

## 5.0 RELEVANT CHEMICAL BEHAVIOR IN THE ENVIRONMENT

The primary contaminants of interest for this analysis are arsenic, copper, chromium, mercury and lead, which were identified as risk drivers in the September 2004 *Baseline Human Health and Ecological Risk Assessment Report* prepared for EPA (M&E,2004). PAHs, specifically benzo(a)pyrene, were identified as minor contributors to risk. PAHs will not be addressed in this analysis since the fate and transport behavior of PAHs is characterized by limited migration potential in groundwater, and very limited phase transfer from sediments to groundwater. The presence of chlorinated VOCs in the aquifer at concentrations that drive risk is widely documented at Wells G and H. Chlorinated VOCs in groundwater were not evaluated as part of this analysis.

### 5.1 Metals Fate and Transport

The potential release and migration of metals in the subsurface environment is a complicated process. The mobility of metals depends on factors such as the overall groundwater composition, pH, metal complex formation, valence state of the metal, and cation-anion exchange capacity. Changes in the oxidation-reduction potential (ORP) in soil or groundwater can affect the chemical species present. Metals occur in the environment as free ions or as complexed species. Complexing generally increases the solubility and mobility of metals in groundwater. Additionally, the type of complex a metal forms depends on whether the species is hard (strongly held electron field) or soft (deformable electron field). Hard species form stronger bonds than soft species. In general, complexation reduces metal toxicity (Campbell, 1995; DiToro et al, 1990).

The distribution between soil and water for metals is much more difficult to estimate than for organic compounds. Since the sorption of metals depends on pH, the metal concentration, the species present, and the type of complex formation, a single distribution coefficient or isotherm equation cannot be used to predict metal adsorption. Literature aqueous partitioning coefficient (K<sub>d</sub>) values can vary by more than two orders of magnitude (ERG, 2003). Generally, metal adsorption increases with pH. Inorganics most often sorb to clay minerals, organic matter, and iron and manganese oxyhydroxides. The surface charge of organic matter and oxyhydroxides is strongly pH-dependent, becoming more negative as pH increases and more positive as pH decreases. Metals may be sorbed on the surface of the soil or fixed to the interior of the soil, where they are unavailable for release to water. After available sorption sites are filled, most metals are incorporated into the structures of major mineral precipitates, as coprecipitates. At very high concentrations, they may be precipitated into pure metal phases.

The solubility of metals is also dependent on several factors. The solubility of cations decreases as pH increases. For a few cations (e.g., Zn<sup>+2</sup>, Al<sup>+3</sup>, and Fe<sup>+2</sup>), metal solubility increases again at alkaline pH values. The solubility of metals may decrease depending on the complex formation. Some cations may complex with oxygen and hydroxide, forming insoluble oxyhydroxides, or may complex with phosphate, sulfate, and carbonate to form insoluble mineral precipitates. Metal sulfide complexes, which form in reducing environments, are extremely insoluble, and their formation tends to reduce the total metals concentrations (EPA, 1979). However, arsenic is the exception to the insolubility of metal sulfides at circumneutral pH (Wilken et al, 2003).

Metals may be removed from the water phase through mechanisms such as precipitation and irreversible sorption (EPA, 1979).

In the water phase, the total metal concentration includes the dissolved metal concentration and the suspended metal concentration, which is sorbed to colloidal particles. As a result, the groundwater data may reflect metals concentrations that are associated with a significant percentage of colloidal material. Although some groundwater samples from the Wells G and H Site were filtered with a 0.45-micron filter, studies indicate that the most mobile particles were in the range of 0.1 to 0.55 micron and contributed as much as 40 percent of the total mobile metals (EPA, 1979). Therefore, elevated metals concentrations in groundwater may be due to the suspended load and not just to the dissolved percentage.

The fate and transport properties of metals identified as being potential risk drivers in the Aberjona River Study (M&E, 2003) are discussed in more detail below.

### ***5.1.1 Iron and Manganese***

Iron (Fe) and manganese (Mn) geochemistry are important to the understanding of Central Area aquifer geochemistry because of their ubiquitous presence, controlling influence on the solubility of arsenic, and because their presence is indicative of the overall redox status of the aquifer. The following summary of iron and manganese fate and transport properties is important to the interpretation of the available iron and manganese data.

Iron and manganese are naturally occurring elements that are ubiquitous in the environment. Manganese is a hard cation, which is often precipitated in soils to manganese minerals. Iron is a hard cation in the  $\text{Fe}^{+3}$  oxidation state and a borderline cation in the  $\text{Fe}^{+2}$  oxidation state. The transport of these elements is dependent on their species and the pH and ORP of the soil or water environment (ERG, 2003). Low pH and redox potential favors ferrous iron (Fe[II]); high pH and/or redox levels create a stable environment for ferric iron (Fe [III]) (Bodek et al, 1988).

In aqueous solution, ferric and ferrous iron hydrolyze to give various hydrolysis species, the distribution of which is a function of pH (Bodek et al, 1988). Both iron (III) oxyhydroxides and manganese oxides are relatively insoluble in oxidizing environments and are strong sorbants of other metals (ERG, 2003). In natural streams, iron occurs as particulate ferric hydroxide or as some form of organic complex. Ferrous iron is the most common form of dissolved iron in groundwater. Colloidal ferric hydroxide is typically present in surface waters (Bodek et al, 1988).

In lakes, ponds, and rivers, water near the bottom may be depleted of oxygen and attain a low oxidation-reduction potential (Eh), and may contain dissolved ferrous (reduced) iron concentrations up to several mg/L. Suspended iron sulfides that can form in the depleted oxygen/low Eh environment may be carried upward by mixing processes and become oxidized when they reach the oxygen containing waters. Subsequent hydrolysis forms amorphous ferric hydroxides, which may be colloidal and remain suspended at the boundary layer between the reduced water and the surface oxygenated water. With further coagulation, the larger particles settle into the anoxic waters, are converted to sulfides, and return to the bottom sediments

(Bodek et al, 1988). Aurilio (1992) described similar phenomena in the Lower Mystic Lake, which led to the formation of a highly turbid boundary layer between aerobic and anaerobic zones. Ford (2004b) also observed a turbidity maximum at the aerobic/anaerobic interface in the HBHA attributable, in part, to an observed maximum in particulate iron.

Iron and manganese oxyhydroxides and oxides can be used by microorganisms as electron acceptors under reducing conditions and are reduced to more soluble forms in a process known as bioreduction or reductive dissolution (ERG, 2003).

Manganese is often precipitated in soils and sediments as manganese minerals. Environmentally, the most important of these minerals are the Mn(III/IV) oxides. These phases are stable and relatively insoluble in oxidized systems above pH 6–7. The manganese oxides are often stronger sorbents of trace metals than are hydrous ferric oxides. Most of the cobalt, nickel, copper, zinc, lead, silver, and cadmium in a Pennsylvania soil were associated with manganese and iron oxides, with the manganese oxides holding the highest metal amounts relative to their abundance (ERG, 2003).

The generally observed Eh-pH regimes for iron and manganese in Central Area aquifer groundwater are illustrated in Figures 3 and 4, respectively. The Eh-pH diagrams in Figures 3 and 4 are graphical representations of aqueous oxidation-reduction (redox) equilibria for the featured inorganic species (in these cases iron and manganese, respectively). The Eh-pH diagrams graphically depict areas of predominance for in an Eh-pH coordinate system for various aqueous chemical species involved in redox, acid-base, precipitation, and complexation equilibria. Each Eh-pH diagram assumes one set of pressure and temperature conditions, and can be constructed for site-specific chemical, temperature, pressure, and concentration regimes. The Eh-pH plots provided herein are based on a water temperature of 25°C. Although groundwater is typically cooler, the 10°C± difference between the Eh-pH plots and typical groundwater temperature (i.e., 15°C) will negligibly affect the depicted equilibrium relationships. The generic Eh-pH diagrams presented herein are nonetheless useful for conceptually illustrating fundamental aqueous equilibrium relationships. For example the site groundwater Eh-pH conditions superimposed on the iron Eh-pH diagram (Figure 3) favor the presence of both soluble and insoluble iron, with a significant fraction of iron hydroxide solids [Fe(OH)<sub>3(s)</sub>]. Hydrous iron oxides have high adsorptive capacity for arsenic and high specific surface area, and therefore are exceptional sinks for arsenic. Consequently, iron oxyhydroxides should exert significant control on arsenic solubility. In contrast, the site groundwater Eh-pH conditions superimposed on the manganese Eh-pH diagram (Figure 4) suggest that manganese is largely soluble even in the presence of sulfur and carbon.

Note that over 90-percent of the manganese analyses from groundwater samples collected on behalf of EPA in 2002 using low stress (low flow) purging protocols outlined by EPA Region 1 exceeded the EPA Secondary MCL (SMCL) of 50 ug/L, with a 100-percent detection rate. Iron groundwater results from these same sampling events were also significant in terms of detection rates and SMCL exceedances, with a detection rate greater than 90-percent, and with 70-percent of results in excess of the SMCL of 300 ug/L. The comparatively lower rate of SMCL exceedances may reflect the condition of the site groundwater Eh-pH regime, which suggests a significant fraction of iron oxyhydroxy solids at equilibrium. Note that both iron and manganese

are present at concentrations several orders of magnitude greater than typical arsenic groundwater concentrations. For example based on recent (2002) low flow groundwater sampling conducted by EPA in the FDDA, wetland, and Central Area (TRC, 2002a,c), the detected concentrations of iron ranged from 49.6 to 43,700 ug/L, with a median value of 1,100 ug/L. Detected concentrations of manganese ranged from and 2.8 to 9,010 ug/L, with a median value of 551 ug/L. Detected arsenic concentrations from the same sampling events ranged from 0.13 to 371 ug/L, with a median concentration of 1.9 ug/L.

Note also that iron concentrations in available soil data suggest that iron is plentiful in Central Area overburden. For example, iron in soil samples from the FDDA at the Olympia site ranged from 6,500 J mg/kg to 14,000 J mg/kg at a 100-percent rate of detection.

## 5.1.2 Arsenic

### 5.1.2.1 Arsenic Fate and Transport

Arsenic is a significant risk driver for human and ecological receptors in Aberjona River and wetland sediments near Wells G and H and in other reaches of the Aberjona River (e.g., the cranberry bog to the south of Salem Street). The presence of the arsenic in the river and wetland sediments and in the groundwater poses a potential threat to potable water development in addition to that posed by chlorinated solvents like TCE. Whether the arsenic will pose an actual threat depends in part on the geochemistry and hydrologic properties of the aquifer. The following summary of arsenic fate and transport properties is important to the interpretation of the available arsenic data and related geochemical/water quality data.

The geochemistry of arsenic is complex and has a significant impact on the mobility and toxicity of arsenic. For example, the principal forms of arsenic found in natural waters are As(V), and As(III). In general, As(V) is the oxidized form and is less toxic, less mobile, and has a greater tendency to adsorb to aquifer solids (especially iron oxyhydroxide [FeOOH]) than does the reduced form As(III). As(III) is most prevalent in reducing environments. As(III) is more toxic, more mobile, and is less likely to adsorb to aquifer solids, although adsorption does take place to a lesser degree. While the equilibrium chemistry of arsenic, especially As(V) and As(III), is well documented, the equilibrium chemistry is not simple, and equilibrium properties cannot readily be assigned to dynamic hydrogeologic or geochemical situations. Arsenic fate and transport behavior is significantly influenced by the presence of other chemical components and species, such as iron, manganese, sulfur and some organics, as well as pH, dissolved oxygen and oxidation-reduction potential. The fate and transport behavior of arsenic is further complicated by arsenic transformation reaction kinetics, which are relatively slow compared to other chemical species like iron. Arsenic redox behavior is also significantly influenced by the presence of highly organic materials, like peat.

Iron and arsenic chemical behavior in aqueous systems are strongly correlated. Because of the ubiquitous presence of iron in the Central Area aquifer, iron plays a dominant role in the behavior of arsenic at the Wells G and H site and is likely to be the dominant solubility control. In oxidized domains, ferric iron (Fe[III]) predominates and tends to precipitate from solution as iron oxyhydroxides (FeOOH). There are various physical forms of FeOOH, including

crystalline. However, the amorphous FeOOH solids tend to predominate when initially formed (precipitated). Amorphous FeOOH solids have a high specific surface area, and therefore can serve as sink of arsenic in oxidized aqueous systems, such as the Aberjona River. If redox conditions were present that allowed the presence of significant quantities of FeOOH solids throughout the aquifer at the pH ranges typically observed in groundwater in the Central Area aquifer, migration of arsenic to municipal wells G and H, or other high-volume potable water supply well would be significantly attenuated. As previously noted, available soil data show that iron is plentiful in Central Area soil. In addition, the presence of iron hydroxide solids is supported by the previously discussed Eh-pH regime for the Central Area aquifer and Eh-pH predominance graphics for iron (see Figure 3). Note, too, that arsenic also sorbs to aluminum oxides ( $Al[OH]_3$ ) and significant concentrations of aluminum (as high as 6,740 ug/L at MW-002S) were detected in Central Area and nearby groundwater. Manganese oxides also oxidize As(III) to As(V), which is more likely to sorb (Oscarson et al, 1981).

The kinetics of arsenic transformation are important, as are the ORP conditions necessary to drive the transformation. The kinetics of arsenic transformation are slow. For example, the transformation of As(III) to As(V) under the imposition of oxidizing conditions can take days (Cherry et al, 1979). Therefore, species of arsenic in dis-equilibrium with their surroundings can exist for some time. The transformation is not instantaneous. Also, the speed with which As(V) is released from FeOOH, under the imposition of reducing conditions varies with the form of FeOOH solid. As(V) adsorbs readily to FeOOH. Amorphous FeOOH solids dissolve more quickly, and thus release their load of arsenic more rapidly than crystallized FeOOH due to thermodynamic differences. In addition, the reduction of FeOOH is facilitated by microbial mediation, which in turn is driven by the metabolism of organic matter. If conditions are not conducive to microbial mediation, then FeOOH transformation, and thus arsenic release, will be attenuated. As later discussed, conditions in medium and deep overburden in the Central Area aquifer are not conducive to biological activity, due in part to low concentrations of natural organic matter.

In oxidizing environments, arsenic exists primarily as oxyanions (hard anions that contain oxygen) and are immobile. In addition to iron oxyhydroxides, arsenic will also adsorb to clays, aluminum hydroxides, manganese compounds, and organic material at acidic and neutral pHs. Arsenic can be reduced from higher to lower valence states by organic matter, divalent metals, and dissolved sulfide. In sulfidic conditions, arsenic can form aqueous arsenic-sulfide complexes called thioarsenates (Wilkin et al, 2003, Rader et al, 2004)

#### *5.1.2.2 Arsenic in the Central Area Aquifer*

Within the glacial aquifer in the Central Area, measured ORP readings were never more than mildly reducing (-94 mV to -168 mV), with areas of groundwater exhibiting oxidizing conditions ranging as high as 270 to 556 mV. Under these conditions the less mobile and more highly sorbed As(V) can be formed. Figure 5 presents the site Eh-pH regime for arsenic superimposed on an Eh-pH diagram for aqueous arsenic species. Under the Eh-pH conditions generally present in the Central Area Aquifer, the majority of arsenic is expected to be present as the less mobile, more readily adsorbed As(V) species.

EPRI (2003) conducted soil leaching experiments with arsenic and determined that  $K_d$  values ranged from 0 to 664.2 milliliters per gram (mL/g). The best predictor of arsenic content in the leachate was soil grain size, and iron and aluminum content.  $K_d$  increased with decreasing grain size (about 3 orders of magnitude or more from sand to clay).

Hemond (1995) indicated that in the Aberjona watershed the pattern of arsenic contamination in the sediment does not seem to correlate to any probable distribution of sources; however, a strong relationship with the fineness of sediment texture and with organic matter content (which themselves are correlated) was observed. Naturally occurring levels of arsenic in soils are in the range of 0.4 to 40 mg/kg for soils with no geologic or anthropogenic arsenic inputs.

Studies by Keon et al (2000) of the arsenic rich and sulfidic peat sediments from the Aberjona watershed indicated that most of the arsenic is strongly adsorbed, with the remainder likely coprecipitated with iron oxyhydroxides. In contrast, riverbed sediments five feet from the wetland samples show a different arsenic distribution: arsenic is distributed among pools including crystalline sulfides, recalcitrant arsenic oxides, strongly adsorbed As, and ionically adsorbed arsenic (Keon et al 2000).

Keon et al (2001) employed a sequential extraction technique to differentiate various "pools" of solid phase arsenic in sulfidic Aberjona River sediments and iron-reducing wetland peat, and sought to quantify mobile arsenic and discern arsenic associations with redox-dependent solid phases (e.g., iron oxyhydroxides and sulfides). Keon et al (2001) suggests a variety of geochemical processes that might liberate the variously bound fractions of arsenic in sediments. These potential arsenic mobilizing processes include, for example increases in the ionic strength of the aqueous medium, which could occur from road salting, or removal of arsenic complexed with iron oxides or humic acids due to phosphate-laden runoff (e.g., agricultural drainage or lawn fertilization). Keon et al (2001) also attempted to discern the mobility of arsenic coprecipitated with manganese oxides and amorphous iron oxyhydroxides, and arsenic adsorbed to particle sulfates using a hydrochloric acid extraction (Keon et al, 2001). However, the Keon et al (2001) extraction procedure did not account for re-precipitation of arsenic as an arsenic sulfide (Ford, 2004c). Wilkin and Ford (2002) note that with sediments containing sulfide minerals, the hydrochloric acid extraction introduces artifacts to the partitioning scheme. Consequently, Keon et al (2001) may not accurately describe the potential mobility of arsenic associated with coprecipitated manganese oxides and amorphous iron oxyhydroxides, as well as arsenic sorbed to particulate sulfate.

Arsenic in the Aberjona River and downstream lakes was analyzed by Hemond (1995). Hemond found that in the Mystic Lakes downstream of Wells G and H, the arsenic concentrations varied seasonally from 1 ug/L during the winter months to 1.3 ug/L during the summer months. Hemond (1995) found that arsenate concentrations in the anoxic hypolimnion actually increased during the summer months and the arsenite increased from one-quarter of the total arsenic in the water during the colder months to one-half of the total between May and October in the mixed layer (epilimnion) despite that fact that the upper water remained well oxygenated. He indicated that these counter intuitive results are evidence that kinetic considerations govern arsenic speciation during much of the year. He also found that organic arsenic monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) followed a temporal and spatial pattern similar to

that of arsenate, reaching maximum concentrations respectively in the excess of 0.3 ug/L and about 0.1 ug/L. Hemond (2001) also indicates that the Nitrogen Cycle impacts arsenic speciation. Nitrification represents a major hypolimnetic oxygen demand following the onset of seasonal stratification. Nitrate controls the redox potential of the bottom waters and is responsible for reoxidizing ferrous iron (Fe[II]) as it diffuses from the lake sediments into the hypolimnion. Studies by Ahmann et al (1994) have isolated two new species of bacteria from Wells G and H wetland that reduce arsenic, one can also precipitate orpiment ( $As_2S_3$ ) and have a key role in controlling the mobility of arsenic in the watershed.

Other site-specific factors will influence the geochemical behavior and mobility of arsenic. As discussed herein, the mildly reducing to oxidizing aqueous environment of the Central Area aquifer should favor the formation of less mobile As(V), and Fe(III), which provides an adsorption surface for arsenic. The formation of As(V) should further be favored along flow paths by the induced infiltration of demonstrably well oxygenated river water under pumping conditions. Induced infiltration of relatively low concentration river water should also act to dilute contaminant concentrations in the aquifer.

Note that Ford (2004b) conducted oxic leaching tests to assess arsenic release under oxic conditions using a leaching solution with a chemical composition consistent with surface water. Sediment pore water measurements and oxic leach test results indicate that sediments may be a long-term source of arsenic to groundwater at Wells G and H. Arsenic concentrations released from sediments collected from the Wells G and H wetland ranged from 23  $\mu\text{g/L}$  to 341  $\mu\text{g/L}$ . Ford (2004b) notes, however, that the greatest risk of arsenic release from sediments occurs under reducing conditions. Under a pumping scenario where aqueous geochemical conditions become increasingly dependent on the influence of induced surface water infiltration, the aquifer becomes more oxidized; as a result, steady concentrations like that found in the batch oxic leach tests are unlikely to be sustainable. This outcome is dependent, however, on the degree of mixing of various water sources within the aquifer and would be influenced by microbial activity (Ford 2005a).

Overall, as discussed later in this document, water quality data collected during operation of Wells G and H, and later data collected during remedial investigations and the USGS pump test, do not trigger criteria noted as indicative of high arsenic groundwater by Smedly and Kinniburgh (2004).

Groundwater data collected from the Central Area aquifer and nearby areas on behalf of EPA in 2002 using low stress (low-flow) purging protocols set forth by EPA Region I detected arsenic in 76 out of 77 groundwater samples. The highest concentrations tended to be located in the Central River Valley. Fourteen out of the 77 groundwater samples exceeded the current 10  $\mu\text{g/L}$  arsenic MCL. In addition, the highest concentrations were also found in the shallow overburden wells. Comparisons between data from historical non-low-flow and the aforementioned 2002 low-flow sampling suggest that non-low-flow samples techniques may have contributed to elevated arsenic concentrations due to aquifer solids entrainment in the samples. However, since arsenic does not partition as strongly to aquifer solids as chromium and lead, which partition very strongly to aquifer solids (see Sections 5.1.3 and 5.1.4), a portion of the reductions in arsenic concentrations could represent natural attenuation.

### 5.1.3 Chromium

Chromium has been identified as a sediment contaminant in the Aberjona River. EPA determined that a significant portion of the chromium found in sediments was chromium III (greater than 99-percent) (M&E, 2004). The Aberjona River Study did not identify chromium in sediment as a risk driver for human health; however, chromium in sediment of the river and the 38-acre wetland does pose a risk to ecological receptors such as the mallard duck and muskrat. The following summary of chromium fate and transport properties will aid in the interpretation of available groundwater chromium data and related geochemical/water quality data.

Chromium is an inorganic chemical that occurs in the earth's crust and is released to soil and groundwater from natural and anthropogenic sources. Chromium can be transported from soil by wind erosion or runoff, or can leach into the subsurface.

In oxidizing environments, these chromium compounds primarily exist as oxyanions (hard anions that contain oxygen) and are relatively mobile. However, they can be absorbed by clays, iron, oxyhydroxides, aluminum hydroxides, manganese compounds, and organic material at acidic and neutral pHs. Chromium can be reduced from higher to lower valence states by organic matter, divalent metals, and dissolved sulfide.

Chromate (Cr[VI]) species predominate and are highly mobile in oxidized systems, except for their tendency to be adsorbed, particularly by Fe(III) and Mn-oxides below pH 8. Chromate is in general weakly complexed. In contrast, Cr(III) dominates in reducing environments and forms strong, hard-acid complexes. Cr(III) complexes with hydroxyl, sulfate, organic ligands, and other species, which increases its stability and increases the solubility of Cr<sub>2</sub>O<sub>3</sub> (chromium oxide – the solid form). Organic matter, Fe(II), and hydrogen sulfide (H<sub>2</sub>S) can reduce Cr(VI) to Cr(III). Manganese oxides in soil can adsorb Cr(III) and oxidize it to Cr(VI). Adsorption of chromate (C<sub>2</sub>O<sub>4</sub>) by hydrous ferric oxide decreases with increasing pH, whereas Cr(III) adsorption increases as the pH rises (ERG, 2003).

In the general Eh-pH regime of the Central Area aquifer (see Figure 6), chromium is expected to be in the Cr(III) state and will likely exist as Cr<sub>2</sub>O<sub>3</sub> solid. In addition, K<sub>d</sub> values for Cr (III) suggest that chromium will be relatively immobile in Central Area groundwater. The following table compares the K<sub>d</sub> values derived from ERG (2003) for arsenic and chromium at various pHs. The K<sub>d</sub> values for Cr(III), the chromium species expected to predominate in the Central Area aquifer, are many orders of magnitude greater than those of As(V), the least mobile of the two primary arsenic species expected in Central Area groundwater in the Central Area aquifer. Thus, chromium is expected to be relatively immobile.

Soil Water Adsorption Partitioning Coefficient (Kd)			
Element	pH 4.9	pH 6.8	pH 8.0
As(V)	25	29	31
Cr (III)	1,200	1,800,000	4,300,000
Cr (VI)	31	19	14

**Notes:**

\*Kd = Cs/Cw where Cs = concentration adsorbed into soil; Cw = concentration in water units = mL/g  
Kd units = mL/g

#### 5.1.4 Lead

Lead has been identified as a sediment contaminant in the Aberjona River. The Aberjona River Study did not identify lead in sediment as a risk driver for human health; however, lead in sediment does pose a risk to ecological receptors such as mallard ducks and muskrats. The following summary of lead fate and transport properties will aid in the interpretation of available groundwater lead data and related geochemical/water quality data.

Lead is present in the earth's crust and may be released from weathering processes and from anthropogenic sources. This element is a borderline hard/soft cation that forms insoluble metal sulfides in anaerobic environments. Lead generally exhibits little mobility in groundwater systems and tends to sorb and be transported in water primarily with suspended colloidal particles (ERG, 2003). The concentration of lead in groundwater is usually controlled by adsorption or coprecipitation with iron, manganese, and aluminum. Lead is relatively immobile in all matrices due to its strong tendency to be sorbed by iron and manganese oxides and the insolubility of many lead minerals. Lead is effectively removed from water by adsorption to organic matter and clay minerals, precipitation as insoluble salt, and the reaction with hydrous iron and manganese oxide.

Lead is relatively immobile in soils, sediments, and groundwaters. This is reflected by its strong tendency to be adsorbed by Fe and Mn oxides under oxidizing conditions, but also the insolubility of a number of lead minerals including lead hydroxycarbonate, which limits lead concentrations in some public water systems, and pyromorphite ( $Pb_5(PO_4)_3Cl$ ), which controls lead concentrations in some soils adjacent to highways affected by road salt and leaded gasoline exhaust. Lead sulfides are also very insoluble at low Eh, even at low metal and sulfide concentrations (ERG, 2003). Mechanisms for sorption of lead by soils and sediments are ion exchange, specific adsorption, co-precipitation with hydrous oxides, and incorporation into cationic lattice sites in crystalline sediments (Bodek et al, 1988). The following table derived from Bodek et al (1988) summarizes typical values of sorption constants (Langmuir constants) for lead on materials such as clays, Fe-oxides, Mn-oxides, organic matter, soils and sediments. The  $A_m$  and  $\log K_L$ , which represent the maximum adsorption capacity of the solid and the sorption constant related to the binding energy of sorbate, respectively, demonstrate the predominance of Fe and Mn oxide as a sink or solubility control for lead under oxidizing conditions.

Langmuir Constants	Clays	Fe Oxides	Mn Oxides	Organic Matter	Soils	Sediments
$A_m$	~40	2400	2700	300-500	31	20
Log $K_L$ ( $\log M^1$ )	3.5	~4	3.8	~4	4.5	4.9

**Notes:**

$A_m$  = maximum adsorption capacity of solid (ugmol/g) – a Langmuir constant

Log  $K_L$  = Sorption constant related to binding energy of sorbate – a Langmuir constant

In the general Eh-pH regime of the Central Area aquifer (see Figure 7), lead is expected to be in the soluble Pb(II) state, but should be readily adsorbed given the extent of Fe and Mn oxides in the Central Area aquifer and the adsorption tendencies expressed by the Langmuir constants.

Groundwater data collected from the Central Area aquifer and nearby areas on behalf of EPA in 2002 using low stress (low-flow) purging protocols set forth by EPA Region I showed that lead was detected in Central Area groundwater at concentrations generally an order of magnitude lower than the EPA Safe Drinking Water Act (SDWA) Action Level of 15 ug/L. The highest concentration detected during the 2002 low stress (low flow) sampling (5.2 ug/L at MW-002M) was lower than the action level by a factor of 3. Historical analytical data between 1979 and 1991 detected lead on a limited number of events. One sample collected on 1/25/81 from Well G anomalously detected lead at a concentration of 270 ug/L. Historical groundwater data from samples collected with the non low-flow sampling techniques may have artificially elevated metals concentrations due to aquifer solids entrainment (turbidity). Comparisons between data from historical non-low-flow and more recent low-flow sampling discussed later in this document support this hypothesis. Low-flow data are considered more representative of actual conditions. No prior or subsequent monitoring detected lead in Wells G or H except at the end of the USGS aquifer pump test on 1/3/1986. Lead was detected in aquifer pump test effluent from Wells G and H at concentrations of 90 ug/L and 80 ug/L, respectively. However, samples collected 10 days prior during the aquifer pump test did not detect lead at a laboratory reporting limit of 50 ug/L. Later sampling unrelated to the pump test conducted on 8/21/91 did not detect lead at a laboratory reporting limit of 5 ug/L. The erratic detections are contrary to the limited transport behavior of lead and could be artifacts of sampling technique (none of the historical data were based on low-flow sample collection) or could reflect another source of contamination. For example, brass or bronze parts on the pump could serve as a source of detectable lead (WWJ, 1994).

### 5.1.5 Copper

Copper was also identified as a sediment contaminant in the Aberjona River. Although the Aberjona River Study did not identify copper in sediment as a risk driver for human health, copper was found to pose a risk to ecological receptors, specifically, mallard ducks. The following summarizes salient properties, and fate and transport properties of copper that are important in evaluating its potential for contamination of Wells G and H.

Copper is strongly adsorbed by organic matter, Fe(III) and Mn oxides, and secondarily by clays (ERG, 2003). Bodek et al (1988) state that copper exceeds lead in its tendency to be sorbed to solids. Sorption is probably the most important controlling mechanism in determining copper

mobility in the environment. Organic complexation, specific adsorption, precipitation, and ion exchange are important mechanisms for sorption of copper onto soils and sediments. Studies have shown that sorption of copper on hydrous iron and manganese oxides is due to co-precipitation of copper in the iron and manganese oxide lattice (Bodek et al, 1988). The following table derived from Bodek et al (1988) summarizes typical values of sorption constants (Langmuir constants) for copper on materials such as clays, Fe-oxides, Mn-oxides, organic matter, soils and sediments. The  $A_m$  and  $\text{Log } K_L$ , which represent the maximum adsorption capacity of the solid and the sorption constant related to the binding energy of sorbate, respectively, demonstrate the predominance of Fe and Mn oxide as a sink or solubility control for copper. Also tabulated is the  $K_d$  for copper on clay, Fe oxides and Mn oxides. The  $K_d$  values for Fe and Mn oxides are consistent with those of Cr (III), which is not very mobile.

Adsorption Properties of Copper						
Sorption Constants	Clays	Fe Oxides	Mn Oxides	Organic Matter	Soils	Sediments
$A_m$	6	130	1670	200	28	34
$\text{Log } K_L$	5	5	4	5	5	5
$K_d$	3	3600	8000	--	--	--

**Notes:**

- $A_m$  – maximum adsorption capacity of solid (ugmol/g) – a Langmuir constant
- $\text{Log } K_L$  – Sorption constant related to binding energy of sorbate – a Langmuir constant
- $K_d$  – Distribution coefficient (mL/g)
- No value provided in Bodek et al (1998)

Copper is insoluble in reduced environments, where it will precipitate as a sulfide. Copper is insoluble above pH 7–8 (because of the precipitation of tenorite, CuO) and in the presence of abundant carbonate of Cu(II) carbonate minerals. Cu(II) forms strong humate complexes, so that in soils >99.9-percent may be complexed (ERG, 2003).

In the general Eh-pH regime of the Central Area aquifer (see Figure 8), copper will largely exist in a precipitated phase, and available soluble Cu(II) species should be readily adsorbed to Fe and Mn oxides given the extent of Fe and Mn oxides in the Central Area aquifer and the adsorption tendencies expressed by the Langmuir constants and distribution coefficient. Copper groundwater data collected on behalf of EPA in 2002 using low stress (low flow) purging protocols set forth by EPA Region 1 showed that copper was detected in Central Area groundwater at concentrations approximately 3 orders of magnitude lower than the EPA drinking water action level of 1,300 ug/L.

### 5.1.6 Mercury

Mercury (Hg) has been identified as a sediment contaminant in the Aberjona River. The Aberjona River Study did not identify mercury in sediment as a risk driver for human health; however, mercury in sediment does pose a risk to ecological receptors such as mallard ducks and muskrats. The following summarizes salient fate and transport properties of mercury that are important in evaluating its potential for contamination of Wells G and H.

Mercury can exist in three oxidation states (elemental mercury Hg(0), mercurous mercury Hg(I), or mercuric mercury Hg(II)). Mercury forms strong complexes with chloride ion (Cl<sup>-</sup>), which may dominate the solution chemistry of this metal. Mercury forms even stronger complexes with other halogens such as bromide and iodide. Mercury is highly insoluble in reduced environments, where it can precipitate as a metal or as a sulfide. Hg(II) is usually complexed—in pure water as Hg(OH)<sub>2</sub><sup>0</sup>, and at chloride concentrations typical of fresh waters (<10E-2 mol/kg) as HgCl<sub>2</sub><sup>0</sup>. Hg(II) forms strong complexes with humic materials, so that in soils >99.9-percent of mercury may be complexed (ERG, 2003).

Mercury is biologically methylated only in environments low in sulfide. The stable methyl mercury species in fresh waters is CH<sub>3</sub>HgOH. The methyl mercury cation, CH<sub>3</sub>Hg<sup>+</sup>, complexes with ligands containing carbon (C), phosphorous (P), oxygen (O), nitrogen (N), and the halogens, and forms very stable complexes with sulfur-containing ligands. In oxidized, fresh waters the Hg(II) methyl hydroxo and methyl chloro complexes dominate (ERG, 2003).

Mercury is strongly adsorbed by organic matter, Fe(III) and Mn oxides, and secondarily by clays (ERG, 2003). Sorption of mercury is very fast and practically irreversible (Bodek et al., 1988). By inhibiting mercury sorption, Hg-Cl complexing helps to mobilize the metal. Dimethyl mercury is very insoluble in water and tends to be volatilized from soils (ERG, 2003)

In the general Eh-pH regime of the Central Area aquifer (see Figure 9), mercury will largely exist in low solubility phases, and available soluble mercury species should be readily adsorbed to Fe and Mn oxides given the extent of Fe and Mn oxides in the Central Area aquifer. In addition, mercury groundwater data collected on behalf of EPA in 2002 using low stress (low flow) purging protocols outlined by EPA Region 1 showed that mercury was rarely detected in Central Area groundwater. Detected concentrations, and laboratory reporting limits for non-detect results, were typically more than an order of magnitude lower than the EPA MCL of 2 ug/L (generally 0.1 ug/L).

Mercury was anomalously detected at the conclusion of the USGS 30-day pump test in Wells G and H at concentrations of 3.8 ug/L and 4.4 ug/L, respectively, which exceeds the mercury MCL of 2 ug/L. Samples collected approximately 10-days prior to the conclusion of the pump test did not detect mercury at a laboratory reporting limit of 0.2 ug/L. The mercury detections at the end of the pump test are anomalous given that groundwater in the surrounding aquifer does not contain mercury at significant concentrations.

## **6.0 ANALYSIS**

Arsenic is the focus of this analysis, although the potential impacts of other metals, including chromium, lead, iron and manganese are also considered. The probable fate of copper and mercury are also discussed. The influence of geochemical parameters such as ORP, DO, and sulfate are included.

### **6.1 Preface to Analysis**

The most straightforward method for evaluating Aberjona River surface water and sediment impacts on potable water development in the Central Area (OU-2) aquifer would be to assess water quality of the former municipal wells G & H during operation. Unfortunately, arsenic data collected during the period of the use of the wells as a potable water supply are not available. However, other secondary data are available to allow a supposition regarding whether Aberjona River water and sediment arsenic concentrations could have an impact on potable water development. The assessment criteria used to evaluate Aberjona River impacts on potable water development include the following:

- Water quality data from Wells G and H from a period shortly after pumping ceased and proxy data from the period of Wells G and H operation (pre-1979) that indicate whether Wells G&H were likely impacted by arsenic; Water quality data for other pumped wells in the proximity of Wells G and H;
- Wells G and H water quality data (non-arsenic parameters) compared to other aquifers where elevated arsenic is present;
- Mobility of arsenic;
- Arsenic concentrations in the Wells G and H area;
- Hydrologic factors controlling the migration of arsenic;
- Influence of peat deposits;
- Measurement of human hair samples; and
- Other issues.

### **6.2 Water Quality Data for Wells G and H**

Wells G and H were used intermittently as a potable water supply, primarily for emergency water demand, by the City of Woburn. The wells were pumped continuously in the summer months at rates of 700-800 gpm and 400 gpm, respectively (USGS, 1987).

Well G was constructed in late 1964. It is screened from a depth of approximately 75 to 85 feet below ground surface. Well H was constructed in 1967. It is screened from a depth of approximately 78 to 88 feet below ground surface. In both wells, the gravel pack extends

upward to within 10 feet of the surface, above which the casing is surrounded with grout or concrete.

Wells G and H were constructed in soils consisting of an upper layer of peat underlain by sand and gravel to a depth of about 80 to 90 feet. When the wells were first pumped, coliform contamination was identified in the wells. The coliform problem was reportedly "corrected by excavating all of the organic soil or peat for 30 feet around the wells and replacing it with clean bank-run sand and gravel" (Dufresne-Henry, 1978). The well logs indicate that the peat was 5 feet thick at Well G and 17 feet thick at Well H.

Water quality data collected by the City of Woburn during the operation of municipal Wells G and H are available from 1967, 1968, 1973, and 1974. Unfortunately, this data set does not include arsenic and anthropogenic metal contaminant data of interest to this analysis. However, this water quality data is useful for evaluating the redox conditions of the aquifer during pumping as well as to provide comparison to indicator parameters for high arsenic groundwater discussed below.

Arsenic and metals data are available for Wells G and H from sampling conducted on September 24, 1979 (approximately 4 months after shutdown) contained 2.0 and 1.5 ug/L of arsenic, respectively. In six subsequent sampling rounds since 1981, arsenic was nondetect at laboratory reporting limits of 5 to 10 ug/L. In 1986, a 30-day combined pumping test of Wells G and H was performed by the USGS to determine the area of influence and the zone of contribution to the two wells. The wells were pumped at rates of 700 and 400 gpm, respectively. During the pump test, groundwater samples were collected for chemical analysis by other parties at approximately 20 days into the test and at the end of the test. Groundwater samples collected at the 20 day point by GeoEnvironmental Consultants and at the end of the pump test by Weston Geophysical Corporation did not detect arsenic at laboratory reporting limits of 10 ug/L and 5 ug/L, respectively (ETC, 1986; Tighe & Bond, 1986). It is possible that the 30-day USGS pumping test may not have been representative of long-term conditions. However, the other constituents present in the groundwater such as manganese, pH and hardness (and others) were at levels similar to those detected at Wells G and H during operation (Table 1), which suggests that the arsenic results are representative. In any case, the results of all these post-shutdown chemical analyses of Wells G and H suggest that arsenic contamination levels would have been relatively low during the long-term operation of the wells and would probably have met current drinking water standards for arsenic (2006 MCL of 10 ug/L).

**Table 1. Comparison Between Historical Wells G and H Water Quality During Pumping to USGS Pump Test Groundwater Analyses Data**

Constituent	Well G During Municipal Pumping	Well G During USGS Pump Test	Well H During Municipal Pumping	Well H During USGS Pump Test
Iron	0.01-0.12	<0.03	0.01-2.4	<0.03
Manganese	0.02-0.55	0.36	0.59-2.16	0.85
pH	6.2-6.9	6.5	6.3-6.6	6.5
Hardness	79-250	122	188	138
Nitrate as N	0.4-4.4	1.67	0.01-4.9	1.57
Chloride	37-120	72.5	107	86
Conductivity	500-700	446	-	487
Copper	<0.01-0.05	<0.02	-	-

**Notes**

Concentration in mg/L except conductivity in umhos/cm and pH in pH units.

- Data not available/reported

**Sources:** Dufresne-Henry (1978), Tighe and Bond (1986) and historical Wells G and H operational chemical analysis data received from Anna Mayor on City of Woburn Department of Public Works well testing (Mayor, 2003).

Just before the start of the USGS aquifer pumping test, measurements of streamflow indicated that the Aberjona River was gaining water at a rate of about 770 gpm between Olympia Avenue and Salem Street. Within one day after starting the test, that same part of the river was losing water at a rate of about 140 gpm. Gradients had been reversed at that time, causing groundwater that would have discharged to the river and seepage from the river and wetlands to move toward the wells. Near the end of the USGS pumping test, when Wells G and H had been pumped at 1,100 gpm combined for 25 to 30 days, the length of river near the wells was losing water at a rate of 550 to 650 gpm. The cone of depression extended beneath this entire length of the river, so the potential existed throughout this area for water to move downward into the aquifer from the river and the wetlands. See Figure 10 for an illustration of the Wells G and H drawdown (zone of influence) after 30 days of pumping (January 3, 1986).

If large-scale groundwater withdrawals were again made from the aquifer at or near Wells G and H, the interactions between the river and the aquifer would probably be similar to those recorded by the USGS in 1987, and seepage from the river into the aquifer would be significant. The Aberjona River currently has a dissolved arsenic level of about 6 ug/L during baseflow at sampling station TT#5, located downstream of the Wells G and H at the Salem Street bridge (TTNUS, 2002), which would be the dissolved arsenic concentration of the water as it entered the underlying sediment. Particulate arsenic in the river water would most likely be filtered out as the water passed through the sediments and the aquifer.

The dissolved arsenic concentration of the river water would most likely be modified to varying degrees, depending on the subsurface conditions along its flow path down into the aquifer.

In addition, the induced infiltration of oxygenated (DO ranging seasonally from 4.2 to 11.8 mg/L) and strongly oxidizing (ORP ranging from +170 mV to +485 mV) surface water from the

stretch of the Aberjona River near Wells G and H during pumping should shift the aqueous chemical equilibrium of the aquifer to more oxidizing conditions along flow paths. The equilibrium of aqueous arsenic would be expected to increase the predominance of less mobile As(V). In addition, increased formation of iron oxyhydroxide solids would also be expected, to which As(V) very strongly sorbs. Note, however, the arsenic redox equilibrium can be slow to achieve, as shown by Cherry et al (1979) and others. In addition, conditions are expected to be more reducing at the sediment/groundwater interface.

The upland groundwater component of the flow toward the wells could also be modified as it moves through the aquifer, although it would not migrate through potentially arsenic-rich riverbed sediments. Unless much of the infiltrating river water developed much higher dissolved arsenic concentrations as it passed through the sediment and peat, the average of the surface water and groundwater concentrations would yield arsenic concentrations less than 10 ug/L, but a detailed groundwater contaminant transport model would be required to confirm this hypothesis. Based on the low hydraulic conductivity of the peat and the high hydraulic conductivity of the glacial stratified drift sediments, the water originating in the peat would be diluted more than 1,000 fold. Although the above-referenced arsenic-bearing water sources may be characterized by low arsenic concentrations on average, due to geochemical and transport dynamics, the source water may become either enriched or lose arsenic due to geochemical reactions in the subsurface due to the partitioning behavior of arsenic and the dissolution/precipitation behavior of iron oxyhydroxides. As later discussed, the dynamics of the well operation could change these equilibrium values; however, sufficient data are not now available to show that high arsenic concentrations would result in the aquifer under the high-capacity groundwater withdrawal scenario.

### **6.3 Water Quality Data for Other Pumped Wells in the Proximity**

Several wells in the proximity of Wells G and H were pumped for many years and in some cases are still being pumped. If the water quality in these wells is low in arsenic, then other wells placed nearby for potable water use would also be low in arsenic, provided the hydraulics are relatively consistent and the screen depths are similar. Nearby pumped wells include the two J.J. Riley Tannery wells located along the southwest boundary of the Wells G and H Site (Riley Wells), and the Atlantic Gelatin well field located southeast of the Wells G and H site on the Woburn/Winchester line.

#### **6.3.1 J.J. Riley Tannery Water Supply Wells**

The two Riley Wells (S47 and S46) were installed in 1945 and 1958, respectively (Delaney and Gay, 1980) and the J.J. Riley Tannery operated until 1988 (TTNUS, 2003). The wells each had rated capacities between 500 to 750 gpm, which is comparable to the capacities of Wells G and H. The well depths were between 35 and 51 feet, which is about half as deep as Wells G and H (Delaney and Gay, 1980). The results of arsenic analysis in both Riley wells from the only sampling event conducted during their period of operation (1980) were non-detect at a laboratory reporting limit of 10 ug/L (GeoTrans, 1994).

### 6.3.2 Atlantic Gelatin Well Field

Atlantic Gelatin is permitted to withdraw up to 1 million gallons per day (MGD) from 4 operational wells. In the 1950s these wells were pumped at a rate of about 1.5 MGD (Lubker and Halpin, 1951). The groundwater is used for process wash water. Wastewater is discharge to the MWRA sanitary sewer system (TTNUS, 2003). The Atlantic Gelatin wells were installed between about 1935 and 1958, and were between 62 to 156 feet deep. The rated capacities of the wells ranged from 372 to 1,000 gpm (Delaney and Gay, 1980). No testing of water quality for arsenic has been conducted.

### 6.4 Comparison to Other Aquifers

A comprehensive review of arsenic contamination in groundwater was compiled by Smedley and Kinniburgh (2004). They determined concentration ranges for 7 water quality parameters that are indicative of high arsenic concentrations. Evaluating the Wells G and H data in comparison to these parameters showed that unfavorable conditions were present in Well G (all 7 parameters unfavorable) and Well H (5 of 7 parameters unfavorable) for the presence of high arsenic levels. The parameters evaluated included iron, manganese, alkalinity, chloride, sulfate, nitrate, and pH. Table 2 presents the results of the indicator parameters.

Analyte	Favored Range for High Arsenic (mg/L) <sup>1</sup>	Well G			Well H			Finding	
		Avg	Low	High	Avg	Low	High	Well G	Well H
Iron	>0.2	0.045	0.000 <sup>2</sup>	0.210	0.631	0.010	2.400	Unfavorable	Favorable
Manganese	>0.5	0.410	0.020	1.170	1.123	0.200	2.160	Unfavorable	Favorable
Alkalinity	>500	50	32	60	50	47	56	Unfavorable	Unfavorable
Chloride	<60	69	19	185	90	25	116	Unfavorable	Unfavorable
Sulfate	<1	89	22	143	114	80	150	Unfavorable	Unfavorable
Nitrate	<1	3	0.4	21	3.8	0.03	32	Unfavorable	Unfavorable
pH	>7 SU	6.6	6.2	7.3	6.5	6.3	6.7	Unfavorable	Unfavorable

**Notes:**

<sup>1</sup> From Smedley and Kinniburgh, 2004.

<sup>2</sup> As posted in Mayor 2003.

SU – Standard units for potential of hydrogen (pH)

**Wells G and H data sources:** Mayor 2003; GeoTrans, 1994; and Dufresne-Henry, 1978

Table 2 includes some of the characteristic chemical features of high arsenic groundwaters noted by Smedley and Kinniburgh (2004), such as high iron concentrations (>0.2 mg/L), high manganese concentrations (>0.5 mg/L), and low concentrations of chloride (<60 mg/L), sulfate (<1 mg/L), and nitrate (<1 mg/L), as well as pH values near or greater than 7. Other chemical characteristics that are indicative of the relative presence of arsenic include bicarbonate and fluoride; however, comparative data from Wells G and H are not available for these parameters and therefore were not included in Table 2. Strong direct correlations between arsenic and iron concentrations in aqueous systems have been noted in the scientific literature and in work

conducted by EPA at the Industri-Plex Superfund Site. Consequently, high aqueous iron concentrations are expected to be indicative of the potential for high concentrations of arsenic. Manganese oxides also undergo reductive desorption and dissolution, and so could contribute to the arsenic load of groundwaters in the same way as iron. As shown in Table 2 iron and manganese levels at Wells G and H exhibit both favorable and unfavorable indications for a presence of arsenic; however, the possibility for arsenic presence needs to be assessed in view of all the parameters. Total arsenic has also been found to be positively correlated with alkalinity and pH. High salinity (monitored by chloride measurements) in fresh water aqueous systems associated with high rates of evaporation in some regions can be associated with high arsenic concentrations in groundwater. However, chloride is not expected to be a significant indicator in the non-arid conditions characteristic of the Woburn-area. Low sulfate concentrations can be indicative of strongly reducing conditions, and high arsenic concentrations are often associated with strongly reducing conditions. Sulfide mobilizes arsenic due to the formation of thioarsenite complexes (Wilken et al, 2003; Rader et al, 2004). Nitrate levels are also indicative of redox conditions, with low nitrate levels indicative of highly reducing conditions favorable to the presence of high arsenic concentrations. Overall, as shown in Table 2, the average geochemical conditions recorded in Wells G and H exhibit conditions unfavorable to the presence of high arsenic concentrations.

## 6.5 Arsenic Mobility

Hinkle and Polette (1999) reported that two categories of processes largely control arsenic mobility in aquifers:

- Adsorption and desorption reactions; and
- Solid-phase precipitation and dissolution reactions.

Arsenic adsorption and desorption reactions are influenced by changes in pH, redox (reduction/oxidation) reactions, presence of competing anions, and solid-phase structural changes at the atomic level. Solid-phase precipitation and dissolution reactions are controlled by solution chemistry, including pH, redox state, and chemical composition.

### 6.5.1 Adsorption and Desorption Processes

Arsenic is a redox-sensitive element that gains or loses electrons in redox reactions, and may be present in a variety of redox states. Arsenate and arsenite are the stable forms of arsenic solution in water (Hem, 1985). As(V) generally predominates under oxidizing conditions. As(III) predominates when conditions become sufficiently reducing. Under the pH conditions of most groundwater, As(V) is present as the negatively charged oxyanions  $\text{H}_2\text{AsO}_4^{-4}$  or  $\text{HAsO}_4^{-2}$ , whereas As(III) is present as the uncharged aqueous species  $\text{H}_3\text{AsO}_3$  (Hem, 1985). The strength of adsorption and desorption reactions between these different arsenic species and solid-phase surfaces in aquifers varies, in part, because of these differences in charge. Differences in species charge affect the character of electrostatic interactions between species and surfaces.

As(V) and As(III) adsorb to surfaces of a variety of aquifer materials, including iron oxides, aluminum oxides, and clay minerals. Adsorption and desorption reactions between As(V) and

iron oxyhydroxide solid surfaces are particularly important controlling reactions because iron oxides are widespread in the hydrogeologic environment as coatings on other solids, and because As(V) adsorbs strongly to iron oxyhydroxide surfaces in acidic and near-neutral-pH water (Pierce and Moore, 1982). However, desorption of As(V) from iron-oxide surfaces becomes favored as pH values become alkaline (Pierce and Moore, 1982; Masscheleyn et al, 1991b). The pH-dependence of As(V) adsorption to iron-oxide surfaces appears to be related to the change in iron-oxide net surface charge from positive to negative as pH increases above the zero-point-of-charge (pH at which the net surface charge is equal to zero) of about 7.7 for goethite, a crystalline iron oxide (Stumm and Morgan, 1996), or 8.0 for ferrihydrite, an amorphous iron oxide (Dzombak and Morel, 1990).

Iron oxyhydroxide surfaces also adsorb As(III) but to a lesser degree than As(V). Both As(V) and As(III) adsorb to aluminum oxides and clay-mineral surfaces. However, these adsorption reactions appear generally to be weaker than is the case for As(V) adsorption to iron-oxide surfaces under typical environmental pH conditions (Manning and Goldberg, 1997). Nevertheless, pH-dependent adsorption and desorption reactions other than those between As(V) and iron oxyhydroxide surfaces may be important controls over arsenic mobility in some settings. As is the case for adsorption of As(V) to iron oxyhydroxide surfaces, adsorption of As(III) to iron oxyhydroxide surfaces tends to decrease as pH increases, experiencing a maximum at pH 7. Unfortunately, As(V) and As(III) adsorption and desorption reactions with other common surfaces are less well characterized, and apparently more complex than is the case for adsorption and desorption reactions with iron oxyhydroxide surfaces (Manning and Goldberg, 1997).

As a result of the pH dependence of arsenic adsorption, changes in groundwater pH can promote adsorption or desorption of arsenic. Because solid-phase diagenesis (water-rock interaction) typically consumes hydronium ion ( $H^+$ ) (Stumm and Morgan, 1996), the pH of groundwater tends to increase with residence time, which, in turn, increases along groundwater flowpaths. Because iron oxyhydroxide surfaces can hold large amounts of adsorbed As(V), geochemical evolution of groundwater to high (alkaline) pH can induce desorption of arsenic sufficient to result in exceedances of the current EPA MCL in some environments (Robertson, 1989). The Central Area groundwater tends to be mildly acidic; therefore high alkalinity desorption is not expected to be a factor at Wells G and H.

Similarly, redox reactions can control aqueous arsenic solubility by their effects on arsenic speciation, and hence, arsenic adsorption and desorption. For example, reduction of As(V) to As(III) can promote arsenic mobility because As(III) is generally less strongly adsorbed than is As(V). Redox reactions involving either aqueous or adsorbed arsenic can affect arsenic mobility (Manning and Goldberg, 1997).

Arsenic adsorption also can be affected by the presence of competing ions. In particular, phosphate and arsenate have similar geochemical behavior, and as such, both compete for sorption sites (Hingston, et al, 1971; Livesey and Huang, 1981; Manning and Goldberg, 1997). Oxyanions in addition to phosphate also may compete for sorption sites. For example, Robertson (1989) suggested that correlation of arsenate with oxyanions of molybdenum, selenium, and

vanadium in groundwater of the Southwestern United States may be evidence for competitive adsorption among those oxyanions.

Finally, structural changes in solid phases at the atomic level also affect arsenic adsorption and desorption. For example, conversion of ferrihydrite to goethite or to other crystalline iron-oxide phases may occur gradually over time (Dzombak and Morel, 1990). Fuller et al (1993) demonstrated that as ferrihydrite crystallizes into goethite, the density of arsenic adsorption sites decreases. This decrease in density of adsorption sites can result in desorption of adsorbed arsenic. Structural changes in other solid phases may possibly affect arsenic mobility, but the role of such solid-phase structural changes on groundwater arsenic concentrations has received little attention to date (Hinkle and Polette, 1999).

### **6.5.2 *Precipitation and Dissolution Processes***

The various solid phases (e.g., minerals, amorphous oxides, organic carbon) of which aquifers are composed exist in a variety of thermodynamic states. At any given time, some aquifer solid phases will be undergoing dissolution, whereas others will be precipitating from solution. Arsenic contained within solid phases, either as a primary structural component of, or as an impurity in, is released to groundwater when those solid phases dissolve. Similarly, arsenic is removed from groundwater when solid phases containing arsenic precipitate from aqueous solution. As an example, because arsenic often coprecipitates with iron oxide (Moore, et al, 1988), iron oxide may act as an arsenic source (in the case of dissolution) or a sink (in the case of precipitation) for groundwater. Furthermore, solid-phase dissolution will contribute not only arsenic contained within that phase, but also any arsenic adsorbed to the solid-phase surface. The process of release of adsorbed arsenic as a result of solid-phase dissolution is distinct from the process of desorption from stable solid phases (Hinkle and Pollette, 1999).

The interplay of redox reactions and solid-phase precipitation and dissolution may be particularly important with regard to aqueous arsenic and solid-phase iron oxides and sulfide minerals. High concentrations of arsenic often are associated with iron oxides and sulfide minerals (Thornton, 1996). Iron oxides frequently dissolve under reducing conditions, but often precipitate under oxidizing conditions. Sulfide minerals generally are unstable under oxidizing conditions, but may precipitate under reducing conditions. Thus, as a result of the redox-sensitive nature of iron oxides and sulfide minerals, transfer of large amounts of arsenic between these solid phases and neighboring water may result from redox-facilitated precipitation and dissolution reactions (Hinkle and Pollette, 1999).

## **6.6 *Arsenic Concentrations in the Wells G and H Area***

### **6.6.1 *Aberjona River Sediment and Surface Water***

The Aberjona River watershed area was a center of industrial activity around the beginning of the century. Wastes from tanning, leather finishing, chemical manufacturing (especially sulfuric acid production) and arsenic-based pesticide production were commonly discharged either directly or indirectly into the Aberjona River. The Industri-Plex Superfund Site, located about 1

mile upstream of the Wells G and H area, released an estimated 200 to 900 metric tons of arsenic to the Aberjona watershed (Aurilio et al, 1995).

Studies have shown that arsenic is widespread in the Aberjona River and an estimated 300 metric tons of arsenic is still present in the watershed (Aurilio, 1992). The wetland sediments in the specific area of Wells G and H have 700 kilograms (kg) of arsenic present, The river south of Wells G and H to the Mystic Lakes has an estimated 500 kg of arsenic present. The concentration of arsenic in the Wells G and H area ranges from about 500 to 1000 mg/kg (Knox, 1991). An estimated 100 kg/year of arsenic is transported in surface water towards the Mystic Lakes. The surface water dissolved arsenic concentrations observed by Zeeb (1996) ranged from about 1 to 11 ug/L and the concentration on particulate matter ranged from 200 to 400 mg/kg. Arsenic riverine transport peaked in 1930 at the height of chemical manufacturing and has since declined (Zeeb, 1996). Recent remedial investigations conducted by EPA for the Industri-Plex site in 2001 to 2002 have shown that arsenic concentrations in the Aberjona River have not substantially changed since these previous studies. For example, average concentrations of arsenic in samples collected over an 18-month period under baseflow and storm flow conditions at the outlet of the Halls Brook Holding Area (HBHA), located approximately 0.5 miles upstream of the Wells G and H wetland, were 6.0 ug/L under average dissolved-baseflow and 37.1 ug/L under average total-baseflow conditions and 7.72 ug/L (dissolved) and 29 ug/L (total) under storm flow conditions (TTNUS, 2002). Samples collected during this same period at the outlet of the Wells G and H wetland showed that arsenic concentrations slightly attenuated to an average concentration of 5.6 ug/L during baseflow and a total concentration of 20.1 ug/L during baseflow, indicating that some deposition may be occurring in the Wells G and H wetland (Bullard, 2004).

The calculated arsenic fluxes during the same study period were 6.7 grams per hour (g/hr) during baseflow conditions and 23.78 g/hr during storm flow conditions at the HBHA outlet and 5.3 g/hr during baseflow conditions and 44.8 g/hr during storm flow conditions at the outlet of the Wells G and H wetland. Based on these flux values, it is estimated that the total mass of arsenic that is transported beyond the Wells G and H wetland is between 46 and 78 kilograms per year (kg/year), depending on the number and duration of storm events (Bullard, 2004).

Zeeb (1996) determined that peat layers in proximity to Well H to a depth of 55 centimeters (cm) represent the period of industrialization (past 50 years). These sediments have high levels of arsenic associated with overbank flow across the historical peat surface. An additional 10 to 20 cm of peat may have been impacted through particulate transport by percolation through the open structure of the peat surface. The redox conditions of the impacted peat is anticipated to vary in a cyclic manner due to periodic air entry and surface recharge. Zeeb (1996) indicates that the presence of such high concentrations of arsenic in the upper 80 centimeters of peat over a 50 year period suggests that arsenic transport away from this zone is not significant. The arsenic initially deposited in the wetland was in the form of As(V), most likely sorbed to iron and other hydroxides or precipitated as ferric hydroxy arsenate,  $\text{Fe}_3\text{AsO}_4$  (Zeeb, 1996). Once buried in saturated anerobic conditions, the reduction of dissolved As(V) to As(III) occurs in a oxidation reduction potential (Eh) range of 70 to 35 millivolts (mV) in the pH range from 6.5 to 7. Amorphous ferric hydroxide dissolves under Eh conditions ranging from 90 to 0 mV. With significant quantities of desorbed As(V) present, ferrous arsenate,  $\text{Fe}_3(\text{AsO}_4)_2$ , could precipitate

and exist in a narrow Eh-pH zone as ferric iron is reduced to Fe(II) (Zeeb, 1996). Under anaerobic conditions the sulfate present reduces to sulfide and the sulfide reacts with any available iron to produce iron sulfide solids (Smedley and Kinniburgh, 2004). The basic factors favoring iron sulfide solid formation are a sufficient supply of sulfate, iron, high organic matter, presence of sulfate reducing bacteria and an anaerobic environment alternated with limited aeration (Hechanova, 1983).

Data from the Aberjona River Study (M&E, 2004) suggest that sufficient iron and sulfide are present in the peat to support iron-arsenic-sulfur related reactions. The following table summarizes arsenic, iron, and sulfide concentrations in the peat underlying the river and wetlands between Route 128 to the north and Salem Street to the south.

<b>Arsenic, Iron, and Sulfide in Peat – Wells G and H (mg/kg)</b>			
	<b>Arsenic</b>	<b>Iron</b>	<b>Sulfide</b>
Minimum	3.7	2,310	1.605
Maximum	4,550	258,000	121,659
Median	105.5	19,200	558.5

Source: Derived from data presented in M&E, 2004

During the formation of iron sulfide minerals arsenic will be coprecipitated. If insufficient iron is present then thioarsenites will predominate (Wilkin et al., 2003). Moore et al (1988) notes that metal and arsenic sulfide minerals have the potential to sequester a large amount of trace elements, which are potential sources of secondary contamination if exposed to oxidizing environments. Without sulfate limitation, Moore et al found that the main controls on elemental distribution are the precipitation of diagenetic sulfides of arsenic and other metals (e.g., copper and zinc). However, Moore et al do not specify parameters/thresholds for sulfate limited environments. If the sulfides are oxidized they will release the arsenic, which can then be adsorbed to iron oxides thus repeating the cycle. The Industri-Plex facility just upstream of the Wells G and H area was a major producer of sulfuric acid between 1880 and 1929 (Aurilio, 1992) and it is likely that a significant quantity of sulfur compounds were released to the watershed. The sulfide wastes would have been released to the environment through disposal of pyrite cinders, flue dusts and spilled products (sulfuric acid). There are some data available on the levels of sulfides in the Aberjona sediments or regarding the presence of sulfide minerals. Peat sediments in the Aberjona watershed contained between 0.2 to 11-percent by weight of sulfur with a range of 0.2 to 1.6 percent near Wells G and H (Ford, 2004a), so a significant sulfur source is available for the formation of iron sulfides.

Zeeb (1996) identified some arsenic contamination at a deeper peat zone 120 to 160 centimeters below ground surface (bgs) and estimated that about 1 kg of arsenic per meter of river reach was present. Zeeb (1996) noted that this contamination likely migrated deeper through preferential downward groundwater flow possibly due to pumping at Wells G and H under a mobile geochemical window that allowed the arsenic to migrate. Zeeb (1996) assessed whether the peat sediments could be a major source of groundwater contamination to pumped wells and determined that “contrary to previous conclusions, as well as assumptions made as part of several watershed-scale models, the peat soils in this wetland are not loose and permeable, although they are in places interbedded with sand.” Due to the low vertical permeability (6E-5

to 1E-4 centimeters per second [cm/sec]) of the peat, Zeeb (1996) indicates that only a small advective flux would occur through the peat and that contaminant transport through the upper peat would be limited because the peat would be dewatered under pumping conditions. Zeeb (1996) indicates that likely potential sources of arsenic contamination would be outside his study area (which was located between Well H and the river channel). Zeeb postulated that the river channel could be a source, if peat layers are thin or absent.

Ford (2004b) conducted short term, 4 hour, leaching tests of Wells G and H area sediments with aerobic test water. Arsenic leached from the cores at concentrations ranging from 21 to 369 ug/l. In all cases the leached water was at a lower concentration than the initial pore water removed from the sediments. In some cases, the leached concentrations could be explained by residual pore water concentrations, but in other cases over 90-percent of the concentration was due to leaching from the sediment. Ford (2005b) suggests that the degree to which arsenic was leached from these sediments may be positively correlated with Total Organic Carbon (TOC), but four sediment samples may not be sufficient to indicate this with certainty. The leach tests were run on whole sediment samples, including plant fragments. The grain size distribution was not determined for these samples. Ford (2004b) notes that in the field the ability of arsenic to migrate is tied to the hydrologic and geochemistry of the in-situ conditions. The results show that under free draining conditions arsenic can be mobilized. However, as previously noted the mildly reducing weakly oxidized ORP conditions in the Central Area aquifer and the significant presence of iron oxyhydroxide solids is expected to attenuate the mobility of arsenic. In addition, the influx of well oxygenated surface water under pumping conditions is expected to shift the aqueous geochemical equilibrium of arsenic and iron equilibrium to less mobile phases and/or dilute contaminants leached from the peat deposits.

### **6.6.2 Wells G and H Geochemistry**

Dufresne-Henry(1978) indicated that Wells G and H had high levels of dissolved manganese, occasional hydrogen sulfide odors and low oxygen levels, which indicate that reducing conditions were present. The hydrogen sulfide odor is the strongest evidence of reducing conditions. Dufresne-Henry (1978) further indicated that oxygen levels tended to decrease with depth within the potable wells, but did not provide supporting analytical/field data. However, dissolved manganese concentrations can still occur in a mildly oxidizing environment because the manganese redox couple occurs at a higher ORP as compared with iron and arsenic (see Figures 3 and 4). In addition, the long term stability of low iron concentrations from Well G is indicative of mildly oxidizing conditions.

Some observation wells installed by Dufresne-Henry in the wetlands adjacent to Well H had elevated levels of iron but only on two consecutive days during the summer of 1977. For example, Dufresne-Henry observation Well "A", located about 30 feet from Well H, had approximately 10 mg/L of iron at 25 and 50 feet bgs and greater than 40 mg/L at depths of 75 and 92 feet bgs. These data tend to support that reducing conditions were present in some portions of the aquifer during the municipal pumping of Wells G and H. Due to the proximity of Well "A" to Well H, the total iron in the soil is probably similar. However, significantly higher concentrations were detected in groundwater in the wetland. Interestingly, municipal Wells G and H did not have high levels of iron, which suggests that the water quality in the swamp was

entirely different than encountered at Wells G and H. Dufresne-Henry (1978) drew a similar conclusion regarding swamp water quality.

The difference in observed geochemistry in Wells G and H versus monitoring wells installed in, or impacted by, wetland deposits, could be explained in part, by the induced infiltration of well oxygenated and highly oxidized river water. Concentrations of iron in water withdrawn by wells G and H could be diluted by the influx of relatively lower concentration river water. In addition, the relatively oxygenated river water could shift the aqueous geochemical equilibrium predominance of iron to a less soluble (iron (III) oxyhydroxide) form. The influx of river water would have little impact on manganese levels. As shown in the Eh-pH diagram for manganese (Figure 4), the predominance field for manganese is very large and significant precipitation of manganese would not occur except at extremely high pH (pH >8 to 9) for natural water systems or unrealistically high oxidation levels.

### **6.6.3 General Wells G and H Aquifer Geochemistry**

TRC compiled select groundwater inorganic and water quality data from the Central Area aquifer for the period of 1987 to 2002 to prepare composite groundwater concentration isopleths for arsenic, chromium, lead, iron, manganese, dissolved oxygen, ORP, and sulfate. Two sets of concentration isopleths were prepared for arsenic, chromium, lead, iron and manganese. One set is based on maximum groundwater concentration values from low-flow and conventionally collected groundwater samples to provide maximum areal coverage. The second set is based only on low-flow groundwater samples, which provide less areal coverage, but may be more representative since the data are more recent (2001 and 2002) and collected consistent with low-flow protocols. One set of plots were prepared for dissolved oxygen, ORP and sulfate.

The following summarizes the groundwater analytical data sources obtained by PRPs and EPA used to prepare the concentration isopleths. Information concerning these data (source, coverage, data range, limitations, etc.) are summarized in the data matrix presented in Table 3.

- Central Area (OU-2) groundwater data documented in GeoTrans (1994);
- Southwest Properties groundwater data documented in RETEC (1994 and 2003);
- Murphy Waste Oil property groundwater data documented in Clean Harbors (1996 and 1998);
- 2002 groundwater data from the EPA investigation of the Former Drum Disposal Area (FDDA) at the Olympia Property documented in TRC (2002a);
- Central Area groundwater data from eight wells sampled for EPA in October 2002 and documented in TRC (2002c); and
- Split sample data associated with EPA oversight of the RETEC 2002 Supplemental Remedial Investigation of the Southwest Property documented in TRC (2004a).