NITRATE IN RAPID CITY'S WATER SUPPLY

Perry H. Rahn
Department of Geology & Geological Engineering
South Dakota School of Mines & Technology
Rapid City, SD 57701

ABSTRACT

Nitrate concentrations are increasing in Rapid City's municipal wells. Wells #5, #6, #8, #9, #10, and #11 were drilled to the Madison Limestone in 1991-92, and yearly samples for 1993-2005 show nitrate (as nitrogen) concentration in these wells fairly consistently increasing from roughly 0.15 to 0.35 mg/L. Well #8 is farthest from the Madison outcrops and has the lowest concentration. The nitrate concentration is still below the EPA drinking water limit of 10 mg/L. Nevertheless, the increasing concentration is disconcerting because it is clearly anthropogenic but its cause is not clear.

Meadowbrook Gallery and Girl Scout Gallery obtain water from alluvium, and by induced infiltration from Rapid Creek. These two water sources show slightly declining nitrate concentrations, roughly from about 1.3 mg/L in 1993 to 1.0 mg/L in 2005. These relatively high values probably reflect fertilizers used in the Meadowbrook golf course and other places and/or high nitrate in Rapid Creek.

Jackson Spring shows nitrate concentration increasing from roughly 0.25 to 0.35 mg/L. This water originates as part of the Jackson Spring/Cleghorn Spring complex; the nitrate probably reflects the general composition of the ground water in the Madison aquifer as well as Rapid Creek.

The nitrate in the Madison wells and Jackson Spring could come from a number of sources: (1) Streams recharging the Madison aquifer at the sinkhole "loss zones" along Rapid, Boxelder, and Spring creeks. (2) On-site wastewater systems upgradient from the city wells. More than 1,000 upgradient on-site wastewater systems exist within three miles of the city wells. (3) Fertilizers from home sites and/or agricultural areas. Commercial agriculture is probably not the main reason for increasing nitrate in the city wells because there are no feedlots and practically no farmlands (where fertilizers would be used) on the recharge areas of the Madison aquifer. (4) Explosives used for mining. This is probably not the cause of nitrate in Rapid City's water supply.

Keywords

Nitrate, Madison Limestone, septic tanks, Rapid City water supply, ground-water recharge

NITRATE IN KARST TERRAINS

Although igneous rocks may contain small amounts of soluble nitrate minerals, most nitrate found in the nation's ground water comes from organic sources or agricultural chemicals (Hitt and Nolan, 2005). High nitrate problems are typically associated with excessive applications of nitrate fertilizer, feedlots, or runoff from barnyards. Organic materials also release nitrate by bacterial decomposition. Nitrates near the surface can be leached by percolating water and eventually reach ground water (Davis and DeWiest, 1966). Nitrate contamination of karstic aquifer systems from agricultural sources has been documented at numerous sites (Katz et al., 2005, and references contained therein). For example, there has been a steady increase in nitrate concentration in the past 40 years in Fannin Springs, northern Florida. The Upper Floridan aquifer consists of Eocene/Oligocene carbonates, and nitrate (as nitrogen) concentration, up to 4.7 mg/L, originates from inorganic sources (fertilizers) as well as organic (manure spreading and waste disposal). Fertilizers are applied at an average rate of 19 kg/ha-year based on 50% agricultural use of the Fannin Springs basin. Solution-enhanced conduits occur in the Biscayne aquifer, a karst aquifer supplying water for Miami; the municipal well field, the largest in Florida, is near the Everglades wetland area. This karst area has also been studied for pathogen contamination including the presence of *Cryptosporidium parvum* (Renken et al., 2005).Anthropogenic (man-made) nutrient sources and resulting eutrophication of Florida's waterways result from elevated nitrate. According to Bacchus and Barile (2005) invasive alien species include aquatic plants such as water hyacinth and cyanobacteria (blue-green algae); these plants grow vigorously if stimulated by nitrate. Nitrate components were indentified using nitrogen isotopes ($\delta^{15}N$), and originate from citrus groves, industrial dairies (manure from animal wastes), municipal effluent spray, and leachate from septic tank drainfields.

NITRATE IN SOUTH DAKOTA WATER

Typical nitrate (as nitrogen) concentration in municipal sewage ranges from 0-10 mg/L, whereas septic tank system concentration ranges from 0-50 mg/L, and barnyard/feedlot concentrations range from 0-200 mg/L (Meyer, 2000). In South Dakota, Meyer (1987) documented nitrate composition in South Dakota. Sources of nitrate include fertilizers, feedlots, landfills, domestic septic systems, and mining. Meyer found that for 1,037 private wells in the Big Sioux River basin, 284 wells had $N0_3$-N above the 10 mg/L drinking water standard. He estimated that, for the State as a whole, several thousand private wells are probably above this standard. Fifty cases of *methemoglobinemia* have been noted. Water containing more than 10 mg/L has been linked to *methemoglobinemia* in infants, a condition in which the blood is deprived of oxygen and the skin turns blue. In South Dakota one fatality is known (Jeanne Goodman, SD Department of Environment and Natural Resources, 2005, pers. comm.).

In the Black Hills, high nitrate is typically associated with domestic waste. Coker (1981) reported up to 19.3 mg/L nitrate (as nitrogen) in shallow alluvial wells in Rapid Valley, downgradient from Rapid City. On-site wastewater systems were responsible for the high nitrates as well as fecal and coliform bacteria. Musa (1984) found high nitrate and other contaminants in alluvial deposits in the eastern part of Rapid City. Hafi (1984) modeled high nitrate associated with domestic waste (on-site wastewater systems) in the flood plain area below Rapid City. A high nitrate (as nitrogen) concentration, 13 mg/L, was found in alluvium under the campus of SDSM&T (Rahn and Davis, 1986); this high value is probably the result of fertilizers used at the campus of South Dakota School of Mines and Technology, but also could include nitrate contributions from downtown Rapid City, which at one time had no municipal sewer system. Davis (1979) found coliform and fecal bacteria associated with domestic sewage in the Belle Fourche infiltration galleries along Spearfish Creek. Johnson (1975) determined nitrate concentration in shallow wells in Keystone; many of the private wells had 10 to 30 mg/L nitrate (as nitrogen), most likely due to private on-site wastewater systems in operation at the time.

Schwickerath (2004) studied the Spring Creek watershed above Sheridan Lake. He reported fecal bacteria exceeded water quality criteria for immersive recreation (swimming). Nitrate concentrations up to 2.8 mg/L occurred in Palmer Gulch, a tributary to Spring Creek.

Sawyer (in prep.) studied bacteria and nitrate in ground and surface waters at various Black Hills locations. He found that Boxelder Creek at Norris Peak Road generally had less than 0.2 mg/L nitrate (as nitrogen). Rapid Creek in Dark Canyon had 0.1 or less mg/L. Spring Creek at the Stratobowl ranged from 0.2 to less than 0.1 mg/L. A well at Rocky Knolls golf course in Custer had high nitrate (4.2 mg/L). Observation wells below the Hill City sewage lagoons were typically 1 mg/L, but one observation well had 10.1 mg/L. Bear Butte Creek near Galena had 4.8 mg/L, possibly due to mining activities on this watershed. Downstream, Sturgis well #2 had 1.2 mg/L, and Bear Butte Creek at Sturgis had concentrations ranging from approximately 2.6 to 3.9 mg/L (Williamson, 2000).

Driscoll et al. (1996) showed two samples of Spring Creek above Mitchell Lake had 0.100 and 0.110 mg/L nitrogen (NO_2 + NO_3). Two samples of Rapid Creek above Victoria Lake had 0.15 and less than 0.05 mg/L, but below Farmingdale reached 3.40 and 0.75 mg/L. They found the highest nitrate in the Black Hills, 4.10 and 9.30 mg/L, to be from Annie Creek near Lead; this is a recently active gold mine area. Carter et al. (2002) reported the elevated nitrate at Annie Creek is caused by a breakdown of blasting agents and cyanide. Heap-leaching at surface gold mines generates nitrate in the leachate from the spent ore (Davis et al., 1996).

Driscoll et al. (2002) showed a median value of nitrate + nitrite nitrogen in the Madison Limestone is less than 1 mg/L.

RAPID CITY WATER SUPPLY

Long and Putnam (2002) described the hydrogeology of the western part of Rapid City, and included an analysis of the ground-water flow patterns in the bedrock aquifers utilized in Rapid City's water supply.

Figure 1 is a map of the western part of Rapid City showing the location of the primary municipal water supply consisting of nine wells, two infiltration galleries and one spring. In the summer, when demand is great, water is also obtained directly from Rapid Creek.

The nine wells include three older wells in the Minnelusa Formation (#1, #3, and #4), and six newer wells (#5, #6, #8, #9, #10, and #11) in the Madison Limestone. Table 1 shows the dates of construction, the total depths, and approximate pumping rates.

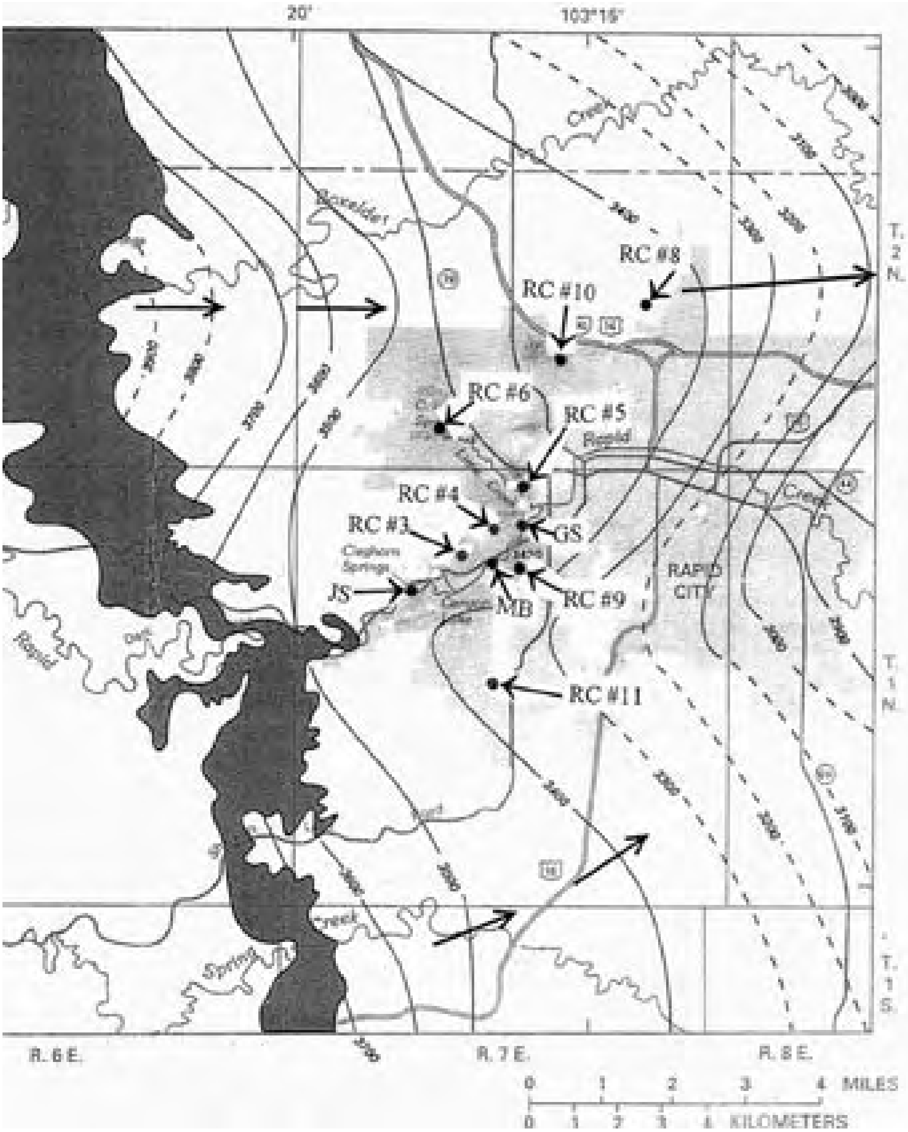

Figure 1. Map of Rapid City showing water supply sources. Modified from Greene (1999) and Anderson et al. (1999). The Madison Limestone is highlighted; its potentiometric surface (feet above sea level) and general ground water flow direction is shown. MB = Meadowbrook gallery. GS = Girl Scout gallery. JS = Jackson Spring.

Table 1. Nitrogen concentration (mg/L) in Rapid City water sources. Data shows "Nitrogen (Nitrate as N)" concentration for annual collection dates: from 1993 to 1996 by Maxim Labs and from 1997 to 2005 by Energy Labs. NA indicates no water sample was taken. [Note: the EPA maximum recommended allowable limit for drinking water is 10 mg/L nitrogen.] The discharge (Q) refers to average withdrawals from 1988 to 1997 (from Long and Putnam, 2002).

	7/12	8/5	12/5	8/14	8/18	8/25	8/13	7/17	8/7	6/25	8/15	6/24	8/3
	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005
Jackson Springs(1)	0.14	0.19	0.28	0.4	0.36	0.33	0.35	0.33	0.27	0.4	0.36	0.34	0.31
Meadowbrook(2)	1.20	0.74	1.52	1.4	2.02	0.85	1.25	NA	1.07	0.6	0.93	1.0	0.83
Girl Scouts(3)	0.68	0.74	1.16	1.2	1.40	0.77	1.64	1.07	0.92	0.9	0.72	0.63	0.64
Well #1(4)	0.16	0.30	NA	NA	NA	0.27	0.34	0.27	0.24	0.3	0.35	0.33	0.31
Well #3(5)	NA	NA	NA	NA	NA	0.28	0.28	NA	NA	NA	NA	NA	NA
Well #4(6)	0.58	NA	0.42	0.5	0.44	0.51	0.43	0.42	0.42	0.5	0.56	0.60	0.53
Well #5(7)	NA	NA	NA	0.2	0.15	0.19	0.2	0.20	0.17	0.2	0.30	0.28	0.28
Well #6(8)	0.14	0.22	0.26	0.2	0.26	0.25	0.27	0.23	0.21	0.2	0.32	0.29	0.28
Well #8(9)	<0.10	0.13	0.14	0.1	0.10	0.15	0.15	0.17	0.14	0.2	0.27	0.24	0.23
Well #9(10)	0.25	0.26	0.27	0.3	0.28	0.36	0.38	0.31	0.32	0.4	0.42	0.40	0.38
Well #10(11)	0.12	0.21	0.21	0.2	0.19	0.26	0.28	0.26	0.22	0.3	0.33	0.31	0.30
Well #11(12)	NA	0.26	0.25	0.3	0.27	0.32	0.33	0.26	0.27	0.3	0.39	0.36	0.39

(1) Jackson Springs has a 22 ft deep "spring box". Built in 1943. Water source is alluvium, Minnelusa Formation and Madison Limestone.
(2) Meadowbrook is a 20 ft deep infiltration gallery. Built in 1950. Water source is alluvium.
(3) Girl Scouts is a 20 ft deep infiltration gallery. Built in 1960. Water source is alluvium.
(4) Well #1 is 1,460 ft deep. Drilled in 1933. Q = 0.13 cfs. Water source is Minnelusa Formation, Madison Limestone, and Deadwood Formation.
(5) Well #3 is 902 ft deep. Drilled in 1935. Q = 0.22 cfs. Water source is Minnelusa Formation, and possibly Madison Limestone.
(6) Well #4 is 1,080 ft deep. Drilled in 1938. Q = 0.70 cfs. Water source is Minnelusa Formation.
(7) Well #5 is 1,272 ft deep. Drilled in 1991.Q = 0.77 cfs. Water source is Madison Limestone.
(8) Well #6 is 1,300 ft deep. Drilled in 1991. Q = 0.32 cfs. Water source is Madison Limestone.
(9) Well #8 is 2,680 ft deep. Drilled in 1991. Q = 0.39 cfs. Water source is Madison Limestone.
(10) Well #9 is 1,051 ft deep. Drilled in 1991.Q = 1.16 cfs. Water source is Madison Limestone.
(11) Well #10 is 1,790 ft deep. Drilled in 1992. Q = 0.91 cfs. Water source is Madison Limestone.
(12) Well #11 is 1,280 ft deep. Drilled in 1992. Q = 0.15 cfs. Water source is Madison Limestone.

The Meadowbrook and Girl Scout galleries consist of collection pipes laid horizontally into the alluvium along Rapid Creek. Most of this water is obtained by induced infiltration from Rapid Creek, although some is derived from ground water flowing downvalley through the alluvium.

Jackson Spring is part of the "Jackson-Cleghorn complex" (Anderson et al., 1999). Ground water discharges into Jackson Spring and nearby Cleghorn Spring, emanating from the Madison Limestone via a breccia pipe extending through the Minnelusa Formation (Long and Putnam, 2002). Jackson Spring is along the bank of Rapid Creek; a pump installed into the spring also induces infiltration from Rapid Creek.

NITRATE DATA

Nitrate data (Table 1) are collected annually for all the Rapid City water sources. Complete water chemistry analyses including radiological data are collected less frequently.

Figure 2 is a graphical plot of the nitrate concentration for the six Madison wells. The rising trends from 1993 to 2005 in all the wells are clearly evident. A best-fit linear line is shown for each well, using an EXCEL spreadsheet. The coefficients of determination (R^2) are all high, indicating a good correlation.

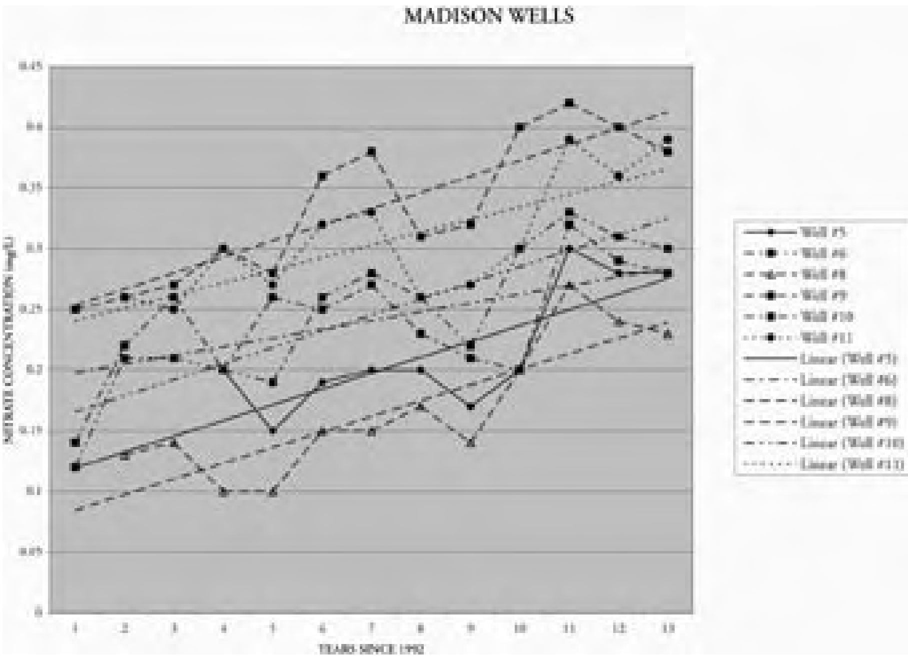

Figure 2. Nitrate plots for Rapid City's six Madison wells.

POSSIBLE SOURCES OF NITRATE

The increasing nitrate concentration in Rapid City's wells is believed to be anthropogenic, i.e., caused by man's influence on the hydrologic regime. There are many possible causes, including mining, agriculture, domestic waste, and lawn fertilizers.

Mining impacts in the northern Black Hills have been shown to cause increased nitrate. There are no active mines in the three watersheds contributing to the Rapid City water supply; however, in the western part of Rapid City there are three active quarries in the Minnekahta Limestone. The rock is used for road base and for the manufacture of cement. The 100 ft thick Opeche Formation underlies the Minnekahta Limestone and probably prevents any appreciable water from seeping to the deeper Minnelusa Formation and Madison Limestone. The potentiometric head of these two deeper formations is approximately 3,420 to 3,500 ft (Long and Putnam, 2002; Carter et al., 2002); this is near the land elevation in the general area of these three quarries. Thus movement of contaminants from the surface down into the Madison aquifer would be unlikely. These quarries do not appear to be affecting Rapid City's wells because the nitrate concentration in the wells near the quarries is not greater than other wells.

Three streams recharge the Paleozoic carbonate aquifer in the vicinity of Rapid City's wells. Boxelder, Rapid, and Spring creeks lose much of their water to the Madison Limestone and Minnelusa Formation. The nitrate in Rapid City's wells could simply reflect an increasing nitrate in these streams. This nitrate probably stems from domestic on-site wastewater systems along the three streams and from the Hill City sewage lagoons along Spring Creek. Dye injected into the loss zone of Boxelder Creek showed up in Rapid City well #6 within 30 days and well #10 within 41 days (Greene, 1999). Spring Creek recharges wells downgradient from its loss zone; Putnam and Long (2002) found that water levels in wells near stream recharge zones rise with increased stream loss rates. Long and Putnam (2004) used stable isotopes of oxygen, $\delta^{18}O$, to estimate water velocity recharged at Spring Creek to a nearby well at Highland Hills. They found "conduit flow" velocity through the Madison Limestone was 540 m/d, resulting in a five-day response time. In November 5, 1993, a nearby well at Copper Oaks had an incident with Giardia bacteria, presumably from water infiltrating from Spring Creek (Miller, 2005). Long and Putnam (2005) concluded that public water supply wells downgradient are very sensitive to potential contamination from Spring Creek.

For each of Rapid City's Madison wells, Greene (1999) estimated the proportion of the water that originates from these three streams. He assumed recharge on local outcrops of the Madison Limestone were minor, and used potentiometric maps, dye test data, and $\delta^{2}H$ and $\delta^{18}O$ isotopes to estimate the percentage of water derived from these three streams as follows:

- Wells #5, #6, #8, and #10 "…obtain approximately 75 percent of their water from Rapid Creek and about 25 percent from Boxelder Creek",
- Well #9 is 40% Rapid Creek water and 60% Spring Creek water,
- Cleghorn Spring is 55% Rapid Creek water and 45% Spring Creek water, and
- Well #11 is primarily recharged by Spring Creek.

If these percentages are accurate, the rising nitrate in the wells simply reflects rising nitrate in the three streams.

The existing data for nitrate concentration in these three streams is not complete enough to evaluate the possibility that they are the source of nitrate in Rapid City's wells. While these streams might be the primary source, there is also local recharge to the Madison Limestone and Minnelusa Formation. Carter et al. (2002) show that between 1 and 2 inches annually recharge these units in the area within a few miles of Rapid City. Therefore the water reaching Rapid

City's wells would also include water infiltrating down from the surface at the outcrop areas near Rapid City as well as water lost by the streams in the sinkhole zones. In a study of recharge to the Madison aquifer just west of Rapid City, extending roughly from Elk Creek to Battle Creek, Long and Putnam (2002, Table 7) estimated 38.8 cfs streamflow recharge and 16.1 cfs infiltration recharge from the surface. Using these numbers, the ratio of stream recharge to infiltration recharge = 38.8/16.1 = 2.41/1. In other words, the water that is found in Rapid City wells originates as 71% stream recharge and 29% infiltration from nearby outcrops. This proportion would vary depending on the well location. For example, well #6 and well #10 would logically contain a greater percentage of stream recharge from Boxelder Creek than the other Madison wells.

The prolonged Black Hills drought (1999 to 2005) may have some influence on the nitrate concentration of stream water in that lower stream discharge typically has higher dissolved constituents. However, the nitrate concentrations were increasing prior to 1999, so the nitrate concentration is not simply due to the drought.

The increasing urbanization surrounding Rapid City is of concern because most of these new houses have on-site wastewater systems. Sawyer and Cowman (2000) inventoried wastewater systems in the Black Hills. In year 2001, approximately 9,000 on-site wastewater systems were identified in the central Black Hills (Sawyer and Lindquist, 2003). The U.S. Environmental Protection Agency (2002) estimates that 10 to 20% of on-site wastewater systems are "failing". Some areas west of Rapid City have very thin soils and are underlain by Paleozoic carbonate rocks that show karst features and contain commercial caves. Sawyer (in prep.) documented the movement of pathogens and contamination in some of these areas. On-site wastewater systems only remove about 10 to 20% of nitrogen, generally in the soil horizon (Anderson, 2003).

Natural recharge occurs by precipitation falling directly on areas underlain by Paleozoic rocks. Rahn and Gries (19763) found that most water discharged by large springs around the perimeter of the Black Hills originates in this way. Carter and Driscoll (2006) estimate that the annual recharge from precipitation on the Madison Limestone and Minnelusa Formation within a few miles of Rapid City ranges from 2.5 to 5 inches. Infiltrating water from septic leach fields would be added to this natural recharge.

Figure 3 shows the location of on-site wastewater systems near Rapid City that were known to exist in 2001. Many new houses are upgradient and are directly on the Madison Limestone and/or Minnelusa Formation. The approximate number of on-site wastewater systems for areas upgradient of the new Madison wells (located west of the contact of the Spearfish Formation and the Minnekahta Limestone as shown in Figure 3) can be summarized into three jurisdictional areas:

205 within the city limits,
170 within 1 mile of the city limits,
652 within 3 miles of the city limits.

The total from these three areas is 1,027 sites. This represents a minimum number because some sites were undoubtedly missed during the initial inventory, and

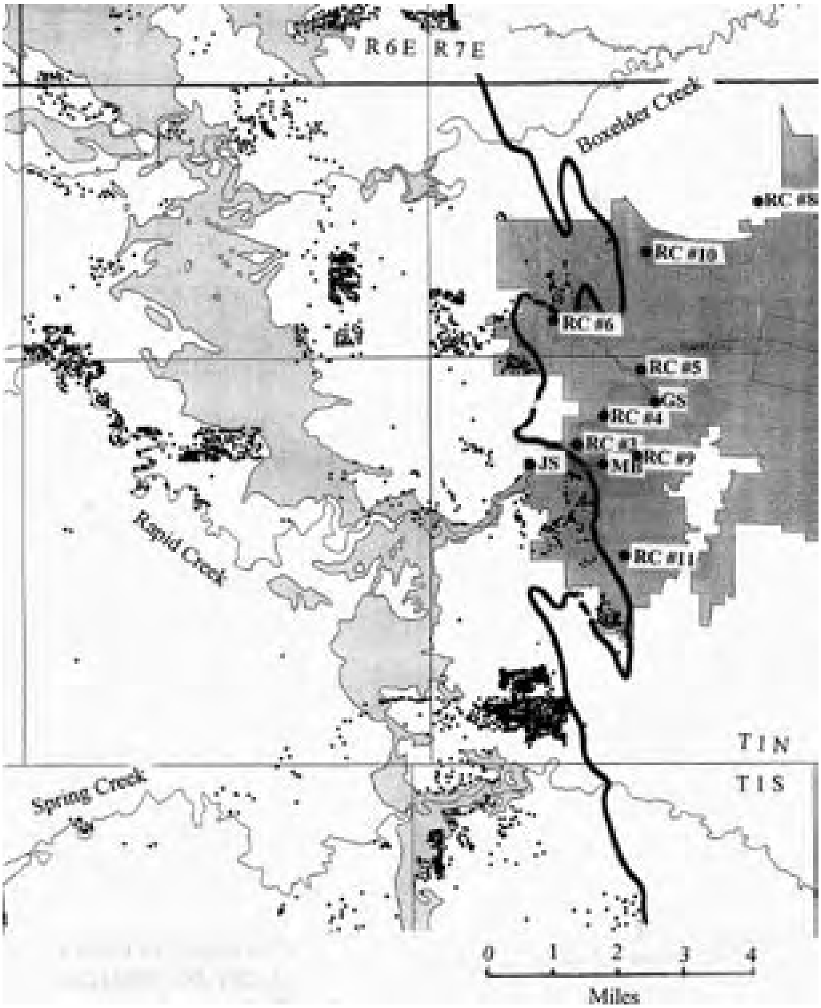

Figure 3. Map of the western part of Rapid City showing the city limits and location of on-site wastewater systems (modified from South Dakota Department of Environment and Natural Resources, unpublished data, 2001). Small circles show the location of on-site wastewater systems; these systems are only shown upgradient of the contact between the Minnekahta Limestone and the Spearfish Formation (heavy line). The outcrop area of the Madison Limestone is highlighted. Large circles show the location of Rapid City's primary water supply.

many new sites have been developed since 2001. The recharge area for the Rapid City wells, as defined by the South Dakota Source Water Assessment and Protection Program, includes the drainage basins of Boxelder, Rapid, and Spring Creeks; an estimated 5,000 on-site wastewater systems exist in this recharge area. There are numerous on-site wastewater systems along Rapid Creek in the Hisega area and Spring Creek below Hill City; these could lead to higher nitrate in these streams.

The nitrate concentration for the two infiltration galleries is somewhat irregular, but generally is greater than the other sources. The concentration seems to be decreasing over the past 13 years. The nitrate concentration probably reflects fertilizers applied to the Meadowbrook golf course.

Fertilizers used in agricultural lands probably contribute little nitrate to Rapid City wells because there are few farms in the recharge area. However, lawn fertilizers used in the expanding urban areas could be a significant nitrate contribution. Range cattle, horses and pets would contribute some nitrate but these are probably not significant.

CONCLUSION

The increasing nitrate in Jackson Spring and Rapid City's six Madison wells is most likely anthropogenic, but its origin is not known with certainty. It probably reflects contamination by water recharging the Madison Limestone and Minnelusa Formation within a few miles upgradient of the wells. The cause of this contamination is most likely a combination of: (1) increasing nitrate in the three streams recharging these aquifers, and (2) water seeping into these aquifers from local on-site wastewater systems and lawn fertilizers.

The general increasing concentrations of nitrate are similar for all the Madison wells. This indicates the nitrate source is widespread rather than a point source such as recharge by Spring Creek, the primary source of recharge for well #11. This supports the hypothesis that on-site wastewater systems are the major source of nitrate.

While the concentration of nitrate is still much less than the drinking water limit, there is concern because the contamination is getting worse every year. Treated sewage wastewater and rural septic systems have been shown to contain pharmaceutical and endocrine-disrupting compounds that make their way into the nation's waters (Stone and Heglund, 2005). If the increasing nitrate in Rapid City's water supply originates from domestic waste, pathogens and pharmaceutical products may eventually reach the water supply.

Future research using nitrogen isotopes could help identify the nitrate sources.

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