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**Differentiating Sources of Recharge and Investigating the Fate of  
Arsenic in the Shallow Groundwater System Adjacent to a  
Losing River, Western Montana**

By

Robyn Cook

B.A., Middlebury College, 2002

Presented in partial fulfillment of the requirements

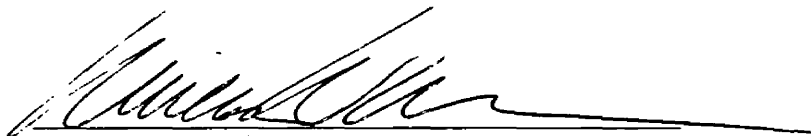
for the degree of

Master of Science

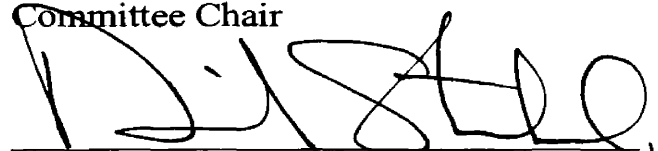
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## **Abstract**

Cook, Robyn C., M.S., 2005

Geology

Defining river recharge and the fate of arsenic in the shallow groundwater system adjacent to a losing river, Western Montana.

Chair/Director: William W. Woessner *WWW 12/23/05*

Groundwater supplies drinking water to approximately 50% of the United States population. The Missoula Valley Aquifer is a Sole Source Aquifer and provides water for over 60,000 residents of the Missoula Valley. It has become largely recognized that rivers and groundwater can be highly connected, and this has implications for water supply wells located near rivers. In these settings the quality of water that is being infiltrated through the river banks is of concern, even though bank storage and infiltration are viewed to serve as a first line of defense to sustain water supplies against pathogens and trace metals.

The Clark Fork River and the Missoula Valley Aquifer are so well connected it is hard to distinguish one from the other. The chemical similarities make it difficult to use a chemical mixing model in this setting. It has been found that groundwater, especially shallow groundwater near the Clark Fork River, follows the same temporal trends for both isotopes and conservative chemistry, suggesting that the river is well connected to shallow groundwater in the Madison area of Missoula. Deeper groundwater near the river and groundwater in more distal areas of the study area have more stable chemistry than the surface water.

This study has shown that there are changes in groundwater arsenic concentrations when there are changes in surface water arsenic concentrations. Unfortunately, due to the complexity of the natural system, the prediction of where, when or to what extent surface water chemistry influences groundwater is limited at best. It is almost certain that if the river ever contained high concentrations of arsenic (or any other hazardous material) that both shallow and deep groundwater will be affected. The Clark Fork River is serving as a source of all chemical constituents to the aquifer. While these constituents may be stored in the vadose zone for periods of time, eventually groundwater throughout the valley will be affected by surface water chemistry. Groundwater on the north side of the river does not appear to be impacted by the Clark Fork River chemistry, especially with distance from the river.

## **Acknowledgements**

Funding for this project was provided by a grant from the Montana Water Center, The University of Montana, and by Mountain Water Company. Thanks to Dr. William Woessner and Dr. Johnnie Moore for their direction and insight with this project. Thanks to Johnnie for being an integral part of this project while on leave and to Bill for his excellent guidance despite traveling for the Birdsall Lecture Series and having fifteen other students. Thanks to Dr. Don Potts for being on my committee. Thanks to Christine and Loreene for everything you do. This project would have floundered with out Amelia Tallman's assistance in the field and lab and her constant advice and counsel. Thanks to the following people for their help in the field: Susan Joy, Sheetal Patel, Paige Williams, Mike Mazzotta, Matt Young, Andy Bookter, and Aaron Fiaschetti. Michael Hofmann's editing was greatly appreciated. Heiko, Donna, Rachel and Matt in the Environmental Biocheochemical Lab provided a great deal of assistance. Thank you John Chandler, statistics guru, for help with my isotope data. The many instrumental problems we encountered in the field would have been detrimental if it were not for the friendly people at ACE Hardware. Finally, I am extremely grateful to have an interested and supportive family, who has cheered me through every one of my endeavors.

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## **Introduction**

Groundwater supplies drinking water to approximately 50% of the United States population [Solley *et al.*, 1993 and 1998]. It has become largely recognized that rivers and groundwater can be highly connected, and this has implications for water supply wells located near rivers [Bowers and Caldwell, 2003; Derouane and Dassargues, 1998; Kelly, 2002; McCarthy *et al.*, 1992]. In these settings the quality of water that is being infiltrated through the river banks is of concern [Eckert *et al.*, 2002; Chen and Chen, 2003], even though bank storage and infiltration are viewed to serve as a first line of defense to sustain water supplies against pathogens and trace metals [Sheets *et al.*, 2002; Herberger *et al.*, 2004].

The Missoula Valley Aquifer is a Sole Source Aquifer and provides water for over 60,000 residents of the Missoula Valley. The aquifer is unconfined and coarse grained. In the eastern portion of the aquifer, including the city of Missoula, the Clark Fork is a source of groundwater recharge, from 50% to over 90% [Woessner, 1988; Miller, 1991; LaFave, 2002]. Several high yield production wells operated by Mountain Water Company are located near the river. The capture zones to these wells and areas of contribution have not been fully derived. The objective of this study was to identify the recharge sources for the eastern portion of the Missoula Valley Aquifer, and to quantify how recharge sources impact produced water quality. Of special concern is determining how dissolved arsenic in river water behaves during infiltration and transport from the surface water to the groundwater. This work assesses the utility of evaluating this complex physical and geochemical system using a mixing model approach.

Mixing models have been used in numerous studies to determine the sources and quantities of water found in streams during storm events [*Hooper and Shoemaker, 1986; Genereux et al., 1993; Ogunkoya and Jenkins, 1993; Durand and Torres, 1996; Vitvar and Balderer, 1997; Kendall et al., 1999; Katsuyama et al., 2001; Joerin et al., 2002*] and to groundwater [*McCarthy et al., 1992; Maulé et al., 1994; Datta et al., 1996*]. End member mixing analysis (EMMA) relies on source waters having distinct chemical signatures. As a result, the stream water being investigated is considered a combination of end-members, depending on the quantity of each component that is contributed to the stream. The same theory can be applied to groundwater. Common chemical constituents used as tracers are calcium, magnesium, potassium, sodium, iron, silica, chloride and fluoride [*Kennedy et al., 1986; Obrdadovic and Sklash, 1987; Joerin et al., 2002; Kelly, 2002*]. Ideally, this study will make it possible to predict the concentrations of chemical elements in groundwater as a function of discernable recharge source chemistry.

In addition to applying standard geochemical constituent analyses, stable isotopes were also assessed. Isotopic data have been used to determine surface water and groundwater mixing. [*Stichler and Moser, 1977; Sklash and Farvolden, 1979; Muir and Coplen, 1981; Payne, 1981; Ferronsky et al., 1982; Payne, 1983; Kennedy et al., 1986; Iacovides, 1988; Darling et al., 1990; Krabbenhoft et al., 1990; McCarthy et al., 1992; Taylor et al., 1992; Kay et al., 2002; Kelly, 2002; Constantz et al., 2003*]. These studies utilized  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  (or  $\delta\text{D}$ ) as tracers because these naturally occurring stable isotopes behave conservatively.

The isotopic composition of river water and groundwater recharge sources often

vary because of isotopic fractionation that occurs as water enters and moves through a watershed. [Coplén, 1993; Coplén *et al.*, 1999]. For example, the process of water evaporating and then being condensed isolates the heavier isotope (Figure 1).

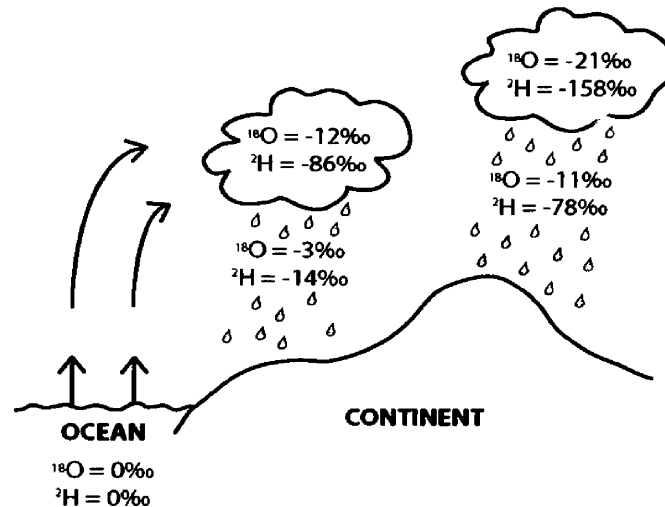


Figure 1. Fractionation of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ . [After Coplén *et al.*, 1999]. Concentrations are shown as the ratio of water (water vapor or rain) to the standard (Vienna Standard Mean Ocean Water or VSMOW) and symbolized as ‰.

The amount of heavy isotopes in any given precipitation event varies spatially depending on altitude, latitude, season, the distance inland from the ocean, and the magnitude of precipitation [Coplén *et al.*, 1999].

Using isotopes in mountainous catchments has allowed investigators to determine source water because precipitation originating at various elevations has different signatures that can be identified [Hooper and Shoemaker, 1986; Sklash, 1990; Mayo *et al.*, 1992; Taylor *et al.*, 1992; Hoeg *et al.*, 2000]. Isotopes may also be used to determine sources of water to a stream, as long as the end members are significantly different. Usually studies seek to isolate pairs of sources such as old groundwater and precipitation, or stored groundwater and snowmelt. Several studies have used  $\delta^{18}\text{O}$  in snowmelt to

calculate the amount of new water that is introduced to a system during runoff [*Hooper and Shoemaker, 1986; Maulé et. al., 1994; Shanley et. al., 2002; Taylor et. al., 2002; Huth et. al., 2004*].

Sklash and Farvolden [1979 and 1982] set up criteria for using isotopes to separate new and old sources of water:

1. The groundwater and baseflow are characterized by a single isotopic content.
2. The rain or snowmelt water is characterized by a single isotopic content or variations in the isotopic content are documented.
3. The isotopic content of the event water is significantly different from the groundwater/baseflow.
4. Vadose water contributions to the stream are negligible.
5. Surface storage water contributions to the stream are negligible.

Study sites that fit all of the above criteria are suitable for using isotopes as tracers.

Unfortunately, two major disadvantages to using isotopes are that the old and new water must have different isotopic signatures, and that can not be known with any certainty before the study. LaFave [2002] collected  $^{18}\text{O}$ , deuterium, arsenic, radioactive isotope and environmental tracer data for the Missoula Valley Aquifer. His work showed a significant seasonal variation in the isotopic composition of the river water and groundwater.

In addition to sorting out the sources of recharge to the Missoula Valley Aquifer, the occurrence of and behavior of dissolved arsenic in recharge sources and within the aquifer were also investigated. This is of particular concern as current river and

watershed conditions contribute arsenic to the river and it is anticipated the levels may rise or become more variable during a dam removal operation planned for the Milltown Dam located approximately 6 river miles upstream of Missoula. Arsenic has been found in groundwater across the U.S., in concentrations both above and below the current EPA limit of 50  $\mu\text{g/L}$  (parts per billion) [Welch, 2000; see Appendix 1]; the proposed new limit, that will be in effect starting January 23, 2006, is 10  $\mu\text{g/L}$ . At the Milltown dam site it is estimated that there is between 1500 and 2650 MT (metric tons) of arsenic being stored in the Milltown reservoir sediments [Moore and Woessner, 2003]. While the Milltown reservoir serves as a sink for arsenic during periods of low flow, it has been shown that during peak flows the sediment in the reservoir is remobilized and contaminated sediment is released downstream [Mickey, 1998; Shifflett, 2002]. Some of the arsenic in the reservoir sediment is also released into the local groundwater and pore water through oxidation of metal sulfides [Mickey, 1998]. The Milltown Dam is scheduled for removal over the winter of 2006-2007 and during this process 2 MT of the most contaminated sediment is scheduled to be removed while the remaining approximately 6 MT will be left in place. The EPA has proposed that dissolved arsenic concentrations in the river will be allowed to increase to 10  $\mu\text{g/L}$  for 30 days and up to 340  $\mu\text{g/L}$  for single 24 hours periods. Concern has been voiced that remediation and restoration actions may impact the Clark Fork River and other possible recharge sources to the Missoula Valley Aquifer.

In general the geochemical conditions that influence the transport of dissolved arsenic from an impacted river to the underlying groundwater are not well understood.



Few studies have focused on how arsenic behaves in the vadose zone between a river and an alluvial aquifer. Nagorski and Moore [1999] found elevated levels of arsenic in a hyporheic zone, containing sediments composed partially of mine waste. Bourg and Bertin [1993] investigated the infiltration of river water to an alluvial aquifer and found that several processes took place to reduce the concentration of manganese along the flowpath. Controls on the occurrence and migration of arsenic include adsorption, dissolution, precipitation and redox reactions. Several studies have found that arsenic is sorbed to iron and manganese oxyhydroxides, and is released when these oxides are dissolved due to changing redox conditions [*Goldberg* , 1986; *Peterson and Carpenter*, 1986; *Aggett and Kreigmann*, 1988; *Moore et. al.*, 1988; *Masscheleyn et. al.*, 1991; *Lucy*, 1996; *Manning and Goldberg*, 1997; *Nicholas et. al.*, 2003 and others].

Hopefully, understanding the fate of arsenic in the Clark Fork River and the Missoula Valley Aquifer will lead to an understanding of arsenic fate and suggest how changes in surface water quality may influence produced groundwater quality.

## **Site Description**

The study area encompasses approximately 5.8 mi<sup>2</sup> in the Missoula Valley of Western Montana (46°52'30"N, 114°0'0"W) (Figure 2). The Clark Fork River, which flows through the valley, drains an area of 6,000 mi<sup>2</sup>, 28% of the entire area of the river's basin in Montana. Average discharge for the Clark Fork in the study area peaks at approximately 10,000 cubic feet per second (cfs) in June, and is usually at a minimum of between 1,200 and 1,500 cfs from September to January [*USGS CFR above Missoula*,

based on a 75 year average]. The hydrograph for this study period, April 28, 2004 to June 16, 2005 (Figure 3) corresponds with a period of drought where stream discharge is less than average.

The city of Missoula receives an average of 13.53 inches of precipitation annually. The average high and low temperatures are 86 °F in July and 31 °F in January [NRIS, based on records from 1893 to 2004]. Currently, the region is in a period of moderate to severe drought, and has been for the past four to seven years [NRIS, 2005]. Snowpack for the 2004-2005 year was close to the thirty year minimum (Figure 4).

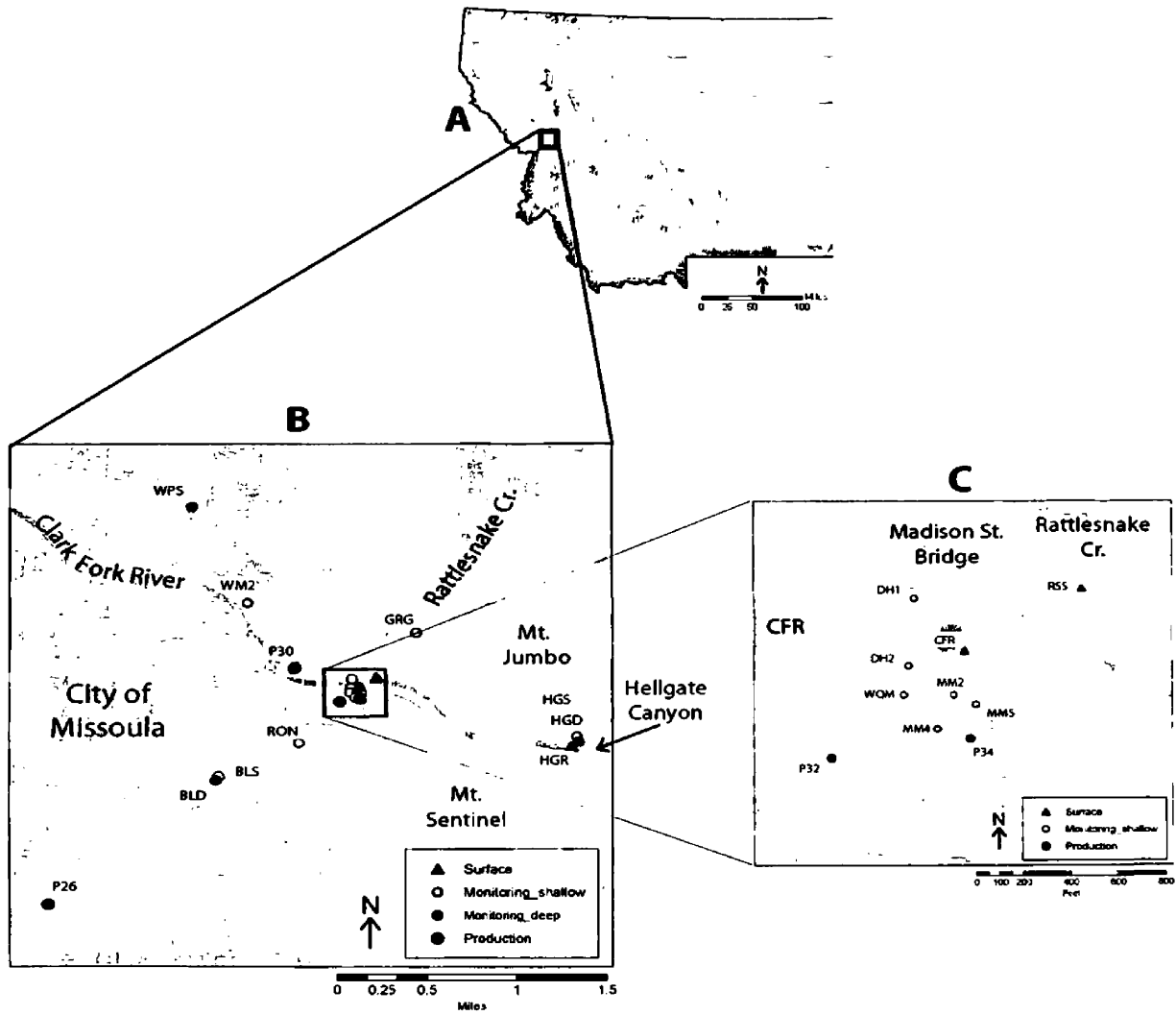


Figure 2. The study area is located in the city of Missoula in Western Montana (A). Sample locations are spaced throughout the city (B), with the highest density in the Madison Bridge area

(C). Samples were taken from surface water, shallow and deep monitoring wells and production wells.

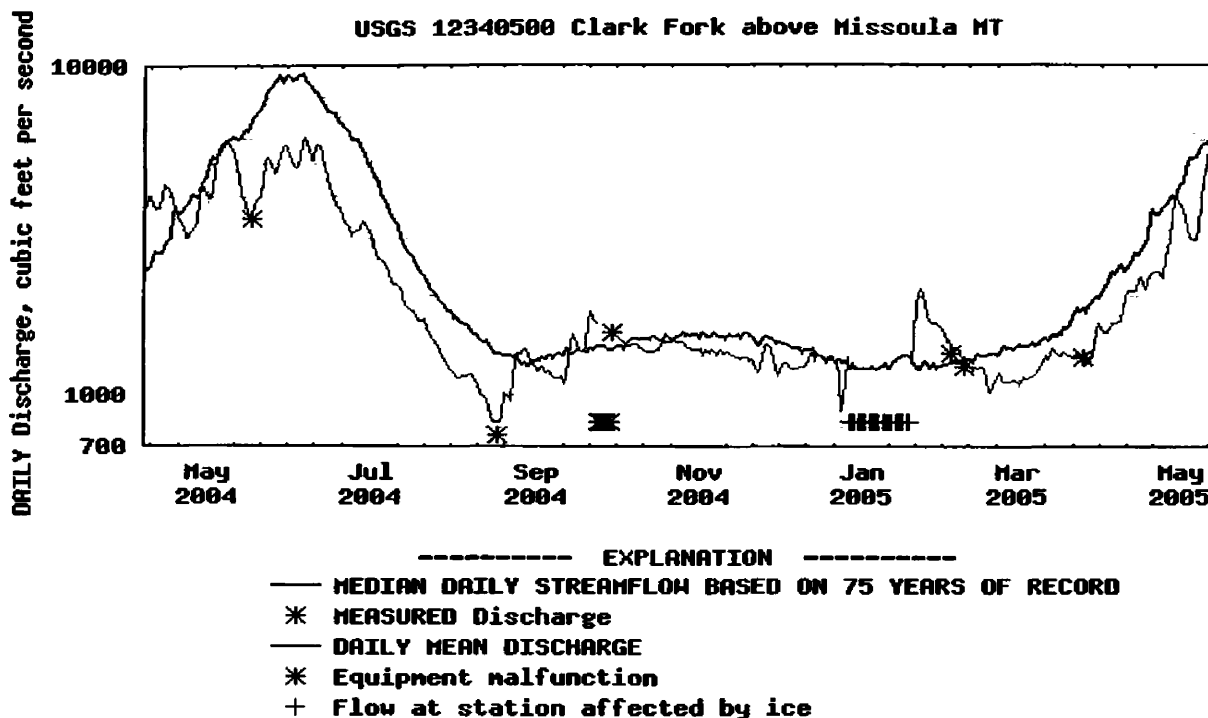


Figure 3. The hydrograph for the Clark Fork River during the study period. There was a period of non-record during January because of ice cover. In general, the hydrograph is below the seventy-five year average (red line).

### Snowpack Trend

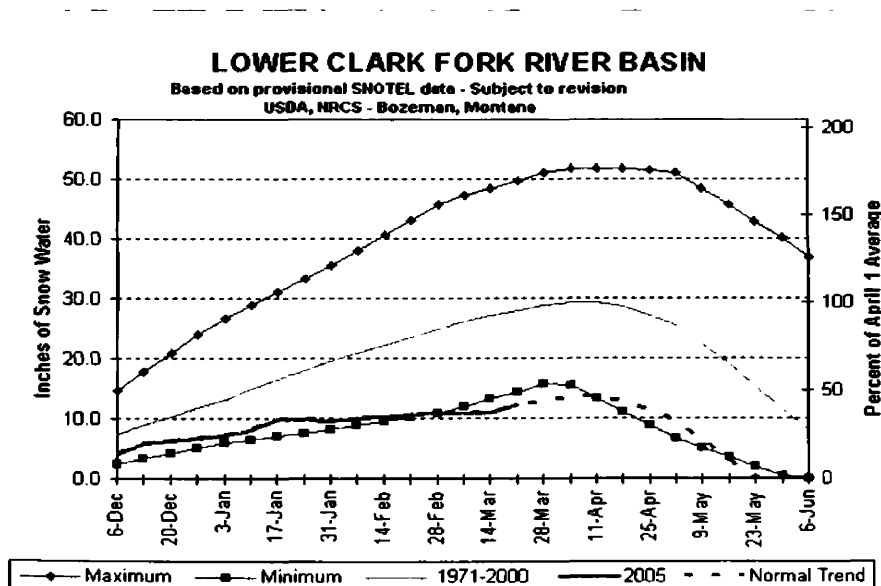
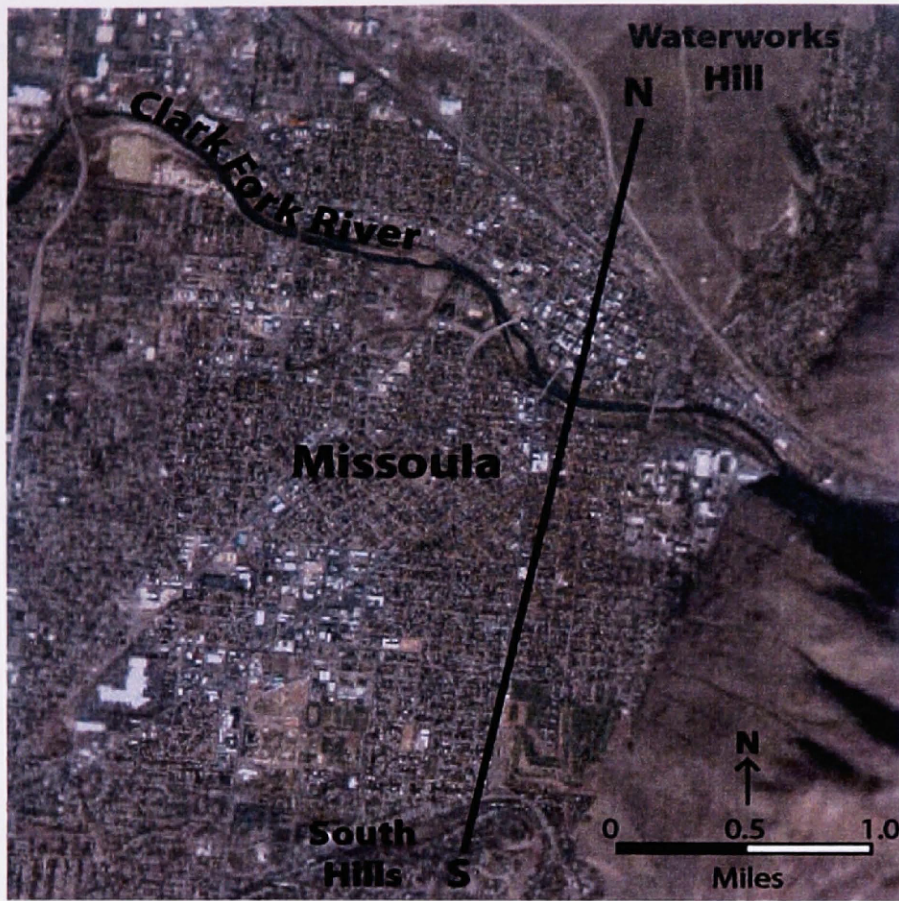
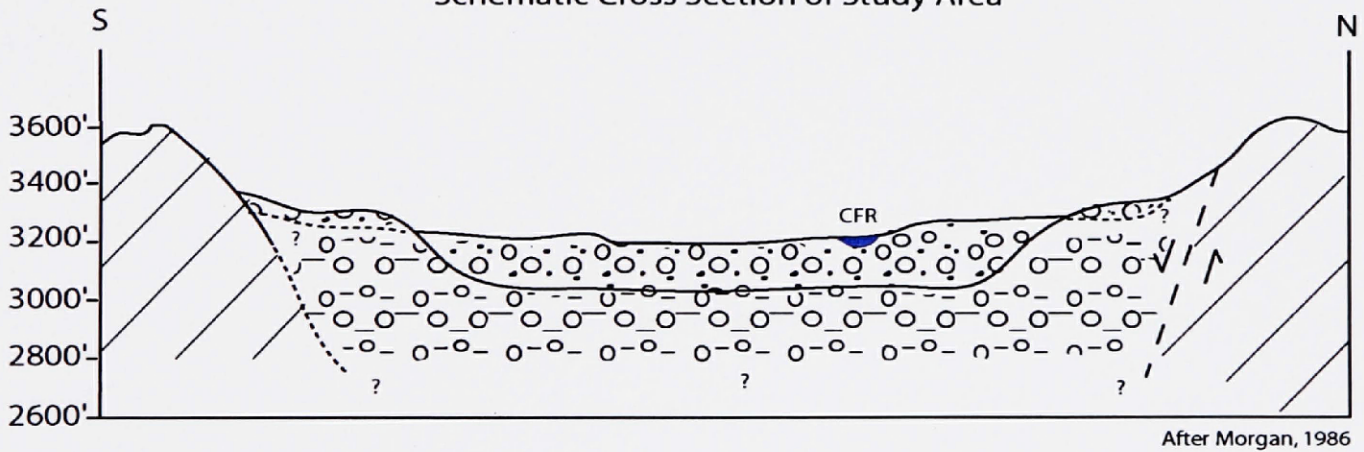


Figure 4. Average snowpack for the Upper Clark Fork River Basin. From December 2004 to May 2005 values were close to or below the 30 year minimum. (From NRIS.)

Underlying the entire valley floor is the Missoula Valley Aquifer. This unconfined aquifer consists of Quaternary glacial and fluvial deposits of silt, sand, gravel, cobbles and boulders. Previous work identified three general layers: The top 10 to 30 ft is coarse but often lies above the saturated zone, and is underlain by roughly 40 ft of finer material. Below the fine material is the primary water bearing unit, which ranges from 50 to 100 ft in thickness and is dominated by coarse material [*Woessner*, 1988]. In the valley the aquifer overlies much finer grained Tertiary sediments [*Clark*, 1986; *Morgan*, 1986; *Woessner*, 1988] (Figure 5), and in Hellgate Canyon the coarse deposits are underlain by the Missoula Group of the Belt Supergroup bedrock [*Gestring*, 1994; *Nyquest*, 2001].



Schematic Cross Section of Study Area



After Morgan, 1986

Legend

- Valley Alluvium
- Tertiary Basin Fill
- Precambrian Bedrock

Figure 5. Location map and schematic cross section of the Missoula Valley. The Missoula Valley Aquifer is in the Valley Alluvium, which is underlain by Tertiary sediments. In Hellgate Canyon the aquifer is directly on top of the Precambrian Bedrock. (After Morgan, 1986)

Groundwater flow through the eastern portion of the valley is generally to the southwest south of the Clark Fork River, and northwest north of the river (Figure 6). Horizontal hydraulic conductivity for the study area ranges from 800 to 20,000 feet per day [Tallman, 2005]. The Clark Fork River is perched above the unconfined aquifer, separated by a vadose zone that is approximately 5 ft thick in Hellgate Canyon and 17 ft in the Madison area [Tallman, 2005]. According to Tallman [2005] recharge contributions to the aquifer are as follows:

<b>Source</b>	<b>Percentage Contributed to Missoula Aquifer</b>
The Clark Fork River	82.6% (148,300 - 510,200 acre-ft/year)
Rattlesnake Creek	2.4% (4,159 - 14,808 acre-ft/year)
Underflow from Hellgate Canyon	11.9% (32,000 - 64,000 acre-ft/year)
Underflow from Rattlesnake Creek	0.5% (1,175 - 2,866 acre-ft/year)
Line Loss from Mt. Water Company	1.6% (4,929 - 7,842 acre-ft/year)
Adjacent Tertiary Hills	0.3% (511 - 2,043 acre-ft/yr)
Inflow from Patty Creek Drainage	0.6% (1,304 - 1,956 acre-ft/year)
Precipitation	0.1% (292 - 438 acre-ft/year)



Figure 6. Groundwater flow for the Missoula Valley. Flow is to the southwest on the southern side of the Clark Fork River, and to the northwest on the northern side of the river. Note the steep gradient in the mouth of the Rattlesnake drainage.

The water purveyor for the city of Missoula is Mountain Water Company. It operates 36 wells in the main valley area; all of their wells generally are 8 to 18 inches in diameter. The wells finished in the eastern portion of the aquifer are completed to a depth of 90 to 270 ft below land surface (one well is finished at 360 ft below land surface) and commonly perforated from 80 to 120 ft at the aquifer base. Well yields range from 220 to 5,600 gallons per minute, the largest of which are obtained from sites adjacent to the Clark Fork River (Figure 6).

## Methods

Sites for geochemical sampling and water level monitoring were selected throughout the Missoula valley based on location, accessibility, and previous investigations and hydrogeological interpretation [Clark, 1986; Woessner, 1988; Miller, 1991; Armstrong, 1991; LaFave, 2002]. Spatial variation was required to allow flow path determination throughout the valley. A variety of well types (production wells, 2, 4 and 6-in monitoring wells) and designs were used to access the groundwater. Surface water samples were collected to represent the quality of various river reaches. Existing monitoring wells were made available for the study by Mountain Water Company and the Missoula Water Quality District. This included access to a network of two-inch monitoring wells between the Clark Fork and a major Mountain Water Company production well near the Madison Street Bridge. In April, 2004, two wells were drilled in Hellgate canyon. A shallow well was drilled to 51 ft and a deep well was finished at 172 ft after drilling to bedrock at 247 ft. In October two additional monitoring wells were installed within 65 ft of the river; one was drilled to 50 feet on the north bank and the other to 70 ft on the south side (Figure 2).

Water chemistry was monitored at 22 sites including 4 production wells, 15 monitoring wells, 3 surface water locations, and one streambed peizometer. Samples were collected weekly from May, 2004 to August, 2004. From August to October each site was sampled biweekly, and from October to February, 2005 each site was sampled on a monthly basis. From February to June samples were collected three times a month. The variations in sampling frequency correlate to the discharge of the Clark Fork and



water chemistry changes anticipated during spring runoff. In addition to sampling for geochemistry, water levels were monitored at 35 sites, 3 production wells, 28 monitoring wells and 4 surface water sites as part of a companion investigation of well capture zones [Tallman, 2005].

Figure 7 is a conceptual model of the possible sources of recharge to the Missoula aquifer. Sampling was designed to monitor these sources and their independent chemical signatures.

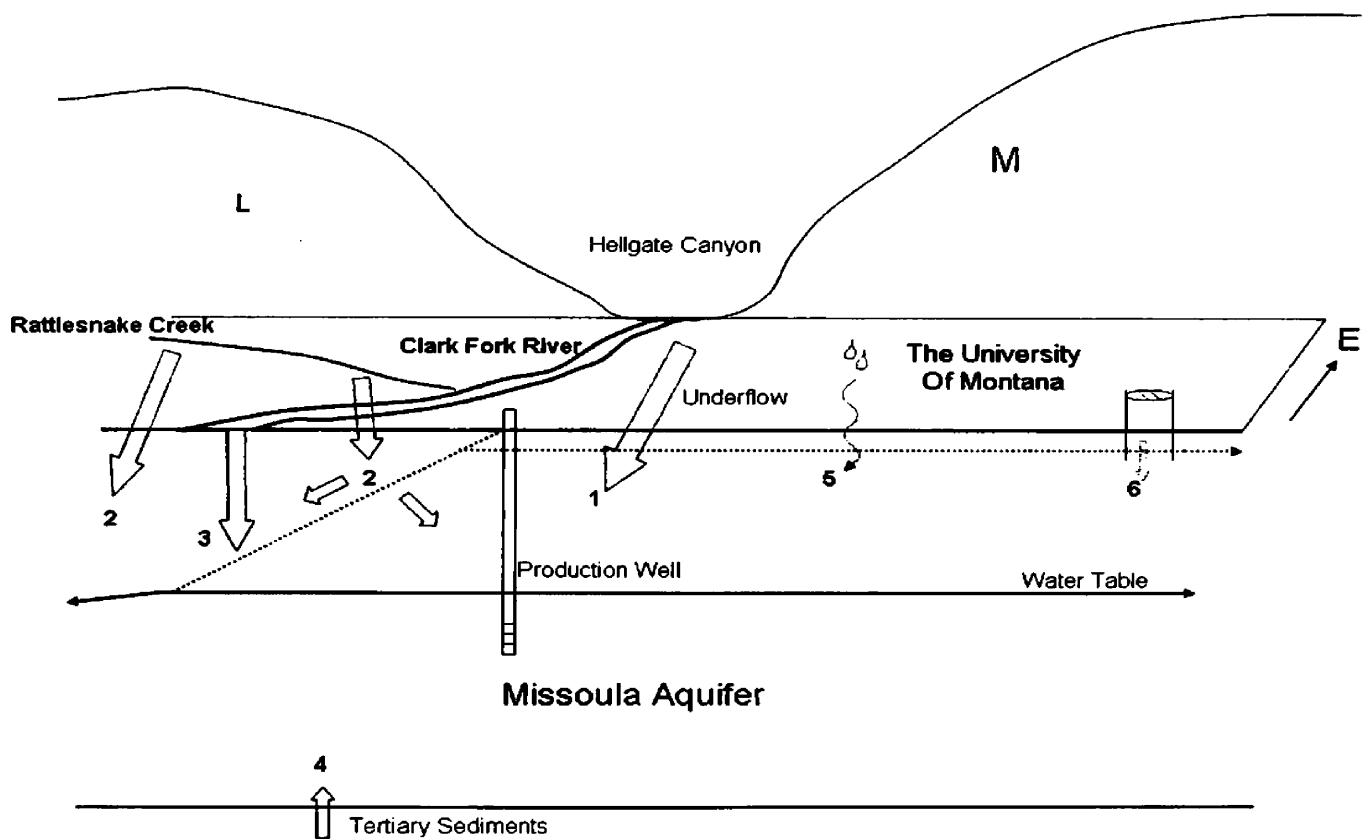


Figure 7. 3-D conceptual model of the sources of recharge to the Missoula Aquifer. Source 1 is underflow from Hellgate Canyon. Source 2 is water from Rattlesnake Creek, including both surface water and underflow from the drainage. (Note that there is a split in the water from Rattlesnake Creek, some of the water may cross under the Clark Fork and be captured by the production well(s) on the south side of the river, while a large portion of the flow stays on the north side of the Clark Fork.) Source 3 is leakage from the Clark Fork River. There is also a possibility that some water is recharged from the Tertiary sediments underlying the Missoula Aquifer (4). Precipitation (5) and recharge from storm drains (6) contribute only a small amount of water to the aquifer.

## Field Methods

Field geochemical parameters (pH, temperature and electric conductivity) were measured during the collection of each sample (see Appendix 2 for pictures of sampling procedures). Monitoring wells were pumped (using a Grundfos pump) until three bore-hole volumes had been removed. A new disposable polyethylene bailer was then used to collect enough water to rinse the bottle and obtain a sample. Production wells were sampled from a spigot before any chemical treatment. The Clark Fork River and Rattlesnake Creek were sampled in the stream channel at a range of depths to obtain a representative sample. The river sample collected on January 19<sup>th</sup> was taken from a hole in the ice. Two different sampling methods were used to access the water just below the river bottom. First, a plastic PVC tube was installed as a piezometer and a peristaltic pump was used to obtain a sample. When that piezometer was flooded with higher spring flows, a suction lysimeter was installed in the channel sediment. The lysimeter had a long piece of tubing that remained above the water surface and was pumped to obtain a water sample. Due to river conditions, this saturated zone was only sampled seven times during the course of the study. During each round of sampling field duplicates and blanks were collected for quality assurance and quality control.

All samples were collected using ultra clean techniques [*Mickey, 1998; EBL Sampling Method #2*]. This process involved using ultra cleaned 120 mL Nalgene bottles that were double-bagged and handled by one set of “clean hands” and one set of “dirty hands.” “Dirty hands” only touched the external bag, while “clean hands” only touched the internal bag and sample bottles. Each bottle was rinsed with sample water three times

before the actual sampling. Surface water samples were collected underwater, and samples from wells were filled to overflowing and capped so that there was minimal head space. “Clean hands” placed the sample in an individual zip-lock bag which was then placed in an open external bag. “Dirty hands” sealed the external bag. Additional samples for anions were collected in non-acid washed bottles. These samples were collected after the ultra clean samples because detection levels for anions are much higher and the same precautions do not need to be taken. All samples were stored on ice and transported to the analytical lab within seven hours of sample collection.

### **Lab Methods**

Samples were filtered in lab as soon as possible (and no longer than 48 hours after sampling) using ultra clean syringes and  $<0.45 \mu\text{m}$  syringe filters (Figure 8) [Tallman EBL SOP 2004\_06\_21]. All filtering took place in a hood [EBL McKinnon and Nagorski, 2000]. New ultra clean 30 mL bottles were rinsed and filled, then acidified with 2% OmniTrace® high purity  $\text{HNO}_3$  for preservation. Anion samples were filtered after the respective ultra clean samples, using the same filter but first rinsing the syringe with the anion sample. Isotope samples were not filtered; instead a 30 mL bottle was filled to an inverted meniscus and capped to incorporate as little air as possible.



Figure 8. Ultra-clean filtering in the hood. Filtering with  $<0.45\mu\text{g}$  filters and acid washed syringes.

Isotopes were analyzed at The University of Alaska at Fairbanks at the Alaska Stable Isotope Facility's Water & Environmental Research Center (WERC). Stable isotope data was obtained using continuous-flow isotope ratio mass spectrometry (CFIRMS). Instrumentation was a Delta+XL with a Thermo Finnigan TC/EA. Isotopes are expressed as a ratio of the heavy to light isotopes compared to a standard. Typically, instrument precision is  $<0.4\text{‰}$  for Oxygen and  $<3.0\text{‰}$  for Hydrogen. The following formula is used to determine  $\delta^{18}\text{O}$  values and data is reported as parts per thousand (per mill, or ‰) relative to the Vienna Standard Mean Ocean Water (VSMOW):

$$\delta^{18}\text{O} = \left( \left[ \frac{{}^{18}\text{O}_{\text{sample}} / {}^{16}\text{O}_{\text{sample}}}{{}^{18}\text{O}_{\text{std}} / {}^{16}\text{O}_{\text{std}}} \right] - 1 \right) * 1000$$

The same formula is applied to  $^2\text{H}$  and is commonly reported as  $\delta\text{D}$  for deuterium. Craig [1961] created a Global Meteoric Water Line (GMWL) by plotting  $\delta^{18}\text{O}$  vs  $\delta\text{D}$  for samples taken around the world. The equation for his line is:

$$\delta\text{D} = 8 \delta^{18}\text{O} + 10$$

This equation has been revised [Kendall and Coplen, 2001] to:

$$\delta\text{D} = 8.11 \delta^{18}\text{O} + 8.99$$

Local Meteoric Water Lines (LMWL) vary from place to place. The Montana LMWL shows a great deal of evaporation and has a very heterogenic cluster around the line:

$$\delta\text{D} = 5.0 \delta^{18}\text{O} - 46.5 \text{ [Kendall and Coplen, 2001]}$$

Plotting data versus a LMWL will show if samples have been subjected to evaporation, or if the isotopes are consistent with local precipitation.

All other analyses were performed at The University of Montana. The ultra clean samples were analyzed for elements (As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, and Zn) on the Perkin-Elmer Sciex ELAN DRCII ICP/MS interfaced with a Perkin-Elmer Series 200 HPLC using EBL EPA6020mod method ICP-MS analysis for metals. Anions ( $\text{F}$ ,  $\text{Cl}$ ,  $\text{NO}_3$ ,  $\text{NO}_2$  and  $\text{SO}_4$ ) were determined on a Dionex DX 400 Ion Chromatography system using EPA method 300.0. Alkalinity was determined in mg/L of  $\text{CaCO}_3$  by titration.

## **Quality control/quality assurance**

Field duplicates and blanks, along with lab splits were used with internal and external standards to ensure precision and accuracy. From the field duplicates and lab splits a confidence level of over 95% was calculated for each result from MS, IC and Isotope analyses by adding two standard deviations to the average calculated error. See Appendix 3 for detailed QA/QC.

## **Results**

Stable isotopes from surface water and groundwater were used to determine the amount of recharge to the Missoula Valley Aquifer from potential recharge sources. These conservative tracers are somewhat useful in this system, but error and a lack of distinct recharge sources limits the use of the isotopic data. Conservative chemistry and arsenic data also provide evidence for the complexity of the interaction between surface water and groundwater. Refer to Figure 2 for all sample locations. Raw data for all sample sites may be found in Appendix 4.

## **Isotopes**

The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  data for the study is scattered around the Local Meteoric Water Line (LMWL) determined by Kendall and Coplen [2001] (Figure 9). Interestingly, groundwater values are quite similar to surface water values, and when accounting for error the differences are hardly distinguishable. The data show similar temporal relationships among shallow and deep groundwater and surface water. Error bars obscure

the data (Figure 10), but because the data follows the same trend, error bars in the following figures will be omitted for clarity. Each data point has an error of +/- approximately 1‰. Shallow and deep groundwater generally follows the river's isotopic signal over time (Figures 11 and 12). The isotopes for the north side of the Clark Fork River share similarities with both the Clark Fork River and Rattlesnake signatures (Figure 13.) With the given sampling frequency, even distal wells appear to peak at the same time as the river. By introducing a lag effect into the data during the time when weekly samples were collected and correlating groundwater  $\delta^{18}\text{O}$  to river  $\delta^{18}\text{O}$ , it becomes clear that wells farther from the river do experience some time lag (Figure 14).

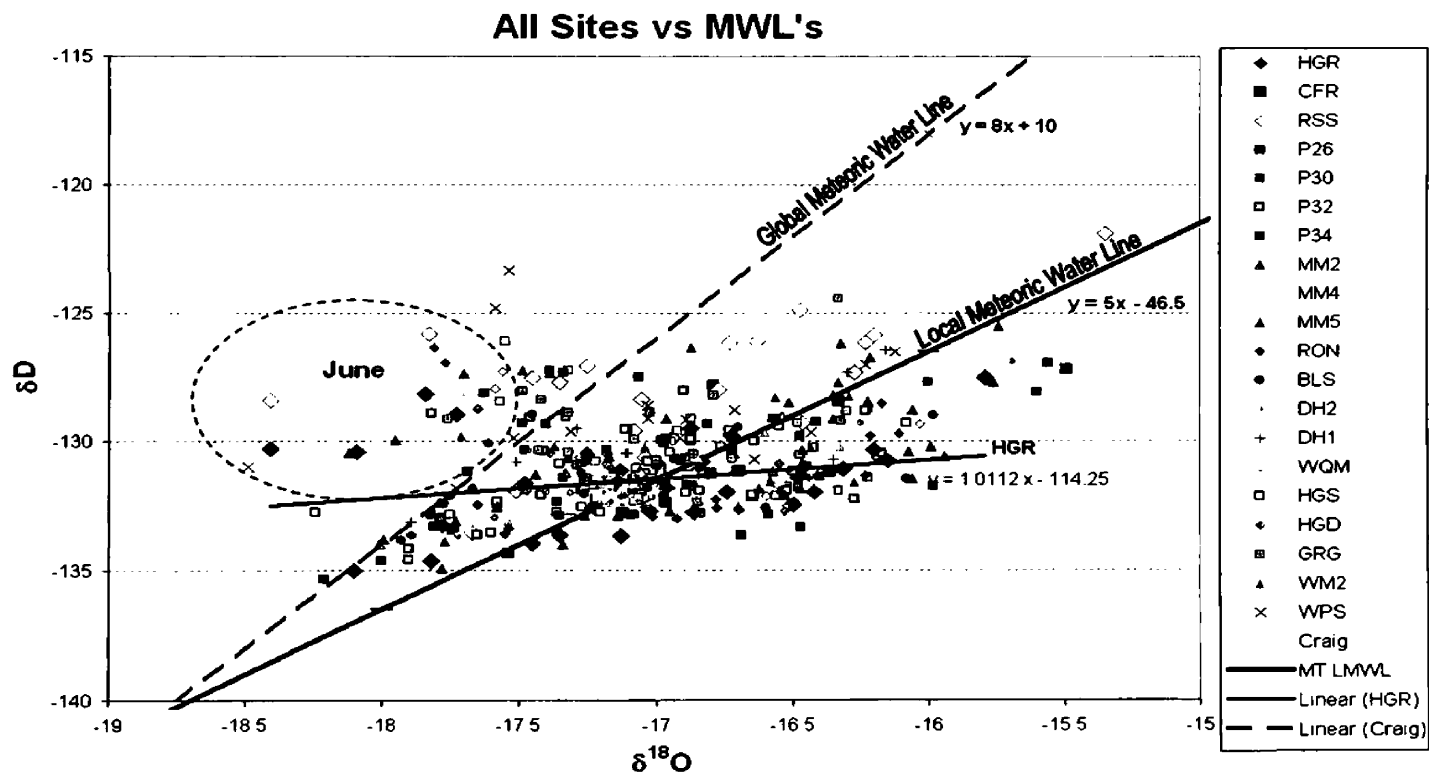


Figure 9. Isotope data for all sample sites over the course of the study. Most of the data are scattered around Montana's Meteoric Water Line, although samples collected in June (labeled) are outliers. The line fit to the Clark Fork River (HGR) samples is as estimation of the regression for the entire data set.

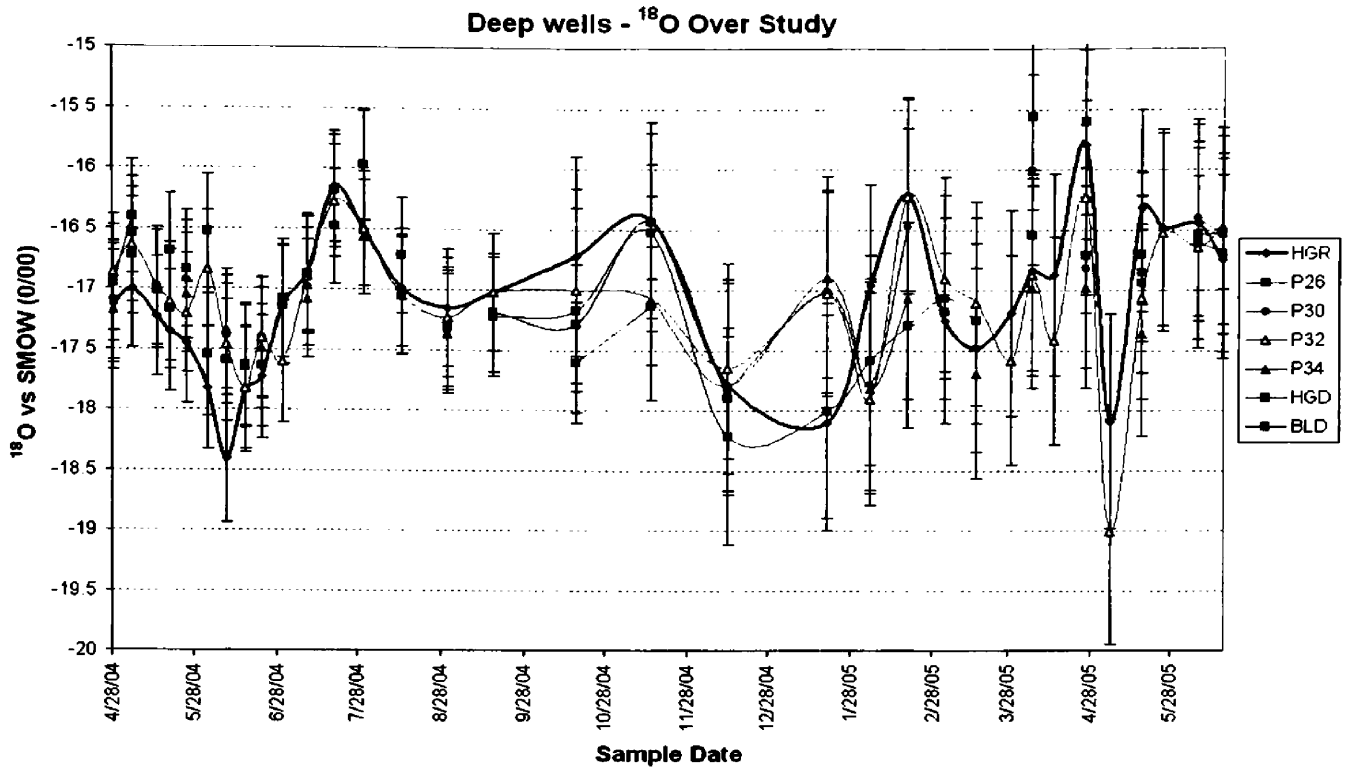


Figure 10. It is hard to distinguish individual points on the time-series due to error bars.

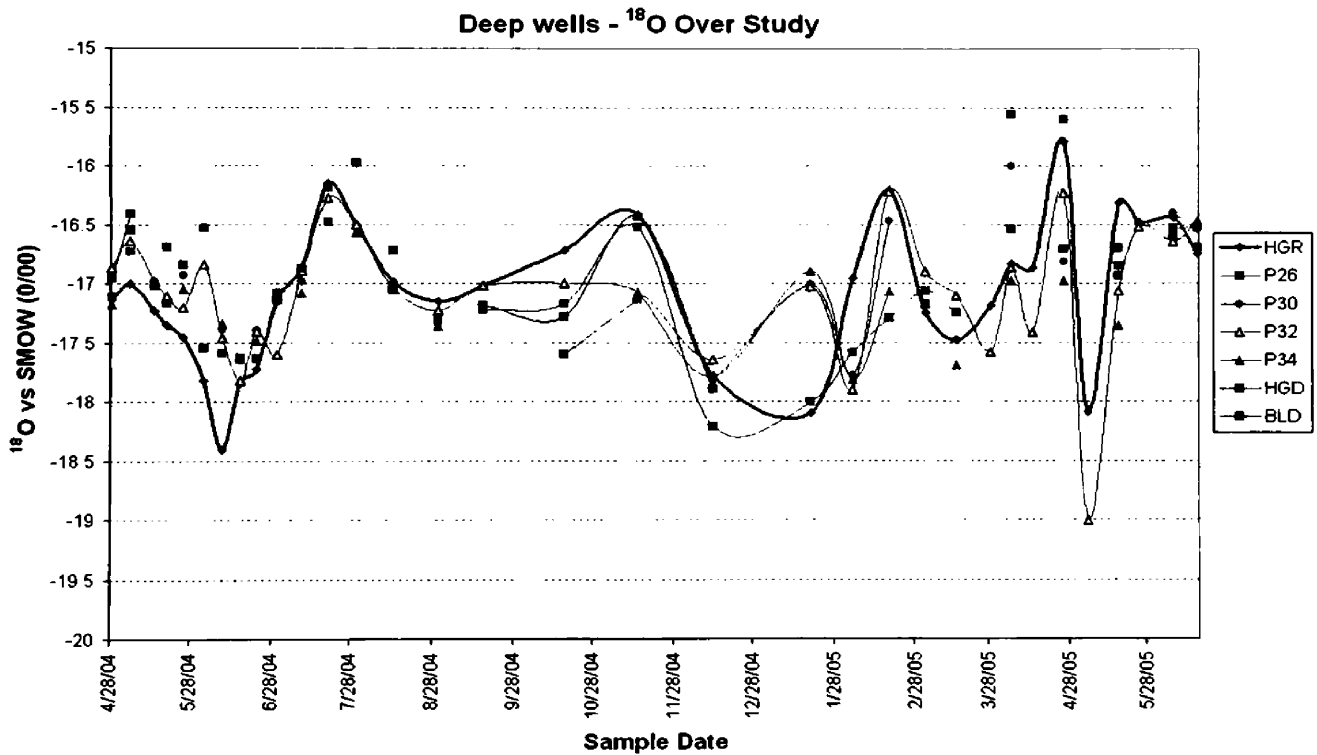


Figure 11. Changes in isotopic signal of the Clark Fork River (HGR) and deep groundwater in production and monitoring wells. In general, the river is isotopically lighter than the groundwater, but all water types follow the same general trend. During periods of frequent sampling (spring and summer) a lag between the surface water and groundwater signals is noticeable.



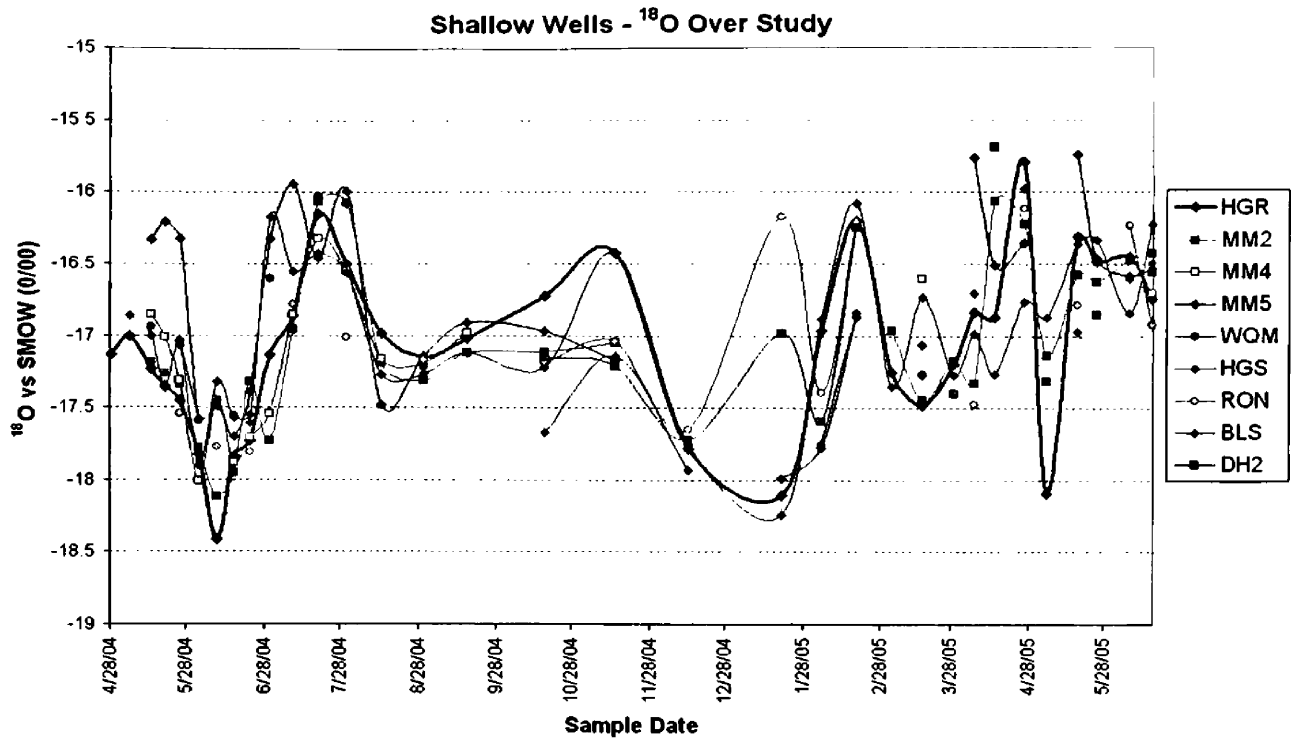


Figure 12. Changes in isotopic signal of the Clark Fork River (HGR) and shallow groundwater. The groundwater signal follows the surface water closely, although groundwater isotopes are slightly heavier than surface water isotopes. The seemingly out of place peaks (RON and DH2) on January 18 correspond to a Rattlesnake Creek peak in  $^{18}\text{O}$  (Figure 13).

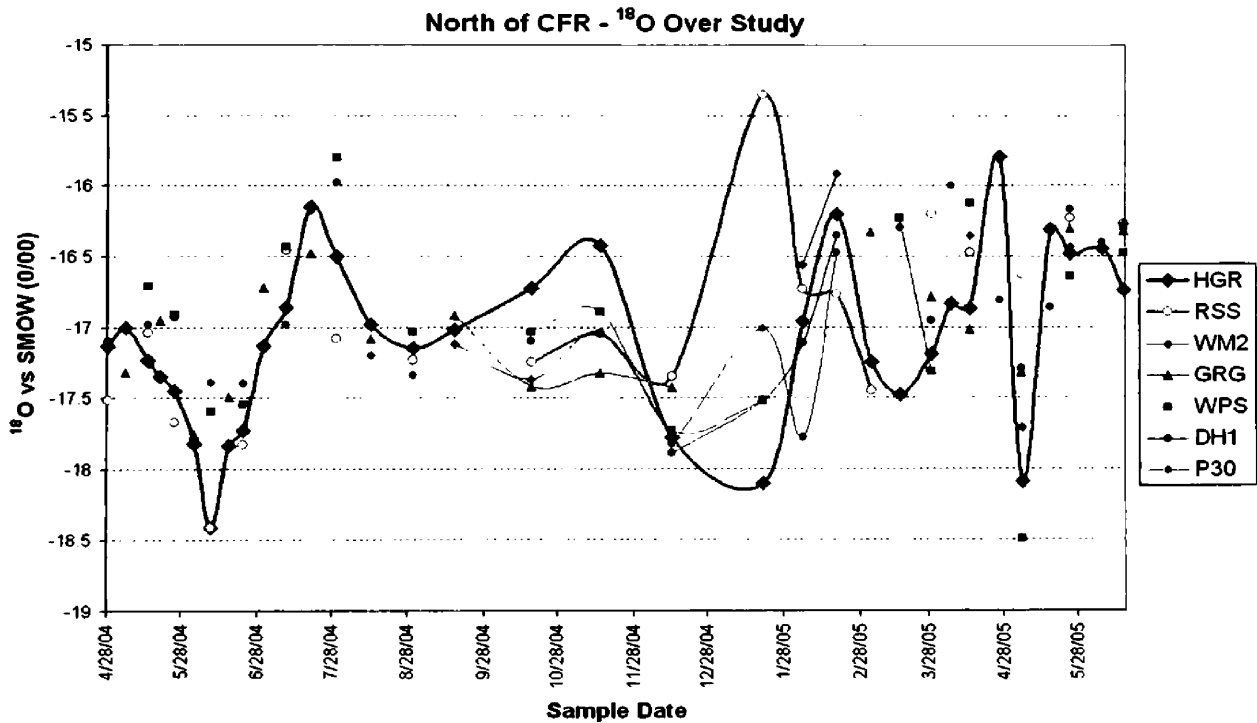


Figure 13. Changes in isotopic signal of the Clark Fork River (HGR), Rattlesnake Creek (RSS) and groundwater on the north side of the Clark Fork River. The large peak in the Rattlesnake Creek signal corresponds to a precipitation event within a local watershed (see Appendix 5).

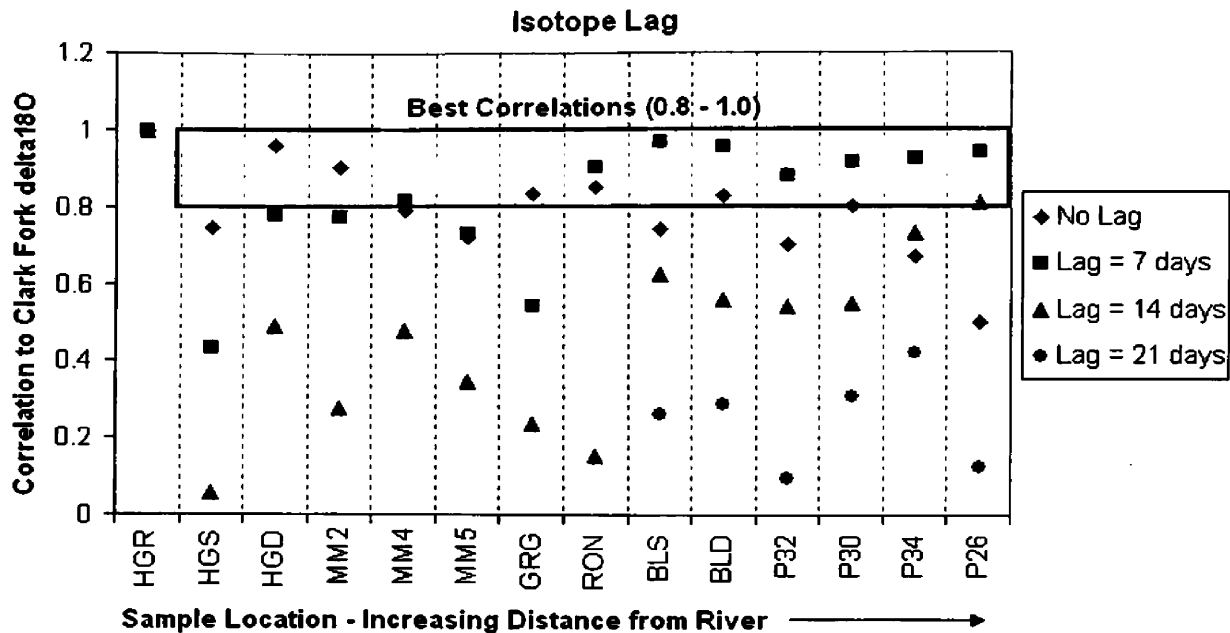


Figure 14. Note that each vertical column represents one site and correlations are given for each of the lag periods. Each lag represents approximately seven days, which was the frequency of sampling for these wells during the spring and summer of 2004. In each column, the symbol that is closest to a correlation of 1 is the best fit. For example, HGD and MM2 fit best with no lag, but RON, BLS, BLD and the production wells all fit better with a lag of seven days. A lag of 14 days also produces a good fit for P26. Introducing a lag in the isotope data makes for better correlation in wells farther down the flow-gradient or deeper in the aquifer.

Introducing lags to the isotope data creates a better correlation between the river and distal groundwater (Figures 15 and 16). Also, the deep groundwater near the river fits better with a lag of seven days (Figures 17 and 18). Correlating the groundwater isotopes with the river isotopes suggests that surface water accounts for 55% to 99% of the variability observed in the isotopic signal of the groundwater. The amount of variability accounted for by surface water trends are show by  $R^2$  values in the figures below. These correlations are only for a short period of time and incorporate a fairly large amount of error, so should not be interpreted as recharge amounts.

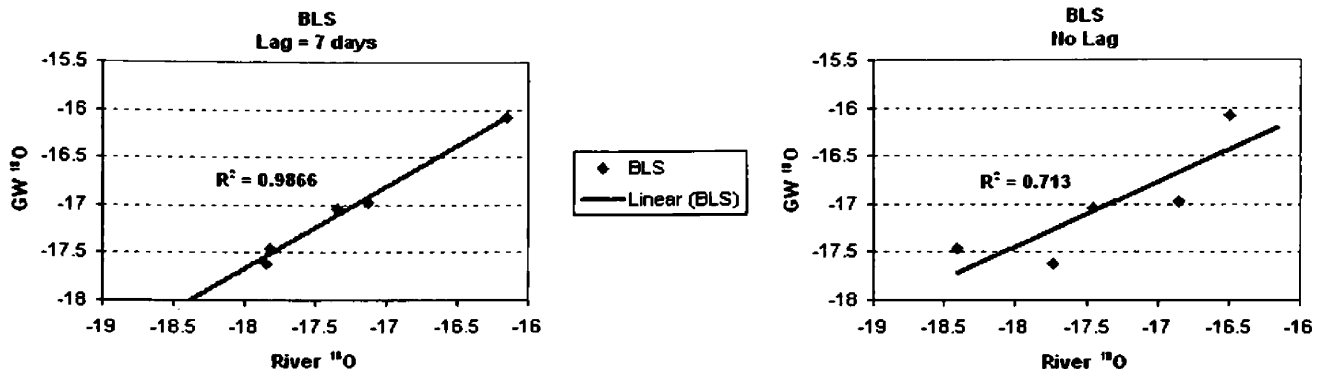


Figure 15. A lag of seven days makes for a better correlation between the surface water and groundwater at BLS.  $R^2$  for the correlation with the lag is 0.99, and without a lag is 0.71.

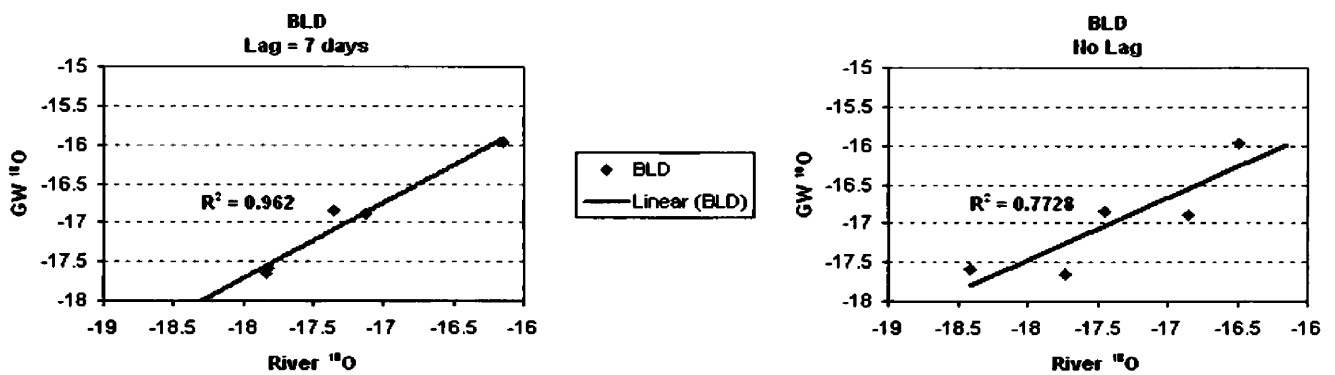


Figure 16. Although there are limited data points, the correlation between surface water and groundwater is better with a lag of seven days at BLD.

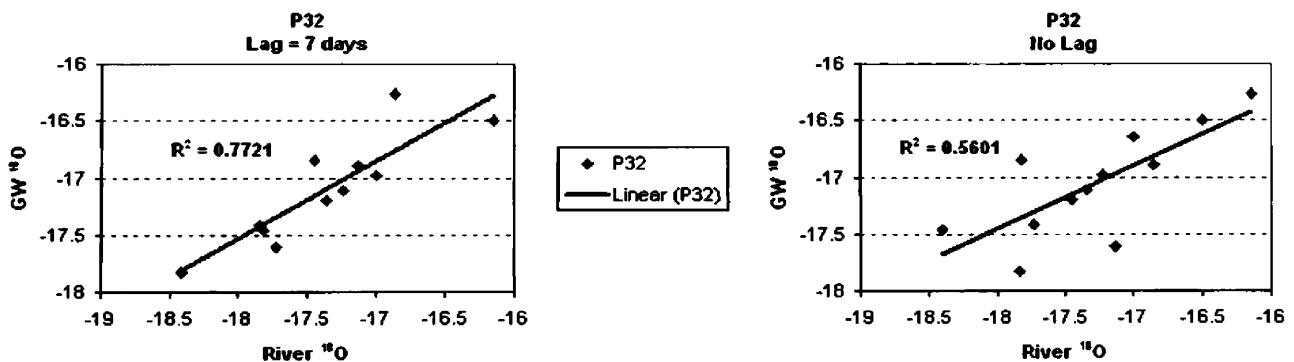


Figure 17. Deep groundwater near the Clark Fork River correlates better to the surface water with a lag of seven days.

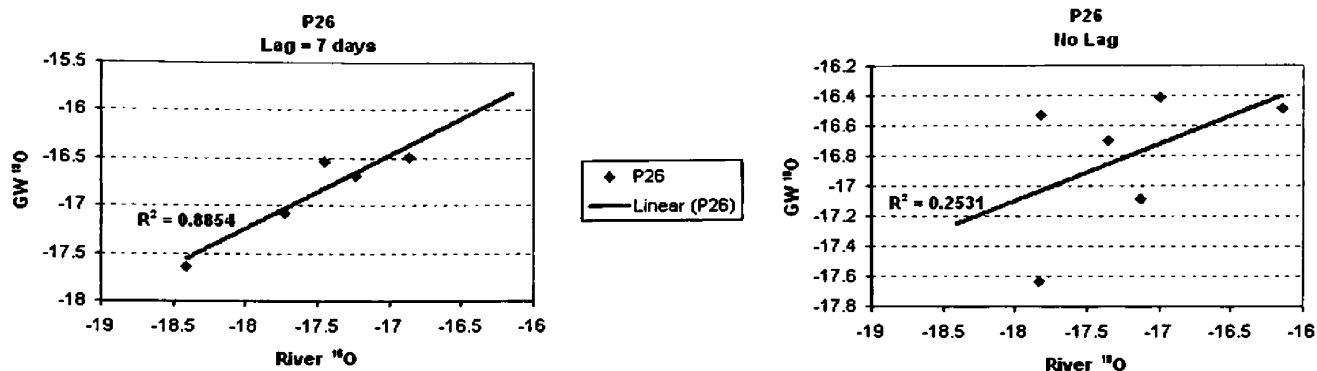


Figure 18. Distal and deep groundwater correlates to the surface water better with a lag of seven days. With no lag the  $R^2$  correlation is 0.25, with a lag of seven days  $R^2$  is 0.88, and with a lag of fourteen days (not shown)  $R^2$  is 0.67. The sampling frequency limits more precise narrowing of the lag window.

Another possible method to determine how much recharge is from the surface water versus underflow from Hellgate Canyon is to compare groundwater isotope values in the valley to HGD, which is the deep well in Hellgate Canyon and represents underflow. Groundwater that is close to the Clark Fork River (MM2) correlates better with the surface water, while deeper groundwater and more distal groundwater correlate better with underflow (Figure 19). A slight problem with these comparisons is the similarity between the isotopic signal of the Clark Fork River and that of the underflow through Hellgate Canyon (Figure 20). This similarity makes it hard to quantify the relative contributions of recharge from the Clark Fork River and from underflow with any precision, possibly because underflow originates as Clark Fork River water upstream.

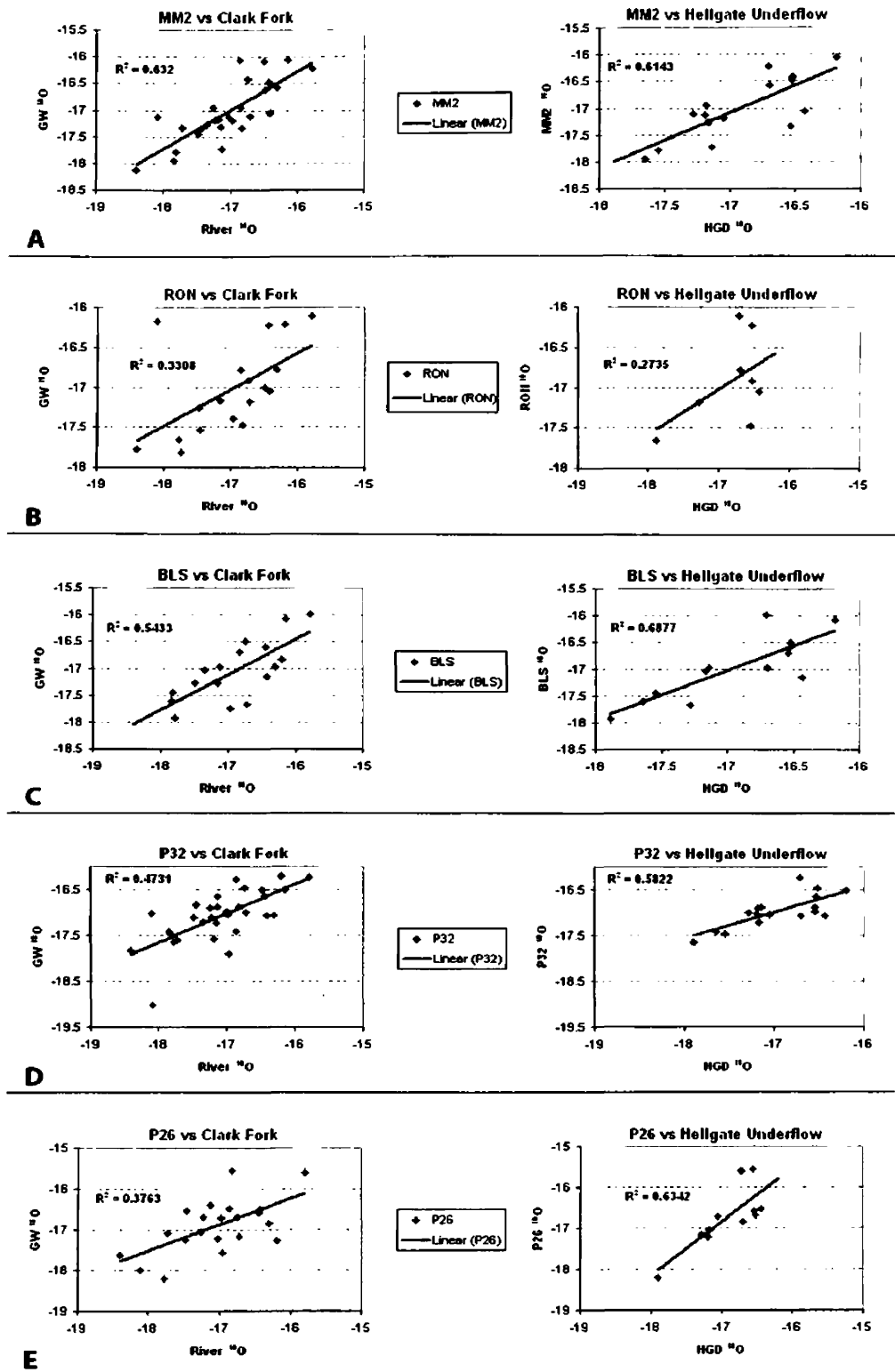


Figure 19. Correlations of groundwater to surface water (River <sup>18</sup>O) and to underflow from Hellgate Canyon (HGD <sup>18</sup>O). A. MM2 near the river correlates to the river slightly better than to underflow. B. RON also shows a better correlation to the Clark Fork River than to underflow. C. BLS, which is farther from the river than RON, shows a slightly better correlation to underflow than to surface water. D. P32, despite its proximity to the river, has a better correlation to underflow than to the river. E. P26, which is the most distal groundwater from the river, shows a much better correlation to underflow than to surface water.

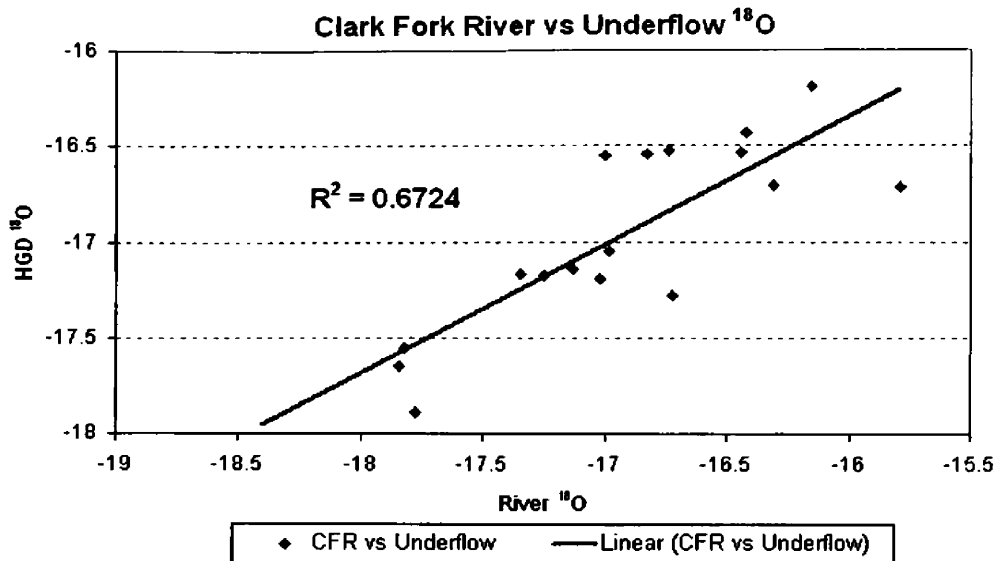


Figure 20. The isotopic composition of the underflow from Hellgate Canyon is very similar to that of the Clark Fork River.

Although stable isotopes are recognized as conservative tracers, there is no correlation between surface water isotopes and conservative chemical elements (Figure 21). This makes it harder to use isotopes in conjunction with conservative chemistry to create a mixing model. Ultimately, the lack of multiple distinct signatures makes it difficult to identify isotopic end members in this system.

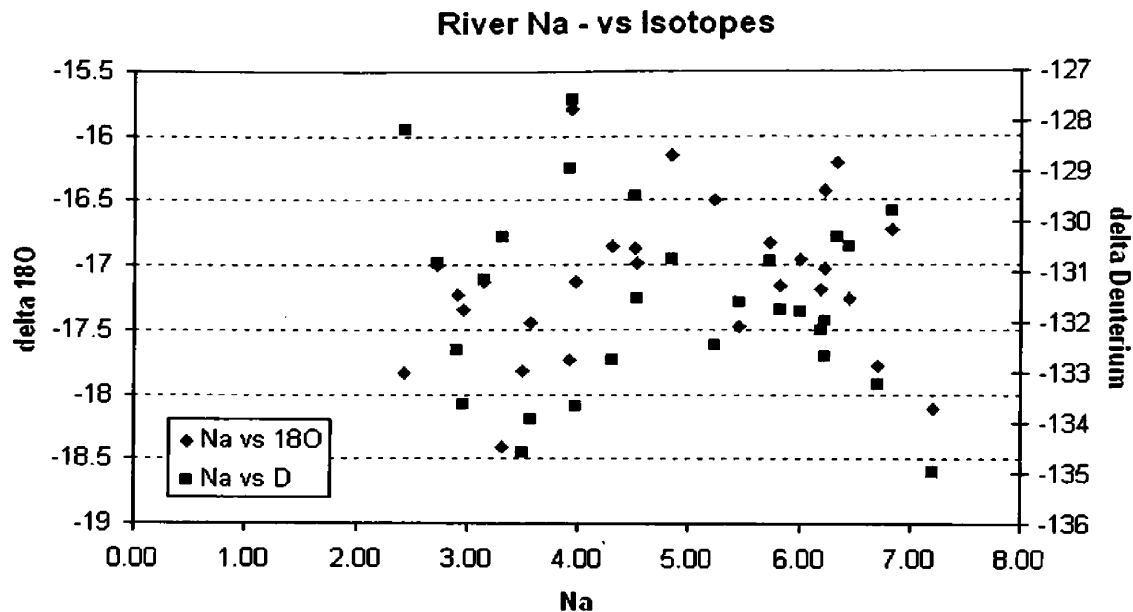


Figure 21. Correlation between Na and both  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in the Clark Fork.

### General Chemistry

All values are for dissolved ions, either in  $\mu\text{g/L}$  or  $\text{mg/L}$ . The concentration of conservative elements (Ca, Na, K, Mg and Cl) in the Clark Fork River is driven by dilution. The same concentrations were found in both our sampling sites on the Clark Fork, reinforcing their conservative behavior in the Clark Fork River (Figure 22 a). Plotting each ion and discharge over time gives a similar correlation as shown by Ca (Figure 22 b). During higher flows ion concentrations were lower, and during baseflow concentrations were higher for all conservative ions. This pattern was slightly disrupted by the drawdown event that took place at Milltown Dam from July 19 through August 13. Comparing upstream values at Turah to values obtained below the dam it is apparent that downstream calcium values decreased during drawdown while concentrations at Turah were increasing (Figure 22 b).

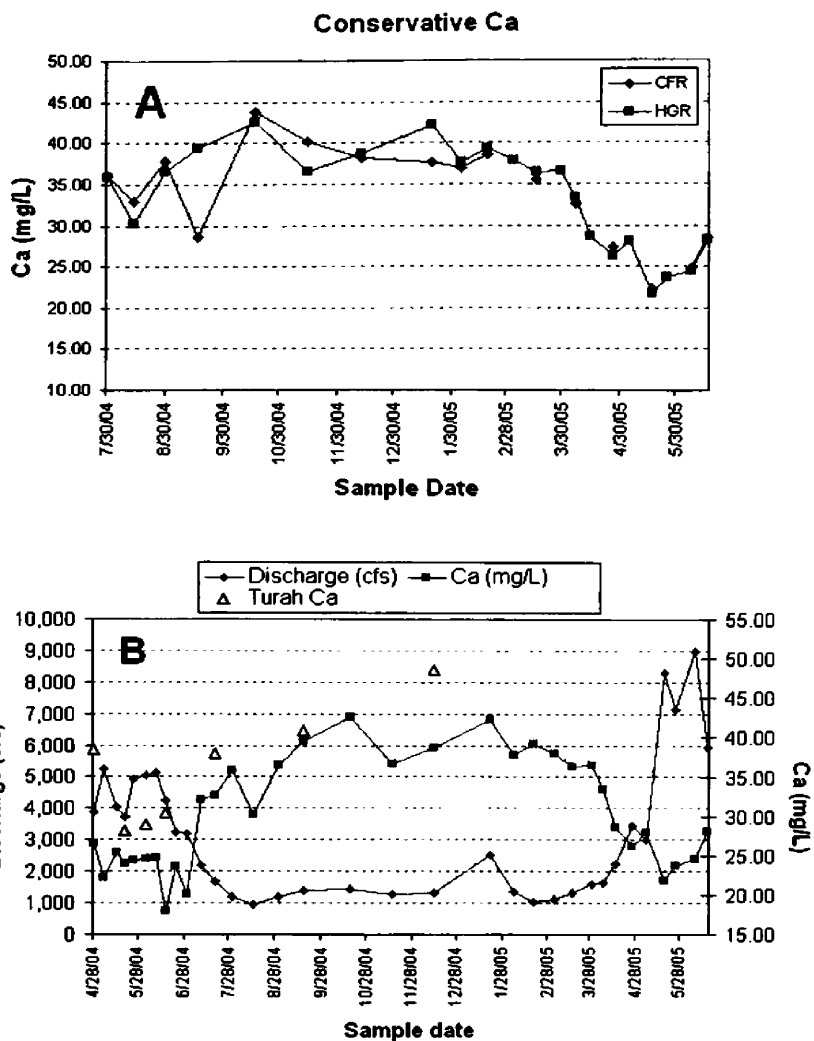


Figure 22. A: calcium concentrations at the upstream (HGR) and downstream (CFR) sites. B: calcium concentration and discharge over time. Limited Turah Bridge (above Milltown Dam, USGS data) values are given for comparison.

Conservative chemical ions all shared similar temporal and spatial trends. All groundwater chemistry was similar among wells throughout the study period, regardless of depth or distance from the river (with the exception of two shallow wells located near the river) (Figure 23 for Ca). Similar trends are found for Na, Mg, K and Cl. Note that while groundwater chemistry remains constant (within a few parts per million), the river chemistry is similar to groundwater chemistry only during baseflow (from August to February). The only wells that show similar trends to the river are shallow monitoring



wells, HGS in Hellgate Canyon and MM2 in the Madison area. The other shallow monitoring wells near the river show an increase in Ca concentration during the spring and summer, coinciding with a higher water table (Figure 24). Wells on the north side also have more constant chemistry, but most concentrations fall below, rather than above surface water concentrations.

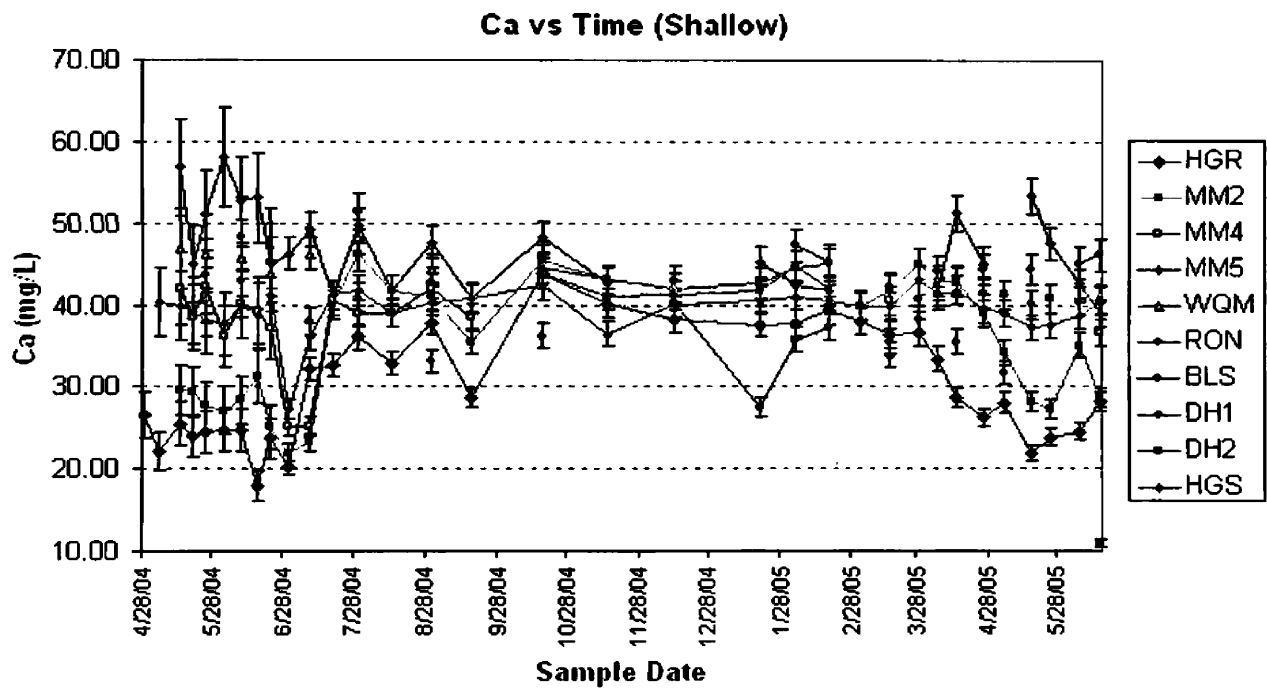
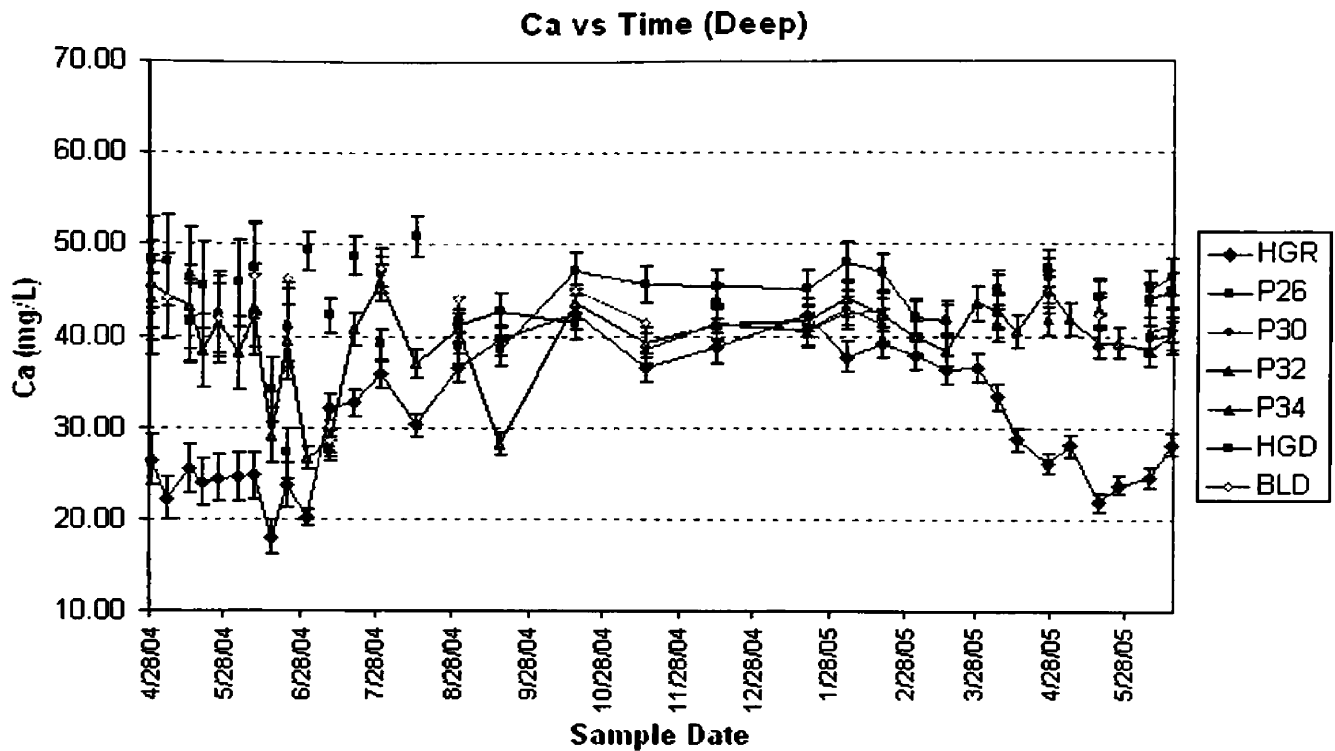


Figure 23. Ca over time in both the deep (top) and shallow (bottom) wells. Deep groundwater (over 80 ft below land surface) concentrations of Ca generally fall between 40 and 50 mg/L. Shallow groundwater (less than 60 ft below land surface) has a wider range of concentrations, with higher concentrations occurring during the spring and summer, and concentrations similar to the river during the winter months. MM2 (light blue) and DH1 (red) have similar chemistry to surface water.

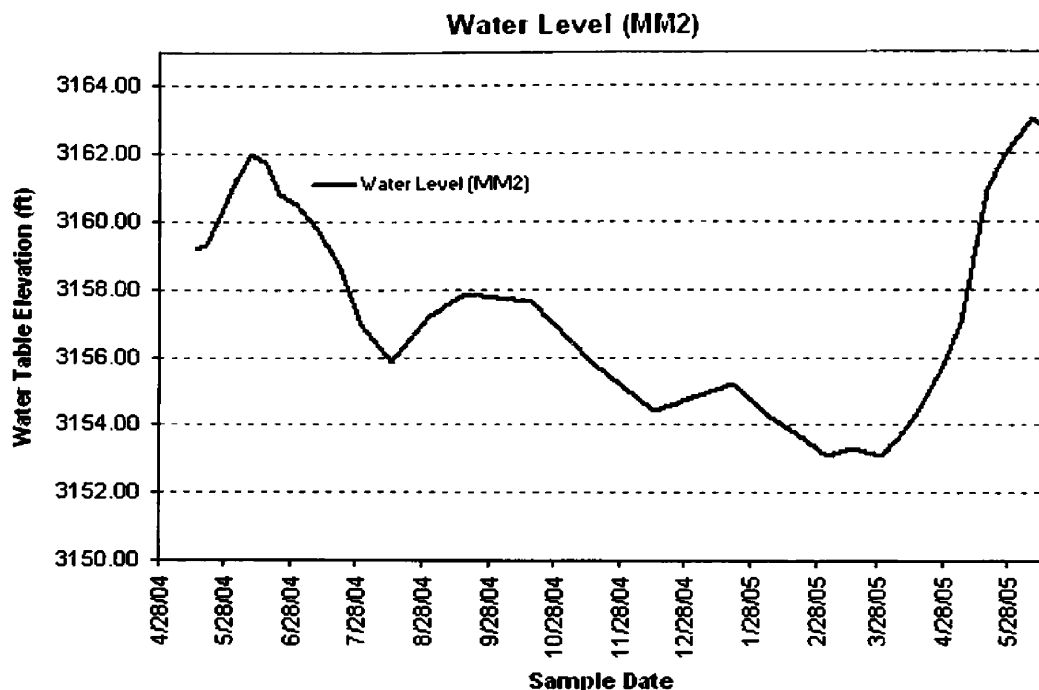
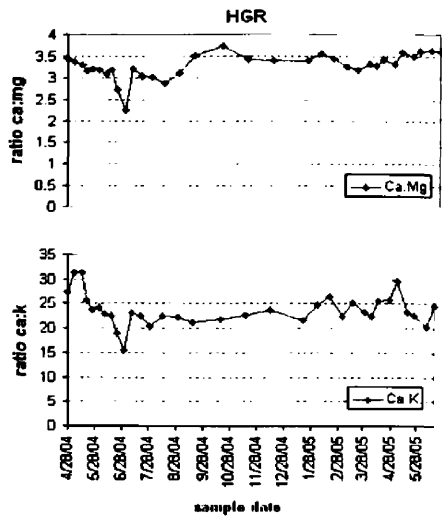
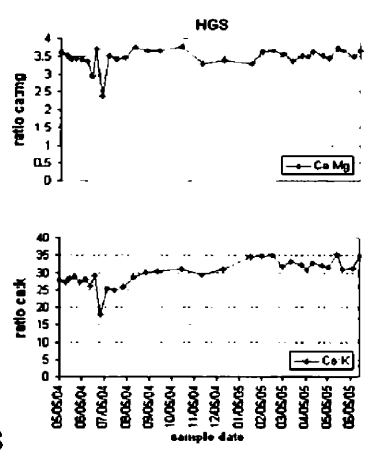


Figure 24. Water table elevations observed at MM2 (a shallow monitoring well 200 ft from the river). The highest elevations are during May and June.

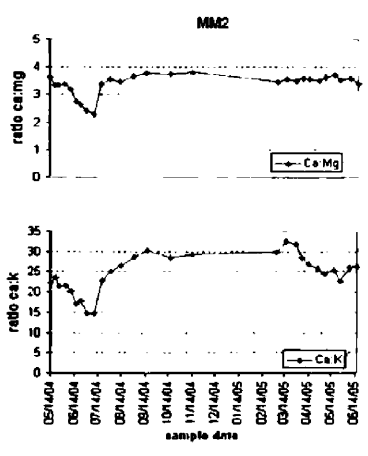
While the concentrations of conservative elements in the shallow groundwater change over time, the ratios of these elements do not. Similarly, the ratios of Ca, Na, Mg and K in deep groundwater stay constant during the study. The only change in these ratios was during June, 2004, when ratios in the Clark Fork River dropped. This decrease was also observed in groundwater near the river, regardless of depth. The decrease is muted or delayed in groundwater farther down the groundwater flow-gradient (Figure 25).



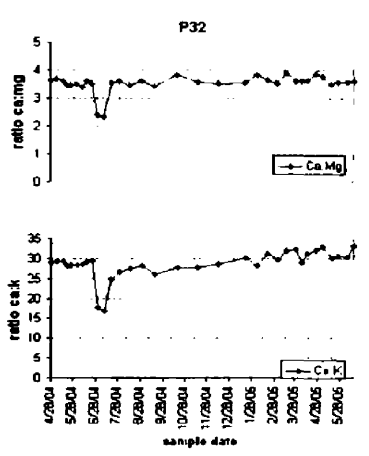
**A**



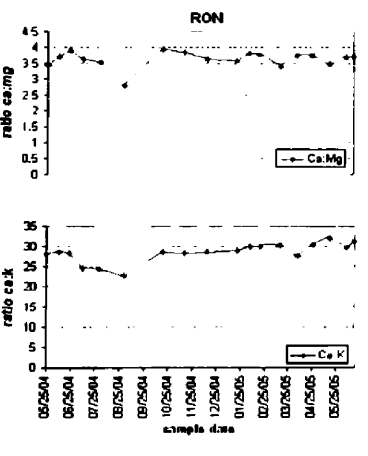
**B**



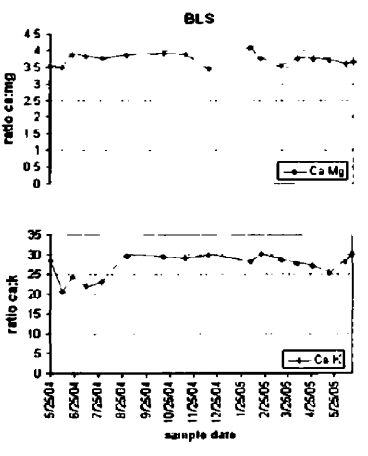
**C**



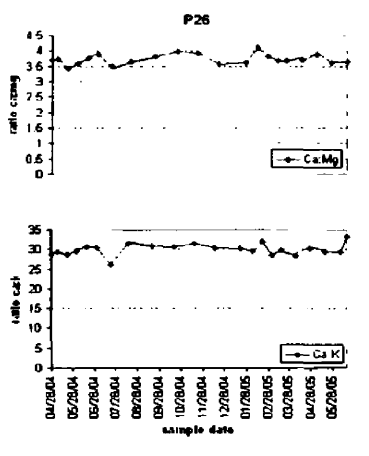
**D**



**E**



**F**



**G**

Figure 25. Ratios of conservative elements in the Clark Fork River (HGR) and in groundwater. A. Ca:Mg and Ca:K in the Clark Fork River. Note the decrease in both ratios in June, 2004. B. HGS mirrors the ratios of HGR. C. MM2 also had decreases in the ratios in June, 2004. D. P32 has the same ratio trend as the river. E. Groundwater at RON saw a delay in the decreased ratios. F. BLS saw a decrease in the ratio of Ca:K, but the timing is delayed from when the decrease occurred in the river, and no notable decrease is observed in the ratio of Ca:Mg. G. P26 only had a slight delayed decrease in Ca:K.

Examining the ratio of two conservative elements throughout the study area reveals that direct river leakage is not the only source of recharge to the Missoula Valley. Examining the ratio Na:Cl for all locations in the study area demonstrates the conservative nature of these two ions in the surface water, and reveals that groundwater is not a simple mixing of two or more end-members (Figure 26).

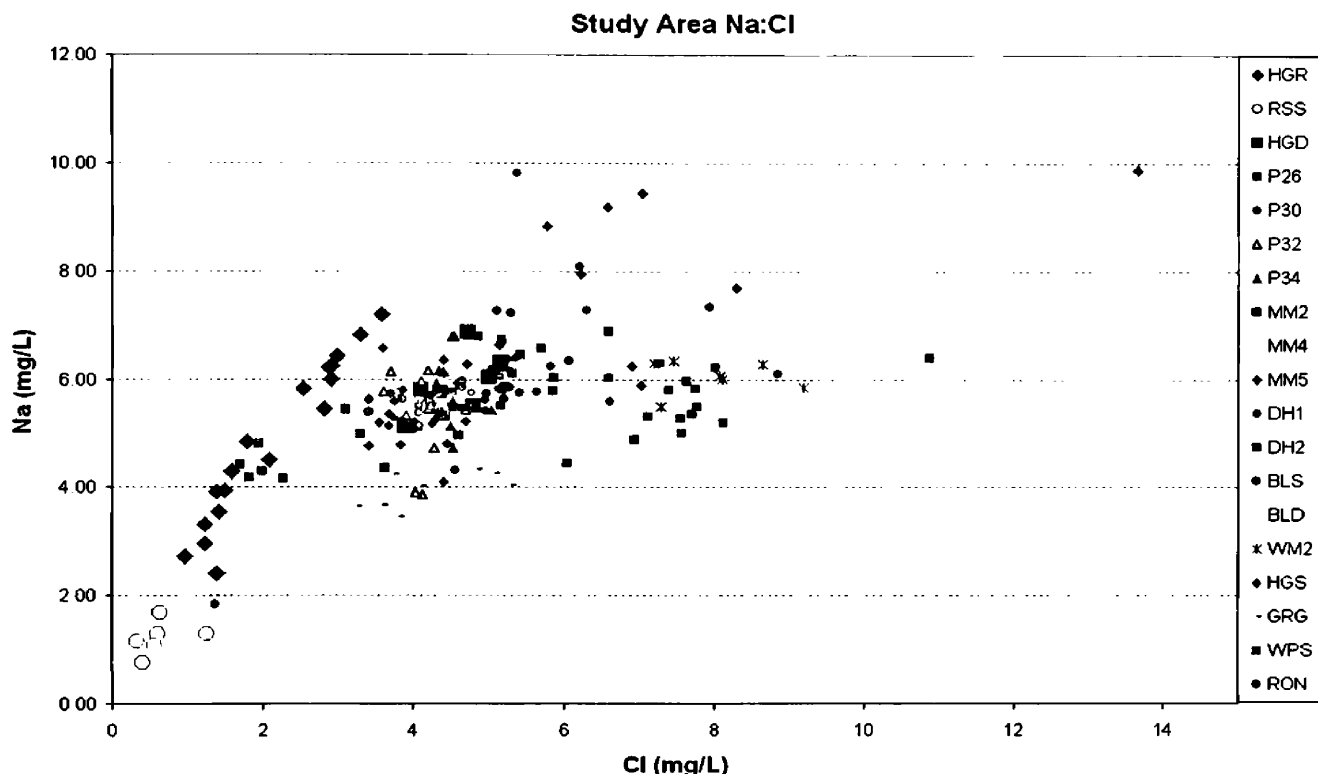


Figure 26. Ratios of Na:Cl for the study area. Note that while surface water values show a linear trend (HGR and RSS), all groundwater values are scattered. HGD, which represents underflow from Hellgate Canyon, is centered in the scattered array of groundwater values.

These trends and similarities between the chemistry data and stable isotope data make it very hard to define end members for a geochemical mixing model.

Other results of interest are that during the course of the study measurable values of manganese (Table 1), cadmium and chromium were detected infrequently (for all values see Appendix 6). These trace concentrations could be from metal contamination

due to instrumentation suspended in a well, from the metal casing in the wells themselves, or from the groundwater. Field blanks and other wells sampled on the same days all contained concentrations below the laboratory quantifiable limit and other wells with the same type of suspended water level monitoring instruments contained no detections in the same sampling period, suggesting that sampling and laboratory error were not the cause of metal contamination.

Table 1. Wells and dates of Mn detection ( $\mu\text{g/L}$ ). Wells are either metal, have metal fittings on the caps, or have stainless steel water level transducers (Instr.).

Date	WQM	DH2	BLS	WM2	GRG	WPS	HGD	HGP	RON
Well Type	Metal	Metal Top	Instr.	Metal Top	Metal	Instr.	Instr.	Metal	Metal
5/5					12.7				
5/14						7.58	High		
5/19					2.21		8.41		
5/25						1.78			
6/2					14.74				
6/9	11.2		2.42			2.48			
6/16					10.4				
6/22	13.7					1.86			
6/30					5.78				
7/9			1.58			1.81			
7/19					5.93			1.67	
7/30			1.16						
8/13				2.91	4.31				
8/30						1.24			10.5
9/16				3.73	24.5				
10/17					1.52	1.72			
12/13		1.61		1.34	3.81	2.60			
1/19						1.28			
3/4								20.6	
4/14					1.22				
5/17			1.95						
5/25					42.1				
6/16					6.81				

The surface water and groundwater chemistry on the north side of the Clark Fork is different than the water quality on the south side of the river. Of special note is groundwater in the Gregory Park area, where the concentrations of all conservative elements were much lower than groundwater sampled south of the river. The lowest

concentrations of constituents was observed on the north side were in Rattlesnake Creek (RSS), these values were usually 0.5 to 4 mg/L lower than Gregory Park (GRG) values.

## Arsenic

**Spatial and Temporal Trends.** All concentrations given are for dissolved arsenic, in parts per billion ( $\mu\text{g/L}$ ). As previously stated, arsenic is a dynamic element. Accordingly, the behavior of arsenic in surface water is quite different than in groundwater. Variability of arsenic in the river is less than 5%, and is fairly conservative between the upstream and downstream sampling locations (Figure 27). However, arsenic does not behave conservatively in the groundwater. In general, groundwater arsenic concentrations decrease with distance from the river, and arsenic concentrations on the north side of the Clark Fork decrease with distance at a greater rate than concentrations south of the river (Figure 28).

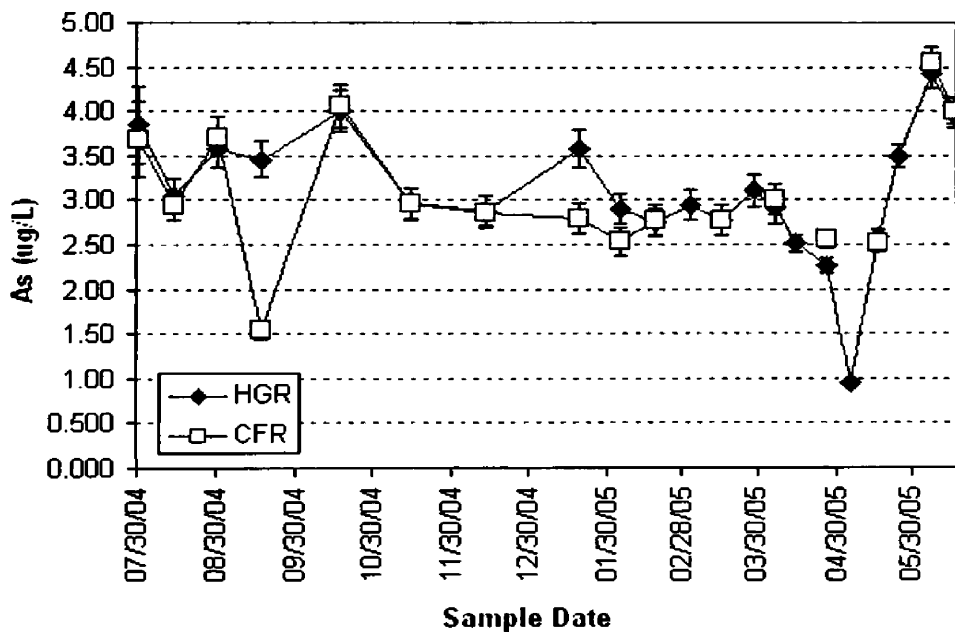


Figure 27. Dissolved arsenic concentrations for upstream (HGR) and downstream (CFR) locations. A rain event on September 19<sup>th</sup> may have caused some dilution in the downstream site (this site is near the confluence of Rattlesnake Creek and the Clark Fork River).

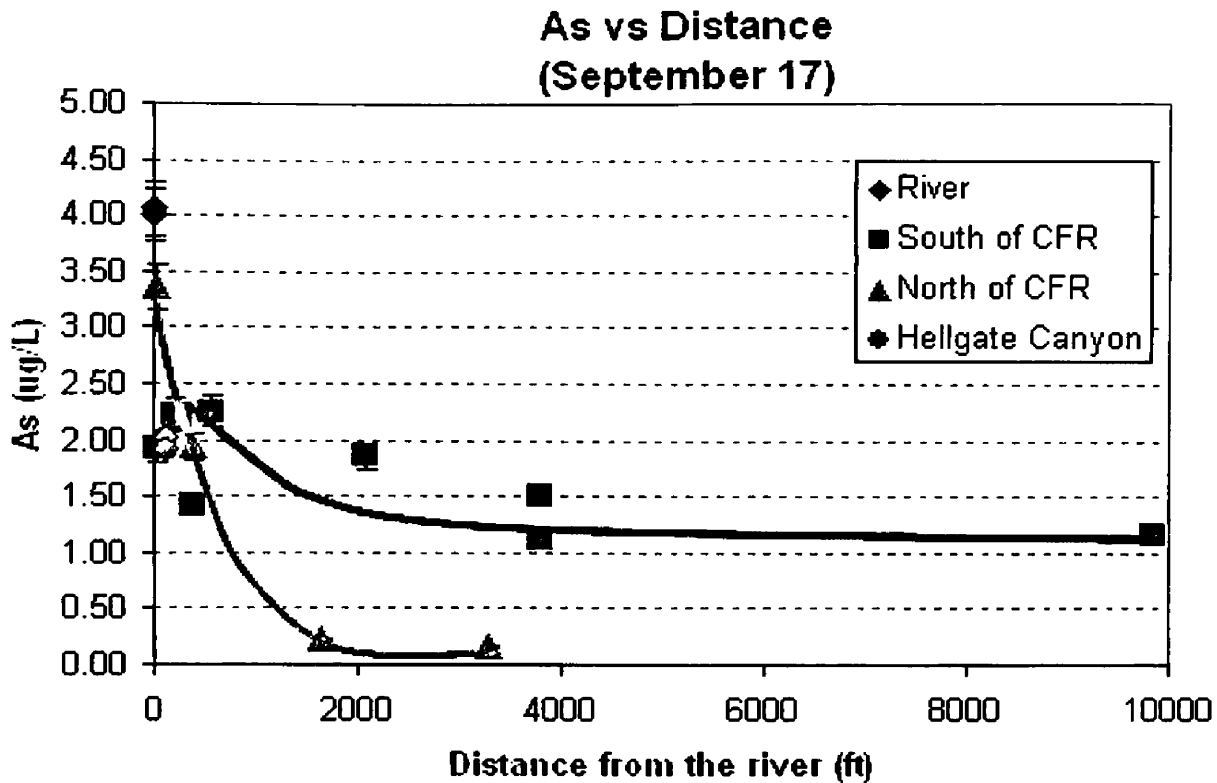


Figure 28. The results from one day of sampling showing the general trend of dissolved arsenic concentrations in groundwater. Concentrations decrease with distance from the river. Error bars are encompassed by the size of the symbol.

Examining the arsenic concentrations of several wells along the groundwater flowpath also shows a similar trend (Figure 29). The two wells closest to the river (DH2 and MM2) show similar concentrations for the winter months, but vary in the spring though the wells are only 160 ft apart. The other three wells (RON, BLS and P26) are roughly 0.4, 0.75 and 2 miles down groundwater gradient from the river, respectively. As the distance from the river increases, the arsenic concentrations generally decrease.



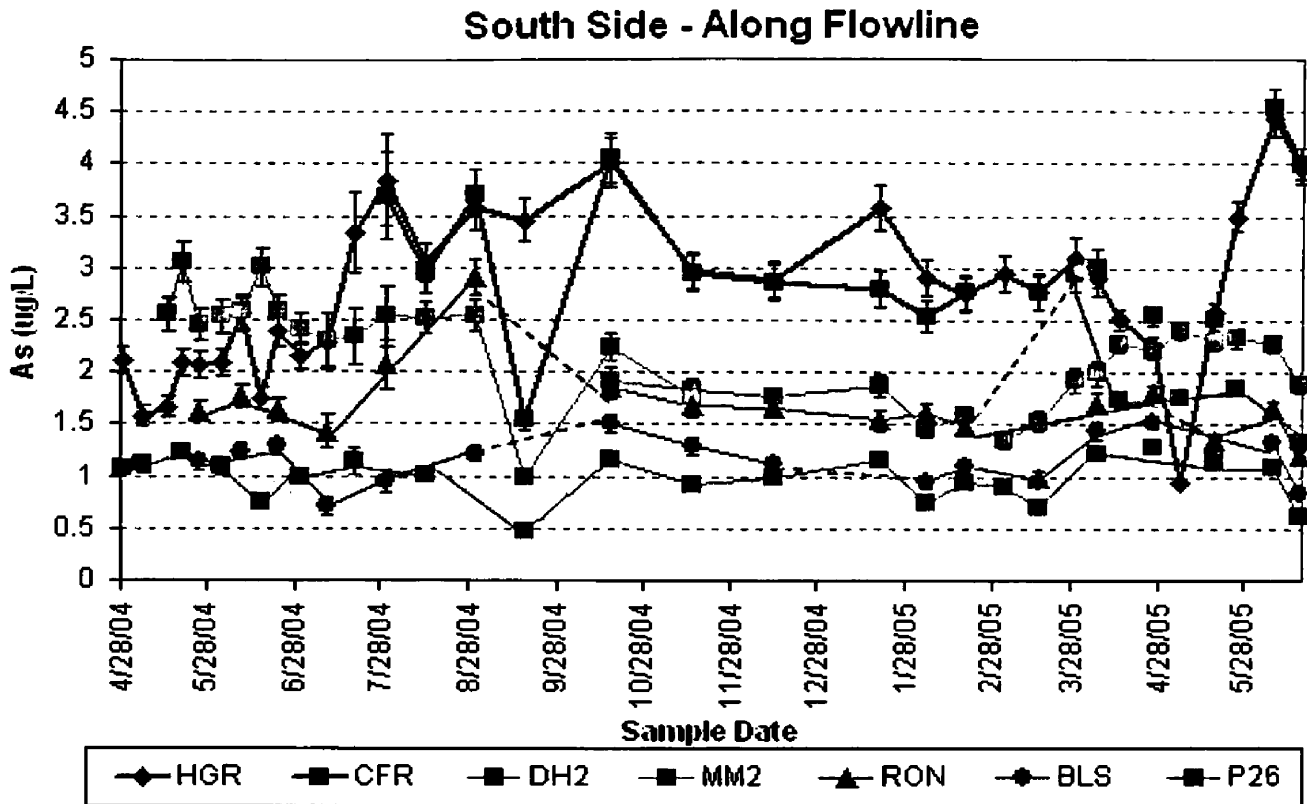


Figure 29. Arsenic concentrations at five wells along the groundwater flowpath from the river to the southwest. In general, concentrations decrease along this flowline.

Locally, the migration of arsenic is more complex. For example, the trends of arsenic concentrations for three monitoring wells near the river (Figure 30) are quite different, despite all of the wells being finished at the same depth and only varying in distance from the river by 100 ft. In the spring of 2004, all three of the wells (MM2, MM4 and MM5) had higher concentrations of arsenic than the river. The water table was at the highest point during this period as well. Following the drawdown event at Milltown reservoir (July 19 through August 13, 2004), the river continued to have elevated arsenic concentrations while the shallow groundwater concentrations were briefly elevated and then declined and remained low through the fall and winter. In the spring of 2005, coinciding with the rising water table, arsenic concentrations began to rise in MM2 and MM5 (due to construction around the production well access to MM4 was limited).

Unlike the previous spring, river concentrations stayed elevated above groundwater concentrations with the exception of two points. The best example of a direct link between surface water arsenic and these shallow monitoring wells was observed during the drawdown event (Figure 31). The level of Milltown reservoir was lowered by eight ft over the course of 18 days and remained at the low stand for just over two weeks. Due to the frequent sampling intervals during the drawdown, an almost immediate increase in groundwater arsenic concentrations was observed corresponding to an increase in the river arsenic concentration. The values above the reservoir, at Turah Bridge, do not match the level of arsenic observed below the dam (Figure 32). During the drawdown event, arsenic concentrations upstream were declining, while below the dam arsenic increased by roughly two parts per billion. This graph also compares how arsenic behaves in the shallow groundwater in Hellgate Canyon and in the Madison area. Apart from the earlier rain event, the shallow groundwater in the Madison area has slightly higher values of arsenic. Deep groundwater in the Madison area is represented by P34.

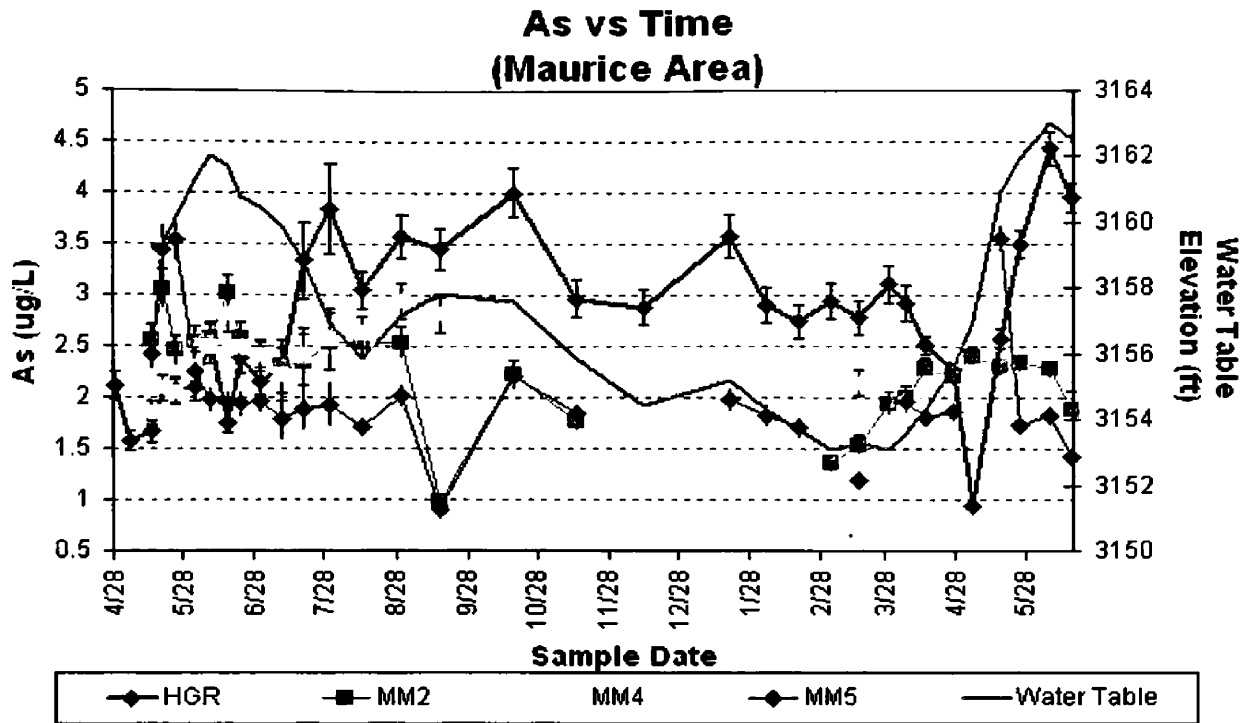


Figure 30. Arsenic concentrations over the course of the study for three monitoring wells near the river. All wells have the same construction and MM2, MM4 and MM5 are 200, 300 and 260 feet from the river, respectively. The water level was taken in MM2, but differences between these wells are negligible (Tallman, 2005).

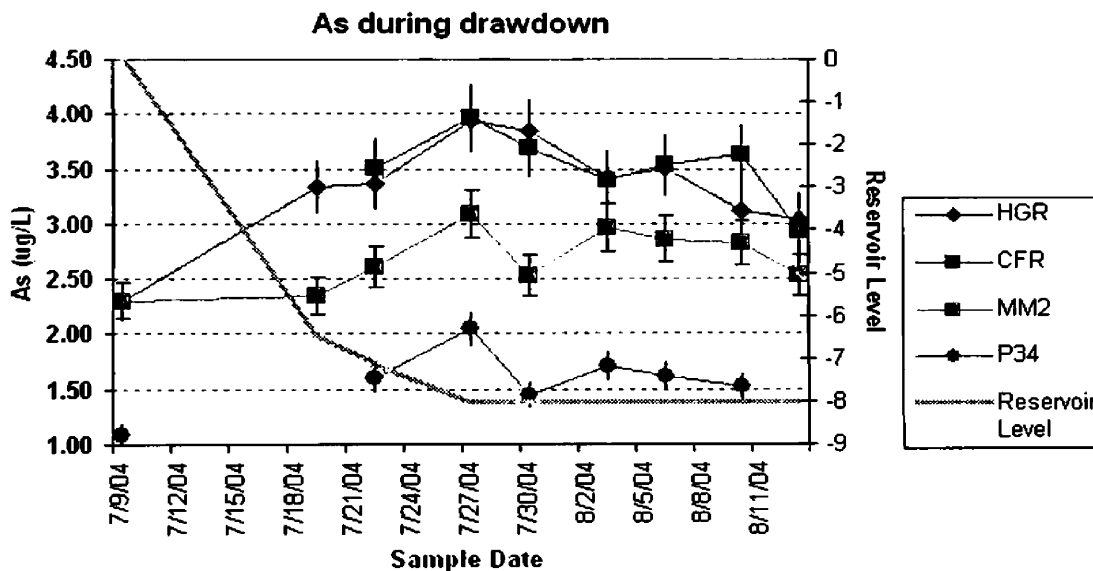


Figure 31. Arsenic concentrations in the river, shallow and deep groundwater during the drawdown event at Milltown reservoir. Samples were taken every three days. Arsenic values increased in surface water and groundwater with the lowering of the reservoir.

## As Over Time (Including Drawdown)

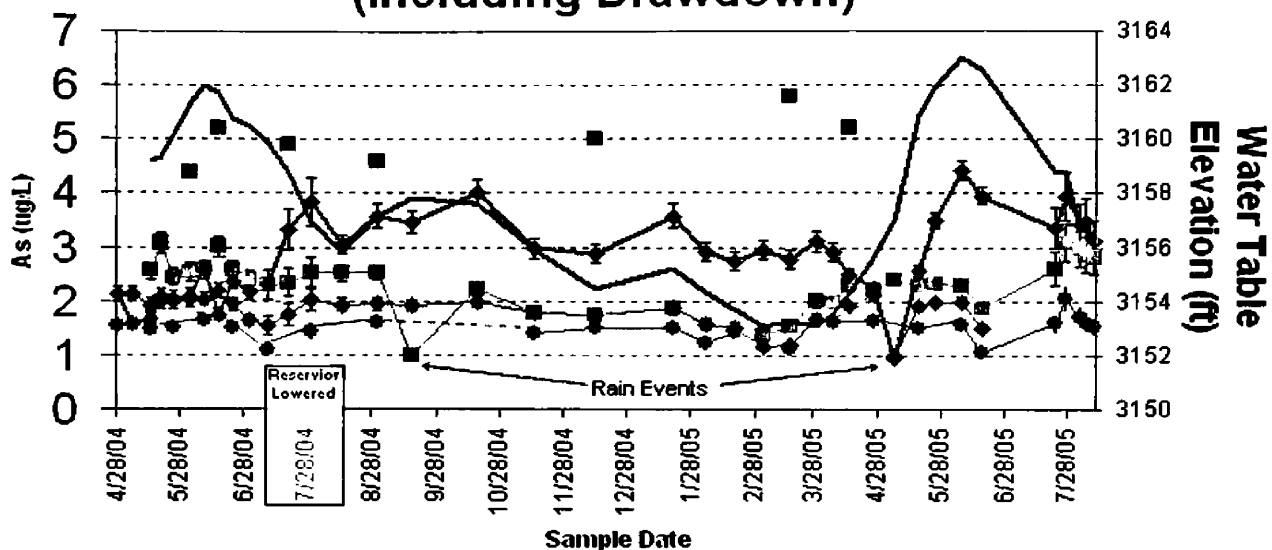


Figure 32. Arsenic values for Turah Bridge, the Clark Fork River, shallow groundwater in Hellgate Canyon and in the Madison area, and for a production well. Historically, Turah Bridge has had higher arsenic values than the Clark Fork River above Missoula (see Appendix 7). During the drawdown (light blue box) arsenic values at Turah declined but arsenic in the Clark Fork increased by about 2 µg/L. Rain events only appear to result in the dilution of the river and the shallow groundwater near the river.

During the rest of the study, changes in arsenic concentration for the production wells near the river are much more muted. Arsenic concentrations for three production wells near the river and one two miles to the southwest of the river (along the groundwater flowpath) do not vary more than a few of parts per billion over the course of the study (Figure 33). Apart from the direct response noted during the Milltown drawdown, deep groundwater arsenic concentrations do not appear to reflect changes in Clark Fork River arsenic concentrations (Figure 34). It is interesting to note that the well with the highest concentrations of arsenic (P32) is not the closest well to the river. The Maurice Street well (P34) is roughly 160 feet closer to the river than the Arthur Street well (P32) (Figure 2), yet the Arthur street well has consistently higher arsenic values.

The Arthur Street well pumps year-round, while the Maurice Street well is an on demand well during peak summer supply. The production well with the lowest values (with the exception of two high values in the spring of 2005) is the Bank Street well (P30), which is the closest well to the river on the north side (230 ft). Values for the Bank Street well are usually just below those of the Benton Street well (P26), which lies in the southwest corner of the study area, two miles from the river.

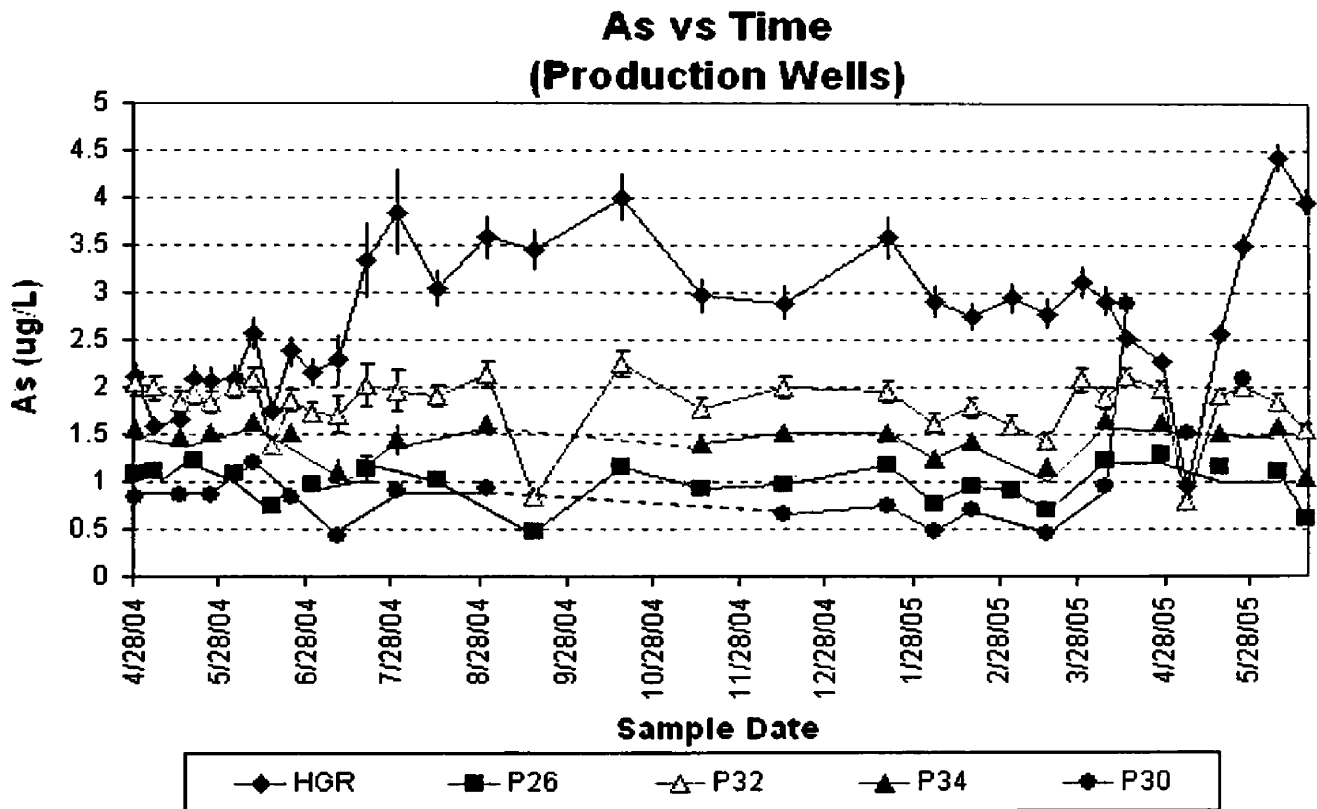


Figure 33. Arsenic concentrations over the course of the study for all four production wells. These wells show little fluctuation in arsenic concentration. The two wells on the south side of the river (P34 and P32) have the highest values, followed by the well which is roughly 2 miles from the river (P26). The well with the lowest concentrations is only 230 ft from the river, on the north side (P30).

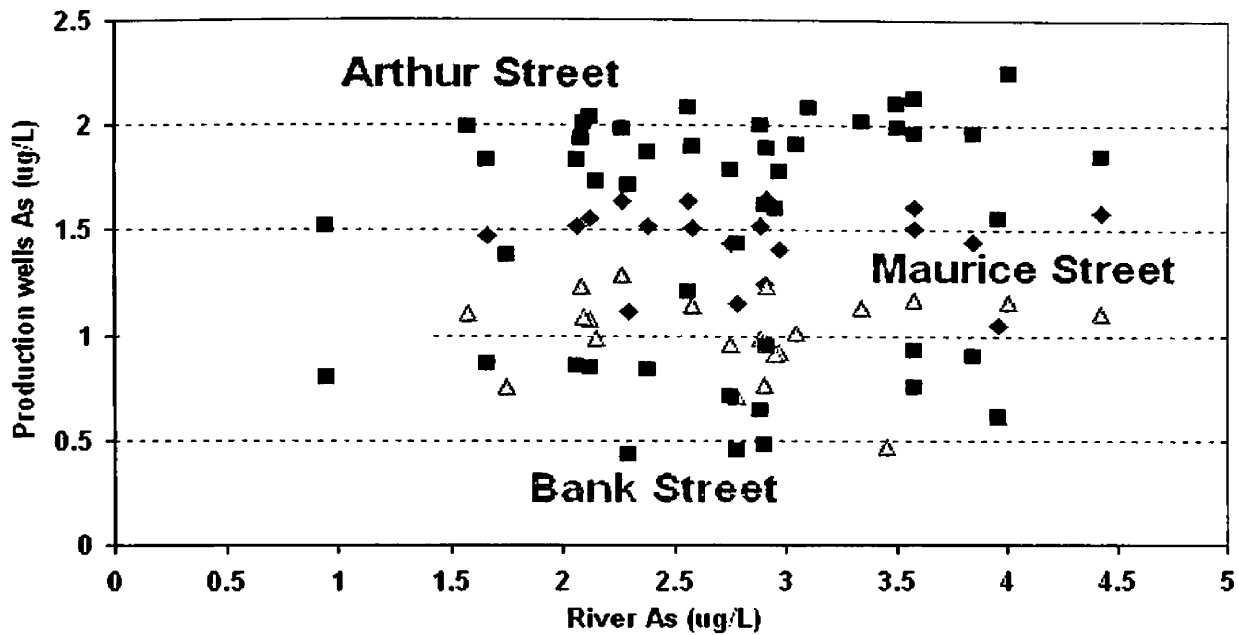


Figure 34. Relationship between river arsenic concentration and production well arsenic concentration. There are no linear correlations between the river and any of the production wells. Instead, each well has a range of values that do not appear to change with or directly correlate to arsenic concentrations in the river.

A pair of nested wells in Hellgate canyon illustrates the difference between shallow and deep groundwater at a single location (Figure 35). The shallow well (HGS) has slightly higher arsenic concentrations, but both wells tend to follow the same general trend as the river. The largest difference between the surface and groundwater arsenic values occurs from the end of June through the winter. The groundwater arsenic values in the spring of 2004 were much closer to river concentrations than in 2005.

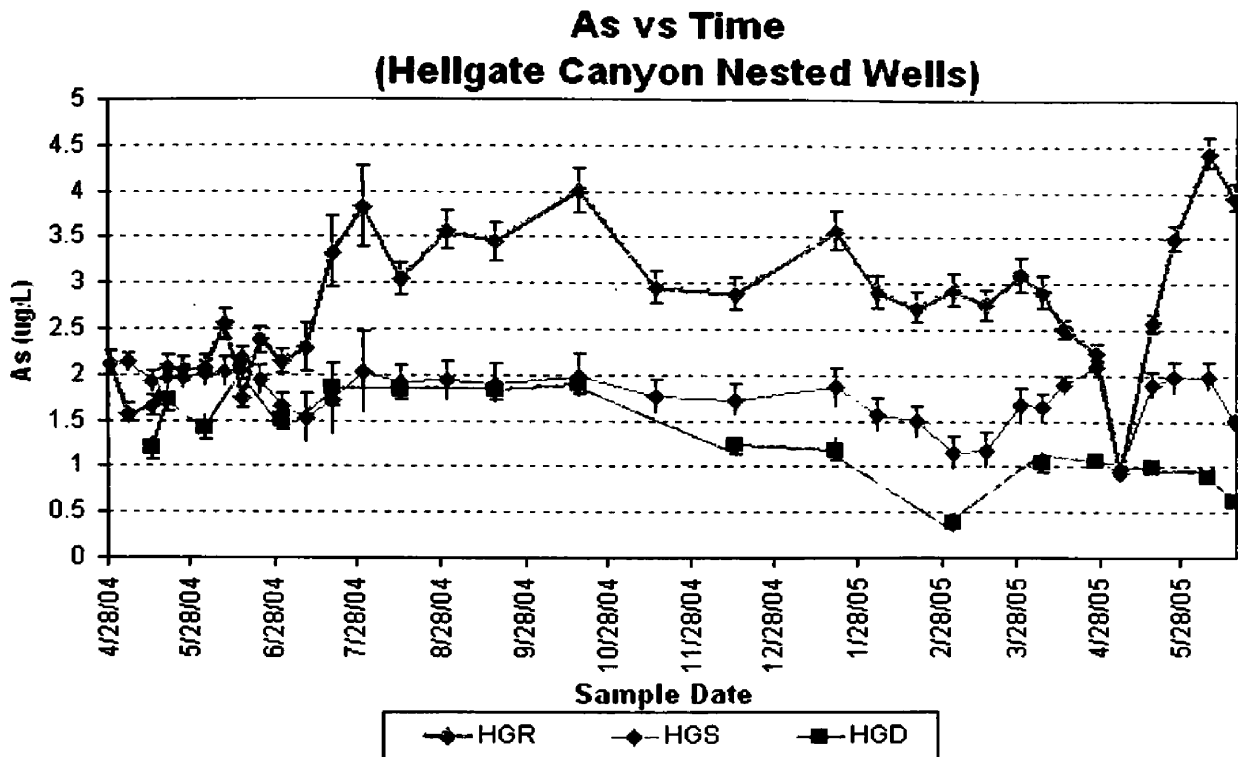


Figure 35. A pair of nested wells in Hellgate Canyon. HGS is the shallow well, HGD is the deep well. Both wells have fairly constant arsenic concentrations, and follow the same trend as the river during the spring. From the late fall through winter there is a greater difference in concentrations between surface and groundwater.

Groundwater arsenic concentrations are much lower on the north side of the Clark Fork River (Figure 28). With the exception of one well that is very close to the river and is finished right at the water table (DH1) all wells have concentrations at or below two parts per billion (Figure 36). Both Rattlesnake Creek and the groundwater in that drainage have very similar arsenic concentrations (less than 1  $\mu\text{g/L}$ ). WM2 is a shallow well, and although it is 400 ft from the river and P30 is only 230 ft from the river (Figure 2), WM2 has higher arsenic concentrations than the production well. The farthest well to the north in our study area is WPS (0.6 mi from the river), and this well has arsenic concentrations below 0.4  $\mu\text{g/L}$ .

### As vs Time (North of Clark Fork)

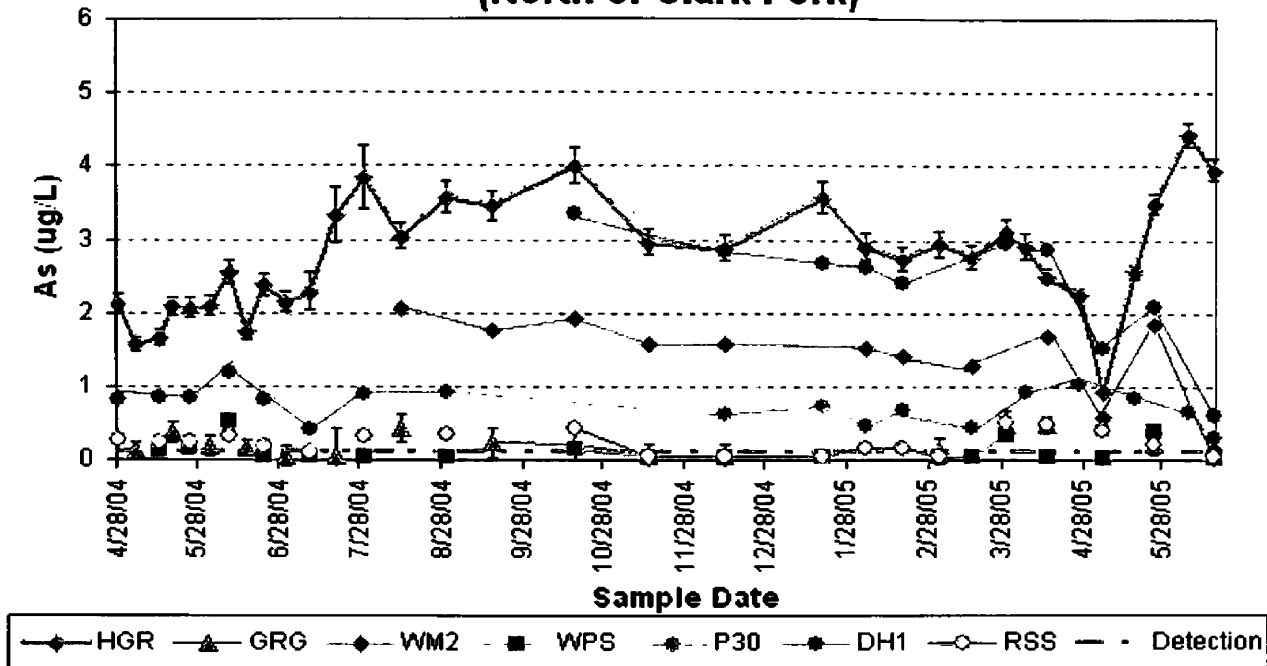


Figure 36. Arsenic concentrations for the Clark Fork, Rattlesnake Creek and wells on the north side of the Clark Fork. The well nearest to the Clark Fork (DH1) follows the river's trend until the late spring of 2005. Rattlesnake Creek and all other wells have consistently low arsenic values. Error bars, where not visible are encompassed by symbols.

**Arsenic and Conservative Elements.** Comparing arsenic to Ca, Na, Mg and K in the Clark Fork shows that arsenic is also conservative in the surface water and that concentrations are controlled by dilution. Arsenic correlates fairly well to any conservative element in the surface water, but does not correlate to isotopic values (Figure 37). This reinforces the fact that although chemical ions and isotopes are both conservative tracers, they do not necessarily correlate with each other. Once arsenic leaves the surface water, the correlation with conservative ions is not present (Figure 38).



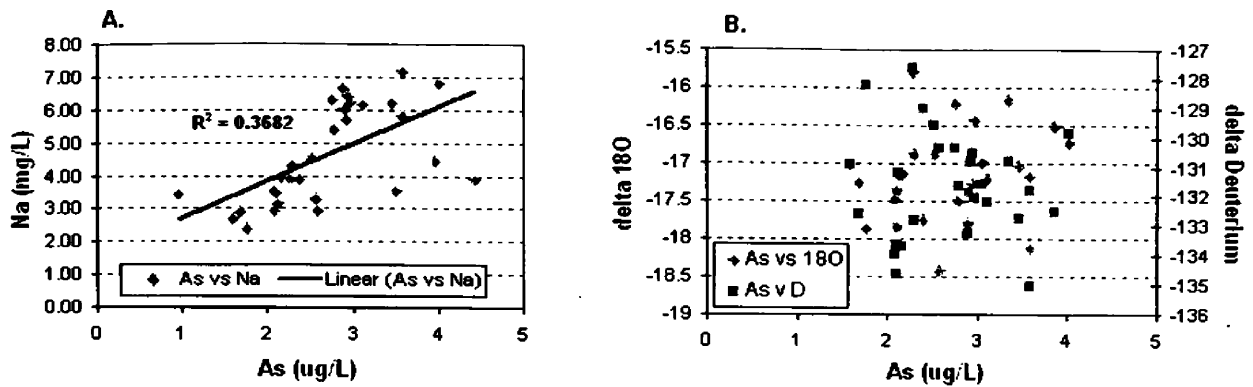


Figure 37. A. Correlation between arsenic and sodium in the Clark Fork River. The relationship suggests that arsenic behaves conservatively in the surface water. B. Lack of correlation between arsenic and both stable isotopes.

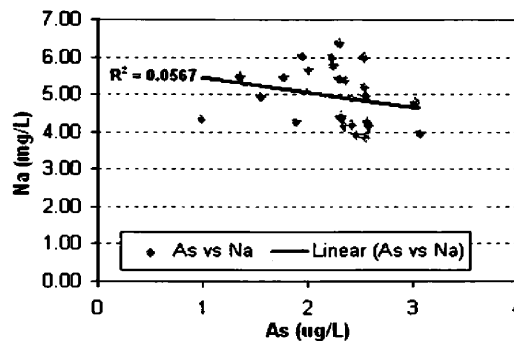


Figure 38. There is a lack of correlation between arsenic and Na, or any other conservative ion, in groundwater.  $R^2$  values for the correlation of the same two elements in surface water is 0.37, but in groundwater the correlation drops to only 0.06.

**Arsenic in the saturated river bed of a losing reach of the Clark Fork River.** Figure 39 is a schematic of the river and groundwater system with arsenic concentrations on one day of sampling for each of the four zones: surface water, the saturated zone beneath the river, shallow and deep groundwater. This zone beneath the river does not fit the normal definition of a hyporheic zone because there is no mixing between surface water and groundwater. Instead it is just a thin saturated zone that water infiltrates through before unsaturated flow begins. Tallman [2005] determined that the thickness of the saturated zone was about 5 ft at this site. Table 2 shows the relative concentrations of arsenic in this zone compared to the river and shallow groundwater, and Figure 40 illustrates the

range of concentrations compared to both surface water and shallow groundwater. During two of the seven sampling periods the saturated zone had higher concentrations of arsenic than the river, and this zone had higher arsenic concentrations than the shallow groundwater with only one exception.

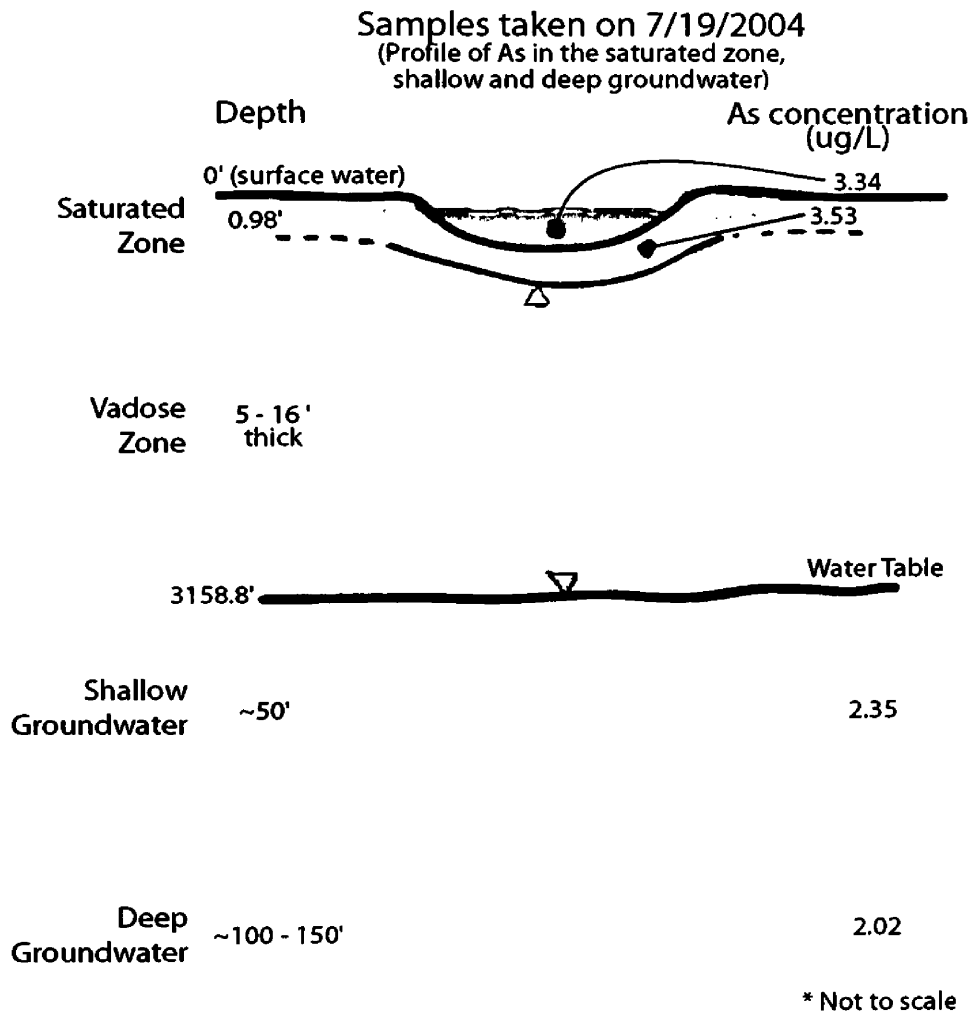


Figure 39. Schematic of the sampling profile. Depths are approximate and may change during different times of the year. Note that on this day of sampling the highest arsenic concentrations were found in the surface water and in the saturated zone.

Table 2. Arsenic concentrations in the Clark Fork and in the saturated zone.

Sample Date	Surface Water	Saturated Zone	Shallow Groundwater
7/19/04	3.34	3.53	1.74
3/4/05	2.95	1.08	1.17
3/29/05	3.11	3.10	1.69
4/6/05	2.92	2.52	1.66
5/17/05	2.58	1.55	1.91
6/7/05	4.43	4.27	2.00
6/16/05	3.96	4.85	1.52

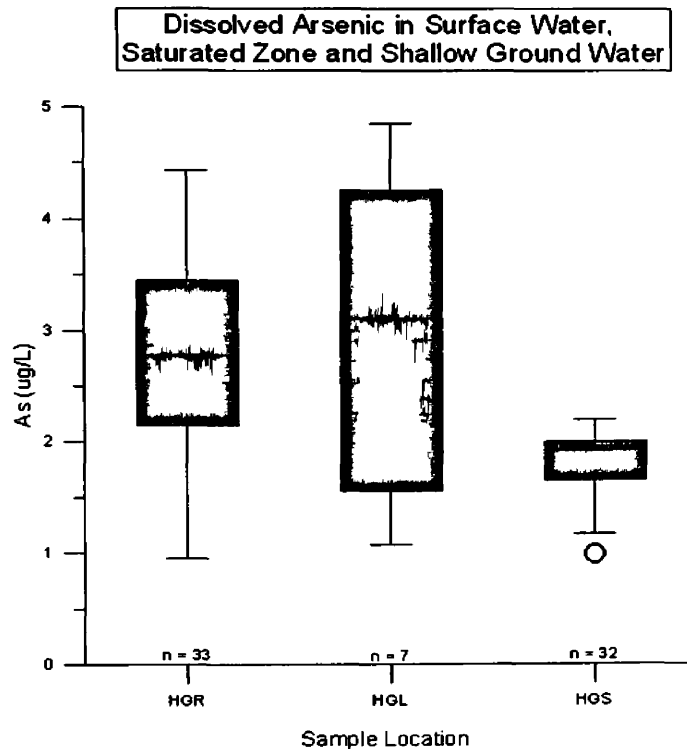


Figure 40. Range of arsenic values for surface water (HGR), the river bed saturated zone (HGL) and shallow groundwater (HGS). Arsenic concentrations are similar between the river and saturated zone, with slightly higher values occurring in the saturated zone. Shallow groundwater has lower arsenic concentrations than either the surface water or saturated zone.

**Controls on Arsenic Mobility.** The presence of dissolved Mn in some wells correlates with higher arsenic values. All but one sampling round showed the presence of Mn in the surface water, but very few groundwater samples contained detectable Mn. The presence of Mn in some of these wells may be attributed to metal contamination, or it may be

naturally occurring. In three wells, all of which are on the north side of the Clark Fork, the occurrence of measurable manganese correlated with higher arsenic concentrations (Figure 41). Other wells showed no correlation between dissolved manganese and arsenic concentrations.

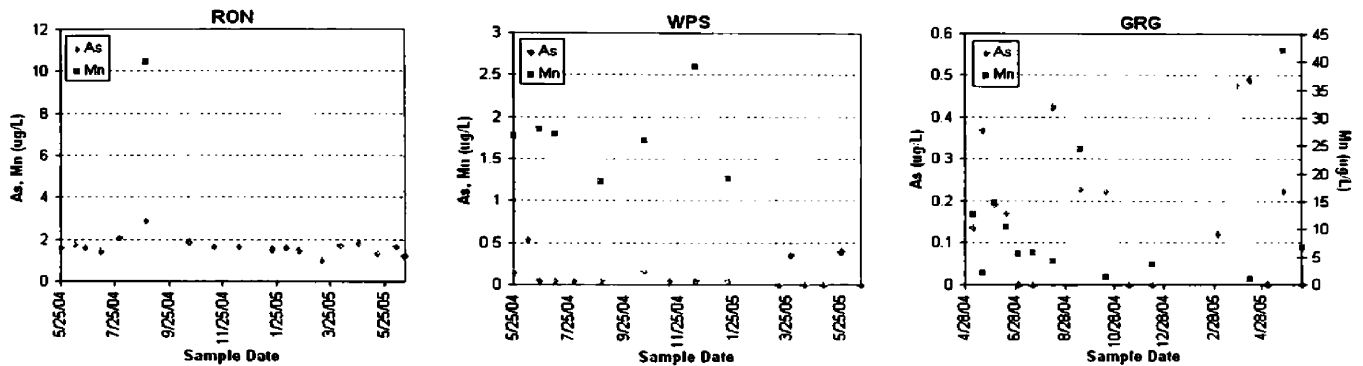


Figure 41. The effect of dissolved manganese on arsenic concentrations. These three wells show that higher concentrations of dissolved Mn generally agree with higher concentrations of dissolved arsenic.

## Discussion

### Contribution of surface water to groundwater

Caution should be taken when interpreting the isotopic results because the total amount of variation over the course of the study is generally within error bars. More frequent sampling might have resolved this problem. Individual data points do follow a similar trend from one sampling period to the next. The fact that there is not a significant difference between the river signal and the groundwater makes it virtually impossible to create a mixing model. These data suggest the groundwater in the Missoula Valley Aquifer is intimately connected to the Clark Fork River. The isotope data can be interpreted to show a lag between peaks in the river signal and in the signal of distal wells. While there are very few data points, overlapping error bars, and it is unclear if

results represent peaks of concentrations, the isotope data supports the general flow direction of groundwater to the southwest through the valley (Figure 42). A study conducted in the Spokane Valley/Rathdrum Prairie Aquifer in Idaho and Washington, which has very similar characteristics to the Missoula Valley Aquifer, found that groundwater closest to the river had similar isotopic signals to the surface water, while distal wells maintained an isotopic signal characteristic of regional groundwater [Caldwell and Bowers, 2003].

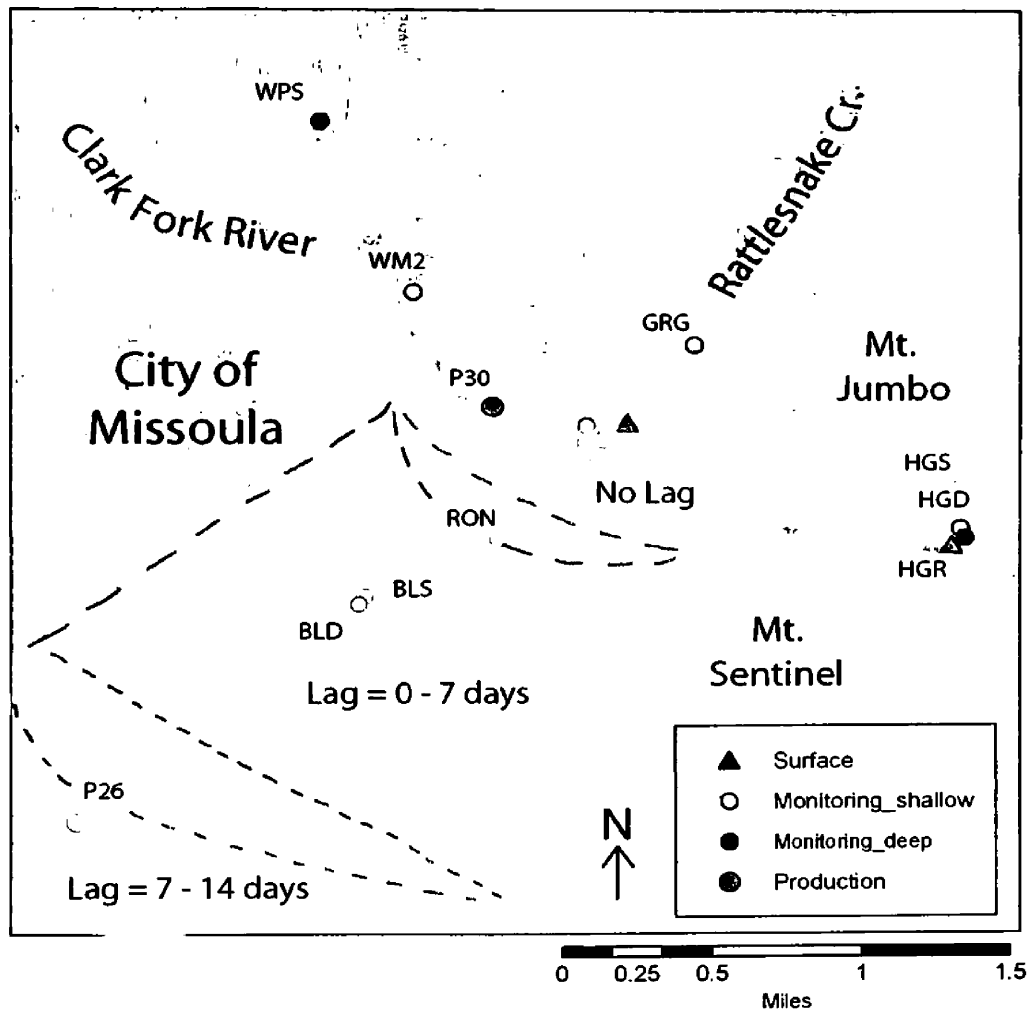


Figure 42. Estimate of the lag time for an isotopic signal to travel through the Missoula valley. Due to the limited number of wells along this flow line, and infrequent sampling, the windows are loosely constrained.

Groundwater velocities south of the river estimated from the sparse isotope data range from 750 to 5,000 ft/day. In comparison, computed groundwater velocities derived from aquifer characterization data (Tallman, 2005; an estimated effective porosity of 0.2, and hydraulic conductivity values of 15,000 ft/day and 20,000 ft/day) yield velocities that range from 330 ft/day to 440 ft/day in this portion of the aquifer. Generally, values are in the same order of magnitude supporting the identified rapid transport of groundwater in this portion of the aquifer.

Although a percentage of river water contribution to recharge can be grossly estimated, the overlapping error bars associated with the isotope data make quantitative separation of the sources of aquifer recharge general estimates only. Based solely on the isotopic data, approximately 65% of the variability in the chemical signature of shallow groundwater near the river can be accounted for by the chemistry of the river water, and for distal or deeper groundwater river water appears to account for ~30% to ~55% of the variability in the groundwater. It also appears as though underflow from Hellgate Canyon is influencing ~25% to ~75% of the variability observed in distal and deeper groundwater.

The similarity between the isotopic signal of the Clark Fork River and underflow from Hellgate Canyon is not surprising. Gestring [1994] studied the connection between the Clark Fork River and the Hellgate Valley Aquifer (HVA) between the Milltown Reservoir and the eastern boundary of this study area. His work suggested that over 50% of the recharge to this up-gradient portion of the Missoula aquifer is from leakage from the Blackfoot and Clark Fork Rivers, and seepage from the Milltown Reservoir.

Additional, though lesser contributions to recharge come as groundwater underflow from the Blackfoot/Bonner canyon and the up-gradient Clark Fork River valley alluvium. The Clark Fork River is reported to be a gaining flow in the reach just below the dam (approximately 600ft [Gestring, 1994]). Beyond that point, the river is reported to begin losing water to the aquifer as the water table becomes lower than the river stage. Generally, groundwater in the Milltown area is composed of Blackfoot River and Clark Fork River leakage and recharge from the Milltown reservoir. Thus, similarities in the water quality of underflow entering and flowing through Hellgate Canyon, and the general Clark Fork River chemistry are expected.

The use of conservative chemical elements to determine recharge percentages was also generally unsuccessful as all of the trends for conservative elements show that the river water is similar to the groundwater during baseflow periods. The shallow groundwater is also geochemically stable during the winter, and is most different from river water in the spring. In addition, the deep groundwater chemistry remains fairly stable in composition and concentrations of components. These observed trends suggest that a physical process, rather than a chemical one is influencing the concentrations of ions present in the shallow groundwater. It was recorded that higher concentrations of constituents in the groundwater correlate to times of a rising water table as well as increased river leakage. Based on this information, the observed increase in concentrations of ions in the shallow groundwater may be the result of the dissolution of vadose zone stored components. The stability of the ratios of the major ions (Figure 25) suggests the conceptual model that processes controlling chemical changes are dominated

by physical factors.

Several studies [Doerr, 1992; Deocampo and Ashley, 1999; Schellpeper and Harvey, 1999; Rosenberg et.al., 2001] have found component storage and release occurring in vadose zones. Wogsland [1988] investigated the impact of storm drain focused runoff on the geochemistry of the receiving groundwater in Missoula. She found an increase in the concentrations of cations as runoff water percolated through the vadose zone. During the spring and summer, she found that the vadose zone was a source of major cations and anions to the groundwater. She attributed these increases to the dissolution of feldspars and carbonates. Possibly a similar process is occurring as water passes through the vadose zone beneath the river and as the water table rises into the vadose zone in the spring. Isotopic data also supports a conceptual model that includes evaporation and temporary storage of constituents in the vadose zone. The surface water isotopic signal is somewhat lighter than the groundwater signal suggesting that there is some slight evaporation of the water before it gets to the groundwater

Distal and deeper groundwater does not reflect the same chemical changes as those observed in the shallow groundwater (Figure 43). Similar variations in the geochemistry of the groundwater were described by Caldwell and Bowers [2003] for the Spokane Valley Aquifer. The authors found that groundwater farther from the river had elevated and stable major-ion concentrations and the groundwater closest to the Spokane River had similar temporal trends as the surface water.



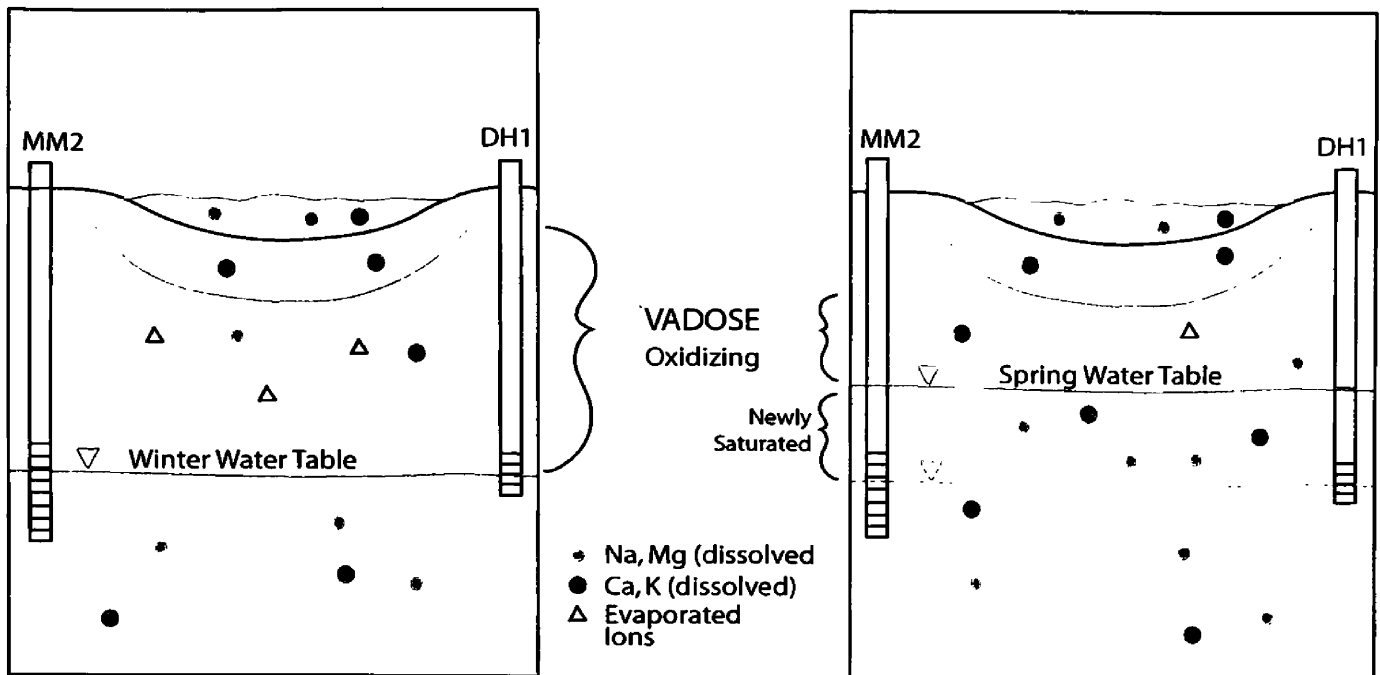


Figure 43. The concentration of Ca, Mg, Na and K by evaporation in the vadose zone during the winter (left). In the spring (right) the fluctuating water table dissolves and flushes out stored precipitates, thus increasing cation concentrations in the shallow monitoring wells near the river.

### **Arsenic Transport and Fate**

Comparing arsenic concentrations to those of conservative chemical ions in the Clark Fork River shows that arsenic behaves conservatively in the river. This is supported by the similar concentrations of arsenic measured at the river monitoring sites and the noted dilution affect of the low arsenic Rattlesnake discharge.

As arsenic infiltrates into the river bed the concentrations in the saturated zone are similar to those in the river (Figure 40; Table 2). It appears, however, that by the time the arsenic is transported to the shallow groundwater adjacent to the stream it has undergone processes that have reduced the concentration (Table 2). However, it should be noted that an exception to this generalization are the arsenic concentrations observed at well DH1 located within 50 ft of the channel on the north side of the river (Madison

area). This well demonstrates the similar concentrations of arsenic in both the shallow groundwater and the river (fall to spring). Concentrations in shallow wells located adjacent to the river track increases and decreases in river arsenic concentrations, though groundwater concentrations are typically lower (e.g. the Milltown drawdown event, Figure 31; fall to spring water quality trends).

There is also evidence that arsenic is not behaving totally conservatively as river and groundwater concentration do not seem to correlate during high surface water discharge and high water table periods observed in the late spring and early summer (Figure 40). It appears that either arsenic is being lost to the aquifer matrix or vadose zone matrix (temporally stored), and later released by changes in infiltration rates or changes in the extent of the saturated zone that correspond to a changing water table position (Figure 30). Each of these processes may be altering the geochemical conditions and enhancing release of arsenic into the water column. Lucy [1996] observed the release of arsenic and metals during a rising water table in Silver Bow Creek sediments, and it is generally accepted that arsenic is released in a reducing environment [e.g. *Moore et. al.*, 1988; *Nagorski and Moore*, 1999; *Nicholas et. al.*, 2003 and others]. Figure 44 presents a conceptual model for the behavior of arsenic in the Clark Fork River and associated underlying groundwater system. Preliminary arsenic speciation data suggests that most of this arsenic is arsenate, but a very small amount of arsenite was detected in one of the wells finished right at the water table (DH2) (Appendix 8).

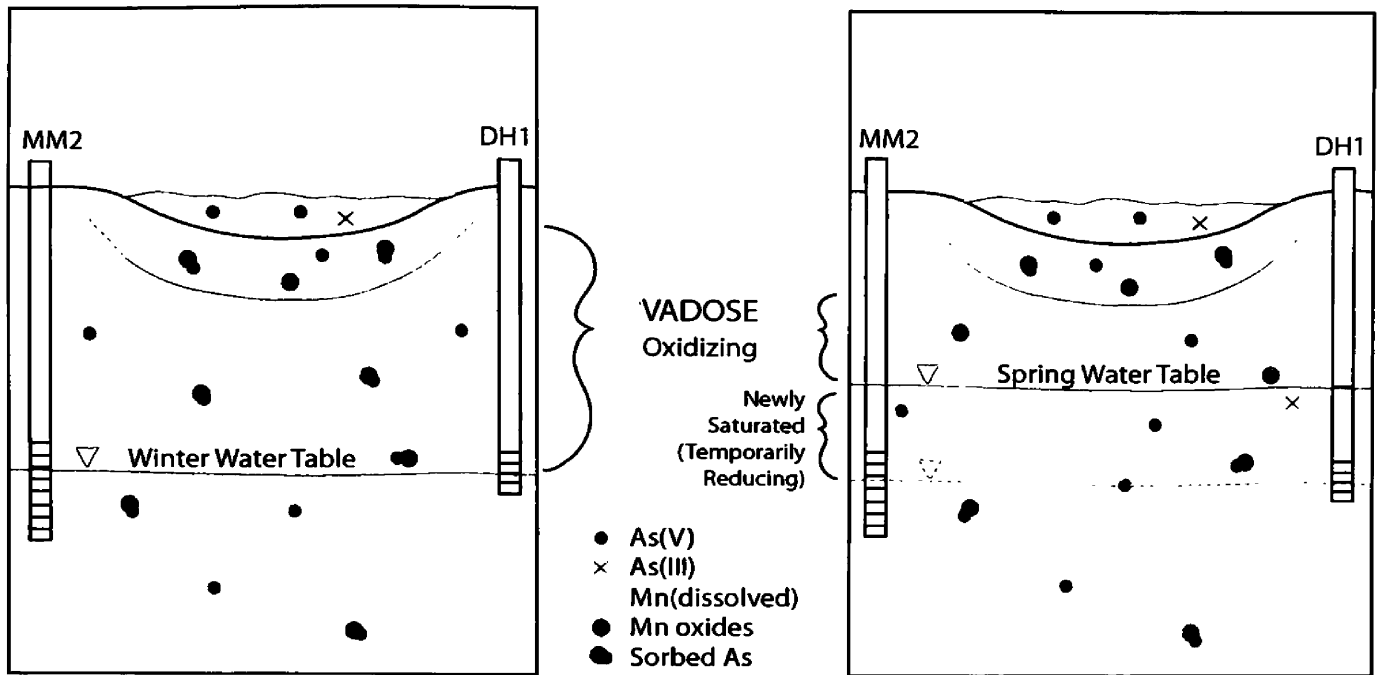


Figure 44. Conceptual model of the fate of As in the shallow groundwater beneath the Clark Fork River. The figure is not to scale. Arsenic is dissolved except where it is sorbed to Mn-oxides. In the winter (left) there is available As in the shallow groundwater, in the form of As(V). When there is a fluctuation in the water table, for example in the spring (right) when the table rises, there is a zone that is saturated (and could be temporarily reducing) and more As is released to the shallow groundwater.

The limited change in arsenic concentrations of shallow wells in Hellgate Canyon during the spring rise in the water table arsenic release may be related to the thinner vadose zone in Hellgate Canyon compared with the unsaturated zone in the Madison area (5 ft thick in Hellgate Canyon versus 17 ft thick in the Madison area). Though it is unknown how river leakage rates impact groundwater arsenic concentrations it should be noted that the stream leakage rates in Hellgate Canyon are roughly one-third the leakage in the Madison area [Tallman, 2005].

Over the course of the study, there are several times where deep groundwater (for example P32 in Figure 33) directly follows the observed trend in arsenic concentrations observed in the study reach of the Clark Fork River. At times when this occurs it appears as though the deep groundwater arsenic concentration increases or decreases by about

40% of the concentration of arsenic observed in the river. However, during some times, no direct connection between river concentrations variations and deep groundwater concentrations are observed. Possibly a clearer understanding of the processes controlling the chemistry of the deeper groundwater can be deciphered from a more complete and longer duration set of water quality data. Comparing the actual concentrations, rather than the percentage of increase or decrease, of arsenic in production well P32 and the river, it appears as though on average, the groundwater concentrations of arsenic are close to 70% of those found in the surface water. Shallow groundwater arsenic concentrations (from monitoring well MM2) average out to 92% of surface water arsenic concentrations. The fact that arsenic concentrations in groundwater are a significant percentage of the concentration found in the Clark Fork River has implications for the future.

The control on arsenic concentrations in the groundwater occurring north of the Clark Fork River in the Madison area appears to be associated with the recharging water of Rattlesnake Creek. The lowest arsenic concentrations in groundwater observed in the study site occur on the north side of the Clark Fork River (with the single exception of well DH1 located within 30 ft of the north bank of the Clark Fork River. The groundwater around Gregory Park never had concentrations above 0.5  $\mu\text{g/L}$ , which is similar to concentrations found in Rattlesnake Creek. Tallman (2005) reported groundwater flow data that show (within the available well network) this low As recharge water stays mostly north of the Clark Fork river.

## **Final Thoughts**

The implications of this research should be clear. The Clark Fork River is a direct and principal source of recharge to the Missoula aquifer as is the river influenced Hellgate Canyon underflow. Changes to the recharge chemistry will have impacts on shallow groundwater and production well water quality. If the chemistry of the river is altered by a short term event, and the constituent acts conservatively, river water will reach the shallow aquifer immediately underneath the river channel within hours to days. Production wells located nearest to the river channel generally receive a higher portion of water from the shallow river water recharge. As observations of the evaluation of arsenic in the river water during the Milltown drawdown showed, arsenic concentrations in near river production wells were directly impacted these variations. These observations suggest that if the dissolved arsenic concentration in the Clark Fork River ever became elevated to levels exceeding the 10 µg/L drinking water standard or near the allowable 24 hour limit during the Milltown Dam removal (340 µg/L), the concentration of near river groundwater production wells may increase by one to two thirds of the river concentration.

For those wells located further from the river channel the produced water would not show as great an impact from short duration degraded river recharge input. Produced water at these sites includes a larger portion of underflow from Hellgate Canyon. However, if river chemistry impacts are of a longer duration where recharging water upgradient of Hellgate Canyon alters the chemistry of the underflow in Hellgate Canyon, this condition combined with longer term alteration of the shallow groundwater being

directly recharged by the river will degrade even the large production wells located 1000's of feet from the river. If degradation of aquifer recharge continued for months it is possible most of the Missoula aquifer south of the river would show some degree of water quality impact. As noted previously, wells located north of the river in the Madison area would likely not be impacted by either short or long term events related to water quality changes in the Clark Fork River. These wells would be degraded if the water quality of Rattlesnake Creek was degraded, however.

## **Conclusions and Recommendations**

The results of this work need to be viewed as part one of a two part evaluation of the sources of water derived from water supply wells located in the eastern portion of the Missoula Valley. The work of Tallman (2005) provided the physical basis for the work described here and her research developed a water balance for the identical study area described here as well as a numerical model used to track and quantify water sources to producing wells. Tallman's (2005) work directly supports the conclusions of this study.

The principle conclusions of this study are that:

1. Recharge sources to the Missoula Valley Aquifer are poorly defined by a geochemical mixing model approach that uses either stable isotopes or conservative chemistry. The two primary sources of recharge the eastern portion of the aquifer are the Clark Fork River and underflow from Hellgate Canyon. It has been demonstrated that these two sources are very well connected (Tallman, 2005; Gestring, 1994).

2. Groundwater chemistry, especially shallow groundwater near the Clark Fork

River, follows the same temporal trends as the river for both isotopes and conservative components, suggesting that the river is well connected to shallow groundwater in the Madison area of Missoula.

3. Isotope data suggests rapid travel times for groundwater moving through the study area.

4. Deeper groundwater near the river and groundwater in more distal areas of the study area has more stable chemistry than the surface water or shallow groundwater near the river. It is similar to the chemistry of the underflow sampled in Hellgate Canyon.

5. Investigations of arsenic behavior and transport in this environment revealed that arsenic acts mostly conservatively in both surface water and groundwater.

6. Increases in shallow groundwater arsenic during non spring periods generally correlated with increases in the arsenic in the river.

7. Arsenic is stored either in the vadose zone or the aquifer during certain times of the year and is released during other times. Changing conditions in the vadose zone, including a change in redox environment, are the most likely mechanisms that release arsenic, but there are undoubtedly many processes that are occurring in this dynamic system.

8. Groundwater arsenic concentrations were always lower on the north side of the Clark Fork River. The dominate recharge source to the north side groundwater system is Rattlesnake Creek.

9. Short term changes in river chemistry are most likely to impact shallow groundwater underneath and adjacent to the river and production wells located adjacent

to the river.

10. Longer duration changes in the river chemistry are most likely to impact both the shallow groundwater and underflow in Hellgate Canyon. As a result, most production wells extracting water from the south side of the river portion of the Missoula aquifer will likely show water quality impacts.

In terms of future management of the aquifer including the production of drinking water for the city and country residents, additional investigations of the processes controlling the transport and fate of potential aquifer contaminants including arsenic are required. Unfortunately, the short duration and level of support for this work allowed for the establishment of preliminary relationships that are insufficient to predict the potentially wide range of variations in recharge supply and quality. Calibrated geochemical models that predict the behavior and transport a number of possible contaminants are needed. These models need to be process based so that the consequences of how changes in river chemistry impact produced water quality can be reasonably forecast. Collecting more speciation data for arsenic and other redox couples would be useful to define the processes controlling arsenic and metal transport, and storage in the vadose zone and in the shallow groundwater. These models should be based on the extensive literature base, and specific instrumentation, sampling, and monitoring of conditions in the river, vadose zone and groundwater.

Specific tools such as stable isotopes should be evaluated further by sampling water during transitional periods, obtaining rain and snow isotope data, and by using analytical techniques to refine errors.



Further analyses should take advantage of activities impacting groundwater and river water quality at the Milltown Reservoir site in preparation and during dam removal, and during stream restoration. Data collection during flow and water quality perturbations of the Clark Fork River should provide a data set useful in calibrating predictive models. Study efforts should be coordinated with activities scheduled at the Milltown site.

Finally, a sentinel monitoring program should be developed and maintained to document how changes in river chemistry and underflow impact produced water quality, especially during reservoir drawdown, dam removal and stream restoration operations at the upstream Milltown site. This work suggests that such a program will require frequent water quality sampling for anticipated constituents such as arsenic, both in the surface water and shallow groundwater. An action plan needs to be developed by the water purveyor that manages the risk of delivering impacted water to the Missoula residents.

## REFERENCES CITED

- Aggett, J. and M.R. Kriegman, 1988. The extent of formation of arsenic(III) in sediment interstitial waters and its release to hypolimnetic waters in Lake Ohakuri. *Water Research*, v. 22: 407-411.
- Armstrong, K.G., 1991. The distribution and occurrence of perchloroethylene in the Missoula Valley Aquifer. Master of Science, Department of Geology, The University of Montana, unpublished.
- Appelo, C.A.J., M.J.J. Van der Weiden, C. Tournassat and L. Charlet, 2002. Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environmental Science and Technology*, v. 36: 3096-3103.
- Bourg, A.C.M. and C. Bertin, 1993. biogeochemical processes during the infiltration of river water into an alluvial aquifer. *Environmental Science and Technology*, v. 27: 661-666.
- Bowers, C.L. and R.R. Caldwell, 2003. Surface-water/ground-water interaction of the Spokane River and the Spokane Valley/Rathdrum Prairie Aquifer, Idaho and Washington. *Water Resources Investigation Report 03-4239*.
- Brannon, J.M and W.H. Patrick, Jr., 1987. Fixation, transformation and mobilization of arsenic in sediments. *Environmental Science and Technology*, v. 21: 450-459.
- Brooks, R. and J.N. Moore, 1989. Sediment-water interactions in the metal-contaminated floodplain of the Clark Fork River, Montana, USA. *GeoJournal*, v. 19, no. 1: 27-36
- Caldwell, R.R. and C.L. Bowers, 2003. Surface-water/Ground-water interaction of the Spokane River and the Spokane Valley/Rathdrum Prairie Aquifer, Idaho and Washington. *USGS Water Resources Investigations Report 03-4239*.
- Castro, N.M. and G.M. Hornberger, 1991. Surface-subsurface water interactions in an alleviated mountain stream channel. *Water Resources Research*, v. 27, no. 7: 1613-1621.
- Chen, X.I and X. Chen, 2003. Stream water infiltration, bank storage, and storage zone changes due to stream-stage fluctuations. *Journal of Hydrology*, v. 280, no. 1-4: 246-264.
- Cherry, J.A., A.U. Shaikh, D.E. Tallman and R.V. Nicholson, 1979. Arsenic species as an indicator of redox conditions in groundwater. *Journal of Hydrology*, v. 43: 373-392.
- Clark, K.W., 1986. Interactions between the Clark Fork River and Missoula Aquifer, Missoula County, Montana. Master of Science, Department of Geology, The University of Montana, unpublished.
- Constanz, J., M.H. Cox and G.W. Su, 2003. Comparison of heat and bromide as groundwater tracers near streams. *Ground Water*, v. 41, no. 5: 647-656.
- Coplen, T.B. 1993. Uses of environmental isotopes. In *Regional ground-water quality*, edited by W.M. Alley, USGS, pp. 226-253, Van Nostrand Reinhold, New York.
- Coplen, T.B., A.L. Herczeg and C. Barnes, 1999. Isotope engineering – using stable isotopes of the water molecule to solve practical problems. In *Environmental Tracers in Subsurface Hydrology*, edited by P.G. Cook and A.L. Herczeg, pp. 79-110, Kluwer Academic Publishers, Boston.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science*, v. 133: 1702-1703.

- Cullen, W.R. and K.J. Reimer, 1989. Arsenic speciation in the environment. *Chemical Reviews*, v. 89: 713-764.
- Darling, W.G., D.J. Allen and H. Armannsson, 1990. Indirect detection of subsurface outflow from a Rift Valley lake. *Journal of Hydrology*, v. 113: 297-306.
- Datta, P.S., S.K. Bhattacharya and S.K. Tyagi, 1996.  $^{18}\text{O}$  studies on recharge of phreatic aquifers and groundwater flow-paths of mixing in the Delhi area. *Journal of Hydrology*, v. 176: 25-36.
- Deocampo, D.M. and G.M. Ashley, 1999. East African groundwater-fed wetlands; roles in the evolution of closed-basin brines. Abstracts with Programs, Geological Society of America Annual Meeting, v. 31, no. 7: 495.
- Derouane, J. and A. Dassargues, 1998. Delineation of groundwater protection zones based on tracer tests and transport modeling in alluvial sediments. *Environmental Geology*, v. 36, no. 1-2: 27-36.
- Deuel, L.E. and A.R. Swoboda, 1972. Arsenic solubility in a reduced environment. *Proceedings - Soil Science Society of America*, v. 36: 276-278.
- Doerr, G.B., 1992. Nitrate contamination of a shallow outwash aquifer in Tippecanoe County, Indiana. Master of Science, Purdue University, unpublished.
- Durand, P. and J.L. Juan Torres, 1996. Solute transfer in agricultural catchments: the interest and limits of mixing models. *Journal of Hydrology*, v. 181: 1-22.
- Eckert, P., S. Kamphausen, R. Irmischer and J. Gotthardt, 2002. The significance of transient flow conditions for well capture zone delineation of bank infiltration well fields. IAHS-AISH Publication, v. 277: 183-189.
- Environmental Biogeochemical Laboratory (EBL), Standard of Procedures. The University of Montana.
- Ferguson, J.F. and J. Gavis, 1972. A review of the arsenic cycle in natural waters. *Water Research*, v. 6: 1259-1274.
- Ferronsky, V.I. and V.A. Polyakov, 1982. *Environmental isotopes in the hydrosphere*. Wiley, Chinchester, 466 p. (Translated by S.V. Ferronsky)
- Genereux, D.P., H.F. Hemond and P.J. Mulholland, 1993. Use of radon-222 and calcium as tracers in a three-end-member mixing model for streamflow generation on the West Fork of Walker Branch Watershed. *Journal of Hydrology*, v. 142, no. 1-4: 167-211.
- Gestring, S.L., 1994. The interaction of the Clark Fork River and the Hellgate Valley Aquifer near Milltown, Montana. Master of Science, Department of Geology, The University of Montana, unpublished.
- Goldberg, S. 1986. Chemical modeling of arsenate adsorption on aluminum and iron oxide minerals. *Soil Science Society of America Journal*, v. 50: 1154-1157.
- Gulens, J., D.R. Champ and R.E. Jackson, 1979. Influence of redox environments on the mobility of arsenic in groundwater. In *Chemical modeling in aqueous systems; speciation, sorption, solubility, and kinetics*, edited by E.A. Jenne, pp. 81-95. American Chemical Society, Washington D.C.
- Herberger, T., A. Mechlinski, B. Fanck, A. Knappe, G. Massmann, A. Pekdeger, and B. Fritz, 2004. Field studies on the fate and transport of pharmaceuticals residues in bank filtration. *Ground Water Monitoring and Remediation*, v. 24, no. 2: 70-77.

- Hoeg, S., S. Uhlenbrook and C. Leibundgut, 2000. Hydrograph separation in a mountainous catchment – combining hydrochemical and isotopic tracers. *Hydrological Processes*, v. 14, no. 7: 1199-1216.
- Hooper, R.P. and C.A. Shoemaker, 1986. A comparison of chemical and isotopic hydrograph separation. *Water Resources Research*, v. 22. no. 10: 1444-1454.
- Huth, A. K., A. Leydecker, J.O. Sickman and R.C. Baless, 2004. A two-component hydrograph separation for three high-elevation catchments in the Sierra Nevada, California. *Hydrological Processes*, v. 18, no. 9: 1721-1733.
- Iacovides, I.S., 1988. Evaluation of the operation of Yermasoyia surface and groundwater reservoirs. IAEA Report: IAEA-R-3976-F, Vienna, 95 p.
- Joerin, C., K.J. Beven, I. Iorgulescu and A. Musy, 2002. Uncertainty in hydrograph separations based on geochemical mixing models. *Journal of Hydrology*, v. 255, no. 1-4: 90-106.
- Katsuyama, M., N. Ohte and S. Kobashi, 2001. A three-component end-member analysis of streamwater hydrochemistry in a small Japanese forested headwater catchment. *Hydrological Processes*, v. 15, no 2: 249-260.
- Kay, R.T., E.R. Bayless and R.A. Solak, 2002. Use of isotopes to identify sources of ground water, estimate ground-water-flow-rates, and assess aquifer vulnerability in the Calumet Region of Northwestern Indiana and Northeastern Illinois, USGS Water-Resources Investigation Report 02-4213.
- Kelly, B.P., 2002. Ground-water flow simulation and chemical and isotopic mixing equation analysis to determine source contributions to the Missouri River Alluvial Aquifer in the vicinity of the Independence, Missouri, Well Field. USGS Water Resources Investigations Report 02-4208.
- Kendall, C. and T.B. Coplen, 2001. Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrological Processes*, v. 15: 1363-1393.
- Kendall, K.A., J.B. Shanley and J.J. McDonnell, 1999. A hydrometric and geochemical approach to test the transmissivity feedback hypothesis during snowmelt. *Journal of Hydrology*, v. 219: 188-205.
- Kennedy, V.C., C. Kendall, G.W. Zellweger, T.A. Wyerman and R.J. Avanzino, 1986. Determination of the components of stormflow using water chemistry and environmental isotopes, Mattole River basin, California. *Journal of Hydrology*, v. 84: 107-140.
- Korte, N.E. and Q. Fernando, 1991. A review of arsenic (III) in groundwater. *Critical Reviews in Environmental Control*, v. 21, no. 1: 1-39.
- Krabbenhoft, D.P., C.J. Bowser, M.P. Anderson, and J.W. Valley, 1990. Estimating ground-water exchange with lakes, 1, The stable isotope mass balance method. *Water Resources Research*, vol. 26: 2445-2453.
- LaFave, J.I., 2002. Tracing ground-water flow in the Missoula Valley Aquifer, southwest Montana. Montana Bureau of Mines and Geology, Ground-Water Assessment Open-file Report 17.
- Lucy, J.K., 1996. Hydrologic and geochemical controls on metals partitioning in the vadose zone and shallow groundwater zone of a highly-contaminated floodplain near Butte, Montana. Master of Science, Department of Geology, The University of Montana, unpublished.
- Manning, B.A. and S. Goldberg, 1997. Adsorption and stability of arsenic(III) at the clay mineral – water interface. *Environmental Science and Technology*, v. 31, no. 7: 2005-2011.

- Masscheleyn, P.H., R.D. Delaune and W.H. Patrick, Jr., 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environmental Science and Technology*, v. 25, no. 8: 1414-1419.
- Maulé, C.P., D.S. Chanasyk and K. Muehlenbachs, 1994. Isotopic determination of snow-water contribution to soil water and groundwater. *Journal of Hydrology*, v. 155: 73-91.
- Mayo, A.L., P.J. Nielsen, M. Loucks and W.H. Brimhall, 1992. The use of solute and isotopic chemistry to identify flow patterns and factors which limit acid mine drainage in the Wasatch Range, Utah. *Ground Water*, v. 30, no. 2: 243-249.
- McCarthy, K. A., W.D. McFarland, J.M. Wilkinson, and L.D. White, 1992. An investigation of the dynamic relationship between groundwater and a river using deuterium and oxygen-18. *Journal of Hydrology*, v. 135: 1-12.
- Mickey, J.W., 1998. The Effects of Discharge Variation on Dissolved Element Concentrations through Milltown Reservoir, Montana. Master of Science, Department of Geology, The University of Montana, unpublished.
- Miller, R.D., 1991. Numerical Flow Model of the Missoula Aquifer: Interpretation of Aquifer Properties and River Interaction. Master of Science, Department of Geology, The University of Montana, unpublished.
- Mok, W.M., J.A. Riley and C.M. Wai, 1988. Arsenic speciation and quality of groundwater in a lead-zinc mine, Idaho. *Water Resources*, v. 22, no. 6: 769-774.
- Moore, J.N., W.H. Fickling and C. Johns, 1988. Partitioning of arsenic and metals in reducing sulfidic sediments. *Environmental Science and Technology*, v. 22, no. 4: 432-437.
- Moore, J.N. and S.N. Luoma, 1990. Hazardous wastes from large-scale metal extraction, A case study. *Environmental Science and Technology*, v. 24, no.9: 1278-1285.
- Moore, J.N. and W.W. Woessner, 2003. Arsenic contamination in the water supply of Milltown, Montana, In: *Arsenic in Groundwater, Geochemistry and Occurrence*, edited by A.H. Welch. Kluwer Academic Publishers, Boston.
- Morgan, W.F., 1986. Geological interpretation of the alluvial aquifer, Missoula basin, Montana. Senior thesis, The University of Montana.
- Muir, K.S. and T.B. Coplen, 1981. Tracing ground-water movement by using stable isotopes of oxygen and hydrogen, Upper Pentencia Creek alluvial fan, Santa Clara Valley, California. USGS Water Supply Paper 2075.
- Nagorski, S.A. and J.N. Moore, 1999. Arsenic mobilization in the hyporheic zone of a contaminated stream. *Water Resources Research*, v. 35, no. 11: 3441-3450.
- Nicholas, D.R., S. Ramamoorthy, V. Palace, S. Spring, J.N. Moore and R.F. Rosenzweig, 2003. Biogeochemical transformations of arsenic in circumneutral freshwater sediments. *Biodegradation*, v. 14: 123-137.
- NRIS, accessed July, 2005. <http://nrisc.state.mt.us>
- Nyquist, D.L., 2001. A depth to bedrock model of the Hellgate Canyon and Bandman Flats area, East Missoula, Montana using constrained inversion of gravity data. Master of Science, Department of Geology, The University of Montana, unpublished.

- Obradovic, M.M. and M.G. Sklash, 1987. An isotopic and geochemical study of seasonal snowmelt runoff in the Apex River Watershed. In *Seasonal Snowcovers: Physics, Chemistry, Hydrology*, edited by H.G. Jones and W.J. Orville-Thomas, pp. 643-659. D. Reidel Publishing Company.
- Ogunkoya, O.O. and A. Jenkins, 1993. Analysis of storm hydrograph and flow pathways using a three-component hydrograph separation model. *Journal of Hydrology*, v. 142, no 1-4: 71-88.
- Oremaland, R.S. and J.F. Stolz, 2003. The ecology of arsenic. *Science*, v. 300: 939-944.
- Payne, B.R., 1981. Practical applications of stable isotopes to hydrological problems. In: J.R. Gat and R. Gonfiantini (Editors), *Stable Isotope Hydrology, Deuterium and Oxygen-18 in the Water Cycle*. IAEA, Vienna, Tech. Report Series 210: 303-334.
- Payne, B.R., 1983. Interaction of surface water with groundwater. In: *Guidebook on Nuclear Techniques in Hydrology*. IAEA, Vienna, Tech. Report Series 91: 319-326.
- Peterson, M.L. and R. Carpenter, 1986. Arsenic distributions in porewaters and sediments of Puget Sound, Lake Washington, the Washington coast and Saanich Inlet, B.C. *Geochimica et Cosmochimica Acta*, v. 50: 353-369.
- Rosenberg, N.D., G.E. Gdowski and K.G. Kevin, 2001. Evaporative chemical evolution of natural waters at Yucca Mountain, Nevada. *Applied Geochemistry*, v. 16, no. 9-10: 1231-1240.
- Schellpeper, J.J. and F.E. Edwin, 1999. Evaporative enrichment of alluvial groundwaters and regional characterization of ground and surface waters in the Republican River basin of Nebraska using chemistry and isotopes. Abstracts with Programs, Geological Society of America Annual Meeting, v. 31, no. 7: 350-351.
- Schifflett, J.A., 2002. The Effect of Discharge Variation on Suspended Sediment and Particulate Contaminant Transport Through Milltown Reservoir, Montana. Master of Science, Department of Geology, The University of Montana, unpublished.
- Shanley, J.B., C. Kendall, T.E. Smith, D.M. Wolock and J.J. McDonnell, 2002. Controls on old and new water contributions to stream flow at some nested catchments in Vermont, USA. *Hydrological Processes*, v. 16, no. 3: 589-609.
- Sheets, R.A., R.A. Darner and B.L. Whitteberry, 2002. Lag times of bank infiltration at a well field, Cincinnati, Ohio, USA. *Journal of Hydrology*, v. 266, no. 3-4: 162-174.
- Sklash, M.G., 1990. Environmental isotope studies of storm and snowmelt runoff generation. In: *Process studies in hillslope hydrology*, edited by M.G. Anderson and T.P. Burt, pp 401-435. J. Wiley and Sons.
- Sklash, M.G. and R.N. Farvolden, 1979. The role of groundwater in storm runoff. *Journal of Hydrology*, v. 43: 45-65.
- Sklash, M.G. and R.N. Farvolden, 1982. The use of environmental isotopes in the study of high-runoff episodes in streams. In *Isotope studies of hydrologic processes; selected papers from a symposium*, edited by E.C. Perry and C.W. Montgomery, pp. 65-73, Northern Illinois Press, De Kalb, IL.
- Solley, W.B., R.R. Pierce and H.A. Pearlman, 1993. Estimated use of water in the United States in 1990, U.S. Geological Survey Circular 1081, 76 pp.

- Solley, W.B., R.R. Pierce and H.A. Pearlman, 1998. Estimated use of water in the United States in 1995, U.S. Geological Survey Circular 1200, 71 pp.
- Stichler, W. and H. Moser, 1977. An example of exchange between lake and groundwater. In: Isotopes in Lake Studies, Proc. Advisory Group Meeting, 29 August – 2 September 1977, Vienna, IAEA Vienna: 115-119.
- Swartz, C.H., N.K. Blute, B. Badruzzman, A. Ali, D. Brabander, J. Jay, J. Besancon, S. Islam, H.F. Hemond, and C.F. Harvey. Mobility of arsenic in a Bangladesh aquifer; inferences from geochemical profiles, leaching data, and mineralogical characterization. *Geochimica et Cosmochimica Acta*, vol.68, no.22: 4539-4557.
- Tallman, A.T. 2005. Identifying the factors controlling the sources and quantities of water captured by Municipal supply wells in the highly conductive Missoula Aquifer, Western Montana. Master of Science, Department of Geology, The University of Montana, unpublished.
- Taylor, C.B., L.J. Brown, J.J. Cunliffe and P.W. Davidson, 1992. Environmental tritium and  $^{18}\text{O}$  applied in a hydrological study of the Wairau Plain and its contributing mountain catchments, Marlborough, New Zealand. *Journal of Hydrology*, v. 138: 269-319.
- Taylor, S., X. Feng, M. Williams and J. McNamara, 2002. How isotope fractionation of snowmelt affects hydrograph separation. *Hydrological Processes*, v. 16, no. 18: 3683-3690.
- Udaloy, A. 1988. Arsenic mobilization in response to draining and filling of the reservoir at Milltown, Montana. Master of Science, Department of Geology, The University of Montana, unpublished.
- USGS, 2001. Accessed July, 2005. [http://water.usgs.gov/nawqa/trace/pubs/geo\\_v46n11/fig3.pdf](http://water.usgs.gov/nawqa/trace/pubs/geo_v46n11/fig3.pdf). Extrapolated arsenic values for the United States.
- USGS, 2004. Accessed July, 2005. <http://waterdata.usgs.gov/mt/nwis/uv?12340500>
- Vitvar, T. and W. Balderer, 1997. Estimation of mean water residence times and runoff generation by  $^{18}\text{O}$  measurements in a Pre-Alpine catchment (Rietholzback, Eastern Switzerland). *Applied Geochemistry*, v. 12: 787-796.
- Welch, A.H., D.B. Westjohn, D.R. Helsel and R.B. Wanty, 2000. Arsenic in groundwater of the United States: Occurrence and geochemistry. *Ground Water*, v. 38, no. 4: 589-604.
- Woessner, W.W., 1988. Missoula Valley Aquifer Study; Hydrogeology of the eastern portion of the Missoula aquifer, Missoula County, Montana. Water Development Bureau, MT Department of Natural Resources and Conservation, Helena, MT. Vol. 1 and Vol. 2.
- Wogslund, K.L., 1988. The effect of urban storm water injection by class V wells on the Missoula Aquifer, Missoula, Montana. Master of Science, Department of Geology, The University of Montana, unpublished.

## **Appendices**



## Appendix 1 – Arsenic in the United States

Concentrations of arsenic in groundwater vary greatly by region but are typically in the  $\mu\text{g/L}$  range [Cullen and Reimer, 1989; USGS, 2000] (Figure A1). Arsenic can exist in several oxidation states: +5, +3, 0 and -3 [Nicholas *et al.*, 2003], although the most common are +5 (arsenate) and +3 (arsenite). Several studies [Gulens *et al.*, 1979; Manning and Goldberg, 1997; Oremland and Stoltz, 2003 and others] have shown that arsenite is more mobile in certain environments and consequently more toxic than arsenate. Arsenic is a concern to human health because it can be highly carcinogenic, particularly when it is in the reduced form of As (III) and when it is in drinking water [Ferguson and Gavis, 1972; Mok *et al.*, 1988; Korte and Fernando, 1991].

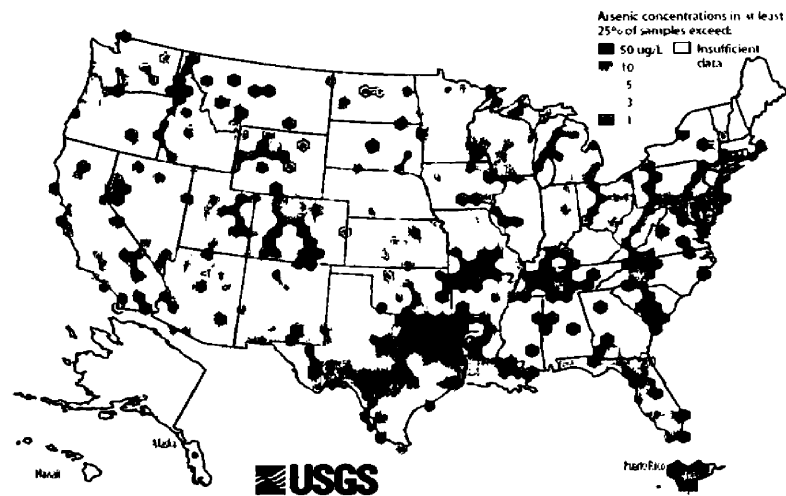


Figure A1. Extrapolated arsenic values for the United States (USGS, 2001)

Many sources can contribute to arsenic appearing in groundwater including mining wastes, geothermal sources, igneous and sedimentary rock and industrial or agricultural products [Welch, 2000; Oremland and Stoltz, 2003].

## Appendix 2 – Sampling and Lab Procedures



A1. Pumping set-up at the nested wells in Hellgate Canyon (HGD and HGS).



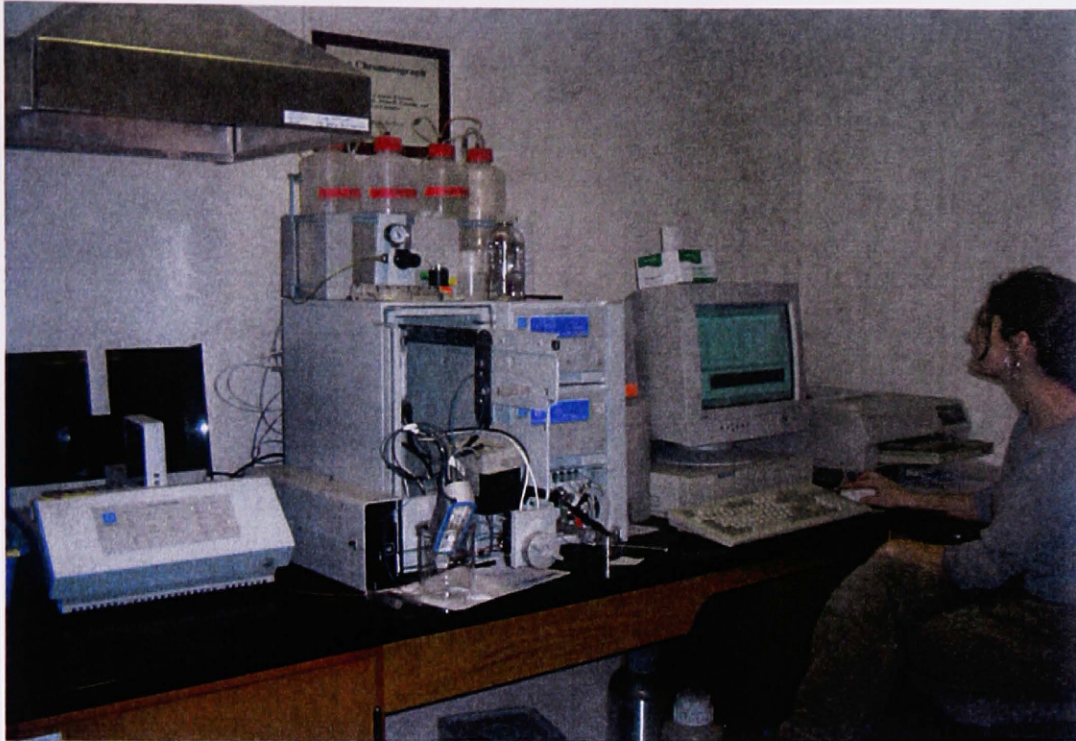
A2. Measuring pH, temperature and conductivity at a well site. The red bucket was filled from water in the pump rather than from a bailer.



A3. Measuring pH, temperature and conductivity in the Clark Fork River.



A4. Ultra clean sampling of one of Mountain Water Co.'s production wells. Robyn (left) is "clean hands" and Amelia (right) is "dirty hands."



A5. Amelia monitoring the process of samples being analyzed on the IC.

## **Appendix 3 – QA/QC**

### QUALITY CONTROL FOR ICP-MS:

With only a few discrepancies, the QA/QC for cations and metals was as follows:

Quantitation was based on a minimum 3 point curve and correlation values were >0.998.

Isotopes for reporting were monitored and chosen based on their QC performance.

Calibration was checked every 10 analyses using a mid point standard (CCV) and an additional varied concentration standard from a separate source (IPC). All recoveries for these standards were with 10%.

Analytical blanks were monitored for contamination and found to contain no elements of interest above the detection limit.

Internal standard recoveries were monitored and used in calculating reported values.

Matrix spike recoveries were monitored and reported for at least every twenty samples analyzed. All spike recoveries were within 75-125% of known values.

Duplicate analyses are reported for at least every twenty samples analyzed. All duplicate recoveries are within 75-125% relative concentration.

### QUALITY CONTROL FOR IC:

According to EPA method 300.0, external standards were run every 10 samples, and were required to pass within 10% of the nominal concentration.

A suite of calibration standards were run twice each session, the first time for calibration and the second for verification.

Spikes and duplicates were run every 10 samples.

At least three lab blanks were run during each session to check for contamination.

### QUALITY CONTROL FOR ISOTOPES:

Pyrolysis Elemental Analysis-Isotope Ratio Mass Spectrometry (pyrolysis-EA-IRMS).

Delta+XL system

$\delta^2\text{H}$  and  $\delta^{18}\text{O}$  value are measured using pyrolysis-EA-IRMS. This method utilizes a ThermoFinnigan MAT high temperature elemental analyzer (TC/EA) and ConFlo III interface with a Delta+XL Mass Spectrometer. The pyrolysis reactor consists of a

reaction tube packed with glassy carbon/graphite and silver wool. Other TC/EA conditions are listed in Table 1.

Table A1. TC/EA Conditions

Pyrolysis tube Temp	1450°C
He Flow rate	120 mL/min
GC column	3 m 5Å mol sieve
GC oven temp	75°C

**Water/Liquid Analysis:**

0.2 uL of water sample are injected into the TC/EA with a CTC Analytics A200SE liquid autosampler. The sample is pyrolyzed into H<sub>2</sub> and CO gases then separated chromatographically. These gases are then transferred to the IRMS, where the isotopes are measured.  $\delta^2\text{H}_{\text{V-SMOW}}$  and  $\delta^{18}\text{O}_{\text{V-SMOW}}$  values are reported in reference to international isotope standards.

Typical Quality Control scheme involves analyzing laboratory working standards every seven replicate samples. Each sequence batch is calibrated to NIST standards to confirm quality assurance.

**Laboratory Working Standards**

DMW-16May2002: Duckering building Millipore Water collected on 16May2002.

NIST standards: REF 8535 (V-SMOW), 8536 (GISP), & 8537 (SLAP)

**Appendix 4**  
**Raw Data for all Study Sites**

P26

Date	Discharge (cfs)	Field Chemistry			Mass Spec ICP (ug/L)													IC (mg/L)				ISO							
		pH	Conductivity (mS)	Temp (deg C)	Alkalinity (mg CaCO <sub>3</sub> /L)	As (10)	Ca (100)	Cd (1.0)	Co (1.0)	Cr (1.0)	Cu (1.0)	Fe (50.0)	K (100)	Mg (100)	Mn (1.0)	Na (100)	Pb (1.0)	Zn (1.0)	F (0.06)	Cl (1.0)	NO <sub>2</sub> (0.06)	SO <sub>4</sub> (1.0)	NO <sub>3</sub> (0.3)	O <sup>18</sup>	H <sup>2</sup>				
4/28	3,890	7.54				1.08	48018.50					1666.00	12901.50		6213.60		9.48										-16.96	-129.86	
5/5	5,260	7.74		10.9	154	1.11	48152.70					1633.30	12924.40		6570.40		6.48	0.15	5.7		20.8	0.57					-16.41	-129.24	
5/14	4,069																												
5/19	3,740	7.75	0.448	10		1.24	45465.90			1.32		1580.00	13271.00		6304.00		23.27										-16.69	-131.07	
5/25	4,930																												
6/2	5,080	7.42	0.459	10.6		1.09	45831.00		2.56	2.83		1545.00	12710.00		6749.00		28.68										-16.53	-131.96	
6/9	5,160																												
6/16	4,270	7.658	0.461	10.6	151	0.76	34066.78					1112.43	9040.72		4461.56		21.81	0.14	6.03		21.23	0.59				-17.63	-128.09		
6/22	3,270																												
6/30	3,200	7.51	0.468	10.1		0.99	49314.61			1.30		1622.63	12653.09		6184.83		24.08										-17.08	-132.82	
7/9	2,200																												
7/19	1,690	7.45	0.467	10.6	137	1.14	48817.36					1866.40	13847.53		6892.59		23.33	0.13	6.6		20.4	0.67				-16.48	-131.76		
7/30	1,210																												
8/13	958	7.46	0.355	10.1		1.01	50882.31			1.38		1606.60	13928.69		6899.14		42.70										-16.72	-130.33	
8/30	1,220																												
9/16	1,395	7.31	0.328	10.9	155	0.47	38469.45			1.06		1241.72	10060.64		4896.05		17.25	0.13	6.93		18.58	0.68				-17.22	-132.18		
10/17	1,430	7.34	0.27	9.9	136	1.16	47233.11					1541.24	11843.20		6030.60		23.24	0.13	6.59		17.95	0.63				-17.17	-131.06		
11/14	1,305	7.5	0.317	9.6	141	0.92	45682.67			4.94		1450.31	11669.37		5793.63		18.53	0.13	5.85		17.89	0.61				-16.52	-131.72		
12/13	1,340	7.4		8.8		0.98	45356.06			4.19		1491.26	12725.61		6193.68		14.39										-18.21	-135.31	
1/19	2,525	7.09	0.347	9.8	134	1.17	45187.21			3.33		1497.52	12436.31		6104.39		20.13	0.13	5.31		17.88	0.54				-18	-134.63		
2/4	1,380	8.12	0.342	9.8	125	0.76	48184.05			3.13		1630.22	11728.13		5860.22		18.37	0.13	5.20		18.26	0.53				-17.58	-132.42		
2/18	1,090	7.27	0.282	9.8		0.96	46884.01			2.78		1469.67	12270.27		6129.11		17.68										-17.29	-130.92	
3/4	1,130	7.66	0.346	9.9	133	0.91	42206.63			2.19		1479.32	11480.81		5819.37		28.40	0.14	5.17		18.56	0.50				-17.06	-127.46		
3/16	1,320	7.69	0.348	9.8	131	0.71	41580.76			5.93		1394.18	11301.83		5510.48		16.42	0.14	5.16		18.67	0.49				-17.25	-131.4		
3/29	1,600																												
4/6	1,660	7.43	0.344	9.9		1.24	45281.78					1600.90	12215.76		6402.94		20.59										-15.56	-126.93	
4/14	2,240																												
4/26	3,450	7.5	0.314	9.9	142	1.29	46576.98			2.34		1537.38	12056.29		6741.49		20.26	0.15	5.18		18.86	0.44				-15.6	-128.05		
5/5	3,000																												
5/17	8,330	7.55	0.352	9.8		1.15	44294.93			1.24	2.16	1509.70	12204.34		6167.30		15.92										-16.85	-132.32	
5/25	7,150																												
6/7	8,980	7.28	0.346	9.9		1.11	45276.13			1.07	1.86	1536.91	12376.37		6454.44		15.92	0.14	5.41	0.00	19.05	0.44				-16.59	-132.84		
6/16	5,950	7.52	0.315	10.1		0.62	46435.39					1395.31	12642.88		6498.32		11.69										-16.69	-133.63	

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WQM

Date	Discharge (cfs)	Depth to water	Field Chemistry			Alkalinity (mg CaCO <sub>3</sub> /L)	Mass Spec ICP (ug/L)										IC (mg/L)					ISO							
			pH	Conductivity (µS)	Temp (deg C)		As (10)	Ca (100)	Cd (1.0)	Co (1.0)	Cr (1.0)	Cu (1.0)	Fe (50.0)	K (100)	Mg (100)	Mn (1.0)	Na (100)	Pb (1.0)	Zn (1.0)	F (0.06)	Cl (1.0)	NO <sub>2</sub> (0.06)	SO <sub>4</sub> (1.0)	NO <sub>3</sub> (0.3)	O <sup>18</sup>	H <sup>2</sup>			
4/28	3,890																												
5/5	5,260																												
5/14	4,069	33.17	7.27	0.43	9.4	140	1.88	46955.00																					
5/19	3,740																												
5/25	4,930	31.95	7.17	0.433	9.1		1.96	46261.00																					
6/2	5,080																												
6/9	5,160	29.96	7.69	0.42	10.5	142	2.02	45716.71																					
6/16	4,270																												
6/22	3,270		7.22	0.413	9.5		1.51	43769.94																					
6/30	3,200																												
7/9	2,200		7.26	0.41	9.4	133	1.91	46200.03																					
7/19	1,690																												
7/30	1,210		7.23	0.419	9.7		1.84	48270.96																					
8/13	958																												
8/30	1,220		7.47	0.305	10.8	152	2.11	44358.68																					

## DH1

Date	Discharge (cfs)	Field Chemistry			Alkalinity (mg CaCO <sub>3</sub> /L)	Mass Spec ICP (ug/L)												IC (mg/L)					ISO					
		pH	Conductivity us	Temp (deg C)		As (.10)	Ca (100)	Cd (1.0)	Co (1.0)	Cr (1.0)	Cu (1.0)	Fe (50.0)	K (100)	Mg (100)	Mn (1.0)	Na (100)	Pb (1.0)	Zn (1.0)	F (0.06)	Cl (1.0)	NO <sub>2</sub> (0.06)	SO <sub>4</sub> (1.0)	NO <sub>3</sub> (0.3)	O <sup>18</sup>	H <sup>2</sup>			
9/16	1,395																											
10/17	1,430	7.18	0.285	12.3	122	3.36	36253.21			1.33	1525.13	10465.50		8083.02		45.29		0.10	6.21	0.00	18.34	0.82				-17.1	-130.45	
11/14	1,305																											
12/13	1,340	7.23	0.324	10.9		2.86	40246.44			1.14	1408.08	12047.84		6308.31		29.30										-17.89	-133.1	
1/19	2,525	7.23	0.236	9.9	81	2.68	27486.79	1.42		3.05	1183.60	8138.84		7347.70		24.46		nd	7.94	0.00	12.49	0.46				-17.51	-130.77	
2/4	1,380	7.85	0.302	9.6	106	2.64	35789.43				1160.08	10079.90		5752.52		35.13		nd	5.40	0.00	18.53	0.67				-17.11	-130.44	
2/18	1,030	7.24	0.329	7.3		2.43	37264.53				1159.47	10438.11		5862.52		15.79											-16.35	-130.69
3/4	1,130																											
3/16	1,320																											
3/29	1,600	7.92	0.261	8		2.96	38257.38				1352.48	10720.72		6209.70		14.15											-16.95	-129.81
4/6	1,660																											
4/14	2,240	7.29	0.31	8.2	120	2.89	35475.40			1.73	1221.34	9685.36		6103.11		16.22		0.09	8.86		18.98	0.49				-16.86	-130.5	
4/26	3,450																											
5/5	3,000	6.93	0.217	8.5		1.53	31685.33			1.10	1088.16	8360.69		7906.84		40.11											-17.29	-129.49
5/17	8,330																											
5/25	7,150	6.53	0.0503	8.1		2.10	6154.85			2.79	474.42	1635.04		1852.48		33.32		<PQL	1.38	0.00	2.42	<PQL				-16.16	-126.43	
6/7	8,980																											
6/16	5,950	6.79	0.0921	8.8		0.62	10874.15				437.59	2847.27		2354.42		23.65											-16.3	-127.32



BLS

Date	Discharge (cfs)	Field Chemistry			Alkalinity (mg CaCO <sub>3</sub> /L)	Mass Spec ICP (ug/L)														IC (mg/L)				ISO				
		pH	Conductivity (uS)	Temp (deg C)		As (.10)	Ca (100)	Cd (1.0)	Co (1.0)	Cr (1.0)	Cu (1.0)	Fe (50.0)	K (100)	Mg (100)	Mn (1.0)	Na (100)	Pb (1.0)	Zn (1.0)	F (0.06)	Cl (1.0)	NO <sub>2</sub> (0.06)	SO <sub>4</sub> (1.0)	NO <sub>3</sub> (0.3)	O <sup>18</sup>	H <sup>2</sup>			
4/28	3,890																											
5/5	5,260																											
5/14	4,069																											
5/19	3,740																											
5/25	4,930	7.16	0.45	10.4		1.14	43505.00				1532.00	12339.00		6921.00		14.89										-17.03	-131.82	
6/2	5,080																											
6/9	5,160	8.1	0.452	12.3	149	1.23	48195.85		3.74		2341.60	13771.54	2.42	7265.91		33.45	0.13	5.11		20.22	0.63				-17.45	-128.94		
6/16	4,270																											
6/22	3,270	7.56	0.447	10.6		1.28	46882.92		1.69		1913.64	12146.70		6302.66		24.67									-17.61	-130.06		
6/30	3,200																											
7/9	2,200	7.62	0.441	10.5	139	0.71	49279.36		4.62		2242.15	12912.79	1.58	7230.46		32.59	0.12	5.30		18.60	0.57				-16.97	-131.55		
7/19	1,690																											
7/30	1,210	7.6	0.435	10.4		0.95	51431.22		2.98		2222.73	13655.70	1.16	7298.46		17.83									-16.08	-131.44		
8/13	958																											
8/30	1,220	7.48	0.303*	11	149	1.21	42683.63				1437.15	11051.41		5637.90		21.23	0.13	5.20		17.16	0.48				-17.26	-132.03		
9/16	1,395																											
10/17	1,430	7.5	0.306	9.2	129	1.51	45824.64				1556.53	11693.75		5856.66		8.81	0.13	5.27		16.91	0.54				-17.67	-131.82		
11/14	1,305	7.52	0.301	8.9	137	1.29	43667.43				1494.75	11187.08		5732.76		13.71	0.14	4.96		17.91	0.47				-17.14	-131.49		
12/13	1,340	7.37	0.337	8.2		1.12	42954.12				1440.89	12344.46		5930.42		11.78									-17.93	-133.81		
1/19	2,525																											
2/4	1,380	8.16	0.333	9.9	126	0.95	47256.13				1672.27	11519.73		5612.11		10.64	0.14	4.96	0.00	19.94	0.41				-17.75	-132.11		
2/18	1,030	7.94	0.345	9.2		1.10	45314.46				1509.38	12011.94		3967.16		17.53									-16.84	-131.01		
3/4	1,130																											
3/16	1,320	7.65	0.34	9.2	127	0.95	42119.08				1470.52	11906.80		5410.92		13.78	0.13	4.96		20.91	0.41				-17.27	-131.25		
3/29	1,600																											
4/6	1,660	7.5	0.34	10.2		1.44	44017.73				1584.81	11655.43		5911.53		20.64									-16.7	-129.45		
4/14	2,240																											
4/26	3,450	7.46	0.308	10.2	144	1.53	44359.07				1633.04	11856.18		6183.45		16.59	0.14	5.12		19.92	0.40				-15.98	-129		
5/5	3,000																											
5/17	8,330	7.63	0.343	10.2		1.26	44306.90		2.06 1.37		1734.20	11911.48	1.95	6017.32		20.97									-16.97	-132.1		
5/25	7,150																											
6/7	8,980	7.34	0.347	10.1		1.33	45082.22				1595.64	12418.11		6348.71		15.72	0.13	6.06	0.00	19.24	0.55				-16.6	-132.56		
6/16	5,950	7.37	0.314	10.3		0.85	46086.51				1529.81	12560.69		6476.08		12.56									-16.49	-132.42		



WM2

Date	Discharge (cfs)	Field Chemistry			Alkalinity (mg CaCO <sub>3</sub> /L)	Mass Spec ICP (ug/L)													IC (mg/L)				ISO					
		pH	Conductivity (µS)	Temp (deg C)		As (10)	Ca (100)	Cd (1.0)	Co (1.0)	Cr (1.0)	Cu (1.0)	Fe (50.0)	K (100)	Mg (100)	Mn (1.0)	Na (100)	Pb (1.0)	Zn (1.0)	F (0.06)	Cl (1.0)	NO <sub>2</sub> (0.06)	SO <sub>4</sub> (1.0)	NO <sub>3</sub> (0.3)	O <sup>18</sup>	H <sup>2</sup>			
7/30	1,210																											
8/13	958	7.19	0.323	11		2.08	39471.27				1676.35	10200.63	2.91	3800.29	35.38											-17.2	-131.51	
8/30	1,220																											
9/16	1,395	7.1	0.283	11.2	136	1.77	39876.12				1846.13	10480.62	3.73	6063.02	20.26						0.1138	8.0814	15.465	0.7987		-17.12	-132.36	
10/17	1,430	7.18	0.287	10.9	122	1.94	39838.80				1811.37	10752.04		6000.56	37.86						0.1089	8.1168	16.979	0.9167		-17.37	-130.16	
11/14	1,305	7.52	0.284	10.4	132	1.60	35354.28				1948.50	10024.58		6279.22	15.67						0.09	8.65	14.80	0.87		-17.04	-130.18	
12/13	1,340	7.2	0.304	10.9		1.59	39623.67				1905.11	11514.79	1.34	6764.17	19.81											-17.77	-132.24	
1/19	2,525																											
2/4	1,380	7.85	0.302	9.5	124	1.54	40065.65				1868.32	10790.61		6313.68	15.08						0.10	7.20	0.00	18.82	0.82		-16.56	-128.28
2/18	1,030	7.26	0.306	9.1		1.43	39162.66				1572.98	10747.47		6112.89	19.49												-15.91	-12835
3/4	1,130																											
3/16	1,320	7.23	0.308	9.1	106	1.29	38486.83				1419.95	11680.79		5502.69	16.08						0.10	7.29	19.36	0.72		-16.29	-128.23	
3/29	1,600																											
4/6	1,660																											
4/14	2,240	7.2	0.305	8.6	130	1.68	40990.45				1762.10	11142.71		6341.66	15.20						0.10	7.46	17.62	0.59		-16.35	-128.16	
4/26	3,450																											
5/5	3,000	7.04	0.284	9.4		0.58	41138.03				2115.71	11277.61		6481.05	15.35												-17.71	-129.79
5/17	8,330																											
5/25	7,150	7.16	0.327	9.1		1.86	38052.08				1482.67	10163.40		5848.72	42.70						0.11	9.19	0.00	17.27	0.56		-16.43	-130.23
6/7	8,980																											
6/16	5,950	7.06	0.335	10		0.15	51344.27				2913.98	12645.77		9207.13	15.27												-16.27	-131.58







HGP/L

Date	Discharge (cfs)	Field Chemistry			Mass Spec ICP (ng/L)													IC (mg/L)				ISO						
		pH	Conductivity mS	Temp (deg C)	Alkalinity (mg CaCO <sub>3</sub> /L)	As (.10)	Ca (100)	Cd (1.0)	Co (1.0)	Cr (1.0)	Cu (1.0)	Fe (50.0)	K (100)	Mg (100)	Mn (1.0)	Na (100)	Pb (1.0)	Zn (1.0)	F (0.06)	Cl (1.0)	NO <sub>2</sub> (0.06)	SO <sub>4</sub> (1.0)	NO <sub>3</sub> (0.3)	O <sup>18</sup>	H <sup>2</sup>			
4/28	3,890																											
5/5	5,260																											
5/14	4,069																											
5/19	3,740																											
5/25	4,930																											
6/2	5,080																											
6/9	5,160																											
6/16	4,270																											
6/22	3,270																											
6/30	3,200																											
7/9	2,200																											
7/19	1,690	8.25	0.394	22.2	97	3.53	33033.68				1.58	1473.94	10827.36	1.67	4949.44		19.48								-16.51	-130.1		
7/30	1,210																											
8/13	958																											
8/30	1,220																											
9/16	1,395																											
10/17	1,430																											
11/14	1,305																											
12/13	1,340																											
1/19	2,525																											
2/4	1,380																											
2/18	1,030																											
3/4	1,130					1.08	34063.43				4.07	1690.69	9620.70	20.56	4946.64		high								-16.88	-129.03		
3/16	1,320																											
3/29	1,600					3.10	38327.76				1.85	1673.84	11243.03		6159.01		18.17											
4/6	1,650					2.52	33102.20					1464.90	9692.05		5377.99		34.90											
4/14	2,240																											
4/26	3,450																											
5/5	3,000																											
5/17	8,330					1.55	22363.03				3.39	804.52	5811.12		2837.65		24.40											
5/25	7,150																											
6/7	8,980					4.27	26085.36				4.58	1185.18	6529.35		3896.12		20.51											
6/16	5,990					4.85	33038.70				5.24	1300.10	8162.38		4597.51		22.90									-15.75	-129.55	



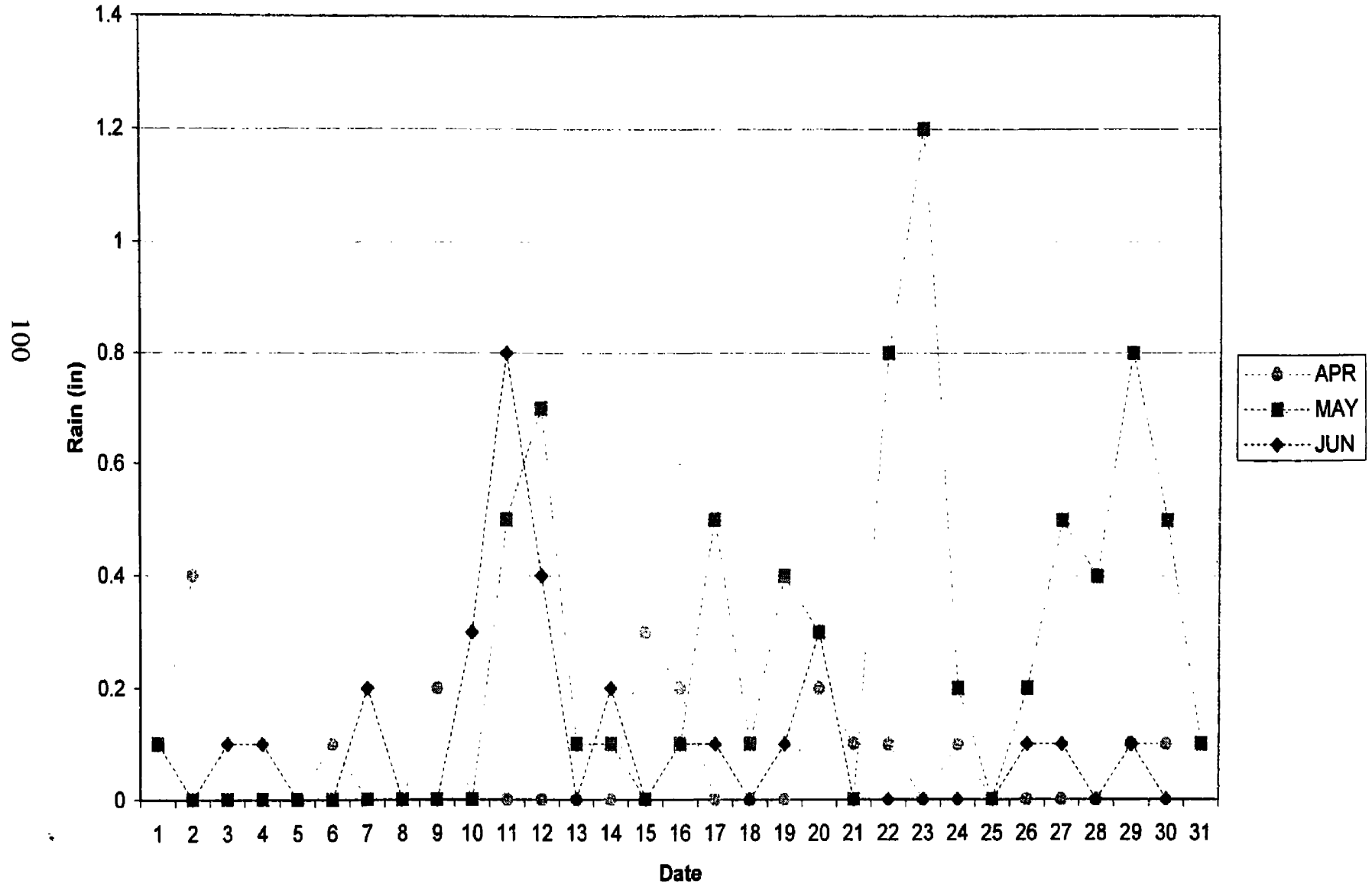
RSS		Field Chemistry			Alkalinity (mg CaCO <sub>3</sub> /L)	Mass Spec ICP (ug/L)													IC (mg/L)				ISO		
Date	Water Elevation	pH	Conductivity (mS)	Temp (deg C)		As (.10)	Cu (100)	Cd (1.0)	Co (1.0)	Cr (1.0)	Cu (1.0)	Fe (50.0)	K (100)	Mg (100)	Mn (1.0)	Na (100)	Pb (1.0)	Zn (1.0)	F (0.06)	Cl (1.0)	NO <sub>2</sub> (0.06)	SO <sub>4</sub> (1.0)	NO <sub>3</sub> (0.3)	O <sup>18</sup>	H <sup>2</sup>
4/28	na	6.96				0.27	2579.00				12.30	212.00	922.50		832.90		24.90							-17.51	-131.91
5/5																									
5/14	3206.6	7.16	0.0287	9	8	0.23	2774.80				4.69	102.00	979.70		960.60		42.20	0			1.39	nd		-17.04	-130.61
5/19																									
5/25	3207.12	6.83	0.0282	8.8		0.23	3617.00				5.97	182.00	987.00		950.00		38.05							-17.67	-133.53
6/2																									
6/9	3206.93	7.42	0.0307	7.47	8	0.32	2752.83				1.09	313.81	851.79	1.14	774.32		48.32	0.01	0.42		1.27	nd		-18.41	-128.41
6/16																									
6/22	3206.88	7.01	0.033	13.4		0.19	2710.25					229.40	906.86		760.53		43.07							-17.83	-125.8
6/30																									
7/9	3206.3	7.22	0.049	13.3	16	0.11	4038.25					321.05	1068.86		1002.58		33.45				1.80	nd		-16.46	-129.28
7/19																									
7/30	3206	8.13	0.0644	16.1		0.33	6231.97				6.72	370.38	1543.58		1914.24		9.71							-17.08	-129.58
8/13																									
8/30	3206.04	7.82	0.0983	13.3	25	0.35	5915.00					310.28	1944.31		1690.64		40.55	0.02	0.65		1.92	nd		-17.23	-131.57
9/16	3206.29																								
10/17	3206.2	7.22	0.0393	7.5	16	0.43	4470.34					430.31	1386.87		1302.81		48.04	0.01	0.61		1.73			-17.25	-127.05
11/14	3206.06	9.17	0.0376	3.9	14	b.d.	4100.47						1272.95		1136.50		34.76				1.81			-17.05	-128.35
12/13	3206.15	6.85	0.0364	0.9		b.d.	4147.11					259.65	1251.29		1124.61		44.40							-17.35	-127.68
1/19	3206.46	6.75	0.0335	0	2	b.d.	3230.11					279.62	1419.97		1288.58		38.42	nd	1.27	0.00	1.49	nd		-15.35	-121.89
2/4	3206.2	7.48	0.0335	3.1	12	0.17	3747.26						1361.23		1160.93		27.80	nd	0.34	0.00	1.90	nd		-16.73	-126.16
2/18	3206.15	6.73	0.0407	0		0.16	4415.73					256.65	1582.29		1431.65		22.94							-16.77	-127.96
3/4	3206	7.4	0.0395	6.3	16	b.d.	4408.88					277.05	1858.39		1082.47		30.06	0.04	0.57		3.03	0.00		-17.45	-127.52
3/16	3206.25																								
3/29	3206.35	7.89	0.0276	5.3		0.52	3696.39						1281.08		1078.14		26.23							-16.2	-125.84
4/6	3206.32																								
4/14		7.04	0.0317	5.6	4	0.47	3592.81					161.14	1407.16		1236.12		21.44	<PQL		n.d.	1.56	n.d.		-16.47	-124.91
4/26	3207																								
5/5		7.26	0.0286	8		0.39	2959.85						1263.51		1248.32		31.62							-16.63	-126.12
5/17	3207.45																								
5/25	3207.33	6.49	0.0223	6.8		0.21	2519.62					184.34	892.23		922.59		32.83	0.00		0.60	1.02	0.00		-16.23	-126.14
6/7	3207.1																								
6/16		6.42	0.0237	10		b.d.	2240.33						747.44		724.12		24.62							-16.27	-127.32



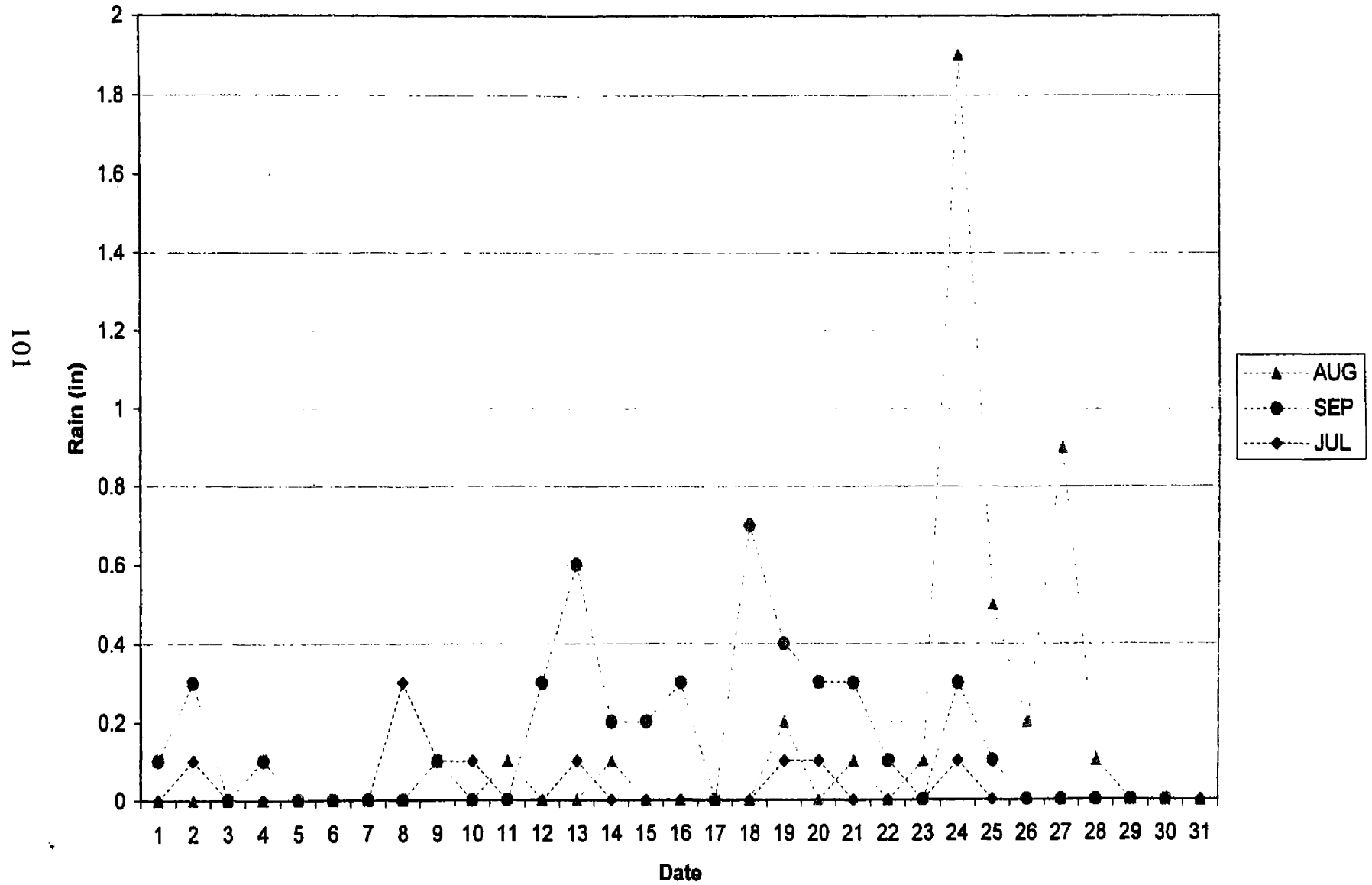


**Appendix 5**  
**Precipitation for the Study Period**

### Daily ppt (Apr - Jun 2004)



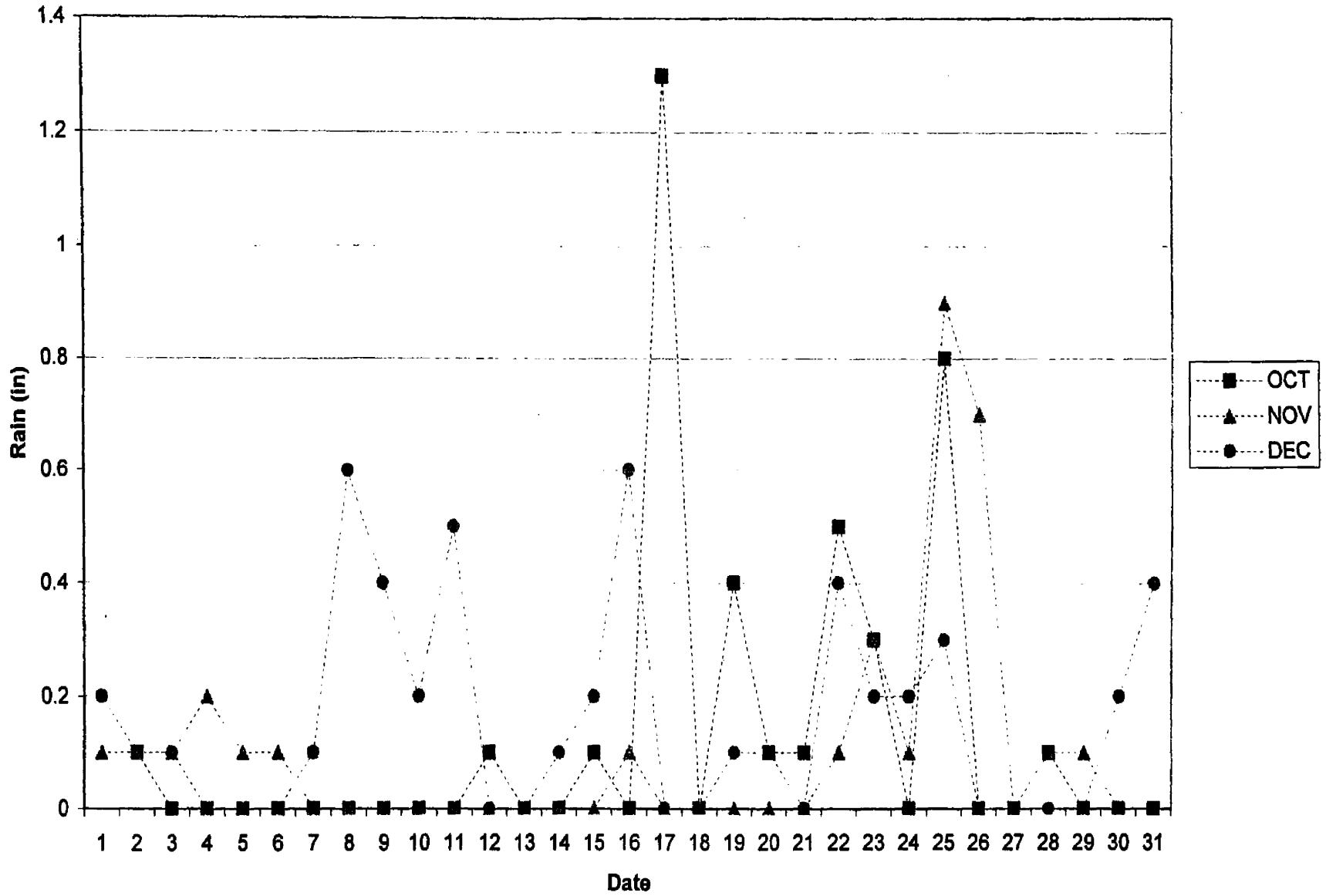
### Daily ppt (Jul - Sep 2004)



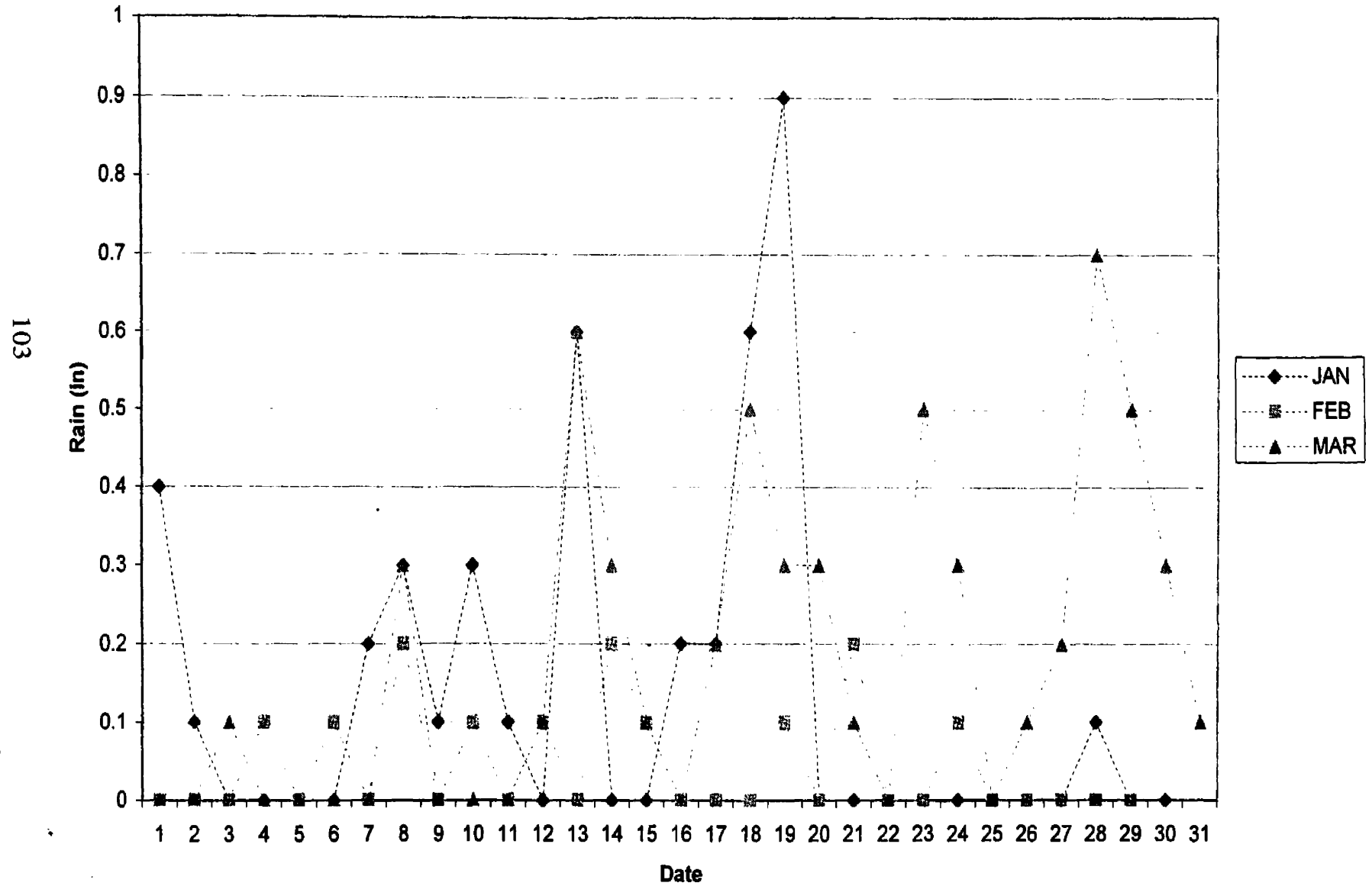


Daily ppt  
(Oct - Dec 2004)

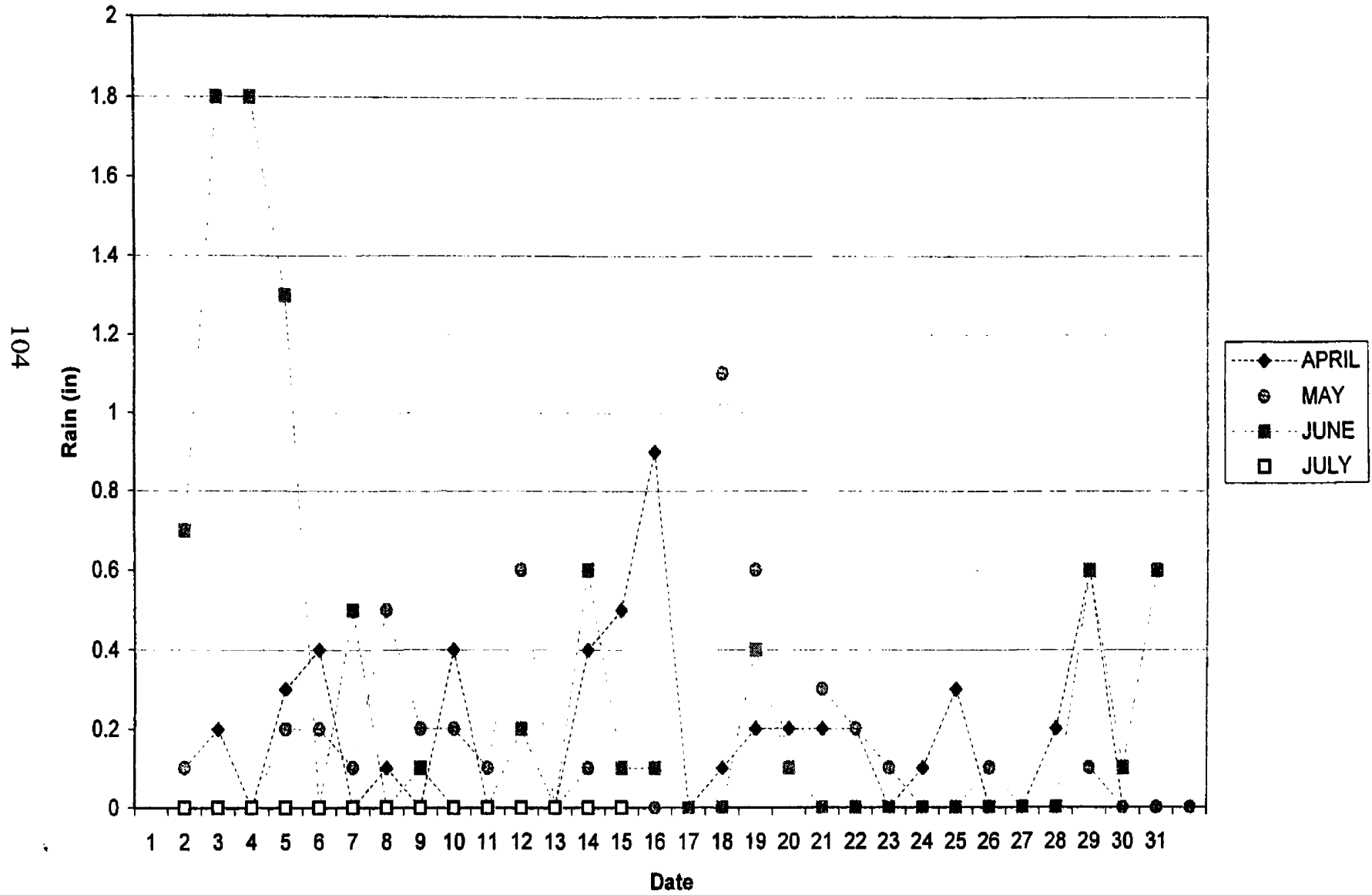
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### Daily ppt (Jan - March 2005)



Daily ppt  
(April - July 2005)

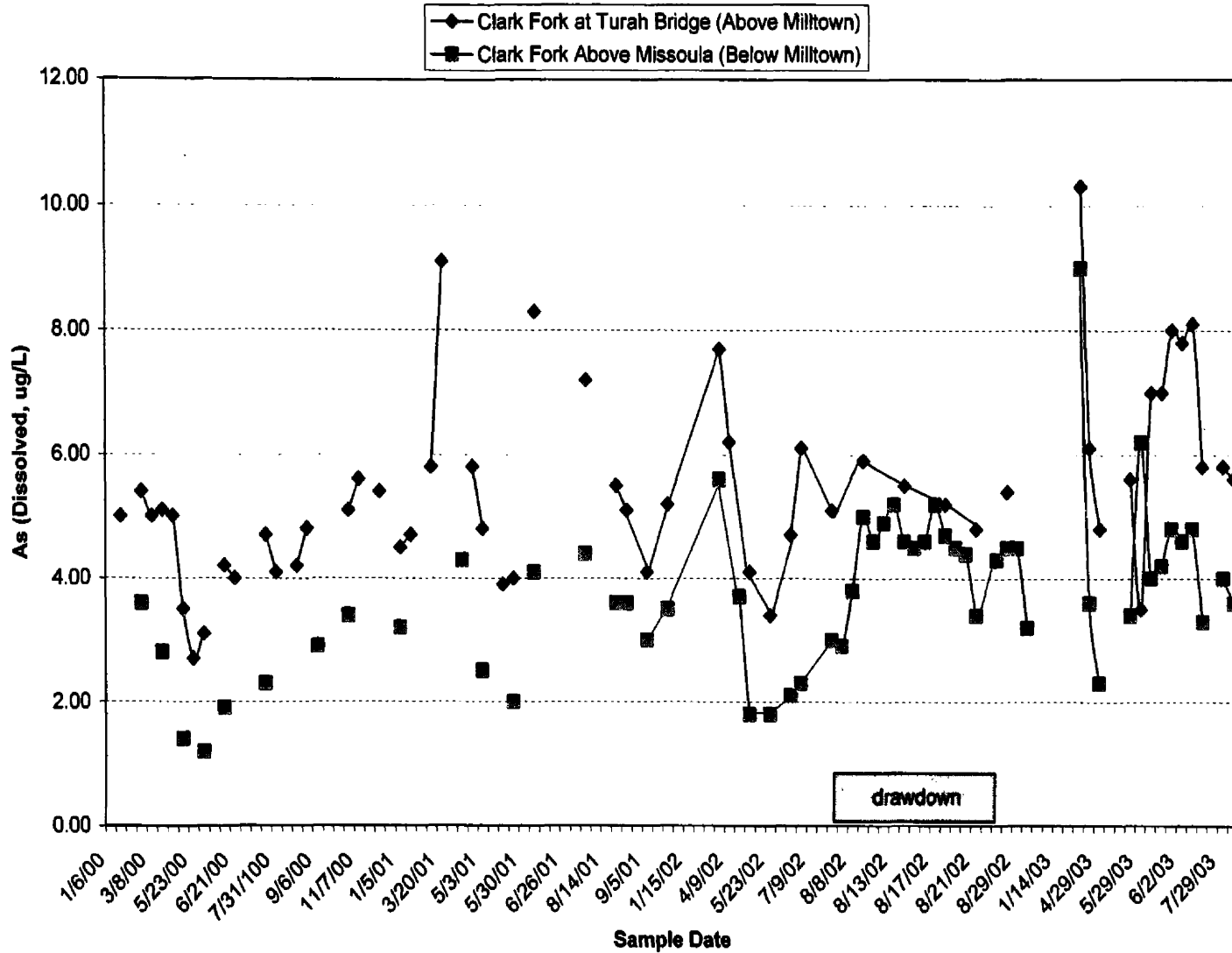


**Appendix 6.** Dissolved cadmium, chromium and manganese detected during the study.

Date	MM2			MM4			MM5			WQM			DH2			BLS			HGS			DH1			GRG			
	Cd	Cr	Mn	Cd	Cr	Mn	Cd	Cr	Mn	Cd	Cr	Mn	Cd	Cr	Mn	Cd	Cr	Mn	Cd	Cr	Mn	Cd	Cr	Mn	Cd	Cr	Mn	
4/28																												
5/5																												13
5/14																												
5/19					1.3																							2.2
5/25					1.6																							
6/2																												15
6/9																												
6/16																												10.4
6/22																												
6/30																												5.78
7/9																												
7/19																												5.93
7/30																												
8/13																												4.31
8/30																												
9/16																												24.5
10/17																												1.52
12/13														1.96		1.61												3.81
1/19																												
3/29														1.20														
4/14														1.76														1.22
5/17		1.11																										
5/25																												42.1
6/7																												
6/16														1.19														6.81



**Arsenic in the Clark Fork River (Above and Below Milltown Reservoir)**



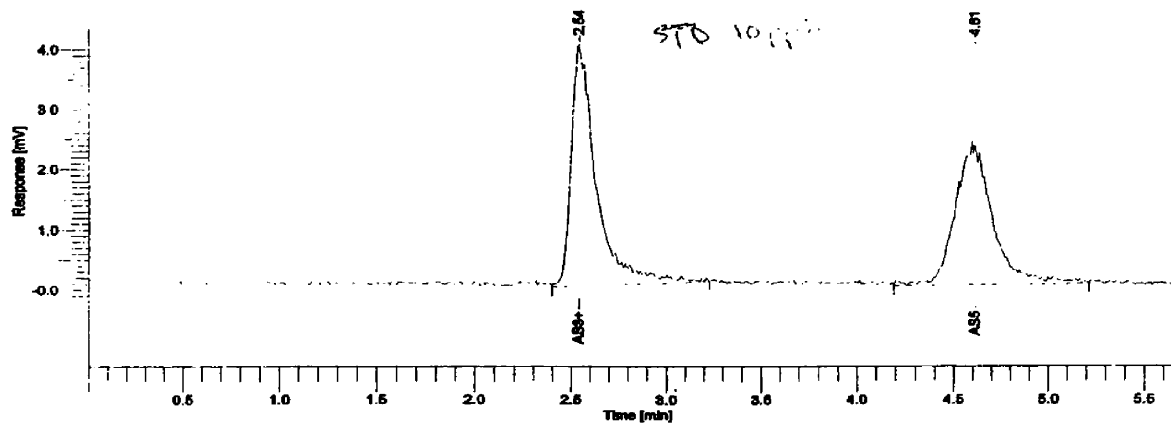
107

**Appendix 7.** Arsenic values for above and below Milltown Dam. The Blackfoot River dilutes the Clark Fork, giving lower arsenic values below the confluence.

**Appendix 8**  
**Speciation Raw Data**

Software Version	: 6.2.1.0.104:0104	Date	: 8/4/2005 15:35:49
Operator	: Administrator	Sample Name	:
Sample Number	:	Study	:
Auto Sampler	:	Rack/Vial	: 0/1
Instrument Name	:	Channel	: A
Interface Serial #	:	A/D mV Range	: 1000
Delay Time	: 0.00 min	End Time	: 6.37 min
Sampling Rate	: 1.9881 pts/s	Area Reject	: 0.000000
Sample Volume	: 1.000000 µL	Dilution Factor	: 1.00
Sample Amount	: 1.0000	Cycle	: 1
Data Acquisition Time	: 8/17/2005 14:32:38		

Raw Data File : C:\EianHPLC\RawData\050617\as 3 and 5 10-050617-144107\_74\_92.raw  
 Inat Method : DEFAULT from C:\EianHPLC\RawData\050617\as 3 and 5 10-050617-144107\_74\_92.raw  
 Proc Method : C:\EianHPLC\Methods\June 8.mth from  
 Calib Method : C:\EianHPLC\Methods\June 8.mth from  
 Report Format File: DEFAULT.rpt  
 Sequence File :



### Arsenic 75 speciation

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Vol% Range	BL	Adjusted Amount	Raw Amount
1	As3+	2.638	36821.61	3977.52	53.20	53.20			BB	10.1589	10.1589
2	as5	4.608	32389.18	2503.97	46.80	46.80			BB	7.0575	7.0575
			69210.79	6281.48	100.00	100.00				17.2164	17.2164

#### Missing Component Report

Component Expected Retention (Calibration File)

dms	2.818
rms	3.811



```

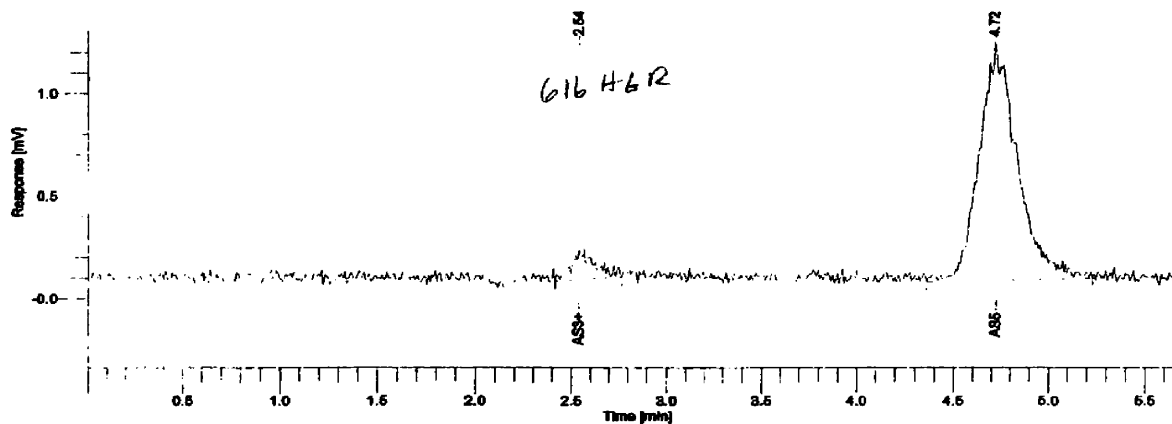
Software Version : 6.2.1.0.104:0104
Operator : Administrator
Sample Number :
AutoSampler :
Instrument Name :
Interface Bortol # :
Delay Time : 0.00 min
Sampling Rate : 1.0881 pts/s
Sample Volume : 1.000000 µL
Sample Amount : 1.0000
Data Acquisition Time : 8/17/2005 17:38:50

Date : 8/4/2006 15:30:39
Sample Name :
Study :
Rack/Vial : 0/1
Channel : A
A/D mV Range : 1000
End Time : 5.70 min

Area Reject : 0.000000
Dilution Factor : 1.00
Cycle : 1
    
```

```

Raw Data File : C:\ElanHPLC\RawData\050617\0606hgr-050617-174452_74_92.raw
Inst Method : DEFAULT from C:\ElanHPLC\RawData\050617\0606hgr-050617-174452_74_92.raw
Proc Method : C:\ElanHPLC\Methods\June 8.mth from
Calib Method : C:\ElanHPLC\Methods\June 8.mth from
Report Format File: DEFAULT.rpt
Sequence File :
    
```



### Arsenic 75 speciation

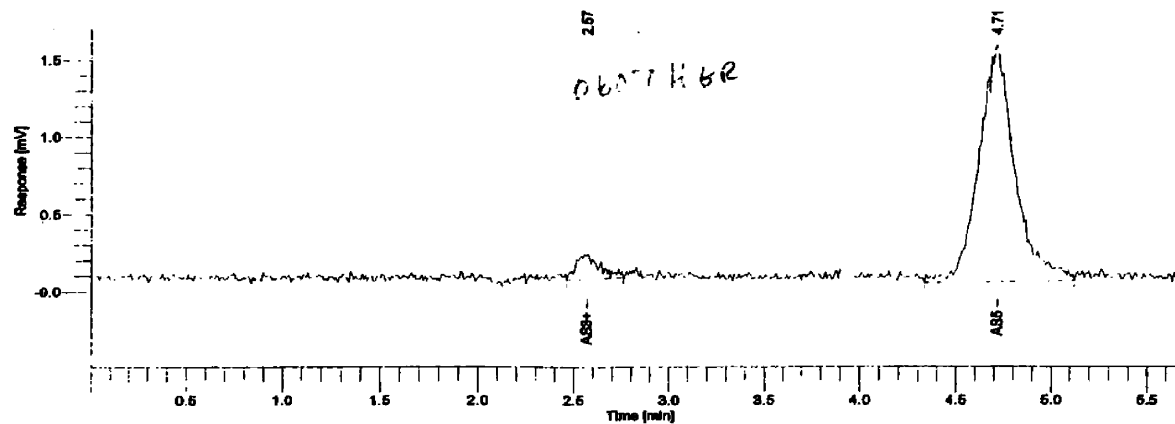
Peak #	Component Name	Time [min]	Area [µV*sec]	Height [µV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Adjusted Amount	Raw Amount
1	As3+	2.539	1204.69	121.60	6.89	6.89	-	-	BB	0.3928	0.3928
2	as5	4.722	16285.63	1121.07	93.11	93.11	-	-	BB	2.8679	2.8679
			17490.32	1242.68	100.00	100.00				3.2607	3.2607

Missing Component Report

Component	Expected Retention (Calibration File)
dma	2.818
mms	3.811

Software Version	: 6.2.1.0.104:0104	Date	: 8/4/2006 17:24:35
Operator	: Administrator	Sample Name	:
Sample Number	:	Study	:
AutoSampler	:	Rack/Vial	: 0/1
Instrument Name	:	Channel	: A
Interface Serial #	:	A/D mV Range	: 1000
Delay Time	: 0.00 min	End Time	: 6.37 min
Sampling Rate	: 1.9881 pts/s	Area Reject	: 0.000000
Sample Volume	: 1.000000 µL	Dilution Factor	: 1.00
Sample Amount	: 1.0000	Cycle	: 1
Data Acquisition Time	: 6/7/2005 19:30:29		

Raw Data File : C:\ElanHPLC\RawData\060607\0607hgr-060607-194033\_74\_92.raw  
 Inet Method : DEFAULT from C:\ElanHPLC\RawData\060607\0607hgr-060607-194033\_74\_92.raw  
 Proc Method : C:\ElanHPLC\Methods\June 8.mth from  
 Calib Method : C:\ElanHPLC\Methods\June 8.mth from  
 Report Format File: DEFAULT.rpt  
 Sequence File :



### Arsenic 75 speciation

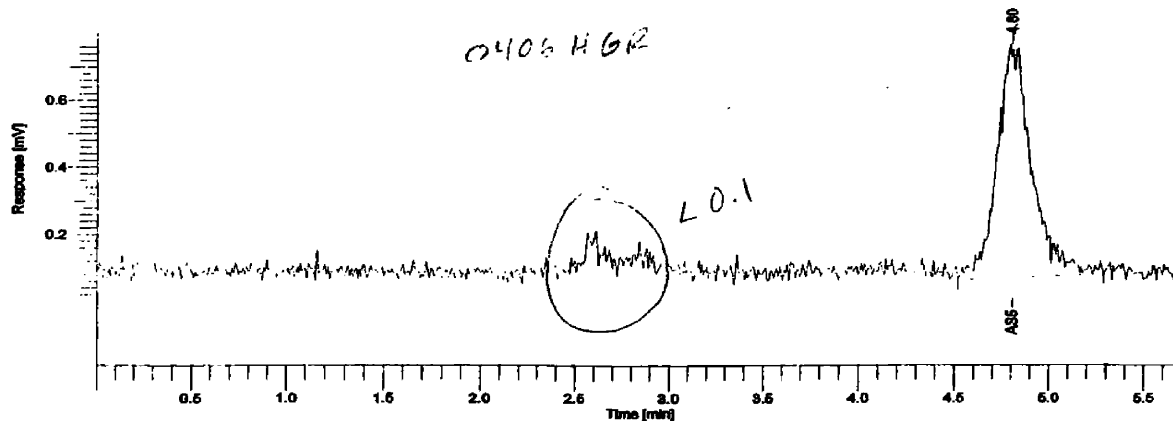
Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Adjusted Amount	Raw Amount
1	As3+	2.566	1391.30	168.62	6.46	6.46	-	-	BB	0.4439	0.4439
2	as5	4.711	20162.26	1642.01	93.54	93.54	-	-	BB	3.8766	3.8766
			21553.55	1698.63	100.00	100.00				4.3204	4.3204

Missing Component Report  
 Component Expected Retention (Calibration File)

dms	2.818
mma	3.811

Software Version : 6.2.1.0.104:0104  
 Operator : Administrator  
 Sample Number :  
 AutoSampler :  
 Instrument Name :  
 Interface Serial # :  
 Delay Time : 0.00 min  
 Sampling Rate : 1.6881 pts/s  
 Sample Volume : 1.000000 µL  
 Sample Amount : 1.0000  
 Data Acquisition Time : 4/7/2005 14:13:20  
 Date : 8/4/2006 17:27:56  
 Sample Name :  
 Study :  
 Rack/Vial : 0/1  
 Channel : A  
 A/D mV Range : 1000  
 End Time : 6.37 min  
 Area Reject : 0.000000  
 Dilution Factor : 1.00  
 Cycle : 1

Raw Data File : C:\EianHPLC\RawData\050310\wc 050406hgr-050407-142333\_74\_82.raw  
 Inst Method : DEFAULT from C:\EianHPLC\RawData\050310\wc 050406hgr-050407-142333\_74\_82.raw  
 Proc Method : C:\EianHPLC\Methods\June 8.mth from  
 Calib Method : C:\EianHPLC\Methods\June 8.mth from  
 Report Format File: DEFAULT.rpt  
 Sequence File :



### Arsenic 75 speciation

Peak #	Component Name	Time [min]	Area [µV*sec]	Height [µV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Adjusted Amount	Raw Amount
1	as5	4.801	9017.28	692.13	100.00	100.00	-		BB	0.9770	0.9770
			9017.28	692.13	100.00	100.00				0.9770	0.9770

Missing Component Report  
Component Expected Retention (Calibration File)

As3+	2.595
dms	2.818
mms	3.811

```

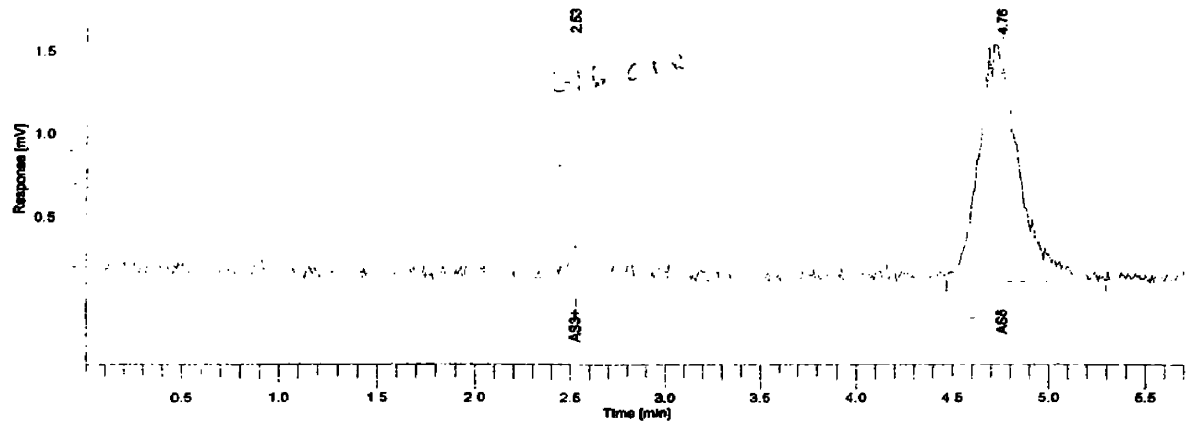
Software Version : 6.2.1.0.104:0104
Operator : Administrator
Sample Number :
AutoSampler :
Instrument Name :
Interface Serial # :
Delay Time : 0.00 min
Sampling Rate : 1.9881 pts/s
Sample Volume : 1.000000 µL
Sample Amount : 1.0000
Data Acquisition Time : 6/17/2005 17:13:12

Data : 6/4/2005 15:28:01
Sample Name :
Study :
Rack/Vial : 0/1
Channel : A
A/D mV Range : 1000
End Time : 5.70 min

Area Reject : 0.000000
Dilution Factor : 1.00
Cycle : 1
    
```

```

Raw Data File : C:\ElanHPLC\RawData\050617\0606cfr-050617-172127_74_92.raw
Inst Method : DEFAULT from C:\ElanHPLC\RawData\050617\0606cfr-050617-172127_74_92.raw
Proc Method : C:\ElanHPLC\Methods\June 8.mth from
Calb Method : C:\ElanHPLC\Methods\June 8.mth from
Report Format File: DEFAULT.rpt
Sequence File :
    
```



### Arsenic 75 speciation

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Cal. Range	Volt Range	BL	Adjusted Amount	Raw Amount
1	As3+	2.527	2038.16	162.14	8.84	8.84	-	-	BB	0.6210	0.6210
2	as5	4.759	21016.35	1283.78	91.16	91.16	-	-	BB	4.0987	4.0987
			23054.50	1445.92	100.00	100.00				4.7197	4.7197

**Missing Component Report**  
 Component Expected Retention (Calibration File)

dma	2.818
mma	3.811

```

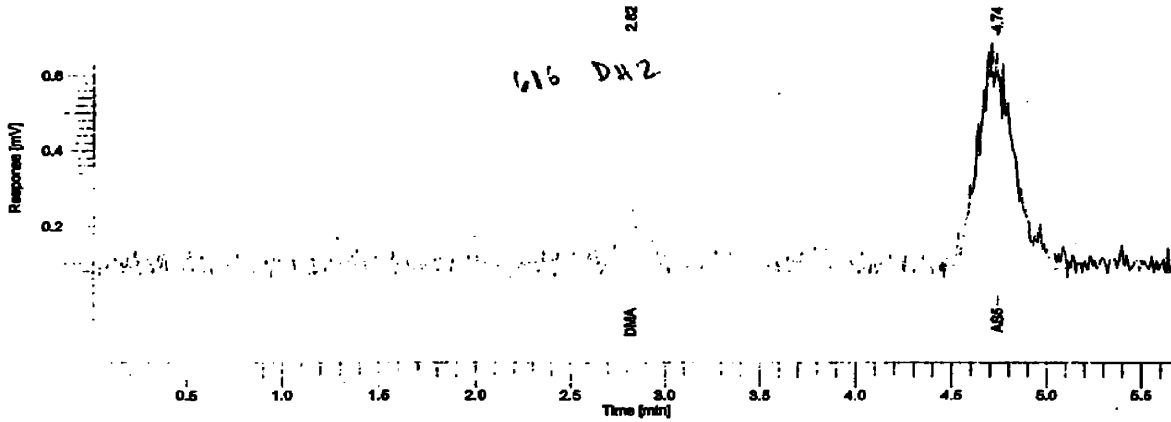
Software Version : 6.2.1.0.104:0104
Operator : Administrator
Sample Number :
Auto Sampler :
Instrument Name :
Interface Serial # :
Delay Time : 0.00 min
Sampling Rate : 1.9881 pts/s
Sample Volume : 1.000000 µL
Sample Amount : 1.0000
Data Acquisition Time : 8/17/2006 19:17:46

Date : 8/4/2006 16:27:31
Sample Name :
Study :
Rack/Vial : 0/1
Channel : A
A/D mV Range : 1000
End Time : 6.70 min

Area Reject : 0.000000
Dilution Factor : 1.00
Cycle : 1
    
```

```

Raw Data File : C:\ElanHPLC\RawData\050617\0606dh2-050617-192531_74_92.raw
Inst Method : DEFAULT from C:\ElanHPLC\RawData\050617\0606dh2-050617-192531_74_92.raw
Proc Method : C:\ElanHPLC\Methods\June 8.mth from
Calib Method : C:\ElanHPLC\Methods\June 8.mth from
Report Format File: DEFAULT.rpt
Sequence File :
    
```



### Arsenic 75 speciation

Peak #	Component Name	Time [min]	Area [µV*sec]	Height [µV]	Area [%]	Norm. Area [%]	Cal. Range	Vol% Range	BL	Adjusted Amount	Raw Amount
1	dma	2.821	1674.99	168.61	16.68	16.68	-	-	BB	0.5381	0.6381
2	as5	4.743	8369.82	536.42	83.32	83.32	-	-	BB	0.8085	0.8085
			10044.81	704.03	100.00	100.00				1.3466	1.3466

Missing Component Report  
Component Expected Retention (Calibration File)

As3+	2.595
mma	3.811