8, and 27.1 mg/L, respectively. Much smaller average concentrations were predicted for Cd, Cu, Ni, Pb, and Zn, specifically 0.57, 48.7, 19.9, 1.31, and 35.3 µg/L, respectively. For Al, Fe, Si, Ni, and Zn, the observed annual average concentrations in the stream water were lower than the predicted values. The difference between the predicted and observed values was particularly large for those elements (Al, Fe, and Si) found in relatively high concentrations in the runoff water. The observed annual average concentrations in the stream water for Al, Fe, Si, Ni, and Zn were 11.1, 8.61, 531, 6.31, and 11.9 µg/L, respectively. Meanwhile, there was reasonable agreement between the predicted and observed concentrations for Cd, Cu, and Pb (Figs. 2a, 2b, and 2d, respectively).

In this study, the predicted element concentration was calculated for runoff water generated at field sites and not stream water. Factors affecting an element's concentration in runoff water after leaving field sites might decrease observed values in the stream water and should be taken into consideration. In previous studies, Elrashidi et al. (2005a,b) reported that P and nitrate-N removal by aquatic weeds and algae in streams has decreased observed element concentrations in water. In addition to the removal of elements from water by biological processes, a chemical precipitation of element oxide, hydroxide, and carbonate could have occurred where the stream water had high pH values. The average annual pH in the stream water was 8.39, compared to the average pH of 6.00 measured in soils. We believe a precipitation of oxide and hydroxide of Al and Fe minerals could be the main factor in removing both Al and Fe from water while biological processes could be playing an important role in removing other elements from water. No effort was made to investigate these assumptions since it was beyond the scope of this study.

One of the objectives of this study was to estimate the impact of agricultural land on water quality (nonpoint source of element contamination) in WT Reservoir. For the agricultural land in WT Watershed, we assumed that most of the elements lost by runoff from soils and those detected in the stream water were transported eventually to WT Reservoir. We used the average element concentration in the stream water and the predicted volume of monthly surface water runoff to estimate the monthly element loading (kg) into WT Reservoir (Table 5).

As expected, the results indicated that element loading into the reservoir was least during winter (December, January, and February). Most of the element loading occurred during spring and summer (April through September) due to the rainfall pattern. For example, the average loading of Fe, Cu, and Zn in winter was 0.96, 7.33, and 1.33 kg/mo, respectively, while that in spring/summer was 4.49, 34.5, and 6.07 kg/mo, respectively. Silicon, with an annual loading of 2.29 Mg/yr, had the greatest quantitative impact on water quality, followed by Cu, with an annual loading of 285 kg/yr. Meanwhile, Zn, Al, Fe, and Ni appeared to have a moderate impact, with an annual loading between 27 and 52 kg/yr. However, when the environmental impact of elements on water quality is evaluated, both the quantitative and qualitative effects of element chemical species should be considered.

Case Study II: Nonpoint Source of Alkaline Earth Element Contamination to Surface Water in Wagon Train Watershed

Introduction

Alkaline earth elements, AEEs (Ca, Mg, Ba, and Sr) share many chemical properties that identify them as a chemical group in soils. These properties contribute to their natural occurrence in carbonate, phosphate, sulfate, and silicate minerals and to their participation in many similar chemical reactions. Calcium and Mg are the most common AEEs in soils (Suarez, 1996). Major Ca-bearing minerals include calcite, dolomite, gypsum, and apatite. Dolomite, talc, brucite, chlorite, tourmaline, and magnesite are the main Mg minerals in soils. The content of Ba and Sr in soils is much lower than the content of Ca and Mg. Barium is most often found in soils as barite (BaSO_4) and witherite (BaCO_3) minerals. However, Ba is usually present as a trace constituent in silicate minerals, such as feldspars and micas. Strontium forms celestite (SrSO_4) and strontianite (SrCO_3) minerals in soils. Similar to Ba, feldspars are the major host minerals of Sr as a trace constituent.

Heavy storms may generate runoff events that remove soil chemical constituents from agricultural land and transport them to surface water bodies (nonpoint source of contamination). Most AEE inputs to streams, rivers, and lakes are from weathering and dissolution of carbonate, sulfate, and silicate minerals in soils (Garrels and Perry, 1974; Brass, 1976). The loss of AEEs from agricultural land through runoff has received little attention from agronomists and soil scientists. However, from an environmental water quality perspective, the concentration and form of alkaline earth elements as well as their total quantity lost from nonpoint sources are important concerns for both agricultural management and subsequent water use.

Excessively large concentrations of AEEs are objectionable for drinking water because of possible physiological effects, unpleasant taste, and greater costs due to corrosion or the need for additional treatment (USEPA, 1986). Calcium and Mg contribute to the hardness of the water and tend to cause encrustations on cooking utensils, in pipes, and in water heaters (Hem, 1989). Large concentrations of Ba in drinking water can cause health problems for human and animals. To protect human health, USEPA (2003) allows no more than 2 mg Ba/L in drinking water sources. The introduction of Sr into the atmosphere due to nuclear weapons testing and the subsequent fallout of Sr on agricultural land and in natural water resources have increased the concern for the adverse effects on human and animal health (Suarez, 1996). Strontium is of particular concern due to the radioisotope ^{90}Sr , which readily enters the food chain (Bowen and Dymond, 1956).

The NRCS technique applies the USDA runoff equation (USDA-SCS, 1991) to estimate loss of runoff water from soils by rainfall. The technique assumes that soluble elements such as Ca, Mg, Ba, and Sr are lost from a specific depth of surface soil that interacts with runoff and leaching water. The objectives of this study were to apply this technique on a watershed (specifically Wagon Train Watershed in southeast Nebraska) to estimate: 1) losses of Ca, Mg, Ba, and Sr from soils by runoff, and 2) element loading into Wagon Train Reservoir.

Materials and Methods

This study was conducted on Wagon Train (WT) Watershed in Lancaster County, Nebraska. Information on the watershed, major soils, streams, and surface water

bodies as well as the methods applied for soil and water sampling and analyses and for estimating alkaline earth elements loss by runoff are given under “Application of the NRCS Technique” (page 5).

Removal of Calcium and Magnesium in Runoff

Using the data on runoff water losses from the 12 soil map units (SMUs) (Table 2) and the amount of elements (Ca and Mg) present in both the water and exchangeable phases in soils (Tables 6 and 7), we calculated how the removal of elements from both the water and exchangeable phases affects the concentration in runoff water. The calculation for Ca could be outlined as follows:

1) For each SMU, the amount of Ca removed in runoff was calculated (kg/SMU) when N% of the exchangeable Ca in soil (interaction zone) is released to the water phase. N is any number between 0 and 100.

2) The amount of Ca removed in runoff from SMUs, calculated in step 1, was summed up (R_N) to determine the total amount of exchangeable Ca (kg) removed in runoff generated from the entire watershed as follows:

$$\sum (\text{SMU}) = R_N (\text{kg}) \quad (8)$$

3) For each SMU, the amount of water-soluble Ca was calculated (kg/SMU) when the element present in the water phase of soil (interaction zone) was removed in runoff.

4) Amounts of calcium removed in runoff from SMUs calculated in step 3 were summed up (W) to determine the total amount of water-soluble Ca (kg) removed in runoff generated from the watershed as follows:

$$\sum (\text{SMU}) = W (\text{kg}) \quad (9)$$

5) The average Ca concentration in runoff (Runoff-Ca) generated from the entire watershed was calculated (mg/L), when both Ca present in the water phase and N% of the exchangeable Ca in soil (interaction zone) were removed in runoff water as follows:

$$\text{Runoff-Ca (mg/L)} = [(R_N + W) \times 1000] \div (V) \quad (10)$$

Where: V = the total volume of runoff water generated from the entire watershed (m^3).

The above calculation (steps 1 through 5) should be performed on two N values (such as 0 and 100) to develop a linear regression equation for Ca. This equation describes the relationship between the average exchangeable Ca% released from all SMUs (independent variable) and runoff-Ca (mg/L) generated from the entire watershed (dependent variable). In this study, we used the data to develop linear regression equations for Ca (Eq. 11) and Mg (Eq. 12).

$$\text{Runoff-Ca (mg/L)} = 7.988 + 3.678 \times (\text{Ca}\%) \quad (11)$$

$$\text{Runoff-Mg (mg/L)} = 4.210 + 0.719 \times (\text{Mg}\%) \quad (12)$$

Results and Discussion

Elements in the Water Phase

The average and standard deviation of Ca, Mg, Ba, and Sr in the water phase for 12 major soils (reported as mg/kg or $\mu\text{g/kg}$ soil) under crop and grass cover in WT Watershed are given in Table 6. For soils under crops, Ca dissolved in the water phase ranged between 41.7 and 93.8 mg/kg with an area-weighted average of 73.4 mg/kg soil. A wider range of Ca concentration (33.1 to 161.0 mg/kg) was observed for soils under grass. However, the area-weighted average for grassland (63.0 mg/kg soil)

was lower than that for cropland. For the 12 major soils, irrespective of land cover, the average amount of Ca in the water phase was 70.3 mg/kg soil.

For soils under crops, Mg dissolved in the water phase ranged between 27.2 and 47.6 mg/kg with an area-weighted average of 41.4 mg/kg soil. A relatively wider range of Mg concentrations (16.1 to 54.2 mg/kg) was observed for soils under grass. However, the area-weighted average (26.9 mg/kg soil) for grassland was much lower than that for cropland. For the 12 major soils, irrespective of land cover, the average Mg concentration in the water phase was 37.0 mg/kg soil.

Compared to Ca and Mg, much smaller concentrations were measured for both Ba and Sr. For soils under crops, Ba dissolved in the water phase ranged between 0.94 and 1.88 mg/kg with an area-weighted average of 1.56 mg/kg soil. A relatively wider range of Ba concentration (0.51 to 2.15 mg/kg) was observed for soils under grass. However, the area-weighted average for grassland (1.09 mg/kg soil) was lower than that for cropland. For the 12 major soils, irrespective of land cover, the average amount of Ba in the water phase was 1.42 mg/kg soil.

For soils under crops, Sr dissolved in the water phase ranged between 0.25 and 0.53 mg/kg with an area-weighted average of 0.40 mg/kg soil. A relatively wider range of Sr concentration (0.23 to 0.66 mg/kg) was observed for soils under grass. Meanwhile, the area-weighted average for grassland (0.38 mg/kg soil) was similar to that for cropland. For the 12 major soils, irrespective of land cover, the average Sr concentration in the water phase was 0.39 mg/kg soil.

Elements in the Exchangeable Phase

The average and standard deviation of Ca and Mg in the exchangeable phase for the 12 major soils (mg/kg) under crop and grass cover in WT Watershed are given in Table 7. For soils under crops, Ca in the exchangeable phase ranged between 2,629 and 3,584 mg/kg with an area-weighted average of 3,199 mg/kg soil. A wider range of Ca concentration (2,265 to 6,172 mg/kg) was observed for soils under grass. Meanwhile, the area-weighted average for grassland (3,329 mg/kg soil) was slightly higher than that for cropland. For the 12 major soils, irrespective of land cover, the average amount of Ca in the exchangeable phase was 3,238 mg/kg soil.

For soils under crops, Mg in the exchangeable phase ranged between 456 and 748 mg/kg with an area-weighted average of 660 mg/kg soil. A similar range of Mg concentration (359 to 742 mg/kg) was observed for soils under grass. Meanwhile, the area-weighted average for grassland (567 mg/kg soil) was slightly lower than that for cropland. For the 12 major soils, irrespective of land cover, the average Mg concentration in the exchangeable phase was 632 mg/kg soil.

Both Ba and Sr occur mainly in the water phase. Negligible amounts were attached to the negatively charged colloid surfaces (exchangeable phase) in soils.

Active Forms of Elements in Soil

Elements dissolved in the soil solution (water phase) within the interactive zone can be removed and lost during the occurrence of runoff events. However, elements attached to the negatively charged colloid surfaces (exchangeable phase) in the soil interactive zone need to be released into the water phase before they can be removed by runoff water. It is assumed that the energy exerted by raindrops on surface soil (interactive zone) and the presence of large amounts of water enhance the release of cations from the exchangeable phase to the water phase. The amount of exchangeable elements released is dependent upon the intensity and duration of the rainfall event in addition to factors related to the soil properties, such as pH, accompanying cations, and electrical conductivity (EC). Thus, element forms present in both the water and exchangeable phases for the soil interactive zone (10-mm depth) are considered environmentally active.

In this study, approximately 98% and 94% of environmentally active Ca and Mg, relatively, were in the exchangeable phase in soils. For Ba and Sr, however, environmentally active forms were present mainly in the water phase because exchangeable forms of these elements are negligible in the 12 soils. Suarez (1996) reported that Ca and Mg are the major components of the exchangeable ions while Ba and Sr are generally insignificant contributors to the sum of the exchangeable cations in soils. For the four elements (Ca, Mg, Ba, and Sr), no apparent differences in the amount of active forms were observed between soils under crops and those under grass.

Element Loss by Runoff

For the rainy season (March through November), Ca, Mg, Ba, and Sr concentrations were measured in surface water samples collected weekly from the main stream in WT Watershed. In this study, we refer to the average element concentration in stream for the rainy season as an annual average. Elrashidi et al. (2005a,b) reported that water samples collected from the main stream in WT Watershed are good representatives for runoff generated from the entire watershed.

Observed Ca concentrations in the main stream ranged from 46.3 to 77.4 mg/L with an annual average of 61.4 mg/L (Fig. 11). Schmidt (2004) reported relatively higher Ca concentrations (ranging between 48 and 120 mg/L and averaging 90 mg/L) in stream-water samples collected from a watershed in northeastern Kansas. In another study on streams in south-central Kansas, Christensen (2001) reported a wide range of Ca concentrations (ranging between 21 and 100 mg/L and averaging 73.0 mg/L).

In this study, observed Mg concentrations in water samples collected from WT Watershed had a narrow range (14.3 to 24.4 mg/L) and an average of 18.6 mg/L annually (Fig. 12). These values are similar to those reported for Mg in the northeastern Kansas watershed, where the average concentration in streams was 22 mg/L (Schmidt, 2004).

In comparison to Ca and Mg, much smaller Ba and Sr concentrations were measured in WT Watershed's stream. The average annual concentration of Ba was 273 $\mu\text{g/L}$ (Fig. 13) and that of Sr was 360 $\mu\text{g/L}$ (Fig. 14). In his study on Ba for 24 Kentucky streams, Crain (2001) reported a wide range of Ba concentrations, between 0.5 and 480 $\mu\text{g/L}$.

We applied the observed annual Ca concentration (61.4 mg/L) in Equation 11 to estimate the percentage of Ca released from the exchangeable phase in soils. Also, the observed annual Mg concentration (18.6 mg/L) was used in Equation 12 to estimate the release from exchangeable Mg. The estimated percentage of exchangeable Ca and Mg released into runoff water was 15% and 20%, respectively. We used these percentages to estimate the amount of exchangeable Ca and Mg released from the 12 major soils in the watershed. Next, we added the amount of exchangeable element released to the amount of element already present in the water phase to calculate total Ca and Mg losses in runoff water. In contrast, Ba and Sr losses in runoff water were determined mainly from elements present in the water phase of soils. The loss of Ca, Mg, Ba, and Sr by runoff water for soils under crop and grass cover are given as kg/ha (Ca and Mg) or as g/ha (Ba and Sr) in Table 8.

As mentioned previously, the loss of Ca by runoff water (from the 10-mm interactive zone) includes 15% of the cation released from the exchangeable phase in addition to the calcium dissolved in soil solution. For soils under crops, Ca loss ranged between 53.2 and 75.6 kg/ha with an area-weighted average of 67.4 kg/ha. A wider range of Ca loss (45.0 to 128.2 kg/ha) was observed for soils under grass. However, the area-weighted average for grassland (67.8 kg/ha) was similar to that for cropland. Figure 15 shows Ca loss by runoff (kg/ha) from soils in relation to their area and location in the watershed. Dark areas in figure 15 reflect high Ca losses (≥ 70 kg/ha), derived mainly from Colo and Nodaway soils. For the 12 major soils, irrespective of land cover, the

average Ca loss by runoff was 67.5 kg/ha. These data indicate an annual Ca loss of 262 Mg from the 12 major soils in the watershed.

Greater Ca losses were reported by Crain (2001) in his study on an agricultural watershed in Kentucky; annual losses from soil ranged from 38.6 to 355 kg/ha and averaged 162 kg/ha. On the other hand, Timmons et al. (1977), in their study on a forested watershed in northern Minnesota, reported much smaller losses, ranging between 3.74 and 4.88 kg/ha and averaging 4.35 kg/ha. The large losses from the Kentucky watershed could be attributed to the dominance of cropland soils amended with lime. In contrast, the acidic forested soils in Minnesota usually have low Ca contents.

The loss of Mg by runoff water (from the 10-mm interactive zone) includes 20% of cations released from the exchangeable phase and Mg ions dissolved in soil solution. For soils under crops, Mg loss ranged between 14.5 and 23.3 kg/ha with an area-weighted average of 21.1 kg/ha. Similar Mg losses (11.2 to 23.0 kg/ha) were observed for soils under grass. However, the area-weighted average for grassland (16.9 kg/ha) was lower than that for cropland. Figure 16 shows Mg loss by runoff (kg/ha) from soils in the watershed. It shows that a large area in the watershed (consisting mainly of Pawnee and Wymore soils) generates Mg losses ranging between 18 and 21 kg/ha. For the 12 major soils, irrespective of land cover, the average Mg loss by runoff was 19.9 kg/ha. This gives an annual magnesium loss of 77.1 Mg from the entire watershed. For an agricultural watershed in Kentucky, Crain (2001) indicated that annual Mg losses ranged from 14.7 to 84.6 kg/ha and averaged 38.6 kg/ha. On the other hand, Schreiber et al. (1976) found smaller Mg losses in runoff water from five southern pine watersheds in northern Mississippi. They reported an average annual loss of 3.05 kg/ha.

In this study, the loss of Ba in runoff water (from the 10-mm interactive zone) included only Ba ions dissolved in soil solution. For soils under crops, barium loss ranged between 114 and 229 g/ha with an area-weighted average of 189 g/ha. A wider range of Ba loss (61 to 259 g/ha) was observed for soils under grass. However, the area-weighted average for grassland (131 g/ha) was lower than that for cropland. Figure 17 shows Ba loss by runoff (g/ha) from soils in relation to their area and location in the watershed. It shows that bottom-land soils (Kennebec, Nodaway, and Judson) have smaller Ba losses than other soils in the watershed. For the 12 major soils, irrespective of land cover, the average Ba loss by runoff was 172 g/ha. These data indicate a total annual Ba loss of 668 kg from the 12 major soils in the watershed. Crain (2001) estimated annual Ba losses in runoff from an agricultural watershed in Kentucky. They reported an annual loss ranging between 77.2 and 386 g/ha and averaging 270 g/ha.

Because of the insignificant amount of exchangeable Sr in soils, the loss of Sr in runoff water (from the 10-mm interactive zone) was derived mainly from ions dissolved in soil solution. The loss of Sr by runoff water for soils under crops and grass is given as g/ha in Table 8. For soils under crops, Sr losses ranged between 30.3 and 63.7 g/ha with an area-weighted average of 48.8 g/ha. A wider range of Sr losses (27.7 to 79.2 g/ha) was observed for soils under grass. Meanwhile, the area-weighted average for grassland (45.7 g/ha) was slightly lower than that for cropland. Figure 18 shows Sr loss by runoff (g/ha) from soils in the watershed. It shows that large areas in the watershed generate Sr losses greater than 45 g/ha. For the 12 major soils, irrespective of land cover, the average Sr loss by runoff was 47.8 g/ha. This gives an annual total Sr loss of 186 kg from the 12 major soils in the watershed.

Element Loading

In this study, losses predicted for water as runoff (Table 2) and losses of alkaline earth elements (AEEs) (Table 8) from soils by runoff were used to predict AEE concentrations in runoff water. The predicted average Ca concentration in runoff

from soils (63.2 mg/L) and the observed average annual concentration in stream water (61.4 mg/L) were in good agreement (Fig. 11). Meanwhile, a perfect agreement was obtained between the predicted (18.58 mg/L) and observed (18.59 mg/L) Mg concentrations (Fig. 12). However, the predicted Ba (161 µg/L) and Sr (45 µg/L) concentrations in runoff water were lower than those concentrations observed in stream water. The average annual Ba and Sr concentrations in stream water were 273 and 360 µg/L, respectively (Figs. 13 and 14).

In this study, the predicted AEE concentration was calculated for runoff water generated at field sites and not stream water. Factors affecting AEE concentration in runoff water after leaving field sites might decrease or increase the observed values in stream water and should be taken into consideration. In previous studies, Elrashidi et al. (2005a,b) reported that P and nitrate-N removal by aquatic weeds and algae in streams has decreased observed concentrations in water. On the other hand, a subsurface seepage that discharges directly into streams might contribute to the high Ba and Sr concentrations observed in water samples collected from the main stream. An investigation of subsurface seepage, however, was out of the scope of this study.

There is another possible explanation for these high Ba and Sr concentrations. In this study, we used a 10-mm top soil interactive zone to estimate elements removed in runoff water. Increasing the depth of the soil interactive zone, where environmentally active Ba is lost by runoff, from a 10-mm to 17-mm soil layer, would increase the average concentration of predicted Ba in runoff to 273.5 µg/L, a value which agrees very well with the observed annual Ba concentration of 273 µg/L in stream water. However, it is impractical to apply this approach for Sr because it would require extending the interaction zone to a depth of 80 mm.

One of the objectives of this study was to estimate the impact of agricultural land on water quality (nonpoint source of Ca, Mg, Ba, and Sr contamination) in WT Reservoir. For the agricultural land in WT Watershed, we assumed that most of the AEE loss from soils by runoff was transported eventually to WT Reservoir. We used the predicted average AEE concentration in runoff and the predicted volume of monthly surface water runoff to estimate the monthly AEE loading (kg) into WT Reservoir (Table 9).

As expected, the results indicated that the monthly AEE loading into the reservoir was least during winter (December, January, and February), averaging 7,063, 2,079, 18, and 5 kg for Ca, Mg, Ba, and Sr, respectively. Most of the element loading in the reservoir occurred during spring and summer (April through September) due to the rainfall pattern. The average monthly loading was 32,937 kg, 9,694 kg, 84 kg, and 24 kg for Ca, Mg, Ba, and Sr, respectively. These values show a greater impact from Ca and Mg on the water quality in WT Reservoir when compared to that from both Ba and Sr. The annual loading was about 273 and 80 megagrams for Ca and Mg, respectively, whereas it was 695 kg for Ba and 193 kg for Sr. Crain (2001) estimated Ca, Mg, and Ba loads for 22 streams in Kentucky. The average annual loads ranged from 8.2 to 3,607 tons for Ca and from 3 to 650 tons for Mg, while the average annual loads of Ba ranged between 0.02 and 3.7 tons.

Summary and Conclusions

Nutrients and other water-soluble chemicals can be transported from agricultural land by surface runoff and subsurface leaching to fresh-water bodies. Management activities on cultivated land in high rainfall areas may pose risks to water quality. The NRCS technique uses existing climatic, hydrologic, and soil survey databases to estimate the loss of elements by runoff and leaching from agricultural land. The technique applies runoff and percolation models to estimate water loss from agricultural watersheds. The interaction between both runoff and leaching waters and dissolved elements in root-zone soil is used to estimate element losses from soil. The GIS software, which uses available spatial soil and land cover layers as well as the predicted data for runoff water and element losses, can be applied to develop digital maps. These maps can improve data presentation and communications with clientele as well as identify trouble areas within a watershed.

In previous studies, the technique has been applied successfully to estimate phosphorus and nitrate-N losses from agricultural watersheds. In this report, it was used to estimate losses of heavy metals (Al, Fe, Si, Cd, Cu, Ni, Pb, and Zn) and alkaline earth elements (Ca, Mg, Ba, and Sr) by runoff from soils.

Phosphorus and most elements (heavy metals and alkaline earth elements) are mainly lost from soils by runoff to surface fresh-water bodies. Only in coarse sandy soil or heavy clay soils that have deep cracks can these elements also be lost by leaching to ground water. Nitrate, however, because of high mobility in the soil profile, can be transported from agricultural land by both surface runoff and subsurface leaching. Elements are released from a thin layer of surface soil that interacts with rainfall and runoff water. The thickness of the interaction zone used in our studies is 10 mm, assuming that only a fraction of the chemical present in this depth interacts with rainfall water.

For WT Watershed, the estimated annual loss of water by runoff was 4.32 million m³. The predicted amount of runoff water was in good agreement with the observed annual inflow for WT Reservoir (4.25 million m³). Significant losses by runoff from the entire watershed were predicted for Si (112 Mg/yr), Al (98.3 Mg/yr), and Fe (53.2 Mg/yr). Relatively lower amounts were predicted for Cu, Zn, Ni, Pb, and Cd (202, 147, 82.7, 5.44, and 2.37 kg/yr, respectively). Some of these elements (i.e., Fe, Cu, Zn, and Si) are either essential nutrients or beneficial for crop production, and their losses should emphasize the need for periodic applications of fertilizers with these elements to agricultural land. Elements such as Cd, Ni, Pb, Al, Cu, and Zn are in the EPA priority or secondary list of pollutants, and high concentrations of them in water can pose a risk to aquatic life, animals, and humans. Therefore, the element concentration in runoff from agricultural land and the impact on surface waters (nonpoint source of pollution) should be understood.

With respect to alkaline earth elements, significant losses by runoff from soils in the watershed were predicted for Ca (67.5 kg/ha/yr) and Mg (19.9 kg/ha/yr). Lower values were predicted for Ba and Sr (172 and 47.8 g/ha/yr, respectively). Both Ca and Mg are essential nutrients for crop production, and their losses should emphasize the need for periodic applications of dolomitic lime on agricultural land.

Water samples were collected weekly throughout the rainy season (March through November) from the main stream before it entered the reservoir. The observed average concentrations of Al, Fe, Si, Ni, and Zn in the stream water were much lower than the predicted concentrations of runoff generated from soils in the entire watershed. The biological uptake of elements by weeds, algae, and aquatic plants might explain the low concentrations of elements in the stream water. Furthermore, a high pH in the stream water could precipitate oxide, hydroxide, and carbonate forms of the elements. On the other hand, the predicted concentrations of Cd, Cu, and Pb

in runoff from the watershed agreed with the concentrations observed in the stream water.

With respect to alkaline earth elements, calcium concentrations in the stream water ranged between 46.3 and 77.4 mg/L and averaged 61.4 mg/L. Magnesium concentrations ranged between 14.3 and 24.4 mg/L and averaged 18.6 mg/L. Barium and Sr had much lower concentrations, averaging from 273 to 360 µg/L, respectively. The predicted annual water and element losses by runoff were used to calculate element concentrations in runoff water. The predicted annual Ca and Mg concentrations in runoff from the watershed were 63.2 and 18.6 mg/L, respectively. Meanwhile, the corresponding Ba and Sr concentrations were 274 and 45 µg/L, respectively. The predicted concentrations of Ca, Mg, and Ba in runoff agreed with the concentrations observed in stream water. The high Sr concentration in stream water could be attributed to a subsurface seepage discharging directly into streams in the watershed.

Assuming that most of the runoff water from the watershed flows into the reservoir, we used the predicted average annual element concentrations in the stream water to estimate annual loadings. The estimated annual loading was relatively high for Si (2,291 kg) and Cu (285 kg), whereas it ranged between 27 and 52 kg for Al, Fe, Ni, and Zn. The estimated annual loading was small (5.78 kg for Pb and 1.94 kg for Cd). For the alkaline earth elements, the estimated annual loading was about 273 Mg for calcium and 80 Mg for magnesium, whereas it was 695 kg for Ba and 193 kg for Sr. These values were slightly higher (about 4%) than those predicted for element losses by runoff from soils. This discrepancy could be attributed to the use of different methods of calculation.

We need to emphasize that the predicted element concentration was calculated for runoff water generated at field sites and not stream water. When we consider the factors (i.e., biological processes and chemical precipitations) affecting element concentrations in runoff after leaving field sites, the technique could provide a reasonable estimation of element concentrations in stream water. In this study, for example, chemical and biological factors resulted in the removal of 109.7, 98.3, and 53.2 Mg of Si, Al, and Fe, respectively, from the stream water in WT Watershed.

Finally, we concluded that the NRCS technique could be used as an exploratory technique to conduct quick evaluations and identify hot spots for large areas of agricultural land. Lengthy and site-specific studies could then focus on certain areas of high risk. With respect to essential nutrients such as Ca, Mg, Fe, Cu, and Zn, the technique could provide useful information for nutrient best management practices.

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Tables

Table 1.—Soil classification and selected properties for 12 major soils under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska

Soil (Map Unit)	Classification	Land Use	Clay	OC	CEC	pH-Water	Hydro-logic Group
			(%)	(%)	(<i>cmol/kg</i>)		
Wymore (WtB)	Fine, montmorillonitic, mesic Aquic Argiudolls	Cropland	37.3	2.14	25.9	5.56	D
		Grassland	32.9	2.44	25.7	5.9	D
Wymore (WtC2)	Fine, montmorillonitic, mesic Aquic Argiudolls	Cropland	37.9	2.23	26.5	5.7	D
		Grassland	35.6	3.46	28.2	5.8	D
Wymore (WtD3)	Fine, montmorillonitic, mesic Aquic Argiudolls	Cropland	41.2	2.16	29.3	5.85	D
		Grassland	34.2	2.78	28.9	6.4	D
Pawnee (PaC2)	Fine, montmorillonitic, mesic Aquic Argiudolls	Cropland	35.2	1.94	24.9	5.64	D
		Grassland	29.3	2.38	21.7	5.55	D
Pawnee (PaD2)	Fine, montmorillonitic, mesic Aquic Argiudolls	Cropland	34.9	1.85	24.5	5.79	D
		Grassland	34.7	2.39	25.5	6.1	D
Nodaway (No, Ns)	Fine-silty, mixed, nonacid, mesic Mollic Udifluvents	Cropland	29.4	2.08	24.4	6.58	B
		Grassland	30.1	2.97	26.4	6.25	B
Sharpsburg (ShC, ShD, ShD2)	Fine, montmorillonitic, mesic Typic Argiudolls	Cropland	39.7	1.94	27.6	5.7	B
		Grassland	37.4	2.05	27	6.15	B
Mayberry (MeC2, MeD2, MhC3)	Fine, montmorillonitic, mesic Aquic Argiudolls	Cropland	31.8	1.96	22.8	5.99	D
		Grassland	26.0	2.08	20.4	6.5	D
Colo (Co, Cp)	Fine-silty, mixed, mesic Cumulic Hapludolls	Cropland	32.1	2.13	25	6.3	C
		Grassland	29.0	2.95	26.1	6.1	C
Judson (JuC)	Fine-silty, mixed, mesic Cumulic Hapludolls	Cropland	32.0	2.26	24.8	6.05	B
		Grassland	30.5	3.06	24	6.0	B
Burchard (BpF, BrD, BrE)	Fine-loamy, mixed, mesic Typic Argiudolls	Cropland	29.8	1.89	21.7	5.96	B
		Grassland	30.1	2.99	23.1	7.0	B
Kennebec (Ke)	Fine-silty, mixed, mesic Cumulic Hapludolls	Cropland	27.6	1.94	20.7	5.95	B
		Grassland	24.7	2.09	19.5	6.1	B

Table 2.—Predicted annual loss of water by runoff[†] (m³/ha) and water present in the soil interaction zone (m³/ha) for 12 major soils under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska

Soil (Map Unit)	Area		Runoff [†]		Interaction Zone	
	Crop	Grass	Crop	Grass	Crop	Grass
	<i>(ha)</i>		<i>(m³/ha/yr)</i>		<i>(m³/ha/yr)</i>	
Wymore (WtB)	391	167	1,167	1,004	59.5	59.5
Wymore (WtC2)	1,270	544	1,167	1,004	59.5	59.5
Wymore (WtD3)	124	53	1,167	1,004	59.5	59.5
Pawnee (PaC2)	240	103	1,167	1,004	60.8	60.8
Pawnee (PaD2)	54	23	1,167	1,004	60.8	60.8
Nodaway (No, Ns)	142	61	901	638	38.4	38.4
Sharpsburg (ShC, ShD, ShD2)	124	53	901	638	57.6	57.6
Mayberry (MeC2, MeD2, MhC3)	110	47	1,167	1,004	51.2	51.2
Colo (Co, Cp)	107	46	1,084	876	64.0	64.0
Judson (JuC)	71	30	901	638	48.4	48.4
Burchard (BpF, BrD, BrE)	57	24	901	638	54.4	54.4
Kennebec (Ke)	31	13	901	638	44.8	44.8
Weighted Average			1,122	942	57.7	57.7
Total	2,719	1,165	3,050,750	1,097,609	156,976	67,275

[†] USDA-SCS (1991).

Table 3.—Average (AV) and standard deviation percentage (SD%) of water-soluble elements for 12 major soils (mg/kg or µg/kg) under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska

Soil Map Unit		Al		Fe		Si		Cd		Cu		Ni		Pb		Zn	
		Crop	Grass	Crop	Grass	Crop	Grass	Crop	Grass	Crop	Grass	Crop	Grass	Crop	Grass	Crop	Grass
		------(mg/kg)-----						------(µg/kg)-----									
WYMORE-WtB	AV	193.63	203.49	104.86	106.90	183.89	218.59	4.83	6.09	388.27	437.67	153.98	182.23	14.51	18.04	272.04	346.46
	SD%	68	65	67	63	67	76	27	25	13	9	40	31	63	82	76	84
WYMORE-WTC2	AV	269.52	77.34	147.10	40.98	235.39	97.09	5.03	4.87	423.53	396.89	201.63	119.89	11.54	8.63	383.12	134.43
	SD%	77	56	79	53	70	67	63	13	20	5	61	21	81	54	94	110
WYMORE-WTD3	AV	293.71	348.97	172.34	181.20	486.58	706.51	6.69	8.03	507.45	613.71	211.06	267.88	14.01	9.67	495.93	600.23
	SD%	34	57	36	57	66	78	41	17	33	35	33	43	72	52	37	42
PAWNEE-PaC2	AV	205.51	155.43	106.79	73.99	223.68	177.60	4.28	5.38	403.09	409.52	181.60	131.05	6.84	16.62	285.12	183.06
	SD%	90	79	93	77	88	88	31	25	6	9	51	34	37	79	88	111
PAWNEE-PaD2	AV	351.88	314.99	192.97	152.43	668.12	567.84	5.92	4.53	541.63	511.89	244.48	188.90	8.32	14.20	470.86	404.49
	SD%	37	45	44	40	67	73	56	51	33	44	43	37	43	76	48	56
NODAWAY	AV	127.91	188.64	72.78	103.61	236.72	231.13	4.32	6.25	474.85	463.95	135.41	212.19	13.10	18.46	215.05	416.50
	SD%	76	91	74	90	79	89	65	21	35	14	51	46	121	83	109	107
SHARPSBURG	AV	221.97	231.36	122.11	116.02	308.05	266.41	5.65	4.67	474.69	398.95	190.84	189.59	13.46	17.16	337.16	380.97
	SD%	64	60	63	55	70	65	32	70	24	22	33	36	101	80	55	52
MAYBERRY	AV	268.24	109.81	137.22	57.40	262.49	88.12	4.14	3.49	380.06	337.45	196.18	105.43	13.60	9.13	379.12	187.00
	SD%	53	64	55	64	60	39	62	61	32	16	48	28	81	49	70	49
COLO	AV	162.71	176.83	94.05	94.04	377.88	127.85	5.17	5.79	514.95	456.46	157.21	200.42	6.88	8.61	247.07	354.13
	SD%	77	26	79	25	89	21	29	9	29	2	39	7	29	32	74	23
JUDSON	AV	161.88	76.93	88.53	40.22	215.95	67.93	3.52	3.33	411.45	345.51	152.30	121.21	7.42	5.30	232.87	100.49
	SD%	53	24	53	23	72	5	36	52	28	12	34	9	48	0	65	77
BURCHARD	AV	304.53	14.48	165.41	8.53	531.79	25.78	5.31	2.98	519.65	340.31	225.26	70.59	10.93	5.30	420.17	8.55
	SD%	55	113	47	112	75	49	42	65	32	20	45	65	40	0	52	35
KENNEBEC	AV	199.95	101.71	109.87	54.89	487.31	223.17	5.23	2.93	584.42	446.73	175.58	99.70	7.35	10.42	356.90	173.85
	SD%	39	72	39	72	45	89	38	51	23	42	28	38	39	57	41	51
Weighted Average (crop and grass)		239.03	136.47	130.46	70.87	265.64	173.47	4.96	5.17	433.21	417.63	187.29	147.32	11.50	11.63	345.58	229.48

Table 4.—Predicted loss of 8 elements by runoff from 12 major soils (kg/ha/yr or g/ha/yr) under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska

Soil Map Unit	Al		Fe		Si		Cd		Cu		Ni		Pb		Zn	
	Crop	Grass	Crop	Grass	Crop	Grass	Crop	Grass	Crop	Grass	Crop	Grass	Crop	Grass	Crop	Grass
	------(kg/ha/yr)-----						------(g/ha/yr)-----									
WYMORE-WtB	23.59	24.59	12.77	12.92	22.40	26.41	0.59	0.74	47.29	52.89	18.75	22.02	1.77	2.18	33.13	41.86
WYMORE-WTC2	32.82	9.35	17.92	4.95	28.67	11.73	0.61	0.59	51.58	47.96	24.56	14.49	1.40	1.04	46.66	16.24
WYMORE-WTD3	35.77	42.17	20.99	21.90	59.26	85.37	0.82	0.97	61.80	74.16	25.70	32.37	1.71	1.17	60.40	72.53
PAWNEE-PaC2	25.00	18.76	12.99	8.93	27.21	21.43	0.52	0.65	49.04	49.43	22.09	15.82	0.83	2.01	34.69	22.09
PAWNEE-PaD2	42.81	38.02	23.48	18.40	81.28	68.53	0.72	0.55	65.90	61.78	29.74	22.80	1.01	1.71	57.29	48.82
NODAWAY	15.70	22.78	8.93	12.51	29.06	27.90	0.53	0.75	58.30	56.01	16.62	25.62	1.61	2.23	26.40	50.29
SHARPSBURG	26.70	27.16	14.69	13.62	37.06	31.28	0.68	0.55	57.11	46.84	22.96	22.26	1.62	2.01	40.56	44.73
MAYBERRY	32.89	13.37	16.83	6.99	32.19	10.73	0.51	0.43	46.60	41.10	24.06	12.84	1.67	1.11	46.49	22.77
COLO	19.67	21.09	11.37	11.22	45.67	15.25	0.63	0.69	62.24	54.45	19.00	23.91	0.83	1.03	29.86	42.24
JUDSON	19.67	9.15	10.75	4.79	26.23	8.08	0.43	0.40	49.98	41.11	18.50	14.42	0.90	0.63	28.29	11.96
BURCHARD	36.76	1.71	19.97	1.01	64.19	3.04	0.64	0.35	62.73	40.14	27.19	8.33	1.32	0.63	50.72	1.01
KENNEBEC	24.38	12.16	13.40	6.56	59.42	26.69	0.64	0.35	71.26	53.43	21.41	11.92	0.90	1.25	43.52	20.79
Weighted Average (crop and grass)	29.10	16.44	15.89	8.54	32.33	20.91	0.60	0.62	52.74	50.35	22.80	17.75	1.40	1.40	42.08	27.63
Weighted Average (watershed)	25.30		13.68		28.90		0.61		52.02		21.29		1.40		37.74	

Table 5.—Predicted average monthly element loading by runoff water (kg) in Wagon Train Reservoir

Month	Predicted Runoff Water <i>(m³)</i>	Loading by Runoff							
		Al	Fe	Si	Cd	Cu	Ni	Pb	Zn
		----- <i>(kg)</i> -----							
January	91,704	1.02	0.79	48.69	0.04	6.06	0.58	0.12	1.09
February	108,241	1.20	0.93	57.48	0.05	7.15	0.68	0.15	1.29
March	327,729	3.65	2.82	174.02	0.15	21.66	2.07	0.44	3.91
April	446,493	4.97	3.84	237.09	0.20	29.51	2.82	0.60	5.33
May	583,297	6.49	5.02	309.73	0.26	38.56	3.68	0.78	6.96
June	602,841	6.71	5.19	320.11	0.27	39.85	3.80	0.81	7.20
July	461,526	5.14	3.97	245.07	0.21	30.51	2.91	0.62	5.51
August	524,667	5.84	4.52	278.60	0.24	34.68	3.31	0.70	6.26
September	508,130	5.66	4.37	269.82	0.23	33.59	3.21	0.68	6.07
October	323,219	3.60	2.78	171.63	0.15	21.36	2.04	0.43	3.86
November	205,958	2.29	1.77	109.36	0.09	13.61	1.30	0.28	2.46
December	135,301	1.51	1.16	71.84	0.06	8.94	0.85	0.18	1.62
Year	4,314,713	48.02	37.15	2291.11	1.94	285.20	27.23	5.78	51.52

Table 6.—Average (AV) and standard deviation (SD) of dissolved calcium, magnesium, barium, and strontium in the water phase for 12 major soils (mg/kg or µg/kg) under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska

Soil Map Unit		Calcium		Magnesium		Barium		Strontium	
		Cropland	Grassland	Cropland	Grassland	Cropland	Grassland	Cropland	Grassland
		----- (mg/kg) -----				----- (µg/kg) -----			
WYMORE-WtB	AV	70.62	48.93	37.06	30.18	1508.14	1325.74	248.79	326.78
	SD	60.75	6.09	14.85	14.70	771.64	475.39	151.84	69.50
WYMORE-WTC2	AV	84.26	61.38	47.56	21.15	1748.33	873.60	478.97	375.90
	SD	66.66	9.50	20.17	2.36	968.41	276.03	262.24	4.00
WYMORE-WTD3	AV	50.16	90.72	41.77	54.21	1881.71	2147.13	358.33	655.11
	SD	27.53	4.21	12.13	19.15	626.40	713.46	123.16	119.27
PAWNEE-PaC2	AV	49.96	33.08	31.93	22.71	1234.96	935.71	329.92	229.76
	SD	19.16	2.02	18.46	9.93	771.85	520.82	163.34	15.41
PAWNEE-PaD2	AV	50.84	69.75	43.50	45.04	1564.70	1606.08	332.83	500.62
	SD	17.13	26.39	13.77	16.16	588.05	729.33	76.48	229.63
NODAWAY	AV	67.00	73.67	27.17	36.49	944.75	1615.56	369.45	493.53
	SD	32.02	14.26	15.05	10.92	667.10	882.68	173.55	52.24
SHARPSBURG	AV	80.72	61.48	44.48	39.81	1781.71	1560.00	316.74	445.59
	SD	71.59	14.27	12.68	16.33	743.27	1032.44	172.65	163.73
MAYBERRY	AV	59.43	65.79	37.59	20.62	1308.31	729.77	327.16	269.13
	SD	26.90	5.19	16.41	7.04	815.83	256.56	140.49	36.19
COLO	AV	93.75	112.69	37.10	43.40	1162.04	1458.42	526.72	542.29
	SD	58.38	4.18	13.02	3.67	515.83	294.69	294.60	21.16
JUDSON	AV	54.62	47.37	27.72	18.54	940.16	706.59	327.40	290.62
	SD	16.19	14.03	11.09	2.67	350.10	48.60	100.91	65.48
BURCHARD	AV	51.77	160.98	39.13	16.07	1465.58	514.40	329.04	376.21
	SD	15.97	65.79	20.06	10.60	726.07	303.86	177.07	179.75
KENNEBEC	AV	41.71	50.10	27.93	17.23	999.94	742.45	279.53	260.11
	SD	11.69	20.55	8.77	6.46	368.62	283.57	85.74	39.88

Table 7.—Average (AV) and standard deviation (SD) of calcium and magnesium in the exchangeable phase for 12 major soils (mg/kg) under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska

Soil Map Unit		Calcium		Magnesium	
		Cropland	Grassland	Cropland	Grassland
		------(mg/kg)-----			
WYMORE-WtB	AV	2949.2	3146.3	607.8	577.4
	SD	386.0	255.1	101.4	43.0
WYMORE-WTC2	AV	3253.2	3466.9	705.0	571.3
	SD	297.2	340.1	171.7	68.8
WYMORE-WTD3	AV	3483.6	3917.8	729.4	680.7
	SD	655.0	496.0	68.8	189.1
PAWNEE-PaC2	AV	3092.8	2264.5	666.6	498.4
	SD	481.9	510.1	134.4	137.5
PAWNEE-PaD2	AV	2989.3	3026.0	672.6	638.2
	SD	472.4	453.5	213.8	60.2
NODAWAY	AV	3583.8	3507.0	573.4	620.0
	SD	1106.2	170.0	257.8	103.1
SHARPSBURG	AV	3219.8	3296.6	747.6	741.5
	SD	394.9	297.6	118.0	137.5
MAYBERRY	AV	3022.7	2955.9	534.9	358.6
	SD	500.7	552.6	109.5	8.6
COLO	AV	3543.7	3426.8	603.7	601.7
	SD	663.1	56.7	122.2	43.0
JUDSON	AV	3243.1	2845.7	530.8	461.9
	SD	441.9	255.1	110.3	120.3
BURCHARD	AV	2635.3	6172.3	478.1	395.1
	SD	699.6	3004.1	308.5	386.8
KENNEBEC	AV	2628.6	2525.0	455.9	443.7
	SD	302.4	1020.3	120.5	266.5

Table 8.—Predicted annual loss of calcium[†], magnesium[‡], barium[§], and strontium[§] (kg/ha/yr or g/ha/yr) by runoff for 12 major soils under crop and grass cover in Wagon Train Watershed, Lancaster County, Nebraska

Soil Map Unit	Calcium [†]		Magnesium [‡]		Barium [§]		Strontium [§]	
	Cropland	Grassland	Cropland	Grassland	Cropland	Grassland	Cropland	Grassland
	------(kg/ha/yr)-----				------(g/ha/yr)-----			
WYMORE-WTC2	69.69	70.26	22.97	16.36	212.93	105.56	58.33	45.42
WYMORE-WTD3	69.75	81.98	22.85	23.00	229.17	259.45	43.64	79.16
PAWNEE-PaC2	62.52	44.99	20.10	14.77	150.25	112.93	40.14	27.73
PAWNEE-PaD2	60.74	63.20	21.66	20.84	190.36	193.84	40.49	60.42
NODAWAY	74.22	72.41	17.41	19.37	115.98	195.05	45.36	59.59
SHARPSBURG	67.82	65.27	23.34	22.09	214.36	183.15	45.73	52.31
MAYBERRY	62.88	62.01	17.73	11.25	160.43	88.88	40.12	32.78
COLO	75.58	74.76	19.08	19.53	140.45	173.97	63.66	64.69
JUDSON	65.73	56.42	16.26	13.20	114.21	84.07	39.77	34.58
BURCHARD	53.96	128.18	16.27	11.21	176.91	60.67	39.72	44.37
KENNEBEC	53.16	51.29	14.52	12.67	121.93	88.8	34.09	31.11

[†] Prediction used calcium ions present in both water phase and 15% of exchange phase in soils.

[‡] Prediction used magnesium ions present in both water phase and 20% of exchange phase in soils.

[§] Prediction used barium or strontium ions present in water phase in soils.

**Table 9.—Predicted average monthly element loading
by runoff water (kg) into Wagon Train Reservoir,
Lancaster County, Nebraska**

Month	Calcium	Magnesium	Barium	Strontium
	------(kg)-----			
January	5,796	1,706	15	4
February	6,841	2,013	17	5
March	20,712	6,096	53	15
April	28,218	8,305	72	20
May	36,864	10,849	94	26
June	38,100	11,213	97	27
July	29,168	8,584	74	21
August	33,159	9,759	84	24
September	32,114	9,451	82	23
October	20,427	6,012	52	14
November	13,017	3,831	33	9
December	8,551	2,517	22	6
Year	272,690	80,254	695	193

Figures

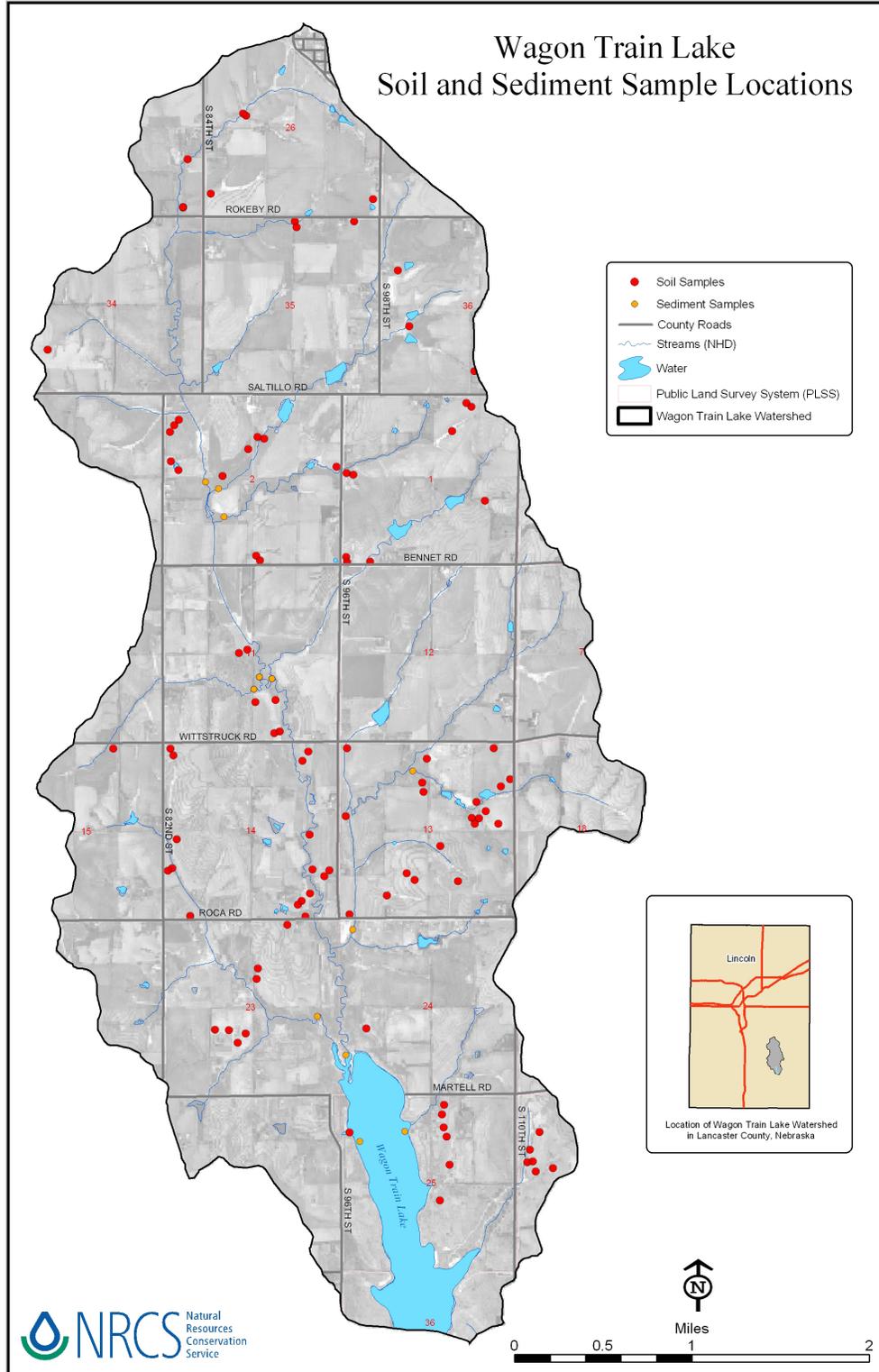


Figure 1.—Soil and water sampling locations in Wagon Train Watershed, Lancaster County, Nebraska.

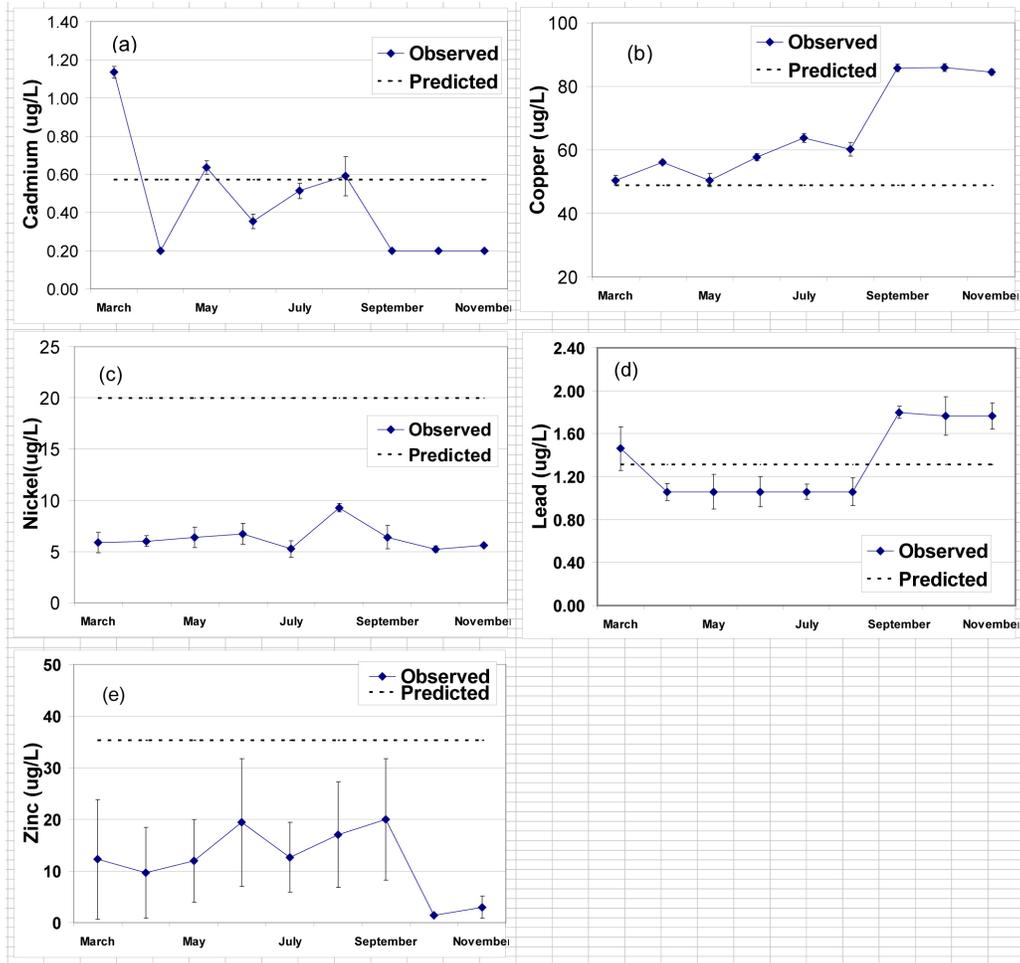


Figure 2.—Predicted amounts in runoff and observed monthly average concentration in stream water ($\mu\text{g/L}$) in Wagon Train Watershed for: (a) Cd, (b) Cu, (c) Ni, (d) Pb, and (e) Zn.

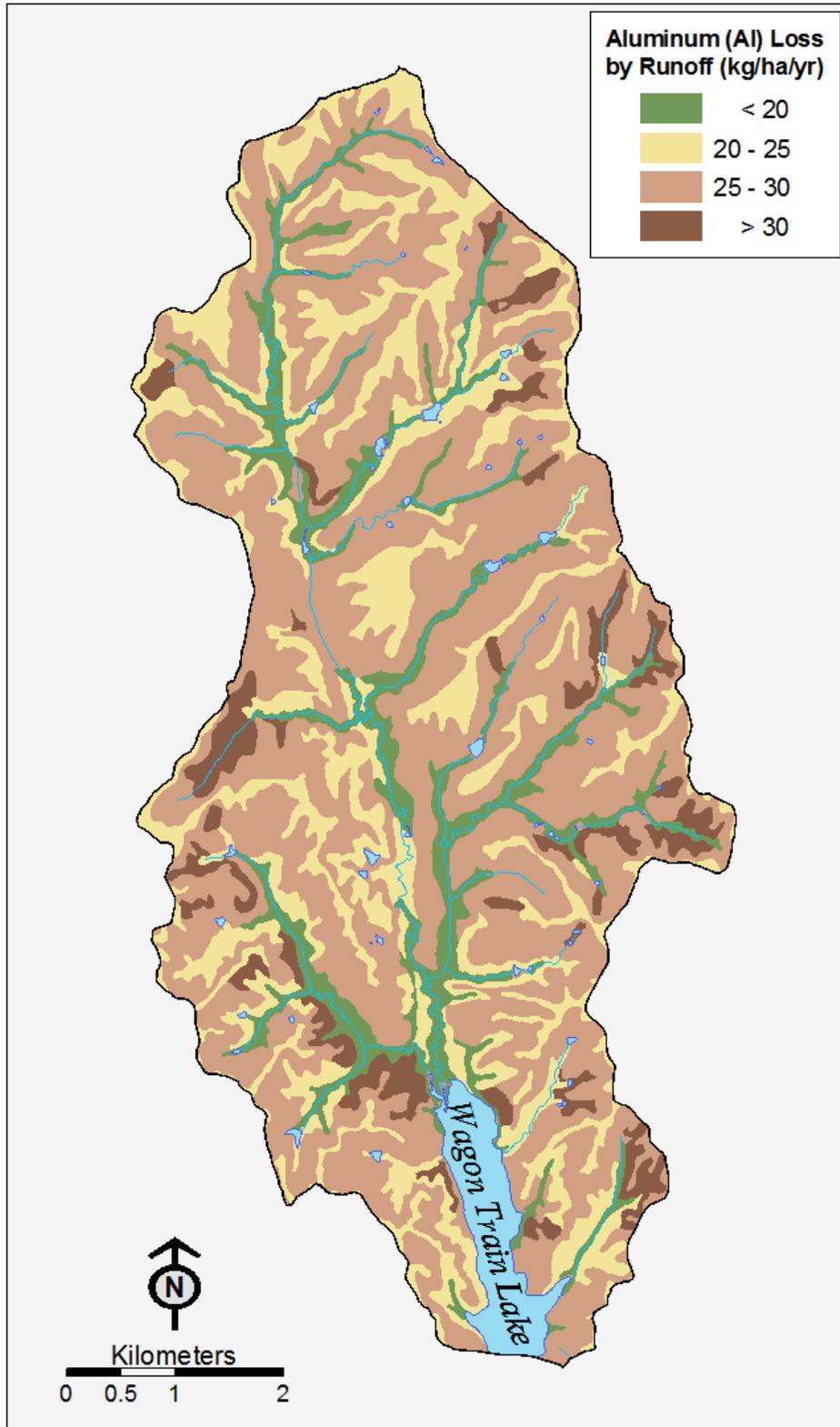


Figure 3.—Aluminum loss by runoff from soils (kg/ha/yr) in Wagon Train Watershed.

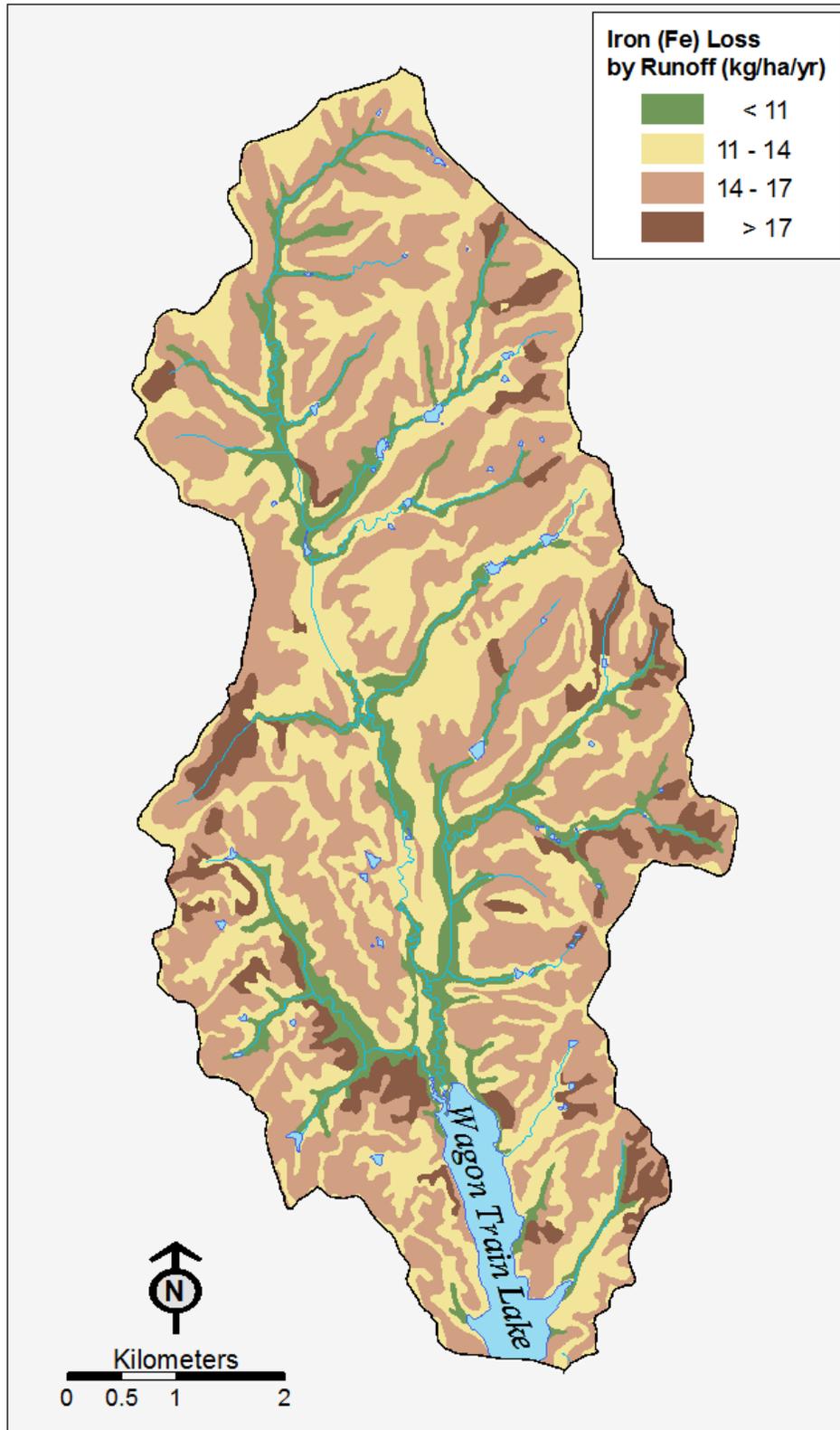


Figure 4.—Iron loss by runoff from soils (kg/ha/yr) in Wagon Train Watershed.

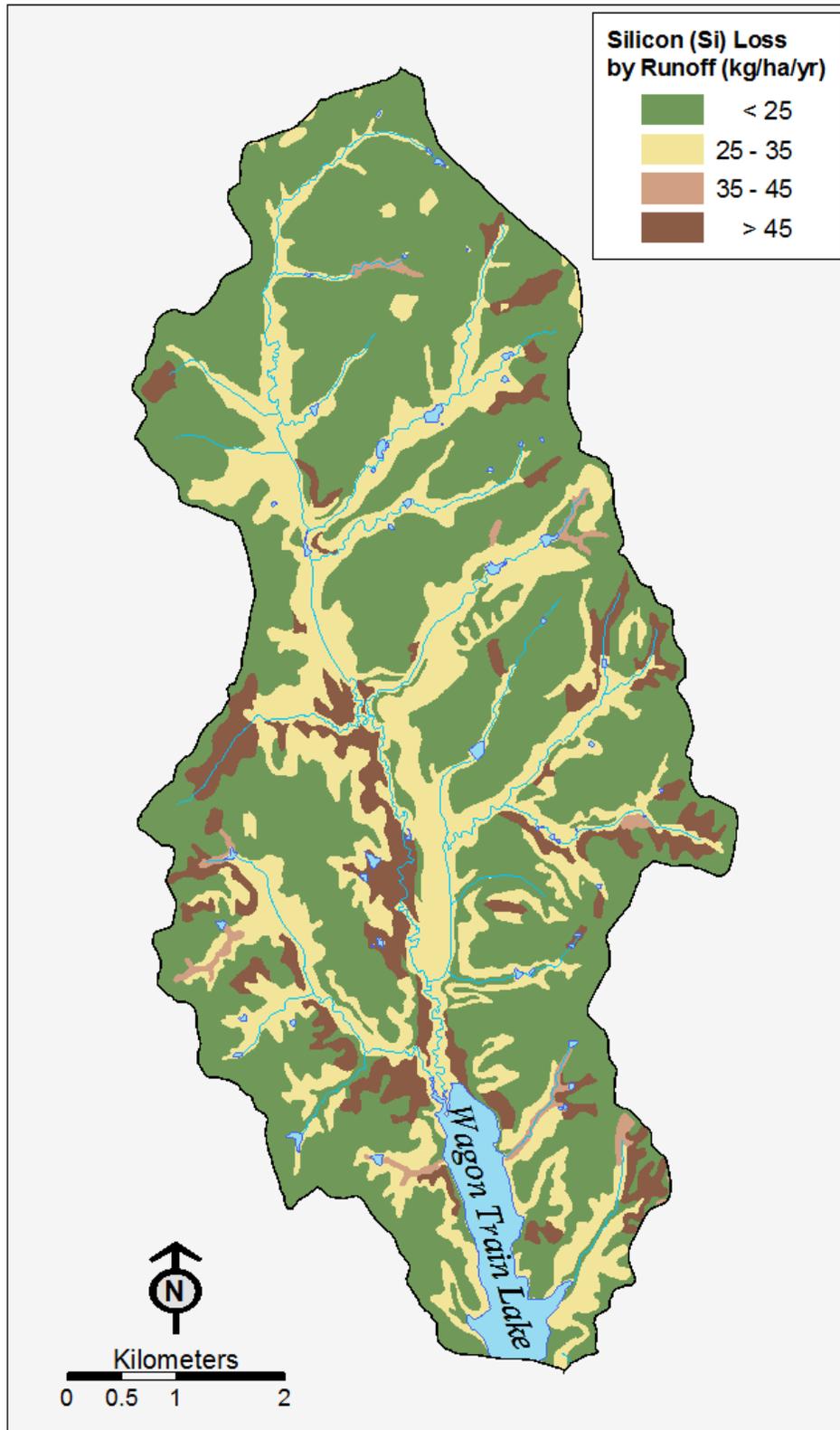


Figure 5.—Silicon loss by runoff from soils (kg/ha/yr) in Wagon Train Watershed.

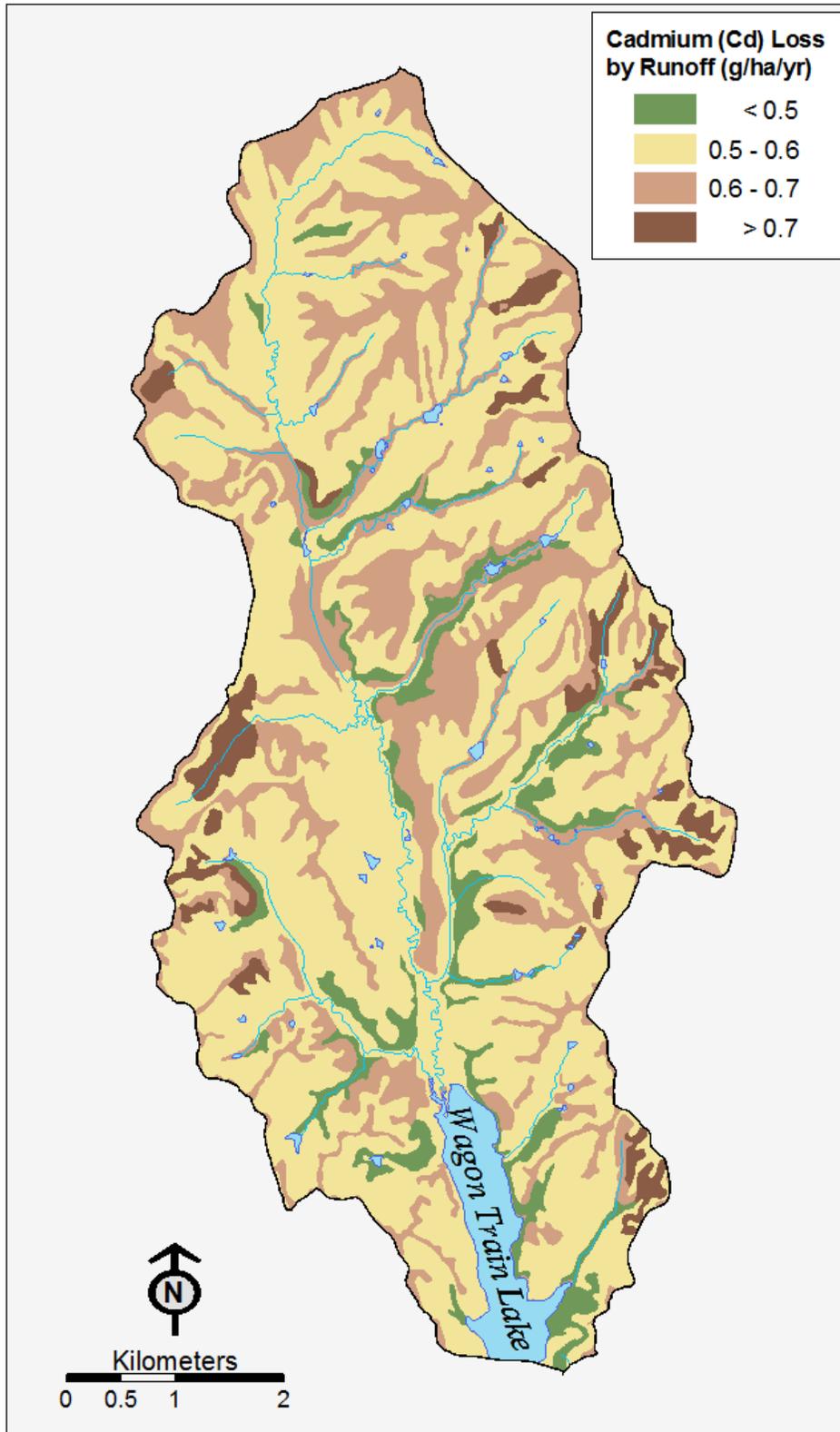


Figure 6.—Cadmium loss by runoff from soils (g/ha/yr) in Wagon Train Watershed.

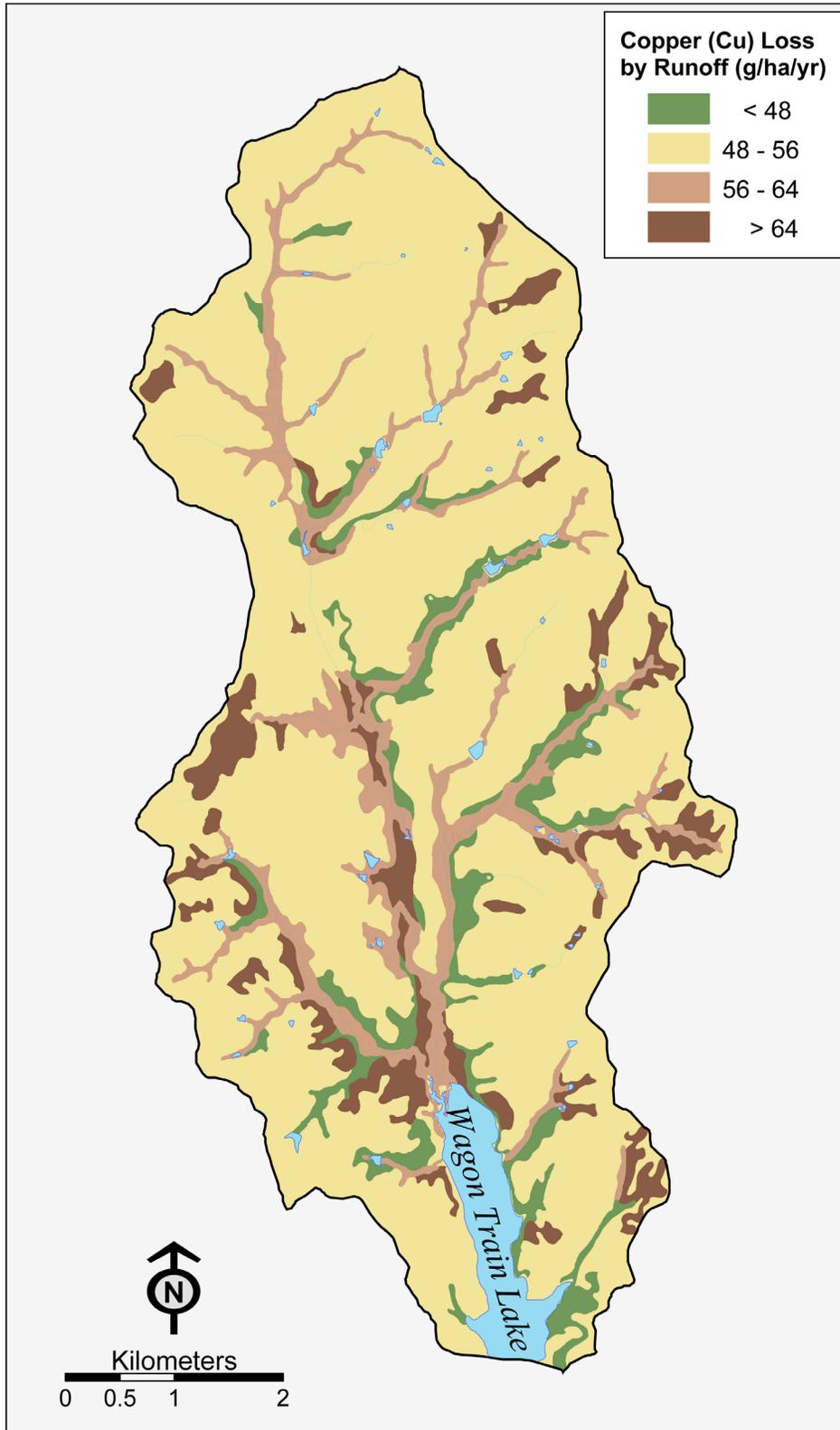


Figure 7.—Copper loss by runoff from soils (g/ha/yr) in Wagon Train Watershed.

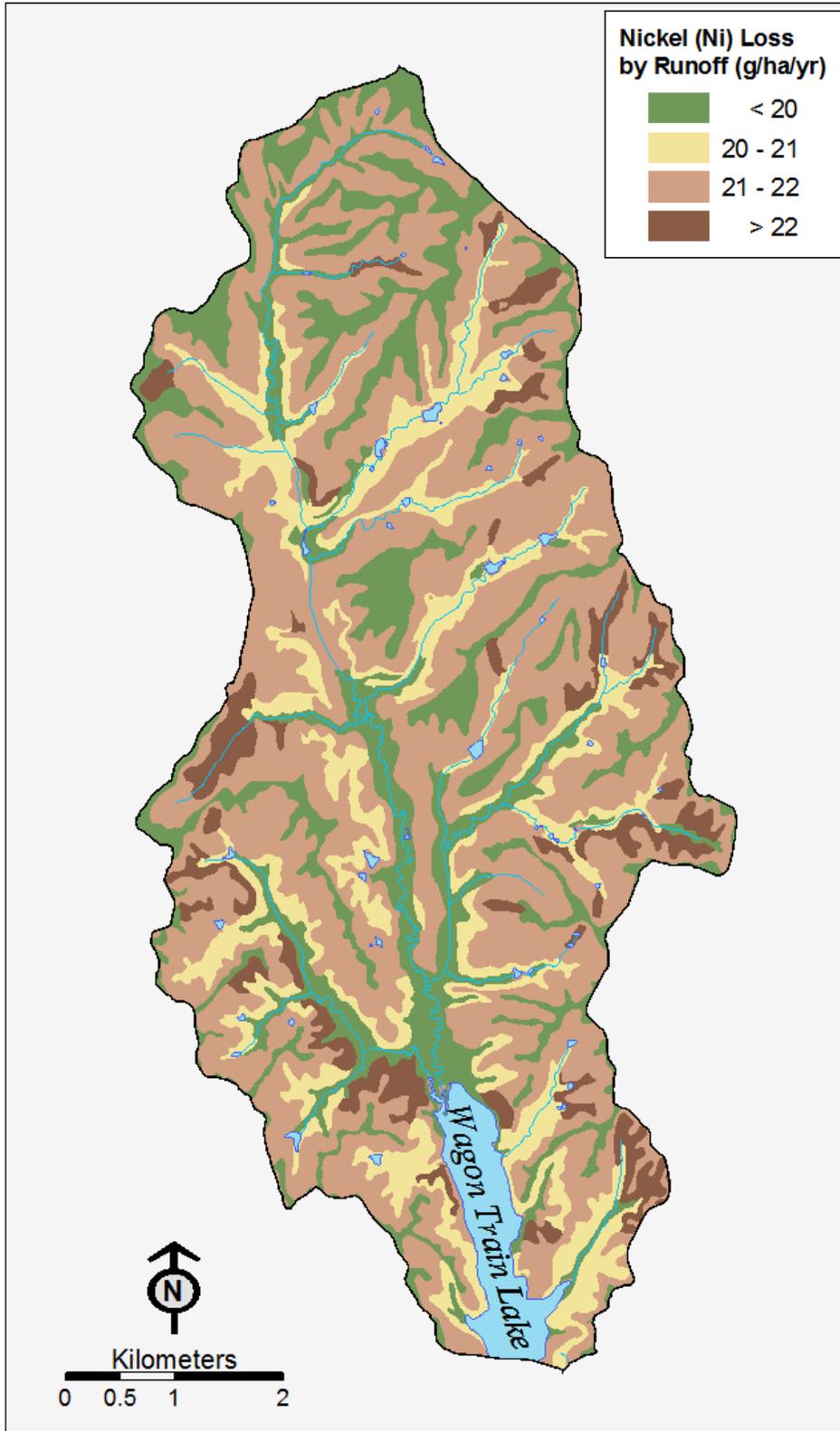


Figure 8.—Nickel loss by runoff from soils (g/ha/yr) in Wagon Train Watershed.

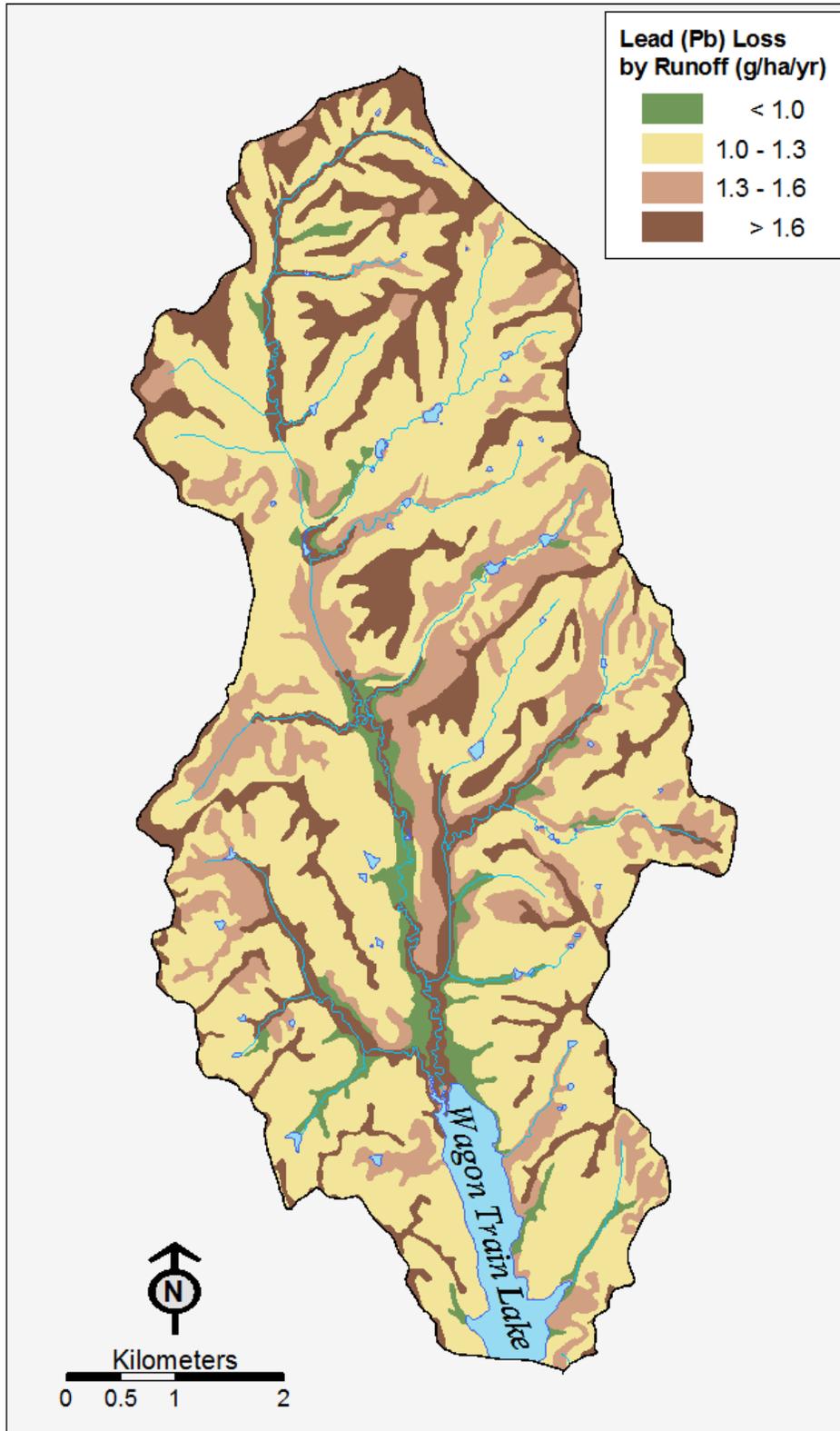


Figure 9.—Lead loss by runoff from soils (g/ha/yr) in Wagon Train Watershed.

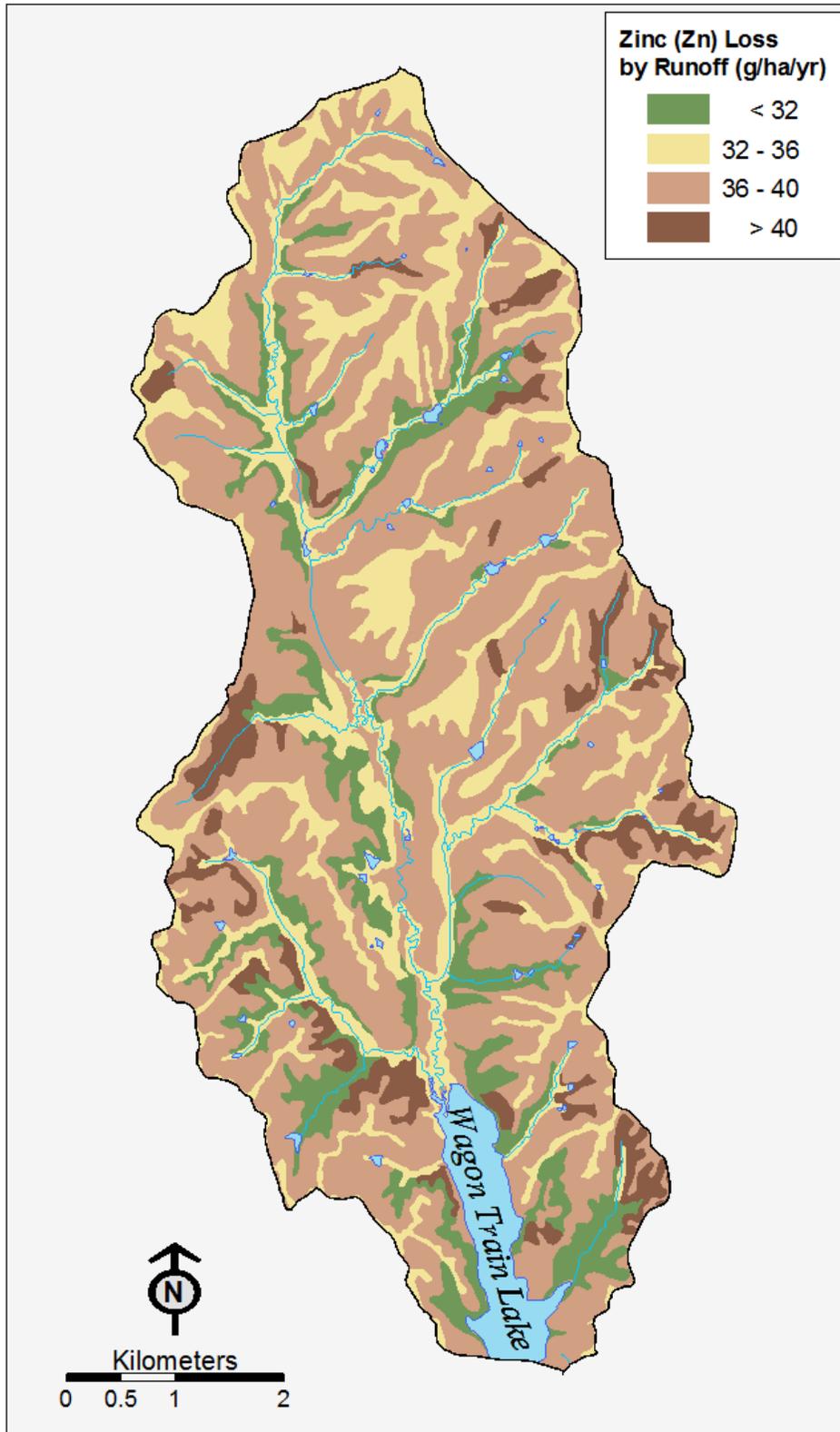


Figure 10.—Zinc loss by runoff from soils (g/ha/yr) in Wagon Train Watershed.

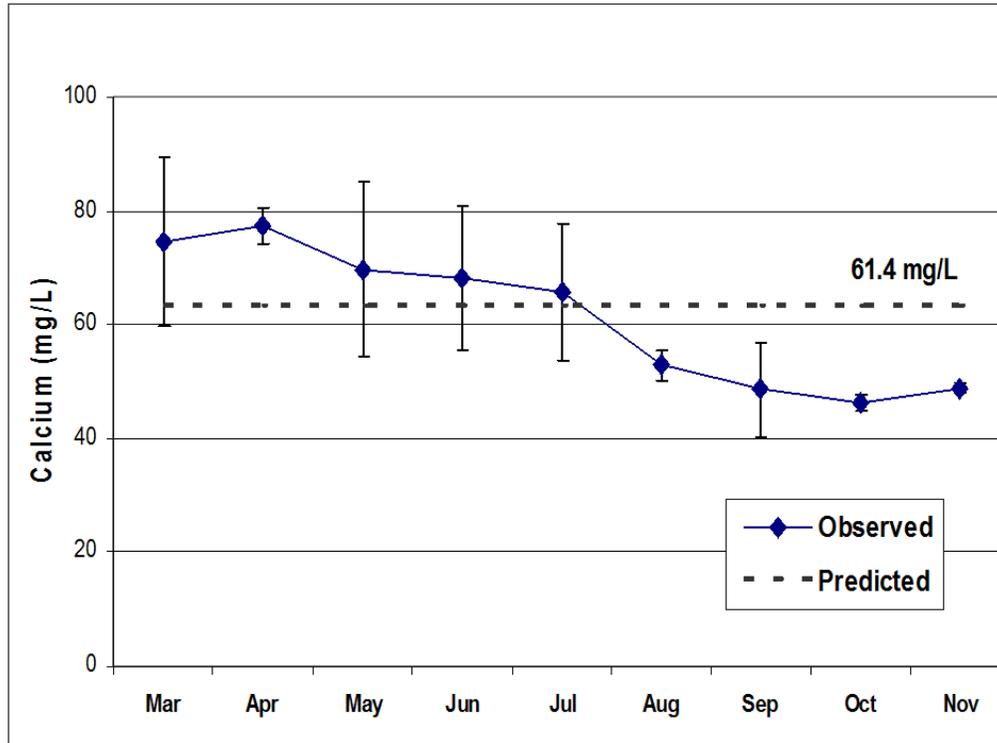


Figure 11.—Predicted calcium in runoff and observed concentration (mg/L) in stream water for Wagon Train Watershed.

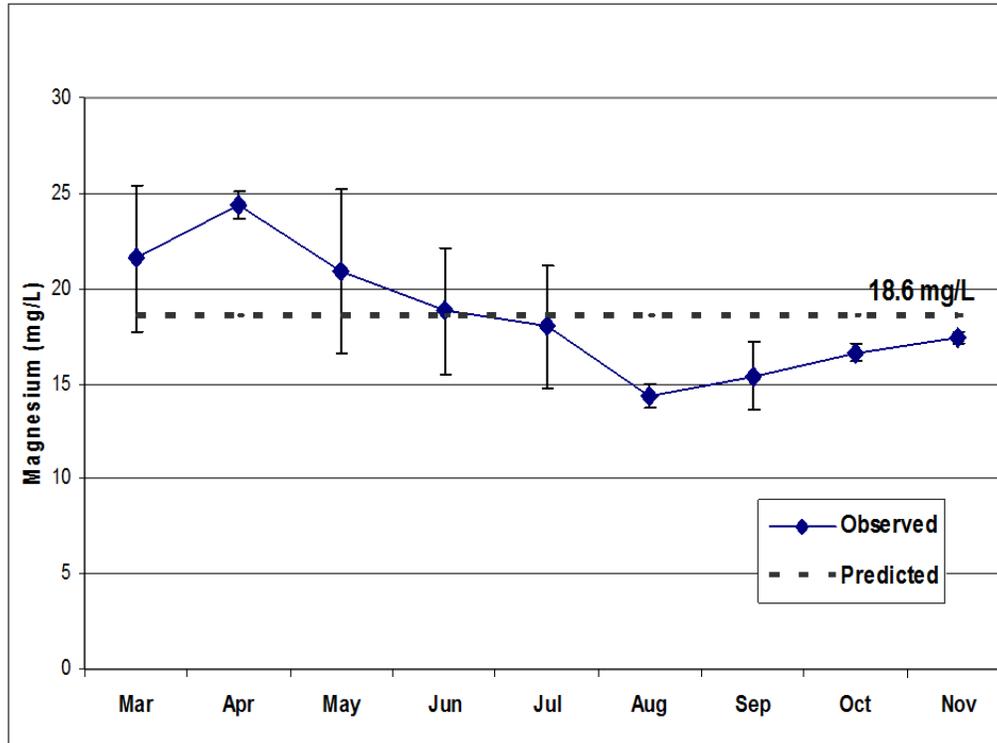


Figure 12.—Predicted magnesium in runoff and observed concentration (mg/L) in stream water for Wagon Train Watershed.

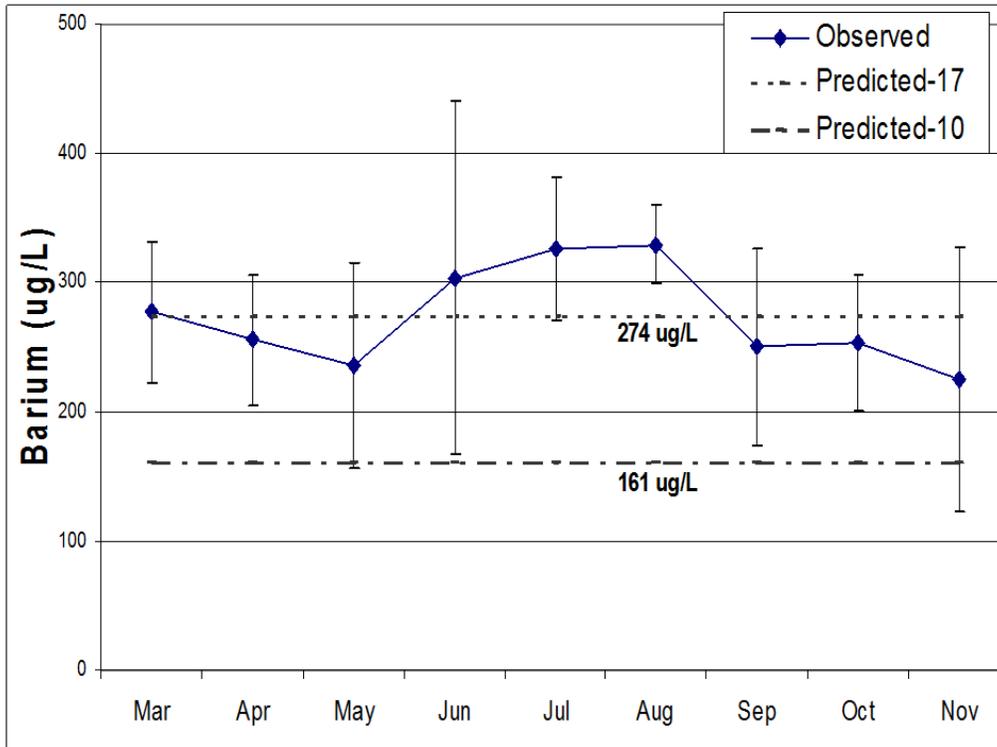


Figure 13.—Predicted barium in runoff from 10- and 17-mm soil depths and observed concentration ($\mu\text{g/L}$) in stream water for Wagon Train Watershed.

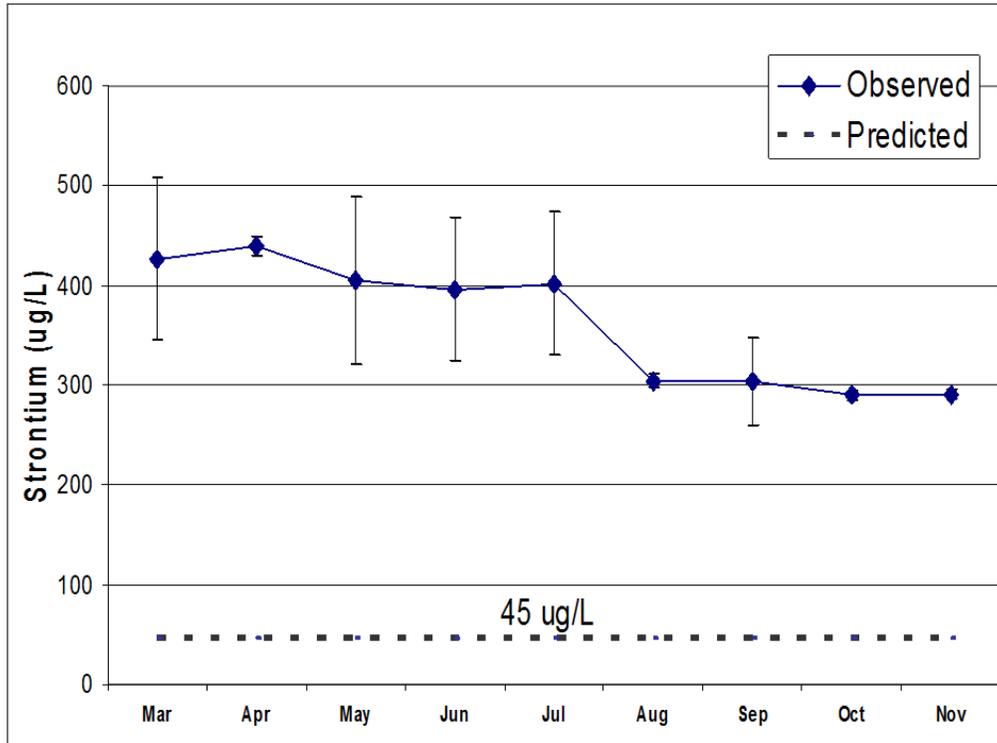


Figure 14.—Predicted strontium in runoff and observed concentration ($\mu\text{g/L}$) in stream water for Wagon Train Watershed.

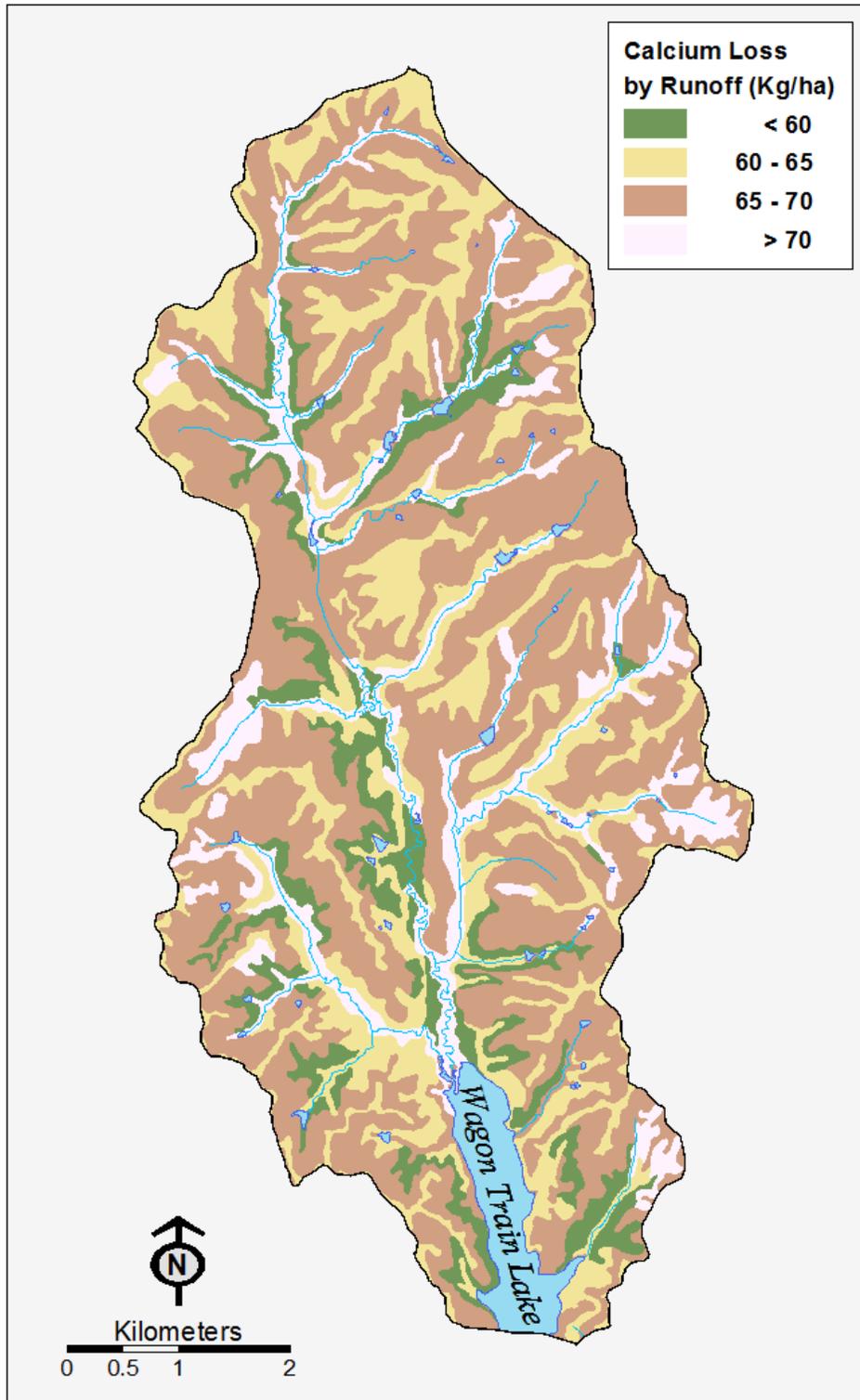


Figure 15.—Calcium loss by runoff from soils (kg/ha) in Wagon Train Watershed.

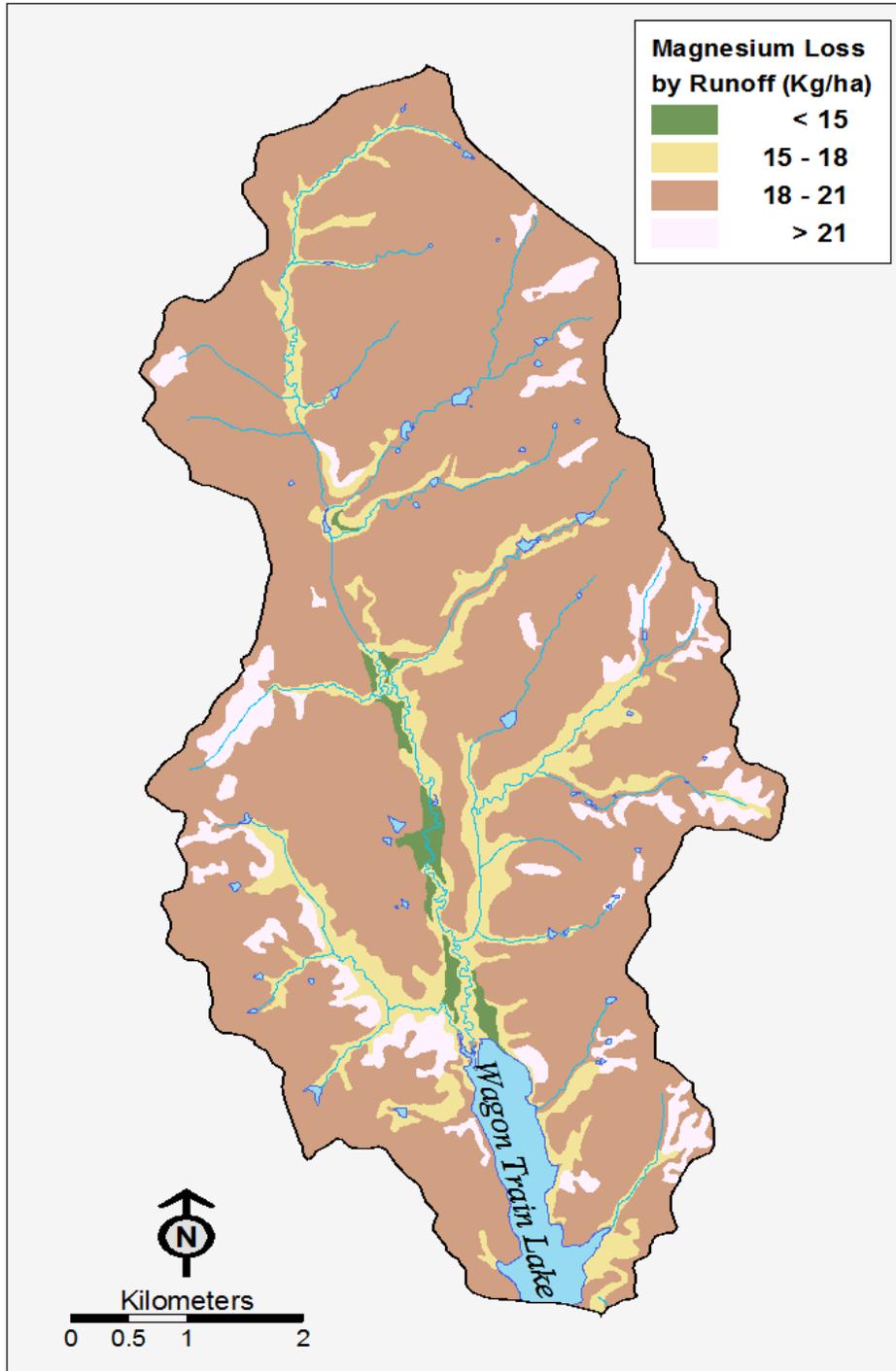


Figure 16.—Magnesium loss by runoff from soils (kg/ha) in Wagon Train Watershed.

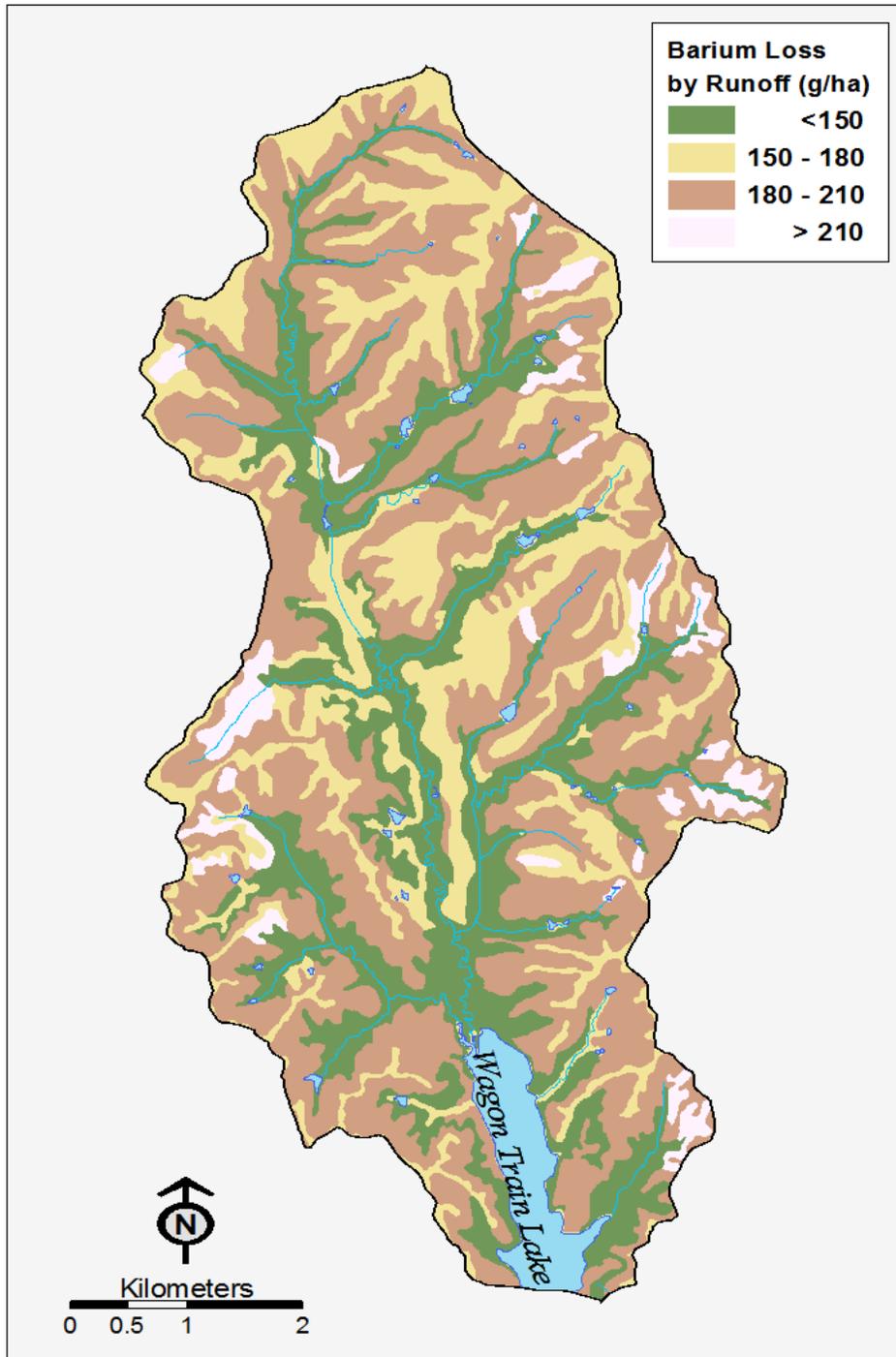


Figure 17.—Barium loss by runoff from soils (g/ha) in Wagon Train Watershed.

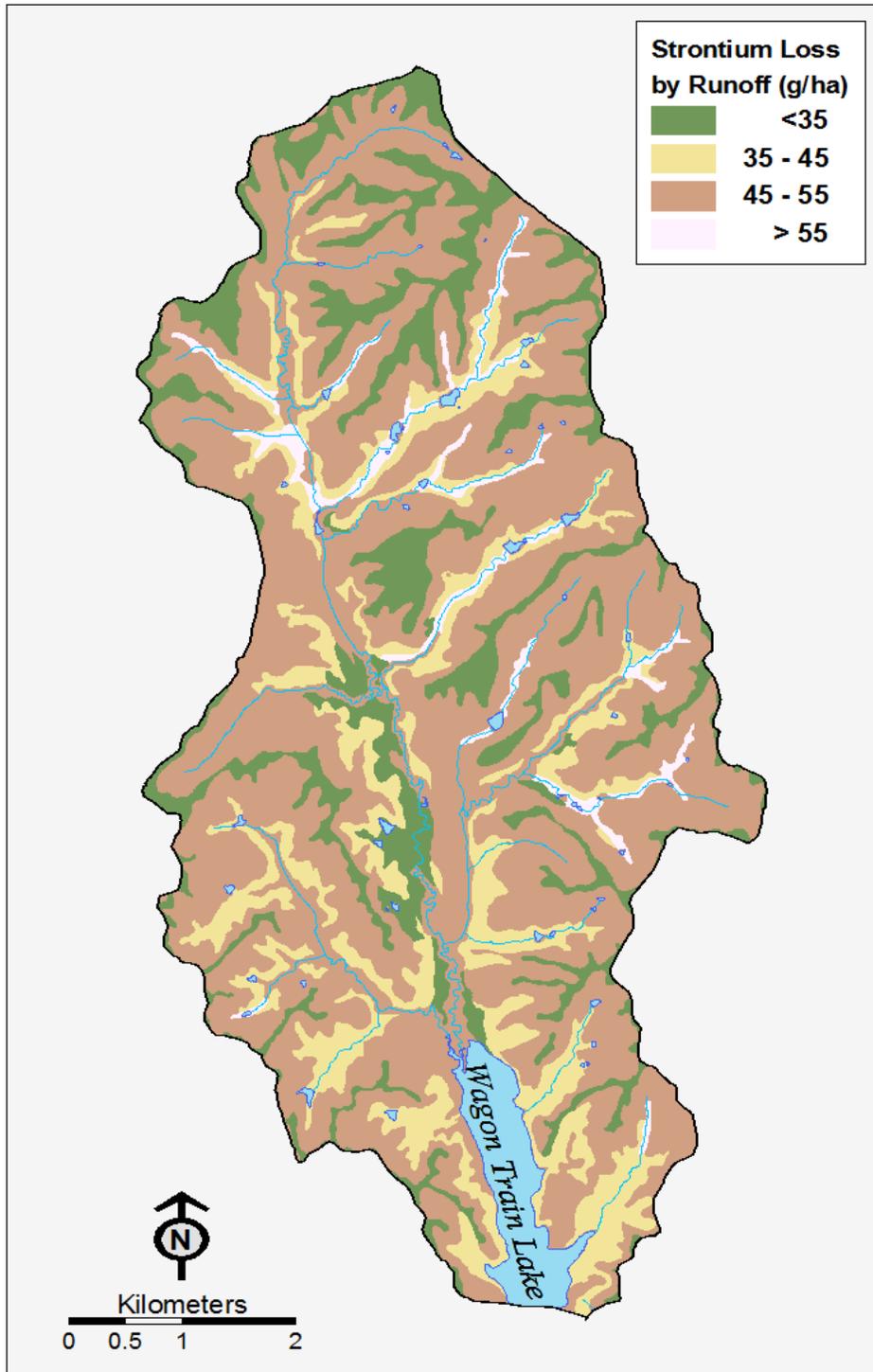


Figure 18.—Strontium loss by runoff from soils (g/ha) in Wagon Train Watershed.