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"REDOX PUMPING" IN THE NEAR SURFACE MISSOULA AQUIFER ON THE FLOODPLAIN OF THE CLARK FORK RIVER: SURFACE WATER AND GROUNDWATERINTERACTIONS AND ARSENIC RELATED CHEMISTRY AT A COMPOST FACILITYNEAR A WASTEWATER TREATMENT PLANT

Donna Lee Smith
The University of Montana

"REDOX PUMPING" IN THE NEAR SURFACE MISSOULA AQUIFER ON THE FLOOD PLAIN OF THE CLARK FORK RIVER: SURFACE WATER AND GROUNDWATER INTERACTIONS AND ARSENIC RELATED CHEMISTRY AT A COMPOST FACILITY NEAR A WASTEWATER TREATMENT PLANT.

By

Donna Lee Smith

B.S., Northern Arizona University, Flagstaff Arizona, USA, 1991

Thesis

presented in partial fulfillment of the requirements
for the degree of

Master of Science
in Geosciences

The University of Montana
Missoula, MT

Spring, 2008

Approved by:

Dr. David A. Strobel, Dean
Graduate School

Dr. Johnnie N. Moore, Chair
Geosciences

Dr. Heiko Langner
Geosciences

Dr. William Woessner
Geosciences

Dr. Michael DeGrandpre
Chemistry

Smith, Donna L., M.S. May 2008   Geosciences

"Redox pumping" in the near surface Missoula Aquifer on the flood plain of the Clark Fork River: Surface water and groundwater interactions and arsenic related chemistry at a compost facility near a wastewater treatment plant.

Chairperson: Johnnie N. Moore

Arsenic transport in groundwater is evaluated at Eko Compost, a site with measurable levels of arsenic, organic carbon and nutrients in the ground water. The compost facility is located adjacent to the Missoula wastewater treatment plant on a contaminated floodplain of the Clark Fork River in the Missoula Valley, Montana, USA.

This site was evaluated over two years for hydrological and chemical characteristics. A series of potentiometric surface maps was created over time and hydraulic conductivity and ground water movement were characterized. Water samples were also collected monthly and results from chemical analyses of the waters were contoured over the site map to evaluate chemical and hydrologic transport.

Arsenic, organic carbon, iron and sulfate increased across the site in summer after water table elevations rose in spring. 'Redox pump' mechanisms were characterized in two locations, where reducing conditions with high levels of iron and organic carbon liberated anomalously high concentrations (60 to150 ug/L) of dissolved arsenic in spring. The source of arsenic appeared to be buried contaminated flood sediments at the site. A conceptual model is presented where the chemical character of the water was influenced vertically by the layer of the sediment that contained the top of the water table, and laterally by the chemical character induced by the path of the groundwater.

Hydraulic conductivities (K) of around 1100 ft/day were estimated for sections of the uppermost layer of the aquifer, K values were higher near the river, and lower in wells finished in the organically enriched zones. During spring and early summer a local flow pattern was described that is seasonally different from the established regional pattern.

Two distinct hydrogeologic occurrences were observed during runoff season while the aquifer was recharging 1) A direct connection developed between the aquifer and the river at the Eko Compost backwater, and 2) potentiometric maps showed flow direction in the aquifer through backfilled channels of organically enriched areas that had been used as sludge ponds for the nearby water treatment plant.

Our findings indicate that both hydrogeology and chemical transport at this site were heavily influenced by the human altered landscape.

INTRODUCTION

Arsenic in ground water used for drinking is a worldwide problem that has caused widespread acute and chronic toxic effects on whole populations and additional thousands of individuals. For example, in Bangladesh and India, shallow drinking water wells may contain hundreds of micrograms per liter (ug/L) of arsenic (Welch et al. 2000; Smedley and Kinniburgh 2002) while the World Health Organization recommended limit for arsenic in drinking water is 10 ug/L. The mechanisms of contamination are varied. Arsenic in groundwater is primarily derived from three sources: naturally occurring minerals, geothermal sources, and mining. In Western Montana, arsenic in surface water and groundwater (Moore and Woessner, 1993) is associated with the artifacts of a significant mining and smelting operation near the headwaters of the Clark Fork River (Moore and Luoma1990; Helgen and Davis 2000).

Currently, EPA Maximum Contaminant Levels (MCLs) for drinking water (US Federal Register, Code of Federal Regulations 40CFR) are based on total aqueous concentration of arsenic without assessing the nature of the complexes present. However, the actual risk may not be completely addressed by this regulatory action limit since differing oxidation states of arsenic result in different reactivity and toxicity (Korte and Fernando 1991; Hughes et al. 2007).

Arsenic is a metalloid that occurs in nature in several oxidation states (-3, 0, +3 and +5) and complexes or species. A key factor in the mobilization and reactivity of arsenic is oxidation state. Arsenic is present in sediment and in surface and groundwater primarily in the oxidation states As(III) (arsenite) and As(V) (arsenate) (Ferguson 1971). Species found in aqueous environments are arsenite anions , $H_3AsO_3^0$, $H_2AsO_3^-$, arsenate anions, $H_2AsO_4^-$, $HAsO_4^{2-}$ and methylated complexes of arsenic, most commonly methyl arsonic acid (MMA),$CH_3AsO(OH)_2$ and dimethyl arsinic acid (DMA), $(CH_3)_2AsO(OH)$, also referred to as cacodylic acid (Stumm and Morgan 1996). Metabolic by-products arsenobetaine (AsB) and arsenocholine (AsC) are both also found in marine environments (Ferguson and Gavis 1971).

The interactions of arsenic in complex environmental systems are influenced by hydrologic, chemical and biological variables. Therefore, analysis for arsenic species and other redox indicators such as dissolved oxygen, iron, sulfate and nitrate should be performed when evaluating arsenic transport systems.

Eko Compost, a commercial composting facility, provides a field model for arsenic behavior relative to redox conditions and surface water and groundwater exchange. The facility is built upon an old landfill/industrial/agricultural site on the floodplain of the CFR and downstream from the municipal wastewater treatment plant. Data from previous monitoring projects by Land and Water Consulting (Land and Water, by permission of Eko Compost) shows concentrations of arsenic varying by well location and season, from less than 10 ug/L, to greater than 100 ug/L. The river water at this location in Missoula contains lower levels of arsenic (1-5 ug/L) (Cook 2005).

The goal of this research was to determine the origin of elevated concentrations of arsenic in the groundwater at Eko Compost, and to identify the likely geochemical controls on arsenic release and transport in the local groundwater system. A conceptual model of the chemical behavior of arsenic underneath the compost yard is presented where transport is unrelated to the composting activity that takes place on the surface. The chemical character of the groundwater is influenced by both the lateral and vertical components of the local hydrologic flow. A reducing plume may be created when 1) the organic enriched, anoxic trending surface waters percolate to the water table from the compost yard above, or 2) laterally flowing groundwater comes into contact with reducing agents and/or nutrients and then encounters arsenic rich sediments, or 3) the water table rises during aquifer recharge periods, coming in contact with contaminated layers of sediment. The following chapters will assess each of these processes and evaluate the degree to which they may explain observed location of arsenic impacted groundwater and its seasonal variability.

BACKGROUND

Description of Study Area

Location

The study area encompasses approximately 150 acres along the Clark Fork River in the Missoula Valley of Western Montana, Township and Range 13N 19W section 18 (Figure 1). The Eko Compost facility is bordered to the east by the Missoula Waste Water Treatment Plant (WWTP) with the CFR less than a quarter of a mile to the east, the property includes groundwater-fed ponds, with a backwater slough and the river to the south (Figure 2). The compost yard itself consists of several large piles of yard waste that are chipped, ground and amended with solid waste from the Missoula and Post Falls, Idaho wastewater treatment plants, and composted over three year cycles. The lower floodplain covers about 20 acres, sitting only 2-3 feet above the river during periods of high flow; the backwater lies west of the floodplain. The composting area is located north of the floodplain at the same elevation. There is little topographic relief, except an engineered terrace to the east about 5 feet higher in elevation, upon which the WWTP facility sits.

When permitting began for the development of the current Eko-Compost facility in 1991, eight monitoring wells were installed by Howard Newman Hydrological Consultants in an attempt to monitor up gradient, central, and down gradient groundwater chemistry. Sampling of several wells indicated high levels of organic carbon and metals including 10 to 100 ug/L arsenic. The site has been subject to biannual groundwater monitoring since 1992.

Activity at the Eko Compost Area

Groundwater flow and chemistry in the aquifer are influenced by artifacts from events and industrial processes at the site in the past. This area may have been particularly influenced by historic floods carrying mining wastes from Butte and Anaconda, before and after construction of the Milltown Dam (Land and

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Water 1992). Around the turn of the century, these floods transported large amounts of metals-contaminated sediments (Moore and Luoma 1990, Helgen and Moore 1996) and may have deposited these sediments on the floodplain at Eko Compost. An air photo from 1941 shows this area of the river was a large meander and flood plain (Figure 3). The main channel gave way to smaller channels and a backwater slough with a large floodplain area. In the 1960s, the property was mainly used as a landfill, including wood disposal and agricultural waste. The entire site was often covered with up to three feet of water (verbal communication, Terry Munnerlyn, operations manager, Eko Compost), when the channel bisecting the property flooded. By the 1970s (Figure 4) the area had been quarried extensively and the original channel and newly excavated lagoons were used for disposal of sludge from the WWTP (Land and Water 1992, Terry Munnerlyn, Eko Compost general manager, personal communication). At this time, Dr Joe Horvath began a small composting operation and attempted to make use of the stockpiled sewage. The photograph in Figure 4 shows the approximate locations of these ponds at the time of development of the Eko Compost facility in the 1980s. Since then, there have been several major flood events that filled many of the old lagoons on the floodplain that had been dredged, and probably saturated buried lagoons that had been backfilled. The most recent occurrence of flooding at the Eko Compost site was documented in 1998.

Currently the major portion of the active compost facility sits just above the described floodplain north and west of the river (Figure 2). The vadose zone is covered with a layer of compost, which holds approximately ten times its weight in water according to a 1992 study (Woods End Research 1992). This study concluded that it is unlikely that significant amounts of moisture will migrate through the compost to the water table (Land and Water 1992). South of the compost yard, the lakes that are remnants of the old floodways sit on the western and northern floodplain, and the southeastern flood plain is a large restored area that has been rehabilitated for wildlife and vegetation.

The WWTP is adjacent to the compost yard to the east. The waste water treatment process influences the site in two ways. First, approximately 0.3 miles upstream from the river backwater at the south edge of the compost yard, effluent is discharged into the river at an average rate of 7.4 cubic feet per second (cfs), representing approximately one tenth of one percent at high flow, to one percent at low flow, of the total volume of the river at this point. This creates a nutrient-enriched zone of surface water upstream of the backwater at Eko Compost. Second, the solid waste generated by the WWTP is deposited immediately for composting at Eko Compost. In this manner the two facilities have established an integrated waste management program, where the disposal needs of one facility can support raw material needs of another.

Possible sources of arsenic contamination in the groundwater beneath Eko Compost

Prior to this work, the sources of arsenic in site monitoring wells had been attributed to buried flood plain sediments from contaminated sources upstream (Newman 1991, Land and Water 1992). This explains the presence of arsenic but does not explain why the concentrations vary across the site seasonally. Other sources that have been postulated to provide the nutrients required for redox release are: the compost above, the river itself after it has been enriched by the effluent from the wastewater treatment plant, or the sludge from the wastewater treatment process that is stored at land surface and used to develop the compost materials. The following chapters will address all of these sources and document evidence to support or refute each scenario.

Previous Studies

Missoula Aquifer

Previous studies in the Missoula valley include basic water quality studies of the Missoula Basin (McMurtrey 1965) and the Missoula Valley (Woessner 1988). Woessner (1988) compiled several studies relating to the Missoula Aquifer including Geldon (1979), Miller (1991), Smith (1992), Morgan (1996) and

Tallman (2005), who characterized the hydrogeology and hydraulic characteristics of the aquifer.

Chemical transport studies are varied, including a study of arsenic in the aquifer as it relates to the losing Clark Fork River (Cook 2005). Pottinger (1988) tracked the source of herbicides in the aquifer. Other organic chemical transport studies included tracing a trichloroethylene (TCE) plume to the White Pine Sash manufacturing facility (Hinman et al. 1990), and PCBs at the Burlington Northern railroad (Stringer 1992). The high transmissivity of the aquifer and the likely presence of channels of higher and lower hydraulic conductivity in the Missoula Aquifer allow for highly varied hydrologic flows. Smaller perched aquifers may have a directional flow that is contrary to the flow direction of the regional aquifer (Stringer 1992). Seasonal regional flow patterns can develop, allowing increased levels of interaction between surface water and groundwater (Miller 1991). Popoff (1985) characterized the ground water contamination in Milltown.

Arsenic in Western Montana surface waters and groundwaters

In Western Montana, surface waters and groundwaters have been evaluated and monitored extensively for arsenic. Arsenic from geothermal sources is present near Yellowstone National Park and in the headwaters of the Madison River (USGS 1987).

Acid mine drainage mobilizes arsenic in the environment in the Butte-Anaconda area (Moore et al. 1988), to areas such as the holding ponds near Anaconda which become secondary sources for arsenic downstream at Silver Bow Creek near Butte (Grant 2006; Gammons et al 2007). Arsenic and other mining waste metals have been found at great distances from the original point sources (Luoma and Moore 1990; Helgen and Davis 2000) such as Milltown Reservoir and associated groundwater above Milltown Dam (Moore and Woessner 2003) less than ten miles upriver from Missoula. Surface water and sediment transport studies show that the primary mode of arsenic transport is in the sediments (Moore et al.1988; Helgen and Moore 1996; Hudson-Edwards et al. 2001; Nicholas et al. 2003). Additionally, hyporheic zone studies have proven

useful for characterization of arsenic in varied redox conditions (Mok et al. 1988; Nagorski and Moore 1999).

<u>Redox phenomena and surface water groundwater interactions</u>

This study will focus on arsenic as it relates to organic carbon and other chemical redox indicators. In the eastern United States, Halls Brook and Mystic Lake are subjects of studies of arsenic as it relates to other nutrients such as iron, sulfate and nitrate seasonally in lakes (Senn and Hemmond 2002) and wetlands (Ford et al. 2006; Wilkin and Ford 2006). Studies of arsenic behavior in surface water and groundwater in the western United States include an evaluation of arsenic transport in the reducing layers in Mono Lake (Spliethoff et al. 1995; Hollibaugh et al. 2005) and Owens Lake, now a dry lakebed and seasonal salt marsh with high levels of arsenic in saline water very near the ground surface (Levy et al. 1999; Ryu et al. 2002). Waters associated with mining sites in Arizona have been evaluated for transport and speciation of arsenic (Foust 2004). Peats and sludges associated with sewage treatment have been shown in the Southern U.S. and Europe to sequester arsenic under certain conditions through reduction and complexation, but these reactions are predictably reversible (Carbonell-Barrachina et al.1999; Juillot et al.1999).

<u>Hydrogeology of Missoula Valley</u>

The Missoula Valley is located in the Missoula Basin and its geology and hydrogeology have been studied extensively beginning with McMurtrey (McMurtrey 1965). The basin is bounded by Precambrian meta-sedimentary rock and filled with over two thousand feet of Tertiary valley fill sediments that are overlain by 100-150 feet of Pleistocene and recent fluvial sediment (Figure 5) (Tallman 2005). The basin floor is dominated by fluvial sediment with isolated deposits of Glacial Lake Missoula sediments mostly along the basin fringe (Geldon 1979, Morgan 1986).

The present drainage system is eroded into these deposits. The valley sits between the Sapphire, the Nine Mile, and Bitterroot ranges with the Clark Fork River bisecting it east to west. The highly conductive aquifer underneath is

the sole source of drinking water for the City of Missoula and has been extensively evaluated for its quality and sustainability as a water resource (Clark 1986; Woessner 1988; Miller 1996). The aquifer occupies the valley alluvium and is bordered at its depth by tertiary sediments. A cross section of the valley at the site is shown in Figure 5.

The Clark Fork River bisects the Missoula Valley and is the primary source of recharge for the Missoula Aquifer. The current mean annual discharge for the CFR above Missoula is approximately 2,000 cfs, with peak discharge of approximately 12,000 cfs in late spring and low discharge of approximately 700 cfs in winter (USGS 2007). The CFR is defined as a losing river, perched 6-12 feet above the aquifer through Missoula to the Reserve Street Bridge, and is influent to the Missoula Aquifer (Woessner 1988). Greater than 80% of the recharge of the aquifer is provided by the CFR as it flows through the valley (Tallman 2005). The river drops by an average of 10 feet of elevation per mile (Woessner 1988).

The Missoula Aquifer is an unconfined aquifer with a saturated thickness of 40-110 feet from depths of 10 to 240 feet below land surface. General groundwater flow is east to west (Woessner 1988; Miller 1996). The near-river water is very young due to the influx of surface water (Clark 1986; Cook 2005). The water table is seasonally 10-20 feet below the land surface in the valley near the CFR. Surface water-groundwater interactions increase with proximity to the CFR and the age of the water in the aquifer increases with distance from the river (McMurtrey 1965, Clark 1986, Woessner 1988).

The Missoula aquifer is divided into three units. The uppermost is Unit One, which is composed of interbedded boulders, cobbles and gravel with silt, sand and some clay interbedded. This unit of the aquifer, where present, is about 10 to 40 feet in thickness. It is fairly productive, with hydraulic conductivity values up to 1,400 ft/d (Woessner 1988), and a porosity of about 20%. Unit Two, which is up to 40 feet thick where present, is composed of tan to yellow, silty, sandy clay, with local layers of coarse sand and gravel; hydraulic conductivity is relatively low in this unit, around 50 ft/d. Unit Three is the deepest most

productive layer, with higher hydraulic conductivities from 1,500 to 10,000 ft/d (Woessner 1988; Miller 1991) materials are interbedded gravels sand, silt and clay. Porosity is 20% and there is a significant vertical hydraulic conductivity. Unit Three is 50 to 100 feet in thickness, resulting in much higher transmissivity.

The CFR generally acts as a hydrologic divide through Missoula with groundwater flow across the valley generally east to west on the north side of the CFR and northeast to southwest south of the CFR (Woessner 1988; Tallman 2006). As the river crosses under the Reserve Street Bridge, it is perched several feet above the aquifer. In the half mile beyond the Reserve Street Bridge, the CFR loses 10 feet of elevation. The river downstream of the bridge is perched above the aquifer only in dry season, and surface water and ground water systems usually intersect in spring (Miller 1991).

Local Hydrogeology

The aquifer beneath Eko Compost has been estimated to be about 130 feet in thickness, and models predict a hydraulic conductivity of about 6000 ft/day (Miller 1991) for the deep aquifer, (Unit Three). The water table is generally twelve to twenty three feet below the ground surface at this site, as predicted by Woessner (1988) for areas of the aquifer near the CFR.

The shallow aquifer at Eko Compost is quite heterogeneous and subsurface flow patterns here vary in direction and velocity (Land and Water 1992). Aquifer materials consist of the coarse gravels expected for the upper section of the Missoula aquifer near the CFR, as well as buried glass, automobile waste, waste wood products, organic debris and flood debris. Sediments impacted by mine wastes transported from upstream areas are also likely present. A representative view of the unsaturated and vadose zone is available in a pit farther west on the property (Figure 6). This outcrop appears to be generally representative of reconstructed well logs (Land and Water 1982; APPENDIX: Well log constructs).

Water Quality

The Missoula Aquifer contains calcium bicarbonate type water, and general water quality is good; microbial and chemical contaminant levels are below drinking water MCLs. Hardness values range from 120 to 160 mg/L $CaCO_3$, which are acceptable drinking water levels. Chloride, sulfate and nitrate increase in the aquifer with distance down hydraulic gradient due to urban activities (Woessner 1988). Trace levels (below drinking water MCLs) of contaminant metals such as copper, arsenic and zinc are present in the CFR and in the regions of the aquifer that are closely associated with the CFR, specifically in areas within a quarter mile of the river (Woessner 1988, Cook 2005).

Arsenic Geochemistry

Arsenate anion, As(V) is the prevalent form of arsenic present in oxygenated waters, but there is a growing body of evidence that arsenite, which is a complex of reduced arsenic As(III), is much more prevalent in ground waters than previously assumed (Mok et al. 1998; Mok and Wai 1994; Moore 1994). Improvements in sample preservation and analytical techniques verify the prevalence of As(III) in ground waters with reducing conditions (Aggett and Kriegman 1988; Korte and Fernando 1991; Masscheleyn et al. 1991; Nagorski and Moore 1999).

Arsenate is stable in oxidized surface waters and is less reactive and therefore less bioavailable than arsenite. The primary mechanism for the toxicity of arsenate is that it acts as a phosphate analog, and may replace phosphorus in bone over time and also interfere with ATP transfer by blocking phosphate binding in the cell (Hughes 2002).

Arsenite is the more labile form of the metalloid. It is available for transport in solution and for biochemical reactions and is therefore the most toxic of the soluble arsenoanions (Korte and Fernando 1991). Arsenite has been shown to react with sulfhydryl groups in cysteine proteins, deactivating the enzymes and increasing the residence time in the body. Acute toxicity measurements for arsenite vs. arsenate are on the order of three times greater, but solubility and

bioavailability affect actual risk associated with each (Hughes 2002). Toxicity is greatly increased (25 to 60 times) in waters containing primarily As(III) vs. As(V) (Korte and Fernando 1991)

Formation of soluble methylated arsenic complexes may affect toxicity characteristics, decreasing the bioavailability of the arsenic. These complexes are formed in biologically active waters where plants are present and nutrients are available. The organically complexed forms DMA and MMA (dimethyl and monomethyl arsenate) are also believed to be less bioavailable since they are more stable complexes than the anions (Ferguson and Gavis1971). These forms are created by organisms as a possible detoxification mechanism (Eisler 1994; Yamuchi and Fowler 1994) and are excreted by mammals as waste products.

Concentration of arsenic in solution is limited by solid phase formation, a process controlled by pH, Eh and reactants. Species present in an oxidizing environment are the arsenate anions $H_2AsO_4^-$ at neutral and lower pH and the doubly charged $HAsO_4^{2-}$ at more alkaline pH values. In reducing environments, the uncharged species of arsenite $H_3AsO_3^0$ is present in waters up to pH 9, where the $H_2AsO_3^-$ anion becomes the predominant species (Figure 7).

The presence of sulfur, manganese and iron complexes can directly affect concentrations and oxidation state of arsenic in solution by adsorbtion and complexation or by affecting redox conditions that affect the chemistry of arsenic. Precipitation of arsenic sulfide complexes and arsenate binding to mineral substrates, primarily iron oxyhydroxides, causes a decrease in available arsenic in solution (Ferguson and Gavis 1971; Manning and Goldberg 1977), while dissolution of arsenic sulfides and arsenic complexed metal oxyhydroxides causes an increase in arsenic in solution (Mok and Wai 1994; Nordstrom and Alpers1999). Figure 8 is a phase diagram for iron and arsenic in natural waters. In general, at higher pH and Eh, iron (oxy)hydroxide (FeOOH) complexes are stable, arsenate is the stable form of arsenic and is adsorbed to the iron oxyhydroxides. At lower Eh values, arsenite is the stable form of arsenic. At low pH and low Eh, iron oxyhydroxides are dissolved as Fe(III) is reduced to Fe(II), and adsorbed arsenite is released into solution. Available sulfides may form

soluble ($AsO(SH)^{2-}$, $H_2As_3 S^{6-}$) and insoluble (As_2S_3 amorphous, As_2S_3 orpiment) arsenic sulfide complexes under reducing conditions (Stumm and Morgan 1996) (Figure 9). Generally, arsenic in groundwater may be present in low concentrations as arsenate. When arsenic is being mobilized in groundwater due to redox conditions, it is present at high concentrations as arsenite.

Iron, sulfate, and organic carbon have direct and indirect effects on arsenic transport involving oxidation/reduction and adsorbtion/dissolution pathways. Table 1 shows several mass action equations for chemical transport mechanisms.

The chemistry of arsenic as it relates to this site is strongly influenced by microbial activity (Bhumbla and Keefer 1994; Nicholas et al. 2003; Oremland et al 2005).This work will address the microbial component in only a general manner. Conditions such as reducing and oxidizing and high or low nutrient content will be referred to without reference to specific microbial components or their mechanisms.

METHODS

Hydrology Field Methods

River stage, water level in wells, and the chemistry of the water were monitored in the effort to evaluate transport and speciation of arsenic at the site. The location of sampling points with respect to the river, the WWTP, compost activities, stratigraphy (via well logs and existing pit excavations) and other sampling points were observed and recorded.

Eleven field measuring events and seven sampling events were performed between January 2006 and September 2006. Maps of the potentiometric surface of the aquifer and chemical data were generated.

Wells

Eight monitoring wells existed at the site. Well logs from Howard Newman Consulting (Newman 1991) show that all wells are 30 feet deep and the 4 inch diameter PVC casing is screened from the bottom to ten feet below the top. These wells were installed in 1991, static water level elevations never reached above the screened intervals of the wells.

Six additional shallow 1 inch diameter wells were added on the floodplain in April 2007, their locations were based on gradients observed on the first seasons potentiometric surface maps. These wells were installed using the Geoprobe with 2 inch diameter steel casing sunk to a level 3 to 12 feet below the ground surface, placing 1 inch PVC with 2 feet of screening (with cuts at 1 inch intervals). Very large cobbles were encountered between 3 and 12 feet below the surface, each well was drilled to the maximum depth attainable. Bentonite was placed around the well bore at land surface. Water was poured into the wells at the time of installation, and rapidly drained, as the wells were completed above the water table at the time of installation, approximately 1 month before high flow.

Additionally, 3 residential wells outside the area, upgradient, on either side of the CFR were monitored for static water levels. One well was equipped with a Global Water level logger from August 2006 to October 2006.

Piezometers

Mini piezometers were driven into the river bottom to evaluate the vertical influence on flow in the backwater of the river and in the White Rock Lake. The piezometers were constructed of 3/4 inch diameter steel pipe 5 feet in length with a conical tip perforated with 1/8 inch diameter holes drilled in the three inch span just below the tip. Water levels were measured inside and outside of the casing, and depth from sediment to water surface was recorded.

Gages

Gages were placed at four points in the CFR, the backwater and White Rock Lake (WRL) in May of 2006. These gages were created by driving long steel fence posts into the bed of the river and attaching a metal ruler. Most locations needed three gages, one each for high, medium and low water. Gage elevations were surveyed and crosschecked by reading water levels off of more than one gage when river surface elevations allowed. Additionally, upstream river stage was measured by dropping a weighted tape off a surveyed point on the Russell Street Bridge (Patel 2004).

Survey

All gages and existing wells and were surveyed in August 2006 using the Trimble Survey Trimmark base station and 5700 receiver with ACU survey controller equipment owned by the Geosciences department. Each point was measured three times with a standard deviation of less than 0.03 feet. Elevations were crosschecked with previous surveys with greater than 98% agreement. Measurements are precise and accurate relative to one another to within .09 feet. Elevations were crosschecked with previous surveys and agreed within 0.2 feet. Error with respect to elevation measurements collected in other studies may be half a foot.

A new survey was completed in May 2007 for the newly installed wells using the Missoula MSOL base station and the above mentioned Trimble survey gear. Elevations of new wells were recorded as well as latitude and longitude data. All wells and gages were resurveyed at this time.

Slug tests were performed for calculations of estimated hydraulic conductivity of the uppermost section of Unit One of the aquifer at Eko Compost (Weight and Sonderegger 2001). A 2 inch diameter slug packed with sand and deionized water was submerged in the well approximately 10 feet below the water surface in each well and static water level was monitored using an in- situ Level troll 500 logger and Win Situ Real Time software. Measurements were taken every 250 milliseconds. The slug was submerged and withdrawn three times at each well, waiting one to two minutes after equilibration for the next perturbation.

Since the wells are screened for the entire depth of the water column, evaluations were performed using the final recovery after removal of the slug and calculated using Bouwer and Rice (1976) equations assuming a porosity of n=0.3.

Lysimeters

Suction lysimeters were placed in the compost yard at varying depths and checked after and during every precipitation event in April and May 2007 (Weight and Sonderegger 2001). The lysimeters were constructed from 2 inch PVC pipe with a micro-porous ceramic cup. A control was placed in my garden. While the garden lysimeter yielded several milliliters of water, no water was found to enter the lysimeters at depths of 6 to 20 inches below the surface at Eko Compost.

Sampling and Analysis Methods

Sampling

Surface water and groundwater samples were collected over the course of seven sampling events from January 2006 through September 2006 at Eko Compost to detect spatial and temporal variations in chemistry and relationships to important redox transitions of, and relating to, arsenic. Representative samples from wells on site and the Clark Fork River adjacent to the site were monitored quarterly for one year beginning January 2006. Additional samples were

collected in late spring and early summer as the hydrology appeared to be heavily influenced at that time by rains and runoff. Control samples from upstream of the WWTP effluent outfall pipe and from the CFR near the effluent outfall pipe were collected, as were compost yard surface and sediment samples. Effluent data from the WWTP monitoring project was included for comparison with site data. Additionally, pilot data was collected from February 2005 through October 2005 and historic data from monitoring by Land and Water dating back to February 1991 were evaluated for comparability. Seasonal data have generally been comparable each year with the exceptions described in the results section.

Surface material, compost and soil and sediment samples were collected at Eko Compost, as well as control samples from the University Lawn near the Clapp Building.

Sampling Technique, Preservation and Preparation

Clean sampling technique for waters according to EPA Method 1669 (U.S. EPA 1983) was practiced. Filtration and preservation took place in the laboratory as described below.

Surface soil, leaf material and compost were collected using a shovel and large plastic bags and refrigerated. Samples were extracted using Milli-Q water and centrifuged. The material did not settle, so samples were left for several days and liquid was decanted and filtered.

Sediment and compost material samples were collected using a large plastic spoon and placed in bags and refrigerated. Samples were extracted with 5% hydrochloric acid (HCl) to evaluate extractable arsenic and analyzed by inductively coupled plasma mass spectrometry (ICPMS) to determine available arsenic.

Wells MW3, MW4 and MW7, which appear to be finished in fine materials with biota present and high levels of contaminants, were pumped for 20 minutes each sampling event using a battery operated submersible pump at 1.5 gallon per minute. To conserve time, wells MW2, MW5 and MW8 which were clear

flowing, low TDS wells with low levels of contaminants, were not pumped prior to sample collection after the first two sampling events. Groundwater samples were collected by submerging the HDPE bailer to one meter below the surface. Two 125 ml wide-mouthed HDPE bottles were filled at low flow to assure the least amount of oxygen introduction in the samples. Samples were immediately placed in a cooler with ice and transported to the lab, filtered using 0.2 micrometer nylon filters and acidified to <pH 3 with Optima nitric acid and stored at 4 degrees C. The pump was decontaminated between wells by submerging in deionized water and running for two minutes.

Analytical

In the field, dissolved oxygen and temperature measurements were taken 25 feet down-well (the length of the cable). Conductivity and pH were taken in the field from a beaker containing the last portion of the bailer sample. Dissolved oxygen was measured in the field with a Global Water YSI 550, which was also used to log temperature. pH was evaluated using an Orion 265A pH meter and 9157BN pH probe. Electrical Conductivity was evaluated using an Orion 0013610 conductivity meter. All meters were calibrated and operated according to manufacturers' specifications. Sufficient time was allowed for equilibration before readings were recorded.

Arsenic Speciation

Determination of arsenic species was carried out using High Performance Liquid Chromatography-Inductively Coupled Mass Spectrometry (HPLC-ICP/MS) is the chromatographic /spectrometric technique that was used to characterize and quantify species of arsenic present in groundwater species readily separated and quantitated by this method are arsenate, arsenite, MMA and DMA (Ritsema 1998; Guerin 1999; Reuter 2003). These are the species most often found in ground waters.

Analyses were performed using a Perkin Elmer Series 2000 LC Pump and Elan DRC-e ICPMS as a detector at mass 75 and mass 91. Two methods were employed beginning with Perkin Elmer 2003, using a phosphate buffer at pH 9

and Hamilton PXRP reverse phase column (PerkinElmer 2003). This method was used for the January and March (unreported) sampling. Results showed decreasing arsenic recoveries over time and required constant recalibration and/or recalculation due to 'salting out' of phosphate compounds in the sample introduction system. Dr. Robert Fisher researched and developed a method using a Shodex Asahipak ES-502N-7C 7.35mmIDx 100mmL porous gel polymer ion exchange column with a citric acid buffer at pH 2 (Martin 2006) that was much more reliable and had the additional benefit of separating MMA(III) and (V) and DMA(III) and (V). This method was used for the remainder of the analyses beginning with June 2006. Detection limits are improved with the new method since signal to noise remains high after several hours of analyses.

Samples were transported immediately to the laboratory in a cooler for immediate filtration and analysis (beginning within 2 hours of returning from the field, concluding within 8 hours) for arsenic species As(III), As(V), MMA and DMA by HPLC-ICP/MS.

Trace Elements by ICP/MS

Trace metals were monitored using Inductively Coupled Plasma Mass Spectrometry (ICP/MS). Total and dissolved arsenic, iron, manganese (substrates for arsenic adsorbtion) and copper, zinc and lead are contaminants that are generated by mining operations upstream and may have been transported downstream in conjunction with arsenic. Group I and II metals calcium, potassium, and magnesium were evaluated for information about reactivity (hardness) and the relationship of the wells to one another, to the surface water (CFR) and to the ground water.

ICPMS analyses were performed on a Perkin Elmer 6100 quadrupole mass spectrometer equipped with dynamic reaction using EPA SW846 modified method 6020 (USEPA 1996).

Anions by Ion Chromatography

Ion Chromatography (IC): Analysis for chloride was performed to evaluate the contribution of WWTP solids to sampling locations. The anions sulfate (SO_4^{2-}), nitrate (NO_3^-), and phosphate (PO_4^{3-}) were analyzed by IC to evaluate

availability of sulfur and nitrogen for complexation and for nutrient availability.

IC analysis was performed on a Dionex ED40 and EP40 Ion Chromatograph using modified EPA Method 300 Analysis for anions (USEPA 1983).

Iron Speciation by FerroZine

Iron oxidation state was determined by dissolved Fe(II) and total Fe analysis by the Ferrozine colorimetric method (To et al 1999) for three sampling events. Redox potentials were calculated from this data.

Ammonia

Ammonia was reported only for sampling events conducted by Land and Water Consulting using EPA method 350.3 (US EPA 1983).

Total Organic Carbon by Combustion

Total organic carbon was analyzed using a Shimadzu Total Organic Carbon analyzer TOC-5000A by EPA method 415.1 (US EPA 1983). Samples were treated with phosphoric acid and purged with helium prior to analysis.

Quality Control

Data were collated and evaluated for quality (precision, accuracy and representativeness. Specific sets of QC criteria were met for each method (APPENDIX: QA/QC). Duplicate analyses, trip blanks and spiked duplicate analyses were performed at a frequency of 25%. All results reported are associated with QC analyses that meet the QA/QC requirements.

Maximum error for all analyses is plus or minus 10%, since the calibration requirements are 90-110% recovery.

Reduced arsenic was spiked into one split of one sample per site visit and evaluated for degradation in transport.

RESULTS AND DISCUSSION: HYDROGEOLOGY

Hydrographs

The runoff event for the 2005 2006 season resulted in sustained elevated surface water elevations in the CFR in April through June (Figure 10). Surface water elevation hydrographs from the United States Geological Society (USGS) gaging station above Missoula were correlated with the site measurements to create a local hydrograph for the CFR at Eko Compost (Figure 11). Highest surface water and static water level elevations in wells were measured on May 24, 2006.

Potentiometric Maps

Potentiometric maps for varying seasons showed flow across the site and the extended hydrologic study area was generally in an east to west direction during the dry winter season and a more southerly direction in summer (in general agreement with maps by Miller (1991) and Woessner (1988)). At its highest measured point, May 25, 2006, the water table elevation at the northeast east edge of the Eko Compost site was 3141.5 feet above sea level, 10 feet above the January 11, 2006 level of 3131.5 feet.

Regional flows from east to west dominated seasonally, as in January, but a local flow regime took precedence at peak runoff season as I will illustrate below. These seasonal patterns were influenced by both the surface water and groundwater exchange with the CFR and the existence of historic backfilled channels across the site. The river did not act as a hydrologic divide after it crossed below the Reserve Street Bridge.

January 2006: Seasonal low water table elevation

On January 11, the water table was well beneath the surface and the bed of the river, around 3132 feet in elevation (Figure 13). The general flow agreed well with Miller (1991), who predicts a general east to west southwest flow in this region at water table elevations around 3130 to 3135 feet above sea level.

Woessner (1988) interpreted this region to have a due easterly influence under the river at this late season water table elevation. At this time the water table is not directly connected with the CFR. Surface water elevations and distant wells were not measured on this date because gages and well locations were not yet established.

<u>May 2006: Seasonal High Water Table Elevation</u>

On May 17, the potentiometric surface map showed that groundwater flow was toward the southwest quadrant of the site (Figure 14) with the general southeast regional pattern of flow and the predicted (Woessner 1988) northward component of flow from under the river. These data were collected three days before peak runoff. CFR was influent to the aquifer upstream and at the site. The water table elevation had risen to near the level of the bottom of the river and surface water elevations were very high. White Rock Lake (WRL) appeared to reflect the water table since there had been little rain, so it was included as a ground water point.

Measurements were collected the following year (2007) for the new wells on the floodplain and corresponding surface water and existing wells. The data were combined based on water table elevation (Figure 15). Surface water elevations did not reach the levels that were reached in 2006; some hydrologic flow patterns may not have been reproduced. Groundwater flow was into the historic channel, and the general northwest flow pattern was confirmed and extended across the southern floodplain.

Piezometers located in the backwater near White Rock Lake showed water levels below the surface water levels and in WRL showed water levels above the surface (Figure 20). These measurements indicated the backwater losing, and WRL gaining on May 20 and 25. Potentiometric maps show that flow is indicated from the backwater incidentally across the WRL and to the north, then meeting up with the channel flow to the northwest.

Measurements from June 8 represent the potentiometric surface of the aquifer as the surface water level receded. A recharge area developed at the site, splitting northward along a diagonal through the compost yard and southward toward the backwater (Figure 16). The local water table elevation had risen above the level of the bottom of the river, and surface water elevations were comparable to local ground water elevations. The gaining reach of the CFR is just beyond this site (Miller 1991), and the southward flow appears to discharge toward the backwater.

Measurements were collected the following year (2007) for the new wells on the floodplain and corresponding surface water and existing wells. The data were combined based on position in the hydrograph (Figure 17). The dates, June 8, 2006 and May 25, 2007, do not agree because the snowmelt hydrograph was decreased from the previous year. Ground water appears to flow from the historic channel, and was confirmed by the 2007 data toward the backwater and crossing the historic (quarried) floodplain.

The WRL may not have reflected ground water elevation due to a large amount of recent precipitation, 1.47 inches on the previous day with a total of 2.7 inches the previous week. The pond may have been leaking to the aquifer rapidly and causing a small hydrologic divide in the area. The map was contoured without WRL but a broken line represents the divide area visible when WRL is included as a data point.

Surface Water and Groundwater Distinction

CFR Upriver, CFR Backwater and White Rock Lake

Water table elevation measurements from wells were plotted with the local hydrograph (Figure 12), showing that the groundwater elevation and CFR surface elevation are closely related. Well water levels are plotted against the CFR Backwater and White Rock Lake (WRL) surface water levels (Figure 18) to illustrate the relationships further. White Rock Lake is an excavated pond near MW4, MW5 and the backwater. All wells showed good correlation with WRL,

which indicated that the pond was a reflection of groundwater. MW7 and MW8 elevations sampled at peak runoff season fall closer to the CFR line. WRL also showed a closer correlation with CFR and the upriver gage, indicating that it was linked to the river more closely than any of the wells. Chemistry confirmed these observations as described in the next chapter.

Static water level elevations in wells located near the river showed good correlation with the upstream hydrograph except MW7 and MW8, which showed better correlation with the CFR backwater.

MW5 and Seep 5

MW5 is near an abandoned lagoon (Seep 5) that fills with groundwater from the rising water table during the spring runoff season (Figure 19). Elevations from the seep are not included in the plots due to the temporary nature of the pond and difficulties in surveying related markers, but chemistry was evaluated and included below for the dates that the seep was present.

This seep appeared to reflect water table elevation, but the surface water chemistry was very different from that in the groundwater due to sludge and waste artifacts congealed on the surface of the bottom of the seep.

Interaction of the River with Area Groundwater

Mini piezometers were placed in the river and backwater and lake to evaluate the vertical gradient of the subsurface flow at the time of runoff as described in the methods chapter. The head elevation of the piezometers in the backwater was lower than the surface water elevations, while head elevations in WRL were higher than surface water elevations (Figure 20).

As discussed in the previous section, piezometer study results indicated the river was losing in the spring at times of high surface water flow, and the nearby pond was receiving groundwater seepage. The WRL reflected ground water elevation in mid May and the river was visually at an elevation close to the elevation of the WRL (Figure 21).

Near-River Wells

Connectivity during the runoff season was evaluated by comparing the static water level elevation in the new (2007) shallow floodplain wells with river stage elevation nearby (Figure 22). Although water table elevations at peak runoff in 2007 did not reach the levels of the previous year, a direct connection with the aquifer developed slowly as the level of the rising water table rose above the level of the river bed.

Hydraulic Conductivity

Hydraulic conductivities (K) were estimated from slug tests performed in wells MW1, MW 2, MW 5, MW 7, and MW 3. MW 3 testing results were inadequate to establish a K value. This may be due to significant amounts of biota and particulate matter in the well. MW 4 has had historically high total dissolved solids (TDS) averaging 400mg/L and total suspended solids (TSS) averaging 40mg/L and a slug test was not attempted due to the presence of large scales or 'skins' of biota (probably iron respiring bacteria) that could clog the screens and contaminate the instruments.

Well Id	MW1	MW2	MW5	MW7
Calculated K	1950 ft/d	1100 ft/d	1700 ft/d	1080 ft/d

Slug tests may generate slightly lower estimates of hydraulic conductivity than actual values(Butler 2003) due to the conditioning response of the well. I have only measured response in the upper 10 feet (Unit One) of the approximately 100 ft thick (including Unit Three) aquifer. These values are best used to compare and contrast general hydrologic conditions between other wells on the site.

Drilling records (Newman 1991) indicate that several wells appear to penetrate layers of fine material which may be the organic layers that are remnants of the backfilled sludge ponds (Land and Water 1992). Well 7 is located in an historic sludge pond area, and has a slightly lower K value than those that are finished in the undisturbed aquifer materials. Wells 3 and 4 are also located in historic pond areas.

RESULTS: CHEMICAL DATA

Arsenic Speciation Analysis and Related Chemistry

Overall water chemistry and geochemistry have been evaluated in order to describe the behavior of arsenic at this site. Chemistry results are presented in this chapter and discussed further in the following chapter in conjunction with the hydrogeology. Samples were collected at Eko Compost on January 11, March 24, May 24, June 13, July 10 and September 22 of 2006.

Results for dissolved arsenic for each well over the duration of the monitoring period are presented in Figure 23. Results for related chemistry (Figure 24, Figure 25 and Figure 26) were evaluated over time by location from the Clark Fork River northward.

Arsenic and related chemistry by location

Arsenic concentrations in the CFR adjacent to the study site ranged from 1ug/L to 4.5 ug/L. Speciation of arsenic in the Clark Fork River was primarily As(V) with less than 10% As(III) as was expected for oxygenated surface waters (Ferguson and Gavis 1971). However, in July as stream flow decreased and algae appeared, the ratio of As(III) to As(V) increased to more than 10% and trace amounts of methylated complexes and arsenocholine (AsC) were present in June through September (Figure 27). Dissolved oxygen, nitrate, sulfate, arsenic and chloride decreased in spring and increased through the summer. Iron and total organic carbon (TOC) increased in May and decreased slowly through the summer (Figure 29).

The WRL, which was at most times a reflection of groundwater, showed between 1 ug/L and 3.5 ug/L arsenic during our sampling period. As(V) was the primary form of arsenic until July (Figure 28). At this time, As(III) and DMA were present at the detection limit under much more reducing conditions. Dissolved oxygen, nitrate, sulfate arsenic and chloride decreased in spring and increased much more slowly through the summer. Iron and TOC increased in May and

decreased through the summer with elevated iron (100 ug/L) again in September.

MW4 indicated reducing conditions that did not vary seasonally. MW4 contained As(III) almost exclusively (Figure 29), at levels from 2 to 8 ug/L, with the highest levels of arsenic found in May. The less than 5% As(V) could be an artifact of oxygenation during sampling. High levels of iron were characteristic of this well. There was no detectable nitrate or dissolved oxygen, sulfate and TOC dropped beginning in March and May respectively and chloride rose slightly through the summer, but was found at relatively low levels of 10 mg/L.

MW3 showed low levels of arsenic from 1 to 5 ug/L, with partial reducing conditions in winter and at low water table elevation, and primarily reduced conditions through summer with more oxidized As(V) present in July and early fall (Figure 30). Winter and summer looked the same with fall and spring showing more oxidizing conditions. Iron was high in winter, low in summer, ranging from10 to100 ug/L. Chloride was low in summer while TOC and sulfate were elevated and then decreased in summer, while low levels of nitrate showed the opposite trend. Very little dissolved oxygen was present.

MW7 indicated complete oxidizing conditions in winter at low water table elevation (Figure 31) and complete reducing conditions in summer at high water table elevation. Levels of arsenic varied from10 ug/L in winter to over 100 ug/L in spring. A discussion section later in this chapter is dedicated to the mechanisms of redox chemistry, hydrogeology and arsenic in this well. Iron increased in summer, chloride, sulfate and TOC spiked in May, then decreased, while nitrate showed the opposite effect.

MW5 had low arsenic, around 2.5 to 3 ug/L, and it was all As(V) (Figure 32). Generally, iron was low, chloride, nitrate sulfate and TOC increased until July and then decreased. Dissolved oxygen was above 3 mg/L in May and then decreased in spring and summer, recovering to about 2 mg/L in September.

MW5 Seep (Seep 5) appeared during the months of May and June. In May there was some biological activity, algal growth and a sulfur smell likely due to microbially induced sulfate reduction, and reduced arsenic. This was believed

to be a surface phenomenon, as there was a large amount (25 mg/L) of TOC in these waters due to rotting vegetation and possibly WWTP solids. High chloride, nitrate and phosphate present in May to June may have influenced the quality of the water in MW5 .

MW8, although detectable levels (5 to 10 ug/L) of arsenic were present in the dissolved acidified fraction, this well did not show enough arsenic to analyze for redox state on the dates collected. This may be due to the interaction of unacidified sample matrix with the mobile phase used in the HPLC method or with the sample bottle. In winter at low water table elevation, MW8 showed elevated levels phosphate, nitrate, chloride sulfate and low levels of iron. Concentrations dropped slightly during summer and recovered in fall. This well was difficult to sample due to large amounts of solid waste being deposited in the area surrounding the well on several sampling dates.

Well MW2 represents a control for groundwater samples, since it is not affected by the system under observation. MW2 showed less than 2 ug/L arsenic. Sulfate and nitrate were elevated, but dissolved oxygen was present, and iron was very low. MW2 was questioned as a control when it was noted that bags of fertilizer had been stored above the well, but the contamination was limited to nitrogen, and the well was deemed representative of downgradient flow for general chemistry other than that associated with the fertilizers stored at the land surface. Additionally, access was complicated due to the temporary storage of large amounts of refuse in the area immediately surrounding the well. MW1 was not sampled since Land and Water Consulting had discontinued sampling because results had never shown detectable (greater than 2.5 ug/L) levels of arsenic historically.

Compost material extraction showed detectable levels of arsenic (Table 3). The finished compost that lies on the surface for long periods of time contained .011 mg/kg extractable arsenic resulting in a concentration of 0.065 mg/L arsenic in the associated water extract. This is not believed to affect the saturated zone as discussed later in the text.

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Sediment leachate analyses showed an elevated level of arsenic (Table 3) in layer three, the gray overbank sediment, which contained ten times more arsenic than layer one (yellow sediment) and the background soil (Clapp Building lawn). Arsenic concentrations in layer two and the compost finished product were five times above the background soil levels. These values are for extractable arsenic, which is a low biased value compared to digested sediment values. Therefore, it is likely that the gray sediment falls above the normal range for background representative soils (0.1 to 55 mg/kg) and sediments (0.6 to 50 mg/kg) (Smedley and Kinniburgh 2002).

Control samples from upstream of the WWTP effluent (CFR Above), and from the CFR near source of effluent (CFR Below), both show less than 2 ug/L arsenic, and oxidizing conditions (APPENDIX: Water and soil chemistry data). CFR below shows elevated chloride (5.7 mg/L) and nitrate is present at a low level (0.35 mg/L). Arsenic values for the two control samples above and below the effluent agree within 2%, but results from three hundred feet upstream are at or below detection limit for chloride and nitrate.

Calculation of redox potentials

Redox potential values (pe) have been calculated using mass balance equations (APPENDIX:Redox Potential) and are presented in Table 2. According to the solubility diagram for arsenic species (Figure 7), for natural waters between pH 6 and 7, the pe value for a reducing environment should fall below a value of 1, and for an oxidizing environment the pe should be greater than 1. This is generally the case when the As(III)/As(V) pairs are used to calculate pe based on the pH of the sample and the pe^0 for the redox half reaction. This does not hold true for calculations using the Fe(II)/Fe(III) pairs, indicating that iron does not control the redox potential in this system. It should be noted that, although the arsenic pairs appear to reflect the redox environment in these wells, it is not likely that they are the primary drivers the of the redox potential of the systems.

DISCUSSION: CHEMISTRY AND HYDROGEOLOGY

<u>Hydrologic maps combined with chemistry contours</u>

The results from the hydrologic study were combined with the results from the soil and water sampling and chemical analyses. Chemical contours in addition to the hydrogeologic potentiometric surface contours provide a conceptual model of interactions between the groundwater and the surface water as well as ground water interaction with aquifer materials in which the wells are finished. These maps show the seasonal variations of the chemistry of each well when the groundwater beneath the site was influenced primarily by the regional aquifer flow or by the influx of surface water of the river to the east and south of the site. When the water table elevation was lowest and the regional flow regime governed flow, the chemistry of the water was influenced by the rest of the aquifer. During local flow high stage regime, the chemical concentrations and reductive/oxidative chemistry of the water were influenced primarily by the geochemistry of the newly saturated sediments.

<u>Chemistry at seasonal low and seasonal high water table elevation</u>

January: The chemical characteristics of the aquifer at the lowest water table elevation (January) are plotted over the site map in Figure 38Groundwater flow at the site reflected the regional flow pattern of the aquifer at this time. The presence of arsenic was consistent across the site. A chemically reducing plume appeared from MW4 in the direction of groundwater flow, reaching to MW3. Arsenic was present in its reduced form at Wells 3 and 4 and in oxidized form in MW7 and MW8. Other reducing actors were present at consistent levels across the site except that MW4 showed high iron (5 mg/L or 5000 ug/L) and reducing character (100% As(III) with 4.4 ug/L present) and MW3 also showed 92% As(III) with 6.2 ug/L arsenic present. Chloride was elevated at MW3. Compared to other months, there was a medium level of sulfate across the flownet, and nitrate was elevated at the eastern border of the site and slightly elevated at MW2; this is an anomaly due to surface contamination as discussed in the previous section.

Chloride concentrations were highest at MW3 and lowest near the CFR and WRL, TOC was consistent around 10 ug/L across the site.

May: The runoff event, discussed previously, was reflected in the May 25 data set, showing the highest elevation of the water table (Figure 35). The groundwater flow lines for this sampling date showed the regional east west component with the local flow northward from the river. The static water level elevations were very high for this sampling event and chemical concentration contours of TOC, sulfate, and reduced arsenic indicated that the water table had reached an elevation that allowed flow into a buried channel. Maps presented in the previous chapter confirm flow into the historic channel.

Influx of river water from the south and east was corroborated by similarities in well chemistry to the CFR chemistry. WRL reflected CFR chemistry at this time as well with low nitrate and chloride concentrations probably due to dilution of the WWTP effluent from runoff and precipitation. Arsenic and iron were present in very high concentration in MW7 (due to the properties of the sediments combined with the reducing environment as I will discuss in the Redox Pump section in the next chapter). MW7 showed high levels of chloride, sulfate and TOC that may indicate ground water flow through organic rich backfilled channels that served as sludge lagoons. Nitrate concentrations dropped off at this time, probably due to the reduced environment in the well. Data from well MW8 were not collected due to inaccessibility of the well for sampling.

There was no apparent connection between MW4 and MW3 for the May sampling event. The reducing plume seen in January along the groundwater flow path was not present. The flow lines from the May 17 potentiometric map indicate that the flow path to MW3 did not cross MW4 or MW7 in May.

Chemistry during changing local groundwater flow regime

June: June 13 (Figure 36) showed an overall change in the local flow regime with the split flow headed toward the backwater to the south as discussed in the hydrogeology section. The concentration of arsenic in MW7 was decreased and the position of the reducing plume was shifting. Chloride levels

decreased along with the direction of flow of clean water from the river. Sulfate and iron had migrated to MW4 and WRL. MW7 showed lower levels of chloride, sulfate and TOC in a delayed response to the CFR levels of these nutrients dropping in May. March data for MW7 and CFR were very similar as was June data, indicating a return from the anoxic, reducing local channel influence to the larger regional flow system.

A direct connection developed following the flow lines from MW4 to WRL and to MW5 and the seep for reducing potential and sulfate, which appeared to have a high concentration centered in the trough of the old channel along with TOC which still increased northward. MW5 had high nitrate concentrations possibly due to the associated seep.

July: Arsenic concentration on July 10 was still high (60 ug/L) due to the reducing environment of MW7(Figure 37).There appeared to still be some association between MW7 and MW4, but there was less association between MW3 and MW4. In MW3, As(III) represented 58% of the total concentration of 2.02 ug/L. The reduced plume was from MW4 to WRL, centering on the historic channel even though regional flow dominated. Arsenic concentration in WRL was high with 90% of the 7.6 ug/L arsenic in the reduced form. Methylated species were also present at this time. Nitrate levels were still very low at the eastern border of Eko Compost and elevated in the CFR and the Seep at MW5. Chloride concentrations remained lower, with levels centered in the old channel ravine.

Chemistry as regional groundwater flow regime returns

September: Measurements from September 20 showed the arsenic and iron returned to baseline values at MW7 and redox conditions returned to oxidizing with nitrate present (Figure 38). TOC concentrations were greatly reduced and centered at MW3, possibly because the water table elevation had dropped below the trough of the old canal and lagoons. Chloride levels were also lower in concentration and centered at MW3 implying that the old channel/lagoons may have been a source of chloride. The redox plume from MW4 lost its influence and was receding, but 56% of the arsenic present was in

the form As(III) reduced arsenic and 27 ug/L of iron remained in WRL. The gradient was reduced and the system appeared to be returning to steady state. Dissolved oxygen in MW5 was recovering slowly toward its steady state value of about 3 mg/L.

<u>Summary of regional flow regime to local flow and flow patterns during aquifer recharge</u>

In January, the water table sits below the historic channels and there is little influence of the local flow regime on the general chemistry except for a high chloride value centered at MW3. The shape of the historic channel diagonally bisecting the compost yard was outlined in spring by the reducing plume and the TOC, nitrate and sulfate concentration contours in May.

The aquifer was recharged and equilibrating with surface water during June and July. The steady state flow from west to east returned although the high water table elevation was still allowing local flow. The historic channel diagonally bisecting the compost yard was still visible in the contours for all chemistry parameters

By September the water table was dropping below the level of the historic channels and returning to regional flow. The shape of the historic channel diagonally bisecting the compost yard was no longer visible in the contours for contaminant chemistry, but concentrations were decreased from previous months.

Discussion: Chemical Mechanism of Arsenic Solublization

<u>Redox Pump</u>

During this study, MW7 showed an elevated concentration of arsenic when the water table was at its highest elevation in spring of 2006. Samples collected May 25 show more than 100 ug/L dissolved arsenic, with subsequent samples in June and July showing about 60 ug/L dissolved arsenic. These results are an order of magnitude higher than previous arsenic concentrations in

this well. The model of a 'redox pump' (Moore 1994) described above in the arsenic geochemistry section appears to fit this MW7 environment.

The seasonal position of the water table relative to contaminated layers in the saturated zone may contribute to high levels of arsenic in the groundwater (Figure 39). Arsenic is present in the gray sediment layer at a relatively high leachable concentration of 45 mg/kg (Table 3). It is most likely present as As(V) adsorbed to iron oxyhydroxides present in the sediment. As the water table rises and saturates the gray sediment layer, amounts of arsenic may be liberated from the more contaminated sediment layer. If a reducing environment is created, as in the case where the well is finished in the area of the historic sludge ponds/channels, the Fe(III) oxyhydroxides are dissolved when Fe(III) is reduced to Fe(II), and reduced As(III) is liberated.

The area at well location MW7 served as a waste lagoon before being backfilled in the 1980s (Figure 4). Fine organic layers lie at the bottom of the pond remnant area, as discussed in the site description. The water table appears to have saturated this layer at MW7 as well as the contaminated sediment layer during the spring recharge season. Other substrates that become present in the aquifer as the water table rises, such as organic carbon, nutrients and bacteria, provide fuel and means for reduction of iron(oxy)hydroxides and solublization of Fe(II) and As(III) as discussed in the Arsenic Geochemistry section of this paper.

Sources of Arsenic and Nutrients Facilitating Transport and Mobilization

Buried sediments are the proposed source of arsenic that was mobilized in this system. Leachate from a possible flood deposited sediment layer yielded a significantly higher amount of arsenic than any of the other soils or sediments tested (Table 3), indicating that arsenic was present at elevated levels in the buried flood sediments. Other possible sources of arsenic are summarized in Table 4, along with possible sources of nutrients and likely pathways to conditions required for arsenic mobilization via this mechanism.

All wells at the site, except MW1 and MW2, likely penetrate this layer of sediment and all of these wells showed detectable levels of arsenic in spring

when the water table elevation corresponded with buried sediments. The wells are located in areas with differing lithology. MW3 is finished near or in the historic channel. MW4 is finished in a reducing environment which may be influenced by buried waste including sludge from one era and automotive parts waste from another era (verbal communication Terry Munnerlyn). This well appears to have functioned as a redox pump, seasonally liberating large amounts of arsenic until about 1994, when arsenic concentration leveled out. MW5 is finished next to an abandoned sludge lagoon that fills with groundwater in the spring and MW7 and MW 8 were finished in backfilled sludge lagoons.

Conditions Contributing to the Development of the Redox Pump at MW7

Analyses for arsenic in MW7 have been performed biannually since 1991. Groundwater sampled from MW7, MW4 and MW8, contained similar concentrations of arsenic each spring from 1991 until 1999, when MW7 showed a tenfold increase in arsenic concentration, and since 2004 has showed elevated levels of arsenic each spring (Figure 40).

Historic data for MW7 were analyzed for relationships between arsenic and other chemical parameters. Static water level elevations in MW7 did not correlate well with concentrations of arsenic over time (Figure 42). There is not a direct relationship between the elevation of the water table and the availablilty of arsenic. TOC and ammonia levels are elevated along with arsenic, but were also elevated at MW7 throughout the monitoring period previous to 1999, suggesting they were not limiting factors for the enhanced arsenic solubility seen since 1999. Comparisons of analytical parameters arsenic, iron, manganese and, biochemical oxygen demand (BOD) after 1999 showed a very good correlation (Figure 40). In summer, iron increased in solution along with arsenic. and the BOD levels decreased below detection limit, inferring anoxic activity and coliform levels may have increased dramatically. Phosphate is present in June of 2004, 2005 and 2006. Results for Total Coliform test (Land and Water 2006) were below detection limits each summer from the early 1990s until the summer of

2004, when they were not reported. Data for 2005 and 2006 were not reported and a level of 214 COL/100ml was reported in summer of 2007.

According to my potentiometric surface maps, groundwater flow during May and June, when arsenic levels were highest, reaches MW7 from directly under the WWTP (Figure 41). Holding tanks were upgraded and sealed at the WWTP in 1999, and between 1999 and 2004, the Missoula WWTP completed a transition to the highly effective Biological Nutrient Reduction process, which has resulted in a much cleaner effluent stream (Figure 45). This process involves both an oxidative and reductive process for the removal of nitrogen from the waste stream. Phosphate levels are extremely high (500 to 800 mg/L) in the media resulting from this process. There is a variable 'swing zone' area in the building that houses aerobic processes in winter and anaerobic and anoxic processes in summer (City of Missoula 2000). The waste product of this process is anoxic and anaerobic and contains high levels of phosphate. Any leakage or drainage from the process when the water table elevation is high (in spring) may have generated a reducing plume, containing low oxygen, anaerobic bacteria or microbes and possibly dissolved phosphate, in the local groundwater. This plume would provide dramatically reduced groundwater conditions down-gradient at nearby MW7, enhancing the efficiency of the redox pump after 2004.

There are several possible pathways for the reduced media to reach the groundwater. The two most readily apparent sources would be 1) from the BNR cell itself about 300 feet upgradient of MW7, which is lined in concrete 1.5 feet thick and extends to approximately 15 feet below the land surface. At high flow on May 17, 2006, when 160ug/l arsenic was present at MW7, the water table was approximately 12 feet below the land surface. 2) Runoff from the centrifuge and solid waste area, where the highly organically and biologically enriched media is centrifuged and the solid phase (sludge) is prepared for transport and the supernatant liquid is piped away. Storm drains are present in this area, and quite a lot of hosing and washing of sludge takes place here.

Mass Balance Estimation for Efficacy of Redox Pump

For the sections of aquifer surrounding MW7 and MW4, calculations were performed to determine the amount of time it would take for the arsenic sequestered in the sediments and sludge to be displaced by the passage of groundwater through the sediment layer (Table 5). Simplifying assumptions have been made in order to create general scenarios for transport of arsenic through the sediments under reducing and non reducing conditions.

The section of aquifer beneath MW7, containing the contaminated sediments and remnant sludge would require approximately 100 years for the groundwater to displace all of the arsenic present in the sediments under the conditions found in the well prior to 1999, at a capacity of 0.01 mg/L of arsenic in the groundwater at that location in spring. However, only about 15 years would be required to displace all arsenic present in the sediments at the current capacity of 0.1 mg/L of arsenic in the groundwater in spring. Beneath MW4, reducing conditions have been constant since prior to 1990 (Figure 44). Calculations indicate that it would take roughly 40 years for the section of aquifer to wash out adsorbed arsenic from contaminated sediments assuming that the water carried 0.05 mg/L arsenic initially, to 200 years at the current capacity 0.01 mg/L arsenic currently during the summer months. The process of mitigation may have already taken place, as detected levels of arsenic were considerably higher, approximately 0.08 mg/L in 1990, and have decreased over the monitoring period.

All of these calculations are approximate and are meant to give a general idea of the time scale for movement of this level of contamination from the sediments under varying conditions[1]. Seasonal flows vary, and changes in

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[1]In calculating the time for the displacement, I consider that the water table only reaches the contaminated layer of sediment for two to three months during the spring. I assumed that the primary source for arsenic was the gray sediment layer. Data from a single analysis was used, a value of 45mg/Kg arsenic. I chose a representative seasonal value of arsenic in groundwater for each scenario in time based on Land and Water sampling analysis results (Land and Water,

hydraulic gradient can cause changes in flux of arsenic. The concentration of arsenic in the groundwater varies more widely than represented here. Also, the representative sample may over or under-represent the true concentration of arsenic in the sediments in these areas. Still, it appears that the time period for removal of the arsenic in the sediments in these areas is on a scale of tens to low hundreds of years.

2007), these values were 10 ug/L arsenic and 100ug/L arsenic for each well. The previously calculated hydraulic conductivity of around 1000 ft/day was used for both wells and the hydraulic gradient (dh/dl) for the surface of the water table was measured using the six potentiometric surface maps from the summer months. The lowest of the calculated values for dh/dl were used for both areas, MW7 was in a higher hydraulic gradient (lower velocity) area than MW4 (Appendix F. Arsenic mass balance worksheet).

CONCLUSION

At this site, interactions of surface and groundwater have been mapped and evaluated with respect to seasonal change and chemical character. A conceptual model for the transport of arsenic at Eko Compost is presented showing the connection between the surface water, groundwater and the sediment layers as well as the compost at the land surface and the water treatment process effluent (Figure 46).

There was little observed or documented connection between the compost activity on the surface and the groundwater. The chemical character of the water was influenced primarily by where it came from vertically, and also by where it came from laterally. The vertical component, the layer of the sediment that featured the top of the water table, changed seasonally with water table elevation. In spring, the water table rose to saturate contaminated sediments and elevated concentrations of contaminants were released. Laterally, the water at the site was influenced by its origins up-gradient in the aquifer either from underneath WWTP to the east or CFR to the east and the south and by shallow aquifer materials encountered by aquifer flow.

An effective 'redox pump' at monitoring well 7, located at the up-gradient edge of the compost yard in a backfilled sewage sludge lagoon, caused a seasonal spike in arsenic, concentrations of up to 0.17 mg/L, in the groundwater. Local hydrologic phenomena combined to make this mechanism effective: a vertical component as the aquifer rose to access the source of contamination in the sediment, and a lateral component to supply the fuel for the transport mechanism in the form of a reducing plume from up gradient in the aquifer. Another area of the site beneath MW4 appeared to have self-remediated by the same mechanism over the last 50 to 100 years. Results from down gradient monitoring wells indicated that the phenomenon was specific to that point location, and did not migrate or pose any direct risk to the aquifer in its present use.

The source of arsenic in the groundwater underneath Eko Compost appeared to be the buried sediments, and did not appear to be the surface compost materials or the sewage sludge. My data and that of other researchers indicate that neither the CFR, the local groundwater or the WWTP process effluent were the source of arsenic.

A source of organic material and drivers for reducing chemistry was required for the solubility and transport of arsenic. The buried sludge on the property may have provided an organic carbon to fuel redox reaction, but groundwater in the area of MW7 appeared to also be under the seasonal influence of a strong reducing plume since 2004. Hydrologic data suggest that the source of this anoxic groundwater is up-gradient in the aquifer and is likely related to the recent implementation of the BNR process at the waste water treatment plant.

In order to investigate the source of this reducing media, one could assess the path of the plume by placing more wells along the seasonal groundwater path. The distance may be very short if the source is nearby due to the enriched sludge or supernatant at the centrifuge and waste transport area, or the source may be up to 300 feet up-gradient where the new anoxic-anaerobic reaction cell is located. Results from down gradient monitoring wells show the results to be specific to that point location, contamination did not migrate further or pose any direct risk to the aquifer in its present industrial use.

As expected based on Woessner's (1988) report, hydraulic conductivity estimations for areas of the yard were generally around 1100 ft/d and higher near the river, but lower in contaminated areas. Regional flows across the site appeared to move seasonally as predicted with a primarily west northwest component in winter and southwest split in summer. The connection of the river with the local aquifer at Eko Compost appeared to be more direct in spring, and a complex local flow regime emerged during this time of year. Interpreted local flow directions were supported by groundwater chemistry.

Tables

Table 1 Chemical mass action equations for arsenic in the aqueous environment.

These are some relationships directly affecting arsenic availability in the field environment. Adapted from Moore 1994.

Oxic Conditions

Diagenetic minerals (pyrite) are oxidized, releasing sulfate and free metals at near neutral pH.

$$2FeS_2 + 7O_2 + 2H_2O -> 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$
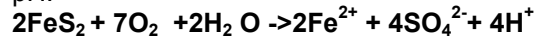
This reaction is facilitated by bacterial activity.

Metals from the first reaction are oxidized forming Fe (and Mn) oxyhydroxides which scavenge the freed arsenic.

$$2Fe^{2+} + 10 H_2O + O_2 -> 4Fe(OH)_3 + 8H^+$$
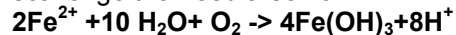
Arsenate tends to adsorb to Fe(III)(hydr)oxides under alkaline oxidizing conditions,

Organic matter (algal cell general formula) if present is oxidized, releasing cations, nitrate, phosphate

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 + 122CaCO_3 ->$$
$$228HCO_3^- + 16NO_3^- + 122Ca^{2+} + 16H_2O + H_3PO_4$$
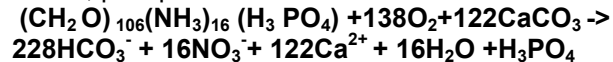
Reducing conditions

Under reducing conditions, the Fe(III)oxides are reduced and dissolved, releasing Fe(II) and adsorbed arsenic into solution as As(III) (arsenite).

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 424FeOOH + 758Ca^{2+} + 652HCO_3^- \rightarrow$$
$$758CaCO_3 + 424Fe^{2+} 16NH_4^+ + 16 H_2O + H_3PO_4$$

In the presence of sulfate

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{-2} ->$$
$$106CO_2 + 16NH_3 + 53S^{2-} + 106 H_2O + H_3PO_4$$
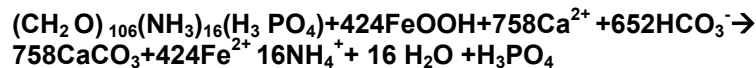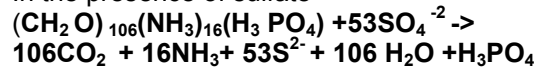
organic matter is reduced, releasing ammonia, carbon dioxide, sulfide, phosphate

$$Fe^{2+} + H_2S \rightarrow FeS + 2H^+$$
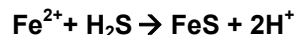
The freed iron is precipitated out as FeS (mackinawite)

In the absence of sulfate, methane is generated

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow$$
$$53CO_2 + 16NH_3 + 53CH_4 + H_3PO_4$$
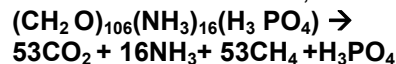
Table 2 Redox Potentials Calculated from As(III)/As(V) and Fe(II)/Fe(III) Pairs.

Redox potentials calculated for the arsenic pairs changes from less than 1 (<1) to greater than 1 (>1) for wells that show reducing character seasonally.

		pH	As(III) ug/L	As(V) ug/L	pe for arsenic couple	Fe(II) ug/L	Fe(III) ug/L	pe for iron couple
MW3	Oct 20 2005	7.1	1.12	0.98	**0.15**			
	Jan 11 2006	7.04	3.2	0.27	**-0.27**	22	.0001	**-10.1**
	March 24	7.2	2.96	0.71	**-3.89**	139	396	**-4.7**
	June 14	6.4	3.043	0.514	**0.84**			
	July 12	7.55	1.95	0.87	**-0.68**			
	Sept 20	6.36	0.6	0.9	**1.37**			
MW4	March 10 2005	6.46	10.75	0.57	**0.50**			
	Oct 20 2005	6.5	4.2	0.43	**0.58**			
	Jan 11 2006	6.71	3.89	0.005	**-0.69**	825	.001	**-8.9**
	March 24	6.70	6.03	0.2	**0.04**	1319	5071	**-2.4**
	June 14	6.28	5.73	0.2636	**0.74**			
	July 12	6.46	5.23	0.005	**-0.37**			
	Sept 20	6.5	3.61	0.26	**0.50**			
MW5	May 24							
	June 14	6.8	.005	2.73	**1.99**			
	July 12	7.43	.005	2.73	**.99**			
	Sept 20	6.81	.005	2.36	**1.95**			
Seep5	May 24					29	2	**-6.4**
	June 14	7.17	0.139	2.88	**0.73**			
	July 12	7.17	0.005	3	**1.46**			
MW7	March 10 2005	6.9	0.05	6.35	**1.53**			
	Oct 20 2005	6.9	1.2	6.1	**0.83**			
	Jan 11 2006	7.1	0.005	2.51	**1.66**			
	March 24	6.9	0.005	3.34	**1.89**	11	.0001	**-9.4**
	June 14	6.5	69.41	2.76	**0.37**	34	3	**-4.2**
	July 12	6.26	44.84	0.65	**0.52**			
	Sept 20	6.95	0.7	6.5	**0.88**			
MW8	June 14	6.76	0.005	6.11	**2.23**			
	July 12	6.95	0.005	5.2	**1.91**			
WRL	March 24	7.5	0.187	1.25	**-0.18**	13	.0001	**-11.2**
	June 14	7.06	0.6318	2.86	**0.56**	26	.0001	**-10.6**
	July 12	7.1	1.97	0.24	**-0.28**			
	Sept 20	6.5	1.4	1.1	**1.02**			
CFR								
	March 24	7.70	0.01	1.812	**0.40**	27	1	**-8.1**
	June 14	7.81	0.3106	3.91	**-0.34**			
	July 12	7.73	0.65	3.36	**-0.41**			
	Sept 20	7.12	0.08	0.86	**0.66**			

Table 3 Solid Samples Trace Element Analysis.

Surface Materials Water Extractable	As (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Cu (mg/kg)
Stage 1 Compost	.011	Non detect	.847	Non detect
Yard Waste	.002	Non detect	3.60	Non detect
Leaves	.0002	Non detect	.738	Non detect
Sand	Non detect	Non detect	Non detect	Non detect

Surface Materials and Sediments Leachable in 5% HCL	As (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Cu (mg/kg)
Layer 1 Yellow Sediment	5.3	0.58	.4	Non detect
Layer 2 Woody Debris	11.4	2.60	.56	0.09
Layer 3 Gray Sediment	45.5	8.52	1.17	0.68
Compost Yard Material	1.94	7.50	0.59	0.17
Geology Lawn	5.0	3.56	.37	0.02
Final Mix	10.9	4.56	.43	0.16
Sludge (From WWTP Lab Results 2002)	5.0	----	----	653

Table 4 Summary of Possible sources and evidence for the availability and transport of arsenic

	Arsenic	Nutrients	Transport
WWTP effluent	Below detection limit <1ug/L.	Nutrient levels have decreased since 2004, effluent chemistry has become more oxidized. Nitrate levels have increased slightly (from 6 mg/L to 12 mg/L), but total nitrogen (from 40 mg/l to <5 mg/L) and ammonia have dropped off dramatically since 2004 (Figure 45). Chloride is not used in the treatment process and should not be a tracer for the waste water treatment process. Samples drawn above and directly below the effluent tube showed an increase from below 1 mg/L to 2 mg/L. The CFR sampling point that day showed 2mg/L.	Surface water Ground water
CFR below effluent	<2 ug/L The same amount of arsenic below effluent tube as above.	Only nitrate and chloride slightly higher (5PPM) likely due to the municipal water source being higher- also sodium and potassium. The total nutrient load in the river downstream of the effluent should be no greater than background plus 1/100 of the values in Figure 45 based on the percent effluent in the river calculated in the introduction. these values generally fall well below any MCLs.	Surface water Ground water under WWTP
Compost Material	10 mg/kg leachate was recorded by this researcher if a large release of compost tea were to take place into the vadose zone, arsenic concentrations in the water would be a maximum of 15 to 64.0 ug/L based on water extract results from the laboratory.	Percolation of rainwater from surface through the compost to the aquifer does not appear likely as discussed in the background section. Lysimeter studies at the site yielded no liquid, while control lysimeters functioned well (discussion: hydrogeology). This should hold true except for events of extraordinary magnitude, when the compost will supersaturate and may expel the liquid. In my experience, the primary result of extreme saturation of the compost is a significant amount of standing water at the surface, although large amounts of water may also move to the vadose zone.	The possibility of increased size of the compost pile causing elevated temperatures in the MW7 groundwater has been suggested, as elevated temperatures may affect reaction kinetics. Field collected temperature data show no measurable elevation in groundwater temperature at MW7 for the years 1999-2006 (APPENDIX: Temps MW7 1991- 2007). The large compost pile does not appear to have caused significantly elevated temperatures in the groundwater at MW7.
Sewage Sludge	around 1 to 5 mg/kg total digestible arsenic in sludge APPENDIX: WWTP sludge metals.	No assay for sludge material but lots of Carbon plus phosphorus sulfur and microbial component. Older sludge (pre 2004, will contain more Chloride, as chlorine was used in the process as a disinfectant until that time. System now uses UV for disinfectant, microbial community is not affected.	Surface water (in effluent) Ground water (buried sludge)
Sediment	40 mg/kg leachable arsenic.		Ground water

Table 5 Calculations for Mass Balance of Arsenic from the Contaminated Sediment Layer

Sediment properties: Assume soil density is 0.96 (Morris and Fan 1997)

45 mg arsenic /kg sediment in layer three (Table 4)

45 mg As/Kg sed x 1000kg sed/m^3sed x 0.96 x 1kg/1000mg

=43.2kg As/ m^3 sed

MW 7

Flux of water through section of aquifer Q/A=KI

=304.9 m/day x 0.0016 x 1 m^2 =0.49 m^3/day

pre-1999 conditions (non-reducing)

0.01 mg/L arsenic present in summer

Flux of arsenic through area Q_{As}= Q_{Tot} *C_{As}

=0.49 m^3/day x 0.01mg As/L x 1000 L/ m^3

Q_{As} =4.88 mg As/day

43.2 kg As/ m^3 sed x /0.0049 kg As/day

=8856 days / 91 days/year (3 months/year)

=**97** years assuming the water table only reaches the sediment layer for three months of the year.

post-1999 conditions (reducing)

0.1 mg/L arsenic present in summer

Flux of arsenic through area Q_{As}= Q_{Tot} *C_{As}

=0.49m^3/day x 0.1mg As/L x 1000 L/ m^3

Q_{As} =49 mg As/day

43.2 kg As/ m^3 sed x /0.049kg As/day

=881 days/ 91 days/year (3 months/year)

=**9.75** years assuming the water table only reaches the sediment layer for three months of the year.

MW4

Flux of water through section of aquifer Q/A=KI

=304.9 m/day x 0.0008 x 1 m^2 =0.24 m^3/day

Pre-monitoring (1991) conditions (reducing, high concentration)

0.05 mg/L arsenic present in summer

Flux of arsenic through area Q_{As}= Q_{Tot} *C_{As}

=0.24 m^3/day x 0.05mg As/L x 1000 L/ m^3

Q_{As} =12.2 mg As/day

43.2 kg As/ m^3 sed x /0.0122 kg As/day

=3542 days / 91 days/year (3 months/year)

=**40** years assuming the water table only reaches the sediment layer for three months of the year.

current conditions (reducing, lower concentration)

0.01 mg/L arsenic present in summer

Flux of arsenic through area Q_{As}= Q_{Tot} *C_{As}

=0.24 m^3/day x 0.01mg As/L x 1000 L/ m^3

Q_{As} =2.44 mg As/day

43.2 kg As/ m^3 sed x /0.0024 kg As/day

=18000 days / 91 days/year (3 months/year)

=**197** years assuming the water table only reaches the sediment layer for three months of the year.

Figures

Figure 1 Missoula valley with Eko Compost and the Missoula Wastewater Treatment Plant located along the Clark Fork River.

Figure 2 Site map showing a recent aerial photograph of the study area.

(U.S. Farm Services Agency, National Agricultural Imagery Program (NAIP)). The compost yard sits adjacent to the wastewater treatment plant. Eight monitoring wells exist at the EKO site, four inches in diameter and 30 feet in depth. Six additional shallow 1 inch diameter wells were added on the floodplain, their locations based gradients observed on the first seasons potentiometric surface maps. Additionally, 3 residential wells up gradient, on either side of the CFR were monitored for static water levels.
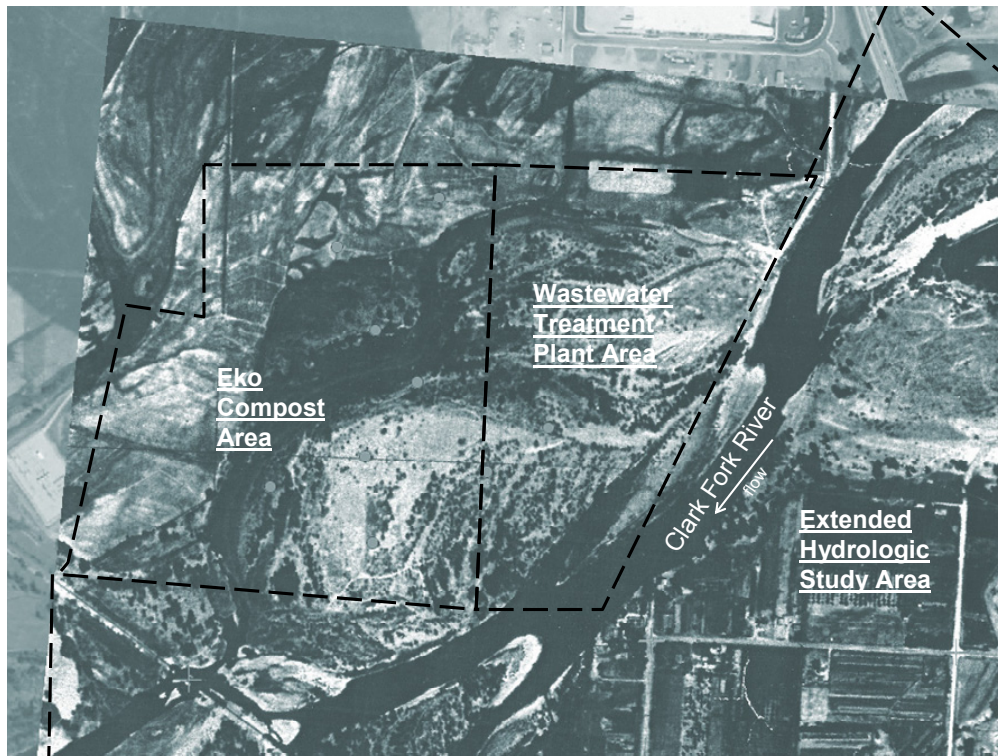
Figure 3 August 1941 air photo (Land And Water 1992) referenced over 2005 aerial photo of the current landscape.

Landmarks were chosen at intersections and points were matched using ARCGIS for georeferencing. This area of the river at the time of the historic photo was a large meander and floodplain, the main channel gave way to smaller channels and a backwater slough with a large floodplain area.

Figure 4 Eco Compost prior to development circa 1977.

Low elevation aerial photo looking north. Note location of channel bisecting property and holding ponds.
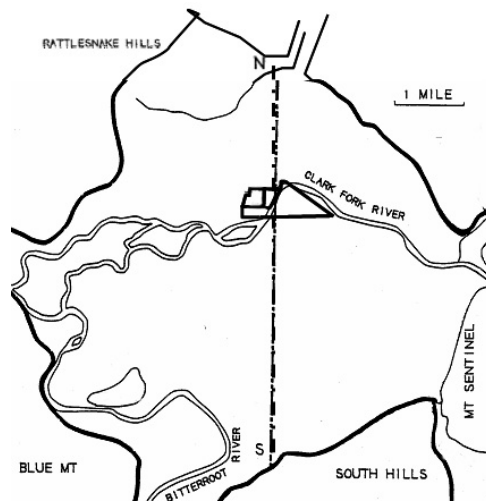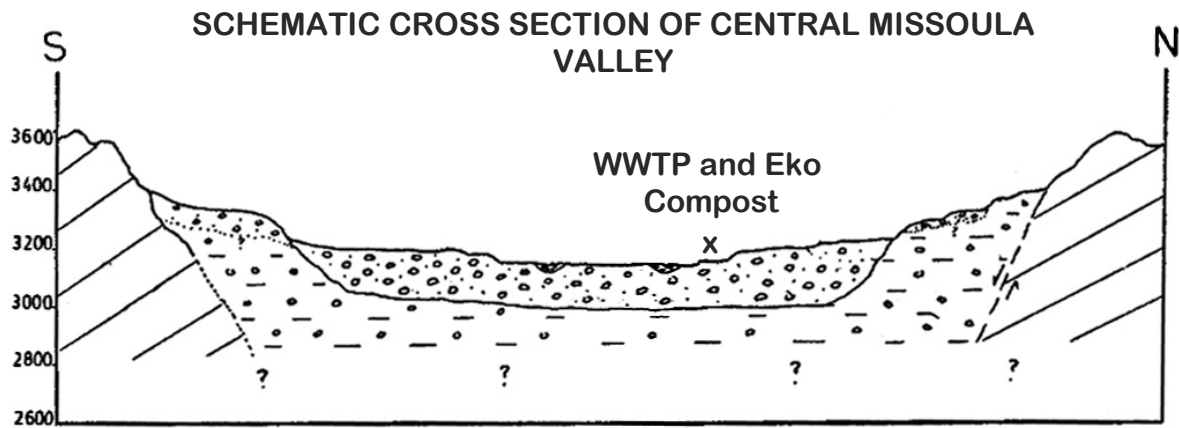
Figure 5 Map view and cross sectional illustration of the Missoula Valley centered at Eko Compost.

The Aquifer is present in the valley alluvium. Adapted from Morgan 1996.

Yellow Sediment

Wood

Gray sediment

~8 ft

Alluvium

Figure 6 Subsurface layering at Eko Compost.

This is an excavated pit in the southwest quadrant of the yard. The photograph above shows a loamy sandy backfill layer (yellow sediment) underlain by a woody layer about three inches thick, with a gray silt layer of about three feet with woody inclusions underlain by a dark well-sorted layer which may be the highest sitting undisturbed overbank sediment layer (gray sediment layers) . Below this are layers of alluvium alternating coarse gravel with smaller pebbles. The surface of the water table lies below the level of the pit bottom in winter, and rises through these layers and into the gray or yellow sediment layer during spring runoff season.
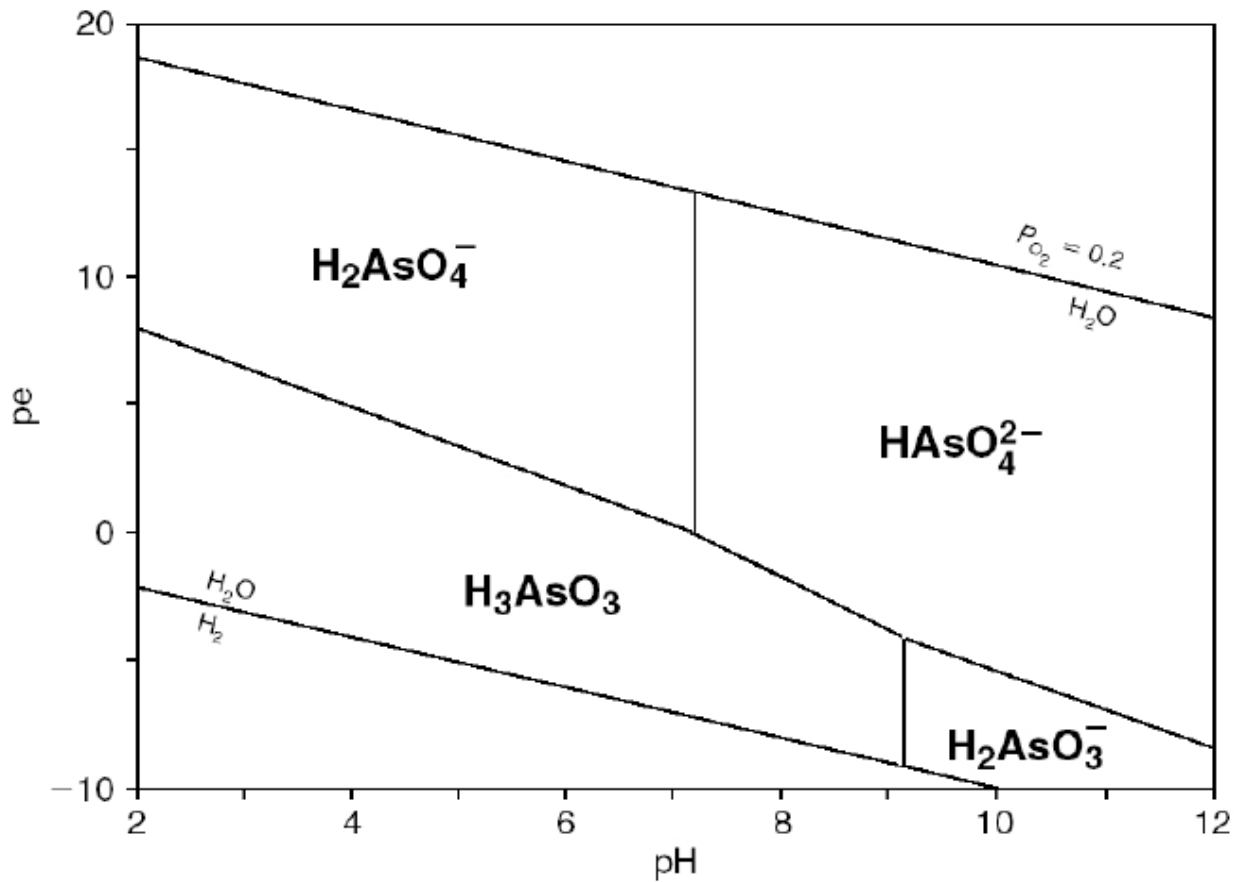
Figure 7 Phase diagram for aqueous arsenic species.

Generated from Log K values for mass action equations for first (and second) dissociations of arsenate and arsenite ions in solution and the reduction of arsenate to arsenite. Activities are assumed 10^{-4} mol/L arsenic.
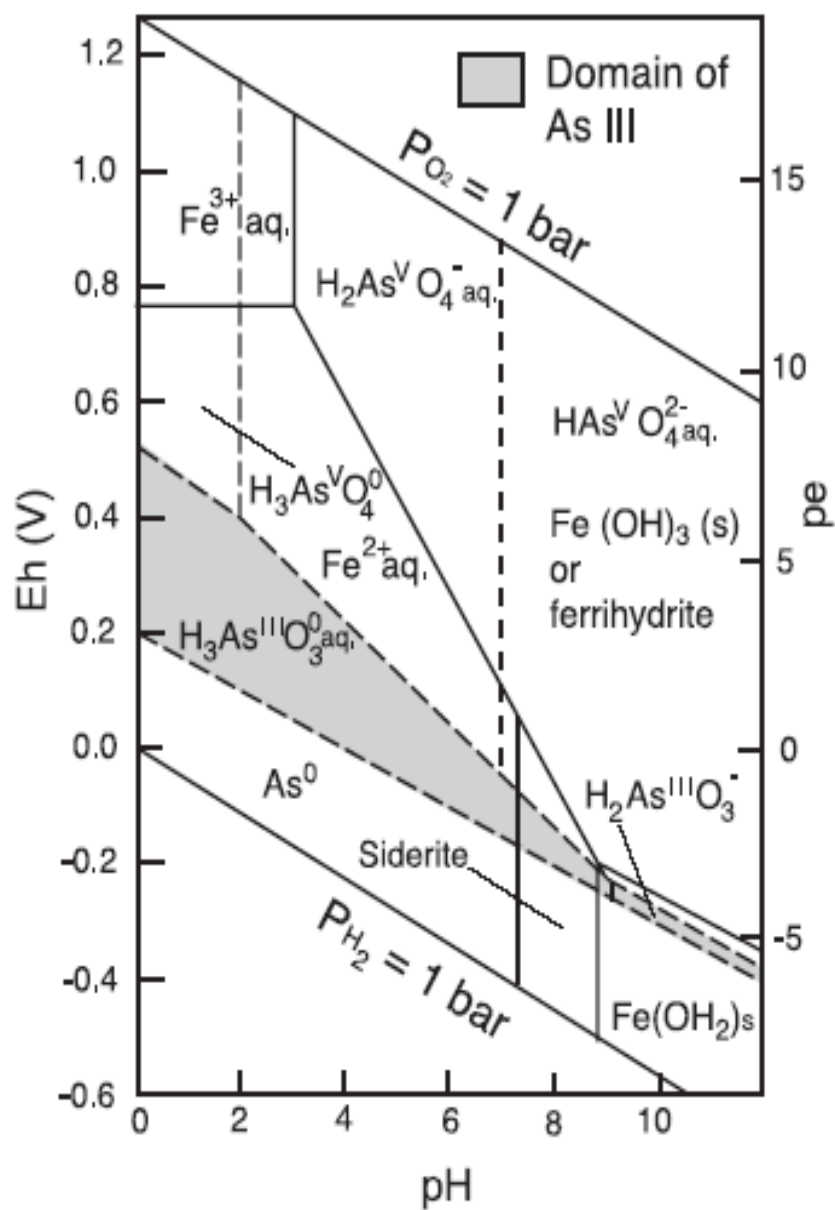
Figure 8 Stability of arsenic complexes and iron compounds as a function of oxidation potential and pH.

Activities are taken to be 10^{-6} mol/L arsenic and 10^{-6} mol/L iron at 25 °c and 1 atmosphere pressure. From Pfeifer 2004.
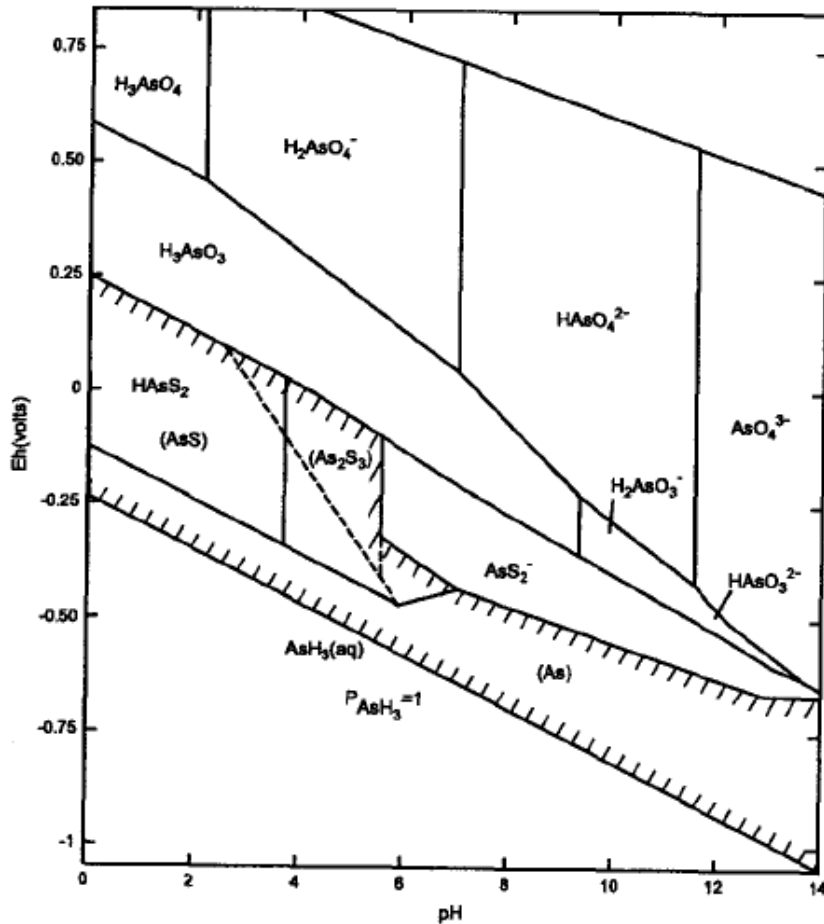
Figure 9 Stability of arsenic and sulfur complexes and compounds as a function of oxidation Eh and pH.

Activities are 10^{-5} mol/L arsenic and 10^{-3} mol/L sulfur at 25 °c and 1 atmosphere pressure. Solid phases form at low pH and mildly reducing conditions. From Ferguson and Gavis 1971.
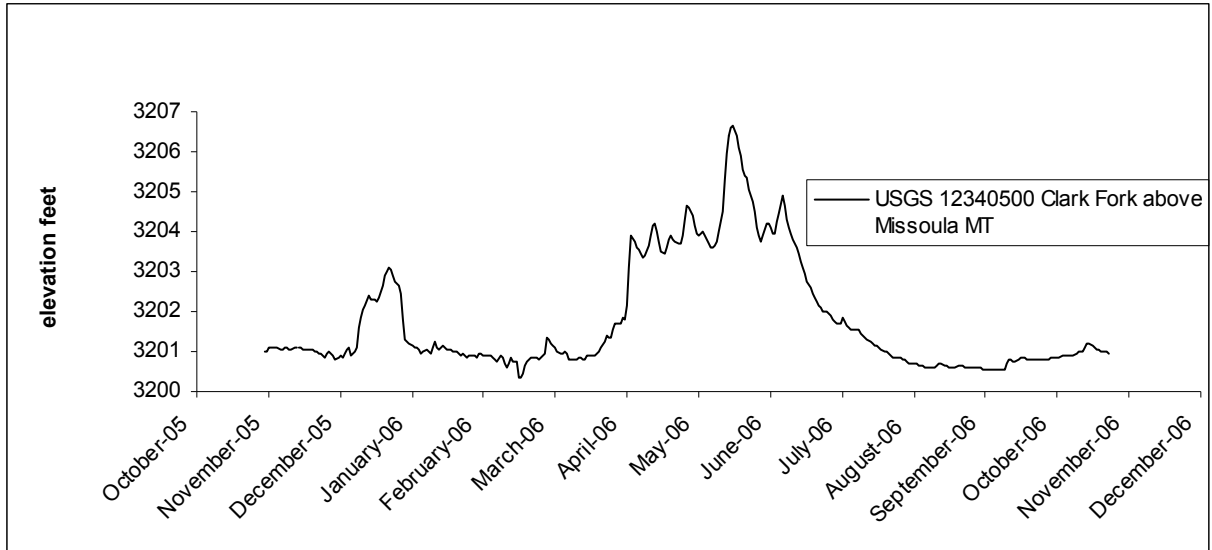
Figure 10 Hydrograph for 2005-2006 CFR above Missoula. (USGS 2006)
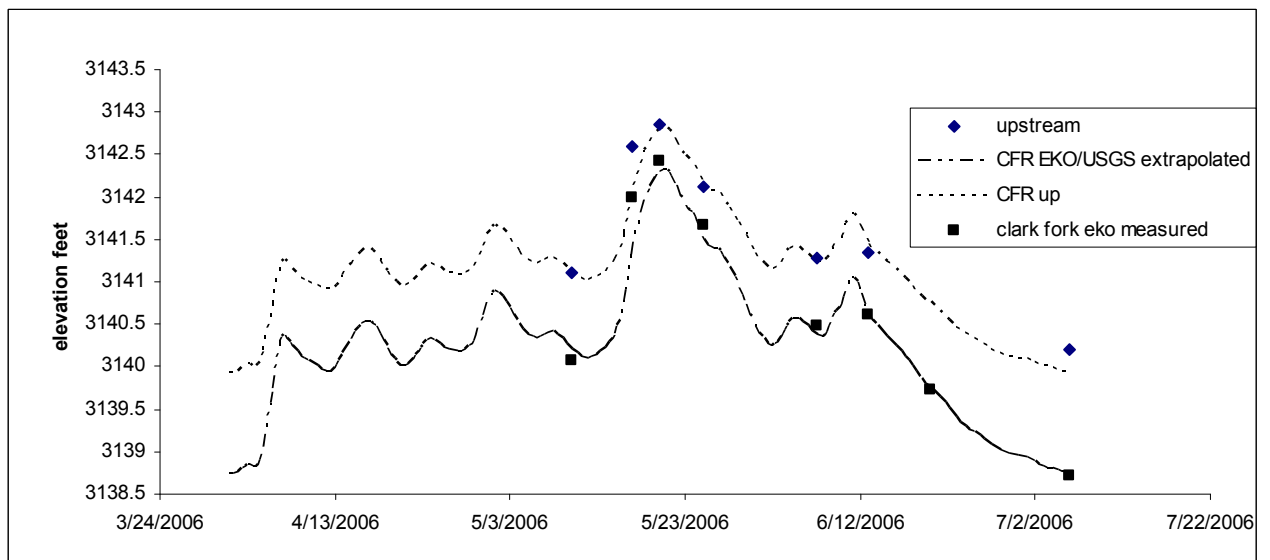
Figure 11 Hydrograph for runoff season at site.

These hydrographs were created using the relationship between measured points at CFR and UP gages and the USGS above Missoula gaging station daily data.
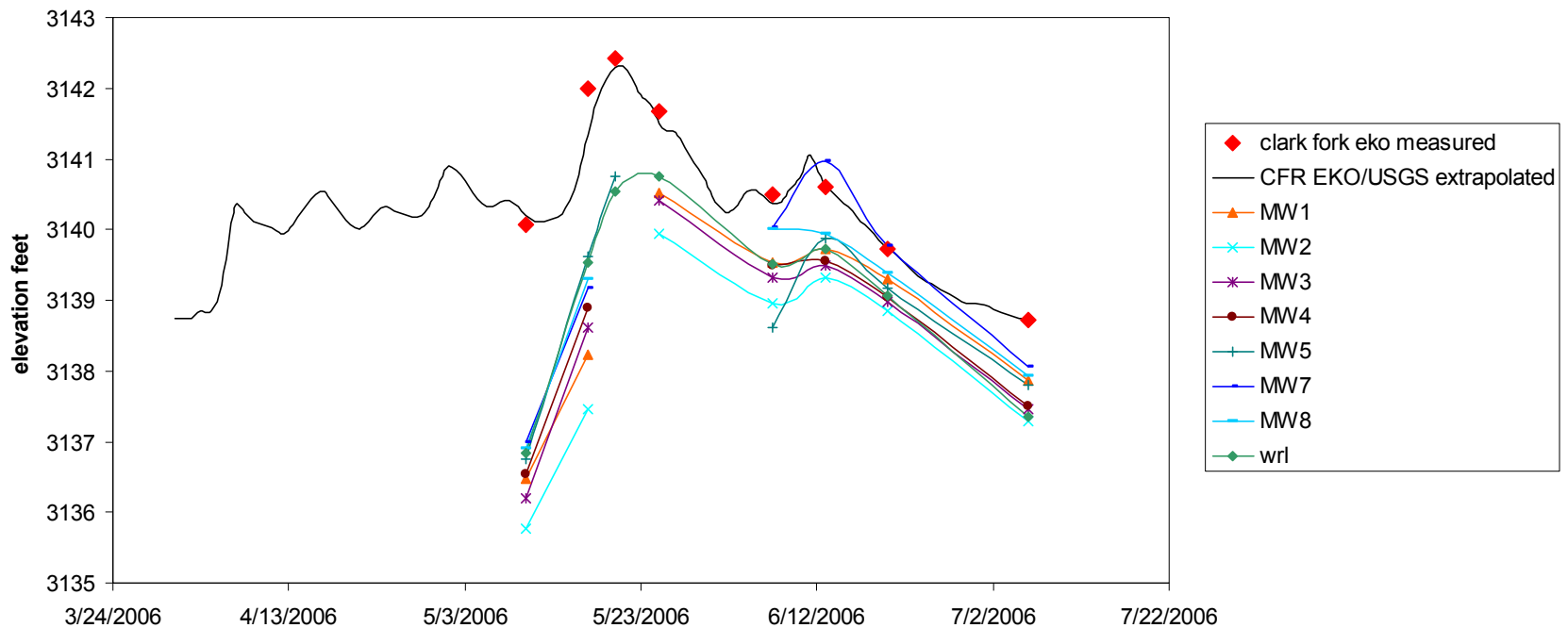
Figure 12 All wells and CFR during runoff.

Static water level elevations for wells are plotted with extrapolated CFR backwater hydrograph and measured points.

Figure 13 January 11, 2006 Potentiometric map of the water table surface at Eko Compost. .

Water table elevation varied across the site from 3131.56 to 3132.24 feet in January, a range of less than 1 foot
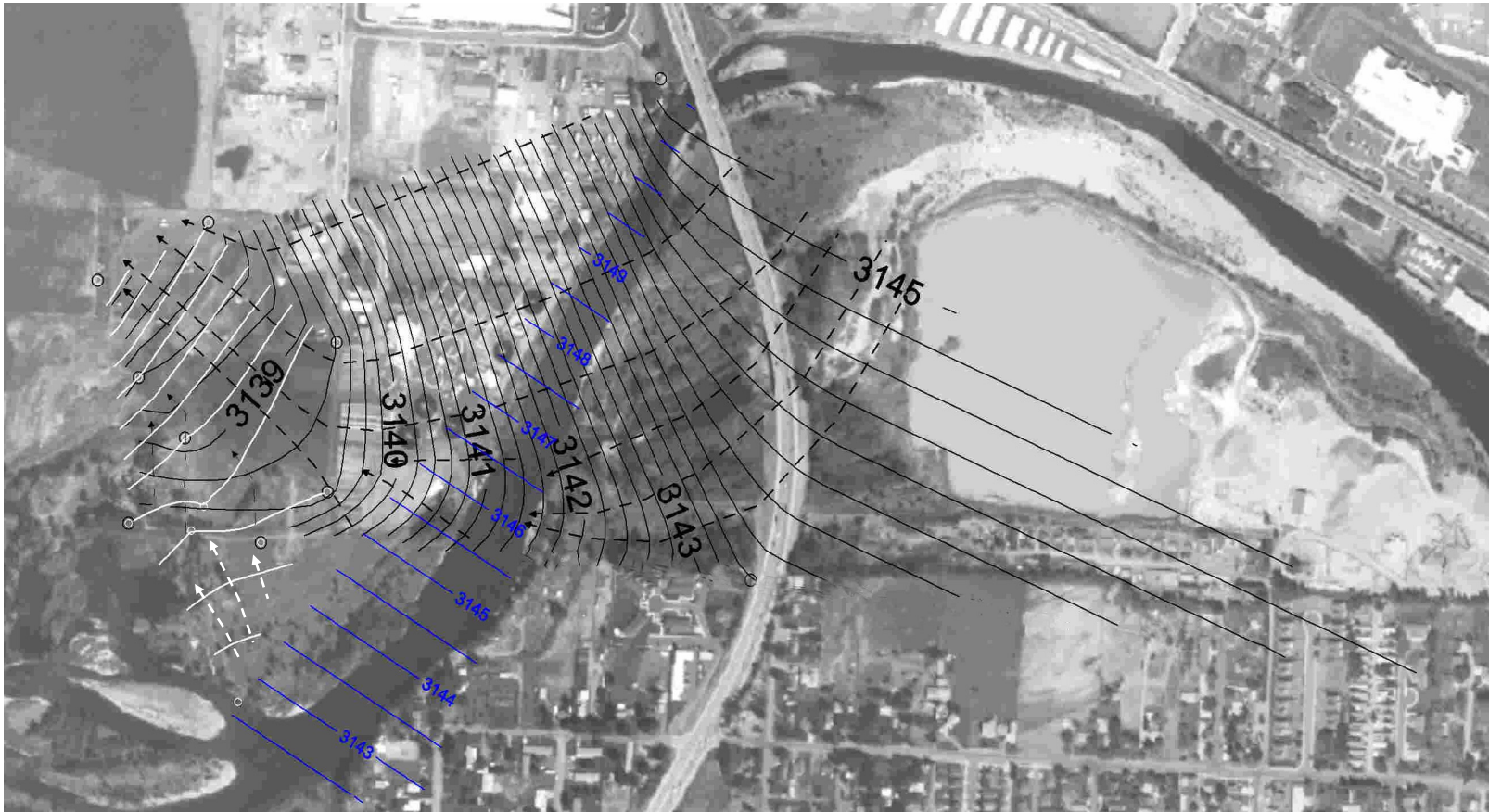
Figure 14 May 17, 2006 Potentiometric surface of the water table with flow lines, including regional wells northeast and southeast of the site.

Surface water elevations are shown in blue (gray) along the river. The surface water at the bridge is 6.3 feet above water table at the boathouse well, and about 6 feet above the water table as mapped at the effluent point. The water table elevation drops 7.2 feet from the boathouse to the site and 1.7 feet across the site.
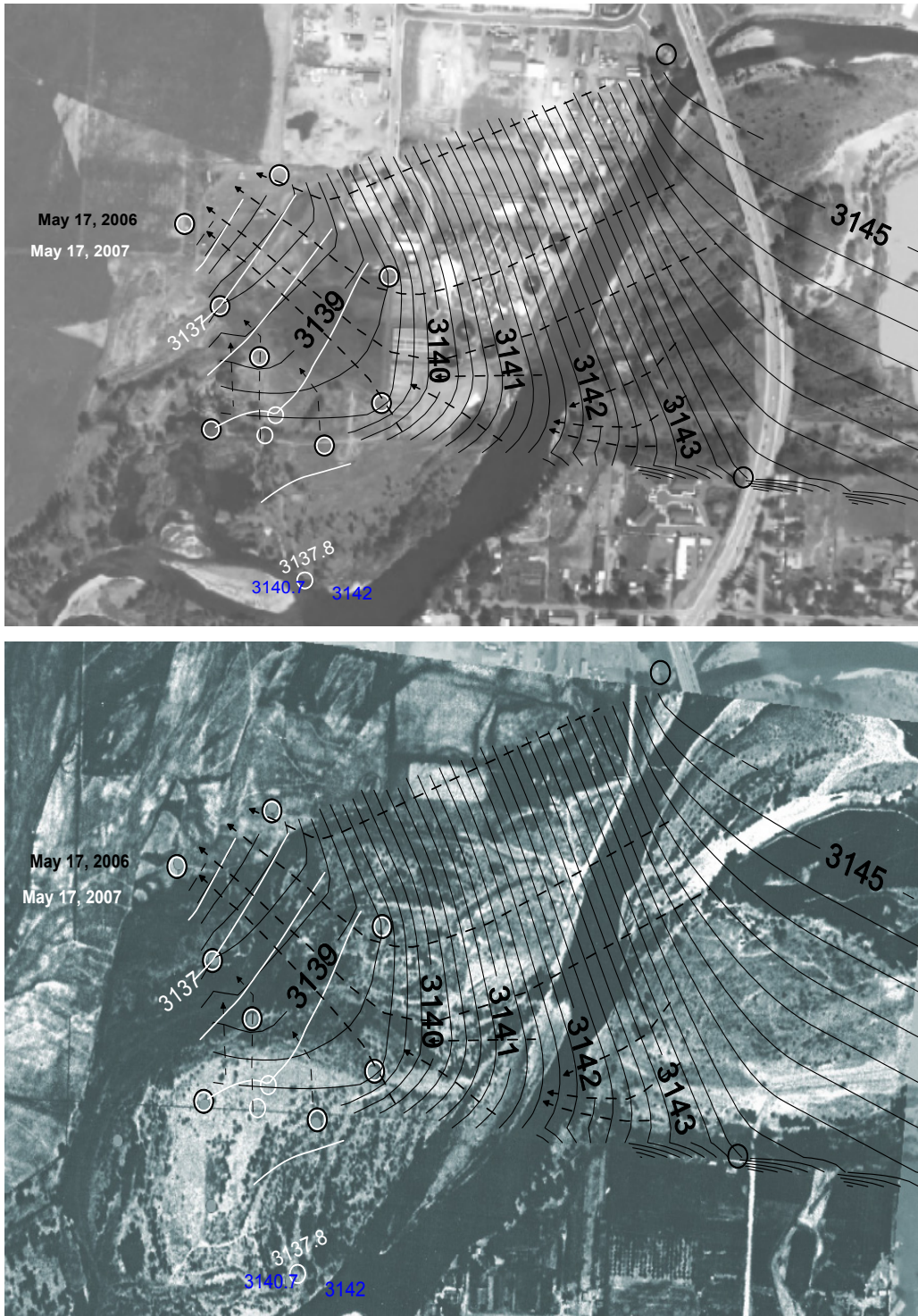
Figure 15 Potentiometric surface at peak runoff. May 17 2006 and May 17 2007 superimposed on 1941 air photo (top) and on the current landscape (below).

The discharge area was centered on the historic channel. White contours represent a potentiometric surface generated from new wells placed on the floodplain the following year, the general northwest flow pattern was confirmed and extended across the southern floodplain.
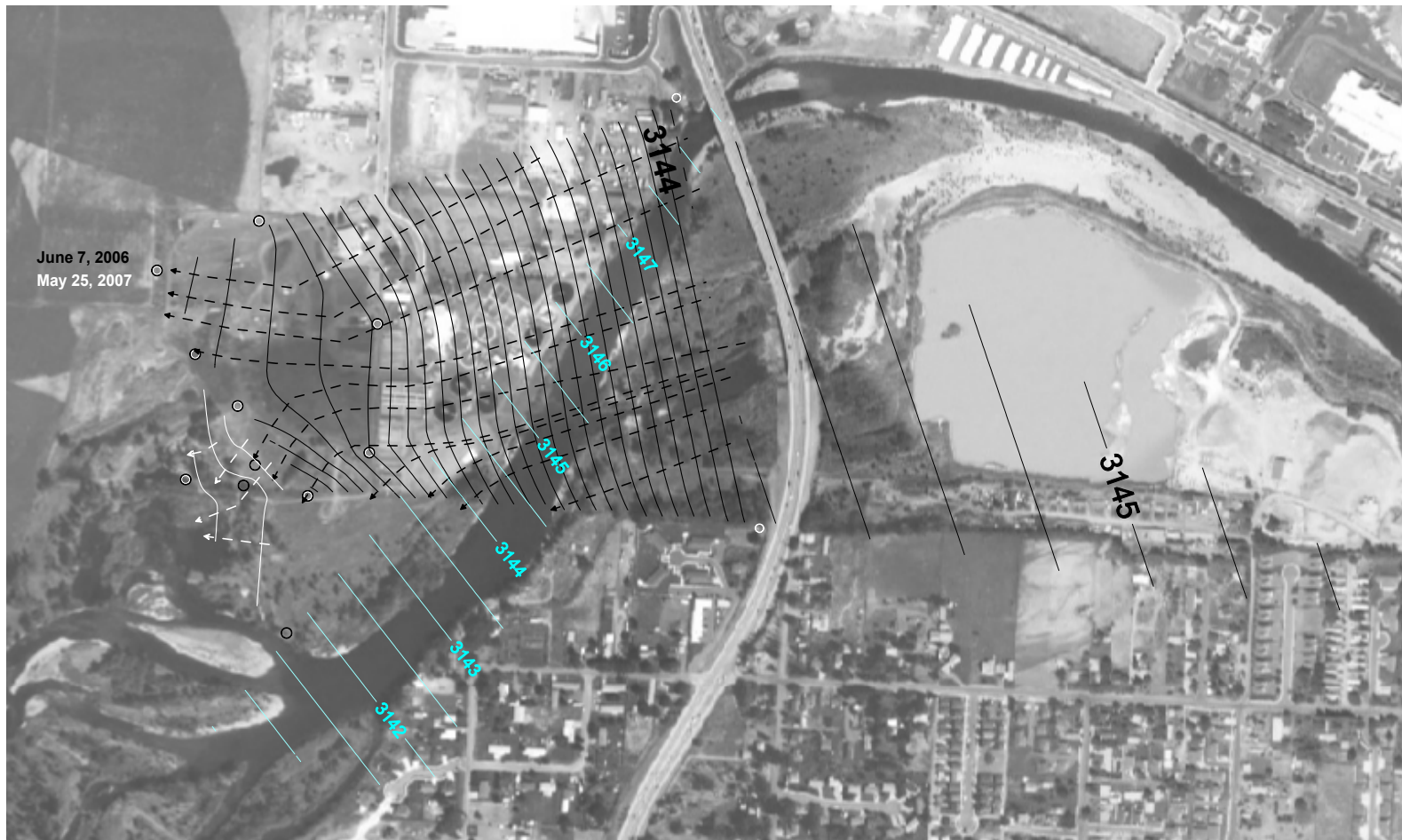
Figure 16 June 8, 2006 Potentiometric surface of the water table with flow lines, including regional wells northeast and southeast of the site.

The surface water at the bridge is 4.8 feet above water table at the boathouse well, and about 3.5 feet above the water table as mapped at the effluent point. The water table elevation drops 4 feet from the boathouse to the site and 1.06 feet across the site.
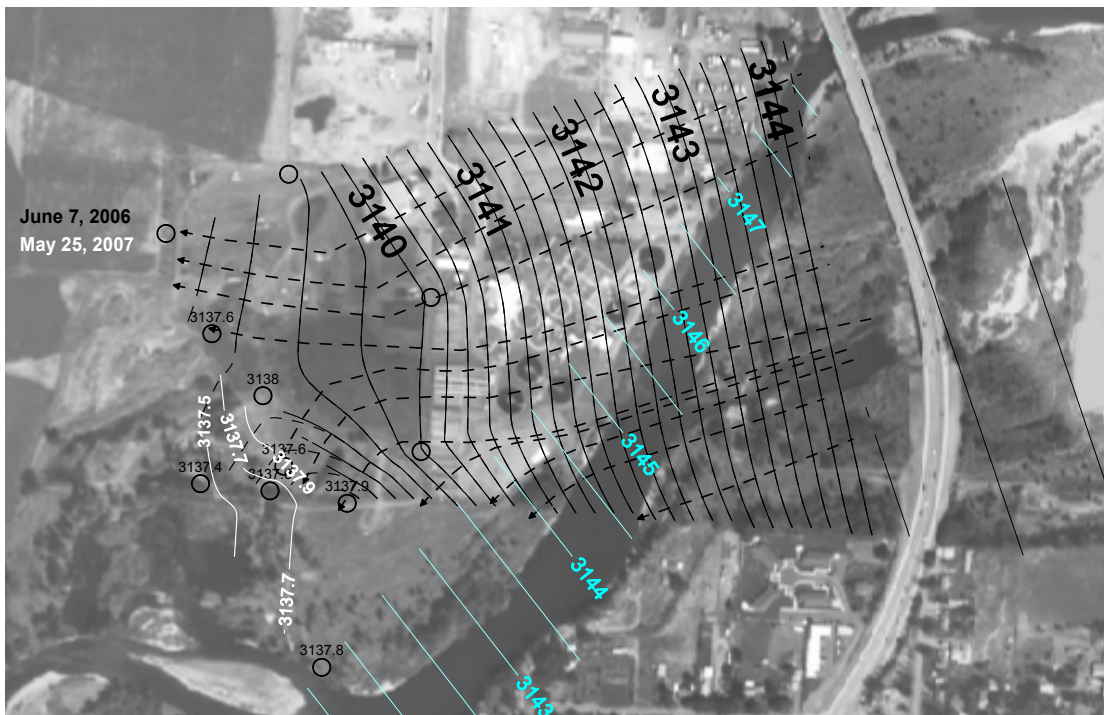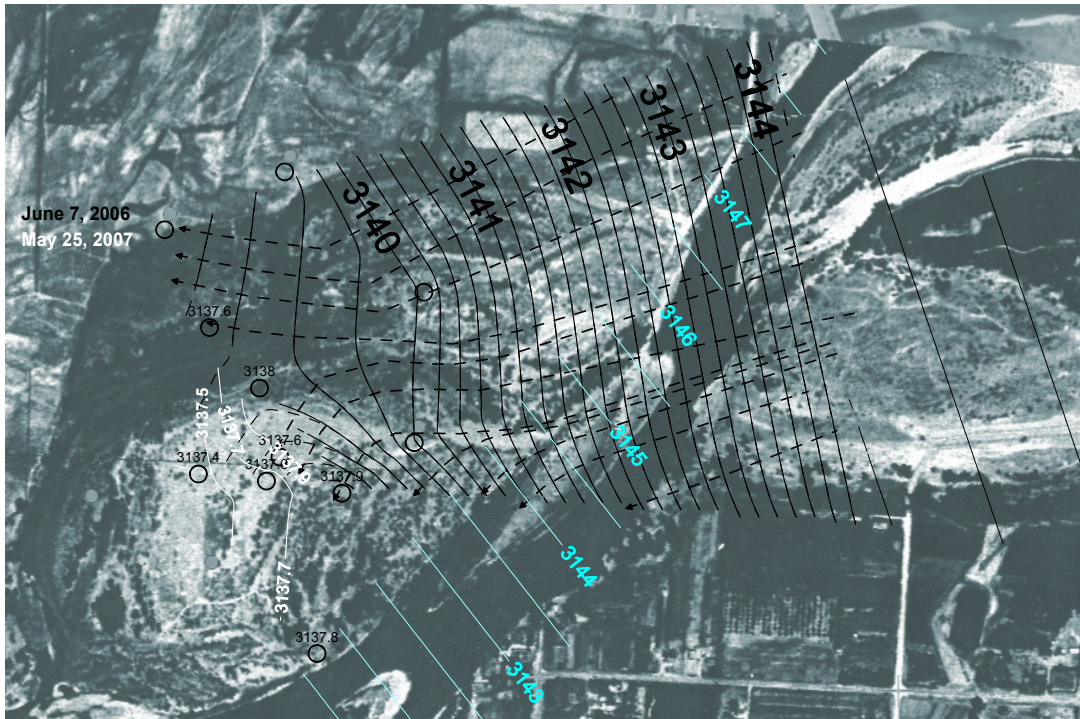
Figure 17 Post peak runoff. June 8, 2006 and May 25, 2007 superimposed on 1941 air photo and on the current landscape.

White contours represent the potentiometric surface generated from new wells placed on the floodplain the following year. The recharge area is centered on the historic channel, the discharge area is toward the backwater and crosses the historic (quarried) floodplain. The southern split flow pattern toward the backwater is confirmed by the 2007 data.
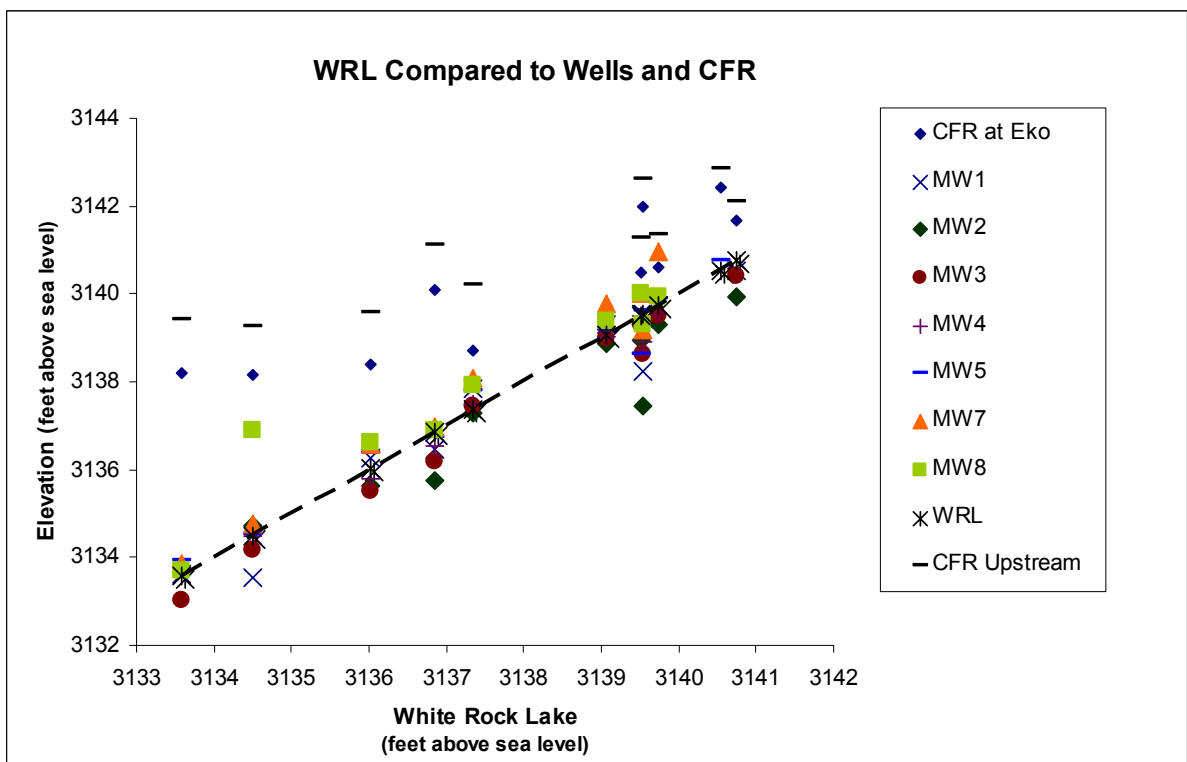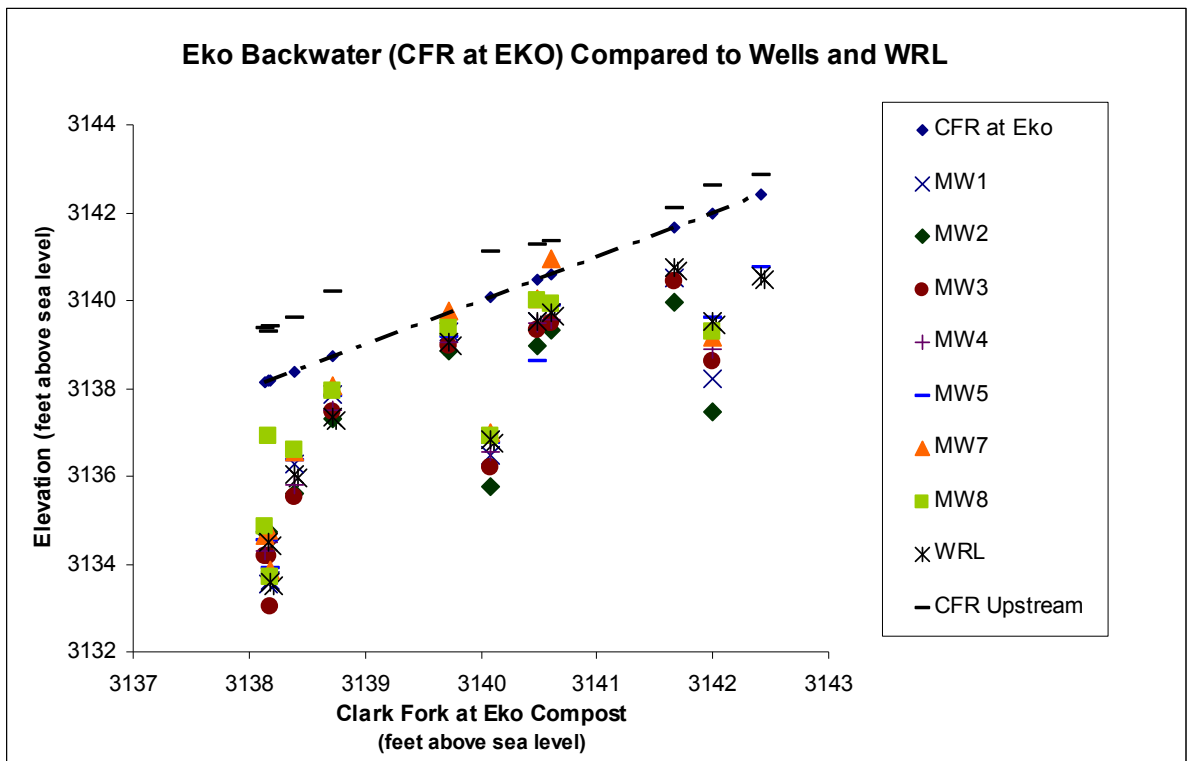
Figure 18 Correlation of water level elevations in wells and surface waters.

Figure 19 MW5 and Seep 5 viewed from the Eko Compost floodplain.

This lagoon fills with groundwater each spring after runoff season. It was present in June and July of 2006. Proximity of the monitoring well allowed for comparison of chemistry and elevation.
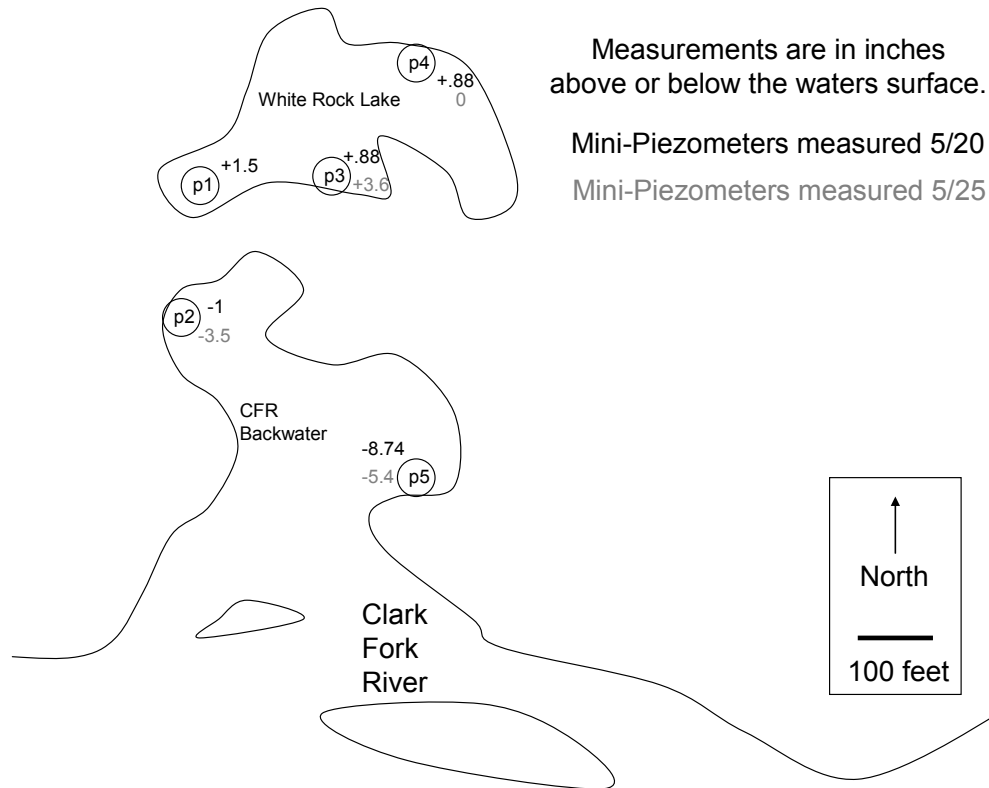
Figure 20 Mini Piezometer locations and measurements showing the backwater influent to the aquifer and the WRL effluent from the aquifer.

Values in the backwater were negative, as level in mini piezometers was below the water surface level. Values in the pond WRL were positive, as measured water level in mini piezometers was above the water surface.

Figure 21 Photograph of CFR Backwater and White Rock Lake May 17.

Surface water (CFR) at left and groundwater (WRL) at right, were at their highest elevations of the season. Photo was taken at midday looking west from the center of WRL.
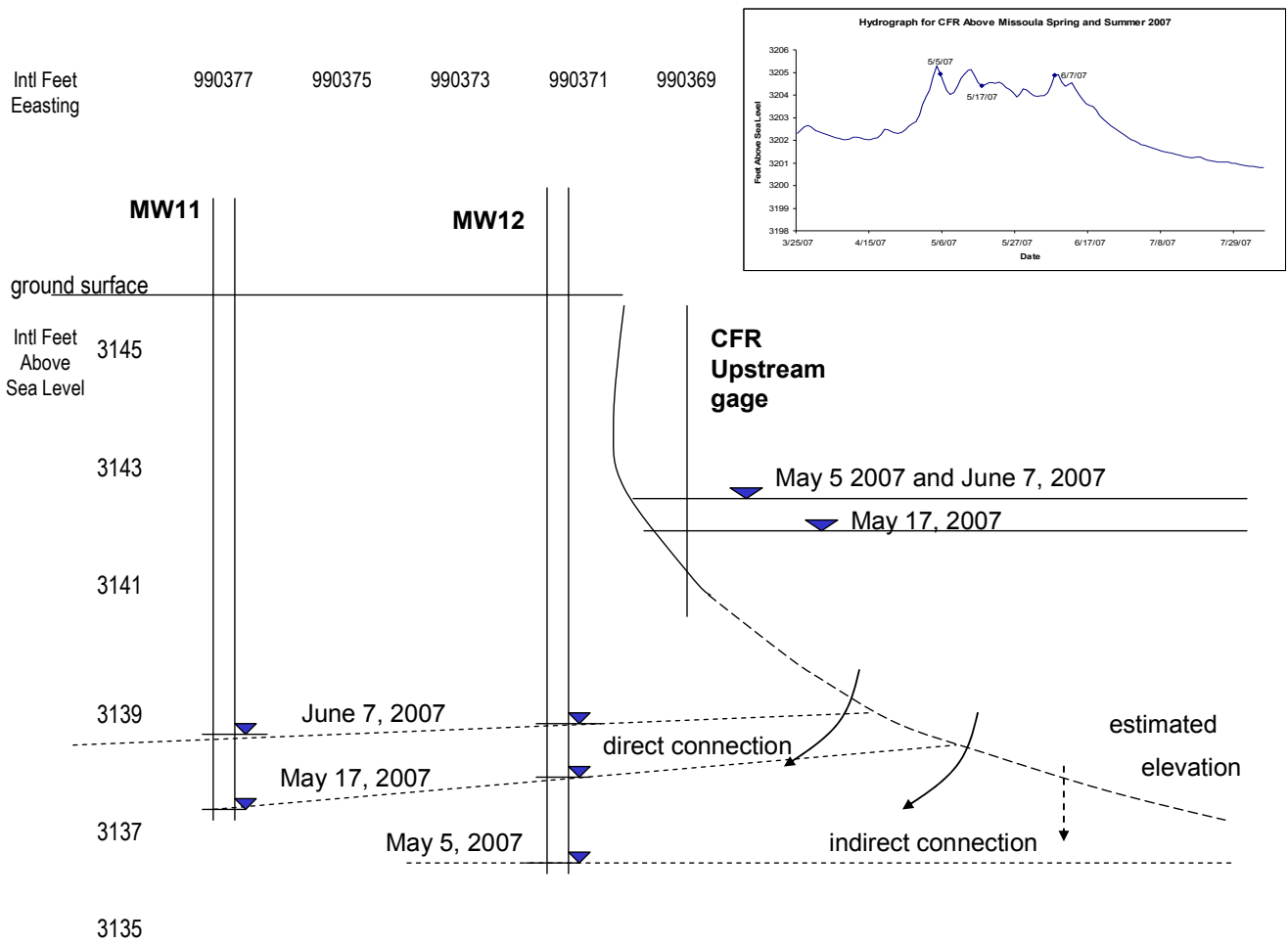
Figure 22 Cross section of floodplain wells and river.

Looking east (up-river) from the river's edge. Static water level measurements in wells UMW11 and UMW12 placed on the floodplain in 2007 indicated close connection with the CFR.
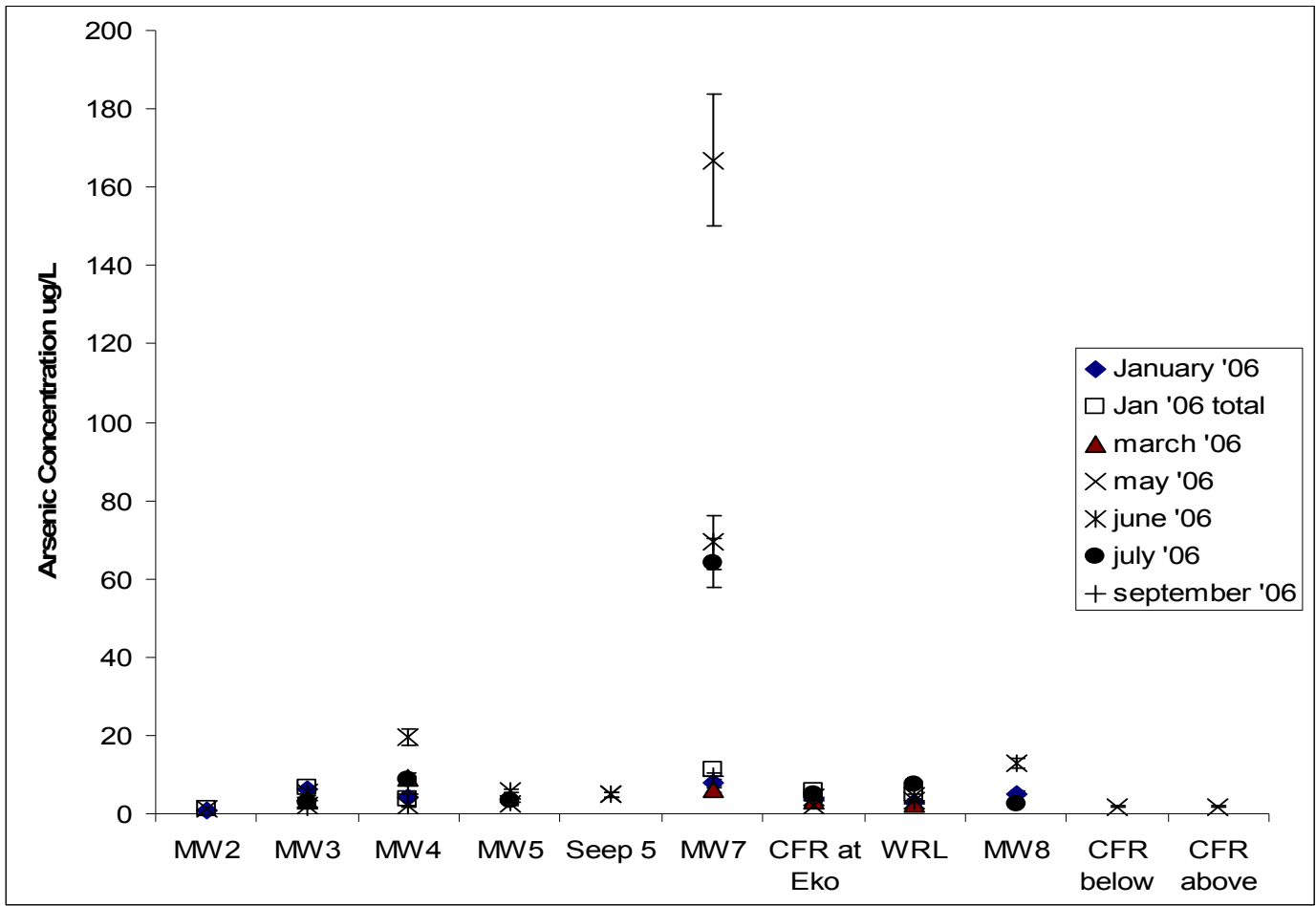
Figure 23 Arsenic concentration in wells at Eko Compost.

MW7 has the highest levels of arsenic seasonally, MW4 and MW8 also have elevated arsenic. MW2, MW5 and CFR above and below show concentrations below the drinking water MCL of 10 ug/L.
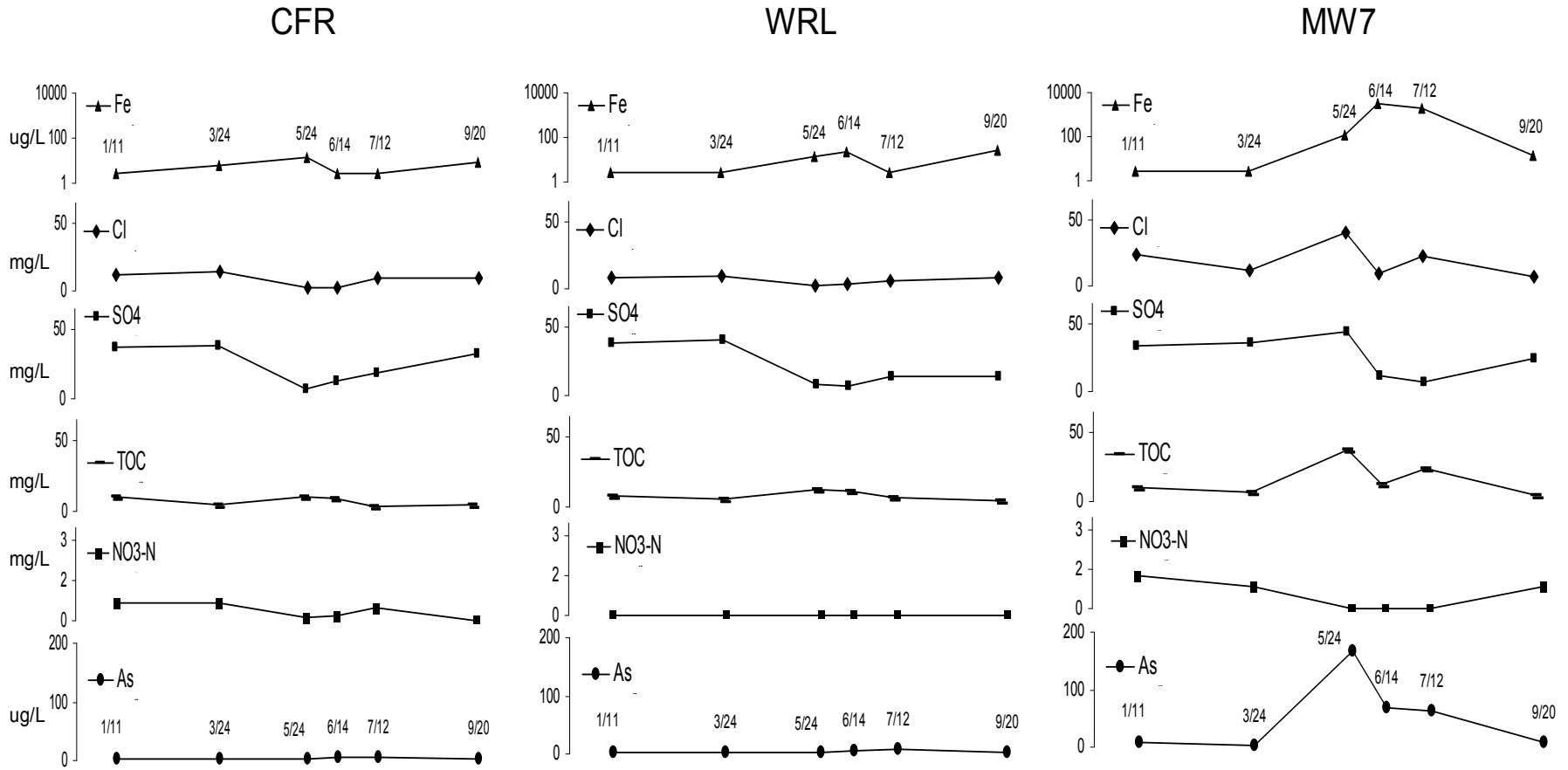
Figure 24 Chemistry of river, surface water and near-river wells at Eko Compost.

Metals results are reported in ug/L, anions are reported in mg/L. Data are stacked for general trend comparisons. Measurement error is encompassed in the size of the sample markers.
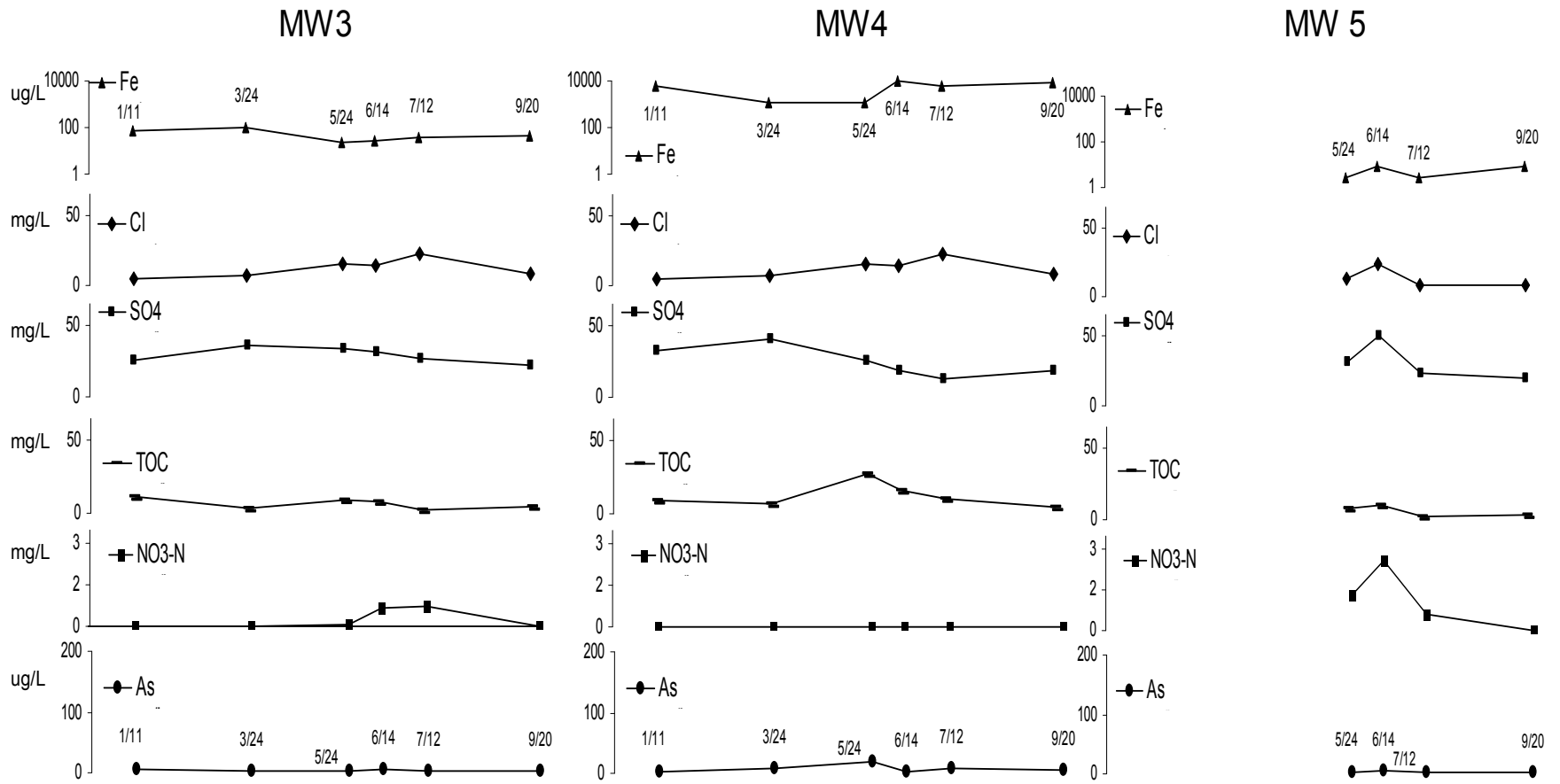
Figure 25 Chemistry of centrally located wells.
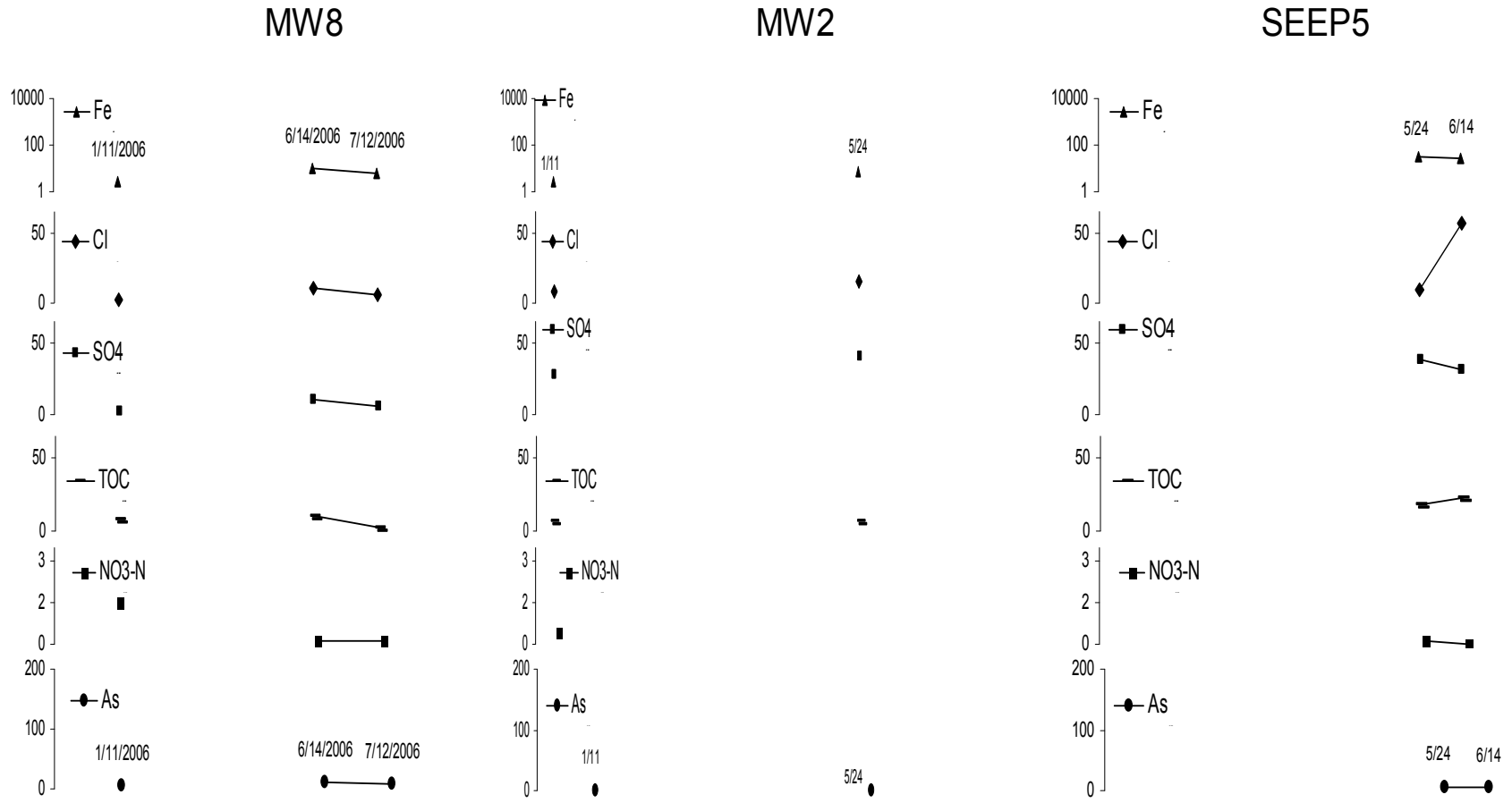
Figure 26 Chemistry of up gradient and down gradient wells and seep.
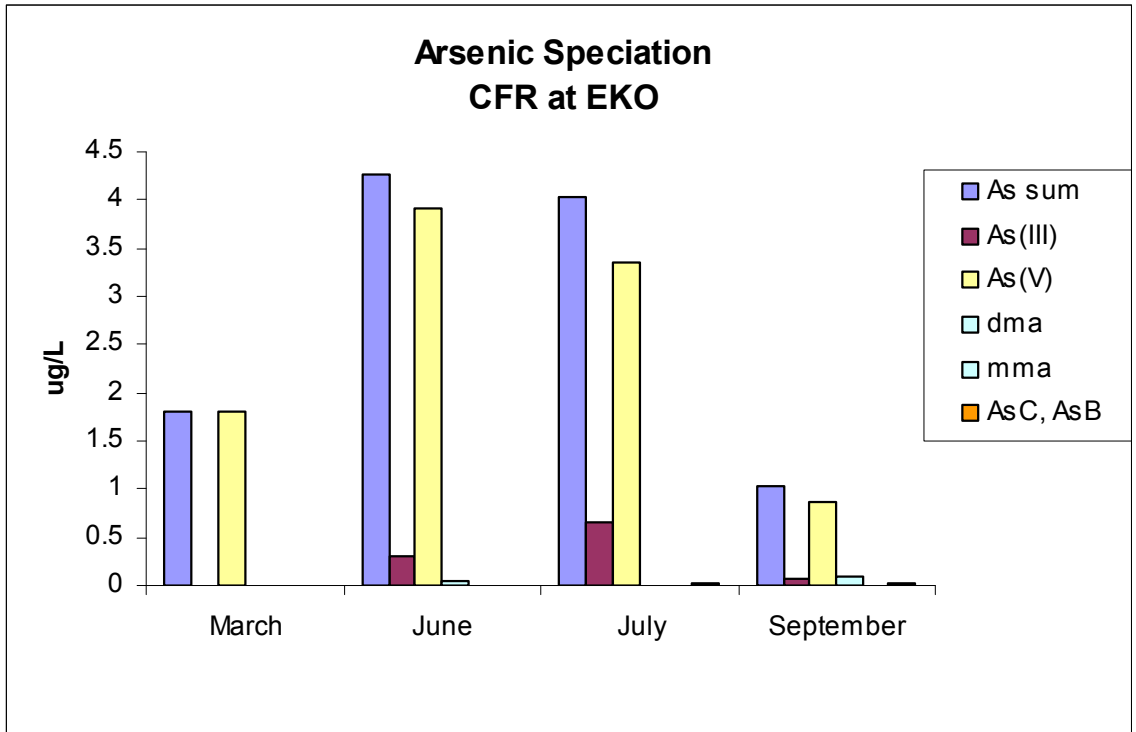
Figure 27 Arsenic Speciation in CFR at Eko Compost.
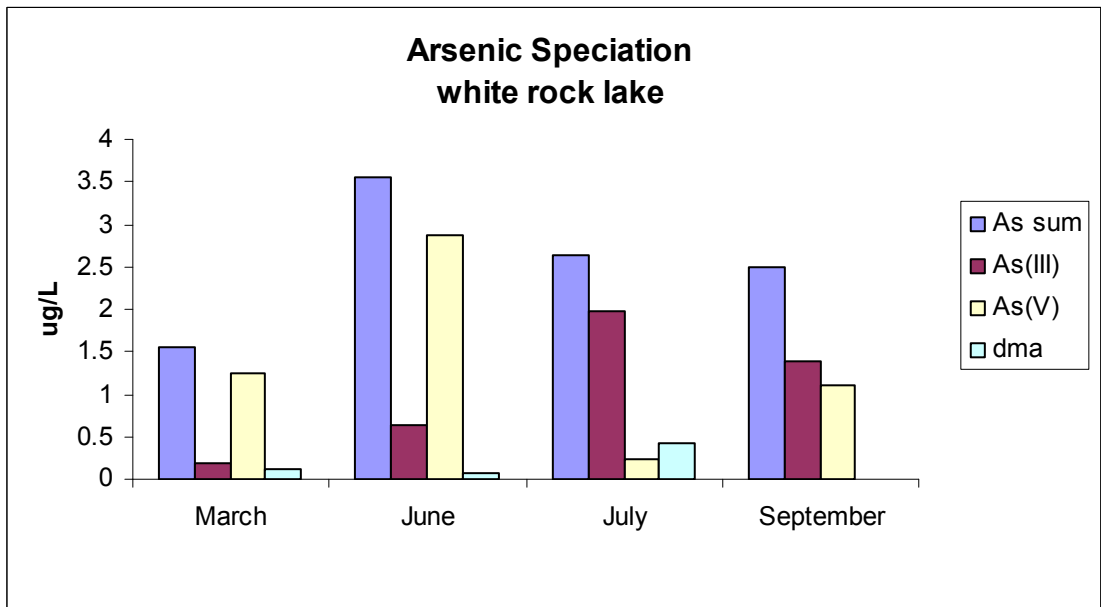
Figure 28 Arsenic Speciation at WRL at Eko Compost.
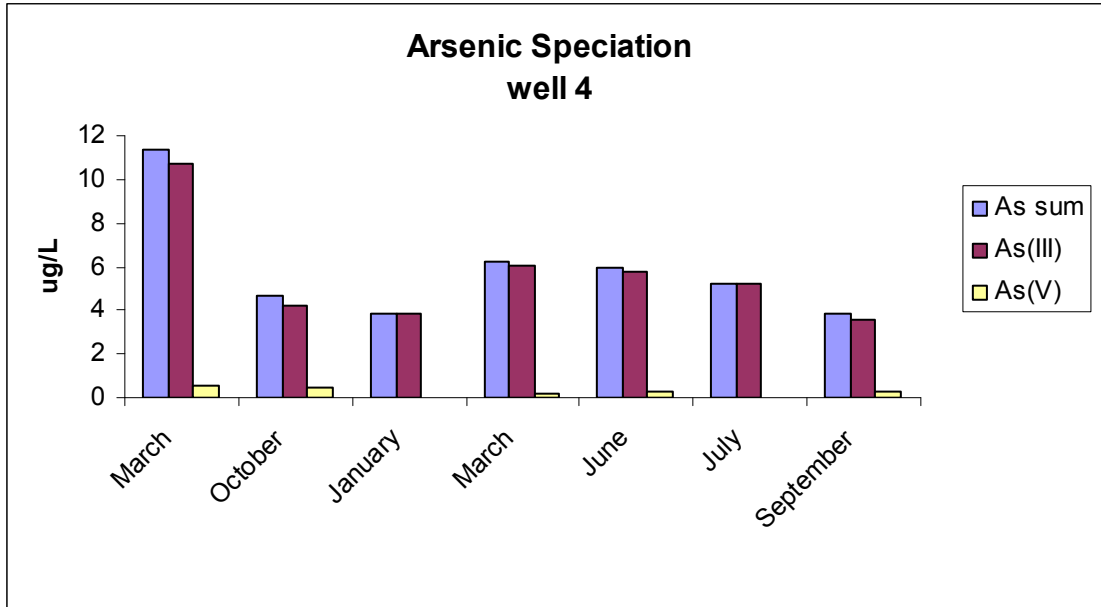
Figure 29 Arsenic Speciation MW4 at Eko Compost.
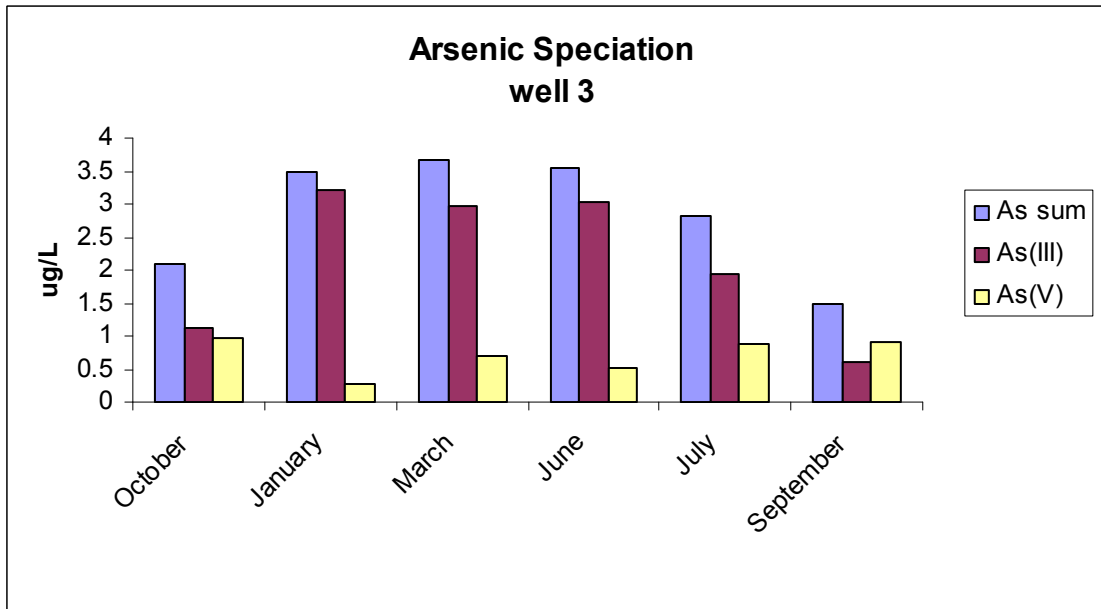
Figure 30 Arsenic Speciation MW3 at Eko Compost.
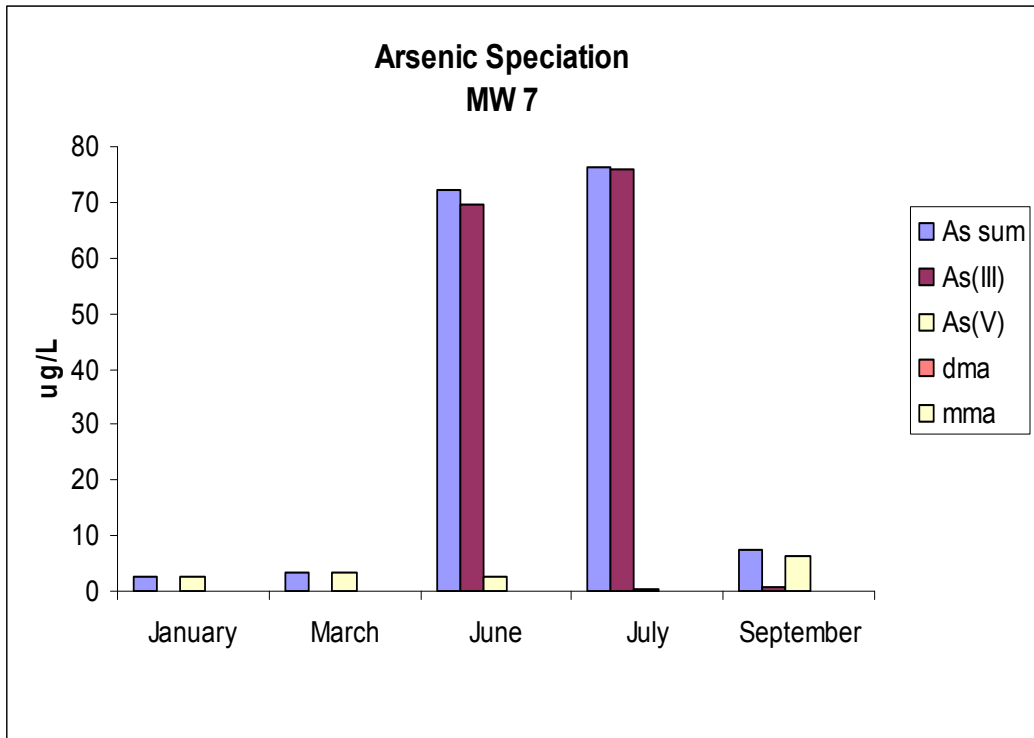
Figure 31 Arsenic Speciation MW7 at Eko Compost.
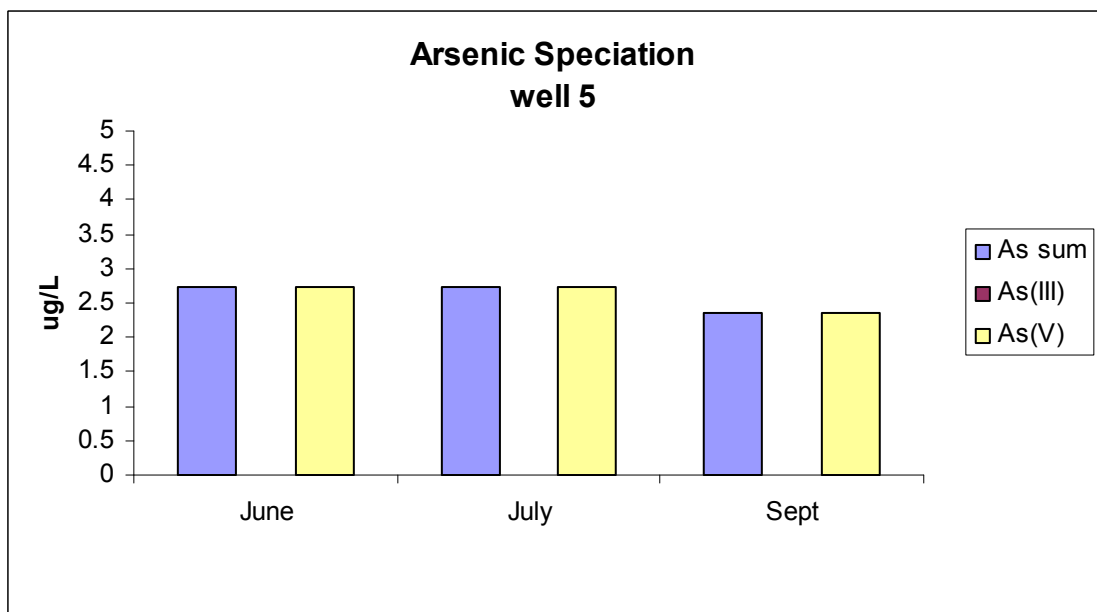
Figure 32 Arsenic Speciation MW5 at Eko Compost.
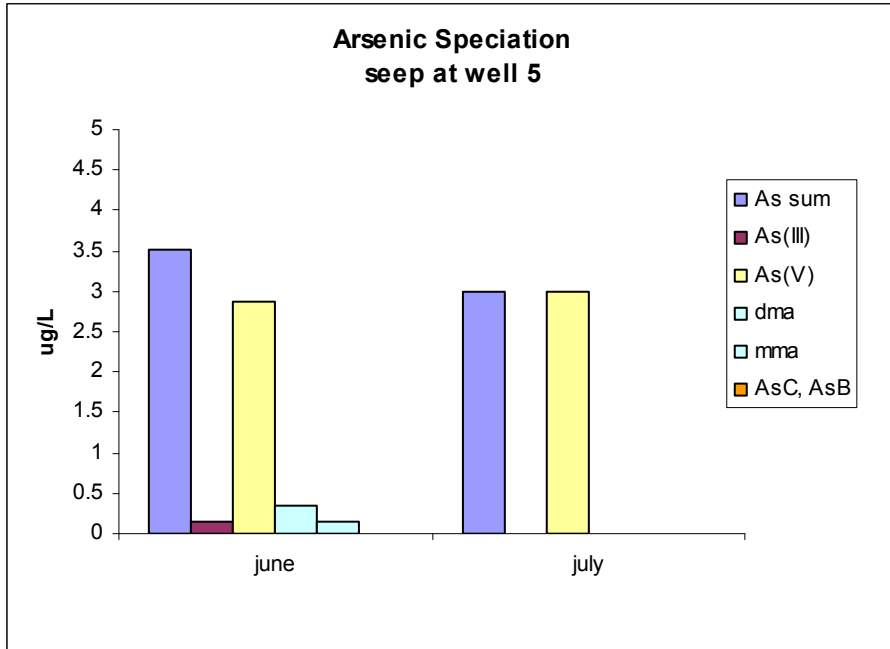
Figure 33 Arsenic speciation for the seep at MW5 (Seep 5) at Eko Compost.
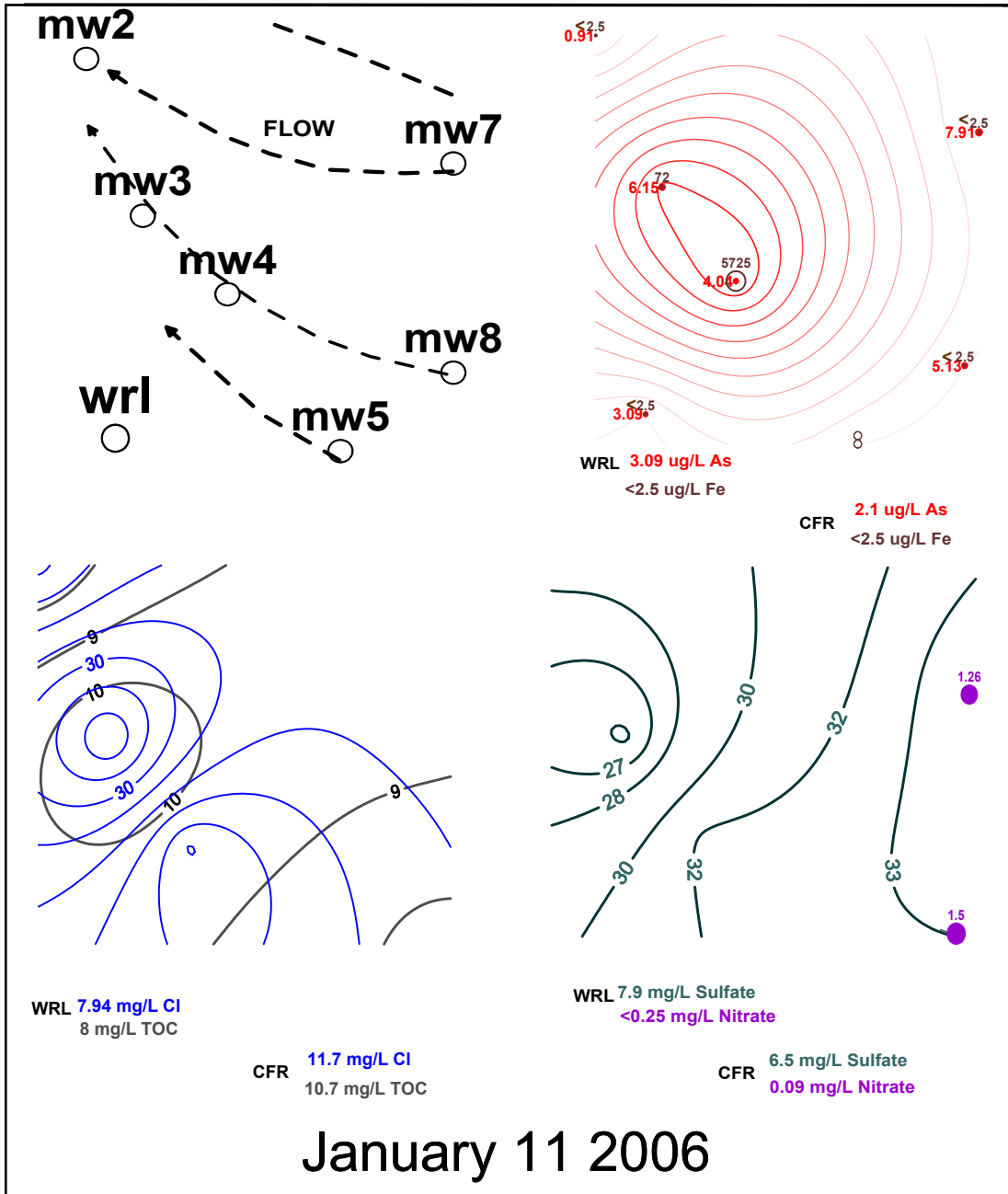
Figure 34 Chemistry contours over the compost yard section of the site for data collected January 11, 2006.

The local flow on these dates is shown in the upper left corner. Arsenic and iron concentrations (in ug/L) are shown by red bubbles and brown circles at upper right of each figure, reducing character is contoured by red lines, darkest being most reducing, lightest being most oxidizing. Total organic carbon and chloride contours are at lower left and sulfate contours and nitrate bubbles are shown at lower right.
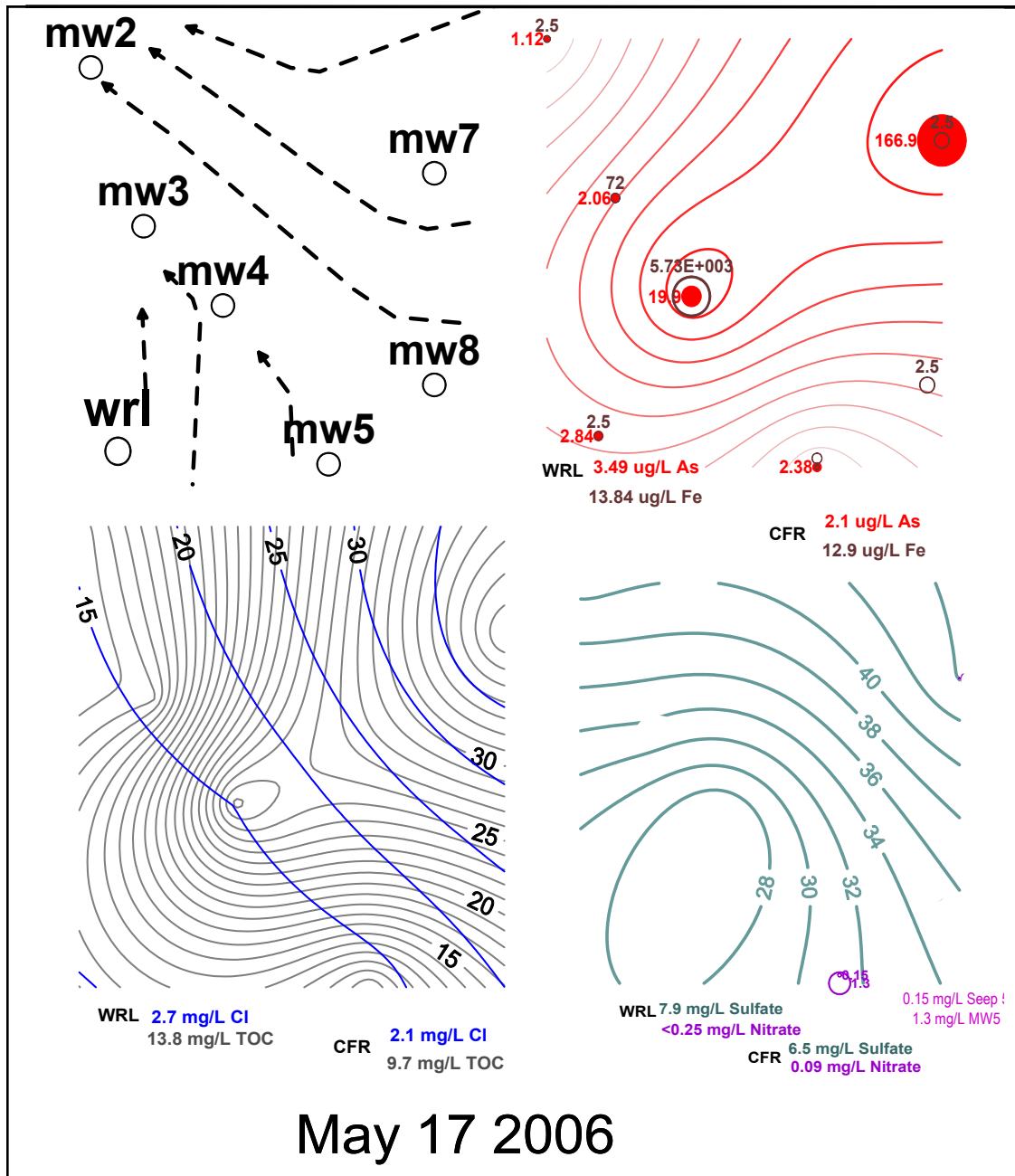
Figure 35 "Redox pump" illustrated with chemistry contours over the compost yard section of the site for data collected May 17, 2006.

In figures 34 and 35, The water table was at its lowest and highest seasonal elevations respectively. In winter, MW 7 showed very little arsenic and the form was As(V). In spring, MW 7 contained high levels of arsenic and iron in a reducing environment, the form was As(III). The historic channel diagonally bisecting the compost yard was outlined in winter and spring by the reducing plume (red lines). In winter there was less indication of the channel in supporting chemistry except for a high chloride value centered around well 3, but the channel was outlined by the total organic carbon, chloride, nitrate and sulfate contours in spring.
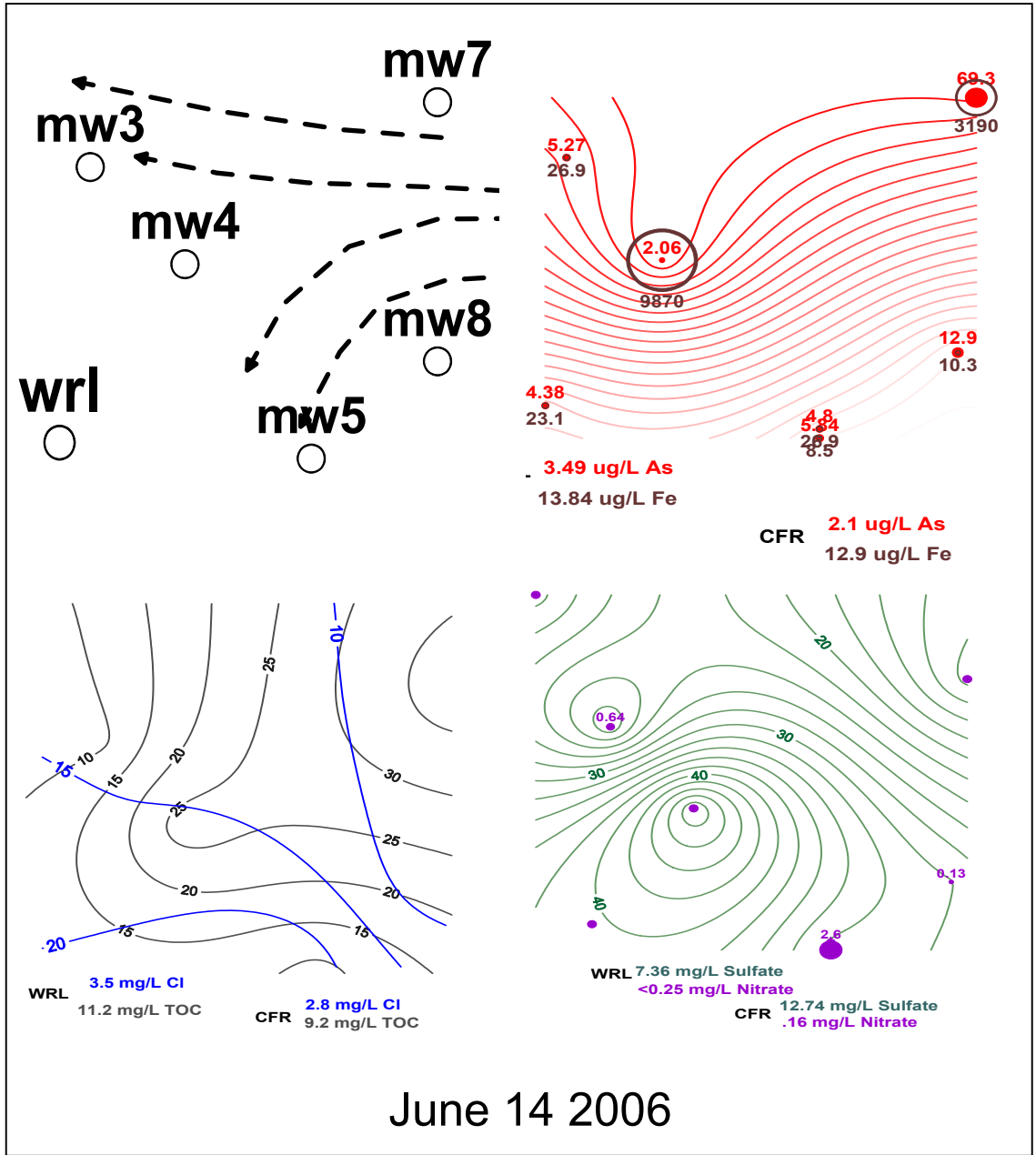
Figure 36 Chemistry contours over the compost yard section of the site for data collected June 14, 2006.
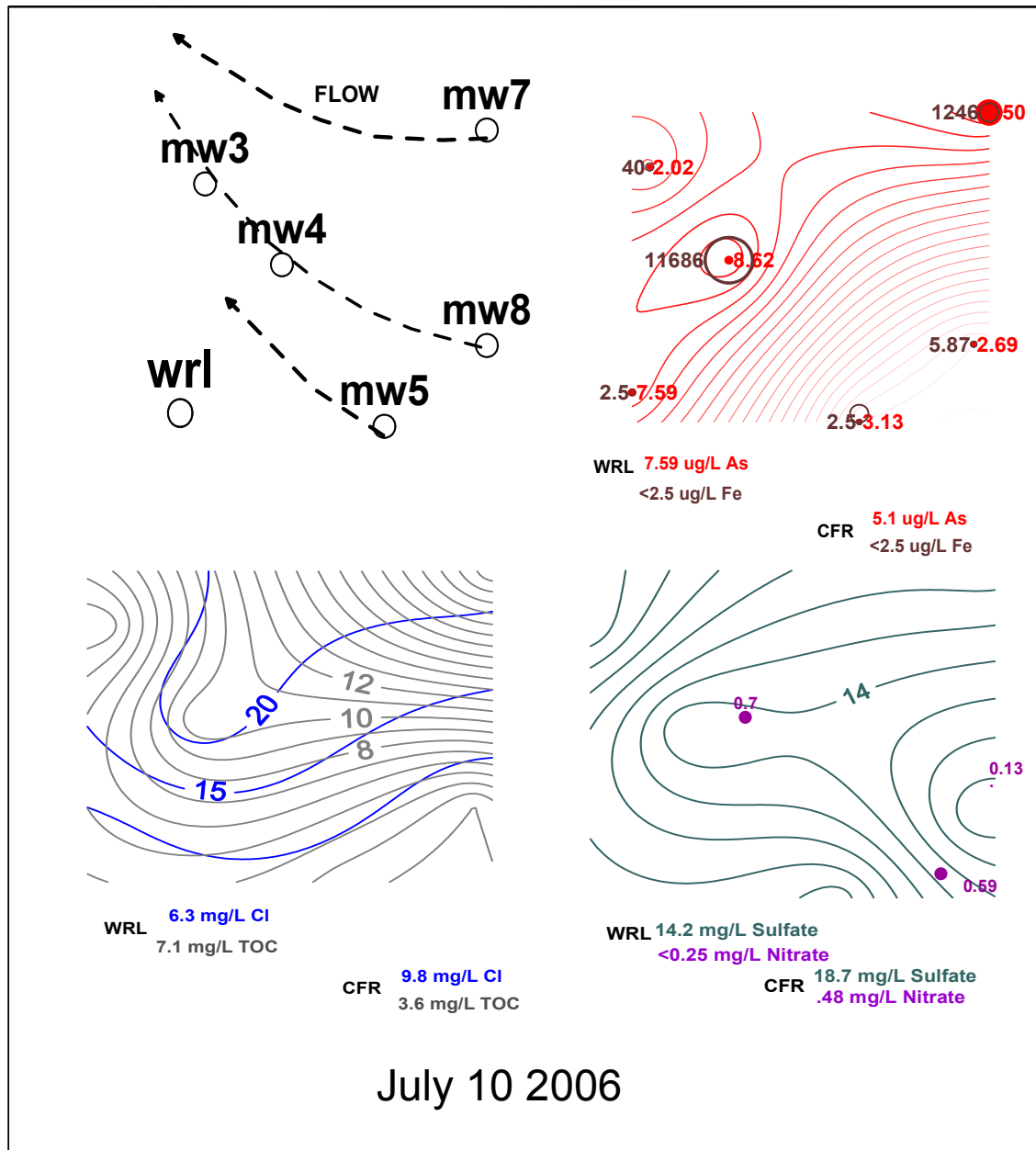
Figure 37 Chemistry contours over the compost yard section of the site for data collected July 10, 2006.

The aquifer was recharged and equilibrating with surface water at this time. MW 7 still contained high levels of arsenic and iron in a reducing environment, the form was As(III), MW 4 showed a consistent amount of As(III) and iron in a reducing environment. Nitrate and redox contours confirm the 2007 extrapolated flowlines shown on July 10 from upriver across the floodplain and into the backwater, as high nitrate in CFR is reflected in well5, and oxygenated river water influences MW5 but not WRL. The historic channel diagonally bisecting the compost yard was still visible in the contours for all contaminant chemistry.

mw7

mw3

mw4

mw8

wrl

mw5

9.42 14

1.72 43

8363
5.03

No
data

27.1
3.51

9 2
3

WRL **3.51ug/L As**
27.1 ug/L Fe

CFR **3.23 ug/L As**
7.9 ug/L Fe

0.82

0.01

0.01

0.01

15 12.5 10

10

4

20

22

20

WRL **7.9 mg/L Su..**
<0.25 mg/L Nitrate

No
data

CFR **32 mg/L Sulfate**
<0.25 mg/L Nitrate

WRL **8.01 mg/L Cl**
4.4 mg/L TOC

CFR **9.5 mg/L Cl**
4.2 mg/L TOC
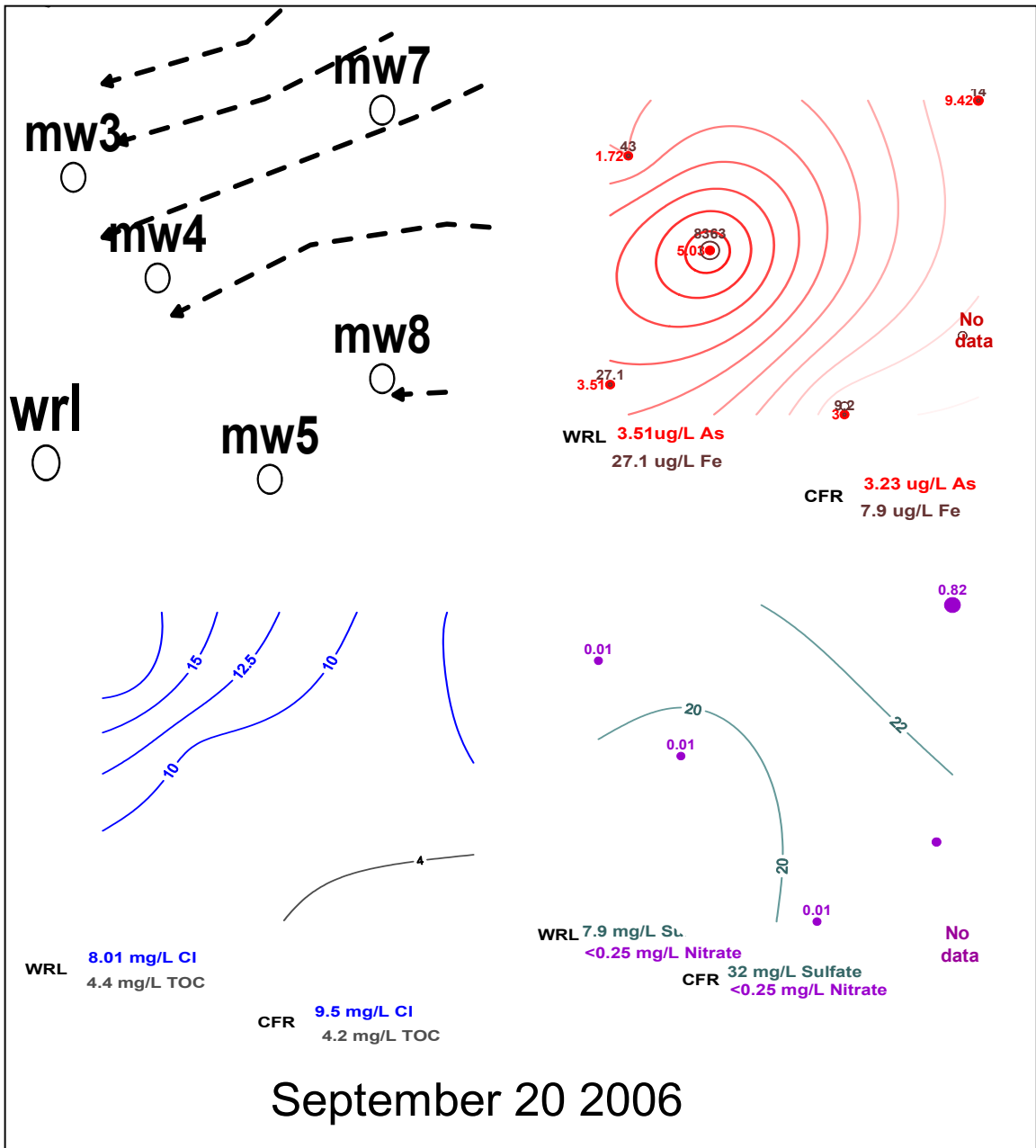
September 20 2006

Figure 38 Chemistry contours over the compost yard section of the site for data collected September 20, 2006.

The water table was dropping below the level of the historic channels and returning to regional flow. Well 4 shows the highest level of arsenic, still in reduced form (As(III)). The historic channel diagonally bisecting the compost yard was no longer visible in the contours for all contaminant chemistry. The local groundwater flow on these dates is shown on the labeled photos in the lower right corners.

Low Water Table Elevation (Winter)

Well MW1
MW1 As <10 ug/L

land surface

Well MW7
MW7 As <10 ug/L

yellow sediment

screened interval

wood

gray sediment

backfilled Channel (high TOC, reducing)

coarse alluvium

30 ft

alluvium

High Water Table Elevation (Spring)

Well MW1
MW1 As <10 ug/L

land surface

Well MW7
MW7 As >100ug/L

yellow sediment

screened interval

wood

gray sediment

backfilled Channel (high TOC, reducing)

30 ft

coarse alluvium

alluvium
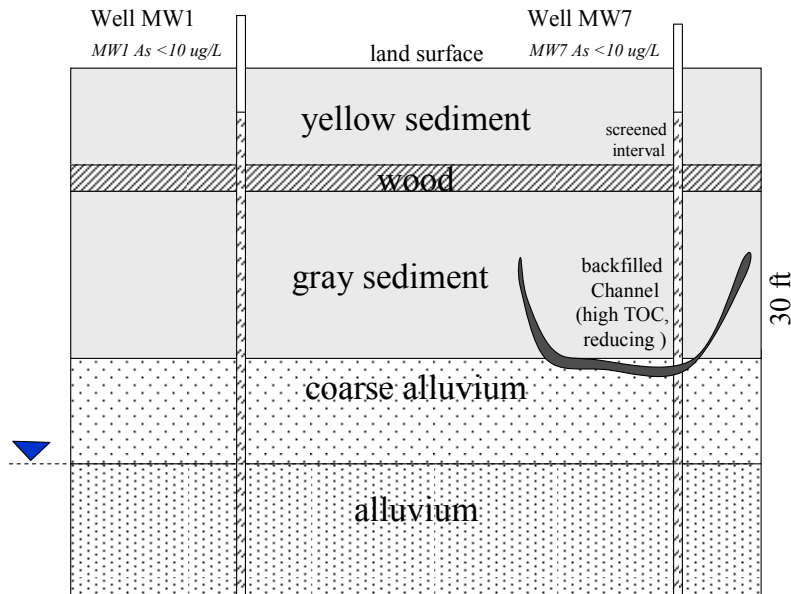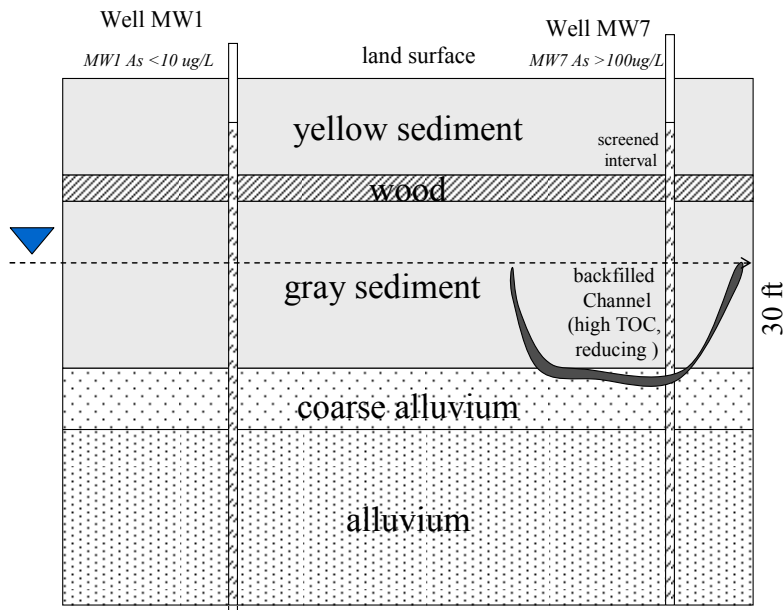
Figure 39 Hydrogeologic mechanism of "redox pump" solublization of contaminants.

The well on the right may show a much higher concentration of arsenic (ten times higher) in the ground water when water table elevation is highest. While many of the wells at the site show the type of increase associated with the well on the left in spring, well 7 appears to be subject to the conditions shown on the right.
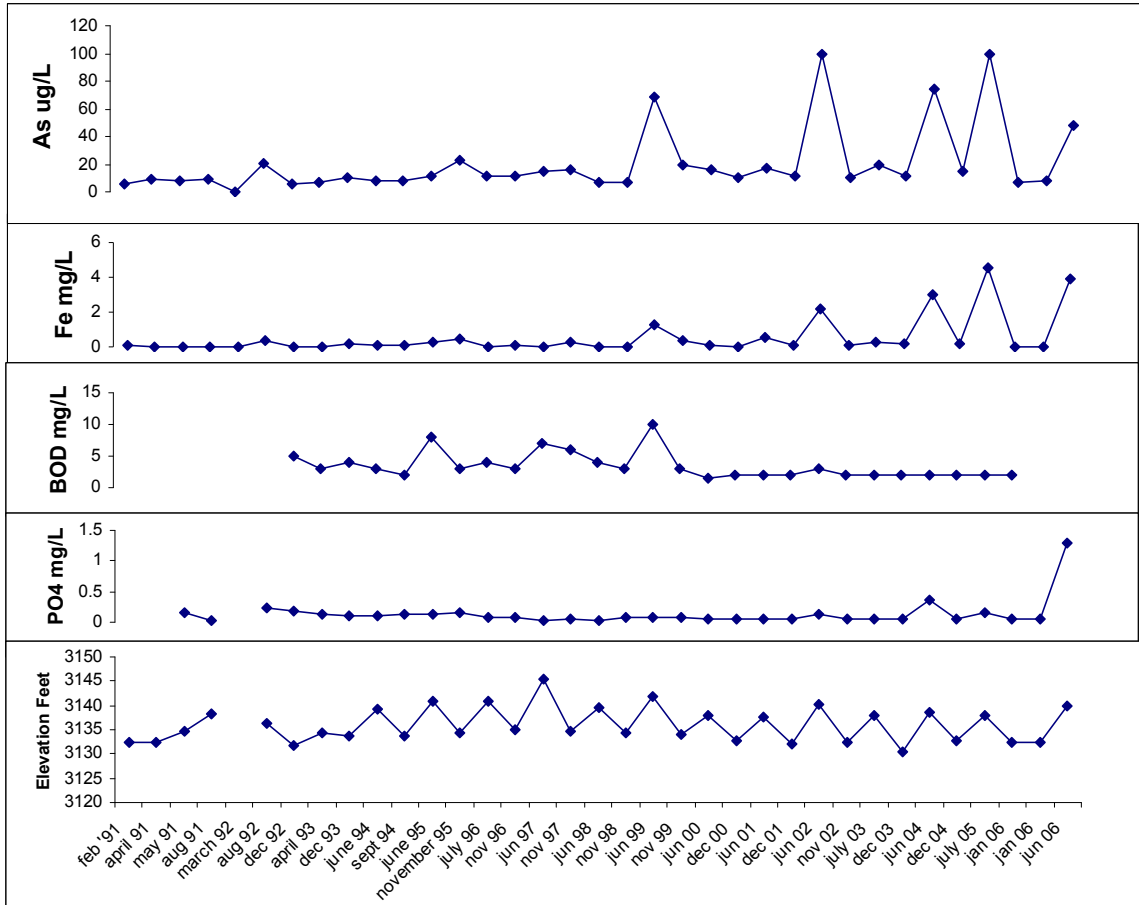
Figure 40 Static water level elevation at time of sampling for MW 7 since 1991, compared with arsenic, iron and phosphate concentrations and Biological Oxygen Demand.

Iron levels increased when arsenic levels increased after 1999. BOD decreases, and phosphate is present at times when arsenic and iron levels are elevated.
Data from Land and Water.

GW Flow May 17 2006

MW7
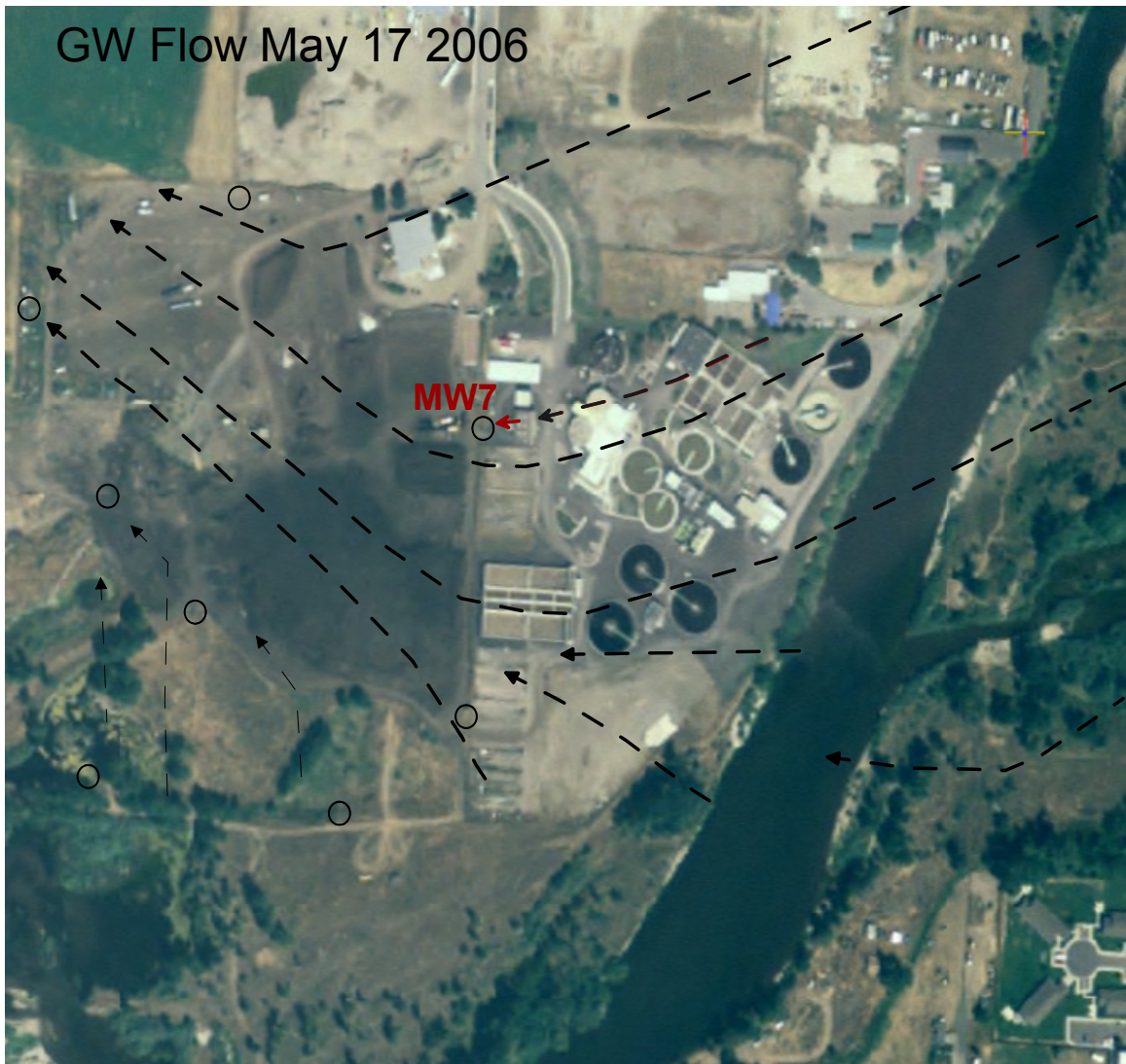
Figure 41 Groundwater flow toward MW7 in spring when 160ug/L arsenic was present.

**As v elevation MW7
Summer Post 1999**
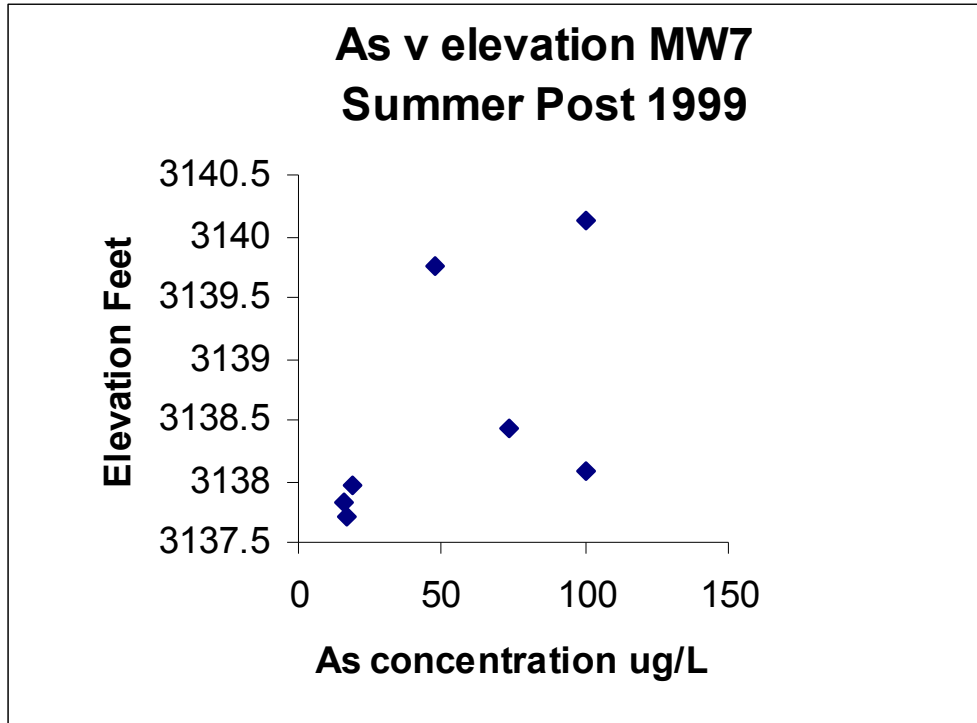
Figure 42 Arsenic concentration vs. static water level elevation for all summer data from MW7 since 1999.

The relationship of arsenic concentration to the position of the water table with respect to sediment layers was tested. Specific elevations of the water table do not directly influence the amount of arsenic in the water directly.
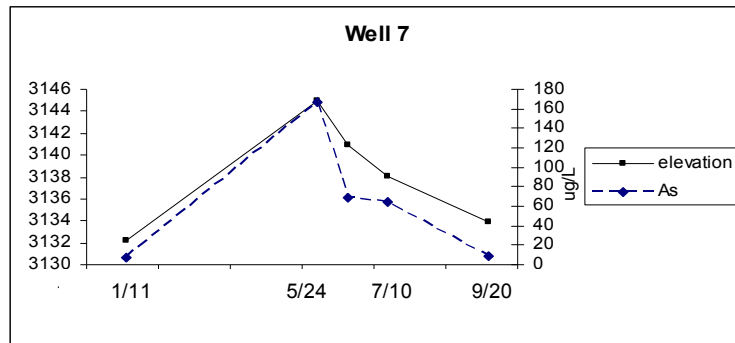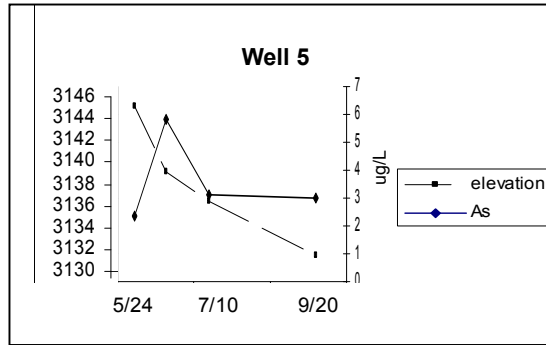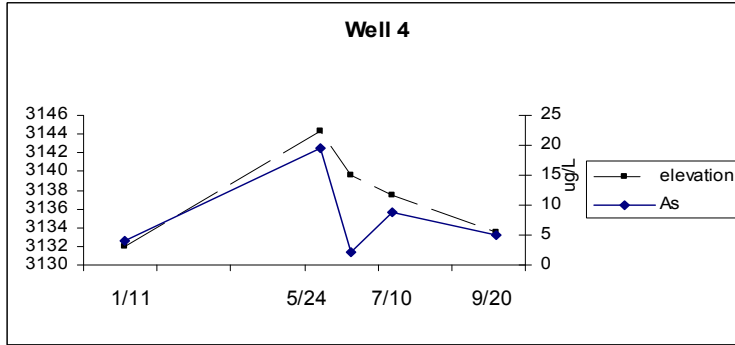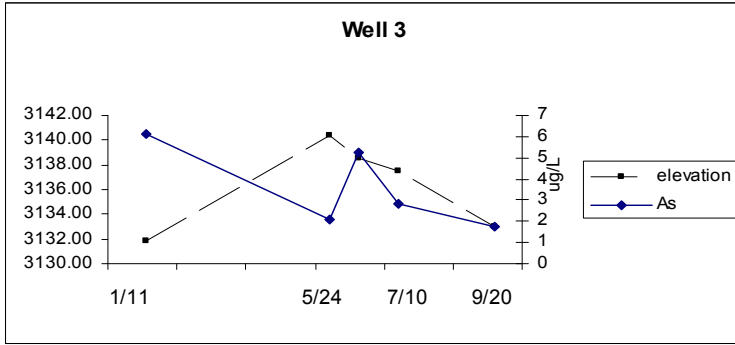
Figure 43 Static water level elevation v. arsenic concentration by well over time

The relationship of arsenic concentration to the position of the water table with respect to sediment layers was tested. In general, arsenic is present at higher concentrations when water table elevations are high. However, specific elevations of the water table do not directly influence the amount of arsenic in the water.
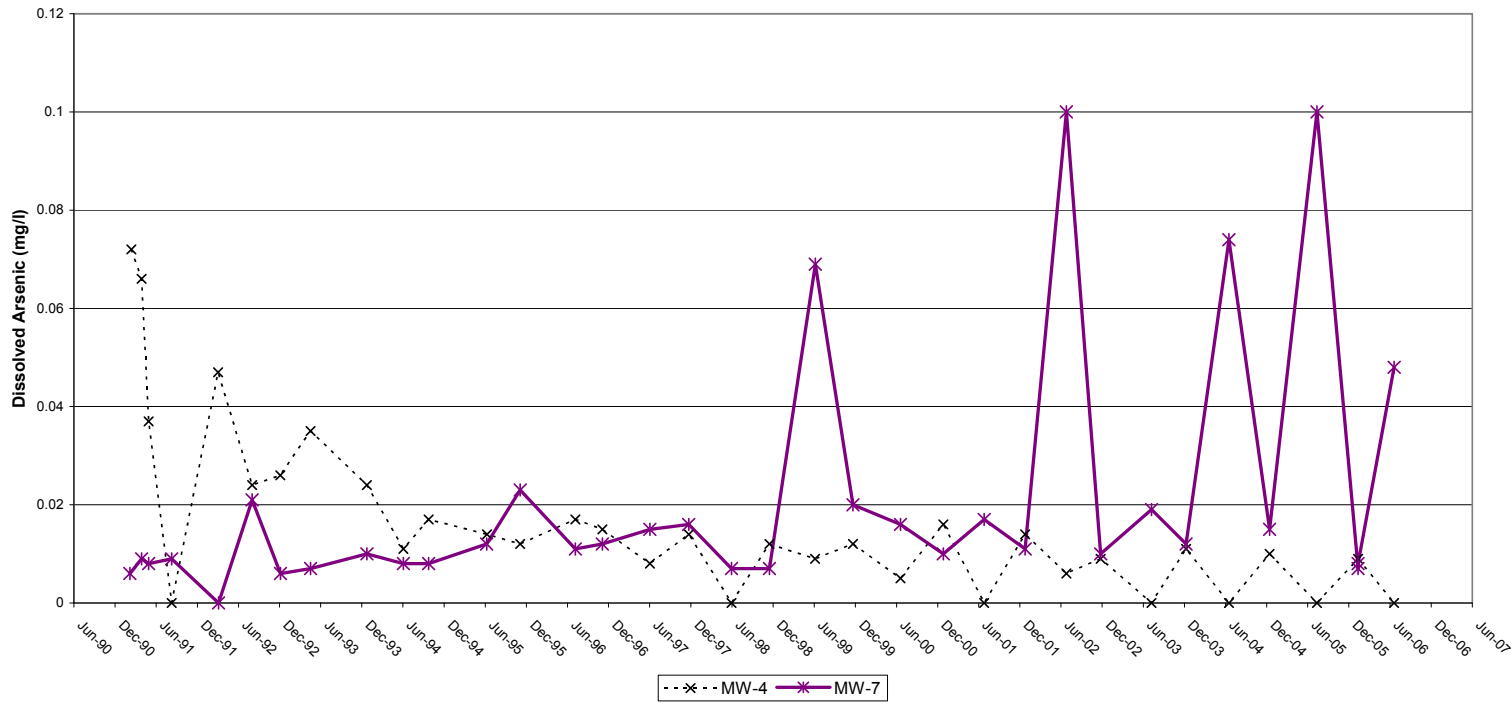
Figure 44 Arsenic concentration at MW4 and MW7 since 1990.

Groundwater at the location of MW4 initially showed elevated concentrations of arsenic, decreasing over time due to reduction and solubilization of adsorbed arsenic in sediments. Concentrations of arsenic in groundwater at the location of MW7 became elevated when reducing conditions were found in this section of the aquifer.
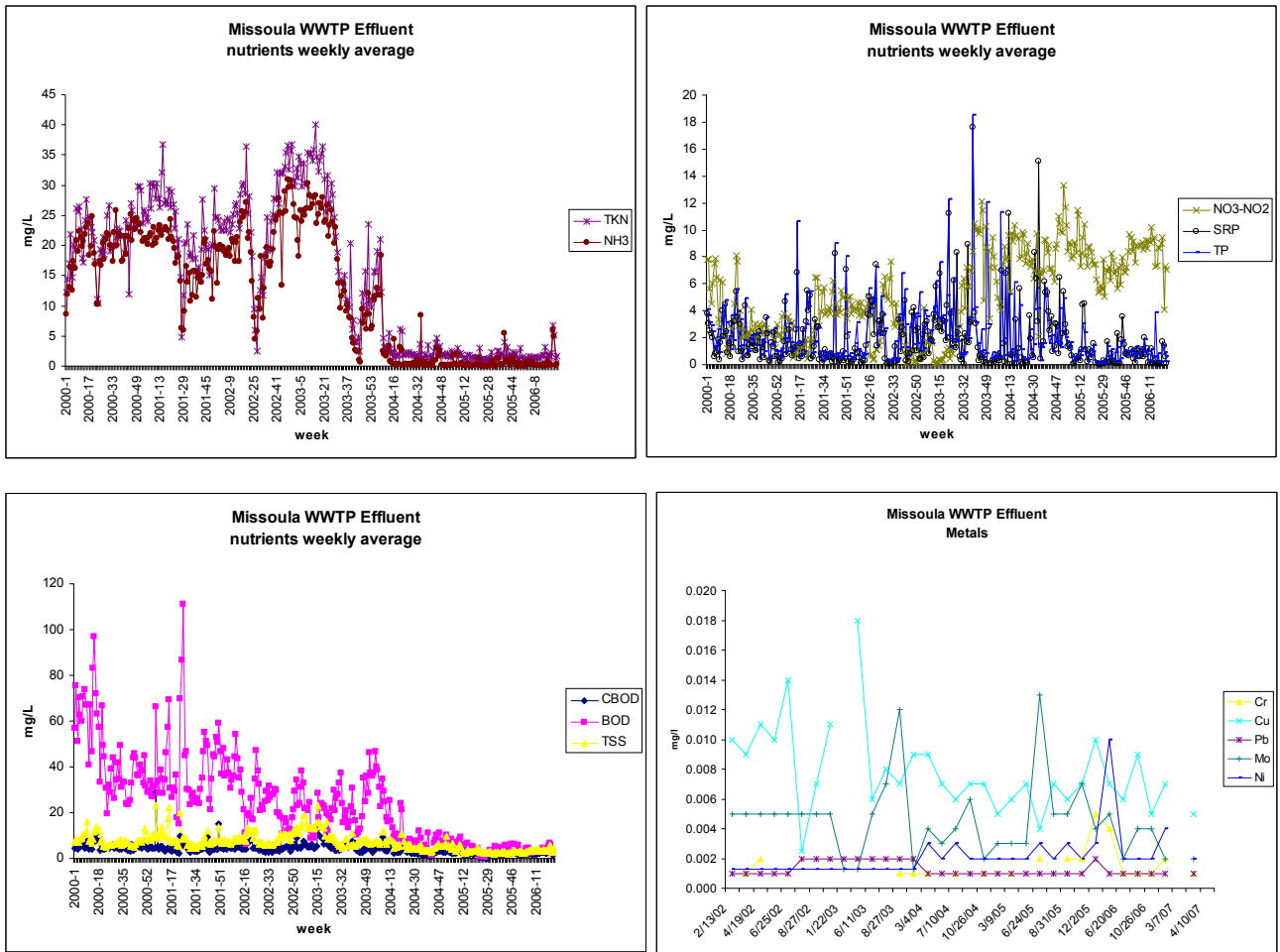
Figure 45 Data from Missoula WWTP Effluent Monitoring

WWTP Effluent prior to 2004 when the new BNR treatment process contains higher levels of most nutrients, nitrogen, TSS, and chemical and biological oxygen demand have decreased significantly. Concentrations of metals have remained the same or increased slightly in the cases of molybdenum and nickel which may be by products of the new BNR treatment process.
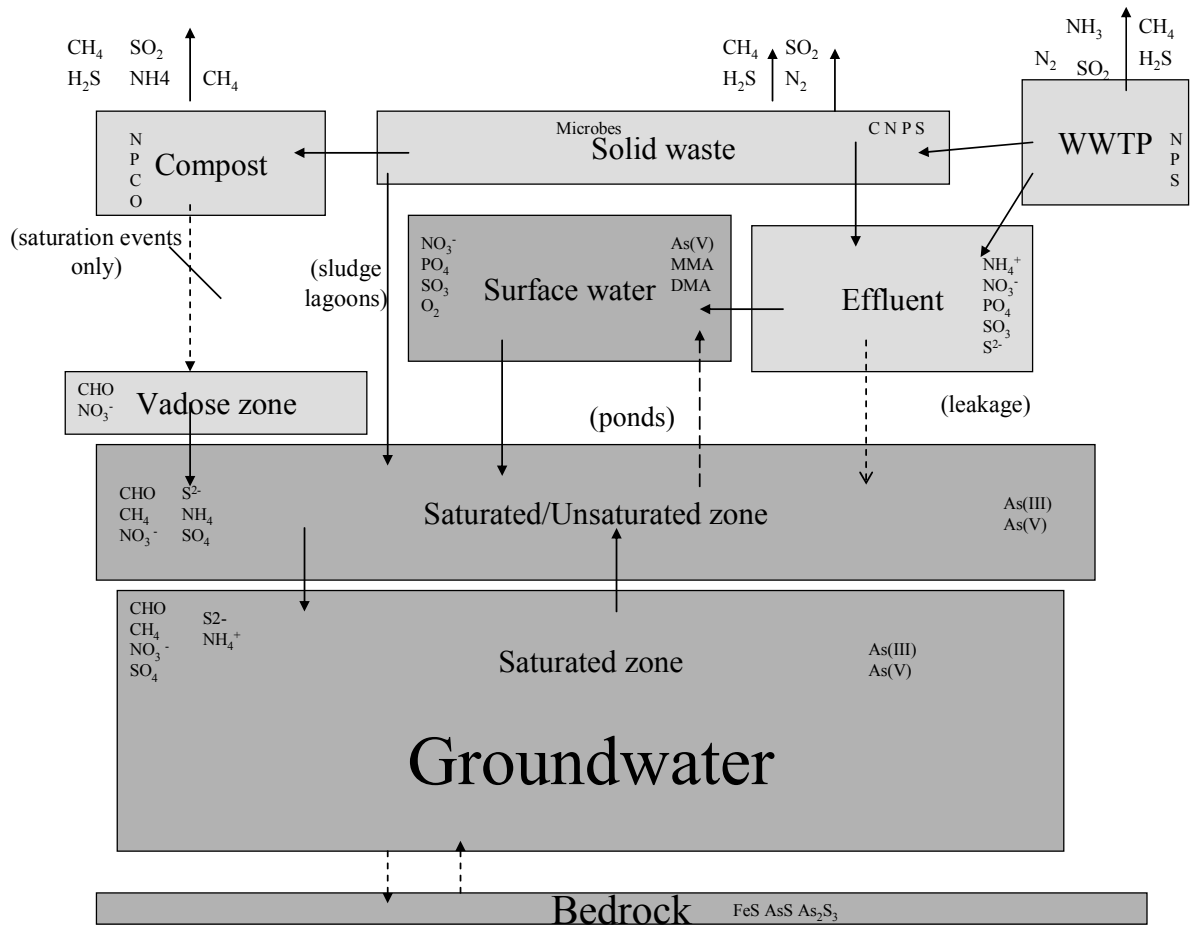
Figure 46 Arsenic and nutrient cycle.

The connection between the effluent, the surface water, groundwater and the sediment layers (saturated/unsaturated zone). Arsenic cycle is in darker shading, nutrient cycle is in lighter shading.

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Sample ID	date collected	As ug/L	Fe ug/L	Ferrizene Fe tot mg/L	Fe 2+ mg/L	Fe 3+ mg/L	Anions F mg/L	Cl mg/L	NO2-N mg/L	SO4 mg/L	NO3-N mg/L	PO43- mg/L	trace elements Mn ug/L	Cu ug/L	major elements Ca ug/L	K ug/L	Mg ug/L	Na ug/L	hardness	TOC mg/L	DO mg/L	temp c	pH
MW2	1/11/2006	0.908	2.50	26	26	0	0.18	8.2	<.1	28.33	0.40		1.10	0.15	41916	2056	11848	5682	153	7.148	3.65	11	7.2
MW2	5/24/2006	1.12	6.94				0.22	15.3	<.1	40.70	6.30		0.119	3.54	56008	2946	14205	18744	198	7.384	1.12	11	6.42
MW3	1/11/2006	6.15	72.00			22	0.22	45.2	<.1	25.81	<0.2		3186.00	0.05	41434	2865	11917	23545		11		13	7.4
MW3	3/24/2006	3.43	94.40	535	139	396	0.23	20.5	<.1	35.78	<0.2		2026.90	4.28	39180	2876	8615	21207	133	3.2			
MW3	5/24/2006	2.06	23.1				0.21	15.9	<.1	33.50	0.09		2728.0	0.883	42375	9587	26213	33542	214	8.7	0.71		7.77
MW3	6/14/2006	5.27	26.90				0.23	13.6	<.1	30.9	0.64	0.025	45.50		51602	4260	13823	23040	186	8.4	0.05	13	6.4
MW3	7/12/2006	2.81	40.16				0.20	17.0	<.1	27.2	0.70	0.025	2073	2.89	34193	4838	9810	23666	126	2.3	0.04	12	7.55
MW3	9/20/2006	1.72	43.70				0.22	19.9	<.1	21.5	n.d.	0.025	3562	5.09	36276	2432	9269	17660	129	4.6	0.04	12	6.36
MW4	1/11/2006	4.04	5725			5332	0.18	4.6	<.1	32.46	<0.2		1443	2.5	33914	3128	8829	6046	121	9.5		12	6.71
MW4	3/24/2006	9.32	1119		824		0.17	6.9	<.1	40.21	<0.2		1613	1.37	43901	3537	8582	6116	145	7.4			
MW4	5/24/2006	19.47	1192	6390	1319	5071	0.17	15.1	<.1	25.10	<0.2		1912	0.671	56772	18118	12675	9582	194	27.36	0.08		
MW4	6/14/2006	2.06	9870				0.21	14.0	<.1	18.4	<0.2	0.025	7165	0.374	78108	16483	15293	12654	258	16.4	0.02	15	6.07
MW4	7/12/2006	8.83	5945				0.23	22.5	<.1	12.6	<0.2	0.025	11687	0.396	49998	5936	11687	11538	173	10.2	0.05	11	6.46
MW4	9/20/2006	5.03	8363				0.22	8.6	<.1	18.8	<0.2	0.025	1764	0.671	36867	4312	7735	7473	124	4.9	0.06	9	6.5
MW5	5/24/2006	2.38	2.50	26	26	0	0.16	12.9	<.1	31.4	1.3	0.025	0.06	2.29	35673	1804	10283	9972	131	6.4	2.79		
MW5	6/14/2006	5.84	8.45				0.13	24.1	<.1	49.9	2.6	0.025	1.35	12.8	46123	7751	29743	28917	238	10.4	1.3	10	6.8
MW5	7/12/2006	3.13	2.50				0.17	7.7	<.1	23.1	0.59	0.025	0.05	4.75	30414	1800	9477	10960	115	2.4	0.42	11	7.43
MW5	9/20/2006	3	9.20				0.11	8.1	<.1	20.3	<0.2	0.025	0.10	3.71	31412	1992	9008	10043	116	3.8	0.06	10	6.81
seep 5	5/24/2006	4.79	31.90	31	29	2	0.16	9.6	<.1	38.50	0.15	0.27	0.65	4.68	40748	6226	10578	9542	145	18.6	3.9		7.17
seep 5	6/14/2006	4.8	26.90				0.11	57.2	<.1	31.2	<0.2	0.025	1.35	1.65	44185	6391	11574	12246	158	22.7	6.3		
MW7	1/11/2006	7.91	2.50				0.14	23.8	<.1	33.75	1.26		53.40	10.2	40758	2816	12455	16839	153	9.7		12	7.01
MW7	3/24/2006	3.04	2.50		11		0.17	11.7	<.1	36.39	0.84		5.97	15.2	44371	2499	9406	8705	150	7			
MW7	5/24/2006	166.9	110.00	37	34	3	0.17	40.0	<.1	44.10	<0.2	3.60	3767	19.2	58875	9666	14319	18372	206	38	0.42		6.5
MW7	6/14/2006	69.3	3190				0.064	9.2	<.1	11.3	<0.2	0.025	1852	14.6	30535	11618	23330	16266	172	12.5	0.73	17	6.5
MW7	7/12/2006	64	1928				0.18	22.3	<.1	6.6	<0.2	0.025	10251	2.73	71495	6514	17567	14246	251	23.9	0.07	15	6.26
MW7	9/20/2006	9.42	14.1				0.11	6.8	<.1	23.9	0.82	0.025	216.00	3.09	40513	3147	10379	8764	144	4.3	0.23	15	6.95
MW8	1/11/2006	5.13	2.50					19.0		33.00	1.50		0.21	12.3	37719	2659	13229	10698	149	7.6		13	7.48
MW8	5/24/2006						-																
MW8	6/14/2006	10.3	10.30				0.11	6.5	<.1	30.1	0.13	0.14	0.09	8.51	52400	4341	14562	18001	191	10.8	0.73	10	6.76
MW8	7/12/2006	7.93	5.87				0.16	6.3	<.1	31.1	0.12	0.025		1.87	42823	2458	12150	8030	157	2	0.13	11	6.95
MW8	7/12/2006								<.1													15	
WRL	1/11/2006	3.09	2.50				0.13	7.9	<.1	37.73	<0.2		16.80	6.72	32607	1723	10896	9709	126	8		3	7.72
WRL	3/24/2006	2.58	2.50			13	0.17	9.0	<.1	40.39	<0.2		15.30	1.86	23893	1163	6507	5655	86	5.2			
WRL	5/24/2006	3.49	13.84	26	26	0	0.11	2.7	<.1	7.90	<0.2		0.59	5.03	19148	1627	5175	3648	69	13	3.9		7.23
WRL	6/14/2006	4.38	23.10				0.12	3.5	<.1	7.4	<0.2	0.025	38.50	7.37	26148	2408	6524	4116	92	11.2	4.5	20	7.8
WRL	7/12/2006	7.59	2.50				0.12	6.3	<.1	14.3	<0.2	0.025	5.87	3.16	27779	2637	8476	12292	104	7.1	6.4	21	8.1
WRL	9/20/2006	3.51	27.10				0.13	8.0	<.1	14.2	<0.2	0.025	110.50	1.24	34380	1843	9777	8601	126	4.4	3.16	15	7.1
CFR	1/11/2006	3.1	2.50				0.23	11.7	<.1	37.12	0.67		1.95	13.1	33811	2210	10975	12856	130	10.7		3	
CFR	3/24/2006	3.89	6.13		2		0.27	14.5	<.1	37.81	0.64		3.15	2.56	30782	2244	7090	8933	106	4.3			
CFR	5/24/2006	2.1	12.90	28	27	1	0.06	2.1	<.1	6.50	0.09		0.74	2.49	17014	853	4726	2814	62	9.7	6.98		
CFR	6/14/2006	4.28	2.50				0.13	2.8	<.1	12.7	0.16	0.025	0.09	4.86	20927	1105	6252	4781		9.2	6	18	8.99
CFR	7/12/2006	5.1	2.50				0.15	9.8	<.1	18.8	0.48	0.025	0.05	2.94	29056	2710	9055	13336	110	3.6	10.22	20	7.73
CFR	9/20/2006	3.23	7.90				0.23	9.5	<.1	32.2	<0.2	0.025	0.74	1.46	28532	1918	10428	10458	114	4.2	8.4	12	7.12
WTP	3/24/2006	1.13	2.50	0	0		0.21	4.0	<.1	30.28	0.32		0.10	2.56						3.7			
CFR below	5/24/2006	1.76	2.50	27	26	1	0.08	5.7	<.1	7.10	0.35		0.18	2.16	17313	1083	4889	5579	63.4	6.4	8.43		
CFR above	5/24/2006	1.73	6.53	74	36	38	0.07	0.7	<.1	6.10	<0.2		0.13	2.86	15459	675	4440	1852	56.9	9.6	8.4		

APPENDIX   Soil Chemistry data Eko Compost Study 2006

Solid sample results (mg/kg)

LEACHATE	dilution	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Sb	Se	Si	Sr	Ti	V	Y	Y	Zn
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Layer1	68	0.45	5.31	0.00	0.05	0.000	69.49	b.d.	0.003	b.d.	0.00	0.58	0.09	0.001	2.68	0.40	0.000	0.04	0.00	0.11	0.01	0.58	b.d.	b.d.	0.35	0.02	0.00	0.00	0.53	0.50	0.01
Layer2	43	1.87	11.36	0.01	0.27	0.000	23.66	0.001	0.003	0.003	0.09	2.60	1.74	0.001	2.06	0.56	0.000	0.05	0.01	1.25	0.05	0.19	b.d.	b.d.	1.26	0.04	0.01	0.00	0.49	0.56	0.17
Layer3	26	5.08	45.47	0.01	0.43	0.001	23.72	0.002	0.009	0.005	0.68	8.52	1.64	0.005	5.03	1.17	0.000	0.19	0.01	1.72	0.18	0.22	b.d.	b.d.	3.91	0.07	0.03	0.02	0.95	1.20	0.39
Yard Matl	15	4.22	1.94	0.05	0.61	0.001	33.06	0.001	0.003	0.008	0.17	7.50	9.02	0.001	5.32	0.59	0.001	1.04	0.01	15.76	0.07	0.43	b.d.	b.d.	1.99	0.10	0.00	0.01	1.11	1.15	0.42
Geology	38	2.86	4.97	0.00	0.21	0.001	9.39	0.000	0.004	0.002	0.02	3.56	1.17	0.002	1.98	0.37	b.d.	0.04	0.01	0.65	0.02	0.07	b.d.	b.d.	2.12	0.02	0.03	0.01	0.63	0.82	0.06
Final Mix	38	4.13	10.91	0.03	0.40	0.000	22.12	0.001	0.002	0.008	0.16	4.56	6.81	0.001	3.65	0.43	0.000	0.81	0.01	13.49	0.05	0.56	b.d.	b.d.	1.51	0.08	0.01	0.01	0.43	0.54	0.37

Water Extract — Leachate:	Ag	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Sb	Se	Sr	Tl	U	V	Zn
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
stage 1 compost	b.d.	42.74	64.78	56.78	high	b.d.	b.d.	high	high	b.d.	b.d.	b.d.	b.d.	0.85	b.d.	14.04	14.94	23.09	45.25	high	4.11	high	4.18	high					high
raw mat'lmilled yard waste	b.d.	high	15.59	16.95	high	b.d.	b.d.	high	high	b.d.	b.d.	b.d.	b.d.	3.60	b.d.	25.79	27.60	high	high	#VALUE!	6.70	high	high	high					high
leaves	b.d.	50.31	2.02	1.75	high	b.d.	b.d.	high	high	b.d.	b.d.	b.d.	b.d.	0.74	b.d.	2.83	3.02	39.16	77.20	high	high	high	high	high					high
clean sand	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	high	high	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	40.40	b.d.	87.62	b.d.	64.49

	solid:	Ag	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	S	Sb	Se	Sr	Tl	U	V	Zn
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
stage 1 compost	6		0.0071	0.0108	0.0094	high	b.d.	b.d.	high	high	b.d.	b.d.	b.d.	b.d.	0.0001	b.d.	0.0023	0.0025	0.0038	0.0075	high	0.0007	high	0.0007	high					high
raw mat'lmilled yard	9.4		high	0.0017	0.0018	high	b.d.	b.d.	high	high	b.d.	b.d.	b.d.	b.d.	0.0004	b.d.	0.0027	0.0029	high	high	high	0.0007	high	high	high					high
leaves	9.6		0.0052	0.0002	0.0002	high	b.d.	b.d.	high	high	b.d.	b.d.	b.d.	b.d.	0.0001	b.d.	0.0003	0.0003	0.0041	0.0081	high	0.0004	high	0.0049	high					high
clean sand	10		b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.					0.0064

Appendix b Arsenic Speciation Data

Perkin Elmer HPLC-ICP/MS
Total arsenic determined using EPA SW 6020 and 3005

Sample ID	date collected	ICP-MS Data As total	As diss	HPLC/ICPMS data As	As(III)	As(V)	dma	mma	AsC, AsB
MW2	1/11/2006	1.13	0.908						
MW2	5/24/2006		1.12						
MW3	10/20/2005	.	2.84	2.1	1.12	0.98			
MW3	1/11/2006	6.57	6.15	3.48	3.2	0.27			
MW3	3/24/2006		3.43	3.66	2.96	0.71			
MW3	6/14/2006		5.27	3.557	3.043	0.514			
MW3	7/12/2006		2.81	2.82	1.95	0.87			
MW3	9/20/2006		1.72	1.5	0.6	0.9			
MW4	3/10/2005		7.6	11.32	10.75	0.57			
MW4	10/20/2005		5.6	4.63	4.2	0.43			
MW4	1/11/2006	3.72	4.04	3.89	3.89				
MW4	3/24/2006		9.32	6.26	6.03	0.2			
MW4	6/14/2006		2.06	5.9918	5.73	0.2636			
MW4	7/12/2006		8.83	5.23	5.23	0			
MW4	9/20/2006		5.03	3.88	3.61	0.26			
MW5	6/14/2006		5.84	2.73		2.73			
MW5	7/12/2006		3.13	2.733		2.733			
MW5	9/20/2006		3	2.36		2.36			
seep 5	6/14/2006		4.8	3.51	0.139	2.88	0.3399	0.1445	
seep 5	7/12/2006			3		3			
MW7	3/10/2005	8.27		6.35		6.35			
MW7	10/20/2005	19.5		7.65	1.2	6.1	0.35		
MW7	1/11/2006	11	7.91	2.51		2.51			
MW7	3/24/2006		3.04	3.34		3.34			
MW7	5/24/2006		166.9						
MW7	6/14/2006		69.3	72.37	69.41	2.76	0.1181	0.085	
MW7	7/12/2006		64	76.18	75.75	0.428			
MW7	9/20/2006		9.42	7.3	0.7	6.5			
MW8	1/11/2006		5.13						
MW8	5/24/2006								
MW8	6/14/2006		10.3	6.11		6.11			
MW8	7/12/2006		7.93	5.2		5.2			
MW8	7/12/2006			na					
MW8	7/12/2006			na					
WRL	1/11/2006	5.76	3.09						
WRL	3/24/2006		2.58						
			3.49	1.56	0.187	1.25	0.124		
WRL	6/14/2006		4.38	3.5567	0.6318	2.86	0.0628		
WRL	7/12/2006		7.59	2.63	1.97	0.24	0.42		0.025
WRL	9/20/2006		3.51	2.5	1.4	1.1			
CFR	1/11/2006	5.11	3.1						
CFR	3/24/2006		3.89	1.81		1.812			
			2.1	4.26	0.3106	3.91	0.0427		
CFR	6/14/2006		4.28	4.02	0.65	3.36			0.025
CFR	7/12/2006		5.1	1.03	0.08	0.86	0.09		0.025
CFR	9/20/2006		3.23	0.437		0.437			
WTP	3/24/2006		1.13						
cfr below	5/24/2006		1.76						
cfr above	5/24/2006		1.73						

Appendix c   Land and Water Data for Eko Compost MW 7 1991 to 2006

			As	SWL elev	temp	Fe	SO4	BOD	COD	TOC	pH	Ca	Cl	NO3	NH4	PO4	TOC	Mn
			ug/L	ft	c	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
MW7	02/01/91	feb '91	6	3132.23		0.13	37		53	16	6.8	74	22	2.86	2.2		16	0.13
MW7	04/01/91	april 91	9	3132.3	7.9	0.04	32		68	25	6.9	114	46	1.77	8.2		25	0.64
MW7	05/03/91	may 91	8	3134.52	9.1	0	33		1	2	7.2	71	24	3.95	1.7	0.15	2	0.24
MW7	08/14/91	aug 91	9	3138.17	10.7	0	40		14	2	7.4	26	5	1.88	1.5	0.03	2	0.22
MW7	03/09/92	march 92	0		8.6	0.04	42		48	3	6.9	81	20	4.08	3.2		3	0.23
MW7	08/05/92	aug 92	21	3136.23	16.3	0.33	37		26	8	6.4	65	8	2.55	16.3	0.22	8	1.9
MW7	12/09/92	dec 92	6	3131.89	9.6	0	32	5	0	0	6.5	53	4	0.64	0.3	0.18	0	0.06
MW7	04/21/93	april 93	7	3134.28	12.8	0	37	3	0	4	6.5	86	41	5.88	0.6	0.12	4	0.17
MW7	12/27/93	dec 93	10	3133.68	11.3	0.19	34	4	1	2	7.43	53	10	0.57	1.4	0.11	2	0.28
MW7	06/07/94	june 94	8	3139.19	12.5	0.05	36	3	12	0	7.2	68	6	2.26	2.9	0.1	0	3.18
MW7	09/27/94	sept 94	8	3133.76	16.4	0.08	27	2	0	0	7.39	51	4	0.79	0.7	0.14	0	0.19
MW7	06/12/95	june 95	12	3140.75	17	0.25	41	8	13	9	6.87	101	11	1.47	2.2	0.14	9	8.78
MW7	11/07/95	november	23	3134.45	13.4	0.42	27	3	0	0	6.92	47	4	0.4	2.1	0.15	0	0.42
MW7	07/09/96	july 96	11	3141.02	17.6	0	48	4	7	4	6.99	49	5	1.93	2.3	0.08	4	3.6
MW7	11/06/96	nov 96	12	3134.99	9.5	0.11	27	3	3	3	8.24	40	4	0.67	1	0.08	3	0.33
MW7	06/05/97	jun 97	15	3145.49	16	0.04	48	7	13	8	7.09	57	9	1.95	3	0.03	8	4.6
MW7	11/24/97	nov 97	16	3134.52	13.2	0.23	32	6	0	2	7.4	48	9	0.41	0.7	0.06	2	0.41
MW7	06/02/98	jun 98	7	3139.64	15.3	0	32	4	11	4	7.23	66	11	2.07	1.3	0.03	4	3.51
MW7	11/17/98	nov 98	7	3134.41	11.9	0	32	3	3	0	7.42	46	5	0.48	1.1	0.07	0	0
MW7	06/09/99	jun 99	69	3141.78	15.3	1.25	37	10	27	9	7.09	113	19	1.26	2.5	0.07	9	8.75
MW7	11/23/99	nov 99	20	3133.94	12.9	0.35	29	3	3	0	6.95	44	4	0.45	0.3	0.08	0	0.45
MW7	06/21/00	jun 00	16	3137.83	13.8	0.11	24	1.5	4	3	7.22	46	9	1.36	0.2	0.04	3	0.7
MW7	12/28/00	dec 00	10	3132.63	12.2	0.03	30	b.d.	0	2	7.07	52	10	1.24	0	0.04	2	0.08
MW7	06/27/01	jun 01	17	3137.7	13.6	0.53	25	b.d.	16	7	6.68	64	14	1.78	1.4	0.06	7	3.49
MW7	12/26/01	dec 01	11	3132.03	13	0.13	32	b.d.	11	0	6.94	50	4	0.41	0	0.05	0	0.22
MW7	06/27/02	jun 02	100	3140.12	13.8	2.18	26	b.d.	19	6.9	6.73	115	15	0.26	1	0.12	6.9	11.4
MW7	11/26/02	nov 02	10	3132.49	13.3	0.07	25	b.d.	4	0	7.1	45	4	0.35	0	0.04	0	0.25
MW7	07/10/03	july 03	19	3137.96	14	0.31	29	b.d.	7	2	6.82	54	8	2.4	1.7	0.05	2	2.55
MW7	12/10/03	dec 03	12	3130.48	13.3	0.14	27	b.d.	0	0.7	7.09	46	4	0.34	0	0.06	0.7	0.2
MW7	06/17/04	jun 04	74	3138.43	12.8	2.98	26	b.d.	11	2.2	7.01	58	19	1.74	0.3	0.36	2.2	1.4
MW7	12/15/04	dec 04	15	3132.64	14.2	0.22	26	b.d.	0	0	6.95	43	6	0.48	0	0.06	0	0.15
MW7	07/13/05	july 05	100	3138.07	14.5	4.51	19	b.d.	32	8.8	6.67	67	11	1.61	4.2	0.16	8.8	5.56
MW7	01/11/06	jan 06	7	3132.24	12.4	0	31	b.d.	0	0	7.01	57	25	1.19	0	0.04	0	0.06
MW7	01/11/06	jan 06	8	3132.24	12.4	0	31		0	0	7.01	55	25	1.14	0	0.04	0	0.05
MW7	06/20/06	jun 06	48	3139.76	14.7	3.91	22		32	9	6.86	84	18	0.52	1.9	1.3	9	5.44

MW7 Temperatures Since 1991
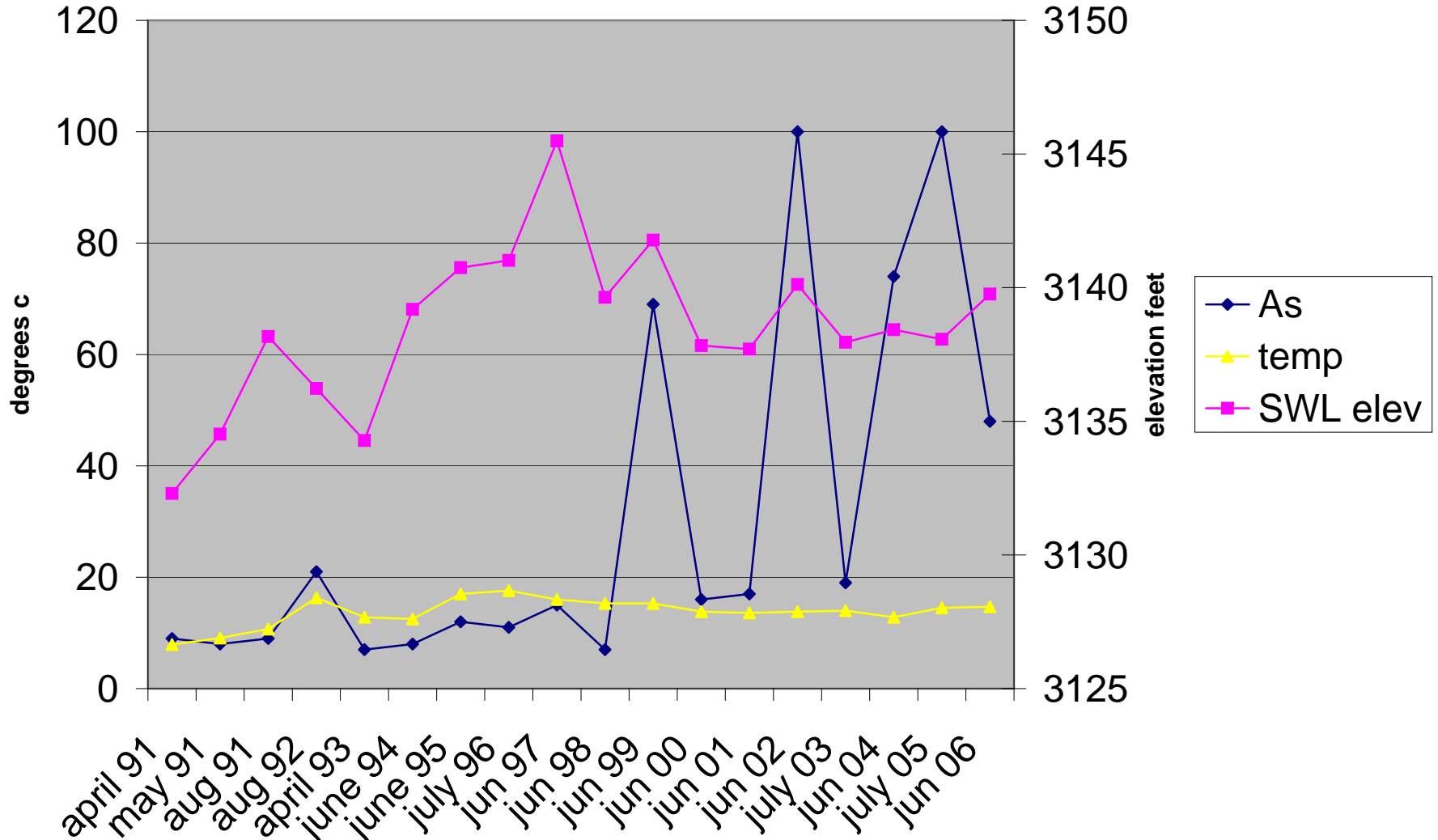
Weekly Averages Missoula WWTP Effluent Jan-2000 through Jul-2006

Appendix e

Years	Months	Weeks	Flow MGD	pH	Temp oC	CBOD mg/L	BOD mg/L	TSS mg/L	NO3-NO2 mg/L	TKN mg/L	NH3 mg/L	SRP mg/L	TP mg/L
2000													
	January	2	7.91	7.21	13.8	4.46	57.1	7.14	7.84	12.32	8.59	3.8	4.07
	January	3	7.33	7.23	12.7	5.62	75.4	8.37	7.81	14.38	11.96	3.07	3.64
	January	4	7.69	7.25	12.4	3.85	51.25	6.91	5.64	16.98	13.13	2.56	3.1
	January	5	7.89	7.27	12.6	4.92	70.4	7.13	4.57	21.82	16.33	2.31	2.88
	February	6	8.09	7.24	11.6	4.92	62.8	8.33	6.01	14.72	12.53	1.98	2.48
	February	7	8.11	7.33	11.7	6.1	60.2	8.7	7.54	20.14	17.39	0.56	1.18
	February	8	8.1	7.37	11.3	5.56	70.8	10.54	7.9	19.21	16.29	0.79	1.36
	February	9	8.3	7.36	11.4	4.61	73.6	10.5	6.45	26.14	20.91	0.9	1.68
	March	10	8.48	7.35	12.3	6.22	67	11.34	3.38	25.64	19.06	1.87	2.58
	March	11	8.48	7.32	12.2	7.76	67	16.13	2.84	26.48	22.29	0.36	0.86
	March	12	8.41	7.36	12.5	4.09	41	7.54	6.32	22.74	21.3	1.67	2.03
	March	13	7.98	7.3	12.4	5.14	67.25	8.39	6.12	17.83	19.9	4.02	4.37
	April	14	8.18	7.31	13.1	3.89	46.6	6.6	2.1	17.21	20.71	2.09	2.44
	April	15	7.95	7.35	13.2	6.58	83	8.63	2.5	24.13	21.78	4.46	4.77
	April	16	7.41	7.35	14	8.53	97	11.69	0.83	27.67	22.95	2.46	3.1
	April	17	8.14	7.34	14.9	10.68	72	13.56	1.17	24.61	23.74	0.92	1.54
	April	18	7.59	7.34	14.8	8.02	63.2	12.2	2.05	24.22	18.43	1.55	2.11
	May	19	7.74	7.38	15.3	7.65	57.2	12.66	1.55	23.01	19.93	0.56	1.09
	May	20	7.78	7.33	15	3.61	33.4	7.07	2.7	22.24	24.82	3.05	3.68
	May	21	8	7.31	16.1	5.45	66.5	8.6	3.38	20.84	18.67	1.28	1.77
	May	22	7.86	7.27	16.8	4.06	49.32	5.49	4.56	17.44	16.86	3.23	3.63
	June	23	7.13	7.27	16.7	4.2	44.4	5.77	8.07	11.16	10.33	5.42	5.58
	June	24	7.07	7.27	17.6	4.45	30.85	4.71	7.68	10.45	10.26	3.56	3.93
	June	25	7.18	7.35	17.2	4.74	19.48	5.69	2.88	19.4	17.38	0.94	1.33
	June	26	6.86	7.36	18	4.58	32.22	5.63	4.03	18.69	16.63	2.95	3.32
	July	27	7.94	7.38	18.3	5.23	28.98	6.44	2	21.3	20.32	1	1.39
	July	28	7.5	7.41	18.2	5.21	38.9	5.69	2.73	18.48	17.71	0.4	0.56
	July	29	8	7.39	19	6.28	44.02	6.27	2.08	21.25	21.07	1.29	1.8
	July	30	7.92	7.37	19.3	4.53	26.12	6.37	2.06	24.92	22.03	4.36	4.92
	July	31	8.06	7.43	19.8	5.55	34.24	6.81	2.01	26.71	21.72	0.67	1.07
	August	32	8.09	7.47	20	4.46	41.8	7.53	2.48	19.02	20.06	0.67	1
	August	33	8.09	7.38	19.7	4.1	34.8	6.46	2	19.81	19.58	1.48	1.94
	August	34	8.09	7.39	19.3	5.45	49.5	8.34	4.1	20.09	17.45	1.73	2.18
	August	35	8.1	7.43	19.4	3.87	30.98	5.9	2.56	20.05	22.19	1.35	1.78
	September	36	8.51	7.43	19.2	5.23	33.38	6.16	2.41	21.37	25.77	1.74	2.21
	September	37	8.51	7.39	18.6	4.31	33.32	7.83	3.07	22.82	20.01	1.07	1.49
	September	38	8.57	7.38	19.1	3.85	23.88	6.5	2.25	22.53	21.82	1.04	1.42
	September	39	8.42	7.4	18.1	3.56	23.54	7.2	1.84	22.4	21.54	2.04	2.32
	September	40	8.4	7.44	17.8	3.43	23.48	6.77	2.97		17.42	2.46	
	October	41	8.53	7.42	17.1	3.16	25.54	5.14	2.62	21.56	17.5	0.38	0.73
	October	42	8.58	7.38	16.6	6.25	32.7	5.74	2.26	18.72	21.44	1.6	1.87
	October	43	8.41	7.4	16.5	3.56	43.9	5.5	2.9	24.15	18.5	1.3	1.65
	October	44	8.26	7.4	15.4	4.26	46	5.09	3.02	22.92	21.43	0.53	0.93
	November	45	8.34	7.44	15.1	4.25	43.9	6.24	2.71	11.97	22.79	3.49	3.5
	November	46	8.17	7.42	14.2	6.16	36.6	8.1	2.34	27.04	25.16	2.33	2.38
	November	47	8.07	7.39	13.5	4.95	36.2	7.37	2.45	25.79	20.85	0.29	0.59

November	48	7.85	7.43	12	5.84	41	7.94	2.3	23.47	24.1	0.23	0.41
December	49	8.22	7.42	12.4	4.32	38.1	7.1	2.42	24.51	22.73	1.61	1.47
December	50	8.03	7.41	12.2	5.61	32.85	8.64	1.64	22.77	24.55	1.35	1.6
December	51	7.61	7.4	11.2	7.5	44.91	13.29	1.84	29.73	23.82	2.37	2.7
December	52	7.92	7.4	10.8	5.08	31.4	12.07	1.28	29.79	23.43	0.62	1.07
December	53	7.51	7.42	11.3	4.03	28.9	8.33	2.97	29.11	22.09	0.57	0.97

2001

January	1	7.9	7.37	11.4	4.33	29.4	8.2	2.2	23.64	20.66	0.16	0.5
January	2	7.77	7.43	10.7	5.13	33.75	8.99	2.26	25.78	20.78	0.19	0.5
January	3	7.79	7.44	10.7	4.3	27.15	9.11	1.87	25.52	21.11	0.85	1.22
January	4	7.97	7.39	10.5	4.4	30.8	10.61	3.58	24.42	21.22	0.45	0.89
February	5	8.21	7.42	10.8	4.3	31.55	9.27	3.76	24.03	20.19	1.74	1.94
February	6	8.12	7.43	10.2	29.05	66.16	22.89	2.51	30.27	21.58	4.66	5.24
February	7	7.95	7.43	10.5	5.44	33.8	10.63	2.64	26.15	22.03	0.78	0.99
February	8	8.28	7.41	11	4.17	28.45	8.99	3.55	30.22	19.96	1.75	1.97
March	9	8.35	7.46	10.5	5.17	38.6	10.93	3.16	29.84	23.07	2.58	3.07
March	10	8.76	7.48	11.3	5.41	34.6	13.56	3.06	27.82	20.29	1.08	1.63
March	11	8.78	7.48	11.5	4.14	28.26	10.8	3.13	30.33	21.21	0.66	1.01
March	12	8.2	7.51	11.5	3.12	34.3	9.27	0.49	27.86	22.55	1.09	1.29
March	13	8.83	7.49	11.9	3.97	46.2	9.9	1	26.37	23.28	1.27	1.55
April	14	8.8	7.48	12	4.66	57.2	17.47	0.69	32.08	21.68	2.63	2.72
April	15	8.93	7.49	11.9	5.11	69.49	22.15	1.01	36.76	22.42	6.86	10.64
April	16	8.8	7.47	12.4	3.54	30.67	7.57	1.34	27.01	22.68	0.42	0.61
April	17	9	7.44	13.8	3.29	26.7	7.07	1.4	27.44	23.04	1.55	1.6
May	18	9.11	7.45	13.6	3.79	30.7	7.97	0.99	26.8	22.46	0.57	0.71
May	19	9.03	7.45	14.4	3.51	29.3	7.49	1.3	29.3	21.07	2.61	2.65
May	20	9.43	7.43	15	4.73	36.5	8.14	1.46	26.35	24.33	0.89	0.94
May	21	8.95	7.44	16.1	2.77	17.9	5.83	1.83	28.89	21.28	3.21	3.01
June	22	8.93	7.4	16.5	2.4	15.07	5.39	0.48	26.84	20.6	5.49	5.46
June	23	9.7	7.4	15.4	10	69.57	20.1	0.74	22.83	19.5	4.05	4.32
June	24	9.35	7.37	16	5.47	86.86	8.63	1.86	25.65	17.12	5.12	5.45
June	25	9.22	7.35	17.2	7.42	111.22	9.19	1.14	18.57	18.11	0.42	0.83
June	26	9.18	7.38	18.1	6.38	44.94	8.63	1.79	21.04	18.25	0.56	0.9
July	27	9.12	7.3	18.8	5.62	46.64	8.7	2.56	14.74	14.14	1.32	1.6
July	28	9.03	7.2	19	4.51	30.4	5.94	6.5	4.88	6.27	3.34	1.7
July	29	8.03	7.27	18.6	3.28	29.78	6.11	6.45	11.82	6.03	2.77	2.69
July	30	8.02	7.39	19.1	2.79	23.46	4.56	5.75	20.35	9.04	2.85	2.72
August	31	8.19	7.43	18.8	3.89	27.32	6.31	2.91	20.46	16.47	0.35	0.66
August	32	8.09	7.37	19.5	3.42	28.34	5.17	3.97	23.51	13.86	0.83	0.94
August	33	8.08	7.41	19.4	2.98	24.44	5.71	5.35	18.22	15.42	0.16	0.32
August	34	7.84	7.41	19.1	2.98	26.18	4.5	5.72	18.68	10.7	0.34	0.53
September	35	8.04	7.43	19.3	3.09	25.54	5.41	3.74	17.73	11.79	1.15	0.7
September	36	8.06	7.4	19.3	3.35	24.16	5.57	3.85	21.64	15.73	0.73	0.92
September	37	8.14	7.42	19	3.84	30.33	6.01	4.01	17.9	15.71	0.5	0.61
September	38	8.13	7.42	18.8	3.79	35.18	5.19	4.21	15.08	11.44	0.63	0.93
September	39	8.12	7.45	18.8	5.04	46.58	7.52	3.82	16.46	14.63	0.58	0.88
October	40	7.92	7.4	17.9	5.15	54.95	9.64	5.43	14.86	15.18	0.22	0.71
October	41	8.12	7.43	16.6	3.84	51.3	6.69	6.27	19.37	13.85	0.51	0.73
October	42	8.19	7.4	16.5	9.2	49.2	12	3.8	27.61	15.09	8.28	8.96
October	43	8.07	7.47	16.2	2.82	25.9	6.6	4.51	22.55	20.37	0.2	0.43

	Month	#											
	November	44	8.19	7.42	16.7	3.24	21.38	6.37	3.73	20.83	21.08	0.58	0.85
	November	45	8.01	7.37	15	3.81	34.58	6.74	4.13	19.7	16.87	0.22	0.52
	November	46	7.94	7.39	15	4.18	45.2	8.4	3.89	19.35	17.59	0.27	0.59
	November	47	7.86	7.36	14.5	3.89	44.56	7.56	5.47	14.98	16.03	0.47	0.67
	December	48	8.22	7.38	13.5	4.2	52.8	7.77	4.97	19.83	15.78	0.96	0.96
	December	49	8.25	7.36	13.6	4.2	50.5	7.53	5.04	20.16	11.07	0.33	0.58
	December	50	8.24	7.45	12.7	14.9	58.9	13.89	3.97	29.38	22.41	7.04	8.05
	December	51	8.07	7.45	12.3	4.81	46.8	8.5	3.44	24.72	19.9	2.11	2.38
	December	52	7.06	7.45	10.5	4.26	37	6.67	4.96	24.7	13.78	0.2	0.56
2002													
	January	1	7.57	7.42	11.5	3.8	48.1	6.84	5.07	24.15	19.4	0.48	0.83
	January	2	8.12	7.44	12.1	5.15	35.83	8.24	3.78	23.01	19.94	0.19	0.51
	January	3	7.84	7.44	11.4	3.98	37.06	6.84	4.48	22.45	19.28	0.15	0.37
	January	4	8.04	7.44	11.3	4.94	42.9	7.06	3.98	22.46	19.65	0.35	0.64
	February	5	7.99	7.45	10.9	4.71	37.3	7.77	4.14	23.96	19	1.21	1.53
	February	6	8.46	7.41	11.3	4.39	30.5	6.27	3.99	22.5	18.31	0.9	3.13
	February	7	8.24	7.39	11.1	4.25	34.06	7.32	4.64	24.47	19	0.82	1.08
	February	8	8.24	7.38	12	5.04	35.8	8.84	3.64	24.19	19.6	0.55	0.99
	March	9	7.78	7.38	9.9	3.89	44.46	8.57	4.62	22.19	18.18	0.12	0.54
	March	10	8.17	7.43	10.3	5.14	54.25	9.09	3.57	23.52	21	0.1	0.83
	March	11	8.7	7.43	11.7	4.79	43.6	7.51	3.97	25.1	20.54	0.27	0.64
	March	12	7.96	7.41	10.2	5.99	35.3	9.46	3.94	26.66	17.3	0.27	0.76
	March	13	8.66	7.42	11.9	4.31	38.5	7.86	4.13	26.9	20.52	1.41	1.61
	April	14	8.44	7.39	11.8	4.2	28.8	8.7	4.5	25.29	21.37	3.72	3.97
	April	15	8.59	7.35	12.8	4.19	21.4	7.81	5.02	22.78	17.43	5.04	5.64
	April	16	8.68	7.36	12.4	5.64	11.14	10.54	0.71	28.44	23.89	3.62	4.14
	April	17	8.53	7.4	13	3.95	6.41	7.61	0.7	29.88	25.62	4.72	4.97
	May	18	8.76	7.39	13.5	7.19	19.7	13.17	0.4	30.29	24.64	4.32	4.59
	May	19	8.79	7.47	13.5	7.16	18.86	12.07	0.47	28.64	25.44	2.22	4.84
	May	20	8.84	7.45	14.7	8.01	26.32	11.2	1.08	36.41	27.14	7.46	7.18
	May	21	9.71	7.42	14.4	8.35	17.24	12.3	1.11	25.25	21.13	1.44	1.42
	June	22	9.82	7.42	15.5	4.24	17.04	8.71	1.43	28.2	22.22	3.16	2.76
	June	23	9.75	7.28	15.3	4.62	34.54	12.27	1.8	22.1	18.81	3.25	2.15
	June	24	9.72	7.28	15.3	5.17	46.92	12.64	2.58	18.13	14.01	2.38	5.02
	June	25	9.55	7.14	16.6	4.1	38.26	7.54	5.96	9.47	8.09	3.75	3.69
	June	26	9.55	7.13	17.8	3.44	32.46	6.31	5.1	6.02	4.4	2.34	2.49
	July	27	8.04	7.16	17.7	4.37	20.78	7.09	6.53	2.43	5.85	0.43	2.7
	July	28	8.27	7.28	18.5	3.6	23.28	6.89	5.05	9.63	11.27	0.11	0.35
	July	29	8.07	7.24	19.6	3.14	21.32	6.3	4.85	12.5	9.46	0.06	0.26
	July	30	8.34	7.27	19.3	2.66	25.1	5.79	6.36	14.8	18.12	0.09	0.31
	August	31	7.95	7.35	19	3.12	29.5	5.99	7.65	11.8	8	0.11	0.33
	August	32	7.99	7.37	18.6	2.81	25.46	6.46	4.57	17.91	12.83	0.11	0.42
	August	33	7.81	7.41	19.3	3.31	31.35	6.57	3.06	19.27	18.22	0.23	0.45
	August	34	7.83	7.41	18.7	3.66	26.82	6.44	2.82	24.68	19.72	1.37	1.74
	August	35	7.9	7.37	19.3	2.69	28.22	5.97	4.5	19.46	17.12	0.2	0.32
	September	36	8.08	7.39	18.9	3.91	27.78	6.13	3.02	19.11	16.54	0.3	0.48
	September	37	8.1	7.37	18.6	3.74	30.1	7.09	3.68	24.04	17.16	3.36	3.69
	September	38	8.21	7.48	18.6	4.23	29.76	8.03	3	25.21	19.36	0.98	1.29
	September	39	8.04	7.45	18.3	3.67	20.16	7.03	2.28	27.82	22.11	2.76	6.74
	October	40	8.04	7.49	17.3	3.09	19.66	7.99	2.7	27.71	24.2	2.21	2.72

October	41	7.9	7.42	17.1	4.67	18.16	10.53	1.39	32.03	24.8	4.77	5.55
October	42	7.9	7.47	15.9	4.05	10.88	9.48	0.11	27.03	27.74	0.28	3
October	43	7.77	7.48	14.8	4.66	17.18	10.66	0.4	32.01	25.55	0.8	1.25
November	44	7.15	7.5	13.5	4.78	17.12	10.49	0.96	32.01	13.48	0.21	0.64
November	45	7.73	7.48	14.1	5.53	15.74	9.44	0.69	32.15	25.34	0.82	2.76
November	46	8.03	7.49	14.4	5	11.86	10.4	1.05	33.06	29	3.9	3.39
November	47	7.75	7.49	14.1	4.84	12.72	10.66	1.03	35.44	25.58	1.04	1.49
November	48	7.22	7.58	12.4	2.9	12.4	8.1	0.21	36.61	30.89	4.23	3.52
December	49	7.29	7.57	13.1	4.69	17.8	10.83	0.3	32.57	29.65	2.54	3.82
December	50	6.95	7.54	13.1	4.67	21.12	12.57	0.16	35.71	30.69	1.02	1.53
December	51	6.94	7.54	13.2	6.22	29.22	12.51	0.49	36.78	29.82	2.71	3.56
December	52	6.24	7.51	11.9	8.85	34.23	13.74	0.73	30.78	26.83	0.44	5.38
2003												
January	1	6.47	7.55	12.6	4.32	23.03	10.9	0.67	29.75	24.68	0.4	0.95
January	2	6.76	7.55	12.7	4.8	23.83	11.23	0.69	32.79	24.56	2.22	2.78
January	3	7.19	7.5	12.8	4.48	30.98	13.76	4.21	31.33	20.78	0.51	1.18
January	4	7.21	7.53	11.2	5.32	38.14	15.11	0.94	34.79	18.23	3.01	4.01
February	5	7.35	7.45	12.2	7.5	33	18.87	1.63	33.52	25.82	3.2	3.57
February	6	6.98	7.49	12	6.39	22	18.63	1.73	29.74	23.96	2.44	1.83
February	7	6.93	7.47	12.2	5.7	21.62	15.41	1.95	33.56	25.89	0.82	1.77
February	8	7.13	7.47	11	4.76	20.9	13.34	2.13	30.25	24.95	1.84	2.53
March	9	6.78	7.48	10.7	4.72	24.61	13.34	1.67	30.16	26.07	1.75	1.55
March	10	6.15	7.49	10.9	5.49	9.01	13.5	0.29	35.37	30.34	3.7	4.34
March	11	6.51	7.45	11.8	6.27	12.2	13.52	0.05	35.14	28.32	3.29	3.88
March	12	6.46	7.43	12.3	4.61	9.08	12.73	0.13	35.25	26.15	5.81	6.17
March	13	6.14	7.46	11.9	4.48	10.21	13.29	0.17	34.15	26.82	2.74	3.4
April	14	6.52	7.48	12.8	5.18	13.36	15.71	0.36	35.89	27.9	2.81	3.52
April	15	6.58	7.47	13	12.95	28.28	23.24	0.27	40	28.21	6.79	7.59
April	16	7.93	7.41	13.2	10.06	17.9	16.09	0.29	34.72	23.59	2.46	3.02
April	17	8.79	7.41	13.8	9.28	23.66	14.07	0.36	32.2	25.21	3.26	3.67
May	18	8.91	7.44	13.9	8.94	24	13.77	0.75	34.13	26.91	3.16	3.28
May	19	8.9	7.38	13.9	6.32	23.32	13.48	0.75	35.21	26.18	1.78	2.13
May	20	8.38	7.4	14.8	7.64	21.7	9.85	1.14	36.38	27.91	4.41	5.1
May	21	7.9	7.35	15.5	11.15	19.6	15.81	1.26	30.92	23.87	11.24	12.28
May	22	9.18	7.37	16.9	6.69	12.17	8.65	0.48	25.67	24.1	2.03	1.23
June	23	8.91	7.4	16.7	5.24	18.48	9.94	1.1	31.65	26.7	3.77	4.11
June	24	8.35	7.41	17.7	4.35	17.08	8.49	0.82	27.02	21.57	1.54	1.84
June	25	8.4	7.37	18.1	5.45	21.98	9.91	1.23	26.77	23.3	6.22	6.37
June	26	8.17	7.43	17.3	4.45	29.75	9.55	1.58	30.22	25.84	1.26	1.87
July	27	7.93	7.43	18.7	3.45	20.67	7.89	1.9	28.52	23.85	8.35	1.7
July	28	8.14	7.45	19	3.41	26.22	7	2.6	24.66	20.28	2.41	2.84
July	29	7.87	7.47	19.6	3.98	28.2	6.23	2.86	21.58	22.96	0.62	0.83
July	30	8.04	7.41	20.2	3.34	33.02	5.47	3.94	18.82	17.76	0.36	0.71
August	31	8.08	7.35	20.5	4.2	37.42	6.17	5.88	15.69	13.65	1.97	0.56
August	32	8.3	7.29	20.5	5.72	23.94	4.63	6.4	14.08	9.62	0.04	0.73
August	33	8.07	7.32	20.4	5.31	15.7	5.43	4.15	13.97	11.5	2.3	0.86
August	34	8.62	7.3	20	5.51	18.28	8.26	7.23	13.03	13.7	1.72	2.19
August	35	8.67	7.29	20.2	5.43	20.93	8.83	5.78	15.01	12.48	8.92	3.46
September	36	8.98	7.29	19.9	4.91	13.14	6.03	5.82	10.5	9.05	1.62	1.95
September	37	9.25	7.3	19.7	6.45	16.08	5.2	7.01	10.94	10.09	3.12	3.47

Month	#											
September	38	9	7.28	18.9	5.17	22.8	5.97	7.23	9.71	8.15	3.28	4.1
September	39	8.51	7.28	18.9	7.56	30.75	10.97	8.4	20.4	7.86	17.62	18.51
October	40	8.49	7.25	18.7	5.89	20.06	6.17	10.49	6.08	4.6	3.86	4.21
October	41	9.17	7.24	18.8	6.7	16.5	5.34	10.07	7.55	3.88	3.07	3.14
October	42	9.34	7.26	17.7	3.44	10.41	6.39	10.04	3.92	2.63	1.25	1.55
October	43	8.82	7.26	17.8	3.29	11.2	7.43	9.74	3.94	2.55	0.33	0.82
November	44	8.91	7.23	15.4	2.6	12.64	7.86	9.93	4.88	2.46	0.66	0.98
November	45	8.68	7.27	13.9	2.65	12.72	7.06	12.12	2.55	1.01	0.51	2.6
November	46	8.93	7.19	14.8	2.75	18.08	7.51	11.44	7.44	0.74	0.78	1.06
November	47	8.44	7.16	14.7	3.78	35.28	7.91	4.77	12.13	9.39	0.2	0.54
November	48	8.45	7.17	13.6	3.44	25	7.31	10.23	10.16	7.09	0.16	0.82
December	49	8.98	7.18	13.9	5.72	35.9	9.09	8.7	15.75	8.52	0.14	12.04
December	50	8.63	7.17	13.5	4.43	28.46	6.79	8.51	9.08	6.12	2.85	2.95
December	51	8.72	7.18	12.9	6.38	46.2	7.29	3.41	23.49	12.12		
December	52	8.23	7.14	11.7	3.85	37.3	6.2	7.22	10.92	8.58	0.08	0.42
December	53	8.07	7.17	11.2	2.87	35.9	6.7	9.41	9.7	6.05	0.28	0.89

2004

Month	#											
January	2	7.83	7.17	10.6	4.36	37.5	7.06	8.06	11.5	6.56	0.14	0.45
January	3	8.71	7.27	10.5	4.13	46.8	7.43	7.24	15.75	10.98	0.35	0.66
January	4	9.47	7.33	11.4	5.02	39.8	7.89	6.19	15.51	11.6	0.17	0.52
January	5	10.19	7.32	11.7	4.99	38.5	7	4.97	18.95	12.96	0.7	0.98
February	6	8.96	7.2	10.9	4.31	30.9	6.31	4.26	12.96	11.81	0.28	0.49
February	7	8.07	7.19	10.7	5.96	22.56	7.03	4.63	21.03	11.69	0.54	11.32
February	8	8.09	7.15	11	9.55	34.75	11.49	4.06	12.25	18.35	6.97	6.76
February	9	8.31	7.08	11.7	6.11	29.13	12.04	7.4	4.71	2.44	1.54	0.64
March	10	8.29	7.11	11.7	3.44	25	6.89	8.76	3.09	1.94	0.23	1.93
March	11	8.09	7.08	12.4	3.27	17.98	6.26	7.77	3.28	1.67	6.74	7.14
March	12	8.71	7.06	12.9	3.4	15.9	8.03	7.94	2.79	2.18	0.06	0.64
March	13	8.52	7.08	13.2	5.19	25.18	8.5	9.62	5.45	3.35	11.24	5.2
April	14	8.01	7.22	13.3	5.09	16.32	7.88	5.45	2.76	0.8	0.73	0.91
April	15	8.5	7.09	14.2	4.42	13.12	7.67	9.73	2.38	0.69	0.66	1.15
April	16	8.54	7.12	14.4	2.33	9.15	4.34	9.16	1.56	0.29	0.06	0.26
April	17	9.33	7.08	14.5	3.44	10.65	6.49	10.36	2.32	4.5	0.06	6.08
May	18	8.91	7.09	15.3	2.83	10.56	4.96	9.52	1.62	0.31	3.32	0.75
May	19	8.45	7.11	16.4	2.83	8.43	5.29	9.56	1.89	0.13	0.08	0.3
May	20	8	7.06	15.5	2.75	9.51	5.17	9.35	2.02	0.37	1.2	1.34
May	21	7.88	7.06	16	8.97	23.86	10.66	7.9	6.06	3.18	5.67	4.38
May	22	7.89	7.11	16.2	5.36	21.28	10.86	8.05	5.71	2.61	0.55	1.11
June	23	7.74	7.11	17.3	4.02	7.18	7.52	9.83	1.88	0.24	0.07	0.54
June	24	8.44	7.11	16.9	3.35	6.99	5.49	9.64	2.05	0.4	0.08	0.34
June	25	8.02	7.12	17.4	2.64	5.57	4.17	7.48	2.05	0.35	0.15	0.36
June	26	8.43	7.1	18.5	3.06	7.2	6.43	8.28	2.07	0.19	0.12	0.39
July	27	7.84	7.12	18.9	3.15	8.63	6.31	9.02	2.31	0.28	0.12	0.46
July	28	7.74	7.11	18.6	2.2	5.35	4.77	7.69	1.95	0.25	3.64	2.63
July	29	7.83	7.1	19.8	2.17	5.85	4.03	7.26	1.79	0.09	1.96	1.14
July	30	7.59	7.14	20.2	2.22	7.35	4.4	7.84	1.97	0.46	0.69	0.62
July	31	7.37	7.13	20.2	2.3	7.73	4.49	6.36	1.73	0.2	0.51	1.52
August	32	7.78	7.14	20.5	2.39	7.54	4.29	7.01	1.7	1	8.29	4.07
August	33	7.51	7.18	20.3	1.86	5.69	3.97	9.72	1.59	0.15	6.39	5.66
August	34	7.81	7.19	20.7	3.61	12.04	5.33	6.75	3.69	0.29	3.18	4.16

August	35	8.25	7.18	19.8	3.21	8.97	5.57	2.07	1.88	8.52	15.06	1.45
September	36	7.96	7.21	19.9	1.33	4.6	3.23	6.95	1.08	0.78	0.43	0.28
September	37	7.74	7.19	19.5	1.58	3.92	3.2	6.69	1.28	0.06	1.41	1.29
September	38	8.41	7.17	19.2	1.62	5.62	3.49	6.98	2.01	0.73	1.72	1.57
September	39	8.47	7.06	18.6	1.99	4.6	3.44	9.33	1.33	0.22	6.19	5.63
October	40	8.76	7.13	18.9	1.83	11.24	3.46	9.24	3.41	0.36	5.37	5.06
October	41	8.27	7.06	18.2	0.82	2.45	3	8.29	1.53	0.36	5.38	3.26
October	42	8.24	7.13	17.4	1.02	1.51	2.86	8.85	1.31	0.09	3.96	2.09
October	43	8.46	7.1	16.6	1.51	2.48	3.2	7.16	1.59	0.11	2.51	1.56
October	44	8.31	7.16	15.7	3	6.69	4.66	7.12	2.56	0.85	3.56	2.15
November	45	8.37	7.15	15.1	2.6	8.02	4.94	6.75	3.82	0.93	0.96	1
November	46	8.52	7.13	15.1	2.59	10.38	5.4	6.19	4.61	2.93	1.36	1.62
November	47	8.47	7.06	14.3	3.53	7.22	6.71	8.59	3.05	1.7	3.07	2.71
November	48	8.28	7.11	13.8	3.07	10.99	5.83	8.89	3.28	2.54	3	1.7
December	49	8.13	7.04	12.9	3.1	7.5	5.54	11.02	1.98	0.19	0.79	1.5
December	50	8.36	7.05	13.2	3.01	7.13	5.41	10.49	1.78	0.14	6.48	4.2
December	51	8.54	7.08	12.8	2.87	6.47	5.26	9.91	1.8	0.12	1.57	1.27
December	52	7.99	7.04	11.9	2.68	6.82	6.87	9.81	1.58	0.07	2.3	2.3
December	53	7.86	6.91	11	3.76	10.26	9.83	13.28	2.09	0.12	5.41	4.94
2005												
January	2	8.02	7.02	9.2	3.12	6.74	5.76	11.65	1.65	0.19	2.97	2.02
January	3	8.16	6.97	9.8	2.8	6.81	4.69	10.34	1.41	0.09	2.36	1.71
January	4	8.61	7.02	10.7	2.43	8.54	3.97	8.39	2.56	0.16	1.33	1.2
January	5	8.8	7.04	11.3	2.19	7.21	6.57	9.08	2.22	1.71	1.41	1.37
February	6	8.59	7.05	11.4	2.04	5.64	3.93	8.92	2.15	0.31	1.18	1.62
February	7	8.29	7.07	11	2.25	5.32	3.2	7.9	1.96	0.3	0.68	0.56
February	8	8.69	7.03	10.8	2.84	7.33	4.14	8.14	3.02	2.03	0.1	0.19
February	9	8.4	7.09	10.5	3.16	6.55	4.77	9.09	1.83	0.11	0.07	0.49
March	10	8.96	7.1	11.4	3.6	8.13	6.04	8.3	2.07	0.37	0.56	0.61
March	11	8.7	7.08	12.1	2.89	9.45	5.14	11.42	1.88	0.45	0.45	0.62
March	12	8.91	7.1	11.7	1.77	5.03	2.9	11.11	1.26	0.19	0.53	1.04
March	13	8.65	7.11	10.9	1.37	4.93	2.43	7.31	1.27	0.2	0.27	0.65
April	14	9.08	7.07	12.1	1.54	6.33	2.33	8.25	1.07	0.18	1.15	1.17
April	15	8.82	7.08	12.8	1.14	5.25	3.03	9.47	1.85	0.38	4.45	3.04
April	16	8.87	7.11	12.5	2.02	6.45	3.94	10.39	1.79	0.27	4.52	2.39
April	17	8.99	7.13	13.3	1.74	4.6	2.63	8.08	1.31	0.05	1.12	0.82
April	18	8.89	7.15	14.1	2.18	5.06	3.31	7.25	1.41	0.19	0.22	0.23
May	19	8.79	7.18	14.8	1.89	5.13	2.91	8.78	1.37	0.14	0.76	0.63
May	20	8.86	7.13	15.7	1.94	3.18	2.94	8.73	1.3	0.09	1.09	1.15
May	21	8.81	7.11	16.1	2.2	3.64	3.77	8.36	1.48	0.32	0.53	0.67
May	22	8.25	7.15	16	2.88	4.13	4.43	7.74	1.46	0.09	0.86	0.94
June	23	8.62	7.14	16.2	2.41	4.44	5.09	7.45	3.05	1.35	1.54	1.4
June	24	8.92	7.19	15.8	0.26	0.91	2.63	7.42	1.23	0.07	0.14	0.23
June	25	8.47	7.18	16.5	0.31	0.73	2.57	6.35	1.15	0.16		0.06
June	26	8.15	7.19	17.5	0.62	1.7	2.71	5.35	1.19	0.05	0.07	0.09
July	27	8.22	7.2	17.8	0.58	0.92	2.11	5.53	1.15	0.04	0.01	0.1
July	28	7.73	7.23	18.4	0.44	0.57	2.58	5.9	1.03	0.03	0.03	0.13
July	29	7.82	7.24	19	0.11	1.93	2.39	5.59	1.17	0.03	0.05	0.08
July	30	7.74	7.22	19.2	0.54	1.65	2.72	7.79	1.31	0.15	0.32	0.33
July	31	8.05	7.23	19.5	1.37	3.37	3.11	5.06	2.34	0.86	0.06	0.17

August	32	7.99	7.24	20	1.36	2.87	2.68	7.08	1.24	0.13	0.21	0.62
August	33	7.85	7.24	20	1.15	1.76	2.09	6.89	1.02	0.09	1.7	1.33
August	34	8.11	7.25	19.5	0.93	1.55	1.67	7.21	1.09	0.02	0.13	0.44
August	35	7.82	7.24	19.8	2.01	5.38	2.67	6.22	2.43	1.28	0.21	0.48
September	36	8.39	7.27	19.4	1.84	4.9	2.57	8.22	2.48	1.32	0.85	1.11
September	37	8.34	7.21	19.3	1.23	3.37	2.63	7.74	1.72	0.38	0.21	0.24
September	38	8.41	7.22	18.5	1.28	4.33	2.16	6.8	2.21	0.2	0.2	0.23
September	39	8.52	7.22	18.4	1.5	3.45	2.24	7.01	1.49	0.32	0.07	0.9
October	40	8.43	7.24	18	1.83	4.86	3.06	5.62	4.04	5.54	2.29	1.23
October	41	8.59	7.22	17.6	1.72	3.72	3	7.24	1.65	0.62	0.05	0.2
October	42	8.2	7.2	17.2	1.77	5.87	2.63	5.93	3.19	1.09	0.08	0.47
October	43	7.98	7.2	17.3	1.54	4.17	2.01	7.33	1.76	0.8	1.87	1.71
October	44	8.12	7.21	16.3	1.57	2.56	1.98	7.94	1.46	0.19	3.55	1.75
November	45	8.4	7.18	15.6	2.01	3.91	2.56	6.89	1.75	0.43	1.51	1.07
November	46	8.5	7.2	14.2	2.09	6.43	2.69	6.86	2.33	1.34	0.81	0.65
November	47	8.29	7.17	13.4	2.57	6.16	3.08	7.2	2.02	0.73	0.71	0.7
November	48	7.74	7.15	12.8	3.07	6.17	3.56	8.41	2	0.47	0.68	0.69
December	49	7.84	7.12	11.6	2.29	3.29	3.19	9.64	1.22	0.07	0.8	0.96
December	50	7.77	7.1	10	1.93	2.7	2.59	9.44	1.16	0.05	1.12	1.1
December	51	7.99	7.09	10.6	1.86	5.77	2.49	8.4	3.01	0.42	0.83	0.75
December	52	7.98	7.08	10.2	2.01	3.66	3.19	9.12	1.5	0.16	0.48	0.8
December	53	7.97	7.06	10.9	1.55	2.97	3.67	7.55	1	0.03	0.17	0.43
2006												
January	1	8.07	7.1	10.6	1.53	3.05	2.2	8.81	1.37	0.04	1.15	1.33
January	2	8.22	7.07	10.8	1.9	3.63	2.32	8.87	0.87	0.73	1.01	0.83
January	3	8.36	7.07	10.4	1.74	3.36	2.64		1.08	0.25	0.69	0.72
January	4	8.69	7.08	10.4	2	4.56	3.2	8.87	1.62	0.79	0.61	1.11
February	5	8.79	7.09	10.8	1.92	4.6	2.96	9.09	1.55	0.45	1.12	1.3
February	6	8.41	7.11	10.2	2.23	4.04	3.64	8.56	1.31	0.67	0.63	0.96
February	7	8.21	7.11	9.1	1.79	2.43	3.8	8.8	1.43	0.23	2	1.84
February	8	8.37	7.1	10.2	1.81	2.76	2.97	9.21	1.21	0.14	0.72	0.76
March	9	8.56	7.06	11.3	1.75	2.7	3.47	8.64	1.26	0.19	1.19	0.94
March	10	8.46	7.1	10.8	2.43	3.2	3.84	9.19	1.44	0.19	0.17	0.32
March	11	8.59	7.1	11	1.85	2.6	3.3	9.05	1.37	0.19	0.04	0.16
March	12	8.79	7.06	11.7	2.01	3.03	4.41	10.17	1.71	0.2	1.16	1.13
April	13	7.97	7.11	11.9	2.06	2.67	3.61	9.21	1.86	0.07	0.09	0.63
April	14	9.14	7.05	12.3	2.55	3.59	3.2	9.45	1.81	0.27	0.22	0.51
April	15	8.86	7.1	12.8	2.56	4.31	3.49	7.25	3.13	0.06	0.04	3.85
April	16	8.63	7.04	13	2.46	3.73	4.06	7.38	1.83	0.11	0.06	0.18
April	17	8.41	7.07	13.8	2.07	3.79	3.43	8.67	1.77	0.83	0.03	0.84
May	18	8.3	7.12	13.9	2.12	3.18	2.94	8.61	1.66	0.34	0.04	0.13
May	19	8.59	7.13	14.6	3.7	5.45	4.16	8.98	2.09	0.22	0.04	0.24
May	20	9.36	7.11	16.6	4.58	6.48	5.64	9.46	6.75	5.94	1.74	1.43
May	21	11.29	7.07	15.9	3.4	5.68	5.34	4.11	5.07	4.95	1.41	0.87
June	22	10.61	7.04	15.4	1.51	2.91	2.76	7.31	1.27	0.15	0.63	0.62
June	23	10.21	7.06	16.5			4.47	7.09	1.73	0.3	0.04	0.19

H3AsO3 + H2O----> H2AsO4- + 3H+ +2e   log K =   -21.65

<div style="text-align:right">

above pH 7.16 use
H3AsO3 + H2O ----> HAsO42- + 4H+ +2e logK=-28.81
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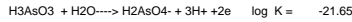
pe zero	-6.40E-01	
Eh=	-RT/nFlnQ	=-.059/2 LogK
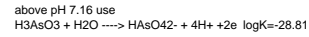
log[HAsO42-] - 4pH - 2pe - log[H3AsO3] = -28.81
pe=-.5*(-16.31+log(h3aso3)+4*pH-log(HAsO4--)

1mol As:1 mol salt so use molarity
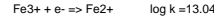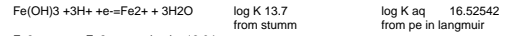log[H2AsO4-] - 3pH - 2pe - log[H3AsO3] = -21.65
pe=-.5*(-21.65+log(h3aso3)+3*pH-log(h2aso4-)   16.46959

	pH	As(III)	As(V)	mol H3AsO3	mol H2AsO4-	K	Eh	Ezero -Eh	pE
Well 3 jan	7.04	3.2	0.27	4.27E-05	0.0000036	6.40E-23	6.55E-01	-1.46E-02	-2.46E-01
well 3 july deep	7.55	1.35	1.08	1.80E-05	0.0000144	5.05E-31	8.94E-01	-2.54E-01	-4.29E+00
july shallow	7.55	1E-11	1.3	1.33E-16	1.73333E-05	8.20E-20	2.82E-01	9.22E-01	1.56E+01

-22.19379

Fe(OH)3 +3H+ +e-=Fe2+ + 3H2O   log K 13.7   log K aq   16.52542
                                     from stumm   from pe in langmuir

Fe3+ + e- => Fe2+   log k =13.04
                                           too many possible equations.
log[fe2+] -log[fe3+]+3pH +pe=13.04

pe=13.04-log[fe2+] + log[fe3+]- 3pH

DO CALCS FOR IRON

	pH	As(III)	As(V)	mol H3AsO3	mol H2AsO4-	pe
Well 3 jan	7.04	10.75	0.57	1.43E-04	0.0000076	-0.37
well 3 july deep	7.55	1.35	1.08	1.80E-05	0.0000144	-0.75
july shallow	7.55	1E-11	1.3	1.33E-16	1.73333E-05	4.86

16.4-LOG(L34)+LOG(M34)-3*I34

1319

	pH	As(III)	As(V)	mol H3AsO3	mol H2AsO4-	pe	pH	Fe(II)	Fe(III)	mol fe2	mol fe3	pe	
Well 3													
10/20/2005	7.10	1.12	0.98	1.49E-08	1.31E-08	0.15	7.20						
1/11/2006	7.04	3.2	0.27	4.27E-08	3.60E-09	-0.27	7.04	22	0.0001	3.92857E-07	1.78571E-12	-10.06242	
3/24/2006	7.20	2.96	0.71	3.95E-08	9.47E-09	-0.31	7.20	139	396	2.48214E-06	7.07143E-06	-4.74532	
5/24/2006							0.00						
6/14/2006	6.40	3.043	0.514	4.06E-08	6.85E-09	0.84	0.00						
7/12/2006	7.55	1.95	0.87	2.60E-08	1.16E-08	-0.87	0.00						
7/12/2006	7.55	1.35	1.08	1.80E-08	1.44E-08	-0.74	0.00						
7/12/2006	7.55	0.29	1.3	3.87E-09	1.73E-08	-0.37	0.00						
9/20/2006	6.36	0.6	0.9	8.00E-09	1.20E-08	1.37	0.00						
							0.00						
							0.00						
							0.00						
well 4													
3/10/2005	6.46	10.75	0.57	1.43E-07	7.60E-09	0.50							
10/20/2005	6.50	4.2	0.43	5.60E-08	5.73E-09	0.58	0.00						
1/11/2006	6.71	3.89	0.005	5.19E-08	6.67E-11	-0.69	6.71						
3/24/2006	6.70	6.03	0.2	8.04E-08	2.67E-09	0.04	6.46	825	0.001	1.47321E-05	1.78571E-11	-8.896454	
5/24/2006							6.46	1319	5071	2.35536E-05	9.05536E-05	-2.395151	
6/14/2006	6.28	5.73	0.2636	7.64E-08	3.51E-09	0.74	0.00						
7/12/2006	6.46	5.23	0.005	6.97E-08	6.67E-11	-0.37	0.00						
7/12/2006	6.46	7.56	0.005	1.01E-07	6.67E-11	-0.45	0.00						
7/12/2006	6.46	6.14	0.005	8.19E-08	6.67E-11	-0.41	0.00						
9/20/2006	6.50	3.61	0.26	4.81E-08	3.47E-09	0.50	0.00						
							0.00						
							0.00						
							0.00						
							0.00						
well 5							0.00						
5/24/2006							0.00						
6/14/2006	6.80	0.005	2.73	6.67E-11	3.64E-08	1.99	0.00						
7/12/2006	7.43	0.005	2.733	6.67E-11	3.64E-08	0.91	0.00						
							0.00						
9/20/2006	6.81	0.005	2.36	6.67E-11	3.15E-08	1.95	0.00						
seep							0.00						
5/24/2006	7.17						7.17	29	2	5.17857E-07	3.57143E-08	-6.271368	
6/14/2006	7.17	0.139	2.88	1.85E-09	3.84E-08	0.73	0.00						
7/12/2006	7.17	0.005	3	6.67E-11	4.00E-08	1.46	0.00						
well 7							0.00						
3/10/2005	6.90	0.05	6.35	6.67E-10	8.47E-08	1.53	0.00						
10/20/2005	6.90	1.2	6.1	1.60E-08	8.13E-08	0.83	0.00						
1/11/2006	7.01	0.005	2.51	6.67E-11	3.35E-08	1.66	0.00						
3/24/2006	6.90	0.005	3.34	6.67E-11	4.45E-08	1.89	6.90	11	0.0001	1.96429E-07	1.78571E-12	-9.341393	
5/24/2006							6.50	34	3	6.07143E-07	5.35714E-08	-4.154358	
6/14/2006	6.50	69.41	2.76	9.25E-07	3.68E-08	0.37	0.00						
7/12/2006	6.26	75.75	0.428	1.01E-06	5.71E-09	0.31	0.00						
7/12/2006	6.26	44.84	0.65	5.98E-07	8.67E-09	0.52	0.00						
7/12/2006	6.26	47.12	0.4459	6.28E-07	5.95E-09	0.42	0.00						
9/20/2006	6.95	0.7	6.5	9.33E-09	8.67E-08	0.88	0.00						
							0.00						
							0.00						
							0.00						
well 8							0.00						
1/11/2006	7.48	0	0	0.00E+00	0		0.00						
------	0.00	0	0	0.00E+00	0		0.00						
5/24/2006	0.00	0	0	0.00E+00	0		0.00						
6/14/2006	6.76	0.005	6.11	6.67E-11	8.15E-08	2.23	0.00						
7/12/2006	6.95	0.005	5.2	6.67E-11	6.93E-08	1.91	0.00						
							0.00						
							0.00						
							0.00						
white rock lake							0.00						
1/11/2006	7.72	0	0	0.00E+00	0.00E+00		0.00						
3/24/2006	7.50	0.187	1.25	2.49E-09	1.67E-08	-0.18	7.50	13	0.0001	2.32143E-07	1.78571E-12	-11.21394	0.475277
5/24/2006	7.20	0	0	0.00E+00	0.00E+00		7.20	26	0.0001	4.64286E-07	1.78571E-12	-10.61497	0.457517
6/14/2006	7.06	0.6318	2.86	8.42E-09	3.81E-08	0.56	0.00						
7/12/2006	7.10	1.97	0.24	2.63E-08	3.20E-09	-0.28	0.00						
9/20/2006	6.50	1.4	1.1	1.87E-08	1.47E-08	1.02	0.00						
							0.00						
							0.00						
							0.00						
cfr							0.00						
1/11/2006	7.72	0	0	0.00E+00	0.00E+00		0.00						
3/24/2006	7.70	0.01	1.812	1.33E-10	2.42E-08	0.40	7.70						#DIV/0!
5/24/2006	7.70	0	0	0.00E+00	0.00E+00		7.70	27	1	4.82143E-07	1.78571E-08	-8.131364	0.69255
6/14/2006	7.81	0.3106	3.91	4.14E-09	5.21E-08	-0.67	7.81						
7/12/2006	7.73	0.65	3.36	8.67E-09	4.48E-08	-0.70	0.00						
7/12/2006	7.73	1.16	3.38	1.55E-08	4.51E-08	-0.82	0.00						
9/20/2006	7.12	0.08	0.86	1.07E-09	1.15E-08	0.66	0.00						

Missoula WWTP Effluent nutrients weekly average

Missoula WWTP Effluent nutrients weekly average

Missoula WWTP Effluent nutrients weekly average

Missoula WWTP Effluent nutrients weekly average
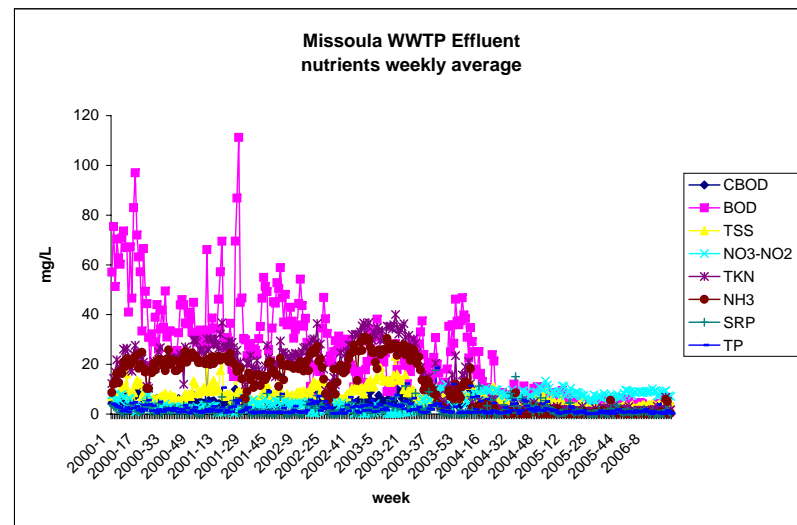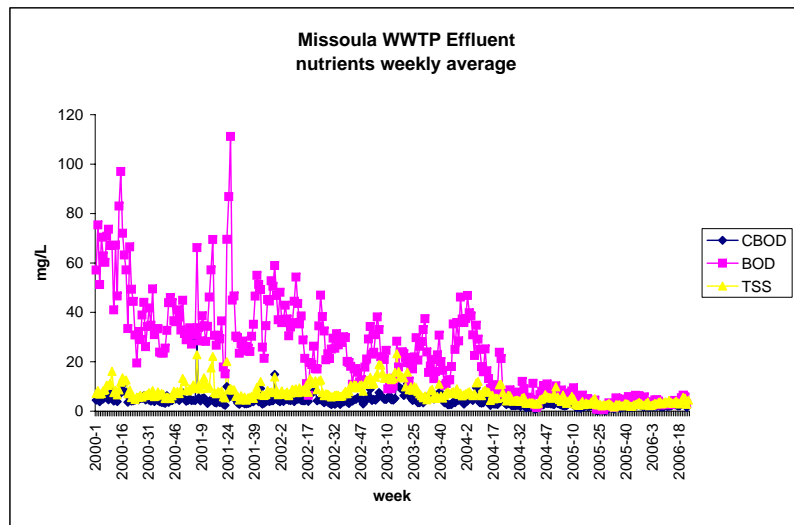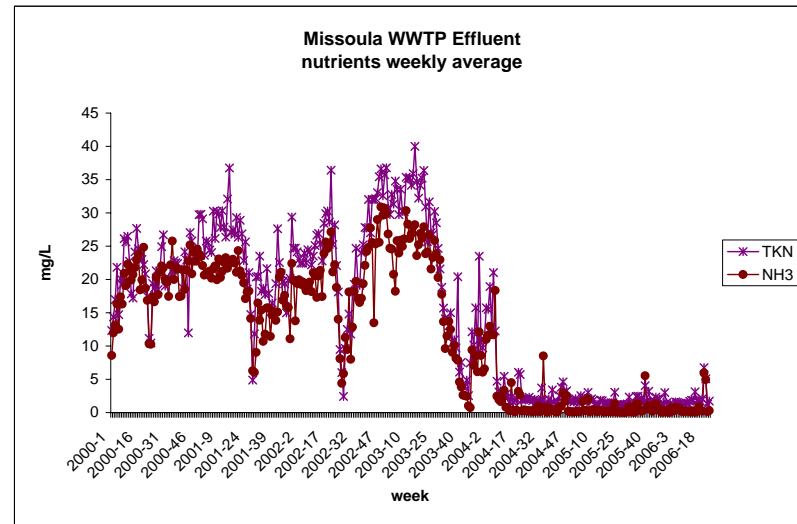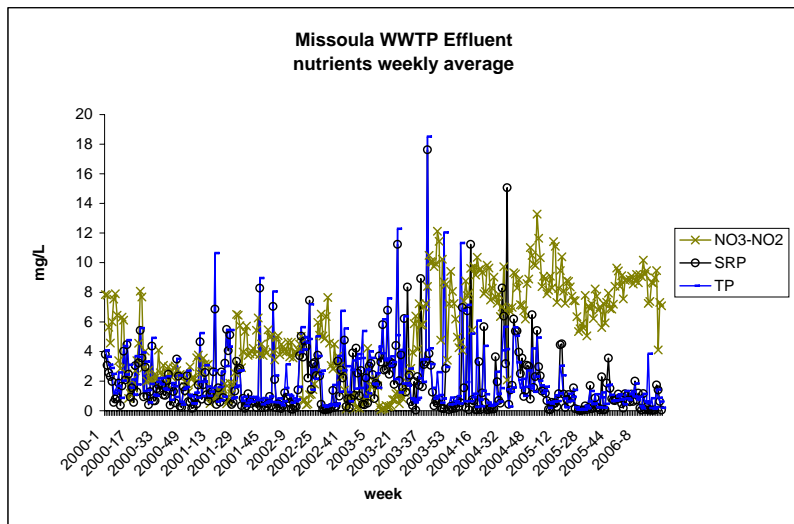
Missoula WWTP Effluent
Metals
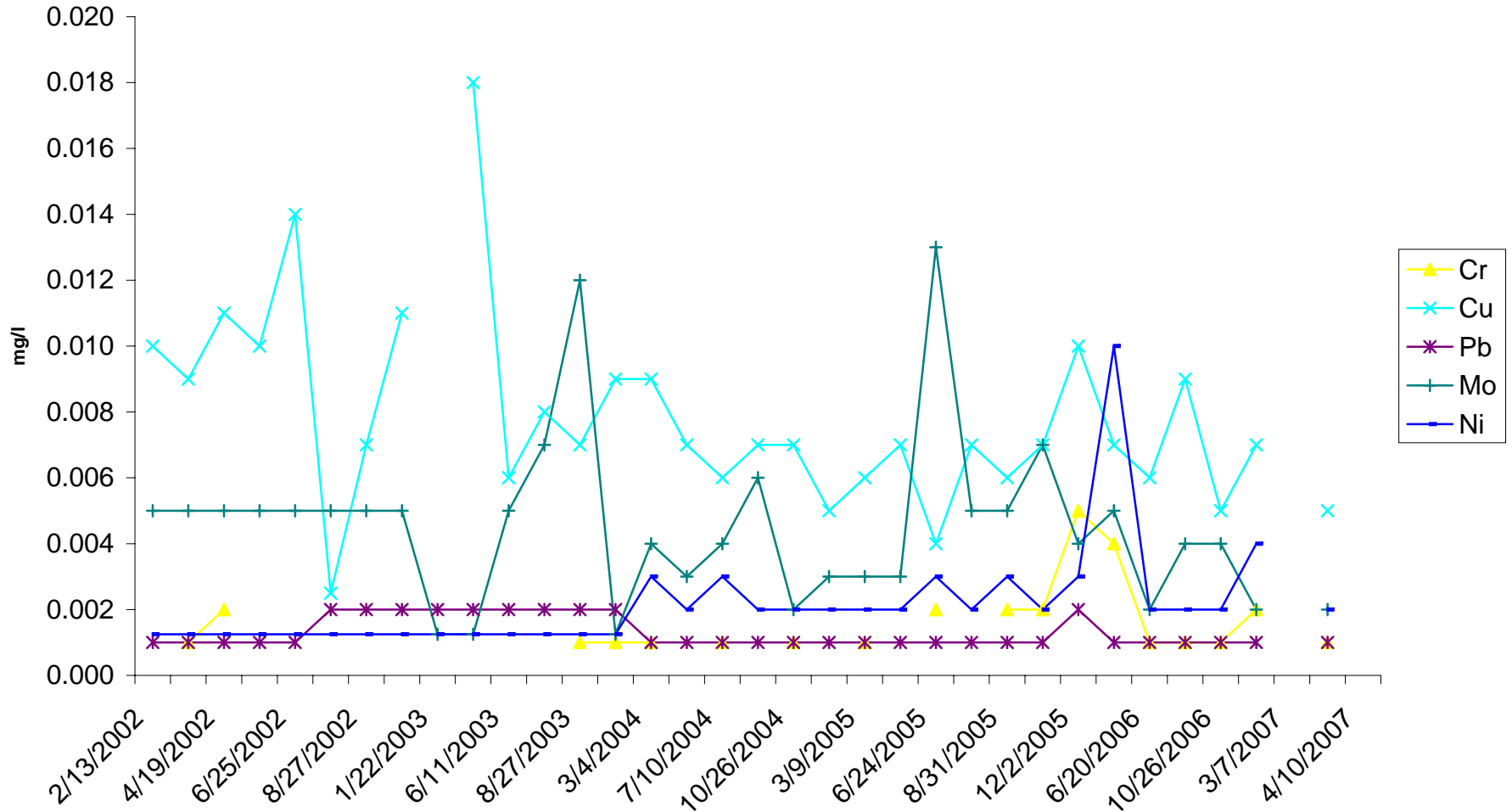
MW7

Mass balance calculation for well 7 under pre 1999 conditions (non reduced)			Mass balance calculation for well 7 under reducing conditions during aquifer recharge		

assuming (left) / **assuming** (right)

soil density	0.96 Fan, Morris Reservoir sedimentation handbook		soil density	0.96 Fan, Morris Reservoir sedimentation handbook	
mg/kg As in sediment	45.00		mg/kg As in sediment	45.00	
mg/L As in water	**0.01**		**mg/L As in water**	**0.10** may-july	
area	1.00 cubic meters		area	1.00 cubic meters	
dh/dl for area may 17	0.0016	0.0016	dh/dl for area may 17	0.0016	0.0016
K well 7	1000.00 ft/d		K well 7	1000.00 ft/d	

SEDIMENT (left)
kg sed/ m^3 sediment	960.00
mg As/m^3 sediment	43200.00
kg As/m^3 sediment	43.20

SEDIMENT (right)
kg sed/ m^3 sediment	960.00
mg As/m^3 sediment	43200.00
kg As/m^3 sediment	43.20

Water (left)
Q/A	1.60 feet/day
Q/A	0.49 meters/day
water Q for area	0.49 cubic meters/day
arsenic Q for area	4.88 mg As/day
	0.0049 kg As/day

Water (right)
Q/A	1.60 feet/day
Q/A	0.49 meters/day
water Q for area	0.49 cubic meters/day
arsenic Q for area	48.78 mg As/day
	0.05

Kg as in system   43.20 area* kg As/L | Kg as in system   43.20 # cubic meters* kg As/L

8856.00 days | 885.60 days

24.26 years   of regular as levels | 2.43 years   if concentration is always 0.1 ug/l

98.63 years assuming that the water table only reaches contaminated layer of sediment for three months of the year. | 9.86 years adjusted for 2 months of high arsenic in water and assuming that the water table only reaches contaminated layer of sediment for three months of the year.

MW4

Mass balance calculation for well 4 INITIAL concentrations 1990			Mass balance calculation for well 4 INITIAL concentrations 1990		

assuming (left) / **assuming** (right)

soil density	0.96 Fan, Morris Reservoir sedimentation handbook		soil density	0.96 Fan, Morris Reservoir sedimentation handbook	
mg/kg As in sediment	45.00		mg/kg As in sediment	45.00	
mg/L As in water	**0.05**		**mg/L As in water**	**0.01**	
area	1.00 cubic meters		area	1.00 cubic meters	
dh/dl for area may 17	0.0008	0.0008	dh/dl for area may 17	0.0008	0.0008
K well 7	1000.00 ft/d		K well 7	1000.00 ft/d	

SEDIMENT (left)
kg sed/ m^3 sediment	960.00
mg As/m^3 sediment	43200.00
kg As/m^3 sediment	43.20

SEDIMENT (right)
kg sed/ m^3 sediment	960.00
mg As/m^3 sediment	43200.00
kg As/m^3 sediment	43.20

Water (left)
Q/A	0.80 feet/day
Q/A	0.24 meters/day
water Q for area	0.24 cubic meters/day
arsenic Q for area	12.20 mg As/day
	0.0122 kg As/day

Water (right)
Q/A	0.80 feet/day
Q/A	0.24 meters/day
water Q for area	0.24 cubic meters/day
arsenic Q for area	2.44 mg As/day
	0.0024 kg As/day

Kg as in system   43.20 # cubic meters* kg As/L | Kg as in system   43.20 # cubic meters* kg As/L

3542.40 days | 17712.00 days

9.71 years   of regular as levels | 48.53 years   of regular as levels

39.45 years assuming that the water table only reaches contaminated layer of sediment for three months of the year. | 197.26 years assuming that the water table only reaches contaminated layer of sediment for three months of the year.

Quality Assurance/ Quality Control

Hydrogeology

Measurement of Static Water Level elevation in wells

Maximum error for existing wells was +-.02 foot or 1/8 inch based on triplicate measurements. All measurements for these wells were reported to .01 and contours are 0.2 feet apart. This contour value is ten times larger than the error, so maps should be representative.

Static water levels in new one inch diameter wells on the flood plain were measured using the tape and ink method, error is +-1/8 inch based on triplicate measurements. Data for plotting maps was rounded to the nearest 0.1 foot to achieve maximum representativeness.

Measurement of Static Water Level elevation in surface water

Maximum error was calculated using trigonometry from a maximum expected slant of the gage. If a 36 inch gage is tilted so that a plumb line drops 6 inches from its base, the maximum measurement error would be -1.5 inches or .125 feet.

<u>Chemistry</u>

Quality Control for HPLC ICP-MS

QA/QC for speciation analysis was as follows:

Quantitation was based on a minimum two point curve. Calibration was checked every 10 analyses using a mid curve standard (CCV). All recoveries for these standards were within 10% of the known value.

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

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

Quality Control for ICP-MS

QA/QC for elemental analysis was as follows:

Quantitation was based on a minimum three point curve.

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

Calibration was checked every 10 analyses using a mid curve standard (CCV) and an additional varied concentration standard from a separate Source (IPC) All recoveries for these standards were within +-10% of the known value.

Analytical blanks were monitored for contamination and found to contain no elements of interest above the practical quantitation 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 were reported for at least every twenty samples analyzed. All duplicate recoveries were within 75-125% relative concentration.

Quality Control for IC

According to EPA method 300.0 QA/QC for elemental analysis was as follows:

Quantitation was based on a minimum three point curve. Calibration was checked every 10 analyses using a mid curve standard (CCV) and an additional varied concentration standard from a separate Source (IPC) All recoveries for these standards were within +-10% of the known value.

nalytical blanks were monitored for contamination and found to contain no anions of interest above the practical quantitation limit.

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

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

Quality Control for TOC

Quantitation was based on a minimum three point curve.

Calibration was checked every 10 analyses using a mid curve standard (CCV). All recoveries for these standards were within +-10% of the known value.

Analytical blanks were monitored for contamination and found to contain no anions of interest above the practical quantitation limit.

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