

Prepared in cooperation with the  
National Park Service

# Ground-Water Flow Direction, Water Quality, Recharge Sources, and Age, Great Sand Dunes National Monument, South-Central Colorado, 2000-2001



Scientific Investigations Report 2004-5027



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By Michael G. Rupert and L. Niel Plummer

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Scientific Investigations Report 2004–5027

**U.S. Department of the Interior**  
**U.S. Geological Survey**

**U.S. Department of the Interior**  
Gale A. Norton, Secretary

**U.S. Geological Survey**  
Charles G. Groat, Director

U.S. Geological Survey, Reston, Virginia: 2004

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## Conversion Factors, Datums, Abbreviations, and Abbreviated Water-Quality Units

| Multiply                       | By             | To obtain                           |
|--------------------------------|----------------|-------------------------------------|
| foot (ft)                      | 0.3048         | meter (m)                           |
| inch (in.)                     | 25.4           | millimeter (mm)                     |
| mile (mi)                      | 1.609          | kilometer (km)                      |
| square mile (mi <sup>2</sup> ) | 2.590          | square kilometer (km <sup>2</sup> ) |
| milligrams per liter (mg/L)    | 1/ionic weight | millimoles per kilogram (mmol/kg)   |

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation: °F = 9/5 (°C) + 32

### Abbreviated water-quality units:

|       |  |
|-------|--|
| mg/L  | milligrams per liter                                 |
| pCi/L | picocuries per liter                                 |
| pmc   | percent modern carbon                                |
| pptv  | parts per trillion by volume                         |
| TU    | tritium units  |
| µg/L  | micrograms per liter                                 |
| µS/cm | microsiemens per centimeter<br>at 25 degrees Celsius |

### Abbreviations used in this report:

|     |                            |
|-----|----------------------------|
| BP  | years before present       |
| CFC | chlorofluorocarbon         |
| DIC | dissolved inorganic carbon |
| DOC | dissolved organic carbon   |
| OD  | outside diameter           |
| PVC | polyvinyl chloride         |

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29); horizontal coordinate information is referenced to the North American Datum of 1927 (NAD27).



# Ground-Water Flow Direction, Water Quality, Recharge Sources, and Age, Great Sand Dunes National Monument, South-Central Colorado, 2000-2001

By Michael G. Rupert and L. Niel Plummer

## Abstract

Great Sand Dunes National Monument is located in south-central Colorado along the eastern edge of the San Luis Valley. The Great Sand Dunes National Monument contains the tallest sand dunes in North America; some rise up to 750 feet. Important ecological features of the Great Sand Dunes National Monument are palustrine wetlands associated with interdunal ponds and depressions along the western edge of the dune field. The existence and natural maintenance of the dune field and the interdunal ponds are dependent on maintaining ground-water levels at historic elevations. To address these concerns, the U.S. Geological Survey conducted a study, in collaboration with the National Park Service, of ground-water flow direction, water quality, recharge sources, and age at the Great Sand Dunes National Monument.

A shallow unconfined aquifer and a deeper confined aquifer are the two principal aquifers at the Great Sand Dunes National Monument. Ground water in the unconfined aquifer is recharged from Medano and Sand Creeks near the Sangre de Cristo Mountain front, flows underneath the main dune field, and discharges to Big and Little Spring Creeks. The percentage of calcium in ground water in the unconfined aquifer decreases and the percentage of sodium increases because of ionic exchange with clay minerals as the ground water flows underneath the dune field. It takes more than 60 years for the ground water to flow from Medano and Sand Creeks to Big and Little Spring Creeks. During this time, ground water in the upper part of the unconfined aquifer is recharged by numerous precipitation events. Evaporation of precipitation during recharge prior to reaching the water table causes enrichment in deuterium ( $^2\text{H}$ ) and oxygen-18 ( $^{18}\text{O}$ ) relative to waters that are not evaporated. This recharge from precipitation events causes the apparent ages determined using chlorofluorocarbons and tritium to become younger, because relatively young precipitation water is mixing with older waters derived from Medano and Sand Creeks.

Major ion chemistry of water from sites completed in the confined aquifer is different than water from sites completed in the unconfined aquifer, but insufficient data exist to quantify if the two aquifers are hydrologically disconnected. Radiocar-

bon dating of ground water in the confined aquifer indicates it is about 30,000 years old (plus or minus 3,000 years). The peak of the last major ice advance (Wisconsin) during the ice age occurred about 20,000 years before present; ground water from the confined aquifer is much older than that.

Water quality and water levels of the interdunal ponds are not affected by waters from the confined aquifer. Instead, the interdunal ponds are affected directly by fluctuations in the water table of the unconfined aquifer. Any lowering of the water table of the unconfined aquifer would result in an immediate decrease in water levels of the interdunal ponds. The water quality of the interdunal ponds probably results from several factors, including the water quality of the unconfined aquifer, evaporation of the pond water, and biologic activity within the ponds.

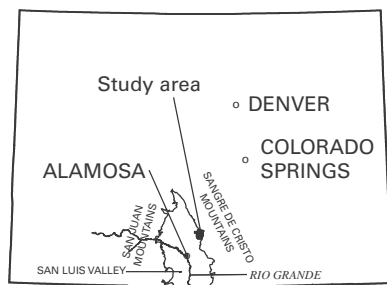
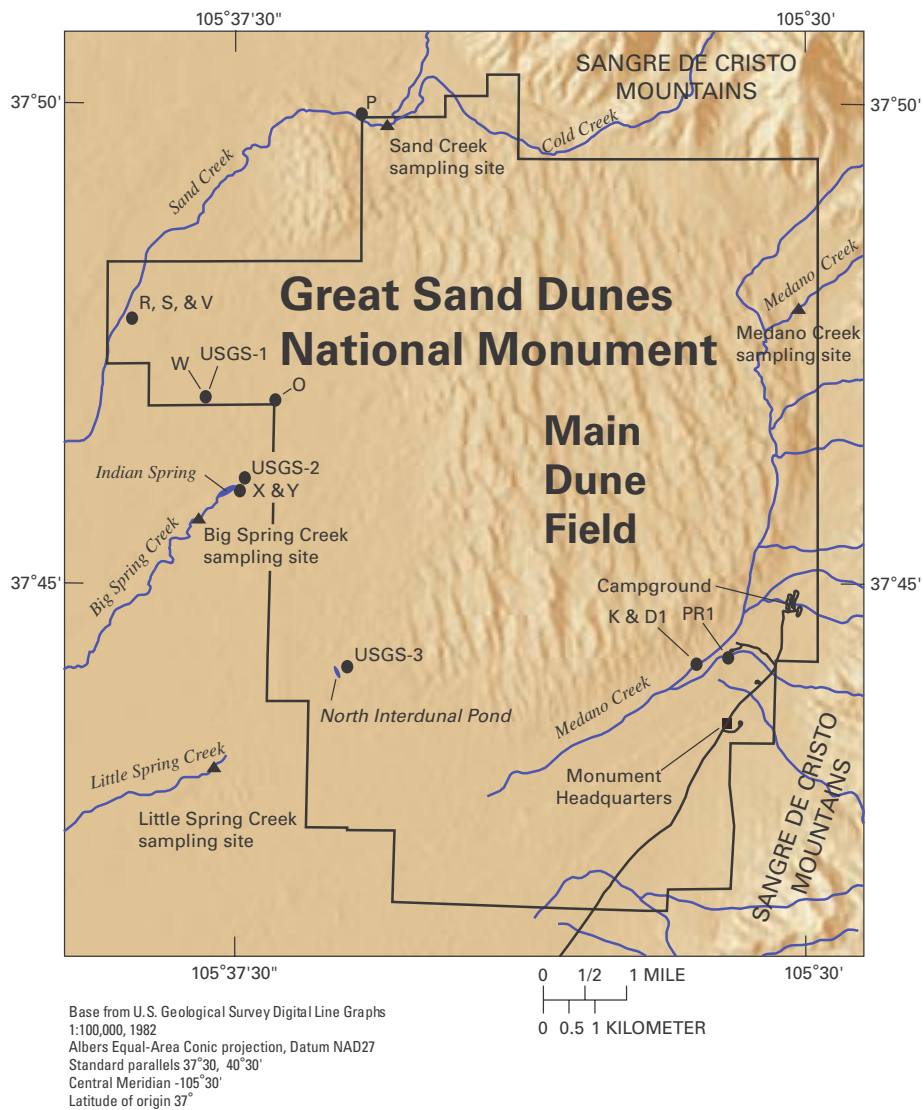
## Introduction

Great Sand Dunes National Monument (hereinafter called Great Sand Dunes) (fig. 1) contains the tallest sand dunes in North America, some of which rise up to 750 feet. As incongruous as it might seem, the sand dunes are dependent on water (Chatman and others, 1997). Prevailing winds transport sand northeastward toward the Sangre de Cristo Mountains. Two streams flowing from the Sangre de Cristo Mountains, one on the northwestern edge (Sand Creek) and one on the east and southeastern edge (Medano Creek) (fig. 1), transport the sand southwestward around the perimeter of the dunes and deposit the sand on the upwind side, where prevailing winds transport the sand northeastward toward the Sangre de Cristo Mountains again. The rate of sand transport northeastward by wind generally is the same as the rate of sand transport southwestward by water; together, the two mechanisms maintain the dune field in a state of quasi-equilibrium (Chatman and others, 1997).

A shallow unconfined aquifer and a deeper confined aquifer are the two principal aquifers at Great Sand Dunes. All the water in Medano and Sand Creeks, except what is lost to evapotranspiration, infiltrates into the shallow unconfined



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- EXPLANATION**
- Ground-water sampling site (table 1)
  - ▲ Surface-water sampling site (table 1)

| Ground-water sampling site name | Well depth (feet) | Depth to water table (feet) | Well screen length (feet) | Aquifer |
|---------------------------------|-------------------|-----------------------------|---------------------------|---------|
| D1                              | 100.0             | 87.83                       | 10                        | U       |
| K                               | 13.0              | 11.49                       | 10                        | U       |
| O                               | 25.0              | 19.64                       | 10                        | U       |
| P                               | 40.0              | 13.70                       | 10                        | U       |
| PR1                             | 350.0             | >200                        | 60                        | *       |
| R                               | 105.0             | 10.88                       | 10                        | U       |
| S                               | 31.3              | 10.29                       | 10                        | U       |
| V                               | 394.0             | 9.54                        | 20                        | C       |
| W                               | 74.0              | 3.51                        | 20                        | U       |
| X                               | 76.0              | 14.02                       | 20                        | U       |
| Y                               | 351.0             | 0                           | 20                        | C       |
|                                 |                   | (flowing)                   |                           |         |
| USGS-1                          | 11.6              | 2.57                        | 5                         | U       |
| USGS-2                          | 14.0              | 3.80                        | 10                        | U       |
| USGS-3                          | 10.3              | 6.09                        | 5                         | U       |

(>, greater than; U, unconfined aquifer; C, confined aquifer; \*, unknown aquifer).

**Figure 1.** Location of sampling sites and well-construction data at the Great Sand Dunes National Monument, south-central Colorado.

aquifer. The existence and natural maintenance of the dune field are dependent on maintaining ground-water levels in the shallow unconfined aquifer at historic altitudes. A drop in local ground-water levels would likely decrease the distance the creeks flow before all water infiltrates into the shallow unconfined aquifer. The capability of the creeks to transport sand back to the upwind side of the dune field would be reduced and, therefore, jeopardize the long-term viability of the dune field.

Important ecological features of Great Sand Dunes are palustrine wetlands associated with interdunal ponds and depressions that nearly intersect the water table. The interdunal ponds and depressions are located primarily on the western edge of the dune field and provide important habitat for a variety of species that depend on a wetland habitat in an otherwise desert environment. The interdunal ponds are of special concern because the number of ponds has decreased in recent years. Analysis of 10 sets of aerial photographs taken from 1936 through 1995 demonstrated that the number of ponds decreased from 36 in 1936 to zero in 1966, and then gradually increased to 9 in 1995 (Chatman and others, 1997, p. 75). The 1930's photographs show that the ponds have well-developed fringing communities of perennial wetland plants, which indicate ground-water levels have been relatively stable for many decades (Chatman and others, 1997, p. 76). The relatively sudden disappearance of ponds seems to indicate a decrease in ground-water levels, and the cause of the change has not been determined. Continued lowering of the water table may lead to continued disappearance of the ponds.

Delineation of a water budget for Great Sand Dunes was identified in 1997 during the Water Resources Management Plan scoping process as the most critical water-resources issue facing Great Sand Dunes (Chatman and others, 1997, p. 71). Quantification of the sources and timing of recharge to the shallow unconfined aquifer, the deeper confined aquifer, the interdunal ponds, and various springs can assist in developing a water budget that will help protect the water rights of Great Sand Dunes and aid in management decisions to maintain historic ground-water levels. To address these concerns, the U.S. Geological Survey (USGS), in collaboration with the National Park Service (NPS), conducted a study of ground-water flow direction, water quality, recharge sources, and age in Great Sand Dunes.

## Purpose and Scope

The purpose of this report is to describe the study of ground-water flow direction, water quality, recharge sources, and age. The recharge source of the unconfined aquifer, interdunal ponds, and Big and Little Spring Creeks is determined. The age of ground waters sampled from the unconfined and confined aquifers is determined using a variety of geochemical methods. The amount of mixing in the unconfined aquifer of (presumably) older waters from the confined aquifer with young waters derived from recharge by local precipitation and

recharge from Medano and Sand Creeks is discussed. Ground- and surface-water samples were collected during 2000 and 2001 from streams, springs, and wells in and adjacent to Great Sand Dunes.

## Study Area Description

Great Sand Dunes is located in south-central Colorado along the eastern edge of the San Luis Valley (fig. 1). The San Luis Valley is nearly flat, drained by the Rio Grande, and is about 100 miles long (north to south) by as much as 50 miles wide (east to west). The San Luis Valley is bounded by the Sangre de Cristo Mountains to the east and the San Juan Mountains to the west. Great Sand Dunes is located at altitudes ranging from 7,500 to 10,300 feet and receives annual average precipitation of about 11 inches at Great Sand Dunes Headquarters. Most of the sediments eroded from the Sangre de Cristo Mountains are derived from gneiss, granite, and granodiorite of Precambrian age (Johnson, 1971). Most of the sediments eroded from the San Juan Mountains are derived from ash flows, tuffs, and breccias of Middle Tertiary age ranging in composition from quartz latite to rhyolite (Johnson, 1971). Surface water in Great Sand Dunes flows generally westward from the Sangre de Cristo Mountains to a closed basin in the San Luis Valley and collects in numerous small playa lakes.

The predominant feature in Great Sand Dunes is the 30 square-mile main dune field. Some of the dunes are as much as 750 feet high. The age of the dunes is estimated to be from 2,000 to 12,000 years old (Chatman and others, 1997). The composition of the sand indicates the predominant source is the San Juan Mountains to the west. The sand was deposited on the floor of the San Luis Valley by the Rio Grande and other local streams and then carried by prevailing southwesterly winds to the Sangre de Cristo Mountain front. The shape of the Sangre de Cristo Mountains modifies the wind regime at the mountain front. Mountain passes funnel northeasterly winds across the dune field. The resulting bimodal wind regime changes dune behavior from migratory to vertically growing (Andrew Valdez, National Park Service, oral commun., 2002). The dune field extends as much as 5 miles westward from the Sangre de Cristo Mountain front. The dune field is part of a much larger eolian sand sheet that extends as much as 20 mi westward from the Sangre de Cristo Mountain front and primarily is composed of low-relief, vegetation-stabilized sand dunes (sand sheet). The interpreted thickness of the eolian sand sheet is about 140 feet (HRS Water Consultants, 1999). The base of the sand sheet is marked by a gradual change to clay-rich fluvial-lacustrine sediments of the Alamosa Formation (HRS Water Consultants, 1999). A variety of dune types exist at Great Sand Dunes, including barchan, reversing, star, and parabolic dunes. Locations of the various types of dunes are determined by localized wind patterns in Great Sand Dunes.

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A shallow unconfined aquifer and a deeper confined aquifer are the two principal aquifers at Great Sand Dunes, which are located in the Alamosa Formation. The Alamosa Formation consists of unconsolidated gravels, sands, clays, and conglomerates (Siebenthal, 1910). A clay layer that is about 8 feet thick and about 300 feet deep separates the aquifers. The clay layer was identified in sites V and Y, near the west edge of the dune field (fig. 1; table 1). It is unknown if the clay layer extends eastward to the base of the Sangre de Cristo Mountains in Great Sand Dunes.

### Acknowledgments

The author appreciates the assistance and information provided by Fred Bunch and Andrew Valdez from the National Park Service. Their assistance during the sampling phase of this study was invaluable and their sense of humor made the long hours in the field much more enjoyable. The author wishes to thank the Nature Conservancy for allowing access to their property for sample collection. The authors also wish to thank Scott Anderholm, Mike Friedel, Gerhard Kuhn, Keith Lucey, and Betty Palcsak, USGS, for their comments during the colleague review process.

### Methods of Investigation

For the study described in this report, ground-water level measurements and ground- and surface-water quality data were collected and three monitoring wells were installed. These data were used to help define the ground-water flow direction, water quality, recharge sources, and age in Great Sand Dunes.

### Well Construction and Nomenclature

All pre-existing wells sampled for this study are ground-water monitoring wells, except site PR1, which is a drinking-water supply well. Sites K, O, P, and S are less than 41 feet deep (fig. 1; table 1) and are completed in the upper part of the unconfined aquifer. Sites R, W, and X are 105, 74, and 76 feet deep, respectively, and are completed in the middle portion of the unconfined aquifer. No wells are completed in the deepest portion of the unconfined aquifer. Site PR1 is a relatively deep well (350 feet), but it is unknown if it is completed in the unconfined or confined aquifer because the site is located close to the mountain front and the well driller's record could not be located.

Three wells were installed for this study; one near site W (USGS-1), one near sites X and Y (USGS-2), and one near the North Interdunal Pond (USGS-3) (fig. 1). Wells were installed by hand auguring and advancing a 4-inch outside diameter (OD) polyvinyl chloride (PVC) well casing as far as possible

(from 10 to 15 feet). A 2-inch OD well then was inserted inside the 4-inch OD PVC casing to the bottom of the hole. The 2-inch OD well consisted of a 5- or 10-foot section of 2-inch OD PVC well screen (0.010-inch slot size), with 2-inch OD solid PVC well casing attached above the well screen and extending to the land surface. The 4-inch OD casing then was removed (leaving the 2-inch OD well in place), and the annulus of the augured hole was packed with auger cuttings (sand and silt). Each well was developed using a portable well pump that ran continuously for several hours.

Sites V and Y are completed in the confined aquifer (fig. 1). During drilling of sites V and Y, the first clay layer interpreted to be the top of the confined aquifer was encountered at 323 feet in site V and at 260 feet in site Y (HRS Water Consultants, 1999). The 8-foot thick, gray clay layer was correlated between sites V and Y using geophysical logs (HRS Water Consultants, 1999). Site V is 394 feet deep (table 1) and penetrates 71 feet into the confined aquifer. Site Y is 351 feet deep and penetrates 91 feet into the confined aquifer.

### Measurement of Ground-Water Levels, Water-Quality Sampling, and Analyses

During this study, ground-water levels were measured at every well using calibrated steel tapes prior to sampling. The NPS also has collected a limited amount of continuous water-level data from selected wells at Great Sand Dunes during 1999 using pressure transducers.

Water-quality samples were collected from wells at Great Sand Dunes that could produce sufficient amounts of water (sites K, O, P, PR1, R, S, USGS-1, USGS-2, USGS-3, V, W, X, and Y; table 1) and from Medano Creek, Sand Creek, Big Spring Creek, and Little Spring Creek (fig. 1). Medano and Sand Creeks were sampled during December and June to determine water quality during low- and high-flow conditions, respectively. Field parameters were measured at each site, including water level, dissolved oxygen, hydrogen sulfide, pH, specific conductance, water temperature, and alkalinity. At most sites, water samples were analyzed for major ions, deuterium ( $^2\text{H}$ ) and oxygen-18 ( $^{18}\text{O}$ ), sulfur hexafluoride ( $\text{SF}_6$ ), tritium ( $^3\text{H}$ ), chlorofluorocarbons (CFC's), and dissolved gases. To facilitate ground-water age dating of waters potentially thousands of years old, water from selected sites also was analyzed for carbon-14 ( $^{14}\text{C}$ ), carbon 13/12 ratio, and dissolved organic carbon (DOC). Ambient air samples were collected at four sites and analyzed for CFC's. All sites except Little Spring Creek were sampled once during September 2000. Five samples of  $^2\text{H}$ ,  $^{18}\text{O}$ , and  $^3\text{H}$  also were collected quarterly from Medano and Sand Creeks starting May 2000 through June 2001 to provide information on seasonal fluctuations of these constituents. Where possible, sites in proximity but at different depths (for instance R, S, and V) were sampled to gain insight into the vertical distribution of water ages and chemical and isotopic composition. Two of the sites (V and Y) are deep wells (greater than 300 feet) and were sampled

**Table 1.** Selected well-construction and ground- and surface-water quality data, Great Sand Dunes National Monument, south-central Colorado, 2000-2001

| Site name<br>(see fig. 1 for<br>location) | Site<br>type | U.S. Geological<br>Survey station<br>identification<br>number | Latitude<br>(in ddmss) | Longitude<br>(in ddmss) | Date of<br>sample<br>collection | Well depth<br>(feet below<br>land<br>surface) | Depth to<br>water table<br>(feet below<br>land<br>surface) | Well screen<br>length<br>(feet) | Altitude of<br>top of well<br>casing (feet<br>above NGVD 29) | Aquifer |
|---|--------------|---|------------------------|-------------------------|---------------------------------|---|--|---------------------------------|--|---------|
| K   | Well         | 374410105312701   | 374410                 | 1053127                 | 9/12/00                         | 13.0  | 11.49  | 10                              | 8019   | U       |
| O   | Well         | 374655105365901   | 374655                 | 1053659                 | 9/11/00                         | 25.0  | 19.64  | 10                              | 7718   | U       |
| P   | Well         | 374954105355101   | 374954                 | 1053551                 | 9/14/00                         | 40.0  | 13.70  | 10                              | 7828   | U       |
| PR1                                       | Well         | 374414105310201   | 374414                 | 1053102                 | 9/25/00                         | 350.0   | >200   | 60                              | 8050   | *       |
| R   | Well         | 374746105385201   | 374746                 | 1053852                 | 9/19/00                         | 105.0   | 10.88  | 10                              | 7689   | U       |
| S   | Well         | 374746105385202   | 374746                 | 1053852                 | 9/18/00                         | 31.3  | 10.29  | 10                              | 7689   | U       |
| V   | Well         | 374746105385203   | 374746                 | 1053852                 | 9/19/00                         | 394.0   | 9.54   | 20                              | 7690   | C       |
| W   | Well         | 374657105375401   | 374657                 | 1053754                 | 9/15/00                         | 74.0  | 3.51   | 20                              | 7682   | U       |
| X   | Well         | 374558105372801   | 374558                 | 1053728                 | 9/13/00                         | 76.0  | 14.02  | 20                              | 7678   | U       |
| Y   | Well         | 374557105372901   | 374557                 | 1053729                 | 9/20/00                         | 351.0   | 0 (flowing)  | 20                              | 7677   | C       |
| USGS 1                                    | Well         | 374657105375402   | 374657                 | 1053754                 | 9/26/00                         | 11.6  | 2.57   | 5                               | 7682   | U       |
| USGS 2                                    | Well         | 374605105372301   | 374605                 | 1053723                 | 9/26/00                         | 14.0  | 3.80   | 10                              | 7760   | U       |
| USGS 3                                    | Well         | 374407105360401   | 374407                 | 1053604                 | 9/27/00                         | 10.3  | 6.09   | 5                               | 7729   | U       |
| Big Spring Creek                          | SW           | 374540105380201   | 374540                 | 1053802                 | 9/26/00                         | --  | --   | --                              | --   | --      |
| Big Spring Creek                          | SW           | 374540105380201   | 374540                 | 1053802                 | 6/15/01                         | --  | --   | --                              | --   | --      |
| Little Spring Creek                       | SW           | 374303105374401   | 374303                 | 1053744                 | 6/15/01                         | --  | --   | --                              | --   | --      |
| Medano Creek                              | SW           | 374752105300801   | 374752                 | 1053008                 | 5/22/00                         | --  | --   | --                              | --   | --      |
| Medano Creek                              | SW           | 374752105300801   | 374752                 | 1053008                 | 7/11/00                         | --  | --   | --                              | --   | --      |
| Medano Creek                              | SW           | 374752105300801   | 374752                 | 1053008                 | 9/12/00                         | --  | --   | --                              | --   | --      |
| Medano Creek                              | SW           | 374752105300801   | 374752                 | 1053008                 | 12/14/00                        | --  | --   | --                              | --   | --      |
| Medano Creek                              | SW           | 374752105300801   | 374752                 | 1053008                 | 6/15/01                         | --  | --   | --                              | --   | --      |
| Sand Creek                                | SW           | 374946105353301   | 374946                 | 1053533                 | 5/25/00                         | --  | --   | --                              | --   | --      |
| Sand Creek                                | SW           | 374946105353301   | 374946                 | 1053533                 | 9/14/00                         | --  | --   | --                              | --   | --      |
| Sand Creek                                | SW           | 374946105353301   | 374946                 | 1053533                 | 12/13/00                        | --  | --   | --                              | --   | --      |
| Sand Creek                                | SW           | 374946105353301   | 374946                 | 1053533                 | 6/14/01                         | --  | --   | --                              | --   | --      |

[--, no data; SW, surface water; >, greater than; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter; µg/L, micrograms per liter; °C, degrees Celsius; ND, not detected; ddmss, degrees, minutes, and seconds; per mil, parts per thousand; U, unconfined aquifer; C, confined aquifer; \*, unknown aquifer; NGVD 29, National Geodetic Vertical Datum of 1929]

**Table 1.** Selected well-construction and ground- and surface-water quality data, Great Sand Dunes National Monument, south-central Colorado, 2000-2001—Continued

[--, no data; SW, surface water; >, greater than; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter; µg/L, micrograms per liter; °C, degrees Celsius; ND, not detected; ddmms, degrees, minutes, and seconds; per mil, parts per thousand; U, unconfined aquifer; C, confined aquifer; \*, unknown aquifer; NGVD 29, National Geodetic Vertical Datum of 1929]

| Site name<br>(see fig. 1 for<br>location) | Sampling<br>date | Oxygen,<br>dissolved<br>(mg/L) | pH, water,<br>whole,         |                            | Specific<br>conductance<br>field<br>(µS/cm) | Specific<br>conductance<br>lab<br>(µS/cm) | Temperature,<br>water<br>(°C) | Acid<br>neutralizing<br>capacity,<br>water,           |   | Bicarbonate,<br>water, filtered,<br>field,<br>HCO <sub>3</sub> | Alkalinity,<br>water,<br>filtered,<br>field<br>(mg/L as<br>CaCO <sub>3</sub> ) | Hydrogen<br>sulfide,<br>water,<br>filtered,<br>field<br>(mg/L) |
|---|------------------|--------------------------------|------------------------------|----------------------------|---|---|-------------------------------|---|---|--|--|--|
|   |                  |                                | field<br>(standard<br>units) | lab<br>(standard<br>units) |   |   |                               | unfiltered,<br>lab<br>(mg/L as<br>CaCO <sub>3</sub> ) | filtered,<br>field<br>(mg/L as<br>CaCO <sub>3</sub> ) |  |  |  |
| K   | 9/12/00          | 2.2                            | 6.9                          | 8.1                        | 145   | 149                                       | 14.7                          | 66.15   | 73  | 60   | ND   |  |
| O   | 9/11/00          | 6.5                            | 7.7                          | 8.1                        | 239   | 247                                       | 14.1                          | 61.21   | 69  | 57   | ND   |  |
| P   | 9/14/00          | 3.0                            | 6.5                          | 8.0                        | 76  | 80  | 7.6                           | 32.26   | 41  | 34   | ND   |  |
| PR1                                       | 9/25/00          | 7.4                            | 7.2                          | 8.3                        | 310   | 333                                       | 11.8                          | 126.67  | 152   | 125  | ND   |  |
| R   | 9/19/00          | 4.1                            | 7.8                          | 7.8                        | 70  | 74  | 13.2                          | 29.85   | 35  | 29   | ND   |  |
| S   | 9/18/00          | 4.9                            | 7.5                          | 7.8                        | 68  | 69  | 13.7                          | 27.59   | 33  | 27   | ND   |  |
| V   | 9/19/00          | 0.4                            | 8.7                          | 8.1                        | 129   | 135                                       | 13.9                          | 61.20   | 72  | 59   | ND   |  |
| W   | 9/15/00          | 5.5                            | 7.8                          | 7.9                        | 114   | 121                                       | 13.5                          | 44.86   | 61  | 50   | ND   |  |
| X   | 9/13/00          | 4.7                            | 7.7                          | 8.1                        | 106   | 109                                       | 13.1                          | 47.22   | 59  | 48   | ND   |  |
| Y   | 9/20/00          | 0.2                            | 8.5                          | 8.2                        | 159   | 168                                       | 15.2                          | 85.31   | 95  | 78   | 0.24   |  |
| USGS 1                                    | 9/26/00          | 1.8                            | 7.4                          | 8.2                        | 214   | 237                                       | 15.9                          | 88.52   | 107   | 88   | ND   |  |
| USGS 2                                    | 9/26/00          | 0.8                            | 6.8                          | 8.2                        | 184   | 197                                       | 12.1                          | 78.84   | 102   | 84   | ND   |  |
| USGS 3                                    | 9/27/00          | 5.0                            | 7.7                          | 8.1                        | 150   | 160                                       | 15.8                          | 53.24   | 62  | 51   | ND   |  |
| Big Spring Creek                          | 9/26/00          | --                             | --                           | --                         | --  | --  | --                            | --  | --  | --   | --   | --   |
| Big Spring Creek                          | 6/15/01          | 1.0                            | 8.3                          | 8.1                        | 116   | 142                                       | 15.4                          | 58.18   | 71  | 58   | --   |  |
| Little Spring Creek                       | 6/15/01          | 6.9                            | 7.9                          | 7.8                        | 169   | 194                                       | 19.5                          | 78.07   | 92  | 76   | --   |  |
| Medano Creek                              | 5/22/00          | 7.7                            | 8.0                          | 7.5                        | 76  | 80  | 14.0                          | --  | 41  | 34   | --   |  |
| Medano Creek                              | 7/11/00          | 6.0                            | 8.1                          | 7.7                        | 100   | 104                                       | 23.7                          | --  | 56  | 46   | --   |  |
| Medano Creek                              | 9/12/00          | --                             | --                           | --                         | --  | --  | --                            | --  | --  | --   | --   | --   |
| Medano Creek                              | 12/14/00         | 10.2                           | 7.8                          | 7.1                        | 102   | 108                                       | 0.0                           | 49.49   | 59  | 48   | --   |  |
| Medano Creek                              | 6/15/01          | 8.3                            | 7.8                          | 7.6                        | 58  | 65  | 13.6                          | 29.56   | 36  | 29   | --   |  |
| Sand Creek                                | 5/25/00          | 8.7                            | 7.7                          | 8.0                        | --  | 50  | 9.5                           | --  | 23  | 19   | --   |  |
| Sand Creek                                | 9/14/00          | --                             | --                           | --                         | --  | --  | --                            | --  | --  | --   | --   | --   |
| Sand Creek                                | 12/13/00         | 11.0                           | 8.0                          | 7.7                        | 85  | 87  | 0.0                           | 33.27   | 38  | 31   | --   |  |
| Sand Creek                                | 6/14/01          | 9.9                            | 7.7                          | 7.3                        | 45  | 48  | 4.7                           | 18.70   | 22  | 18   | --   |  |

**Table 1.** Selected well-construction and ground- and surface-water quality data, Great Sand Dunes National Monument, south-central Colorado, 2000-2001—Continued

[--, no data; SW, surface water; >, greater than; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter; µg/L, micrograms per liter; °C, degrees Celsius; ND, not detected; ddmms, degrees, minutes, and seconds; per mil, parts per thousand; U, unconfined aquifer; C, confined aquifer; \*, unknown aquifer; NGVD 29, National Geodetic Vertical Datum of 1929]

| Site name<br>(see fig. 1 for<br>location) | Sampling<br>date | Solids  |   |  |  |  |                                      |   |  |  |  |   |
|---|------------------|---|---|--|--|--|--------------------------------------|---|--|--|--|---|
|   |                  | Hardness,<br>dissolved<br>(mg/L as<br>CaCO <sub>3</sub> ) | residue at<br>180°C,<br>dissolved<br>(mg/L) | Calcium,<br>dissolved<br>(mg/L as<br>Ca) | Magnesium,<br>dissolved<br>(mg/L as<br>Mg) | Potassium,<br>dissolved<br>(mg/L as K) | Sodium,<br>dissolved<br>(mg/L as Na) | Chloride,<br>dissolved<br>(mg/L as<br>Cl) | Fluoride,<br>dissolved<br>(mg/L as<br>F) | Silica,<br>dissolved<br>(mg/L as<br>SiO <sub>2</sub> ) | Sulfate,<br>dissolved<br>(mg/L as<br>SO <sub>4</sub> ) | Dissolved<br>organic<br>carbon<br>(mg/L as C) |
| K   | 9/12/00          | 60.6  | 103.0                                       | 16.57                                    | 4.67                                       | 4.23                                   | 3.87                                 | 0.81                                      | 0.23                                     | 28.00  | 5.30   | 0.72  |
| O   | 9/11/00          | 79.5  | 144.0                                       | 20.32                                    | 6.98                                       | 8.11                                   | 11.59                                | 1.18                                      | 0.39                                     | 46.29  | 12.34  | --  |
| P   | 9/14/00          | 32.7  | 52.9  | 9.46                                     | 2.20                                       | 0.70                                   | 2.09                                 | 0.59                                      | 0.50                                     | 13.00  | 5.06   | 0.36  |
| PR1                                       | 9/25/00          | 135.0   | 199.0                                       | 39.91                                    | 8.60                                       | 1.14                                   | 15.05                                | 7.38                                      | 0.45                                     | 22.00  | 28.79  | 0.45  |
| R   | 9/19/00          | 25.7  | 73.7  | 6.69                                     | 2.17                                       | 3.58                                   | 2.07                                 | 0.46                                      | 0.44                                     | 36.00  | 4.36   | 0.27  |
| S   | 9/18/00          | 24.9  | 66.6  | 7.29                                     | 1.63                                       | 2.61                                   | 1.87                                 | 0.44                                      | 0.38                                     | 32.00  | 3.82   | 0.45  |
| V   | 9/19/00          | 36.7  | 113.0                                       | 14.06                                    | 0.39                                       | 1.82                                   | 12.81                                | 1.44                                      | 0.47                                     | 40.81  | 4.55   | <0.15   |
| W   | 9/15/00          | 34.3  | 105.0                                       | 9.37                                     | 2.65                                       | 5.92                                   | 6.66                                 | 0.93                                      | 0.35                                     | 49.13  | 3.54   | <0.15   |
| X   | 9/13/00          | 32.6  | 98.2  | 8.63                                     | 2.67                                       | 4.32                                   | 6.40                                 | 0.93                                      | 0.27                                     | 44.44  | 2.20   | <0.15   |
| Y   | 9/20/00          | 41.9  | 160.0                                       | 15.62                                    | 0.71                                       | 3.39                                   | 17.31                                | 1.80                                      | 0.85                                     | 68.66  | 0.44   | 0.48  |
| USGS 1                                    | 9/26/00          | 62.4  | 168.0                                       | 15.13                                    | 5.98                                       | 8.63                                   | 19.41                                | 1.41                                      | 0.87                                     | 52.32  | 10.60  | 0.70  |
| USGS 2                                    | 9/26/00          | 76.1  | 173.0                                       | 18.00                                    | 7.57                                       | 4.84                                   | 10.77                                | 1.53                                      | 1.12                                     | 65.70  | 12.34  | 5.22  |
| USGS 3                                    | 9/27/00          | 48.7  | 116.0                                       | 13.35                                    | 3.72                                       | 4.97                                   | 9.59                                 | 1.18                                      | 0.43                                     | 43.96  | 7.23   | 0.30  |
| Big Spring Creek                          | 9/26/00          | --  | --  | --                                       | --   | --                                     | --                                   | --  | --                                       | --   | --   | --  |
| Big Spring Creek                          | 6/15/01          | 43.2  | 112.0                                       | 11.42                                    | 3.55                                       | 5.53                                   | 8.62                                 | 0.88                                      | 0.31                                     | 41.64  | 5.05   | --  |
| Little Spring Creek                       | 6/15/01          | 62.0  | 137.0                                       | 17.78                                    | 4.28                                       | 5.97                                   | 11.86                                | 0.87                                      | 0.24                                     | 40.99  | 8.00   | --  |
| Medano Creek                              | 5/22/00          | 32.5  | --  | 8.58                                     | 2.69                                       | --                                     | --                                   | --  | --                                       | --   | 2.66   | --  |
| Medano Creek                              | 7/11/00          | 43.8  | --  | 11.95                                    | 3.39                                       | --                                     | --                                   | --  | --                                       | --   | 2.30   | --  |
| Medano Creek                              | 9/12/00          | --  | --  | --                                       | --   | --                                     | --                                   | --  | --                                       | --   | --   | --  |
| Medano Creek                              | 12/14/00         | 46.8  | 67.1  | 12.66                                    | 3.68                                       | 0.77                                   | 3.17                                 | 0.83                                      | 0.20                                     | 12.00  | 4.02   | --  |
| Medano Creek                              | 6/15/01          | 26.5  | 43.7  | 7.05                                     | 2.16                                       | 0.60                                   | 2.04                                 | 0.35                                      | 0.16                                     | 11.31  | 2.46   | --  |
| Sand Creek                                | 5/25/00          | 20.8  | --  | 6.37                                     | 1.18                                       | --                                     | --                                   | --  | --                                       | --   | 3.22   | --  |
| Sand Creek                                | 9/14/00          | --  | --  | --                                       | --   | --                                     | --                                   | --  | --                                       | --   | --   | --  |
| Sand Creek                                | 12/13/00         | 35.8  | 50.4  | 10.79                                    | 2.15                                       | 0.60                                   | 1.97                                 | 0.78                                      | 0.43                                     | 7.00   | 6.71   | --  |
| Sand Creek                                | 6/14/01          | 19.3  | 29.1  | 5.91                                     | 1.10                                       | 0.40                                   | 1.04                                 | 0.22                                      | 0.36                                     | 5.63   | 3.24   | --  |



**Table 1.** Selected well-construction and ground- and surface-water quality data, Great Sand Dunes National Monument, south-central Colorado, 2000-2001—Continued

| Site name<br>(see fig. 1 for<br>location) | Sampling<br>date | Boron,<br>dissolved<br>(µg/L as B) | Iron,<br>dissolved<br>(µg/L as Fe) | Manganese,<br>dissolved<br>(µg/L as Mn) | Carbon<br>13/12 ratio<br>(per mil) | Carbon-14,<br>water,                      |   | Carbon-14,<br>count<br>error<br>(percent<br>modern<br>carbon) | Hydrogen<br>2/1 ratio<br>(per mil) | Oxygen<br>18/16<br>ratio<br>(per mil) | Tritium<br>(tritium<br>units) | Tritium<br>precision<br>estimate<br>(tritium<br>units) |
|---|------------------|------------------------------------|------------------------------------|---|------------------------------------|---|---|---|------------------------------------|---------------------------------------|-------------------------------|--|
|   |                  |                                    |                                    |   |                                    | filtered<br>(percent<br>modern<br>carbon) | Carbon-14,<br>count<br>error<br>(percent<br>modern<br>carbon) |   |                                    |                                       |                               |  |
| K   | 9/12/00          | <13                                | <10                                | <3.2                                    | --                                 | --  | --  | --  | -89.8                              | -12.0                                 | 7.9                           | 0.5  |
| O   | 9/11/00          | 42.7                               | <10                                | <3.2                                    | --                                 | --  | --  | --  | -84.3                              | -9.5                                  | 12.9                          | 0.8  |
| P   | 9/14/00          | <13                                | <10                                | 1.8                                     | --                                 | --  | --  | --  | -98.2                              | -13.6                                 | 11.2                          | 0.8  |
| PR1                                       | 9/25/00          | 33.8                               | 13.3                               | <3.2                                    | -11.50                             | 84.87                                     | 0.57  | 0.57  | -106.2                             | -14.4                                 | 10.5                          | 0.8  |
| R   | 9/19/00          | <13                                | <10                                | <3.2                                    | -9.54                              | 115.10                                    | 0.73  | 0.73  | -102.6                             | -14.1                                 | 10.7                          | 0.8  |
| S   | 9/18/00          | <13                                | <10                                | <3.2                                    | --                                 | --  | --  | --  | -98.5                              | -13.7                                 | 6.8                           | 0.6  |
| V   | 9/19/00          | 8.5                                | <10                                | 19.1                                    | -11.15                             | 38.89                                     | 0.34  | 0.34  | -100.9                             | -13.6                                 | 0.0                           | 0.3  |
| W   | 9/15/00          | 14.1                               | 20.1                               | 1.8                                     | -6.07                              | 86.70                                     | 0.64  | 0.64  | -89.4                              | -10.8                                 | 0.0                           | 0.3  |
| X   | 9/13/00          | 11.1                               | <10                                | <3.2                                    | -7.29                              | 90.77                                     | 0.59  | 0.59  | -100.1                             | -13.1                                 | 0.0                           | 0.3  |
| Y   | 9/20/00          | 27.3                               | <10                                | 35.1                                    | -8.61                              | 1.55                                      | 0.07  | 0.07  | -102.7                             | -14.0                                 | 0.0                           | 0.3  |
| USGS 1                                    | 9/26/00          | 35.9                               | <10                                | 54.0                                    | -10.39                             | 109.60                                    | 0.62  | 0.62  | -85.2                              | -9.8                                  | 6.4                           | 0.4  |
| USGS 2                                    | 9/26/00          | 18.9                               | 3364                               | 116.3                                   | -15.32                             | 75.27                                     | 0.51  | 0.51  | -84.9                              | -9.9                                  | 4.1                           | 0.3  |
| USGS 3                                    | 9/27/00          | 20.1                               | <10                                | <3.2                                    | -7.78                              | 103.50                                    | 0.68  | 0.68  | -85.0                              | -10.2                                 | 9.6                           | 0.5  |
| Big Spring Creek                          | 9/26/00          | --                                 | --                                 | --                                      | --                                 | --  | --  | --  | -92.1                              | -11.7                                 | 2.2                           | 0.3  |
| Big Spring Creek                          | 6/15/01          | 16.2                               | 11.2                               | 1.7                                     | --                                 | --  | --  | --  | --                                 | --                                    | 2.2                           | 0.3  |
| Little Spring Creek                       | 6/15/01          | 17.9                               | 15.4                               | 3.5                                     | --                                 | --  | --  | --  | -93.3                              | -12.0                                 | 2.6                           | 0.3  |
| Medano Creek                              | 5/22/00          | --                                 | --                                 | 7.0                                     | --                                 | --  | --  | --  | -109.3                             | -14.8                                 | 13.2                          | 1.0  |
| Medano Creek                              | 7/11/00          | --                                 | --                                 | 12.7                                    | --                                 | --  | --  | --  | -104.7                             | -14.1                                 | 13.5                          | 1.0  |
| Medano Creek                              | 9/12/00          | --                                 | --                                 | --                                      | --                                 | --  | --  | --  | -97.8                              | -13.5                                 | 13.9                          | 1.0  |
| Medano Creek                              | 12/14/00         | <13                                | 76.0                               | 15.1                                    | --                                 | --  | --  | --  | -106.5                             | -14.7                                 | --                            | 1.0  |
| Medano Creek                              | 6/15/01          | <13                                | 51.4                               | 7.7                                     | --                                 | --  | --  | --  | -108.9                             | -15.2                                 | 14.6                          | 0.8  |
| Sand Creek                                | 5/25/00          | --                                 | --                                 | 1.6                                     | --                                 | --  | --  | --  | -105.7                             | -14.7                                 | 11.9                          | 0.8  |
| Sand Creek                                | 9/14/00          | --                                 | --                                 | --                                      | --                                 | --  | --  | --  | -91.9                              | -12.9                                 | 11.5                          | 0.8  |
| Sand Creek                                | 12/13/00         | <13                                | 9.7                                | <3.2                                    | --                                 | --  | --  | --  | -94.0                              | -13.3                                 | 11.3                          | 0.8  |
| Sand Creek                                | 6/14/01          | <13                                | 20.4                               | 2.6                                     | --                                 | --  | --  | --  | -106.0                             | -14.9                                 | 11.4                          | 0.8  |

[--, no data; SW, surface water; >, greater than; <, less than; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter; µg/L, micrograms per liter; °C, degrees Celsius; ND, not detected; ddmmss, degrees, minutes, and seconds; per mil, parts per thousand; U, unconfined aquifer; C, confined aquifer; \*, unknown aquifer; NGVD 29, National Geodetic Vertical Datum of 1929]

to provide information on the deeper, and presumably older, water in the confined aquifer.

Ground-water samples were analyzed for a variety of geochemical constituents, which helped to verify the results of this study through multiple lines of evidence. Waters that are thousands of years old can be dated using  $^{14}\text{C}$ . Waters less than 50 years old can be dated using  $^3\text{H}$  and CFC's (Plummer and Friedman, 1999). Waters less than 30 years old can be dated using  $\text{SF}_6$ , but  $\text{SF}_6$  is best suited for waters less than 10 years old (Busenberg and Plummer, 2000). If conditions are favorable, accuracy of ages determined with CFC's and  $\text{SF}_6$  can be plus or minus 1 or 2 years. The source of recharge waters and the amount of evaporation those waters have undergone prior to recharge can be determined using  $^2\text{H}$  and  $^{18}\text{O}$ . Major ions can be used to characterize ground-water types, determine sources of ground water, and evaluate chemical reactions that may be occurring as water moves through the aquifer. The Isotope Laboratory at the University of Waterloo located in Ontario, Canada, analyzed the  $^{14}\text{C}$  samples. The USGS Isotope Tracers Laboratory located in Menlo Park, California, analyzed the  $^3\text{H}$  samples. The USGS Reston Chlorofluorocarbon Laboratory located in Reston, Virginia, analyzed CFC and  $\text{SF}_6$  samples. The USGS Reston Stable Isotope Laboratory located in Reston, Virginia, analyzed  $^2\text{H}$  and  $^{18}\text{O}$  samples. The USGS National Water Quality Laboratory in Denver, Colorado, analyzed the major ion samples.

Ground- and surface-water sampling and field-processing methods specified by the USGS (U.S. Geological Survey, 1997 to present) were used in this study. Ground-water samples were collected using a 2-inch Grundfos™ Redi-flow submersible pump powered by a portable electrical generator. Surface-water samples were collected using equal-width increment sampling methods (U.S. Geological Survey, 1997 to present). Special sampling procedures are required for CFC and  $\text{SF}_6$  samples to avoid contact with ambient air. Sampling procedures for CFC and  $\text{SF}_6$  samples specified by the USGS Reston Chlorofluorocarbon Laboratory in Reston, Virginia (U.S. Geological Survey Reston Chlorofluorocarbon Laboratory, 2000) were used. A minimum of five replicate CFC water samples in flame-sealed glass containers were collected at each site. At a minimum, three of the five replicate CFC water samples were analyzed. If a large variation in CFC concentrations was measured in those three replicate samples, then all five replicate CFC water samples were analyzed, which helped to ensure that consistent results were obtained. Replicate  $\text{SF}_6$  samples were collected and analyzed to help ensure consistent results.

## Age-Dating and Isotopic Characterization Techniques

The following is an overview of the concepts, geochemical constituents, and geochemical modeling methods used by this study to determine ground-water ages, to estimate ground-water quality changes along a flowpath, to determine

the amount of mixing of different types of water, to identify sources of water, and to identify water that has undergone evaporation since precipitation in the source area.

## Ground-Water Age, Piston Flow, and Mixing

Ground-water ages are often termed “apparent age” because the ages are modeled using simplifying assumptions regarding transport processes that may affect the age-dating constituent (such as CFC's) in the water (Plummer and Busenberg, 1999). The simplest and most common transport assumption in ground-water age dating is to assume piston flow, which assumes that the constituent concentration was not altered by transport processes (such as mixing or dispersion) from the point of entry to the measurement point in the aquifer. Some ground-water ages determined with a piston-flow model may be an oversimplification, because mixing and dispersion can occur during ground-water flow.

All ground water pumped from wells is, to some extent, water mixed within the well bore (Plummer and Busenberg, 1999). It is common to have the youngest waters near the top of an aquifer (near the source of recharge) and the oldest waters near the bottom of an aquifer. If the well screen is long, water flowing into a well can be drawn from multiple portions of the aquifer, where it mixes within the well bore. Mixing of water in the well bore produces mixed ages, which can complicate modeling of apparent age. Apparent ages of water sampled from narrow intervals of an aquifer probably are affected less by mixing than those ages interpreted from water samples pumped from large open intervals or from well bores open to multiple fractures of water-bearing zones. The simplest case of mixing occurs if the water is a binary mixture of old (CFC-free) and young waters; the problem becomes unsolvable if more than two waters mix. Most researchers model apparent ages based upon binary mixing because it is difficult to quantify mixing of more than two water types.

For the most part, sites sampled at Great Sand Dunes had relatively narrow screened intervals, which decreases the amount of mixing in the well bore. Sites USGS-1 and USGS-3 have screened intervals of 5 feet; sites K, O, P, R, S, and USGS-2 have screened intervals of 10 feet; sites V, W, X, and Y have screened intervals of 20 feet; and PR1 has a screened interval of 60 feet (table 1, fig. 1).

## Hydrogen and Oxygen Stable Isotopes

The isotopic composition of hydrogen ( $^1\text{H}$  and  $^2\text{H}$ ) and oxygen ( $^{16}\text{O}$  and  $^{18}\text{O}$ ) in the water molecules of ground and surface water at Great Sand Dunes were examined to determine sources of water and the effects of evaporation. Isotopes are atoms of the same element that differ in mass because of a difference in the number of neutrons in the nucleus. For example, deuterium ( $^2\text{H}$ ) is hydrogen with one proton and one neutron in the nucleus and is distinguished from hydrogen ( $^1\text{H}$ )



that has one proton and no neutrons in the nucleus. In application to ground water in Great Sand Dunes,  $^2\text{H}$  and  $^{18}\text{O}$  can be used to trace ground water along a flowpath, to determine the amount of mixing of different types of water, and to identify water that has undergone evaporation since precipitation in the source area (Coplen, 1993; Coplen and others, 2000).

The isotopic compositions of stable isotopes  $^2\text{H}$  and  $^{18}\text{O}$  are expressed in per mil units, or parts per thousand, as deviation of the isotope ratio relative to a standard by using delta notation ( $\delta$ ), as shown in equation 1:

$$\delta = \left[ \frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \right] \times 1,000 \quad (1)$$

where

$R$  is the measured isotopic ratio. The delta symbol in this report is followed by the chemical symbol for the heavier isotope of the isotopic pair (for instance  $\delta^{18}\text{O}$ , because  $^{18}\text{O}$  is heavier than  $^{16}\text{O}$ ). Per mil values in this report are presented relative to the standardized reference compound, which is Vienna Standard Mean Ocean Water (Coplen, 1994) for hydrogen ( $\delta^2\text{H}$ ) and oxygen ( $\delta^{18}\text{O}$ ). As an example, an  $^{18}\text{O}/^{16}\text{O}$  measurement that is +50 per mil ( $\delta^{18}\text{O} = +50$ ) is enriched in  $^{18}\text{O}$  by 5 percent relative to the standard; the sample is isotopically heavy relative to the standard.

Isotopic variations of  $^2\text{H}$  and  $^{18}\text{O}$  are usually covariant because they are part of the water molecule. The isotopic composition of precipitation varies globally according to the World Meteoric Water Line (Craig, 1961) (fig. 2), computed from equation 2:

$$\delta^2\text{H (per mil)} = 8 \delta^{18}\text{O (per mil)} + 10 \quad (2)$$

Although the isotopic composition of most precipitation varies with a slope of approximately 8 on plots of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , the intercept of  $\delta^{18}\text{O}$  at 0 per mil, known as the deuterium excess (Dansgaard, 1964) can vary widely depending on relative humidity in the moisture source and local climatic conditions where precipitation forms. As water evaporates, the lighter isotopes  $^1\text{H}$  and  $^{16}\text{O}$  in water vapor are removed preferentially, and the stable isotopic compositions of the remaining water are shifted toward greater enrichment in  $^2\text{H}$  and  $^{18}\text{O}$ . Because of the kinetic isotope fractionation effect of evaporation, the isotopic composition of the residual water typically shifts off the World Meteoric Water Line along slopes of 3 to 6, partly because of a complicated function of humidity, temperature, salt concentration, and other factors (Coplen, 1993, p. 235). The residual water undergoing evaporation becomes enriched in  $^2\text{H}$  and  $^{18}\text{O}$ . Water undergoing multiple cycles of evaporation is enriched further along the expected evaporation path (fig. 2).

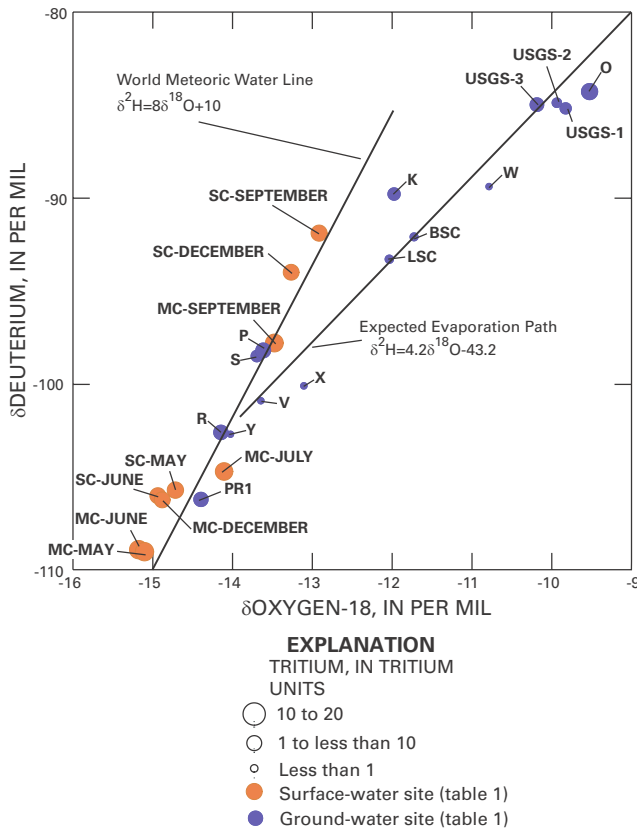
## Sulfur Hexafluoride

Sulfur hexafluoride ( $\text{SF}_6$ ) is a colorless, odorless, non-flammable, nontoxic, stable gas with excellent electrical insulating and arc-quenching properties (Busenberg and Plummer, 2000). Industrial production began in 1953 with the introduction of  $\text{SF}_6$ -filled electrical switches, and annual production has increased continually since that time. Studies of  $\text{SF}_6$  as a potential environmental tracer for dating young ground water are being done because  $\text{SF}_6$ : (1) has a high rate of increase in the atmosphere (6 percent per year), (2) is stable in soils, (3) resists biodegradation, (4) does not substantially sorb onto organic matter, and (5) does not substantially degrade under highly reducing conditions (Busenberg and Plummer, 2000). The age of young ground waters can probably be determined using  $\text{SF}_6$  in most geologic environments except areas with igneous and volcanic rocks, where concentrations of naturally occurring  $\text{SF}_6$  can be much greater than from anthropogenic sources. The age-dating range of  $\text{SF}_6$  for ground water is currently about 30 years (Busenberg and Plummer, 2000).

Ground-water ages of water from most sites sampled at Great Sand Dunes could not be estimated using  $\text{SF}_6$ . Almost all of the samples collected for this study had  $\text{SF}_6$  concentrations that were much greater than that expected in current precipitation (table 2). The anomalously high concentrations of  $\text{SF}_6$  are probably due to naturally-occurring  $\text{SF}_6$  in the igneous rocks near Great Sand Dunes. Even samples collected from Medano and Sand Creeks had anomalously high  $\text{SF}_6$  concentrations;  $\text{SF}_6$  was presumably leached from the igneous rocks located in the Sangre de Cristo Mountains.

## Carbon-14

Carbon-14 ( $^{14}\text{C}$ ) has a relatively long radioactive half-life (5,730 years), which makes it suitable for dating ground waters that are thousands of years old. The upper atmosphere produces  $^{14}\text{C}$  naturally; the  $^{14}\text{C}$  activity is balanced by decay and removal by precipitation to maintain a steady-state atmospheric  $^{14}\text{CO}_2$  activity (Clark and Fritz, 1997). High neutron fluxes associated with above-ground thermonuclear testing produced large quantities of  $^{14}\text{C}$  so that by 1964 the atmospheric activities in the northern hemisphere had almost doubled. The increased activity of  $^{14}\text{C}$  has now been almost washed out of the atmosphere, but can be found in plant material, the oceans, and ground water that was recharged during that time in history. Dating of ground water with  $^{14}\text{C}$  is accomplished by measuring  $^{14}\text{C}$  activities of dissolved inorganic and organic carbon in the water (DIC and DOC). Dissolved  $\text{CO}_2$ , carbonic acid, bicarbonate, and carbonate are the four main species of DIC in ground water (Clark and Fritz, 1997). The concentrations of bicarbonate and carbonate together comprise carbonate alkalinity. Old ground water can be dated if sufficient time has passed for measurable decay of the initial  $^{14}\text{C}$  activity ( $A_0$ ), which depends on the analytical reporting limits of the laboratory. Measured  $^{14}\text{C}$  activities are expressed



**Figure 2.** Relative hydrogen isotope ratios, relative oxygen isotope ratios, and tritium activities measured in ground- and surface-water samples collected at Great Sand Dunes National Monument, 2000-2001 (2H, deuterium; <sup>18</sup>O, oxygen-18; δ, per mil; MC, Medano Creek; SC, Sand Creek; BSC, Big Spring Creek; LSC, Little Spring Creek).

as a percent of modern carbon; the activity of modern carbon is defined as 95 percent of the <sup>14</sup>C activity in 1950 of the National Bureau of Standards (NBS) oxalic standard (Clark and Fritz, 1997, p. 18), which approximates the <sup>14</sup>C activity of wood grown in 1890 that was relatively free of CO<sub>2</sub> from fossil-fuel sources.

Several models can be considered in <sup>14</sup>C dating (see for example, Kalin, 1999). The “unadjusted age” is that which has not been corrected for geochemical reactions, and is always the oldest possible <sup>14</sup>C age. The <sup>14</sup>C age, t, is calculated from the <sup>14</sup>C radioactive decay equation:

$$t = \frac{5,730}{\ln 2} \ln \frac{A_o}{A_{Meas}} \quad (3)$$

where

$A_o$  is the initial <sup>14</sup>C activity in the initial water, in percent modern carbon;

$A_{Meas}$  is the measured <sup>14</sup>C activity of DIC in the final water (in pmc), in percent modern carbon; and  
5,730 is the half-life of <sup>14</sup>C, in years.

A more accurate estimated <sup>14</sup>C age can be obtained by accounting for geochemical reactions that could affect carbon concentrations in water. A computer program, NETPATH (Plummer and others, 1994), was used to calculate the <sup>14</sup>C ages of the ground-water samples, to calculate calcite saturation indices of ground-water samples, and to calculate mixing of two sources of ground water. NETPATH models net geochemical mass-balance reactions of minerals (and gases) that dissolve or precipitate in the aquifer material as the initial water evolves chemically into the final water.

To calculate <sup>14</sup>C ages of ground water using NETPATH, two water analyses are used: an initial water and a final water. The initial water is determined by sampling water from a well that was recharged just before the advent of above-ground thermonuclear tests. The final water is determined by sampling a well suspected of having water thousands of years old. NETPATH adjusts the <sup>14</sup>C activity (in percent modern carbon, pmc) of the initial water for all sources and sinks of carbon that affect the carbon mass transfer between initial and final water. Examples include dissolution of carbonate minerals, oxidation of organic matter, and addition of CO<sub>2</sub> gas from the unsaturated zone. This procedure calculates the <sup>14</sup>C activity of the final water, adjusted for chemical reaction but not radioactive decay; <sup>14</sup>C dating based upon radioactive decay then is applied to the final water.

### Tritium

The radioactive isotope of hydrogen, <sup>3</sup>H, was used to identify recent ground-water recharge or ground-water mixtures that contain some recent water. <sup>3</sup>H substitutes for a hydrogen (<sup>1</sup>H) atom or deuterium (<sup>2</sup>H) atom in the water molecule and can serve as an excellent tracer because water containing a <sup>3</sup>H atom follows the same pathway through the environment as water containing no <sup>3</sup>H atoms (Plummer and others, 1993, p. 256–257). The half-life of <sup>3</sup>H is 12.32 years (Lucas and Unterweger, 2000) and commonly is measured in picocuries per liter (pCi/L) or tritium units (1 TU = 3.19 pCi/L).

Low concentrations of <sup>3</sup>H are produced naturally by the interaction of the atmosphere with cosmic rays from the solar wind. Atmospheric thermonuclear weapons testing from 1952 to the mid-1960’s introduced a large amount of <sup>3</sup>H to the atmosphere that was incorporated directly into water molecules of precipitation. Concentrations in precipitation have been decreasing since that time because of the exchange of water with the oceans, short half-life of <sup>3</sup>H, and because most atmospheric thermonuclear weapons testing has been discontinued. Because the concentration of <sup>3</sup>H in the atmosphere was high for a relatively short period of time, its presence in ground water can identify water that has been recharged during the last 50 years or mixtures that contain a fraction of

**Table 2.** Mean concentrations and calculated atmospheric mixing ratios of chlorofluorocarbons and mean concentrations of sulfur hexafluoride measured in ground water and surface water, Great Sand Dunes National Monument, south-central Colorado, 2000-2001

[CFC, chlorofluorocarbon; mean concentration, mean CFC concentration normally calculated from three replicate samples collected at each site; pg/kg, picograms per kilogram; pptv, parts per trillion by volume; SF<sub>6</sub>, sulfur hexafluoride]

| Site name    | CFC-11<br>mean<br>concentration in<br>solution<br>(pg/kg) | CFC-11<br>calculated<br>atmospheric<br>mixing ratio<br>(pptv) | CFC-12<br>mean<br>concentration in<br>solution<br>(pg/kg) | CFC-12<br>calculated<br>atmospheric<br>mixing ratio<br>(pptv) | CFC-113<br>mean<br>concentration in<br>solution<br>(pg/kg) | CFC-113<br>calculated<br>atmospheric<br>mixing ratio<br>(pptv) | SF <sub>6</sub> mean<br>concentration in<br>solution (pptv) |
|--------------|---|---|---|---|--|--|---|
| K            | 322   | 146   | 157   | 303   | 56.7   | 60.6   | 15.6  |
| O            | 940   | 437   | 220   | 447   | 65.3   | 72.0   | 13.8  |
| P            | 536   | 190   | 294   | 470   | 84.1   | 69.0   | 23.0  |
| PR1          | 324   | 142   | 101   | 196   | 18.6   | 19.3   | 2.6   |
| R            | 1,005   | 400   | 253   | 449   | 68.9   | 64.1   | 30.9  |
| S            | 821   | 369   | 242   | 478   | 82.1   | 87.3   | 10.5  |
| V            | 517   | 209   | 164   | 295   | 37.7   | 35.8   | 22.5  |
| W            | 2.2   | .9  | 1.0   | 1.8   | 1.3  | 1.3  | 12.8  |
| X            | 1,168   | 470   | 294   | 530   | 68.1   | 65.0   | 21.0  |
| Y            | .4  | .2  | .6  | 1.5   | .0   | .0   | 13.1  |
| USGS -1      | 115   | 56  | 91  | 192   | 15.8   | 18.3   | 2.2   |
| USGS -2      | 45.1  | 21  | 34  | 69  | 8.2  | 9.1  | 1.6   |
| USGS -3      | 154   | 71  | 77  | 156   | 18.1   | 19.9   | 1.6   |
| Medano Creek | 613   | 268   | 340   | 655   | 96.9   | 100  | 13.6  |
| Sand Creek   | 404   | 292   | 267   | 726   | 65.3   | 107  | 13.3  |

post-1950's water. <sup>3</sup>H concentrations in precipitation prior to thermonuclear weapons testing are not well known but probably did not exceed 2 to 8 TU (Plummer and others, 1993, p. 260). Because <sup>3</sup>H has a half-life of 12.32 years, water derived from precipitation before thermonuclear weapons testing would contain a maximum <sup>3</sup>H concentration of 0.12 to 0.5 TU by the early 2000's. Clark and Fritz (1997, p. 185) state that waters with <sup>3</sup>H activities above about 30 TU contain a considerable component of recharge from the 1960's or the 1970's, and activities above 50 TU indicate recharge predominantly from the 1960's.

Historic <sup>3</sup>H activities in precipitation can be used to estimate present <sup>3</sup>H activities measured in ground water recharged from precipitation in the past. Albuquerque, New Mexico, is the closest station to Great Sand Dunes for which a long-term record of <sup>3</sup>H in precipitation exists. The U.S. Geological Survey low-level <sup>3</sup>H laboratory has measured the activity of <sup>3</sup>H in precipitation collected at Albuquerque over sampling intervals of weekly to quarterly since August 1958 (International Atomic Energy Agency, 2001). Winter-spring precipitation at Albuquerque during the past several years contained 8 to 9 TU. Precipitation from about 1985 to date of sampling for this study (September 2000) would contain on average about 7.4 TU in September 2000. Precipitation from about 1975 to 1985 would average about 12 plus or minus 5 TU if sampled in September 2000. Precipitation from approximately 1970 would contain considerably higher <sup>3</sup>H content (about 40 TU) than more recent precipitation, if sampled in September 2000. Actual <sup>3</sup>H concentrations in precipitation at Great Sand Dunes may be larger than those measured at Albuquerque due to the latitudinal gradients of <sup>3</sup>H concentrations in precipitation

(Plummer and others, 2004). Rozanski and others (1991) estimate that the average latitudinal variation of <sup>3</sup>H in the northern hemisphere is approximately 0.023 log TU per degree latitude. As an example, Great Sand Dunes is approximately 3 degrees latitude north of Albuquerque, so the average <sup>3</sup>H content of precipitation during 2000 should be about 10.5 TU relative to 9 TU at Albuquerque.

## Chlorofluorocarbons

CFC's were used to determine ages of recently recharged ground water and the effects of mixing of different ground waters. CFC's are stable, synthetic organic compounds that were developed in the early 1930's as safe alternatives to ammonia and sulfur dioxide in refrigeration and have been used in a wide range of industrial and refrigerant applications (Plummer and Friedman, 1999). Production of CFC-12 (dichlorodifluoromethane, CF<sub>2</sub>Cl<sub>2</sub>) began in 1931, followed by CFC-11 (trichlorofluoromethane, CFCl<sub>3</sub>) in 1936, and then by many other CFC compounds, most notably CFC-113 (trichlorotrifluoroethane, C<sub>2</sub>F<sub>3</sub>Cl<sub>3</sub>). At ordinary (room) temperatures, CFC-113 is liquid (boiling point 47.6°C), and CFC-11 and CFC-12 are gases (boiling points -23.6 and -29.8°C, respectively). CFC-11 and CFC-12 were used as coolants in air conditioning and refrigeration; as blowing agents in foams, insulation, and packing materials; as propellants in aerosol cans; and as solvents (Plummer and Busenberg, 1999). CFC-113 has been used primarily by the electronics industry in semiconductor chip manufacturing, in vapor degreasing and cold immersion cleaning of microelectronic components, and

in surface cleaning. Probably better known as Freon™, CFC's are nontoxic, nonflammable, and noncarcinogenic, but they contribute to ozone depletion. Therefore in 1987, 37 nations signed an agreement to limit release of CFC's and to halve CFC emissions by 2000. This agreement was strengthened in 1990 and 1992 to establish a cutoff date of 1996 for production of CFC's in industrialized nations. The United States ceased production on January 1, 1996, as a regulatory requirement under the Clean Air Act (Plummer and Friedman, 1999).

CFC's provide excellent tracers and dating tools of young water (50-year time scale). Ground-water age dating with CFC's is based on Henry's law solubility, which is, the concentration of the gas dissolved in water in equilibrium with air is proportional to the partial pressure of the gas in air (Plummer and Busenberg, 1999). Under favorable conditions, sufficient concentrations of CFC-12, CFC-11, and CFC-113 can dissolve into water and allow dating of ground water recharged since approximately 1941, 1947, and 1955, respectively. Ground-water age dating with CFC-11, CFC-12, and CFC-113 is possible because: (1) the atmospheric mixing ratios (concentrations of the compounds in air) of these compounds are known and(or) have been reconstructed over the past 50 years, (2) the Henry's law solubilities in water are known, and (3) concentrations in air and young water are relatively high and can be measured (Plummer and Busenberg, 1999). Atmospheric concentrations of CFC-11, CFC-12, and CFC-113 in air in North America are shown in figure 3.

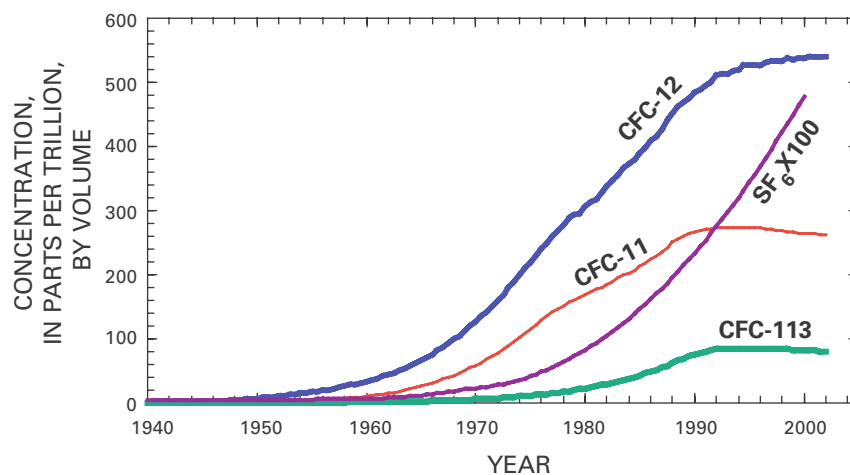
## Dissolved Gases

Ground-water age dating with CFC's is based on gas solubility, which is affected by the recharge temperature and excess air in the water sample (Plummer and Busenberg, 1999), and altitude at location of recharge. The recharge temperature is the temperature of the recharge water at the water table during recharge; over-estimation of recharge temperature

results in apparent ages that are too young, and under-estimation gives apparent ages that are too old. Dissolved gases of  $N_2$ , Ar, methane ( $CH_4$ ),  $O_2$ , and  $CO_2$  in ground water were used to estimate recharge temperature and excess air of the water samples. The concentration, as well as the ratios of concentrations of dissolved gases, can be used to calculate the recharge temperature of a ground-water sample using Henry's law. Excess air is air dissolved in ground water in relative proportions equal to that of the troposphere, and in excess of that determined by solubility equilibrium. Excess air is trapped and dissolved under increased hydrostatic pressure in ground water at the capillary fringe or in fractures as the water table rises. High concentrations of excess air are common in fractured rock aquifers and in aquifers in semi-arid areas. Introduction of excess air adds CFC's to ground water, and if not accounted for in age interpretation, causes a young-age bias (Plummer and Busenberg, 1999). Excess air is determined by comparing the ratio of  $N_2$  to Ar in air to the equilibrium solubility-ratio of  $N_2$  to Ar in water. The altitude at location of recharge was estimated to be the altitude of Medano and Sand Creeks at the Sangre de Cristo mountain front.

## Water-quality sampling results

This section describes the results of water-quality sampling from sites completed in the unconfined and confined aquifers and from Medano, Sand, Big Spring, and Little Spring Creeks. Ground-water samples were analyzed for major ions,  $^2H$  and  $^{18}O$ ,  $^{14}C$ ,  $^3H$ , and CFC's; surface-water samples were analyzed for major ions,  $^2H$  and  $^{18}O$ ,  $^3H$ , and CFC's. The results of the laboratory analyses are presented in this section; results then are synthesized in later sections entitled "Ground-Water Flow Direction, Water Quality, Recharge, and Age in the Unconfined Aquifer" and "Ground-Water Age and Water Quality in the Confined Aquifer."



**Figure 3.** Atmospheric concentrations of CFC-11, CFC-12, CFC-113, and SF<sub>6</sub> in air in North America (from Plummer and Busenberg, 1999).

### Major Ions

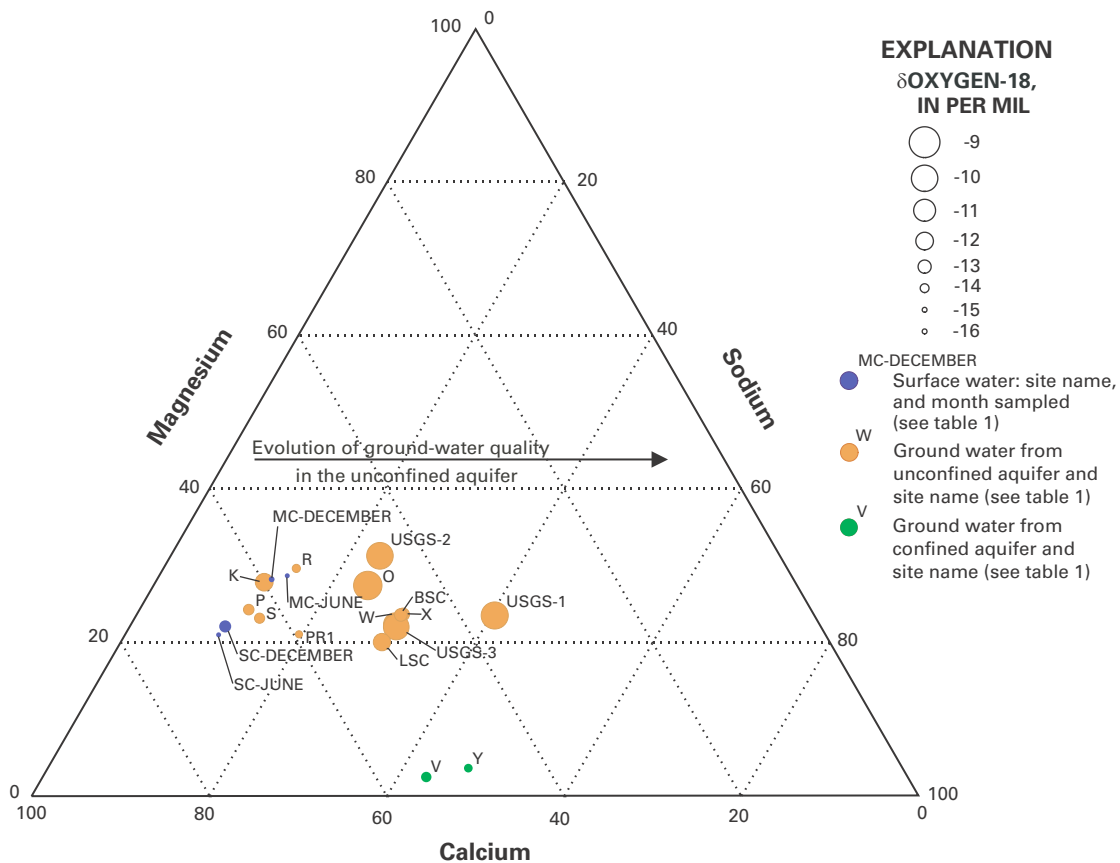
A trilinear diagram of the major cations measured in samples collected for this study is shown in figure 4. Trilinear diagrams show the relative percentages of cations in milliequivalents per liter (Hem, 1992). Trilinear diagrams also were made for anions, but no detectable trends were observed.

Major ion samples collected from Medano and Sand Creeks plot on the left-hand portion of figure 4. Sites K and P are located adjacent to Medano and Sand Creek, respectively (fig. 1). The cation composition of water samples collected from sites K and P is similar to that from Medano and Sand Creeks (fig. 4). Samples collected from sites O, W, X, USGS-1, USGS-2, USGS-3, and Big and Little Spring Creeks have a smaller percentage of calcium and a larger percentage of sodium (fig. 4) than samples collected from Medano and Sand Creeks. The percentage of calcium tends to decrease and the percentage of sodium tends to increase with increasing distance from Medano and Sand Creeks. Water samples collected from sites completed in the confined aquifer (sites V and Y) plot in a different portion of figure 4 than water samples collected at the other sites, indicating that the major ion chemistry

of water from sites V and Y is different than that of water from wells completed in the unconfined aquifer.

### Hydrogen and Oxygen Stable Isotopes

The <sup>2</sup>H and <sup>18</sup>O isotopic compositions of samples collected from Medano and Sand Creeks correspond with the World Meteoric Water Line (fig. 2), indicating that precipitation in the Sangre de Cristo Mountains east of Great Sand Dunes has undergone very little evaporation after reaching the land surface. Five quarterly samples were collected from Medano and Sand Creeks beginning May 2000 to observe seasonal differences in isotopic composition. May and June samples collected from Medano Creek have light isotopic compositions compared to most samples collected for this study (fig. 2); these samples are composed mostly of snowmelt derived from precipitation during the coolest time of the year. Isotopic compositions of samples collected from sites P, PR1, R, and S plot along the same World Meteoric Water Line as samples collected from Medano and Sand Creeks, indicating the waters did not undergo substantial amounts of evaporation prior to recharge.



**Figure 4.** Trilinear diagram of cation percentages and  $\delta$ oxygen-18 of ground water and surface water sampled at Great Sand Dunes National Monument, 2000-2001 (MC, Medano Creek; SC, Sand Creek; BSC, Big Spring Creek; LSC, Little Spring Creek;  $\delta$ , per mil).



Samples collected from sites O, USGS-1, USGS-2, and USGS-3 have the heaviest isotopic compositions compared to other samples and plot along a line of slope approximately 4.4, consistent with the expected evaporation path, which indicates that the waters underwent evaporation prior to recharge. Samples collected from site K, site W, Big Spring Creek, and Little Spring Creek probably underwent about half of the evaporation prior to recharge than samples collected at sites O, USGS-1, USGS-2. With the exception of site K, water with heavier isotopic compositions was sampled from sites relatively distant from Medano or Sand Creek, and water with the lightest isotopic compositions was sampled from sites relatively close to Medano or Sand Creek. The  $^2\text{H}$  and  $^{18}\text{O}$  isotopic compositions of waters sampled from the confined aquifer (sites V and Y) plot near the World Meteoric Water Line, as do the surface water samples (fig. 2).

## Carbon-14

Water samples from sites completed in the unconfined aquifer (sites PR1, R, W, and X) were analyzed for  $^{14}\text{C}$  to establish initial  $^{14}\text{C}$  activities for modeling ground-water ages of water from the confined aquifer. Activities of  $^{14}\text{C}$  in DIC ranged from about 84.9 pmc in water from site PR1 to 115.1 pmc in water from site R, indicating these waters were recharged in the last few hundred years (table 1).

The  $^{14}\text{C}$  activities of DIC in water from sites completed in the confined aquifer (sites V and Y) are about 38.9 and 1.6 pmc, respectively (table 1). Unadjusted ground-water ages calculated with the  $^{14}\text{C}$  decay equation (equation 3) indicates maximum  $^{14}\text{C}$  ages of 6,600 and 33,300 years before present (BP) for water from sites V and Y, respectively. These are the oldest possible ages for these water samples (if they are not mixtures); adjusted ages based upon NETPATH geochemical modeling will be presented later in this report.

## Tritium

Samples of  $^3\text{H}$  were collected quarterly from Medano and Sand Creeks during 2000; minimum  $^3\text{H}$  activities were 11.3 TU, maximum  $^3\text{H}$  activities were 14.6 TU, and median  $^3\text{H}$  activities were 12.7 TU (table 1). If the Albuquerque, New Mexico, record for  $^3\text{H}$  in precipitation can be applied to the study area, the data for  $^3\text{H}$  activity in surface water indicate that Medano and Sand Creeks may contain a fraction of ground water recharged prior to about 1985, indicating that a portion of the base flow in the Creeks is probably bedrock discharge from the Sangre de Cristo Mountains. The size of the dots in figure 2 is scaled to  $^3\text{H}$  activities;  $^3\text{H}$  activities of water from sites O, P, PR1, R, and USGS-3 are similar to those measured in Medano and Sand Creeks. Activities of  $^3\text{H}$  in water from sites V, W, X, and Y are zero (table 1), indicating the age of the water is older than 1953. Activities of  $^3\text{H}$  in water from sites K, S, USGS-1, USGS-2, Big Spring Creek, and Little Spring Creek are between 1 and 10 TU, indicating

that they contain at least a portion of waters younger than 1953 (table 1). Water samples collected from the confined aquifer (sites V and Y) had zero  $^3\text{H}$  activities (table 1), indicating that the waters are older than 1953.

## Chlorofluorocarbons

The measured CFC concentrations and the calculated atmospheric mixing ratios of ground and surface water sampled at Great Sand Dunes are listed in table 2. Water samples collected from sites W and Y contained no substantial concentrations of CFC's, indicating the ground water ages are older than 1941 (table 2). These results are consistent with that expected because site Y is 351 feet deep and is completed in the confined aquifer. The CFC results obtained for water from sites W and Y, in addition to indicating the presence of old, pre-1941 water in the study area, confirm that the sampling procedures and equipment did not introduce CFC's into the samples.

Ground-water samples collected from site V contained detectable amounts of CFC's, which was not expected because site V is completed in the confined aquifer. Water from site V had zero  $^3\text{H}$  activities, suggesting the water is older than 1953. Geochemical mixing models were constructed using NETPATH (Plummer and others, 1994) to determine if CFC's in water from site V could be the result of a leaky well seal, which would result in a mixture of water from the confined aquifer (site Y) and water from the unconfined aquifer (site R or S). Those geochemical models indicated that water from site V is probably not a mixture of waters from the unconfined and confined aquifers. Figure 4 confirms the results of the mixing models, because the ionic composition of water from site V does not lie between water from site Y and waters from the unconfined aquifer. Site V was drilled using the reverse air rotary drilling method. It is possible that air from the drilling process injected CFC-containing air into the aquifer and contaminated the ground water with CFC's; because site V is a monitoring well, it is possible that it hasn't been pumped sufficiently to flush out the CFC contamination.

## Ambient Air Samples

In most samples, it was not possible to estimate dates using CFC-11 because most CFC-11 concentrations in ground water were anomalously high. This high concentration may be caused by anomalously high concentrations of CFC-11 in local air. Ambient air samples were collected near sites S, USGS-2, USGS-3, and Medano Creek (table 3) to determine CFC concentrations in the atmosphere at Great Sand Dunes. The CFC-12 and CFC-113 concentrations (about 540 and 80 pptv, respectively) were within the expected range of air in North America (fig. 3). The CFC-11 concentrations (between about 300 and 1350 pptv) were higher than the 270-pptv concentration expected in air in North America. The cause

of the high CFC-11 concentrations is not known; Great Sand Dunes is not downwind of an urban area. The predominant land use upwind from Great Sand Dunes is agriculture, so perhaps CFC-11 is used as a propellant or inert ingredient in crop protection chemicals or other chemicals used in the area. Plummer and others (2000) measured anomalously high concentrations of CFC-11 in air and unsaturated zone air samples from south-central Idaho, which has similar cropping practices as the San Luis Valley. U.S. Environmental Protection Agency regulations (U.S. Environmental Protection Agency, 1998) permit use of CFC-11, CFC-12, and CFC-113 as inert ingredients in crop protection chemicals. Data were not available to determine if crop protection chemicals used in the region contain CFC-11.

Dissolved-gas samples were collected in replicate from each site; samples were analyzed for N<sub>2</sub>, Ar, O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> (table 4). Most sites had recharge temperatures ranging from 5.3 to 9.9 degrees Celsius (table 4), but ground water collected from USGS-2 had a recharge temperature of 22.5 °C. The dissolved-gas sample collected from USGS-2 is believed to be representative because a replicate sample provided an identical result. The higher recharge temperature at USGS-2 may be the result of focused recharge from a summer storm event(s). The excess air is larger than most other samples, indicating air was trapped and dissolved during a rapid recharge event. The mean annual air temperature at Great Sand Dunes measured during 1980-2000 is 6.6 °C (Colorado Climate Center, 2002), and the mean air temperatures measured during June, July, and August

**Table 3.** Chlorofluorocarbon data analyzed from air samples collected at Great Sand Dunes National Monument, south-central Colorado, 2000-2001

[CFC, chlorofluorocarbon; pptv, parts per trillion by volume; percent modern CFC mixing ratios in air are based on mean values for North American air of 264, 540, and 80 pptv during the period of sampling (<http://water.usgs.gov/lab/cfc/>)]

| Site name<br>(see fig. 1<br>for<br>location) | Date of<br>sample<br>collection | CFC-11,<br>standard<br>deviation of<br>measurement |        |                             | CFC-12,<br>standard<br>deviation of<br>measurement |        |                             | CFC-113,<br>standard<br>deviation of<br>measurement |        |                              |
|--|---------------------------------|--|--------|-----------------------------|--|--------|-----------------------------|---|--------|------------------------------|
|  |                                 | CFC-11<br>(pptv)                                   | (pptv) | Percent<br>modern<br>CFC-11 | CFC-12<br>(pptv)                                   | (pptv) | Percent<br>modern<br>CFC-12 | CFC-113<br>(pptv)                                   | (pptv) | Percent<br>modern<br>CFC-113 |
| S  | 09/19/2000                      | 502.10   | 0.17   | 190.2                       | 537.60   | 5.42   | 99.6                        | 84.11   | 0.27   | 102.6                        |
| USGS-2                                       | 09/26/2000                      | 302.18   | 1.73   | 114.5                       | 538.93   | 1.80   | 99.8                        | 80.45   | 0.21   | 98.1                         |
| USGS-3                                       | 09/27/2000                      | 305.64   | 0.78   | 115.8                       | 534.27   | 1.86   | 98.9                        | 79.54   | 0.45   | 97.0                         |
| Medano<br>Creek                              | 09/25/2000                      | 1353.54  | 12.36  | 512.7                       | 540.57   | 1.37   | 100.1                       | 79.83   | 0.21   | 97.4                         |

## Dissolved Gases

Ground-water age dates determined using CFC's are based on Henry's law solubility, so it is important to estimate the temperature at time of recharge and altitude at location of recharge. Recharge temperatures were determined for this study using dissolved-gas concentrations measured from water samples collected at the same time as the CFC samples were collected (table 4).

of 1980-2000 are 16.1 °C, 18.6 °C, and 17.4 °C, respectively. Water sampled from site USGS-2 must have been recharged under conditions slightly above the mean summer air temperatures. An alternative explanation for the higher recharge temperature is decomposition of organic matter in the aquifer matrix at the site, which would produce the larger methane and CO<sub>2</sub> concentrations and smaller dissolved oxygen concentrations measured in water from USGS-2. Decomposition of organic matter is probably not the process that lead to higher recharge temperatures of water from USGS-2 because organic decomposition would produce negative excess air; water from USGS-2 has relatively large excess air.

**Table 4.** Dissolved-gas data analyzed from ground-water samples collected at Great Sand Dunes National Monument, south-central Colorado, 2000-2001

[°C, degrees Celsius; mg/L, milligrams per liter, NAVD 29, National Geodetic Vertical Datum of 1929]

| Site name (see fig. 1 for location) | Water temperature at time of collection (°C) | Nitrogen (N <sub>2</sub> ) (mg/L) | Argon (Ar) (mg/L) | Oxygen (O <sub>2</sub> ) (mg/L) | Carbon dioxide (CO <sub>2</sub> ) (mg/L) | Methane (CH <sub>4</sub> ) (mg/L) | Estimated recharge altitude (feet above NAVD 29) | Calculated recharge temperature (°C) | Average recharge temperature (°C) | Excess air in water sample (cubic centimeters per liter at standard temperature and pressure) | Average excess air in water sample (cubic centimeters per liter at standard temperature and pressure) |
|-------------------------------------|--|-----------------------------------|-------------------|---------------------------------|--|-----------------------------------|--|--------------------------------------|-----------------------------------|---|---|
| K                                   | 14.7   | 15.432                            | 0.547             | 0.06                            | 14.62                                    | 0.0000                            | 8,013  | 9.5                                  |                                   | 1.8   |   |
| K                                   | 14.7   | 15.545                            | 0.551             | 0.19                            | 14.50                                    | 0.0000                            | 8,013  | 9.2                                  | 9.4                               | 1.8   | 1.8   |
| P                                   | 7.6  | 18.307                            | 0.631             | 1.14                            | 20.87                                    | 0.0000                            | 7,813  | 5.3                                  |                                   | 3.2   |   |
| P                                   | 7.6  | 18.452                            | 0.634             | 1.21                            | 20.94                                    | 0.0000                            | 7,813  | 5.3                                  | 5.3                               | 3.4   | 3.3   |
| PR1                                 | 11.8   | 17.345                            | 0.586             | 3.92                            | 20.22                                    | 0.0000                            | 8,300  | 8.2                                  |                                   | 3.5   |   |
| PR1                                 | 11.8   | 16.880                            | 0.579             | 4.03                            | 20.25                                    | 0.0000                            | 8,300  | 8.1                                  | 8.2                               | 3.0   | 3.3   |
| R                                   | 13.2   | 19.154                            | 0.630             | 4.05                            | 2.33                                     | 0.0000                            | 8,300  | 6.6                                  |                                   | 4.8   |   |
| R                                   | 13.2   | 19.051                            | 0.631             | 3.38                            | 2.83                                     | 0.0000                            | 8,300  | 6.2                                  | 6.4                               | 4.6   | 4.7   |
| S                                   | 13.7   | 17.722                            | 0.591             | 2.97                            | 4.19                                     | 0.0000                            | 8,300  | 8.4                                  |                                   | 4.0   |   |
| S                                   | 13.7   | 17.718                            | 0.590             | 2.42                            | 4.74                                     | 0.0000                            | 8,300  | 8.6                                  | 8.5                               | 4.0   | 4.0   |
| V                                   | 13.9   | 17.193                            | 0.595             | 0.05                            | 0.35                                     | 0.0014                            | 8,300  | 6.7                                  |                                   | 2.9   |   |
| V                                   | 13.9   | 17.150                            | 0.593             | 0.05                            | 0.36                                     | 0.0015                            | 8,300  | 6.8                                  | 6.8                               | 2.9   | 2.9   |
| W                                   | 13.5   | 15.143                            | 0.554             | 4.19                            | 3.12                                     | 0.0000                            | 8,300  | 7.5                                  |                                   | 1.0   |   |
| W                                   | 13.5   | 15.141                            | 0.554             | 3.44                            | 3.66                                     | 0.0000                            | 8,300  | 7.5                                  | 7.5                               | 1.0   | 1.0   |
| X                                   | 13.1   | 14.628                            | 0.560             | 2.82                            | 3.59                                     | 0.0005                            | 8,300  | 5.6                                  |                                   | -0.2  |   |
| X                                   | 13.1   | 14.591                            | 0.558             | 2.81                            | 3.36                                     | 0.0005                            | 8,300  | 5.7                                  | 5.7                               | -0.1  | -0.1  |
| Y                                   | 15.2   | 16.475                            | 0.573             | 1.40                            | 0.59                                     | 2.4666                            | 8,300  | 7.9                                  |                                   | 2.5   |   |
| Y                                   | 15.2   | 16.174                            | 0.565             | 1.38                            | 0.60                                     | 2.3978                            | 8,300  | 8.4                                  | 8.2                               | 2.4   | 2.5   |
| USGS-1                              | 15.9   | 15.169                            | 0.535             | 0.04                            | 7.16                                     | 0.0000                            | 8,300  | 10.1                                 |                                   | 1.9   |   |
| USGS-1                              | 15.9   | 18.776                            | 0.600             | 0.06                            | 7.23                                     | 0.0000                            | 8,300  | 9.7                                  | 9.9                               | 5.4   | 3.7   |
| USGS-2                              | 12.1   | 15.836                            | 0.477             | 0.13                            | 32.23                                    | 0.1619                            | 8,300  | 22.5                                 |                                   | 5.5   |   |
| USGS-2                              | 12.1   | 15.890                            | 0.478             | 0.13                            | 32.13                                    | 0.1483                            | 8,300  | 22.5                                 | 22.5                              | 5.6   | 5.5   |
| USGS-3                              | 15.8   | 14.091                            | 0.525             | 3.06                            | 4.44                                     | 0.0000                            | 8,300  | 8.9                                  |                                   | 0.4   |   |
| USGS-3                              | 15.8   | 13.883                            | 0.518             | 3.72                            | 3.80                                     | 0.0000                            | 8,300  | 9.4                                  | 9.2                               | 0.4   | 0.4   |



## Ground-Water Flow Direction, Water Quality, Recharge, and Age in the Unconfined Aquifer

The following conceptual model of ground-water flow direction, ground-water quality, ground-water recharge sources, and ground-water age in the unconfined aquifer was constructed using the data collected and analyzed by this study:

Ground water in the unconfined aquifer is recharged from Medano and Sand Creeks near the Sangre de Cristo Mountain front, flows southwestward underneath the main dune field, and discharges to Big and Little Spring Creeks. As ground water flows underneath the main dune field, the percentage of calcium decreases and the percentage of sodium increases due to cation exchange with clay particles in the aquifer matrix. As ground water flows underneath the main dune field, it also mixes with recharge waters from precipitation on the dune field. Those recharge waters undergo evaporation prior to recharge, resulting in isotopically heavier  $^2\text{H}$  and  $^{18}\text{O}$  stable isotopes of those recharge waters. Recharge from precipitation is verified using ground-water age dates; ground water near the western edge of the dunefield, near sites USGS-1, USGS-2, and USGS-3 is a mixture of relatively older waters recharged near the mountain front with younger recharge waters that fell as precipitation on the western edge of the dune field. CFC and  $^3\text{H}$  data indicate that it takes over 60 years for the old fraction of the ground water to travel from the mountain front to sites USGS-1, USGS-2, and USGS-3. A portion of the ground water discharges to Big and Little Spring Creeks. The remaining portion travels southwestward towards a closed basin in the San Luis Valley. The interdunal ponds are located in areas where depressions in the dune field intercept the water table of the unconfined aquifer; the interdunal ponds receive little or no water from the confined aquifer.

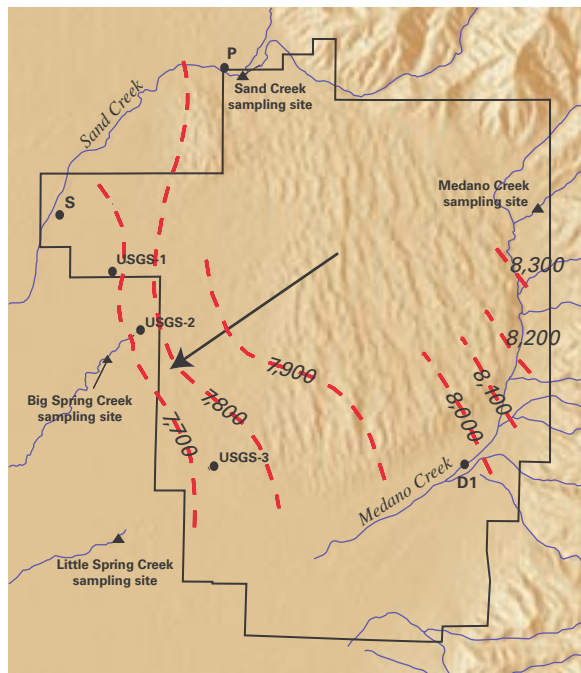
To help confirm this conceptual model, information indicating ground-water recharge near the mountain front, ground-water flow direction, downgradient changes of ground-water quality, ground-water recharge by precipitation on the dune field, evaporation of recharge waters, ground water ages, and quality of water from Big and Little Spring Creeks and the interdunal ponds are discussed. Wherever possible, multiple lines of evidence are presented to support the hypotheses.

## Ground-Water Recharge Near the Mountain Front

Water from wells located near Medano and Sand Creeks (sites P, PR1, R, S) is recently recharged water from Medano and Sand Creeks because  $^2\text{H}$  and  $^{18}\text{O}$  isotopic compositions (fig. 2), cation ratios (fig. 4), and  $^3\text{H}$  activities (fig. 2) are similar to those observed in samples from Medano and Sand Creeks. Little, if any, ground water is supplied to creeks or shallow ground water by upwelling from the confined aquifer in this area. This concept is corroborated by several other studies at Great Sand Dunes. HRS Water Consultants (2002) found that Medano Creek is in hydraulic connection with the regional unconfined water table upstream from site K at least on a seasonal basis. HRS Water Consultants (2002) observed a strong downward flow gradient in the vicinity of site K, as demonstrated by progressively deeper water levels in progressively deeper monitoring wells. McCalpin (1999) observed that water levels in monitoring wells installed in the Medano Creek floodplain near site K vary seasonally, roughly in phase with discharge of Medano Creek. Wurster and Cooper (2000) installed 120 hand-dug piezometers near sites O, R, S, V, W, and USGS-1 to determine the altitude of the water table. Mounding of ground water in the vicinity of Sand Creek was observed that was attributed to localized recharge from Sand Creek during snowmelt runoff. Harmon and others (1999) observed that surface flow in Sand Creek near sites R, S, and V is in hydraulic connection with the unconfined aquifer in the San Luis Valley and that a “well-defined ground-water mound” exists that is indicative of recharge from Sand Creek to the unconfined aquifer.

## Ground-Water Flow Direction in Unconfined Aquifer

A water-table map for the unconfined aquifer was constructed that indicates that ground water flows from the Sangre de Cristo mountain front towards Big and Little Spring Creeks (fig. 5). Water levels measured from sites completed in the upper part of the unconfined aquifer (less than 40 feet) were used. Only six sites sampled for this study were suitable for the water-table map, so additional altitudes were approximated where the water table is thought to coincide with land surface. Near the mountain front, altitudes of the beds of Medano and Sand Creeks were assumed to approximate the water level in the unconfined aquifer where perennial flow exists. Altitudes of the creek beds were determined from USGS 1:24,000 topographic maps. In the discharge area of the flow system, the altitudes of the sample sites on Big and Little Spring Creeks were used because these sites are located in an area of ground-water discharge from the unconfined aquifer. The water-table map shows an approximate northeast to southwest ground-water flow direction (fig. 5) in the unconfined aquifer; Wurster and Cooper (2000, p. 42) also observed that the dominant ground-water flow direction in the unconfined aquifer gener-



**EXPLANATION**  
 - 7,700 - Approximate water-level contour—Contour interval is 100 feet. Datum is NGVD of 29.  
 ← Generalized direction of ground-water flow  
 ● USGS-3 Well and site name (see table 1)

**Figure 5.** Water table in the unconfined aquifer, Great Sand Dunes National Monument, 2000.

ally is southwestward from the Sangre de Cristo Mountains toward the center of the San Luis Valley.

### Downgradient Changes of Major Ion Chemistry

Major ion chemistry of ground water in the unconfined aquifer changes as ground water moves downgradient through the unconfined aquifer. The percentage of calcium tends to decrease and the percentage of sodium tends to increase with increasing distance from Medano and Sand Creeks (fig. 4). Two explanations are possible for the relative change in calcium and sodium percentages. One explanation is evaporation combined with precipitation by calcite. The other is cation exchange on clay particles in the aquifer matrix. Calcite saturation indices are the maximum concentrations of Ca and CO<sub>3</sub> that can exist in the ground water before calcite precipitation occurs. Calcite saturation indices calculated using NETPATH for water from sites O, USGS-1, USGS-2, USGS-3 and W indicate that concentrations of Ca and CO<sub>3</sub> are not large enough for calcite precipitation; in other words, the water is undersaturated with respect to calcite. This indicates that the percentage of calcium decreases and the percentage of sodium

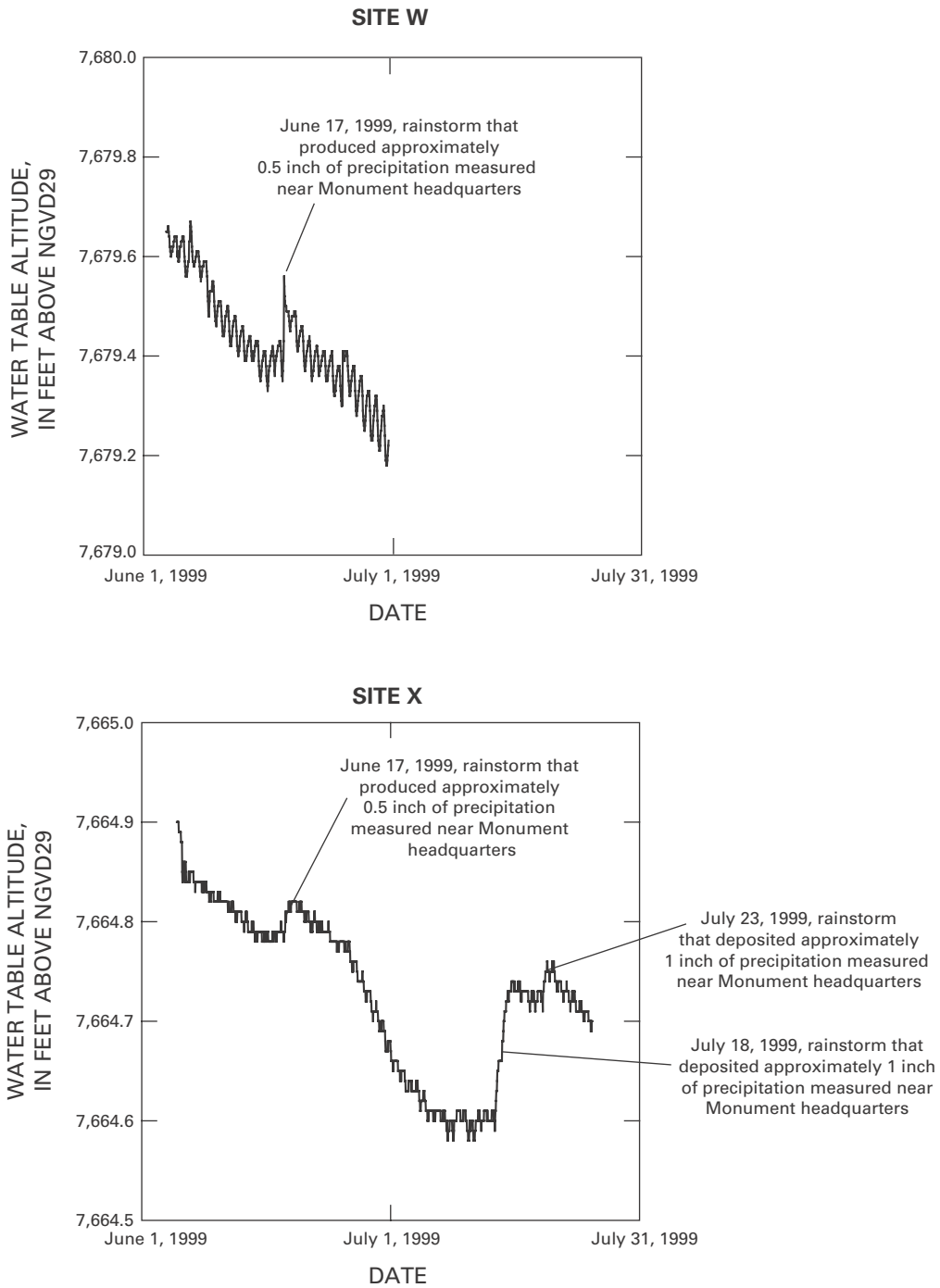
increases as the result of cation exchange with clay minerals as ground water moves downgradient through the unconfined aquifer. Even a deposit that appears to be composed of clean sand or gravel can have a sufficient amount of clay minerals for ion exchange to occur (Freeze and Cherry, 1979). These changes in cations with increasing distance from Medano and Sand Creeks results in an evolutionary change of ground-water quality as ground water moves downgradient in the unconfined aquifer. Mayo and Associates (1991, p. 53) observed a similar decrease in calcium and increase in sodium in an area just west of Great Sand Dunes and attributed the change to cation exchange with clay particles.

### Ground-Water Recharge by Precipitation on the Dune Field

Long-term water-level data collected by the NPS (Andrew Valdez, National Park Service, electronic commun., 2002) indicate that the unconfined aquifer is being recharged by precipitation events. Wells completed in the unconfined aquifer show an immediate response to rainstorm events. A hydrograph of ground-water levels measured hourly in sites W and X, which are 74 and 76 feet deep, respectively, is shown in figure 6. On June 17, 1999, approximately 0.5 inch of precipitation was measured at a weather station located near Great Sand Dunes Headquarters (Colorado Climate Center, 2002) that resulted in a water-level increase of almost 0.2 inch at site W and a water-level increase of about 0.05 inch at site X (fig. 6). Site X has a longer period of record than Site W; two additional precipitation events were reflected in water levels measured at Site X. About 1 inch of precipitation was measured on July 18 and July 23, 1999, respectively (Colorado Climate Center, 2002), that resulted in water levels at Site X increasing over 0.1 inch and almost 0.05 inch, respectively. Continuous water levels measured at sites W and X indicate a water-table response on the western edge of the dune field soon after a large precipitation event. Wurster and Cooper (2000) also observed that ground-water levels in the Indian Springs area rose immediately after storm events and declined in the absence of precipitation. The recharge water reaching the water table may not be water from the current precipitation event; soil moisture from previous events may be pushed into the saturated zone by the increase in head.

### Evaporation of Recharge Waters

Isotopic compositions of <sup>2</sup>H and <sup>18</sup>O indicate that precipitation on the dune field is evaporated prior to recharging the ground water in the unconfined aquifer. Isotopic compositions of samples collected from Medano and Sand Creeks correspond with the World Meteoric Water Line (fig. 2), indicating that precipitation in the Sangre de Cristo Mountains east of Great Sand Dunes has undergone very little evaporation after reaching the land surface. Five quarterly samples were col-



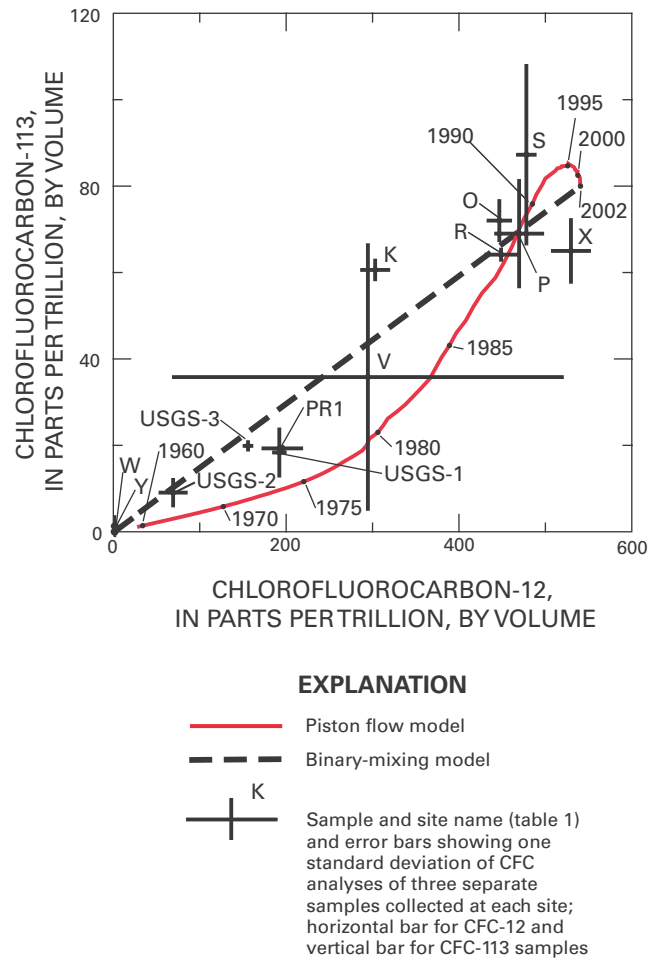
**Figure 6.** Ground-water levels measured in sites W and X and selected precipitation events, Great Sand Dunes National Monument, south-central Colorado, 1999.

lected from Medano and Sand Creeks beginning May 2000 to observe seasonal differences in isotopic composition. May and June samples collected from Medano Creek have the lightest isotopic compositions of all the samples collected for this study (fig. 2); these samples are composed mostly of snowmelt from precipitation during the coolest time of the year. Isotopic compositions of samples collected from sites P, PR1, R, and S plot along the same World Meteoric Water Line as samples collected from Medano and Sand Creeks, indicating the waters did not undergo substantial amounts of evaporation prior to recharge.

Samples collected from sites O, USGS-1, USGS-2, and USGS-3 have the heaviest isotopic compositions of all the samples collected for this study and plot along a line of slope approximately 4.4, consistent with the expected evaporation path, which indicates that the waters underwent evaporation prior to recharge. Samples collected from site K, site W, Big Spring Creek, and Little Spring Creek probably underwent about half of the evaporation prior to recharge than samples collected at sites O, USGS-1, USGS-2 and USGS-3. With the exception of site K, water with heavier isotopic compositions was sampled from sites relatively distant from Medano or Sand Creek, and water with the lightest isotopic compositions was sampled from sites relatively close to Medano or Sand Creek. Evaporation of precipitation immediately after it is deposited on the dune surface, combined with kinetic isotopic fractionation during evaporation in the shallow unsaturated zone, probably leads to enrichment in stable isotope composition. Mayo and Associates (1991, p. 46) also reported that ground water in the unconfined aquifer sampled from wells located west of Great Sand Dunes have undergone considerable evaporation prior to recharge. Wurster and Cooper (2000, p. 57) reported that isotopic ratios became heavier with increasing distance from Sand Creek.

## Ground-Water Age

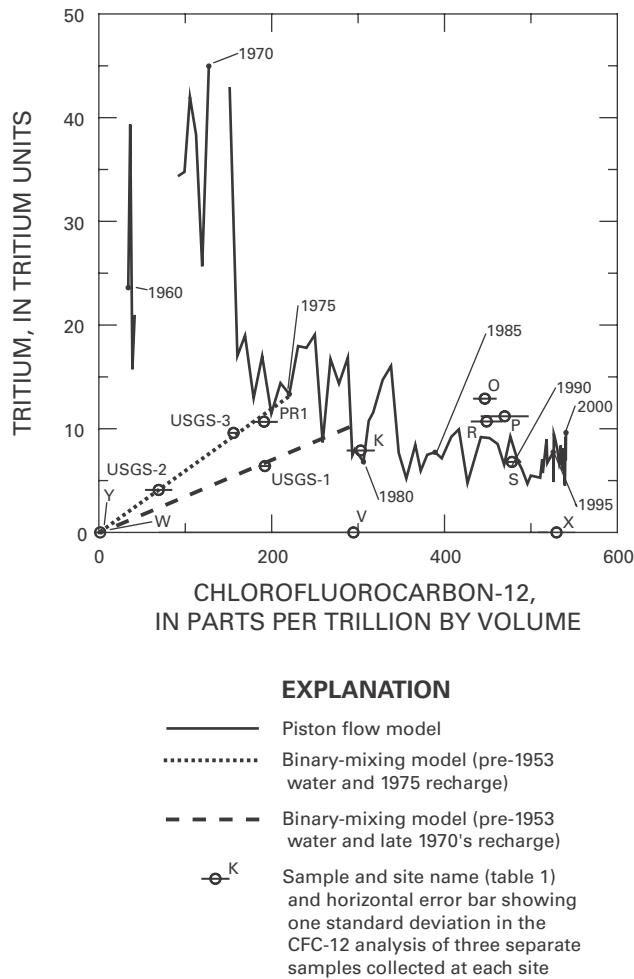
Ground-water ages and the amount of mixing of old ground waters with young recharge waters was determined for water from wells completed in the unconfined aquifer by examining ratios of CFC-113 and CFC-12 (fig. 7), ratios of  $^3\text{H}$  and CFC-12 (fig. 8), and ratios of  $^{14}\text{C}$  and CFC-12 (fig. 9). Figure 7 shows a comparison of the measured concentrations of CFC-113 and CFC-12 (converted to gas atmospheric mixing ratios in parts per trillion by volume using the measured recharge temperature) with the piston-flow and binary-mixing models of CFC-113 and CFC-12. The model air composition data are those measured at Niwot Ridge, Colorado (U.S. Department of Commerce, 2002). The solid curved line on figure 7 corresponds to unmixed piston flow, and the dashed line represents binary mixing of modern (year 2000) and old (pre-1941, pre-CFC) water. The horizontal and vertical error bars show one standard deviation of CFC analyses of three separate samples collected at each site. The analytical precision is better than 3 percent for most of the samples. A few of



**Figure 7.** Measured CFC-12 and CFC-113 concentrations in ground-water samples and models of piston flow and binary mixing of modern (year 2000) and old (pre-1941) water, Great Sand Dunes National Monument.

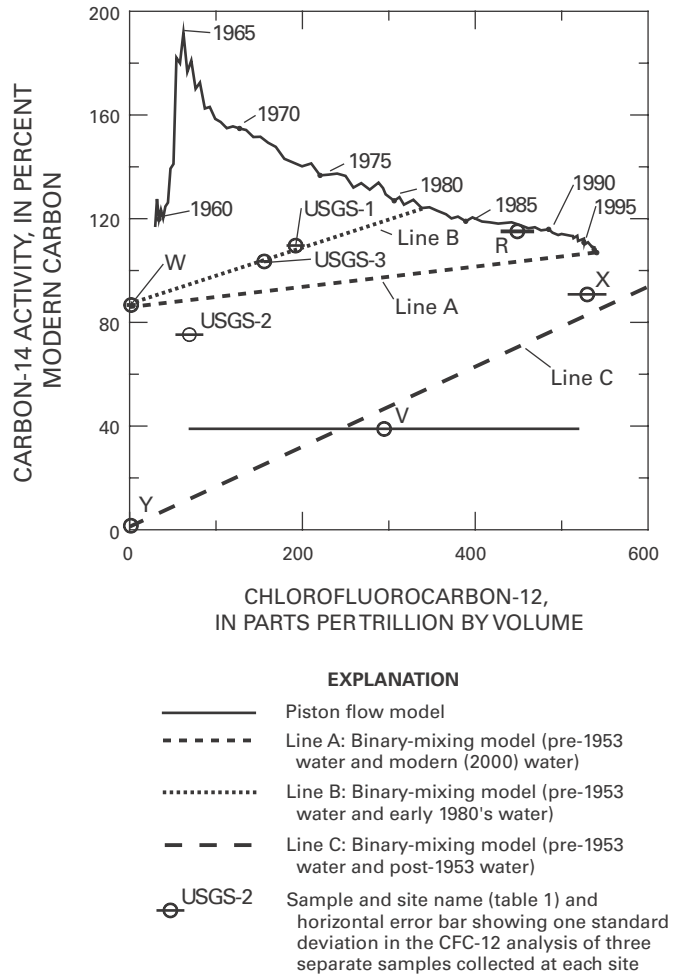
the samples show very large variations in CFC composition between separate samples, indicating unsteady mixing conditions during sampling or problems with sampling methods (sites V and S in particular). Dates of recharge are noted along the piston-flow curve.

Samples from sites located near Sand Creek (P, R, and S) have recharge dates in the late 1980's, indicating they are recently recharged waters from Sand Creek (fig. 7). Samples from sites O and X also have recharge dates in the late 1980's, though sample X may contain a small excess of CFC-12. Samples W and Y are free of CFC's and, thus, do not contain a fraction of post-1941 water. Sample K contains an excess of CFC-113, but has a piston-flow CFC-12 age from the late 1970's. Samples USGS-1, USGS-2, USGS-3, and PR1 appear to be mixtures of young and old water because they lie between the binary mixing and piston flow lines. Site V was drilled using the air rotary method; sample V was probably contaminated with CFC's as the result of that drilling method.



**Figure 8.** Measured tritium and CFC-12 in ground-water samples and models of piston flow and binary mixing, Great Sand Dunes National Monument.

Mixing of old and young waters also is demonstrated in relations of measured <sup>3</sup>H (tritium units) and CFC-12 concentrations (parts per trillion by volume) in ground-water samples and models of piston flow (solid line) and binary mixing (dashed lines) (fig. 8). The <sup>3</sup>H values for the piston-flow curve are based on tritium in precipitation recorded at Albuquerque, New Mexico (International Atomic Energy Agency, 2001) decayed to the sample date of September 2000. The CFC values for the piston-flow curve are those measured at Niwot Ridge, Colorado (U.S. Department of Commerce, 2002). Dates of recharge are noted along the piston-flow curve. Two dashed lines show binary mixing of old water (<sup>3</sup>H-free; pre-1953) with water recharged about 1975 (samples PR1, USGS-2, and USGS-3) and mixing of old water with recharge from the late 1970's (USGS-1). The horizontal error bars show one standard deviation in the CFC-12 analysis of three separate samples collected at each site. Samples O, P, R, S, and K are relatively unmixed samples recharged in the late 1980's (O, P, R, S) and early 1980's (K). Samples O, P, and R plot



**Figure 9.** Measured carbon-14 activity of dissolved inorganic carbon and CFC-12 concentrations in ground-water samples and models of piston flow and binary mixing, Great Sand Dunes National Monument.

above the piston flow line possibly because of the latitudinal gradients of <sup>3</sup>H concentrations in precipitation (Rozanski and others, 1991), which would increase <sup>3</sup>H concentrations of precipitation above those measured in Albuquerque by approximately 0.023 log TU per degree latitude. Samples V and X are old (pre-thermonuclear testing) waters that have been contaminated in some way with CFC-12. Samples Y and W are free of CFC-12 and <sup>3</sup>H indicating a pre-1940's age.

Further evidence of mixing can be seen by comparing <sup>14</sup>C and CFC-12 data (fig. 9). The solid line on figure 9 shows <sup>14</sup>C activities of atmospheric CO<sub>2</sub> from measurements made at Schauinsland, Germany (1977-1997) (Levin and Kromer, 1997), and Vermont, Austria (1959-1983) (Levin and others, 1994), as a function of atmospheric CFC-12 concentrations (parts per trillion by volume). The <sup>14</sup>C activity data for CO<sub>2</sub> are considered representative of northern-hemisphere <sup>14</sup>C atmospheric activities. From the 1950's until the mid-1960's, the <sup>14</sup>C activity in the atmosphere nearly doubled (from 100 pmc, pre-1953, to nearly 200 pmc in 1964) as a result of



atmospheric thermonuclear testing. Dates of recharge are indicated along the solid line (piston-flow curve). Water from site R plots near the piston-flow curve and is apparently unmixed. Water from site W represents pre-1953 water indicating an initial  $^{14}\text{C}$  activity of about 85 pmc for the study area. Line A on figure 9 denotes binary mixtures of pre-1953 water and modern (2000) water. Water from sites USGS-1 and USGS-3 plot along a binary-mixing line of pre-1953 water and water from the early 1980's (Line B). Water from sites USGS-2, X, and V contain water recharged prior to 1953, but have mixed with a fraction of post-1953 water. Water from sites V and X appear to plot along a hypothetical mixing line of modern water that is somewhat contaminated in CFC-12 (Line C); water from site V is probably contaminated with CFC's from the air rotary drilling methods used to install the well.

In summary, ground-water age dating indicates that water from sites located near Sand Creek (P, R, and S) was recharged in the late 1980's. CFC data collected from sites USGS-1, USGS-2, and USGS-3 indicate the waters are mixtures of pre- and post-1941 waters. The post-1941 fraction probably is composed of recharge of evaporated waters from numerous precipitation events on the dune field. The pre-1941 fraction probably is composed of waters recharged by Medano or Sand Creek near the mountain front, which indicates a traveltime of at least 60 years from the mountain front to the western edge of the dune field. A traveltime of over 60 years is consistent with water from site W, which is located adjacent to site USGS-1 but is completed 62 feet deeper in the unconfined aquifer than site USGS-1 (fig. 1). Water from site W contained no CFC's or  $^3\text{H}$ , and, therefore, is more than 60 years old. Age-dating results for water from site X also indicates a traveltime of more than 60 years. Water from site X has a zero  $^3\text{H}$  activity (table 1), has  $^2\text{H}$  and  $^{18}\text{O}$  compositions similar to Medano and Sand Creeks (fig. 2), and has a large percentage of sodium (fig. 4), indicating water from site X was recharged from Medano or Sand Creek more than 60 years ago and has flowed to its current location with out detectable effects by recharge from precipitation events on the dune field.

## Big and Little Spring Creeks

Ground water discharging into Big and Little Spring Creeks is from a deeper portion of the unconfined aquifer than water sampled from sites O, USGS-1, USGS-2, and USGS-3. Cation ratios of water from Big and Little Spring Creeks are similar to those measured in sites O, USGS-1, USGS-2, and USGS-3 (fig. 4), indicating a similar flowpath. Isotopic compositions of  $^2\text{H}$  and  $^{18}\text{O}$  of water from Big and Little Spring Creeks are lighter and  $^3\text{H}$  activities are less than those measured in water from sites O, USGS-1, USGS-2, and USGS-3 (fig. 2), indicating these waters have had less recharge from precipitation on the dune field, probably because they are discharging from a deeper portion of the aquifer. Big and Little Spring Creeks are gaining streams, which means their flow

continually increases in a downstream direction as the result of continual ground-water discharge.

## Interdunal Ponds

The interdunal ponds intercept the water table of the unconfined aquifer (Wurster and others, 2002), and their occurrence is directly affected by fluctuations in the water table of the unconfined aquifer. Any lowering of the water table of the unconfined aquifer decreases water levels of the interdunal ponds. Lowering of the water table could occur during periods of drought, during periods of overpumping of the unconfined aquifer, or through lowering of local base level by downcutting of Big or Little Spring Creek. Sites USGS-1, USGS-2, and USGS-3 are located on the upgradient sides of interdunal ponds and help to characterize ground-water quality of recharge waters to the interdunal ponds. The evolutionary change in major ion chemistry shown in figure 4 indicates that ground water in the interdunal ponds and Big and Little Spring Creeks probably originated as recharge from Medano and Sand Creeks. The ground water traveled downgradient underneath the main dune field, where the percentage of calcium decreased and the percentage of sodium increased probably because of cation exchange with clay minerals. The  $^2\text{H}$  and  $^{18}\text{O}$  isotopic compositions also became heavier due to recharge by evaporated precipitation on the dune field. The water quality of the interdunal ponds is the result of the water quality of the unconfined aquifer, plus changes due to evaporation off the water surface and changes supplied by biologic activity within the interdunal ponds. Waters from the confined aquifer do not affect water quality and water levels of the interdunal ponds.

This hypothesis is supported by data collected by HRS Water Consultants (1999), who determined that the altitude of the water surface of Indian Spring is equal to the static altitude of water in site X. HRS Water Consultants (1999) stated that these water-level data, plus the absence of any near-surface confining bed in the drill record of site X, indicates that Indian Spring is supported by the regional unconfined water table. Wurster and Cooper (2000) installed 13 shallow piezometers in the Indian Spring area. Water levels measured in these sites showed a northeast to southwest flow direction, and the water table was roughly equivalent to the surface of Indian Spring. Indian Spring appears to be a flow-through system (Wurster and Cooper, 2000, p. 83), meaning that water discharges into the pond near the northeast shore and discharges from the pond on the southwest shore with the shallow regional ground-water flow direction. Site USGS-2 is located upgradient from Indian Spring, and samples from site USGS-2 reflect ground-water quality that enters Indian Spring.

## Ground-Water Age and Water Quality in the Confined Aquifer

The following conceptual model of ground-water age and water quality in the confined aquifer was constructed using the data collected and analyzed by this study:

The adjusted  $^{14}\text{C}$  age of water from well Y is about 30,000 years before present (BP). The adjusted  $^{14}\text{C}$  age of water at well Y is only about 3,000 years younger than the unadjusted age because, as shown by NETPATH calculations, geochemical reactions in the aquifer have only minor influence on the  $^{14}\text{C}$  activities of DIC in the ground water. The major ion composition of water from wells completed in the confined aquifer is distinct from waters from the upper portion of the unconfined aquifer and from Medano and Sand Creeks, but insufficient data exist to quantify whether the unconfined and confined aquifers are hydrologically disconnected.

To help confirm this conceptual model,  $^{14}\text{C}$  age dates and major ion chemistry are discussed. Wherever possible, multiple lines of evidence are presented to support the hypotheses.

### Ground-Water Age in the Confined Aquifer

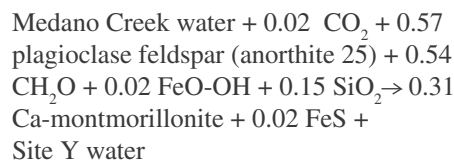
The  $^{14}\text{C}$  activities ( $A_{\text{Meas}}$ ) of DIC in water from sites V and Y are 38.9 and 1.6 pmc, respectively (table 1). Unadjusted ground-water ages calculated with the  $^{14}\text{C}$  decay equation (equation 3) indicates maximum  $^{14}\text{C}$  ages of 6,600 and 33,300 years BP for water from sites V and Y, respectively.

NETPATH (Plummer and others, 1994) was used to test uncertainty in the unadjusted  $^{14}\text{C}$  age and to model the effects of geochemical reactions that might affect the  $^{14}\text{C}$  ages. NETPATH uses two water analyses for  $^{14}\text{C}$  dating: an initial water and a final water. Unfortunately, wells are not located directly upgradient from sites V and Y that can be used to establish initial water. The most likely source of recharge to the confined aquifer is from surface-water runoff along the mountain front. Water samples collected during the month of June from Medano Creek were used as initial waters for modeling of  $^{14}\text{C}$  ages of water from site Y, and water samples collected during the month of June from Sand Creek were used as initial waters for modeling of  $^{14}\text{C}$  ages of water from site V. Samples collected from the creeks during the month of June were used for initial water because snowmelt runoff commonly is largest during June, so the recharge probably is largest during June.

The  $^{14}\text{C}$  activity of the initial waters,  $A_0$ , also must be estimated.  $^{14}\text{C}$  samples collected from Medano and Sand Creeks would not be representative of  $A_0$  for very old waters because they probably contain anomalously large  $^{14}\text{C}$  activities

from above-ground thermonuclear testing. Water samples collected from site W provide a good representation of  $A_0$  of the initial waters (86.7 pmc) because they were collected from a relatively shallow well (74 feet) and did not contain CFC's or  $^3\text{H}$ , indicating the recharge date is prior to the year 1941.

Because the solute chemistry of the initial and final waters is relatively dilute (table 1), geochemical corrections to the  $^{14}\text{C}$  activity of the final waters were small. Taking the local geology into account, possible reactions affecting the chemical evolution of water from Medano Creek to water at site Y and water from Sand Creek to water at site V include the dissolution of calcite ( $\text{CaCO}_3$ ), goethite ( $\text{FeO-OH}$ ), and plagioclase feldspar (anorthite 25); oxidation of organic carbon ( $\text{CH}_2\text{O}$ ); and the precipitation of Ca-montmorillonite, iron sulfide ( $\text{FeS}$ ), kaolinite,  $\text{CH}_4$ , and silica ( $\text{SiO}_2$ ). Possible cation exchange of sodium for calcium was considered, in addition to methanogenesis, evaporation, and exchange of  $\text{CO}_2$  gas during the recharge process. All geochemical reactions that could be considered result in more recent adjusted  $^{14}\text{C}$  ages. The geochemical reactions were modeled in NETPATH to account for observed chemical changes in concentrations of C, Ca, Na, Si, Fe, and S, and conservation of electrons in redox reactions between the initial and final waters. The modeling results are not unique but still are useful in assessing possible uncertainties in the adjusted  $^{14}\text{C}$  age. Among the geochemical reactions just described, the NETPATH modeling resulted in 33 combinations of phases (models) that could describe the chemical evolution of water from Medano Creek to site Y. One possible model shown in a generalized form is:



The coefficients listed above are in millimoles per kilogram of water. The  $^{14}\text{C}$  activities of the carbon sources  $\text{CO}_2$ ,  $\text{CaCO}_3$ , and  $\text{CH}_2\text{O}$  were assumed to be 100, 0, and 0 pmc, respectively.

From the 33 models found by NETPATH for the chemical evolution of water from Medano Creek to water Y, the average adjusted  $^{14}\text{C}$  age was 30,000 plus or minus 3,000 years BP. The average adjusted  $^{14}\text{C}$  age is about 3,500 years younger than the unadjusted age, which indicates that the effects of geochemical reactions are relatively small in ground water at Great Sand Dunes. The peak of the last major ice advance (Wisconsin) during the ice age occurred about 20,000 years BP (U.S. Geological Survey, 1992); ground water from Site Y is much older than that. NETPATH found 7 models for the chemical evolution of water from Sand Creek to water at site V with an average adjusted  $^{14}\text{C}$  age of 4,300 plus or minus 900 years BP, which is about 2,300 years younger than the unadjusted age.

It is unknown why water from site V is younger than water from site Y. Geochemical mixing models developed

using NETPATH indicate that water in site V did not mix with waters from the unconfined aquifer (perhaps through a leaky well seal), which would decrease its apparent age. An insufficient number of sites are completed in the confined aquifer in Great Sand Dunes to determine ground-water flow direction or velocity, which would help explain the younger age of water from site V.

For comparison,  $^{14}\text{C}$  ages of water from site Y also were modeled using water from site W as the initial water. The average adjusted  $^{14}\text{C}$  age of water evolving from site W to site Y is 26,400 plus or minus 3,700 years BP, which is 3,400 years younger than water evolving from Medano Creek to site Y. Taking the error margins into account,  $^{14}\text{C}$  ages of water from site Y using initial water from site W and initial water from Medano Creek overlap, suggesting there is no significant difference in  $^{14}\text{C}$  ages. The average adjusted  $^{14}\text{C}$  age of water evolving from site W to site V is 5,600 plus or minus 500 years BP, which is 1,300 years older than water evolving from Sand Creek to site V. Taking the error margins into account,  $^{14}\text{C}$  ages of water from site V using initial water from site W and initial water from Sand Creek overlap, suggesting there is no significant difference in  $^{14}\text{C}$  ages.

## Major Ion Chemistry and Connection Between Unconfined and Confined Aquifers

Water samples collected from sites completed in the confined aquifer (sites V and Y) plot in a different portion of figure 4 than water samples collected at the other sites, indicating that the major ion chemistry of water from sites V and Y is different than water from wells completed in the unconfined aquifer. On first examination, this might indicate that there is limited hydrologic connection between the confined and unconfined aquifers. However, there are insufficient data to determine if any leakage exists between the confined and unconfined aquifer. Water levels measured in sites V and Y are artesian, or above the top of the confined aquifer, indicating an upward gradient from the confined aquifer to the unconfined aquifer. A clay layer about 8 feet thick separates the two aquifers (HRS Water Consultants, 1999), suggesting that there should be limited hydrologic connection between the two aquifers. However, all the wells completed in the unconfined aquifer and sampled by this study are completed in the upper half of the unconfined aquifer; the deepest well is only 105 feet deep. No samples were collected from the lower half of the unconfined aquifer. Ground water could be seeping from the confined aquifer to the lowermost portion of the unconfined aquifer and be undetected by this study.

Previous studies have presented opposing hypotheses concerning whether the confined aquifer is isolated from the unconfined aquifer. Magee and Mueller (1999) observed a distinct geochemical difference between waters from the unconfined and confined aquifers, suggesting the two aquifers are isolated. Mayo and Associates (1991) believe no upward vertical leakage into the unconfined aquifer occurs from the

confined aquifer. HRS Water Consultants (1999) performed pump tests on sites V and Y, and did not observe any changes in water levels in adjacent wells completed in the unconfined aquifer, suggesting there is no hydrologic connection. However, HRS Water Consultants (2001, p. 5) observed an increase in water levels measured in site V with the onset of flow in Sand Creek, indicating some amount of vertical leakage does occur between the confined and unconfined aquifers, probably near the mountain front.

## Summary and Conclusions

Great Sand Dunes National Monument (hereinafter called Great Sand Dunes), located in south-central Colorado along the eastern edge of the San Luis Valley, contains the tallest sand dunes in North America; some rise up to 750 feet above the San Luis Valley floor. The existence and maintenance of the dunes is dependent on water, because Medano and Sand Creeks, located on either side of the dune field, transport sand that is blown to the downwind side of the sand dunes back to the upwind side. This recycling of sand maintains the dune field in a state of quasi-equilibrium. If local ground-water levels drop, the capability of the creeks to transport sand back to the upwind side will be reduced, which jeopardizes the long-term viability of the dune field.

Important ecological features of Great Sand Dunes are palustrine wetlands associated with interdunal ponds and depressions that nearly intersect the water table near the western edge of the dune field. The interdunal ponds and depressions provide important habitat for a variety of species that depend on a wetland habitat in an otherwise desert environment. The interdunal ponds are of special concern because their numbers have decreased markedly in recent years. The relatively sudden disappearance of ponds appears to indicate a considerable change in Great Sand Dunes hydrology, the cause of which has yet to be determined. Lowering of the water table may lead to continued disappearance of the ponds.

A shallow unconfined aquifer and a deeper confined aquifer are the two principal aquifers at Great Sand Dunes. Knowledge of the sources and timing of recharge to the shallow unconfined aquifer, the deeper confined aquifer, the interdunal ponds, and Big and Little Spring Creeks is critical to understanding the complexities of the ground-water flow system at Great Sand Dunes. To address these concerns, the U.S. Geological Survey conducted a study, in collaboration with the National Park Service, of ground-water flow direction, water quality, recharge sources, and age in Great Sand Dunes.

Geochemical methods and models were used to quantify ground-water ages and to determine recharge sources of waters sampled in Great Sand Dunes. Ground-water samples were analyzed for major ions, deuterium ( $^2\text{H}$ ) and oxygen-18 ( $^{18}\text{O}$ ), carbon-14 ( $^{14}\text{C}$ ), tritium ( $^3\text{H}$ ), and chlorofluorocarbons (CFC's). Data from multiple geochemical constituents compli-



ment each other, helping to verify the results. Major ions were used to identify sources of water and to quantify the change of ground-water chemistry as it moves downgradient. Hydrogen and oxygen isotopes of the water molecule ( $^2\text{H}$  and  $^{18}\text{O}$ ) were used to help identify sources of recharge water and identify waters that underwent evaporation prior to recharge. Waters that are thousands of years old were dated using  $^{14}\text{C}$ . Waters less than 50 years old were dated using  $^3\text{H}$  and CFC's.

The results of this study indicate that ground water in the unconfined aquifer is recharged from Medano and Sand Creeks near the Sangre de Cristo Mountain front, flows underneath the main dune field, and discharges from Big and Little Spring Creeks. It takes over 60 years for ground water to travel from Medano and Sand Creeks to Big and Little Spring Creeks. As the ground water travels underneath the dune field, the percentage of calcium decreases and the percentage of sodium increases due to cation exchange with clay minerals. The ground water in the upper part of the unconfined aquifer is recharged by numerous precipitation events as it travels underneath the dune field. This recharge from precipitation events causes the  $^3\text{H}$  and  $^{18}\text{O}$  isotopic compositions to become heavier, because the precipitation waters undergo evaporation prior to reaching the water table. Evaporation of precipitation immediately after it falls on the dune surface, combined with kinetic isotopic fractionation during evaporation in the shallow unsaturated zone, probably leads to enrichment in stable isotope composition. This recharge from precipitation events is confirmed by  $^3\text{H}$  and CFC age dating, because the waters on the western edge of the dune field are mixtures of pre- and post-1941 waters; the pre-1941 waters were recharged at the mountain front, and the post-1941 waters were recharged by precipitation on the dune field.

The age of ground water from the confined aquifer determined with  $^{14}\text{C}$  is about 30,000 years before present, plus or minus about 3,000 years. The peak of the last major ice advance (Wisconsin) during the ice age occurred about 20,000 years before present (U.S. Geological Survey, 1992); ground water from the confined aquifer is much older than that. The major ion composition of water from wells completed in the confined aquifer is distinct from waters from the upper part of the unconfined aquifer and from Medano and Sand Creeks, but insufficient data exist to quantify whether the unconfined and confined aquifers are hydrologically disconnected.

The results of this study indicate that the water quality and water levels of the interdunal ponds are not affected by waters from the confined aquifer. Instead, the interdunal ponds intercept the water table of the unconfined aquifer, and their occurrence is directly affected by fluctuations in the water table of the unconfined aquifer. Any lowering of the water table of the unconfined aquifer will result in an immediate decrease in the water levels of the interdunal ponds. Lowering of the water table could occur during periods of drought, during periods of overpumping of the unconfined aquifer, or through lowering of local base level by dncutting of Big or Little Spring Creeks. The water quality of the interdunal

ponds is probably a combination of the water quality supplied by the unconfined aquifer, plus changes due to evaporation off the water surface and changes supplied by biologic activity within the interdunal ponds.

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