

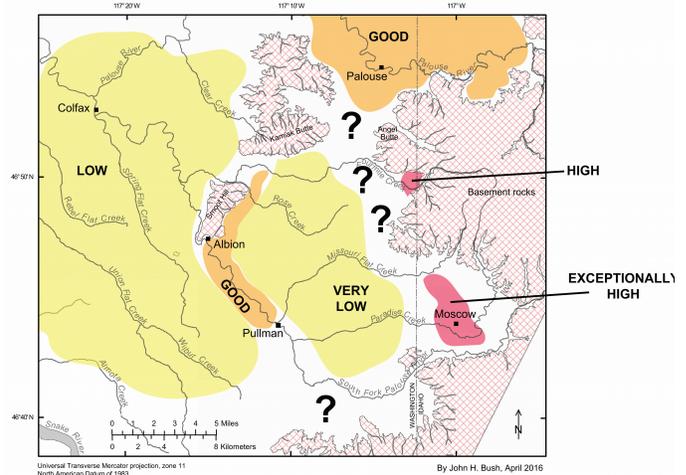
Funding Opportunity: Geochemical Tracers for Improving the Palouse Basin Recharge Model and Understanding Travel Time in Columbia River Basalt Group Aquifers

Proposed Project: Tracing Recharge in the Palouse Basin Aquifers within the Columbia River Basalt Group

Project Institution: University of Idaho

Problem: Groundwater recharge and travel time in the Palouse Basin are not well understood. This lack of knowledge about the movement and storage of water in the aquifers restricts protection and management of the resource.

Generalized Wanapum (Upper Aquifer) Water Supply Map, Palouse Basin



Research Goal: Assess local-to-regional flowpaths and source waters using geochemical tracers.

Previous Work: Past studies have developed information about regional groundwater geochemistry, but this knowledge has not been properly evaluated to understand recharge and travel time.

Proposed Evaluation: Build on the existing geochemical data for the Wanapum and Grande Ronde aquifers through a new groundwater sample collection from Palouse Basin supply wells, analysis of geochemical tracers, and an initial source-water tracking investigation.

Project Framework: Implement the source-water tracking investigation as a graduate student class project for Dr. Langman's Geochemistry of Natural Waters and Environmental Hydrogeology courses offered in the 2016/17 academic year.

Utility of the Project: This project represents a developmental process for improving groundwater knowledge to understand the movement and storage of water within the Wanapum and Grande Ronde aquifers. Results of the study will improve our understanding of recharge and travel time in the aquifers, which is necessary to evaluate aquifer dynamics under future conditions of increased withdrawals, drought, and(or) artificial recharge.

Tracing Recharge in the Palouse Basin Aquifers within the Columbia River Basalt Group

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1. Introduction

Previous analyses of geochemical tracers in groundwater from the basalt aquifers of the Palouse Basin have produced conclusions of early Holocene to late Pleistocene age groundwater with small amounts of modern water^{1,2}. The Wanapum Formation of the Columbia River Basalt Group (CRBG) contains the shallowest of the basalt aquifers and the most recently recharged water³. The underlying Grande Ronde Formation of the CRBG is the primary aquifer of the Palouse Basin and contains older water, but the aquifer can be discriminated chemically as containing an upper and lower aquifer^{1,4}. The most widely analyzed age tracer in Palouse groundwater has been carbon-14 (¹⁴C)^{1,5,6}, and the most recent interpretation of ¹⁴C estimates that the groundwater ranges in age from 4,400 to 26,400 years before present (BP) for the Grande Ronde Aquifer and 3,300 to 14,600 years BP for the Wanapum Aquifer¹. These conclusions were based on uncorrected ¹⁴C and supported by Larson et al.⁴ who inferred recharge during the colder and wetter climate of the Pleistocene from depleted water isotope (δ^{2H} and $\delta^{18}O$) values. The theory of primarily “old” water in the aquifers has not been fully embraced because of a lack of correlation between groundwater ages and flow direction, inner-basin recharge that appears to be contributing to both aquifers, seasonal modern precipitation that contains similarly depleted $\delta^{18}O$ values, and substantially greater recharge rates to local production wells^{1,4,7-9}.

The lack of conclusive evidence of old water and closed aquifer systems within the Palouse Basin led to additional investigations examining potential inner-basin recharge areas and the introduction of young water. Carey³ used a young water tracer (helium-3 or ³H) to identify inner-basin areas of modern recharge (<60 years BP) that had been previously proposed by O'Brien et al.¹⁰ and were outside of the theorized mountain-front recharge zone¹¹⁻¹³. Although, Carey³ did indicate the likely presence of only old groundwater in the lower aquifer. Use of the ³H tracer helped to identify modern recharge where Douglas et al.¹ had indicated younger water near Pullman and Colfax compared to older water upgradient near Moscow and Palouse. The existence of younger water downgradient was previously hypothesized to have occurred because of a potential groundwater divide between Moscow and Pullman¹.

Continuing questions about groundwater ages and travel times in the basalt aquifers of the Palouse Basin and lack of potential flowpath connectivity (highly variable age distributions) led to investigations by Dijkma et al.¹⁴ and Moxley¹⁵ to examine inner-basin stream recharge. Dijkma et al.¹⁴ estimated that within the Paradise Creek sub-basin recharge likely was reaching the Wanapum Formation through mountain-front pathways and creek loss where paleochannels

had thinned hydraulically-restrictive layers. Moxley¹⁵ found modern recharge that originated from the Palouse River between Pullman and Albion. Additionally, Moxley¹⁵ identified $\delta^{18}\text{O}$ values more depleted in seasonal storms than present in the lower Grande Ronde Aquifer, which confirmed results by Moravec et al.⁹. The work of Carey³, Dijkema et al.¹⁴, and Moxley¹⁵ indicate greater complexity of potential recharge pathways and travel times, which require a refinement of the Palouse Basin recharge model that has been created from the ^{14}C and $\delta^{18}\text{O}$ values. The ^{14}C concentrations and depleted $\delta^{18}\text{O}$ values of the CRBG aquifers have not been evaluated holistically to integrate the various “signals” of the tracers that can bring greater clarity to the age interpretation and potential recharge and travel times within the aquifers.

2. Uncertainty in the Recharge Model

The application of groundwater tracers to determine an apparent age or travel time requires the rigorous analysis of potential inputs that can “contaminate” tracer concentrations and increase the potential error^{16,17}. The application of ^{14}C (“old” tracer) for age dating or determining recharge and travel time of groundwater can be problematic because of the error associated with estimating dead carbon input and variations in carbon forms and their transport¹⁶. The application of a “young” tracer such as ^3H also may produce age errors because of mixing with older waters¹⁷. The current interpretation of ^{14}C groundwater ages discounts the input of dead carbon at the mountain-front recharge area, from the basin surface (e.g., creek infiltration), from the aquifer matrix (e.g., carbonate dissolution), or basement rock (e.g., deep CO_2 input). An acceptance of the ^{14}C ages infers a potential travel time of a few feet per year in the aquifers, which is an extremely slow rate for any productive aquifer matrix and unrealistic given the known recharge to pumping supply wells. Additionally, the current conceptual recharge model in the Palouse Basin contradicts physical flow characteristics of the aquifer such as high hydraulic conductivity zones¹⁸ and a lack of correlation between age estimates and direction of flow⁸. This investigation proposes the collection of new tracer data (noble gases, water and carbon isotopes, and water chemistry) to compliment existing data (^{14}C and ^3H) for updating the recharge model and understanding travel time in the aquifers. An integration of old and new tracer data can provide the means of appropriately interpreting solution and solute transport applicable to conceptual or numerical lumped parameter (tracer) or hydraulic (flow) models and a better understanding of recharge, storage, and travel time of groundwater in the Palouse Basin aquifers.

3. Study Design

This study will be completed as a graduate student project for Dr. Langman’s Geochemistry of Natural Waters and Environmental Hydrogeology courses offered in the 2016/17 academic year. Use of the graduates students for sample collection will drastically minimize personnel costs and provide an applicable case study of modern aqueous geochemical research for better understanding and managing groundwater resources.

3.1 Three-Part Investigation

1. Compilation of the existing tracer data for water supply wells in the CRBG aquifers in the Palouse Basin.
2. Collection of water samples from water supply wells for analysis: 1) noble gases of Ar, Kr, Xe, Ne, and ^4He including the $^3\text{He}/^4\text{He}$ ratio, 2) stable isotope ratios of $\delta^{18}\text{O}$, $\delta^2\text{H}$, and $\delta^{13}\text{C}$, 3) ^{39}Ar mid-age tracer, 4) and water chemistry (pH, conductivity, temperature, cations, anions).
3. Re-examination of recharge and travel times for creation of a new Palouse Basin recharge model that can be used for flowpath (tracer) analysis or integrated into a future physical flow model.

3.2 Age Tracer Utility

The current tracer data has not been used to its full extent—limited or no correction of dead carbon for ^{14}C and no examination of He with ^3H or ^{14}C . Relatively large mantle inputs of He into deep groundwater have been mapped in eastern/central Washington and eastern Idaho, and ^{14}C -free CO_2 accompanied the He input¹⁹. The Palouse Basin lies in an area of relatively higher crustal p-wave velocities that would correlate with the addition of mantle CO_2 to deep groundwater¹⁹. Additionally, a better understanding of the cosmogenic and anthropogenic ^3He can be used to improve the calculated age using the mother/daughter ratio of $^3\text{H}/^3\text{He}$ ²⁰. In addition to the ^{14}C reinterpretation, the Pacific Northwest National Laboratory has offered free analysis of groundwater samples for ^{39}Ar as part of its Ultra Sensitive Nuclear Measurements Initiative. ^{39}Ar is useful for dating submodern groundwater (~40 to ~1000 years BP) because it fills this gap of uncertainty between ^3H and ^{14}C .

3.3 Noble Gas, Water Chemistry, and Isotope Data

The noble gas method of identifying groundwater sources works best at mid and high latitudes such as northern Idaho because of the larger temperature changes for these latitudes²¹. Since noble gases tend not to react with other elements, their concentrations in groundwater remain fairly constant once cut off from the atmosphere, except for Ar and He because of possible additions from the decay of ^{40}K to ^{40}Ar , ^3H to ^3He , U decay and release of ^4He , or inputs of terrigenous He. Noble gas concentrations in water may be used to reconstruct the temperature (noble gas thermometer) at the time of the recharge and evaluate potential source-water mixing²²⁻²⁴. The noble gases act as complimentary data set to the age-dating tracers by indicating changes in recharge pathways or seasonality through an integrated examination with the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of water, $\delta^{13}\text{C}$ of dissolved inorganic carbon, and water chemistry.

3.4 Recharge Model

The initial improvement of the recharge model will allow for future evaluation of groundwater movement through flowpath analysis or particle tracking within a physical flow

model based on the discrimination of source-water mixing (i.e., differences in recharge pathways). The integration of the various geochemical tracers will allow for identification of source (upgradient) waters and an interpretation of their possible geologic source such as high flow zones or inner-basin recharge. This discrimination according to an integrated tracer-based recharge model will allow “old” or “young” water to be separated as part of a mixed water packet moving through the system from an origin point to downgradient locations.

4. Methods and Analyses

4.1 Existing Data Compilation

Existing water chemistry and tracer data are available in published articles, theses, and through the Palouse Basin Aquifer Committee. The data will be compiled into a database for use in the source-water tracking analysis.

4.2 Sampling of Supply Wells

Water supply wells (Table 1) will be sampled according to pumping regimes from September 2016 through March 2017. The alternation of well pumping according to supply needs will require sampling to be dispersed across the academic year. The Latah Formation wells are included to assist with discriminating a near-surface recharge component.

Table 1. Supply wells potentially available for groundwater sample collection.

Entity	Latah Fm.	Wanapum Fm.	Grande Ronde Fm.
City of Moscow	Elks and Parker	2 and 3	6, 8, and 9
University of Idaho		Aquaculture	3 and 4
Washington State Univ.		Dairy Farm	4, 6, 7, and 8
City of Pullman			4, 5, 6, 7, and 8
City of Palouse			1 and 3

4.3 Water Sample Analysis

All groundwater samples will be analyzed for field parameters of dissolved oxygen, temperature, pH, and conductivity using a Hanna multi-parameter water-quality meter. Groundwater samples will be subdivided and sent to the appropriate laboratories (Table 2).

Table 2. Laboratory analyses for groundwater samples collected from water supply wells.

Entity	Constituents	Method	Precision
University of Utah	Noble gases	Quadrupole MS	± 1 %
University of Idaho	Cations, anions	ICP-MS, IC	< 0.5 µg/L
University of Arizona	^{13/12} C	Gas-ratio MS	± 0.30 ‰
Pacific Northwest National Laboratory	³⁹ Ar	ultra-low-background proportional counters	± 50 yrs
Boise State University	^{2/1} H, ^{18/16} O	Spectroscopic, cavity ring	< 0.5 ‰

4.4 Recharge Analysis

The recharge model will be refined through scenario testing of conservative tracers and geochemical modeling of conservative and nonconservative tracers to partition select groundwater locations between likely source waters. Scenario testing of conservative tracers consists of a linear optimization of possible mixing scenarios given feasible limits and constraints of the conservative solutes. This analysis will provide an initial view of the mixing relations of waters along flowpaths within and between aquifers. The geochemical modeling (USGS PHREEQC) will allow for refinement of the mixing scenarios through incorporation of nonconservative (reactive and/or decay) tracers. This work is considered an initial stage of analysis that would lead to lumped parameter (tracer) or physical flow modeling that fully incorporates the physical space of the aquifers.

- Values of ^{14}C will be adjusted for a dead carbon input according to new data evaluation.
- ^3H values will be paired with new ^3He and ^{39}Ar values to refine the modern water component.
- He isotopes will be evaluated for indicators of modern water components (^3H presence) and(or) deep gas inputs that can correspond to CO_2 additions.
- Noble gas data will be combined with updated tracer data to evaluate changes to composite water samples because of likely differences in source waters.

5. Resources, Timeline, and Indicators of Success

5.1 Resources and Costs

The investigation will be overseen by Jeff Langman, Hydrogeochemist, University of Idaho, and implemented by students participating in Dr. Langman's Geochemistry of Natural Waters and Environmental Hydrogeology courses (2016/17 academic year). Included in the costs are expenses for travel (PNNL and sampling) and supplies to collect and analyze samples. Approximately 25 groundwater samples will be targeted for sample collection.

Table 3. Project costs.

Funding Category	Cost
PI Salary	\$5,291
Fringe	\$1,672
Travel	\$4,000
Supplies	\$2,500
Analyses	\$22,250
Overhead	\$0
Total	\$35,713

5.2 Timeline

The study will begin in August 2016 (Table 4) if funding is approved and the Geochemistry of Natural Waters course proceeds as planned. It is expected that the investigation will occur over 1.5+ year. Progress presentations will be completed by each class at the end of each semester and a final presentation will be given by Dr. Langman at the completion of the study. Manuscripts derived from the work will be submitted for publication in 2018.

Table 4. Project timeline.

Timeline:	2016 (quarters)			2017		
Task:	3	4	1	2	3	4
Data compilation	█					
Field sampling		█		█		
Lab analyses		█	█			
Data review			█			
Data evaluation				█		
Presentation		█				█
Manuscript					█	

5.3 Indicators of Success

- Refinement of the Palouse Basin recharge model.
- Ability to numerically discriminate source waters and recharge pathways.
- Training and graduation of University of Idaho students with regards to geochemical tracers.
- Publication of the recharge model and refinement of the tracer application for this fractured basalt aquifer.

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