# GEOCHEMICAL ASSESSEMENT OF AQUIFER RECHARGE EFFECTS IN THE SOUTHWEST DENVER BASIN

by

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Colorado Water

Resources Research Institute

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# IN THE SOUTHWEST DENVER BASIN

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ABSTRACT

Recharge of the Denver groundwater basin by injection recharge has been proposed as a result of increasing depletion of the water supply. However, injection recharge can cause physical and chemical changes in the geologic materials of the recharged aquifer, depending on the chemistry of both the host and injected waters, as well as the mineralogy of the aquifer's rock matrix.

The Denver groundwater basin contains four principal bedrock aquifers, of which the Arapahoe aquifer is considered to be the best in terms of water quality and quantity. Some preliminary field injection tests have been undertaken using drinking water supplies. However, water that meets drinking water standards contains constituents which may react upon injection, resulting in aquifer damage. The field injection test results have not been publically released.

As a preliminary step in designing future field tests, analyses of aquifer water and Denver Water Board municipal drinking water were evaluated by a geochemical equilibrium computer model (PHREEQE), developed by the U.S. Geological Survey, to determine the potential for reaction. The results of these simulations confirm that the AQrapahoe aquifer is a good candidate for injection recharge. No fatal flaw appears to exist, from a geochemical standpoint, which would prevent the use of drinking water to recharge the Arapahoe aquifer.

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## 1.0 INTRODUCTION

Population growth projections have been developed by the Denver Regional Council of Governments (DRCOG) for the next several decades (see Table 1.). Increases in water demand due to population growth are depleting ground water resources south of the Denver metropolitan area where a number of suburban water districts rely on ground water for their primary supplies. Accordingly, the Denver basin aquifers constitute a vital source of water for thousands of residents.

Costa and Bilodeau (1982) summarize the history and development of the Denver Water Board system, which utilizes trans-mountain water diversions to supply many thousands of Denver and suburban customers. They reported that the raw water stored by the Denver Water Board in the period 1977-82 ranged from 58 to 89 percent of the maximum available raw-water storage capacity. This captured water must be treated before distribution to customers. Since an estimated 40 percent of the treated residential water is used for lawn watering, a marked seasonality in water demand occurs, with a summertime peak. This variation in demand has created both problems and potential opportunities. During the summer of 1973, the Denver water treatment facilities were over-taxed on five days (Costa and Bilodeau; 1982, p.303). This led to conservation measures which reduced per capita consumption to 197 gallons per capita per day (GCD) in 1979 from a peak of 225 GCD in 1974 (Costa and Bilodeau; 1982, p.304).

By combining the DRCOG population projections with these water consumption rates, the estimated demand may be projected. As shown in Figure 1., these projected demands will exceed the current water treatment capability in the period 1990-2010, depending on

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Table 1.  Estimated Future Water Demands in the Denver Metropolitan Area Based on Denver Regional Council of Governments (DRCOG) Population Projections and Historical Water Consumption Patterns.

| Year | DRCOG Denver Metropolitan Area Population Forecast | Estimated Daily Water Use (million-gallons/day) | |
| | | LOW USE (197 gal/day/person) | HIGH USE (225 gal/day/person) |
| --- | --- | --- | --- |
| 1980 | 1,618,461 | 318.84 | 364.15 |
| 1985 | 1,815,050 | 357.56 | 408.39 |
| 1990 | 2,028,900 | 399.69 | 456.50 |
| 2000 | 2,340,800 | 461.14 | 526.68 |
| 2010 | 2,629,900 | 518.09 | 591.73 |
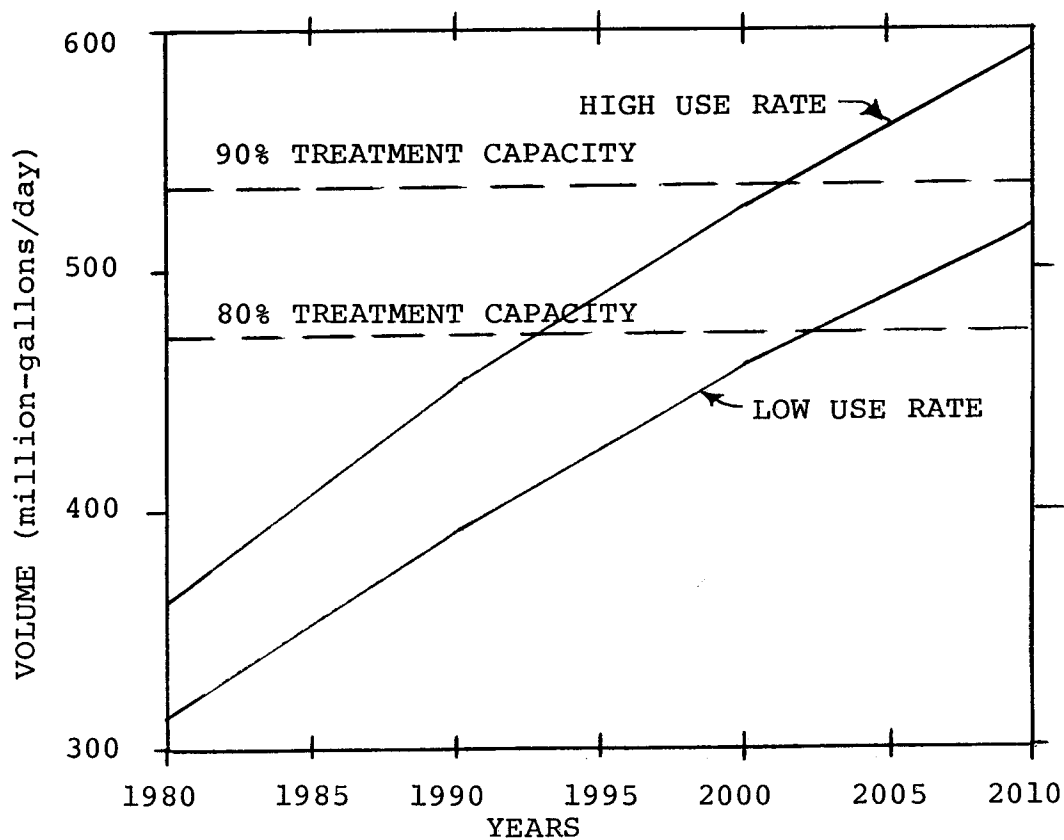


Figure 1.  Estimated Supply and Demand Curves for the Denver Metropolitan Area.

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assumed consumption rates and treatment facility operating levels. Currently, the Denver Water Board can theoretically treat up to 645 million gallons per day (MGD) of raw water. However, this assumes 100% capacity at all plants, including the Kassler water treatment plant which has been shut-down for environmental reasons. Without the Kassler plant, and assuming 80 percent production efficiency over a longer period, a treated water capacity of about 476 MGD is possible. This assumes adequate raw water storage reserves. There is obviously excess water treatment capacity available in the winter months. Again, provided adequate raw water reserves are available, some treated water could be recharged to the Denver groundwater basin by injection, and used to maintain or replenish ground water aquifers which are currently being depleted. Such a scenario has been proposed, and current knowledge suggests that the strategy would be successful. However, injection recharge can cause physical and chemical changes in the geologic materials of the recharged aquifer, depending on the chemistry of both the host and injected waters as well as the mineralogy of the aquifer's rock matrix.

The Denver groundwater basin contains four principal bedrock aquifers, of which the Arapahoe aquifer is considered to be the best in terms of water quality and quantity (Stollar, 1981). Some preliminary field injection tests have been undertaken using drinking water supplies. Water that meets drinking water standards still contains appreciable contaminants which may react upon injection, resulting in aquifer damage.

As a preliminary step in designing future tests, analyses of aquifer water and Denver Water Board municipal drinking water were used in a U.S. Geological Survey developed computer geochemical equilibrium model (PHREEQE) to determine the potential for reaction. The results of these simulations confirm that the Arapahoe aquifer is a good

candidate for injection recharge. No fatal flaw appears to exist from a geochemical standpoint in the theory of using drinking water to recharge the Arapahoe aquifer.

## 2.0 BACKGROUND

### 2.1 Types of Artificial Recharge

There are two principal methods for performing artificial recharge: surface recharge and injection recharge. Surface recharge includes a variety of methods and engineering concepts. Injection recharge requires injection wells and facilities to support the movement of water to and through these wells.

### 2.1.1 Surface Recharge

Surface recharge techniques for artificiallly recharging ground water generally involve "water spreading", meaning the release of water over the ground surface so as to increase the quantity of water infiltrating into the ground and reaching the water table (Todd, 1987). Surface recharge is only effective for recharging unconfined or "water-table" aquifers. The recharge effect can be intentional, as when facilities are designed specifically to recharge a water table aquifer, or unintentional, as in the case of excess irrigation which results in recharge to the water table. Water spreading techniques include:

- basins
- stream channels
- ditches and furrows
- flooding
- irrigation
- pits and shafts (Todd, 1987).

All of these methods are effective only if several conditions are met. There must be sufficient storage space for the recharged water between the water table and the ground surface. Percolation rates must be sufficient for the recharge water to reach the water table in a reasonable period of time. The subsurface geology must permit water to move downward and laterally away from the surface recharge site. Climate must also be considered, since loss of recharge water through evaporation of a standing water body could make surface recharge ineffective. Once these conditions are met and an available water supply is identified, surface recharge becomes possible.

Surface recharge directly impacts only the water table aquifer. Aquifers below the water table aquifer may be affected indirectly over time. Methods other than surface spreading must be employed to recharge deeper, confined or semiconfined, aquifers.

2.1.2 Injection Recharge

Injection wells must be used to recharge deep aquifers directly. While surface spreading methods face problems from clogging the base of the spreading area, injection wells face more complicated clogging problems due to their depth and the relatively small area of the well screen.

Previous experience with several injection recharge field operations (Resource Seminars in Water Resources, 1987) have shown Transmissivity declines during each injection run due to the formation of a plugging film on the well screen and on the surface of the well annulus. Three problem-causing factors have been identified:

1) entrained air clogging the well;

2) suspended particulate matter in the recharge water clogging the well; and

3) an inappropriate well design for a recharge well.

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## 2.2 Previous Work on Artificial Recharge

Recently several books have been published on the topic of artificial recharge. O'Hare, et al (1986) describes the concepts of artificial recharge and includes methods for site selection and evaluation as well as an annotated bibliography on the subject. Asano (1985) edited a collection of articles concerning groundwater recharge with reclaimed wastewater, groundwater recharge operations, and the fate of micropollutants during recharge. Several annotated bibliographies are available covering different time spans (Todd, 1959; Signor, et al., 1970; Knapp, 1973; NTIS, 1987). Recently an increasing number of conferences and seminars have been conducted on the topic of artificial recharge (Resource Seminars in Water Resources, 1987; Salt River Project, 1987). The number of existing publications demonstrates that the topic of artificial recharge is becoming one of increasing concern in this country, especially in the arid and semi-arid western states.

Within the state of Colorado, artificial recharge studies have been conducted in northeastern Colorado and in Colorado Springs(Emmons, 1977; Jenkins and Hofstra, 1969; Taylor, 1975). These studies have concentrated on pit and surface recharge rather than injection recharge.

The 1985 Urban Storm Runoff Quality Control Conference (American Public Works Association, 1985) included several sessions which were applicable to artificial recharge in the Denver basin. Session II included discussions on controlling phosphate levels in the Cherry Creek reservoir and drainage basin through the use of detention ponds. Phosphate levels in the Cherry Creek Reservoir drainage system in and near Denver, Colorado are currently higher than the State of Colorado mandated level. The U.S. Environmental Protection Aqency's National Urban Runoff Program has shown that phosphorus removal

from urban runoff using detention is reasonably effective (Urbonas, 1985). One method of retaining this runoff is through the use of detention ponds (see Fig. 2). At the present time, approximately thirty such ponds are located throughout the drainage basin, generally at the junctures of tributaries to Cherry Creek. Each pond would trap urban runoff and remove phosphorus as well as some suspended particulates. Water tapped from the pond outflow could be routed to a nearby recharge well and injected to recharge the bedrock aquifer. This procedure would utilize previously unused and unappropriated runoff water; however further treatment of the runoff water would be necessary.

Artificial recharge by injection has already been field tested within the Denver basin by the Willows Water District. The District is located in the southeastern Denver metropolitan area. Arapahoe aquifer water which has been run through a water treatment facility to attain drinking water standards was used as the source water to be injected into wells in the Arapahoe aquifer.

## 2.3 Comparison with Previous Studies

Many examples of artificial recharge studies can be found in the current literature (see section 2.2). While the on-going research into artificial recharge at the Colorado School of Mines (CSM) has built on this knowledge, it has also shifted the focus from that found in previous studies in significant ways. Other studies of artificial recharge sites have concentrated on unconfined and alluvial aquifers (Taylor, 1975), whereas the current CSM studies have bedrock aquifers as their primary focus.

Within the state of Colorado, all of northeastern Colorado previously has been considered as opposed to restricting and concentrating research on the Denver basin.

OUTLET STRUCTURE
FOR LARGER STORMS

100 YR. WATER SURFACE
WATER QUALITY
POND SURFACE

FILTRATION PIPING
(IF REQ'D)
OVERFLOW
STRUCTURE

OVERFLOW

WIDTH(W)

BAFFLE
STRUCTURE

INFILTRATION OR
FILTRATION BASIN

L/4

LENGTH (L)

WATER QUALITY OUTLET STRUCTURE
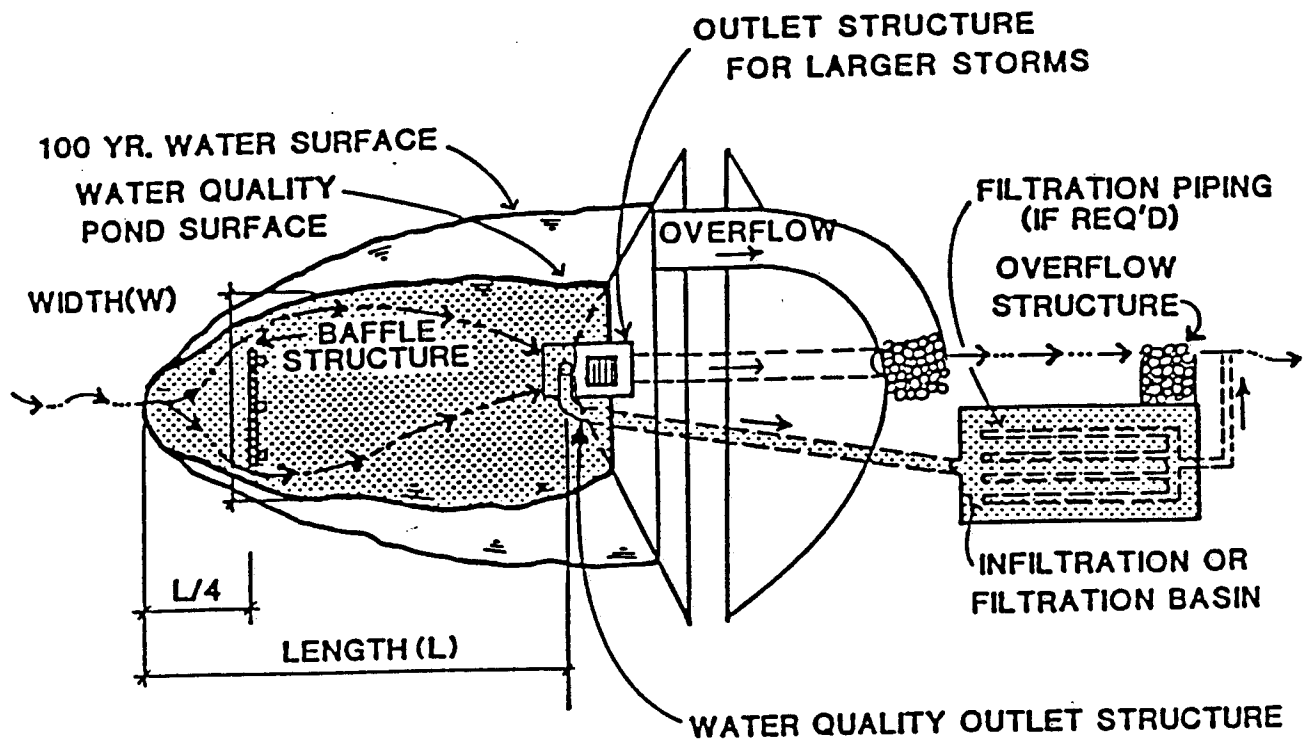
Figure 2.   Example of the standardized layout for a phosphorous
detention pond (Urbonas, 1985).

Table 2. A comparison between the orientations of previous recharge studies and studies at CSM.

| Previous Work | CSM Research |
|---|---|
| unconfined and alluvial aquifers | confined and unconfined bedrock aquifers primary focus |
| all of northeastern Colorado | restricted to the Denver basin |
| pit recharge is primary recharge method | injection recharge is primary recharge method |
| models use hydrological and physical constraints | model considers geochemical and geological constraints as well as hydrological and physical constraints |

Historically, pit recharge has been the principal recharge method employed. The CSM research focuses primarily on injection wells and on the constraints involved with this approach. Past studies have utilized computer models which accounted for hydrological and physical variables. For the CSM studies, the computer model used considered geochemical and geological constraints as well. Table 2 compares these differences between past studies and the research at CSM.

2.4 Geologic and Hydrologic Setting of the Denver Basin

The Denver groundwater basin covers a 6700 square mile area extending from the Front Range of the Rocky Mountains eastward to Limon and from Greeley in the north to Colorado Springs in the south (see Fig. 3). The Denver metropolitan area is located on the western edge of the basin. Structurally, the basin is asymmetrical, with steeper dipping beds to the west and a thicker sequence of rocks in the south (see Fig. 3). Data quantifying the water resources within the Denver basin were compiled by Robson (1983 and 1984). Publications are also available which discuss the geologic structure, hydrology, and water quality of the individual bedrock aquifers (Robson and Romero, 1981a and 1981b; Robson, et al, 1981a and 1981b).
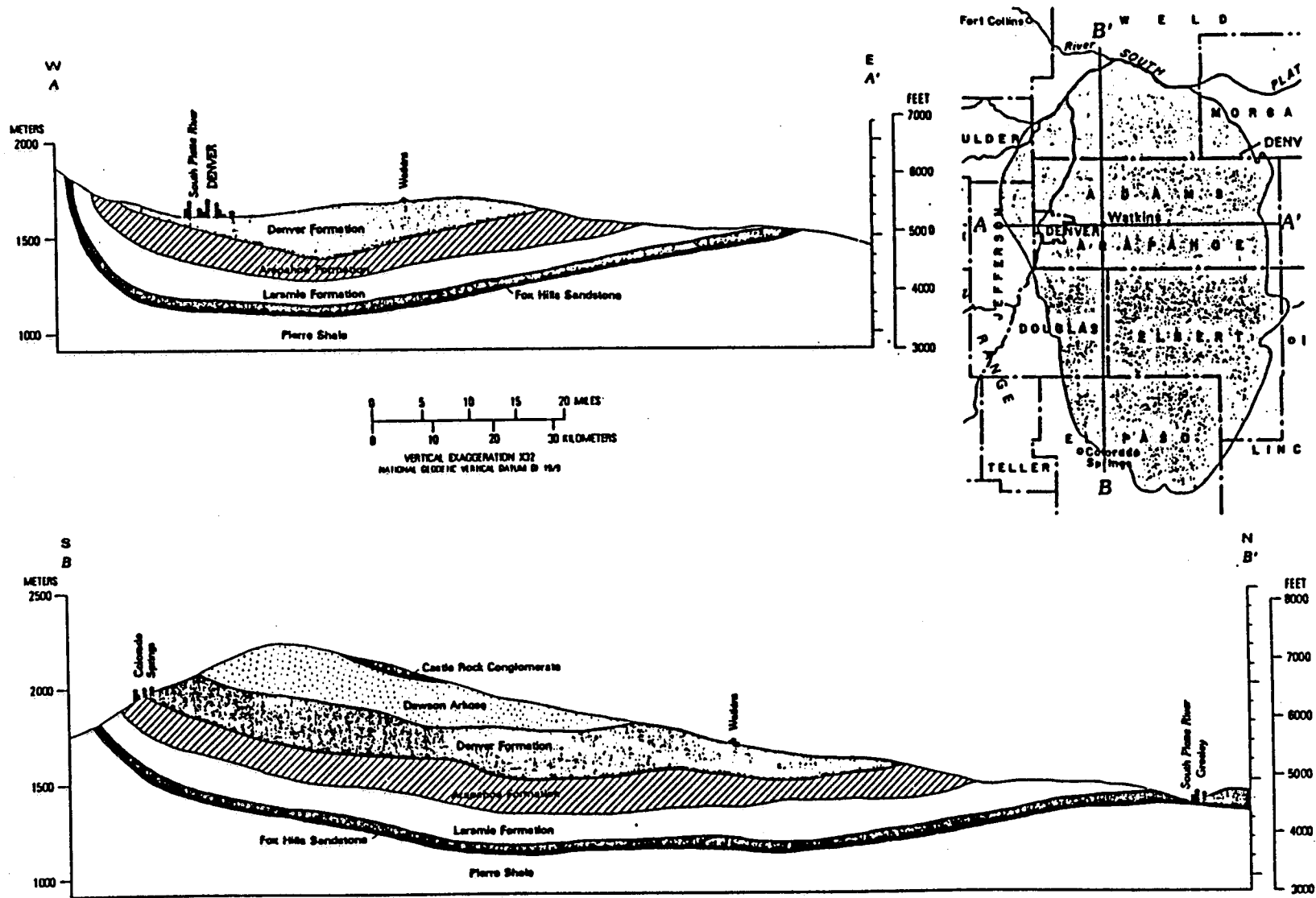
Figure 3. Location of study area and generalized geologic cross-sections through the Denver basin (Robson, 1984).

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## 2.4.1 Climate

The Denver basin has a semi-arid continental climate with 50 to 70 inches of mean annual potential evaporation and only 11 to 18 inches of mean annual precipitation (Robson, 1984). Using this precipation rate, an average of 5.0 million acre-feet of water enters the basin every year. Most of this volume of water is lost through evaporation, transpiration, and runoff, and less than one percent recharges the bedrock aquifers (Robson, 1984).

## 2.4.2 Hydrologic Setting

Water is obtained from five separate hydro-geologic units. While these units generally correspond to the lithologic formations found in the basin, the correspondence is not exact. This results in the borders between the aquifers being close to, but not exactly the same as, the formation divisions. The units, going from oldest to youngest, are: 1) the Laramie - Fox Hills aquifer; 2) the Arapahoe aquifer; 3) the Denver aquifer; 4) the Dawson aquifer; and, 5) the Quaternary alluvial aquifer (see Figs. 3 and 4). For the purposes of this project, the four bedrock aquifers, numbers 1 through 4 above, received the most study, with the Arapahoe aquifer receiving the most concentrated research.

## 2.4.3 The Arapahoe Formation and Aquifer

The Arapahoe formation consists of a 400 to 700 foot (ft) thick sequence of interbedded conglomerate, sandstone, siltstone, and shale. The formation occurs stratigraphically below the Denver formation and above the Laramie formation (see Fig 3.). The Arapahoe formation can be distinguished from the adjacent formations by the larger

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proportion of conglomerate and sandstone with respect to shale, the absence of significant carbonaceous beds, and a lighter color. Individual conglomerate and sandstone beds are generally lens-shaped, moderately consolidated, and range in thickness from a few inches to 30 to 40 ft. In some places, these beds are closely spaced and form a single hydrologic unit that is 200 to 300 ft thick (Robson, 1984).

Major et al (1983, p. 5) give the following description of the Arapahoe formation:

> Sandstone, conglomeratic sandstone, shale and siltstone. Light gray
> to pale orange and grayish-yellow, fine- to coarse-grained quartzose
> sandstone and conglomeratic sandstone with interbeds of light gray,
> light brown, and yellowish-gray shale and siltstone. Reddish-brown
> iron staining is common. Sandstones and conglomerates are lenticular
> but are closely spaced and cover large areas; the horizons frequently
> exceed 250 feet in thickness.

There is inadequate data to define the potentiometric surface for the entire Arapahoe aquifer. A major trough occurs in the potentiometric surface along the South Platte River. Water from the north and west drain into this trough. The trough was originally shallower prior to well drilling in the area and has been deepened and expanded during the past 100 years by flowing wells and pumpage (Robson, 1984). Along the southern, eastern, and south-eastern edges of the aquifer, water is flowing toward the aquifer margins. In most of the eastern section of the aquifer, water is flowing toward the north (Robson, 1984).

Water movement within the Arapahoe aquifer is principally lateral (see Fig. 5). Recharge to the aquifer is in small part from precipitation and in large part from the downward movement of water percolating from the overlying Denver Aquifer.
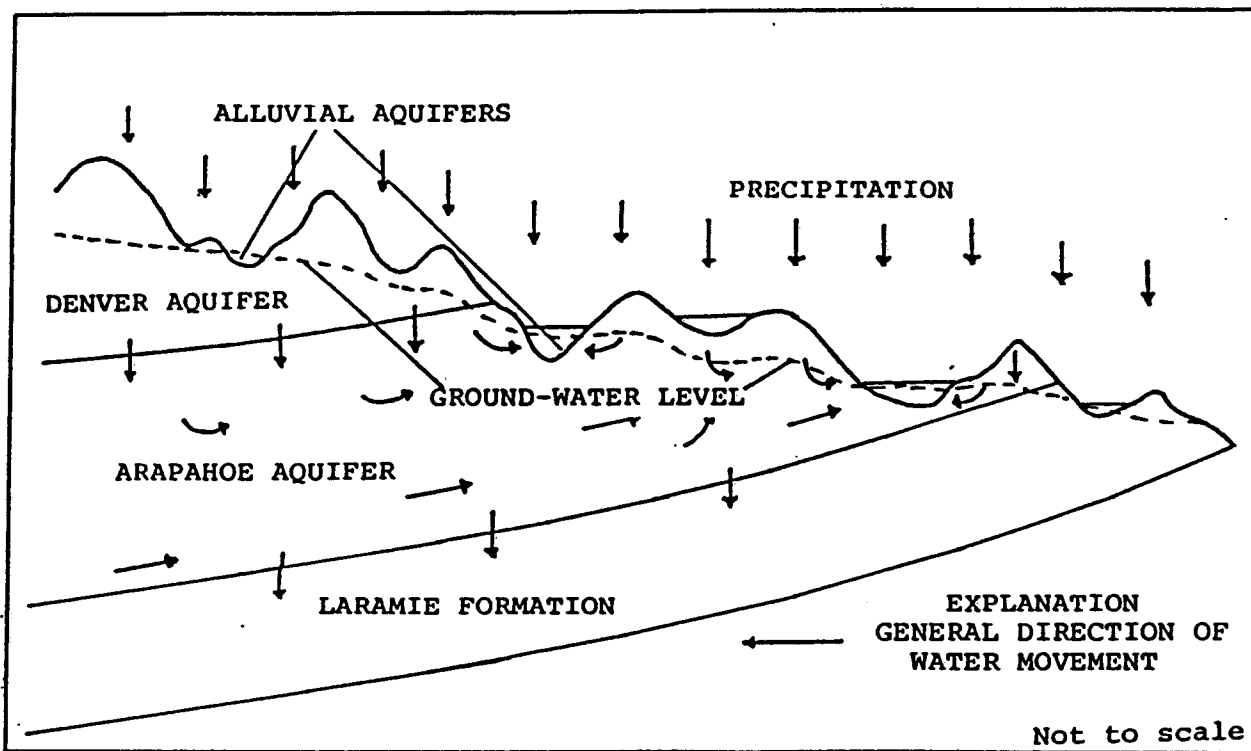
Figure 5. Schematic diagram of water movement within the
Arapahoe aquifer (Robson, et al., 1981a).

Discharge from the aquifer occurs through surface discharge to drainages, downward percolation to the Laramie-Fox Hills aquifer, and pumpage. Downward percolation is limited by the 400 to 500 feet of low-permeability materials that overlie the water-bearing portion of the Laramie formation.

Using computer simulation to develop a transient-state 20-year budget for the Arapahoe aquifer, Robson (1984) calculated recharge from precipitation to be 41,000 acre-feet, and net inter-aquifer flow as 77,000 acre-feet.

When pumping from the Arapahoe aquifer began in the early 1880's, artesian conditions existed. Water levels rapidly declined, as shown in Figure 6. Between 1958 and 1978, water levels declined 250 feet or more under some parts of Aurora. Water levels rose up 200 feet under parts of Denver during the same period due to decreased use of wells in that area. In 1981, the average water level declines in the aquifer were 15 ft/yr (Robson, 1981). More recently, declines have increased to 50 ft/yr. As of 1981, the aquifer was tapped by some 6000 stock, domestic, and municipal wells (Stollar, 1981).

The Arapahoe aquifer is the primary source of water for the Denver suburban area and for rural areas of central Adams and El Paso counties, east Elbert County, and parts of Arapahoe County (Robson, 1984). This is because of its accessibility, high productivity, and good to excellent water quality. Because of the basin configuration, part of the aquifer occurs under water table conditions and part occurs under confined conditions, as shown in Figure 7. The thickness of water-yielding material in the aquifer averages 100 ft but is as thick as 300 ft. Hydraulic conductivities range from 0.5 ft/day to 7 ft/day, with transmissivities ranging from 0 at the edge of the aquifer to 15700 gpd/ft (Robson, 1984).
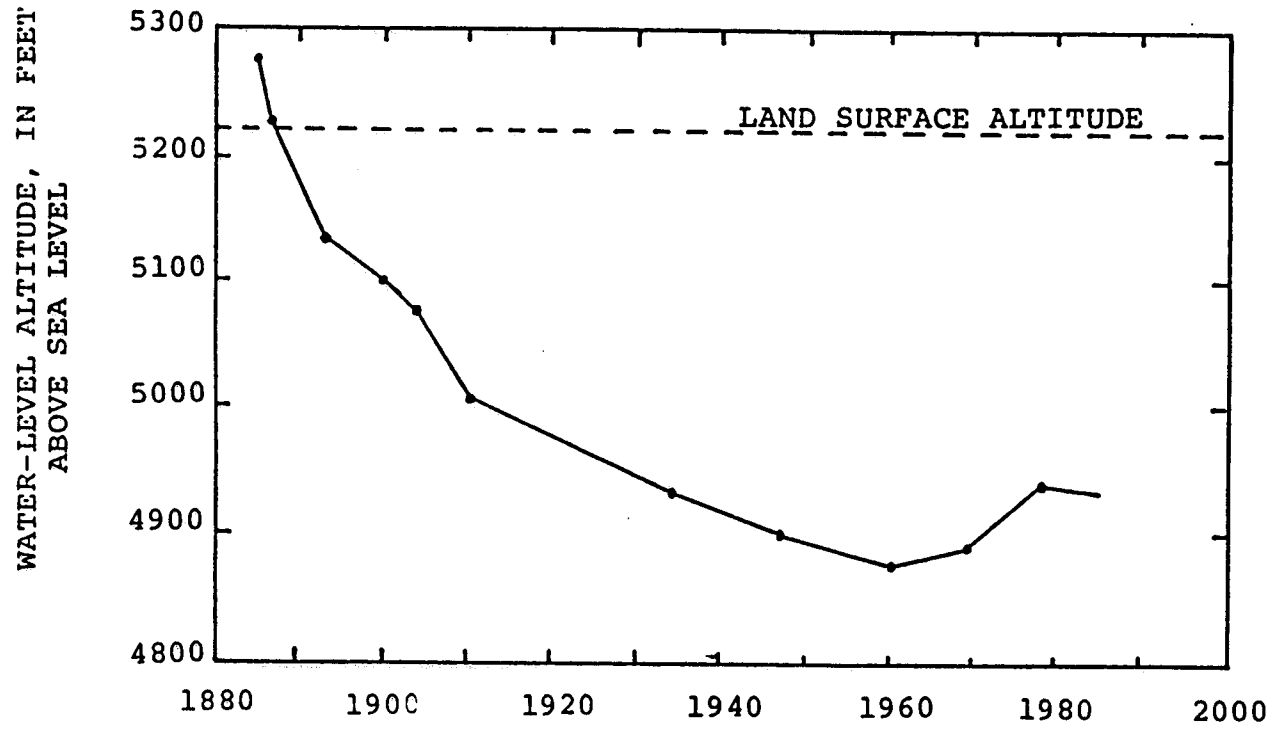
Figure 6.  Water-level hydrograph for the Arapahoe aquifer near the Colorado Capital Building (Robson, 1984).

LARIMER

WELD

MORGAN

BOULDER

ADAMS

JEFFERSON

WASHINGTON

ARAPAHOE

ELBERT

DOUGLAS

LINCOLN

EL PASO

0  5  10  15 miles

0  5 10 15  Km
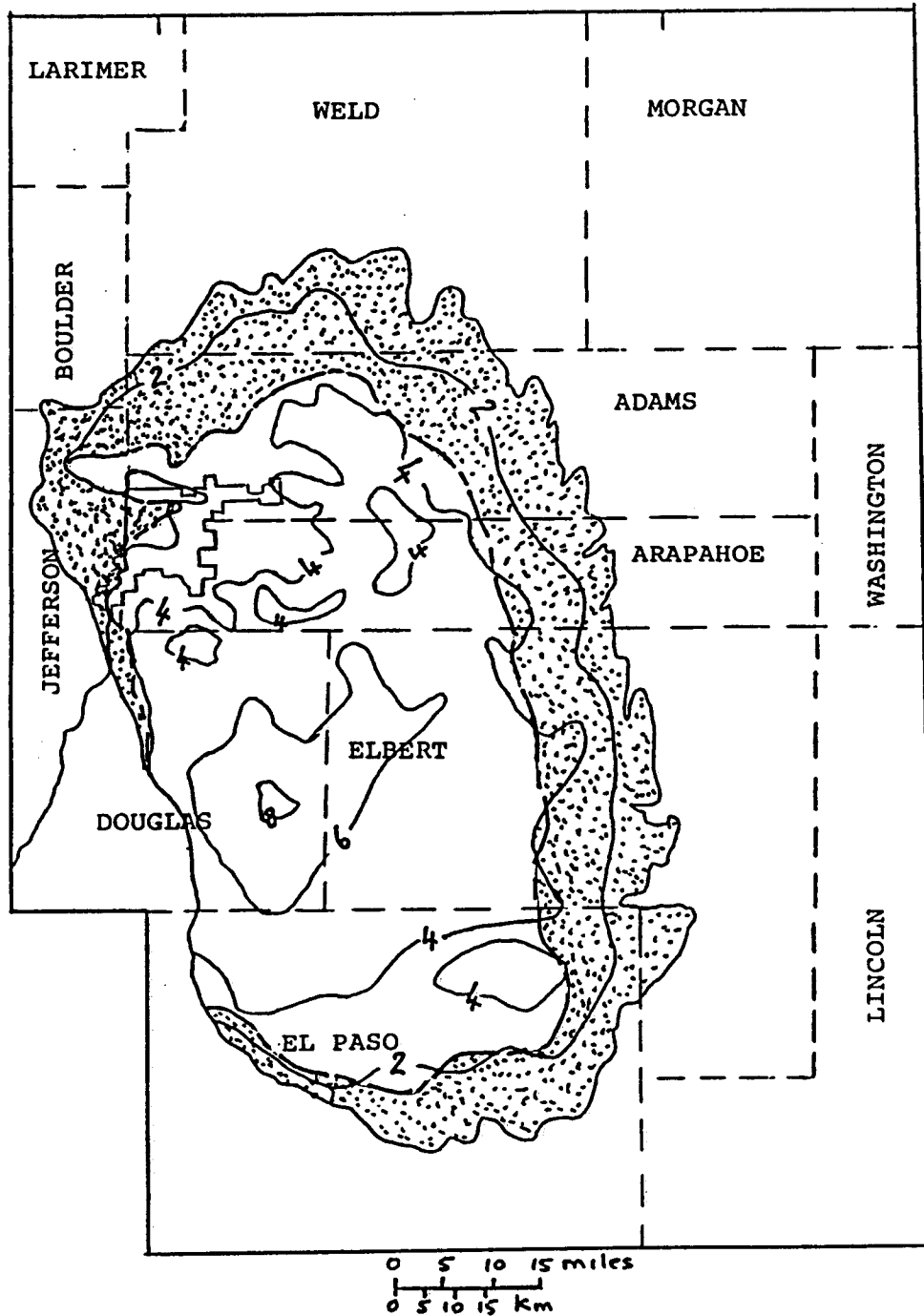
Area where water-table conditions commonly observed
in the upper part of the Arapahoe aquifer.

Area where confined conditions commonly occur.

Contour of storage coefficient ( x10$^{-4}$) for the confined
conditions.

Figure 7.   Confined storage coefficient of the Arapahoe Aquifer
and location of water-table and confined conditions.
(After Robson, 1984)

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Robson (1984) reports that porosity in the Arapahoe aquifer ranges from 12% to 46% with a mean of 30%, based on laboratory analysis of 33 samples. Specific yields, based on laboratory analysis of 25 samples, range from 3.3% to 33%, with a mean of 16%. Estimated storage coefficients range from 0.0002 to 0.0008. Water reserves stored in the aquifer are estimated at 150 million acre-ft with 80 million acre-ft of water recoverable (Robson, 1984).

Water in the Arapahoe aquifer is generally of good chemical quality and meets the drinking water standards of the Colorado Department of Health and the Environmental Protection Agency (Robson, et al 1981a). The water is classified as a sodium bicarbonate type, with calcium bicarbonate type water occurring in the aquifer at scattered locations (Robson, 1984). At some margins of the aquifer, sodium sulfate type water occurs, mainly due to percolation from the overlying Denver aquifer. Table 3 lists water quality analyses for the selected water samples, along with an average value compiled for the aquifer.

Dissolved sulfate concentratins vary from 5 to 249 mg/L under parts of Denver and Lakewood, with 1000 mg/L of more on the eastern edge of the aquifer, and as much as 1500 mg/L near the northern margin. Dissolved solids concentrations are highest along the eastern margin ( > 2000 ppm), where water is moving toward the aquifer edges. Total dissolved solids are lowest in the central part of the aquifer, near the source of recharge from the overlying Denver aquifer. Water hardness is highest in the same areas as high sulfate concentration. In the central part of the aquifer, water is classified as soft. Dissolved iron concentrations generally range from 20 to 200 ug/L, with concentrations as much as 6500 ug/L in a few widely scattered wells (Robson, 1984; Robson, et al, 1981a). This iron becomes insoluble when exposed to air.

# Table 3. Water Quality Analyses for the Arapahoe Aquifer water and the Maximum and Minimum Drinking Water Range samples used in this study.

| Constituent mg/l | A-1 | A-2 | A-3 | A-4 | A-5 | A-6 | A-7 | A-8 | A-9 | Average | Drinking Water Maximum | Minimum | Constituent mg/l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 20.0 | 3.1 | 70.0 | 13.0 | 150.0 | 350.0 | 110.0 | 18.0 | 8.7 | 82.5 | 28.5 | 7.0 | Ca |
| Mg | 1.9 | 3.0 | 10.0 | 1.3 | 20.0 | 86.0 | 35.0 | 1.0 | 2.7 | 17.9 | 9.2 | 1.3 | Mg |
| Na | 110.0 | 140.0 | 89.0 | 190.0 | 76.0 | 170.0 | 150.0 | 220.0 | 160.0 | 145.0 | 24.0 | 2.8 | Na |
| K | 2.1 | 4.1 | 4.0 | 2.6 | 6.6 | 8.6 | 6.9 | 1.0 | 1.6 | 4.2 | 2.1 | 0.6 | K |
| Fe | 0.19 | 0.17 | 1.10 | 0.05 | 0.03 | 0.09 | 0.11 | 0.01 | 0.03 | 0.20 | 0.21 | 0.01 | Fe |
| Mn | 0.05 | 0.03 | 0.07 | 0.00 | 0.01 | 0.21 | 0.00 | 0.00 | 0.02 | 0.04 | 0.03 | 0.01 | Mn |
| Al | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | 0.97 | 0.01 | Al |
| Si | 14.0 | 9.6 | 7.9 | 10.0 | 21.0 | 9.5 | 27.0 | 11.0 | 6.7 | 13.0 | * 14.2 | * 4.5 | Si |
| Cl | 13.0 | 57.0 | 4.8 | 13.0 | 60.0 | 8.2 | 34.0 | 8.5 | 13.0 | 23.5 | 31.2 | 1.2 | Cl |
| HCO3 | 160.0 | 250.0 | 210.0 | 280.0 | 290.0 | 300.0 | 280.0 | 220.0 | 420.0 | 267.8 | ** 90 | ** 20 | HCO3 |
| SO4 | 130.0 | 110.0 | 220.0 | 180.0 | 270.0 | 1300.0 | 440.0 | 300.0 | 7.2 | 328.6 | 38.8 | 16.0 | SO4 |
| NO3-N | 0.03 | 0.04 | 0.01 | 0.59 | 7.70 | 13.00 | 5.20 | 1.30 | 0.20 | 3.12 | 0.52 | 0.03 | NO3-N |
| P | 0.000 | 0.000 | 0.000 | 0.020 | 0.120 | 0.000 | 0.130 | 0.010 | 0.000 | 0.031 | 0.087 | 0.004 | P |
| F | 1.0 | 1.1 | 0.8 | 1.0 | 0.6 | 1.5 | 2.1 | 1.4 | 1.9 | 1.3 | 1.4 | 0.7 | F |
| pH | 7.9 | 8.1 | 7.3 | 8.2 | 7.0 | 8.3 | 7.0 | 8.4 | 7.5 | 7.7 | @ 8 | @ 7.2 | pH |
| Eh | -0.0096 | -0.0421 | 0.0515 | -0.0280 | 0.1970 | -0.0610 | -0.0137 | -0.1990 | -0.0688 | -0.1530 | -0.0300 | 0.1900 | Eh |
| pE | -0.1620 | -0.7115 | 0.8690 | -0.4790 | 3.3300 | -1.0330 | -0.2320 | -0.0406 | -1.1620 | -2.5840 | -0.5040 | 3.2100 | pE |
| T (C) | 19.0 | 16.0 | 18.0 | 20.0 | 12.0 | 13.0 | 17.5 | 22.5 | 16.0 | 17.1 | 22.0 | 1.0 | T (C) |
| % difference | 2.06 | -0.42 | 0.54 | 1.61 | -0.17 | -1.63 | -0.40 | 0.40 | 0.94 | NA | NA | NA | % difference |

* reported as SiO2
** reported as CaCO3
@ lab value; all other pH values reported as field values
NA not analyzed

# 3.0 METHODS

## 3.1 Conceptual Design

Figure 8 shows the conceptual design set up for the CSM research. As outlined on the flow chart, the first steps were to define potential sources of recharging water and potential recharge locations. From there, potential supply and location scenarios were identified and modeled from a geochemical standpoint. Using the results of the geochemical modeling, the appropriateness of injection recharge was evaluated, and conclusions and recommendations for future research described.

## 3.2 Identification of Potential Sources

While artificial recharge of ground water has been performed in other areas of the country, Federal and State regulations impact the types of water that can be used for recharge. In the state of Colorado, appropriation is the method used for determining water rights. People with the oldest water rights must be satisfied before more junior claims will be considered. Because of this, identifying unclaimed sources is a problem. The quality of water already in an aquifer cannot be degraded when recharge water is injected into the aquifer. This regulation also limits the types of water that can be considered for use in artificial recharge projects.

Much research has been done on the design of artificial recharge systems when the recharging water source is known. However, little has been published on the selection of a water supply where the identification of surplus water sources is difficult. Under-utilized

```
┌─────────────────────────────┐
│    Potential sources of     │
│  surface and ground water   │
│      supply and demand      │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│      legal constraints      │────┐
└─────────────────────────────┘    │        ┌──────────────┐
              │                    │        │ unavailable  │
              ▼                    └───────▶│ sources or   │
┌─────────────────────────────┐    │        │ locations    │
│       hydro-geologic        │    │        └──────────────┘
│        constraints          │────┘
└─────────────────────────────┘
      │                    │
      ▼                    ▼
┌──────────────────────┐  ┌──────────────────────────────┐
│ potential supply and │  │      supplies/locations      │
│ location "scenarios" │  │  requiring further research  │
└──────────────────────┘  │          to assess           │
       │                  └──────────────────────────────┘
       ▼
┌─────────────────────────────────┐
│  GEOCHEMICAL ASSESSMENT         │
│                                 │
│  - Obtain Arapahoe Aquifer      │
│    chemical data from WATSTORE  │
│  - Obtain Drinking Water data   │
│  - Model mixing effects using   │
│    program PHREEQE              │
└─────────────────────────────────┘
              ▼
┌─────────────────────────────────┐
│  Evaluation of Results          │
│    - precipitation              │
│    - dissolution                │
└─────────────────────────────────┘
              ▼
┌─────────────────────────────────┐
│  RECOMMENDATIONS                │
│    - future field tests         │
│    - regional hydrologic modeling│
└─────────────────────────────────┘
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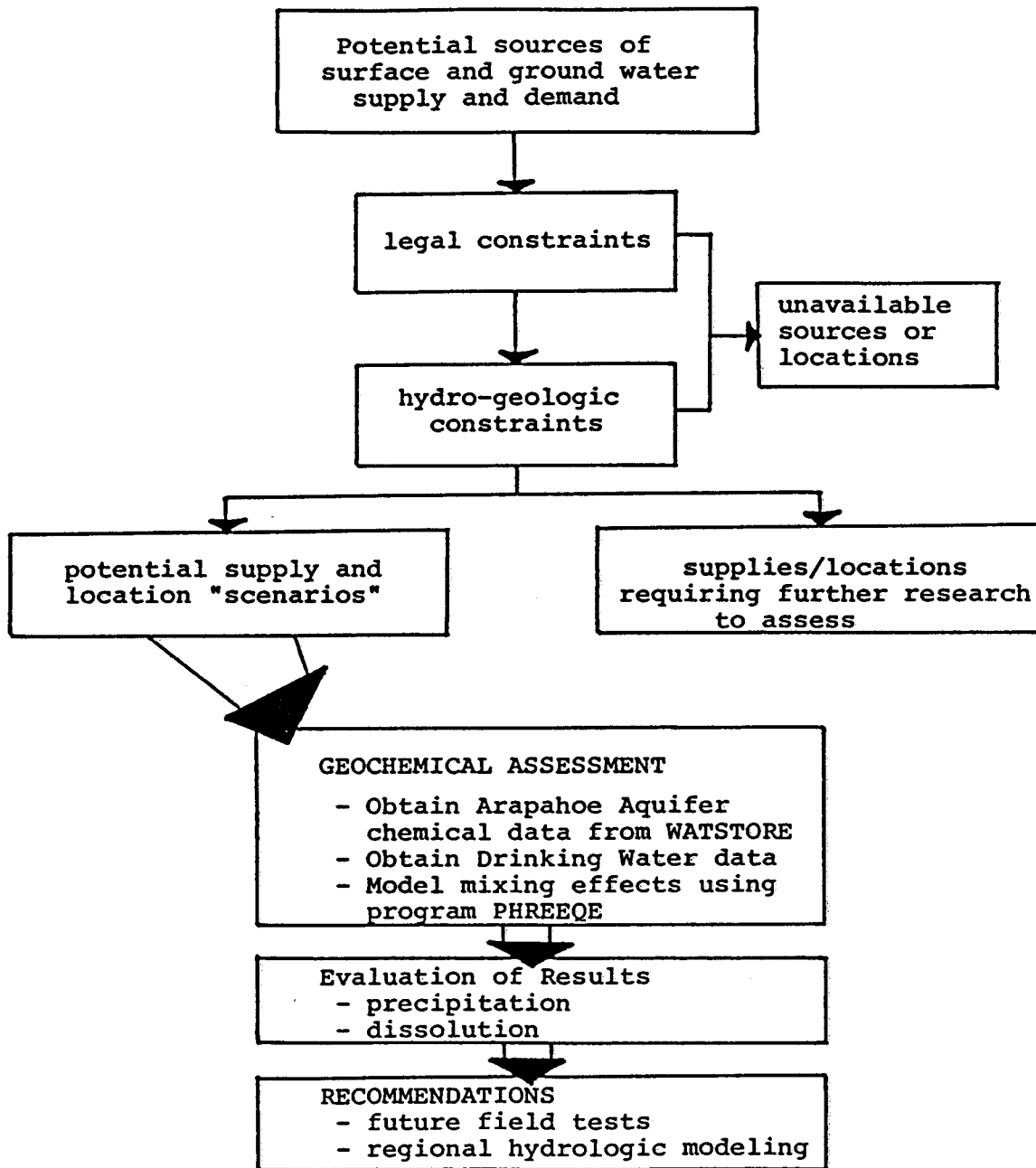
Figure 8.    Conceptual design of the study.

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water resources are not obvious within the Denver basin, and finding water for artificial recharge becomes a major hurdle to overcome in any design specification.

Recharge methods that depend on diversion of existing surface waters are not possible in the Denver basin as non-appropriated surface waters do not exist. This also applies to water in both the South Platte and the Arkansas Rivers as both of these rivers are bound by interstate compacts. Diversionary and flood control structures exist within the basin and form reservoirs; however, use of this water for artificial recharge would be inefficient. Recharging of aquifers from reservoir waters can only be considered viable for long-term, multi-year storage needs. This also requires larger reservoir storage capacities to account for unexpected seasonal fluctuations. Such larger capacities are not currently available, thus researvoir sources are not a suitable source of recharge water at this time.

Once the unattainable water sources have been identified and discarded, several more subtle sources remain. In order of potential importance, these are:

1) municipal drinking water - This refers to the excess water in the Denver treatment system during the off-season. Figure 9 shows the basin's seasonal fluctuations in water demand. The plot begins in January and shows the highest demand during the summer months of July and August. Since water supply facilities are built to meet peak demand, they are idle during the rest of the year. This seasonal fluctuation results in the potential for having excess drinking water available during the off-peak months. This excess could be recycled through artificial recharge.

2) "urban" storm waters - Urbanization increases runoff above that experienced in an undeveloped environment. This "surplus" runoff could be retained and used as an injection source. In effect, the artificial recharge system is compensating for the reduced natural

## WATER CONSUMPTION DATA   1977 – 1980
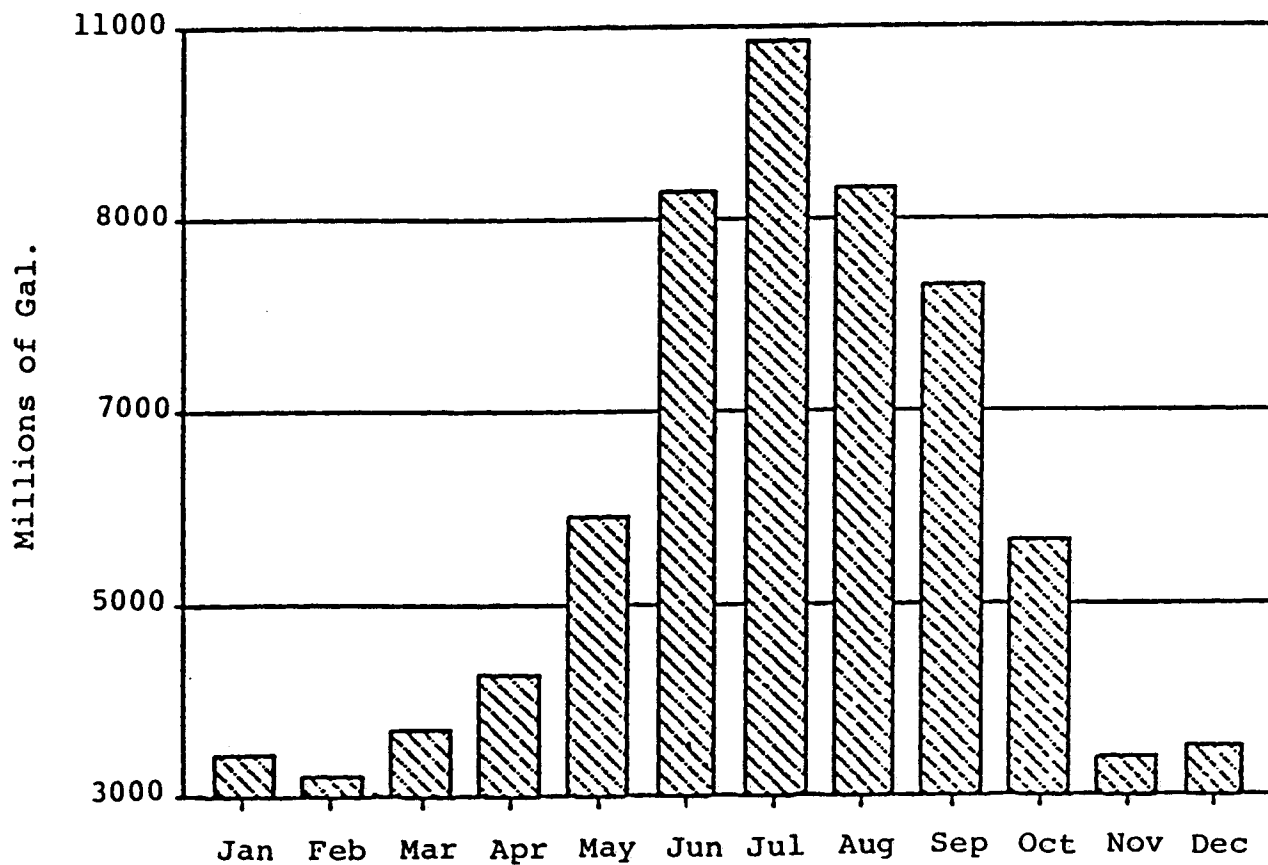### Denver Water Board



Figure 9.   Seasonal fluctuations in water demand within the
Denver basin (Halepaska, 1986).

infiltration. Between 1975 and 1977, urban storm-runoff data was collected in the Denver metropolitan area (Ellis, 1978). These data indicate that trace elements are not of particular concern for runoff water. However, arsenic, copper, iron, lead, and zinc were detected at sufficient concentrations to be of potential concern for any use of runoff as recharge water. The principal concern is that the particulate phase is considerably more prevalent than the dissolved phase. This suggests that runoff water would need to be treated to at least drinking water standards prior to any form of injection recharge. For this reason the chemistry of runoff water was not included in subsequent modeling attempts.

3) peak flows during storm events - During storm events, water above that already appropriated moves through the system. This surplus water could be retained and used as a source for injection. Since the chemistry of this peak flow water tends to be variable, chemistry data specific to peak flows is not available. However, peak flow water is much like runoff water in terms of its turbidity and particulate phase. Any peak flow water would have to be treated to at least drinking water standards prior to use as an injection source.

4) industrial heating/cooling water - Various industrial processes use water for temperature control. This thermally polluted water could be treated and re-injected if enough is available to make the operation feasible.

5) treated municipal wastewater - Excess water which has received secondary or tertiary treatment could be used as a recharge source. Recent reports indicate El Paso, Texas is operating such a system (Resource Seminars in Water Resources, 1987). This potential source was identified in the progress report for this research (Aikin, et al., 1986).

However, as with the other sources, any recharged water would need to be treated to high standards before injection.

### 3.3 Requirements for Successful Recharge Projects

Public Law 98-434, the "High Plains States Groundwater Demonstration Program Act of 1983", lists several requirements which must be met for a given location to be an acceptable artificial recharge site. These requirements are: 1) an available surface water supply; 2) the presence of a declining water table which provides adequate aquifer storage; and, 3) the commitment of a minimum of twenty percent non-Federal cost-sharing. Other important considerations include: 1) the current and future land usage patterns at the prospective installation; 2) the public acceptability of the program; and, 3) the lack of serious environmental problems. Deficiency in any one characteristic should not necessarily permanently preclude artificial recharge planning, as conditions can change within a relatively short period of time. Initial development and construction of artificial recharge mechanisms will occur where all three components are manifest. A summary of the available recharging waters, aquifer storage, and land usage patterns will allow site delineation within the Denver groundwater basin.

The identification of available recharging water sources has already been discussed in section 3.2.

The existence of adequate aquifer storage can be used to give a rough areal approximation of where initial development will occur. Instead of using storage potential, it is simpler to use the directly related quantity of aquifer depletion as an indicator. By charting occurrences of groundwater depletion, it is possible to determine where

unsaturated aquifer materials exist. Based on this analysis, the main area of bedrock aquifer depletion exists in the southwest central portion of the basin just south of the Denver metropolitan area. Depletion exists in the unconfined northern aquifers as well.

Correlations can be made between aquifer declines and current land usage. In the southwestern region, depletion of confined aquifers is indirectly related to urbanization, while in the northern region, depletion of the unconfined aquifers is due primarily to irrigation. Trend patterns for land consumption into the year 1990 indicate that present day agricultural lands will be replaced by urbanized areas as contiguous development spreads throughout the Front Range.

## 3.4 Geochemical Assessment

### 3.4.1 Methodology

The scenario of recharging the Arapahoe aquifer with drinking water was developed using the previously described potential water sources and known areas of depletion. The computer model PHREEQE was used to study the potential geochemical impacts of injecting drinking water. The results from PHREEQE were used to identify and predict the geochemical processes and potential problems associated with injection recharge of drinking water into the Arapahoe aquifer. This scenario has already been field-tested within the Denver basin by the Willows Water District; however, the geochemical results of the Willows tests are still proprietary.

The chemistry of drinking water and Arapahoe aquifer water had to be characterized for use in the model. "Watstore" is a database maintained by the U.S. Geological Survey.

The database contains the results of chemical analyses on water samples collected from wells throughout the basin. The analyses are separated by aquifer. Thirty-nine analyses were readily available for water from wells tapping only the Arapahoe aquifer. These analyses were evaluated using two criteria. The first criteria was completeness of the analysis - i.e., had the sample been analyzed for all of the applicable constituents. The second criteria was the charge imbalance. The number of positive and negative ions in a solution are totaled and the totals compared to determine charge imbalance. Since solutions must be electrically neutral, the imbalance should be zero. Deviations from zero occur if an important constituent is left out of the analysis, or if an error was made in the analysis. A range of plus or minus three was set for the charge imbalance. Most of the selected analyses are within plus or minus two. Using these criteria, nine analyses were selected for input into PHREEQE. Based on the thirty-nine available Arapahoe aquifer analyses, the nine chosen samples appear to be representative of the basin. The values for the nine samples were also averaged to create a tenth "average" sample.

The chemistry of drinking water is set within a given narrow range by federal regulations (see Table 3). The two end members of this range (identified as the MAX and the MIN samples) were each combined with every Arapahoe water sample run through the model. The chemistry of drinking water is closely regulated and is constant within the given range; however, the chemistry of water in the Arapahoe aquifer varies throughout the basin.

## 3.4.2 Description of PHREEQE

PHREEQE is a computer program designed to model geochemical reactions that occur between ground water and aquifer-rock systems. The acronym PHREEQE stands for "pH-redox-equilibrium-equations". The original program was designed by U.S. Geological Survey personnel. A manual is available through the Survey which provides the original code for the program as well as a summary of the basic chemical and thermodynamic concepts and assumptions involved in PHREEQE (Parkhurst, et. al, 1980). Many variations on the original program have been written to deal with specific problems or situations. For the CSM research, the original program was modified for IBM microcomputers (Kooper, 1986).

The program uses thermodynamic principles to calculate low temperature chemical reactions which can occur between ground water and aquifer rock systems. PHREEQE has the capability to simulate three types of reactions:

1) the reactions occurring when reactants are added to a solution; 2) the reactions occurring when one solution is titrated by another; and, 3) the reactions occurring when two or more solutions are mixed. For this project, the mixing capability of the program was used to predict whether or not precipitation or dissolution of minerals will be a problem for a particular combination of injection and aquifer waters.

The model is based on an ion-pairing aqueous model, and is capable of calculating pH, redox potential, and mass transfer as a function of reaction progress (Parkhurst, et. al, 1980). The model calculates pH, pE (a quantity directly related to Eh or oxidation potential, see Section 3.4.3), total concentration of elements, the distribution of aqueous species, and the saturation state of the aqueous phase with respect to specified mineral

phases. This model was used because of its provision for mixing separate solutions in proportions specified by the user. The model defines each solution separately, and then defines the saturation indices of the compounds contained in the specified mix. The saturation index of a compound is a measure of how close the compound is to equilibrium with the rest of the solution. If a compound has an index of zero, it is saturated with respect to the solution; if the index is positive, the compound is supersaturated; and, if the index is negative, the compound is undersaturated.

When the program models a mixing scenario, chemical analyses are required on the solutions being mixed. The type of data needed includes things such as pH, pE, temperature, and the concentrations of the elements present in the solution. These data are entered into the program for the two solutions which are to be mixed. The user then tells the program the proportions to use when mixing the two solutions. From the computer-generated results, the user can identify those minerals which are most likely to precipitate or dissolve in a given situation. In the case of artificial recharge, we are most concerned with those minerals which could precipitate and clog a well.

### 3.4.3 Limitations of PHREEQE

There are limitations inherent in the use of computer simulations of natural water systems. While the program solution is unique, it may not be representative of the actual system. Mineral phases may exist in the natural system that are not included in the data base. The reverse could also be true, mineral phases may be included in the data base which are not found in the natural system. The most fundamental limitations lie in the chemical data entered into the program to characterize the solutions to be mixed.

Assumptions had to be made when data required by the program was missing from the available analyses.

Nitrogen was listed in the analyses as nitrate-nitrite. It is unlikely that these compounds exist as such in the aquifer; however, the amounts under consideration are small. Due to the reducing conditions found in the aquifer, relative to surface water, nitrogen would probably exist as ammonia rather than a nitrate-nitrite.

Analyses of aquifer water samples do not include aluminum. Aluminum is important for predictions concerning clay minerals. While aluminum should be present in aquifer waters, the low charge imbalance indicates it is presnt in very small amounts.

The chemical analyses of aquifer water provided through the Geological Survey Watstore database did not include Eh, or the associated pE, measurements. Eh is a measure of the oxidation potential of a reaction and is directly related to pE by the following Equation 1 (Garrels and Christ, 1965).

$$pE = Eh/0.0592 \qquad (1)$$

PHREEQE requires the pE of each of the solutions to be mixed in order to simulate the reactions occurring during mixing. With Eh missing from the chemical data provided, approximations had to be made.

Since the iron in the samples was not given in species form, the assumption was made, based on pH, that the principal iron reaction involves the formation of amorphous ferric oxyhydroxide from ferrous iron as the aquifer water becomes oxidized during mixing. From

the Eh-pH diagram for the system iron-water-carbon dioxide (see Fig 10), ferric oxyhydroxides are converted to ferrous iron by the following equation:

$$Fe(OH)_3 + 3H^+ + e^- = Fe^{2+} + 3H_2O \qquad (2)$$
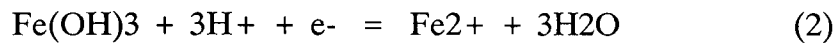
Based on the relatively low levels of iron in drinking water, the solution cannot be said to be dominated by iron, so Equation 2 is not the only control of the solution pE (Langmuir and Whitcombe, 1971). However, based on the pH, the iron in the Arapahoe aquifer water exists in the form of ferrous iron and is converted to ferric oxyhydroxides as mixing with the oxygenated injection water occurs. Thus, the iron chemistry is controlled by equation 2. This understanding was used in estimating pE's for the chosen solutions.

This estimation of pE for the solutions is potentially the weakest step in the geochemical calculations. A sensitivity analysis was performed using the average chemical data for Arapahoe aquifer samples. This showed that changes in pE over ranges greater than shown on the Eh-pH diagram (see Fig. 10) have little effect on the resulting chemistry of the two solutions or of the final mix. The minerals showing the most impact during the sensitivity analysis were those containing iron, an Eh sensitive element, but one which fortunately is present in low concentrations. Therefore, while these minerals are theoretically possible, they can form only minor constituents in the aquifer. Based on the above analysis, the assumptions involved in estimating pE values were deemed acceptable for this research.
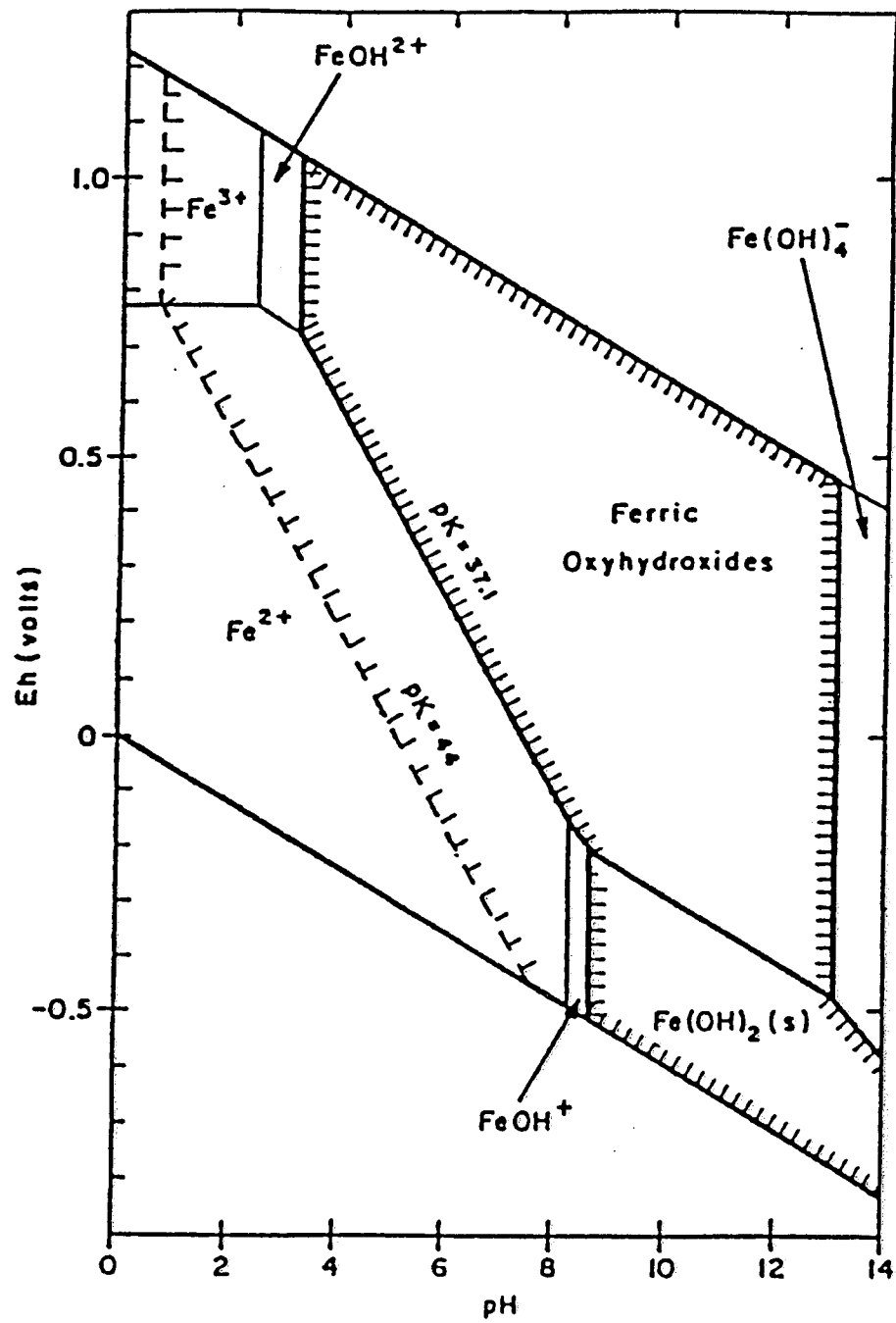
Figure 10. Eh-pH diagram for the system Fe-H2O-O2 (Langmuir and Whittemore, 1971).

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A 1:1 mix of aquifer water and treated water was assumed during the simulations. It is assumed that this mixing ratio will occur at some distance from the injection well, within the aquifer. This allows comparisons of saturation states at different points in the injection process.

4.0 RESULTS

PHREEQE produces data on the saturation states of the components of solutions before and after mixing. These saturation indices can be positive or negative. Values close to zero indicate saturation, negative values indicate undersaturation, and positive values indicate supersaturation. Changes in these values from before to after mixing indicate that reactions are occurring as a result of mixing. These reactions are affecting the precipitation state of the particular constituent.

Because of their length, the detailed results from the PHREEQE computer simulations have not been reproduced in this report. Copies may be obtained by writing to the Colorado Water Resources Research Institute at Colorado State University.

Tables 4 and 5 show the changes which have occurred as a result of mixing Arapahoe aquifer water with drinking water. Table 4 shows the results when the minimum drinking water value is used, while Table 5 shows the results when the maximum drinking water value is used. A key is provided at the base of each table. A blank value indicates that no significant change in saturation indices occur for that constituent. Values of P or SP

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## Table 4. Changes in Saturation Indices due to mixing Arapahoe Aquifer water with Minimum Drinking Water.

| | A-1 | A-2 | A-3 | A-4 | A-5 | A-6 | A-7 | A-8 | A-9 | AVG | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| calcite | | SS | | SS | | | | SS | | SS | calcite |
| dolomite | | | | | | | | | SS | | dolomite |
| siderite | | D | D | | | | | | | | siderite |
| rhodochrosite | | | | | | | | | | | rhodochrosite |
| gypsum | | | | | | D | | | | | gypsum |
| hydroxyapatite | | | | | SS | | | | | | hydroxyapatite |
| fluorite | | | | | | SS | SS | | | | fluorite |
| chalcedony | | S | | S | | S | | S | D | | chalcedony |
| quartz | | | | | | | | | SS | | quartz |
| gibbsite | | | | | | | | | | | gibbsite |
| kaolinite | | | | | | | | | | | kaolinite |
| sepiolite | | | | | | SS | | | | | sepiolite |
| hematite | | | | | | | | | | | hematite |
| goethite | | | SS | | | | | | SS | | goethite |
| FeOH3a | | | | SP | | | P | | | | FeOH3a |
| vivianite | | | | | | | | | | | vivianite |
| pCO2 | | | | | | | | | | | pCO2 |
| pH | -0.06 | -0.05 | 0.07 | -0.04 | 0.07 | 0.07 | 0.09 | 0.05 | 0.06 | 0.03 | pH |
| pE | -2.77 | -2.55 | -3.39 | 0.95 | -1.17 | -2.50 | 3.53 | 0.47 | -3.48 | 3.62 | pE |
| Act H2O | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | Act H2O |
| ionic strength | -0.0030 | -0.0040 | -0.0050 | -0.0050 | -0.0080 | -0.0190 | -0.0092 | -0.0061 | -0.0034 | -0.0073 | ionic strength |
| temp | -9.0 | -7.5 | 8.5 | -9.5 | -5.5 | -6.0 | -8.3 | -10.8 | -7.5 | -8.1 | temp |

LEGEND: SP=strong precipitation; P=precipitation; D=dilution;
S=dissolution of rock matrix; SS=strong dissolution of rock matrix

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Table 5. Changes in Saturation Indices due to mixing Arapahoe Aquifer water with Maximum Drinking Water.

| | A-1 | A-2 | A-3 | A-4 | A-5 | A-6 | A-7 | A-8 | A-9 | AVG | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| calcite | | | | | | | | | | | calcite |
| dolomite | | | | P | | | | SP | | SS | dolomite |
| siderite | | D | D | | | | | | | | siderite |
| rhodochrosite | | | | | | | | | | | rhodochrosite |
| gypsum | | | | | | D | | | | | gypsum |
| hydroxyapatite | | | | P | | | | SP | | | hydroxyapatite |
| fluorite | | | | | | S | SS | | | | fluorite |
| chalcedony | | S | | S | | S | | | P | | chalcedony |
| quartz | | | | | | | | | | | quartz |
| gibbsite | | | | | | | | | | | gibbsite |
| kaolinite | | | | | | | | | | | kaolinite |
| sepiolite | | | | | | SS | | | | | sepiolite |
| hematite | | | | | | | | | | | hematite |
| goethite | | | | | | | | | | | goethite |
| FeOH3a | P | P | | SP | | | SP | | SP | SP | FeOH3a |
| vivianite | | | | | | | | | | | vivianite |
| pCO2 | | | | | | | | | | | pCO2 |
| pH | 0.03 | -0.03 | 0.10 | -0.05 | 0.05 | -0.03 | 0.09 | -0.10 | 0.03 | 0.05 | pH |
| pE | 0.11 | 0.13 | -3.27 | 0.46 | -0.59 | -2.60 | 3.04 | -0.50 | 0.58 | 3.46 | pE |
| Act H2O | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | Act H2O |
| ionic strength | -0.0020 | -0.0900 | -0.0040 | -0.0030 | -0.0060 | -0.0180 | -0.0078 | -0.0047 | -0.0018 | -0.0058 | ionic strength |
| temp | 0.5 | 3.0 | 2.0 | 1.0 | 5.0 | 4.5 | 2.3 | -0.3 | 3.0 | 2.5 | temp |

indicate that the constituent is becoming supersaturated as a result of mixing. Values of S or SS indicate that dissolution is occurring as a result of mixing.

Dissolution (values of S or SS) would be advantageous for minimizing aquifer plugging. This is the case for almost all mixtures of "minimum" treatment water with Arapahoe aquifer water. Precipitation (values of P or SP) indicates the possibility of aquifer plugging. Potential plugging is indicated with some mixtures of "maximum" treatment water and Arapahoe aquifer water.

It is important to keep the geochemical results of this study in perspective with regard to time. In the short term, suspended material may be a more significant cause of well screen and aquifer plugging than precipitation of saturated mineral phases. Also, the saturated phases indicated can be expected to precipitate at different rates, if they precipitate at all.

## 5.0 CONCLUSIONS AND RECOMMENDATIONS

This study has used the computer model PHREEQE as a way to examine potential artificial recharge problems. While several assumptions were made in order to use the model, the computer-generated results do give an indication of the reactions likely to occur in the field. Analyses were made using injection water having the maximum and minimum ion concentrations allowed by EPA drinking water standards. Within this range, some water mixtures may promote precipitation of minerals by increasing their saturation indices. Other mixtures decrease saturation indices and may be beneficial to recharge programs due to an eventual increase in porosity and hydraulic conductivity as dissolution occurs. Such

an increase may also weaken the aquifer structure over the long term, but this would only be a problem if groundwater withdrawal increased so that the weakened area was unsaturated.

The injection process was examined at the well before mixing and within the aquifer at the point where a 1:1 mixture was occurring. Use of other mixtures would give a more complete picture of saturation and precipitation processes that could occur around a well during aquifer recharge. The 1:1 mix will occur at some distance from the recharge well. Computer runs using different proportions would give a better idea of reactions occurring within a halo around the well.

More accurate results could be obtained by using water analyses that included Eh and aluminum concentration values, which were not available in the U.S. Geological Survey Watstore database. Also, it may be beneficial to rewrite equations in the PHREEQE data base using $NH_4+$ as a master species rather than $NO_3-$, and assume that nitrogen is occurring as ammonia. However, these more accurate results would require a much greater expenditure of time and money. Sample collection and analysis following strict procedures would be required.

This study can serve as a first estimate in choosing the location for an injection well and choosing the injection water. Problematic constituents in the injection water can be identified so that the practicality of removing them can be assessed. This study has not discovered any severe geochemical problem which would prevent the injection recharge of drinking water into the Arapahoe aquifer.

At this time, research is beginning which will assess the long-term hydrologic effects of artificial recharge. Augmentation of the water supply in a portion of the Denver

groundwater basin will be evaluated by designing recharge scenarios and modeling them with a three-dimensional finite- difference flow model. Results of this research into the geochemical aspects of injection recharge, when combined with this hydrologic modeling, will offer a clearer understanding of the possibility of using artificial recharge to augment groundwater supply in the Denver basin.

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