

Prepared in cooperation with the Metro Wastewater Reclamation District

Preliminary Assessment of Sources of Nitrogen in Groundwater at a Biosolids-Application Area near Deer Trail, Colorado, 2005



Scientific Investigations Report 2012–5056

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By Tracy J.B. Yager and Peter B. McMahon

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Conversion Factors

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in)
kilometer (km)	0.6214	mile (mi)
meter (m)	3.281	foot (ft)
micron (μm)	0.000039	inch (in)
Area		
square kilometer (km^2)	0.3861	square mile (mi^2)
Volume		
cubic centimeter (cm^3)	0.06102	cubic inch (in^3)
liter (L)	0.2642	gallon (gal)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

Temperature in degrees Celsius ($^{\circ}\text{C}$) may be converted to degrees Fahrenheit ($^{\circ}\text{F}$) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25°C).

Concentrations of chemical constituents in liquids are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

Concentrations of chemical constituents in solid materials are given either in milligrams per kilogram (mg/kg) or micrograms per gram ($\mu\text{g}/\text{g}$).

Isotopic composition data are provided in delta (δ) notation in units of per mil (parts per thousand or 0/00).

Preliminary Assessment of Sources of Nitrogen in Groundwater at a Biosolids-Application Area near Deer Trail, Colorado, 2005

By Tracy J.B. Yager and Peter B. McMahon

Abstract

Concentrations of dissolved nitrite plus nitrate increased fairly steadily in samples from four shallow groundwater monitoring wells after biosolids applications to nonirrigated farmland began in 1993. The U.S. Geological Survey began a preliminary assessment of sources of nitrogen in shallow groundwater at part of the biosolids-application area near Deer Trail, Colorado, in 2005 in cooperation with the Metro Wastewater Reclamation District. Possible nitrogen sources in the area include biosolids, animal manure, inorganic fertilizer, atmospheric deposition, and geologic materials (bedrock and soil). Biosolids from the Metro Wastewater Reclamation District plant in Denver and biosolids, cow manure, geologic materials (bedrock and soil), and groundwater from the study area were sampled to measure nitrogen content and nitrogen isotopic compositions of nitrate or total nitrogen. Biosolids also were leached, and the leachates were analyzed for nitrogen content and other concentrations. Geologic materials from the study area also were sampled to determine mineralogy. Estimates of nitrogen contributed from inorganic fertilizer and atmospheric deposition were calculated from other published reports.

The nitrogen information from the study indicates that each of the sources contain sufficient nitrogen to potentially affect groundwater nitrate concentrations. Natural processes can transform the nitrogen in any of the sources to nitrate in the groundwater. Load calculations indicate that animal manure, inorganic fertilizer, or atmospheric deposition could have contributed the largest nitrogen load to the study area in the 13 years before biosolids applications began, but biosolids likely contributed the largest nitrogen load to the study area in the 13 years after biosolids applications began.

Various approaches provided insights into sources of nitrate in the groundwater samples from 2005. The isotopic data indicate that, of the source materials considered, biosolids and (or) animal manure were the most likely sources of nitrate in the wells at the time of sampling (2005), and that inorganic fertilizer, atmospheric deposition, and geologic materials were not substantial sources of nitrate in the wells in 2005. The

large total nitrogen content of the biosolids and animal-manure samples and biosolids leachates also indicates that the biosolids and animal manure had potential to leach nitrogen and produce large dissolved nitrate concentrations in groundwater. The available data, however, could not be used to distinguish between biosolids or manure as the dominant source of nitrate in the groundwater because the nitrogen isotopic composition of the two materials is similar. Major-ion data also could not be used to distinguish between biosolids or manure as the dominant source of nitrate in the groundwater because the major-ion composition (as well as the isotopic composition) of the two materials is similar. Without additional data, chloride/bromide mass ratios do not necessarily support or refute the hypothesis that biosolids and (or) animal manure were the primary sources of nitrate in water from the study-area wells in 2005. Concentrations of water-extractable nitrate in the soil indicate that biosolids could be an important source of nitrate in the groundwater recharge. Nitrogen inventories in the soil beneath biosolids-application areas and the nitrogen-input estimates for the study area both support the comparisons of isotopic composition, which indicate that some type of human waste (such as biosolids) and (or) animal manure was the source of nitrate in groundwater sampled from the wells in 2005. The nitrogen-load estimates considered with the nitrogen isotopic data and the soil-nitrogen inventories indicate that biosolids applications likely are a major source of nitrogen to the shallow groundwater at these monitoring wells.

Introduction

The Metro Wastewater Reclamation District (Metro District) applied biosolids from their wastewater treatment process in Denver, Colo., to their agricultural land near Deer Trail, Colo. (fig. 1). The wastewater treatment processes that produced the biosolids included an industrial-waste pretreatment program, trash and grit screening, primary clarification, aeration, secondary clarification, solids concentration, solids blending, anaerobic digestion, and centrifugation (<http://www.metrowastewater.com/>, accessed August 9, 2011).

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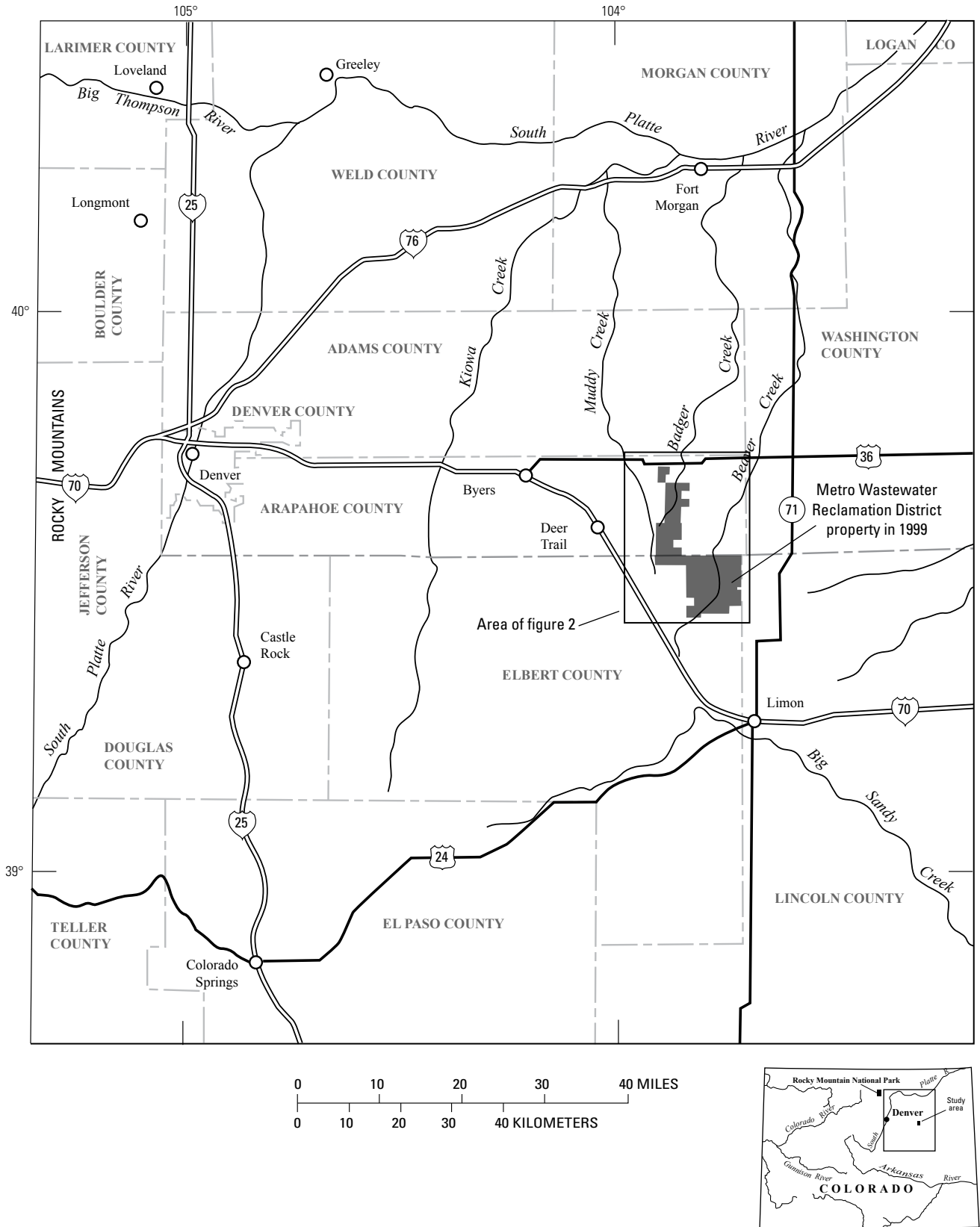


Figure 1. Location of the nitrogen source study near Deer Trail, Colorado.

Biosolids applications to the area have been permitted by the State of Colorado (Colorado Department of Public Health and Environment, 2003) and documented by the wastewater treatment plant. The biosolids were applied intermittently as a fertilizer and soil amendment at agronomic loading rates to the Metro District properties beginning in late 1993.

Groundwater-quality monitoring by the U.S. Geological Survey (USGS) at the Metro District properties near Deer Trail (fig. 2) indicated that concentrations of dissolved nitrate in water from some shallow wells increased after monitoring began in 1993 (Yager and others, 2004, 2009; unpub. data on file at U.S. Geological Survey Colorado Water Science Center, 2011). The increase in nitrate concentration in samples from one well in particular, well D6, was of interest to the Metro District because (1) the well was located near a property boundary (fig. 2), (2) measured nitrate concentrations were largest at this location, and (3) nitrate concentration increased from about 5 milligrams per liter as nitrogen (mg-N/L) in 1993 before biosolids were applied to about 40 mg-N/L in 2007 (fig. 3). Nitrate concentrations also increased in water from three other shallow monitoring wells in the drainage area upgradient from well D6, although to a lesser extent. The gradual increase in nitrate concentration in water from well D6 during a period of intermittent biosolids applications led to concerns that biosolids were causing the nitrate increase. However, nitrate concentrations were at least 5 mg-N/L in some of these monitoring wells before biosolids applications to the area began, which indicates that biosolids applications were not the only source of nitrogen to groundwater in the area. The cycling of nitrogen between organic nitrogen, ammonia, oxidized forms such as nitrate, and other nitrogen forms is well documented (Russell-Hunter, 1970; Freeze and Cherry, 1979; Odum, 1989; Hem, 1992), so nitrate in the groundwater could have been derived from sources that contained nitrogen in some form other than nitrate.

Biosolids, animal manure, inorganic fertilizer, atmospheric deposition, and geologic materials (bedrock and soil) are possible nitrogen sources in the area. Because of the multiple possible sources of nitrogen at the Metro District properties, the USGS began a preliminary assessment of sources of nitrogen in shallow groundwater at part of the biosolids-application area in 2005 in cooperation with the Metro District. The Metro District properties near Deer Trail and the surrounding land (fig. 2) constitute the study area. Biosolids from the Metro District plant in Denver (fig. 1) and biosolids, cow manure, geologic materials (bedrock and soil), and groundwater from the study area (fig. 2) were sampled to measure nitrogen content and nitrogen isotopic compositions of nitrate or total nitrogen. Biosolids also were leached, and the leachates were analyzed for nitrogen content and other constituent concentrations. Geologic materials from the study area (fig. 2) also were sampled to determine mineralogy. Estimates of nitrogen contributed from inorganic fertilizer and atmospheric deposition were calculated from other published reports.

Purpose and Scope

This report presents a preliminary assessment of sources of nitrogen in shallow groundwater at part of a biosolids-application area near Deer Trail, Colo., in 2005. Results from mineralogical, chemical, and isotopic analyses of possible source materials are evaluated with respect to groundwater characteristics. The preliminary assessment of nitrogen sources in groundwater pertains to conditions in 2005, although data from 1993 through 2008 were used to support the assessment. This report includes the data collected from the study area that were used to evaluate sources of groundwater nitrate. This report does not include all the data collected by the USGS from the study area or the Metro District plant in 2005; those data are included in Yager and others (2009) and Crock and others (2008).

Description of Study Area

The study area (described in more detail in Yager and Arnold, 2003, and Yager and others, 2004) is located on the eastern plains of Colorado about 16 kilometers (km) east of the town of Deer Trail (fig. 1). The study area is on the eastern margin of the Denver Basin, a bowl-shaped sequence of sedimentary rocks that was formed in an ocean or near-ocean environment. The geology of the study area consists of interbedded shale, siltstone, and sandstone, which is overlain in some areas by clay, windblown silt and sand, or alluvial sand and gravel (Sharps, 1980; Major and others, 1983; Robson and Banta, 1995). The primary water-supply aquifer is the Laramie–Fox Hills aquifer, which is a bedrock aquifer that ranges from 0 to about 61 meters (m) thick in the study area and is the lowermost aquifer in the Denver Basin aquifer sequence (Robson and others, 1981; Robson and Banta, 1995; Yager and Arnold, 2003). Multiple alluvial aquifers are present in the study area. These aquifers are associated with the surficial drainage network and contain water of variable quality, are of limited extent, and generally yield little water (Stevens and others, 2003; Yager and Arnold, 2003). The study area is within the South Platte River drainage basin; all streams in this area drain northward to the South Platte River (fig. 1; Yager and Arnold, 2003). Short segments of some of the streams are intermittent, but in general, the streams are ephemeral and flow only after storms. No surface water flows from the Metro District properties except after storms. Most ponds in the area have been created by detention structures. Soils in the area generally are sandy or loamy on flood plains and stream terraces, clayey to loamy on gently sloping to rolling uplands, and sandy and shaley on steeper uplands (Larsen and others, 1966; Larsen and Brown, 1971).

Land use in the study area was historically rangeland or cropland and pasture (U.S. Geological Survey, 1980). Some petroleum exploration was done in the area (Drew and others, 1979), but no oil or gas production took place on the Metro

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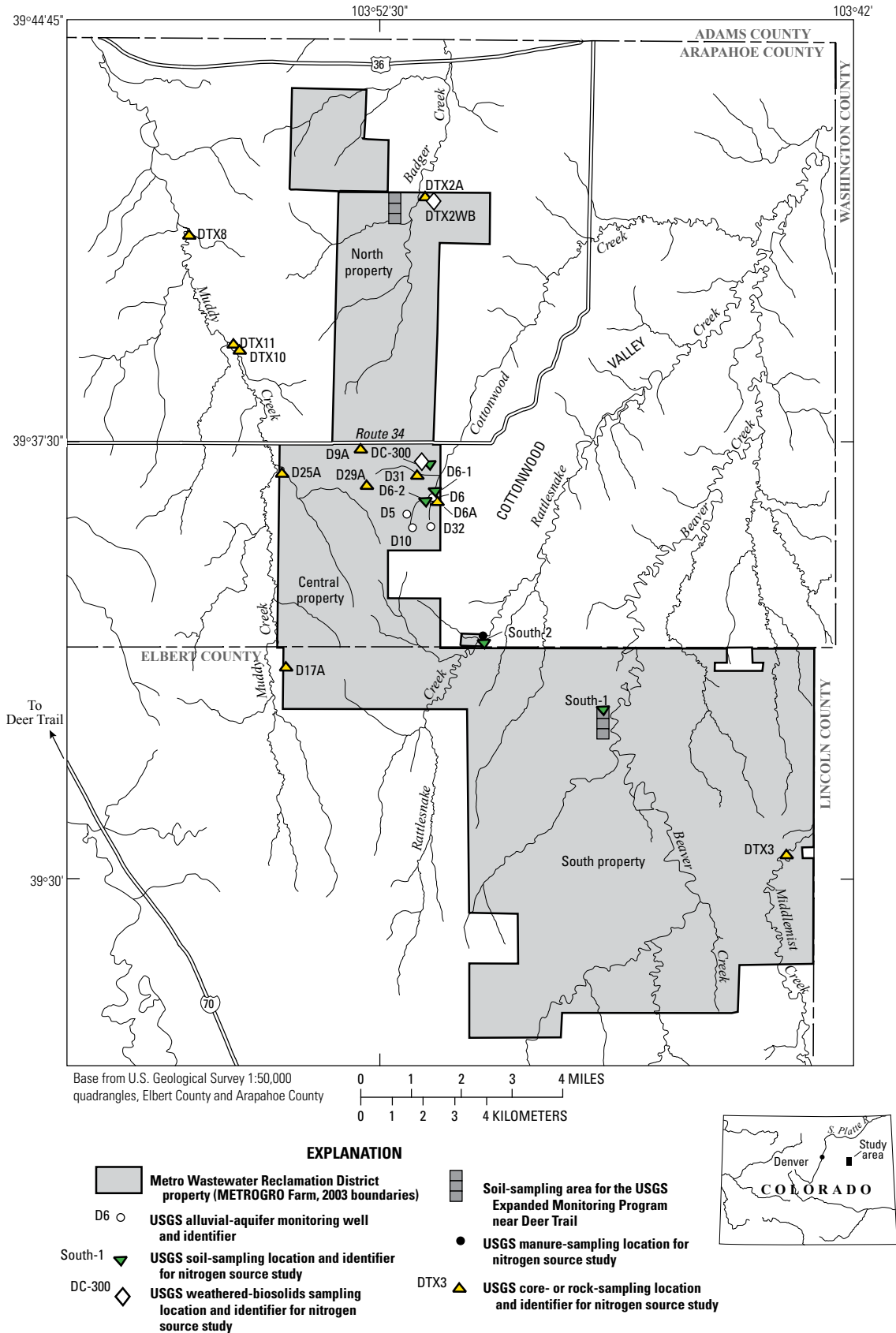


Figure 2. Locations of U.S. Geological Survey sampling sites related to the nitrogen source study near Deer Trail, Colorado.

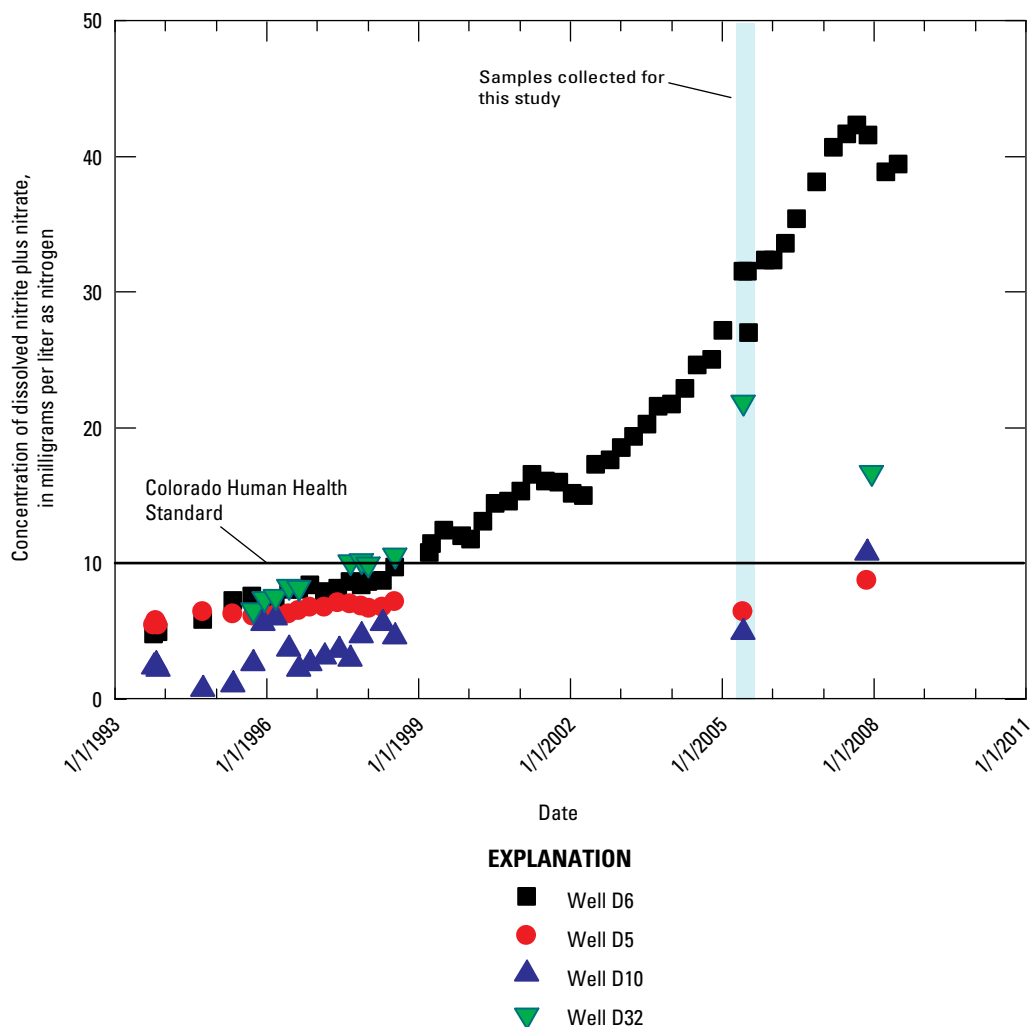


Figure 3. Concentrations of dissolved nitrite plus nitrate in water from selected monitoring wells as a function of time using data from this study (in blue column), Stevens and others (2003), Yager and others (2004), and U.S. Geological Survey (unpub. data on file at U.S. Geological Survey Colorado Water Science Center, 2011).

District properties during 1993 through 2005 (N. Crews, Metro Wastewater Reclamation District, written commun., April 13, 2011). Land in the study area was used as rangeland or cropland during 1993 through 2005. Cattle and sheep were the primary domesticated animals grazing the area, and wildlife also were present. No concentrated animal-feeding operations were located on or near the Metro District properties during 1993 through 2005; no evidence of large confined or unconfined animal feeding or dairy operations has been produced for the period before 1993. Wheat was the primary crop; farmland was not irrigated. Herbicides and other chemicals were applied to the study area during 1993 through 2005 for farming purposes. Pesticides and fertilizers also may have been applied to the Metro District properties historically, but little information is available about these historical applications. Inorganic fertilizer has not been used in the area since

1993 (N. Crews, Metro Wastewater Reclamation District, oral commun., April 13, 2011); no documentation of type or quantity of inorganic fertilizer use in the area has been produced for the period before 1993. Biosolids were applied as a fertilizer and soil amendment only on the Metro District properties.

Monitoring well D6 is located on the east side of the Metro District Central property (fig. 2). This area is drained by Cottonwood Creek, and the contributing surficial drainage area for the D6 location is about 2.8 square kilometers (km^2) (<http://water.usgs.gov/osw/streamstats/colorado.html>, accessed March 6, 2012). About 80 percent of this surficial drainage area is Metro District property. The topography of this drainage area is steep to gently rolling hills. Well D6 was located in a lowland depositional area at the confluence of ephemeral Cottonwood Creek and an unnamed tributary. Groundwater in well D6 likely was a mixture of water from

alluvium in paleochannels and water from the unconfined part of the Laramie–Fox Hills aquifer (Yager and Arnold, 2003). Completion information for this well and other monitoring wells in the study is provided in the Groundwater Characteristics section of the report. Biosolids were applied intermittently in the surficial drainage area that contained well D6, but this drainage area is not known to contain any current or former pit toilets or septic tanks.

Approach

Samples of fresh biosolids were collected from the Metro District wastewater treatment plant in Denver (fig. 1), and samples of weathered biosolids were collected from the study area near Deer Trail (fig. 2). The study area near Deer Trail was the same as that used by the USGS Expanded Monitoring Program near Deer Trail (Yager and others, 2009). Fresh biosolids were collected into large jars from an active centrifuge at the Metro District plant by Metro District personnel then were refrigerated and provided to the USGS. A fresh biosolids sample obtained in September 2004 was dried and archived at the laboratories of the USGS in Denver prior to grinding and analysis. The drying process included compositing all containers of fresh sample material into a large, shallow tray, substantially stirring the sample to homogenize, and leaving the sample in forced-air conditions (typically under a heat lamp) until dry before splitting the sample in a stainless-steel soil splitter. The aliquot of dried biosolids for analysis was ground to less than (<) 150 microns (μm) and analyzed for nitrogen by methods 350.1, 351.2, and 353.2 (U.S. Environmental Protection Agency, 1993) or by elemental analyzer (Révész and Qi, 2006). In contrast, fresh biosolids samples obtained in 2010 were analyzed for nitrogen compounds in chilled, hydrated, unground materials within one month of collection and analyzed for nitrogen by methods 350.1, 351.2, and 353.2 (U.S. Environmental Protection Agency, 1993). Weathered biosolids were sampled by the USGS from site DTX2WB (fig. 2) in 2002 and from site DC-300 (fig. 2) in 2005 by hand picking biosolids aggregates from the land surface using laboratory-cleaned spatulas and tweezers. The biosolids sampled at site DC-300 in late May 2005 and the fresh biosolids from September 2004 were produced at the same wastewater treatment plant at approximately the same time. The dried, ground 2004 fresh biosolids sample and corresponding weathered biosolids sample (from site DC-300) were analyzed for nitrogen concentration and the isotopic composition of total nitrogen at the USGS Stable Isotope Laboratory using methods described by Révész and Qi (2006).

To better understand how biosolids could be a source of inorganic constituents in groundwater, leachate samples were analyzed. The leachates were prepared from three types of biosolids materials using procedures that were based on the methods described by Hageman (2007). Fresh, wet biosolids for leachates were subsampled from the wet material bottled at the Metro District the day previous to leaching before any

drying or grinding of the sample and then refrigerated. Frozen, partly thawed biosolids for leachates also were subsampled from fresh, wet biosolids from the Metro District before any drying or grinding of the sample; they were then frozen for 2 months, then partially thawed. Laboratory-dried biosolids for leachates were subsampled from the air-dried, ground aliquot of Metro District biosolids that had been prepared for analysis. The target mass of biosolids material to leach with 1 liter (L) of solution (Hageman, 2007) was 50 grams (g). The leaching solution was laboratory-grade deionized water (known as inorganic blank water). For wet samples, the mass of biosolids and the volume of deionized water were adjusted for water content of the material so that the final leachate volume was consistent among the samples; water content ranged from about 75 to 85 percent by weight (%). After mixing, the leachate was filtered through a 0.45- μm nitro-cellulose filter. Leachate samples were analyzed for major ions, nutrients, and trace elements by the USGS National Water Quality Laboratory according to methods described by Fishman (1993). Leachate concentrations are reported as mass (milligram or microgram) per 1 L of total leachate solution (mg/L or $\mu\text{g/L}$).

Samples of fresh and weathered cow manure were collected from the study area in 2005. The manure samples were obtained from the land surface at South-2, a part of the study area that had not received biosolids (fig. 2). Both the fresh and weathered manure samples were collected with laboratory-cleaned utensils, then were air-dried and ground (<150 μm) at the laboratories of the USGS in Denver prior to analysis. These samples were analyzed for their total nitrogen concentration and the isotopic composition of total nitrogen at the USGS Stable Isotope Laboratory using methods described by Révész and Qi (2006).

Information about inorganic fertilizer and atmospheric deposition is available in the literature (for example, Zublena and others, 1991; Kendall and Doctor, 2004; Ruddy and others, 2006). Site-specific information for these sources were not collected as part of this study but were estimated from literature information.

Samples of geologic materials that were used in the nitrogen source assessment included bedrock and soil. Nitrogen in soil is from the bedrock minerals or from other sources of nitrogen that are applied or transported to the soil.

Samples of rock were collected at various times from the study area (fig. 2). A few samples were collected from the soil surface or from surficial outcrops. Most samples were collected from cores obtained from split-spoon core barrels in hollow-stem augers during the drilling of exploratory boreholes or monitoring wells. Rock samples were analyzed for mineralogy by using X-ray diffraction (Cullity and Stock, 2001) with and without the Rietveld Method (Young, 1995). Most of the rock samples that were analyzed for nitrogen concentration were ground prior to analysis and submitted to a commercial or research laboratory through a contract with the USGS. A single rock sample (shale) from the study area was analyzed for total nitrogen concentration and the isotopic composition of total nitrogen at the USGS Stable Isotope

Laboratory using methods described by Révész and Qi (2006). The sample was from archived core of unweathered shale that underlies the site at DTX11 (fig. 2) at about 11.6 m below land surface. The core was obtained from a borehole in 2000 when a monitoring well was installed at this location.

In 2005, samples of soil from five sites in the study area (fig. 2) were collected, dried, and ground. Soil samples were collected at approximately every 0.15-m depth in the top 1.5 m of the soil column. Samples from the upper 0.3 m were analyzed for the total nitrogen concentration and the isotopic composition of total nitrogen at the USGS Stable Isotope Laboratory (<http://isotopes.usgs.gov/>) in Reston, Va., using procedures described by Révész and Qi (2006). The remaining soil samples were analyzed for concentrations of water-extractable nitrate and chloride, as described below. Soil-sampling sites D6-1, D6-2, and DC-300 (fig. 2) were located in or adjacent to cultivated fields to which biosolids had been applied. Grazing also may have occurred at sites D6-1 and D6-2. Site South-1 (fig. 2) was located in a cultivated field that was not grazed during 1995 through 2005 and to which biosolids had not been applied; this site was in one of the soil-sampling fields used by the USGS Expanded Monitoring Program near Deer Trail (Yager and others, 2004). Site South-2 was located in a pasture to which biosolids had not been applied (fig. 2).

Nitrate and chloride concentrations in the soil samples were determined by first extracting the anions from the oven-dried soil using deionized water and then quantifying the concentrations of nitrate and chloride in the extracts by ion chromatography (McMahon and others, 2003). The measured concentrations were corrected for dilution by the added deionized water and then normalized to the dry weight of the soil used in the extraction. Concentrations are reported in micrograms as nitrogen per gram of dry sediment ($\mu\text{g-N/g}$) for nitrate or micrograms per gram of dry sediment ($\mu\text{g/g}$) for chloride.

Water samples were collected from four USGS monitoring wells (D5, D6, D10, D32) (fig. 2) during May through July 2005. Detailed information about these monitoring wells is provided by Yager and Arnold (2003). The sampling protocols are described in detail elsewhere (Stevens and others, 2003; McMahon and others, 2004) and are only briefly summarized here. Approximately three casing volumes of water were purged from the wells prior to sampling using a submersible pump. Values of pH, specific conductance, and water temperature and concentrations of dissolved oxygen were monitored in the field using a flow-through chamber during purging. Samples for the laboratory analysis of dissolved nutrients; dissolved nitrogen gas (N_2), argon, and methane; nitrogen and oxygen isotopes of nitrate ($\delta^{15}\text{N}[\text{NO}_3]$ and $\delta^{18}\text{O}[\text{NO}_3]$); and nitrogen isotopes of N_2 ($\delta^{15}\text{N}[\text{N}_2]$) were collected after the field properties stabilized. Nutrient samples were analyzed at the USGS National Water Quality Laboratory in Denver using procedures described by Fishman (1993). Analyses of the dissolved gases— N_2 , argon, and methane—were done at the USGS Chlorofluorocarbon Laboratory (<http://water.usgs.gov/lab/dissolved-gas/>) in Reston, Va., using procedures described

by Busenberg and others (1993). Analyses of $\delta^{15}\text{N}[\text{NO}_3]$, $\delta^{18}\text{O}[\text{NO}_3]$, and $\delta^{15}\text{N}[\text{N}_2]$ were done at the USGS Stable Isotope Laboratory (<http://isotopes.usgs.gov/>) in Reston, Va., using procedures described by Böhlke and Denver (1995), Casciotti and others (2002), and Böhlke and others (2003). The delta “ δ ” notation, in per mil (parts per thousand or ‰), is defined by equations 1 and 2, where ^{15}N , ^{14}N , ^{18}O , and ^{16}O are stable isotopes of nitrogen (N) and oxygen (O) and the superscripts are the approximate atomic masses of the isotopes.

$$\delta^{15}\text{N} = \left[\frac{^{15}\text{N}/^{14}\text{N}_{\text{sample}}}{^{15}\text{N}/^{14}\text{N}_{\text{standard}}} - 1 \right] \times 1,000 \quad (1)$$

$$\delta^{18}\text{O} = \left[\frac{^{18}\text{O}/^{16}\text{O}_{\text{sample}}}{^{18}\text{O}/^{16}\text{O}_{\text{standard}}} - 1 \right] \times 1,000 \quad (2)$$

Values of $\delta^{15}\text{N}[\text{NO}_3]$ and $\delta^{18}\text{O}[\text{NO}_3]$ were measured using the denitrifier method (Casciotti and others, 2002) and reported relative to atmospheric N_2 (AIR) and Vienna Standard Mean Ocean Water (VSMOW), respectively (Böhlke and others, 2003). The 2-sigma precisions of the $\delta^{15}\text{N}[\text{NO}_3]$ and $\delta^{18}\text{O}[\text{NO}_3]$ isotopic results are ± 0.5 per mil and ± 1.0 per mil, respectively. Values of $\delta^{15}\text{N}[\text{N}_2]$ are reported relative to AIR with a 2-sigma precision of ± 0.2 per mil.

Values of $\delta^{15}\text{N}[\text{NO}_3]$ in groundwater can be altered from their original values at the time of recharge by natural microbial processes in the aquifer that reduce nitrate to N_2 gas, potentially reducing the usefulness of nitrogen isotopes for understanding nitrate sources. This process is referred to as denitrification and generally occurs when concentrations of dissolved oxygen in groundwater are less than about 2 mg/L (Böhlke and others, 2002). Thus, if nitrogen isotopes are to be used to assess sources of nitrate in groundwater, it is important to correct for denitrification effects. When necessary, measured values of $\delta^{15}\text{N}[\text{NO}_3]$ in the water samples were corrected for denitrification effects produced in the aquifer using the approaches described by Vogel and others (1981), Böhlke (2002), and McMahon and Böhlke (2006).

Nitrogen Sources in the Study Area

Information about nitrogen sources is important to the understanding of variability of nitrogen concentrations in groundwater over time and space (Ruddy and others, 2006). One of the largest sources of nitrogen in an agricultural environment can be farm fertilizer, although animal manure and atmospheric deposition also are nitrogen sources in agricultural environments (Ruddy and others, 2006). Farm fertilizers can include biosolids, livestock manure, and inorganic fertilizers. Holloway and Dahlgren (2002) reported that rocks can

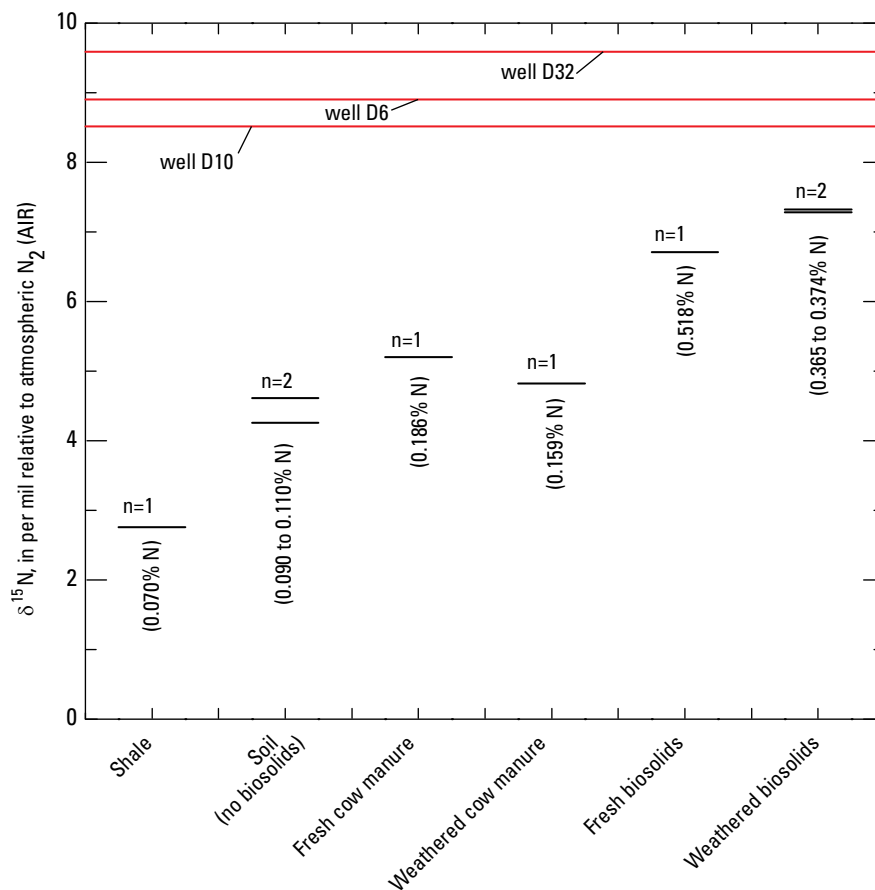
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be a natural source of nitrogen to groundwater and streams. In addition to biosolids, other forms of human sewage such as pit toilets or septic tanks can be present in rural environments and contribute nitrogen. Because no known current or former pit toilets or septic tanks are located in the vicinity of well D6 and because the source-assessment tools used for this study do not distinguish between different types of human sewage, these potential nitrogen sources are not discussed further. Total nitrogen content and isotopic composition of total nitrogen in samples of biosolids, animal manure, and geologic materials from the study area are shown in figure 4. Total nitrogen content measured for the sources in 2005 ranged from 0.070% in shale to 0.518% in fresh biosolids. The nitrogen isotopic

values measured for the sources in 2005 ranged from about +2.8 per mil in shale to +7.3 per mil in weathered biosolids.

Biosolids

Biosolids have been applied to parts of the study area (fig. 5) intermittently since 1993. Fresh biosolids from the Metro District were measured by the USGS to contain as much as 71,000 milligrams per kilogram as nitrogen (mg-N/kg) in 2010 (table 1), which is 7.10%. The nitrogen in fresh biosolids is primarily in the reduced forms, organic nitrogen and ammonia (table 1) or ammonium. These forms of nitrogen are transformed to nitrate in the presence of oxygen



EXPLANATION

- Nitrogen isotopic composition ($\delta^{15}\text{N}$) of total nitrogen in solid source materials
- Nitrogen isotopic composition ($\delta^{15}\text{N}$) of nitrate in groundwater (corrected for denitrification effects)

(0.365% N) Total nitrogen content of solid measured in 2005 sample, in percent by weight

n=2 The number of samples analyzed for that material—The composition of groundwater was based on analysis of a single sample from each well.

Figure 4. Nitrogen isotopic composition of selected solid source materials and of nitrate in groundwater (corrected for denitrification effects produced in the aquifer, if necessary; see table 5) from this study and total nitrogen content of the solids.

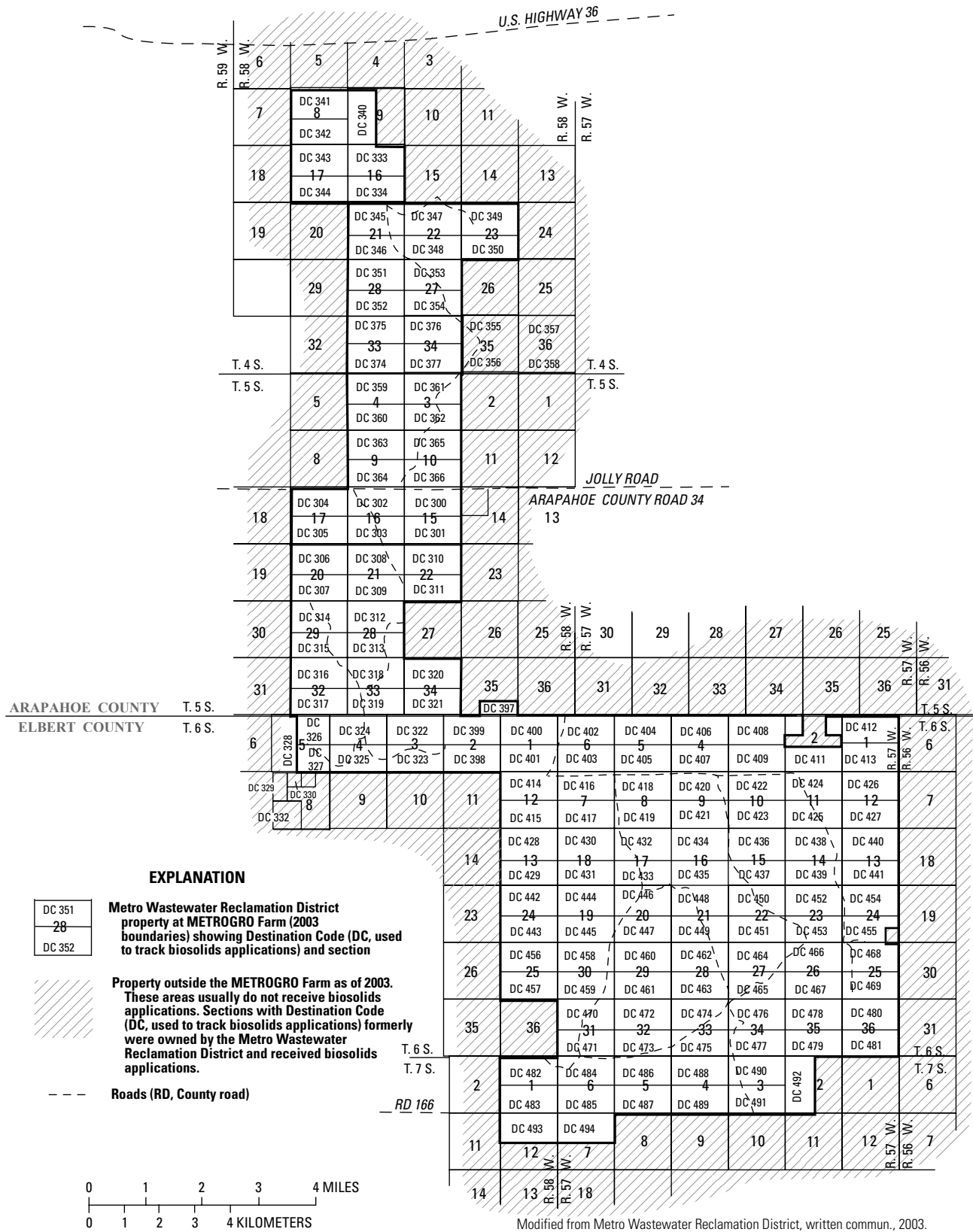


Figure 5. Metro Wastewater Reclamation District biosolids-application areas near Deer Trail, Colorado.

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Table 1. Nitrogen data for biosolids and manure materials related to the Metro Wastewater Reclamation District properties near Deer Trail, Colorado.

[All data reported as dry weight; mg-N/kg, milligram per kilogram (parts per million) as nitrogen; DSAC, distillation with semi-automated colorimetry, method 350.1 (U.S. Environmental Protection Agency, 1993); KSAC, Kjeldahl with semi-automated colorimetry, method 351.2 (U.S. Environmental Protection Agency, 1993); LSAC, deionized water leaching procedure with semi-automated colorimetry, method 353.2 (U.S. Environmental Protection Agency, 1993); CEA, combustion by elemental analyzer (Révész and Qi, 2006); --, not determined; <, less than]

Sample description (sites are shown in fig. 2)	Sample date	Analysis date	Ammonia, ¹ soluble (mg-N/kg, by DSAC)	Organic nitrogen plus ammonia, ¹ soluble (mg-N/kg, by KSAC)	Nitrite plus nitrate, soluble (mg-N/kg, by LSAC)	Nitrogen, total (mg/kg, by CEA)
Biosolids, field weathered (applied to the land surface at site DTX2WB several months before sample was collected)	2002	2002	440	4,200	1,100	--
Biosolids, fresh (from a centrifuge at the wastewater treatment plant, then dried in a laboratory and archived prior to analysis)	September 2004	2005	--	--	--	5,180
Biosolids, field weathered (applied to the land surface at site DC-300 between 9/30/04 and 10/4/04, about 8 months before sample was collected)	May 2005	2005	--	--	--	3,740
Biosolids, field weathered, replicate (applied to the land surface at site DC-300 about 8 months before sample was collected)	May 2005	2005	--	--	--	3,650
Biosolids, fresh, wet (from a centrifuge at the wastewater treatment plant)	October 2010	October 2010	15,000	71,000	<47	--
Biosolids, fresh, wet, replicate (from a centrifuge at the wastewater treatment plant)	October 2010	October 2010	15,000	57,000	<47	--
Biosolids, fresh, wet (from a centrifuge at the wastewater treatment plant)	November 2010	November 2010	9,000	71,000	<40	--
Biosolids, fresh, wet, replicate (from a centrifuge at the wastewater treatment plant)	November 2010	November 2010	8,000	63,000	6.0	--
Biosolids, fresh, wet (from a centrifuge at the wastewater treatment plant)	December 2010	December 2010	15,000	68,000	<44	--
Biosolids, fresh, wet, replicate (from a centrifuge at the wastewater treatment plant)	December 2010	December 2010	15,000	70,000	<44	--
Cow manure, fresh (collected from the land surface at site South-2)	June 2005	2005	--	--	--	1,860
Cow manure, field weathered (collected from the land surface at site South-2)	June 2005	2005	--	--	--	1,590

¹Analyses for "ammonia" quantify ammonia plus ammonium.

through ammonification (mineralization) and nitrification (Barbarick and Ippolito, 2000; Gilmour and others, 2003; Kadlec and Wallace, 2009). The substantial nitrogen content measured by the USGS in Metro District biosolids (table 1) confirms that biosolids have fertilizer potential and also indicates that biosolids are one potential source of nitrogen in groundwater of the study area. Biosolids applications are regulated for content, application method, and record keeping through the Colorado Department of Public Health and Environment (2003). The regulation specifies how to calculate nitrogen content for biosolids applications. Using the approach specified by the regulation, the nitrogen applied to all the Metro District properties in the study area during 1993–2008 was calculated from Metro District application records to be 4,930 kilograms per square kilometer as nitrogen (kg-N/km²) per biosolids application (median from 614 applications).

Biosolids applications are documented by the Metro District by half-section (Destination Codes or DCs), not by watershed (fig. 5), and multiple watersheds are included in the DCs that have drainage area contributing to the D6 location (DC 301 in section 15 and DCs 310 and 311 in section 22). About 70–80 percent of the approximately 2.8-km² area draining to the D6 location received biosolids applications. Most of the biosolids-application area likely to directly affect the D6 location is contained within areas DC 310 and DC 311 (fig. 5). Biosolids were applied to areas DC 310 and DC 311 during 1994, 1997, 2000, 2001, and 2003; no biosolids were applied to these areas during 1993, 1995, 1996, 1998, 1999, 2002, or 2004 through 2008. Applications to areas DC 310 and DC 311 during the application years ranged from 103 to 7,695 kg-N/km² (N. Stefonick, Metro Wastewater Reclamation District, written commun., October 2009).

Various values for nitrogen isotopic composition are provided for biosolids. Buck (2003) reported a nitrogen isotopic composition for biosolids of +9.6 per mil. Kendall and Doctor (2004) reported a large range of isotopic nitrogen values for human waste (about -5 to +25 per mil for $\delta^{15}\text{N}[\text{NO}_3]$ with a corresponding $\delta^{18}\text{O}[\text{NO}_3]$ range of about -7 to +14 per mil). The fresh biosolids sample from the Metro District had a higher nitrogen content (0.518%) and a lower isotopic nitrogen value (+6.6 per mil) than the corresponding weathered biosolids sample (0.365 to 0.374% and +7.3 per mil) from this study area (fig. 4). Thus, weathering can affect the nitrogen content and isotopic composition of biosolids. It was observed by the USGS that biosolids weathered longer than about 9 months at this site disaggregated so completely that pure biosolids could no longer be sampled from the land surface, although the biosolids-derived material may continue to weather and change chemically and isotopically in the soil after this stage.

Concentrations of nitrogen (including nitrate), chloride, and other inorganic constituents in leachate from fresh biosolids are listed in table 2. Concentrations of ammonia plus organic nitrogen in leachate from biosolids materials ranged from 249 to 650 mg-N/L of leachate, whereas concentrations of nitrate were less than 0.1 mg-N/L. These data and those

in table 1 indicate that most of the nitrogen in fresh biosolids was in reduced forms such as organic nitrogen and ammonia. The data in tables 1 and 2 also indicate that nitrogen was lost from the fresh biosolids during the drying process, which could reflect the loss of volatile forms of reduced nitrogen such as ammonia. This result is similar to field results that were reported by Robinson and Polglase (2000) documenting ammonia volatilization following biosolids application. The leachate data (table 2) also indicate the chemical heterogeneity of the biosolids materials, which likely results from distinct clay masses that are present with organic-rich material in the final biosolids product.

Animal Manure

Manure from domestic livestock and wildlife is a potential source of nitrate in the groundwater at the Metro District properties. Nitrogen in manure is primarily in the reduced forms, organic nitrogen and ammonium (University of Minnesota, 2002; Sullivan, 2008). These forms of nitrogen are transformed to nitrate in the presence of oxygen through ammonification (mineralization) and nitrification (Hartz and others, 2000; Gilmour and others, 2003; Sullivan, 2008; Kadlec and Wallace, 2009). Manure freshly deposited on the land surface can contain less nitrogen (less than 2,000 mg-N/kg or 0.2% according to fig. 4; Gormly and Spalding, 1979; Lysyk and others, 1985) than fresh biosolids (fig. 4; table 1). However, manure can be concentrated in a single location whereas a small volume of biosolids is distributed over a large area during the Metro District application process. The estimated annual nitrogen input from livestock manure in Arapahoe County was about 160 kg-N/km² from unconfined or confined operations (median of the annual values from 1982, 1987, and 1992 from Ruddy and others, 2006). The estimated annual nitrogen input from livestock manure in Elbert County was about 480 kg-N/km² from unconfined operations and 58 kg-N/km² from confined operations (median of the annual values from 1982, 1987, and 1992 from Ruddy and others, 2006).

No data for site-specific annual nitrogen input from livestock or wildlife manure are available for the study area. No confined livestock operations were observed at or near the Metro District properties by the USGS during 1993 through 2005. The nearest animal-feeding operation on record with the State of Colorado (S. Scott, Colorado Department of Public Health and Environment, written commun., August 16, 2011) is about 24 km northwest of well D6, which is much farther than the ammonia concentration and deposition distances from feedlots that were documented by McGinn and others (2003) but less than those documented by Occhipinti and others (2008). Cattle occasionally were observed on the Metro District properties by the USGS during 1993 through 2005, but not in the D6 drainage area. Wildlife was observed in the study area by the USGS, particularly herds of deer and pronghorn in addition to various birds. No identifiable, subsurface deposits of livestock or wildlife manure were observed in

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Table 2. Chemical data from analyses of leachates prepared from biosolids materials and associated quality-control samples.

[All leachates were prepared 12/18/2007 from Metro Wastewater Reclamation District biosolids according to procedures that were based on the methods of Hageman (2007). Analyses were done by the U.S. Geological Survey National Water Quality Laboratory on filtered leachates according to methods described by Fishman (1993). Oct., October; Dec., December; µg/L, micrograms per liter; ICP-MS, inductively coupled plasma–mass spectroscopy; DA, discrete analyzer; mg-N/L, milligrams per liter as nitrogen; <, less than; cICP-MS, collision-cell inductively coupled plasma–mass spectroscopy; IC, ion chromatography; mg/L, milligrams per liter; E, estimated by laboratory; +, plus; N, nitrogen; mg-P/L, milligrams per liter as phosphorus; std., standard; µS/cm, microsiemens per centimeter at 25 degrees Celsius; --, not applicable; °C, degrees Celsius; IBW, inorganic blank water]

Analyte, analytical method	Units	Concentration or characteristic in leachate from indicated biosolids material ¹				
		Laboratory dried (from Oct. 2007)	Frozen, partly thawed, nondried (from Oct. 2007)	Fresh, wet (from Dec. 2007)	Replicate of fresh, wet (from Dec. 2007)	None (leachate equipment blank)
Aluminum, ICP-MS	µg/L	21.6	99.7	115	213	<1.6
Antimony, ICP-MS	µg/L	2.1	1.6	2.4	1.7	<0.1
Arsenic, cICP-MS	µg/L	7.0	9.0	6.0	5.4	<0.06
Barium, ICP-MS	µg/L	2.1	2.4	6.5	2.2	<0.4
Beryllium, ICP-MS	µg/L	<0.008	<0.008	<0.008	<0.008	<0.008
Boron, ICP	µg/L	73.5	55.3	51.5	43.5	<1.2
Bromide, IC	mg/L	0.07	E0.07	0.08	0.08	<0.02
Cadmium, ICP-MS	µg/L	0.28	0.13	0.19	0.11	<0.04
Calcium, ICP	mg/L	9.54	7.67	4.89	4.49	E0.04
Chloride, IC	mg/L	48.4	61.0	59.6	58.0	<0.12
Cobalt, cICP-MS	µg/L	5.86	8.43	5.13	4.57	<0.02
Copper, cICP-MS	µg/L	24.6	3.16	2.0	2.2	<1
Chromium, cICP-MS	µg/L	0.6	1.7	0.8	0.9	<0.1
Fluoride, IC	mg/L	0.37	1.18	1.21	1.12	<0.12
Iron, ICP	µg/L	288	1,220	322	373	<8
Lead, ICP-MS	µg/L	0.65	0.45	0.84	0.38	<0.08
Magnesium, ICP	mg/L	2.92	1.77	1.71	1.3	<0.02
Manganese, ICP-MS	µg/L	32.5	25.6	8.2	7.8	<0.2
Molybdenum, ICP-MS	µg/L	85.1	40.8	61.5	58.0	<0.2
Nickel, cICP-MS	µg/L	77.1	74.9	27.9	28.4	<0.2
Nitrogen, ammonia, ² colorimetry, DA, salicylate-hypochlorite	mg-N/L	110	323	224	258	0.086
Nitrogen, nitrite + nitrate (NO ₂ +NO ₃), colorimetry, continuous flow, cadmium-reduction	mg-N/L	E0.024	0.041	0.044	0.042	<0.04
Nitrogen, nitrite, colorimetry, DA	mg-N/L	<0.100	E0.073	E0.055	<0.100	<0.002
Nitrogen, ammonia ² + organic, alkaline persulfate	mg-N/L	249	519	650	379	E0.03
Orthophosphate, colorimetry, DA, phosphomolybdate	mg-P/L	1.97	10.4	15.2	13.3	<0.006
pH, electrode	std. units	6.9	8.4	8.6	8.7	5.6
Potassium, ICP	mg/L	15.9	27.5	25.8	23	<0.02
Selenium, cICP-MS	µg/L	16.0	18.1	8.1	8.4	<0.04
Silica, ICP	mg/L	3.31	2.49	6.29	5.57	<0.02
Silver, ICP-MS	µg/L	0.34	0.11	<0.1	<0.1	<0.1
Sodium, ICP	mg/L	11.3	18.0	15.4	13.9	<0.12
Specific conductance, Wheatstone bridge	µS/cm	575	2,280	1,400	1,340	2
Strontium, ICP	µg/L	31.2	23.9	16.9	16.2	<0.4

Table 2. Chemical data from analyses of leachates prepared from biosolids materials and associated quality-control samples.— Continued

[All leachates were prepared 12/18/2007 from Metro Wastewater Reclamation District biosolids according to procedures that were based on the methods of Hageman (2007). Analyses were done by the U.S. Geological Survey National Water Quality Laboratory on filtered leachates according to methods described by Fishman (1993). Oct., October; Dec., December; mg/L, micrograms per liter; ICP-MS, inductively coupled plasma–mass spectroscopy; DA, discrete analyzer; mg-N/L, milligrams per liter as nitrogen; <, less than; cICP-MS, collision-cell inductively coupled plasma–mass spectroscopy; IC, ion chromatography; mg/L, milligrams per liter; E, estimated by laboratory; +, plus; N, nitrogen; mg-P/L, milligrams per liter as phosphorus; std., standard; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; --, not applicable; oC, degrees Celsius; IBW, inorganic blank water]

Analyte, analytical method	Units	Concentration or characteristic in leachate from indicated biosolids material ¹				
		Laboratory dried (from Oct. 2007)	Frozen, partly thawed, nondried (from Oct. 2007)	Fresh, wet (from Dec. 2007)	Replicate of fresh, wet (from Dec. 2007)	None (leachate equipment blank)
Sulfate, IC	mg/L	192	20	38.1	49.6	<0.18
Uranium, ICP-MS	μ g/L	0.41	74.3	37.1	33.2	<0.02
Tungsten, cICP-MS	μ g/L	7.0	18.2	14.1	12.4	<0.06
Zinc, cICP-MS	μ g/L	38.6	27.1	12.8	14.5	<1.8
Chloride:Bromide	none	691	871	745	725	--
Sample temperature at time of preparation, thermistor of pH meter	$^{\circ}$ C	25	25	25	25	25
Mass of biosolids material leached	grams	50.01	216.32	216.54	216.20	0
Volume of IBW added	liter	1.00	0.82	0.82	0.82	1.00
Estimated water content of solid material	percent	7	78.5	78.5	78.5	100 (all water, no solid)

¹All biosolids samples were collected from the centrifuges at the wastewater treatment plant (1- to 2-day composites) in Denver, Colorado.

²Analyses for “ammonia” quantify ammonia plus ammonium.

the cores obtained from the drilling of exploratory boreholes or monitoring wells in the study area. No fresh or weathered concentrated manure-deposition areas were observed on the surface of the Metro District properties by the USGS during 1993 through 2005. Therefore, the estimated annual nitrogen input that was calculated from Ruddy and others (2006) was assumed to apply to the surficial drainage area that contains well D6.

Various values for nitrogen isotopic composition are provided for animal manure. Gormly and Spalding (1979) reported a range of nitrogen isotopic composition for live-stock manure of +4.8 to +44 per mil. Kreitler and Jones (1975) reported a nitrogen isotopic composition of +14 per mil for barnyard soils with definite animal-waste contribution. Kendall and Doctor (2004) reported a large range of isotopic composition values for animal manure (about -5 to +25 per mil for $\delta^{15}\text{N}[\text{NO}_3]$ with a corresponding $\delta^{18}\text{O}[\text{NO}_3]$ range of about -7 to +14 per mil). The fresh cow-manure sample from the study area had a higher nitrogen content (0.186%) and a higher $\delta^{15}\text{N}[\text{NO}_3]$ (+5.2 per mil) than the corresponding weathered cow-manure sample (0.159% and +4.8 per mil) from this study area (fig. 4). Thus, weathering can affect the nitrogen content and isotopic composition of animal manure.

Inorganic Fertilizer

Inorganic fertilizer used in farming is a possible source of nitrate in the groundwater of the study area. Parts of the Metro District properties near Deer Trail were farmed before biosolids applications began in 1993. The nitrogen content of inorganic fertilizers can range from about 5 to about 80% (Zublena and others, 1991), which is as much as 800,000 mg-N/kg. The forms of nitrogen in inorganic fertilizer vary by product but commonly include ammonium or nitrate (Zublena and others, 1991). If the nitrogen is not already in nitrate form, the nitrogen can be transformed to nitrate in the presence of oxygen through nitrification. Estimated median annual nitrogen input from fertilizer use on farmland during 1987 through 1992 is calculated from Ruddy and others (2006) as about 190 kg-N/km² for Arapahoe County and about 120 kg-N/km² for Elbert County. No inorganic fertilizers reportedly were used at the Metro District properties near Deer Trail during 1993 through 2005 (Metro Wastewater Reclamation District, written commun., 2007), but this type of fertilizer could have been used on the properties before the Metro District acquired the properties.

Various values for nitrogen isotopic composition are provided for inorganic fertilizer. The nitrogen isotopic composition of inorganic fertilizers can range from less than +1 to +5.6 per mil ($\delta^{15}\text{N}[\text{NO}_3]$) but generally is characterized by low isotopic values (Vitoria and others, 2004). Gormly and Spalding (1979) reported a nitrogen isotopic composition of -1.1 ± 1.0 per mil for inorganic fertilizers. Kendall and Doctor (2004) reported a range of about -3 to +3 per mil for $\delta^{15}\text{N}[\text{NO}_3]$ with a corresponding $\delta^{18}\text{O}[\text{NO}_3]$ ranging from about -7 to about +23 per mil in inorganic fertilizer. Kreitler (1979) reported a nitrogen isotopic composition of -38 to +1.9 per mil for inorganic fertilizer.

Atmospheric Deposition

Atmospheric nitrogen is a possible source of nitrate in groundwater at the Metro District properties. Natural sources of nitrogen in arid environments include precipitation, eolian deposition of nitrate salts, and biological assimilation of atmospheric nitrogen by biota (Walvoord and others, 2003). The nitrogen content of atmospheric deposition in eastern Colorado can be about 0.7 mg-N/L in precipitation (National Atmospheric Deposition Program, <http://nadp.sws.uiuc.edu/>, accessed April 28, 2011), but the nitrogen content of atmospheric deposition varies. Estimated median annual nitrogen input from atmospheric deposition during 1985 through 2001 is calculated from Ruddy and others (2006) to be about 280 kg-N/km² for Arapahoe County and about 250 kg-N/km² for Elbert County based on median values. The nitrogen input from precipitation can be small compared to other sources in agricultural environments.

Various values for nitrogen isotopic composition are provided for precipitation. The nitrogen isotopic composition of atmospheric deposition generally is characterized by low isotopic values. Billy and others (2010) reported $\delta^{15}\text{N}[\text{NO}_3]$ for precipitation in France as -7 to -2 per mil with a mean of -4 per mil. Nanus and others (2008) reported $\delta^{15}\text{N}[\text{NO}_3]$ for precipitation in Rocky Mountain National Park (a higher elevation area about 161 km northwest of the study area) as ranging from -3.6 to -2.1 per mil with a corresponding $\delta^{18}\text{O}[\text{NO}_3]$ for precipitation ranging from +71.2 to +74.8 per mil. Kendall and Doctor (2004) reported $\delta^{18}\text{O}[\text{NO}_3]$ for precipitation ranging from about +17 per mil to about +67 per mil.

Geologic Materials

Another potential source of nitrate in groundwater at the Metro District properties is nitrogen naturally present in geologic materials (bedrock and soil) of the study area. The forms of nitrogen in bedrock of the study area are most likely organic nitrogen in recalcitrant organic matter and ammonium in silicate minerals (Holloway and Dahlgren, 2002). Nitrogen in rocks can result in increased nitrogen in terrestrial and aquatic systems when bedrock weathers (Holloway and Dahlgren, 2002). Nitrogen can be substantial in coal (Holloway and Dahlgren, 2002; Schweinfurth, 2003), and

coal is found in the Laramie Formation west of the Metro District properties (Kirkham and Ladwig, 1979). Only trace amounts of coal were detected in or above the geologic materials that contain groundwater at well D6 as determined by exploratory drilling at sites D6A, D9A, and D25A (fig. 2) in 2002 (table 3). However, geologic materials (both bedrock and soil) of the study area contained nitrogen. Samples of weathered and unweathered shale, siltstone, sandstone, loess, and near-surface soil from the study area contained nitrogen (table 3), and nitrogen content was largest in the shale samples (as much as 2,344 mg-N/kg). Soil that received biosolids applications (sites D6-1 and DC-300) contained as much as 1,700 mg-N/kg nitrogen (table 3). Soil that did not receive biosolids applications (sites South-1 and South-2) contained as much as 1,100 mg-N/kg nitrogen (table 3). Soil nitrogen is from surficial applications (biosolids, animal manure, and inorganic fertilizer), plant materials, atmospheric deposition, and bedrock. A mineralogical analysis did not identify any of the nitrogen-bearing minerals listed by Holloway and Dahlgren (2002, table 1) in the geologic materials from the vicinity of the Metro District properties. However, nitrogen concentrations of shale samples from sites DTX3 and DTX8 (fig. 2, table 3) were substantially larger than the range reported by McMahan and others (1999) for Pierre Shale and larger than many other rock concentrations reported by Holloway and Dahlgren (2002). This study did not assess annual nitrogen input from bedrock in the study area, but Holloway and others (2001) reported cumulative nitrogen release from rocks in laboratory experiments as 3.6×10^{-12} moles per square centimeter (mol/cm²) (0.0005 kg-N/km²) for slate and 4.2×10^{-11} mol/cm² (0.0059 kg-N/km²) for greenstone. Holloway and others (2001) reported cumulative nitrogen release from soils derived from nitrogen-bearing bedrock in laboratory experiments at similar or slightly smaller levels (0.0002 to 0.0004 kg-N/km²).

Various values for nitrogen isotopic composition are provided for geologic materials. Kendall and Doctor (2004) reported $\delta^{15}\text{N}[\text{NO}_3]$ for soil as ranging from about +2 per mil to +7 per mil with a corresponding $\delta^{18}\text{O}[\text{NO}_3]$ for soil ranging from about -7 per mil to about +13 per mil. The isotopic composition of total nitrogen in geologic materials from the study area was +2.8 per mil in shale and +4.3 per mil to +4.7 per mil in soil. The nitrogen isotopic composition of the geologic materials from the study area was lower than that measured for biosolids or animal manure (fig. 4).

Concentrations of water-extractable nitrate and chloride in the soil samples are shown in figure 6. The largest concentrations of nitrate occurred in the upper 0.6 m at sites D6-1 and DC-300 where concentrations exceeded 75 $\mu\text{g/g}$. Those two sites also had the largest inventories of nitrate stored in the upper 1.5 m of the soil column. Both of those sites received biosolids applications and were cultivated. Some grazing probably occurred at both sites as well. Sites South-1 and South-2 were cultivated and grazed, respectively, but received no biosolids applications. The largest nitrate concentrations

at those sites were less than 35 $\mu\text{g/g}$. Site D6-2 received biosolids applications, but it had by far the smallest nitrate concentrations and largest chloride concentrations of any site. The presence of large chloride concentrations in the soil zone in semiarid regions has been interpreted to mean that little to no water movement has occurred through the soil (Scanlon and Goldsmith, 1997; Walvoord and others, 2003; McMahon and others, 2006) because otherwise the chloride would be flushed from the soil. This interpretation assumes no application of chemical amendments, such as potassium chloride, to a cultivated field. Although historical chemical-application data for the site are lacking, the relatively small chloride concentrations at the other cultivated sites indicate that land applications of potassium chloride probably did not occur (fig. 6). A general lack of water movement through the soil at site D6-2 is supported by the small concentrations of nitrate in the soil zone at that site (fig. 6). In contrast, all of the other sites had larger nitrate concentrations and smaller chloride concentrations than site D6-2, consistent with the interpretation that water movement through the soil did occur at those other sites.

Source Contributions

The nitrogen information from the study indicates that each of the sources contain sufficient nitrogen to potentially affect groundwater nitrate concentrations. Natural processes can transform the nitrogen in any of the sources to nitrate in the groundwater. Nitrogen information for each source in the study area is summarized in table 4 and was used to estimate nitrogen loads. The nitrogen load from biosolids applications in areas DC 310 and DC 311 during 1993 through 2008 ranged from 75 to 9,310 kilograms of nitrogen (kg-N) per application. The annual nitrogen load to this area ranged from 0 during non-application years to 16,482 kg-N in 1997. The total nitrogen load (summation from all applications to areas DC 310 and DC 311) was about 48,300 kg-N for 1993 through 2005 (table 4). The actual load of biosolids-applied nitrogen to the surficial drainage area contributing to the D6 location cannot be calculated from available application records. However, estimates calculated from Metro District application records indicate that the load of biosolids-applied nitrogen to the drainage area contributing to the D6 location did not exceed 72,440 kg-N for the period 1993 through 2005 or 74,770 kg-N for the period 1993 through 2008.

Estimated annual nitrogen input was used to estimate the nitrogen load to the contributing surficial drainage area of well D6 from animal manure, inorganic fertilizer, atmospheric deposition, and geologic materials (bedrock and soil) (table 4). Because biosolids applications began in the study area in 1993, the nitrogen load was calculated separately for the 13 years prior to biosolids application (1980 to 1993) and for the 13 years after biosolids applications began (1993 through 2005). Estimates calculated from Ruddy and others (2006) indicate that the nitrogen load from animal manure likely did not exceed 17,000 kg-N for the period 1993 through 2005. The nitrogen load from inorganic fertilizer is estimated

as 0 kg-N for the period 1993 through 2005 because only biosolids were used as the fertilizer. Estimates calculated from Ruddy and others (2006) and the National Atmospheric Deposition Program (<http://nadp.sws.uiuc.edu/>) indicate that the nitrogen load from atmospheric deposition likely did not exceed 11,000 kg-N for the period 1993 through 2005. Using nitrogen-release rates from Holloway and others (2001), the nitrogen load from bedrock is estimated as 0.20 kg-N or less and the nitrogen load from soil is estimated as 0.01 kg-N or less for the period 1993 through 2005. Thus, calculated estimates from Holloway and others (2001) indicate that the nitrogen load from all geologic materials likely did not exceed 0.21 kg-N for the period 1993 through 2005, which is much less than the estimated nitrogen load from biosolids, animal manure, and atmospheric deposition for the same period. The load estimates (table 4) indicate that animal manure, inorganic fertilizer, or atmospheric deposition could have contributed the largest nitrogen load to the study area in the 13 years before biosolids applications began, but biosolids likely contributed the largest nitrogen load to the study area in the 13 years after biosolids applications began.

Groundwater Characteristics

Groundwater information for the study area indicates that nitrate concentration varied both temporally and spatially. In 1993, before any biosolids applications began, dissolved nitrite plus nitrate concentrations were about 5 mg-N/L or larger in groundwater samples from monitoring wells D5, D6, and D9 (well D9 was at the D9A location shown in fig. 2); concentrations were about 2.4 mg-N/L in groundwater samples from monitoring well D10 in 1993 (unpub. data on file at U.S. Geological Survey Colorado Water Science Center, 2011). Concentrations of dissolved nitrite plus nitrate increased fairly steadily in samples from well D6 after biosolids applications began; concentrations of dissolved nitrite plus nitrate also increased similarly at monitoring well D32 and to a lesser extent at wells D5 and D10 (fig. 3). Wells D5 and D6 were completed at similar depths (table 5); well D10 was completed about 3 m shallower, and well D32 was completed about 3 m deeper (table 5). Wells D5, D10, and D32 were upgradient topographically as well as hydrogeologically from well D6 and located in the same drainage basin as well D6, so they are of the most interest in understanding well D6 nitrogen sources. Concentrations of dissolved nitrite plus nitrate were much lower at 24 other monitoring wells during the same period, but spiked as high as 25–31 mg-N/L in late 1995 and 1998 at well D9 and in late 1996 at well D25 (well D25 was at the D25A location shown in fig. 2) (unpub. data on file at U.S. Geological Survey Colorado Water Science Center, 2011). This information indicates that (1) groundwater in the study area had a nitrogen source before biosolids applications started, and (2) concentration patterns for dissolved nitrite plus nitrate in groundwater were diverse and highly variable throughout the study area during 1993–2005.

Table 3. Mineralogy and nitrogen concentration of geologic materials collected near Deer Trail, Colorado.

[Samples were obtained from borehole cores when monitoring wells were installed (DTX3, DTX8, DTX10, DTX11, D6A, D25A, and D31), from exploratory coreholes (D9A, D17A, D6-1, DC-300, South-1, and South-2), from outcrops (D29A), and from recently tilled fields (DTX2A). mg-N/kg, milligram per kilogram (parts per million) as nitrogen; DSAC, distillation with semi-automated colorimetry, method 350.1 (U.S. Environmental Protection Agency, 1993); +, plus; KSAC, Kjeldahl with semi-automated colorimetry, method 351.2 (U.S. Environmental Protection Agency, 1993); LSAC, deionized water leaching procedure with semi-automated colorimetry, method 353.2 (U.S. Environmental Protection Agency, 1993); °C, degrees Celsius; ±, plus or minus; std. dev., standard deviation; mg/kg, milligram per kilogram; CEA, combustion by elemental analyzer (Révész and Qi, 2006); --, not determined; <, less than; n, number of samples analyzed; cm, centimeter; ~, approximately; major, minerals that compose greater than 25 percent by weight; minor, minerals that compose between 5 and 25 percent by weight; trace, minerals that compose less than 5 percent by weight]

Site (fig. 2)	Sample depth, meters below land surface	Sample date	Sample description	Mineralogy ¹	Ammonia, ² soluble (mg-N/kg, by DSAC)	Organic nitrogen + ammonia, ² soluble (mg-N/kg, by KSAC)	Nitrate + nitrite, soluble (mg-N/kg, by LSAC)	Nitrogen, total (mg/kg, by pyrolysis at 1,050°C [± std. dev.])	Nitrogen, total (mg/kg, by CEA)
DTX3	4.3–4.5	2/12/1999	Black unweathered shale	--	--	850	<1	2,344 ± 34 (n=3)	--
DTX8	42.2–42.4	3/2/1999	Hard, black, unweathered shale with silt	--	--	750	<1	2,101 ± 65 (n=3)	--
DTX8	48.9–49.1	3/2/1999	Gray silt (weathered siltstone and shale) with shale	--	--	370	<1	869 ± 49 (n=2)	--
DTX8	49.8–50.0	3/2/1999	Gray silt (weathered siltstone and shale) with shale	--	--	360	<1	874 ± 6 (n=2)	--
DTX10	25.0–25.2	2/24/1999	Shale, clay (weathered shale), and silt (weathered siltstone)	--	--	500	<1	798 ± 51 (n=2)	--
DTX10	26.1–26.3	2/24/1999	Gray silt (weathered siltstone and shale) with shale	--	--	450	<1	1,031 ± 37 (n=2)	--
DTX10	31.2–31.4	2/24/1999	Black shale with silt (weathered shale) and fossil fragments	--	--	400	<1	1,086 ± 17 (n=3)	--
DTX10	109.9–110.8	2/24/1999	Hard black clay (weathered shale) with shale and silt (weathered siltstone)	--	--	470	1	1,358 ± 6 (n=2)	--
DTX2A	0 (surface)	7/6/2000	Tabular, clear to white crystal (9 cm × 5 cm × 2 cm)	Gypsum with trace of quartz sand	--	--	--	--	--
DTX11	~1.2	1/18/2000	Dense, semi-consolidated, grey, silty clay (loess) with white crystalline rootlet deposits	Quartz (major), microcline, (minor), with trace of albite, gypsum, muscovite, (possible kaolinite or chlorite, clinocllore), dolomite; White crystalline deposits identified as gypsum	--	--	--	--	--
DTX11	8.2	1/18/2000	Unconsolidated pink, brown, black, white, and gray silt and sand with arkosic fragments	Quartz, microcline (major), albite (minor), with trace of gypsum, muscovite	--	--	--	--	--
DTX11	~10.7	1/18/2000	Consolidated fragments of grey sandstone and darker siltstone in unconsolidated, homogeneous, grey, very fine sand and silt	Quartz (major), albite, microcline (minor), with trace of montmorillonite clay, muscovite, (possible kaolinite, clinocllore), gypsum, pyrite, dolomite	--	--	--	--	--
DTX11	~11.6	1/18/2003	Hard, black, unweathered shale	--	--	--	--	--	700
D6A	0.6–0.8	2/6/2002	Semi-consolidated, brown clay balls in dark grey-brown loam (loess)	Quartz (major), albite, orthoclase (minor), with trace of montmorillonite, muscovite, calcite, kaolinite, magnesiohornblende	--	--	--	--	--
D6A	3.0–3.2	2/6/2002	Unconsolidated, light brown loam with black flecks that possibly are coal (loess)	Quartz (major), gypsum (minor), with trace of albite, montmorillonite, muscovite, orthoclase, kaolinite (sample has smectite, probably montmorillonite)	--	--	--	--	--
D6A	19–19.5	2/6/20024	Unconsolidated, dense, brown, clayey silt (loess) with white megascopic crystals lining a vertical planar void	Quartz (major), gypsum (minor), with trace of albite, montmorillonite, muscovite, orthoclase, and possible kaolinite (sample has smectite, probably montmorillonite); White crystals identified as gypsum	<2	94	<1	--	--
D6A	8.7–9.1 (below screen)	2/6/2002	Consolidated, dark grey to black shale	Quartz (major), gypsum (minor), with trace of orthoclase, albite, montmorillonite, muscovite, and possible kaolinite (sample has smectite, probably montmorillonite)	--	--	--	--	--
D9A	8.7–10.2	2/7/20024	Black amorphous-mineral vein (0.3–0.6 cm thick) in semiconsolidated brown silty loess	Quartz (major), albite (minor), with trace of orthoclase, montmorillonite, muscovite; Black mineral is amorphous, consistent with coal	<2	51	5.2	--	--
D9A	17.1	2/7/2002	Consolidated, friable, orange sandstone with unconsolidated, homogeneous, orange loamy sand (weathered sandstone)	Quartz (major), albite (minor), with trace of orthoclase, montmorillonite, muscovite; Black mineral is amorphous, consistent with coal	--	--	--	--	--

Table 3. Mineralogy and nitrogen concentration of geologic materials collected near Deer Trail, Colorado.—Continued

[Samples were obtained from borehole cores when monitoring wells were installed (DTX3, DTX8, DTX10, DTX11, D6A, D25A, and D31), from exploratory coreholes (D9A, D17A, D6-1, DC-300, South-1, and South-2), from outcrops (D29A), and from recently tilled fields (DTX2A). mg-N/kg, milligram per kilogram (parts per million) as nitrogen; DSAC, distillation with semi-automated colorimetry, method 350.1 (U.S. Environmental Protection Agency, 1993); +, plus; KSAC, Kjeldahl with semi-automated colorimetry, method 351.2 (U.S. Environmental Protection Agency, 1993); LSAC, deionized water leaching procedure with semi-automated colorimetry, method 353.2 (U.S. Environmental Protection Agency, 1993); °C, degrees Celsius; ±, plus or minus; std. dev., standard deviation; mg/kg, milligram per kilogram; CEA, combustion by elemental analyzer (Révész and Qi, 2006); --, not determined; <, less than; n, number of samples analyzed; cm, centimeter; ~, approximately; major, minerals that compose greater than 25 percent by weight; minor, minerals that compose between 5 and 25 percent by weight; trace, minerals that compose less than 5 percent by weight]

Site (fig. 2)	Sample depth, meters below land surface	Sample date	Sample description	Mineralogy ¹	Ammonia, ² soluble (mg-N/kg, by DSAC)	Organic nitrogen + ammonia, ² soluble (mg-N/kg, by KSAC)	Nitrate + nitrite, soluble (mg-N/kg, by LSAC)	Nitrogen, total (mg/kg, by pyrolysis at 1,050°C [± std. dev.])	Nitrogen, total (mg/kg, by CEA)
D9A	17.4–17.5	2/7/2002	Consolidated, friable, weathered, yellow sandstone and gray shale with heterogeneous gray, black, and yellow loamy sand and shale	Quartz (major), with trace of orthoclase, montmorillonite, albite, gypsum, jarosite, muscovite, possible kaolinite (sample has amorphous smectite, probably montmorillonite); Yellow mineral identified as jarosite surrounded by minerals quartz and gypsum	--	--	--	--	--
D9A	17.7	2/7/2002	Consolidated, friable, heterogeneous, weathered, grey, black, yellow and red loamy siltstone, sandstone, and shale with vein of clear/white crystalline mineral	Quartz (major), gypsum, orthoclase, montmorillonite (minor), with trace of albite, jarosite, muscovite; Clear/white mineral identified as gypsum with a trace of quartz sand	--	--	--	--	--
D9A	18.1	2/7/2002 ⁴	Consolidated, weathered, friable red-orange siltstone and sandstone with concretions, just above grey shale	Quartz (major), gypsum (minor), with trace of albite, montmorillonite, orthoclase, muscovite, jarosite	<2	52	<1	--	--
D9A	18.29	2/7/2002	Consolidated, friable, weathered, orange and brown sandstone with orange, black, and yellow shale	Quartz (major), gypsum and microcline (minor), with trace of albite, montmorillonite, muscovite, jarosite	--	--	--	--	--
D9A	18.35	2/7/2002	Clear crystals in consolidated, friable, weathered, grey shale with yellow and orange minerals; semi-consolidated weathered, yellow, orange, grey, and brown siltstone, shale, and sandstone	Clear crystals identified as gypsum	--	--	--	--	--
D9A	18.38–18.41	2/7/2002	Clear crystals in consolidated, friable, weathered grey shale with yellow and orange minerals; semi-consolidated weathered, yellow, orange, grey, and brown siltstone, shale, and sandstone	Quartz and gypsum (major), jarosite and montmorillonite clay (minor), with trace of microcline, albite, jarosite, muscovite; Clear crystals identified as gypsum	--	--	--	--	--
D9A	18.44	2/7/2002	Consolidated, friable, weathered, grey clayey shale with yellow, clear, and orange minerals; unconsolidated weathered, yellow, orange, grey, and brown siltstone and sandstone	Quartz and gypsum (major), jarosite and montmorillonite clay (minor), with trace of microcline, albite, muscovite; Yellow minerals identified as natrojarosite, jarosite; clear minerals identified as quartz, gypsum; orange minerals identified as natrojarosite, jarosite, amorphous iron hydroxides	--	--	--	--	--
D17A	~32.0	10/22/1997	Consolidated, dense, dark grey shale and siltstone	Quartz (major), microcline, albite, montmorillonite (minor), with trace of gypsum, muscovite, (possible kaolinite or chlorite, clinochlore), dolomite	--	--	--	--	--
D17A	51.5	10/22/1997	Consolidated, dense, dark grey shale and siltstone	Quartz (major), dolomite (minor), with trace of microcline, albite, muscovite, montmorillonite, gypsum, possible kaolinite or chlorite and clinochlore	--	--	--	--	--
D25A	7.0	2/5/2002	Semi-consolidated to unconsolidated orange-brown sand or weathered sandstone	Quartz (major), microcline and albite (minor), with trace of muscovite, montmorillonite, possible kaolinite or chlorite, clinochlore	--	--	--	--	--
D29A	0 (surface)	3/6/1997	Consolidated, hard, light brown sandstone on top of field along road	Quartz and calcite (major), albite (minor), with a trace of microcline, muscovite	--	--	--	--	--
D31	1.4–2.7	5/4/1995	Unconsolidated, hard, dry balls of brown clay and clay-loam (loess) with 0.2- to 0.3-cm pods of anhedral white crystals; light brown silty loam to clay loam (loess)	White crystals identified as gypsum surrounded with a trace of quartz	--	--	--	--	--
D6-1	0.2–0.3	5/31/2005	Soil in valley area that has received biosolids applications, cultivation, and possibly grazing		--	--	--	--	1,000
D6-1	0.4–0.6	5/31/2005	Soil in valley area that has received biosolids applications, cultivation, and possibly grazing		--	--	--	--	1,700
DC-300	0.2–0.3	5/31/2005	Soil on south-facing hillslope that has received biosolids applications and cultivation		--	--	--	--	700
South-1	0.2–0.3	5/31/2005	Soil on lowland terrace that has received cultivation but no biosolids applications		--	--	--	--	900
South-2	0.1–0.2	5/31/2005	Soil on upland terrace that has had grazing but has not received biosolids applications or cultivation		--	--	--	--	1,100

¹Analyzed in 2005 by X-ray diffraction (Cullity and Stock, 2001) with and without Rietveld Method (Young, 1995).

²Analyses for “ammonia” quantify ammonia plus ammonium.

³Chemical analysis done in 2005.

⁴Chemical analysis done in 2002; mineralogic analysis done in 2005.

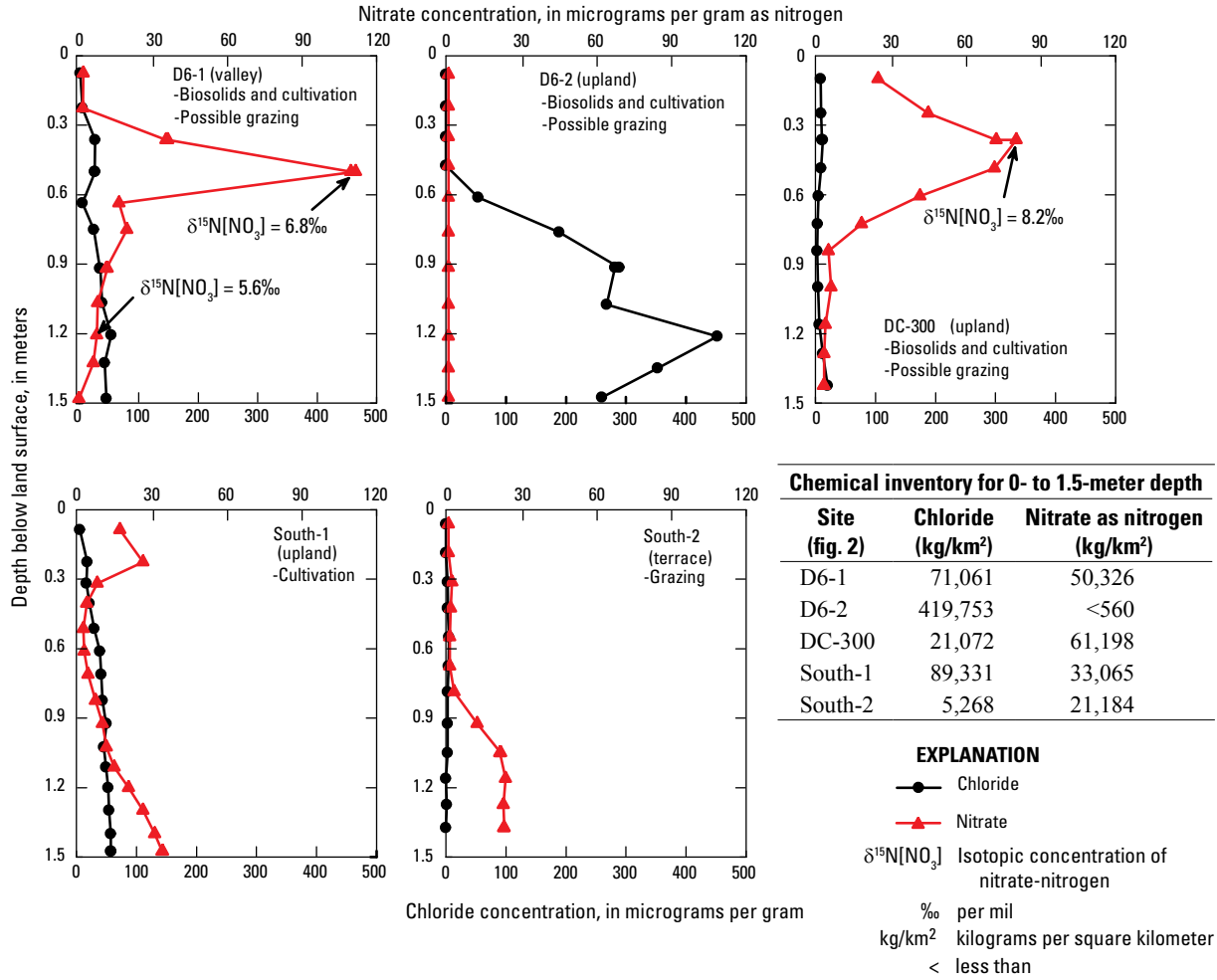


Figure 6. Concentrations of water-extractable chloride and nitrate in the upper 1.5 meters of the soil column at five sites with variable land-use histories, $\delta^{15}\text{N}[\text{NO}_3]$ values for selected samples, and table of chemical inventories of total mass of chloride and nitrate stored in the soil column.

Chemical and isotopic data collected from wells D5, D6, D10, and D32 in 2005 for this study are listed in table 5. Although nitrite concentrations were not measured in the 2005 samples, other measurements from the site in 2005 and from historical data (Stevens and others, 2003, table 14) indicate that nitrite probably represents less than 1% of the dissolved nitrite plus nitrate concentration in groundwater; therefore, dissolved nitrite plus nitrate in groundwater is referred to as nitrate in the remainder of this report. Nitrate concentrations for the 2005 samples ranged from a low of 4.91 mg-N/L in well D10 to a high of an estimated 31.5 mg-N/L in well D6. Nitrate concentration in the sample collected from well D5 in 2005 (6.40 mg-N/L) is not consistent with the apparent long-term trend of increasing nitrate concentrations in the well (fig. 3); the 2005 concentration was substantially less than that of a subsequent sample collected in late 2007 (fig. 3; Yager

and others, 2011, table 10). Nitrate concentrations in the samples collected from well D6 in 2005 and in late 2007 are consistent with the apparent long-term trend of increasing nitrate concentrations in the well (fig. 3). Nitrate concentration in the sample collected from well D10 in 2005 is consistent with the apparent long-term trend of irregularly increasing nitrate concentrations in the well (fig. 3); however, the 2005 concentration was substantially less than that of a subsequent sample collected in late 2007 (fig. 3; Yager and others, 2011, table 10). Nitrate concentration in the sample collected from well D32 in 2005 is consistent with the apparent long-term trend of increasing nitrate concentrations in the well observed for 1995 through 1998 (fig. 3); however, the 2005 concentration was substantially greater than that of a subsequent sample collected in late 2007 (fig. 3; Yager and others, 2011, table 10).

Table 5. Chemical data for groundwater from selected monitoring wells sampled in 2005.

[NWIS, U.S. Geological Survey National Water Information System database; m, meters; mg/L, milligrams per liter; --, not measured; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; $^{\circ}\text{C}$, degrees Celsius; mg-N/L, milligrams per liter as nitrogen; E, estimated by laboratory; <, less than; N_2 , nitrogen gas; Ar, argon; CH_4 , methane; nd, not determined; cc STP/L, cubic centimeters at standard temperature and pressure per liter; $\delta^{15}\text{N}[\text{NO}_3^-]$, the delta N-15 isotope composition of the nitrate nitrogen; ‰, per mil or parts per thousand; AIR, atmospheric N_2 ; $\delta^{18}\text{O}[\text{NO}_3^-]$, the delta O-18 isotope composition of the nitrate oxygen; VSMOW, Vienna Standard Mean Ocean Water; $\delta^{15}\text{N}[\text{N}_2]$, the delta N-15 isotope composition of the nitrogen gas]

	Well name				
	D5	D6	D6	D10	D32
NWIS station number ¹	19103515500	33103512300	33103512300	09103514600	09103513900
Screen interval, m below land surface	4.9 to 7.9	4.0 to 7.0	2.3 to 5.3	2.3 to 5.3	8.5 to 11.6
Sample date	5/31/2005	6/1/2005	7/13/2005	5/31/2005	6/1/2005
Depth to top of screen, m below water level	0.76	1.84	1.74	-0.46	0.27
Dissolved oxygen, mg/L	2.6	--	3.0	4.1	--
Field pH, standard units	7.2	7.0	7.0	7.2	6.9
Specific conductance, $\mu\text{S}/\text{cm}$ at 25 $^{\circ}\text{C}$	4,140	17,600	17,000	4,400	3,600
Ammonia plus organic nitrogen, dissolved, mg-N/L as N	0.20	E1.7	--	0.30	0.18
Ammonia, dissolved, mg-N/L	<0.040	0.067	--	<0.040	E0.029
Nitrite plus nitrate, dissolved, mg-N/L	6.40	E31.5	² E27	4.91	21.9
N_2 , mg/L	degassed	degassed	16.434	14.690	18.085
Ar, mg/L	degassed	degassed	0.5212	0.5487	0.6350
CH_4 , mg/L	degassed	degassed	<0.001	<0.001	<0.001
Recharge temperature, $^{\circ}\text{C}$	nd	nd	E15	E12	E8
Excess air, cc STP/L	nd	nd	1.0	0.7	2.5
Excess N_2 , mg-N/L	nd	nd	2.0	<0.5	<0.5
Measured $\delta^{15}\text{N}[\text{NO}_3^-]$, ‰ relative to AIR	15.5	--	10.1	8.5	9.6
Measured $\delta^{18}\text{O}[\text{NO}_3^-]$, ‰ relative to VSMOW	6.79	--	0.62	-0.94	-0.39
Measured $\delta^{15}\text{N}[\text{N}_2]$, ‰ relative to AIR	degassed	degassed	-0.29	0.84	0.44
Corrected ³ nitrate, mg-N/L	nd	nd	E29	4.91	21.9
Corrected ³ $\delta^{15}\text{N}[\text{NO}_3^-]$, ‰ relative to AIR	nd	nd	E8.9	8.5	9.6

¹Last 11 digits, only. First four digits are "3936" for each of these sites.

²Value is nitrate as nitrogen analyzed by ion chromatography (estimated because of chloride interference).

³Corrected for denitrification effects in the aquifer; these corrected values are graphed in figure 4.

Measured $\delta^{15}\text{N}[\text{NO}_3^-]$ values in water samples from the wells ranged from +8.5 to +15.5 per mil for samples collected in 2005 (table 5). The lowest $\delta^{15}\text{N}[\text{NO}_3^-]$ value was measured in the sample from well D10 (table 5). The highest $\delta^{15}\text{N}[\text{NO}_3^-]$ value was measured in the sample from well D5 (table 5).

Denitrification probably affected the nitrogen isotopic composition of nitrate in water from wells D5 and D6 more than it did nitrate in water from wells D10 and D32. The samples from wells D5 and D6 plot farther along isotope-fractionation trend lines characteristic of denitrification (Böttcher and others, 1990; Granger and others, 2004) than the samples from D10 and D32 (fig. 7). Analysis of the dissolved-gas data for wells D6, D10, and D32 also indicates that water

from wells D10 and D32 contained little or no excess N_2 from denitrification, whereas water from well D6 apparently contained a small amount of excess N_2 , about 2 mg-N/L (table 5). The nitrogen isotopic composition of nitrate in water from well D6 was corrected for denitrification effects using the chemical and isotopic data (Böhlke and others, 2002), resulting in a shift in the measured value from +10.1 to +8.9 per mil (table 5). The dissolved-gas sample from well D5 apparently was degassed (probably during sampling), so the measured nitrogen isotopic composition of nitrate in water from that well could not be corrected for denitrification effects. Thus, isotopic data from well D5 is not discussed further.

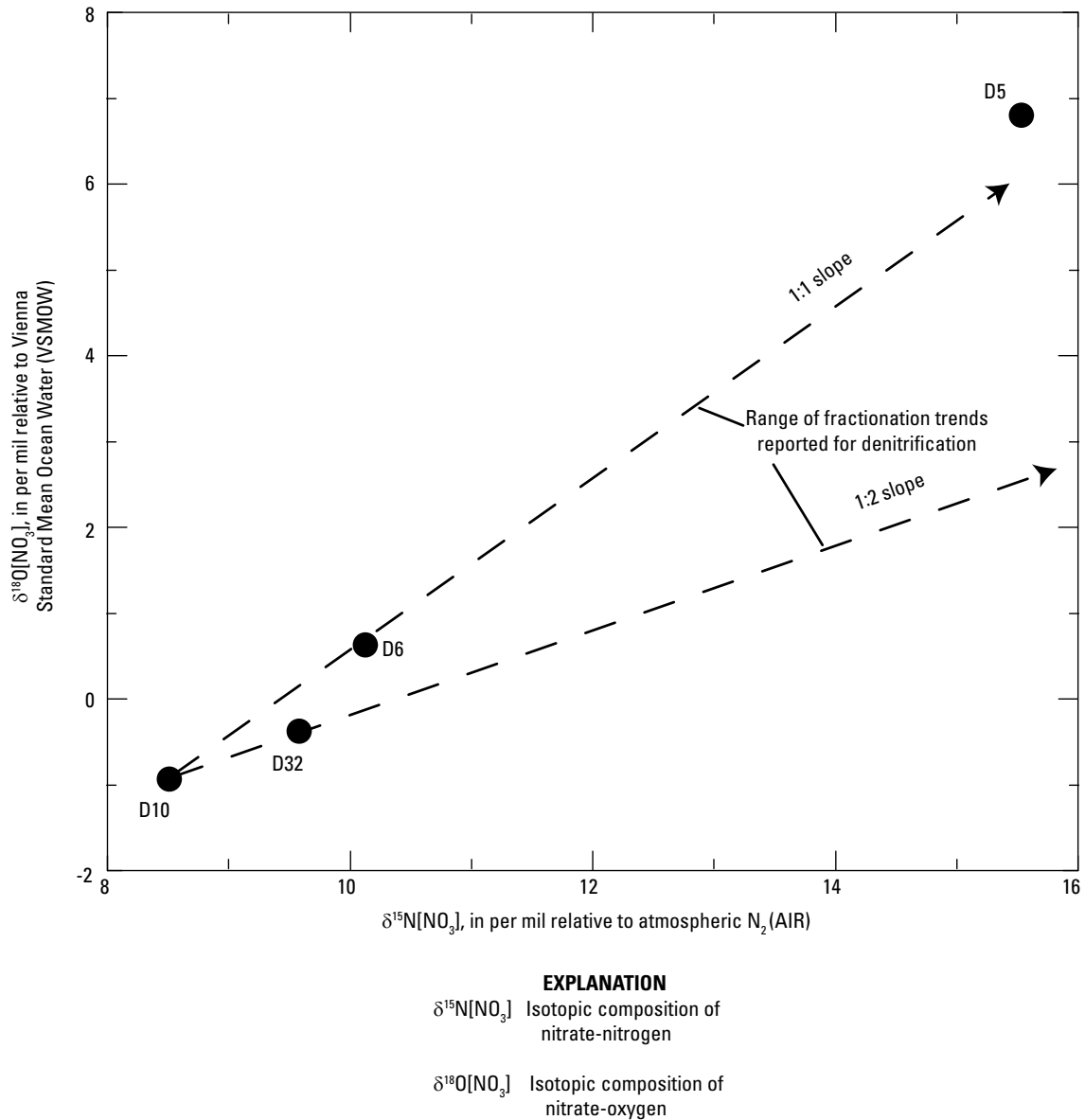


Figure 7. Measured values of $\delta^{15}\text{N}[\text{NO}_3]$ and $\delta^{18}\text{O}[\text{NO}_3]$ in water from the monitoring wells.

Preliminary Assessment of Sources of Nitrogen in the Groundwater

Various approaches provided insights into sources of nitrogen in the groundwater samples from 2005. Nitrogen isotopic composition of source materials was compared to that of the groundwater samples. Major-ion concentrations of the groundwater samples were evaluated for source information. Chloride/bromide mass ratios of source materials were evaluated for source information. Characteristics of water-extractable nitrate in soil also were evaluated for source information.

Nitrogen Isotopic Composition

Nitrate-nitrogen isotopic values for water samples from wells D6, D10, and D32 (fig. 4, table 5) were not similar to the isotopic values commonly observed for nitrate derived from inorganic fertilizers, atmospheric deposition, bedrock, or soil (fig. 4, table 4). Nitrate-nitrogen isotopic values for the groundwater samples were similar to the isotopic values commonly observed for nitrate derived from organic waste materials, such as animal manure and sewage (including biosolids) (fig. 4, table 4). Among the source materials considered in this study, however, weathered biosolids had the closest nitrogen isotopic values to those for nitrate in water from the

wells (fig. 4). The isotopic values for total nitrogen in the three biosolids samples analyzed for this study were somewhat smaller than the isotopic values for nitrate in the water from wells D6, D10, and D32. However, a nitrogen isotopic value of +9.6 per mil was reported for biosolids from Oregon (Buck, 2003), which is similar to the values for nitrate in water from the selected Deer Trail area wells.

The weathered biosolids had larger nitrogen isotopic values than the fresh biosolids (fig. 4), which probably reflects the preferential loss of ^{14}N during volatilization of ammonia, or other volatile nitrogen species, from the biosolids as they dried and weathered. As discussed previously, a substantial amount of nitrogen was lost from fresh biosolids when they were dried in the laboratory (tables 1 and 2). A similar loss of nitrogen can be observed in the nitrogen data from fresh and field-weathered biosolids (table 1). Thus, one possible explanation for the difference in isotopic values between nitrate in water samples from the wells and total nitrogen in biosolids, assuming biosolids were the source of that nitrate, could be that nitrate in water from the wells was derived from biosolids that were more highly weathered than those measured in this study.

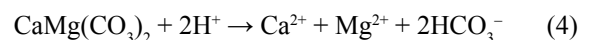
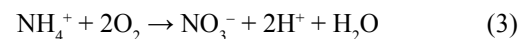
The isotopic values for total nitrogen in samples of animal manure, shale, and soil from this study were smaller than the isotopic values for total nitrogen in biosolids and for nitrate in water from the wells (fig. 4). Typically, the preferential loss of ^{14}N from animal manure as it weathers results in larger isotopic values for the nitrogen that still remains in the animal manure, as was observed with the biosolids samples, but the weathered animal-manure sample from this study actually had a smaller nitrogen isotopic value than the fresh animal-manure sample. The reason for this is unclear, but it could simply indicate that the fresh animal manure from which the weathered sample was derived had a smaller initial nitrogen isotopic value to begin with than the fresh animal-manure sample collected for this study. Nonetheless, nitrate derived from animal manure commonly has nitrogen isotopic values in the range of the values for nitrate in water samples from the wells, or higher (Gormly and Spalding, 1979). In contrast, nitrate derived from shale and soil commonly has nitrogen isotopic values smaller than what was measured in nitrate in water samples from the wells (McMahon and others, 1999; Kendall and Doctor, 2004; McMahon and Böhlke, 2006).

The isotopic data indicate that, of the source materials considered, biosolids and (or) animal manure were the most likely sources of nitrate in the wells at the time of sampling (2005) and that inorganic fertilizer, atmospheric deposition, and geologic materials were not substantial sources of nitrate in the wells in 2005. The large total nitrogen content of the biosolids and animal-manure samples (table 1) and biosolids leachates (table 2) also indicates that the biosolids and animal manure had potential to leach nitrogen and produce large dissolved nitrate concentrations in groundwater. The available data, however, cannot distinguish between biosolids or manure

as the dominant source of nitrate in water from well D6 because the nitrogen isotopic composition of the two materials is similar. Additional isotopic measurements of biosolids and groundwater nitrate could indicate whether those values change with time.

Major-Ion Concentrations

Major-ion concentrations sometimes are helpful in differentiating sources. Concentrations of several major ions in water from well D6 increased with time along with the nitrate concentrations. Concentrations of sodium, potassium, calcium, magnesium, sulfate, and bromide exhibited significant positive correlations with time. The correlations of sodium concentrations with time and sulfate concentrations with time were the strongest among the time correlations examined here (fig. 8). In figure 8, *p* values less than 0.05 indicate statistically significant correlations at the 95-percent confidence level, and the correlation coefficient (r^2 ; 0 to 1 for positive correlations) indicates the strength of the correlation (Helsel and Hirsch, 1992). Increases in concentrations of major ions in shallow groundwater under cropland have been reported in other studies (Böhlke, 2002; McMahon and others, 2007) and have been attributed to a combination of processes. Soil amendments or fertilizers such as calcium sulfate (gypsum), calcium magnesium carbonate (dolomite), and potassium chloride are applied in some cropland settings to improve soil properties, and dissolution of those chemicals in the soil zone can increase concentrations of major ions in recharge. It is unlikely that gypsum and dolomite were used at the Deer Trail site because the soils already contain those minerals (table 3). As discussed previously, it appears that potassium chloride also was not used to any substantial degree at the site. In fact, chloride concentrations in well D6 appear to have decreased slightly over time (fig. 8). Nitrogen in fresh biosolids and manure occurs primarily in reduced forms (table 1), but upon exposure to air those reduced forms of nitrogen can be oxidized to nitrate, thereby producing protons (acidity) that may react with and dissolve minerals in the soil:



The positive correlations of nitrate concentrations with time and major-ion concentrations with time for samples from well D6 are consistent with the interpretation based on isotope data that nitrate in water from well D6 was derived from biosolids, animal manure, or a combination of the two source materials. The major-ion data, however, could not be used to distinguish between biosolids or manure as the dominant source of nitrate in water from well D6 because the major-ion composition (as well as the isotopic composition) of the two materials is similar.

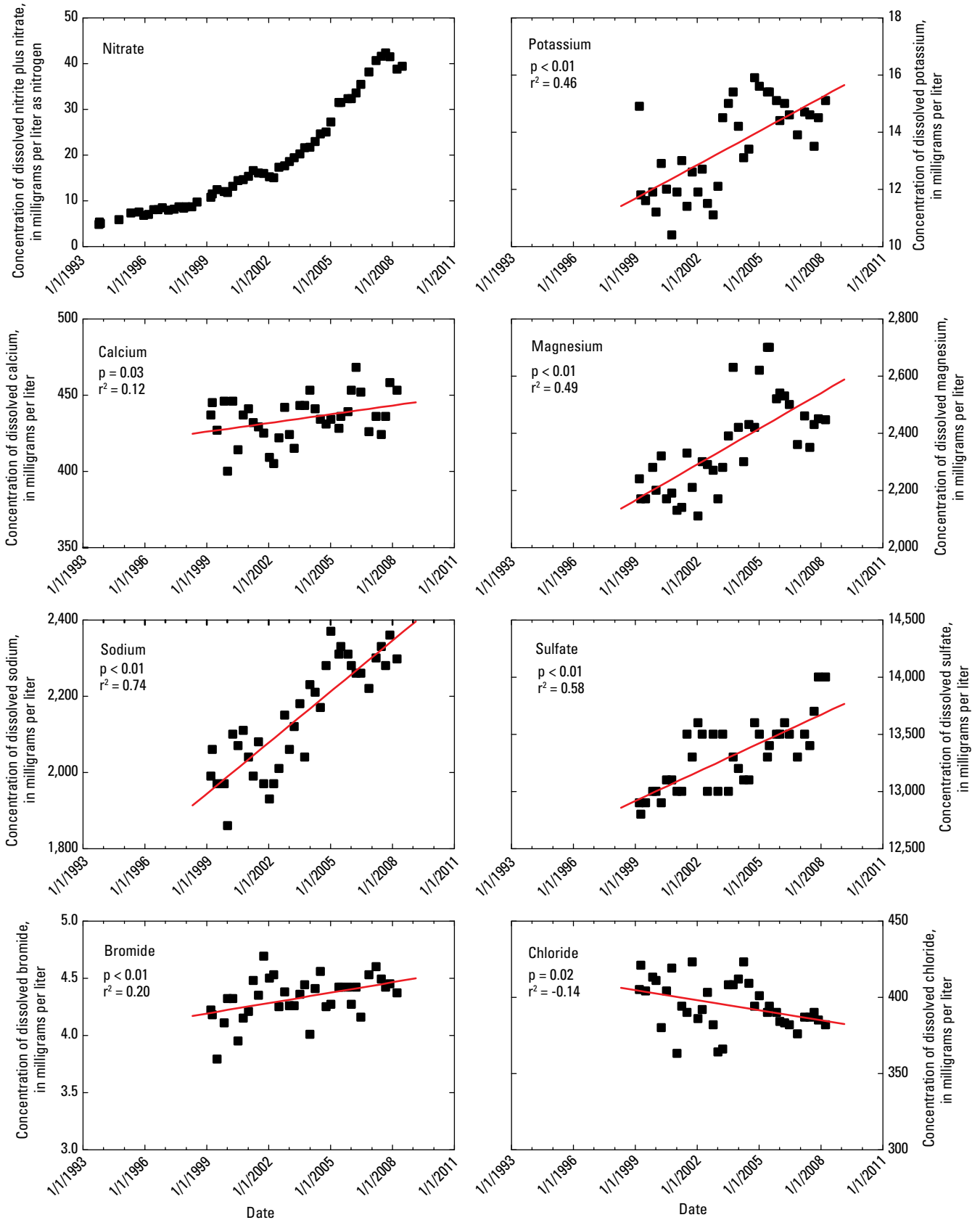


Figure 8. Concentrations of nitrate and selected major ions in water from well D6 with solid lines for linear regressions (regression statistics are shown in each plot).

Chloride/Bromide Mass Ratios

Chloride/bromide mass ratios can be used to assess sources of chloride and groundwater contamination (Davis and others, 1998). Chloride/bromide mass ratios in water from the wells near Deer Trail were substantially smaller than the ratios measured in leachate from fresh biosolids and in some domestic sewage effluent and animal manure (Davis and others, 1998; Panno and others, 2006; Mullaney and others, 2009) but were similar to chloride/bromide mass ratios reported by Hudak (2003) and Katz and others (2011) for some animal wastes and atmospheric deposition (fig. 9). These data imply that atmospheric deposition and animal manure may be sources of the nitrate in groundwater from well D6 and that biosolids or other sewage materials cannot have been an important nitrate source. However, a large range of chloride/bromide mass ratios are reported in the literature for animal wastes (Katz and others, 2011), and chloride/bromide ratio

data for animal waste at the Deer Trail site are not available, so chloride/bromide mass ratios are not definitive in differentiating animal-waste sources of chloride or nitrate for this site. It is also possible that the large baseline concentrations of chloride and bromide in the groundwater from this site (fig. 8) overwhelmed any contribution of those anions from biosolids or other sewage, thus reducing the sensitivity of the ratio method for detecting contributions from those sources at this site. It is unknown whether the chloride/bromide ratio of biosolids changes as biosolids weather in the field. This is important to know because biosolids were not applied on a regular basis in the vicinity of well D6, which means that the chloride/bromide ratio of weathered biosolids could be more relevant than the ratio for fresh biosolids in characterizing biosolids-affected recharge. A reduction in chloride/bromide ratios in biosolids during weathering would bring these ratios in closer agreement with the ratios measured in water from the wells.

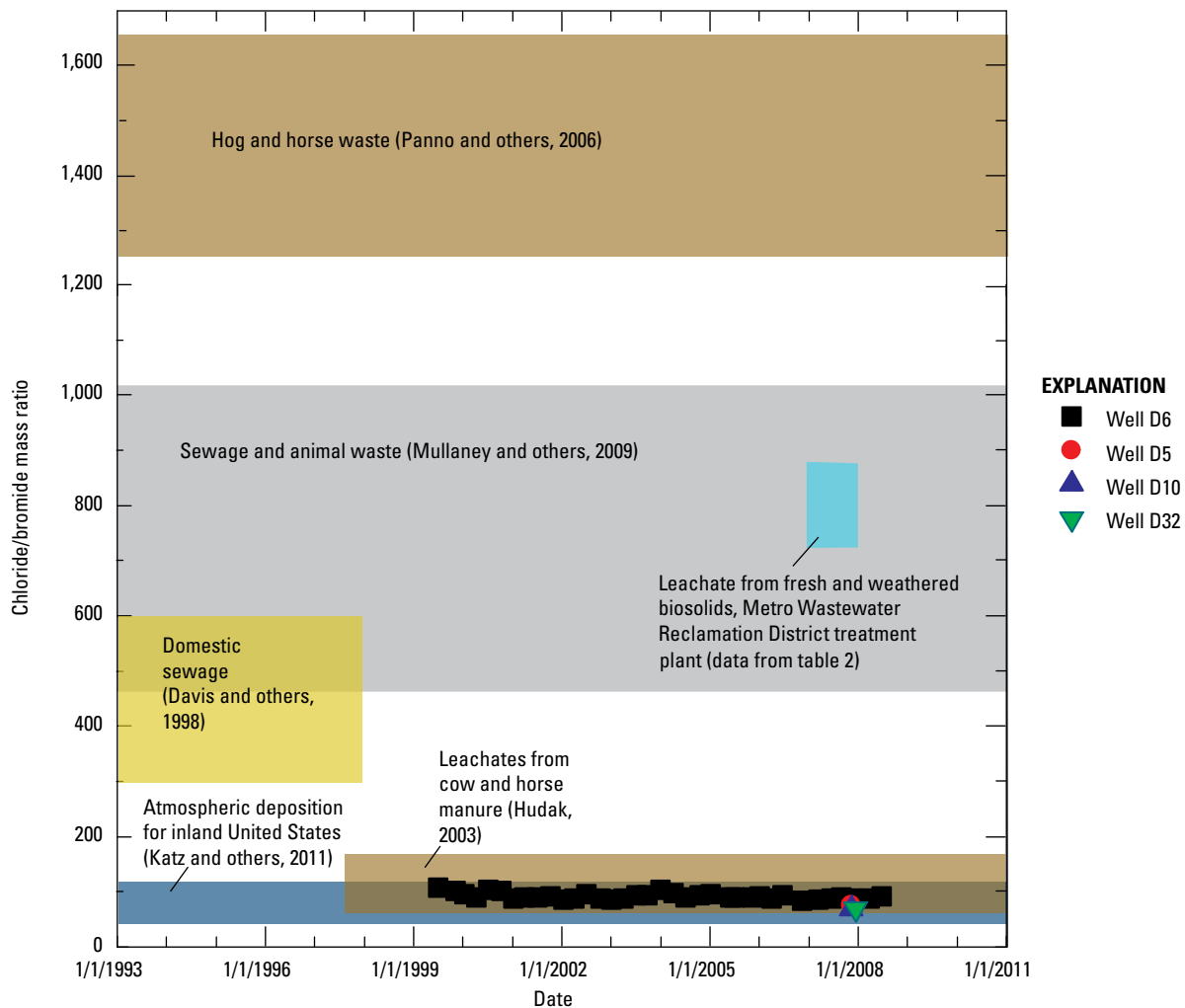


Figure 9. Chloride/bromide mass ratios in water from selected monitoring wells near Deer Trail as a function of time and the ratios measured in domestic sewage, leachate from biosolids, animal waste, and atmospheric deposition.

A reduction in chloride/bromide ratios of biosolids during weathering would mean that chloride is preferentially lost during that process. There is some evidence from the literature that chloride is preferentially lost relative to bromide from organic matter as weathering proceeds. Shotyk (1997) reported that the percentage of bromide retained in Scottish peat bogs was 50 to 60 times greater than that of chloride. Similarly, Biester and others (2004) reported that 7.5% to 50% of the bromine in Chilean peat bogs was retained compared with 0.2% to 2% of the chlorine. The organic matter in biosolids may be similar to that of peat bogs with respect to retention of bromide. Although the chloride/bromide ratio of weathered animal manure in the study area is not known, it is possible that the organic matter in animal manure could retain more bromide than chloride as was the case for the peat bogs. Thus, without additional data, the chloride/bromide mass ratios do not necessarily support or refute the hypothesis that biosolids and (or) animal manure were the primary sources of nitrate in water from the study-area wells in 2005.

Water-Extractable Nitrate in Soil

Characteristics of water-extractable nitrate in soil can provide information about likely nitrogen sources. Concentrations of water-extractable nitrate in the soil indicate that biosolids could be an important source of nitrate in recharge at well D6. As discussed previously, the soil samples with the largest concentrations of water-extractable nitrate were from the two sites where biosolids had been applied (D6-1 and DC-300) (fig. 6). Site D6-2 was not included in this group, even though biosolids were applied there, because it appears that very little water movement through the soil zone occurred at that site (fig. 6). Sites D6-1 and DC-300 also were cultivated and may have been grazed at times, but they still had much larger soil nitrate inventories than the two sites that were only cultivated (South-1) or grazed (South-2) (fig. 6). Values of $\delta^{15}\text{N}[\text{NO}_3]$ for the largest concentrations of water-extractable nitrate at sites D6-1 and DC-300 were +6.8 and +8.2 per mil, respectively (fig. 6), which are similar to the values for nitrate in water from wells D6, D10, and D32 (fig. 4). The concentrations of water-extractable nitrate were used to evaluate nitrogen inventories in the soil (fig. 6), which can provide additional information about likely nitrogen sources. The nitrogen inventories in the soil beneath biosolids-application areas (fig. 6) and the nitrogen-input estimates for the study area (table 4) both support the comparisons of isotopic composition (fig. 4), which indicate that some type of human waste (such as biosolids) and (or) animal manure was the source of nitrate in groundwater sampled from well D6 in 2005. Measurements of water-extractable nitrate in soil profiles at more sites would help to determine how representative the data in figure 6 are with respect to the larger study area.

Of the various methods used to evaluate nitrate sources in the study area, isotopic composition is better established and

better constrained by end-member data than other methods like chloride/bromide mass ratios. Therefore, isotopic composition (which indicates that inorganic fertilizer, atmospheric deposition, and geologic materials were not the source of nitrate at well D6) was given more weight than chloride/bromide mass ratios (which indicate that atmospheric deposition or animal manure was the source of nitrate at well D6). The nitrogen-load estimates considered with the nitrogen isotopic data and the soil-nitrogen inventories indicate that biosolids applications likely are a major source of nitrogen to the shallow groundwater in the vicinity of well D6 (table 4). The isotopic and other data collected for this study appear to be useful for identifying the likely sources of nitrate in groundwater from well D6 (biosolids and (or) animal manure), but the data only represent a single point in time relative to the 15-year apparent trend of increasing nitrate concentrations (fig. 3). To reduce uncertainty in identifying the dominant source of nitrate in groundwater from well D6, additional characterization of the nitrogen isotopic composition and chloride/bromide ratios of fresh and weathered biosolids and manure, as well as additional soil-nitrogen inventories, would be useful.

Summary

Biosolids from municipal wastewater treatment in Denver, Colo., have been applied intermittently as a fertilizer and soil amendment to some nonirrigated farmland near Deer Trail, Colo., since 1993. Biosolids applications to the area have been permitted by the State of Colorado and documented by the wastewater treatment plant.

Concentrations of dissolved nitrate have increased over time in some of the shallow monitoring wells at the biosolids-application area. The increase in nitrate concentration in samples from one well in particular, well D6, was of interest to the Metro Wastewater Reclamation District (Metro District) because (1) the well was located near a property boundary, (2) measured nitrate concentrations were largest at this location, and (3) nitrate concentration increased from about 5 milligrams per liter as nitrogen (mg-N/L) in 1993 before biosolids were applied to about 40 mg-N/L in 2007. Nitrate concentrations also increased in water from three other shallow monitoring wells in the drainage area upgradient from D6, although to a lesser extent. The gradual increase in nitrate concentration in water from well D6 during a period of intermittent biosolids applications led to concerns that biosolids were causing the nitrate increase. However, nitrate concentrations were at least 5 mg-N/L in some of these monitoring wells before biosolids applications to the area began, which indicates that biosolids applications were not the only source of nitrogen to groundwater in the area.

Biosolids, animal manure, inorganic fertilizer, atmospheric deposition, and geologic materials (bedrock and soil) are possible nitrogen sources in the area. Because of the multiple possible sources of nitrogen at the Metro District

properties, the USGS began a preliminary assessment of sources of nitrogen in shallow groundwater at part of the biosolids-application area in 2005 in cooperation with the Metro District. The Metro District properties near Deer Trail and the surrounding land constitute the study area. Biosolids from the Metro District plant in Denver and biosolids, cow manure, geologic materials (bedrock and soil), and groundwater from the study area were sampled to measure nitrogen content and nitrogen isotopic compositions of nitrate or total nitrogen. Biosolids also were leached, and the leachates were analyzed for nitrogen content and other concentrations. Geologic materials from the study area also were sampled to determine mineralogy. Estimates of nitrogen contributed from inorganic fertilizer and atmospheric deposition were calculated from other published reports.

The geology of the study area consists of interbedded shale, siltstone, and sandstone, which is overlain in some areas by clay, windblown silt and sand, or alluvial sand and gravel. The primary water-supply aquifer is the Laramie–Fox Hills aquifer, and multiple alluvial aquifers are associated with the surficial drainage network in the study area.

Land use in the study area was rangeland or cropland and pasture. Cattle and sheep were the primary domesticated animals grazing the area, and wildlife also were present. No concentrated animal-feeding operations were located on or near the Metro District properties during 1993 through 2005; no evidence of large confined or unconfined animal feeding or dairy operations has been produced for the period before 1993. Wheat was the primary crop. Inorganic fertilizer has not been used in the area since 1993; no documentation of type or quantity of inorganic fertilizer use in the area has been produced for the period before 1993. Biosolids were applied intermittently in the surficial drainage area that contained well D6, but this drainage area is not known to contain any current or former pit toilets or septic tanks.

Fresh biosolids from the Metro District contained as much as 71,000 milligrams per kilogram as nitrogen (mg-N/kg), primarily in the reduced forms, organic nitrogen and ammonia or ammonium. A fresh biosolids sample from the Metro District had a higher nitrogen content and a lower nitrogen isotopic composition than the corresponding weathered biosolids sample from this study area. The leachate data indicate that nitrogen was lost from the fresh biosolids during the drying process, which could reflect the loss of volatile forms of reduced nitrogen such as ammonia.

Manure freshly deposited on the land surface can contain less nitrogen (less than 2,000 mg-N/kg) than fresh biosolids, however manure can be concentrated in a single location whereas a small volume of biosolids is distributed over a large area. The fresh cow-manure sample from the study area had a higher nitrogen content and a higher nitrogen isotopic composition than the corresponding weathered cow-manure sample from this study area.

Inorganic fertilizers can contain as much as 800,000 mg-N/kg. No inorganic fertilizers reportedly were used at the Metro District properties near Deer Trail during 1993 through

2005, but this type of fertilizer could have been used on the properties before the Metro District acquired the properties. The nitrogen isotopic composition of inorganic fertilizers generally is characterized by low isotopic values.

Atmospheric deposition in eastern Colorado can contain about 0.7 mg-N/L in precipitation, but the nitrogen content of atmospheric deposition varies. The nitrogen isotopic composition of atmospheric deposition generally is characterized by low isotopic values.

Geologic materials (both bedrock and soil) of the study area contained nitrogen. Nitrogen content was largest in shale samples (as much as 2,344 mg-N/kg). Soil that received biosolids applications contained as much as 1,700 mg-N/kg nitrogen. Soil that did not receive biosolids applications contained as much as 1,100 mg-N/kg nitrogen. The nitrogen isotopic composition of the geologic materials from the study area was lower than that measured for biosolids or animal manure.

The nitrogen information from the study indicates that each of the sources contain sufficient nitrogen to potentially affect groundwater nitrate concentrations. Natural processes can transform the nitrogen in any of the sources to nitrate in the groundwater. Nitrogen information for each source was used to estimate nitrogen loads to the surficial drainage area contributing to the well D6 location. Estimates calculated from Metro District application records indicate that the load of biosolids-applied nitrogen did not exceed 72,440 kilograms as nitrogen (kg-N) for the period 1993 through 2005. Calculated estimates indicate that the nitrogen load from animal manure to the drainage area contributing to the D6 location likely did not exceed 17,000 kg-N for the period 1993 through 2005. The load of inorganic-fertilizer nitrogen to the drainage area contributing to the D6 location is estimated as 0 kg-N for the period 1993 through 2005. Calculated estimates indicate that the load of atmospheric-deposition nitrogen likely did not exceed 11,000 kg-N for the period 1993 through 2005. Calculated estimates indicate that the nitrogen load from all geologic materials likely did not exceed 0.21 kg-N for the period 1993 through 2005, which is much less than the estimated nitrogen load from biosolids, animal manure, and atmospheric deposition for the same period. The load estimates indicate that animal manure, inorganic fertilizer, or atmospheric deposition could have contributed the largest nitrogen load to the study area in the 13 years before biosolids applications began, but biosolids likely contributed the largest nitrogen load to the study area in the 13 years after biosolids applications began.

Concentrations of dissolved nitrite plus nitrate increased fairly steadily in samples from well D6 after biosolids applications began. Concentrations of dissolved nitrite plus nitrate also increased at three other shallow monitoring wells in the vicinity. Water-quality data indicate that (1) groundwater in the study area had a nitrogen source before biosolids applications started, and (2) concentration patterns for dissolved nitrite plus nitrate in groundwater were diverse and highly variable throughout the study area during 1993–2005.

Various approaches provided insights into sources of nitrate in the groundwater samples from 2005. The isotopic

data indicate that, of the source materials considered, biosolids and animal manure were the most likely sources of nitrate in the wells at the time of sampling (2005) and that inorganic fertilizer, atmospheric deposition, and geologic materials were not substantial sources of nitrate in the wells in 2005. The large total nitrogen content of the biosolids and animal-manure samples and biosolids leachates also indicates that the biosolids and animal manure had potential to leach nitrogen and produce large dissolved nitrate concentrations in groundwater. The available data, however, could not be used to distinguish between biosolids or manure as the dominant source of nitrate in water from well D6 because the nitrogen isotopic composition of the two materials is similar. Major-ion data also could not be used to distinguish between biosolids or manure as the dominant source of nitrate in water from well D6 because the major-ion composition (as well as the isotopic composition) of the two materials is similar. Without additional data, chloride/bromide mass ratios do not necessarily support or refute the hypothesis that biosolids and (or) animal manure were the primary sources of nitrate in water from the study-area wells in 2005. Concentrations of water-extractable nitrate in the soil indicate that biosolids could be an important source of nitrate in recharge at well D6. Nitrogen inventories in the soil beneath biosolids-application areas and the nitrogen-input estimates for the study area both support the comparisons of isotopic composition, which indicate that some type of human waste (such as biosolids) and (or) animal manure was the source of nitrate in groundwater sampled from well D6 in 2005. The nitrogen-load estimates considered with the nitrogen isotopic data and the soil-nitrogen inventories indicate that biosolids applications likely are a major source of nitrogen to the shallow groundwater at these monitoring wells. To reduce uncertainty in identifying the dominant source of nitrate in groundwater from well D6, additional characterization of the nitrogen isotopic composition and chloride/bromide ratios of fresh and weathered biosolids and manure, as well as additional soil-nitrogen inventories, would be useful.

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