4.3.2 Wilson Ditch

Wilson Ditch is an agricultural supply ditch used to convey irrigation and stock water from Prickly Pear Creek to fields northwest of the plant site. Flow in Wilson Ditch is controlled by a headgate at the head of the ditch on Upper Lake. The position of the headgate and the flow in the ditch are controlled by a "ditch rider" hired by the water users, who ensures that downstream water right allocations are met.

Prior to 1997, the initial segment of the ditch conveyed water through the plant site in an underground pipe. The plant site segment transported water from its intake at Upper Lake, past the acid plant cooling towers along the southwest side of the plant, through the Lower Old Ore Storage Yard, and past the thawhouse to the secondary highway crossing (features shown on Exhibit 2-2-1; note that the Exhibit shows the relocated Wilson Ditch as described below). The potential for infiltration of process water or groundwater into the plant site portion of the ditch was first examined in 1978, and leaking joints were pressure grouted in 1984.

In 1997, the plant site portion of Wilson Ditch was relocated from its intake point at Upper Lake to the point where it crosses the secondary highway. The replaced segment consists of an underground 30" HDPE pipe located along the south and west plant boundary fence lines. The replacement segment connects with the remainder of the Wilson Ditch corridor at the secondary highway.

From the crossing at the secondary highway, the remainder of the ditch consists of an open earthen channel. In 1993, this portion of the ditch downstream of the secondary highway to the U.S. Highway 12 crossing (about 3700 feet) was remediated by removing approximately 18" of material from the bottom and 12" from the sides of the ditch.

4.3.2.1 Surface Water Flow in Wilson Ditch

Wilson Ditch flows only during the irrigation season (approximately April through September). Flow in the ditch was measured in 1984 and 1985 at site WD-2 (Figure 4-3-1), and averaged 3.5 cfs. Additional flow measurements were collected at sites WD-2, WD-3, WD-4 in May 1993, and flows ranged from 7.42 to 8.26 cfs (about 3300 to 3700 gpm). The surface water flow data are summarized in Table 4-3-<u>3</u>. Compared to the late April 1993 flow of 90.7 cfs in Prickly Pear Creek upstream of the Upper Lake diversion (PPC-3), the diversion to Wilson Ditch represents slightly less than 10% of the total creek flow during the spring. The water right to the ditch owned by the downstream Prickly Pear Simmental Ranch amounts to slightly over 5000 gpm (11 cfs). Total water rights claimed in the ditch are about 15 cfs.

Date	WD-2 flow (cfs)	WD-3 flow (cfs)	Date	WD-2 flow (cfs)	WD-3 flow (cfs)
11/5/84	Dry		7/5/85	3.2	
4/19/85	3.9		7/12/85	3.2	
4/26/85	3.5		7/19/85	3.2	
5/3/85	6.5		7/26/85	2.6	
5/8/85	5.6	3.5	8/2/85	1.3	
5/17/85	6.4		8/12/85	2.1	
5/31/85	4.8		8/15/85	1.8	
6/5/85	5.8		8/29/85	1.7	
6/14/85	2.6		9/4/85	2.4	
6/21/85	2.8		9/10/85	2.5	
7/1/85	3.6		5/11/93	7.42	
			5/14/93	7.51	8.26

 TABLE 4-3-3.
 FLOW MEASUREMENTS FOR WILSON DITCH

4.3.2.2 Wilson Ditch Water Quality

Water quality in Wilson Ditch has been measured at sites WD-1 through WD-4 (Exhibit 3-2-1 and Figure 4-3-1). Site WD-5 has no water quality data and has been used for flow monitoring only. Site WD-1 is at the head of the ditch at Upper Lake, and site WD-2 is at the secondary highway crossing where the ditch leaves the plant site. The remaining sites (WD-3 and WD-4) are located various distances downstream of the plant site. All water quality results for Wilson Ditch are in Appendix 3-1-1.

The 1990 Comprehensive RI/FS concluded that water quality in Wilson Ditch was not significantly different from water quality in Prickly Pear Creek (sites PPC-3 and PPC-4) or Upper Lake. The 1990 RI cited the following average concentrations at site WD-2: 34 mg/L sulfate, 185 mg/L TDS, 0.012 mg/L dissolved arsenic, 0.008 mg/L dissolved lead, and 0.029 mg/L dissolved zinc. Total metals concentrations were generally several times higher than dissolved metals concentrations in Wilson Ditch samples.

During remediation of the off-plant segment of the ditch between WD-2 and WD-3, the plant site portion of the ditch above the crossing at the secondary highway was dammed using a temporary earthen berm. The temporary dam, installed in spring 1993, was needed to keep the open ditch portion dry so sediments could be removed. A sample of water was collected that had accumulated behind the temporary dam and was analyzed as a field check of water quality. The results indicated a total arsenic concentration of 8 ppm. The elevated arsenic concentration was considered indicative of the continued infiltration of smelter site water into the upper (piped) portion of the ditch, even after grouting of leaking joints in 1984.

Several additional water quality samples were collected from Wilson Ditch at sites WD-2, WD-3, and WD-4 in May 1993. These data results are in Appendix 3-1-2. Dissolved arsenic concentrations ranged from 0.04 to 0.25 mg/L, and total arsenic concentrations ranged from 0.046 to 0.26 mg/L. The May 1993 sample results demonstrate the potentially wide variations in Wilson Ditch water quality, presumably due to varying degrees of plant site water infiltration to the ditch. For example, a sample collected at WD-2 on May 11, 1993 had a dissolved arsenic concentration of 0.25 mg/L, while a sample collected several days

later on May 14 had a dissolved arsenic concentration of 0.036 mg/L; the dissolved zinc concentrations from the same two samples were 0.215 mg/L and 0.05 mg/L, respectively.

Based on the potential for elevated concentrations of arsenic and metals to infiltrate from the plant site into Wilson Ditch, and to be transported downstream to other water users, the ditch relocation project was completed in 1997 as discussed above. The new ditch route from Upper Lake to the secondary highway eliminated the potential for smelter site-derived water to impact water in Wilson Ditch.

4.3.2.3 <u>Sediment Quality</u>

Wilson Ditch bottom sediments were initially sampled during the Phase I Investigation (1984 and 1985), and again during the Comprehensive RI sampling activities. All sediment quality results are in Appendix 3-1-3. In general, high concentrations of arsenic, cadmium, lead, and zinc were observed in bottom sediments from the ditch. Samples collected across 30-inch depth intervals showed that concentrations decreased rapidly with depth, with the highest concentrations present in the upper 8 inches of sediment. The maximum arsenic concentration was 2658 mg/kg at site WD-2 (4-8 inch depth), and the maximum lead concentration was 6528 mg/kg at the same site (0-4 inch depth).

Bottom sediments from WD-2 to WD-3 were removed as part of remedial actions in 1993. The excavated sediments were temporarily stockpiled in the East Field, and were subsequently consolidated with soils from the residential clean-up action as stipulated in the Wilson Ditch Work Plan (Hydrometrics, 1993). Average concentrations of metals in the stockpiled sediments were 1492 mg/kg lead, 146 mg/kg arsenic, 57 mg/kg cadmium, and 1040 mg/kg zinc. Post-excavation sampling of ditch sediments was performed to confirm that materials with elevated metals concentrations had been removed. Backfill material specifications required lead and arsenic concentrations of <200 mg/kg and <100 mg/kg, respectively (Hydrometrics, 1993).

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4.3.3 Storm Water Runoff

The Asarco East Helena Plant occupies approximately 142 acres on the south edge of the City of East Helena. Approximately 45 acres of the Plant are paved and the remainder consists of 61 acres of stockpiled slag (4 acres of which are in the Zinc Plant area), 7 acres encompassing Lower Lake, and approximately 28 acres of graveled working, storage, and drive areas. Storm water runoff from approximately 26 acres in the central plant area (21 paved, 6 unpaved) collects in the drain system of the main (central) plant water circuit (see Section 4.2) and gravity drains to Thornock Tank. From Thornock Tank, the water is pumped to the one-million gallon storage tanks. As described in Section 4.2, excess water in the main plant process water circuit is treated at the HDS facility and discharged to Lower Lake under the provisions of MPDES permit No. MT-0030147.

The 24-hour storm event runoff volumes referred to in this storm water runoff section (5year, 25-year, and 100-year) were calculated using published precipitation-frequency data (NOAA, 1983). Rainfall depths (24-hour) used for calculations were 1.7 inches for the 5year storm, 2.3 inches for the 25-year storm, and 2.8 inches for the 100-year storm. Detailed hydrologic modeling calculations for storm water runoff from the Asarco plant site are given in the Asarco East Helena Storm Water System Improvement Project Design Criteria & Conceptual Design Summary (Hydrometrics, 1996).

The Plant has three areas where there is no runoff resulting from the 100-year, 24-hour storm event. Storm water from the 14 acre Zinc Plant drainage area near the Plant's west access road flows to a topographically low area by the main plant parking and zinc plant and drains into alluvial material underlying the plant. Therefore, there is no storm water runoff from this area. Similarly, there is no runoff from the remaining 57 acres of stockpiled slag (61 acres total minus four acres by the zinc plant) because precipitation rapidly infiltrates or evaporates. Last, no runoff occurs from the seven acre Lower Lake.

Runoff from the remainder of the Plant is from the 38 acre ore storage yard, and from the 5.8 acres of access roads and parking areas outside the fenced area of the Plant (formerly Outfall No.2).

In December 1997, a storm water containment facility was completed west of the plant, (see Figure 4-3-<u>13</u>). The system is designed to collect storm water runoff that previously discharged to the Outfall No. 1 at the northwest end of the plant site. Water from the containment tank is pumped to Thornock Tank where it is introduced into the plant water circuit. The storm water control facility consists of the following components:

- A primary capture and settling tank (625,000 gallons, sized to capture the 5-year, 24hour storm) where flocculants and coagulants are passively added to settle suspended sediment;
- A secondary containment tank surrounding the primary tank sized to contain the 625,000 gallon containment tank (representing the 25-year, 24-hour storm);
- A containment system downstream of the primary and secondary containment that routes any water in excess of the 25-year, 24-hour storm and excessive runoff from former Outfall No. 2 to an impoundment against a railroad embankment, with a discharge culvert under the railroad and U.S. Highway 12. A riser on the culvert was installed to ensure no water discharges through the culvert until the 100-year, 24-hour storm is exceeded.

A field inspection by Montana Department of Environmental Quality personnel in April 1998 confirmed that the system had been installed as designed.

4.3.3.1 Storm Runoff Flow

Storm water runoff calculations in the plant Storm Water Management Plan indicate that, for the 37.8-acre drainage reporting to former Outfalls 1 and 2 west of the plant site, the 100year



24-hour storm would generate 1.6 million gallons of runoff. As noted previously, storm water runoff from the 32 acres on the northwest end of the plant site is routed to a collection system sized to contain the 25-year, 24-hour storm (1.2 million gallons).

4.3.3.2 Storm Runoff Water Quality

Complete water quality results for storm water runoff monitoring sites are in Appendix 3-1-1. The database includes samples taken prior to and during the RI study period (1985 and 1987), and samples collected under storm water discharge authorization MPDES Permit No. MTR-000072 (1993 through 1997).

Storm water quality analyses performed in 1985 and 1987 showed that total metals concentrations in runoff were much higher than dissolved metals concentrations, due to the entrainment of large quantities of suspended solids in all samples (TSS ranged from 393 to 4320 mg/L during the 1985 and 1987 events). For example, the average total arsenic concentration measured during the 1985 sampling event was 4.3 mg/L, while the average dissolved arsenic concentration was 0.52 mg/L. In 1987, average total arsenic concentration in runoff was 132 mg/L, and average total lead concentration was 554 mg/L.

Under the terms of the MPDES permit authorization for storm water discharge, water quality samples were collected in May 1993, with subsequent first flush and composite samples collected from 1994 through 1997. Table 4-3-<u>4</u> shows summary statistics for storm runoff water quality from 1994 through 1997, during the period when first flush and composite samples were collected for each monitoring event. As shown in the Table 4-3-4, total metals concentrations in runoff are typically 10 to 100 times greater than dissolved metals concentrations.

				A	verage	Concentr	ation (m	g/L)			
Sample Type		As	As	Cd	Cd	Cu	Cu	Pb	Pb	Zn	Zn
	TSS	(Dis)	(Tot)	(Dis)	(Tot)	(Dis)	(Tot)	(Dis)	(Tot)	(Dis)	(Tot)
First <u>Flush</u>	1519	0.05	2.42	0.626	6.04	0.074	8.12	0.223	26.3	0.448	14.1
Composite	645	0.04	1.53	0.557	3.19	0.073	4.95	0.162	23.2	0.872	8.78

TABLE 4-3-4. QUALITY OF STORM WATER RUNOFF (1994-1997)

The storm water containment and impoundment system installed in 1997 will contain storm water from the plant up to and including the 100-year, 24-hour storm. Collection of water quality samples from the storm water containment tank are planned in 1998 as part of a plant-wide water balance study being conducted by Asarco. Results from these samples will be used to evaluate the effectiveness of the coagulant/flocculant and settling tank at removing suspended solids and the accompanying particulate phase metals from storm water.

It should be noted that Outfall No.2 no longer requires an MPDES storm water permit since storm water is directed to a surface depression where it is impounded before reaching Prickly Pear Creek. The MPDES storm water permit must be maintained in the unlikely event that storm waters discharge under extreme events (greater than 100-yr).

4.4 GROUNDWATER

Hydrostratigraphic data, groundwater flow data, and groundwater quality data have been collected in the plant-site and surrounding area, as part of numerous investigations including:

- Phase I Hydrogeologic Investigation of the Asarco East Helena Plant (1984 through 1985);
- Phase II Remedial Investigation (1986 though 1987);
- Comprehensive RI/FS (1987 through 1990);

- Post-RI/FS Monitoring (1989 through 1997);
- Lower Lake Remedial Design (1992 through 1994);
- Lower Lake Remediation Project Monitoring (1994 through 1996); and
- Storm Water Remedial Design (1991 through 1994).

Asarco presently maintains 27 monitoring wells (wells installed for groundwater level measurement and quality sampling) in the plant site area (DH series wells), 15 monitoring wells in the East Helena area (EH series wells), 11 monitoring wells in the vicinity of the former sediment drying area (APSD series wells) and three monitoring wells south of the plant area. In addition to the monitoring wells, 11 piezometers (P series and ST series) were installed for water level measurement and aquifer testing purposes. Monitoring well and piezometer locations are shown on Exhibit 3-2-1 and a well inventory summarizing well completion data is in Table 4-4-1.

Asarco conducts semi-annual water level and water quality monitoring at various monitoring wells and surface water sites as part of their Post-RI Monitoring Program. Monitoring requirements for the Post-RI Monitoring Program were reviewed in Section 3. The primary objective of the Post-RI monitoring program is to assess effects to groundwater and surface water from Process Pond Remedial Actions implemented on the plant site.

Post-RI data collected from 1990 through 1994 were summarized in the Post-RI Well and Surface Water Monitoring Report (Hydrometrics, 1995). The Post-RI report summarizes data with a minimum of interpretation; as per direction by EPA at the time of its preparation (see responses to EPA comments in Appendix 1). Subsequent data summaries, including maps, tabulations and graphs have also been submitted to EPA in August 1996 and during several RCRA transition briefing meetings in 1997. On March 13, 1997 EPA provided comments to Asarco that discussed issues related to the Asarco East Helena Post-RI Well and Surface Water Monitoring Report (Hydrometrics, 1995). On October 15, 1997, EPA compiled a summary of the RCRA program comments to the groundwater investigations and

			TABLE 4-4-1.	MONITORIN	NG WELL AND I	PIEZOMETER I	NVENTORY			
Well Name	Location	Date Installed	Ground Surface Elevation (ft)	Measuring Point Elev. (ft)	Northing	Easting	Total Depth Drilled (ft bgs)	Total Depth Cased (ft)	Casing Size (ID) (in)	Screened Interval (ft bgs)
MONITORING W	VELLS									
APSD-1	Lower Lake	8/20/91	3917.75	3918.16	9716.54	8719.30	11.75	11.75	2"	1.75-11.75
APSD-2	Lower Lake	8/20/1991	3918.44	3919.80	9633.03	8665.22	18	18	2"	8-18
APSD-3	Lower Lake	8/21/1991	3918.50	3919.21	9549.27	8644.32	12.5	12.5	2"	2.5-12.5
APSD-4	Lower Lake	8/21/91	3920.65	3921.95	9476.20	8550.21	14	14	2"	4-14
APSD-7	Lower Lake	10/12/1993	3919.00	3920.58	9809.69	9547.31	16	16	2"	8.5-16
APSD-8	Lower Lake	10/13/1993	3919.18	3920.52	9563.36	9579.65	15	15	2"	5-15
APSD-9	Lower Lake	10/13/1993	3922.17	3923.62	9371.12	9062.25	16	16	2"	6-16
APSD-10	Lower Lake	10/13/1993	3921.60	3923.14	9418.76	8712.87	16	16	2"	6-16
APSD-11	Lower Lake	10/14/1993	3921.37	3923.36	9501.90	9287.47	16	16	2"	6-16
APSD-12	Lower Lake	10/14/1993	3919.27	3920.78	9654.90	8950.59	16	15.5	2"	5.5-15.5
APSD-13	Lower Lake	10/15/1993	3921.23	3923.95	9647.25	8332.04	23	23	2"	13-23
APSD-14	Lower Lake	10/15/1993	3917.6	removed durin	g soil excavation		16	16	2"	6-16
DH-1	S of Smelter	12/8/84	3905.99	3907.77	11555.37	7175.93	50	50	4"	40-50
DH-2	SW of Smelter	12/9/84	3933.68	3935.31	10275.19	6738.32	65.5	65.5	4"	55.5-65.5
DH-3	Smelter	12/10/84	3944.68	3946.05	8426.67	8269.54	55	54	4"	44-54
DH-4	Smelter	12/14/84	3913.74	3914.42	10002.09	9438.54	23.6	23	4"	17-23
DH-5	Smelter	1/7/85	3917.42	3917.98	10099.25	9009.34	17	17	4"	9-17
DH-6	Smelter	12/13/84	3886.68	3886.37	11962.20	8390.30	25	25	4"	15-25
DH-7	Smelter	12/12/84	3893.91	3895.74	11772.67	9728.56	28.5	28.5	4"	18.5-28.5
DH-8	Smelter	1/5/85	3912.75	3913.39	11092.94	7578.44	50	49	4"	39-49
DH-9	Smelter	1/4/85	3894.15	3893.29	11010.94	8548.58	17	11.5	4"	6.5-11.5
DH-10	Smelter	12/11/84	3882.49	3883.28	11906.85	8749.24	10	10	4"	5-10
DH-11	Smelter	1/5/85	3908.19	3910.31	10439.08	9780.63	29	29	4"	19-29
DH-12	Smelter	11/3/86	3907.67	3906.60	10965.42	7983.65	30	30	4"	0-20
DH-13	Smelter	11/3/86	3907.66	3907.43	10977.71	7973.69	45	45	4"	35-45
DH-14	Smelter	10/22/86	3912.92	3912.81	10003.66	9446.34	46	46	4"	34-46
DH-15	Smelter	11/1/86	3885.9	3886.96	11977.03	8393.90	50	50	4"	41.5-50
DH-16	Smelter	11/20/86	3902.28	3901.35	11407.22	7829.09	30	28	4"	23-28
DH-17	Smelter	11/25/86	3902.04	3902.27	11407.22	7838.90	41	41	4"	31-41
DH-18	Smelter	12/2/86	3907.72	3907.33	10952.88	7994.13	68	63.5	4"	55.5-63.5
DH-19	Smelter	4/22/87	3916.44	3915.85	9889.92	8307.84	30	30	4"	20-30
DH-20	Smelter	4/22/87	3926.74	3927.50	9419.48	8372.15	31	30	4"	20-30
DH-20	Smelter	4/23/87	3920.74	3927.50	10711.47	8187.00	30	29	4"	19-29
DH-22	Smelter	4/23/87	3903.33	3921.79	10105.98	8030.91	35	34	4"	24-34
DH-22 DH-23	Smelter	4/28/87	3922.28	3921.79	10704.29	8407.90	20	20	4"	10-20
DH-23 DH-24	Smelter	4/28/87	3897.33	3897.47	11813.79	7586.54	35	35	4"	27-35
DH-24 DH-26		4/30/87	3071.33	abandoned	11013./7	1300.34	35	35	4"	25-35
DH-26 DH-27	Smelter		3909.22	3908.81	10350.61	8251.30	35	35 29	4"	19-29
DH-27 DH-28		5/1/87	3909.22	3908.81					4"	26-36
	Smelter	12/14/87			10666.08	8105.12	36	36		
DH-29	Smelter Fast Halana	12/11/87	3918.64	3918.79	9658.38	8554.64	17	17	4"	7-17
EH-50	East Helena	11/6/86	3885.36	3885.83	12571.59	6927.62	45	45	4"	25-45
EH-51	East Helena	10/24/86	3875.50	3876.56	12604.66	7938.30	30	30	4"	10-30
EH-52	East Helena	11/7/86	3877.36	3877.35	12648.14	8861.76	13	13	4"	5-13
EH-53	East Helena	11/11/86	3868.23	3869.31	13737.44	6327.66	35	35	4"	25-35
EH-54	East Helena	11/20/86	3866.66	3866.57	13762.18	7882.82	18	18	4"	8-18

			TABLE 4-4-1.	MONITORIN	G WELL AND	PIEZOMETER	INVENTORY			
Well Name	Location	Date Installed	Ground Surface Elevation (ft)	Measuring Point Elev. (ft)	Northing	Easting	Total Depth Drilled (ft bgs)	Total Depth Cased (ft)	Casing Size (ID) (in)	Screened Interval (ft bgs)
EH-57A	East Helena	11/23/87	3881.19	3881.79	12952.72	5823.60	45	45	4"	35-45
EH-58	East Helena	11/23/87	3883.16	3884.46	12474.91	9671.54	35	31	4"	21-31
EH-59	East Helena	5/6/87	3873.67	3873.24	13233.30	9108.96	18	18	4"	8-18
EH-60	East Helena	12/1/87	3885.24	3884.86	12488.82	7409.79	29	29	4"	22-28
EH-61	East Helena	11/30/87	3885.80	3886.22	12490.70	7396.00	45	45	4"	36-45
EH-62	East Helena	11/20/87	3867.32	3871.59	13746.86	6872.50	46.5	46.5	4"	25-45
EH-100	East Helena	11/5/1986	3885.52	3886.25	12572.46	6910.53	60	60	4"	52-60
EH-101	East Helena	11/5/1987	3875.70	3876.81	12603.17	7951.39	45	45	4"	34-45
EH-102	East Helena	11/7/86	3877.50	3877.04	12630.31	8861.50	35	35	4"	25-35
MW-1	CAMU	6/26/97	3948.00	3949.65	9145.74	7019.35	68	68'	2"	58-68
MW-2	CAMU	6/27/1997	3940.76	3942.52	9564.62	6981.24	66	66'	2"	56.0-66.0
MW-3	CAMU	6/30/1997	3936.04	3937.55	9585.79	7367.42	50	48'	2"	38.5-48.0
PIEZOMETERS										
P-1	Smelter	12/7/87	3907(est)	na	na	na	45	45	2"	35-45
P-2	Smelter	12/4/87	3907(est)	na	na	na	45	45	2"	35-45
P-3	Smelter	12/3/87	3902(est)	na	na	na	41	41	2"	31-41
P-4	Smelter	12/3/87	3902(est)	na	na	na	41	41	2"	31-41
P-5	East Helena	11/16/87	3877.14	na	na	na	13	13	2"	5-13
P-6	East Helena	11/20/87	3875.90	na	na	na	30	30	2"	10-30
P-8	East Helena	12/15/87	3877.14	na	na	na	21	21	2"	14-21
P-9	East Helena	12/16/87	3876(est)	na	na	na	33	33	2"	30-33
ST-3	Smelter	8/16/91	3910(est)	na	na	na	27	27	2"	17-27
ST-4	Smelter	8/16/91	3910(est)	na	na	na	30	30	2"	20-30
ST-5	Smelter	8/19/91	3900(est)	na	na	na	27	27	2"	17-27

restated comments on the Post-RI Well and Surface Water Monitoring Report that were previously provided by EPA. These comments addressed:

- Conclusions and recommendations from the RCRA program's review of groundwater data,
- The RCRA program evaluation of May 1997 organic sampling results of monitoring wells DH-27 and DH-28, and
- Comments on the Post-Remedial Investigation (RI) Well and Surface Water Monitoring Report (Hydrometrics 1995).

In October 1997, Asarco elected to respond to these comments in the CC/RA Report. Responses to these comments are in Appendix 4-1-1. These responses include crossreferences to specific sections of the CC/RA where information is presented and which updates the Post-RI report, as well as additional information requests by EPA.

This CC/RA report provides a summary of information on hydrostratigraphic units, aquifer characteristics and groundwater flow conditions in the plant site area based on these previous investigations and a discussion of current water level and water quality conditions based on recent monitoring data.

4.4.1 Hydrostratigraphic Units

As described in the Comprehensive RI (Hydrometrics, 1990a), hydrostratigraphic units in the East Helena area are based on data from soil core drill holes and monitoring wells. These data are augmented by driller's logs of private wells, and from existing hydrological and geological literature.

Six hydrostratigraphic units have been defined in the plant site and surrounding area for purposes of characterizing groundwater flow conditions. From shallowest to deepest, they are as follows:

- A perched groundwater system is found in surficial slag/fill deposits on portions of the plant site where the slag and fill are underlain by relatively low permeability marsh deposits.
- An unconfined or partially confined shallow groundwater system is present in the Quaternary/Tertiary alluvium present beneath the plant site and in downgradient areas.
- Where the Quaternary/Tertiary alluvium become thicker at the north end of the Plant Site and in East Helena there is also an intermediate groundwater system.
- Tertiary volcanic ash/clay forms a laterally extensive confining unit that underlies the shallow and intermediate alluvial units.
- Deeper Tertiary alluvium underlies the volcanic ash/clay unit.
- Precambrian metasedimentary bedrock underlies the Tertiary deposits at depth.

Figure 2-2-1, in Section 2 of this report shows the surficial geology of the East Helena area. Fill, alluvium and Tertiary volcanic ash units are all exposed at the surface in the plant site area. Exhibits 4-4-1 and 4-4-2 are geologic cross-sections of the stratigraphy in the East Helena area.

The marsh deposits composed of organic clay and silt overlie the coarse-grained Quaternary alluvium on portions of the plant site. The marsh deposits are found in the vicinity of Upper and Lower Lakes but have also been encountered at monitoring wells in the Plant site area north of Lower Lake sites (DH-4, DH-9 and DH-23). In these areas, fine-grained organic clays and silts have been covered by slag (a siliceous smelting by-product) and other fill from Plant operations, including cobbles, gravel, silt, clay, and debris. Geological cross sections (Exhibit 4-4-2, cross sections D-D', and F-F') show up to 15 feet of organic fine-grained sediments beneath Lower Lake. These sediments generally are soft, have a low density and resemble peat. Old photographs (circa 1920) and early plant blueprints also show Quaternary flood-plain deposits from Prickly Pear Creek underlying the slag piles (Hydrometrics, 1990a).

The water levels in monitoring wells DH-5 and DH-23 (see cross sections F-F' on Exhibit 4-4-2) show that the slag is partially saturated in locations that are underlain by the organic, fine-grained marsh deposits. These deposits inhibit downward percolation. The RI noted that DH-23 water levels are anomalously high and attributed this to perched conditions on the organic silt and clay layer. This conclusion was supported by saturated conditions above the clay layer during drilling of DH-9, prior to advancing the hole through the two foot clay layer. Once the drill hole was advanced through the clay, measured water levels were six to seven feet deeper. The approximate extent of the area where perched groundwater conditions may be present is shown on the cross sections and site maps on Exhibits 4-4-1 and 4-4-2.

Groundwater is present in the shallow alluvium under most portions of the plant site and this shallow alluvial unit is the primary receptor for plant site infiltration. Subsurface information collected during the RI and the Post-RI drilling efforts show the alluvial unit consists of varying mixtures of cobbles, gravel, sand, silt, and clay which are present in complex layers and lenses. The coarser grained materials (cobbles, gravel, and sand) provide a good medium for groundwater movement.

The shallow alluvium is the thinnest at the southern end of the plant site and along the western plant boundary where the underlying Tertiary ash unit rises close to the ground surface. The alluvium ranges in thickness from less than 30 feet along the southern and western plant site boundaries to over 60 feet in the East Helena area (Exhibits 4-1-1 and 4-1-2, Cross Sections A-A' & E-E'). The actual saturated thickness of the alluvium is typically 10 feet or less in the plant site area and 20 to 30 feet in the East Helena area. Where the alluvium thickens to the north and east, it forms shallow and intermediate groundwater systems separated by thin (2 to 9 feet) clay and silt lenses. These fine-grained layers are generally discontinuous (Exhibits 4-4-1 and 4-4-2).

The Tertiary volcanic ash unit consists of yellow-white to light gray, compact, siliceous ash/tuff. Samples from this unit consist of 90 percent siliceous ash. The unit commonly h:\files\007 asarco\0867\ccra report\r99cra1.doc\HLN\2/2/07\065\0096 2/2/07/7:59 AM

contains clasts of angular basalt, ranging in size from sand to cobbles. Based on drilling conducted during the RI, the ash unit is partially to totally altered to clay in the City of East Helena.

Where borings fully penetrate the ash unit, it is typically 25 feet or more in thickness. The ash unit lies at depths as shallow as 24 feet beneath the ground surface in the plant site area and as deep as 68 feet in off-plant areas in the City of East Helena. Figure 4-4-1 is a contour map showing the depth to top of the ash unit beneath the plant site. The ash unit generally dips to the northeast, with an apparent ridge underlying the Lower Ore Storage Area within the plant site. Where the shallow water table encounters this ash ridge on the western boundary of the plant site, the unconsolidated sediments overlying the ash unit are above the water table and unsaturated. No shallow groundwater is found in this area (as indicated on Exhibit 4-4-1 and 4-4-2).

The ash unit forms a confining unit that is typically underlain at depth by deeper alluvial gravel. However, there are very limited data with which to describe the extent and characteristics of this deeper alluvial unit. Where it has been encountered to the north of the plant site, it is typically at depths of 70 to 90 feet.

Driller's logs for several water supply wells indicate that bedrock has also been encountered locally beneath the Tertiary Ash unit. Four industrial water supply wells owned by American Chemet (AMCHEMET 1 through AMCHEMET 4), and a water supply well owned by Asarco are completed in the deeper bedrock strata that underlies the Tertiary ash and alluvium. The Asarco water supply well was plugged with bentonite and abandoned as part of the RI/FS investigation activities in 1987 (Hydrometrics, 1987). The drilling logs from these bedrock wells indicate they are completed in fractured shale bedrock. Although the drilling logs are not sufficiently detailed to clearly distinguish various sediments, the RI surmised



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these deep units may be Precambrian meta-sedimentary rock of the Belt Supergroup (Hydrometrics, 1990a).

Most private wells in the East Helena area are completed in the intermediate or deep aquifers underlying one or more discontinuous clay layers of Quaternary or Tertiary age. These private wells generally range in depth from 34 to 80 feet. One 160 foot deep well in East Helena (Jensen, see Exhibit 4-4-1, Cross Section A-A') is completed in bedrock underlying the ash unit and other Tertiary alluvial sediments. Three private wells located west of the plant (D. Hulst, K. Hulst and L Hulst) are also completed in bedrock aquifers (see well logs in Appendix 4-4-1). The ash unit, which underlies much of the plant site and the City of East Helena, is exposed at the ground surface near the three Hulst wells.

4.4.2 Hydrologic Characteristics

4.4.2.1 Aquifer Permeability

Forty-five monitoring wells in and around the plant site have been aquifer tested as part of the RI/FS (Hydrometrics, 1990a) and Lower Lake Remedial Design (Hydrometrics, 1994b). The results of individual tests are shown in Table 4-4-2 and summarized by area and unit in Table 4-4-3. The hydraulic conductivity (K) results for the shallow alluvium range from 1 ft/day to 702 ft/day reflecting the heterogeneous composition of the alluvium. While the permeability of the alluvium is highly variable, there is a general trend of increasing permeability from upgradient (south of the plant site) to downgradient (north of the plant site) (see Table 4-4-3). With the exception of results from EH-100, the intermediate alluvium generally shows lower hydraulic conductivities than the shallow system. No data are available for the deeper alluvium.

The hydraulic conductivity values derived from the slug test and pumping tests should be considered high-end estimates since many of the wells displayed evidence of lower permeability boundary conditions during testing. This reflects the heterogeneous stratigraphy

Monitoring Well	Hydrostratigraphic Unit/ Location	Transmissivity	Hydraulic C	Conductivity
weil	Hydrostratigraphic offic Location	(ft2/day)	(ft/day)	(cm/sec)
DH-1	Shallow - Upgradient	40	4	1.42E-03
DH-2	Shallow - Upgradient	43	1	5.19E-04
DH-3	Shallow - Upgradient	6	5	1.84E-03
DH-4	Shallow - Upper Plant Site	1077	180	6.34E-02
DH-5	Shallow - Upper Plant Site	788	79	2.78E-02
DH-6	Shallow - Lower Plant Site	6972	702	2.48E-01
DH-7	Shallow - NE of Plant Site	2286	227	8.02E-02
DH-8	Shallow - Central Plant Site	2440	244	8.61E-02
DH-10	Shallow - Lower Plant Site	293	67	2.36E-02
DH-11	Shallow - East of Plant Site	1805	180	6.37E-02
DH-13	Shallow - Central Plant Site	1421	142	5.02E-02
DH-14	Intermediate - Upper Plant Site	99	8	2.83E-03
DH-15	Intermediate - Lower Plant Site	76	9	3.16E-03
DH-17	Shallow - Lower Plant Site	2521	253	8.92E-02
DH-19	Shallow - Upper Plant Site	406	41	1.44E-02
DH-20	Shallow - Upgradient	1318	264	9.30E-02
DH-21	Shallow - Central Plant Site	159	18	6.23E-03
DH-22	Shallow - Central Plant Site	464	58	2.05E-02
DH-24	Shallow - Lower Plant Site	1509	269	9.48E-02
DH-26	Shallow - Central Plant Site	854	100	3.54E-02
DH-27	Shallow - Central Plant Site	566	56	1.98E-02
DH-28	Shallow - Central Plant Site	747	106	3.75E-02
DH-29	Shallow - Upper Plant Site	561	67	2.36E-02
EH-50	Shallow - Downgradient	174	10	3.63E-03
EH-51	Shallow - Downgradient	2888	289	1.02E-01
EH-52	Shallow - Downgradient	1108	222	7.83E-02
EH-53	Shallow - Downgradient	92	13	4.72E-03
EH-54	Shallow - Downgradient	35	5	1.65E-03
EH-57A	Shallow - Downgradient	3433	381	1.34E-01
EH-58	Shallow - Downgradient	463	46	1.63E-02
EH-59	Shallow - Downgradient	160	16	5.66E-03
EH-60	Shallow - Downgradient	1988	374	1.32E-01
EH-61	Shallow - Downgradient	605	60	2.12E-02
EH-62	Shallow - Downgradient	9809	511	1.80E-01
EH-100	Intermediate - Downgradient	1013	127	4.48E-02
EH-101	Intermediate - Downgradient	182	18	6.42E-03
EH-102	Intermediate - Downgradient	1215	122	4.29E-02
APSD-1	Shallow - Upper Plant Site	156	16	5.50E-03
APSD-2	Shallow - Upper Plant Site	37	4	1.29E-03
APSD-7	Shallow - Upper Plant Site	363	36	1.28E-02
APSD-9	Shallow - Upper Plant Site	530	53	1.87E-02
APSD-10	Shallow - Upper Plant Site	377	38	1.33E-02
APSD-11	Shallow - Upper Plant Site	278	28	9.79E-03
APSD-12	Shallow - Upper Plant Site	354	35	1.25E-02
P-1	Shallow - Central Plant Site	3592	359	1.27E-01
P-2	Shallow - Central Plant Site	2379	238	8.39E-02
P-3	Shallow - Lower Plant Site	3042	304	1.07E-01
P-4	Shallow - Lower Plant Site	2883	288	1.02E-01
P-6	Shallow - Down Gradient	2445	245	8.63E-02

TABLE 4-4-2 SUMMARY OF AQUIFER TEST RESULTS

Source: P, DH & EH series wells - Comprehensive RI/FS (Hydrometrics, 1990a) APSD series - Lower Lake 90% Design Report (Hydrometrics, 1994b)

Location	No. Sites Tested	H	Iydraulic Conc (ft/day)	•
		Min	Max	Mean
Perched Aquifer	1			Inconclusive*
TOTAL	1			
Shallow Groundwater				
Upgradient	3	1	5	4
Upper Plant Site	12	4	264	70
Central Plant Site	7	18	244	152
Lower Plant Site	5	67	702	323
E. Helena	12	13	511	181
(downgradient)				
TOTAL	39			
Intermediate				
Upper Plant Site	1			8
Lower Plant Site	1			9
E. Helena (downgradient)	3	18	127	89
TOTAL	5			
Deep Alluvium	No Data			
Deep Bedrock	No Data			

TABLE 4-4-3. SUMMARY OF HYDRAULIC CONDUCTIVITY DATA BY AREA

* A pumping test at DH-23 (completed in perched water within the slag) produced no measurable drawdown at a discharge rate of 85 gpm.

encountered throughout the site. Finer grained materials with relatively low permeability are present in most areas and potentially effect the bulk permeability characteristics of the aquifer. Under these conditions, average hydraulic conductivity values calculated from short-term pumping tests and slug tests are likely to overestimate the bulk permeability of the aquifer.

4.4.2.2 Depth to Groundwater

Shallow groundwater is present in the alluvial aquifer beneath most of the plant site with the exception of the ore storage area on the western edge of the site where the fine-grained Tertiary ash unit rises close to the surface and the overlying alluvium is unsaturated. Depth to water in the shallow alluvium beneath the remainder of the plant site and in the downgradient East Helena area ranges from 6 to 60 feet. Depth to groundwater is shallowest near Upper Lake, Lower Lake and Prickly Pear Creek. The depth to groundwater generally increases to the north.

Seasonal fluctuations in groundwater levels range from several tenths of a foot up to several feet. The smallest seasonal water table fluctuations are observed near Lower Lake and the largest in downgradient wells northwest of the site. Fluctuations in groundwater levels tend to mirror fluctuations in Prickly Pear Creek. Groundwater levels generally begin rising in May in response to spring runoff and gradually increase over the next few months. There is a progressive decline in groundwater levels from September through April, however, water level trends often vary considerably in response to increases in streamflow in Prickly Pear Creek.

A graph of water levels from representative monitoring well sites is shown in Figure 4-4-2. Hydrographs for all of the monitoring wells are included with the water quality trend graphs in Appendix 4-3-1. Two notable increases are evident in the graphs. First, water levels at many of the monitoring wells show a gradual increase from 1990 to 1993. The timing of this increase corresponds to the period when Asarco was attempting to eliminate groundwater gains to their plant water system. However, the increase in 1992 is also evident in upgradient DH-2 and to a lesser extent in upgradient monitoring well DH-3 (see DH-3 hydrograph in Appendix 4-3-1), suggesting this is a regional rather than plant site water level trend. A second more pronounced increase is evident in the fall of 1997. Again, this trend is evident in all of the wells, though it is most pronounced in the plant site area. As noted in the



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February 1998 Plant Water Investigation Report (Hydrometrics, 1998), water levels have subsequently declined in 1998.

Groundwater Flow Directions

Regional groundwater flow in the East Helena area is northward toward Lake Helena. Potentiometric maps (Figure 4-4-3) for the shallow groundwater system of the site illustrate seasonal groundwater trends. Both maps show a general direction of groundwater flow to the north and northwest. The spring potentiometric map, however, shows more variability in the area downgradient of the plant site reflecting the influence of Prickly Pear Creek on the shallow water table. Water levels in Prickly Pear Creek are higher than adjacent groundwater levels below the plant site, resulting in surface water recharge to the shallow groundwater system. Consequently, the potentiometric surface is higher and less prone to seasonal fluctuations in the vicinity of Prickly Pear Creek. Water levels to the west of Prickly Pear Creek in the East Helena area tend to show greater seasonal decline resulting in an increased northwesterly flow component in the early spring when the water table is lowest.

Local variations in groundwater flow direction are also evident near Lower Lake based on 1993 and 1995 water level data (data collected as part of Remedial Design and Remediation Monitoring for Lower Lake). A review of data collected as part of the Lower Lake remedial action monitoring (1993 and 1995) shows a general pattern of groundwater flow from Upper Lake to Lower Lake. The potentiometric surface shows a multi-directional flow pattern from Upper Lake; eastward to Prickly Pear Creek, northward toward East Helena, and westward from Lower Lake (see Figures 4-4-4 and 4-4-5). Based on water levels in Lower Lake and adjacent monitoring wells, the potentiometric surface shows a pattern of steep gradients immediately to the north and east of Lower Lake toward Prickly Pear Creek. As noted in Sections 4.2 and 4.3, surface water quality data indicate a component of flow from Lower Lake to Prickly Pear Creek.





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The potentiometric pattern to the west of Lower Lake is complicated and indicates a corridor of groundwater flow to the northwest with steeper gradients from both Upper Lake and Lower Lake. The 1995 potentiometric surface (Figure 4-4-5) suggests a flow depression in the area underlying the acid plant sediment storage area near Lower Lake. This is the same general area in which the Lower Lake sediments were dewatered after dredging from the pond (see Section 4.2). A similar flow pattern was noted in the discussion of 1993 potentiometric data (Figure 4-4-4) in the 90% Report for the Lower Lake Remediation Project (Hydrometrics 1994b). However, the water levels for wells DH-29 and ASPD-2 were about 3 feet lower in 1995, resulting in an even steeper flow gradient from Upper Lake and Lower Lake toward this area. A review of the groundwater level trend data (Appendix 4-3-1) shows that wells DH-29 and ASPD-2 showed a temporary drop in water level in 1995. Since 1995, water levels have returned (risen 3 feet) to their approximate previous level. The cause of the temporary water level decline in these wells is not known, but corresponds in time with the period of sediment dewatering of Lower Lake sediments. The effects of plant activities and remedial actions on groundwater conditions is discussed further in Section 5.0.

The 1990 Comprehensive RI/FS reported a regional hydraulic gradient in the East Helena area of 0.0162 (about 85 feet/mile) to the north and northwest. The hydraulic gradient was steeper in the plant site area, and decreased downgradient in the East Helena area. The 1997 potentiometric data in Figure 4-4-3 show similar trends to those in the RI. Hydraulic gradients range from 0.025 to 0.01 with the steepest hydraulic gradients at the south end of the plant site and the lowest gradients downgradient in the East Helena area. The average hydraulic gradient across the plant site is 0.0176 and there is little change seasonally in the site-wide gradient.

<u>Vertical hydraulic gradients are generally downward between the shallow and intermediate</u> alluvium and upward across the ash unit that separates the deep groundwater system from the overlying alluvium. Water level differences at paired monitoring well sites are summarized in Table 4-4-4.

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TABLE 4-4-. SUMMARY OF HEAD CHANGE AND VERTICAL HYDRAULIC GRADIENTS OBSERVED AT MONITORING WELL PAIRS

Average Difference in Observed Head Direction of (feet) Hydraulic Gradient	-0.38 Downward	-0.10 Downward	1.09 Upward	-1.17 Downward	-0.34 Downward	-0.18 Downward	-1.54 Downward
Ave Ave	shallow to intermediate	shallow to intermediate	intermediate to deep	shallow to intermediate	shallow to intermediate	shallow to intermediate	shallow to intermediate
LOCATION	Lower Lake	Central Plant Site	Central Plant Site	N. Plant Site Boundary	East Helena	East Helena	East Helena
WELL PAIRS	DH-4 to DH-14	DH-12 to DH-13	DH-13 to DH-18	DH-6 to DH-15	EH-50 to EH-100	EH-51 to EH-101	EH-52 to EH-102

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Observed head changes between paired wells in the shallow and intermediate alluvium range from several tenths of a foot up to 1.5 feet. While the hydraulic gradients indicate a potential for vertical flow within the upper and intermediate alluvial groundwater systems, intervening fine grained sediments are present in many areas which restrict flow. Aquifer tests conducted during RI/FS investigation showed varying degrees of vertical interconnection between the shallow and intermediate alluvial groundwater systems.

An upward hydraulic gradient is evident at DH-18 where deeper groundwater levels are typically a foot or more above water levels in adjacent shallower wells (MW-12 and MW-13). The presence of an upward gradient and a laterally continuous confining layer of volcanic ash prevent downward migration of groundwater from the overlying alluvial groundwater system.

Groundwater Velocity and Flux

Groundwater velocity and flux estimates were presented for the east and west portions of the plant site in the Comprehensive RI (Hydrometrics, 1990a). These estimates were calculated based on average aquifer permeabilities and hydraulic gradients. However, the discussion in the RI qualifies the results, pointing out the limitations of using average characteristics in a heterogeneous aquifer. Calculated groundwater velocities were 6.5 ft/day on the east half of the site and 11 ft/day to 17 ft/day on the west half of the site. Groundwater flux was estimated at 70 gpm on the east half of the site and approximately 200 gpm on the west half of the site.

4.4.3 Groundwater Quality

Groundwater quality upgradient of the plant site, within the plant site boundaries, and downgradient of the plant site has been monitored since 1985 with a network of monitoring wells completed in the shallow, intermediate, and deep aquifers. Forty-three monitoring wells (DH and EH series wells) were drilled and sampled prior to and during the RI/FS study (Hydrometrics, 1990a) (1985-1988). Twelve additional wells (APSD series) were

subsequently installed as part of the acid plant sediment drying area investigation. In addition to these monitoring wells, various private wells have been included in the groundwater monitoring program. All groundwater monitoring locations are shown on Exhibit 3-2-1. Monitoring well construction details are in were previously shown in Table 4-4-1, and a historic summary of the sampling frequency and parameters measured during various phases of monitoring at the East Helena plant site is in Section 3.2 (Tables 3-2-1 and 3-2-2).

This evaluation of groundwater quality addresses:

- Inorganic parameters measured in:
 - Upgradient groundwater
 - On-plant groundwater which is discussed for the
 - East portion of the plant
 - West portion of the plant
 - Downgradient groundwater (the community of East Helena, including a number of private wells)
- Organic parameters detected in groundwater on the plant and downgradient of the plant.

Since inorganic constituents (particularly arsenic) are of greatest concern for the plant site and downgradient areas, this groundwater quality evaluation focuses on inorganic parameter concentrations, trends, and interrelationships. A brief review of groundwater organic parameter results follows the evaluation of inorganics, including a discussion of the effect of low concentrations of organic constituents on the mobility and transport of arsenic and metals. Chemical fate and transport are further discussed in Section 4.5.

Groundwater quality trends and interrelationships were evaluated using temporal/ concentration plots, statistical analyses, plume concentration maps, and analysis of interparametric relationships. Detailed discussion and interpretation of groundwater quality relative to source areas, source area remediation, and potential downgradient transport of contaminants are in Sections 4.5 and 5.5.

4.4.3.1 Inorganic Constituents

In general, groundwater analytical parameters have included a suite of inorganics (common constituents, major anions, and dissolved trace constituents). Arsenic speciation analyses (differentiation of arsenic (III) and arsenic (V)) also have been performed during the RI/FS and post-RI/FS groundwater sampling periods. Analytical results for all groundwater samples are included in the sample database in Appendix 3-1-1, and complete summary statistics for all monitoring wells are in Appendix 4-3-2. Plots of concentration changes over time for the following parameters are in Appendix 4-3-1:

- Dissolved arsenic and arsenic speciation;
- Sulfate;
- pH;
- Dissolved oxygen;
- Groundwater elevation;
- Total dissolved solids;
- Chloride;
- Dissolved iron and manganese; and
- Dissolved cadmium, lead, copper, and zinc.

Interparametric scatter plots and correlation coefficient tables are in Appendix 4-4-2. The correlation matrix scatter plots and correlation tables are prepared to help evaluate potential relationships between chemistry parameters. The scatterplots show each of the parameters as a function of other parameters, along with a histogram of the data to give a general representation of the data distribution. Each of the individual scatterplots also shows a linear best-fit regression line through the data; however, this is not meant to imply that linear relationships exist between all or any of the pairs of parameters. The scatterplot matrices are

intended to be used with the corresponding correlation tables to identify anywhere one parameter covaries with another (for example, whether or not dissolved arsenic concentrations systematically increase or decrease as pH increases). The correlation tables show calculated linear correlation coefficients for the parameters shown on the scatter plots. For the purposes of this evaluation, correlation coefficients (r values) of 0.7 or higher are considered good indicators of interparametric relationships.

Upgradient Wells

Two shallow aquifer monitoring wells located south of the plant site (DH-2 and DH-3) were installed to characterize upgradient groundwater conditions. Groundwater flow in the vicinity of the plant site is to the north or northwest; therefore, groundwater from wells DH-2 and DH-3 are not influenced by plant site activities.

Groundwater from these wells are very hard, alkaline, calcium-bicarbonate types with low concentrations of TDS, arsenic and metals. Table 4-4-<u>5</u> shows upgradient well summary statistics for selected parameters (dissolved oxygen, pH, sulfate, chloride, arsenic (III), arsenic (V), and dissolved arsenic, cadmium, copper, lead, and zinc). Key constituents of concern were selected for presentation in summary tables; as mentioned previously, complete statistics are included in Appendix 4-3-2. As shown in Table 4-4-<u>5</u>, average dissolved arsenic concentrations upgradient of the plant site are low (0.009 mg/L at DH-2 and 0.014 mg/L at DH-3). Concentrations of metals, sulfate, and chloride are also low in upgradient wells.

Arsenic speciation results for upgradient wells may not be representative because of the low concentrations of arsenic present in upgradient groundwater. As described in Section 3.0, the speciation method employed by the analytical laboratory results in dilution of the sample by a 1:1 ratio, and an accompanying twofold increase in the detection limit. For samples with low dissolved arsenic concentrations (near the detection limit), speciation results are probably not meaningful.

	Site	
Data	DH-2	DH-3
DO (Average)	5.13	4.60
DO (Minimum)	3.5	2.7
DO (Maximum)	6.04	7.5
pH (Average)	7.22	7.00
pH (Minimum)	5.62	6.02
pH (Maximum)	8.55	8.23
SO4 (Average)	56	70
SO4 (Minimum)	37	52
SO4 (Maximum)	71	81
Cl (Average)	17	11
Cl (Minimum)	6.6	7.2
Cl (Maximum)	25	13
As (Average)	0.009	0.014
As (Minimum)	0.005	0.006
As (Maximum)	0.018	0.06
As+3 (Average)	0.038	0.020
As+3 (Minimum)	0.001	0.004
As+3 (Maximum)	0.56	0.16
As+5 (Average)	0.018	0.022
As+5 (Minimum)	0.004	0.005
As+5 (Maximum)	0.073	0.1
Cd (Average)	0.0014	0.0013
Cd (Minimum)	0.001	0.001
Cd (Maximum)	0.005	0.005
Cu (Average)	0.006	0.006
Cu (Minimum)	0.004	0.004
Cu (Maximum)	0.008	0.008
b (Average)	0.006	0.006
Pb (Minimum)	0.005	0.005
b (Maximum)	0.02	0.02
Zn (Average)	0.028	0.024
Zn (Minimum)	0.006	0.006
Zn (Maximum)	0.138	0.18

Table 4-4-5. Upgradient Well Summary Statistics

NOTE:

Metals and arsenic concentrations are dissolved.

Below detect values replaced with the detection limit for calculations.

Values are in mg/L except for pH (standard units).

Discrepancies between dissolved arsenic and arsenic speciation concentrations likely due to laboratory contamination and/or the inherent low accuracy of speciation results at low arsenic concentrations (see report text for discussion).

Interparametric correlations (Appendix 4-4-2) showed no values higher than 0.5, and that no strong correlations exist between parameters in upgradient groundwater. No notable trends in upgradient groundwater quality have occurred over the period of record.

Plant Site Wells

Monitoring wells on the Asarco East Helena plant site have been classified in two groups for the purposes of discussing groundwater quality: wells located in the western portion of the plant site, and those located in the eastern portion of the plant site. Table 4-4- $\frac{6}{6}$ lists the plant site monitoring wells by category.

TABLE 4-4-6. ASARCO EAST HELENA EAST AND WEST PLANT SITE WELLS

East Plant	Site Wells			
APSD-1	APSD-7	APSD-11	DH-6	DH-11
APSD-2	APSD-8	APSD-12	DH-7	DH-14*
APSD-3	APSD-9	DH-4	DH-9	DH-15*
APSD-4	APSD-10	DH-5	DH-10	
West Plant	Site Wells			
APSD-13	DH-12	DH-18**	DH-23	DH-28
APSD-14	DH-13	DH-19	DH-24	DH-29
DH-1	DH-16	DH-21	DH-26	
DH-8	DH-17	DH-22	DH-27	

NOTE: * = intermediate aquifer well ** = deep aquifer well Remaining wells are shallow aquifer wells.

Separation of monitoring wells into east and west plant site was based on geographic, groundwater flowpath (see potentiometric maps; Figure 4-4-3), water quality, and consideration of known or anticipated sources of arsenic and metals to groundwater. In general east plant site wells are located on a northward flow path from the berm between Upper and Lower Lakes, underneath the slag pile, to the region where Prickly Pear Creek borders U.S. Highway 12 (see Figure 4-4-3). Groundwater quality in these wells have historically appeared to be similar to Lower Lake water quality.

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West plant site wells are located on a more northwesterly flowpath, from the Former Sediment Drying Area adjacent to Lower Lake through the main plant facilities toward East Helena monitoring well EH-60. Known or suspected source of impacts to groundwater quality in this portion of the plant site include the former acid plant sediment drying areas near Lower Lake, the acid plant process water solids reclaim facility and the former acid plant sediment drying area adjacent to the acid plant, the former speiss pond and speiss granulating pit areas, the ore storage area in the southwest region of the plant site, and the area near the former zinc plant. For reference, wells located along the approximate border between the east and west plant site areas are DH-20, DH-29, DH-9, and DH-6 (Figure 4-4-3).

East Plant Site

Summary statistics (average, minimum, and maximum) for selected water quality constituents in east plant site wells are shown in Table 4-4-7. Groundwater quality in this area of the plant is variable, with average sulfate concentrations ranging from 4 mg/L at DH-20 to 1,278 mg/L at APSD-2, and average dissolved arsenic concentrations ranging from 0.005 mg/L at DH-11 to 23.2 mg/L at APSD-3. Groundwater pH values are near neutral or slightly acid (average pH ranges from 6.6 at APSD-3 to 7.6 at APSD-7). Metals concentrations are generally low, with the exception of cadmium and zinc at APSD-3, and zinc at APSD-10 and DH-5 (Table 4-4-7).

Arsenic speciation results indicate that arsenic (III) predominates in wells near Lower Lake (except for well DH-5), while arsenic (V) is prevalent in wells downgradient of Lower Lake such as DH-9, DH-6, and DH-10. Well DH-5 is distinct in terms of both arsenic speciation (dominated by As(V) rather than As(III)) and dissolved oxygen concentration (average of 7.2 mg/L, much higher than other east plant site wells) compared to nearby wells on the north side of Lower Lake (DH-4 and APSD-7). The RI noted that this well had lower concentrations of TDS and common ions than any other monitoring site (including

East Plant Site Wells Summary Statistics Table 4-4-7.

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	Site														1	+	+	+	1	
Data	APSD-1	APSD-10	APSD-11	APSD-12	APSD-2	APSD-3	APSD-4	APSD-7	APSD-8	4PSD-9	DH-10	DH-14	DH-15	DH-20	DH-4	-		-	DH-II	DH-7
DO (Average)	1.86	1.93	2.26	3.81	2.58	2.38	2.92	2.21	2.23	1.94	2.90	1.95	1.95	3.13	1.69	7.20	2.74	4.71	2.50	3,26
DO (Minimum)	0.76	0.77	0.59	1.4	0.58	0.81	0	0.73	0.62	0.65	15	0.72	0.8	0.8	0.7	3.6	-	1.7	1.4	1.7
DO (Maximum)	5.12	3.38	6.12	10.09	LL	6.04	7.37	5.4	7.15	3.55	9	4.89	4.9	8.99	3.1	10	4.94	8.4	4	6.4
pH (Average)	7.08	7.05	7.13	7.21	6.71	6.64	7.08	7.56	7.27	7.31	6.92	6.84	6.78	7.20	1.07	7.15	7.23	7.30	7.03	6.83
pH (Minimum)	6.46	6.18	5.68	6.64	4.67	6.16	6.41	5.5	6.12	6.4	5.39	5.25	6.56	6.6	5.96	6.1	6.43	5.94	5.94	5.63
pH (Maximum)	7.65	7.94	16.7	8.21	7.15	7.23	7.57	8.56	167	8.1	7.69	8.25	7.03	8.23	7.62	7.85	7.74	8.43	7.68	1912
SO4 (Average)	311	415	44	163	1278	451	68	615	237	83	364	9	439	4	84	50	710	459	72	75
SO4 (Minimum)	47	49	23	59	174	219	41	54	3.6	48	45	2	400	-	14	6	2	242	16	4
SO4 (Maximum)	1491	1107	129	505	2288	923	110	1523	1015	133	1258	17	490	12	426	93	1805	768	299	156
Cl (Average)	19	4	4	51	304	52	6	242	62	4	16	8	38	2	36	00	37	63	17	~
Cl (Minimum)	8.7	-	2.1	6	65	23	3.3	86	3	2	1.7	0.007	35	4	8.2	2.8	11	40	-	-
CI (Maximum)	50	7.4	9	417	553	151	13	433	178	6	75	13	44	8.1	168	18	-	-	106	53
As (Average)	1.83	0.897	0.028	0.124	19.80	23,19	0.301	20.43	1.90	1.09	2,10	0.007	0.011	0.127	3.04	0.578	4.22	4.50		0.006
As (Minimum)	0.311	0.261	0.008	0.028	1.17	6.04	160'0	2.5	0.17	0.568	0.513	0.004	0.004	0.076	1.57	-		-	-	0.004
As (Maximum)	3.47	1.88	0.146	0.161	74.74	136	1.26	49	14	1.7	5.75	0.049	0.043	0.19	11.4	3	-	-	-	0.01
As+3 (Average)	1.81	0.528	0.023	0.089	17.35	35.77	0.106	20.54	0.711	0.133	0.486	0.014	0.014	0.117	2.96	-	-	0.395	-	0.015
As+3 (Minimum)	0.156	0.182	0.004	0.042	0.949	1.34	0.02	3.61	0.056	0.009	0.004	0.004	0.008	0.04	1.71	_		-		0.004
As+3 (Maximum)	3.8	16.0	0.127	0.141	48.84	167	0.259	53	5.475	0.54	4.6	0.042	0.027	0.331			4.7	6.6	0.124	0.092
As+5 (Average)	0.286	0.242	0.015	0.040	2.32	4.38	0.153	4.249	0.121	0.827	1.23	0.017	210'0	0.047	-	-	-	2.87	0.016	0.023
As+5 (Minimum)	0.032	0.026	0.005	0.011	0.176	2.19	0.074	0.34	0.014	0.471	0.024	0.004	0.008	0.009		-	-	-	_	0.004
As+5 (Maximum)	0.84	0.739	0.027	0.078	4.806	10.8	0.297	28.2	0.656	1.066	4.68	0.036	0.035	0.137	0.5	1.35	4.6	-	0.101	0.106
Cd (Average)	0.002	0.083	0.002	0.003	0.002	2.33	0.003	0.130	0.002	0.007	0.002	0.001	0.002	0.001	0.001	-			0.001	100.0
Cd (Minimum)	0.001	0.001	0.001	0.001	100'0	0.54	0.001	0.015	0.001	0.003	0.001	0.001	0.001	0.001	0.001	0.001 (0.001	-	-	0.001
Cd (Maximum)	0.011	0.725	0.01	0.014	0.01	5,08	0.023	0.347 -	10:0	0.012	0.005	0.004	0.01	0.006	0.005	-	-	-	0.006	0.005
Cu (Average)	0.005	0.007	0.005	0.005	0.007	0.007	0.005	0.006	0.005	0.006	0.008	0.006	0.008	0.005	0.006	-	-	-	-	0.006
Cu (Minimum)	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.008	0.004	0.004	-		-	-	0.004
Cu (Maximum)	0.008	0.052	0.008	0.008	0.024	0.025	0.01	0.016	0.014	0.011	0.014	0.022	0.008	0.008	0.017	-	-	0.016	0.008	0000
Pb (Average)	0.005	0.036	0.005	0.005	0.006	0.005	0.005	0.007	0.005	0.007	0.006	0.005	0.005	0.005	0.005	-	-	0.007		0.005
Pb (Minimum)	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	-	-	0.005	0.005	0.001
Pb (Maximum)	0.005	0.117	0.005	0.005	0.024	0.006	0.005	0.02	0.005	0.016	0.02	0.006	0.0066	0.02	0.02	0.048 (-	0.02	0.02	0.02
Zn (Average)	0.075	3.30	0.027	0.047	0.031	12.47	0.046	0.117	0:020	0.281	0.054	0.020	0.016	0.013	0.017		0.012	0.351	0.012	0.012
Zn (Minimum)	0.006	0.108	0.006	0.006	0.008	5.906	0.022	0.01	0.006	0.13	0.008	0.006	0.008	0.006	0.006	0.69 0		0.051	0.006	0.006
Zn (Maximum)	1.26	9.61	0.084	0.37	0.11	30.4	0.141	0.316	0.064	0.675	0.2	0.099	0.045	0.032	0.095	-	0.025	0.975	0.038	0.033

NOTE:

Wells DH-14 and DH-15 are intermediate aquifer wells, other wells completed in the shallow aquifer. Metals and arcenic concentrations are dissolved. Below detect values replaced with the detection limit for calculations Values are in mg/L except for pH (standard units). Federal Maximum Contantinant Levels (MCLs): As = 0.05 mg/L, Cd = 0.005 mg/L, Pb = 0.015 mg/L. State of Montana human health standards for parameters of interest: As = 0.018 mg/L, Cd = 0.005 mg/L, Pb = 0.015 mg/L.

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upgradient monitoring wells and Prickly Pear Creek upstream of the plant site. The RI also noted that DH-5 is located adjacent to the City of East Helena potable water supply line that supplies water to the plant site from its source on McClellan Creek, about 5 miles south of the Plant site. McClellan Creek is an upstream tributary to Prickly Pear Creek and water from McClellan Creek supplies the majority of the potable water supply for the City of East Helena. As described in the RI, it is likely the nearby potable water line adjacent to DH-5 leaks and is the source of the general water quality characteristics observed at DH-5; including the high oxidation state of groundwater (high DO and high ratio of As (III) to As (V).

Interparameter correlation coefficients and matrix scatterplots (Appendix 4-4-2) show positive correlations are apparent between dissolved cadmium and dissolved zinc (R=0.78), and between chloride and sulfate (R=0.73), as well as between dissolved arsenic and arsenic (III) (R=0.95). Zinc and cadmium typically show similar behavior in groundwater and are probably derived from the same sources on the plant site. The arsenic (III)/dissolved arsenic correlation contrasts with the lack of relationship between arsenic (V) and dissolved arsenic (see Appendix 4-4-2). The correlation is driven by the predominance of arsenic (III) in the relatively high arsenic concentrations wells near Lower Lake.

Trends in groundwater dissolved arsenic concentration on the east plant site are variable (Appendix 4-3-1). Many wells have shown decreases in arsenic concentration over time (APSD-1, APSD-3, APSD-9, and DH-9). Downgradient wells DH-4, DH-6, and DH-10 have recently shown very slight increases in arsenic concentrations, after a long period of decreasing concentrations. Figure 4-4-6 shows dissolved arsenic, dissolved zinc, and sulfate concentration trends for Lower Lake and a number of monitoring wells downgradient of Lower Lake. As described in Section 4.2, Lower Lake arsenic concentration peaked in 1993 at 87 mg/L, and subsequently decreased to 0.24 mg/L in November 1997. The 1993 peak had little or no observable effect on downgradient wells DH-4 and DH-6. Well APSD-7 has shown seasonal fluctuations in arsenic concentration at this well (8.6 mg/L in November 1997).

1997) remains higher than the concentration in Lower Lake (0.24 mg/L in November 1997). Groundwater arsenic concentrations at APSD-7 are probably affected both by recharge from Lower Lake and by loading of arsenic from historically impacted soils and sediments between Lower Lake and APSD-7; most recently from the high concentrations in Lower Lake in 1993 (see Section 4.2).

The trends shown on Figure 4-4-6 suggest that Lower Lake is one of several potential source areas affecting groundwater on the east plant site. Well DH-5, for example, has relatively high zinc concentrations and low sulfate concentrations compared to Lower Lake. Low sulfate concentrations are probably the influence of fresh water leakage from the City of East Helena potable water supply line. However, high zinc concentrations at DH-5 probably reflect the historic water quality of discharges from the old zinc plant (operated by The Anaconda Company until 1982). The zinc plant discharges were combined with the Asarco plant main process fluid circuit discharges to Lower Lake until 1982. The location of the outfall to Lower Lake was just adjacent to the location of DH-5.

Sulfate concentrations in Lower Lake have recently increased from about 600 mg/L to about 1600 mg/L (an effect of HDS treatment of arsenic and metals) (Figure 4-4-6). Wells APSD-7, DH-6, and DH-4 also have shown recent increases in sulfate concentration beginning in 1994, although the increase at DH-4 was not apparent until 1996. Sulfate concentrations at wells DH-5 and DH-9 do not show a direct relationship with Lower Lake sulfate concentrations. As described above, DH-5 is affected by the probable potable water supply leak. DH-9 is located downgradient of Thornock Tank. Until recently, the sulfate trend in DH-9 was generally downward and reflected the removal of Thornock Lake from the main process circuit and the subsequent sediment removal actions. However, DH-9 shows a recent rise in sulfate concentration. Recent water quality trends were evaluated in the February 1998 Plant Water Investigation Report as discussed in Section 5.0.



Figure 4-4-6.

Dissolved Arsenic, Zinc, and Sulfate Trends in Groundwater Downgradient of Lower Lake

Well DH-11, located across Prickly Pear Creek to the northeast of Lower Lake, has shown an increasing trend in sulfate, chloride, and total dissolved solids concentration over the past three years, corresponding to the increase observed in Lower Lake (Appendix 4-3-1). The sulfate concentration trend seems to indicate that the influence of Lower Lake on shallow groundwater may extend across Prickly Pear Creek in this region; however, arsenic concentrations at DH-11 have always been low at this site (<0.005) even when Lower Lake previously exhibited elevated arsenic concentrations. This indicates geochemical attenuation of arsenic due to redox conditions beneath Prickly Pear Creek (See discussion in Section 4.5).

West Plant Site

Summary statistics (average, minimum, and maximum) for selected water quality constituents in west plant site wells are shown in Table 4-4-8. Groundwater quality in this area of the plant is more variable than on the east plant site, due to the presence of numerous historical source areas, including the Former Acid Plant Water Treatment Facility and Sediment Drying Area, the Former Speiss Pond and Pit, and the ore storage area (Exhibit 2-1-1). Average sulfate concentrations in shallow groundwater on the west plant site range from 399 mg/L at APSD-13 to 2,771 mg/L at DH-28, and average dissolved arsenic concentrations range from 0.007 mg/L at DH-1 to 420 mg/L at DH-21. Arsenic speciation is typically dominated by arsenic (III), although sites immediately downgradient of the former settling speiss pond and pit have shown (on average) nearly equal concentrations of both arsenic (III) and arsenic (V), and wells near the southern end of the plant and the former (V).

Groundwater pH values on the west plant site are typically near neutral or slightly acidic, with the exception of groundwater near the speiss settling pond and pit which is basic and groundwater near the acid plant water treatment facility which is acidic. Average groundwater pH at well DH-21 adjacent to the speiss pond replacement tank is 10.9, and average groundwater pH at DH-19 next to the acid plant water treatment area is 4.4 (Table 4-

Table 4-4-8.

West Plant Site Shallow Wells Summary Statistics

4 DH-1 DH-13 DH-14 DH-14 DH-15 DH-16 DH-17 DH-17 DH-24 DH-24 DH+24 DH+24 DH+24 DH+24 DH+24 DH+26 DH+27 DH+27 DH+27 DH+27 DH+27 DH+27 DH+27 DH+27 DH+26 DH+26 DH+26 DH+26 DH+26 <thdh+26< th=""> DH+26 DH+2</thdh+26<>		Site																
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Data	APSD-13	APSD-14	DH-1	DH-12	DH-13		DH-17	01-H0	DH-21	DH-22	DH-23	DH-24	DH-26	DH-27	DH-28	DH-29	DH-8
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	DO (Average)	3.73	2.34	8.05	2.62	2.38		2.18	2.42	1.88	2.29	2.76	2.22	2.03	2.43	1.56	4.52	4.93
	DO (Minimum)	0.79	1.5	5.1	1.4	0.35		1.2	1.1	0.4	1.1	1.6	1.07	1.25	-	0.4	1.4	3.24
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	DO (Maximum)	9.1	3.4	6	6.98	4.77		5.06	4.16	8.6	4.96	3.91	5.8	2.7	5.5	3.42	10.28	8
	pH (Average)	6.41	6.20	7.17	6.55	6.17		6.55	4.35	10.94	5.17	7.32	5.83	5.31	6.20	10.38	6.66	6.71
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c $	pH (Minimum)	5.41	3.97	5.83	5.91	5.19		5.63	3.58	10.25	4.29	6.16	3.61	4.86	5.32	9.08	5.95	6.01
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	pH (Maximum)	6.93	6.9	8.15	7.68	7.04		7.22	5.39	11.68	6.54	8.01	6.9	5.75	6.84	12.09	7	7.28
	SO4 (Average)	399	488	1046	1557	1548		1725	1315	2527	707	566	1304	1575	1523	2771	1260	1451
0) 723 665 1534 2630 3000 2140 2811 4872 3519 1153 1153 173 771 2100 88 155 90 10 63 54 115 133 178 97 223 150 432 109 88 156 37 4 104 69 165 3373 110.071 65.085 100.000 117.466 420.172 20.000 4181 65.073 72.883 112 9,22 0,007 83.703 110.071 65.085 100.000 117.466 420.172 20.000 4181 259 123 1112 9,22 0,007 93.71 17.322 33.31.44 35.56 15.57 0.03 10.97 50.84 44.76 7.84 166 7.73 123 7.88 0 0.012 0.062 0.011 97.77 9.74 15.46 6.7 7.8 19.7 7.88 19.1	SO4 (minimum)	165	310	368	217	161		774	520	42	75	341	616	1338	514	1491	538	685
63 54 115 153 178 97 223 150 432 109 88 156 90 27 39 57 17 12 24 52 29 56 37 57 4 70 60 165 372 382 277 117 580 565 37 57 4 7.056 5.622 0.001 83703 110071 65085 100000 117.46 65.733 72.883 72.883 11.2 92 0.012 0.007 0.001 92.773 10.8477 70.766 97.888 10.91 123 72.883 0 0.012 0.007 0.001 17.322 33.124 10.58 153 73.88 123 72.883 0 0.004 2771 11.322 33.124 10.58 153 72.1 98.7 55.7 55.79 61.96 65.933 102 90.00 10.25 53.468	SO4 (Maximum)	723	665	1534	2630	3000		2811	4872	3519	1153	1152	11/1	2100	3200	4150	3029	2549
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cl (Average)	63	54	115	153	178		223	150	432	109	88	156	90	222	301	243	286
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	CI (Minimum)	27	39	57	17	12		52	29	5.6	9	37	57	4	80	8.9	63	110
7.056 5.622 0.007 83.703 110.071 65.085 100.000 11.746 420.175 20.000 4.181 65.073 72.883 3.4 3.4 3.711 17.322 3.29 1.294 33.59 165 6.339 1.175 25.79 61 11.2 9.2 0.004 0.001 2.773 108.477 70.776 97.688 109.141 178.407 1.847 1.645 61.966 69.300 0.012 0.0062 0.011 9.2773 108.477 70.776 97.688 109.141 178.407 1.847 1.645 61.966 69.300 0.004 0.007 0.004 2.7772 11.325 33.124 1.058 43.27 43.5 43.56 69.300 0.011 4.244 5.844 1.861 4.276 0.193 22.7550 10.725 26.35 4.682 2.7456 0.004 0.0018 0.1334 0.0053 0.024 1.877 0.025 0.001 10.225 0.001 0.001 0.002 1.246 0.023 0.125 0.73 0.0046 0.004 0.0018 0.011 0.001 0.001 0.001 0.002 1.246 0.73 0.73 0.73 0.004 0.004 0.0018 0.001 0.001 0.001 0.004 0.004 0.004 0.004 0.004 0.004 0.004 0.0018 0.001 0.001 0.001 0.001 <	Cl (Maximum)	104	69	165	352	382		417	580	656	319	281	229	123	745	545	106	651
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	As (Average)	7.056	5.622	0.007	83.703	110.071		100.000	117.466	420.172	20.000	4.181	65.073	72.883	44.907	294,685	113.953	0.036
11.2 9.2 0.02 198 240 116.3 156 416 750 72.1 9.7 98.2 88.8 m 0.0012 0.062 0.011 92.773 108.477 70.776 97.688 109.141 178.407 1.847 1.645 61.966 69.300 m 0.003 0.0117 0.05 290 2.772 11.325 33.124 1.058 10.914 178.407 1.847 1.645 61.966 69.300 m 0.03 0.0117 0.05 290 2.772 11.325 33.124 1.058 0.152 0.094 0.004 0.004 19.804 60 m 0.03 0.011 4.344 5.844 1.861 4.276 10.193 227.550 17.257 2.635 4.682 2.458 m 3.66 3.91 0.004 0.225 0.379 1.133 0.2244 0.13 1.645 61.926 69.73 m 3.56 3.91 0.004 0.004 0.204 0.004 0.004 0.004 0.004 0.002 m 9.53 1.7257 2.635 4.682 2.456 0.73 m 9.53 1.7257 2.035 1.7257 2.035 4.682 2.456 m 0.0011 0.0013 0.0012 0.0012 0.0012 0.0012 0.0012 0.0012 0.0021 0.0012 m 0.0023 0.0012 0.0014 $0.$	As (Minimum)	3.4	3.8	0.004	3.771	17.322		1.294	33.59	165	6:339	1.175	25.79	61	15	74.76	18.9	0.005
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	As (Maximum)	11.2	9.2	0.02	198	240		156	416	750	72.1	P.7	98.2	88.8	145	690	430	0.101
n) 0.004 0.007 0.004 0.004 0.004 0.004 0.004 0.004 0.004 19.804 60 n) 0.03 0.117 0.05 290 250 147.2 157 435 468 6.7 7.8 102 90 n) 3.56 3.91 0.004 0.225 0.113 0.224 1.861 4.726 1.0193 2.57550 17.257 2.635 4.682 2.456 90 n) 9.53 10 0.004 0.2044 1.861 4.276 10.132 2.974 1.9 0.125 2.468 4.72 2.456 0.018 0.233 0.1725 2.682 4.682 2.456 0.73 0.234 0.73 0.1725 3.9117 n) 0.004 0.001 0.001 0.001 0.001 0.244 0.132 0.132 0.002 0.215 0.73 0.216	As+3 (Average)	0.012	0.062	0.011	92.773	108.477		97.688	109.141	178.407	1.847	1.645	61.966	69.300	42.658	148.734	142.648	0.019
00.030.1170.05290250147.2157435468 6.7 7.8102906.5356.9550.0114.3445.8441.8614.27610.193227.55017.2572.6354.6822.4563.663.910.0040.2250.3791.1330.2240.131.60.1520.0180.2350.739.53100.00180.13340.00530.00150.00121.049127.55017.2572.6354.6822.45651.60.0010.00180.13340.00530.00150.00120.10291.454150.005210.42970.23560.27233.911751.60.0010.0010.0010.0010.0010.0010.0010.0021.240.0130.25460.0810.0251.870.1500.0040.0010.0010.0010.0010.0010.0021.240.0021.80.1500.0040.0040.0010.0010.0010.0040.0050.0260.0110.0120.0330.0040.0040.0040.0040.0040.0040.0020.0260.0110.0110.0360.0050.0050.0050.01430.0060.0060.0010.0040.0060.0010.0360.0050.0050.0150.0150.0150.0120.0050.0120.0020.008<	As+3 (Minimum)	0.004	0.007	0.004	2.772	11.325		1.058	0.152	6.0	0.004	0.004	19.804	60	12.5	57.65	17.1	0.004
6.535 6.955 0.011 4.344 5.844 1.861 4.276 10.193 227.550 17.257 2.635 4.682 2.456 3.66 3.91 0.004 0.225 0.379 1.133 0.224 0.13 1.6 0.152 0.018 0.235 0.73 3.66 3.91 0.004 0.225 0.379 1.133 0.224 0.13 1.6 0.235 0.73 5 1.6 0.0018 0.1334 0.0053 0.0015 0.001	As+3 (Maximum)	0.03	0.117	0.05	290	250		157	435	468	6.7	7.8	102	60	148	439	392	0.096
m) 3.66 3.91 0.004 0.225 0.379 1.133 0.224 0.13 1.6 0.152 0.018 0.235 0.73 m) 9.53 10 0.038 15.7 30 2.974 19 98.9 532.4 51.5 8 12.16 4.7 n 10.0916 2.2600 0.001 <th< th=""><th>As+5 (Average)</th><th>6.535</th><th>6.955</th><th>0.011</th><th>4.344</th><th>5.844</th><th></th><th>4.276</th><th>10.193</th><th>227.550</th><th>17.257</th><th>2.635</th><th>4.682</th><th>2.456</th><th>2.620</th><th>105.387</th><th>5.824</th><th>0.029</th></th<>	As+5 (Average)	6.535	6.955	0.011	4.344	5.844		4.276	10.193	227.550	17.257	2.635	4.682	2.456	2.620	105.387	5.824	0.029
m) 9.53 10 0.038 15.7 30 2.974 19 98.9 532.4 51.5 8 12.16 4.7 10.0916 2.2600 0.0018 0.1334 0.0053 0.0015 0.001	As+5 (Minimum)	3.66	3.91	0.004	0.225	0.379		0.224	0.13	1.6	0.152	0.018	0.235	0.73	0.008	2.5	0.37	0.004
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	As+5 (Maximum)	9.53	10	0.038	15.7	30		19	98.9	532.4	51.5	~	12.16	4.7	10.6	491.1	19.9	0.095
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cd (Average)	10.0916	2.2600	0.0018	0.1334	0.0053		0.0029	14.5415	0.0052	10.4297	0.2536	0.2723	3.9117	0.0040	0.0049	0.0858	1.5694
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Cd (Minimum)	2	1.6	0.001	0.001	0.001		0.001	1.24	0.001	0.546	0.081	0.002	1.8	0.001	0.001	100'0	0.001
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cd (Maximum)	24.5	2.9	0.005	1.24	0.013		0.008	87	0.02	23.6	0.46	0.57	8	0.022	0.024	2	10.1
0.032 0.004 0.004 0.004 0.004 0.004 0.004 0.006 0.006 0.012 0.011 0.004 0.004 0.008 0.363 0.005 0.033 0.015 0.015 0.015 0.015 0.015 0.015 0.013 0.004 0.005 0.043 0.004 0.005 0.013 0.010 0.005 0.023 0.010 0.001 0.010 0.003 0.010 0.001 0.003 0.011 0.140 0.506 0.030 0.001 0.003 0.0	Cu (Average)	0.150	0.004	0.008	0.008	0.007		0.007	0.014	0.047	0.161	0.026	0.011	0.011	0.008	0.013	0.006	0.012
0 0.363 0.005 0.038 0.013 0.015 0.015 0.013 0.014 0.204 0.506 0.029 0.023 0.023 0.008 0.010 0.008 0.010 0.001 0.001 0.001 0.001 0.001 0.001 0.001 0.003 0.011 0.140 0.043 0.009 0.011 0.031 0.004 0.005	Cu (Minimum)	0.032	0.004	0.004	0.004	0.004		0.004	0.006	0.008	0.012	0.011	0.004	0.008	0.004	0.004	0.004	0.004
0.008 0.010 0.008 0.010 0.010 0.001 <th< th=""><th>Cu (Maximum)</th><th>0.363</th><th>0.005</th><th>0.038</th><th>0.033</th><th>0.015</th><th></th><th>0.015</th><th>0.043</th><th>0.204</th><th>0.506</th><th>0.059</th><th>0.029</th><th>0.023</th><th>0.045</th><th>0.037</th><th>0.018</th><th>0.031</th></th<>	Cu (Maximum)	0.363	0.005	0.038	0.033	0.015		0.015	0.043	0.204	0.506	0.059	0.029	0.023	0.045	0.037	0.018	0.031
0.004 0.005 <th< th=""><th>Pb (Average)</th><th>0.008</th><th>0.010</th><th>0.008</th><th>0.010</th><th>0.010</th><th></th><th>0.011</th><th>0.140</th><th>0.043</th><th>0.009</th><th>0.030</th><th>0.011</th><th>0.031</th><th>0.010</th><th>0.018</th><th>0000</th><th>0.011</th></th<>	Pb (Average)	0.008	0.010	0.008	0.010	0.010		0.011	0.140	0.043	0.009	0.030	0.011	0.031	0.010	0.018	0000	0.011
0.023 0.02 0.056 0.075 0.05 0.0125 0.05 0.05 0.05 0.05 0.06 0.038 0.061 0.05 0.063<	Pb (Minimum)	0.004	0.005	0.005	0.005	0.005		0.005	0.043	0.005	0.005	0.009	0.005	0.005	0.005	0.005	0.005	0.005
14.192 5.880 0.049 4.038 16.261 2.591 3.013 39.579 0.031 7.239 2.251 19.675 40.958 5.87 3.3 0.006 0.315 1.811 0.696 0.04 11.8 0.01 0.388 1.179 6.741 27	Pb (Maximum)	0.023	0.02	0.056	0.075	0.05	-	0.05	0.6	0.238	0.025	0.061	0.05	0.063	0.05	0.1	0.05	0.075
5.87 3.3 0.006 0.315 1.811 0.696 0.04 11.8 0.01 0.388 1.179 6.741 27	Zn (Average)	14.192	5.880	0.049	4.038	16.261		3.013	39.579	0.031	7.239	2.251	19.675	40.958	3.160	0.045	4.284	3.093
	Zn (Minimum)	5.87	3.3	0.006	0.315	1.811		0.04	11.8	10.0	0.388	1.179	6.741	27	0.595	0.008	0.053	0.006
0.388 10.4 49.1 5.73 8.2 1.50 0.118 1.3.1 6.2 35.8 63.75	Zn (Maximum)	35	7.1	0.388	10.4	49.1	5.73	8.2	150	0.118	13.1	6.2	35.8	63.75	12.3	0.25	23	14.8

NOTE:

Metals and arsenic concentrations are dissolved. Below detect values replaced with the detection limit for calculations

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Metals concentrations are variable, with cadmium and zinc present in higher concentrations than copper and lead at most monitoring locations. Average dissolved cadmium concentrations in west plant site shallow groundwater range from near the detection limit (0.002 mg/L at DH-16 and 0.002 mg/L at DH-1) to 14.5 mg/L at DH-19. Average dissolved zinc concentrations range from 0.031 mg/L at DH-21 to 40.9 mg/L at DH-26. Copper and lead concentrations are low with the highest average dissolved copper concentration on the west plant area of 0.16 mg/L at well DH-22. The highest average dissolved lead concentration is 0.14 mg/L at DH-19 (Table 4-4- $\underline{8}$).

Similar to the east side of the plant, west plant site correlation coefficients (Appendix 4-4-2) are positive between dissolved cadmium and dissolved zinc (R=0.74), and between chloride and sulfate (R=0.78), as well as between dissolved arsenic and arsenic (III) (R=0.76), and dissolved arsenic and arsenic (V) (R=0.84). Arsenic and sulfate also show a moderately positive correlation (R=0.64). The arsenic (V)/dissolved arsenic correlation was not apparent on the east plant site. In addition, Figure 4-4-7 shows that high arsenic (V) concentrations occur where pH values are high, generally downgradient of the former speiss pond and pit area.

Trends in groundwater dissolved arsenic concentration on the west plant site (Figure 4-4-7) show that the majority of wells in this area have exhibited decreasing arsenic concentrations over the last several years. These decreases have been accompanied in many cases by decreasing concentrations of sulfate and chloride. For example, the arsenic concentration at well DH-24 (near the northwest boundary of the site) has decreased from about 80 mg/L prior to 1991 to 25.8 mg/L in November 1997, while at the same time sulfate concentration decreased from about 1,600 mg/L to 688 mg/L. Many other wells have shown similar decreasing trends over time (e.g., DH-12, DH-13, DH-17). Monitoring wells immediately downgradient of known sources, however, show periodic spikes in arsenic, sulfate, and/or metals concentrations. Well DH-8, on the western side of the plant site near the ore storage area, showed a large spike in cadmium, zinc, and sulfate concentrations in 1993 and 1994,



Figure 4-4-7. Dissolved Arsenic, Zinc, and Sulfate Trends in Groundwater Downgradient of the Acid Plant and Former Sediment Drying Area

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followed by subsequent decreases (Appendix 4-3-1). This metals and sulfate spike occurred at approximately the same time that the well sustained damage from equipment being used on the plant site.

Wells <u>DH-21</u> and DH-28, downgradient of the former speiss settling pond and granulating pit, have shown considerable variability in arsenic concentrations (from about 75 to 750 mg/L), consistently high pH values, and spikes in arsenic concentration at various times over the last ten years.

Groundwater arsenic spikes observed at these wells have presumably been caused by historic process uses, as well as residual effects from arsenic-bearing soils and aquifer material. As described in Section 4.2, runoff from the speiss storage area has high concentrations of arsenic and sulfate and may also be a source of these constituents to groundwater if the existing speiss tank storm water containment facility is not completely effective. Potential sources to groundwater are discussed in detail in Section 5.0. Although arsenic concentrations are high, the rest of the metal parameter concentrations at wells DH-21 and DH-28 have remained relatively low, due primarily to limited solubility of metals under the localized high pH conditions.

In contrast to the former speiss pond and pit area groundwater chemistry (high pH, high arsenic, low metals), groundwater in the vicinity of the former acid plant water treatment facility (DH-19 and DH-22) is characterized by low pH and high concentrations of both metals and arsenic (Table 4-4-7). Groundwater pH is higher near the former sediment storage and drying areas (DH-29), but metals and arsenic concentrations are relatively high. In general, arsenic and metal concentrations in both DH-19 and DH-29 increased from 1989 through 1991. Since 1991 there has been a consistent trend of water quality improvements in the area. The concentration increases occurred when monitoring well DH-29 was covered with saturated acid plant sediments in the acid plant drying area adjacent to Lower Lake. The surface casing on the well was extended to prevent future incidents and the sediment dry

pad was subsequently taken out of use. The effects of plant operations on groundwater are discussed further in Sections 4.5 (Fate and Transport) and 5.0 (Release Assessment).

One of the shallow groundwater quality concerns on the plant site is the effect of observed spikes in arsenic or metals concentrations at source area wells (DH-21, DH-28, DH-29 and DH-19) on downgradient arsenic concentrations. Figures 4-4-7 and 4-4-8 (as well as Appendix 4-3-1) show trend plots for acid plant/former sediment drying area wells, and speiss pond/pit wells, along with downgradient wells. The acid plant/sediment drying area well graph (Figure 4-4-7) shows dissolved zinc, dissolved arsenic, and sulfate trends, and the speiss pond and pit well graph (Figure 4-4-8) shows dissolved arsenic, arsenic (III), and sulfate trends. Since the former speiss pond and pit are themselves located downgradient from the former acid plant water treatment facility and the sediment drying area, a number of "downgradient" wells appear on both figures.

As shown on Figure 4-4-7, a large spike in zinc concentration at DH-19 in 1991 apparently did not significantly affect zinc concentrations in downgradient wells. Most of the groundwater zinc load contributed by the DH-19 spike may have been precipitated as the zinc-bearing groundwater moved into contact with the high pH groundwater near the speiss pond and pit. Zinc concentrations at well DH-24 (averaging 19.7 mg/L), which is the most downgradient well on the west plant site, have historically been higher than at any of the other wells except DH-19, implying that a zinc-specific source area exists in the area just upgradient of DH-24.

Groundwater shows pattern of diminishing arsenic concentration peaks with distance from the acid plant sediment drying area. Highest arsenic concentrations were measured at DH-29 (430 mg/L) in late 1990, with subsequently lower arsenic concentrations at DH-19 (416 mg/L) in late 1991, and at DH-27 (145 mg/L) in 1993. This pattern may indicate gradual migration and attenuation of an arsenic plume downgradient of the former sediment drying area (Figure 4-4-7). Based on the distance between wells DH-29, DH-19, and DH-27, and



Figure 4-4-8. Dissolved Arsenic, Arsenic (III), and Sulfate Trends in Groundwater Downgradient of the Speiss Pit and Speiss Pond

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the time lapse between observed arsenic concentration peaks at these wells, an approximate arsenic front travel rate of 1 ft/day can be calculated for shallow groundwater in this region of the Plant. However further downgradient, arsenic concentrations at wells DH-24 and DH-17 show no corresponding peaks. This indicates that migration of arsenic from the acid plant sediment drying areas is limited, or decreased to extent that it is masked by groundwater inputs at the speiss pond and pit.

Figure 4-4-8 shows that, despite wide fluctuations in shallow groundwater arsenic and sulfate concentrations at DH-21 and DH-28 (near the former speiss pond and speiss pit, respectively), downgradient arsenic and sulfate concentrations have generally shown a consistent decrease and no indication of increases in concentration related to upgradient spikes. In addition, the high groundwater pH values at DH-21 and DH-28 do not persist downgradient; the nearest wells downgradient of DH-21 and DH-28 (DH-12 and DH-13) have average pH values of 6.5 and 6.2, respectively (Table 4-4- $\underline{8}$).

As discussed in the groundwater contaminant fate and transport section of the CC/RA report (Section 4.5), the overall behavior of arsenic in the subsurface may be controlled to a large extent by interactions with redox-active elements, particularly iron and manganese. Iron and manganese compounds are typically present in appreciable quantities in aquifer material, and the presence of soluble (dissolved) iron and manganese can be an indicator of the general redox status of groundwater. The data for iron and manganese in groundwater are limited to several samples collected during the RI/FS investigations in the 1980s, and a recent sample collected in support of the 1998 Plant Water Investigation. Addition of iron and manganese to the groundwater analytical parameter list for future monitoring events within and downgradient of the plant site should be considered, as it may be help refine predictions of arsenic plume behavior (see Section 6.0 (Summary and Conclusions)).

The mobility and geochemical behavior of arsenic in the subsurface is closely related to its oxidation state (+3 vs. +5), and thus to the oxidation/reduction (redox) status of groundwater, and the concentrations of redox-active constituents such as iron and manganese. h:\files\007 asarco\0867\ccra report\r99ccra1.doc\HLN\2/2/07\065\0096 2/2/07/7:59 AM Figure 4-4-9 is a comparison of dissolved arsenic, iron, and manganese concentrations in groundwater along a flow path downgradient of the former speiss pond on the west plant site (DH-21, DH-13, DH-17, DH-24, and EH-60). The data in the upper graph are presented in the Comprehensive RI/FS (Hydrometrics, 1990a), and represent average concentrations at each well as of April 1989. The data in the lower graph were collected as part of the February 1998 Water Release Assessment for the plant site. Well EH-60 was not sampled as part of this investigation, and wells DH-12 and DH-16 were sampled rather than DH-13 and DH-17. Wells DH-12 and DH-16 are located immediately adjacent to DH-13 and DH-17, but are screened at shallower depths.

Figure 4-4-9 indicates that decreasing arsenic concentrations downgradient of the former speiss pond are typically associated with increasing concentrations of iron and manganese. Overall concentrations of all three constituents were lower in February 1998 than in the RI/FS period (prior to April 1989). One possible explanation for the observed relationship between arsenic and manganese is the heterogeneous oxidation of soluble arsenic (III) to arsenic (V) by solid manganese oxides present in aquifer materials (Manning and Goldberg, 1997; Scott and Morgan, 1995). Under this scenario, as arsenic (III) from the speiss pit area moves downgradient and into contact with solid MnO₂, the manganese oxide oxidizes arsenic (III) to arsenic (V), and manganese is reduced from Mn (IV) to the more soluble Mn (II), which is released to groundwater. Thus, downgradient trends might include:

- Decreasing arsenic concentrations (due to adsorption of the less mobile arsenic (V));
- A movement in arsenic speciation ratio from predominantly arsenic (III) to more contribution from arsenic (V); and
- Increasing manganese concentrations due to solubilization of MnO₂.









Note: EH-60 data from May 1998; other data from February 1998.





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Arsenic speciation results reported in the RI/FS show that in general, the arsenic (III)/arsenic (V) ratio increased from DH-21 to DH-17, then decreased from DH-17 to EH-60. While arsenic concentrations in west plant site shallow groundwater are probably controlled by a complex interaction of source area inputs and geochemical interactions with aquifer materials, the consistent relationship between decreasing arsenic concentrations and increasing iron and manganese concentrations suggests that reactions with manganese and iron may exert significant control on arsenic concentrations. Geochemical factors affecting the mobility of arsenic in groundwater are discussed in more detail in Section 4.5 (Fate and Transport).

Plant Site Well Summary

Overall groundwater quality on the East Helena plant site is generally depicted in Figures 4-4-10 <u>through 4-4-14</u>. Figures 4-4-10 and 4-4-11, show historic and recent isocontour plots of arsenic and sulfate for spring 1990 and spring 1997 data sets. <u>Figures 4-4-12, 4-4-13, and 4-</u> 4-14 are isocontour maps showing November 1997 cadmium, lead and zinc concentrations in groundwater. _-Additional isocontour plots from spring 1990 through fall 1997 for arsenic, sulfate, chloride, and zinc are in Appendix 4-4-3. <u>Examination</u> of isocontour plots suggests that:

- The high concentration arsenic plume areas (shown in yellow and gold) have decreased significantly near the former acid plant water treatment facility, the former sediment drying area, and in the area downgradient of the former speiss pond. An exception is well APSD-2, near the former acid plant sediment drying area adjacent to Lower Lake, which still shows a localized area of high arsenic concentrations.
- A high concentration groundwater arsenic plume remains in the former speiss pond area.











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- A low concentration arsenic plume appears at the eastern edge of Lower Lake in the Spring 1997 map that is not evident in the Spring 1990 map. This appears to be a contouring phenomena associated with the addition of data at APSD –7 in 1997 rather than an actual water quality trend.
- A slight increase in arsenic concentrations is evident at DH-10 at the downgradient boundary of the plant site.
- An expansion of the sulfate plume is evident downgradient of Lower Lake.
- Cadmium and lead concentrations in groundwater are elevated within the immediate plant site area, but remain at or below the limits of detection in East Helena area monitoring wells. Similarly, elevated zinc concentrations persist throughout the west plant site, but are near or below detection limits in East Helena shallow monitoring wells (with the exception of the St. Clair private well).
- Arsenic and metals concentrations in some monitoring wells throughout the plant site exceed applicable water quality standards (previously presented in Table 4-3-2); however, these exceedances are limited to the plant site area and generally do not persist in downgradient (East Helena) wells. Arsenic concentrations exceed water quality standards in a limited area downgradient of the plant site, as shown in the arsenic isocontour map (Figure 4-4-10). Metals concentrations (cadmium, lead, and zinc) are currently below human health standards and MCLs in all downgradient wells, as shown on Figure 4-4-12, 4-4-13, and 4-4-14.

Downgradient Wells

Downgradient wells include monitoring wells and private wells within and near the city of East Helena. Several of the private wells are located upgradient, on the plant site itself, or to the east or west of the plant site, rather than directly downgradient (to the north or northwest). Summary statistics for downgradient monitoring wells and private wells are in Tables 4-4-9 and 4-4-10, respectively. With the exception of the St. Clair well completed in the shallow aquifer, all private wells are completed in the intermediate or deep portions of the aquifer. Average sulfate concentrations in the shallow aquifer downgradient of the plant

Table 4-4-9.

Downgradient (East Helena) Wells Summary Statistics

Data	EH-100	EH.101	C01-H2	EH.SO	EH S1	CH.57	EU C2	DIL 24	17 H C7 A	1711 59	1711 50	BU 60	EH.61	CA.HG
DO (Average)	1.57	2.39	2.83	5.07	4.21	4.55	7.75	5.35	197	4.91	5.32	2.11	3.63	5.62
DO (Minimum)	-	1.1	0.35	2.4	1.9	1.6	4.4	1.2	5.2	2.6	2.8	0.6	1.2	3.9
DO (Maximum)	2.3	3.5	7.8	7.8	6.11	8.3	11.2	10.2	9.72	10.2	8.15	2.97	8.78	7.2
pH (Average)	6.03	6.37	7.04	6.74	6.88	6.97	6.75	7.11	7.25	6.95	7.03	6.52	7.08	6.81
pH (Minimum)	5.36	4.92	6.14	6.15	5.93	5.99	5.63	5.67	6.3	6.13	6.28	6.05	6.58	5.86
pH (Maximum)	6.52	6.93	8.05	7.8	7.6	8.09	7.28	8.32	8.08	8.09	7.81	7.43	8.06	7.56
SO4 (Average)	1079	413	156	889	516	161	684	84	139	88	84	934	502	306
SO4 (Minimum)	878	243	70	480	145	50	407	31	54	45	57	593	470	68
SO4 (Maximum)	1362	516	268	1097	1006	910	960	930	434	201	III	1329	560	553
Cl (Average)	123	26	6	117	23	13	86	80	24	4	S	158	46	23
Cl (Minimum)	105	9.2	4.4	64	6.4	2.7	43	2	5.4	2	3	93	38	6.5
Cl (Maximum)	155	42	13	166	48	100	140	120	112	7.8	8.7	247	60	72
As (Average)	0.015	0.007	0.008	0.006	0.472	0.769	0.007	0.018	0.005	0.006	0.008	5.910	0.011	0.008
As (Minimum)	0.006	0.005	0.004	0.004	0.006	0.006	0.004	0.004	0.004	0.004	0.004	1.23	0.006	0.004
As (Maximum)	0.051	0.016	0.062	0.01	1.52	1.45	0.023	0.04	0.008	0.014	0.015	9666	0.021	0.051
As+3 (Average)	0.010	0.015	010.0	0.009	0.092	0.205	0.009	0.042	0.009	0.010	0.008	2.078	0.019	0,009
As+3 (Minimum)	0.008	0.008	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.008	0.008	0.004
As+3 (Maximum)	0.014	0.0336	0.036	0.036	1.1	1.4	0.044	0.837	0.037	0.037	0.022	5.492	0.038	0.039
As+5 (Average)	0.021	0.035	0.013	0.014	0.436	0.579	0.011	0.024	010'0	0.011	0.014	3.645	0.021	0.010
As+5 (Minimum)	0.008	600.0	0.004	0.004	0.008	0.01	0.004	0.004	0.004	0.004	0.004	0.006	0.008	0.004
As+5 (Maximum)	0.056	0.0804	0.0648	0.06	2.1	1.75	0.0432	0.072	0.03	0.0414	0.042	6.8	0.031	0.028
Cd (Average)	0.0012	0100.0	0.0012	0.0015	0.0015	0.0016	0.0015	0.0013	0.0014	0.0012	0.0015	0.0034	0.0023	0.0019
Cd (Minimum)	0.001	0.001	0.001	100'0	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	100.0	0.001
Cd (Maximum)	0.002	0.001	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.006	0.01	0.005	0.014
Cu (Average)	0.011	0.009	0.006	0.007	0.007	0.006	0.007	0.006	0.006	0.006	0.005	0.011	0.008	0.005
Cu (Minimum)	0.008	0.008	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.008	0.008	0.004
Cu (Maximum)	0.013	0.012	0.008	0.018	0.02	0.016	0.013	0.008	0.01	0.01	0.008	0.02	0.008	0.01
Pb (Average)	0.011	0.005	0.006	0.010	0.006	0.006	0,009	0.006	0.006	0.006	0.005	0.007	0.021	0.006
Pb (Minimum)	0.005	0,005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Pb (Maximum)	0.022	0.005	0.02	0.05	0.02	0.02	0.05	0.02	0.02	0.02	0.006	0.022	0.038	0.02
Zn (Average)	0.106	0.011	010.0	0.013	0.013	0.015	0.021	0.009	0.011	0.009	0.010	0.033	0.016	0.011
Zn (Minimum)	0.018	0.008	0.006	0.006	0.006	0.008	0.006	0.006	0.006	0.006	0.006	0.017	0.008	0.006
Zn (Maximum)	0.356	0.023	0.02	0.037	0.052	0.026	0.25	0.02	0.02	0.021	0.02	0.115	0.03	0.02

NOTE:

Wells EH-100, -101, -102 are intermediate aquifer wells; remaining wells are completed in the shallow aquifer. Metals and arsenic concentrations are dissolved. Below detect values replaced with the detection limit for calculations Values are in mg/L except for pH (standard units).

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Table 4-4-10. Private Well Summary Statistics (page 151)

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Data	AMCHEMI	AMCHEM2	AMCHEM3	AMCHEM4	ASRWELL	BERRY	BRNHAMI	CASEY	COX	DHULST	DUEL	EHC1
DO (Average)	2.75	2.44	2.35	2.86	2.00	1.40			5.80	8.64	5.42	6.55
DO (Minimum)	2.3	0.87	2.35	0.94	1.9	0.4			5.8	6.1	2.5	5.8
DO (Maximum)	3.2	5.4	2.35	5.5	2.1	6			5.8	10.6	8.8	7.9
pH (Average)	7.10	7.00	7.18	7.01	6.54	6.40			6.86	7.45	7.10	6.93
pH (Minimum)	6.6	5.43	7.18	5.17	6.03	6.15			6.86	5.25	9	6.72
pH (Maximum)	7.6	7.9	7.18	7.73	7.04	6.68			6.86	8.52	7.94	7.25
SO4 (Average)	27	54	213	29	17	484	50	52	85	84	46	59
SO4 (Minimum)	25	24	32	23	13	436	49.6	52	85	38	34	53
SO4 (Maximum)	28	600	394	34	21	544			85	241	56	64
Cl (Average)	5	7	22	3	3	36	4	3	9	21	3	2
CI (Minimum)	4.7	2	4	2	3	33	4.3	3	5.7	10	-	ю
Cl (Maximum)	4.7	86	39	4	3	39			5.7	41	3.9	5.5
As (Average)	0.006	0.005	0.005	0.027	0.015	0.006	0.017	0.004	0.006	0.020	0.006	0.006
As (Minimum)	0.006	0.004	0.004	0.004	0.01	0.004	0.004	0.004	0.006	0.006	0.004	0.005
As (Maximum)	0.006	0.009	0.006	0.467	0.024	0.008			0.006	0.05	0.014	0.006
As+3 (Average)	0.010	0.078	0.012	0.093	0.023	0.009		0.004	0.018	0.047	0.023	0.065
As+3 (Minimum)	0.008	0.004	0.012	0.004	0.008	0.008		0.004	0.0184	0.004	0.004	0.008
As+3 (Maximum)	0.0112	1.3	0.012	1.6	0.047	0.01			0.0184	0.55	0.187	0.27
As+5 (Average)	0.029	0.022	0.009	0.016	0.008	0.012		0.032	0.013	0.031	0.021	0.026
As+5 (Minimum)	0.0088	0.004	0.0088	0.004	0.0047	0.0096			0.0132	0.004	0.004	0.0108
As+5 (Maximum)	0.049	0.113	0.0088	0.094	0.012	0.014			0.0132	0.135	0.096	0.044
Cd (Average)	0100'0	0.0014	0.0023	0.0013	0.0010	0.0010	0.0020	0.0020	0.0010	0.0012	0.0011	010070
Cd (Minimum)	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001
Cd (Maximum)	0.001	0.005	0.005	0.005	0.001	0.001			0.001	0.005	0.002	0.001
Cu (Average)	0.008	0.006	0.014	0.007	0.008	0.008	0.014	0.008		0.009	0.064	0.008
Cu (Minimum)	0.008	0.004	0.014	0.004	0.008	0.008	0.012	0.008		0.004	0.005	0.008
Cu (Maximum)	0.008	0.018	0.014	0.039	0.008	0.008			0	0.022	0.77	0.008
Pb (Average)	0.005	0.007	0.005	0.006	0.005	0.005	0.013	0.020	0.005	0.006	0.006	0.005
Pb (Minimum)	0.005	0.005	0.004	0.005	0.005	0.005	0.005	0.02	0.005	0.005	0.005	0.005
Pb (Maximum)	0.005	0.03	0.005	0.02	0.005	0.005			0.005	0.02	0.02	0.005
Zn (Average)	0.014	0.062	0.045	0.088	0.011	0.023	0.033	0.008	0.015	0.011	0.011	0000
Zn (Minimum)	0.008	0.006	0.0125	0.006	0.008	0.008	0.03	0.008	0.015	0.006	0.006	0.008
Zn (Maximum)	0.010	0.35	10	1 1	0.018	0.053	0.035	0.008	0.015	0.03	0.033	0.011

NOTE:

Metals and arsenic concentrations are dissolved. Below detection values replaced with the detection limit for calculations Values are in mg/L except for pH (standard units).

Blanks indicate no data for well. Federal Maximum Contaminant Levels (MCLs): As = 0.05 mg/L, Cd = 0.005 mg/L, Pb = 0.015 mg/L. State of Montana human health standards for parameters of interest: As = 0.018 mg/L, Cd = 0.005 mg/L, Pb = 0.015 mg/L.

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Table 4-4-10. Private Well Summary Statistics (page 152)

Data	EHC2	EARNST	FLAGE	HELFERT	HOFF	JENSENA2	KAMRMN	KHULST	LAMPC	LAMPF1	LAMPR	THULST
DO (Average)	5.47	1.30	5.40	3.98	3.92	2.95	3.90	8.15			3.93	8.68
DO (Minimum)	2.4	0.7	5.4	2.8	3.7	2	3.9	8.1			3.3	6.6
DO (Maximum)	~	1.9	5.4	4.5	4.13	3.7	3.9	8.2			4.5	11.1
pH (Average)	6.57	6.28	6.67	6.86	6.78	6.66	6.65	7.38			6.77	7.35
oH (Minimum)	6.3	5.99	6.67	6.72	6.52	60.9	6.65	7.07			6.68	5.3
pH (Maximum)	7	6.46	6.67	6.95	7.03	7.22	6.65	7.69			6.91	7.96
SO4 (Average)	55	519	46	89	508	149	130	93	330	82	87	55
SO4 (Minimum)	51	442	42	74	420	133	130	86	330	82	56	14
SO4 (Maximum)	60	581	49.1	115	660	165	130	104			135	83
Cl (Average)	4	39	3	3	41	16	6	43	09	7	3	20
Cl (Minimum)	4	34	2	2.8	41	15.5	9	18	09	6.6	2.3	3
Cl (Maximum)	4.1	44	3.1	3.8	41	16	9	06			3.3	158
As (Average)	0.009	0.007	0.005	0.006	0.005	0.006	0.006	0.023	0.009	0.006	0.006	0.021
As (Minimum)	0.006	0.004	0.004	0.004	0.004	0.004	0.006	0.021	0.004	0.004	0.004	0.01
As (Maximum)	0.012	0.013	0.006	0.01	0.006	0.01	0.006	0.026			0.007	0.05
As+3 (Average)	0.015	0.010	0.008	0.008	0.026	0.010	0.014	0.022			0.008	0.014
As+3 (Minimum)	0.008	0,008	0.008	0.008	0.008	0.008	0.014	0.016			0.008	0.004
As+3 (Maximum)	0.0256		0.008	0.008	0.044	0.014	0.014	0.028			0.008	0.048
As+5 (Average)	0000	0.023	0.010	0.020	0.010	0.022	0.008	0.031			0.016	0.027
As+5 (Minimum)	0.0084		0.01	0.008	0.008	0.0108	0.008	0.008			0.0136	0.006
As+5 (Maximum)	0.01	0.036	0.01	0.051	0.012	0.04	0.008	0.054			0.02	0.112
Cd (Average)	0.0010	0.0010	0.0010	0.0011	0.0020	0.0010	0.0010	0.0010	0.0020	0100'0	0.0012	0.0013
Cd (Minimum)	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Cd (Maximum)	0.001	0.001	0.001	0.002	0.004	0.001	0.001	0.001			0.002	0.005
Cu (Average)	0.008	0.008	0.036	0.027	0.027	0.047	0.008	0.008	600'0	0.011	0.062	0,006
Cu (Minimum)	0.008	0.008	0.036	0.018	0.022	0.008	0.008	0.008	0.004	0.011	0.023	0.004
Cu (Maximum)	0.008	0.008	0.036	0.036	0.035	0.085	0.008	0.008			0.1	0.017
Pb (Average)	0.005	0.005	0.005	0.007	0.033	0.005	0.005	0.005	0.013	0.005	0.011	0.006
Pb (Minimum)	0.005		0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0,005	0.005
Pb (Maximum)	0.005		0.005	0.02	0.12	0.006	0.005	0.005			0.033	0.02
Zn (Average)	0.008	0.014	0100	0.015	0.024	0.009	0.031	0.012	0.052	0.151	0.012	0.021
Zn (Minimum)	0.008	0.008	0.008	0000	0.011	0.008	0.031	0.008	0.038	0.071	0.008	0.008
	0 000	2000	1100	0000	2200	1100	0.021	0.016	0.065	0.731	0.00	0.114

NOTE:

Metals and arsenic concentrations are dissolved. Below detection values replaced with the detection limit for calculations

Values are in mg/L except for pH (standard units).

Blanks indicate no data for well.

Federal Maximum Contaminant Levels (MCLs): As = 0.05 mg/L, Cd = 0.005 mg/L, Pb = 0.015 mg/L. State of Montana human health standards for parameters of interest: As = 0.018 mg/L, Cd = 0.005 mg/L, Pb = 0.015 mg/L.

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Table 4-4-10. Private Well Summary Statistics (page 153)

Data	MANION	NORDSTR	ROMASKO	SIMAC	STCLAIR	VETSCH	WALTER	WESTON	WOJCIK
DO (Average)	1.15	3.50	1.73	5.08	4.02	1.37	4.40	3.68	4.15
DO (Minimum)	0.3	2.8	0.4	4.7	2.4	0.4	2.4	2.3	3
DO (Maximum)	2	4.2	2.6	5.5	5.9	2.2	6.9	4.5	4.9
pH (Average)	5.88	6.68	6.61	6.87	6.86	6.54	6.68	6.75	6.60
pH (Minimum)	5.76	6.65	6.35	6.58	6.08	6.39	5.75	6.3	6.43
pH (Maximum)	5.99	6.7	6.75	7.04	7.61	6.67	7.44	7.09	6.72
SO4 (Average)	880	93	419	88	134	454	45	P9	55
SO4 (Minimum)	500	83	384	86	96	420	22	58	47
SO4 (Maximum)	1160	103	446	90	200	478	52	101	09
CI (Average)	121	2	28	5	2	31	3	3	2
CI (Minimum)	121	2	26	4	6.4	30	2.5	2	2
CI (Maximum)	121	2	30	5.9	9.6	31	3.9	3.2	2.2
As (Average)	0.005	0.005	0.006	0.007	0.073	0.006	0.007	0.006	0.006
As (Minimum)	0.004	0.004	0.004	0.006	0.008	0.004	0.004	0.004	0.004
As (Maximum)	0.006	0.006	0.007	0.008	0.144	0.006	0.009	0.006	0.006
As+3 (Average)	0.013	0.012	0.009	0.009	0.010	0.011	0.228	0.010	0.010
As+3 (Minimum)	0.008	0.008	0.008	0.008	0.004	0.008	0.008	0.008	0.008
As+3 (Maximum)	0.018	0.016	0.01	0.0108	0.059	0.018	1.51	0.0168	0.014
As+5 (Average)	0.018	0.010	0.018	0.019	0.077	0.025	0.028	0.019	0.019
As+5 (Minimum)	0.008	0.008	0.008	0.0084	0.01	0.008	0.01	0.012	0.01
As+5 (Maximum)	0.027	0.011	0.031	0.034	0.165	0.044	0.094	0.029	0.031
Cd (Average)	0.0019	0.0010	0.0010	0.0010	0.0010	0.0010	0.0011	0.0010	0.0010
Cd (Minimum)	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Cd (Maximum)	0.004	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001
Cu (Average)	0.057	0.013	0.025	0.008	0.013	0.012	0.040	0.015	0.028
Cu (Minimum)	0.008	0.013	0.019	0.008	0.008	0.008	0.008	0.014	0.014
Cu (Maximum)	0.18	0.013	0.031	0.008	0.028	0.016	0.118	0.015	0.041
Pb (Average)	0.024	0.005	0.006	0.005	0.005	0.005	0.007	0.005	0.005
Pb (Minimum)	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Pb (Maximum)	0.07	0.005	0.0078	0.005	0.005	0.007	0.02	0.005	0.005
Zn (Average)	0.044	0.051	0.010	0.073	0.087	0.012	0.038	0.011	010.0
Zn (Minimum)	0.015	0.022	0.008	0.044	0.008	0.008	0.008	0.01	0.008
Zn (Maximum)	0.005	0.106	0,015	0.085	0.217	0.02	0.096	0.014	0.015

NOTE:

Metals and arsenic concentrations are dissolved. Below detection values replaced with the detection limit for calculations

Values are in mg/L except for pH (standard units).

Blanks indicate no data for well.

Federal Maximum Contaminant Levels (MCLs): As = 0.05 mg/L, Cd = 0.005 mg/L, Pb = 0.015 mg/L. State of Montana human health standards for parameters of interest: As = 0.018 mg/L, Cd = 0.005 mg/L, Pb = 0.015 mg/L.

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from 84 mg/L to 934 mg/L; concentrations in the three intermediate/deep aquifer monitoring wells cover nearly the same range, from 156 mg/L to 1079 mg/L. Groundwater pH is near neutral or slightly acidic (averages range from 6.0 to 7.3), and average dissolved oxygen (DO) concentrations range from 1.57 to 7.75 mg/L, with lower concentrations generally present in the intermediate/deep aquifer wells. Well EH-60 differs somewhat from the other shallow monitoring wells, with a lower average DO concentration, and a lower range of observed concentrations (i.e., the maximum observed DO at EH-60 was 2.97 mg/L, while maximum values at other wells range from 6.11 mg/L to 11.2 mg/L).

Metals and arsenic concentrations are low at most downgradient monitoring wells. Exceptions include EH-60 (average dissolved arsenic = 5.91 mg/L), EH-52 (average dissolved arsenic = 0.769 mg/L), and EH-51 (average dissolved arsenic = 0.472 mg/L). Well EH-100 (a deep monitoring well) has the highest average zinc concentration of any downgradient monitoring well (0.106 mg/L), along with the highest average sulfate concentration (Table 4-4-9). Isocontour maps showing arsenic, sulfate, cadmium, lead and zinc were previously shown in Figures 4-4-10 through 4-4-14.

Private wells show some variability in water quality, with relatively low concentrations of arsenic and metals (Table 4-4-<u>10</u>). Average sulfate concentrations range from 17 mg/L to 880 mg/L, average arsenic concentrations range from below laboratory detection limits (0.005 mg/L) to 0.073 mg/L, and average zinc concentrations range from 0.008 mg/L to 0.151 mg/L. Cadmium and lead are at or below detection limits in downgradient wells. Average groundwater pH in private wells ranges from 5.9 to 7.5.

The highest average arsenic concentration is present in the one private well completed in the shallow aquifer (St. Clair). This well is not used and the pump has been removed. All residences within the city of East Helena use city water and none of the private wells are used for potable water supplies.

Interparameter correlations for downgradient monitoring wells (Appendix 4-4-2) show positive correlations between sulfate and chloride, arsenic and arsenic (III), and arsenic and arsenic (V). Correlations also were evaluated for private wells, but no statistically strong (0.07 or above) relationships exist.

Water quality trends downgradient of the plant site are shown in Appendix 4-3-1. The nearest off-plant downgradient monitoring well (EH-60) shows a consistent increasing trend in arsenic concentration since monitoring began in 1987. Well EH-51, where arsenic concentrations have historically fluctuated seasonally, also has recently shown a slight upward trend. Other downgradient monitoring wells have remained constant or decreased in arsenic concentration (e.g., EH-52). Downgradient trends for arsenic, along with dissolved oxygen and sulfate, are shown for selected downgradient monitoring wells on Figure 4-4-1<u>5</u>.

Figure 4-4-15 shows a clearly increasing arsenic trend at well EH-60, as well as the decreasing trend at EH-52 and relatively low arsenic concentrations at other wells. The low dissolved oxygen concentrations at EH-60, and seasonal fluctuations in dissolved oxygen concentrations at wells near Prickly Pear Creek (EH-51 and EH-52) are evident on the plot of DO concentrations. Seasonal fluctuations in dissolved oxygen also occur at well EH-50, although the trend is the opposite of that at wells EH-52 and EH-51. Well EH-53 tends to show very high dissolved oxygen concentrations for groundwater (4.4 to 11.2 mg/L), indicating that the influence of oxygenated water from Prickly Pear Creek probably extends over a significant portion of the western East Helena area.

Sulfate concentration trends on Figure 4-4-15 show increases at several downgradient monitoring wells over the last several years (EH-51, EH-52, EH-62). Although not shown on Figure 4-4-15, sulfate concentrations in intermediate aquifer monitoring well EH-102 also have increased consistently since 1991, after a period of concentration decreases. Since 1996, sulfate concentrations at well EH-60 show a decreasing trend similar to trends in immediately upgradient plant site wells DH-24, DH-17, DH-13, after historical increases and



Figure 4-4-15. Dissolved Arsenic, Dissolved Oxygen, and Sulfate Trends in Groundwater Downgradient of the East Helena Plant Site

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peaks in 1992 and 1995. A comparison of the wells immediately north of the plant site (EH-50, EH-51, and EH-60) with wells further downgradient (EH-53 and EH-62) suggests that, in general, sulfate concentrations peaked at the near downgradient wells in 1994 and 1995, and have since remained steady or decreased. At the further downgradient wells, concentrations peaked later (at EH-53 in 1996), or are continuing to increase (EH-62).

The interrelationships between arsenic, oxidation conditions and sulfate are key factors that control arsenic and metal mobility. These <u>G</u>roundwater quality trends <u>relative to and</u> the physical and geochemical mechanisms that <u>likely</u> control arsenic <u>and</u> metals <u>concentrations</u> in plant site and downgradient groundwater are discussed in Section 4.5.

4.4.3.2 Organic Constituents

Analyses for organic constituents in groundwater have been performed for selected monitoring wells within and downgradient of the East Helena plant site. Complete results for organics, including data collected as part of the RI are in the water quality database (Appendix 3-1-1). Figure 4-4-16 highlights monitoring wells that have shown evidence of organic constituents including observed petroleum/organic staining or odors noted in well construction logs. The figure shows the results of the May 1997 sample event for organics superimposed on a recent (Nov. 1997) contour map of groundwater arsenic concentrations.

Samples for organics analysis have generally been collected for wells that showed evidence of organic constituents during drilling, and for several downgradient wells. Figure 4-4-16 shows that the locations with evidence of organic constituents coincides roughly with the high concentration portion of the arsenic plume, and also with the portion of the plume dominated by the reduced (+3) form of arsenic. The coincidence of locations with organic constituents and the arsenic plume are probably due to similar source areas (i.e., historic organic releases in the same areas where historic arsenic occurred). Organic compounds could potentially affect the mobility of arsenic and other metals in the subsurface, directly through complexation, or indirectly through their influence on groundwater redox state.



While the presence of organics could potentially result in a reduced oxidation state in groundwater, dissolved oxygen concentrations on the west plant site in the region of organic contamination are generally in the range of 1 to 3 mg/L, indicating that the presence of organics has not stimulated the formation of a highly reducing environment.

Table 4-4-11 shows average organic parameter concentrations for the highlighted wells on Figure 4-4-16, as well as several downgradient wells. The data in Table 4-4-11 show that organic constituents are generally low with the exception of the area near DH-27 and downgradient well DH-28.

TABLE 4-4-11. ORGANIC PARAMETER AVERAGE GROUNDWATER CONCENTRATIONS, WEST PLANT SITE AND DOWNGRADIENT WELLS

				Mo	nitoring `	Well			
Parameter	DH-6	DH-13	DH-17	DH-21	DH-24	DH-26	DH-27	DH-28	EH-60
ТРН	Na	1.12	1.19	na	0.91	na	na	na	0.92
Oil & Grease	0.7	1.00	16.1	11.1	0.41	17.5	6.0	na	30.0*
DRO as Diesel	Na	na	na	na	na	na	207	0.74	na
GRO	Na	na	na	na	na	na	42.7	13.3	na

NOTES:

Averages calculated from period of record data; in general, TPH samples were collected from 1988-1997, Oil & Grease samples in 1987-1988, DRO and GRO samples in 1996-1997. See Appendix 3-1-1 for complete analytical results.

BTEX analyses at wells DH-13 (<0.005 mg/L) and DH-26 (<0.001 mg/L) were below analytical detection limits. BTEX parameters were not analyzed at other well sites.

na = not analyzed

All concentrations in mg/L.

TPH = Total Petroleum Hydrocarbons

DRO = diesel range organics

GRO = gasoline range organics

* This site showed an unusually broad range of oil & grease results; for two sample dates, results included one value of 60 mg/L and a subsequent value of 0.08 mg/L.

Table 4-4-12 is a correlation matrix for arsenic, arsenic speciation, and general organics data for the wells listed in Table 4-4-11. A correlation analysis was performed to assess whether groundwater data indicated any relationship between dissolved arsenic concentrations, concentrations of a particular arsenic species, and general indicators of organic contamination. The results in Table 4-4-12 show no statistical correlation between arsenic (dissolved, +3, or +5) and the organic constituents oil & grease and TPH.

TABLE 4-4-12. CORRELATION COEFFICIENTS (R) FOR ARSENIC, TPH, AND OIL & GREASE WEST PLANT SITE AND DOWNGRADIENT WELLS

	As (Dis)	As+3	As+5	Oil & Grease	TPH
As (Dis)	1				
As+3	0.75	1			
As+5	0.88	0.38	1		
Oil & Grease	-0.08	-0.04	-0.10	1	
ТРН	0.10	0.09	0.00047	NC	1

NOTES: NC = not calculated (no samples with both oil & grease and TPH analyses). Wells included in correlation: DH-6, DH-13, DH-17, DH-21, DH-24, DH-26, DH-27, DH-28, and EH-60.

A general pattern of organic constituents in soils and groundwater is present on the west plant site, presumably due to historic spills and/or equipment leakage. Analyses of volatile and semi-volatile organics were conducted <u>at selected wells</u> during the <u>Comprehensive</u> RI/FS (pre-1990), and also during the post-RI monitoring period (1990-1997). The results from both periods of monitoring showed no detectable volatile organics and only low or trace concentrations of semi-volatile acid and base/neutral compounds that are typical of heavier fuel oils. Based on historical information and the weathered broken down signature of the detected organics, the RI report concluded the source of organics observed on the plant site was fuel oil, probably used to fire sinter machines in the 1920s and 1930s.

As noted above, the highest concentrations of organics are at DH-27. Free product was observed in monitoring well DH-27 during Post-RI/FS monitoring in November 1996. Samples <u>for</u> organic analyses were subsequently collected from DH-27 and an adjacent well, DH-28, on December 9th and 10th, respectively. Asarco environmental personnel investigated possible sources of the diesel and believe that it may have been the result of leaking mobile equipment. An Asarco contractor was working in the New Direct Smelt Building (located upgradient of DH-27) during the fall of 1996. Some of his equipment was reported to be leaking diesel or hydraulic fluid. However, the exact quantity and timing of the release was unknown. The equipment was repaired and removed from the area in October 1996.

Since that time, DRO concentrations in the three subsequent biannual sampling events of DH-27 have progressively decreased (May 1997, November 1997, May 1998) were 91 mg/l, 39 mg/l, and 30 mg/l, respectively. None of the subsequent sampling events encountered free product on the static water surface. During these four sampling events, the DRO concentration in the adjacent DH-28 well has remained relatively unchanged at approximately 1 mg/l.

Based on the low concentrations of organics present throughout most of the site (excluding DH-27) compared to arsenic concentrations, along with the lack of any statistical correlation between these constituents in groundwater, organics do not appear to be a significant factor governing subsurface arsenic transport on the East Helena Plant site.

4.5 FATE AND TRANSPORT

This fate and transport discussion addresses:

- Potential routes of contaminant migration
- Environmental chemistry
- Groundwater transport of arsenic including:

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- The Comprehensive RI/FS conceptual model of arsenic mobility, and
- Updated conceptual model

As part of the Comprehensive RI (Phase II) activities, EPA identified four primary sources of potential contamination at the East Helena plant: smelter emissions; ore storage areas; slag pile; and process fluids including process ponds and process fluid transport circuits (EPA, 1987). These sources were identified based on elevated metals concentrations found in various media in the plant site. In groundwater and surface water environments, the constituent of greatest concern is arsenic, due to its potential mobility and toxicity. Arsenic is the only constituent that is typically present in shallow groundwater downgradient of the plant site at levels exceeding MCLs (see Section 4.4.3.1). As a result, this fate and transport discussion focuses on arsenic. Visual Evidence of petroleum hydrocarbons (e.g. hydrocarbon sheen or odor) was also observed in plant site area groundwaters; however, concentrations typically do not exceed MCLs (see Section 4.4.3.2). In addition, as discussed in Section 4.4.3.2, with the exception of a localized area on the plant site, only low or trace concentrations of organics constituents have been detected, and a statistical evaluation of organic parameters and arsenic concentrations shows no correlation for these parameters at the plant site.

4.5.1 Potential Routes of Migration

Primary contaminant pathways are identified in Figure 4-5-1. The CC/RA examines plant site soil, groundwater and surface water pathways. As indicated in Section 1.1, air emissions pathways to off-site receptors are not addressed in this CC/RA.

4.5.1.1 <u>Process Water (Process Water Ponds and Process Water Circuits) to</u> <u>Groundwater</u>

The RI identified the primary cause of elevated arsenic and metals in groundwater as seepage from process ponds and losses from process water circuits. Of the metal parameters examined during the RI and post-RI investigation periods, arsenic is the most mobile in the



groundwater system. The major source of arsenic in groundwater is associated with process fluid losses from the former speiss pond and pit area, and from the acid plant water treatment facilities and its associated drying areas. In the past, losses from the main process water circuit, and from process ponds including Lower Lake and Thornock Lake contributed lesser amounts of arsenic to groundwater. The process water circuits, including the main plant water circuit and the acid plant water circuit, remain potential sources of arsenic and metals to groundwater.

4.5.1.2 Soil to Groundwater Pathway

Arsenic and metal bearing soils are present on the plant site (Section 4.1.2) above and below the water table. Since the majority (estimated 63 percent) of the site is paved, only a portion of soils on the plant site are exposed to rainfall infiltration. Water that infiltrates through exposed soils can dissolve or desorb arsenic and metals from the soils, carrying soluble constituents to groundwater. In addition to precipitation infiltration, soils also may be contacted and constituents solubilized by water released from leaking subsurface lines on the plant site. Last, arsenic and metals present in soils below the water table may be mobilized by groundwater. In the groundwater system the concentrations and forms of arsenic and metals can change significantly due to adsorption, redox changes, pH changes and other contaminant attenuation mechanisms (see Section 4.5.3).

4.5.1.3 Groundwater to Surface Water Pathway

Arsenic and metals derived from historic plant site activities are present in groundwater beneath the site. Based on hydrogeologic information, the direction of groundwater flow beneath the plant site is generally to the north and northwest. However, local groundwater flow to Prickly Pear Creek (the primary surface water resource in the vicinity of the plant site) occurs as seepage from Lower Lake through the earthen berm that separates the pond and the creek. As a result, there is a component of groundwater flow on the northeast side of Lower Lake that flows toward Prickly Pear Creek. Although groundwater flow at the Lower Lake berm is evident, there appears to be little interaction between groundwater and Prickly Pear Creek north of Lower Lake (see Sections 4.3.1.1 and 4.4.2). Data collected as part of the Comprehensive RI/FS have shown a small but measurable increase in dissolved manganese and arsenic in Prickly Pear Creek adjacent to Lower Lake (see Section 4.3.1.2).

4.5.1.4 Surface Water to Groundwater Pathway

Streamflow losses provide a potential pathway for transport of contaminants from surface water to groundwater. Although potential Prickly Pear Creek losses to groundwater in the vicinity of the plant site are of small enough magnitude to be within flow measurement errors and cannot be quantified (see Section 4.3.1.1), monitoring wells north of the plant show evidence of seasonal groundwater chemistry and water level elevation changes due to seasonal recharge of groundwater from Prickly Pear Creek. Because arsenic and metal concentrations in Prickly Pear Creek are less than concentrations in groundwater, surface water is not considered to be an important source or pathway of arsenic and metals loading to groundwater.

Surface water runoff from the plant site is a potential pathway of arsenic and metals to groundwater. In 1997, a storm water containment tank system was installed to contain runoff north of the plant site (see Section 4.3.3). As described above, the tank is designed to contain the 25-year 24-hour storm. Secondary containment in surface basins are designed to retain up to the 100-year 24-hour storm event and offer a potential pathway for surface water infiltration to groundwater.

4.5.1.5 Soil to Surface Water Pathway

Erosion and transport of soil as overland runoff to surface water provides a potential contaminant pathway. With the completion of the large storm water improvements project in 1997 (see Section 4.3.3), storm water discharges to surface water could potentially occur only when the 100-year, 24-hour storm event is exceeded. Even under these conditions there would be no direct outfall to surface water bodies, since storm runoff overflow would run into a large field.
Erosion of the slag pile, particularly in the area where the slag pile abuts and is in contact with Prickly Pear Creek, is also a potential pathway to surface water and Prickly Pear Creek (see Section 6.3 Comprehensive RI/FS and Section 4.3 of this report). Stream sediment sampling results show very limited evidence of water quality effects, however, there is visual evidence of slag in Prickly Pear Creek sediments adjacent to the plant site.

4.5.2 Environmental Chemistry

A detailed description of the environmental chemistry of arsenic, metals (cadmium, copper, iron, lead, manganese, and zinc) and petroleum hydrocarbons is in Section 8.2 of the Comprehensive Remedial Investigation/Feasibility Study (Hydrometrics, 1990a). In general, the fate of arsenic and metallic contaminants is determined by their chemical properties, and geochemical changes (e.g., pH, redox potential, ionic strength, etc.) that take place in the environment. <u>Brief summations of the environmental chemistry of arsenic, cadmium, lead, and zinc are presented in this section, with emphasis on arsenic, the contaminant of greatest concern on the site.</u>

Arsenic

Several biogeochemical processes including chemical speciation, precipitation, adsorption, biotransformation, and volatilization affect the fate and transport of arsenic in environmental media. Although arsenic can exist in several oxidation states (+5, +3, +1, -3, and 0) in the natural environment, the most predominant oxidation states found in natural waters are the +5 (As V) and +3 (As III) oxidation states. Both As (V) and As (III) hydrolyze to form triprotic acids in water. The dominant aqueous species of arsenic is determined by pH and redox (Eh) conditions as shown by the Eh-pH diagram in Figure 4-5-2. Although the Eh-pH diagram in Figure 4-5-2 applies to conditions at 25° C, adjustment of equilibrium constants to temperatures more representative of groundwater temperatures (e.g., 10° C) does not appreciably alter the general stability fields shown in Figure 4-5-2. —In oxidizing environments likely to exist in most surface waters and shallow groundwaters without long



residence times, As (V) species predominate. In reducing conditions, As (III) species predominate. Because of the variations in redox state and pH found in plant process waters and groundwaters, chemical speciation is likely an important factor controlling the fate of arsenic on site, particularly in the groundwater.

In soil and aquatic environments, the transport of arsenic is dominated by adsorption/ desorption mechanisms. Although both As (III) and As (V) species adsorb to metal oxide and clay surfaces, As (V) has been demonstrated to have greater adsorption affinities under most conditions (As III can be more strongly adsorbed at high pH; Raven et al., 1998). Adsorption of both As (III) and As (V) decreases with increasing pH above pH 7 to 9 and with increasing salinity (Gupta and Chen, 1978). These results suggest that arsenic adsorption is most important in aerobic, neutral to acidic, fresh waters. Under anoxic, alkaline, or saline conditions, arsenic is expected to be weakly adsorbed. Because aquifer materials on the site contain abundant clay and metal oxide materials, adsorption is believed to be an important mechanism for attenuation of arsenic in groundwater. The varying redox, pH, and salinity conditions in site groundwater suggest that adsorption behavior of arsenic in site groundwater will be variable.

Under certain conditions, coprecipitation of arsenic with hydrous oxides of iron and manganese, and/or adsorption of arsenic on freshly precipitated hydrous iron and manganese oxides, appears to be a dominant pathway for the removal of dissolved arsenic from aqueous systems. Both As (III) and As (V) have been reported to adsorb/coprecipitate with hydrous iron and manganese oxides (Ferguson and Gavis, 1972; Raven et al. 1998, Belzile, 1988; Belzile and Tessier, 1990; Peterson and Carpenter, 1986; Agett and Roberts, 1986). Several lines of evidence suggest that adsorption and/or coprecipitation of arsenic with iron and manganese oxides is the dominant mechanism for attenuation of arsenic in site groundwater:

• Iron and manganese oxides are abundant in aquifer materials on site;

- Sequential extraction analyses of aquifer materials (discussed in Sections 4.4.3 and 8.3.1 of the Comprehensive RI/FS) indicate enrichment of arsenic in iron and manganese mineral phases; and
- Groundwater chemical data suggest removal of iron and manganese from groundwater by oxidation and subsequent precipitation (see Section 4.5.3), providing a mechanism for coprecipitation and fresh oxide surfaces for adsorption.

<u>Eh-pH diagrams for iron and manganese, showing stable species under various redox and pH</u> conditions, are shown on Figures 4-5-3 and 4-5-4.

Arsenic is also subject to biotransformation and volatilization, however, these mechanisms are not believed to be important for plant site waters. Biologically mediated transformation of As (III) to methylarsines can occur under very reducing conditions such as occur in flooded soils. Such conditions do not commonly occur on the plant site. Similarly, although volatilization of methylated arsenic compounds and arsine (in highly reducing environments) can occur, highly reducing environments necessary to produce methylated arsenic compounds are not believed to exist on the plant site with the possible exception of marsh deposits associated with Upper and Lower Lakes.

<u>Cadmium</u>

Cadmium exists in the +2 oxidation state in the natural aqueous environment, and changes in the redox status of the system do not affect this oxidation state. Solids that may exert an influence on cadmium mobility include cadmium sulfide (CdS) under reducing conditions, and cadmium hydroxide (Cd(OH)₂) or cadmium carbonate (CdCO₃) under oxidizing conditions. Carbonate forms may be especially important in calcareous soils (Baes and Mesmer, 1976).

<u>Cadmium can be found in several chemical forms, ranging from simple equated ions and metal-</u> inorganic complexes to metal-organic forms. It has been shown to interact with ligands such as

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OH-, Cl-, CO_3^{-2} , and SO_4^{-2} in aqueous solutions (Long and Angino, 1977). Bingham et al. (1984) reported that cadmium complexes readily with chloride and sulfate in soil solutions in such a way that its availability and transport is significantly influenced. This mechanism may be important in plant site groundwaters with elevated chloride and sulfate concentrations. Humic substances can also account for most of the complexation in natural waters.

Sorption processes are considered the most important factor in reducing the aquatic load and transport velocity of cadmium. Adsorption onto mineral surfaces and organic materials, in addition to co-precipitation with hydrous metal oxides and isomorphous substitution in carbonate minerals decreases the aqueous concentrations of cadmium. During adsorption, competition between cations for adsorption sites strongly influences the behavior of cadmium. The presence of alkaline earth metal ions such as Ca⁺² and Mg² reduces the adsorption of cadmium by soils, aluminum, manganese and iron oxides, and clay minerals.

<u>Lead</u>

Lead is a metal that can exist in three stable oxidation states: 0, +2, and +4. Metallic lead and the common lead minerals (sulfide, sulfate, and carbonate) are normally insoluble in water, but can be solubilized by some acids. In groundwater systems, the small amount of leachable lead contained in most lead ores is readily readsorbed by ferric hydroxide or combines with carbonate or sulfate ions to form insoluble compounds (Hem 1976). Throughout most of the natural environment, the divalent form Pb⁺² ion is the stable species of lead. The more oxidized solid (PbO₂) is stable only under highly oxidizing conditions and probably has little significance in the aquatic environment (Callahan et al., 1979).

Except for severely contaminated environments, where precipitation is important, the concentration of lead in aquatic systems is controlled by sorption processes. Some researchers found that in the presence of kaolinite, illite, and montmorillonite clays at pH ranging from 5.0 to 7.0, most lead ions were precipitated and sorbed probably as low solubility ions such as PbOH⁺ and Pb₄(OH)₄⁺⁴ (Demayo et al, 1982). The capacity of soils to adsorb lead increases

with pH, cation exchange capacity, organic carbon content, and phosphorus levels. Huang et al. (1977) reported that at low pH, lead may actually be negatively sorbed (repelled from the adsorbent surface).

The presence of suspended or dissolved organic material in water can also greatly effect the chemical form in which lead will be present. Lead may be adsorbed directly onto particulate organic matter, or form organo-metallic complexes, which increase the affinity of lead for particle surfaces such as clays and other minerals. Overall, only a small percent of the total lead contained in soils is expected to be readily available to groundwater.

<u>Zinc</u>

Zinc in the aqueous environment occurs exclusively in the +2 oxidation state and is insensitive to redox conditions. Common zinc minerals include sphalerite (ZnS), smithsonite (ZnCO₃), willemite (Zn₂SiO₄) and zincite (ZnO). Zinc complexes with common organic and inorganic ligands are quite soluble in near neutral or acidic waters, such that zinc is one of the most mobile of the transition metals (Callahan, 1979). In very reducing environments, precipitation of zinc sulfide may exert control over zinc concentrations; however, the dominant fate of zinc is probably sorption to hydrous metal oxides, clays or particulate organics in soils and sediments. Association of zinc with particle surfaces is highly dependent on the chemical speciation of zinc (i.e., the relative abundances of inorganic complexes, organic complexes, and the free zinc ion).

Manganese and iron oxides are the predominant phases controlling the adsorption behavior of zinc in soils (Kinniburgh and Jackson, 1982; Balistrieri and Murray, 1982). Zinc may be incorporated into manganese and iron oxides during formation (coprecipitation), or may adsorb to the surface of preexisting materials. Zinc may also associate with calcite phases in the soil environment (Zachara et al., 1993). Adsorption and coprecipitation of zinc are favored at higher pH values

In some waters, adsorption of zinc can be reduced due to the presence of high concentrations of divalent alkaline metals (Mg^{+2} , Ca^2) which can compete with zinc for the adsorption sites in soils. As salinity increases, zinc may be desorbed from sediments due to displacement by major cations (Callahan, 1979).

4.5.3 Groundwater Transport of Arsenic

An evaluation of groundwater transport of arsenic including a conceptual model describing arsenic mobility and arsenic attenuation mechanisms, and a numeric groundwater transport model is presented in Section 8.3 of the Comprehensive RI/FS (Hydrometrics and MDI, 1987). The following sections discuss and summarize conclusions reached in the Comprehensive RI/FS and present further documentation in support of the conceptual model based on data collected after the RI/FS.

4.5.3.1 Comprehensive RI/FS Conceptual Model of Arsenic Mobility

Although post-RI data (Sections 4.3 and 4.4) show some water quality changes have occurred since the completion of the RI/FS, the general concepts and mechanisms governing chemical mobility remain relevant to current conditions on the site. This section recounts the water quality relationships and the fate and transport mechanisms established in the RI/FS. In Section 4.5.3.2 the RI/FS transport model is then compared to recent water quality trends.

The primary conclusion reached in the Comprehensive RI/FS regarding arsenic mobility in plant groundwater is that the mobility of arsenic is controlled by groundwater pH and redox conditions, and adsorption/coprecipitation of arsenic by iron and manganese oxides. Mobility of arsenic from the speiss granulating pond and pit area (the primary source of arsenic to the groundwater system) and Lower Lake (a secondary source of arsenic to groundwater) is limited by redox and pH changes that occur in groundwater downgradient of the sources.

Speiss Pond and Pit Area and Downgradient Groundwater

Based on calculated redox potential (Eh), As(III)/As(V) ratios, dissolved oxygen concentrations, and pH, the RI/FS transport analysis divided groundwater downgradient of the speiss pond into distinct redox and pH regions exhibiting distinct differences in arsenic behavior.

Figure 4-5- $\frac{5}{2}$ shows RI and post-RI groundwater concentration trends in arsenic, sulfate and chloride. Dissolved oxygen concentrations and groundwater pH values during the RI period (as well as other recent data) are shown on Figure 4-5- $\frac{6}{2}$. At the time of the RI, process water in the speiss pond and groundwater immediately downgradient (0 to 600 feet downgradient of the speiss pond) were reduced (mean dissolved oxygen concentrations are less than 1 mg/L) and had high pH values ranging from approximately 10 to 12. Groundwater in this region contained high arsenic concentrations (e.g. average of 496 mg/L at DH-21). In spite of the reducing conditions, both speiss pond water and groundwater in this region contained high alkalinity of these waters.

Groundwater further downgradient of the speiss pond (approximately 600 to 1600 feet downgradient) was near neutral in pH and somewhat less reducing (As (III) dominant with dissolved oxygen concentrations ranging from 1 to 3 mg/L). Arsenic concentrations remained high, slightly less than upgradient concentrations, and little attenuation of arsenic was indicated. Iron and manganese concentrations in this groundwater region were also quite high (approximately 50 mg/L and 30 mg/L, respectively). The RI concluded that the observed increase in iron and manganese in this region was likely due to dissolution of iron and manganese from aquifer materials. Iron speciation data collected at wells DH-17 and DH-24 indicated that dissolved iron was essentially all in the reduced (Fe (II)) form.

Further downgradient of the speiss pond (approximately 1,600 to approximately 2,000 feet downgradient, represented by well EH-60) there was an abrupt, approximately 100 fold



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decrease in groundwater arsenic concentrations (the average arsenic concentration at EH-60 was 1.43 mg/L at the time of the RI). Dissolved iron concentrations also were much lower than upgradient (average of 0.025 mg/L vs average of 50 mg/L upgradient) and Fe (II) was not detected. Manganese concentrations in groundwater in this region remained high (approximately 40 mg/L) suggesting groundwater redox conditions were not sufficiently high for manganese removal by oxidation/precipitation mechanisms. Although dissolved oxygen concentrations, and iron (II) data indicate that groundwater in this region was more oxidized than upgradient groundwater. In this region, arsenic was present almost exclusively as As (V). The RI/FS concluded that the pronounced decrease in arsenic concentrations in this region was supported by the following findings:

- Groundwater data show removal of iron accompanied by an increase in the oxidation state of groundwater.
- Iron is known to be insoluble in neutral, slightly reducing to oxidizing waters and is known to form hydrous iron oxide/hydroxides mineral phases (typically ferrihydrite (Fe(OH)₃) or goethite (FeOOH)) under these conditions.
- Arsenic is known to readily adsorb/coprecipitate with hydrous iron oxide/hydroxide materials.
- Sequential extraction analyses of aquifer materials indicate enrichment of arsenic in amorphous iron phases.
- In contrast to the major reductions in arsenic concentrations, there are only minor decreases in concentrations of conservative ions such as sulfate and chloride downgradient of the speiss pond. The much greater decrease in arsenic indicates processes other that mixing and dilution must be responsible for the removal of arsenic from solution.

At further distances downgradient (approximately 3,200 feet downgradient, represented by well EH-62), dissolved oxygen concentrations increased (approximately 4 to 5 mg/L), arsenic concentrations (approximately 0.01 mg/L) were near background levels for the Helena Valley, arsenic (III) was not detected, and iron and manganese concentrations were low (approximately 0.02 mg/L).

In summary, based on the transport analysis presented in the RI, migration of arsenic in groundwater from the speiss pond was controlled primarily by the redox state of groundwater. Under the reducing conditions present in the speiss pond and adjacent groundwater, arsenic is mobile. Under the more oxidizing conditions present in ambient off-plant site groundwater, arsenic is much more readily attenuated.

In general, redox conditions in natural (uncontaminated) groundwater are determined by the relative rates of introduction of oxygen by circulation and the consumption of oxygen by decomposition of organic matter or occasionally by oxidation of sulfides or ferrous silicates. The most important variables in natural systems (Drever, 1982) appear to be:

- 1. The oxygen content of recharge water.
- 2. The distribution and reactivity of organic matter and other potential reductants in the aquifer.
- 3. The distribution of potential redox buffers in the aquifer (e.g. iron and manganese oxide/hydroxides).
- 4. The circulation rate (or residence time) of groundwater within the aquifer.

Redox conditions in groundwater on and off the plant are variable and in many cases are likely determined by the four factors listed above. Examples of these factors are:

- Groundwater adjacent to Prickly Pear Creek in the City of East Helena which contain higher than average dissolved oxygen levels presumably due to recharge by oxygenated surface water in Prickly Pear Creek; and
- Groundwater downgradient of Lower Lake (DH-4) which contains lower than average dissolved oxygen levels, presumably due to recharge that occurs from leakage through the organic-rich (i.e., reducing) sediments in Lower Lake and the likely presence of organic-rich deposits underlying the slag pile.

The redox state of groundwater downgradient of the speiss pond may potentially be influenced by additional factors. The arsenic content of speiss pond water (an average concentration of approximately 1,600 mg/L) represents a very large potential reductant source and/or redox buffer. Although no arsenic speciation data is available for speiss pond water, groundwater approximately 50 feet downgradient of the speiss pond (well DH-21) contains an average of approximately 390 mg/L arsenic (III). These high concentrations of reduced arsenic may produce reducing conditions in groundwater downgradient of the speiss pond.

Evidence of petroleum hydrocarbon contamination has been observed in and downgradient of the speiss pond area in both soils and groundwater (see Section 4-4-2). Although volatile and semi-volatile fractions of the petroleum hydrocarbons have apparently been degraded by weathering, some long-chain residuals remain in soils at and just above the water table. While it is possible that petroleum hydrocarbons may contribute to the reducing conditions in the area and thus exhibit some influence on metals mobility, there does not seem to be a statistical correlation between the presence of organics and either redox state or arsenic concentrations at the site (see discussion in Section 4.4.3.2).

Lower Lake and Downgradient Groundwater

Graphs of parameter concentration trends (similar to Figures 4-5-5 and 4-5-6 for the speiss pond flowpath) have been prepared for Lower Lake and downgradient wells. Figure 4-5-7 shows RI and post-RI groundwater concentration trends in arsenic, sulfate and chloride. h:\files\007 asarco\0867\ccra report\r99cra1.doc\HLN\2/2/07\065\0096 2/2/07/10:09 AM





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Dissolved oxygen concentrations and groundwater pH values during the RI period (as well as other recent data) are shown on Figure 4-5-8. Unlike the speiss pond area, monitoring wells are not present along a distinct flowpath on the plant site downgradient of Lower Lake, due to the presence of the slag pile and associated difficulties with well completion; however, wells downgradient of the slag pile are present along a flow path. Figures 4-5-7 and 4-5-8 summarize available data for key parameters downgradient of Lower Lake.

The RI/FS transport analysis showed that the changes in groundwater redox conditions and arsenic concentrations downgradient of Lower Lake, although not as dramatic, were similar to those observed downgradient of the speiss pond. Groundwater near Lower Lake and downgradient for a distance of approximately 2,600 feet was found to be relatively reducing with low dissolved oxygen concentrations, elevated iron and manganese concentrations, and the arsenic (III) or reduced form of arsenic predominant. Over this distance of 2,600 feet, arsenic concentration decreases generally paralleled decreases in concentrations of the conservative ions sulfate and chloride indicating that arsenic reductions were due primarily to dilution/dispersion processes and that little geochemical attenuation of arsenic was occurring. Between 2,600 and 3,200 feet (where recharge of oxygen-rich water from Prickly Pear Creek is evident) groundwater arsenic concentrations were reduced by a factor of approximately 300. This decrease in arsenic concentration is coincident with a change from arsenic (III) dominant to arsenic (V) dominant conditions, large decreases in iron and manganese concentrations, and increases in dissolved oxygen concentrations. Sulfate and chloride concentrations only decline slightly over this same distance, indicating reduction in arsenic concentrations by attenuation rather than dilution/dispersion. Similar to the speiss pond area, groundwater data downgradient of Lower Lake suggest removal of arsenic by coprecipitation/adsorption with hydrous iron oxides/hydroxides in response to increasing oxidation state in groundwater. Thus, groundwater chemistry changes downgradient of Lower Lake provide further indications of redox control of arsenic mobility.



FIGURE 45.8. LOWER LAKE AND DOWNGRADIENT WELL WATER QUALITY TRENDS (BY TIME INTERVAL)

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4.5.3.2 Updated Conceptual Model Based on Post-RI/FS Data

Speiss Pond and Downgradient Groundwater

Groundwater chemistry data collected downgradient of the former speiss pond since the Comprehensive RI/FS (i.e., after 1989) continue to support the conceptual model of control of arsenic mobility by redox conditions. However, groundwater quality downgradient of the former speiss pond has shown some changes since the RI/FS due to remediation of the speiss pond and speiss pit areas, and possibly due to other factors including remediation of the acid plant area. As a result, downgradient arsenic concentrations and arsenic behavior in groundwater have changed somewhat.

Briefly, remedial activities and process changes in the vicinity of the Speiss Pond and Pit have included:

- Installation of an HDPE liner in the speiss pond prior to completion of the Comprehensive RI/FS (August 1988);
- Construction of a new speiss settling tank with secondary leak detection to replace the speiss pond in summer/fall 1989. During construction of the new speiss settling tank, soils under approximately one half of the former pond and under the new tank were excavated to a depth of 20 feet (the depth of the water table);
- Replacement of water granulation of speiss with air water mist granulation of speiss in the plant operation (April 1991);
- Excavation of soils under the remaining half of the former speiss pond (not excavated in 1989) in November 1992; and
- Excavation and removal of soils in the speiss pit area in July 1995.

These changes in the construction and operation of the speiss processing area likely resulted in a reduced contribution of process-water-derived arsenic to soils and groundwater from the speiss processing area. Excavation and removal of contaminated soils in the area also likely reduced the potential loading of arsenic from soils to groundwater.

Downgradient and temporal changes in groundwater chemistry (As (III), As (V), sulfate, chloride, pH, zinc, and dissolved oxygen) for various time periods generally corresponding to periods of construction/remediation activities are shown in Figure 4-5-3 and Figure 4-5-4. The graphs show average concentrations for five general time periods:

- 1. The RI (1986-1988) (averages based on data collected during the RI);
- 2. Pre-1993 (averages based on data collected during 1990-1992);
- 3. Post-1993 (averages based on data collected during 1993 through 1995, following completion of remediation of the speiss pond area);
- 4. Post-1996 (averages based on data collected during 1996 and 1997, representing "current" plant site conditions); and
- 5. Overall Mean (averages based on the entire period of record);

In general, the changes in groundwater chemistry downgradient of the former speiss pond and pit area since the Comprehensive RI/FS indicate:

- Highly variable arsenic concentrations in groundwater (well DH-21) immediately adjacent to the former speiss pond area;
- Reductions in concentrations of arsenic and metals in plant site monitoring wells downgradient of the former speiss pond and pit area coincident with reductions in sulfate and chloride concentrations and reduction in As (III)/As (V) ratios (increase in oxidation state);
- Increases in concentrations of arsenic near the edge of the contaminant plume (near well EH-60) coincident with decreasing sulfate concentrations and decreasing oxidation state of groundwater in the area.

At DH-21 in the immediate source area, arsenic concentrations have fluctuated over a wide range with no clear long-term trends. Arsenic concentrations ranged from over 600 mg/L in 1989 to about 200 mg/l in the 1990 to 1993 period. Since 1990, concentrations show alternating rising and falling patterns suggestive of continued periodic inputs of arsenic to the groundwater system. While residual arsenic in soils may be a contributing source to groundwater in this area (excavation of soils could not be conducted below the water table, or where railroad tracks or buried utilities were present), the elimination of surface sources of arsenic to groundwater in this area has not been confirmed. Runoff from the speiss loading areas has been determined to have extremely high arsenic concentrations (section 4.2) and therefore may also be a factor if an infiltration pathway exists. A discussion of the potential sources of arsenic to groundwater is included in Section 5.0.

While source area reductions are not evident at monitoring well DH-21, water quality improvements are clearly evident in downgradient plant site wells, including DH-13, DH-17, and DH-24. An exception is well EH-60, located just north of the plant site near the lower boundary of the plume, where arsenic concentrations have continued to increase. These water quality trends are generally consistent with the conceptual model presented in the Comprehensive RI/FS (described above), as follows: source reductions will initially result in reduced arsenic concentrations in nearby downgradient wells, while residual arsenic from the source continues to migrate (limited by retardation and geochemical attenuation) at the downgradient limits of the plume. Thus, wells further downgradient from the former source will require a longer period to show the effects of source removal relative to nearby wells.

Concentrations of sulfate, chloride, and arsenic in downgradient wells DH-13, DH-17 and DH-24 have declined steadily since 1990 (as described in Section 4.4.3). These wells are downgradient of the former speiss pond at distances of about 400 feet, 900 feet and 1400 feet, respectively (Figure 4-5-5). Reduction in concentrations of arsenic, sulfate and chloride have been the greatest closest to the former speiss pond area. As shown on Figure 4-<u>5-9</u>, in the





Figure 4-5-9.

Percent Reductions in Dissolved Arsenic and Sulfate in Plant Site Wells Downgradient of the Speiss Pond/Pit Area

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period following remediation of the speiss pond area arsenic concentrations have shown reductions of 87% at DH-13, 68% at DH-17, and 60% at DH-24.

At well EH-60 (approximately 2,000 feet downgradient of the speiss pond area), sulfate concentrations also have shown a decreasing trend since 1992, similar to that observed for wells DH-13, DH-17 and DH-24. Arsenic concentrations, however, do not show a similar decreasing trend at EH-60. As described in Section 4.4.3, arsenic concentrations have steadily increased (from approximately 1 mg/L in 1988 to approximately 10 mg/L in 1997). Coincident with this increase in arsenic concentrations, the dominant form of arsenic has changed from essentially all As (V) in 1988 to approximately equal amounts of As (III) and As (V) during the post-1996 period.

Potential causes of the arsenic concentration trend at EH-60 are:

- 1. Organic constituents present in groundwater at well EH 60 have previously been considered (in Section 4.4.3.2 of this report) as a potential explanation for increased arsenic mobility near EH 60 in plant site and downgradient groundwater. The presence of organic constituents in groundwater can generate reducing conditions and result in increased arsenic mobility. In this case, At well EH-60, however, organics concentrations are detectable but low (with the exception of a single oil & grease result of 60 mg/L obtained in December 1987), and have shown no indication of any recent concentration changes. As discussed in Section 4.4.3.2 no statistical correlation is evident between organic concentrations and concentrations or oxidation states of arsenic. The presence of low level organics at EH-60, therefore, is probably not the primary cause of the observed arsenic increases.
- 2. Another factor (other than organics) may be stimulating formation of a more reduced groundwater environment at well EH-60, thereby resulting in increased mobilization of arsenic (III). While there has been a progressive increase in As (III) concentration at EH-60 over the last few years, there has been no observable reduction in dissolved oxygen concentrations or increase in dissolved iron concentrations, which would be

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indicative of a lower redox state. Based on the absence of change in these other indicators, the observed arsenic concentration increases (including As (III)) may simply reflect gradually increasing inputs of the reduced species of arsenic.

3. Alternatively, the increase in arsenic concentrations at EH-60 may be indicative of a very gradual advance of arsenic in groundwater as the geochemical mechanisms for attenuation at the plume front (e.g., adsorption sites, amounts of iron or manganese oxides) are slowly depleted. Such an advance, over a period of decades, is predicted by the RI/FS solute transport model.

Although arsenic in groundwater is believed to be attenuated by adsorption/coprecipitation with iron oxides/hydroxides upgradient of well EH-60, a gradual advance of the plume front would result in increasing As(III). While the RI/FS solute transport model indicated there would be a gradual advance of the plume, the accompanying discussion of the model also notes that the predicted concentrations and rate of advance reflect a worse case scenario since the model does not account for removal of arsenic through processes of geochemical attenuation. Indeed, while the model correctly notes a plume advance, it greatly overpredicts the present concentrations and the estimated time for reductions to occur. For example, the model predicts arsenic concentrations at DH-24 would take 50 years to decrease to their current concentrations after speiss pond remediation. The model also predicts arsenic concentrations should be in the range of 1 to 2 mg/L near downgradient well EH-62. In fact, EH-62 and other wells in this area show no evidence of arsenic increases.

The arsenic plume has advanced very little since the RI period (ten years), and downgradient arsenic concentrations have remained at background levels due to processes of natural attenuation such as coprecipitation and adsorption of arsenic with hydrous iron oxide/hydroxide materials. Groundwater data reflect increasingly more oxidizing conditions in groundwater downgradient of EH-60, apparently due to additional influence from Prickly Pear Creek. For example, there is a five-fold increase in dissolved oxygen concentrations between EH-60 and EH-62. As explained previously, under increasingly oxidizing

conditions arsenic is much less mobile and more likely to be attenuated. For this reason, the RI predicted that it is unlikely significant arsenic increases will be observed in downgradient areas affected by Prickly Pear Creek. Despite the observed increase in concentrations near well EH-60, the absence of arsenic concentration increases in the downgradient East Helena area is consistent with the RI conceptual model of limited downgradient migration.

Groundwater Downgradient of Lower Lake

Recent groundwater quality trends downgradient of Lower Lake are generally consistent with the RI/FS conceptual model. Groundwater quality downgradient of Lower Lake generally reflects Lower Lake water quality trends, but is also affected by local redox conditions in groundwater.

Temporal changes and in groundwater chemistry trends for Lower Lake and downgradient wells are shown in Figure 4-5-7 and Figure 4-5-8. The graphs show average concentrations of key parameters for four general time periods:

- 1. <u>The RI (1986-1988) (averages based on data collected during the RI);</u>
- 2. <u>Pre-1996 (averages based on data collected during 1990-1996);</u>
- 3. <u>Post-1996 (averages based on data collected after 1996, following the dredging of Lower Lake sediments); and</u>
- 4. <u>Overall Mean (averages based on the entire period of record).</u>

Post-RI monitoring data show increasing sulfate concentrations^{*} in Lower Lake (a byproduct of the HDS water plant) and an improving (decreasing) arsenic concentrations. These trends are generally evident in downgradient wells, although arsenic concentrations in

* The HDS water treatment plant withuses hydroxide and sulfide precipitation followed by filtration to remove arsenic and metals from excess plant water and acid plant scrubber blowdown. The primary contributor of sulfate is the reagent ferric sulfate which is added to promote coprecipitation of arsenic. The HDS plant discharges to Lower Lake. h:\files\007 asarco\0867\ccra report\r99ccra1.doc\HLN\2/2/07\065\0096 22/2/07/10:09 AM downgradient plant site wells appear to be variable. As discussed in Section 4.4.3, the water quality trends at these wells may show the influence of sources other than Lower Lake.

Recent data suggest that, as concluded in the RI, groundwater redox conditions downgradient of Lower Lake appear to control arsenic mobility. In particular, water quality data show an increase in groundwater oxidation state and a decrease in arsenic concentrations in the general vicinity of Prickly Pear Creek (e.g., average arsenic concentrations decrease from 3.04 mg/L to 0.005 mg/L from DH-4 to DH-11, and from 2.31 mg/L at DH-10 to 0.769 mg/L at EH-52). Consistent with this redox change, monitoring wells downgradient of Prickly Pear Creek have shown little effect from past arsenic increases in Lower Lake or plant site wells. There are, however, low level increases in sulfate concentrations in many of the East Helena wells along the Lower Lake flow path, corresponding to increasing sulfate trends in Lower Lake as a result of the discharge of treated water from the HDS water treatment plant. The fact that sulfate increases are evident in East Helena area wells, but arsenic increases generally are not, is a further indication that geochemical attenuation in the vicinity of Prickly Pear Creek is limiting arsenic migration rather than simply dilution and mixing effects.

4.5.4 Groundwater Transport of Cadmium, Lead, and Zinc

Figures 4-4-12, 4-4-13, and 4-4-14 are isocontour plots showing the current (as of November 1997) distribution of dissolved cadmium, lead, and zinc in groundwater beneath and adjacent to the plant site. As indicated on the figures, the highest concentrations of all three metals are near the acid plant and the former acid plant sediment drying area. During November 1997, the highest concentration of cadmium on the plant site, 11.4 mg/L, was observed at well APSD-13 (near the former acid plant sediment drying area). Well DH-19, downgradient of the acid plant, showed the highest November 1997 concentrations of lead (0.161 mg/L) and zinc (30.1 mg/L). Elevated concentrations of cadmium and zinc in groundwater are present throughout the west plant site area, while elevated lead concentrations are generally limited to an area near the source area (acid plant). Elevated concentrations of these three metals do not persist downgradient of the plant site (Figures 4-4-12, 4-4-13, 4-4-14).

Overall, cadmium, lead, and zinc in plant site groundwater are present at significantly lower concentrations than the primary constituent of concern, arsenic. The observed groundwater concentration distributions of cadmium, lead, and zinc relative to source areas and likely controls on subsurface mobility are discussed individually in the following sections.

4.5.4.1 Cadmium

As shown on Figure 4-4-12, high cadmium concentrations at well APSD-13 decrease downgradient to 3.38 mg/L at DH-19 and 0.546 mg/L at DH-22. Concentrations near the former speiss pit and pond are relatively low (<0.01 mg/L), presumably due to the high groundwater pH in this area. Wells DH-8 (1.8 mg/L) and DH-23 (0.45 mg/L) also show elevated cadmium with concentrations decreasing downgradient at well DH-24 to 0.131 mg/L, and then to 0.001 mg/L or less at East Helena wells immediately downgradient of the west plant site (EH-50, EH-60, EH-51). The conspicuous decrease in cadmium concentrations from well DH-24 to well EH-60 (two orders of magnitude) occurs in a region where iron and manganese in groundwater primarily through coprecipitation and adsorption on iron and manganese oxides, as well as other soil minerals and/or organic materials.

Cadmium concentrations in groundwater generally correlate with high soil concentrations of cadmium (the lower ore storage area near DH-8, the acid plant sediment drying area near APSD-13). Well DH-23 is completed in a shallow perched aquifer (Exhibit 4-4-2), and thus is more susceptible to impacts from historical plant water seepage and other plant site activities. Soils in the former upper ore storage area between Upper and Lower Lakes have relatively high cadmium concentrations (see Section 4.1.2). However, groundwater in this area at wells APSD-11 and APSD-12 is low in cadmium (0.002 mg/L or less), indicating that cadmium is not readily leachable from the soils under existing groundwater geochemical conditions (i.e., near-neutral pH).

Slightly elevated cadmium in groundwater is also apparent at well APSD-7 east of Lower Lake (0.233 mg/L). This concentration is higher than the current concentration in Lower Lake (0.021 mg/L), thus, the source of cadmium at APSD-7 is presumed to be historically impacted soils. Low concentrations of cadmium in groundwater and Prickly Pear Creek surface water downgradient of APSD-7 (Figure 4-4-12) suggest that cadmium mobility and impacts in this area are probably limited by adsorption of cadmium to soils, and perhaps by limited groundwater flux in the area of APSD-7.

4.5.4.2 Lead

As discussed in Section 4.5.2, lead is relatively immobile in most subsurface environments due to its strong tendency to adsorb to particle surfaces. Figure 4-4-13 indicates that lead concentrations are elevated only near source areas (e.g. the acid plant soils near well DH-19), and that lead concentrations quickly decrease with distance from sources. Low groundwater pH at well DH-19 creates an environment conducive to lead mobilization from soils. As noted previously, well DH-23 (November 1997 lead concentration of 0.45 mg/L) is completed in a shallow perched aquifer (Exhibit 4-4-2), and thus is more susceptible to impacts from historical plant water seepage and other plant site activities. Concentrations decrease to near or below detection limits (0.005 mg/L) well upgradient of the plant site boundary on the west plant site (wells DH-16 and DH-8; Figure 4-4-13). Data collected to date indicate very little potential for migration of lead off the plant site.

Soils in the former upper ore storage area between Upper and Lower Lakes are relatively high in lead, as well as cadmium (Section 4.1.2). Like cadmium, however, these soils do not appear to impact groundwater lead concentrations, which are currently below laboratory detection limits (<0.005 mg/L) at wells APSD-11 and APSD-12.

4.5.4.3 Zinc

Zinc typically shows greater mobility in groundwater systems than lead, and is generally similar in geochemical behavior to cadmium. Figures 4-4-12 (cadmium distribution in