GROUND WATER RECHARGE AND FLOW IN THE REGIONAL TREASURE VALLEY AQUIFER SYSTEM

GEOCHEMISTRY AND ISOTOPE STUDY

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Executive Summary

Ground water in a regional system of deep, confined aquifers is increasingly targeted for the Treasure Valley's growing municipal and industrial water needs. Additional development of these aquifers requires greater knowledge about ground water recharge and flow in the regional system. The purpose of this study was to (1) refine the conceptual model of regional ground water recharge and flow in the Treasure Valley using hydrochemical data, and (2) provide new information for estimating regional-scale hydraulic parameters. The study objectives were to:

- Describe hydrochemical characteristics of principal aquifers that comprise the regional ground water flow system.
- Assess likely sources of recharge.
- Examine patterns in dissolved ion concentrations and abundance of carbon isotopes along regional ground water flow paths.
- Determine whether known geochemical processes describe the observed patterns.
- Estimate residence times for regional ground waters.

Results from the study show distinctive relationships between ground water chemistry and the unique depositional environments of the principal aquifers. Specifically, the study found that:

- Tritium was non-existent in samples from deeper, regional ground water, except where poor well construction may have allowed inter-aquifer mixing. This finding indicates that ground water in deeper aquifers entered the flow regime prior to atmospheric nuclear testing during the 1950s and 1960s.
- Specific conductance (and by inference, total dissolved solids) is greatest in shallow alluvial aquifers and decreases with depth. This finding indicates that water in deeper aquifers did not enter the ground water regime through the carbon-rich sediments found in Treasure Valley soils.
- Concentrations of major ions and other dissolved constituents varied consistently with depth among aquifer zones. The high degree of consistency suggests that these hydrochemical data can be used to identify discrete aquifer zones in other areas of the basin.
- Comparisons between measured constituents and established models of geochemical processes showed that (1) ground water near the northeastern basin margin has experienced little interaction with aquifer minerals and (2) ground water beyond the northeastern basin margin has experienced substantial interaction with aquifer minerals. Geochemical evolution of Treasure Valley ground water appears to be influenced by solution of both carbonate and silicate minerals.
- Residence times of Treasure Valley ground water generally increase with depth and with distance along a regional east-to-west trending flow path. Residence

times range from thousands to tens of thousands of years. The youngest waters entered the subsurface a few thousand years ago and are found along the northeastern boundary of the basin, adjacent to the Boise foothills. The oldest waters entered the subsurface between 20,000 and 40,000 years ago and are found in the western reaches of the basin near the Snake River. Ground water in the deep deltaic aquifers beneath Boise was recharged between 10,000 and 20,000 years ago. The proximity of these paleo-ground waters to the mountain front recharge area suggests that there is little natural flow in these aquifers.

- Contemporary seepage from rivers and/or irrigation diversions is not the primary source of recharge for most deeper, regional aquifers. Paleo-river channels, fractured granite aquifers in the Idaho Batholith and tributary sedimentary aquifers are the most likely sources of recharge to the regional flow system.
- A strong relationship between concentrations of dissolved constituents and depositionally-defined aquifer units, observed geochemical patterns consistent with the apparent evolution of ground water geochemistry, and the general east-to-west increase of ground water residence times support a conceptual model of regional ground water flow consisting of (1) recharge in alluvial sediments in southeast Boise and at the base of the mountain front north of Boise, (2) movement of ground water from the recharge areas into the deeper Boise area fluvial-lacustrine aquifers, and (3) movement of ground water from the Boise area aquifers into regional deep-lake aquifers of Nampa and Caldwell.

Table of Contents

List of Figures

List of Tables

Abbreviations for Wells and Other Waters

Am	Amity production
BCW	Banner Creek wells
BC	Blacks Creek production
BFS	Boise Front springs
BR	Boise River
C15	Caldwell No. 15 production
C16	Caldwell No. 16 production
CM	Cassia monitoring
C1	Cassia No. 1 production
C2	Cassia No. 2 production
Ch	Christiansen domestic
Edg	Edgeview (Braddock) production
G1	Goddard No. 1 production
G2	Goddard No. 2 production
Gy	Guyer domestic
HP	Hewlett-Packard production
In	Inouye domestic
J	Johnson domestic
JR	JR Flat production
Kn	Knox domestic
Ku	Kuespert domestic
L	Lete domestic
MAC	MAC production
MH	Maple Hills
MSt	Market Street production
McN	McNabb domestic
M8t	Meridian No. 8 test
M15	Meridian No. 15 production
M19	Meridian No. 19 production
M19t	Meridian No. 19 test
MD	Micron monitoring deep
MS	Micron monitoring shallow
M5	Micron No. 5 production
N12	Nampa No. 12 production
N19	Nampa No. 19 production
P10	Parma No. 10 production
StL	Saint Lukes fire control
Sch	Schwisow domestic
SH	State Hospital production
SW	Sunset West production
TV1	TVHP1 multi-level monitoring 1
TV2	TVHP1 multi-level monitoring 2
UI	University of Idaho production
Wm	Westmoreland production
Wr	Wright domestic

1. INTRODUCTION

1.1. Problem Statement

Ground water in a system of deep, confined aquifers is a primary source of potable water for Treasure Valley residents. These aquifers are tapped by most of the region's municipal and industrial wells and are increasingly targeted for additional development as the Treasure Valley population grows. Expanding use of ground water resources necessitates greater knowledge about recharge and flow in the regional ground water system. The goal of this study is to develop a better understanding of the regional flow system, with emphasis on recharge mechanisms and ground water residence times. The following introduction (1) describes a basic conceptual model of the regional system, (2) provides background on the geochemical tools used in the analysis, (3) reviews previous and related work, and (4) presents the purpose and objectives of the present study.

1.2. Regional Ground Water System

The Treasure Valley region of southwestern Idaho (Figure 1) has a complex history of lacustrine and alluvial deposition that influences regional ground water movement. In general, basin sedimentary deposits grade from coarser, more permeable sediments near the Boise Front[1] to finer, less permeable sediments at the distal end of the basin. At the basin scale, sediments are a finer grade with depth. These regional trends are interrupted by a complex arrangement of highly permeable deposits associated with paleo-river channels, river deltas, alluvial fans, and other features characteristic of a dynamic lacustrine history. Productive units are often surrounded by lower permeability deep-lake deposits, which, in some cases, limit interaction between productive units. The complexity of the ground water environment is well documented in the Boise area (Wood, 1997; Squires et al., 1992) and near Caldwell (Wood, 1994).

Additional influences on the movement of ground water are attributed to structural processes, including downwarping of the basin and faulting along the basin margin. Basin downwarping and an associated downslope trend in sediment deposition contribute to steeply dipping sedimentary deposits along the northern basin margin, which may cause deeper aquifer units to pinch out at depth (Wood, 1997). An erosional unconformity associated with changing lake levels in Pliocene Lake Idaho

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[1] Boise Front describes the portion of the Idaho Batholith that forms the northern boundary of the lower Boise River basin.

truncates down-dipping units along the basin margin near Boise (Wood, 1997; Squires et al., 1992). The relationship between ground water above the unconformity and ground water in the underlying delta deposits, while unclear, is thought to be significant to the regional system (Wood, pers. comm.). In addition to complexity inherent in deposition and erosion, a series of major faults bisect the stratigraphic section along the northern basin margin. The hydrologic impact of these faults is poorly understood, but they are likely to be an important influence on ground water flow in Boise-area aquifers.

Less is known about the western portions of the valley. The relatively stable deep-water lake that covered this portion of the basin probably resulted in a less complex depositional environment than is found near the basin margin. Within this more uniform geologic environment, productive aquifers are interspersed with less permeable sediments, and vertical stratification of ground water is apparent from changes in water quality. Natural mixing between shallow aquifers and underlying regional ground water appears to be minimal and deep aquifers are generally confined.

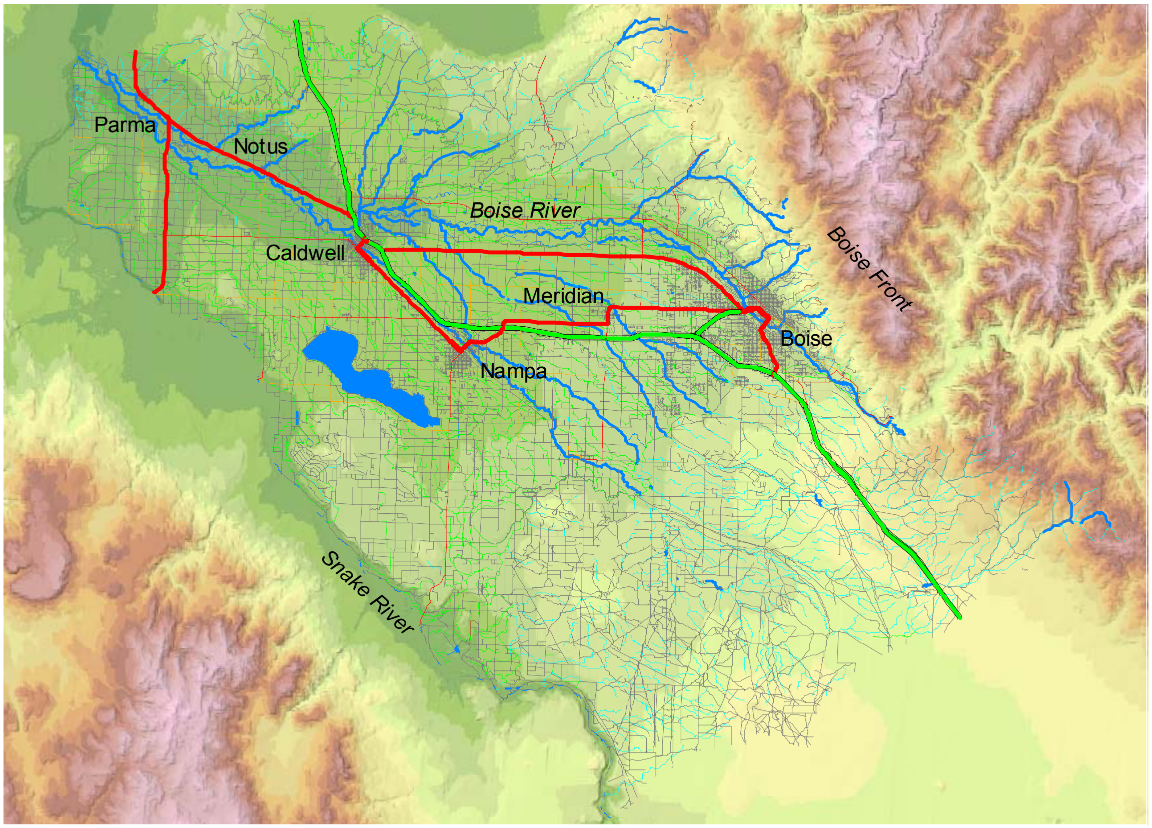

Figure 1. Map of the Treasure Valley project area.

Recharge to shallow aquifers in the basin is dominated by seepage from the dense network of irrigation canals and percolation from irrigation water (Urban and Petrich, 1998). Additional sources include mountain front recharge, underflow from the granitic Idaho Batholith and tributary sedimentary aquifers, and direct precipitation. There is no doubt that irrigation represents the primary source of recharge to shallow aquifers; however, the extent that surface water contributes to deep, regional aquifers, or that shallow aquifers recharge deep, regional aquifers, remains unclear.

The present conceptual model of ground water recharge and flow in the Treasure Valley consists of (1) aquifers contained in shallow alluvium and (2) aquifers contained in deeper Idaho Group sediments. Shallow alluvial aquifers are recharged by seepage from canals and deep percolation below irrigated fields. These aquifers discharge locally at nearby irrigation drains, creeks, or rivers. Deep Idaho Group aquifers are confined or semi-confined and do not appear to be in direct hydraulic connection with surface water. Deep ground water most likely originates as underflow from the granitic rocks and paleo-river channels that border the northern margin of the Treasure Valley near Boise. It may also originate as river or canal seepage in the northeastern portion of the valley. These deeper waters are thought to comprise a regional ground water system that ultimately discharges to the Snake River. A series of NW-SE trending faults is thought to influence both vertical and horizontal ground water flow.

1.3. Geochemical Tools for Analyzing Ground Water Flow

The developing body of scientific knowledge about chemical interactions between ground water and aquifer minerals provides a unique set of tools for interpreting changes in dissolved ions and other constituents along ground water flow paths. These interpretations allow hydrologists to (1) investigate the relative importance of various recharge sources, (2) confirm likely ground water flow paths, and (3) gain insight into the evolution of ground water chemistry within a flow system. Recent applications of these tools include the Milk River Aquifer, Canada (Hendry and Schwartz, 1990); the Cambrian-Ordovician Sandstone Aquifer, eastern Wisconsin (Weaver and Bahr, 1991); and the Mahomet Bedrock Aquifer, east-central Illinois (Panno et al., 1994).

Environmental isotopes are useful tracers of water movement because unique isotopic signatures are related to particular recharge environments. Analysis of isotopic tracers allows one to (1) establish the environment in which ground water recharge took place and/or (2) constrain the window of time during which recharge occurred. These techniques have proven useful for analyzing a number of ground water systems in the western U.S., including San Juan Basin, New Mexico (Phillips et al., 1989); Aravaipa Valley and Tucson Basin, Arizona (Adar and Neuman, 1988; Adar et al., 1988; Campana and Simpson, 1982); Santa Clara Valley, California (Muir and Coplen, 1981); White River Flow System, Nevada (Kirk and Campana, 1990); and the Eastern Snake River Plain, Idaho (Plummer et al., 2000).

Tritium (^{3}H), carbon-14 (^{14}C), and carbon-13 (^{13}C) are environmental isotopes used in the present study. Tritium and ^{14}C are radioisotopes, and although they differ in application, these radioactive species are both used to estimate the time that a unit of water resides in the ground water system. Tritium is used to identify "modern" ground waters, while ^{14}C is used to date "paleo" ground waters.[2] The potential for dating ground water using atmospheric ^{3}H has been explored by numerous researchers, beginning with Kaufman and Libby (1954). Worldwide atmospheric testing of thermonuclear weapons during the 1950s and 1960s resulted in relatively high concentrations of ^{3}H in rain water.[3] This well-documented influx of ^{3}H into the ground water environment has become a standard for the definition of "modern" ground water (Clark and Fritz, 1997). Ground water with ^{3}H concentrations greater than ~10 picoCuries per liter (pCi/L) is "modern" in that a substantial portion of that water entered the subsurface during the past 50 years. Present-day precipitation contains very little ^{3}H because most of the bomb ^{3}H has been removed (rained) from the atmosphere.

The discovery in 1946 of naturally-occurring ^{14}C (radiocarbon) in atmospheric CO_2, the estimation of its 5,730-year half-life, and the early recognition of its utility for dating carbon-rich material, resulted in development of a useful ground water dating technique. Most ^{14}C in ground water is introduced when recharge water percolates through the soil zone. Carbon dioxide released in the soil from decomposing plants accumulates at a concentration between 10 and 100 times greater than that of the atmosphere. The high CO_2 pressure of the soil increases the concentration of ^{14}C-containing dissolved inorganic carbon (DIC) in percolating water. Once beyond the influence of the soil zone, percolating water ground water is no longer exposed to ^{14}C-rich DIC. With time, the dissolved ^{14}C slowly decays to carbon-12 (^{12}C), leaving measurably less ^{14}C behind in the water.

Estimating the residence time of ground water using ^{14}C-dating requires quantifying the decrease in ^{14}C from radioactive decay after the initial CO_2 charging. Two key assumptions must be evaluated in order to establish residence times: (1) the original concentration of ^{14}C in the charged water must be known; and (2) sources or sinks of ^{14}C (other than radioactive decay) encountered after leaving the soil zone must be quantified. If these two assumptions are valid, then the residence time of ground water in the aquifer is calculated using an exponential model of radioactive decay and the

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[2] In practical terms, "modern" ground waters are those recharged during the past five decades, while "paleo" ground waters are those recharged thousands to tens-of-thousands of years ago.

[3] Even at peak atmospheric concentrations, tritium fallout was not a direct threat to human health (Clark and Fritz, 1997).

known half-life of ^{14}C. To address the first assumption, two independent historic records have been developed that establish the activity of ^{14}C in the atmosphere. These records are Holocene tree rings and late Pleistocene coral. The records provide convincing evidence that atmospheric ^{14}C has decreased about 40% during the past 30,000 years (Clark and Fritz, 1997).

The second assumption, that sources and sinks of ^{14}C along a ground water flow path can be quantified, is much more problematic in ground water systems. Ground water is subjected to perpetual changes in its chemical make-up caused by reaction with the mineral assemblages through which it passes. This process, known as geochemical evolution, often results in dilution of dissolved ^{14}C by biogenic and mineral carbon that, because of its extreme age, no longer contains ^{14}C. In addition, certain chemical and biological reactions partition different carbon isotopes into various reaction products, resulting in isotopic fractionation of the dissolved carbon. In general, these geochemical and biological reactions reduce the amount of ^{14}C in ground water and, if not accounted for, may cause ground water ages to be grossly overestimated. The practical range of ground water ages that can be determined using ^{14}C analysis is 5,000 to 30,000 years (Clark and Fritz, 1997). Even when the sources and sinks of ^{14}C are known and ground water age falls within this range, mixing between different aquifers may add considerable uncertainty to travel time estimations.

Measuring the relative abundance of the stable isotope ^{13}C in ground water provides another means of tracing carbonate evolution and is particularly useful for determining the importance of biogeochemical reactions in the ground water system. Large differences in $\delta^{13}C$ among the various carbon reservoirs in a regional flow system make this technique a useful diagnostic tool. The evolution of DIC in ground water begins with atmospheric CO_2 ($\delta^{13}C \approx -7‰$).[4] Photosynthetic uptake of atmospheric CO_2 is accompanied by a substantial depletion in $\delta^{13}C$ (approximately 22‰ for C_3 plants, resulting in plant $\delta^{13}C$ values of between -24 and -30‰).[5] Subsequently, when dead vegetation is decomposed in the soil and converted back to CO_2, the isotopically-light CO_2 accumulates in the soil at concentrations between 10 and 100 times that of the atmosphere. The CO_2 is further fractionated by diffusion away from the production zone. As a result of these processes, soil CO_2 typically has a $\delta^{13}C$ value of about -23‰.

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[4] Del notation is used to describe the proportion of ^{13}C relative to the more ubiquitous isotope ^{12}C. The defining relationship is $^{13}C/(^{13}C+^{12}C)$. The ratio is expressed per mille (‰), which is, one unit per thousand.

[5] The amount of fractionation depends on the type of plant and its particular photosynthetic pathway. Most terrestrial ecosystems are dominated by C_3 plants. A good discussion of these pathways can be found in Clark and Fritz (1997).

As soil CO_2 dissolves into percolating water some of it becomes hydrated and dissociates into HCO_3^- and CO_3^{2-}. This geochemical process fractionates ^{13}C once again. The extent of this ^{13}C fractionation is dependent on pH, but is close to -15‰ for ground waters with pH greater than 7.5. In carbonate terranes, weathering of calcite and other carbonate minerals causes DIC concentrations to increase and $\delta^{13}C$ to evolve to higher values until calcite saturation is reached. The saturation $\delta^{13}C$ value depends on the starting P_{CO_2}, the $\delta^{13}C$ value of the carbonate material and whether the ground water system is open or closed to exchange with atmospheric CO_2.

Several complicating factors associated with chemically reduced ground waters are also recorded in the ^{13}C signature, namely oxidation of organic matter and methanogenesis. Microbial oxidation of organic matter adds additional CO_2 to the ground water system. The added CO_2 is depleted in ^{13}C because of fractionation during the biochemical reaction. This process can add carbon to the ground water DIC pool that has $\delta^{13}C$ of between -25 and -30‰. Methane-producing bacteria strongly affect $\delta^{13}C$ of DIC by adding CO_2 with $\delta^{13}C$ of about +10‰.

1.4. Previous Geochemistry and Isotope Studies in the Treasure Valley

Although no existing geochemical studies directly address regional-scale ground water recharge and flow in the Treasure Valley, a number of studies contribute to understanding particular parts of the system. Previous investigators have used naturally occurring stable isotopes to describe recharge of cold-water springs in the granitic foothills above Boise (Mariner et al., 1989). Stable isotopic signatures (^2H and ^{18}O) of spring water suggest that these shallow aquifers on the mountain-front have contemporary and local recharge sources. On the other end of the age continuum, ^{14}C-ages of geothermal water emanating from structural faults deep beneath Boise suggest recharge some 14,000 to 30,000 years ago (Mariner et al., 1989; Mayo et al., 1984). Radiocarbon-ages have also been determined for ground water from the Goddard, Westmoreland, and MAC wells, which penetrate non-thermal aquifers near Boise (Parliman and Spinazola, 1998). These data show that some deep ground water beneath Boise originated as much as 11,000 years ago. The existence of paleo-ground water precludes a direct, dynamic connection to shallow aquifers or surface water. This distinction is supported by measurements of ^3H in ground water samples from five shallow wells adjacent to the New York Canal. These measurements indicate that downward movement of surface water originating from canal seepage and flood irrigation has been limited to a depth of about 200 feet since the 1950s (D. Parliman, pers. comm. 1999).

A general, basin-scale geochemical and isotope study of ground water in the Eastern Snake River Plain evaluated geochemical controls on non-thermal and geothermal water using major ion chemistry (Wood and Low, 1988). The study also addressed the source of recharge to the geothermal system using both stable isotopes and radioisotopes. Results suggested that non-thermal aquifers of the Eastern Snake River Plain recharge from tributary basins and local irrigation. In contrast, geothermal waters are on the order of 20,000 years old. These geothermal aquifers are thought to derive recharge from precipitation in the high mountains of central Idaho (Wood and Low, 1988). The layered sedimentary aquifers of the Treasure Valley are clearly different from the basalt aquifers of the Eastern Snake River Plain; however, a similar geochemical and age dating approach is likely to provide similar information for the Treasure Valley ground water system.

1.5. Purpose and Objectives

The primary purpose of this investigation was to refine the present conceptual model of ground water recharge and flow. A secondary purpose was to provide data for estimating regional-scale hydraulic parameters. The specific objectives were to:

1. Describe hydrochemical characteristics of principal aquifers that comprise the regional ground water flow system.
2. Assess likely sources of recharge.
3. Examine patterns in dissolved ion concentrations and abundance of carbon isotopes along regional ground water flow paths.
4. Determine whether known geochemical processes describe the observed patterns.
5. Estimate residence times for regional ground waters.

2. METHODS

2.1. Ground Water Sampling and Chemical Analysis

The completion of several preliminary tasks was necessary to acquire an appropriate data set that represents the regional ground water system. The tasks included: (1) selecting wells for ground water sampling, (2) collecting samples, (3) measuring the appropriate constituents, and (4) determining the most suitable analytical tools. This section describes the methodology used to accomplish these tasks.

2.1.1. Well Selection

Thirty-eight wells were selected for ground water sampling (Figure 2). The wells, all completed in Idaho Group sediments, lie about the axis of the basin between southeast Boise and Parma, generally along the hypothesized path of ground water flow.[6] Particular attention was given to driller's logs and as-built drawings to ensure that sampling wells had (1) adequate surface seals; (2) grout seals, packers, and/or formation seals at all casing reductions; (3) minimal overbore; and (4) clearly identified water bearing zones (WBZs) defined by a screened and/or gravel packed interval. The tops of the WBZs were between 338 and 800 feet below ground surface and the WBZs were less than 213 feet thick. Exceptions to these criteria were multi-level monitoring wells, which are completed over several discrete WBZs; and the United Water Idaho, Inc., Market Street well, which is completed in a WBZ between depths of 510 and 912 feet. The Market Street well has undergone rigorous geophysical examination and, although open for 402 feet, is considered important for interpreting estimates of ground water residence times in nearby wells.

2.1.2. Ground Water Sampling and QA/QC

The Idaho Department of Water Resources contracted with the U.S. Geological Survey to obtain water samples from the wells shown in Figure 2. Sampling was conducted during the 1999 and 2000 field seasons. Sampling protocol closely followed Standard Operating Procedures (SOPs) developed for the Statewide Ambient Ground Water Quality Monitoring Program (Statewide Program). Each water sample required a field site inventory (SOP 1.00); well purging (SOP 3.00); equipment decontamination (SOP 4.00); proper collection (applicable parts of SOP 5.00); quality control sampling

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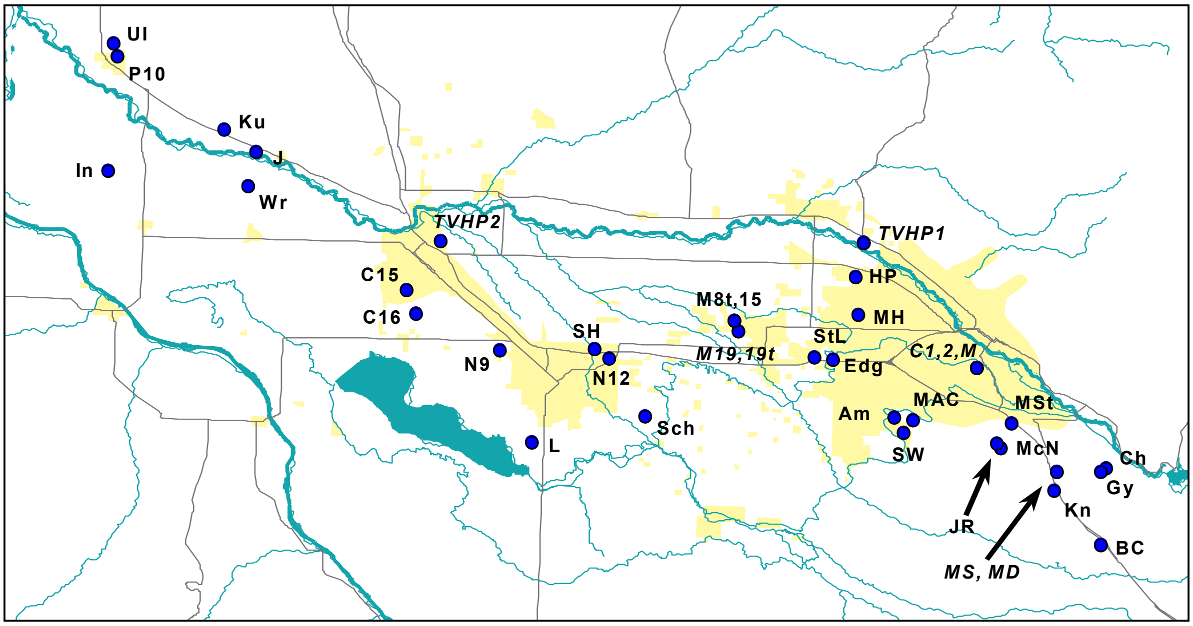
[6] Petrich and Urban et al. (1999) gives a full analysis of water level measurements in the basin.

(SOP 9.00); appropriate labeling (SOP 8.00); and storage (SOP 6.00) (IDWR, 1998a). Quality control checks consisted of duplicate samples, an equipment blank per month of sampling, and one blind reference of each analyte per month of sampling. Following this plan ensured that (1) data were collected in a manner consistent with the research objectives, (2) data accurately represented the actual ground water conditions, and (3) data were technically defensible.



Italics identify multi-level wells. Well information is provided in Appendix 1.

Figure 2. Sampling well locations and labels.

The Quality Assurance (QA) Plan for the Statewide Program was adopted to evaluate the sampling and analysis protocol used during the present study. The Statewide Program QA plan was selected because sampling requirements were similar to the present study and because the Statewide Program benefited from state and federal review (IDWR, 1998b). Quality assurance observations were conducted at the field and laboratory level. These observations included: (1) previewing laboratory QA procedures prior to sample submission; (2) reviewing laboratory QA data upon receipt by TVHP personnel; (3) observing field sampling techniques; and (4) evaluating quality control (QC) data, including ion balances, precision of duplicate analyses, and accuracy of blind references.

2.1.3. Measurements and Reporting

Temperature, pH, dissolved oxygen (DO), and specific conductance (C_s) were measured in a flow-through cell connected to the discharge of each well. After these parameters stabilized, samples were collected and stored according to the procedures described in Section 2.1.2. Alkalinity was titrated immediately after each sample was collected. All ground water samples were submitted to the USGS National Laboratory in Arvada, Colorado, for chemical analyses of major ions (Ca, Mg, Na, K, HCO_3, CO_3, Cl, and SO_4), NO_3, SiO_2, F, Fe, Mn, and ^3H.[7]

Twenty-eight samples from deep wells in the central basin were selected for ^{14}C age-dating from the pool of 38 wells. The selection criteria described in Section 2.1.2, together with the chemical information, were used to establish that the 38 wells produced water exclusively from the regional ground water system. The absence of ^3H and NO_3 in the age-dating samples ensured that no modern water contaminated the wells. The University of Waterloo Radioisotope Laboratory conducted measurements of ^{13}C and prepared graphite targets for ^{14}C analysis from DIC extracted from the ground water samples. Carbon-13 was measured using standard Mass Spectroscopy methods. Carbon-14 was measured using Accelerator Mass Spectroscopy (AMS) methods.[8] Carbon-14 measurements were conducted at The Canadian Centre for Accelerator Mass Spectroscopy (ISOTRACE), Toronto, Canada, and at the Rafter Radioisotope Laboratory, Lower Hutt, New Zealand.

All data except P_{CO_2} and isotope measurements are reported using International System of Units (SI).[9] For direct comparison with historic data, P_{CO_2} data are given in bars and ^3H measurements are given in units of picoCuries per liter (pCi/L). Carbon isotope reporting follows protocol outlined by Stuvier and Polach (1977). Values of $\delta^{13}C$ are reported as per mil (‰) with respect to the PDB standard. Carbon-14 ages based on the activity of ^{14}C relative to the absolute international standard activity, normalized to ^{14}C activity in 1950 wood, and corrected for isotopic fractionation are reported as conventional radiocarbon ages. All age calculations are based on the Godwin half-life for ^{14}C (5730 y). Radiocarbon ages are reported in years before present (ybp) with AD 1950 equal to 0 ybp. Statistical certainty based on the number of accumulated sample counts, oxalic acid standard counts, and background counts, plus analytical uncertainty and instrument error are given as ± one standard deviation. Elevations are reported in feet above mean sea level (MSL).

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[7] Specific information about analytical methods can be found at http://www.nwql.cr.usgs.gov/.

[8] Accelerator Mass Spectrometry employs a particle accelerator to count the number of atoms of each carbon isotope in the target material. Additional information about AMS can be found at http://www.gns.cri.nz/atom/rafter/measure.htm.

[9] A reference of SI units can be found at http://www.unc.edu/~rowlett/units/sipm.html.

2.2. Data Analysis

2.2.1. Aquifer Correlation and Geochemical Evolution

Analysis of chemical data collected from poorly constructed wells or from natural mixing zones could clearly bias the results of our study. To establish confidence in our analysis we identified and rejected data that showed evidence of mixing between discrete zones in the stratigraphic section. Tritium and NO_3 were used as the primary indicators of mixing with contemporary waters. Elevated DO and SO_4 indicated mixing in cases where deep ground water was known *a priori* to be chemically reduced. Samples that showed elevated concentrations of fluoride, very high Na/Ca ratios, and elevated temperatures were identified as possibly mixed with hydrothermal water.

Hydrochemical data were mapped, compared to previous interpretations of hydrogeologic unit boundaries, and considered relative to aquifer stratigraphy. Values of C_s, pH, relative molar concentrations of major ions, redox status (DO and SO_4), and P_{CO_2} were used to correlate chemistry with detailed geophysical and stratigraphic interpretations.[10] Saturation indices for the most important mineral phases, including dissolved CO_2 gas, were calculated using the chemical equilibrium model WATEQF (Plummer et al., 1976). Analysis of basin-scale ground water evolution closely followed seminal works by Garrels (1967) and Garrels and Mackenzie (1967).

2.2.2. Carbon Isotope Analysis

Flow path geochemistry was also evaluated using $\delta^{13}C$ data from both dissolved and mineral-phase inorganic carbon. Dissolved inorganic carbon measurements in well samples were supplemented by $\delta^{13}C$ measurements of drill cuttings from the Cassia, Julia Davis, and Simplot Geothermal wells. The carbonate data were used to strengthen the analysis of geochemical evolution and to correct ^{14}C-age calculations.

2.2.3. Carbon-14 Age Dating

Four reservoir correction techniques were considered to adjust the conventional radiocarbon ages for geochemical processes that influence ^{14}C activity in the Treasure Valley ground water system. These techniques include: (1) an empirical model, (2) a chemical mass balance model, (3) a $\delta^{13}C$-mixing model, and (4) a Matrix Exchange model. All of these models assume that the diluting source of carbon is old enough to

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[10] Dissolved CO_2 gas is often expressed in terms of partial pressure as P_{CO_2}.

be ^{14}C-free and that carbonate dissolution occurs below the water table. Results from the correction models were subjected to an additional correction for long-term changes in atmospheric ^{14}C.

2.2.3.1. Empirical Model

An empirical approach proposed by Vogel (1970) assumes that measurements of ^{14}C activity in ground water located near the recharge zone accurately represent the initial activity of ^{14}C. In this model of ground water recharge and flow, water percolating through the soil and into the first part of the flow system is rapidly charged with CO_2 (and therefore ^{14}C). Beyond the recharge zone, ground water is shut off to CO_2 inputs (a closed-system model). The only reaction addressed by this model is the addition of old carbon via carbonate dissolution beyond the recharge zone. The correction factor (q) is introduced to adjust the ^{14}C activity ($a\,^{14}C$) of DIC entering ground water from the recharge zone. The correction factor is found using

$$q = a^{14}C_{DIC} / a\,^{14}C_{rech}\,,$$

where $a^{14}C_{rech}$ is obtained by estimating (or preferably, measuring) ^{14}C in the recharge zone. Often ^{3}H is used to identify recharge zone water. The important assumption underlying the empirical approach is that the recharge environment of paleo-ground water is the same as that of modern recharge water.

2.2.3.2. Chemical Mass Balance (CMB) Model

A more robust approach to correcting ^{14}C data is to use measured geochemical parameters. Several variations of this approach, including the alkalinity correction model (CMB-ALK) of Tamers (1975) and the chemical mass balance model (CMB-CHEM) of Fontes and Garnier (1979), are collectively known as geochemical models. Generically, a geochemical mass balance is simply a budget that accounts for all inputs and outputs of dissolved constituents. The basic CMB correction model consists of a two-step correction. The steps are (1) correct ^{14}C in the recharge zone for carbonate loading using assumed P_{CO_2} and pH values; and (2) correct for carbonate dilution during movement through the aquifer using either titrated alkalinities or mass balance based on major ion data. The correction factor is obtained using

$$q = m\mathrm{DIC}_{rech} / m\mathrm{DIC}_{final},$$

where $m\mathrm{DIC}_{rech}$ is the molar concentration of DIC gained during transit through the recharge zone and $m\mathrm{DIC}_{final}$ is the sum of the ^{14}C-active (recharge) DIC and the “dead” DIC gained during transit through the aquifer. The CMB approach does not apply to ground waters open to atmospheric CO_2 or to systems in which carbonate is precipitated from solution.

2.2.3.3. $\delta^{13}C$-mixing Model

Carbon-13 measurements provide a useful tool for estimating corrections to ^{14}C-age calculations, because ^{13}C is a good tracer of carbonate evolution in ground water. The underlying assumption is that any process affecting ^{14}C during ground water recharge and flow, other than radioactive decay, affects ^{13}C in a similar fashion. The working conceptual model begins with soil CO_2 gas at equilibrium with the soil solution, resulting in open system dissolution of soil carbonate in the recharge zone. Once the solution passes beyond the recharge zone, carbonate dissolution is controlled by the amount of dissolved CO_2 in the water. The primary difference between the $\delta^{13}C$ mixing model and other correction models is that it allows incorporation of ^{14}C-active DIC during carbonate dissolution under open-system conditions in the recharge zone. The biggest limitation of this approach is that ground water age calculations are profoundly affected by small changes in the enrichment factor used to estimate isotope exchange in the soil zone. The enrichment factor depends heavily on the pH chosen for the recharge water, which is difficult to quantify for waters recharged thousands of years ago. The $\delta^{13}C$-mixing model correction factor is calculated using the following:

$$q = (\delta^{13}C_{DIC} - \delta^{13}C_{carb})/(\delta^{13}C_{soil} + \varepsilon^{13}C_{DIC\text{-}CO2} - \delta^{13}C_{carb}),$$

where: $\delta^{13}C_{DIC}$ = measured $\delta^{13}C$ in ground water

$\delta^{13}C_{carb}$ = $\delta^{13}C$ of calcite being dissolved (between +5‰ and -15‰)

$\delta^{13}C_{soil}$ = $\delta^{13}C$ of soil CO_2 (usually close to -23‰)

$\varepsilon^{13}C_{DIC\text{-}CO2}$ = the pH dependent enrichment of $\delta^{13}C_{soil}$ by fractionation between soil CO_2 and DIC_{soil}

2.2.3.4. $\delta^{13}C$-Matrix Exchange Model

Isotopic exchange between $^{14}C_{DIC}$ and primary calcite along the ground water flow path is recorded by closed system enrichment of ^{13}C. This exchange process is accounted for in the $\delta^{13}C$-mixing model above. A second exchange process, which is not accounted for in the basic $\delta^{13}C$-mixing model, is exchange of $^{14}C_{DIC}$ with carbon contained in secondary calcite minerals. This exchange process may play an important role in controlling $^{14}C_{DIC}$ of waters that remain at equilibrium with calcite along much of their flow path. The $\delta^{13}C$-matrix exchange model proposed by Fontes and Garnier (1979; 1981) uses (1) a cation mass balance to estimate the contribution of ^{14}C-free carbonate from the aquifer matrix and (2) isotope mass balance to distribute $^{14}C_{DIC}$ into that exchanged with soil CO_2 (open-system exchange) and/or the carbonate matrix (matrix exchange).

The total matrix-derived DIC ($m\mathrm{DIC}_{\mathrm{carb}}$) is estimated from a cation mass balance equation proposed by Fontes and Garnier (1979):

$$m\mathrm{DIC}_{\mathrm{carb}} = m\mathrm{Ca}^{2+} + m\mathrm{Mg}^{2+} - m\mathrm{SO}_4^{2-} + 1/2(m\mathrm{Na}^{+} + m\mathrm{K}^{+} - m\mathrm{Cl}^{-})$$

This portion of the correction model accounts for carbonate dissolution based on Ca and Mg, with a correction for evaporite dissolution ($m\mathrm{SO}_4^{2-}$) and cation exchange ($m\mathrm{Na}^{+} + m\mathrm{K}^{+} - m\mathrm{Cl}^{-}$).

The total matrix-derived DIC is then distributed into the open-system exchange (containing ^{14}C-active carbonate) component and the matrix exchange component (containing old, ^{14}C-dead carbonate) based on $\delta\,^{13}$C. The open-system component is calculated using

$$mDIC_{CO_2-exch} = \frac{\delta^{13}C_{meas} \cdot mDIC_{meas} - \delta^{13}C_{carb} \cdot mDIC_{carb} - \delta^{13}C_{soil} \cdot (mDIC_{meas} - mDIC_{carb})}{\delta^{13}C_{soil} - \varepsilon^{13}C_{CO_2-CaCO_3} - \delta^{13}C_{carb}}.$$

Using this calculation to estimate the open-system contribution, the correction factor becomes

$$q = (m\mathrm{DIC}_{\mathrm{meas}} - m\mathrm{DIC}_{\mathrm{carb}} + m\mathrm{DIC}_{\mathrm{CO2\text{-}exch}})/m\mathrm{DIC}_{\mathrm{meas}}.$$

2.2.3.5. Which Model to Use?

All of these models for correcting ^{14}C-ages are gross simplifications of processes occurring in real ground water flow systems. Deciding which correction model is most appropriate for the Treasure Valley system is not straightforward; however, a model selected using reasoned consideration of the actual geochemical environment provides ground water ages that are more accurate than uncorrected ^{14}C-ages. A well-characterized recharge environment is the main assumption underlying the empirical approach. This assumption is not valid in the Treasure Valley where the recharge environment is not characterized well enough to allow adequate empirical determination of q and long-term climatic changes have clearly altered the recharge environment. For these reasons the empirical approach is not used in our analysis. The CMB models are sensitive to pH and P_{CO_2} conditions in the recharge zone. These values are rarely known for older ground waters and are especially difficult to resolve in complex recharge environments. Regional ground water in the Treasure Valley may be quite old and may be recharged from a variety of sources, including underflow from fractured granite aquifers, underflow from tributary sedimentary aquifers, seepage from rivers and canals, and percolating irrigation water. In addition, it is unclear whether the stringent closed-system assumption is valid for this system. As a result, the suitability of the CMB model for correcting ^{14}C in this ground water system is questionable. Like the CMB model, the δ^{13}C-mixing models are also strongly dependent on unknown recharge conditions; however, when combined with the matrix exchange approach of Fontes and Garnier (1979, 1981), this class of models offers a correction that is less dependent on knowledge of recharge conditions and can be applied to both open and closed systems. Based on this analysis, our approach to evaluating which model best represents the Treasure Valley is based on comparing the results from the CMB models and δ^{13}C-mixing models and weighing other geochemical information.

3. HYDROGEOLOGIC SETTING

Aquifers that supply most municipal and industrial ground water in the Treasure Valley lie in the Idaho Group of sediments that are, roughly, the upper 1,000 feet of a sedimentary section that extends to depths of several thousand feet. Idaho Group aquifers underlie a system of shallow aquifers that exist in the upper 100 to 300 feet of surficial Pleistocene sediments and recent alluvium. A review of the hydrogeologic characteristics of the Idaho Group aquifers that may be part of the regional flow system provides a framework from which to correlate and interpret geochemistry data. The following review describes (1) geographical boundaries of the Idaho Group aquifers, (2) relative position of the aquifers in the flow system, (3) depositional environments, (4) important physical and chemical characteristics, and (5) representative sampling wells used for this study. The review is followed by a discussion of a regional geologic unconformity that appears to play an important role in regional ground water flow.

3.1. Review of Principal Aquifers

Our review of the important aquifers of the Treasure Valley begins in the Boise area and relies heavily on geophysical and stratigraphic interpretations of Burnham and Wood (1992), Squires et al. (1992), and Squires and Wood (2001). Interpretation of seismic data by Wood and Anderson (1981) and Wood (1994) provide the basis for our understanding of the hydrogeology near Meridian, Nampa, and Caldwell. Stratigraphic work by Beukleman (1997) gives insight into the hydrogeology of the down-valley reaches of the basin.

Squires et al. (1992) segregate Boise area aquifers by depositional boundaries based largely on detailed analysis of well cuttings and interpretation of geophysical logs. Distinct hydrogeologic units are described in relation to sediment deposition in a dynamic paleo-river delta system that entered shallow water at the head of a large lake that once covered much of the Treasure Valley. The units identified by Squires et al. (1992) are (1) southeast Boise alluvial fan deposits, (2) south Boise fan-to-lake transition deposits, (3) central Boise shallow-water lacustrine deposits, (4) west Boise deep-water lacustrine and alluvial deposits, and (5) north Boise lake-margin deposits.

3.1.1. Southeast Boise alluvial fan deposits

Southeast Boise alluvial fan deposits are thought to be remnants of an ancient alluvial fan and/or fan-delta system emanating from the mountain front near Lucky Peak Reservoir (Figure 3). These interbedded silt, sand, and gravel deposits underlie the Tenmile Ridge area and include the Old Penitentiary, Micron Technology, Inc.

campus, and Blacks Creek area. Ground waters in the southeast Boise alluvial fan deposits lie in an upgradient position relative to the central portion of the basin. Geophysical logs obtained from wells in these deposits exhibit a "spikey" character, which reflects the heterogeneous nature of the strata, and high resistivity, which indicates low dissolved solids in the ground water.[11] No substantial aquitards are apparent in geophysical logs (Squires et al., 1992); however, lack of water level responses in shallow wells during the Micron No. 5 pumping test indicates some hydraulic separation between aquifer zones (Scanlan, 1998). Sediments in these deposits are oxidized and the regional hydraulic gradient is downward. These characteristics are consistent with the hypothesis that the southeast Boise alluvial fan deposits constitute a recharge area. Two authors have suggested that seepage from the New York Canal near its diversion from the Boise River is the primary source of recharge to the alluvial fan aquifers (Robison and Brockway, 1999; Squires et al., 1992). This important hypothesis has not been confirmed. Six wells sampled during this study are believed to draw from the southeast Boise alluvial fan deposits: Guyer, Christiansen, Micron Shallow, Micron Deep, Knox, and Blacks Creek (Figure 2).

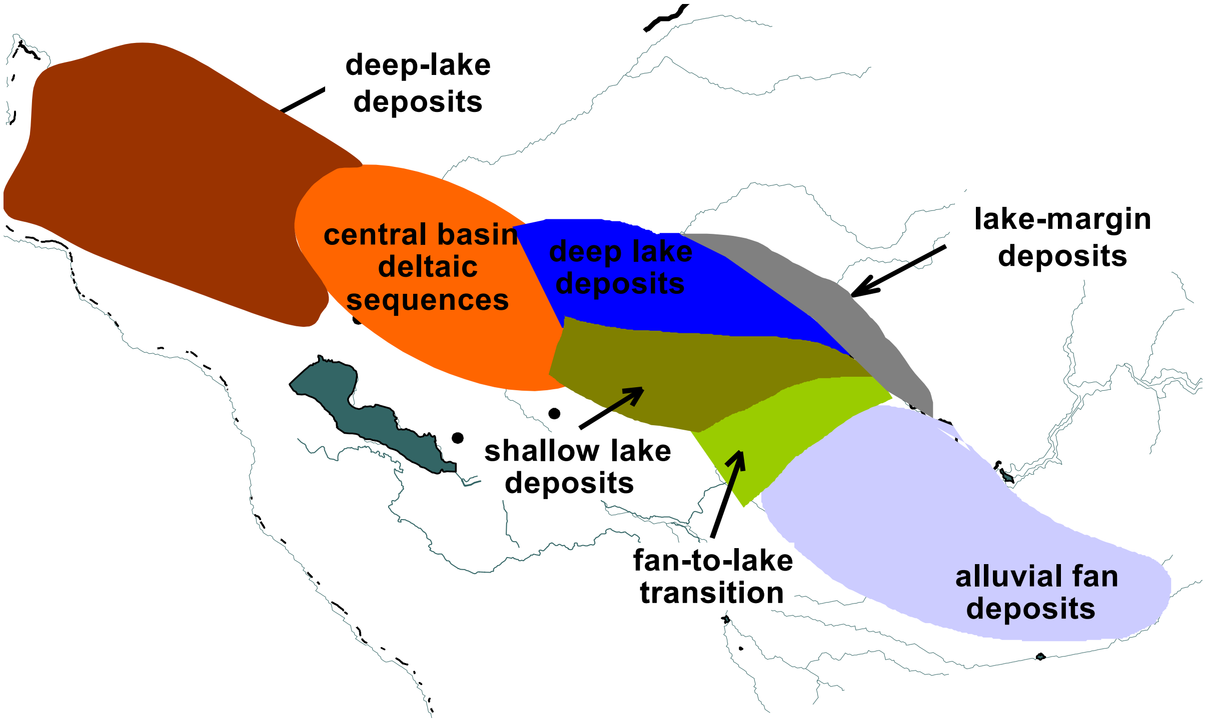

Figure 3. Important hydrogeologic units of the Treasure Valley regional ground water system (after Squires et al., 1992 and Wood, 1994).

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[11] Resistivity is a measure of resistance of the aquifer to an induced electrical current. The measure is indicative of the concentration of dissolved ions in ground water.

3.1.2. South Boise Fan-to-Lake Transition Deposits

The south Boise fan-to-lake transition deposits embody a change from coarse-grained fluvial sands and gravels of the alluvial fan to finer-grained lake sediments. The zone of transition lies west of the fan sediments in approximately a three-mile-long crescent centered along the New York Canal (Figure 3). Ground water mounding from canal seepage affects hydraulic gradients in some aquifers in the transition deposits; however, it is likely that these deposits were hydraulically down-gradient from the alluvial fan aquifers prior to surface water diversion. The transition zone consists of layers of oxidized fluvial deposits interbedded with reduced lake sediments. Coarse-grained oxidized sands are thought to have been deposited by fluvial activity when lake levels were low, while finer, reduced silts and clays were deposited in a lacustrine environment associated with high lake levels. Some organic matter is found in silt and clay beds. The silt and clay beds are thicker than those found in the fan deposits, ranging from 50 to 100 feet thick (Squires et al., 1992). These authors suggest that these thicker layers may be more laterally extensive than those of the fan deposits. Seepage from the local canal system is reported to be a primary source of recharge to aquifers in the transition deposits (Squires et al., 1992). Six wells are completed in the south Boise transition deposits: JR Flat, Market Street, McNabb, MAC, Amity, and Sunset West (Figure 2).

3.1.3. Central Boise Lacustrine Deposits

The central Boise lacustrine deposits are located along a 2- to 3-mile-wide band centered approximately on I-184, north and west of the transition deposits (Figure 3). The western boundary has not been characterized and may extend west to Meridian. The deposits are characterized by oxidized sediments in the uppermost 200 to 300 feet of the section underlain by reduced sands, silts, and clays. The oxidized zone is marked by the existence of oolites and organic detritus, which indicates proximity to a shoreline (Squires et al., 1992). A blue color in the deeper sediments reflects deposition in an anoxic lacustrine environment. The deeper section is marked by an angular unconformity (Wood and Anderson, 1981; Squires et al., 1992). Units above the unconformity have relatively horizontal bedding, while the units below the unconformity dip 3° to 7° west. Four wells are completed in the central Boise lacustrine deposits: Cassia monitoring well, Cassia 2, Edgeview, and St. Lukes.

3.1.4. West Boise Lacustrine Deposits

The west Boise deep-water lacustrine deposits lie generally north and northwest of the central Boise lacustrine deposits. Where the deep-water deposits abut the Boise Foothills, they are often juxtaposed beneath lake-margin fluvial sand and gravel deposits (Figure 2). The western extent of the deep-water deposits has not been identified, but they probably extend beyond Meridian, Nampa, and Caldwell, toward the western end of the basin. Stratigraphic interpretation of these facies is similar to the central Boise lacustrine deposits in that a thick layer of oxidized, horizontally-interbedded sands, silts, and clays overlie a reduced section of steeply-dipping beds. Drill cuttings show the presence of reduced sediments below an elevation of approximately 2,100 feet. Squires et al. (1992) note that the top of the reduced section is marked by an unconformity at about 500 feet below ground surface and perhaps by a layer of red alluvial gravel. The range of 3° to 7° west-trending dip translates to between 400 and 650 feet of elevation per mile, making stratigraphic correlation of individual aquifer units difficult (Squires et al., 1992). Geophysical logs show that the deep-water deposits lie below the unconformity and consist of monotonous silt and clay layers interspersed with thin sand beds. Examples of the sand aquifers of the deeper section are found in the Hewlett-Packard (HP) well. These depositional units are described as "Gilbert-type" deltas that were formed by streams draining the Boise foothills (Wood, 1997). Stratigraphic offset across the east Boise-Eagle fault zone allows correlation of these delta sands with similar deposits in the foothills (Wood, 1997). The deep sand beds contain water under confined conditions. Some production wells have experienced substantial drawdowns when pumped at about 1,000 gpm, suggesting a limited lateral extent of the productive zones. A number of wells may be completed in these deposits, including: HP, Goddard 1, Goddard 2, Meridian 19, Meridian 19-test, and Meridian 15 production wells (Figure 2).

3.1.5. North Boise Fluvial Lake-Margin Deposits

A zone of laterally continuous arkosic sands, river gravels, and silts lies in an apron along the contact with the Boise Foothills (Figure 3). These horizontally bedded deposits make up the first 400 to 500 feet of sediment along the basin margin (Squires et al., 1992). Because they are located proximate to the basin margin, wells drilled below an elevation of 2,200 feet in these deposits often encounter volcanic rocks and signs of underlying geothermal aquifers. Proximity to the basin margin also explains the occurrence of numerous structural faults that offset the stratigraphic section as much as 1,200 feet (Burnam and Wood, 1992). In west Boise, a similar zone of silts, sands and gravels overlies the west Boise lacustrine deposits (Squires et al., 1992). The TVHP 1 multi-completion monitoring well appears to be completed in north Boise lake-margin deposits.

3.1.6. Nampa and Caldwell Lacustrine and Delta Deposits

Deep pro-grading sand aquifers east of Caldwell are also identified with a river delta system (Wood and Anderson, 1981). These units occur between 2,000 and 2,300 feet below land surface, far beyond depths penetrated by most production wells. Wood (1994) addresses the morphology of similar delta deposits near Caldwell. His study correlates seismic data to geophysical and stratigraphic data from the Simplot Geothermal Well. Here, a number of river delta facies are revealed in the upper 1,500 feet of the section. A lower unit consists of a pro-delta sequence of north-dipping calcareous mudstones between depths of 1,200 and 1,500 feet (830 to 1,130 feet above mean sea level). This unit is overlain by a delta front sequence between 1,000 and 1,200 feet (1,130 to 1,330 feet above mean sea level). The delta front consists of 9- to 20-foot-thick fine sands interspersed with thin clay lenses, which grade upward into interbedded sand and mud of a delta plain. The delta plain section, which occurs between 350 feet and 1,000 feet (1,330 to 1,980 feet above mean sea level), is characterized as well-sorted fine sand interbedded with moderately to slightly calcareous mud (Wood, 1994). The sand beds are between 10 and 40 feet thick. Wood and carbonized organic matter are reported in the silt beds. Most of the large-capacity production wells in the Nampa and Caldwell areas are completed between 350 and 1,000 feet below ground surface, including Nampa 12, State Hospital, Nampa 9, Caldwell 15 and Caldwell 16. Sediments above 350 feet are characterized by non-calcareous mudstones and medium-grained sands with some coarser material.

3.1.7. Down-Valley Lacustrine Deposits

In the far western, or down-valley reaches of the Treasure Valley, between Caldwell and Parma, many wells penetrate confined or semi-confined aquifers in the upper few hundred feet of the sedimentary section. Reports of hydrogen sulfide odor and methane gas in wells drawing water from depths of less than 100 feet are not uncommon (D. Parliman and E. Squires, pers. com. 1999) and provide evidence that a transition between oxidized sediments and reduced sediments occurs at relatively shallow depths. These observations are confirmed by a distinct color change from yellow and brown sediments to gray-blue and gray sediments in a series of three NE-SW trending geologic cross-sections of the area (Beukelman, 1997). The redoximorphic transition occurs uniformly at elevations between 2,150 and 2,250 feet deep in all the three cross-sections. The uniform elevation of the transition and the existence of a similar feature near the Boise and Snake Rivers (where oxygen-containing surface waters could percolate downward and oxidize sediments below the contact) are construed to mean that the feature is a result of original diagenesis rather than post-depositional geochemical processes (Beukleman, 1997). Based on this information, the color change is probably akin to similar color changes observed in the eastern part of the Treasure Valley near Boise. These redoximorphic features appear to mark the transition between surficial alluvial deposits and underlying deep-lake deposits. Sampling wells in the down-valley lacustrine deposits include: Wright, Johnson, Kuespert, Inouye, Parma 10, and UI (Figure 2).

3.2. Significance of Redoximorphic Features and the Boise Unconformity

Recent stratigraphic interpretations indicate that, in the Boise area, redoximorphic color changes are related to an angular unconformity found at depths between 300 and 450 feet below ground surface (Squires and Wood, 2001). The abrupt color changes may be a useful indication of the transition between shallow aquifers and the regional ground water flow system. The purpose of this section is to explore the importance of these features and to set the stage for distinguishing regional ground water from shallow ground water using hydrochemical data.

With exception of the north Boise lake-margin deposits, the southeast Boise alluvial fan deposits, and the south Boise fan-to-lake transition deposits, all aquifer units discussed in the previous subsections exhibit redoximorphic color changes in the vertical section. Transitions from brown or yellow sediments to gleyed blue and gray sediments are reported valley-wide in driller's logs. Stratigraphic work by Wood (1994) suggests that the transition to reduced sediments occurs deeper in the stratigraphic section near Caldwell than in the Boise area. Cuttings from the Simplot Geothermal well near Caldwell indicate that blue or gray sediments first appear at elevation of approximately 1,130 feet. This compares to 1,950 feet in Caldwell 16; 2,080 feet in the State Hospital well; 1,970 feet in Nampa 12; 2,120 feet in Meridian 19-test; 2,260 feet in St. Lukes, and 2,350 in the Cassia wells. Blue clays are noted at elevations between 2,150 and 2,250 feet in down-valley wells near Notus and Parma.

Near Boise, the redoximorphic transition may be related to an angular unconformity that appears in two stratigraphic cross-sections that extend from the Boise Foothills out to the fluvial-lacustrine sediments that underlie the city (Squires and Wood, 2001). The main features of the unconformity are tilted silt and clay-stone beds overlain by horizontally-bedded gravel, overlain by mudstone. Squires et al. (1992) propose that receding lake levels in Pliocene Lake Idaho caused previously uplifted and/or depositionally-tilted strata to be eroded by river systems, truncating the dipping sediments. The authors argue that occurrence of these paleo-river systems is marked by gravel deposits found atop the erosional surface. Subsequent sediment deposition on top of the gravel would have occurred at a much lower angle than the truncated strata, resulting in nearly horizontal beds overlying steeply dipping beds. The horizontal deposits overlying the gravel layer consist of lake-bed muds interbedded with delta sands and lake-shore sands. Delta and lake-shore sediments indicate that recession of the lake was followed by an episode of lake filling.

Influence of the unconformity(s) on local and regional hydrology is presently the subject of much discussion. Horizontal ground water movement between wells completed in different aquifer units below the unconformity would have to flow across highly reduced low conductivity clay/mudstone interbeds. Such a configuration suggests low horizontal flow rates within the dipping beds. If the high conductivity fluvial gravel atop the erosional surface is in contact with the truncated, dipping aquifer units below, ground water may be distributed rapidly along the unconformity when the deeper units are pumped. In this scenario, drawdown of aquifers in the steeply dipping beds below the unconformity could induce recharge from a large area along the plane of the unconformity. Atop the fluvial gravels, mudstone deposits from subsequent lake filling may inhibit downward movement of shallow ground water across the unconformity. Correlation between the apparent redoximorphic transition and the erosional unconformity has not been extended beyond the Boise–Meridian area.

4. HYDROCHEMICAL INTERPRETATION OF PRINCIPAL AQUIFERS

In the previous section we describe a set of contiguous aquifers bounded by mountains and a major river that, conceptually at least, are the framework for ground water flow in the Treasure Valley. We show that each aquifer rests in a unique position in the flow system and that each aquifer has a characteristic depositional history. We call these hydrogeologic units principal aquifers to highlight their function in the regional ground water system. The following analysis expands the interpretation of principal aquifers by (1) comparing hydrochemical characteristics of recharge waters to characteristics of principal aquifers located near the northeastern margin of the basin; (2) comparing hydrochemical characteristics among principal aquifers located in the central portion of the basin; and (3) considering regional trends in hydrochemistry data.

Several criteria are used to determine whether data from our sampling wells represent the principal aquifers listed in Section 3. The sampling wells are considered to uniquely represent a given aquifer unit if: (1) they are located within the boundary of the unit as described in Section 3; (2) their screened intervals are located in the same stratigraphic section with respect to oxidized and reduced sediments; and (3) they exhibit hydrochemical characteristics similar to other wells in the unit. A record of all physical and hydrochemical data compiled during this study is contained in Appendix 1.

4.1. Characteristics of Potential Recharge Sources

A substantial portion of recharge to deep aquifers in the basin is thought to originate in the mountains north and east of Boise. We hypothesize that aquifers located adjacent to the mountain front convey a substantial amount of recharge water into deep aquifers in the central portion of the basin. To evaluate this hypothesis, we compare the hydrochemical characteristics of mountain front recharge waters to the hydrochemical characteristics of ground waters in adjacent recharge zone aquifers.

Water in the Boise River at Diversion Dam is chiefly a mixture of surface runoff and shallow ground water from smaller drainages in the upper Boise River system. As noted in Section 3.1.1, contemporary seepage from the river and its many irrigation diversions has been suggested to be an important source of recharge to portions of the regional aquifer system; and there is some indication of a longer-term connection between the upper Boise River system and aquifers in southeast Boise (Squires and Derricott, 1992). Our hydrochemical data from the Boise River at Diversion Dam allows us to characterize the river system as a source of recharge. A second plausible recharge source is direct underflow from mountain front aquifers that are tributary to the basin. Hydrochemical data from wells in shallow alluvium beneath Banner Creek, a drainage in the Silver Creek Experimental Watershed in the Boise National Forest (J. Clayton, unpublished data) and data from spring waters emanating from the mountain front above Boise (Young et al., 1988) provide a range of hydrochemical data for characterizing mountain front recharge.

Dissolved gasses typically remain near equilibrium with atmospheric pressure in surface waters and in shallow ground waters near recharge areas (Drever, 1988). The concentration of DO in the Boise River at Diversion Dam is 11 mg/L and the partial pressure of CO_2 (P_{CO_2}) is $10^{-3.3}$ bar (Table 1). Dissolved oxygen was not measured in the Banner Creek wells or in the Boise Front springs, so no comparisons can be made with respect to DO; however, we used measurements of pH and dissolved HCO_3 to calculate P_{CO_2} values between $10^{-1.6}$ and $10^{-2.3}$ bar in the three Boise Front springs and $10^{-2.2}$ bar for an average of 20 shallow monitoring wells in the Banner Creek drainage (Table 1). The subsurface waters, unlike water in the Boise River, are charged with CO_2 as they pass through the soil zone, hence the greater values of P_{CO_2} in the mountain front springs and shallow wells. For the same reason, pH of river water is 7.9, while the pH of mountain front ground water ranges between 5.8 and 6.6 (Table 1). Water in the Boise River and shallow ground water on the mountain front have low specific conductance (C_s) (Table 1). Low C_s reflects a scarcity of dissolved ions due to minimal contact with weathering minerals. Dissolved ions are dominated by Ca and HCO_3 in all of the recharge waters, with the Boise Front springs showing slightly greater influence of Na, SO_4 and other ions (Figure 4).

Recharge Source/ Aquifer Unit	C_s (uS/cm)	DO (mg/L)	NO_3 (mg/L)	SO_4 (mg/L)	pH	PCO_2 (mg/L)
Banner Creek wells	58	nd	.01	1.16	6.6	$10^{-2.2}$
Boise Front springs	nd	nd	<0.2-1.1	3.6-5.2	5.8-6.2	$10^{-1.8}$-$10^{-1.6}$
Boise River	62	11	0.1	1.5	7.9	$10^{-3.3}$
north Boise margin	135-247	0.1-0.9	<0.1	5.3-10	7.1-7.3	$10^{-2.5}$-$10^{-2.0}$
alluvial fan north	138-185	3.6-4.0	1.5-1.6	4.2-7.8	8.1-7.8	$10^{-3.3}$-$10^{-2.9}$
alluvial fan south	208-230	3.8-6.2	1.8-2.1	6.9-7.5	7.4-7.6	$10^{-2.6}$-$10^{-2.3}$
transition zone east	217-288	2.1-5.2	0.6-1.6	14-20	7.6-7.7	$10^{-2.5}$-$10^{-2.7}$
transition zone west	317-374	0.8-1.2	<0.1-0.2	24-44	7.6-7.8	$10^{-2.7}$-$10^{-2.4}$

Table 1. A comparison of selected hydrochemistry data from recharge waters and aquifers near the mountain front. Banner Creek Watershed data are from J. Clayton (unpublished data). Boise Front spring data are from Young et al. (1988).

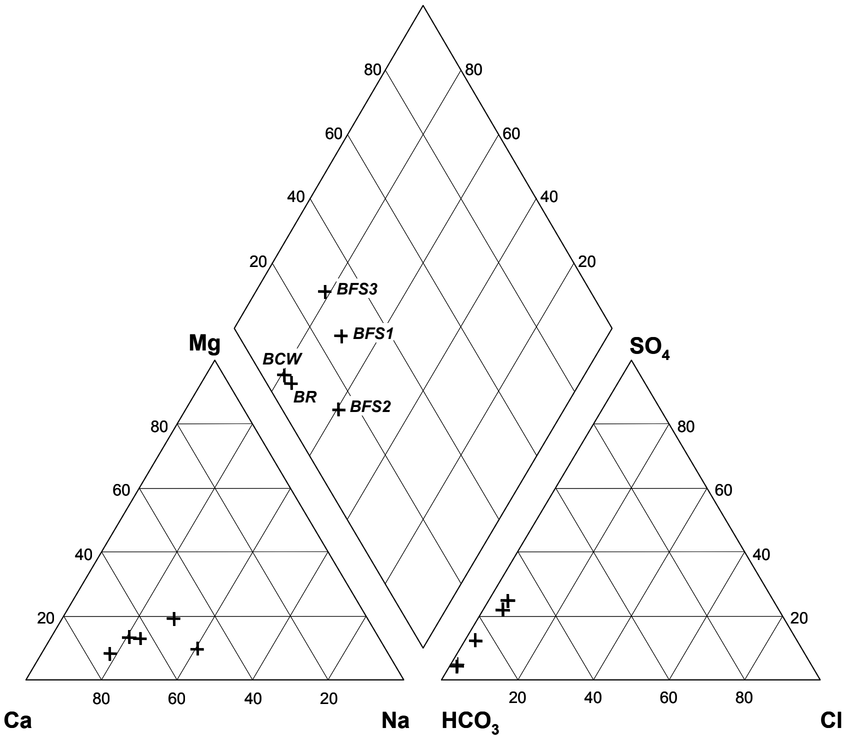

Figure 4. Distribution of cations and anions in selected mountain front recharge waters. The data are for the Boise River at Diversion Dam (BR), springs on the Boise Front (BFS), and shallow wells in the Banner Creek drainage of the Silver Creek Experimental Watershed (BCW).

4.2. Characteristics of Recharge Zone Aquifers

Ground water in the southeast Boise alluvial fan deposits and the north Boise basin margin are hydrochemically midway between mountain recharge waters and aquifers in the central portion of the basin. Specific conductance is lower in the recharge waters than in the recharge-zone aquifers (Table 1). The Banner Creek wells and Boise Front springs exhibit substantially lower pH values than are found in the recharge-zone aquifers (this does not hold true for the Boise River, because pH in the river is buffered by atmospheric CO_2). Like the recharge waters, dissolved ions in the recharge zone aquifers are dominated by Ca and HCO_3; however, there is a greater influence of Na and SO_4 in the recharge zone ground waters than in the river and Boise Front springs (Figure 5).

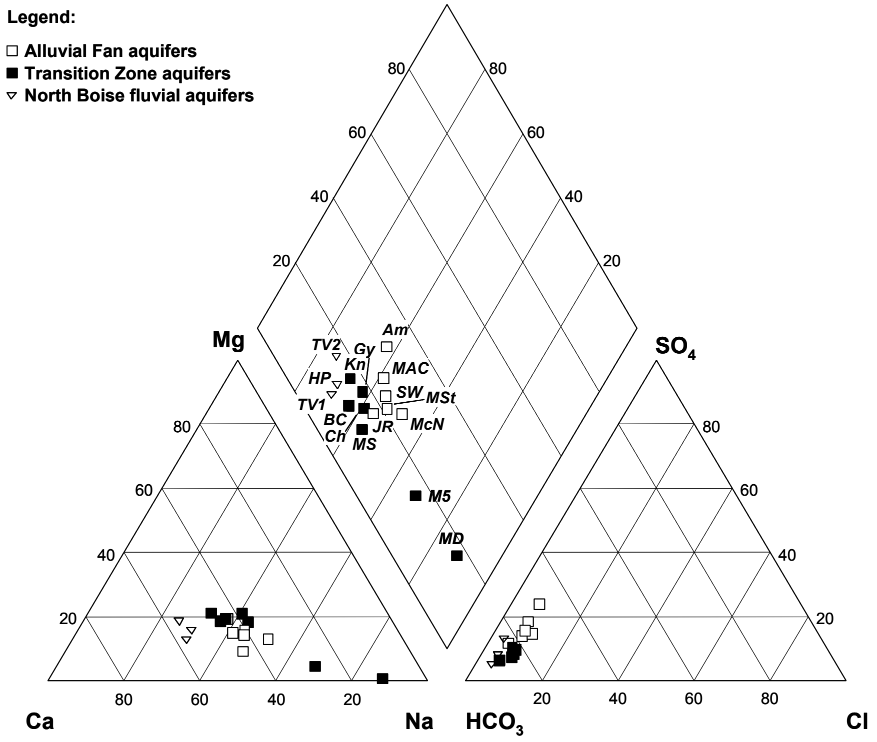

Figure 5. Distribution of cations and anions in selected ground water wells located near the Boise mountain front.

4.2.1. Aquifers in the Southeast Boise Alluvial Fan

Wells in the southeast Boise alluvial fan sediments can be grouped according to their proximity to the Boise River. The Guyer and Christiansen wells penetrate more than 500 feet of unsaturated sediments in the northeastern portion of the alluvial fan region, not far from the New York Canal diversion from the Boise River at Diversion Dam (Figure 2). Water samples from the Guyer well and Christiansen well have P_{CO_2} similar to the atmospheric equilibrium values observed in the river (Table 1). These relatively low P_{CO_2} values are an indication that the source of recharge is direct seepage from a surface water source, rather than percolation through the soil zone.[12] This finding supports the idea that ground water entering the subsurface in the upper reaches of the river and major irrigation diversions is a source of recharge to unconfined or semi-confined aquifers in the northeastern portion of the alluvial fan. Based on the fact that we detected no ^3H in these wells, the water that is presently in these aquifers must have originated as seepage prior to 1950's bomb testing. Another plausible recharge scenario is that the alluvial fan ground waters originated in the Boise river system long

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[12] Recall that P_{CO_2} is generally two to three orders of magnitude higher in soil water than in surface waters. Details about CO_2 charging in soil are discussed in Section 5.

ago and moved slowly into the fan sediments through paleo-river channels (Squires et al., 1992).

The Alluvial Fan aquifer is represented by Christiansen (Ch), Guyer (Gy), Knox (Kn), Blacks Creek (BC), Micron monitoring shallow (MS), Micron monitoring deep (MD), and Micron production no. 5 (M5). The Transition Zone aquifer is represented by McNabb (McN), JR Flat (JR), Market Street (MSt), Amity (Am), Sunset West (SW), and MAC. The north Boise basin margin is represented by TVHP1 multilevel monitoring wells 1 and 2 (TV1 and TV2) and the Hewlett-Packard production well (HP).

The Micron Technology, Inc., monitoring wells, the Knox well, and the Blacks Creek rest area wells are in a similar production zone as the Guyer and Christiansen wells and also penetrate more than 500 feet of unsaturated sediments before encountering unconfined or semi-confined ground water. The Micron, Knox, and Blacks Creek wells are located several miles further from the Boise River and New York Canal than Guyer and Christiansen. Water samples from the more distant wells contain no measurable ^3H but slightly higher C_s and P_{CO_2} than the Guyer and Christiansen wells. Higher C_s and P_{CO_2} indicate that a portion of aquifer recharge comes from deep percolation of soil water. The influence of Na is substantially greater in the Micron No. 5 production well and the Micron Deep monitoring well than in other wells in the southeast Boise alluvial fan (Figure 5). We conclude that these deeper wells are influenced by geothermal water because (1) Boise area geothermal waters typically have Na/Ca ratios between 60 and 100 (Mariner et al., 1989), so that any mixture of cold water and geothermal water would result in a substantial increase in the proportion of Na in the mixture; (2) the Micron No. 5 well and Micron Deep monitoring well pump water at temperatures in the range of low-temperature geothermal wells (27°C and 24°C, respectively); and (3) both wells exhibit slightly elevated concentrations of fluoride. In spite of our conclusion, we are somewhat skeptical about the reliability of the ion data from the Micron Deep well because drilling mud was noted in the well discharge during sampling. Even so, high Na concentrations in Micron No. 5, which penetrates the same zone as the Micron Deep monitoring well, is reason for a more detailed analysis of the influence of geothermal water on these deeper alluvial aquifers.

All of the alluvial fan ground waters have NO_3 concentrations between 1.5 and 2.1 mg/L. Some have informally suggested that these slightly elevated NO_3 concentrations result from land application of wastewater at the Micron facility. Elevated NO_3 concentrations in drinking water is a public health concern; therefore, it is worthwhile to use our new data to shed some light on the feasibility of waste-water as the source. Land application at the Micron facility occurred post-atmospheric bomb testing, so any percolating wastewater would have carried ^3H into the aquifer. Because ^3H concentrations are below the detection limit in all of the wells we sampled in the alluvial fan deposits, it is unlikely that land application is the cause of elevated NO_3.

Two natural hydrogeologic processes could explain these elevated NO_3 concentrations. First, natural downward percolation of water through the unsaturated sediments overlying the aquifer could cause a small, long-term NO_3 flux to the water table. Second, weathering of alluvial fan sediments in the oxic ground water environment could introduce N into the ground water. These hypotheses could be tested by (1) measuring the concentrations of NO_3 and CO_2 in unsaturated-zone water; (2) analyzing N in archived well cuttings from the Micron No. 5 well; and (3) reviewing existing water quality data.

4.2.2. Aquifers in the South Boise Fan-to-Lake Transition Zone

Ground water in the fan-to-lake transition zone contains less DO, less NO_3 and greater SO_4 than ground water in the alluvial fan aquifer (Table 1). In addition, the relative proportion of the various dissolved ions found in transition zone water is shifted toward a greater influence of Na over Ca and SO_4 over HCO_3 (Figure 5). These distinctions are particularly relevant considering that the Amity, Sunset West and MAC wells in the western portion of the transition zone have less DO, less NO_3 and greater SO_4 than the McNabb, JR Flat, and Market Street wells in the eastern part of the transition zone. The trends are consistent with ground water flowing from the alluvial fan aquifers and through the transition zone.

With the exception of the Market Street well, all of the transition zone wells draw water from above the unconformity described in Section 3.2. In fact, the Market Street well at the eastern margin of the transition zone is the easternmost occurrence of this unconformity, which is observed in the stratigraphic section as far west as Meridian (Squires and Wood, 2001). In spite of substantial mudstone units overlying the unconformity, ground water above and below the mudstone remains chemically undifferentiated at the Market Street well. The basis for original determination of the fan-to-lake transition zone is the observation that thick shoreline or lacustrine deposits do not appear in the alluvial fan aquifer(s), but that shoreline and lacustrine deposits begin to appear in the transition zone (Squires et al., 1992). The trends observed in the hydrochemical data support this interpretation and perhaps extend it by suggesting that the transition zone may mark the initial divergence of ground water into regional-scale flow paths. Unfortunately, no sampling wells fully penetrate the transition-zone mudstones west of Market Street; therefore, it is not possible to confidently resolve that hydrochemical differences between shallow and deep ground water first occur in the transition zone.

4.2.3. Aquifers at the North Boise Basin Margin

Ground water in the north Boise fluvial deposits differs from ground water in the southeast Boise alluvial fan in some important aspects. First, ground water in the north

Boise area has substantially lower DO (Table 1). Second, NO_3 is below detection in all wells in this aquifer (Table 1). Third, some north Boise wells (TVHP1 monitoring wells 3 and 4) exhibit an odor of hydrogen sulfide. Fourth, the relative proportion of Na is less than observed in the southeast Boise alluvial fan aquifer (Figure 4). Very low DO combined with the odor of hydrogen sulfide and NO_3 concentrations below detection reflect reducing conditions in the recharge zone directly adjacent to the mountain front. At first glance, this condition does not fit our conceptual model of ground water recharge from the mountain front, because ground water near a recharge source is expected to retain evidence of the oxic environment from which it originated. However, pyrite is documented in the deep lake deposits along the north Boise margin and SO_4 is present in ground water at concentrations between 5 and 10 mg/L.[13] Given that sulfide oxidation uses DO and forms sulfate, pyrite and other sulfide minerals in aquifer sediments may be rapidly oxidized by oxygen-rich recharge water, resulting in reduced conditions immediately adjacent to the mountain front recharge source.

The significance of reduced ground water in the recharge zone is that the flow rate of oxygen-rich recharge water through the aquifer must be relatively small. With respect to identifying a primary source of recharge, the range of P_{CO_2} calculated for north Boise ground water and the distribution of dissolved ions are most similar to the characteristics of the Banner Creek wells. Most importantly, P_{CO_2} values indicate that the ground water once percolated through a soil zone (Table 1). This finding contradicts the possibility that recharge to these aquifers originates in the Boise River or in the Farmers Union Canal; however, because of the complexity of the north Boise aquifer system, too much should not be made of similarities to the Banner Creek waters. Using well log correlations, geophysical logs and seismic data, Squires and Wood (2001) make a convincing argument for a paleo-delta system that originates in the Boise foothills and extends out into the basin in the vicinity of the TVHP 1, Goddard and HP wells. These authors describe a series of southwest dipping fluvial sand and gravel aquifers bounded above and below by mudstone aquitards and terminated by prodelta mudstone deposits. Squires and Wood (2001) conclude that long-term hydraulic connection may exist between aquifer zones, but that local lenses of mudstone lead to short-term responses to well pumping. The idea that productive sand and gravel units in deeper portions of the north Boise aquifers are discontinuous and somewhat isolated is supported by the chemically reduced ground water. This observation, along with the presence of NW-SE trending structural faults that may also inhibit ground water flow, gives credence to the idea that these aquifers are not capable of rapidly conveying large quantities of recharge from the mountain front to aquifers in the central portion of the basin.

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[13] Dittus et al. (1998) document pyrite in the completion zones of TVHP 1.

4.3. Hydrochemical Characteristics of Central Basin Aquifers

4.3.1. Aquifers in Central and West Boise Lacustrine Deposits

Shallow ground water is readily distinguished from ground water in deeper zones in the lacustrine environments of central and west Boise. Ground water from aquifers above thick mudstone deposits is oxic, contains ^3H, exhibits elevated P_{CO_2}, has relatively high C_s, and is enriched in SO_4 compared with groundwater below the mudstone (Table 2, Figure 6). Ground water below the mudstone exhibits substantially greater Na/Ca ratios than overlying aquifers (Table 2, Figure 6). Where two mudstone layers exist, ground water between them exhibits mixed characteristics. Wells that exhibit these differentiated hydrochemical characteristics include the Goddard wells, the three Cassia Street wells in central Boise, Edgeview and St. Lukes in west Boise/Meridian, and the Meridian 19 production and test wells in Meridian (Table 2).

Well Name	TWBZ Elev. feet	C_s (uS/cm)	DO (mg/L)	pH	P_{CO2} (mg/L)	SO_4 (mg/L)	Na/Ca
Goddard 2	2,199	349	nd	6.8	$10^{-2.7}$	32	0.5
Goddard 1	1,771	204	nd	7.8	$10^{-1.6}$	2.5	1.7
Cassia 1	2,551	432	1.7	7.3	$10^{-2.1}$	32	1.2
Cassia Monitor	2,226	209	0	8.0	$10^{-3.0}$	12	1.4
Cassia 2	1,901	198	0	8.2	$10^{-3.6}$	7.2	20.9
Edgeview	2,268	304	0.1	7.5	$10^{-2.4}$	30	1.1
St. Luke's	1,980	220	0	7.7	$10^{-2.7}$	1.4	1.5
Meridian 19-Test	2,210	370	4.7	7.2	$10^{-2.2}$	59	0.5
Meridian 19	2,010	135	0	8.0	$10^{-3.2}$	4.7	1.4

These wells represent aquifers above and below mudstone layers. The acronym TWBZ means top of the water-bearing zone as determined from well logs.

Table 2. Selected hydrochemical data from wells in central and west Boise lacustrine deposits.

High P_{CO_2} in aquifers above the mudstone layers show that a substantial portion of their recharge is derived from percolating surface water - probably associated with irrigation. Additionally, SO_4 is comparatively high. Where the ground water is oxic and sulfide minerals are absent from the aquifer matrix, SO_4 is often derived from dissolution of evaporite minerals in the unsaturated zone. Interestingly, very little NO_3 is measured in these shallow regional aquifers.[14] In comparison to these shallow aquifers, ground water in deep aquifers below the mudstone is probably recharged through a system of paleo-deltas extending into the basin from the Boise foothills

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[14] Recall that these "shallow" regional aquifers are distinct from overlying shallow alluvial aquifers that are affected by anthropogenic activities on the land surface.

(Squires and Wood, 2001). From a hydrochemical standpoint the recharge scenario appears to be similar to the scenario we described for the north Boise system. Reduced conditions and relatively high Na/Ca ratios prevail in these ground waters.

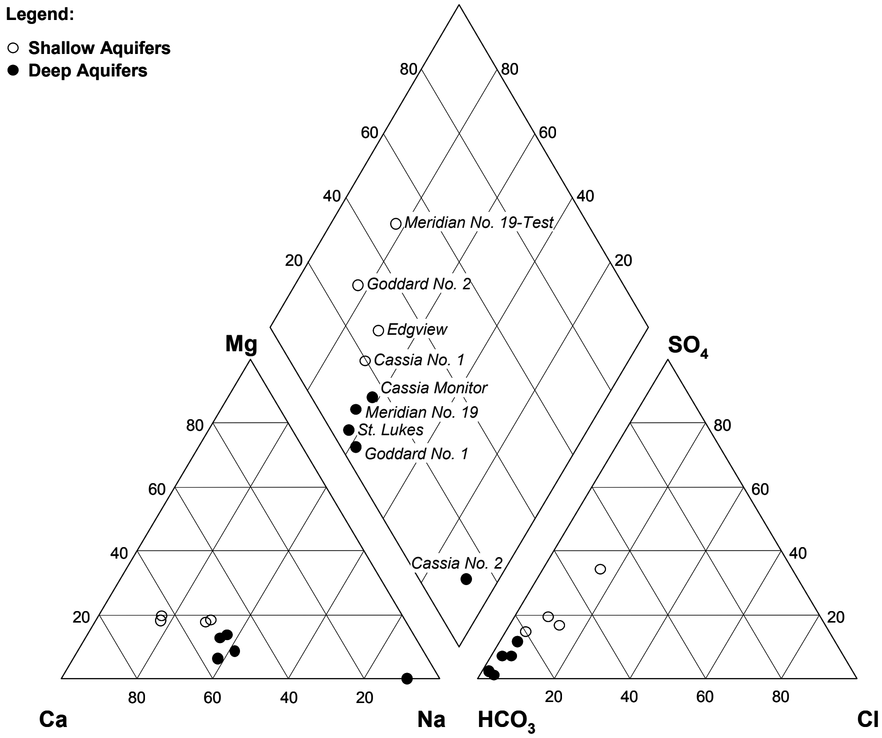

Figure 6. Distribution of cations and anions in selected ground water wells located in central and west Boise lacustrine aquifer.

4.3.2. Meridian to Caldwell Lacustrine Deposits

Distinct shallow and deep hydrogeologic units also are apparent in ground water chemistry data from wells located between Meridian and Caldwell. A comparison between wells drawing water from aquifer units above and below an elevation of about 2,100 feet above mean sea level shows clear differences in C_s, DO, and Na/Ca (Table 3, Figure 7). The differences are similar to those observed in the central and west Boise deposits. All three sampling wells drawing water from above 2,100 feet contain ^3H at levels indicative of modern recharge.

Well Name	TWBZ Elev. feet	C_s (uS/cm)	pH	DO (mg/L)	SO_4 (mg/L)	P_{CO2} (mg/L)	Na/Ca
State Hospital	2,181	547	7.6	5.3	84	$10^{-2.5}$	1.2
Nampa 12	2,166	505	7.6	5.7	81	$10^{-2.6}$	1.2
Caldwell 15	2,220	615	7.8	4.2	89	$10^{-3.1}$	1.6
Nampa 9	2,082	247	7.7	2.2	8.1	$10^{-2.6}$	4.1
Caldwell 16	2,012	276	8.2	0.5	14	$10^{-2.6}$	3.0
Down-valley wells	1,900-2,040	261-360	7.9-8.1	0	0.1-2.1	$10^{-2.9}$-$10^{-2.5}$	2.4-6.5

The acronym TWBZ means top of the water-bearing zone as determined from well logs.

Table 3. Selected hydrochemical data from wells between Meridian and Parma.

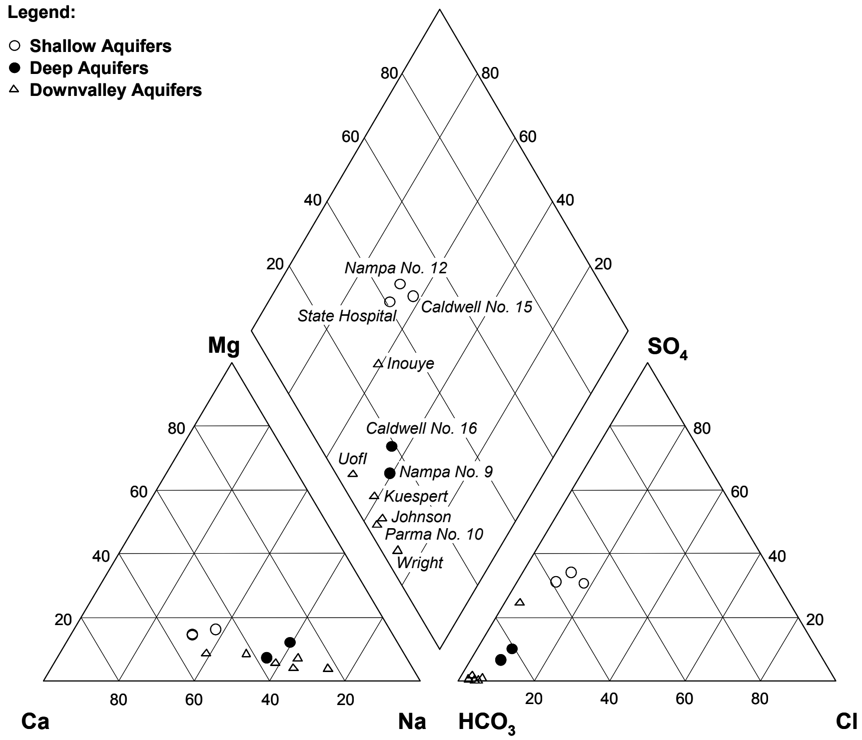

Figure 7. Distribution of cations and anions in selected ground water wells in Nampa, Caldwell, and down-valley locations.

In spite of similarities with the central and west Boise lacustrine aquifers, all of the ground waters we sampled near Nampa and Caldwell unexplainably contain higher concentrations of DO and SO_4 (Table 3). The Nampa 9 and Caldwell 16 wells, both below the 2,100-foot elevation, have measurable DO and SO_4 concentrations near 10 mg/L. This contrast with the Boise aquifers may be explained by the observation made in Section 3.2, that thick mudstones associated with erosional unconformities occur deeper in the section near Caldwell than they do in the deltaic environment near Boise.

4.3.3. Caldwell to Parma Down-Valley Lacustrine Deposits

Ground water in down-valley aquifers is more distinctive than anywhere else in the basin. Very low SO_4 concentrations in combination with DO and NO_3 below the analytical detection limit suggest highly reduced conditions (Table 3, Figure 7). Highly reduced ground water environments are commonly caused by anaerobic oxidation of organic matter by microbes. Sulfate reduction and methane fermentation are the main anaerobic processes thought to contribute to reduced conditions in down-valley aquifers, because hydrogen sulfide odor and methane have been observed emanating from several wells in the area (D. Parliman, E. Squires, pers. com. 1999).

Another characteristic of down-valley aquifers is high Na/Ca ratios (Table 3, Figure 7). Excluding aquifers influenced by geothermal water, down-valley aquifers exhibit greater Na/Ca ratios than aquifers east of Caldwell. Assuming that aquifer mineralogy is similar throughout the central basin, higher Na/Ca ratios may indicate longer ground water residence times.

5. THE CARBONATE SYSTEM

Bicarbonate is the dominant anion in nearly all waters in the Treasure Valley ground water system in spite of the fact that carbonate minerals are not ubiquitous in the basin. The prevalence of bicarbonate reflects the importance of carbonate reactions in the geochemical evolution of regional ground water. A thorough analysis of the carbonate system is important for evaluating sources of recharge and evaluating ground water flow between principal aquifer units. In addition, analysis of carbonate geochemistry is essential for determining ground water residence times from ^{14}C data.

Near the recharge zone, where ground waters are relatively young, calcium carbonates are often the dominant weathering minerals. This is because carbonates are more readily weathered than silicate minerals, so even in small amounts they dominate the ionic signature of ground water. The capacity of recharge waters to dissolve carbonate minerals in the aquifer is defined by temperature, pH, and P_{CO_2}. When compared quantitatively with the state of DIC in ground water, this information can be used to validate or invalidate recharge hypotheses. In more evolved waters farther along a regional ground water flow path, analysis of carbonate geochemistry must be enhanced by isotopic information about carbon cycling, and silicate weathering must be considered. The ensuing analysis ties geochemical concepts of carbonate dissolution and ^{13}C tracing into the present conceptual model of ground water recharge and flow.

5.1. Carbonate Geochemistry

Our study of carbonate geochemistry in the Treasure Valley system involves calculating carbonate equilibria for each recharge source and sampling well and comparing the state of carbonate mineral saturation among the principal aquifers. Carbonate geochemistry is the subject of numerous texts including Garrels and Christ (1965) and Drever (1997). We refer readers to these sources for detailed discussion of the analytical methods.

The amount of calcium carbonate that recharge water can dissolve is controlled by the temperature, pH, and P_{CO_2} conditions imposed in the soil zone. The higher the CO_2 concentration of the water, the lower its pH and the more aggressively the water dissolves aquifer minerals. The Saturation Index (SI) is a measure of how much calcite a particular ground water has dissolved relative to how much it can potentially hold. The logarithm of SI (logSI) is often used to express SI graphically because values of SI commonly range over several orders of magnitude. Ground waters that are under-saturated with respect to calcite have logSI values less than zero. In simple terms, under-saturation means that the ground water has not dissolved as much carbonate as it has capacity to dissolve. Ground waters saturated with respect to calcite have logSI values near zero. Saturation means that the ground water has dissolved as much carbonate as it can hold. Ground waters that are super-saturated with respect to calcite have logSI values greater than zero. Super-saturation indicates that carbonate is precipitating from the ground water solution.

As expected, all of the recharge waters are far under-saturated with respect to calcite. Values of logSI are -3.1 for the Boise Front springs, -2.5 for Banner Creek wells, and -1.1 for the Boise River. Most ground waters in the Boise area are slightly under-saturated, having logSI values less than zero (Figure 5). In contrast, most ground waters in the western portion of the basin exhibit logSI values near zero (Figure 5). These waters are saturated with respect to calcite. In a simplistic way, these observations bear out our conceptual model of relatively fresh recharge water entering the system along the eastern basin margin and becoming more saturated with respect to carbonate further along the flow path.

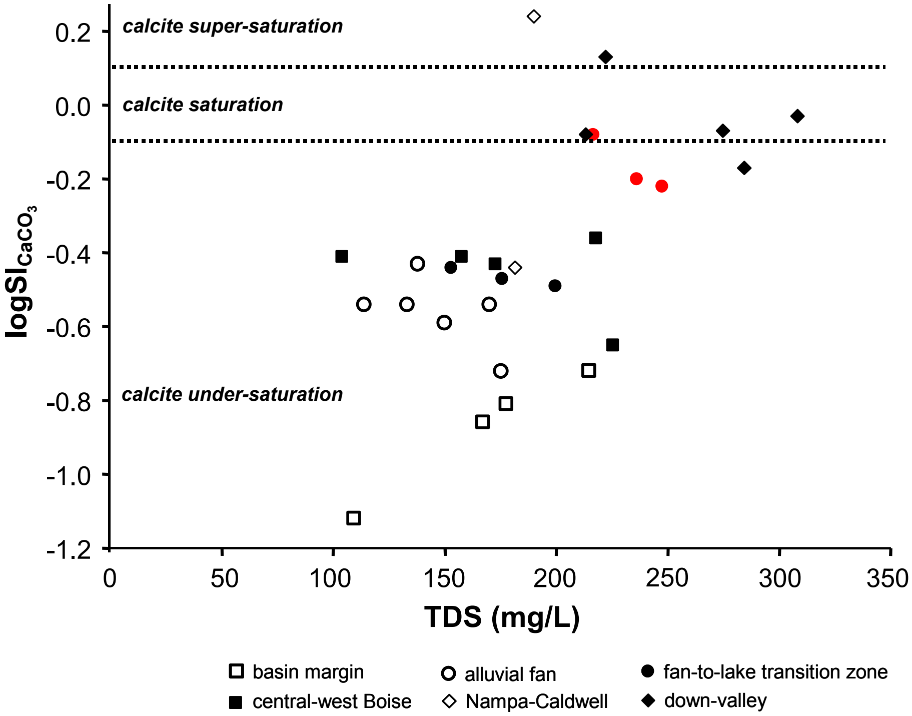

Figure 5. Calcite saturation indices for principal aquifers of the Treasure Valley ground water system. Data for Amity, Sunset West and MAC wells are shown in red.

An interesting deviation from what we are calling a regional trend in carbonate saturation is found in the transition zone. Waters from the Amity, Sunset West, and MAC wells are much closer to saturation with respect to calcite than are other wells in the Boise area (Figure 5). Although we can offer no clear explanation for this anomaly, it is instructive to recall that there are several other notable differences between chemical parameters in the Amity, Sunset West, and MAC wells, and the other transition zone wells (Table 1). In spite of the inconsistency, regional progression of carbonate saturation fits plausibly into the general conceptual model of regional recharge and flow. Because ground water radiocarbon dates must be corrected for carbonate dissolution along the flow path, this conclusion bodes well for obtaining realistic ground water residence times.

5.2. Open versus Closed Carbonate System

In the previous section we developed a conceptual relationship between the capacity for recharge waters to dissolve aquifer minerals, and the amount of dissolved calcium carbonate measured in the principal Treasure Valley aquifers. Taking this relationship a step further, we evaluate recharge conditions by comparing open-system and closed-system models of carbonate dissolution.

The evolution of DIC in ground water begins with weathering reactions in the recharge zone. These reactions are driven by acidity created during the solution of CO_2 gas and organic acids in the soil. Under *open-system* conditions, where ground water acidity is continuously replaced by CO_2-rich recharge from the soil, weathering reactions persist until chemical equilibrium is reached between aqueous phases and aquifer minerals. Under *closed-system* conditions, where there is no continuous flux of CO_2-rich recharge, weathering reactions neutralize the ground water acidity. The net result is that chemical equilibrium is reached sooner than in an open-system and less weathering occurs relative to open-system conditions. In other words, greater weathering occurs in aquifers open to continuous recharge from the soil zone.[15]

Plotting the molar concentrations of dissolved Ca^{2+} in the ground waters as a function of P_{CO_2} and considering where the data lie relative to theoretical calcite weathering trajectories based on open and closed-system assumptions is a useful method of accomplishing this task (Drever, 1988). It is important to recognize that the theoretical calculations are based solely on calcite equilibria and do not account for silicate weathering, biological fluxes, or any other biogeochemical process that may affect Ca^{2+} concentrations in the aquifer. This problem is likely to be particularly acute in the older, more evolved ground waters down-valley; therefore, the following discussion focuses on ground waters in the eastern portion of the basin.

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[15] Under some closed-system conditions, oxidation of organic matter and reduced minerals such as pyrite (FeS_2) may contribute additional acidity to ground water.

Measured concentrations of dissolved carbonate species, pH, and temperature from the (1) Boise River, (2) Boise Front springs, and (3) Banner Creek wells are used to define starting conditions for the theoretical carbonate dissolution trajectories. A set of open-system and closed-system trajectories for each starting condition is shown in Figure 6, together with measured data from Boise area aquifers. Note that all of the open-system trajectories increase along the ordinate axis with no change in P_{CO_2}. This is because the primary assumption of the open-system model is that CO_2 gas is continuously replenished, so P_{CO_2} is held constant. The closed-system model trajectories deviate toward less P_{CO_2} as the calcium concentration increases. This is because the total amount of CO_2 in the system is fixed before calcite dissolution begins and, as dissolution occurs, CO_2 gas is used up.

Of the six possible trajectories shown in Figure 6, a closed-system trajectory beginning with the range of mountain front recharge waters is the best model for most of the aquifers in the Boise area. This conclusion follows from:

1. The geochemical data describe a curvilinear trend along a generalized closed-system trajectory that has initial conditions similar to the Boise Front springs and Banner Creek wells.
2. Shallow oxic ground waters appear to be physically separated from deeper waters in all but the alluvial fan aquifers.
3. Low permeability blue clay deposits exist in all but the alluvial fan aquifers.
4. Water level measurements show upward hydraulic gradients in deep aquifers west of the transition-zone (Petrich et al., 1999).

The southeast Boise alluvial fan may be exception to the closed-system model. As noted in Section 3.2, the alluvial fan lacks redoximorphic color changes in the vertical section. Ground water is unconfined, oxic, has low C_s, and exhibits a downward hydraulic gradient. It stands to reason that ground water in the alluvial fan should be described using an open-system model.

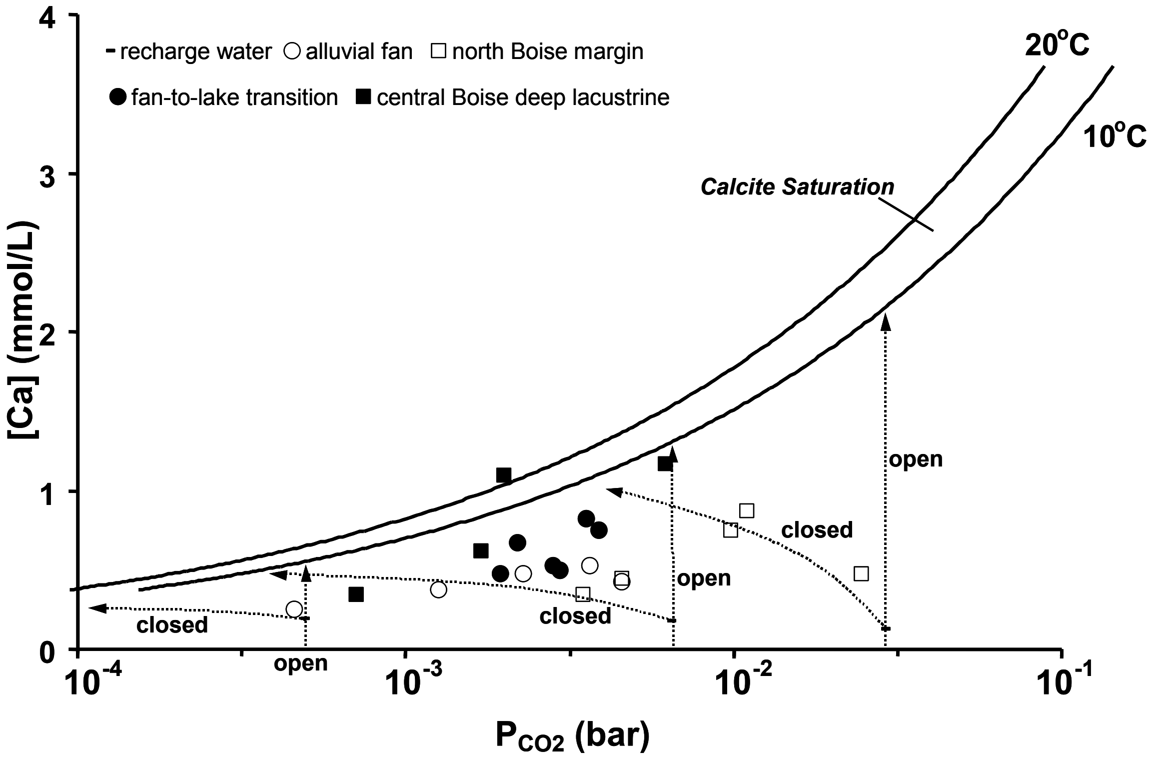

Figure 6. Open versus closed-system trajectories for calcite dissolution in basin margin aquifers.

5.3. Carbon Isotopes and the Carbonate System

Processes that control the quantity of DIC in ground water also affect the relative proportion of carbon isotopes; therefore, changes in isotopic character of ground water DIC can be used to evaluate the magnitude of carbonate dissolution on a regional scale. The first step in this analysis is to determine the range of $\delta^{13}C_{DIC}$ for recharge waters.[16] In the recharge zone, where substantial carbonate dissolution has not yet occurred, $\delta^{13}C_{DIC}$ is controlled by the distribution of carbonate species. Estimates of $\delta^{13}C_{rech}$ for the Boise Front springs, Banner Creek wells and Boise River were determined using a ^{13}C mixing-model (Appendix 2). Carbon-13 enrichment factors ($\varepsilon^{13}C$) for the distribution of DIC species depend on water temperature and were determined from relationships described by Vogel et al. (1970) and Mook et al. (1974). The fundamental mixing equation is:

$$\delta^{13}C_{rech} = \delta^{13}C_{soil} + \frac{mDIC_{H_2CO_3(aq)}}{mDIC}\cdot\varepsilon^{13}C_{H_2CO_3(aq)} + \frac{mDIC_{HCO_3^-}}{mDIC}\cdot\varepsilon^{13}C_{HCO_3^-},$$

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[16] Refer to footnote 4 for discussion of del (δ) notation.

where $\delta^{13}C$ of soil CO_2 gas ($\delta^{13}C_{soil}$) is taken to be -23‰ (Clark and Fritz, 1997). Applying the mixing-model to our representative recharge waters provides the following $\delta^{13}C_{rech}$ values:

Boise Front springs, –21.4‰;
Banner Creek wells, –18.0‰;
Boise River, –13.7‰.

Note that these values are quite different. The acidic Boise Front springs, at pH 6, are weighted more to $\delta^{13}C$ of carbonic acid (-24.1‰) than $\delta^{13}C$ of bicarbonate (-15.1‰).[17] The opposite is true for Boise River water at pH 7.9. The Banner Creek wells, at pH 6.6, fall between these extremes.

Away from the recharge zone, where ground water is largely closed to soil CO_2, carbonate dissolution is the primary control on $\delta\ ^{13}C_{DIC}$. Potential sources of carbon in Treasure Valley aquifers include (1) oolites, carbonized wood and shells in shoreline deposits (-2‰ to +4‰), (2) calcareous muds and shells in deep lake areas (-3‰ to -6‰), and (3) biogenic CO_2 from oxidation of organic matter in confining beds (-25‰ to -30‰). With the exception of biogenic CO_2, dissolution of lacustrine carbonates introduces ^{13}C-enriched carbon to the recharge DIC pool. As $\delta\ ^{13}C_{DIC}$ evolves to greater values along the flow path, it becomes less and less diagnostic of the controlling open or closed-system conditions. This is because silicate dissolution becomes increasingly important, and the difference between $\delta\ ^{13}C_{DIC}$ and $\delta\ ^{13}C_{CaCO3}$ diminishes as ground water is enriched. Measurements of ^{14}C can increase the utility of $\delta\ ^{13}C_{DIC}$ measurements, because under open-system conditions ^{14}C in ground water is continually replenished and is maintained near 100 pmC. In contrast, ^{14}C is isolated from the soil atmosphere under closed-system conditions and radioactive decay reduces its activity. The longer ground water resides in isolation from soil CO_2, the lower the ^{14}C activity.

Ground water $\delta\ ^{13}C_{DIC}$ in the recharge-zone aquifers ranges between –12‰ and –15‰, while ground water in the deep deltaic aquifers beneath Boise and in down-valley locations have $\delta^{13}C_{DIC}$ values between -8‰ and -12‰ (Figure 7). One down-valley well (Parma No. 10) has a $\delta^{13}C_{DIC}$ of –5‰. Increasing $\delta^{13}C_{DIC}$ in wells west of Meridian is consistent with a regional flow model of carbonate evolution, because carbonate dissolution from $\delta^{13}C$-enriched calcareous muds in the deep lake environment adds $\delta^{13}C$-enriched DIC to the ground water. Calcareous silt stones and mud stones are documented in the Simplot Geothermal well near Caldwell (Wood, 1994). The substantial differences between $\delta^{13}C_{DIC}$ of ground water in the central

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[17] Recall the discussion of ^{13}C fractionation in Section 1.1.

Boise deltaic sequences and ground water in the recharge-zone aquifers may reflect the closed-lake depositional environment of the shoreline sediments. These differences are consistent with isolated aquifers in the deep deltaic aquifers.

Like $\delta^{13}C_{DIC}$, $^{14}C_{DIC}$ also differentiates the various aquifers. Figure 7 shows that the highest ^{14}C-activities are in waters near the recharge area, while the lowest activities are found in down-valley wells and in wells penetrating the deep deltaic aquifers beneath Boise. In the western reaches of the basin increasing $\delta^{13}C$ generally accompanies decreasing ^{14}C-activity. This relationship is as it should be for a closed ground water system undergoing carbonate dissolution.

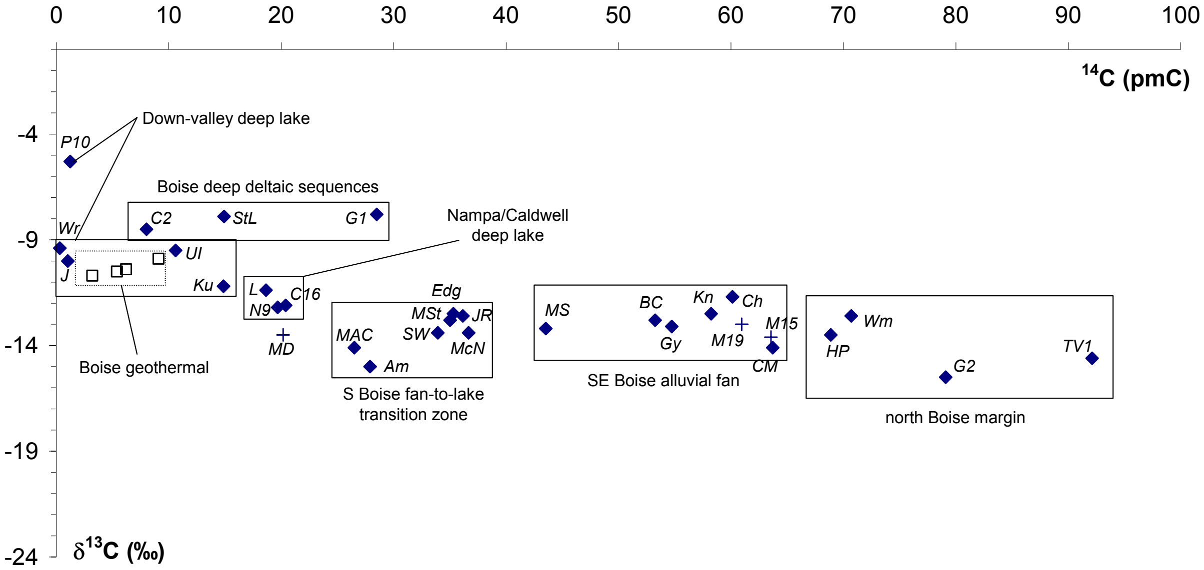

Figure 7. Isotopic trends of DIC in principal aquifers of the Treasure Valley ground water system. Plus symbols represent wells that do not conform to their principal aquifer designation.

Geochemical evolution of ground water often involves more than CO_2-driven dissolution of aquifer minerals. Carbon dioxide produced by microbial oxidation of organic carbon ($\delta^{13}C=-25$‰) can dilute ground water DIC with lighter ^{13}C, thereby reducing $\delta^{13}C_{DIC}$. Denitrification and sulfate reduction are examples of microbial oxidation. Under highly reduced conditions, methanogenic fermentation can contribute CO_2 with $\delta^{13}C$ greater than +10‰. Mixing of large quantities of methanogenic CO_2 would substantially increase $\delta^{13}C_{DIC}$ of ground water. No decreasing trend is observed in the $\delta^{13}C_{DIC}$ data, ruling out a strong influence of sulfate reduction, or a similar oxidation process. With the exception of the Parma No. 10 well ($\delta^{13}C_{DIC}$=-5.3‰), there are no wells that show exceptionally large increases of $\delta^{13}C_{DIC}$, suggesting that methanogenesis does not play a major role in regional geochemistry (although it may be very important in isolated areas). The absence of these processes and the subtle evolution of $\delta\ ^{13}C$ along the flow path imply that carbonate dissolution, rather than microbial activity, is the primary control on ground water DIC.

5.4. Controls on Ground Water DIC–Silicate versus Carbonate

Our analysis of carbon cycling in the regional aquifer system leads to three main conclusions about geochemical processes in the regional ground water system: (1) dissolution of carbonate minerals is an important control on DIC in ground water near the recharge zone, (2) regional ground water is closed to inputs of CO_2 except along the basin margin, and (3) sulfate reduction and/or methanogenesis do not contribute gross amounts of CO_2 to ground water in the central portion of the basin. These conclusions explain in a regional sense how carbonate dissolution adds DIC to ground water; however, silicate weathering is also an important aspect of geochemistry in central basin aquifers. Silicate weathering is addressed in the following section.

6. SILICATE MINERAL WEATHERING

Beginning with aquifers at the northeastern margin of the basin and moving west toward the Snake River, we observe decreasing water levels, decreasing hydraulic conductivity, decreasing P_{CO_2}, decreasing DO, and decreasing ^{14}C activity. At the same time, we observe greater aquifer confinement, increasing C_s, increasing Na/Ca ratio, and increasing $\delta^{13}C_{DIC}$. Collectively, these trends implicate a continuous, interconnected, east-to-west-flowing regional ground water system. Given that the basin is bounded by silicate-rich geologic terrains and that these terrains are the source of much of the basin fill through which regional ground water flows, the implication is much more compelling if we can demonstrate that our hydrochemical data can be described by an appropriate model of silicate mineral weathering. Put another way, we can test our conceptual model of regional recharge and flow by evaluating ground water chemistry as it relates to established models of silicate mineral dissolution and precipitation. In this analysis, our objectives are to identify important silicate mineral phases and determine whether our hydrochemical data can be described as a function of primary silicate mineral dissolution and secondary silicate mineral formation.

6.1. Important Silicate Mineral Phases

Aquifers in the Treasure Valley are composed mainly of detrital sediments weathered from the granitic Idaho Batholith. Studies of mineral weathering in the Banner Creek watershed, located in the southwestern part of the Idaho Batholith, show the composition of the parent granite rock. The granite in the Banner Creek area consists of nearly equal amounts of quartz, orthoclase, and An_{19} plagioclase, with minor amounts of biotite (Clayton, 1988). Sand and silt-sized sediments weathered from similar material make up most of the important regional aquifers in the Treasure Valley (S. Wood, pers. com. 1999). Along paleo-shorelines the arkosic sediments are often interspersed with carbon-rich evaporite and biogenic mineral. Volcanic ash is present in many stratigraphic sections. In relation to geochemical evolution of ground water in the Treasure Valley, the most important mineral phases are (1) arkosic sediments, (2) evaporites or biogenic minerals associated with shoreline deposits, (3) volcanic glasses, and (4) secondary clay minerals. Particular mineral phases of geochemical importance are listed in Table 4.

Classification	Mineral Phase	Chemical Formula	Depositional Environment
Primary Arkose	quartz	SiO_2	basin-wide detritus
	CaNa plagioclase feldspars	$(Ca,Na)AlSi_3O_8$	basin-wide detritus
	K feldspars	$KAlSi_3O_8$	basin-wide detritus
	biotite	$K(Mg,Fe)_3(Al,Fe)Si_3O_{10}(OH,F)_2$	basin-wide detritus
Biogenic or Evaporite	calcite	$CaCO_3$	shoreline deposits
	aragonite	$CaCO_3$	shoreline deposits
Evaporite or Hydrothermal	gypsum	$CaSO_4$	shoreline deposits or hydrothermal vents
	pyrite	FeS_2	shoreline deposits or hydrothermal vents
Volcanic	rhyolite glass	SiO_2	basin-wide
	basalt glass	SiO_2	basin-wide
Secondary Clays	Ca-montmorillonite		weathering product
	halloysite		weathering product
	palagonite		weathering product
	zeolites		weathering product
Organic Matter		CH_2O	basin-wide detritus

Table 4. Plausible phases for ground water reactions in Treasure Valley aquifers (S. Wood, pers. com. 1999).

Like most waters that evolve in the presence of feldspathic igneous rock, deep Treasure Valley ground water is dominated by Na-Ca-HCO_3 and is rich in silica. The genesis of ground water in this environment is summarized below, following Garrels (1967).

1. The ionic make-up of ground water is driven by weathering reactions and is controlled by the P_{CO_2} of the recharge water.
2. Plagioclase feldspars, biotite, and other dark minerals are weathered much more rapidly than K-feldspars or quartz.
3. The high percentage of plagioclase feldspars relative to other rapidly-weathered silicate minerals results in a high percentage of Ca^{2+} and Na^+ in the ground water.
4. K^+ and Mg^{2+} are derived primarily from biotite.
5. Dissolved silica is almost entirely derived from plagioclase and related minerals.
6. Cl^- and SO_4^- are not derived from silicate weathering (except for pyrite oxidation) and generally indicate mixing of water from other sources.
7. The first alteration product formed by silicate weathering is often kaolinite, although a wide range of clay minerals and metal oxides may be present.

6.2. Weathering of Primary Minerals

Using these observations as a framework for evolution of regional Treasure Valley ground waters, several methods can be employed to evaluate whether the ground water system can be considered as a continuously evolving silicate system. The first method is based on the observation that Na/Ca mole ratios in feldspathic ground waters generally reflect the feldspar composition of the aquifer matrix (Drever, 1988). To evaluate the progressive dissolution of silicate minerals, the relationship between molar concentrations of Na^+, Ca^{2+}, and SiO_2 is evaluated with respect to theoretical Na/Ca ratios for plagioclase minerals present in Treasure Valley aquifers. A general trend is observed in which the Na/Ca ratio increases with increasing SiO_2 concentration (Figure 8). The trend is not completely consistent with the position of the sampled aquifer in the regional flow system. For example, SiO_2 decreases between the alluvial fan and transition zone aquifers, while the Na/Ca ratio increases slightly. Even so, the Na/Ca ratio is greatest in waters farthest from the northeastern basin margin even though these waters are influenced by $CaCO_3$ dissolution. Ground waters west of Nampa exhibit Na/Ca close to that of An_{19} plagioclase (Figure 8). This regional relationship reasonably suggests that ground water chemistry is not fully evolved in recharge area aquifers, but moves toward geochemical equilibrium as ground water transits the central basin. Alternatively, mineral assemblages could have been distributed in a systematic fashion during deposition and subsequent redistribution, resulting in different (but predictable) accumulations of minerals at varying distances from the batholith. The argument is that these mineral accumulations would prescribe the contemporary distributions of dissolved constituents like Na^+, Ca^{2+}, and SiO_2. By this explanation alone, the regional trend seen in Figure 8 is unlikely, because the depositional history of the Treasure Valley spans millions of years and is extremely complex; however, when combined with a continuous ground water flow system, the patterns observed in Figure 8 make sense. Our conclusion from the preceding discussion is that the geochemical trends observed in Figure 8 are an expression of a regionally-connected ground water flow system that moves through a locally heterogeneous, but regionally systematic, arrangement of sedimentary deposits.

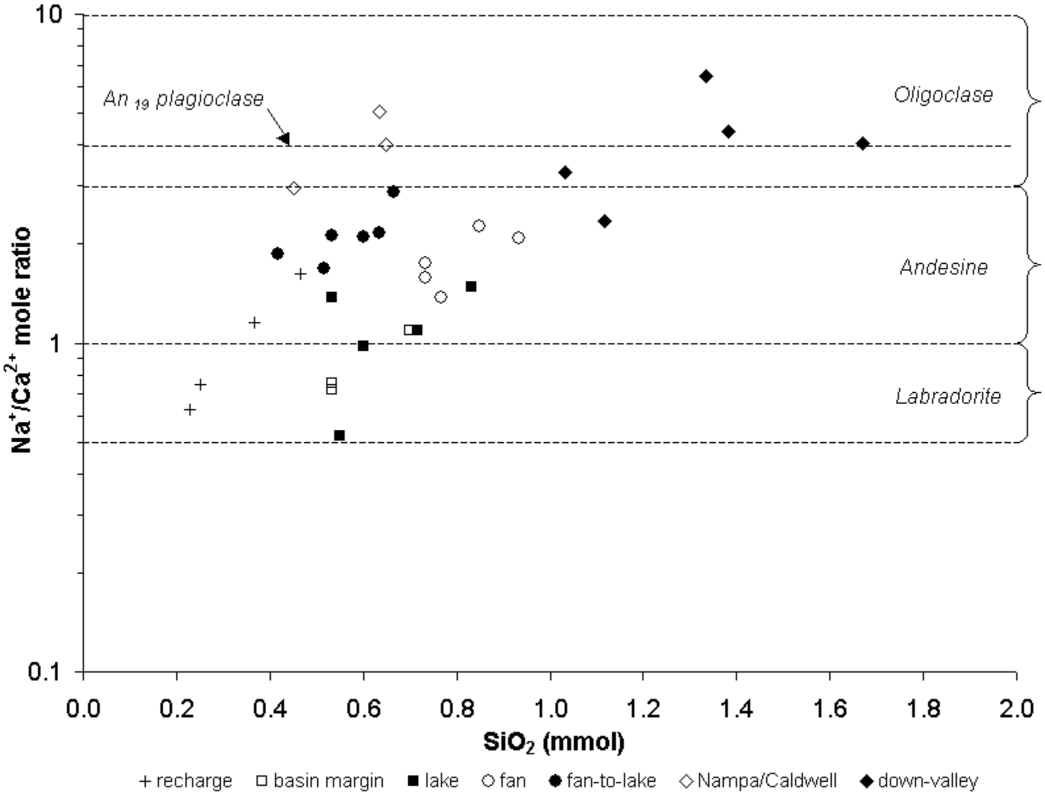

Figure 8. Relationship between Na/Ca mole ratios in regional ground waters and theoretical Na/Ca ratios for selected silicate minerals. Ranges of Na/Ca for Labradorite, Andesine and Oligoclase are taken from Garrels (1967).

6.3. Formation of Secondary Minerals

Weathering of primary silicate minerals is only one factor that controls Na/Ca ratios in evolving ground water systems. Another factor is the formation of silicate weathering products (i.e., secondary minerals such as kaolinite and montmorillonite clays). Evaluating the influence of secondary clay minerals on the ground water solution is a rather tenuous science because the composition of clays can be quite variable and because reliable free-energy data is not available. However, an analysis of the important kaolinite-montmorillonite[18] system offers valuable insight into the regional evolution of ground water in the Treasure Valley.

Kaolinite is often an early weathering product during the evolution of ground water in silicate terranes (Garrels, 1967). Formation of kaolinite may be accompanied by the formation of smectite clays later in the geochemical process. The important associations between the weathering minerals and weathering products, and their effect

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[18] In this context the terms smectite and montmorillonite are equivalent.

on dissolved concentrations of cations and SiO_2 are (1) weathering of plagioclase feldspars releases cations and silica into solution; (2) formation of kaolinite removes silica, but does not affect cation chemistry; and (3) formation of smectite clays removes both silica and cations from solution.

Stability diagrams are the basic tools for examining equilibrium conditions of waters with respect to various aquifer minerals. Stability diagrams show which of a prescribed group of minerals is more stable in contact with a particular solution. When overlain by Na-mineral stability fields, data from the Treasure Valley wells show that some waters lie in the kaolinite field, the smectite field, or on the border between the kaolinite and smectite fields (Figure 9). One can deduce from Figure 9 that waters near the recharge source at the basin margin should form kaolinite, which according to Garrels (1967) is generally the first weathering product of Na-Ca-HCO_3 waters in feldspathic rocks. In contrast, Figure 9 suggests that waters in the down-valley locations are supersaturated with respect to Na-bedeillite (or a similar clay mineral). Waters from most of the central basin appear to be simultaneously at equilibrium with both kaolinite and Na-smectite minerals. A similar stability relationship exists for Ca mineral phases, although, because of the influence of calcite dissolution, the data plot entirely in the Ca-bedeillite field (Figure 10). The trajectory of water chemistry data in a K mineral stability diagram is odd because it suggests that ground water is at equilibrium with the primary K-feldspar mineral near the recharge zone, evolves to a condition in which kaolinite is formed, but then shifts away from that condition as ground water passes the Nampa-Caldwell aquifers on its way down-valley (Figure 11). This seemingly contradictory trend may be an indication that we have oversimplified the geochemical model by not representing an important K-mineral phase in our analysis.

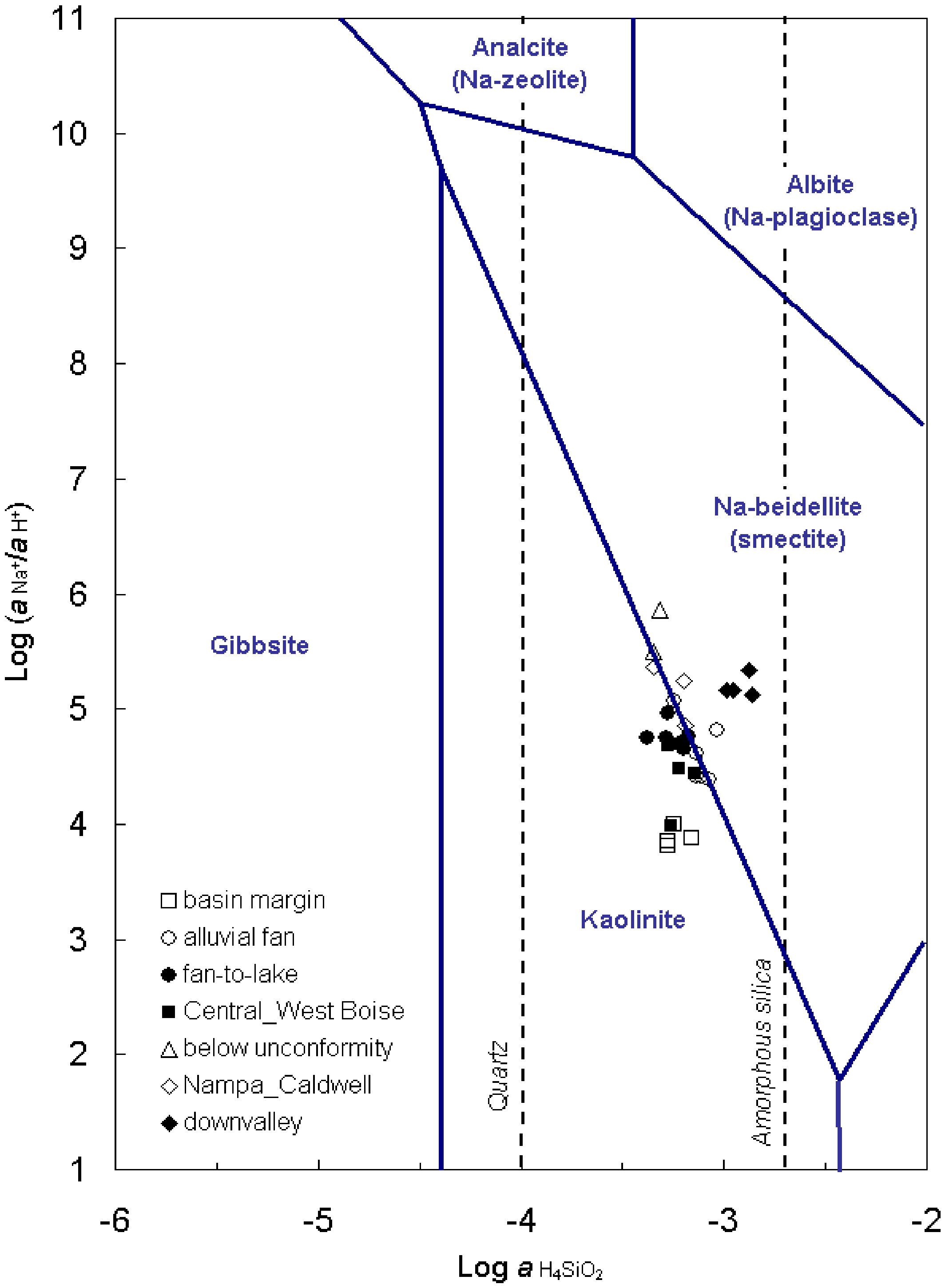

Figure 9. Relationship between regional Treasure Valley ground waters and stability fields for minerals in the system Na_2O-Al_2O_3-SiO_2-H_2O at 25°C (after Drever, 1988).

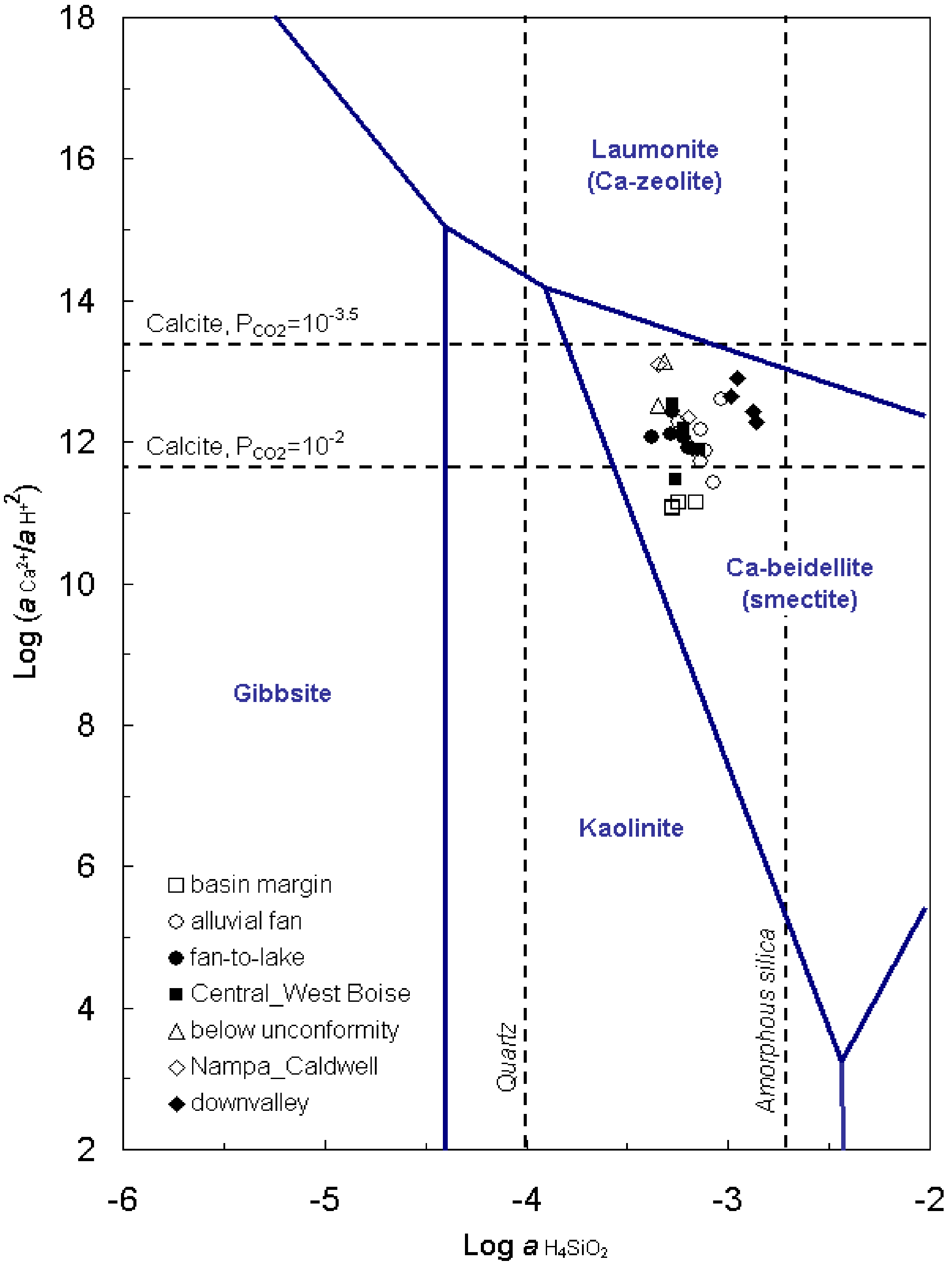

Figure 10. Relationship between regional Treasure Valley ground waters and stability fields for minerals in the system CaO-Al_2O_3-SiO_2-H_2O at 25°C (after Drever, 1988).

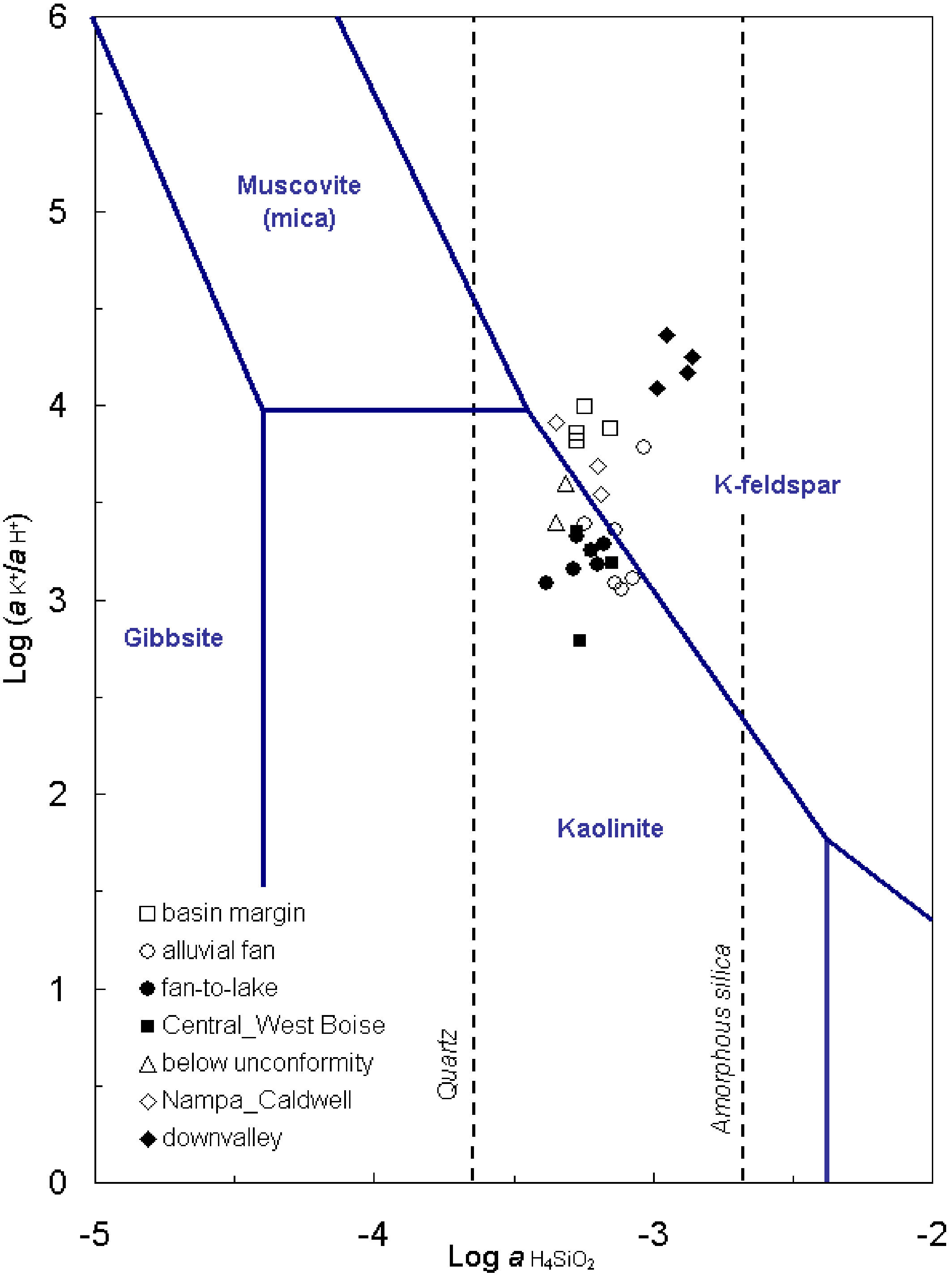

Figure 11. Relationship between regional Treasure Valley ground waters and stability fields for minerals in the system K_2O-Al_2O_3-SiO_2-H_2O at 25°C (after Drever, 1988).

The final step in our analysis of weathering products involves further development of the idea that regional ground waters progress toward an equilibrium condition between kaolinite and a smectite clay. Our evaluation is based on the suggestion that feldspars are altered to kaolinite early in the evolutionary process, while more geochemically evolved waters may be controlled by concurrent formation of kaolinite and smectite minerals (Garrels, 1967). Kaolinite-smectite reaction quotients for our data exhibit an asymptotic increase from about –20 (recharge) to about –10 (down valley aquifers) (Figure 12). The curve becomes asymptotic where equilibrium exists between kaolinite and the idealized Ca-montmorillonite (smectite) (Garrels, 1967).

Two important conclusions can be drawn from this analysis: (1) ground waters exist in equilibrium with a single weathering product (kaolinite) in the eastern portion of the basin; and (2) ground waters exist in equilibrium with both kaolinite and smectite in the western portion of the basin. These conclusions are another indication that ground water presently located at the western end of the valley once existed further east (upgradient) in a less geochemically evolved state.

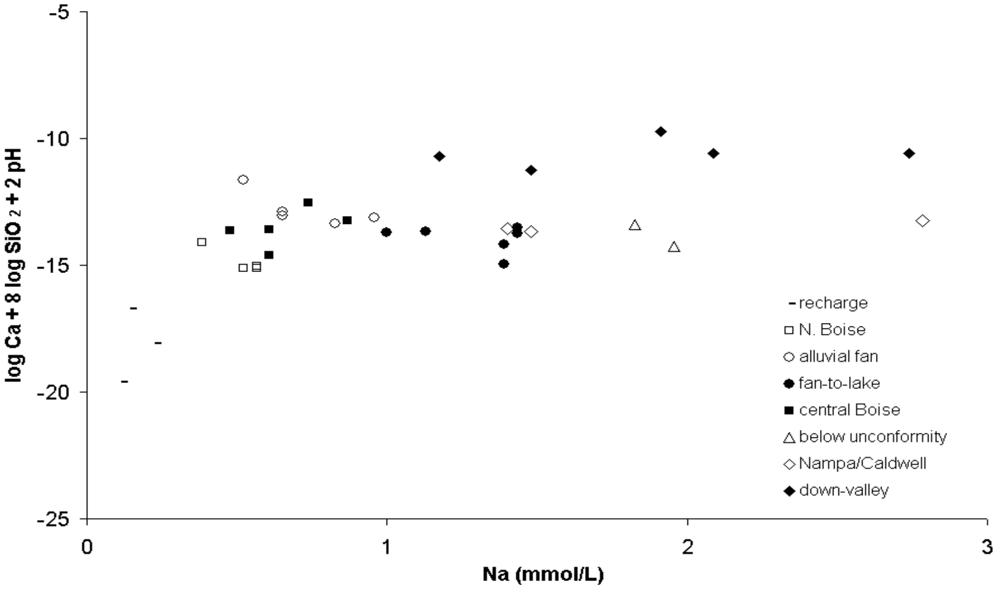

Figure 12. Changes in the kaolinite-smectite reaction quotient for regional ground waters in the Treasure Valley. After Garrels (1967).

7. GROUND WATER RESIDENCE TIMES

The previous sections focused on defining the most appropriate conceptual and geochemical models for the Treasure Valley regional ground water system. In this section, we use those models as the basis for estimating ground water ages and comparing ground water residence times among the principal regional aquifers.

7.1. Age Dating

Ground water ages are calculated from the activity of ^{14}C ($a^{14}C$) in ground water using the decay equation

$$t = -8267 \ln(a^{14}C/a_0{}^{14}C), \qquad [1]$$

where $a^{14}C$ is the measured ^{14}C activity in the ground water and $a_0{}^{14}C$ is the ^{14}C activity of water in modern soil (100 pmC). In carbonate terranes, where carbonate dissolution dilutes $^{14}C_{DIC}$ with ^{14}C-free carbon, equation [1] cannot be applied without correction. Our analysis of regional-scale carbon cycling in the Treasure Valley system shows that carbonate dissolution contributes to ground water DIC (Section 5). Consequently, ^{14}C-ages calculated directly from the measured $^{14}C_{DIC}$ data would over-estimate ground water residence times. To establish ^{14}C-ages when carbonate dissolution occurs along the ground water flow path, a dilution factor (q) is determined that accounts for additions of ^{14}C-free DIC. When multiplied by $a_0{}^{14}C$, q gives a dilution-corrected value for the ^{14}C activity of DIC in recharge water. Substituting this value into [1], the corrected ground water age is given by

$$t = -8267 \ln(a^{14}C/\ q\ a_0{}^{14}C) \text{ (Clark and Fritz, 1997).} \qquad [2]$$

Dilution of ground water DIC by old carbonate generally results in $q<1$; therefore, corrections for dilution reduce the estimated age. In practice, values of q range between 0.60 and 1.0 (Clark and Fritz, 1997).

The simplicity of correcting ^{14}C data for flow path carbon inputs is deceiving. Estimating reasonable values of q requires detailed understanding of the carbonate system, particularly with respect to the recharge environment. Before considering the correction techniques in detail, it is useful to review our present conceptual model of carbon cycling in the flow system.

1. Recharge water is charged with ^{14}C-rich CO_2 as it passes through the soil.
2. Holocene carbonates slightly depleted in ^{14}C may be dissolved into the DIC pool in the recharge zone beyond the soil.

3. Beyond the recharge zone, where carbonate dissolution is controlled by closed-system assumptions, old (^{14}C-free) carbonate dilutes the ground water ^{14}C pool. Occurrence of these old carbonates is not uniform throughout the basin.
4. Isotopic exchange of dissolved ^{14}C for solid-phase ^{12}C and ^{13}C may occur along the flow path.
5. In isolated aquifers, free CO2 may be introduced from biochemical oxidation of old organic matter.

According to this model, carbon fixed from the atmosphere by plants is released into the soil as CO_2 gas when the plants decompose. High CO_2 pressure in the soil causes increased concentration of DIC in percolating water and charges the water with ^{14}C. When percolating water leaves the soil zone it may pass through late Pleistocene or Holocene carbonate deposits having a level of ^{14}C activity that is slightly less than that of modern carbonate. Dissolution of these carbonates would alter the ^{14}C activity of recharging water from the activity expected in a modern DIC pool (*i.e.*, 100 pmC) to a slightly lower value. At the present time there are no studies addressing the ^{14}C activity of contemporary vadose zone water in the Boise area, so for the purposes of our age corrections, ^{14}C activity of vadose zone carbonates are assumed to be 100 pmC. In light of long-term variations in atmospheric ^{14}C activity and considering the wide range of uncorrected ages of Treasure Valley ground waters, this assumption will have little influence on our corrections.

The decrease in atmospheric a^{14}C during the past 30,000 years further confounds estimates of the activity of recharge water. A rough estimate of the decrease is obtained from a composite diagram of atmospheric ^{14}C activity compiled by Clark and Fritz (1997). The estimated rate of decrease is 2×10^{-3} pmC y^{-1} for ground waters recharged since the last glacial maximum. This rate corresponds roughly to an a^{14}C value of 100 pmC for waters recharged during the past 2,500 years and 140 pmC for waters recharged 20,000 years ago. The data are too sparse to extend the estimate beyond 20,000 years.

In contrast to recharge-zone carbonates, carbonate deposits formed before the late Pleistocene have, by now, lost most of their original ^{14}C to radioactive decay. These carbonates do not contain measurable ^{14}C activity; therefore, ^{14}C in the DIC fraction is substantially diluted by dissolution of these carbonate minerals. Most carbonate in deep, regional aquifers falls in this category. Biochemical oxidation of organic matter can also have a profound effect on estimates of ^{14}C ages. Carbon-14-free organic matter contained in the aquifer matrix may be oxidized by sulfate reducing microbes. Another common biochemical reaction in sedimentary ground water environments is methanogenesis. Methanogenesis occurs when methane-producing bacteria break down organic carbon into methane and carbon dioxide. Biogenic sources of ^{14}C-free carbon would have the same diluting effect as dissolution of old carbonate minerals.

Fortunately, our analysis of ^{13}C data suggests that these biogenic sources do not contribute a great deal to dilution of DIC in the regional system (see Section 5.3).

7.2. Application of Correction Models

Corrections for sources and sinks of carbon along the ground water flow path were determined using the CMB-ALK, CMB-CHEM, $\delta^{13}C$-mixing and Matrix Exchange models (Section 2.2.3). Spreadsheets containing the complete calculations are contained in Appendix 3. Uncertainty about the source of recharge to the Treasure Valley aquifers and sensitivity of correction models to recharge water pH and P_{CO_2} required that corrections be evaluated for a range of recharge chemistries. Corrected ^{14}C ages were calculated using the range of recharge pH and P_{CO_2} values represented by the Boise Front springs, Banner Creek wells, and Boise River waters.

Comparisons among ground water ages determined using the CMB-ALK, CMB-CHEM, $\delta^{13}C$-mixing and Matrix Exchange models are shown in Figure 13. Two important observations from these comparisons are:

1. Except for the relatively young basin margin waters, all corrections result in decreased ages. Corrected ages greater than uncorrected ages in aquifers near the recharge zone result from incorrectly applying the restrictive closed-system assumptions;
2. The magnitudes of corrections are generally consistent among the various methods and among the various recharge conditions.

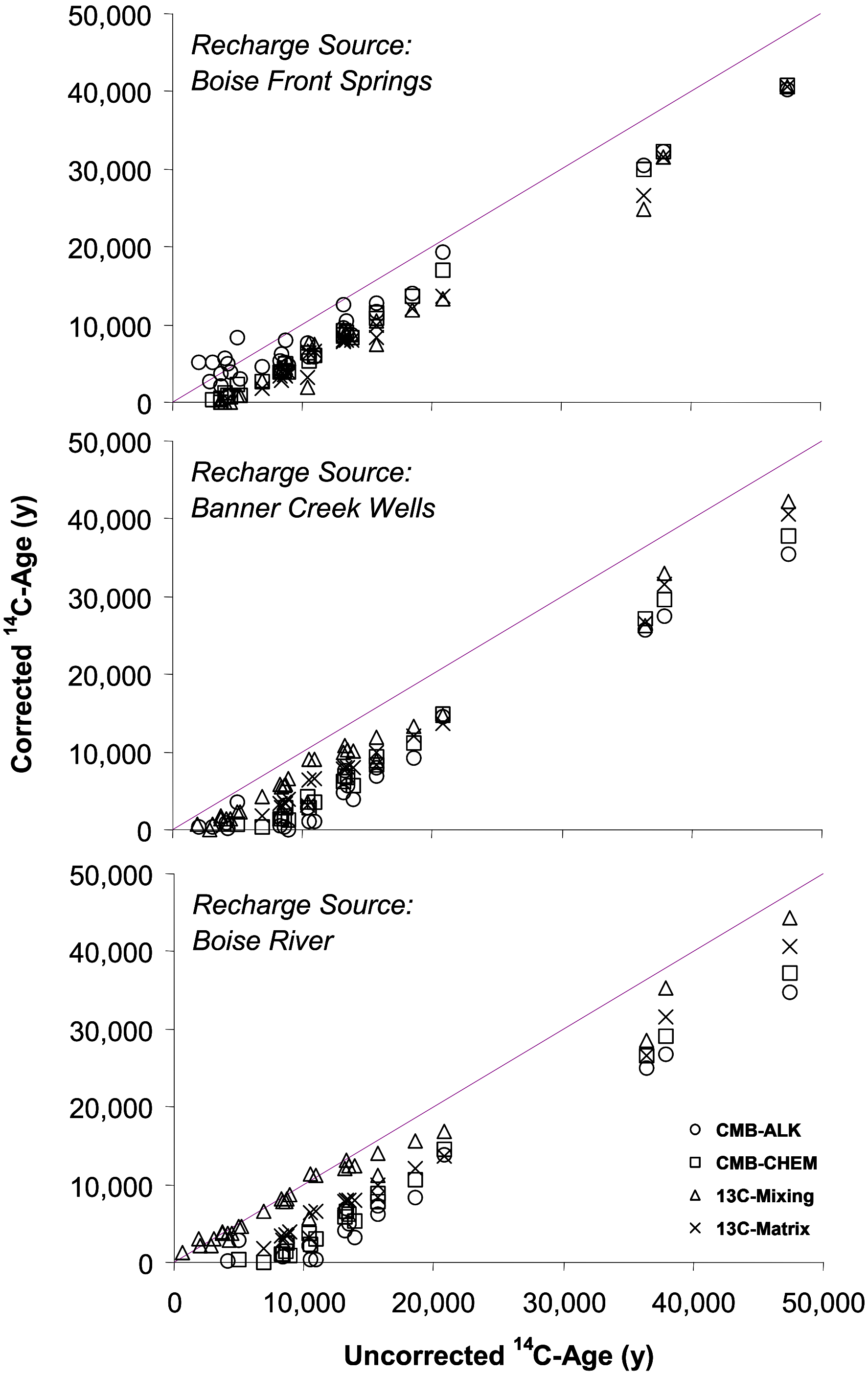

Figure 13. Comparison of ^{14}C-ages calculated for three recharge scenarios using the CMB-ALK, CMB-CHEM, δ^{13}C-Mixing and δ^{13}C-Matrix Exchange models. The 1:1 line represents the condition where corrected ages are the same as uncorrected ages.

These observations give us confidence that the corrected ages are reasonable estimates of true ground water residence times. The fact that the four models give relatively consistent results indicates that carbonate dissolution is indeed the primary geochemical factor affecting regional-scale ground water age calculations. The fact that the greatest differences between the strictly closed-system models (CMB) and the combined open/closed-system models (δ^{13}C-mixing) occur in younger waters near the recharge zone confirms that the closed-system assumption are too restrictive for the basin margin aquifers. Based on agreement between the CMB models and the δ^{13}C-mixing models for ground waters in the central basin, and considering that the δ^{13}C-mixing model is not constrained by closed-system assumptions, we consider ground water ages estimated using the δ^{13}C-mixing model to most accurately represent ground water residence times.

7.3. Ground Water Residence Times

We further constrain the range of residence times for each ground water by selecting the most appropriate recharge data for the aquifer as determined by previous discussions. For example, Boise River water was used as the starting condition to estimate the residence times of ground water in the alluvial fan and transition zone aquifers. This approach provides “best estimates” of ground water residence times that can be used to represent ground water flow in the regional system. These “best estimates” are shown in Table 5 along with a tabulation of the range of calculated residence times. Note that the practical limits of the ^{14}C-age dating method are 5,000 to 30,000 years; therefore, residence time estimates for the basin margin aquifers and some down-valley aquifers must be considered accordingly.

Principal Aquifer	Well Name	Top of Water Bearing Zone	Ground Water Residence Time		
			Minimum	*Maximum*	*Best Est.*
		(feet above msl)		*(years)*	
North Boise	TVHP 1	2,282	0	1,000	<1,000
fluvial sands	HP	2,065	0	3,000	<3,000
Central and West Boise	Goddard 2	2,199	0	2,000	<2,000
lacustrine deposits	Cassia Monitor	2,226	0	4,000	<3,000
	Meridian 15	2,105	0	4,000	<4,000
	Meridian 19	2,010	0	4,000	<4,000
Southeast Boise	Christiansen	2,636	0	4,000	<2,000
alluvial fan deposits	Guyer	2,565	1,000	5,000	<2,000
	Micron Shallow	2,512	3,000	7,000	<4,000
	Knox	2,567	0	4,000	<5,000
	Blacks Creek	2,510	1,000	5,000	<5,000
South Boise	JR Flat	2,476	0	8,000	6,000
fan-to-lake transition	Market Street	2,382	0	8,000	6,000
deposits	McNabb	2,542	0	8,000	6,000
	MAC	2,372	0	11,000	9,000
	Amity	2,279	0	11,000	9,000
	Sunset West	2,295	0	9,000	7,000
	Edgeview	2,268	0	8,000	6,000
Below Unconformity	Micron Deep	2,266	7,000	13,000	11,000
deep deltaic deposits	Cassia 2	1,901	13,000	21,000	15,000
	Goddard 1	1,771	4,000	10,000	<10,000
	St. Luke's	1,890	7,000	13,000	9,000
Nampa and Caldwell	Lete	2,126	4,000	13,000	10,000
lacustrine deposits	Nampa 9	2,082	6,000	13,000	10,000
	Caldwell 16	2,012	5,000	13,000	10,000
Down-valley	Wright	1,898	35,000	47,000	42,000
lacustrine deposits	Johnson	2,010	28,000	38,000	32,000
	Keuspert	1,985	7,000	16,000	12,000
	Parma 10	2,036	24,000	31,000	26,000
	UofI	1,984	9,000	19,000	13,000

Table 5. Ground water residence times for principal aquifers in the Treasure Valley regional ground water system. Residence times are based on ^{14}C-age dates using the CMB and δ^{13}C-mixing models. Minimum and maximum represent the full range of possible recharge conditions, while best estimates are based on the δ^{13}C-mixing model combined with the most appropriate recharge conditions as described in the text.

8. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

8.1. Summary and Conclusions

The purpose of this study was to use principles of ground water geochemistry to refine the conceptual model of ground water recharge and flow in the Treasure Valley. Our objectives were to:

1. Describe hydrochemical characteristics of principal aquifers that comprise the regional ground water flow system.
2. Assess likely sources of recharge.
3. Examine patterns in dissolved ion concentrations and abundance of carbon isotopes along regional ground water flow paths.
4. Determine whether known geochemical processes describe the observed patterns.
5. Estimate residence times for regional ground waters.

To meet these objectives, the following tasks were completed:

1. Principal aquifers and associated mineral assemblages were delineated base on the work of previous researchers.
2. Thirty-eight ground water wells representing waters from the principal aquifers were identified and sampled.
3. Concentrations of a variety of dissolved constituents, including ^{3}H, were measured in all water samples; 28 samples representing deep, regional waters were analyzed for ^{14}C; and archived well cuttings from several deep wells were analyzed for carbon isotopes.
4. Spatial distributions of hydrochemical data were compared and used to substantiate the principal aquifer delineations.
5. Recharge sources were differentiated using ion chemistry and isotope-mixing models.
6. Likely regional flow paths were evaluated by observing patterns in dissolved ion concentrations and carbon isotope abundance, and by applying geochemical processes models.
7. Regional ground water residence-times were estimated from the measured abundance of ^{14}C.

Despite tremendous regional geologic complexity, results from the study show distinctive relationships between ground water chemistry and the unique depositional environments of the principal aquifers. These relationships are embodied in the following conclusions:

1. Tritium is non-existent in deeper, regional ground waters, except where poor well construction may allow inter-aquifer mixing. This finding indicates that ground water in deeper aquifers entered the flow regime prior to atmospheric nuclear testing during the 1950s and 1960s.
2. Specific conductance (and by inference, total dissolved solids) is greatest in shallow alluvial aquifers and decreases with depth. This finding indicates that water in deeper aquifers did not enter the ground water regime through the carbon-rich sediments found in Treasure Valley soils.
3. Concentrations of major ions and other dissolved constituents vary consistently with depth among aquifer zones. The high degree of consistency suggests that these hydrochemical data can be used to identify discrete aquifer zones in other areas of the basin.
4. Comparisons between measured constituents and established models of geochemical processes show that (1) ground water near the northeastern basin margin has experienced little interaction with aquifer minerals, and (2) ground water beyond the northeastern basin margin has experienced substantial interaction with aquifer minerals. Geochemical evolution of Treasure Valley ground water appears to be influenced by solution of both carbonate and silicate minerals.
5. Residence times of Treasure Valley ground water generally increase with depth and with distance along a regional east-to-west trending flow path. Residence times range from thousands to tens of thousands of years. The youngest waters entered the subsurface a few thousand years ago and are found along the northeastern boundary of the basin, adjacent to the Boise foothills. The oldest waters entered the subsurface between 20,000 and 40,000 years ago and are found in the western reaches of the basin near the Snake River. Ground water in the deep deltaic aquifers beneath Boise was recharged between 10,000 and 20,000 years ago. The proximity of these paleo-ground waters to the mountain front recharge area suggests that these aquifers sustain little natural flow.
6. Contemporary seepage from rivers and/or irrigation diversions is not the primary source of recharge for most deeper, regional aquifers. Paleo-river channels, fractured granite aquifers in the Idaho Batholith, and tributary sedimentary aquifers are the most likely sources of recharge to the regional flow system.

7. A strong relationship between concentrations of dissolved constituents and depositionally-defined aquifer units, the relevance of established geochemical principles to the apparent evolution of ground water geochemistry, and the general east-to-west increase of ground water residence times support a conceptual model of regional ground water flow consisting of (1) recharge in alluvial sediments in southeast Boise and at the base of the mountain front north of Boise, (2) movement of ground water from the recharge areas into the deeper Boise area fluvio-lacustrine aquifers, and (3) movement of ground water from the Boise area aquifers into regional deep-lake aquifers of Nampa and Caldwell. Although not specifically addressed in this study, a reasonable extension of this conceptual model includes regional upwelling at the distal end of the basin and removal of discharging ground water via surface drains to the Boise River system.

8.2. Recommendations

This study of regional-scale geochemistry in the Treasure Valley has provided new insight into basin recharge and flow-system processes. The following recommendations are offered as guidance toward aspects of the ground water system that warrant additional attention.

1. <u>Recharge along the Boise Front</u>. The present study underscores the inherent complexity of basin recharge and suggests that the basin/batholith interface plays an important role in the distribution of recharge of water to Boise area aquifers. Quantifying the contribution of natural recharge to Boise area aquifers from the various sources along the Boise mountain front would provide important information about the long-term impacts of present and future development in these aquifers. This information could be obtained using multi-level monitoring wells (e.g., Marden Lane), additional ground water level data, additional geophysical and stratigraphic work, and a recharge-focused geochemistry study.
2. <u>Recharge and hydraulic connection in southeast Boise</u>. The southeast Boise alluvial fan aquifers have been an area of recent concern because of depressed ground water levels. Using additional stratigraphic interpretations and geochemical work to (1) identify sources of recharge and (2) understand the connection of the alluvial fan to other Boise area aquifers would enhance the scientific basis for sound aquifer management. Related subjects of interest include identifying sources of elevated nitrate in water containing no tritium and evaluating the hydraulic connection of the southeast Boise aquifers to the Boise River system above the New York Canal diversion.
3. <u>Discharge from down-valley aquifers</u>. Regional ground water flow in the Treasure Valley appears to be constrained at the discharge end of the basin.

That is, fine-grained sediments at the western reaches of the basin may be the primary control on the amount of water moving through the system. Water level and hydrochemistry data obtained from the recently drilled multi-level monitoring well in Caldwell provide the first appropriate data for evaluating this theory. Similar wells in Nampa, Notus, and Parma would provide key information for a more complete understanding of regional discharge.

4. <u>Improved estimates of ground water residence times</u>. Regional-scale estimates of ground water residence times require broad assumptions about ground water flow and basin geochemistry. With more localized study, it is possible to address these assumptions with greater resolution and to improve estimates of ground water residence times. A focus on establishing residence times for smaller portions of the regional system may benefit from using a new inverse mass balance approach to evaluating ground water chemistry and isotope compositions (Zhu and Murphy, 2000). Inverse mass balance models can be developed for ground water flow between a series of wells along a flow path based on local geology, mineralogy, petrographic information, saturation indices, and specific knowledge about mineral dissolution.

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Appendix 1

Well Information and Laboratory Analyses of Water Samples

Well Name	Owner	USGS Station Name	LAT deg	LAT min	LAT sec	LON deg	LON min	LON sec	T	R	Sec
Christiansen	Micron Corporation	Christiansen Replacement	43	31	50	116	6	18	02N	03E	09BAA2
Blacks Creek	Idaho Deptartment of Transportation	Blacks Creek Rest Area	43	28	41	116	6	28	02N	03E	28CAC1
Blacks Creek	Idaho Deptartment of Transportation	Blacks Creek Rest Area	43	28	41	116	6	28	02N	03E	28CAC1
Guyer	Vern Guyer	Guyer-new deepened	43	31	39	116	6	34	02N	03E	09BCA2
Micron Shallow	Micron Corporation	Micron Shallow Monitor	43	31	37	116	8	43	02N	03E	07DBB1
Micron Deep	Micron Corporation	Micron Deep Monitor	43	31	37	116	8	46	02N	03E	07DBB2
Micron No. 5[1]	Micron Corporation	Micron No. 5	43	31	42	116	8	0	02N	03E	07ACD1
Knox	Tim Knox	Tim Knox	43	30	50	116	8	50	02N	03E	18BAC1
Market St.	United Water Idaho	BWC Market St.	43	33	34	116	11	6	03N	02E	35BAB1
JR Flat	United Water Idaho	BWC J.R. Flat Prod.	43	32	33	116	11	32	02N	02E	02BBC2
McNabb	Walter McNabb	1333 Lk Hazel	43	32	43	116	11	45	02N	02E	03AAB2
Cassia No. 1	United Water Idaho	UWID Cassia No. 1	43	35	47	116	12	53	03N	02E	16DAA1
Cassia No. 2	United Water Idaho	UWID Cassia No. 2	43	35	47	116	12	53	03N	02E	16DAA2
Cassia Monitor	United Water Idaho	UWID Cassia Monitor	43	35	47	116	12	53	03N	02E	16DAA3
MAC[2]	United Water Idaho	BWC MAC	43	33	26	116	15	8	03N	02E	32BBC1
Sunset West	United Water Idaho	BWC Sunset West	43	33	4	116	16	24	03N	01E	36DAD1
Amity	United Water Idaho	BWC Amity	43	33	40	116	16	54	03N	01E	36ABB1
Westmoreland[2]	United Water Idaho	BWC Westmoreland	43	38	21	116	16	11	04N	02E	31CBD1
Goddard No. 1[2]	United Water Idaho	BWC Goddard No. 1	43	38	43	116	17	16	04N	01E	36BAC1
Goddard No. 2[2]	United Water Idaho	BWC Goddard No. 2	43	38	42	116	17	16	04N	01E	36BAC2
TVHP No. 1	TVHP, State Street, Star	TVHP No. 1-zone 1	43	40	48	116	18	44	04N	01E	14CCB1
TVHP No. 2	TVHP, State Street, Star	TVHP No. 1-zone 2	43	40	48	116	18	44	04N	01E	14CCB2
TVHP No. 3	TVHP, State Street, Star	TVHP No. 1-zone 3	43	40	48	116	18	44	04N	01E	14CCB3
TVHP No. 4	TVHP, State Street, Star	TVHP No. 1-zone 4	43	40	48	116	18	44	04N	01E	14CCB4
HP	United Water Idaho	HP	43	39	22	116	19	2	04N	01E	27ADC1
Edgview	United Water Idaho	S. Co. Braddock (Edgeview)	43	35	58	116	20	2	03N	01E	16ADDA1
Edgview	United Water Idaho	S. Co. Braddock (Edgeview)	43	35	58	116	20	2	03N	01E	16ADDA1
St. Lukes	Saint Lukes Hospital	St. Lukes Med. Ctr.-887'	43	36	5	116	21	0	03N	01E	16BCA1
Meridian No. 15	City of Meridian, 8th St., Meridian	Meridian No. 15	43	37	3	116	24	48	03N	01W	11AADA1
Meridian No. 19-Test	City of Meridian, UstickxTen Mile	Meridian No. 19-Test	43	37	30	116	25	0	03N	01W	03AAA2
Meridian No. 19	City of Meridian, UstickxTen Mile	Meridian No. 19-Production	43	37	30	116	25	0	03N	01W	03AAA3
Schwisow	Duane Schwisow	4410 N. Star Rd., Nampa	43	33	30	116	29	20	03N	01W	32BBD1
Nampa No. 12	City of Nampa	Nampa No. 12	43	35	47	116	31	10	03N	02W	13DBBD1
State Hospital	State of Idaho	ID SS & State Hosp. No. 4	43	36	9	116	31	58	03N	02W	14ADA1
Lete	Inake Lete	3212 S. Stanford	43	32	18	116	34	54	02N	02W	04DBB1
Nampa No. 9	City of Nampa	Nampa No. 9	43	36	2	116	36	38	03N	02W	17BCB1
Caldwell No. 16	City of Caldwell	Caldwell No. 16 (Valley View School)	43	37	24	116	40	54	03N	03W	03DBC2
Caldwell No. 15	City of Caldwell	Caldwell No. 15	43	38	23	116	41	25	04N	03W	34CBB1
Johnson	Travis Johnson	21381 Hwy 20-26	43	43	49	116	49	11	05N	04W	33ACBA1
Wright	George Wright, 21626 Howe Rd, Caldwell	SQW-Wright	43	42	25	116	49	31	04N	04W	04CDC1
Kuespert	Paul Kuespert	25595 Don Lane	43	44	43	116	50	49	05N	04W	29BCAA1
Parma No. 10	City of Parma	Parma No. 10	43	47	33	116	56	15	05N	05W	04DCD1
Inouye	Kris Inouye	23605 Rodeo Lane	43	42	52	116	56	30	04N	05W	04BDD1
U of I	University of Idaho	Parma Research Sta.	43	48	5	116	56	30	05N	05W	04BDDA1

Well Name	Land Surf Elev ft (NGVD)	Total Depth ft	DTW ft	WL Elev[3] ft	TWBZ ft	TWBZ Elev[3] ft	BWBZ ft
Christiansen	3140	522	485	2655	504	2636	514
Blacks Creek	3355	975	672	2683	845	2510	900
Blacks Creek							
Guyer	3135	620	494	2641	570	2565	620
Micron Shallow	3067	561	491	2576	555	2512	nd
Micron Deep	3066	811	501	2565	800	2266	nd
Micron No. 5[1]	3088	1217	475	2613	598	2490	1212
Knox	3070	642	371	2699	503	2567	642
Market St.	2892	944	270	2622	510	2382	912
JR Flat	2911	567	258	2653	435	2476	536
McNabb	2910	395	0	2910	368	2542	392
Cassia No. 1	2751	410	75	2676	200	2551	400
Cassia No. 2	2751	1124	150	2601	850	1901	1105
Cassia Monitor	2751	1088	120	2631	525	2226	605
MAC[2]	2790	525	115	2675	418	2372	525
Sunset West	2810	620	120	2690	515	2295	603
Amity	2798	675	120	2678	519	2279	670
Westmoreland[2]	2683	900	25	2658	800	2373	901
Goddard No. 1[2]	2673	1005	12	2661	902	1771	960
Goddard No. 2[2]	2673	551	41	2632	474	2199	545
TVHP No. 1	2582	1005	-1	2583	300	2282	340
TVHP No. 2	2582	1005	-0.7	2583	270	2312	290
TVHP No. 3	2582	1005	0.5	2582	210	2372	250
TVHP No. 4	2582	1005	2.4	2580	130	2452	170
HP	2645	700	15	2630	580	2065	700
Edgview	2680	495	21	2659	412	2268	477
Edgview							
St. Lukes	2660	902	3.2	2657	770	1890	900
Meridian No. 15	2570	765	0	2570	465	2105	765
Meridian No. 19-Test	2550	1040	-4.7	2555	340	2210	420
Meridian No. 19	2550	732	-22.5	2573	540	2010	732
Schwisow	2555	456	-1	2556	454	2101	nd
Nampa No. 12	2570	602	72	2498	404	2166	598
State Hospital	2558	560	65	2493	377	2181	544
Lete	2570	458	80	2490	444	2126	nd
Nampa No. 9	2450	461	110	2340	368	2082	460
Caldwell No. 16	2432	553	19	2413	420	2012	535
Caldwell No. 15	2420	600	32	2388	200	2220	460
Johnson	2300	290	2	2298	290	2010	nd
Wright	2285	420	-1	2286	387	1898	nd
Kuespert	2295	320	0	2295	310	1985	nd
Parma No. 10	2281	505	68	2213	245	2036	479
Inouye	2423	325	126	2297	317	2106	nd
U of I	2305	397	95	2210	321	1984	385

nd=no data

[1] data from Micron Corp.

[2] data from USGS

[3] Elevation Above Mean Sea Level

Well Name	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HCO3 mg/L	Cl mg/L	SO4 mg/L	F mg/L	SiO2 mg/L	NO3 mg/L	Fe ug/L	Mn ug/L	TDS[3] mg/L	USGS TDS mg/L	Hardness mg/L as CaCO3
Christiansen	15	4.1	15	1.4	84	4.8	7.8	0.3	44	1.51	10	4.3	133	141	55
Blacks Creek	21	5.2	19	1.5	120	4.3	6.9	0.27	44	1.81	7.5	1.5	170	167	75
Blacks Creek	21	5.1	19	1.5	120	5.2	7.2	0.27	44	1.87	5.5	1.9	171	162	73
Guyer	10	3.3	12	1.9	61	3.4	4.2	0.29	56	1.66	32	3	114	128	40
Micron Shallow	17	4.9	22	2	120	4.2	7	0.31	51	2.08	96	28	175	176	64
Micron Deep	5.2	0.063	45	0.62	100	4	11	0.82	27	1.65	10	1.6	147	155	13
Micron No. 5[1]	11.9	1.2	33.6	1.22	88	3.13	8.55	0.38	34.2	1.79	nd	nd	138	190	nd
Knox	19	5.2	15	1.1	97	5.7	7.5	0.34	46	1.93	10	1.5	150	156	69
Market St.	19	2.4	23	1.4	100	5.7	14	0.39	36	0.562	20	1.9	153	154	57
JR Flat	21	4.9	26	1.5	120	5.7	12	0.39	38	1.55	10	3	176	175	73
McNabb	20	4.4	33	1.9	130	9.9	20	0.57	40	0.997	10	3.8	199	197	68
Cassia No. 1	46	10	31	1.5	220	8.1	32	0.65	30	0.65	280	85	295	271	160
Cassia No. 2	3.5	0.04	42	0.39	110	3.7	7.2	1.3	29	0.05	5.5	7.7	149	140	9
Cassia Monitor	23	1.6	18	0.53	110	3.5	12	0.58	20	0.05	10	31	142	131	65
MAC[2]	30	6.2	32	1.2	169	9.4	33	0.5	25	0.05	16	200	236	219	100
Sunset West	27	5.7	33	1.3	150	8.5	24	0.38	32	0.182	10	3	216	204	91
Amity	33	8.9	32	1.4	160	9.7	44	0.53	31	0.104	5.5	13	247	237	120
Westmoreland[2]	18	2.7	11	1.1	94	0.7	9.3	0.4	38	0.05	54	94	131	127	56
Goddard No. 1[2]	19	2	18	2.3	127	1.2	2.5	0.4	48	0.05	100	140	167	156	56
Goddard No. 2[2]	44	8.3	13	1.8	169	18	32	0.3	37	0.91	6	30	250	239	140
TVHP No. 1	30	5.1	13	1.4	140	2.1	9.6	0.32	32	0.099	10	12	178	162	97
TVHP No. 2	29	5	12	1.4	130	2.7	8.9	0.32	32	0.091	5.5	8.4	168	155	93
TVHP No. 3	35	7.1	18	1.7	160	3.7	20	0.38	34	0.05	600	37	215	200	120
TVHP No. 4	35	4.8	21	1.3	170	4.4	7.8	0.39	32	0.05	20	40	212	188	110
HP	14	2.5	8.8	1.3	72	2	5.3	0.37	42	0.086	10	3.4	109	112	45
Edgview	32	6.5	20	1.9	140	9.7	30	0.43	43	0.084	320	71	218	211	110
Edgview	32	6.6	20	1.9	140	9.6	30	0.41	43	0.082	320	71	218	208	110
St. Lukes	20	3.4	17	2.3	130	2.7	1.4	0.4	50	0.052	270	230	173	163	64
Meridian No. 15	25	4.6	14	1.4	92	10	25	0.29	36	0.103	30	63	158	162	80
Meridian No. 19-Test	47	8.1	14	1.5	110	19	59	0.24	33	1.31	10	3	225	240	150
Meridian No. 19	14	2.1	11	0.87	75	1.3	4.7	0.35	32	0.05	35	131	104	104	44
Schwisow	12	2.2	9.5	0.91	63	0.58	2.9	0.34	33	0.174	10	3	90	94	40
Nampa No. 12	54	9.1	37	1.7	160	22	81	0.44	32	1.68	10	1.5	310	325	170
State Hospital	61	10	42	1.9	200	20	84	0.31	33	1.71	10	3	354	355	190
Lete	22	4.2	64	3	170	19	45	1.5	38	0.171	5.1	1.9	284	279	72
Nampa No. 9	14	3.6	33	2.7	130	6.8	8.1	0.94	39	0.363	10	3	182	172	51
Caldwell No. 16	20	2.4	34	2	140	9	14	0.59	27	0	23	5.7	190	177	61
Caldwell No. 15	56	12	52	4.5	190	38	89	0.35	36	1.92	10	3	375	393	190
Johnson	19	1.4	44	4.8	180	5.8	0.1	1.4	70	0.05	83	91	252	nd	52
Wright	17	1.7	63	7.2	220	5.7	0.1	1.9	80	0.05	79	114	308	nd	50
Kuespert	18	1.7	34	4.8	150	5.5	1	1.1	62	0.05	450	114	213	203	52
Parma No. 10	19	2.8	48	11	186	3.4	0.73	0.94	83	0.05	74	126	275	280	58
Inouye	53	5.2	45	13	241	7.9	65	0.78	82	0.05	127	131	401	391	150
U of I	20	2.4	27	7.2	160	2.7	2.1	0.74	67	0.05	86	125	222	206	59

nd=no data

[1] data from Micron Corp.

[2] data from USGS

[3] sum of dissolved constituents

Well Name	Ca mmol/L	Mg mmol/L	Na mmol/L	K mmol/L	HCO3 mmol/L	Cl mmol/L	SO4 mmol/L	F mmol/L	SiO2 mmol/L	NO3 mmol/L	TDS[3] mmol/L
Christiansen	0.374	0.169	0.652	0.036	1.377	0.135	0.081	0.016	0.733	0.108	3.681
Blacks Creek	0.524	0.214	0.826	0.038	1.967	0.121	0.072	0.014	0.733	0.129	4.639
Blacks Creek	0.524	0.210	0.826	0.038	0.000	0.146	0.075	0.014	0.733	0.134	2.701
Guyer	0.249	0.136	0.522	0.049	1.000	0.096	0.044	0.015	0.933	0.119	3.162
Micron Shallow	0.424	0.202	0.957	0.051	1.967	0.118	0.073	0.016	0.850	0.149	4.807
Micron Deep	0.130	0.003	1.957	0.016	1.639	0.113	0.114	0.043	0.450	0.118	4.582
Micron No. 51	0.297	0.049	1.461	0.031	1.439	0.088	0.089	0.020	0.570	0.128	4.173
Knox	0.474	0.214	0.652	0.028	1.590	0.161	0.078	0.018	0.767	0.138	4.119
Market St.	0.474	0.099	1.000	0.036	1.639	0.161	0.146	0.021	0.600	0.040	4.215
JR Flat	0.524	0.202	1.130	0.038	1.967	0.161	0.125	0.021	0.633	0.111	4.911
McNabb	0.499	0.181	1.435	0.049	2.131	0.279	0.208	0.030	0.667	0.071	5.549
Cassia No. 1	1.147	0.412	1.348	0.038	3.607	0.228	0.333	0.034	0.500	0.046	7.693
Cassia No. 2	0.087	0.002	1.826	0.010	1.803	0.104	0.075	0.068	0.483	0.004	4.463
Cassia Monitor	0.574	0.066	0.783	0.014	1.803	0.099	0.125	0.031	0.333	0.004	3.830
MAC2	0.748	0.255	1.391	0.031	2.770	0.265	0.343	0.026	0.417	0.004	6.250
Sunset West	0.673	0.235	1.435	0.033	2.459	0.239	0.250	0.020	0.533	0.013	5.890
Amity	0.823	0.366	1.391	0.036	2.623	0.273	0.458	0.028	0.517	0.007	6.522
Westmoreland2	0.449	0.111	0.478	0.028	1.541	0.020	0.097	0.021	0.633	0.004	3.382
Goddard No. 12	0.474	0.082	0.783	0.059	2.082	0.034	0.026	0.021	0.800	0.004	4.364
Goddard No. 22	1.097	0.342	0.565	0.046	2.770	0.507	0.333	0.016	0.617	0.065	6.358
TVHP No. 1	0.748	0.210	0.565	0.036	2.295	0.059	0.100	0.017	0.533	0.007	4.570
TVHP No. 2	0.723	0.206	0.522	0.036	2.131	0.076	0.093	0.017	0.533	0.007	4.343
TVHP No. 3	0.873	0.292	0.783	0.043	2.623	0.104	0.208	0.020	0.567	0.004	5.517
TVHP No. 4	0.873	0.198	0.913	0.033	2.787	0.124	0.081	0.021	0.533	0.004	5.566
HP	0.349	0.103	0.383	0.033	1.180	0.056	0.055	0.019	0.700	0.006	2.885
Edgview	0.798	0.267	0.870	0.049	2.295	0.273	0.312	0.023	0.717	0.006	5.609
Edgview	0.798	0.272	0.870	0.049	0.000	0.270	0.312	0.022	0.717	0.006	3.314
St. Lukes	0.499	0.140	0.739	0.059	2.131	0.076	0.015	0.021	0.833	0.004	4.516
Meridian No. 15	0.623	0.189	0.609	0.036	1.508	0.282	0.260	0.015	0.600	0.007	4.130
Meridian No. 19-Test	1.172	0.333	0.609	0.038	1.803	0.535	0.614	0.013	0.550	0.094	5.761
Meridian No. 19	0.349	0.086	0.478	0.022	1.230	0.037	0.049	0.018	0.533	0.004	2.806
Schwisow	0.299	0.091	0.413	0.023	1.033	0.016	0.030	0.018	0.550	0.012	2.486
Nampa No. 12	1.347	0.374	1.609	0.043	2.623	0.620	0.843	0.023	0.533	0.120	8.135
State Hospital	1.521	0.412	1.826	0.049	3.279	0.563	0.874	0.016	0.550	0.122	9.212
Lete	0.549	0.173	2.783	0.077	2.787	0.535	0.468	0.079	0.633	0.012	8.096
Nampa No. 9	0.349	0.148	1.435	0.069	2.131	0.192	0.084	0.049	0.650	0.026	5.133
Caldwell No. 16	0.499	0.099	1.478	0.051	2.295	0.254	0.146	0.031	0.450	0.000	5.302
Caldwell No. 15	1.397	0.494	2.261	0.115	3.115	1.070	0.926	0.018	0.600	0.137	10.133
Johnson	0.474	0.058	1.913	0.123	2.951	0.163	0.001	0.074	1.167	0.004	6.926
Wright	0.424	0.070	2.739	0.184	3.607	0.161	0.001	0.100	1.333	0.004	8.622
Kuespert	0.449	0.070	1.478	0.123	2.459	0.155	0.010	0.058	1.033	0.004	5.839
Parma No. 10	0.474	0.115	2.087	0.281	3.049	0.096	0.008	0.049	1.383	0.004	7.546
Inouye	1.322	0.214	1.957	0.332	3.951	0.223	0.676	0.041	1.367	0.004	10.086
U of I	0.499	0.099	1.174	0.184	2.623	0.076	0.022	0.039	1.117	0.004	5.836

nd=no data

[1] data from Micron Corp.

[2] data from USGS

[3] sum of dissolved constituents

Appendix 2

Calculation of DIC_{rech} and $\delta^{13}C_{rech}$ for Specified Recharge Conditions

Recharge Conditions: Boise Front Springs			pP_{CO2}	pH	T (C)				
			1.7	6.0	9				
pK_{CO2}	pK_1	$p[H_2CO_3]$	$p[HCO_3^-]$	**DIC_{rech}**	$\delta^{13}C$ Fractionation Factors				**$\delta^{13}C_{rech}$**
				mmol	$CO_{2(aq)}$-$CO_{2(g)}$	HCO_3-$CO_{2(g)}$	$CO_{2(g)}$-$CaCO_3$	DIC-$CO_{2(g)}$	**‰**
1.25	6.48	2.95	3.43	**1.50**	-1.10	9.70	12.79	1.58	**-21.42**

Recharge Conditions: Banner Cr. Wells			pP_{CO2}	pH	T (C)				
			2.2	6.6	8				
pK_{CO2}	pK_1	$p[H_2CO_3]$	$p[HCO_3^-]$	**DIC_{rech}**	$\delta^{13}C$ Fractionation Factors				**$\delta^{13}C_{rech}$**
				mmol	$CO_{2(aq)}$-$CO_{2(g)}$	HCO_3-$CO_{2(g)}$	$CO_{2(g)}$-$CaCO_3$	DIC-$CO_{2(g)}$	**‰**
1.23	6.49	3.43	3.32	**0.84**	-1.10	9.81	12.94	5.04	**-17.96**

Recharge Conditions: Boise River			pP_{CO2}	pH	T (C)				
			3.3	7.9	9				
pK_{CO2}	pK_1	$p[H_2CO_3]$	$p[HCO_3^-]$	**DIC_{rech}**	$\delta^{13}C$ Fractionation Factors				**$\delta^{13}C_{rech}$**
				mmol	$CO_{2(aq)}$-$CO_{2(g)}$	HCO_3-$CO_{2(g)}$	$CO_{2(g)}$-$CaCO_3$	DIC-$CO_{2(g)}$	**‰**
1.25	6.48	4.55	3.13	**0.77**	-1.10	9.70	12.79	9.31	**-13.69**

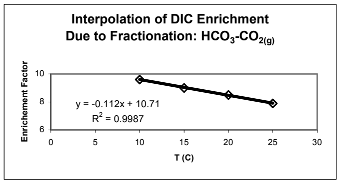
Notes:

(1) Equilibrium constants K_{CO2} and K_1 determined using regression equations shown on p. 117 of Clark and Fritz (1997).

(2) Fractionation factors for the transition from HCO_3 to $CO_{2(g)}$ and from $CO_{2(g)}$ to $CaCO_3$ determined from regressed data shown in Clark and Fritz (1997) Table 5-3. Regression data are plotted below.

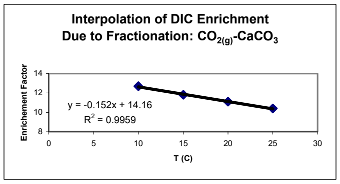
HCO_3-$CO_{2(g)}$

T(C)	$\varepsilon^{13}C$
10	9.6
15	9
20	8.5
25	7.9



$CO_{2(g)}$-$CaCO_3$

T(C)	$\varepsilon^{13}C$
10	12.7
15	11.8
20	11.1
25	10.4



Appendix 3

Ground Water ^{14}C-Age Corrections

Data Used for ^{14}C-Age Corrections

Well Name	Water Temp (deg C)	Field pH	^{14}C pmC	δ^{13}C ‰	Ca mmol/L	Mg mmol/L	Na mmol/L	K mmol/L	Cl mmol/L	SO4 mmol/L	HCO3 mmol/L	Chg Bal Error	ALK mmol/L	$DIC_{MassBal}$ mmol/L
Christiansen	20.4	7.8	60.14	-11.7	0.37	0.17	0.65	0.04	0.14	0.08	1.38	0.18	1.38	0.74
Blacks Creek	21.3	7.5	53.25	-12.8	0.52	0.21	0.83	0.04	0.12	0.07	1.97	0.18	1.9	1.04
Guyer	20.5	8.1	54.73	-13.1	0.25	0.14	0.52	0.05	0.10	0.04	1.00	0.20	1	0.58
Micron Shallow	21.9	7.4	43.53	-13.2	0.42	0.20	0.96	0.05	0.12	0.07	1.97	0.10	1.92	1.00
Micron Deep	24.4	8.2	20.17	-13.5	0.13	0.00	1.96	0.02	0.11	0.11	1.64	0.37	1.8	0.95
Knox	19.8	7.6	58.24	-12.5	0.47	0.21	0.65	0.03	0.16	0.08	1.59	0.23	1.6	0.87
Market St.	22.5	7.7	35.02	-12.8	0.47	0.10	1.00	0.04	0.16	0.15	1.64	0.24	1.64	0.86
JR Flat	19.5	7.6	36.15	-12.6	0.52	0.20	1.13	0.04	0.16	0.12	1.97	0.37	1.94	1.10
McNabb	18	7.6	36.67	-13.4	0.50	0.18	1.43	0.05	0.28	0.21	2.13	0.22	2.08	1.07
Cassia No. 2	30	8.6	8.02	-8.5	0.09	0.00	1.83	0.01	0.10	0.07	1.80	0.03	1.74	0.88
Cassia Monitor	20	8	63.72	-14.1	0.57	0.07	0.78	0.01	0.10	0.12	1.80	0.05	1.74	0.86
MAC	20	7.6	26.5	-14.1	0.75	0.26	1.39	0.03	0.26	0.34	2.77	0.05	2.7	1.24
Sunset West	20.1	7.8	33.93	-13.4	0.67	0.23	1.43	0.03	0.24	0.25	2.46	0.34	2.4	1.27
Amity	17.9	7.6	27.91	-15	0.82	0.37	1.39	0.04	0.27	0.46	2.62	0.45	2.54	1.31
Westmoreland	20.5	7.3	70.7	-12.6	0.45	0.11	0.48	0.03	0.02	0.10	1.54	-0.03	1.5	0.71
Goddard No. 1	23.5	7.8	28.5	-7.8	0.47	0.08	0.78	0.06	0.03	0.03	2.08	-0.19	2.04	0.93
Goddard No. 2	17.5	6.8	79.1	-15.5	1.10	0.34	0.57	0.05	0.51	0.33	2.77	-0.12	2.68	1.16
TVHP No. 1	15.7	7.1	92.12	-14.6	0.75	0.21	0.57	0.04	0.06	0.10	2.30	0.06	2.26	1.13
HP	19.9	7.3	68.88	-13.5	0.35	0.10	0.38	0.03	0.06	0.06	1.18	0.03	1.18	0.58
Edgview	18.7	7.5	35.32	-12.5	0.80	0.27	0.87	0.05	0.27	0.31	2.30	0.17	2.22	1.08
St. Lukes	19.8	7.7	14.92	-7.9	0.50	0.14	0.74	0.06	0.08	0.01	2.13	-0.15	2.16	0.99
Meridian No. 15	19.9	7.7	63.54	-13.6	0.62	0.19	0.61	0.04	0.28	0.26	1.51	0.22	1.5	0.73
Meridian No. 19	19.8	8	60.95	-13	0.35	0.09	0.48	0.02	0.04	0.05	1.23	0.06	1.24	0.62
Schwisow	13.6	8.5	77.96	-13.7	0.30	0.09	0.41	0.02	0.02	0.03	1.03	0.14	1.04	0.57
Lete	18.2	7.8	18.65	-11.38	0.55	0.17	2.78	0.08	0.54	0.47	2.79	0.51	2.72	1.42
Nampa No. 9	24.1	7.7	19.68	-12.2	0.35	0.15	1.43	0.07	0.19	0.08	2.13	0.09	2.08	1.07
Caldwell No. 16	20.6	8.2	20.4	-12.1	0.50	0.10	1.48	0.05	0.25	0.15	2.30	0.03	2.28	1.09
Johnson	16.5	7.9	1.02	-10	0.47	0.06	1.91	0.12	0.16	0.00	2.95	-0.02	2.9	1.47
Wright	19.2	7.9	0.32	-9.4	0.42	0.07	2.74	0.18	0.16	0.00	3.61	0.14	3.6	1.87
Kuespert	16.9	8	14.86	-11.2	0.45	0.07	1.48	0.12	0.15	0.01	2.46	0.01	2.46	1.23
Parma No. 10	24.3	7.8	1.23	-5.3	0.47	0.12	2.09	0.28	0.10	0.01	3.05	0.39	3.72	1.72
U of I	19.6	8.1	10.61	-9.5	0.50	0.10	1.17	0.18	0.08	0.02	2.62	-0.17	2.6	1.22

Calculation of DIC derived from matrix exchange processes

	Total DIC derived from exchange with aquifer carbonates	**Portion of total DIC derived from CO_2 exchange in soil zone**					
		Boise Front Springs		*Banner Creek Wells*		*Boise River*	
		$CO_{2(g)}$-$CaCO_3$	*12.79*	$CO_{2(g)}$-$CaCO_3$	*12.94*	$CO_{2(g)}$-$CaCO_3$	*12.79*
		$\delta^{13}C_{carb}$	$\delta^{13}C_{carb}$	$\delta^{13}C_{carb}$	$\delta^{13}C_{carb}$	$\delta^{13}C_{carb}$	$\delta^{13}C_{carb}$
		0	*-5*	*0*	*-5*	*0*	*-5*
Well Name	**DIC_{carb} (mmol)**	**$DIC_{CO2\text{-}exch}$ (mmol)**					
Christiansen	0.74	0.04	-0.07	0.04	-0.07	0.04	-0.07
Blacks Creek	1.04	0.11	-0.05	0.11	-0.04	0.11	-0.05
Guyer	0.58	0.10	0.02	0.09	0.02	0.10	0.02
Micron Shallow	1.00	0.10	-0.04	0.10	-0.04	0.10	-0.04
Micron Deep	0.95	0.17	0.05	0.17	0.05	0.17	0.05
Knox	0.87	0.09	-0.03	0.09	-0.03	0.09	-0.03
Market St.	0.86	0.09	-0.04	0.09	-0.04	0.09	-0.04
JR Flat	1.10	0.14	-0.02	0.14	-0.02	0.14	-0.02
McNabb	1.07	0.12	-0.04	0.12	-0.04	0.12	-0.04
Cassia No. 2	0.88	-0.17	-0.33	-0.16	-0.33	-0.17	-0.33
Cassia Monitor	0.86	0.11	-0.02	0.11	-0.02	0.11	-0.02
MAC	1.24	0.11	-0.08	0.11	-0.08	0.11	-0.08
Sunset West	1.27	0.16	-0.02	0.16	-0.02	0.16	-0.02
Amity	1.31	0.25	0.08	0.25	0.08	0.25	0.08
Westmoreland	0.71	0.01	-0.11	0.01	-0.11	0.01	-0.11
Goddard No. 1	0.93	-0.28	-0.48	-0.28	-0.48	-0.28	-0.48
Goddard No. 2	1.16	0.16	0.00	0.16	0.00	0.16	0.00
TVHP No. 1	1.13	0.19	0.03	0.19	0.03	0.19	0.03
HP	0.58	0.06	-0.03	0.06	-0.03	0.06	-0.03
Edgview	1.08	0.02	-0.15	0.02	-0.15	0.02	-0.15
St. Lukes	0.99	-0.27	-0.47	-0.27	-0.47	-0.27	-0.47
Meridian No. 15	0.73	0.08	-0.03	0.08	-0.03	0.08	-0.03
Meridian No. 19	0.62	0.05	-0.04	0.05	-0.04	0.05	-0.04
Schwisow	0.57	0.10	0.02	0.10	0.02	0.10	0.02
Lete	1.42	0.00	-0.22	0.00	-0.22	0.00	-0.22
Nampa No. 9	1.07	0.04	-0.12	0.04	-0.12	0.04	-0.12
Caldwell No. 16	1.09	0.00	-0.18	0.00	-0.17	0.00	-0.18
Johnson	1.47	-0.13	-0.39	-0.13	-0.39	-0.13	-0.39
Wright	1.87	-0.17	-0.50	-0.17	-0.49	-0.17	-0.50
Kuespert	1.23	-0.02	-0.22	-0.02	-0.22	-0.02	-0.22
Parma No. 10	1.72	-0.40	-0.75	-0.40	-0.75	-0.40	-0.75
U of I	1.22	-0.21	-0.44	-0.21	-0.44	-0.21	-0.44

Corrected Values of $^{14}C_{rech}$ Used in Ground Water Age Calculations Based on Boise Front Spring Recharge Conditions

Recharge Conditions	pP_{CO2}	pH	T(C)	$\delta^{13}C_{carb}$	DIC_{rech}
Boise Front Springs	1.7	6.0	9	0	1.50

Well Name	Uncorrected	CMB-ALK	CMB-CHEM	δ^{13}C-Mixing $\delta^{13}C_{rech}$ (‰)		MATEXCH
				-23.0	-21.4	
		closed system (Tamers, 1975)	closed system (Fontes and Garnier, 1979)	closed system (Pearson, 1965)[1]	open and closed system (Pearson, 1965)[2]	open and closed system (Fontes and Garnier, 1979; 1981)
Christiansen	100	108.9	67.0	50.9	54.7	49.3
Blacks Creek	100	76.3	59.1	55.7	59.8	52.7
Guyer	100	150.0	72.2	57.0	61.2	51.7
Micron Shallow	100	76.3	60.1	57.4	61.7	54.5
Micron Deep	100	91.5	61.3	58.7	63.1	52.8
Knox	100	94.3	63.3	54.3	58.4	51.1
Market St.	100	91.5	63.4	55.7	59.8	52.7
JR Flat	100	76.3	57.6	54.8	58.9	50.9
McNabb	100	70.4	58.3	58.3	62.6	55.2
Cassia No. 2	100	83.2	63.0	37.0	39.7	42.0
Cassia Monitor	100	83.2	63.5	61.3	65.9	58.0
MAC	100	54.1	54.8	61.3	65.9	59.2
Sunset West	100	61.0	54.1	58.3	62.6	54.7
Amity	100	57.2	53.4	65.2	70.1	59.8
Westmoreland	100	97.3	68.0	54.8	58.9	54.6
Goddard No. 1	100	72.0	61.6	33.9	36.4	41.5
Goddard No. 2	100	54.1	56.4	67.4	72.4	64.1
TVHP No. 1	100	65.4	57.1	63.5	68.2	58.9
HP	100	127.1	72.2	58.7	63.1	56.0
Edgview	100	65.4	58.2	54.3	58.4	53.9
St. Lukes	100	70.4	60.4	34.3	36.9	41.3
Meridian No. 15	100	99.5	67.1	59.1	63.6	56.3
Meridian No. 19	100	122.0	70.8	56.5	60.7	54.1
Schwisow	100	145.2	72.5	59.6	64.0	54.3
Lete	100	53.8	51.5	49.5	53.2	49.4
Nampa No. 9	100	70.4	58.4	53.0	57.0	51.9
Caldwell No. 16	100	65.4	57.9	52.6	56.5	52.6
Johnson	100	50.8	50.6	43.5	46.7	45.9
Wright	100	41.6	44.5	40.9	43.9	43.4
Kuespert	100	61.0	54.9	48.7	52.3	49.1
Parma No. 10	100	49.2	46.6	23.0	24.8	30.4
U of I	100	57.2	55.2	41.3	44.4	45.7

[1] Assumes a value of $\delta^{13}C_{rech}$ equal to that of soil DIC, with no fractionation. This assumption may be reasonable for waters with pH<7.5.

[2] Fractionation factor estimated from regression of Table 5.3, Clark and Fritz (1997).

Corrected Values of $^{14}C_{rech}$ Used in Ground Water Age Calculations Based on Banner Creek Well Recharge Conditions

Recharge Conditions	pP_{CO2}	pH	T(C)	$\delta^{13}C_{carb}$	DIC_{rech}
Banner Cr. Wells	2.2	6.6	8	0	0.84

Well Name	Uncorrected	CMB-ALK	CMB-CHEM	δ^{13}C-Mixing $\delta^{13}C_{rech}$ (‰)		MATEXCH
				-23.0	-18.0	
		closed system (Tamers, 1975)	closed system (Fontes and Garnier, 1979)	closed system (Pearson, 1965)[1]	open and closed system (Pearson, 1965)[2]	open and closed system (Fontes and Garnier, 1979; 1981)
Christiansen	100	61.0	53.2	50.9	65.0	49.3
Blacks Creek	100	42.7	44.7	55.7	71.1	52.7
Guyer	100	84.0	59.2	57.0	72.8	51.7
Micron Shallow	100	42.7	45.7	57.4	73.3	54.5
Micron Deep	100	51.2	47.0	58.7	75.0	52.8
Knox	100	52.8	49.1	54.3	69.4	51.1
Market St.	100	51.2	49.3	55.7	71.1	52.7
JR Flat	100	42.7	43.2	54.8	70.0	50.9
McNabb	100	39.4	43.9	58.3	74.4	55.2
Cassia No. 2	100	46.6	48.8	37.0	47.2	42.0
Cassia Monitor	100	46.6	49.3	61.3	78.3	58.0
MAC	100	30.3	40.4	61.3	78.3	59.2
Sunset West	100	34.2	39.8	58.3	74.4	54.7
Amity	100	32.0	39.1	65.2	83.3	59.8
Westmoreland	100	54.5	54.3	54.8	70.0	54.6
Goddard No. 1	100	40.3	47.4	33.9	43.3	41.5
Goddard No. 2	100	30.3	42.0	67.4	86.1	64.1
TVHP No. 1	100	36.6	42.7	63.5	81.1	58.9
HP	100	71.2	59.3	58.7	75.0	56.0
Edgview	100	36.6	43.8	54.3	69.4	53.9
St. Lukes	100	39.4	46.0	34.3	43.9	41.3
Meridian No. 15	100	55.7	53.4	59.1	75.6	56.3
Meridian No. 19	100	68.3	57.6	56.5	72.2	54.1
Schwisow	100	81.3	59.6	59.6	76.1	54.3
Lete	100	30.1	37.2	49.5	63.2	49.4
Nampa No. 9	100	39.4	44.0	53.0	67.8	51.9
Caldwell No. 16	100	36.6	43.5	52.6	67.2	52.6
Johnson	100	28.5	36.4	43.5	55.6	45.9
Wright	100	23.3	30.9	40.9	52.2	43.4
Kuespert	100	34.2	40.6	48.7	62.2	49.1
Parma No. 10	100	27.5	32.8	23.0	29.4	30.4
U of I	100	32.0	40.8	41.3	52.8	45.7

[1] Assumes a value of $\delta^{13}C_{rech}$ equal to that of soil DIC, with no fractionation. This assumption may be reasonable for waters with pH<7.5.

[2] Fractionation factor estimated from regression of Table 5.3, Clark and Fritz (1997).

Corrected Values of $^{14}C_{rech}$ Used in Ground Water Age Calculations Based on Boise River Recharge Conditions

Recharge Conditions	pP_{CO2}	pH	T(C)	$\delta^{13}C_{carb}$	DIC_{rech}
Boise River	3.3	7.9	9	0	0.77

Well Name	Uncorrected	CMB-ALK	CMB-CHEM	δ^{13}C-Mixing $\delta^{13}C_{rech}$ (‰)		MATEXCH
				-23.0	-13.7	
		closed system (Tamers, 1975)	closed system (Fontes and Garnier, 1979)	closed system (Pearson, 1965)[1]	open and closed system (Pearson, 1965)[2]	open and closed system (Fontes and Garnier, 1979; 1981)
Christiansen	100	55.9	51.1	50.9	85.4	49.3
Blacks Creek	100	39.1	42.6	55.7	93.4	52.7
Guyer	100	77.0	57.1	57.0	95.6	51.7
Micron Shallow	100	39.1	43.6	57.4	96.4	54.5
Micron Deep	100	47.0	44.8	58.7	98.5	52.8
Knox	100	48.4	47.0	54.3	91.2	51.1
Market St.	100	47.0	47.1	55.7	93.4	52.7
JR Flat	100	39.1	41.1	54.8	92.0	50.9
McNabb	100	36.1	41.8	58.3	97.8	55.2
Cassia No. 2	100	42.7	46.7	37.0	62.0	42.0
Cassia Monitor	100	42.7	47.1	61.3	102.9	58.0
MAC	100	27.8	38.3	61.3	102.9	59.2
Sunset West	100	31.3	37.7	58.3	97.8	54.7
Amity	100	29.4	37.0	65.2	109.5	59.8
Westmoreland	100	50.0	52.1	54.8	92.0	54.6
Goddard No. 1	100	37.0	45.2	33.9	56.9	41.5
Goddard No. 2	100	27.8	39.9	67.4	113.1	64.1
TVHP No. 1	100	33.6	40.5	63.5	106.6	58.9
HP	100	65.2	57.2	58.7	98.5	56.0
Edgview	100	33.6	41.7	54.3	91.2	53.9
St. Lukes	100	36.1	43.9	34.3	57.7	41.3
Meridian No. 15	100	51.1	51.2	59.1	99.3	56.3
Meridian No. 19	100	62.6	55.5	56.5	94.9	54.1
Schwisow	100	74.6	57.5	59.6	100.0	54.3
Lete	100	27.6	35.2	49.5	83.1	49.4
Nampa No. 9	100	36.1	41.9	53.0	89.1	51.9
Caldwell No. 16	100	33.6	41.4	52.6	88.3	52.6
Johnson	100	26.1	34.4	43.5	73.0	45.9
Wright	100	21.4	29.1	40.9	68.6	43.4
Kuespert	100	31.3	38.5	48.7	81.8	49.1
Parma No. 10	100	25.3	31.0	23.0	38.7	30.4
U of I	100	29.4	38.8	41.3	69.3	45.7

[1] Assumes a value of $\delta^{13}C_{rech}$ equal to that of soil DIC, with no fractionation. This assumption may be reasonable for waters with pH<7.5.

[2] Fractionation factor estimated from regression of Table 5.3, Clark and Fritz (1997).

Corrected Ground Water ^{14}C-Ages Based on Boise Front Spring Recharge Conditions

Recharge Conditions	pP_{CO2}	pH	T(C)
Boise Front Springs	1.7	6.0	9

Well Name	uncorrected	CMB-ALK closed system (Tamers, 1975)	CMB-CHEM closed system (Fontes and Garnier, 1979)	δ^{13}C-mixing closed system (Pearson, 1965) for recharge waters w/ pH<7.5	δ^{13}C-mixing open and closed system (Pearson, 1965); fractionation factors calculated from Table 5.3	MATEXCH open and closed system (Fontes and Garnier, 1979; 1981)
Christiansen	4,204	4,911	896	-1,384	-788	-1,647
Blacks Creek	5,210	2,968	863	365	961	-93
Guyer	4,983	8,335	2,285	330	926	-478
Micron Shallow	6,876	4,634	2,661	2,285	2,881	1,858
Micron Deep	13,235	12,501	9,187	8,831	9,427	7,955
Knox	4,469	3,987	689	-572	24	-1,078
Market St.	8,674	7,940	4,912	3,829	4,425	3,372
JR Flat	8,412	6,170	3,850	3,437	4,033	2,825
McNabb	8,294	5,390	3,830	3,827	4,423	3,376
Cassia No. 2	20,860	19,337	17,043	12,630	13,226	13,697
Cassia Monitor	3,726	2,203	-33	-320	277	-774
MAC	10,979	5,906	6,003	6,934	7,530	6,639
Sunset West	8,936	4,849	3,857	4,469	5,065	3,946
Amity	10,550	5,930	5,366	7,017	7,613	6,303
Westmoreland	2,866	2,644	-324	-2,109	-1,513	-2,143
Goddard No. 1	10,377	7,667	6,376	1,438	2,034	3,107
Goddard No. 2	1,938	-3,134	-2,791	-1,324	-728	-1,737
TVHP No. 1	679	-2,837	-3,961	-3,079	-2,483	-3,690
HP	3,082	5,063	393	-1,323	-727	-1,712
Edgview	8,604	5,088	4,134	3,563	4,159	3,496
St. Lukes	15,728	12,824	11,554	6,893	7,489	8,415
Meridian No. 15	3,749	3,704	456	-595	1	-994
Meridian No. 19	4,093	5,737	1,239	-624	-27	-989
Schwisow	2,058	5,144	-603	-2,225	-1,629	-2,989
Lete	13,883	8,762	8,390	8,066	8,662	8,050
Nampa No. 9	13,439	10,535	8,990	8,197	8,793	8,016
Caldwell No. 16	13,142	9,626	8,627	7,832	8,428	7,827
Johnson	37,907	32,314	32,270	31,022	31,618	31,472
Wright	47,491	40,238	40,789	40,093	40,690	40,596
Kuespert	15,761	11,675	10,806	9,812	10,408	9,886
Parma No. 10	36,360	30,495	30,050	24,225	24,821	26,519
U of I	18,546	13,926	13,636	11,236	11,832	12,073

Corrected Ground Water ^{14}C-Ages Based on Banner Creek Well Recharge Conditions

Recharge Conditions	pP_{CO2}	pH	T(C)
Banner Cr. Wells	2.2	6.6	8

Well Name	uncorrected	CMB-ALK closed system (Tamers, 1975)	CMB-CHEM closed system (Fontes and Garnier, 1979)	δ^{13}C-mixing closed system (Pearson, 1965) for recharge waters w/ pH<7.5	δ^{13}C-mixing open and closed system (Pearson, 1965); fractionation factors calculated from Table 5.3	MATEXCH open and closed system (Fontes and Garnier, 1979; 1981)
Christiansen	4,204	117	-1,009	-1,384	642	-1,647
Blacks Creek	5,210	-1,825	-1,440	365	2,391	-93
Guyer	4,983	3,542	650	330	2,356	-478
Micron Shallow	6,876	-159	405	2,285	4,312	1,858
Micron Deep	13,235	7,708	6,992	8,831	10,857	7,955
Knox	4,469	-807	-1,406	-572	1,455	-1,078
Market St.	8,674	3,146	2,824	3,829	5,856	3,372
JR Flat	8,412	1,377	1,472	3,437	5,463	2,825
McNabb	8,294	597	1,485	3,827	5,854	3,376
Cassia No. 2	20,860	14,544	14,935	12,630	14,657	13,697
Cassia Monitor	3,726	-2,590	-2,119	-320	1,707	-774
MAC	10,979	1,113	3,489	6,934	8,960	6,639
Sunset West	8,936	56	1,312	4,469	6,496	3,946
Amity	10,550	1,137	2,787	7,017	9,043	6,303
Westmoreland	2,866	-2,150	-2,180	-2,109	-82	-2,143
Goddard No. 1	10,377	2,874	4,197	1,438	3,464	3,107
Goddard No. 2	1,938	-7,927	-5,225	-1,324	702	-1,737
TVHP No. 1	679	-7,631	-6,364	-3,079	-1,052	-3,690
HP	3,082	270	-1,239	-1,323	704	-1,712
Edgview	8,604	294	1,788	3,563	5,589	3,496
St. Lukes	15,728	8,031	9,313	6,893	8,920	8,415
Meridian No. 15	3,749	-1,089	-1,442	-595	1,432	-994
Meridian No. 19	4,093	944	-469	-624	1,403	-989
Schwisow	2,058	350	-2,221	-2,225	-198	-2,989
Lete	13,883	3,969	5,718	8,066	10,092	8,050
Nampa No. 9	13,439	5,742	6,651	8,197	10,223	8,016
Caldwell No. 16	13,142	4,832	6,265	7,832	9,858	7,827
Johnson	37,907	27,520	29,557	31,022	33,048	31,472
Wright	47,491	35,445	37,795	40,093	42,120	40,596
Kuespert	15,761	6,881	8,299	9,812	11,839	9,886
Parma No. 10	36,360	25,702	27,155	24,225	26,252	26,519
U of I	18,546	9,133	11,143	11,236	13,263	12,073

Corrected Ground Water ^{14}C-Ages Based on Boise Front Spring Recharge Conditions

Recharge Conditions	pP_{CO2}	pH	T(C)
Boise River	3.3	7.9	9

Well Name	uncorrected	CMB-ALK closed system (Tamers, 1975)	CMB-CHEM closed system (Fontes and Garnier, 1979)	δ^{13}C-mixing closed system (Pearson, 1965) for recharge waters w/ pH<7.5	δ^{13}C-mixing open and closed system (Pearson, 1965); fractionation factors calculated from Table 5.3	MATEXCH open and closed system (Fontes and Garnier, 1979; 1981)
Christiansen	4,204	-602	-1,353	-1,384	2,899	-1,647
Blacks Creek	5,210	-2,545	-1,845	365	4,648	-93
Guyer	4,983	2,822	349	330	4,613	-478
Micron Shallow	6,876	-878	7	2,285	6,568	1,858
Micron Deep	13,235	6,988	6,602	8,831	13,114	7,955
Knox	4,469	-1,526	-1,779	-572	3,711	-1,078
Market St.	8,674	2,427	2,451	3,829	8,112	3,372
JR Flat	8,412	657	1,056	3,437	7,720	2,825
McNabb	8,294	-122	1,074	3,827	8,111	3,376
Cassia No. 2	20,860	13,825	14,559	12,630	16,913	13,697
Cassia Monitor	3,726	-3,309	-2,491	-320	3,964	-774
MAC	10,979	394	3,053	6,934	11,217	6,639
Sunset West	8,936	-663	871	4,469	8,753	3,946
Amity	10,550	418	2,342	7,017	11,300	6,303
Westmoreland	2,866	-2,869	-2,516	-2,109	2,174	-2,143
Goddard No. 1	10,377	2,154	3,811	1,438	5,721	3,107
Goddard No. 2	1,938	-8,647	-5,649	-1,324	2,959	-1,737
TVHP No. 1	679	-8,350	-6,784	-3,079	1,205	-3,690
HP	3,082	-449	-1,539	-1,323	2,960	-1,712
Edgview	8,604	-425	1,376	3,563	7,846	3,496
St. Lukes	15,728	7,312	8,917	6,893	11,176	8,415
Meridian No. 15	3,749	-1,809	-1,786	-595	3,689	-994
Meridian No. 19	4,093	224	-782	-624	3,660	-989
Schwisow	2,058	-369	-2,519	-2,225	2,058	-2,989
Lete	13,883	3,249	5,260	8,066	12,349	8,050
Nampa No. 9	13,439	5,023	6,241	8,197	12,480	8,016
Caldwell No. 16	13,142	4,113	5,851	7,832	12,115	7,827
Johnson	37,907	26,801	29,092	31,022	35,305	31,472
Wright	47,491	34,725	37,291	40,093	44,377	40,596
Kuespert	15,761	6,162	7,864	9,812	14,095	9,886
Parma No. 10	36,360	24,982	26,665	24,225	28,508	26,519
U of I	18,546	8,413	10,710	11,236	15,519	12,073

Costs associated with this publication are available from the Idaho Department of Water Resources in accordance with Section 60-202, *Idaho Code*. IDWR-21000-20-03/2004.