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### Title

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**Determining flow, recharge, and vadose zone drainage in an unconfined aquifer  
from groundwater strontium isotope measurements, Pasco Basin, WA.**

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## 1 Abstract

Strontium isotope compositions ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) measured in groundwater samples from 273 wells in the Pasco Basin unconfined aquifer below the Hanford Site show large and systematic variations that provide constraints on groundwater recharge, weathering rates of the aquifer host rocks, communication between unconfined and deeper confined aquifers, and vadose zone-groundwater interaction. The impact of millions of cubic meters of wastewater discharged to the vadose zone ( $10^3$ - $10^5$  times higher than ambient drainage) shows up strikingly on maps of groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$ . Extensive access through the many groundwater monitoring wells at the site allows for an unprecedented opportunity to evaluate the strontium geochemistry of a major aquifer, hosted primarily in unconsolidated sediments, and relate it to both long term properties and recent disturbances. Groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  increases systematically from 0.707 to 0.712 from west to east across the Hanford Site, in the general direction of groundwater flow, as a result of addition of Sr from the weathering of aquifer sediments and from diffuse drainage through the vadose zone. The lower  $^{87}\text{Sr}/^{86}\text{Sr}$  groundwater reflects recharge waters that have acquired Sr from Columbia River Basalts. Based on a steady-state model of Sr reactive transport and drainage, there is an average natural drainage flux of 0-1.4 mm/yr near the western margin of the Hanford Site, and ambient drainage may be up to 30 mm/yr in the center of the site assuming an average bulk rock weathering rate of  $10^{-7.5}$  g/g/yr.

## 2 Introduction

Groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  variations that result from water-rock interactions can be used to identify flow paths and document interaction between different aquifers (e.g., Musgrove and Banner, 1993; Banner et al., 1994; Johnson and DePaolo, 1994, 1996, 1997a, b; Bullen et al., 1996; Johnson et al., 2000; Woods et al., 2000; Gosselin et al., 2001). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of groundwaters is governed by input of Sr from mineral dissolution, and is therefore determined by the Sr concentration, age, and Rb/Sr ratio of the minerals in communication with the water. The extent to which the  $^{87}\text{Sr}/^{86}\text{Sr}$  in pore water approaches that of the mineral is related to both the chemical processes of mineral dissolution and the physical rate of transport. Adsorption and ion exchange have no direct effect on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the dissolved Sr at steady state, but will affect the temporal response of  $^{87}\text{Sr}/^{86}\text{Sr}$  in a groundwater system to changes in boundary conditions.

The fluid-rock interaction that governs  $^{87}\text{Sr}/^{86}\text{Sr}$  is coupled to transport rates. Measurements of  $[\text{Sr}]$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  in pore water can provide constraints on drainage rates through the vadose zone (e.g., Sonnethal and Bodvarsson, 1999; Maher et al., 2003a). Since both the dissolution rate and transport rates affect the evolution of  $^{87}\text{Sr}/^{86}\text{Sr}$  in pore fluids, a detailed understanding of the effects of mineral weathering on the isotopic composition of dissolved Sr (e.g., Blum and Erel, 1995; Bullen et al., 1997; Taylor et al., 2000a, b; White et al., 2001; White and Brantley, 2003) is necessary to determine drainage rates in the vadose zone. In groundwater systems it is often easier to determine the transport rate, thereby constraining the rate of dissolution. For unconfined aquifers, communication between the vadose zone and the groundwater system must be

6/29/04

considered in addition to the effects of weathering. Assuming the rate of transport can be determined, it should then be possible to constrain maximum rates for both weathering and drainage in unconfined aquifer systems.

The Pasco Basin is unique as a subject of groundwater geochemical study because the unconfined aquifer is penetrated by more than a thousand wells drilled for monitoring groundwater contamination related to the Hanford Site, and hence a detailed characterization of the isotopic patterns is possible. Most previous studies of Sr isotopes in groundwater have been conducted in host rocks that are volcanic (e.g., Johnson and DePaolo, 1994; Johnson et al., 2000), limestone (Banner et al., 1994; Woods et al., 2000) or in situations where flow paths were nearly normal to stratigraphy (Johnson and DePaolo, 1997). One exception is Bullen et al.'s (1996) study of  $^{87}\text{Sr}/^{86}\text{Sr}$  in a shallow sandy aquifer. The Hanford Site represents a different situation because the host rocks are unconsolidated sediments with large variations in lithology, and the groundwater flows through the same units for the entire length of the aquifer. The Hanford Site also differs in that the flow is not fracture-controlled. The pattern of groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios at the Hanford Site reflects groundwater transport, weathering of the sediments in the aquifer, upwelling from deeper confined aquifers, and recharge from runoff, springs and vadose zone drainage. The Sr isotope data are incorporated into models of Sr isotope transport to derive estimates of vadose zone drainage that are independent of vadose zone hydrologic models, and to constrain field-scale weathering rates in this important aquifer.

### **3 Setting**

The Hanford Site is located in the Pasco Basin in south-central Washington state, approximately 10 km north of the confluence of the Columbia and Yakima rivers (Figure

6/29/04

1). The Pasco Basin consists of sedimentary deposits overlying gently folded and faulted Miocene tholeiitic basalt flows of the Columbia River Basalt Group. Unconformably overlying the basalt is the Pliocene Ringold Formation, which consists of fluvial deposits of gravel, silt, and clay. A zone of pedogenic carbonate, part of the Cold Creek Unit (CCU), was developed on top of the eroded surface of the Ringold Formation and in overlying gravel deposits during arid climate conditions (Slate, 1996; US DOE, 2002).

During the Pleistocene epoch, the collapse or floatation of ice dams released vast amounts of floodwater from Glacial Lake Missoula, which formed the Channeled Scabland of eastern Washington, and deposited a sequence of sands and gravels in Pasco Basin (Bretz, 1969; Waitt, 1985). These mostly unconsolidated sediments of broadly granitic provenance are known as the Hanford formation (informal designation, see discussion in US DOE 2002). Recently reported radiometric and paleomagnetic data suggest that catastrophic floods occurred episodically throughout the Pleistocene, hence the Hanford formation may be as old as 2 million years at its base and as young as 10,000 years at the top (Bjornstad et al., 2001; Clague et al., 2003). Holocene deposits of alluvial and eolian sands overlie the Hanford formation sediments in some areas of the Hanford Site (Lindsey, 1994).

The contrast in composition and mineral age between the flood deposits of the Pasco Basin and the surrounding highlands of basalt provide distinct isotopic compositions for the sources of Sr in groundwater. Maher et al. (2003a) report  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.710-0.712 for bulk analyses of the Hanford formation sands and silts. Members of the Columbia River Basalt Group (CRBG) that are observed in and around the Hanford Site include the Wanapum, Grande Ronde, and Saddle Mountain flows.

6/29/04

Hooper and Hawkesworth (1993) report  $^{87}\text{Sr}/^{86}\text{Sr}$  values of 0.704-0.705 for the Wanapum and Grand Ronde flows, but their  $^{87}\text{Sr}/^{86}\text{Sr}$  measurements of Saddle Mountain flows are in the range 0.706 to 0.710. It is not known if this large variation in  $^{87}\text{Sr}/^{86}\text{Sr}$  is present in the Saddle Mountain basalts within the Pasco Basin.

Natural recharge to the unconfined aquifer primarily comes from springs, drainage through the vadose zone, and runoff from basalt ridges that comprise the western border of the Hanford Site (Gee et al., 1992). The unconfined aquifer flows from the basalt ridges west of the Hanford Site through the predominantly granitic sediments of the Ringold and Hanford Formations, to the Columbia River along the eastern boundary of the site. An underlying system of confined aquifers is present in the fractured basalt and sedimentary interbeds of the Columbia River Basalt Group (Spane and Webber, 1995). Communication between the unconfined and confined aquifers may occur where vertical hydraulic gradient and local permeability permit.

Plutonium for nuclear weapons was produced in reactors along the Columbia River (the "100 Areas") and chemically separated from other reactor products near the center of the Hanford Site (the "200 Areas") from the mid 1940's until the late 1980's. The byproducts of Pu production and purification at the Hanford Site now comprise some of the most serious and complex environmental problems in the USA. High-level radioactive waste generated from these activities was initially stored in single-shelled tanks, many of which are known to have leaked. Large quantities of low-level waste were discharged directly to the ground through infiltration ponds (e.g., "U Pond"), trenches, and cribs (buried, open-bottomed containers). As a result, there is considerable mixed waste and radionuclide contamination in the vadose zone at Hanford, and a

6/29/04

number of contaminant plumes have been documented in the unconfined aquifer below the site (Hartman et al., 2002). The extent to which the vadose zone contaminants will impact regional water resources such as the Columbia River depends on the degree of geochemical and hydrologic interaction between vadose zone drainage and the aquifer waters.

## **4 Samples and Methods**

### **4.1 Samples**

More than 300 samples were collected for isotopic analysis from 273 Hanford groundwater monitoring wells between 1999 and 2003 (Figure 2). Most of the samples are collected from near the top of the unconfined aquifer, just below the water table. Samples were filtered, acidified with HNO<sub>3</sub> (ULTREX) and sealed in 250 mL polyethylene bottles. These data are augmented by a vast amount of chemical and hydrological information published as part of the ongoing environmental monitoring effort at Hanford (Hartman et al., 2002).

### **4.2 Analytical Methods**

For Sr isotopic analysis of water samples, acidified 20 ml aliquots were spiked (in order to obtain Sr concentrations) and evaporated to dryness. All samples were then purified by ion exchange chromatography using Eichrom Sr- Spec resin in 0.250 ml Teflon columns. Yields for the chemical separations are about 98%. Total procedural blanks were approximately 200 pg. Given the small contribution from blank relative to the total amount of Sr analyzed, no blank corrections were applied. Sr isotopic ratios



6/29/04

were measured on a VG354 multi-collector thermal ionization mass spectrometer. The average value for NBS 987 during the analyses was  $0.710286 \pm 0.000020$  ( $2\sigma$ ). The generally accepted value for this standard is between 0.71024 and 0.71025, but no corrections have been made to the data reported here. Any corrections would be insignificant for the purposes of this study.

### **4.3 Contouring and Profiles**

In order to contour and calculate profiles through the data, the available samples are first gridded by kriging using the GSTAT package (Pebesma and Wesseling, 1998). Contours and profiles are calculated from gridded data using the Generic Mapping Tools software (Wessel and Smith, 1998).

## **5 Results**

### **5.1 $^{87}\text{Sr}/^{86}\text{Sr}$ in Hanford area rivers**

The Hanford Site lies just north of the confluence of the Columbia and Yakima rivers. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of samples from these two rivers reflect the contrast in geochemistry of rocks within the Columbia and Yakima watersheds upstream of the Hanford Site. Above its confluence with the Yakima, the Columbia River receives most of its input from the Cascades and the Canadian Rockies. Thirteen samples of the Columbia River (Table 1) have an average  $^{87}\text{Sr}/^{86}\text{Sr}$  of  $0.7141 \pm 0.0002$  ( $2\sigma$ ), consistent with input from relatively old mid-continental rocks of its drainage area. Sr is relatively dilute in Columbia River waters along the Hanford Site, with concentrations that range from 61 to 99  $\mu\text{g}/\text{L}$ . One sample collected from the Yakima River has a Sr concentration

6/29/04

of 136  $\mu\text{g/L}$ , and a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.70731, consistent with input from a lower  $^{87}\text{Sr}/^{86}\text{Sr}$  source such as the Columbia Plateau flood basalts and Cascade volcanic rocks found in the Yakima River watershed.

Samples collected from the Priest Rapids Dam, upstream of the Hanford Site, had  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios that are mostly indistinguishable from samples collected on the same dates at the Hanford Townsite and Richmond Pump House, downstream from Hanford (Table 1). Samples collected during 1999 show small but measurable variability in  $^{87}\text{Sr}/^{86}\text{Sr}$  and [Sr] with the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.71469), highest [Sr] (99  $\mu\text{g/L}$ ) samples collected in April, and the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.71349), lowest [Sr] (61  $\mu\text{g/L}$ ) samples collected in June. These differences may indicate seasonal variability in the strontium geochemistry of the Columbia River along the Hanford Site, but additional sampling is needed to define the annual variations. The maximum range of  $^{87}\text{Sr}/^{86}\text{Sr}$  in the Columbia River is small ( $\sim 0.001$ ) relative to range of values observed in groundwater across the Hanford Site ( $\sim 0.007$ ). Hence, the water used for engineering activities, which was derived exclusively from the Columbia River, can generally be expected to have a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.714.

## **5.2 $^{87}\text{Sr}/^{86}\text{Sr}$ variations in groundwater**

Groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the unconfined aquifer generally increase from 0.707 to 0.712 as groundwater flows from west to east across the Hanford Site (Figure 2A). Groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  is close to 0.708 at the northwest and southwest margins of the site, adjacent to the Yakima Ridge and northern Rattlesnake Hills. This low  $^{87}\text{Sr}/^{86}\text{Sr}$  groundwater is attributed to recharge from springs and runoff from the basalt ridges that form the western boundary of the Hanford Site.

6/29/04

An increase of  $^{87}\text{Sr}/^{86}\text{Sr}$  to values of 0.711-0.712 occurs in the central part of the Hanford Site, especially in areas where hydraulic gradients are relatively low. This central zone of higher  $^{87}\text{Sr}/^{86}\text{Sr}$  values extends east-northeast to the Columbia River. Groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.711-0.712 is within the range of values measured from bulk sediments from the Hanford formation, and deep vadose zone pore waters (Maher et al., 2003a).

The disturbances on groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  caused by discharges at the surface are readily apparent in the 200 West and 200 East Areas (Figures 2B and C), where chemical processing of fuel rods and disposal of vast volumes of wastewater took place. The 200 West Area has relatively high hydraulic gradients, while in the 200 East Area it is often difficult to discern the direction of groundwater flow due to the very low hydraulic gradients and high transmissivity. Groundwater appears to move mainly to the south-southeast from the 200 East Area, based on contaminant plume migration (Hartman et al., 2002). The large volumes of water that were dumped at the surface have substantially altered the head profile across the 200 Areas, increasing head in some wells by more than 22 m. The resulting groundwater mounds are transitory and have decreased by more than 6 m in the past 20 years (Hartman, 2000).

In the vicinity of the highly impacted 200 Areas (Figures 2B and 2C), gradients in groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  are much higher than in other parts of the Hanford Site. For example, in the 200 West Area  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios increase from 0.708 west of the U pond to 0.713, just 1 km to the east. East of this “plume” of high  $^{87}\text{Sr}/^{86}\text{Sr}$ , groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  decreases to 0.710.

6/29/04

A zone of  $^{87}\text{Sr}/^{86}\text{Sr}$  values between 0.711 and 0.712 is centered on the 200 East Area. Groundwater from several wells just east of the 200 E Area have lower  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.709-0.710), in apparent reversal to the general increase of  $^{87}\text{Sr}/^{86}\text{Sr}$  from west to east across the site. This shift to conspicuously low groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  south of Gable Mountain is accompanied by lower Sr concentration (around 100  $\mu\text{g}/\text{L}$ ). Correlated decreases in Sr concentration and  $^{87}\text{Sr}/^{86}\text{Sr}$  are indicative of recharge from basalt-hosted aquifers, and probably reflect upwelling of confined aquifer waters south of Gable Mountain. This area coincides with the inferred location of the May Junction normal fault (shown in cross section on Figure 1B), and is near a documented erosional window in the Elephant Mountain basalt unit, where the hydraulic head of the confined aquifer system exceeds that of the unconfined aquifer (Hartman, 2000; Vermeul et al., 2002).

A large variation in groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  is observed between Gable Mountain and the Columbia River, in the vicinity of the 100 Area nuclear reactors (Figure 2A). Groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  is generally high (0.712-0.714) to the northwest of Gable Mountain near the 100B/C, 100-K, 100-N, and 100-D Areas. In the eastern 100 areas (H and F), groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  is significantly lower (0.709-0.711). The elevated  $^{87}\text{Sr}/^{86}\text{Sr}$  in wells from the western 100 areas can be explained by input from the Columbia River, since groundwater levels in this area respond to changes in river stage (Hartman, 2000).

The input of high  $^{87}\text{Sr}/^{86}\text{Sr}$  water from the Columbia River apparently does not extend to the east, where  $^{87}\text{Sr}/^{86}\text{Sr}$  is 0.709-0.711. This low  $^{87}\text{Sr}/^{86}\text{Sr}$  is consistent with upwelling from the deeper basalt-hosted aquifers. The hydraulic head in the confined aquifer system exceeds that of the unconfined aquifer by more than 20 m in this area of low  $^{87}\text{Sr}/^{86}\text{Sr}$ .

6/29/04

Approximately 15 km north of their confluence, the elevation of the Yakima River is 16m higher than the Columbia River. This elevation difference provides a hydraulic gradient across the southern Hanford Site. Groundwater samples from 18 wells located in the southern corner of the Hanford Site have low  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.707-0.710), within the range of values expected for input from the Yakima River. These data indicate that the unconfined aquifer likely receives input from the Yakima River

Two wells with anomalously high  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.716 and 0.718 respectively) near the Energy Northwest area are plotted in Figure 2 (black triangles), but are not included in the contoured data set. These wells are located in a low-hydraulic conductivity window within a southeast trending zone of high hydraulic conductivity (Vermeul et al., 2001). Flow may be channeled around this area, as evidenced by a low-concentration window within the tritium contamination (Hartman et al, 2002). A source of high  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $>0.714$ ) has yet to be identified at the Hanford Site. Maher et al. (2003a) report pore water  $^{87}\text{Sr}/^{86}\text{Sr}$  up to 0.720 in the very near surface of the 200W Area, but the high  $^{87}\text{Sr}/^{86}\text{Sr}$  did not appear to be linked to any identifiable mineralogic component of the sediment. High  $^{87}\text{Sr}/^{86}\text{Sr}$  groundwater (up to 0.715) is also observed in and around the 300 and Richland North areas, just north of the confluence of the Columbia and Yakima rivers. This higher  $^{87}\text{Sr}/^{86}\text{Sr}$  may be caused by the application of Columbia River water for irrigation and groundwater storage activities by the city of Richland.

### **5.3 Sr concentration**

Groundwaters from unconfined aquifer wells sampled for this study have Sr concentrations between 31 and 868  $\mu\text{g}/\text{L}$ , and average 255  $\mu\text{g}/\text{L}$ . As shown in Figure 3, groundwater samples of average Sr concentration have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios that span the total

6/29/04

variation for the Hanford Site (0.707 to 0.716). Groundwater samples from the 200 E Area and outlying areas (600 Area) with Sr concentrations above 400 ppb tend to have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios clustered around 0.712. The source of high  $^{87}\text{Sr}/^{86}\text{Sr}$ , high [Sr] groundwaters is most likely pore water and exchangeable Sr naturally present in the Hanford vadose zone sediments that has been flushed into the groundwater.

Relatively undisturbed vadose zone pore fluids have Sr concentrations of 1000 to 4000  $\mu\text{g}/\text{L}$  (Maher et al., 2003a) plus additional exchangeable Sr of similar isotopic composition. Hence the vadose zone sediments contain much more labile Sr than is present in the underlying groundwater, since the thicknesses of the vadose zone and the aquifer are similar. The effect of vadose zone leaching is most clearly shown by the 200E groundwaters (Figure 4), which can be modeled as mixtures between vadose zone pore water with  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.712 to 0.713 and a concentration of 1000 - 2000  $\mu\text{g}/\text{L}$ , and local normal groundwater with values of 0.710 – 0.711 and 100  $\mu\text{g}/\text{L}$ . A large quantity of water introduced at the surface increases the water content (or saturation) in the vadose zone and consequently greatly increases the effective permeability and drainage rates through the vadose zone. Mixing of the discharge waters with high [Sr] unsaturated zone pore waters results in a significant volume of relatively fast moving, high [Sr] water that passes through the Hanford vadose zone and mixes with the unconfined aquifer. The magnitude of these effects will be considered in more detail below.

In the 200W Area the relationships between  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr concentrations are more complex than for the 200E Area. Most of the 200W groundwaters have relatively low  $^{87}\text{Sr}/^{86}\text{Sr}$  values, mainly because the ambient groundwater in this part of the aquifer has low  $^{87}\text{Sr}/^{86}\text{Sr}$ . Some of the 200W groundwaters have high [Sr] with  $^{87}\text{Sr}/^{86}\text{Sr}$  that is

6/29/04

too low to be explained by soil water-groundwater mixing (Figure 4). This may be a result of the presence of carbonate-rich Cold Creek units that are just above the water table in this area. The Cold Creek carbonates have a  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.710 (Singleton et al., 2002), and dissolution of the Sr from these units would tend to make the vadose zone fluids entering the aquifer lower in  $^{87}\text{Sr}/^{86}\text{Sr}$ .

## 6 Discussion

The contour patterns of  $^{87}\text{Sr}/^{86}\text{Sr}$  (Figure 2A) roughly mirror contours of hydraulic head (Figure 1A), and thus the observed Sr isotope values appear to be a consequence of the lateral advection of pore fluids coupled with the addition of Sr from weathering sediments and/or drainage from the overlying vadose zone. The overall pattern of  $^{87}\text{Sr}/^{86}\text{Sr}$  in groundwater at the Hanford Site is construed to be a result of recharge water entering the aquifer with a Sr isotope composition close to that of the Columbia River Basalts then gradually acquiring the isotopic values reflective of the sedimentary units during transport. Natural recharge from the Hanford vadose zone is relatively small, 0.01 to 100 mm/yr (Gee et al., 1992; Murphy et al., 1996). However, the Sr concentrations of the pore waters in the vadose zone are typically high (1000-4000  $\mu\text{g}/\text{L}$ ) (Maher et al., 2003a), compared to 100-300  $\mu\text{g}/\text{L}$  in groundwater. Consequently, even relatively small amounts of diffuse recharge can affect the groundwater Sr isotope ratios. The following sections develop a mathematical representation of this conceptual model, estimate likely values for the various components of this model, and then use hydrologic, chemical, and isotopic measurements from the Hanford Site to evaluate the importance of each Sr flux.

## 6.1 Sr isotope transport model

Following the approach of Johnson and DePaolo (1997a), the lateral advective-dispersive transport equation describing the change in concentration with time for an adsorbing solute such as Sr, with contributions from both weathering and the vadose zone in a saturated porous medium can be written as:

$$K_{ret} \frac{\partial C_f}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C_f}{\partial x} \right) - v \frac{\partial C_f}{\partial x} + J_d + I \quad (1)$$

Where  $x$  is the distance along the flow path (assumed to be approximately horizontal),  $D$  is the longitudinal hydrodynamic dispersion coefficient, and  $C_f$  is the solute concentration in the pore fluid. The mean pore water velocity is represented by  $v$ ,  $J_d$  is the reaction flux representing dissolution (positive value) and precipitation (negative value) and the last term,  $I$ , is the flux of Sr entering the groundwater through the vadose zone. The parameter to the left of Equation 1,  $K_{ret}$ , is the retardation factor. See Appendix I, for a list of notation and units used in models for this study.

The reaction flux,  $J_d$ , is a result of dissolution processes only, as precipitation does not change the Sr isotopic composition of the fluid. Each mineral that is undergoing weathering (dissolution) provides a contribution to this bulk flux:

$$J_d = MR_d C_s \quad (2)$$

Where  $R_d$  is the bulk dissolution rate ( $\text{time}^{-1}$ ),  $C_s$  is the bulk solid Sr concentration (per unit mass), and  $M$  is the local solid/fluid mass ratio.



## **6.2 Sr input from the vadose zone**

Estimates of vadose zone recharge at the site vary spatially depending on groundcover, soil hydraulic properties and anthropogenic disturbances. Maher et al. (2003a) estimate that the isotopic composition of Sr in a 1-D column of the Hanford unsaturated zone would take between 1,800 and 20,000 years to reach a steady state. Given this estimate, it is likely that the near surface pore water Sr isotope compositions are evolving with time, but near the base of the Hanford formation, where the water table is located, the flux of Sr is approximately constant with time. Thus we begin by assuming that the input of Sr is constant over time (but spatially variable) at the vadose zone-groundwater interface. This assumption is not valid near areas of wastewater discharge (e.g. the 200W and 200E Areas), where the drainage of large volumes of water since the 1940's has perturbed the Sr geochemistry of the aquifer.

We assume that vertical mixing is sufficiently rapid within the aquifer that concentration and isotopic gradients are negligible with depth. This assumption is reasonable based on the expected magnitude of transverse dispersion in the aquifer relative to the aquifer thickness. The longitudinal dispersion coefficient is in the range  $10^4$  to  $10^5$  m<sup>2</sup>/yr, based on a dispersivity of 95 m (Kincaid et al., 1998). If the transverse dispersion coefficient is ten times smaller (e.g., Freeze and Cheery, 1979), then the characteristic distance for mixing over a period of 1 year (during which time the groundwater flows about 100m to 1 km horizontally), is in the range 30 to 100 meters, comparable to the thickness of the aquifer. The net transfer of Sr to the aquifer can then be expressed in terms of the drainage flux,  $q$ :

6/29/04

$$I = \frac{q}{\phi h} (C_f' - C_f) \quad (3)$$

Where  $C_f'$  is the concentration of Sr in the pore water entering the aquifer from the vadose zone. The term  $h$  is the vertical thickness of the aquifer, and  $\phi$  is the effective porosity. Recasting equation (1) in terms of an isotope ratio (in this case  $^{87}\text{Sr}/^{86}\text{Sr}$ ) yields:

$$K_{ret} \frac{\partial r_f}{\partial t} = D \left( \frac{\partial^2 r_f}{\partial x^2} \right) - v \frac{\partial r_f}{\partial x} + R_d M \frac{C_s}{C_f} (r_d - r_f) + \frac{q}{\phi h} \frac{C_f'}{C_f} (r_f' - r_f) \quad (4)$$

The longitudinal dispersivity ( $\lambda$ ), in the unconfined aquifer is approximately 95 m (Kincaid et al., 1998), where:

$$\lambda = \frac{D}{v} \quad (5a)$$

The effect of dispersion on the evolution of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the groundwaters can be assessed by comparing the dispersivity to the isotopic “reaction length” for Sr isotopes, which is given by (Johnson and DePaolo, 1994):

$$L_{Sr} = \frac{v C_f}{M R_d C_s} \quad (5b)$$

For  $v$  in the range 20 to 50 m/yr, the value of  $L_{Sr}$  is in the range 4800 to 12000 m ( $M = 6$ ,  $R_d = 5 \times 10^{-7}$  g/g/yr,  $C_s/C_f = 1400$ ). Because  $L_{Sr}$  is about 50 to 130 times larger than  $\lambda$ , dispersion has little effect on the results. To be more accurate, the combined effects of weathering and diffuse recharge should be accounted for in  $L_{Sr}$ , which decreases the reaction length by half, but still leaves it much larger than  $\lambda$ .

As a test of the above analysis, models were run with dispersion included. The inclusion of dispersion changed the calculated model  $^{87}\text{Sr}/^{86}\text{Sr}$  values by less than 0.001 % relative to models with no dispersion. The models discussed in the following sections do not include dispersion.

### **6.3 Steady state models**

The time for the isotopic composition of an adsorbing solute such as Sr to approach steady state, i.e. the time ( $\tau$ ) for an exchange front to traverse a length (L) depends on the pore fluid velocity and retardation factor ( $K_{ret}$ ) according to:

$$\tau = \frac{LK_{ret}}{v} \quad (6)$$

Based on Sr  $K_d$  values of 5-15 mL/g (Kincaid et al., 1998), and a saturated porosity of 0.25, Sr retardation factors in Hanford groundwater range from 30 to 90. The time ( $\tau$ ) required for a Sr exchange front from groundwater recharge at the western margin of the site near the start of profiles A-A' and B-B' (Figure 2A) to reach the Columbia River is approximately 30,000 to 90,000 years. At the current depth of the water table, most of the sediments are older than 750 ka (Bjornstad et al., 2001). However, periodic outbursts from glacial Lake Missoula may have perturbed the groundwater system in the Pasco Basin up until the cessation of flooding at around 12 ka. In addition, Quaternary climate changes occur on 10 - 100 kyr time scales. Sr isotope compositions in the unconfined aquifer at Hanford may be close to steady state, but this is not guaranteed by any means. For example, groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  near the Columbia

River and in areas that were disturbed by infiltration ponds are unlikely to be at steady state.

Once the system has reached steady state, the exchange reactions have no effect on the isotope ratio of the groundwater, rather the isotope ratio at a given position is a function of dissolution and vadose zone input only (Johnson and DePaolo, 1997a,b).

Neglecting any input from the vadose zone the Sr isotope ratios along a transect can be modeled according to:

$$\frac{dr_f(x)}{dx} = \frac{MR_d C_s}{vC_f} [r_d - r_f(x)] \quad (7)$$

This model can be used to assess the effects of varying the weathering rate parameter  $R_d$ .

The isotopic effect of Sr input from vadose zone drainage is evaluated by considering the coupled processes of Sr dissolution, drainage, and transport described by:

$$\frac{dr_f(x)}{dx} = \frac{MR_d C_s}{vC_f} [r_d - r_f(x)] + \frac{q}{\phi v h} \frac{C_f'}{C_f} [r_f' - r_f(x)] \quad (8)$$

Where  $q$ , is the average drainage rate from the vadose zone to the unconfined aquifer of pore waters with concentration  $C_f'$  and isotope ratio  $r_f'$ . The thickness of the unconfined aquifer ( $h$ ) is documented in Hartman (2000). It should be noted that, because  $r_d \approx r_f'$ , equation 8 can be written to a good approximation as:

$$\frac{dr_f(x)}{dx} \approx \frac{MR_d C_s + (q/\phi h) C_f'}{vC_f} [r_d - r_f(x)] \quad (8b)$$

Equation 8b shows that the data give us directly a value for the term on the far right hand side, which includes the additive effects of weathering reactions in the aquifer and diffuse recharge through the vadose zone. To the extent that we can constrain  $R_d$  we can derive estimates for  $q$ , and vice versa.

## **6.4 Groundwater velocity**

Average linear pore fluid velocity ( $v$ ) is calculated based on Darcy's law. The head gradient is calculated every 500 m across the Hanford Site from published records of well head data (Hartman et al., 2002). Hydraulic conductivity is estimated by dividing the transmissivity at the top of the water table determined from well-pumping tests and flow model calibrations (Cole et al., 1998; Vermeul et al., 2001) by the saturated thickness of the unconfined aquifer (Hartman, 2000). An effective porosity value of 0.25 is used for the unconfined aquifer based on previous groundwater flow studies (Kincaid et al., 1998).

## **6.5 $^{87}\text{Sr}/^{86}\text{Sr}$ and concentration of Sr inputs:**

The parameter ( $r_d$ ) represents the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of Sr released by weathering of the bulk sediments. This bulk parameter characterizes the isotopic and chemical composition of Sr-bearing minerals, and their relative dissolution rates (Johnson and DePaolo, 1996; Maher et al., 2003a). A first approximation of  $r_d$  can be obtained from the bulk  $^{87}\text{Sr}/^{86}\text{Sr}$  of the sediments. These values are consistently in the range 0.7095 to 0.7115 for Hanford formation samples. There are no data for the Ringold Formation. Studies of vadose zone pore fluids and leaching experiments on the Hanford sediments suggest that  $r_d$  is typically close to the bulk sediment  $^{87}\text{Sr}/^{86}\text{Sr}$ , but tends to be somewhat higher in general, and can be considerably higher in surface soils where there may be rapidly weathering mica. Maher et al. (2003a) used  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios determined for  $\text{HNO}_3$  leachates of the soils as a best estimate of the  $r_d$  values, and these values were 0.7134

6/29/04

$\pm 0.0014$  for the Hanford formation (19 samples) and  $0.7140 \pm 0.0015$  for the Ringold Formation (6 samples). Two samples from the Cold Creek units gave a lower value of  $0.7113 \pm 0.0010$ . Based on these results, and assuming most groundwater in the unconfined aquifer is in contact with either the Ringold or Hanford sediments, we assign a value of 0.7135 to  $r_d$ .

The change in pore water  $^{87}\text{Sr}/^{86}\text{Sr}$  due to mineral dissolution is proportional to the concentration of Sr in dissolving solids (Equation 4). Bulk Sr concentrations in the the Hanford formation sediments range from 215 to 358 ppm (Serne et al., 2002; Maher et al., 2003a), with an average value of 325 ppm. Limited data exist on the bulk Sr concentration of Ringold Formation sediments, but a measurement from Serne et al. (2002) suggests that the concentration of Sr in Ringold sediments is lower by a factor of 2, or about 170 ppm.

Based on the results of Maher et al. (2003a), the average Sr concentration of pore waters from Hanford sediments in the deep vadose zone is  $1700 \mu\text{g}/\text{L}$ , and the  $^{87}\text{Sr}/^{86}\text{Sr}$  at the depth of the water table is close to 0.712. The thickness of the unconfined aquifer is 20m to 175m as documented in Hartman (2000).

## **6.6 Weathering Rates for the Hanford and Ringold sediments**

The determination of weathering rates in natural systems is difficult due to the variety of factors that control dissolution and the lack of correspondence between field and laboratory determined rates (White and Brantley, 2003). As a starting point we follow the approach of Maher et al., (2003a) by estimating the bulk dissolution rates ( $R_d$ ) in the vadose zone for Hanford and Ringold sediments based on the data of White et al. (1996) for Sr-bearing minerals of the Merced chronosequence in Northern California.

6/29/04

The Merced and Hanford sediments are both derived from granitic parent material, have comparable ages and mineralogical compositions, and are affected by similar climates, such that bulk dissolution rates are likely to be comparable between the sites. Plagioclase and alkali-feldspar dissolution rates in the vadose zone are estimated to range from  $10^{-6.0}$  to  $10^{-5.5}$  g/g/yr and from  $10^{-6.4}$  to  $10^{-5.9}$  g/g/yr respectively (Maher et al., 2003a). The bulk dissolution rates ( $R_d$ ) for Hanford and Ringold sediments in the vadose zone can then be estimated according to the mineralogical composition of the sediments. The abundance of primary Sr-bearing minerals in the Pasco Basin sediments is approximately 15% plagioclase and 40% K-spar for the Hanford formation, and 10% plagioclase and 20% K-spar for the Ringold Formation (Serne et al., 2002). Taking these mineral compositions into account, the bulk dissolution rates in the vadose zone are approximately  $10^{-6.5}$  to  $10^{-6}$  g/g/yr for the Hanford formation and  $10^{-6.7}$  to  $10^{-6.2}$  g/g/yr for the Ringold Formation.

Measurements of isotopic disequilibrium for the uranium decay series in pore waters and sediments provide a method for determining *in situ* weathering rates. Preliminary determinations of dissolution rates for the Ringold and Hanford sediments based on the U-series method are consistent with the estimates based on the Merced chronosequence used for the Hanford vadose zone, but suggest rates that are a factor of 5-10 lower in the unconfined aquifer (Maher et al., 2003b). This relation is consistent with a U-series disequilibrium study on a sandy unconfined aquifer in Long Island, NY, which calculated lower dissolution rates in groundwater than in the vadose zone (Tricca et al., 2001). For these reasons, we estimate that dissolution rates in the unconfined aquifer range from  $10^{-6.5}$  to  $10^{-7.5}$  g/g/yr in Hanford sediments and from  $10^{-6.7}$  to  $10^{-7.7}$  g/g/yr in Ringold sediments. Uncertainties in the value of  $R_d$  are significant because the shifts in

6/29/04

groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  with time and distance are the sum of contributions from weathering and from diffuse recharge, and the contributions from the two sources appear to be subequal. The relationship between derived values for vadose zone recharge and weathering rates are discussed further below.

## **6.7 Ambient drainage and weathering**

Our model for Sr isotope evolution in the unconfined aquifer provides a method to couple the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in groundwater to the observed hydraulic head and aquifer thickness. To evaluate the impact of ambient weathering and vadose zone drainage on groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$ , we consider a profile that begins at Dry Creek Valley and follows an approximate streamline of flow toward the Columbia River (A-A' on Figure 2A). This profile was chosen so that it: 1) is oriented approximately perpendicular to contours of hydraulic head, 2) passes near the greatest possible number of wells where  $^{87}\text{Sr}/^{86}\text{Sr}$  has been measured, 3) is far enough from wastewater discharge areas so as not to be strongly affected by water discharged at the surface, and 4) is within 20 km of the assumed recharge from the basalt ridges to the west, so that it should be close to steady state even with a disturbance at 12 Ka.

The ambient increase in  $^{87}\text{Sr}/^{86}\text{Sr}$  across the Pasco Basin is given by a profile through the kriged data set along A-A' which pass near 6 wells where  $^{87}\text{Sr}/^{86}\text{Sr}$  was measured (Figure 5). Groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  increases from 0.7075 to slightly lower than 0.712 along profile A-A', and is accompanied by an increase in Sr concentration from about 100  $\mu\text{g}/\text{L}$  in the recharge zone at the western end to 220  $\mu\text{g}/\text{L}$  at the center of the site.



Figure 6A shows the expected groundwater Sr profile for different values of the weathering rate with no diffuse recharge from drainage through the vadose zone along the flow path. Even at low values of  $R_d$ , weathering of the unconfined aquifer sediments increases the  $^{87}\text{Sr}/^{86}\text{Sr}$  along profile A-A' to some extent. If the weathering rate is  $10^{-7.2}$  g/g/yr in the aquifer sediments, then it is possible to account for all of the observed increase in  $^{87}\text{Sr}/^{86}\text{Sr}$  along A-A' without any input from the vadose zone. Thus, based on our model,  $R_d$  can not be higher than  $10^{-7.2}$  g/g/yr, in order to match the observed  $^{87}\text{Sr}/^{86}\text{Sr}$  profile A-A'. For lower values of  $R_d$ , the disparity between observed and model results in Figure 6A, may indicate a small, but measurable contribution of Sr from vadose zone drainage.

Figure 6B shows the predicted groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  profiles for uniform vadose zone drainage fluxes ( $q$ ) of 0, 0.3, 1, and 10 mm/yr, based on a lower estimate for the weathering rate constant  $R_d$  ( $10^{-7.5}$  g/g/yr) of the Ringold Formation sediments that host the unconfined aquifer along most of this transect. Addition of a constant 0.3 mm/yr flux ( $q$ ) from the vadose zone produces a reasonable fit to the observed  $^{87}\text{Sr}/^{86}\text{Sr}$  profile along most of profile A-A' (Figure 6B). A vadose zone drainage rate of 1 mm/yr captures the general shape of the profile A-A', but results in predicted  $^{87}\text{Sr}/^{86}\text{Sr}$  values that are higher than those observed. Increasing this flux to 10 mm/yr produces model  $^{87}\text{Sr}/^{86}\text{Sr}$  results that approach 0.712 much closer to the beginning of the profile than the observed values. The maximum value of  $q$  that is allowed for  $R_d = 0$  is 1 mm/yr, for constant drainage across the site.

Previous studies of net infiltration predict a variable flux of natural drainage vadose zone across the Hanford Site that ranges from 0 mm/yr up to 100 mm/yr,

6/29/04

depending on soil cover and vegetation (Gee et al., 1992; Fayer and Walters, 1995). The observed groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  profile can be matched exactly using Equation 8 by allowing the steady-state drainage flux ( $q$ ) vary across the site (assuming a weathering rate of  $10^{-7.5}$  g/g/yr). The steady-state values of  $q$  required to fit the model  $^{87}\text{Sr}/^{86}\text{Sr}$ , range from 0 to 0.4 mm/yr along the first 5000m of profile A-A'. From 8000m to 10000m, where the slope of  $^{87}\text{Sr}/^{86}\text{Sr}$  vs. distance steepens, the required drainage rate  $q$  increases to about 0.4-1.4 mm/yr. From 10000 m to 15000 m the value of  $q$  may increase up to 30 mm/yr. Once the groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  is close to the value for the drainage Sr flux (beyond about 15000m on A-A')  $q$  is not constrained.

The steady state values of  $q$  (0 to 1.4 mm/yr) required to match the observed profile from 0 to 10000 m along A-A', and the predicted increase in  $q$  beyond 10000 m are consistent with the drainage estimates based on soil cover and vegetation, which changes from vegetated loam to stabilized sand dunes in this part of the Hanford Site (Gee et al., 1992; Fayer and Walters, 1995). As the drainage estimate derived from our study is based on groundwater compositions, it should be considered an average flux across the vadose zone-water table boundary integrated over the thousands of years needed to establish steady state. Modern drainage rates may increase considerably in other parts of the Hanford Site due to recent activities such as the disposal of water through infiltration ponds in the 200 Areas and removal of vegetation.

## **6.8 Sensitivity of results to input parameters**

We have derived estimates for natural recharge fluxes in the central and western parts of the Hanford Site based on 1-dimensional models for the Sr isotopic balance in the groundwaters. The derived values, which are 0 to 1.4 mm/yr in the west central part

6/29/04

of the site along transect A-A', and of order 30 mm/yr in the east limit of transect A-A', are subject to uncertainty due to natural variability of the input parameters; in particular  $r_d$ ,  $r_f'$ , and  $R_d$ ; and because a 1-D model was used. We have not performed a full Monte Carlo evaluation of the variations, but it is possible to give reasonable estimates of the uncertainties. In general, if the estimates of the weathering rate ( $R_d$ ) are increased, the estimated recharge decreases. It is possible to fit almost all of the groundwater data with zero recharge if the weathering rate is of order  $10^{-7}$  yr<sup>-1</sup> and varies appropriately along the flow path (Figure 6a). Changing the value of  $r_d$  within the range  $0.7135 \pm 0.0015$ , would change the inferred weathering rates for zero recharge by less than a factor of 2 (or  $\pm 0.3$  log units). It is likely that the weathering rate is substantially smaller than  $10^{-7}$  yr<sup>-1</sup>; but it is unlikely that the rate is much below  $10^{-8}$  yr<sup>-1</sup>. For weathering rate of  $10^{-8}$  yr<sup>-1</sup>, the inferred values for recharge would increase by only 0.1 to 0.3 mm/yr for the western part of the site. However, the low value of  $R_d$  would mean that a value of  $q = 0$  would not be possible, and that the minimum values for recharge would be about 0.5 mm/yr in the western part of transect A-A'. Changing the value of  $r_f'$  within the limits  $0.712 \pm 0.001$  also has a small effect on the inferred recharge rates. The use of a 1-D model has little effect on the inferred values of the natural recharge rates because the isotopic contours are not strongly curved along the transect and they are oriented nearly perpendicular to the flow direction.

## **6.9 General comments on results**

The density of water wells drilled and regularly sampled at the Hanford Site allows us to map the variations in Sr isotopic composition with unprecedented detail. The Hanford unconfined aquifer is now characterized in sufficient detail for Sr isotopes (also

6/29/04

for O and C isotopes – a subject to be reported elsewhere), that we can assess the value of Sr isotope data for understanding flow and chemical processes in aquifers. The data show that the isotopic variations are quite large and regular. It was not known beforehand whether the Hanford Site geology was conducive to finding systematic Sr isotopic variations. However, because the primary recharge areas are in Columbia River Basalt at the western margin of the aquifer, the initial Sr isotopic composition of the groundwater is greatly different from that in the sedimentary rocks, and even though there is substantial variability in the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the sediments, the average sediment values are sufficiently different from the basalt values that the change in groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  is systematic across the site.

In the central part of the Hanford site, the isotopic pattern is relatively simple except for the disturbances associated with the 200 areas. The  $^{87}\text{Sr}/^{86}\text{Sr}$  of the groundwater increases gradually as a result of both weathering of the host sediments and diffuse recharge along the flow path. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio reflects the sum of recharge plus weathering contributions. Because we can place constraints on the weathering contribution, we can make some estimates of recharge fluxes. The estimates are entirely independent of any model for the vadose zone hydrology. The fact that the magnitude of the estimates with the Sr isotope approach are roughly in accord with the estimates based on systematics of soil grain size and vegetation cover (Gee et al., 1992; Fayer and Walters, 1995) and chloride mass balance (Murphy et al., 1996) is suggestive both that the Sr isotope data analysis is reasonable and that the overall recharge estimates are accurate.

6/29/04

Areas that have received large amounts of water disposed to the surface, such as the 200 Areas and the Richland North site, show up strikingly on the Sr isotope map (Figure 2). These effects are not specifically correlated with contamination plumes, because the Sr isotope compositions reflect the amount of water disposed to the vadose zone rather than the amount of any specific contaminant. The groundwater Sr isotopic composition is modified as a result of flushing of dissolved and adsorbed Sr from the vadose zone into the groundwater. In the 200 West Area the increase of  $^{87}\text{Sr}/^{86}\text{Sr}$  with distance is much greater than it is immediately to the north and south. The biggest groundwater effects in the 200 West Area appear to be related to the U Pond, where the largest amounts of water were disposed. In the Richland North Area the groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  values are much higher than almost anywhere else on the Hanford Site, and the high values are confined to areas to the south and east of the site.

The northern area of the Hanford Site, north of Gable Mountain and Gable Butte, also has a distinctive isotopic pattern. In the 100 B,C, 100K and 100N areas the Sr isotope map shows the effects of infiltration of Columbia River waters. The general decrease of  $^{87}\text{Sr}/^{86}\text{Sr}$  from west to east indicates that the vadose zone Sr and weathering fluxes have  $^{87}\text{Sr}/^{86}\text{Sr}$  that is lower than 0.713, and also shows the effects on upwelling from the deeper confined aquifer. Other areas of upwelling from the deeper confined aquifer also show up well on the Sr isotope maps of Figure 2. Recharge from the Yakima River in the southern part of the Site is also apparent.

## 7 Conclusions

A contour map of Sr isotope compositions in groundwater provides a method to image groundwater recharge, drainage, and disturbances to the unconfined aquifer below the Hanford Site. Sr isotopes reflect groundwater flow paths and record the effects of anthropogenic disturbances to the groundwater system at Hanford. Natural recharge to the unconfined aquifer primarily comes from the Yakima Ridge and northern Rattlesnake Hills at the western margin of the site, and thus has lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $\sim 0.707$ ) than either Columbia River water (0.714) or water that has equilibrated with the granitic sediments ( $\sim 0.712$ ). Large volumes of low-level wastewater discharged at the surface leaches Sr out of the vadose zone, obscuring the shift of Sr isotopes caused by natural vadose zone drainage and weathering of aquifer sediments.

Groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  in the Hanford unconfined aquifer depends on the coupled effects of drainage through the vadose zone and dissolution of the Pasco Basin sediments. The extent to which groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  approaches the weathering or vadose zone fluxes of Sr is governed by the groundwater velocity, drainage flux, dissolution rate, and aquifer thickness. Combining measurements of hydraulic head and aquifer thickness with measurements of groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr concentration allows for estimates of vadose zone drainage flux in areas that are not significantly impacted by site activities using a steady-state model, and a transient model can be used to investigate the effects of discharging large volumes of water through the vadose zone and into the unconfined aquifer. The  $^{87}\text{Sr}/^{86}\text{Sr}$  increase along a “background” profile across the Hanford Site is consistent with an average vadose zone flux of 0-1.4 mm/yr near the western margin of the site, and may indicate values up to 30 mm/yr in the central part of the site.

6/29/04

Discharges of water to the vadose zone have had a significant impact on groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  in the Pasco Basin due to large amounts of mobile Sr in the vadose zone.

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6/29/04

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6/29/04

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## 10 Figure Captions

Figure 1 A) Location of the Hanford Site, with groundwater monitoring wells, and contours of hydraulic head superimposed on geologic units present at the water table of the unconfined aquifer (contours from Hartman et al., 2002; geology from Hartman, 2000). B) Geological cross section across the Hanford Site after Hartman (2000), along profile W-E.

Figure 2 A) Contour map of  $^{87}\text{Sr}/^{86}\text{Sr}$  in the Hanford unconfined aquifer based on wells sampled for this study (dot color corresponds to the measured value). Two wells (triangles) with anomalously high  $^{87}\text{Sr}/^{86}\text{Sr}$  are not included in the contour map. Profile A-A' is used to discuss  $^{87}\text{Sr}/^{86}\text{Sr}$  variation across the Hanford Site. B) Detailed map of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the Hanford unconfined aquifer at the 200 West Area. C) Detailed map of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the Hanford unconfined aquifer at the 200 East Area.

Figure 3. Sr concentration and  $^{87}\text{Sr}/^{86}\text{Sr}$  in groundwater of the Hanford unconfined aquifer. Boxes depict the observed ranges of  $^{87}\text{Sr}/^{86}\text{Sr}$  in bulk sediment (data from Maher et al., 2003a) and buried carbonates (data from Singleton et al., 2002).

Figure 4. Sr concentration and  $^{87}\text{Sr}/^{86}\text{Sr}$  in groundwater of the Hanford unconfined aquifer. Compositions for typical vadose zone soil water (SW, 0.712, 1700  $\mu\text{g}/\text{L}$ ), Columbia River water (RW, 0.714, 90  $\mu\text{g}/\text{L}$ ) and groundwater (GW, 0.709, 150  $\mu\text{g}/\text{L}$ ) are connected by mixing curves.

Figure 5. Profile of groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  (solid blue) calculated along A-A' (Figure 2A) from the kriged dataset of wells sampled for this study. Measurements of groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  at nearby wells are shown as blue squares. Measurements of Sr concentration at nearby wells are shown as red dots, and are connected by a line between well locations. The water table and depth of the unconfined aquifer are indicated by the shaded blue area.

Figure 6. Groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  (solid blue) profile along A-A' (Figure 2A), calculated from the kriged dataset and compared with a steady state model of groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$ . Measurements of groundwater  $^{87}\text{Sr}/^{86}\text{Sr}$  at wells near A-A' are shown as blue squares. A) The weathering rate has a strong effect on predicted steady state  $^{87}\text{Sr}/^{86}\text{Sr}$  values. We estimate a weathering rate ( $R_d$ ) of  $10^{-7.5}$  g/g/yr along A-A'. B) For a  $R_d$  value of  $10^{-7.5}$  g/g/yr a constant vadose zone drainage ( $q$ ) of 0.3 mm/yr (dashed) results in a steady state model profile that closely matches the observed increase in  $^{87}\text{Sr}/^{86}\text{Sr}$  along A-A'.

6/29/04

Table 1. Sr concentration and  $^{87}\text{Sr}/^{86}\text{Sr}$  from river waters collected near the Hanford Site.

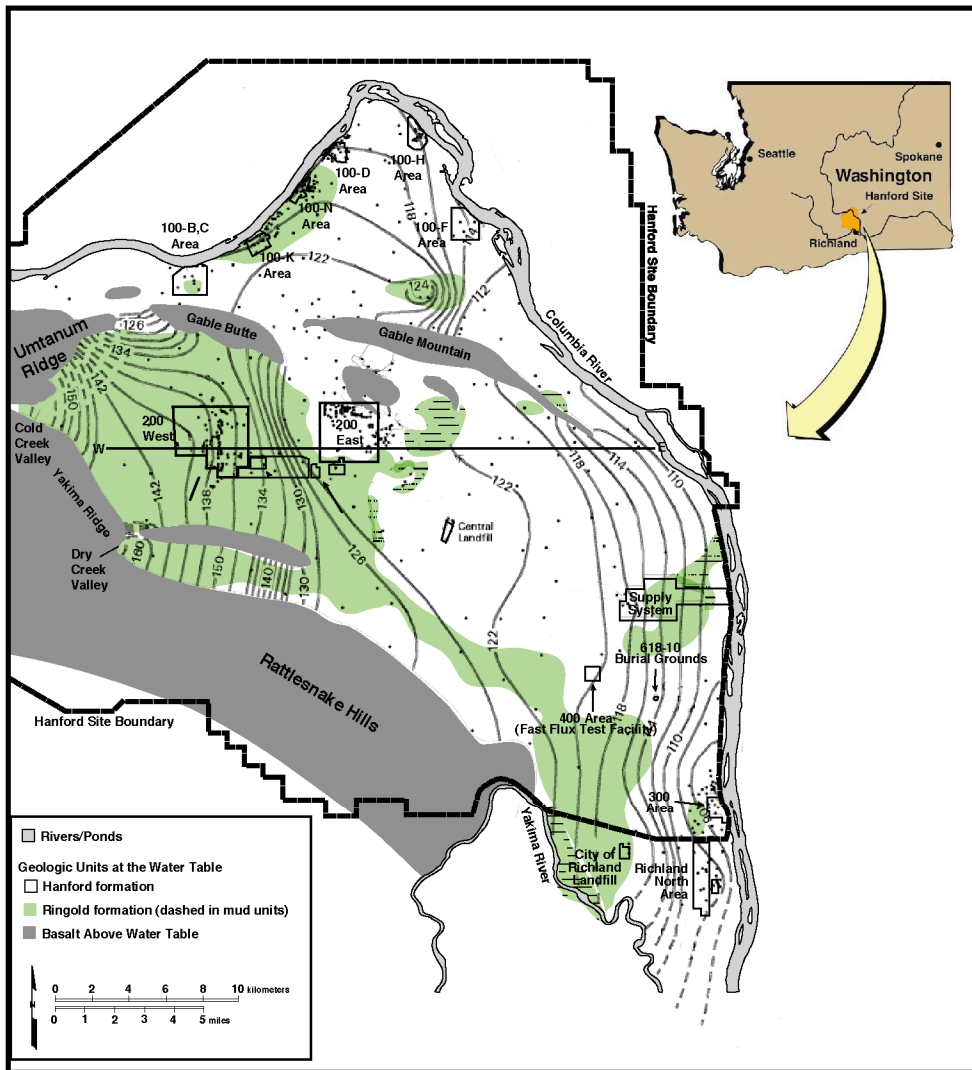
<b>Sample</b>	<b>Location</b>	<b>Date</b>	<b><math>^{87}\text{Sr}/^{86}\text{Sr}</math></b>	<b>[Sr] <math>\mu\text{g}/\text{L}</math></b>
<i>Columbia River</i>				
B0V828	Priest Rapids	04/20/99	0.71469	95
B0V830	Richland Pump House	04/20/99	0.71468	99
B0V832	Richland Pump House	04/20/99	0.71469	97
B0VCX5	Hanford Townsite	05/13/99	0.71441	93
B0VCX3	Priest Rapids	05/13/99	0.71396	93
B0VK77	Priest Rapids	06/30/99	0.71349	68
B0VK79	Richland Pump House	06/30/99	0.71374	61
B0VPP0	Priest Rapids	07/21/99	0.71414	66
B0VPP2	Richland Pump House	07/21/99	0.71419	64
B0W189	Priest Rapids	08/05/99	0.71398	70
B0W191	Richland Pump House	08/05/99	0.71398	70
B0W8R8	Priest Rapids	09/01/99	0.71370	97
B0W8T0	Richland Pump House	09/01/99	0.71366	96
<i>Yakima River</i>				
Yak1	Yakima River at S. Richland	10/10/03	0.70731	136



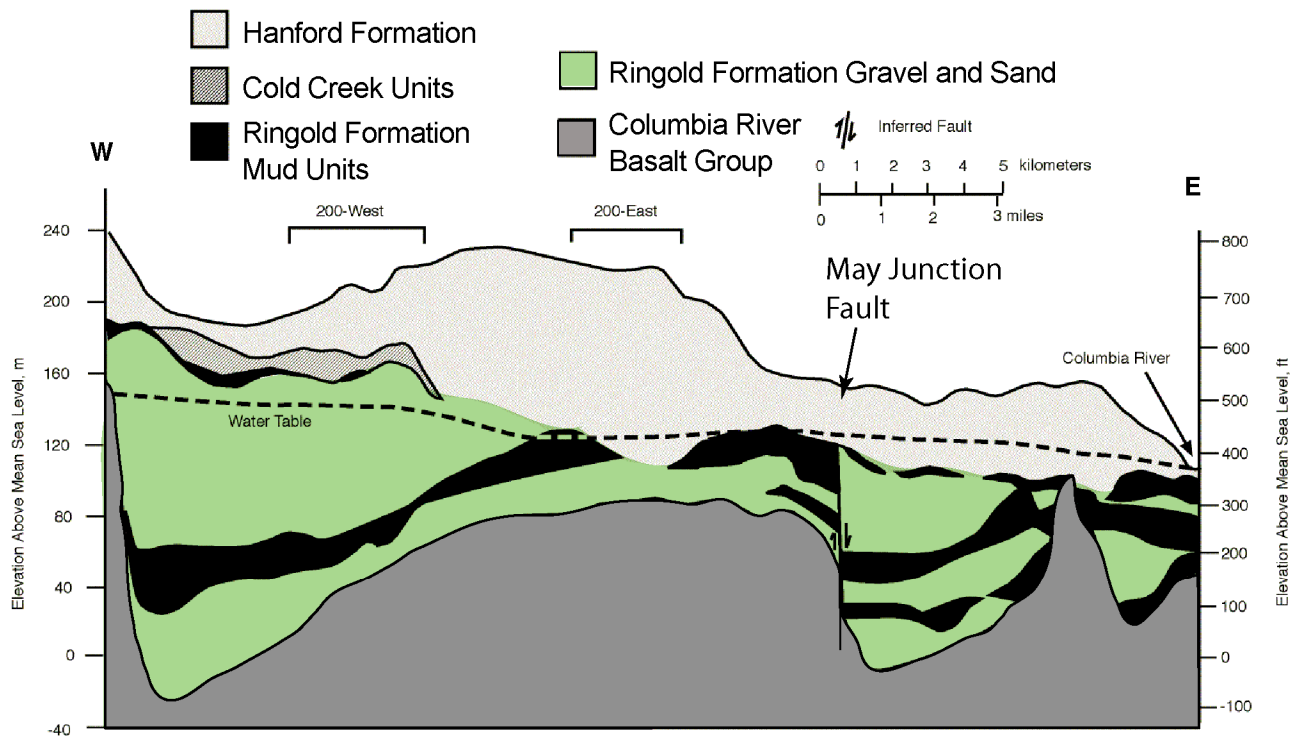
6/29/04

Appendix I. Notation used in models.

Notation		Units
$C_f, C_f', C_s$	Concentration of Sr in the groundwater, vadose zone drainage, and the bulk solid respectively	Mass per volume for fluid, Mass per total mass for solid
$D$	Longitudinal dispersion coefficient	$(\text{Length})^2$ per time
$h$	Aquifer thickness	Length
$I$	Flux of Sr diffusing into the liquid from vadose zone drainage	Mass per unit vol. fluid per unit time
$J_d$	Flux of Sr diffusing into the liquid phase from dissolution	Mass per unit vol. fluid per unit time
$K_{ret}$	Retardation factor ( $= 1 + \rho_b K_d / \phi$ ) where $\rho_b$ is bulk density	
$K_d$	Distribution coefficient	Volume per mass
$L_{Sr}$	Isotopic reaction length	Length
$M$	Ratio of solid mass to fluid volume in a representative volume ( $= \rho_b (1/\phi - 1)$ )	
$q$	Vadose zone drainage flux	Volume per area per time
$R_d$	Bulk solid dissolution rate	Mass per total solid mass per time
$r_f, r_f', r_d$	$^{87}\text{Sr}/^{86}\text{Sr}$ of groundwater, vadose zone drainage and bulk dissolving solid respectively	
$t$	time	
$v$	Linear groundwater velocity	Length per time
$x$	Profile location	length
$\phi$	Effective porosity	
$\lambda$	Longitudinal dispersivity	Length
$\tau$	Characteristic time for an exchange front to traverse a system	Time



**Figure 1A**



**Figure 1B.**

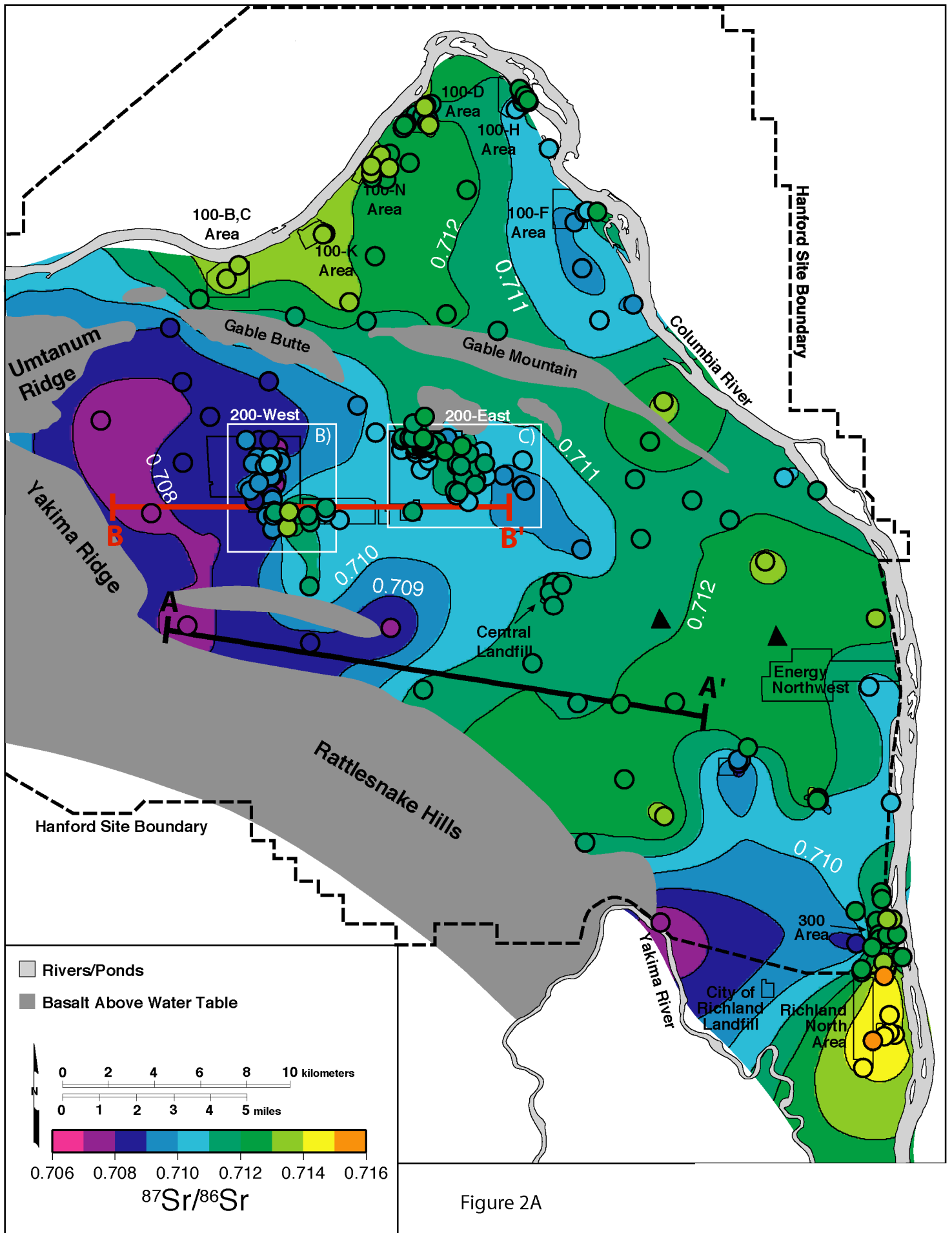


Figure 2A

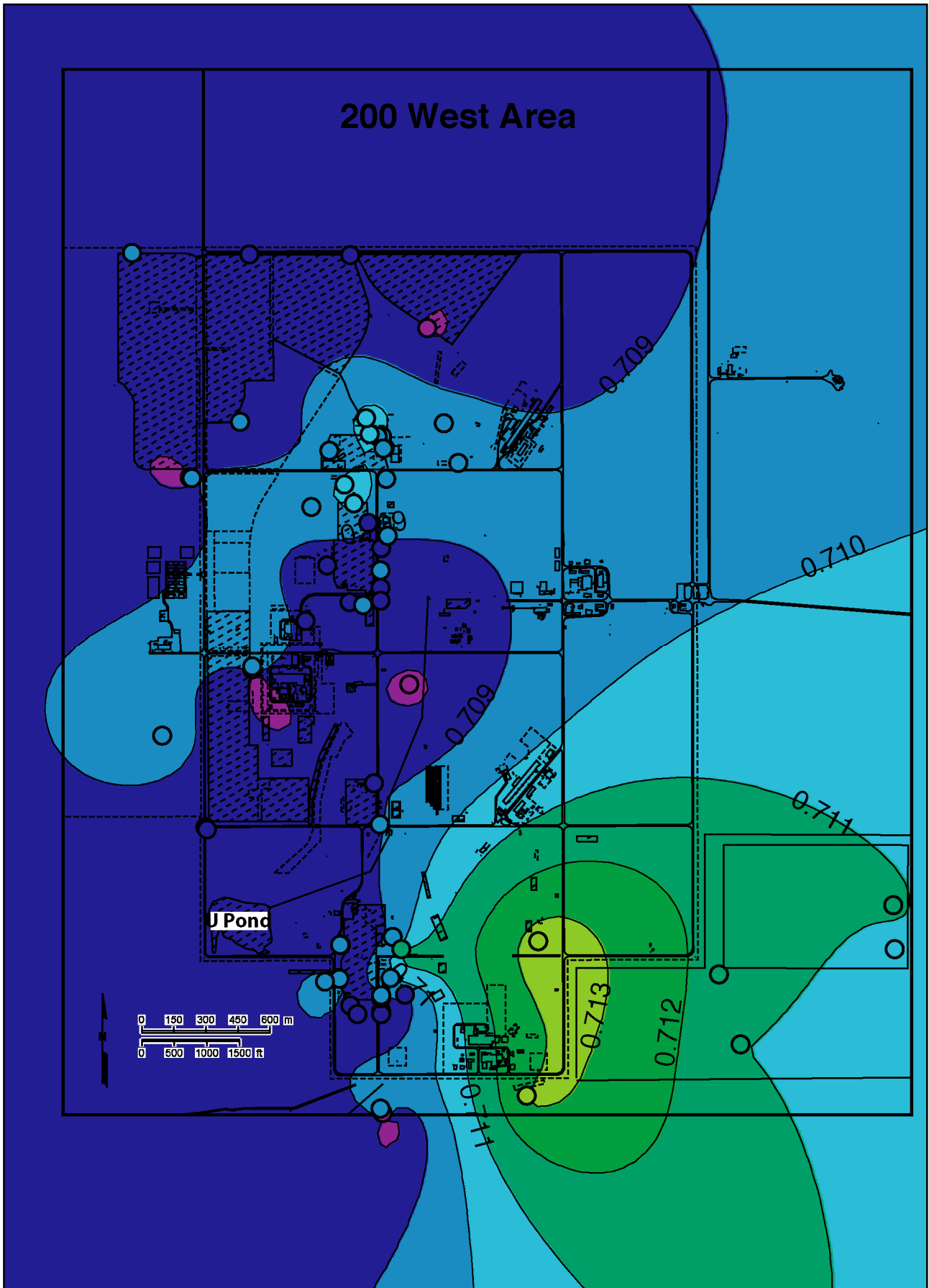


Figure 2B.

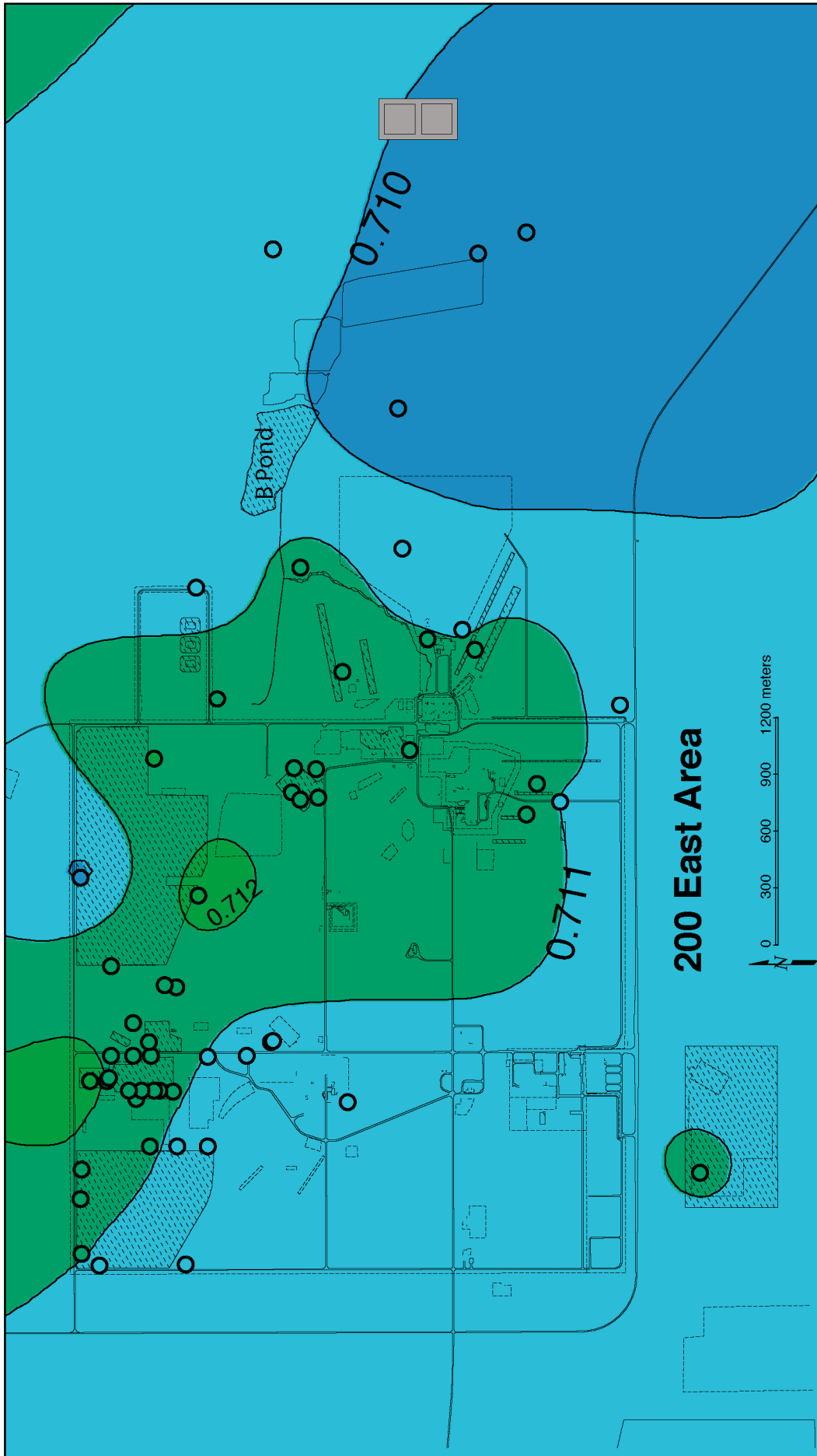


Figure 2C.

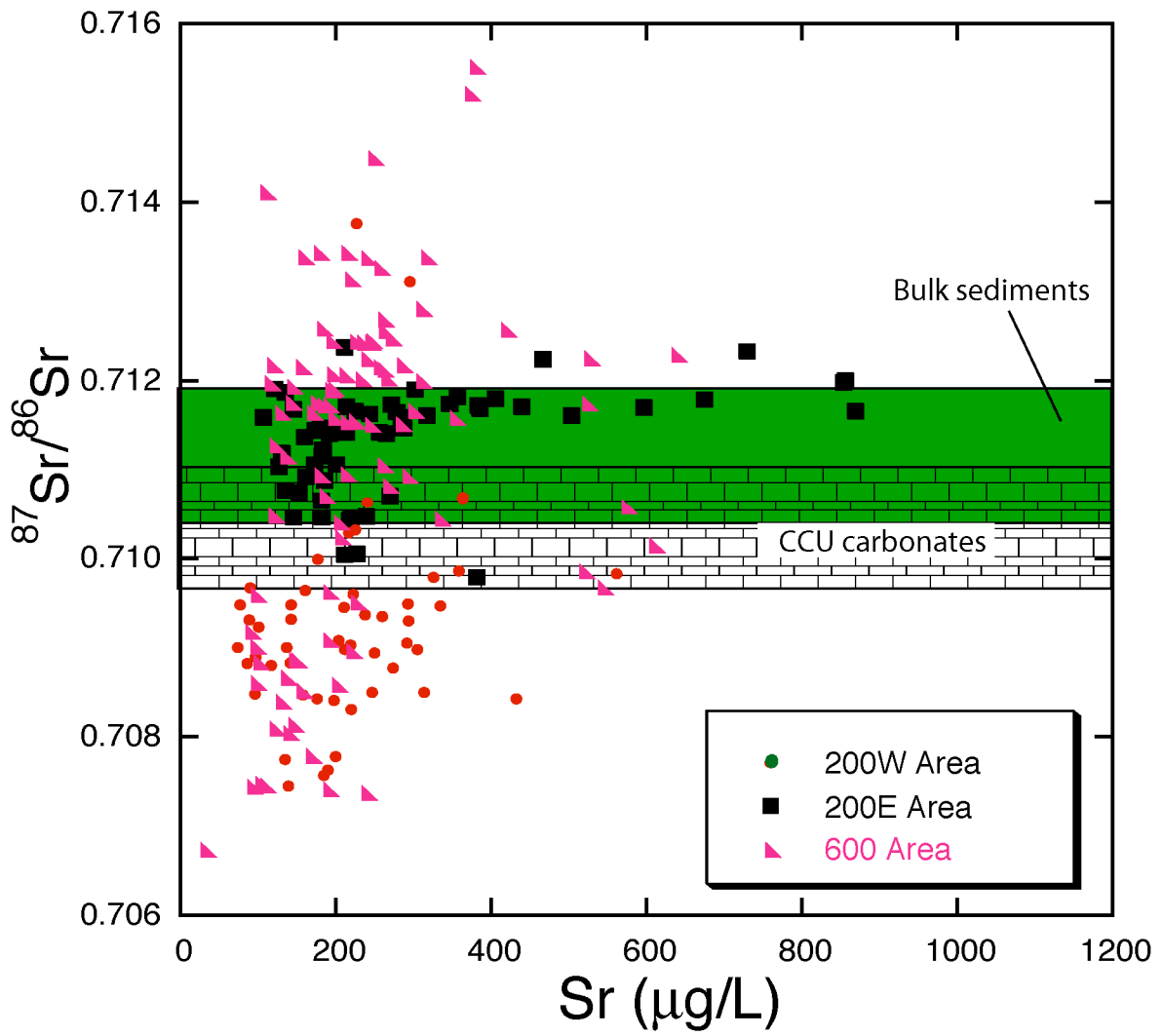


Figure 3.

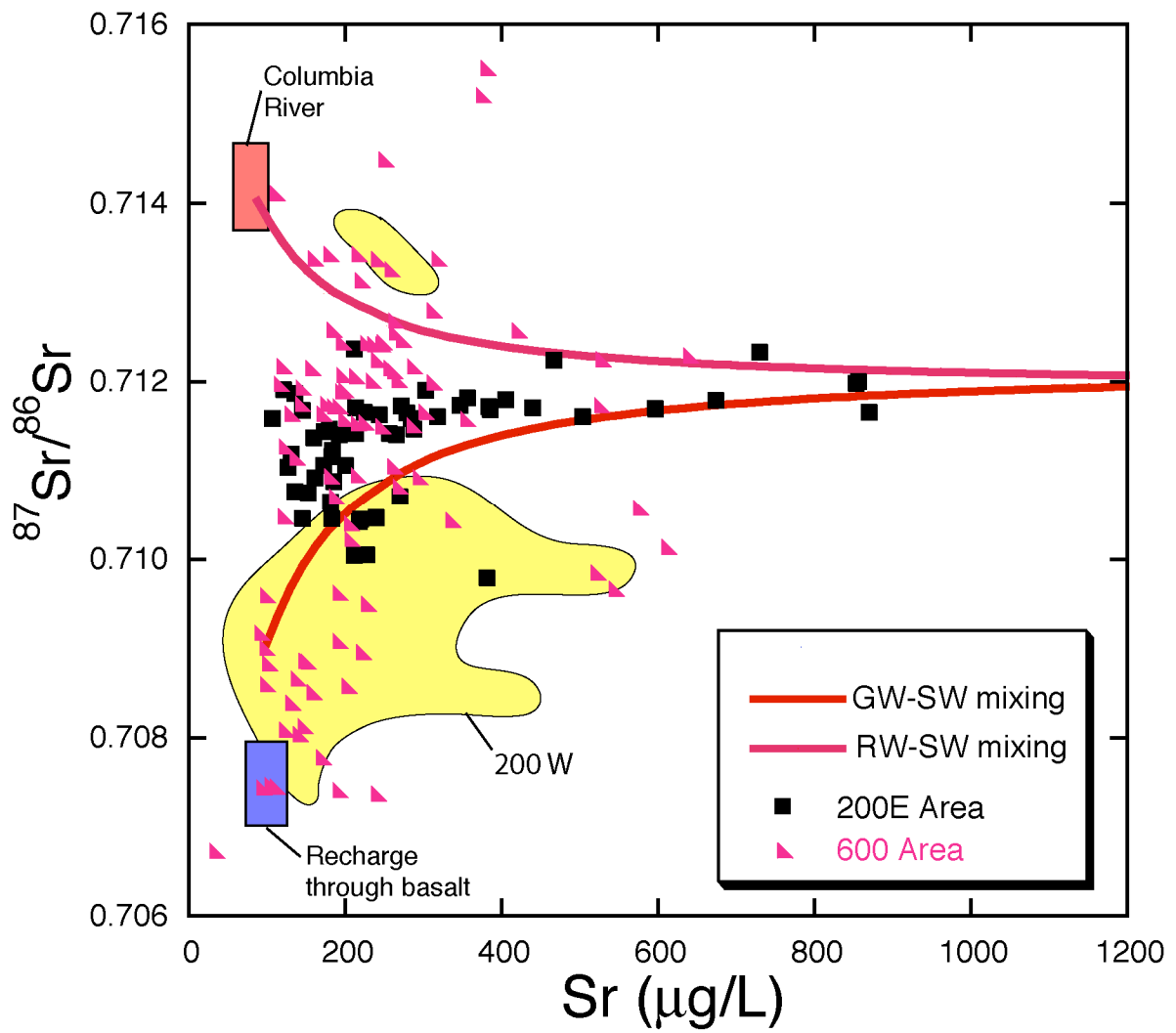


Figure 4.



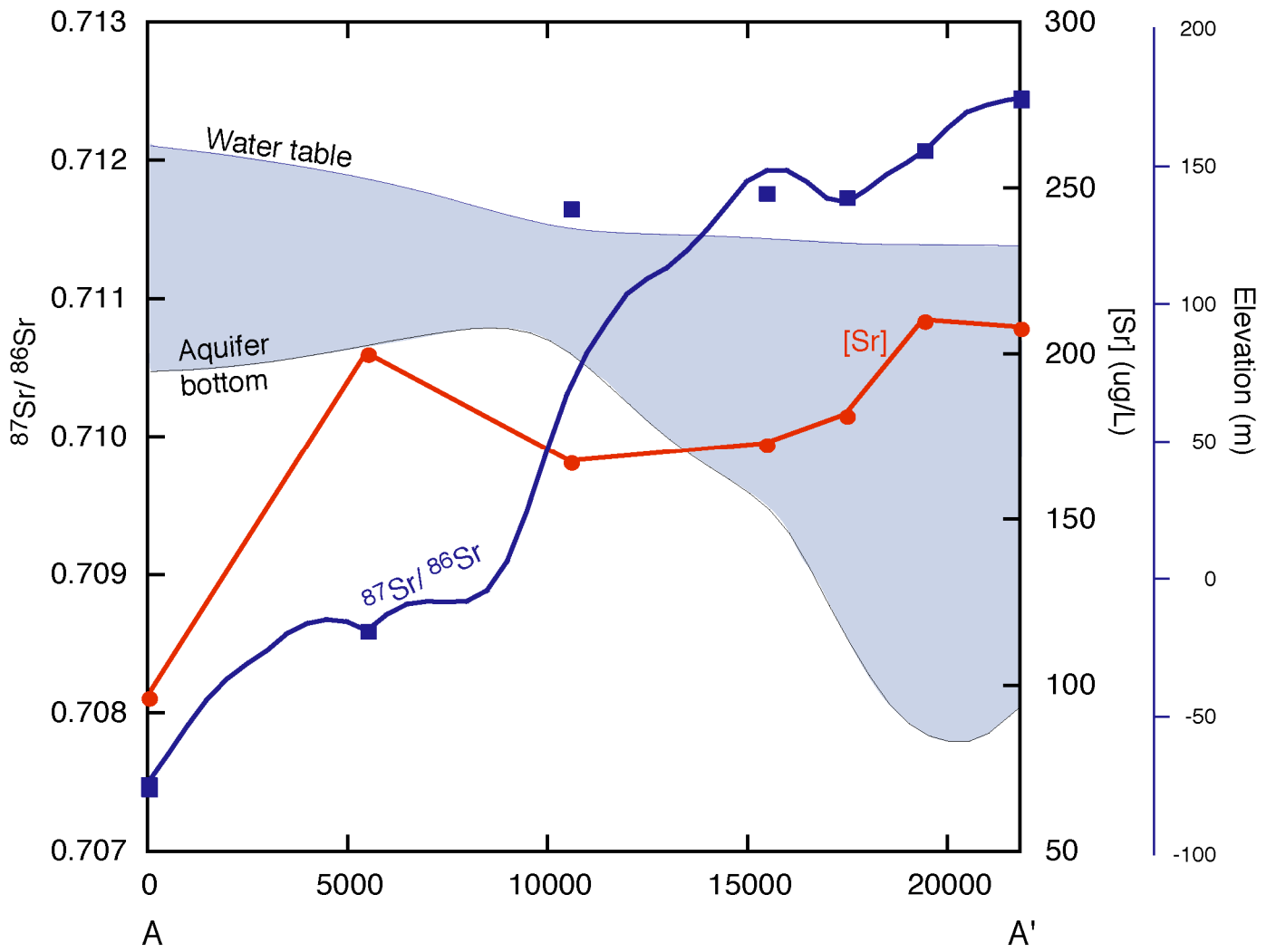


Figure 5.

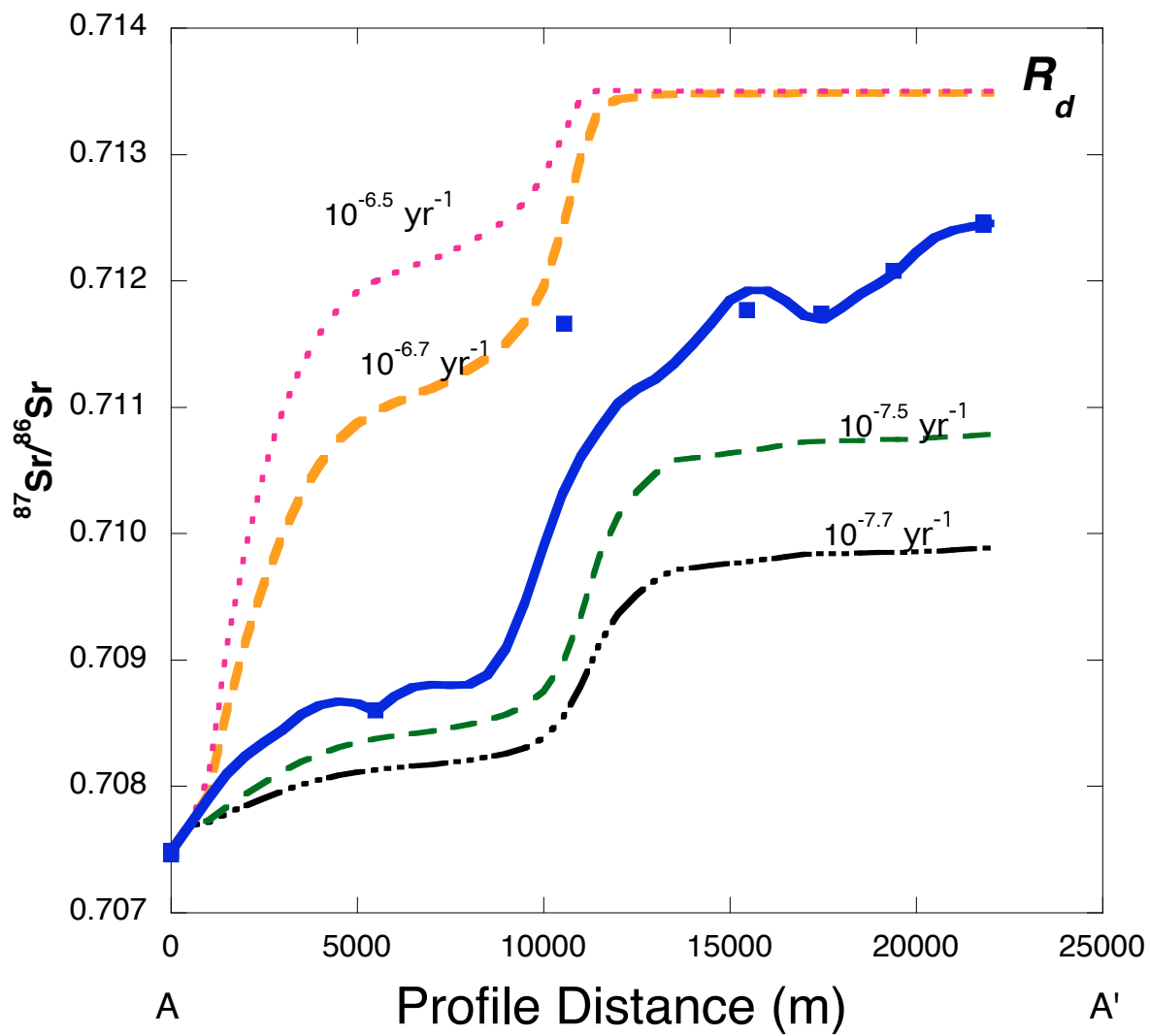


Figure 6A.

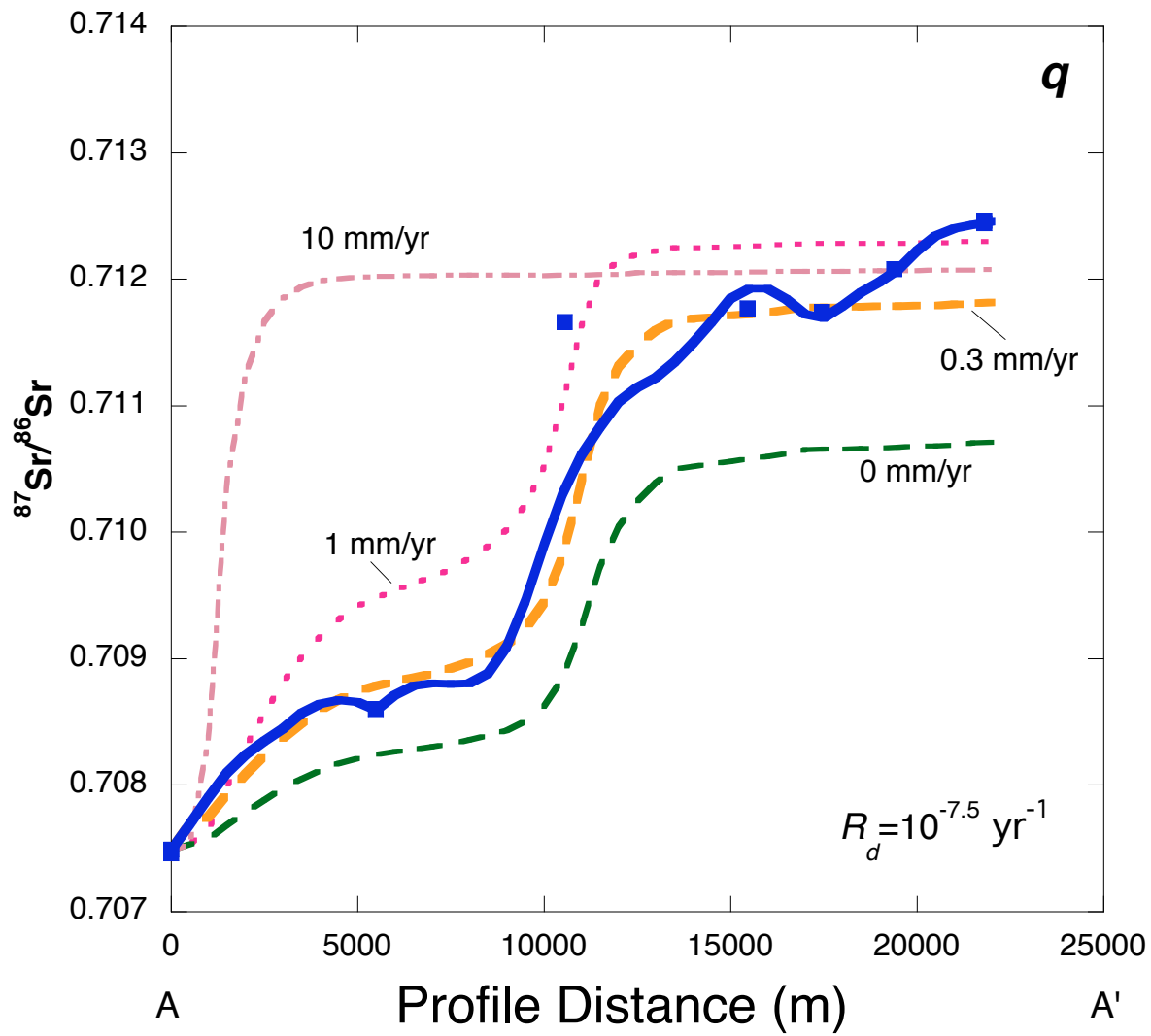


Figure 6B.