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Margot Truini
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THESIS APPROVAL

The abstract and thesis of Margot Truini for the Master of Science in Geology were presented February 16, 1996, and accepted by the thesis committee and the department.

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An abstract of the thesis of Margot Truini for the Master of Science in Geology presented February 16, 1996.

Title: The use of hydrochemistry to identify potential processes operating in the Saddle Mountains Basalt aquifer and the use of the nitrate-nitrogen isotope to distinguish between potential sources of nitrate to the shallow alluvial aquifer in the Lower Umatilla Basin, Oregon.

Nitrate concentration in excess of national drinking-water standards (10 mg/l) are present in the shallow alluvial aquifer and Saddle Mountains Basalt (SMB) aquifer in the Lower Umatilla Basin, Oregon. To determine sources responsible for elevated nitrate concentrations in the SMB aquifer mass-balance and reaction-path models (NETPATH and PHREEQE) were used to understand observed geochemical trends. Nitrate-nitrogen isotopes were used to distinguish potential nitrate sources in the shallow alluvial aquifer.

NETPATH-validated simple water/rock reactions in the SMB aquifers in Irrigon (dissolving glass, precipitating smectite, dissolving or precipitating calcite, and cation exchange) using constituents (calcium, magnesium, sodium and carbon). Diversity of composition for the shallow alluvial water and limited number of wells available made

obtaining a mass balanced solution for the SMB aquifer near Boardman impossible. Irrigon basalt groundwaters were consistent with the PHREEQE models prediction of natural hydrochemical trends, where Boardman basalt groundwaters plotted consistently with impacted alluvial groundwater.

Nitrogen-isotopic values of nitrate ($\delta^{15}\text{N}_{\text{NO}_3}$) were measured in the shallow alluvial groundwater from 17 wells in 4 land-use settings, 3 lysimeter samples and 1 surface water effluent sample. The landuse setting and corresponding average ranges for nitrate concentrations (as N) and $\delta^{15}\text{N}_{\text{NO}_3}$ values for wells near: commercial fertilizer-irrigated fields range from 25-87 mg/l, +3.5 to +4.6 per mil; explosive washout lagoons ranged from 10-18 mg/l, +4.6 to +4.9 per mil; potato waste water application ranged from 6.4-17.8 mg/l, +4.4 to +35 per mil; past confined animal feeding operations (CAFO) ranged from 16-56 mg/l, +4.9 to 10.4 per mil; lysimeters 5.4-39.9 mg/l, +9.1 to +21.9 per mil; surface water effluent ranged from 60-61 mg/l, +3.5 to 6.5 per mil; and varying landuse ranged from 9.3-19.5 mg/l, +2.7 to +7.1 per mil. Commercial fertilizer $\delta^{15}\text{N}_{\text{NO}_3}$ signatures are consistent for this source. Explosive $\delta^{15}\text{N}_{\text{NO}_3}$ values are consistent with an atmospheric signature. CAFO $\delta^{15}\text{N}_{\text{NO}_3}$ signatures probably result from mixing between currently applied commercial fertilizer and past CAFO's. High

$\delta^{15}\text{N}_{\text{NO}_3}$ signatures (+22 to +35 per mil) imply denitrification. Potato waste water and varying land-use $\delta^{15}\text{N}_{\text{NO}_3}$ signatures indicate probable mixing of nitrate-nitrogen sources in the groundwater.

THE USE OF HYDROCHEMISTRY TO IDENTIFY POTENTIAL
PROCESSES OPERATING IN THE SADDLE MOUNTAINS BASALT
AQUIFER AND THE USE OF THE NITRATE-NITROGEN ISOTOPE
TO DISTINGUISH BETWEEN POTENTIAL SOURCES OF NITRATE
TO THE SHALLOW ALLUVIAL AQUIFER IN THE LOWER
UMATILLA BASIN, OREGON

by

MARGOT TRUINI

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE
in
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TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	i
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
INTRODUCTION.....	1
Location and Geography of Study Area.....	2
Background.....	4
GEOLOGY.....	7
Stratigraphic Units.....	9
Columbia River Basalt and Ellensburg Formation..	9
Pleistocene Deposits.....	14
Geologic Structure.....	18
Groundwater Hydrology.....	19
Alluvial Unconfined Aquifer.....	19
Saddle Mountains Basalt Aquifer.....	22
METHODS.....	25
NITROGEN.....	28
The Nitrogen Cycle.....	31
Nitrogen Stable Isotopes.....	34
Isotopic Fractionation in the Soil Zone.....	38
DATA SECTION.....	44
Hydrochemistry Data.....	44
Common ion composition.....	48
Conceptual geochemical model.....	58
Simple geochemical model.....	62

NETPATH modeling concepts.....	66
PHREEQE modeling concepts.....	67
NETPATH results	69
NETPATH model for 11M01 and 17K01.....	74
UMA 165 TO UMA 28 and UMA 29.....	75
PHREEQE results.....	77
Nitrate-Nitrogen Isotopic Data.....	82
DISCUSSION.....	102
Geochemistry.....	102
Nitrate-Nitrogen Isotopic Analysis.....	104
CONCLUSION.....	117
REFERENCES.....	121

LIST OF TABLES

v

TABLE	PAGE
1 Common Ion Data.....	45
2 NETPATH Data and Stoichiometric Data for Glass, Smectite, and calcite.....	63
3 Data expressed as Activities for wells in Basalt and Alluvial Aquifers.....	71
4 Output for NETPATH model 11M01-17K01.....	74
5 Output for NETPATH model UMA 165-UMA 281....	75
6 Well Construction Data for selected wells...	84
7 Compilation of Nitrate-Nitrogen Isotopic Analysis.....	86

FIGURES	PAGE
1. Study Area Location.....	3
2. Stratigraphic Units in the Lower Umatilla Basin.....	8
3. Basalt flow zone stratigraphy and relation to groundwater.....	10
4. Geologic structure and surface geology...	13
5. Cross sections A-A' and B-B'.....	15
6. Pleistocene coarse grained facies and the potentiometric surface map for the shallow alluvial aquifer.....	20
7. Comparison of geologic and hydrologic units.....	21
8. General scheme for the transfer of nitrogen between the atmosphere, marine and terrestrial environments....	29
9. Mechanisms of nitrate formation.....	30
10. The nitrogen cycle.....	32
11. Chemical species found in the nitrogen cycle.....	35
12. Nitrate-Nitrogen isotopic ranges for $^{15}\text{N}_{\text{NO}_3}$ signatures.....	40
13. Location of wells used for geochemical evaluation of Saddle Mountains Basalt aquifer.....	47

14.	Divalent cations Ca^{2+} and Mg^{2+} versus total dissolved solids.....	vii 49
15.	Monovalent cations Na^{+} and K^{+} versus total dissolved solids.....	50
16.	Anions NO_3^{-} and SO_4^{2-} versus total dissolved solids.....	51
17.	Chloride versus total dissolved solids.....	52
18.	Piper diagram of common ion data for alluvial and basalt aquifers.....	56
19.	Saturation indexes for calcite and dolomite.....	72
20.	Stability relationship to demonstrate waters in equilibrium with smectite.....	73
21.	Perceived geochemical trends in the groundwater for calcium and sodium.....	79
22.	Perceived geochemical trends in groundwater for calcite and magnesium.....	81
23.	Location of wells used for nitrate-nitrogen isotopic sampling.....	87
24.	All the data for the ^{15}N -nitrogen isotopic study.....	88

25.	^{15}N -nitrate isotopic values for wells sample for the U. S. Army Depot.....	viii 90
26.	^{15}N -nitrogen isotopic values for wells sampled for argiculture fertilizer application.....	92
27.	^{15}N -nitrogen isotopic values for potato waste water application.....	93
28.	Denitrification curve for UMA 258.....	95
29.	^{15}N -nitrate isotopic values for wells sampled for confined animal feeding operations.....	98
30.	^{15}N -nitrate values down gradient from confined animal feeding operations and potato waste water.....	100

INTRODUCTION

Elevated levels of nitrate-nitrogen (greater than 10 mg/l) in the shallow alluvial and basalt aquifers in the Lower Umatilla Basin, Oregon, necessitated declaration of the region as a groundwater management area by the Oregon Department of Environmental Quality in 1990. High levels of nitrate in drinking water are of concern because of health hazards such as methemoglobinemia ("blue baby" disease) (Winton et al., 1971) and chronic toxicity and possible development of cancer from nitrosamine (U.S. Environmental Protection Agency, 1975). The Lower Umatilla Basin Groundwater Management Area is characterized by diverse land uses, some of which are potential nitrate sources such as: confined animal feeding operations (CAFO), septic systems, the application of food processing waste water, the application of commercial fertilizers to fields, and munitions storage for the Umatilla U.S. Army Depot.

The Oregon Department of Environmental Quality (DEQ), Oregon Water Resource Department (OWRD), and the Drinking Water Section for the Health Division (DWSHD) collectively worked with a citizens committee comprised of 20 citizens who live in the groundwater management

area to determine the sources of nitrate in the groundwater.

The purpose of this thesis is to identify processes affecting the groundwater chemistry of the Saddle Mountains Basalt (SMB) aquifer along with distinguishing land uses potentially contributing nitrate to the alluvial and basalt groundwater. These tasks: 1) employ the geochemical models NETPATH (Plummer et al., 1994) and PHREEQE (Parkhurst et al., 1990) to identify potentially operating processes that produced the observed groundwater compositions in the SMB aquifers; and 2) use the isotopic composition of nitrate-nitrogen in groundwater from the shallow alluvial aquifer to potentially distinguish differing land use sources of nitrate.

LOCATION AND GEOGRAPHY OF STUDY AREA

The study area is roughly 550 square miles (884 km²) in northern Morrow and Umatilla counties, Oregon. Boundaries consist of the Columbia River to the north, the township line between 2N and 3N to the south, the county line between Morrow and Gilliam counties to the west, and the range line between R29E and R30E to the east (figure 1). The study area is part of the Umatilla Lowlands, a portion of the Deschutes-Columbia Plateau

Figure 1. Location of study area.

physiographic province adjacent to the northern foothills of the Blue Mountains (Hogenson, 1964; Orr et al., 1992). Topography is basically a flat northward-sloping plain. Elevation ranges from 275 feet (84 m) to 700 feet (213 m).

The climate is semiarid and dry, with typically hot summers and cold winters. Average precipitation by water year (October through September) is 8.75 inches (222 mm) at Hermiston and believed similar for the entire study area. Most of the precipitation occurs in the winter months, October through March, as rain.

Access is provided by state, county, and local roads throughout the area.

BACKGROUND

Water quality data are used to understand the geochemical evolution of water along a groundwater flow path (Jacks, 1973; Edmunds et al., 1982; Plummer et al., 1990). Grondin and Nelson (1995) characterized the chemistry of groundwater from specific wells in the study area as a means of identifying potential geochemical processes contributing to elevated levels of calcium, sodium, magnesium, potassium, sulfate, chloride, and nitrate in the shallow alluvial aquifer. An important process identified by Grondin and Nelson

(1995) affecting groundwater composition is mixing of ambient groundwater with the infiltration of surface waters from irrigation, potato waste water effluent, septic tank effluent and explosives-washout lagoons, canals, and rivers.

Elevated concentrations of nitrate in the SMB aquifer suggest some of the wells constructed in the basalt aquifer are in hydraulic connection either naturally or aided by improper well construction, with the shallow alluvial aquifer. This suggests mixing of impacted alluvial groundwater with groundwater in basalt as an ongoing process affecting the hydrochemistry of the SMB aquifer in some locations.

To further distinguish the initial sources of nitrate to the alluvial groundwater, the delta value of the $^{15}\text{N}/^{14}\text{N}$ ratio relative to the atmospheric standard is employed as a useful tool to potentially discriminate among different nitrate sources. Nitrogen isotopes have been utilized to discriminate between suspected sources of nitrate in contaminated groundwater (Wolterink et al., 1979; Krietler, 1975; Krietler, 1979; Flipse et al., 1985; Spalding et al., 1982; Heaton, 1986; Komor et al., 1993). As Nitrogen compounds are altered chemically within a system, the stable isotopes ^{14}N and ^{15}N may undergo isotopic fractionation. Semiquantitative

distinctions between groundwater nitrate derived from human or animal waste, or cultivated sources such as inorganic fertilizers or soil organic nitrogen is possible on the basis of the $^{15}\text{N}/^{14}\text{N}$ ratio. Nitrogen isotopic compositions have also been used to characterize processes such as denitrification, recognized by a trend toward high $^{15}\text{N}/^{14}\text{N}$ ratio of the nitrate-nitrogen and low concentrations of nitrate (Mariotti et al., 1982; Mariotti et al., 1988; Myrold, 1990).

One other nitrate-nitrogen isotopic study has been conducted in the study area by Sweet, Edwards and Associates (1985), an environmental consulting firm. This nitrogen isotopic study was site-specific for one of the potato processing plants and looked at nitrate in the surface-water, unsaturated zone, and groundwater. Results from their study indicated the primary source of nitrogen contamination in the alluvial aquifer was waste-water irrigation.

GEOLOGY

The Lower Umatilla Basin is located in the southern edge of the Columbia Plateau, a regional downwarp between the Rocky Mountains and Cascade Range. The study area in the Lower Umatilla Basin is located at the south east margin of the Yakima Fold Belt, which is characterized by east-west trending sets of narrow anticlinal ridges and broad synclinal basins (Riedel et al., 1989). The Columbia Plateau is underlain by flood basalts of the Miocene Columbia River Basalt Group and Miocene-to-Holocene sediments.

From oldest to youngest, the principle stratigraphic units in the basin are the Columbia River Basalt Group, the Ellensburg Formation, the Alkali Canyon Formation, and what are interpreted to be Pleistocene catastrophic flood deposits (figure 2). Major structures in the Basin are the Dalles-Umatilla syncline, a structural trough forming the axis of the basin, and the Service anticline, a north-south trending fold and fault complex aligned with Umatilla and Emigrant Buttes (Wozniak, 1995). Unless otherwise cited primary citation for the following discussion is from the work of Wozniak (1995).

System	Series	Group	Formations	Age (Ma)	Member or Unit
Quaternary	Holocene		Surficial Sediments		Wind-blown Silt and Sand
			Holocene Alluvium		Alluvial Flood Plain Sediments
	Pleistocene		Pleistocene Deposits	.013 - ?	<div>Fine-grained Sediments</div> <div>Coarse-grained Sediments</div>
Tertiary	Pliocene		-?- -?- -?-		Erosional Unconformity
			Alkali Canyon		Undifferentiated Sediments
	Miocene	-?- -?- -?-		Local Erosional Unconformity	
		Columbia River Basalt Group	Saddle Mountains Basalt	10.5	Elephant Mountain Basalt
					Local Eros. Unconf. < Rattlesnake Ridge Interbed*
				12	Pomona Basalt
				Local Eros. Unconf. < Selah Interbed*	
				Umatilla Basalt	
				Local Eros. Unconf. < Mabton Interbed*	
Wanapum Basalt		14.5 - 15.6	Undifferentiated Basalt		
Grande Ronde Basalt	15.6 - 16.5				
				Ellensburg Formation	

Modified from Tolan and others, 1989.

* Ellensburg Formation

Figure 2. Stratigraphic units in the Lower Umatilla Basin.

STRATIGRAPHIC UNITS

Columbia River Basalt Group and Ellensburg Formation:

From the middle to late Miocene (17.5 to 6.0 Ma), extremely large outpourings of basaltic lavas flooded the Columbia Plateau. The outpourings are collectively called the Columbia River Basalt Group (Swanson et al., 1975). Most of the lava flows originated in southeastern Washington and northeastern Oregon (Davis-Smith et al., 1988). Decreasing volumes of successive basalt outpourings and concurrent regional evolution of folds and faults caused each successive flow to halt farther to the north, resulting in a thinning of the basalt sequences from south to north in Oregon. Magneto-telluric data suggest the basalt may be more than 2000 feet (610 m) thick in the Boardman area and greater than 10,000 feet (3050 m) thick in the center of the regional structural basin located in the Horse Heaven Hills region (Davis-Smith et al., 1988).

Basalt flows range from a few feet up to 298 feet (91 m) in thickness. Typically the flows are vertically jointed with a dense interior zone and a scoriaceous or brecciated zone at the top and bottom (figure 3). These porous zones between basalt flows have significance hydrologically and are called interflow zones (figure 3). Sedimentary beds ranging from a few feet to

Modified from Grondin et al., 1995.

Figure 3. Basalt flow zones stratigraphy and relation to groundwater.

more than 200 feet (61 m) thick may occur between the porous zones of neighboring flows. These interbeds are composed of clay, silt, and sand, with gravel in some areas. Because of the general pattern of diminishing volume between successive flows and increased time intervals between flows, the interbeds are thickest and most significant between the younger basalt flows. These sedimentary interbeds are known as the Ellensburg Formation (Schminke, 1967) (figure 2).

In the study area the Columbia River Basalt Group comprises three formations. From oldest to youngest they are, the Grande Ronde Basalt, Wanapum Basalt, and Saddle Mountains Basalt (Swanson et al., 1979). Each formation contains multiple members and each member contains one or more individual lava flows. The Grande Ronde and Wanapum Formations both occur at considerable depth in the study area and will not be discussed further in this thesis. The Saddle Mountains Basalt overlies the Wanapum Basalt and occurs near or at the surface in the study area.

Three members of the Saddle Mountains Basalt are relevant. From oldest to youngest these are the Umatilla, Pomona, and Elephant Mountain basalts (Swanson et al., 1979). There are three major sedimentary interbeds between flows of the Saddle Mountains Basalt.

The Rattlesnake Ridge interbed between the Elephant Mountain and Pomona Members; the Selah interbed between the Pomona and Umatilla Members; and the Mabton interbed between the Umatilla Member of the Saddle Mountains Basalt and the underlying Priest Rapids member of the Wanapum Formation (figure 2).

The Umatilla and older members of the Saddle Mountains Basalt do not crop out in the study area, but are penetrated by area wells. The Umatilla member is medium-to-dark gray, and aphyric. Correlations based on well log descriptions indicate the flow varies from 60 to 100 feet (18 to 30 m) thick.

The overlying Selah interbed contains vitric tuffs and weakly indurated siltstones which accumulated in the river bank and flood plains prior to the eruption of the Pomona Basalt (Schminke, 1967). The Selah interbed near Umatilla is 15 feet (4.6 m) thick and up to 147 feet (49 m) thick near Boardman. Driller's logs typically describe this interbed as blue or green clay.

The Pomona Member is exposed east of the Service anticline (figure 4). The basalt is light-to-medium gray, characterized by thick entablature with slender undulating columns, sparse phenocrysts of olivine and plagioclase, and scattered glomerocrysts of olivine and clinopyroxene. Outcrop and surface data suggest a

Figure 4. Showing the structure and surface geology in the study area with the cross-section lines A-A' and B-B', (Modified from Wozniack, 1995).

thickness of about 150 feet (45 m).

The Rattlesnake Ridge interbed is typically 10 to 20 feet (3 to 6 m) thick. Drill cuttings reveal silts, clays, and vitric tuffs commonly described as blue or green clays.

The Elephant Mountain Member is the youngest of the Columbia River Basalts in the study area. The flow(s) are exposed extensively west of Service Anticline. The basalt is aphyric and weathers to dark-gray or black. The maximum thickness of the flow(s) in the study area is 69 to 79 feet (21 to 24 m) near the Columbia River. The stratigraphic relation of the three members of the Saddle Mountains Basalt and interbeds across the study area are shown in cross sections A-A' and B-B' (figure 5; Wozniak, 1995).

Pleistocene Deposits:

In the Pleistocene Epoch, dams of glacial ice periodically blocked the drainage of the Clark Fork River in north Idaho near Purcel Lake. This damming of the river formed a large body of water known as glacial Lake Missoula (Waitt, 1985). Tremendous volumes of water released during episodic failure of the ice dam swept across southeastern Washington and down the Columbia River drainage basin (Bretz, 1969; Waitt, 1985).

Figure 5. Showing cross-section A-A' and B-B'
(Modified from Wozniack, 1995).

Each flood released a torrent of water that stripped the land of soil and sediments, scoured underlying rock surfaces, and deposited extensive tracks of boulders, gravels, sand, and silt. Faroquio et al. (1981) referred to these Pleistocene gravels and boulders as catastrophic flood deposits. Widespread sands and gravels were deposited in the lowlands of the Umatilla Basin. These deposits are the principle groundwater producing zones that overlie the Columbia River Basalt Group.

The flood deposits are divided into two assemblages: a predominately coarse-grained assemblage of boulders, gravels, and medium- to coarse-grained sands (Pscfc) and a predominately fine-grained assemblage of silts, fine-grained sands and clays with interbeds of sands and gravels (Pscff) (figure 5). These assemblages will be referred to as coarse-grained Pleistocene deposits and fine-grained Pleistocene deposits, respectively.

Coarse-grained Pleistocene deposits (Pscfc) occur at or near land surface in most of the Lower Umatilla Basin at elevations below 750 feet (228 m). Wozniak (1995) equates these sediments to the glacio-fluvial deposits of Hogenson (1964), the older alluvium of Robinson (1971), and the fluvial glacial deposits of

Walker (1973). The deposits typically occur as unconsolidated, poorly sorted, clast-supported gravels with lenticular interbeds of medium- to coarse-grained sand, or, as thick, cross-bedded sequences of fine- to coarse-grained sand with lenticular beds of gravel. Roughly 70 percent of the gravel clasts are angular fragments of basalt; the remaining are rounded fragments of granitic, metamorphic, and volcanic rocks which are not indigenous to the Umatilla Basin.

Fine-grained Pleistocene deposits (Pscff) occur at elevations between 748 and 1148 feet (228 and 350 m). Wozniak (1995) equates these deposits to pebbly silts described by Allison (1933) and mapped as glacial lake sediments by Hogenson (1964) and Walker (1973). The deposits typically occur as silts, fine silty sands, and clays with interbeds of sand and gravel. The total thickness of predominantly fine-grained Pleistocene deposits ranges up to 197 feet (60 m). Wozniak (1995) found that these sediments thicken away from the erosional troughs which are filled with thick accumulations of coarse-grained flood deposits.

GEOLOGIC STRUCTURE

The structural features that control the attitude of the Columbia River Basalts and geometry of the land surface are the Dalles-Umatilla syncline and the Service anticline (figure 4).

A regional topographic low in the area is controlled by the Dalles-Umatilla syncline (Newcomb, 1967) which appears to control the modern course of the Columbia River between Arlington and Umatilla, Oregon. In the study area, outcrop patterns and subsurface correlation indicate that the syncline plunges to the west between Umatilla and Irrigon and to the east between the western boundary of the study area and Boardman (figure 4). Using well correlations Wozniak (1995) found that the Oregon limb of the fold dips about 50 feet per mile (15 meters per kilometer) to the north.

An alignment of buttes and ridges extending from Sillusi Butte in Washington to Service Butte in Oregon form the topographic expression of the Service Anticline. In the study area between Umatilla Butte and Service Butte, the structure is expressed as a chain of isolated basalt buttes surrounded by alluvial sediments. Hogenson (1964) and Shannon & Wilson Inc. (1973) describe minor faults associated with the structure. Robinson (1971) infers bounding faults on both sides of

the buttes may obscure the folding along the structure. Wozniak (1995) suggests from outcrop data and well log data, that faulting has produced at least 250 feet (76 m) of throw on the west side of Hermiston Butte.

GROUNDWATER HYDROLOGY

The aquifers of concern for the present study are the shallow alluvial aquifer consisting of the coarse-grained and fine-grained Pleistocene deposits and the Saddle Mountains Basalt aquifer(s) (figure 6).

Alluvial Unconfined Aquifer

Pleistocene deposits are the principle water-bearing unit in the alluvial aquifer system. The permeability of the coarse-grained deposits is much higher than that of the fine-grained deposits.

The coarse-grained Pleistocene deposits (Pscfc) occur as broad tracts of open-framework gravels and medium to coarse-grained sands. Significant quantities of unconfined groundwater occur in three extensive areas within these deposits (figure 7). In these areas saturated thickness exceeds 10 feet (3 m), hydraulic gradients are low less than 10 feet per mile (3 m per/km) and well yields are high 1,000 to 4,000 gallons per minute (3,785 to 15,140 liters per minute).

Geologic Unit						Hydrogeologic Unit		
System	Series	Group	Formation	Age (Ma)	Member or Unit	Aquifer or Confining Bed		
Quaternary	Holocene	Columbia River Basalt Group	Surficial Sediments		Wind-blown Silt and Sand	Alluvial Aquifer		
			Holocene Alluvium		Alluvial Flood Plan Sediments			
	Pleistocene		Pleistocene Depoists	.013 - ?	Fine-grained Sediments			Coarse-grained Sediments
Tertiary	Pliocene		-? - -? -	Alkali Canyon	-? - -? -	Erosional Unconformity		
						Undifferentiated Sediments		
						Local Erosional Unconformity		
	Miocene	Saddle Mountains Basalt	10.5	Elephant Mountain Basalt	Confining Bed			
				L.E.U. Rattlesnake Ridge Interbed*	Basal Elephant Mountain Aquifer			
			12	Pomona Basalt	Confining Bed			
				L.E.U. Selah Interbed*	Basal Pomona Aquifer			
				Umatilla Basalt	Confining Bed			
				L.E.U. Mabton Interbed*	Basal Umatilla Aquifer			
						Confining Bed		
			Wanapum Basalt	14.5 - 15.6	Undifferentiated Basalts		Confining Bed	
Grande Ronde Basalt	15.6 - 16.5	Undifferentiated Columbia River Basalt Aquifers						

Modified from Grondin et al., 1995.

* Ellensburg Formation

Figure 6. Comparison of geologic and hydrogeologic units.

Figure 7. Showing the Pleistocene coarse grained facies and the potentiometric surface for the shallow alluvial aquifer (Modified from Wozniack, 1995).

The predominately fine-grained Pleistocene deposits (Pscff) occur as clays, silts, sandy silts, and gravelly silts. Cumulative thicknesses of saturated sand and gravel beds range from 29 feet (9 m) to less than 5 feet (1.5 m). These beds appear to be relatively discontinuous over a scale of miles. The hydraulic gradient in these saturated areas is typically greater than 23 feet per mile (7 meters per km), and well yields are low to moderate (100 to 500 gallons per minute (378.5 to 1,892.5 liters per minute)).

Saddle Mountains Basalt Aquifers

Thin brecciated or fractured zones typically represent the water-bearing zones within the Saddle Mountains Basalt. These zones are located at the top and base of individual flows (figure 3). The dense interior of the flows are believed to be relatively impermeable. Brecciated and fractured zones in the basalt flows account for less than 10 percent of the thickness of a flow (Lindholm et al., 1988).

The Saddle Mountains Basalt contains three shallow aquifers: the basal Elephant Mountain aquifer, the basal Pomona aquifer, and the basal Umatilla aquifer (figure 6). A thin interbed of silt and clay separates the water bearing zones at the base of each flow and the

top of the underlying flow.

The Columbia River breaches each flow, some at more than one locality. Structural troughs within the Saddle Mountains Basalt expose margins of some of the flows beneath various sections of saturated alluvium (figure 5). This suggests a hydraulic connection between the groundwater in the basalt aquifers, the Columbia River and the alluvial aquifer. Where the basalt dips toward the river, recharge from the Columbia River will be limited to portions of an aquifer that are at or below river level. Where flow margins are exposed beneath saturated alluvial sediments, recharge from the alluvial aquifer is possible.

Wozniak (1995) constructed a potentiometric surface map for the shallow alluvial aquifer system with generalized flow lines (figure 7). The alluvial aquifer is recharged by precipitation, leakage from streams, canals and reservoirs, deep percolation of irrigation water, and inflow from adjacent highlands. Recharge water that reaches the saturated zone (water table) flows down gradient toward the Umatilla and Columbia rivers where it discharges from the system. Some alluvial groundwater is discharged to the underlying basalt aquifers where margins of basalt flows are exposed at the base of the alluvial aquifer (figure 5).

Wozniak (1995) found the direction of groundwater flow within the alluvial aquifer is locally controlled by subsurface "topography" at the top of the basalts (figure 4). Here the rate of flow is controlled by lateral variation in grain size and cementation within the sediments.

Recharge sources for basalt aquifers, similar to those of the alluvial aquifer, differ in that the effective recharge area is smaller with a lower recharge efficiency. This is due to porous and permeable zones in the basalts being restricted to tabular breccia or fracture zones at the top or bottom of flows (figure 3). The water that percolates into the basalts is largely confined to tabular aquifers at the top or base of the flows. In most areas of the study area (figure 5), the basalt dips towards the north and groundwater flow in the basalt aquifers is towards the Columbia River.

METHODS

An investigation of the groundwater in the Lower Umatilla Basin have demonstrated that differing land use in the study area has impacted the shallow alluvial aquifer and in some locations the SMB interbed aquifers (Wozniak, 1995). Methods used to investigate impacted groundwater include 1) water chemistry analysis and 2) nitrate-nitrogen isotopic analysis.

The groundwater collection for the water chemistry technical investigation includes multiple state agencies in the Lower Umatilla Basin Groundwater Management Area and related groundwater sampling and laboratory analysis. The groundwater sampling included reconnaissance, bi-monthly, synoptic, and selected nitrogen-isotopic samples. The groundwater samples were chemically analyzed at Oregon Department of Environmental Quality, Oregon Department of Agriculture, Oregon State University Department of Agricultural Chemistry, and Boston University Stable Isotope Laboratories.

Selection of wells used for this thesis considered several factors: 1) the relationship between land use and wells sampled by state agencies in a synoptic sampling conducted in July of 1992. Wells were sampled for common ions, the nutrients NO_3^- , PO_4^- , SO_4^{2-} ,

metals, volatile organic compounds, soluble organic compounds, and the groundwater field parameters pH, specific conductance, and temperature. 2) the connection between land use and the presumed groundwater flow paths in the shallow alluvial aquifer (Grondin and Nelson, 1995) where the $\delta^{15}\text{N}$ isotopic signature would reflect groundwater directly under the potential surface source of nitrate or directly down gradient; 3) the land use associated with high levels of nitrate in the groundwater exceeding EPA drinking water standards ($\text{NO}_3^- > 10\text{mg/l}$); 4) wells for $\delta^{15}\text{N}$ isotopic analysis were screened in the alluvial aquifer only; 5) investigation of impacted and non-impacted SMB interbed aquifers was based on previously collected groundwater chemistry; and 6) accessibility of wells for nitrogen isotopic sampling.

All samples used for nitrate-nitrogen isotopic analysis were collected by the author in a consistent manner using the following procedures: wells were purged for twenty-minute periods and/or until the temperature and specific conductance of the groundwater remained constant. One liter teflon bottles previously rinsed with deionized water, were rinsed twice with well water before the sample was collected. The samples were then placed in a cooler on ice. All the samples were

filtered in the field using a peristaltic hand pump and 4 micro-meter filters. Sulfuric acid was added to the samples until the pH read between 2 and 4. The samples were kept iced until shipping for isotopic analysis.

NITROGEN

Elements that make up the Earth are continually circulated through the atmosphere, to the oceans, in and out of biota by way of photosynthesis, growth and decay, and through the lithosphere by means of sedimentation, weathering, and erosion. Each element follows a particular path or set of pathways through the natural system that is determined by the biogeochemical and physical properties of the element (Atlas, 1988). Each element has its own natural biogeochemical cycle. The nitrogen cycle is very complex, and in some aspects not well understood. The mechanisms by which nitrogen is transferred involve large numbers of pathways and many forms of nitrogen (Figure 8) (Wolterink et al., 1979).

The major input of nitrogen to the soil-water-biomass is the fixation of atmospheric N_2 accomplished primarily through natural bacterial fixation (Atlas, 1988). This is accomplished when N_2 is reduced to ammonium and the ammonium is converted to an organic form. To a lesser degree ammonium and nitrate are directly deposited to the land surface through rain-out of natural atmospheric and pollutant ammonium nitrate and ammonium sulfate (Heaton, 1986). Figure 9 shows several reaction paths and sources for the production of

Modified from Burns and Hardy, 1975.

Figure 8. General scheme for transfer of nitrogen between the atmosphere, marine, and terrestrial environments indicating relative transfer rates (numbers are millions of tonnes/yr) and interconversions within the terrestrial and aquatic reservoirs.

nitrate. Some of these sources include: 1) nitrate from fertilizers; 2) nitrate from decaying plants; 3) nitrate from animal and human waste; and 4) nitrate that results from atmospheric nitrogen fixation by free-living bacteria (Wolterink et al., 1979).

THE NITROGEN CYCLE

The active cycling of carbon, hydrogen, and oxygen can be carried out by micro-organisms, plants, and animals. However, the biogeochemical cycling of nitrogen is largely dependent on the metabolic activities of micro-organisms alone (figure 10) (Burns and Hardy, 1975).

No plants or animals are able to use atmospheric nitrogen directly, and only a few microorganisms are capable of breaking the N_2 triple bond of the elemental nitrogen gas and reduce it to ammonia (Atlas, 1988). The process of converting nitrogen gas to ammonia is called nitrogen fixation. Globally it is estimated that microorganisms convert 200 million tonnes of nitrogen to fixed forms of nitrogen per year in comparison to 30 million tonnes produced by industrial production of nitrogen fertilizers (Atlas, 1988). The first detectable product of nitrogen fixation is ammonia

Modified from Atlas, 1988.

Figure 10. The nitrogen cycle showing chemical forms and key processes in biogeochemical cycling of nitrogen. The left portion of the cycle represents anaerobic, the right portion aerobic processes. The critical steps of nitrogen fixation, nitrification, and denitrification are all mediated by bacteria. $R-NH_2$ represents amino groups in cell protein.

(reaction 1;Atlas, 1988). Free-living bacteria and bacteria in the soil zone in symbiotic association with plants carry out the microbial fixation of atmospheric nitrogen in terrestrial habitats (Atlas, 1988).

Ammonification is the process whereby plants, animals and many microorganisms convert organic amino nitrogen to ammonia, (Krietler, 1975; reaction 2). This is where nitrogen is transferred from organic to an inorganic form.

Nitrification is the process by which ammonium (N-oxidation level = -3) is converted to nitrite (N-oxidation level = +3; reaction 3), and nitrite is converted to nitrate (N-oxidation level = +5; reaction 4). This is an example of aerobic respiration. The two steps of nitrification are carried out by two different microbial populations (Atlas, 1988). In soils this is an important process because of the transformation of the ammonium cation to the nitrate anion.

Positively charged cations are bound by negatively charged soil clay particles and consequently are preferentially retained in soils; however, negatively charged anions, i.e. nitrate, are not absorbed by the

soil and therefore are readily leached from the soil (figure 11) (Drever, 1988). This transference of nitrogen from the soil to the groundwater is critical because it is an important loss of nitrogen from the soil.

High concentrations of nitrate and nitrite in drinking water are a serious health hazard to humans. Nitrite is hazardous because it can combine with blood hemoglobin to block the normal exchange with oxygen and nitrate can be reduced to nitrite in the stomach of infants to produce methemoglobinemia or "blue baby syndrome".

Denitrification is the microbial reduction of nitrate and nitrite to nitrogen gas by aerobic bacteria as a result of anaerobic respiration (reaction 5; Krietler, 1975; Wolterink et al., 1979; Atlas, 1988). This process produces N_2O or N_2 which returns nitrogen to the atmosphere and completes the nitrogen cycle (figure 10).

THE NITROGEN STABLE ISOTOPE

There are two naturally occurring light stable isotopes of nitrogen, ^{14}N and ^{15}N (Atlas, 1988). The

Reactions

1 fixation	4 ammonification
2 nitrification	5 denitrification
3 assimilation	6 nitrate-containing precipitation,
often as nitric acid in acid rain

micro-organisms play a part in reactions 1, 2, 4, and 5

Modified from Brock et al., 1988.

Figure 11. Chemical species found in the nitrogen cycle, illustrating changes in oxidation state and relative stability.

nucleus of a ^{14}N atom contains seven protons and seven neutrons while the nucleus of a ^{15}N atom contains seven protons and eight neutrons.

The isotopic composition of N is expressed in terms of the nitrogen isotope ratio delta (δ) value in parts per thousand (ppt) or (per mil), and is defined as follows:

$$\delta^{15}\text{N} = \frac{{}^{15}\text{N}/{}^{14}\text{N}(\text{sample}) - {}^{15}\text{N}/{}^{14}\text{N}(\text{air})}{{}^{15}\text{N}/{}^{14}\text{N}(\text{air})} \times 1000$$

Air is composed of 99.632% ^{14}N and 0.368% ^{15}N , (Wolternik et al., 1979). The nitrogen isotope ratio of air is used as a reference and therefore has a delta value of zero. The delta ^{15}N values of naturally occurring substances generally range from -20 per mil to +20 per mil. Nitrogen with a positive $\delta^{15}\text{N}$ value has a $^{15}\text{N}/^{14}\text{N}$ ratio greater than atmospheric nitrogen, nitrogen with a negative $\delta^{15}\text{N}$ value has a $^{15}\text{N}/^{14}\text{N}$ ratio smaller than atmospheric nitrogen.

The process of changing the isotopic ratio during a reaction or process is referred to as isotopic fractionation. Fractionation of the ^{15}N and ^{14}N isotopes occur because of the difference in mass between the two atoms (Wolterink et al., 1979). The ^{15}N atom contains an extra neutron giving it a mass approximately

7% greater than the ^{14}N atom (Wolterink et al., 1979). This greater mass causes the ^{15}N atom to behave slightly differently from the ^{14}N in chemical and physical processes (Wolterink et al., 1979). It is these differences that produce the variation in the $^{15}\text{N}/^{14}\text{N}$ ratio of different nitrogen compounds.

Isotopic fractionation mechanisms are:

1. Physical fractionation;
2. Chemical equilibrium fractionation;
3. Chemical kinetic fractionation.

Physical fractionation can occur through diffusion, evaporation and sublimation (Krietler, 1975). In diffusion, molecules containing the lighter ^{14}N isotope will have a higher velocity. In evaporation and sublimation the lighter ^{14}N isotope will have a higher vapor pressure leading to preferential transfer of the comparatively lighter isotope to the vapor (Krietler, 1975).

Chemical equilibrium fractionation (isotope exchange equilibrium) is the preference of an isotope to concentrate in one species of a chemical reaction, either on the reactant or product side depending on the reaction. This means when two chemical species are in equilibrium, the isotopic distribution also reaches an equilibrium (Wolterink et al., 1979). The value of the

isotopic equilibrium constants are dependant on the different energy levels of the molecules and bond strength. These strongly temperature dependant isotopic equilibrium constants have been calculated and/or determine experimentally (Krietler, 1975).

Chemical kinetic fractionation will occur in non-equilibrium fractionation where the same chemical species containing the two isotopes react at different rates when undergoing the same reaction, e.g. progressive denitrification. In an incomplete reaction, the lighter isotope will often be concentrated in the product, while the heavier isotope is concentrated in the reactant. The isotopic ratio for the product will depend upon the initial isotopic ratio of the reactants and the extent of reaction that occurred.

ISOTOPIC FRACTIONATION IN THE SOIL ZONE RELATED TO THE NITROGEN CYCLE

Nitrogen isotopic studies on the $\text{NO}_3\text{-N}$ molecule have been used to differentiate between different surface sources of nitrate contamination in groundwater (Krietler, 1975; Wolterink et al., 1979; Heaton, 1986; Myrold, 1990). As nitrogen moves through the soil it can be isotopically fractionated by a variety of microbially induced chemical reactions; the intermediate

nitrogen compounds having different isotopic compositions (Krietler, 1975). Based on the fractionation mechanism that occurs in the soil, the delta values for nitrate in groundwater typically reflect distinct isotopic signatures (figure 12).

The $\delta^{15}\text{N}$ composition of nitrate from fertilizers used for agricultural purposes typically ranges from -4 per mil to +4 per mil (Heaton, 1986). Ammonium and nitrate in fertilizers usually are derived from the industrial fixation of atmospheric nitrogen by quantitative processes i.e. complete conversion resulting in little isotopic deviation from the initial source; typically these products have $\delta^{15}\text{N}$ values close to zero (Heaton, 1986).

The $\delta^{15}\text{N}$ composition of nitrate from soil organic nitrogen originating from cultivated fields with no animal waste or fertilizer application typically range from +4 per mil to +9 per mil (Heaton, 1986). The process by which organic nitrogen is transformed to nitrate is called mineralization where the oxidation of soil humus takes place as a result of plowing and aerating soils (Kreitler, 1975; Wolterink et al., 1979).

Figure 12. Nitrate-nitrogen isotopic ranges for different $^{15}\text{N}_{\text{no}_3}$ signatures.

The process of mineralization can be considered in terms of three steps:

1st step: organic-N - NH_4^+

2nd step: NH_4^+ - NO_2^-

3rd step: NO_2^- - NO_3^-

The isotopic fractionation depends on which reaction is the rate-limiting step (Mariotti et al., 1982). The first step involves little isotopic fractionation as indicated by a separation factor (E) (where $E_{\text{product-reactant}} = \delta^{15}\text{N}_{\text{product}} - \delta^{15}\text{N}_{\text{reactant}}$), thus $E_{\text{NH}_4^+ - \text{organic nitrogen}}$ is equal to approximately 0.0 per mil. Step 2 (and/or 3), however, involves a large kinetic fractionation with a separation factor (E) ($E_{\text{NO}_3^- - \text{NH}_4^+}$) from -35 to -5 per mil (Mariotti et al., 1982).

Mariotti et al. (1982) recognized two situations: 1) If relatively large amounts of ammonium are available, the process is limited by step two where the first formed nitrate is strongly depleted in ^{15}N . Bacterial involvement, however, will promote an increase in the rate of steps two and three; and 2) when little ammonium is available the mineralization process is limited by the non-fractionation step, step one, leaving the nitrate with the isotopic composition similar to that of the organic nitrogen.

The $\delta^{15}\text{N}$ composition of nitrate from animal/human

waste typically ranges from +10 per mil to +20 per mil (Kreitler, 1979; Wolterink et al., 1979; Heaton, 1986). Isotopic fractionation of ^{15}N and ^{14}N results from ammonia volatilization (Krietler, 1975). The hydrolysis of urea:

fractionates the isotopes through a physical fractionation such that ammonia with the lighter ^{14}N isotope ($^{14}\text{NH}_3$) will volatilize more rapidly than the heavier isotope ($^{15}\text{NH}_3$) (Krietler, 1975; Heaton, 1986). This physical fractionation process is the reason that nitrate derived from animal/human waste has a delta range of +10 per mil to +20 per mil (Heaton, 1986).

Denitrifying bacteria typically prefer the ^{14}N -O bond over the ^{15}N -O bond (Mariotti et al., 1988). This microbial kinetic fractionation produces nitrate with a heavy $\delta^{15}\text{N}$ signature. Mariotti et al. (1988) used the reduction of NO_2^- to N_2O as a simple single-step unidirectional process: NO_3^- to NO_2^- to NO to N_2O to N_2 , resulting in an enrichment of the ^{15}N in the substrate, and ^{15}N depletion of the gaseous product (N_2) (Mariotti et al., 1988). Denitrifying bacteria are typically found in saturated, anaerobic environments where a carbon source is available as an electron donor. Commonly shallow groundwater aquifers provide this

environment because a carbon source typically would not reach deeper groundwater environments.

DATA

This section presents data on hydrochemistry of the SMB aquifer and a $\delta^{15}\text{N-NO}_3^-$ analysis of potential sources of nitrate in the groundwater from the shallow alluvial aquifer in the Lower Umatilla Basin.

HYDROCHEMISTRY DATA

To evaluate possible anthropogenic impacts to groundwater in the basalt aquifers, the composition of groundwater from wells in the basalt aquifer in the Lower Umatilla Basin was examined. Variations in groundwater chemistry for wells completed in the SMB aquifers indicate that recharge of nitrate-contaminated water from the shallow alluvial aquifer is more pronounced in some areas than in others.

Figure 13 shows the location of wells completed in the basalt and alluvium used to evaluate groundwater in SMB aquifers. Table 1 contains common ion data for the selected wells from a synoptic sampling event conducted in 1991 by the Oregon Department of Environmental Quality and other agencies.

Table 1. Common ion data collected by the Oregon Department of Environmental Quality for the Lower Umatilla Basin Management area.

LOWER UMATILLA BASIN GROUNDWATER MANAGEMENT AREA

All Project Wells and Surface Water Sites Sampled by DEQ
July 1990 through March 1993
Selected Inorganic Constituents

ND = Non-Detectable

Site-id	NO3- mg/L	NA mg/L	CA mg/L	MG mg/L	K mg/L	HCO3- mg/L
11M01	ND	40	18	5.9	6.1	170
17K01	ND	65	11	3.3	9.0	172
UMA 085	24	51	67	25.0	7.3	191
UMA 002	15	45	77	41.0	4.5	310
UMA 176	29	40	120	34.0	10.0	350
UMA 178	19	42	89	26.0	8.7	300
UMA 177	7	32	75	22.0	7.1	263
UMA 031	21	49	88	27.0	8.7	278
UMA 086	7	32	65	25.0	6.5	294
UMA 167	1	49	71	22.0	4.4	374
UMA 133	18	54	100	30.0	5.8	350
UMA 182	13	42	89	27.0	6.2	372
UMA 183	29	46	120	51.0	5.4	455
UMA 180	1	80	93	47.0	7.1	529
UMA 144	2	30	46	12.0	6.7	228
UMA 053	5	31	78	20.0	9.1	294
UMA 102	4	25	61	15.0	6.6	251
UMA 269	0	73	3	0.8	9.2	183
UMA 281	0	80	11	4.8	8.2	211
UMA 147	0	99	12	5.7	10.0	252
UMA 164	3	18	54	13.0	5.6	235
UMA 027	0	75	7	2.5	7.4	207
UMA 165	1	16	29	8.6	3.4	148
UMA 003	40	58	110	58.0	5.7	161
UMA 028	2	27	68	44.0	5.4	415
UMA 129	12	65	50	26.0	9.0	258
UMA 029	24	60	84	53.0	6.1	270

Table 1. Continued

<u>Site-id</u>	<u>SO4- mg/L</u>	<u>CL mg/L</u>	<u>PO4- mg/L</u>	<u>TDS mg/L</u>	<u>pH</u>	<u>Sp. COND uS/cm2</u>
11M01	30	5.5	--	190	8.2	305
17K01	33	8.5	--	225	8.4	360
UMA 85	64	58.0	0.05	500	7.9	802
UMA 002	54	61.0	0.02	540	7.4	884
UMA 176	57	40.0	0.04	630	7.6	1014
UMA 178	57	40.0	0.04	530	7.4	831
UMA 177	60	26.0	0.07	420	7.4	641
UMA 031	57	55.0	0.03	550	7.7	900
UMA 086	28	24.0	0.03	400	7.8	655
UMA 167	24	25.0	0.04	440	7.7	720
UMA 133	60	51.0	0.03	600	7.7	918
UMA 182	26	24.0	0.05	500	7.5	767
UMA 183	43	42.0	0.14	720	7.6	1092
UMA 180	78	63.0	0.04	670	7.7	1099
UMA 144	20	12.0	0.13	270	7.8	415
UMA 053	34	25.0	0.04	400	7.9	666
UMA 269	1	18.0	0.04	260	8.7	327
UMA 281	12	22.0	0.03	270	8.1	434
UMA 147	23	22.0	0.03	320	8.5	484
UMA 164	20	8.5	0.06	280	7.7	426
UMA 165	6	4.1	0.01	190	7.9	262
UMA 003	120	140.0	0.02	850	7.4	884
UMA 028	25	17.0	0.02	430	7.6	720
UMA 129	47	52.0	0.01	460	7.6	770
UMA 029	130	75.0	0.02	750	7.9	1046

Figure 13. Showing the location of the wells used for the geochemical evaluation of the Saddle Mountains Basalt aquifer, (Modified from Wozniack, 1995).

The mass balance model NETPATH (Plummer et al., 1994) and reaction path model PHREEQE (Parkhurst et al., 1990) were utilized to identify possible operating processes and offer theoretical geochemical explanations for observed compositions.

Common Ion Compositions

The solutes present in groundwater are controlled by several factors: 1) the composition of the water when it enters the aquifer; 2) the solid phases the water encounters and their respective solubilities; and 3) the residence time of the water in the aquifer (Hearn et al., 1985). The total dissolved solids (TDS) represents the content of dissolved constituents in the groundwater (Hem, 1989). A higher TDS generally relates to a longer residence time of the groundwater in an aquifer (Hem, 1989). Groundwater from the SMB aquifers along with groundwater from the shallow alluvial aquifer were examined using graphs of (TDS) versus different constituents in order to estimate relative groundwater residence time, and the relationship of the constituents with respect to their associated aquifers (figures 14-17).

Chloride, sulfate and nitrate are useful constituents to examine in basalt aquifers. When

Figure 14. Showing divalent cations Ca^{2+} and Mg^{2+} vs. Total Dissolved Solids. All the wells except those labeled alluvial wells are in Saddle Mountains Basalt.

Figure 15. Showing monovalent cations Na^+ and K^+ vs. Total Dissolved Solids. All the wells except those labeled alluvial wells are in Saddle Mountains Basalt.

Figure 16. Showing anions NO_3^- and SO_4^{2-} vs. TDS. a) NO_3^- concentrations for Saddle Mountain Basalt wells (11M01 and 17K01) below detection. All wells except those labeled alluvial wells are in Saddle Mountains Basalt.

Figure 17. Showing Chloride vs. Total Dissolved Solids.
All wells except those labeled alluvial wells are in Saddle Mountains Basalt.

unimpacted by anthropogenic activities, these aquifers typically yield low values for these ions relative to groundwater because these ions are generally absent or at low concentrations in the minerals comprising the rock itself. Therefore, high levels of these constituents suggest another influence contributing to the composition of the groundwater outside natural water/rock reactions.

To assess deviation from natural water/rock reactions in this study, data from wells representing groundwater from an aquifer known to be relatively unimpacted are used for reference. Two wells in the SMB, 11M01 and 17K01, sampled by Ebbert et al. (1995) as part of a nitrate study in the Columbia Plateau, Washington, yielded tritium levels below detection, presumably representing waters infiltrated prior to the nuclear bomb tritium spike in 1953. 17K01 is down gradient from 11M01 along the same flow path and defining a flow path known to be relatively unimpacted from surface infiltration. Expected patterns of hydrochemical evolution in a basalt aquifer as groundwater evolves along a flow path include: 1) low concentrations of nitrate, and chloride; 2) increasing sodium concentrations relative to calcium and magnesium concentration; and 3) lowering concentrations of

potassium. Wells 11M01 and 17K01 in figures 14-17 are indicated by open and solid diamond boxes. In figures 14-17 groundwater from wells 11M01 and 17K01 are consistent with the expected geochemical trends and allow relatively unimpacted groundwater from a SMB aquifer to be compared to what are perceived to be impacted SMB aquifers in the Lower Umatilla Basin.

Based on nitrate concentrations (figure 16) data from wells in basalt near Irrigon suggest very little impact, while wells in basalt near Boardman suggest a high degree of impact. From figures 14 and 15, wells in basalt near Irrigon plot similarly to wells 11M01 and 17K01, yielding a higher sodium content, with lower calcium and magnesium concentrations. Several Boardman wells in basalt, however, plot comparable to shallow alluvial wells, with lower sodium content and higher concentrations of calcium and magnesium. The similarity between these Boardman wells in basalt and shallow alluvial wells provides evidence the Boardman basalt wells are being influenced through recharge from shallow alluvial waters. This influence is further illustrated for Boardman wells in basalt in figures 16, and 17, where high levels of nitrate, sulfate, and chloride plot similarly to shallow alluvial wells. This contrasts greatly with Irrigon wells in basalt where nitrate

levels are near detection limits, and with sulfate and chloride levels once again similar in concentration to 11M01 and 17K01.

This initial evaluation of groundwater from basalt aquifers in Boardman and Irrigon is followed by further analysis of the data using a trilinear diagram as another method to qualify and define the water chemistry (table 1). The trilinear diagram expresses the major ionic constituents in milliequivalents per liter, where cations are plotted separately from anions. This is accomplished by grouping potassium with sodium on one axis, fluoride, nitrate and chloride on another axis, leaving magnesium, calcium and sulfate by themselves on their own axes, and finally combining carbonate and bicarbonate for the final axis. By expressing the values as percentages of the total milliequivalences per liter of cations and of anions, the water composition can be expressed with a trilinear diagram (Hem, 1989). Figure 18 shows a trilinear diagram of the data from table 1. The cations from wells in basalt near Boardman and shallow alluvial wells plot primarily in the middle of the diagram, yielding waters with high proportions of calcium and magnesium. Wells in basalt near Irrigon plot with a high percent of sodium and potassium

Figure 18. Showing piper diagram of common ion data for alluvial, and basalt aquifers in the Lower Umatilla Basin used for hydrochemical evaluation of the Saddle Mountains Basalt aquifer.

relative to magnesium and calcium. With respect to anions the trilinear diagram shows a high proportion of bicarbonate ions relative to chloride and sulfate ions for groundwater from wells located in Boardman and Irrigon basalt aquifers, along with groundwater from wells in the alluvial aquifers, and wells 11M01 and 17K01.

Due to the fact both trilinear diagrams are in percentages, the proportions of a given cation or anion relative to the sum of equivalents for all cation and anions must be one hundred. This allows the analysis to be expressed as a single point on a two coordinate diagram (Hem, 1989). In figure 18 wells in basalt near Boardman and shallow alluvial wells plot similarly, trending towards high (sulfate + chloride) and (calcium + magnesium) waters. Irrigon basalt wells and wells 11M01 and 17K01, however, trend towards high (carbonate + bicarbonate) sodic waters. This difference in perceived evolutions for Boardman and Irrigon basalt waters can be quantified using the geochemical models NETPATH (Plummer et al., 1994) and PHREEQE (Parkhurst et al., 1990). To help define the mineralogical constraints used in these models, the conceptual geochemical model for basalt water/rock reactions defined by Benson and Teague (1982) and later by Hearn

et al. (1985) and Steinkampf et al. (1985) is addressed.

Conceptual geochemical model for basalt water/rock reactions

Between 17.5 and 6.0 million years ago, large outpourings of fluid basaltic lava flooded the Columbia Plateau from linear vents in eastern Washington and Oregon. This resulting huge lava field is collectively known as the Columbia River Basalt Group (Swanson et al., 1975). The mineralogy of the basalt consists of plagioclase, pyroxene, and opaque metal oxides (Benson and Teague, 1982). Plagioclase has a composition between labradorite (An_{50-70}) and andesine (An_{30-70}); pyroxene has a composition between augite ($((Ca,Na)(Mg,Fe,Al)(Si,Al)_2O_6)$) and sub-calcic augite, and the opaque metal oxides are titanium-iron oxides of the illmenite ($FeTiO_3$)-magnetite (Fe_3O_4) series (Ames, 1980). These minerals are present in a matrix of cryptocrystalline material and volcanic glass (Ames, 1980).

Differing cooling rates within the flows controlled the composition and relative abundance of glassy and crystalline components along with the crystal size (Hearn et al., 1985). Rapidly cooled flows usually have a fine-grained and glass-rich zone at their base. Slow

cooling within the interior of the flow, however, promotes crystal growth, leading to more coarse-grained crystalline phases and less glass (Hearn et al., 1985).

The terms colonnade and entablature describe the two most commonly observed jointing patterns (Long and Wood, 1986). Columns in the colonnade zone, about 3 feet (1 m) in diameter are generally straight and tightly jointed. Columns in the entablature zone are smaller and more irregular. Seventy percent of the total volume of the flows are typically entablature (Swanson et al., 1979).

Secondary alteration as described by Benson and Teague (1982) typically takes place along fractures, in vesicles, and in brecciated zones between flows known as the interflow zone. These are the major ground-water flow paths in the basalt flows. Secondary mineral assemblages found by Benson and Teague (1982), include: smectite $((1/2\text{Ca}, \text{Na})_{.7}(\text{Al}, \text{Mg}, \text{Fe})_4[(\text{Si}, \text{Al})_8\text{O}_{20}](\text{OH})_4)$, celadonite (part of the illite group), clinoptilolite $(\text{Na}_{.88}, \text{Ca}_{.48}, \text{K}_{.94})\text{Mg}^{10}\text{Fe}_{.20}\text{Al}_3(\text{Al}_{.66}, \text{Si}_{1.34})\text{Si}_{13}\text{O}_{36}$ and four silica phases (SiO_2)- (opal, quartz, cristobalite, and tridymite). These minerals occur in both vesicular and non-vesicular samples. Less common vesicle filling minerals include gypsum and calcite (Benson and Teague, 1982).

Smectite occurs at all depths within the samples from drill cores. Celadonite has an extensive but patchy occurrence; silica typically occurs as quartz, and calcite occurred between 0 and 1148 feet (0 to 350 m) and 3199 and ~4757 feet (975 to ~1450 m) in depth. Clinoptilolite occurs in samples only from depths in excess of 1243 feet (379 m) (Benson and Teague, 1982).

The solubilities of the major crystalline and glassy components of the Columbia River Basalt Group are not known. However, due to a lack of crystal structure and extensive surface area, volcanic glass is found to be more soluble than crystalline silicate minerals (Jones, 1966). Pyroxene and iron-titanium oxide minerals were observed to be more altered than plagioclase feldspar (Benson and Teague, 1982). Therefore, the principle phases that react with groundwater, in order of decreasing reactivity, are thought to be glass, poorly crystalline matrix, pyroxene and titanomagnetite, and plagioclase (Hearn et al., 1985).

Hearn et al. (1985) indicate carbon dioxide-charged waters infiltrate into the basalt and come in contact with the various solid phases. The volcanic glass, cryptocrystalline matrix, pyroxene, and labradorite begin to dissolve because of the mildly acidic nature of

the water and hydrolysis of the less-crystalline and silicate mineral phases. The glassy and cryptocrystalline materials being the most soluble phases contribute the most dissolved constituents to the water. Dissolved oxygen reacts with dissolved ferrous iron, oxidizing it to ferric iron, which precipitates as amorphous oxyhydroxide. The dissolving aluminum and silicon precipitate as amorphous aluminosilicates and silica. With time these non-crystalline phases become structurally more ordered, forming minerals such as goethite, smectite, and quartz. The formation of smectite incorporates significant amounts of iron and magnesium.

The contribution of hydroxyl ions to solution as dissolution progresses through hydrolysis raises the pH. Carbonate minerals (primarily calcite) at elevated pH exceed their stability limits and precipitate. This removes the divalent cations calcium and magnesium from the water. In contrast, concentrations of the monovalent cations sodium and potassium increase with groundwater residence time, mostly because these constituents do not participate in the reactions forming early solid phases. Eventually at depth, the saturation of clinoptilolite, a sodium-potassium zeolite, is reached. The general diagenic sequence seems to be

smectite-clinoptilolite-silica and/or clays and carbonates (Benson and Teague, 1982; Hearn et al., 1985).

Simple Conceptual Model for the Lower Umatilla Basin

For the purposes of this thesis a simplified version of the conceptual geochemical model of Benson and Teague (1982) and Hearn et al. (1985), can be used to create a conceptual model for the study area. The lack of data for solid phases for this study makes it difficult to create a model that represents true phases within the basalt groundwater system. However, the conceptual models by Benson and Teague (1982) and Hearn et al. (1985) allow for a reasonable hypothetical model to be explored in an attempt to describe processes that may be contributing to the hydrochemistry of the basalt ground water systems in Irrigon and Boardman.

Due to the highly soluble nature of volcanic glass (Jones, 1966), glass is the only primary phase used in the following NETPATH models. Stoichiometric data for the glass to enter into the models is available from Hearn et al. (1985) (table 2). Because clinoptilolite is found below depths of 1150 feet (350 m) (Benson and Teague, 1982; Hearn et al., 1985) and this system is between 100 and 150 feet (30 and 45 m) below land

Table 2. a) NETPATH input data for 11M01-17K01 and UMA 165-UMA 281 groundwater models. The concentrations are in mmol/l per kg of H₂O.
b) Stoichiometric compositions of phases used in the model, entered by the author.

a)

UMA 11M01-17K01 model

Initial well: 11M01

Final well : 17K01

<u>WELL#</u>	<u>Calcium</u>	<u>Sodium</u>	<u>Magnesium</u>
11M01	.4493	1.7405	.2428
17K01	.2746	2.8284	.1358

UMA 165-UMA 281 model

Initial well:UMA 165

Final well :UMA 281

<u>WELL#</u>	<u>Calcium</u>	<u>Sodium</u>	<u>Magnesium</u>
UMA 165	.7238	.6962	.3538
UMA 281	.2746	3.4812	.1975

b)

Chemical compositions of minerals used in the NETPATH models

Entablature Glass (Allen and Strope, 1983)

Sis.804Tio.169Feo.918Mgo.105Cao.558Na1.254Ko.466Po.083O24

Smectite (Hearn et al., 1985)

Na0.07Cao.15Ko.09Mgo.71Fe1.11Al0.76Si3.67

Calcite (Default NETPATH formula)

Ca1.0C1.0O3.0

surface (assuming similar heat flow patterns and little erosion), smectite and calcite are the only reasonable secondary minerals to use.

Anthropogenic sources directly influencing the alluvial ground water that may in some areas be recharging to the SMB aquifer, include potato waste-water application, fertilizer application, confined animal feeding operations, and septic systems (Grondin and Nelson, 1995). The addition of contaminants to groundwater, in many cases, is found to be accompanied by the addition of other more common constituents (e.g. calcium, sodium, chloride, sulfate, etc.; Grondin and Nelson, 1995). For the purposes of this thesis, potato waste water, fertilizer application and confined animal feeding operations are important sources for elevated levels of calcium, sodium, and magnesium.

Through the application of NETPATH (Plummer et al., 1994), Grondin and Nelson (1995) found processes influencing the alluvial groundwater to be the composition of the recharge water, evapotranspiration, interaction of CO₂ gas within the unsaturated zone, mixing between other groundwater or surface water, and chemical reactions between solid material in the aquifer, such as dissolution/precipitation and cation exchange. Important processes believed to be taking

place in the basalt aquifers are mixing between the shallow alluvial aquifer and basalt aquifers and chemical reactions with solid material in the aquifer.

The elevated levels of sodium relative to calcium in the groundwater for wells in Irrigon SMB, and wells 11M01 and 17K01 (figure 15), suggest cation exchange may occur within the various systems, where the interlayer cations in smectite are exchangeable and calcium is exchanging for sodium within the clay layers. The constituents used in the model are the cations magnesium, calcium, sodium and carbon. Through keeping the initial model simple with respect to mineral phases (glass, smectite, calcite, and cation exchange), and ionic constituents (calcium, magnesium, sodium, and carbon), departure from that model allows exploration of other processes that are perceived to be affecting the given groundwater system.

To validate the conceptual model, the numerical models NETPATH (Plummer et al., 1994) and PHREEQE (Parkhurst et al., 1990) were employed to model simple fluid rock reactions. In order to understand the nature of the numerical models NETPATH and PHREEQE, a brief discussion of the concepts behind the models follows.

NETPATH Modeling Concepts

NETPATH is an interactive Fortran 77 computer program used to interpret net geochemical mass-balance reactions between an initial and final water along a flow path (Plummer et al., 1994):

initial water + reactant phase = final water + product phase

NETPATH can also be used to compute the mixing proportions between two or more initial waters and net geochemical reactions that can account for the observed compositions of a final water.

initial water + one or more mixing water(s) + reactant phase = final water + product phase

Previously defined chemical and isotopic data from a hydrochemical system are utilized by the program. Every possible geochemical mass balance reaction model is examined between selected evolutionary waters for a given set of chemical constraints and a set of plausible phases in the system.

The chemical state of the water can be determined by entering data from table 1 into NETPATH. WATEQF an ion-association model is used to calculate the distribution of aqueous species. This includes a determination of the phases of individual minerals and their saturation indices expressed as the $\log_{10}$ of the

ion activity product (IAP) divided by the equilibrium product (KT). When $\text{LOG}(\text{IAP}/\text{KT}) = 0$ the system is saturated with respect to the given phase; when $\text{LOG}(\text{IAP}/\text{KT}) < 0$, the system is undersaturated with respect to the phase; and when $\text{LOG}(\text{IAP}/\text{KT}) > 0$ the system is supersaturated with respect to the phase.

PHREEQE Modeling Concepts

PHREEQE is a Fortran IV computer program designed to model geochemical reactions based on an ion pairing aqueous model (Parkhurst et al., 1990). PHREEQE can calculate pH, redox potential, and mass transfer as the function of a reaction, as well as simulate several types of reactions including (1) addition of reactants into solution, (2) mixing of two waters, and (3) titrating one solution with another (Parkhurst et al., 1990). The program will calculate the following parameters during the reaction simulation:

1. pH.
2. pe.
3. Total concentration of elements.
4. Amounts of minerals (or other phases) transferred into or out of the aqueous species.
5. Distribution of aqueous species.
6. Saturation state of the aqueous phase with respect to specified mineral phases.

In addition, the aqueous model is exterior to the computer code and is completely user definable with respect to the input data for elements and aqueous

species included in the data base (Parkhurst et al., 1990). This allows the user to define constituents and relative amounts of a given mineral to be added to the aqueous model. The general types of reactions that can be simulated are:

1. Mixing of two solutions.
2. Titrating one solution with a second.
3. Adding or subtracting a net stoichiometric reaction (changing total concentration of elements in proportion to a given stoichiometry).
4. Adding a net stoichiometric reaction until the phase boundary of a specified mineral is reached.
5. Equilibrating with mineral phases (mineral equilibrium can be specified with reaction types 1, 2, 3, 4, or 6 as well).
6. Changing temperature.

Selection of number 3 allows the user to start with a system undersaturated with respect to a given mineral phase. The user adds in proper stoichiometric proportions increments of a reaction until the mineral reaches saturation. This reaction is based on the conceptual model and, therefore, represents a natural evolution of groundwater. If the user plots change in concentration of a particular constituent against other constituents, a perceived natural evolutionary trend is modeled. This selection is used in this study to further our understanding of the groundwater systems and perceived operating processes.

NETPATH Modeling

One well from Irrigon SMB aquifers, UMA 281, and one well from Boardman SMB aquifers, UMA 29 were chosen for evaluation. Due to consistently low TDS (figures 14-17) groundwater from well UMA 165 is used as the initial unevolved basalt groundwater. Geographically neither UMA 281, UMA 29 or UMA 165 are along the same groundwater flow path. The concept lies in the notion that UMA 281, and UMA 29, both represent more evolved waters than UMA 165 based on the levels of TDS (figures 14-17). However, the different geochemical trends (figure 18) for UMA 281 and UMA 29 suggest different processes influencing the basalt waters represented by the common ion data in table 1. By allowing UMA 165 to represent initial, relatively unevolved waters, possible NETPATH models can be constructed using the simple conceptual model previously discussed, starting with the dissolution of volcanic glass evolving to the precipitation of smectite, the precipitation or dissolution of calcite ($\text{Ca}^{2+} + 2\text{HCO}_3^- = \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$), and cation exchange.

In order to deduce if the respective mineral phases used in the NETPATH models are precipitating or dissolving with respect to groundwater systems, thermodynamic data from WATEQF is useful. Saturation

indices from WATEQF indicate that the groundwater from the Boardman well UMA 29 is supersaturated with respect to calcite, whereas groundwater from Irrigon well UMA 281 is undersaturated with respect to calcite, and groundwater from UMA 165 is at saturation (figure 19). Unfortunately the data base for WATEQF doesn't contain the other major secondary mineral smectite.

Consequently it is not possible to determine if the system is saturated or undersaturated with respect to this phase. However, activities calculated for concentrations of ions from table 3, enable a graph of the $\log a_{H_4SiO_4}$ vs. $\log(a_{Ca^{2+}}/a_{H^+})$ to be constructed. This is based on calculating the theoretical stability relationships among minerals in the system $CaO-Al_2O_3-SiO_2-H_2O$ at $25^\circ C$, (Drever, 1988; figure 20). By examining the activity of H_4SiO_4 for different values of $\log a_{H_4SiO_4}$ vs. $a_{(Ca^{2+}/H^+)}$ theoretical stability relationships for various secondary minerals in solution can be determined at some particular values of P_{CO_2} (Drever, 1988). Figure 20 suggest groundwater from the basalt aquifers in Irrigon and Boardman, along with groundwater from the shallow alluvial wells, are in equilibrium with smectite.

Table 3. Data expressed as activities for alluvial and basalt wells used to plot the smectite equilibrium diagram.

<u>Well #</u>	<u>Log_a (Ca/H₂)</u>	<u>Log_a (H₄SiO₄)</u>
UMA 167	12.44	-2.988
UMA 133	12.57	-2.973
UMA 182	12.14	-2.993
UMA 183	12.43	-2.870
UMA 164	12.36	-3.136
UMA 281	11.69	-3.002
UMA 165	12.53	-2.968
UMA 28	12.22	-3.071
UMA 29	12.87	-3.048
UMA 179	12.21	-3.088
UMA 30	12.31	-3.089
UMA 129	12.09	-3.046
UMA 3	12.19	-3.054
UMA 27	13.06	-3.027
UMA 269	13.17	-3.105
UMA 147	13.31	-3.082
11M01	12.51	-3.062
17K01	12.48	-3.131

Figure 19. Showing saturation indices for calcite and dolomite.

Figure 20. Stability relationship diagram to demonstrate waters in equilibrium with smectite. Horizontal dashed lines are solubility of calcite.

NETPATH model for wells 11M01 and 17K01

WATEQF data for groundwater from wells in the SMB, 11M01 and 17K01, suggests these wells saturated with respect to calcite and dolomite (figure 19). Figure 20 also suggests these groundwaters, like groundwater from the basalt aquifers in Boardman and Irrigon, are in equilibrium with smectite. Therefore, 11M01 and 17K01 are used to initially evaluate the validity of the simple conceptual model for the Lower Umatilla Basin study area.

For the model 11M01 to 17K01 the model input is in table 2 in mmols/kg H₂O. The output for the model is in table 4:

Table 4, The output for model 11M01 and 17K01.

ENTABLATURE GLASS	+.3601	Dissolution
SMECTITE	-.20393	Precipitation
EXCHANGE	-.32528	Ca ²⁺ for Na ⁺
CALCITE	-.01977	Precipitation

The output from the model run uses (-) to indicate precipitation and (+) to indicate dissolution. This model retains the net reactions within the simple conceptual model derived from Benson and Teague (1982) and Hearn et al. (1985). The initial dissolution of glass (+) is a source of calcium, sodium and magnesium

to the groundwater. The subsequent precipitation of smectite (-) removes magnesium ions from the groundwater and some of the calcium ions. Cation exchange (+) continues to remove calcium ions as the sodium ions increase in solution. Finally the model precipitates calcite (-) removing the calcium ions from solution.

UMA 165 to UMA 281 AND UMA 29

The Irrigon UMA 165 to UMA 281 numerical model maintains the simple basalt water/rock reactions. Output for the model is in table 5.

Table 5, The output for model UMA 165 to UMA 281.

ENTABLATURE GLASS	+.07748	Dissolution
SMECTITE	-.23163	Precipitation
CALCITE	+.89437	Dissolution
EXCHANGE	+1.35206	Exchanging Ca^{2+} for Na^+

The NETPATH model indicates dissolution of entablature glass (+), and precipitates smectite (-). UMA 281 is undersaturated with respect to calcite (figure 19), consequently groundwater dissolves calcite (+) that may have precipitated in vesicles, increasing the calcium ion concentration in the groundwater. Cation exchange (+) removes calcium and contributes sodium into the groundwater.

Elevated concentrations of nitrate in UMA 29 (table 1) indicated a hydraulic connection between the shallow alluvial aquifer and SMB aquifer. Mixing between the two aquifers is a suspected process explaining the hydrochemistry for UMA 29. Attempts to achieve a valid mass balance equation for Boardman SMB groundwater well UMA 29 proved to be ineffectual. The simple conceptual model used calcium, magnesium, sodium, and carbon. Extremely high levels of magnesium and calcium in UMA 29 (table 1) frustrated all attempts of constructing a reasonable mixing model involving the chosen end members. Eventually it became clear efforts to achieve the correct mixture resulted in forcing the numerical model. The diversity of sources contributing nitrate to the shallow alluvial aquifer in the area (Grondin et al., 1995) suggest a great variability in the shallow groundwater composition needed to mix with the deeper basalt groundwater. This diversity restricted the use of a simple mixing model. Because of an incomplete understanding of the composition of the shallow groundwater, the initial concentrations of constituents from the alluvial aquifer to be mixed with the basalt aquifer would be educated guesses at best.

PHREEQE Model Results

The numerical model PHREEQE is used to evaluate the perceived geochemical trends and further illustrate the natural water/rock reactions seen in the 11M01-17K01 and UMA 165-UMA 281 NETPATH models, and apparent departure from natural water/rock reactions for Boardman well UMA 29.

The PHREEQE model uses the chemistry of an initial groundwater and allows the user to add increments of one or more reactants into the solution until a certain saturation state, defined by the user, is arrived at. The results of the model are then compared to actual measured concentrations for constituents from specific groundwater systems. The model presented here uses constituents (calcium, magnesium, and sodium) from well UMA 165 (table 1) as initial concentrations for unevolved groundwater. Using the stoichiometric coefficients from Allen and Strope (1983) for glass (table 2), defined concentrations of calcium, magnesium, and sodium are incrementally added to the system. Calcium and magnesium are added until calcite, and then dolomite reach saturation:

Calcite and dolomite are used in the model as a means of

capturing calcium and magnesium in a solid phase in order to establish a perceived geochemical trend. In fact, these phases would naturally limit the concentration of calcium and magnesium in groundwater, i.e. the calcium content will not by and of itself continue to increase after calcite saturation is reached. The author recognizes the unlikelihood of dolomite existing as a phase in this particular ground water system. However, in order to determine a perceived geochemical trend for each of the constituents a mineral containing calcium and magnesium such as dolomite can be brought to saturation. The model allows sodium to be added to the system through dissolving glass, however, no specific mineral is brought to saturation. Perceived trends as defined by the model for calcium, sodium, and magnesium are subsequently plotted.

From figure 21 showing calcium versus sodium it can be seen the PHREEQE model trend plots similarly to trends using data from table 1 for Irrigon wells in basalt, and the 11M01_17K01 system. All three systems trend towards decreasing calcium concentrations with increasing sodium concentrations. The slope of the perceived geochemical trend for the 11M01-17K01 system and the PHREEQE model support the hydrochemical

groundwater system of increasing sodium concentrations coinciding with decreasing calcium concentrations. This contrasts with data for wells in basalt near Boardman, UMA 29, and alluvial wells (table 1) which indicate a hydrochemical system of increasing sodium and calcium concentrations (figure 21).

Figure 19 shows wells 11M01 and 17K01 to be saturated with respect to dolomite. This forces the model to precipitate dolomite removing magnesium from solution. UMA 165 is undersaturated with respect to dolomite or other magnesium-bearing mineral phases therefore dissolving dolomite and contributing magnesium to the solution. The PHREEQE model using UMA 165 as an initial well would, therefore, add magnesium to solution. This is why in figure 22 the perceived geochemical trend for the numerical PHREEQE model compared to the perceived natural geochemical trend for the wells 11M01 and 17K01 do not coincide. The perceived trend depicted for UMA 29 (figure 22) describes a hydrochemical system with high magnesium concentrations. Figure 19 indicates groundwater from well UMA 29 to be oversaturated with respect to dolomite. This suggests a source of magnesium outside natural water/rock reactions.

Figure 22. Graph showing perceived geochemical trends. Arrows depict the perceived trends for each system .

NITRATE-NITROGEN ISOTOPIC DATA

Increased concentrations of sodium, magnesium and calcium are perceived to be associated with elevated levels of nitrate in the SMB aquifer and shallow alluvial aquifer. In order to further distinguish sources of nitrate to the shallow alluvial aquifer selected wells were sampled for $^{15}\text{N}\text{-NO}_3^-$ isotopic analysis.

Groundwater samples were collected for isotopic analysis to help identify potential sources of NO_3^- in groundwater in the alluvial aquifer in the Lower Umatilla Basin. Seventeen groundwater samples were collected, three lysimeter samples from the unsaturated zone, and one surface-water effluent sample. Fourteen wells were sampled at three separate times of the year to determine if there were variations due to environmental factors i.e. seasonal variations and soil type, affecting the $\delta^{15}\text{N}$ isotopic signature. Studies by Krietler (1975) and Wolternik et al. (1979) determined environmental factors such as climate and soil type can potentially affect isotopic compositions of a soil nitrate sample by affecting the types of bacteria present and the reaction pathways leading to nitrate formation. However, the scope of this study was not able to include: 1) site specific soil sampling to

determine microbial activity, and/or soil matrix; 2) types of fertilizers used to determine the initial nitrogen species; and 3) determination of redox boundaries within the unsaturated and saturated zones. Therefore, although the $\delta^{15}\text{N}$ isotopic results of this study may be affected by processes going on in the unsaturated and saturated zone, as to what these specific processes are and how they affected the $\delta^{15}\text{N}$, the author can only speculate.

Duplicate analyses for delta ^{15}N isotopic composition indicated an analytical uncertainty of less than 1 ppt (per mil). The duplicate isotopic range in the value reported for the surface-water effluent sample showed a difference of 3 per mil. Due to the assumption that the nitrogen for this sample at the time of collection was in a reduced form, this uncertainty is probably due to the time between sampling and analysis rather than analytical error.

Depth to water, open intervals, and whether the well is located in the fine-grained or coarse-grained facies of the shallow alluvial aquifer for groundwater $\delta^{15}\text{N}$ isotopic samples are listed in table 6. The open interval with respect to the static water level and nitrate concentration with respect to the $\delta^{15}\text{N}$ values for all of the groundwater samples did not appear to

Table 6. Selected well construction data for wells used to sampled for nitrate-nitrogen isotopic analysis.

<u>UMA #</u>	<u>Well Finish</u>	<u>Open Interval (feet)</u>	<u>Static Water Level (feet)</u>	<u>Aquifer Unit</u>
133	P	50-80	40	FG
183	P	110-125	95	FG
182	P	76-100	76	FG
224	S	61-80	65	CG
225	S	61-71	62	CG
226	S	45-55	48.5	CG
159	S	82-92	62	FG
173	-	-----	--	FG
161	P	93-133	67	FG
122	O	71	30	FG
134	O	68	44	FG
69	O	53	30	FG
58	O	198	118	FG
258	S	8-18	10.68	CG
248	S	8-18	10.19	CG
246	S	115-125	10.46	CG

Well Finish

O=Open Hole

S=Screened

P=Perforated

Aquifer Type

FG=Fine Grained Alluvial Aquifer

CG=Coarse Grained Alluvial Aquifer

play a significant role in the results of this study.

Table 7 presents the $\delta^{15}\text{N}$ values in per mil and the concentration of $\text{NO}_3\text{-N}$ in mg/l for each sampling event and type of sample collected. The Environmental Protection Agency (EPA) drinking water standard for nitrate as nitrogen is 10 mg/l. The location of wells used in the study are in Figure 23. Figure 24 contains a graph of all the data, where figures 25-29 present the data based on sampling proximity to specific anthropogenic sources of nitrogen. Anthropogenic sources include: 1) U.S. Army explosive washout lagoon; 2) fertilizer application; 3) confined animal feeding operations, and 4) potato waste water application.

Figure 23 shows the location of wells UMA 224, UMA 225, and UMA 226, in the U.S. Army Depot near the explosive washout lagoon. These sites were sampled for $\delta^{15}\text{N}$ analysis in the fall of 1993 from monitoring wells installed to monitor munitions contamination to the groundwater from an unlined explosive washout lagoon (Grondin and Comach, 1995). The $\delta^{15}\text{N}$ values ranged from +4.6 per mil to +4.9 per mil, with nitrate concentrations ranging from 10 mg/l to 18 mg/l (figure 25).

Figure 23 shows the location of wells UMA 161, UMA 173, and UMA 159, sampled from groundwater directly

Table 7. Compilation of nitrate-nitrogen analysis.

10-29-93 = F93 UMA = WELL IDENTIFICATION NUMBER
 5-18-94 = SP94 LYSIM = LYSIMETER SAMPLE
 8-30-94 = SU94 EFFLU = SURFACE WATER SAMPLE
 * = DUPLICATE ANALYSIS RESULTS

LAND USE	SAMPLE	DATE COLLECTED	NO ₃ -N (mg/l)	DELTA 15N (per mil)
CAFO	UMA 183	F93	37	5.1
	UMA 183	SP94	55-56 *	6.3-6.4 *
	UMA 183	SU94	52	5.4
	UMA 182	F93	11	5.3
	UMA 182	SP94	15	4.5
	UMA 182	SU94	16	4.9
	UMA 133	F93	17	10.4
	UMA 133	SP94	17	8.5
	UMA 133	SU94	16.8-17.1 *	9.9-10.0 *
AGRICULTURE FERTILIZER	UMA 173	F93	48-50 *	4.0-4.1 *
	UMA 173	SP94	48	4.1
	UMA 173	SU94	48	3.2
	UMA 161	F93	72	4.7
	UMA 161	SP94	81-87 *	4.1-4.6
	UMA 161	SU94	---	---
	UMA 159	F93	28	3.1
	UMA 159	SP94	29	2.9-3.0 *
	UMA 159	SU94	25.0-28.5 *	2.8-3.0 *
CAFO AND POTATO WASTE WATER	UMA 122	F93	12	5
	UMA 122	SP94	18.1	2.7
	UMA 122	SU94	9.3	4.5
	UMA 069	F93	10	7.1
	UMA 069	SP94	19.5	6.5
	UMA 069	SU94	6.2	6.1
	UMA 134	F93	19	6.8
	UMA 134	SP94	21	6.9
	UMA 134	SU94	15.2	6.8
POTATO WASTE WATER APPLICATION	UMA 248	F93	15	7.3
	UMA 248	SP94	---	4.4
	UMA 248	SU94	0.1	1.8
	UMA 058	F93	8	4.8
	UMA 058	SP94	9	5.5
	UMA 058	SU94	17.8	5.1
	UMA 246s	F93	15	7.6
	UMA 246s	SP94	13	5.5
	UMA 246s	SU94	9.9	5.9
	UMA 246d	SU94	2	3.3
	UMA 258	F93	11	29.5
	UMA 258	SP94	6.4	33.4-33.7 *
	UMA 258	SU94	22.6	20.3
	LYSIM1	SU94	37.9-39.9 *	21.1-21.9 *
	LYSIM2	SU94	3.0-3.1 *	6.4-6.5 *
	LYSIM4	SU94	5.4	9.1
	EFFLU	SU94	60.5-60.9 *	3.5-6.5 *
	WELL 38	SU94	8	6.1
DEPOT: EXPLOSIVE WASHOUT LAGOON	UMA 224	F93	18	4.6
	UMA 225	F93	13	4.9
	UMA 226	F93	10	4.7
	UMA 227	F93	10	4.8

Figure 23. Showing the location of the wells used for nitrate-nitrogen isotopic sampling,
(Modified from Wozniack, 1995).

Figure 24. Showing all the data from the 15N-Nitrate isotopic study in the Lower Umatilla Basin.

EXPLANATION	
● UMA 183 FALL	◻ UMA 134 SPRING
■ UMA 183 SPRING	△ UMA 134 SUMMER
▲ UMA 183 SUMMER	● UMA 248 FALL
● UMA 182 FALL	■ UMA 248 SPRING
■ UMA 182 SPRING	▲ UMA 248 SUMMER
▲ UMA 182 SUMMER	○ UMA 58 FALL
● UMA 133 FALL	◻ UMA 58 SPRING
■ UMA 133 SPRING	△ UMA 58 SUMMER
▲ UMA 133 SUMMER	● UMA 246s FALL
○ UMA 173 FALL	■ UMA 246s SPRINGS
■ UMA 173 SPRING	▲ UMA 246s SUMMER
▲ UMA 173 SUMMER	▲ UMA 246d SUMMER
● UMA 161 FALL	● UMA 258 FALL
■ UMA 161 SPRING	■ UMA 258 SPRING
● UMA 159 FALL	▲ UMA 258 SUMMER
■ UMA 159 SPRING	✦ LYSIMETER 1 SUMMER
▲ UMA 159 SUMMER	✦ LYSIMETER 2 SUMMER
○ UMA 122 FALL	✦ LYSIMETER 4 SUMMER
◻ UMA 122 SPRING	• WELL 38 SUMMER
△ UMA 122 SUMMER	○ UMA 224 FALL
● UMA 60 FALL	○ UMA 225 FALL
■ UMA 69 SPRING	○ UMA 226 FALL
▲ UMA 69 SUMMER	○ Duplicate sample for UMA 226
⊙ UMA 134 FALL	

Figure 24. Continued, Explanation for all the wells sampled for nitrate-nitrogen isotopic sampling.

Figure 25. Showing 15N-Nitrate isotopic values for wells sampled for the U.S. Army washout lagoon/explosives. Dotted lines show isotopic ranges (+ or - 1 per mil).

beneath fields where commercial fertilizer for agricultural purposes had been applied. The $\delta^{15}\text{N}$ values for UMA 161 range from +4.1 per mil to +4.6 per mil, with nitrate concentrations from 72 mg/l to 81 mg/l; the $\delta^{15}\text{N}$ for UMA 173 ranged from +3.2 per mil to +4.1 per mil, with nitrate concentrations from 48 mg/l to 50 mg/l; and $\delta^{15}\text{N}$ values for UMA 159 ranged from +2.8 per mil to +3.1 per mil, with nitrate concentrations from 25 mg/l to 29 mg/l (figure 26). Isotopic data for groundwater from well UMA 173 may suggest environmental factors apparently affect the $\delta^{15}\text{N}$ value in summer, lowering the delta ^{15}N isotopic value from groundwater samples collected in the fall and spring. UMA 161 demonstrated a similar trend from fall to spring, where no sample was collected in the summer. UMA 159 however, demonstrates very little isotopic variation for any of the three sampling events. All three wells maintained consistent groundwater nitrate concentrations for all three sampling periods.

Figure 23 shows the location of monitoring wells UMA 58, UMA 248, UMA 258, and UMA 246s, where groundwater is receiving recharge from fields where potato waste water is applied, placement of lysimeters 1, 2, and 4, and the potato waste water lagoon. Figure 27 shows a graph of $\delta^{15}\text{N}$ vs. nitrate concentration in

Figure 26. Graph showing delta 15N-Nitrate values vs. NO₃- for agricultural fertilizer application. Dotted line shows isotopic ranges (+ or - 1 per mil).

Figure 27. Showing 15N-Nitrate isotopic values for wells, lysimeters, and effluent for potato waste water. Dotted lines show isotopic ranges (+ or - 1 per mil).

(mg/l) for groundwater, lysimeter, and surface water samples.

The $\delta^{15}\text{N}$ for groundwater sample UMA 58 ranged from +4.8 per mil to +5.5 per mil, while nitrate concentrations increased from 8 mg/l to 17.8 mg/l. The $\delta^{15}\text{N}$ for groundwater sample UMA 246s ranged from +5.5 per mil to +7.6 per mil, where nitrate concentrations decreased from 15 mg/l to 9.9 mg/l. The groundwater sample UMA 248, unlike UMA's 58 and 246s, yielded $\delta^{15}\text{N}$ from +7.3 per mil to +1.8 per mil, and nitrate concentrations of 15 mg/l and 0.1 mg/l. The $\delta^{15}\text{N}$ groundwater values for UMA 258 were considerably higher than the other three wells (figure 28), ranging from +20.3 per mil to +33.7 per mil, with nitrate concentrations varying from 22.6 mg/l to 6.4 mg/l, respectively. Groundwater from wells UMA 58 and UMA 246s show similar trends with an apparent increase the $\delta^{15}\text{N}$ isotopic signature in the fall with respect to spring and summer sampling events. The high $\delta^{15}\text{N}$ values for UMA 258 suggest that environmental factors i.e. saturated soils and anaerobic conditions favoring denitrifying bacteria, are probably influencing the isotopic signature.

Soil water samples for $^{15}\text{N}\text{-NO}_3^-$ isotopic analysis were collected from lysimeters used to collect water

Figure 28. Showing denitrification curve for UMA 258.

percolating down from the surface. The lysimeters are emplaced in the unsaturated zone (Barlow et al., 1992) five feet (1.27 m) below land surface in the unsaturated zone under fields where potato waste water is applied. These samples were collected only once in late summer 1994. Lysimeter 1 and lysimeter 2 are one foot (.3 m) apart and lysimeter 4 is one hundred feet (39.48 m) away. Results (figure 27; table 7) from lysimeter 1 yielded a $\delta^{15}\text{N}$ value of +21.1 per mil and a nitrate concentration of 39.9 mg/l; lysimeter 2 yielded a lower $\delta^{15}\text{N}$ value of +6.5 per mil, and nitrate concentration of 3.1 mg/l; lysimeter 4 yielded $\delta^{15}\text{N}$ value of +9.1, with a nitrate concentration of 5.4 mg/l. The variation in the lysimeter samples indicates there may be micro-environmental, i.e. soil bacteria and/or soil-pore processes, factors controlling the $\delta^{15}\text{N}$ isotopic signature and nitrate concentrations. Well 38 located down-gradient from the fields that contained the lysimeters yielded a $\delta^{15}\text{N}$ value of +6.1 and nitrate concentration of 8.0 mg/l. This $\delta^{15}\text{N}$ value and nitrate concentration from well 38 are consistent with values for groundwater from wells UMA 248, UMA 58, and UMA 246s.

Surface water effluent from a potato waste water settling pond, yielded a $\delta^{15}\text{N}$ value of +3.5 per mil and

duplicate analysis of +6.5 per mil, with nitrate concentrations of 60.5 mg/l and 60.9 mg/l respectively (figure 27).

UMA 248d is located in the same drill hole as UMA 248s ($\delta^{15}\text{N}$ 5.5-7.6 per mil and NO_3^- 9.9-15 mg/l), but draws groundwater from a deeper aquifer below a confining layer of clay (Sweet, Edwards and Associates, 1985). The $\delta^{15}\text{N}$ value for UMA 248d measured at +3.3 per mil, and nitrate concentration measured 2.0 mg/l.

The groundwater, lysimeter extractions, and surface water effluent samples consistently yielded delta ^{15}N between +3.0 per mil and +10.0 per mil, with only a few samples yielding isotopic values outside this range. Nitrate concentrations for groundwater range from .1 mg/l to 17.8 mg/l, from lysimeters 5.4 mg/l to 40.0 mg/l, and surface water effluent of 60.5-60.9 mg/l.

Figure 23 shows the location of irrigation wells UMA 183, UMA 182, and domestic well UMA 133, all down-gradient from past confined animal feeding operations. Figure 29 shows $\delta^{15}\text{N}$ values versus nitrate in (mg/l) for the groundwater collected at these sights. UMA 183 yields $\delta^{15}\text{N}$ from +5.1 per mil to +6.4 per mil, and nitrate concentration of 37 mg/l to 56 mg/l. UMA 182 yielded slightly lower $\delta^{15}\text{N}$ values of +4.5 per mil to

Figure 29. Showing ^{15}N -Nitrate isotopic values for wells sampled for Confined Animal Feeding Operations. Dotted lines show isotopic ranges (+ or - 1 per mil).

+5.3 per mil, and nitrate concentrations of 11 mg/l to 16 mg/l. UMA 133 yielded $\delta^{15}\text{N}$ values higher than UMA 183 and UMA 182 of +8.5 per mil to +10.4 per mil, with consistent nitrate concentrations of 17 mg/l (figure 29). UMA 182 and UMA 183 fall outside the reported range of +10 per mil to +20 per mil for animal waste (Krietler, 1975) and UMA 133 falls within the low end of this range. The higher $\delta^{15}\text{N}$ isotopic signatures for groundwater from UMA 133 for summer and fall with respect to spring suggest possible seasonal variation. This same influence is not apparent for wells UMA 183 and UMA 182 whose groundwater ^{15}N isotopic signatures are clustered fairly tightly (figure 29).

Figure 23 shows the location of UMA 69 and UMA 134, domestic wells located 0.1 mile (0.16 km) from each other are directly down-gradient from both confined animal feeding operations and potato waste water application. The $\delta^{15}\text{N}$ values for both wells range from +6.5 per mil to +7.1 per mil, with nitrate concentrations from 10 mg/l to 21 mg/l (figure 30). Both wells fluctuate in nitrate concentration; increasing in the fall and spring and decreasing in the late summer (figure 30). The $\delta^{15}\text{N}$ value remained consistent for UMA 134, and demonstrated an apparent shift for UMA 69, where the fall signature increased

Figure 30. Showing ^{15}N -Nitrate values down gradient from CAFO's and potato waste water application. Dotted line shows isotopic ranges (+ or - 1 per mil).

with respect to spring and summer. UMA 122 is a domestic well located upgradient of UMA 134 and UMA 69, and down-gradient primarily from potato waste water application and commercial fertilizer application (figure 30). The $\delta^{15}\text{N}$ values for UMA 122 ranged from +2.7 per mil in the spring to +5.0 per mil in the fall. Nitrate concentrations for UMA 122 ranged from 9.3 mg/l in the summer to 18 mg/l in the spring (figure 30).

DISCUSSION

The Lower Umatilla Basin is characterized by diverse landuses, some of which are potential nitrate sources to groundwater, e.g. confined animal feeding operations, septic systems, the application of food processing water and/or fertilizers to fields, and munitions storage for the Umatilla U.S. Army Depot. Grondin and Nelson (1995) demonstrated impact to the shallow alluvial aquifer through recharge from irrigation, land application of potato waste water, septic systems and settling ponds as contributing nitrate to the groundwater. Consequently, recharge of impacted shallow groundwater to the deeper SMB groundwater has apparently influenced the hydrochemistry providing deviation from natural basalt water/rock reactions.

GEOCHEMISTRY

Typical basalt water/rock reactions yield low concentrations of nitrate, chloride, and sulfate because these constituents are not usually incorporated in the mineralogy of basalt. Elevated concentrations in a basalt aquifer of these constituents in most cases would imply impact outside expected water/rock reactions. Elevated levels of nitrate, TDS, and chloride from

groundwater wells screened in the SMB aquifer suggest that recharge from the shallow alluvial aquifer has adversely impacted the SMB aquifers near Boardman. Substantially lower concentrations of nitrate in Irrigon groundwater from wells in the SMB aquifer suggest recharge from the shallow alluvial aquifer is minimal (figure 16).

Wells 11M01 and 17K01 are used in both the NETPATH and PHREEQE numerical models to represent SMB groundwater known to be unimpacted. The NETPATH numerical model for Irrigon well UMA 281 validates simple water/rock reactions involving the most basic phases (entablature glass, smectite, calcite), and constituents (sodium, calcite, magnesium, and carbon) and assimilating them into a valid mass balance reaction. A PHREEQE model, involving progressive dissolution of calcite and dolomite, yielded a perceived geochemical trend for sodium and calcium coinciding with groundwater from wells 11M01 and 17K01. This agrees with apparent trends perceived for groundwater from wells in the Irrigon SMB aquifer (figure 21).

Grondin and Nelson (1995) found a direct relationship between high levels of nitrate and high TDS for wells screened in the shallow alluvial aquifer throughout the study area. Boardman basalt wells

consistently yielded high TDS and high concentrations of nitrate (figure 16). Analysis of groundwater from well UMA 29 screened in the SMB aquifer yielded high levels of nitrate, chloride, sulfate, calcium, magnesium, and sodium. This contrasts with groundwater from wells 11M01 and 17K01 and compatibly plots with groundwater from the alluvial aquifer (figures 14-17). Wells in basalt near Boardman and UMA 29 deviate from the PHREEQE model trend for natural water/rock reactions, plotting once again with groundwater from the alluvial aquifer (figure 22). The groundwater geochemistry from wells in the Boardman basalt indicates substantial recharge and subsequent impact from the shallow alluvial aquifer. Therefore, analysis of the $^{15}\text{N}\text{-NO}_3^-$ stable isotope is used to further understand processes impacting the shallow alluvial aquifer and distinguish potential surface sources of nitrate to the groundwater.

$^{15}\text{N}\text{-NO}_3^-$ ISOTOPIC ANALYSIS

In the study area the application of the isotopic composition of NO_3^- -N to identify potential anthropogenic sources of nitrate-nitrogen contamination to groundwater in the alluvial aquifer, yielded results that were not always unambiguous. Some samples yielded $\delta^{15}\text{N}$ values reflecting possible mixing of nitrate

sources in the groundwater and/or soil zone. However, other samples yielded $\delta^{15}\text{N}$ isotopic signatures that corresponded to the reported literature ranges (Krietler, 1975; Krietler, 1979; Heaton, 1986) for a specified primary source of nitrogen. Within the literature there is an overlap within the $\delta^{15}\text{N}$ for specific sources of nitrate (figure 12).

Three irrigation wells, UMA 159, UMA 161, and UMA 173, in fields where commercial fertilizer application is the primary source of nitrate to the groundwater were used to evaluate the impact of irrigation and the application of fertilizer. Figure 26 shows $\delta^{15}\text{N}$ values versus nitrate concentrations in (mg/l) for the three irrigation wells. UMA 161 has $\delta^{15}\text{N}$ values for only fall and spring months, while UMA 159 and UMA 173 have $\delta^{15}\text{N}$ values for fall, spring and summer. All three wells reflect $\delta^{15}\text{N}$ isotopic values consistent with commercial fertilizer as the source of the nitrate (Krietler, 1975; Krietler, 1979; Wolterink et al., 1979; Spalding et al., 1982; Herbel and Spalding, 1993).

The lower summer $\delta^{15}\text{N}$ isotopic values for UMA 173 suggest factors other than the source of the nitrate that may be affecting the isotopic signature are: the time the fertilizer is applied, flushing of nitrate to the groundwater through irrigation, and plant nutrient

uptake. The consistency in nitrate concentrations for wells UMA 159 and UMA 173 suggest a consistent source of nitrate to the groundwater, where the $\delta^{15}\text{N}$ variation in UMA 173 may suggest differing sources of nitrogen are being flushed into the groundwater. A study by Wells and Krothe (1989) indicated fertilizer-derived nitrate to the aquifer can continue only as long as a supply of such nitrate exists. Their study found as long as the nitrogen reservoir is depleted by plant intake the impact of fertilizer-derived nitrate on the isotopic composition of groundwater nitrate may be correspondingly diminished. Therefore, the summer isotopic value for UMA 173 may indicate a full reservoir of fertilizer derived nitrate, whereas fall and spring isotopic values may reflect a diminishing reservoir in conjunction with mixing from ambient groundwater, raising the isotopic signature. UMA 159 yields a $\delta^{15}\text{N}$ value no higher than +3.2 per mil and very little isotopic variation. Communication with the farmer indicated that fertilizer is applied only in May for fields irrigated by wells UMA 161 and UMA 173, but in May, June and July near irrigation well UMA 159. Therefore the lack of isotopic variation for UMA 159 suggests the reservoir stays fairly full due to the constant application of fertilizer to this field.

Monitoring wells UMA 224, UMA 225, and UMA 226, selected to sample groundwater in the U.S. Army Depot, are wells installed to investigate contamination to the groundwater near an unlined explosive-washout lagoon. A duplicate sample was collected for UMA 226. Explosive manufacturing uses atmospheric nitrogen (Heaton, 1986). This would suggest $\delta^{15}\text{N}$ signatures from explosives would yield low isotopic values similar to the $\delta^{15}\text{N}$ isotopic range for manufactured inorganic fertilizer which also uses atmospheric nitrogen for its manufacture. The $\delta^{15}\text{N}$ values from this study are similar to the expected range (-4 per mil to +4 per mil) for fertilizer and correlate to $\delta^{15}\text{N}$ isotopic values from a similar study for explosives (Grondin and Nelson, 1995).

Two irrigation wells UMA 183, and UMA 182, were selected because they are down gradient from a past confined animal feeding operation (figure 29). However, the current landuse is agricultural with commercial fertilizer application. Both wells yielded $\delta^{15}\text{N}$ isotopic signatures ranging from +4.5 per mil to +6.3 per mil, with little isotopic variation. The intermediate $\delta^{15}\text{N}$ isotopic signature (figure 29) may reflect mixing of the fertilizer application and residual animal waste (Mariotti et al., 1988). This is consistent with Grondin and Nelson (1995), who

determined mixing of anthropogenic nitrate sources is an ongoing process in the groundwater of the alluvial aquifer in the study area. However, the intermediate isotopic value for these two wells makes it difficult to distinguish a single source of nitrate to the groundwater.

Figure 23 shows a domestic well directly down gradient from another past confined animal feeding operation and yields $\delta^{15}\text{N}$ values ranging from +8.5 per mil to +10.4 per mil. These isotopic values are closer to the isotopic signature for animal waste (figure 29) (Mariotti et al., 1988). The reason for the increase of the $\delta^{15}\text{N}$ value for summer and fall with respect to spring for this well is speculative. The predominant landuse in the area is agriculture with some dairy farm activity. The high isotopic signature suggest a predominance of animal waste with respect to fertilizer, and/or an organic fertilizer opposed to an inorganic fertilizer. However, the consistent concentration of nitrate for groundwater from this well suggest a constant source of nitrate to the groundwater. Therefore, the shift in the $\delta^{15}\text{N}$ isotopic signature during the spring to a lower value with the consistency in nitrate concentration may reflect differing seasonal landuse, however reconciling the variable $\delta^{15}\text{N}_{\text{NO}_3}$ and

constant NO_3^- -N is difficult.

In many areas potato waste water from a food processing plant is applied to fields as a source of nitrogen to crops. Figure 23 shows the location of sites where $\delta^{15}\text{N}$ analyses were collected for potato-waste water effluent, lysimeter samples from the unsaturated zone, and wells reflecting groundwater directly under fields where potato waste water is applied.

From figure 27 it can be seen the potato-waste water effluent has a high concentration of nitrate 60.5-60.9 mg/l and $\delta^{15}\text{N}$ +3.5-6.5 per mil. This $\delta^{15}\text{N}$ value is considerably lower than one would expect for organic waste. However, elevated $\delta^{15}\text{N}$ generally results from fractionation resulting from ammonia loss through volatilization preferentially removing the lighter isotope. The combination of a high nitrate concentration and low $\delta^{15}\text{N}$ value, suggest rapid oxidation of NH_4^+ to NO_3^- , with little NH_3 volatilizing. The effluent sample was acidified for preservation, reducing the ammonia to ammonium ions. Perhaps this limited the volatilization of the ammonia. Subsequently there was complete oxidation of ammonium to nitrate as the sample waited to be analyzed. As a result, the fractionation of the isotope did not occur. DEQ data

collected from the effluent pond yielded a nitrate concentration of 0.73 mg/l, and total Kjeldahl nitrogen of 72 mg/l (Grondin and Nelson, 1995). The low DEQ nitrate concentration contrast with the high nitrate concentration in samples collected for the isotopic analysis. The difference in nitrate concentrations seems to indicate an initial high concentration of reduced species of nitrogen that oxidized rapidly to nitrate. When this transformation of the nitrogen occurred is speculative and may reflect sampling procedures, and/or shelf time. However, the $\delta^{15}\text{N}$ isotopic range is consistent with the isotopic signature of most of the groundwater and lysimeter samples associated with potato waste water (table 7).

The $\delta^{15}\text{N}$ value and nitrate concentration for soil water from lysimeter 1 are +21.9 per mil and 33 mg/l. Lysimeter 2 one foot away yielded values +6.4 per mil and 3 mg/l. Both are 5 feet (1.5 m) below the surface. Physical micropore processes in the soil zone may be responsible for the difference in nitrate concentration between lysimeters 1 and 2. These are processes that have to do with the negative charge from anions on the soil micropores that attract cations and repel anions in solution. This results in a "double layer" which consists of cations attracted to the solid surface, and

outer diffuse layer known as the Gouy layer in which ions are free to move (Drever, 1988). In the Gouy layer, the concentration of cations unbalanced by the anions will decrease exponentially away from the boundary in the fixed layer (Drever, 1988). Depending upon the thickness of the Gouy layer, anions passing through the pore holes will be repelled or attracted. The repulsion is known as the anion exclusion principle. Anions such as NO_3^- will tend to pass preferentially through the micropore because the repulsion by the negative charge of the solid surface forces them into the central higher velocity portion of the pore often influenced by the ionic strength of the solution.

However, depending on the size of the micropore and thickness of the second layer of cations, the NO_3^- may be retained in the micropore attracted to the cations. The size of the micropore itself exerts an important influence. The soil solution is held in the soil micropores at different surface tensions depending on the pore hole size (Magid and Christensen, 1993). This means solute concentration sampled at different surface tensions are expected to vary according to the various biological and physicochemical processes taking place in the pores (Magid and Christensen, 1993). Therefore even though lysimeters 1 and 2 are adjacent to each other,

the concentration of nitrate may vary based on the micropore processes going on in the soil zone.

Fractionation processes producing the $\delta^{15}\text{N}$ value differences between nitrate from lysimeters 1 and 2 (table 7; figure 27), are speculative at this time. Possibilities for the differences are physical fractionation of the NO_3^- molecule as it passes through the soil zone, and/or microbial fractionation where bacteria prefer the nitrate-nitrogen molecule containing the lighter ^{14}N . One additional possibility in this case is that mice occasionally gain access to the lysimeters, and the high concentrations of nitrate with a high $\delta^{15}\text{N}$ value in lysimeter 1 may reflect mouse waste collecting in the lysimeter (Bart Barlow, Cascade Earth Sciences, personal communication, 1995).

Groundwater collected from UMA 248, UMA 58 and UMA 246s for all three sampling periods, yielded $\delta^{15}\text{N}$ isotopic values +1.8 per mil to +7.6 per mil, with an average of +5.5 per mil. Nitrate concentrations ranged from 0.1 mg/l to 17.8 mg/l (figure 27). Conceivable processes previously discussed affecting the nitrate concentration in relation to the $\delta^{15}\text{N}$ value for the surface water effluent sample where little ammonia volatilization combined with the rapid oxidation of ammonia/ammonium to nitrate, suggest the $\delta^{15}\text{N}$ values for

the groundwater samples range (+4.0 per mil to +6.0 per mil) are not unreasonable and are consistent with the $\delta^{15}\text{N}$ isotopic value of the surface-water effluent +3.5-6.5 per mil.

However, UMA 258, a well sampled for groundwater for potato waste yielded isotopic signatures of +20.3 per mil to +33.7 per mil, and nitrate concentrations varying from 22 mg/l to 6 mg/l, figure 27. These high $\delta^{15}\text{N}$ values, associated with a lower nitrate concentration suggest denitrification (Mariotti et al., 1982; Mariotti et al., 1988; Bottcher et al., 1990; Smith et al., 1988; Fustec et al., 1991; Korom, 1992), the process by which denitrifying bacteria reduce the nitrate to nitrogen gas. Environmental conditions favoring denitrification include (a) average temperature; (b) no exceptional concentration of organic carbon; and (c) humid or saturated conditions (Mariotti et al., 1982). These conditions typically occur in the saturated zone. Studies conducted at different depths to groundwater by Bottcher et al. (1990) found denitrification to exist between depths of 13-23 feet (4-7m) below land surface. For well UMA 258 depth to groundwater from the surface is 10 feet (3 m) and the well is screened from 8-18 feet (2.2-5.5 m) below land surface (table 5) favoring conditions for denitrifying

bacteria.

Using the equation from Mariotti et al. (1988),

$$\delta_f = \delta_i + E * \ln(C_f/C_i) \quad (8)$$

where δ_f is the isotopic composition of the reactant at time (t) in $\delta^{15}\text{N}$ in per mil; δ_i is the initial isotopic composition of the initial reactant before reaction and isotopic change in $\delta^{15}\text{N}$ in per mil; C_f is the final concentration of NO_3^- in mg/l; C_i is the initial concentration of NO_3^- in mg/l; and E is the isotopic enrichment factor of the reaction, related to the isotopic fractionation factor, the ratio of the rate constants of the two isotopic species (Mariotti et al., 1988). In order to determine an initial nitrate concentration C_i , one must first solve for E, then substitute a $\delta^{15}\text{N}$ value for δ_i from groundwater sites sampled for potato waste water.

Using isotopic values and concentrations from UMA 258 to solve for E, where $\delta_i=20.3$ per mil, $C_i=22$ mg/l, $\delta_f=33.7$ per mil, and $C_f=6$ mg/l, $E=-10.63$. This value for E is reasonable and consistent with data presented by Mariotti et al. (1982), who looked at the enrichment factor in soil with respect to the environmental conditions temperature, availability of organic carbon, and the initial soil water content. Mariotti et al. (1982) found the fractionation factor varied between -33

per mil and -11 per mil, primarily affected by temperature and availability of an electron donor.

Using $E = -10.63$ and $\delta_1 = 5.5$ per mil as an average $\delta^{15}\text{N}$ value for potato waste water samples from groundwater an initial nitrate concentration (C_1) can be found. Solving for C_1 , an initial concentration of 84 mg/l of nitrate would have had to have been present in the groundwater to produce this denitrification curve, figure 28 (see also Grondin and Nelson, 1995).

Domestic wells UMA 69, UMA 134, and UMA 122, sampled down gradient from two different sources of waste, CAFOs and potato waste water (figure 23), yielded isotopic signatures primarily between +4.0 per mil and +8.0 per mil (figure 30). UMA 69 and UMA 134 are domestic wells within 0.1 miles (0.16 km) from each other down gradient from a large ongoing CAFO and fields where potato waste water is applied. UMA 122 is a domestic well primarily down gradient from fields where there is potato waste water application, (figure 23).

High nitrate concentrations (table 7) for domestic wells UMA 134, UMA 69, and UMA 122 indicate an anthropogenic source of nitrate. However, the intermediary $\delta^{15}\text{N}$ isotopic values (table 7) precluded identifying the different anthropogenic sources of nitrate because the landuse associated with these wells

is not specific enough to suggest which potential anthropogenic nitrate sources are mixing in the groundwater to produce these intermediary $\delta^{15}\text{N}$ isotopic values.

CONCLUSIONS

Recharge from irrigation, application of potato waste water and septic effluent have adversely impacted the shallow alluvial aquifer yielding elevated levels of nitrate associated with high concentrations of calcium, magnesium, sodium, chloride, and total dissolved solids (Grondin and Nelson, 1995). Groundwater composition of SMB groundwater in Irrigon indicates minimal recharge from the shallow alluvial groundwater. However, elevated levels of nitrate, chloride, magnesium, and high total dissolved solids in Boardman basalt groundwater indicate substantial recharge from the shallow alluvial groundwater.

Irrigon basalt groundwater consistently plotted with wells 11M01 and 17K01, two unimpacted SMB aquifer samples, where Boardman basalt groundwater consistently plotted with shallow alluvial groundwater. The numerical model NETPATH (Plummer et al., 1994) validated simple water/rock reactions (dissolving entablature glass, precipitating smectite, dissolving calcite, cation exchange) for constituents (calcium, magnesium, sodium, carbon) for Irrigon SMB groundwater. However, due to the diversity of compositions from potential anthropogenic sources of nitrate mixing in the shallow alluvial aquifer and limited number of wells available,

finding the actual endmember for a mass balanced solution to basalt groundwater from the wells near Boardman in basalt was not possible.

Use of the numerical model PHREEQE (Parkhurst et al., 1990) allowed the prediction of natural hydrochemical trends using constituents calcium, sodium and magnesium for Irrigon and Boardman wells in SMB groundwater. Irrigon basalt groundwater were consistent with the PHREEQE model that reproduced groundwater trends for wells 11M01 and 17K01, where Boardman basalt groundwater plotted with alluvial groundwater hydrochemical trends.

Wells sampled for groundwater in the shallow alluvial aquifer to potentially distinguish between differing sources of nitrate using the $^{15}\text{N}-\text{NO}_3^-$ stable isotope in some situations was successful agreeing with literature isotopic values, and in other situations were ambiguous where mixing of nitrate sources in the groundwater as indicated by other groundwater studies (Grondin and Nelson, 1995) produced a mixed $\delta^{15}\text{N}$ isotopic signature.

Wells UMA 173, UMA 161 and UMA 159 sampled for groundwater where commercial fertilizer application to fields was the only landuse, yielded $\delta^{15}\text{N}$ isotopic signatures that agreed with literature values. UMA 173

indicated temporal variation where changing nitrate reservoirs and/or the time of year commercial fertilizer is applied may be influencing the $\delta^{15}\text{N}$ isotopic signature.

Wells sampled for groundwater under the Umatilla U.S. Army Depot yielded $\delta^{15}\text{N}$ isotopic signatures consistent with the nitrogen source used in explosive manufacturing: atmospheric nitrogen.

Wells UMA 246, UMA 58, UMA 248, and UMA 258, lysimeters 1, 2, and 4, and surface water effluent all sampled for potato waste water yielded varying $\delta^{15}\text{N}$ isotopic signatures. Groundwater $\delta^{15}\text{N}$ isotopic composition were consistent between many wells varying from +3 per mil to +6 per mil. However, well UMA 258 yielded $\delta^{15}\text{N}$ isotopic values of +20 per mil to +35 per mil. The correlation of high $\delta^{15}\text{N}$ with low nitrate concentrations is characteristic of denitrification.

Groundwater samples for lysimeters 1 and 2, 1 foot (0.3 m) apart samples yielded $\delta^{15}\text{N}$ isotopic compositions +6 per mil to +22 per mil, and nitrate concentrations 5 (mg/l) to 40 (mg/l), consistent with soil micropore processes and bacterial populations influencing both the nitrate concentration and $\delta^{15}\text{N}$ isotopic signature.

High concentrations of nitrate (60 mg/l) for the potato waste water effluent where the nitrogen was

expected to be in its reduced form as $\text{NH}_3/\text{NH}_4^+$ suggest rapid oxidation to nitrate with little ammonia volatilization between sampling and analysis. The isotopic composition, (+3.5 per mil to +6.5 per mil), is consistent with minimal ammonia loss, and agreed with isotopic values obtained from groundwater sampled under fields receiving potato waste water.

Domestic well UMA 133 yielded an $\delta^{15}\text{N}$ isotopic composition (+8.5 per mil to +10.4 per mil) consistent with animal waste as a potential source of nitrate.

Groundwater collected from wells UMA 183, UMA 182, UMA 69, UMA 134, and UMA 122 where mixing of groundwater between multiple suspected sources of nitrate is indicated by water chemistry, yielded $\delta^{15}\text{N}$ isotopic compositions (+4 per mil to +8 per mil) and did not clearly distinguish between differing landuse. Although this value is in the expected range depicting soil organic nitrogen, it also is the suspected value for mixing of organic waste and commercial fertilizer, the common landuse in the area. Wells UMA 182 and UMA 183 $\delta^{15}\text{N}$ isotopic signature, (+4.5 per mil to +6.3 per mil), are therefore interpreted to involve mixing between currently applied fertilizer and a past confined animal feeding operation.

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