

# METAL AND ARSENIC LEVELS IN DRINKING WATER AT TWO MONTANA SUPERFUND SITES<sup>1</sup>

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**Abstract:** Surveys of the concentrations of arsenic, cadmium, and lead in potable waters collected from domestic wells, springs, and creeks were conducted in 2007 within the Clark Fork River Superfund Site, and in 2009 within the Basin Creek Superfund Site, both located in western Montana. These sites were named to the Superfund list as a result of uncontrolled releases of contaminants from hard rock mine, mill and smelter activities. The purpose of these sampling and analysis efforts was to quantify the levels of these elements in drinking water sources on private lands and to assess any human health risks from the ingestion of water. Arsenic has been identified as a human health risk at both of these sites. Surface soil concentrations of this element greater than 150 mg/kg for residential yard soils represent an unacceptable risk at the Clark Fork River Site. A residential surface soil human health risk concentration has not been established for the Basin Creek Site. Concentrations of arsenic as well as cadmium and lead were determined in waters used by residents for drinking and other household uses. Samples were collected from wells, natural springs, and creek. Results are presented and are compared to Environmental Protection Agency's Maximum Contaminant Levels and Montana's Numeric Water Quality Standards.

**Additional Key Words:** water quality, metals, arsenic, Superfund, human risk

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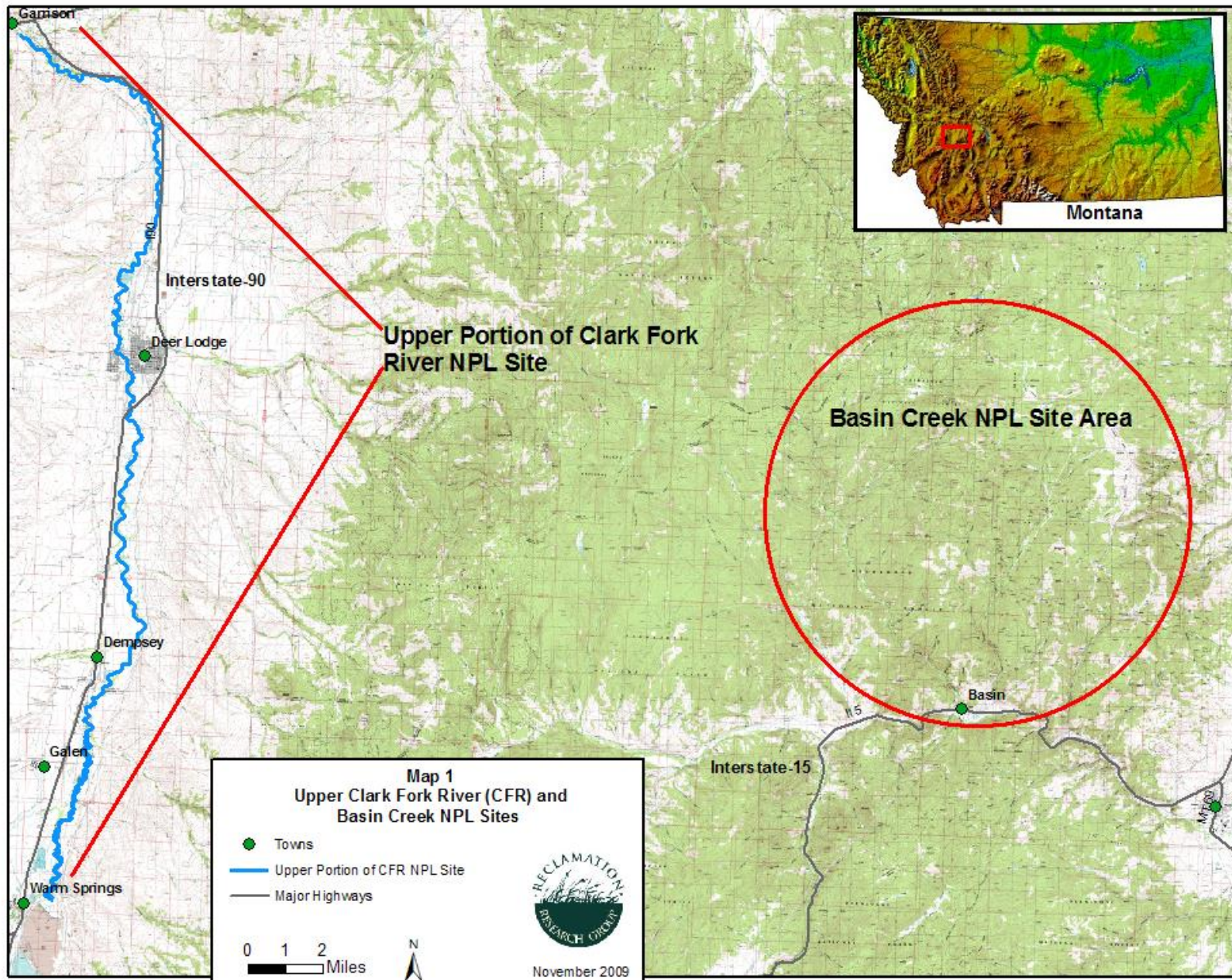
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## **Introduction**

Montana has several large contaminated areas that have been placed on the Environmental Protection Agency' National Priority List as Superfund Sites. Two of these are the Clark Fork River Operable Unit (OU) of the Milltown Reservoir Site and the Basin Creek Watershed Operable Unit of the Basin Creek Site. Both sites are located in western Montana as exhibited on Map 1. The entire flood plain of the Clark Fork River has been impacted by the fluvial deposition of mine, mill, and smelter wastes from mining activities in Butte and Anaconda, Montana. The Clark Fork River OU consists of surface water, stream bed sediments, tailings, impacted soils, groundwater, aquatic resources, terrestrial resources, irrigation ditches and related sediment deposition and contaminated property, and air located within and adjacent to the 100-year historic floodplain of the Clark Fork River. From its headwaters, the Clark Fork River flows north for approximately 43 river miles past the towns of Galen, Deer Lodge, and Garrison. This upper portion of the OU was designated by EPA as Reach A and is the area shown on Map 1. The river then runs northwest for approximately 77 river miles to the Milltown Reservoir near Bonner, Montana. A Record of Decision (ROD) for the remediation of the Clark Fork River OU was released by EPA in 2004 (EPA, 2004a). A 1987 sampling and analysis of waters from 76 domestic wells indicated four wells with arsenic levels in excess of the current Maximum Contaminant Level (MCL) of As of 10 µg/L (CH2M Hill et al., 1991). The concentrations were 12, 13, 15 and 42 µg/L. In the ROD, EPA specified waters from these wells, as well as others were to be sampled and determination of concentrations of As and metals were to be made.

The Basin Creek Watershed OU consists of surface water, stream bed sediments, tailings, impacted soils, groundwater, aquatic resources, terrestrial resources, sediment deposition and contaminated property located within a 77 square mile watershed, a tributary to the Boulder River in Jefferson County, Montana. The watershed extends from the northern edge of the Basin City limits into the surrounding headwaters of Basin and Cataract Creeks. Mining for Ag, Au, Cu, Pb and Zn began in the late 1800s in the watershed. Approximately 300 documented historic mine sites within the watershed have been documented rock, mill tailings, and mill process waters that were released into Basin/Cataract Creeks and associated tributaries as late as the 1960s and continue to be re-released to the present day..



Drinking water sources (wells) for the Town of Basin at the mouth of the Basin sub drainage were sampled in 2000 (CDM, 2005). However, drinking water sources upstream of the Basin City limits were not identified, nor sampled during the Remedial Investigation. The watershed supports a number of full and part time residents who may be at additional risk if their water supply is compromised by mining-related wastes.

### **Objectives**

The objective of these investigations was to quantify concentrations of As, Cd, and Pb in waters used by residents for drinking and other household uses. Samples were collected from wells, natural springs, and creeks. Results are compared to Environmental Protection Agency's Maximum Contaminant Levels, action levels, and secondary standards. The Maximum Contaminant Levels for As and Cd are 10 µg/L and 5µg/L, respectively, while the action level for Pb is 15 µg/L (EPA, 2009). Secondary standards for Cu and Zn in drinking water are 1000 µg/L and 5000 µg/L, respectively (EPA, 1992).

### **Methods and Sampling Locations**

Residential home owners were identified and access agreements to sample their drinking water source were obtained. The sampling methodology for the domestic wells sampled in the Clark Fork River OU was detailed in the Quality Assurance Project Sampling Plan (CH2M Hill, 2007). A Quality Assurance Project Sampling and Analysis Plan (CH2M Hill and RRG, 2009) was prepared for the collection of water from sources of drinking water in the Basin Creek Watershed. These sources included wells, creeks, and springs. The documents required that water supply be sampled at a collection point closest to the well. Any water treatment devices such as carbon or other filters, water softeners, ion exchange columns, reverse osmosis were noted and sampling occurred prior to water reaching such treatment devices, if possible. Water from the sampling point was allowed to flow for at least 5 minutes prior to collection. New one liter polyethylene bottles that contained approximately 2 ml of HNO<sup>3</sup> acid as a preservative were used to hold water samples from each well. One bottle was filled directly from the well's tap and this sample was designated for determination of total metals and As concentrations. Water from the well's tap passing through a 0.45 µ membrane filter into a second pre-acidified polyethylene bottle was designated for determination of dissolved metals and As levels. Both total and dissolved concentrations were determined in waters collected within the Clark Fork



River OU, while total concentrations only were determined in water samples collected within the Basin Creek Watershed OU.

Sample containers were then placed in an iced cooler for holding and transportation, under chain of custody to analytical laboratories. In the field, the location of each sampled well, spring, and creek was recorded using a Global Positioning System (GPS) and a digital image of the well head sampling port, spring or creek were taken. The domestic water samples were analyzed for the following field parameters: specific conductance, temperature, and pH using calibrated field instruments. *[Note: specific sampling location data for these field measurements are not reposted in this paper. The pH values were all circum-neutral, specific conductance levels were low (100 - 500 $\mu$ S), and temperature ranged from about 9°C to about 24°C].* For the Clark Fork River OU samples, filtered and unfiltered samples from each location were analyzed for dissolved and total concentrations of As, Cd, Cu, Pb, and Zn . For the Basin Creek Watershed OU samples, unfiltered samples from each location were analyzed for total levels of As, Cd, and Pb. Standard analytical methods were EPA Method 200.7- Trace Elements in Water, Solids, and Biosolids by Inductively Coupled Plasma-atomic Emission Spectrometry (EPA 2001) for the Clark Fork River OU samples, and EPA Method 200.8 – Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-mass Spectrometry (EPA 1994) for the basin Creek Watershed OU samples. Resulting data were validated using EPA’s Contract Laboratory Program, National Functional Guidelines for Inorganic Data Review (EPA 2004b).

## **Results**

Sampling well locations within the Clark Fork River OU are exhibited on Map 2a and 2b. Locations of the wells, springs, and creeks that were sampled within the Basin Creek Watershed are shown on Map 3.

### **Clark Fork River OU**

A total of 47 domestic water supply wells were identified for sampling as part of this study. Twenty eight (28) corresponded to previously sampled wells (1987 screening study) and 18 represented new wells constructed after the 1987 study. During the field activities, two well owners (Well No. 3 and Well No. 13) declined to have their wells sampled, and one of the residences had two wells serving potable water on their property (Wells No. 9 and 46). In total,

46 well samples were drawn from 45 residences for this study. Analytical data for total concentrations of As, Cd, Pb, Cu, and Zn are shown in Table 1.

Table 1. Concentrations ( $\mu\text{g/L}$ ) of total arsenic, cadmium, lead, copper, and zinc in domestic waters collected from wells within the Clark Fork River OU in 2007.

<b>Sample Name</b>	<b>Water Source</b>	<b>Total Arsenic <math>\mu\text{g/L}</math></b>	<b>Total Cadmium <math>\mu\text{g/L}</math></b>	<b>Total Lead <math>\mu\text{g/L}</math></b>	<b>Total Copper <math>\mu\text{g/L}</math></b>	<b>Total Zinc <math>\mu\text{g/L}</math></b>
DW-01	Well	5.1	< 1.0	0.4	2.2	30.2
DW-02	Well	3.3	< 1.0	3.4	19.0	42.8
DW-04	Well	4.4	< 1.0	1.9	4.3	82.2
DW-05	Well	3.5	< 1.0	5.9	50.6	38.2
DW-06	Well	4.2	< 1.0	< 1.0	5.7	16.3
DW-07	Well	4.1	< 1.0	1.1	6.1	24.7
DW-08	Well	3.7	< 1.0	1.6	27.5	6.9
DW-09	Well	3.3	< 1.0	3.8	16.1	14.8
DW-10	Well	2.4	< 1.0	1.1	25.8	13.0
DW-11	Well	4.3	< 1.0	1.9	19.6	33.4
DW-12	Well	3.6	< 1.0	0.3	60.8	66.5
DW-14	Well	4.2	< 1.0	< 1.0	0.93	4.4
DW-15	Well	3.6	< 1.0	< 1.0	28.5	9.7
DW-16	Well	3.7	< 1.0	0.38	0.94	10.4
DW-17	Well	4.8	< 1.0	< 1.0	5.5	30.9
DW-18	Well	5.2	< 1.0	< 1.0	3.3	20.2
DW-19	Well	4.6	< 1.0	< 1.0	9.4	8.7
DW-20	Well	6.4	< 1.0	< 1.0	3.1	13.6
DW-21	Well	4.6	< 1.0	< 1.0	0.99	10.9
DW-22	Well	4.5	< 1.0	< 1.0	0.73	5.6
DW-23	Well	4.4	< 1.0	0.78	6.7	62.2
DW-24	Well	6.5	< 1.0	9.0	42.1	11.3
DW-25	Well	3.3	< 1.0	4.2	134	41.1
DW-26	Well	2.8	< 1.0	3.4	6.1	76.0
DW-27	Well	8.3	< 1.0	0.67	49.4	20.9
DW-28	Well	8.8	< 1.0	< 1.0	3.2	3.5
DW-29	Well	3.9	< 1.0	0.34	6.6	16.4
DW-30	Well	9.3	< 1.0	< 1.0	3.3	15.8
DW-31	Well	6.4	< 1.0	5.8	53.1	182
DW-32	Well	4.9	< 1.0	2.2	30.5	35.6
DW-33	Well	7.2	< 1.0	< 1.0	2.6	14.4
DW-34	Well	3.1	< 1.0	3.6	47.4	168
DW-35	Well	2.5	< 1.0	0.34	2.9	18.0
DW-36	Well	2.5	< 1.0	198*	71.8	14.5
DW-37	Well	3.0	< 1.0	6.9	96.0	90.8

Sample Name	Water Source	Total Arsenic µg/L	Total Cadmium µg/L	Total Lead µg/L	Total Copper µg/L	Total Zinc µg/L
DW-38	Well	14.6**	< 1.0	1.7	76.0	61.1
DW-39	Well	5.4	< 1.0	4.0	22.7	25.2
DW-40	Well	4.7	< 1.0	2.8	26.2	48.2
DW-41	Well	3.6	< 1.0	1.1	11.6	117
DW-42	Well	2.5	< 1.0	< 1.0	7.9	53.8
DW-43	Well	5.8	< 1.0	14.3	160	533
DW-44	Well	6.8	< 1.0	< 1.0	0.68	3.7
DW-45	Well	6.3	< 1.0	1.8	31.1	15.9
DW-46	Well	4.6	< 1.0	< 1.0	2.0	2.3
DW-47	Well	6.5	< 1.0	16.8	110	8.5
EPA's Maximum Contaminant Level (MCL) for As and Cd; Action Level for Pb; Secondary Standard for Cu and Zn	10	5	15	1000	5000	

\* According to the well owner, this well services two trailers on his property that are vacant. The well had not been used in several months. Initial flow of water was quite turbid and remained so during the approximately 15 minute purging period prior to sample collection. The water contained a significant sediment load. After passing a portion of the water through a 0.45 µ filter, the water appeared to be visually free of sediment. Results of initial sampling and analysis in June 2007 and re-sampling and analysis in November for Well DW- 36 were as follows:

Sample Time	Total Pb (µg/L)	Dissolved Pb (µg/L)
June '07	198	4.7
November '07	185	< 1.0

\*\* Results of initial sampling and analysis in June 2007 and re-sampling and analysis in November of Well DW-38 were as follows:

Sample Time	Total As (µg/L)	Dissolved As (µg/L)
June '07	14.6	15.6
November '07	15.0	15.0

EPA recommended this water not be used for drinking or in food preparation.

#### Arsenic levels in wells sampled in 1987 and 2007

In 1987, two of the wells within the upper portion of the Clark Fork River OU (Reach A), had total As levels that exceeded the current 10 µg/L standard. These were the 2007-numbered

wells, DW-16 and DW-25. Well DW-16 is a dewatering well that is used to dewater farmland to allow for the production of hay and is not used for domestic drinking water purposes. DW-25 is a domestic household well. In 1987, DW-16 had a total As concentration of 42 µg/L. In the 2007 sampling event, total As concentrations dropped substantially with a measured total As concentration of 3.7 µg/L. In 1987, DW-25 had a total As concentration of 13 µg/L. In the 2007 sampling event, total As concentration decreased to 3.3 µg/L. Based on these results, the two wells in Reach A that had total arsenic concentrations above 10 µg/L have both decreased since the 1987 sampling event, and concentrations are less than the current MCL standard of 10 µg/L.

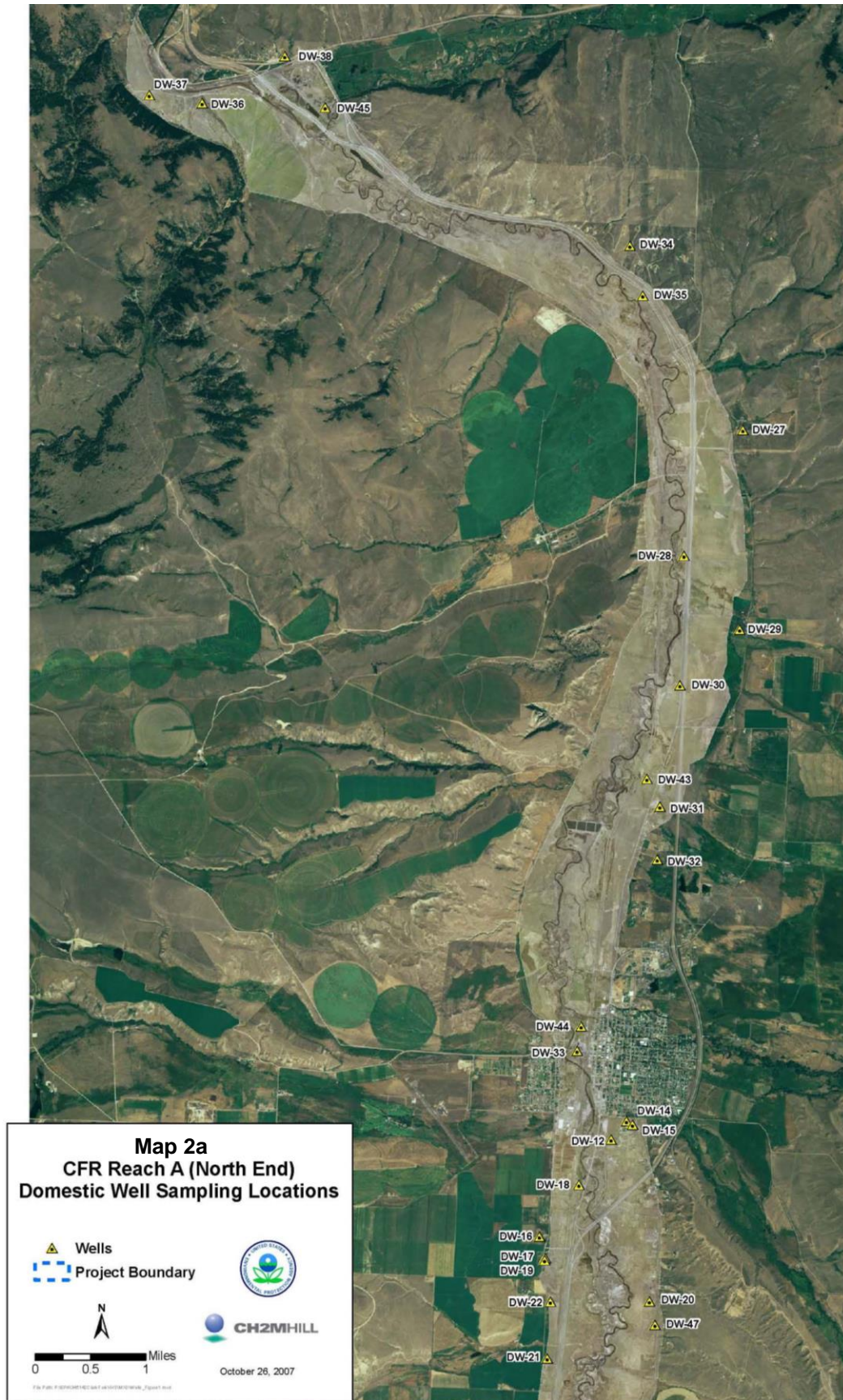
#### Basin Creek Watershed OU

Water samples were collected from fifteen domestic drinking water sources in the Basin Creek watershed (Map 3) during July, August, and September 2009. Concentrations of total As, Cd and Pb are displayed in Table 2.

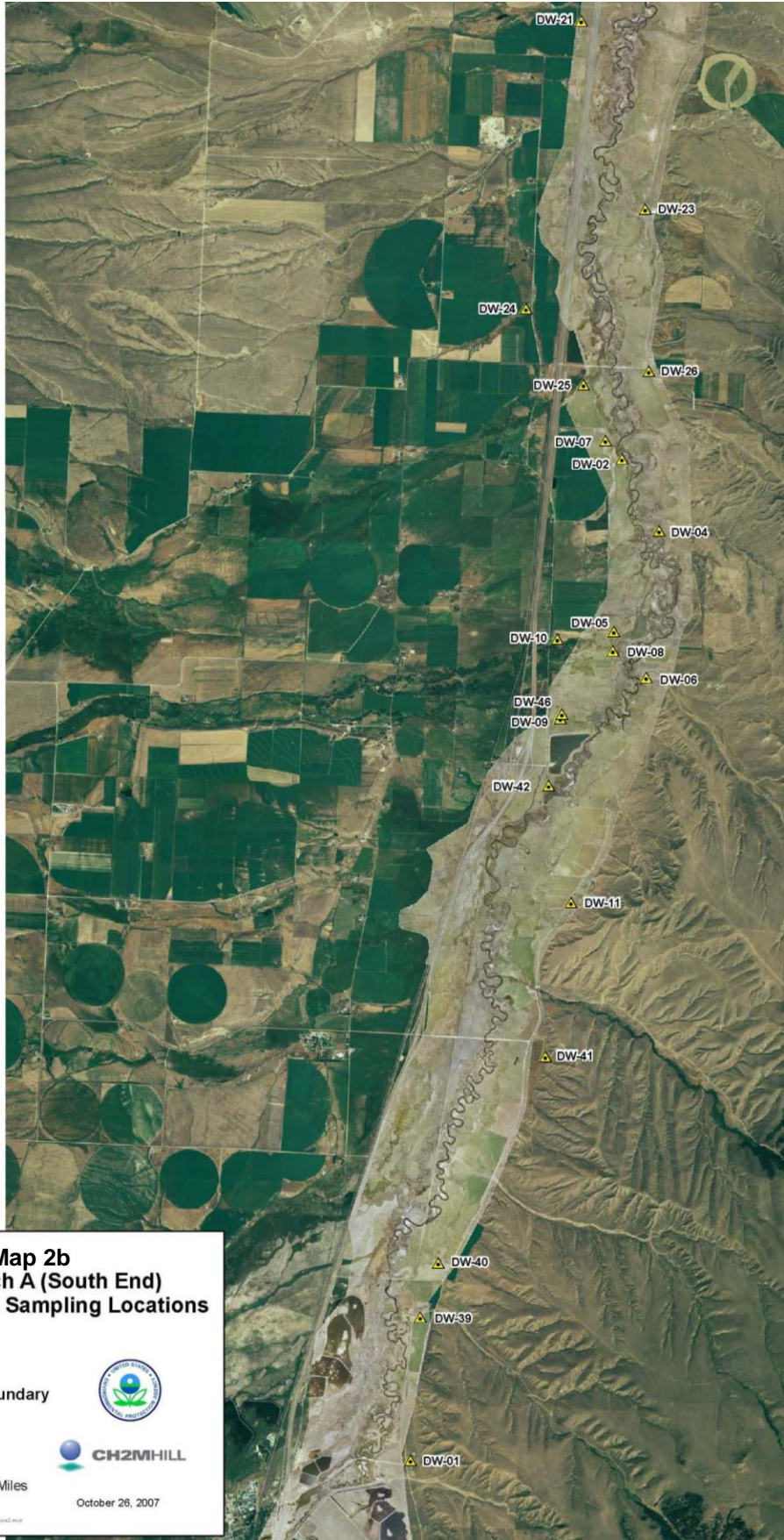
Table 2. Concentrations (µg/L) of total arsenic, cadmium, and lead in domestic waters collected from wells, springs, and creeks within the Basin Creek Watershed OU in 2009.

<b>Sample Name</b>	<b>Water Source</b>	<b>Total Arsenic µg/L</b>	<b>Total Cadmium µg/L</b>	<b>Total Lead µg/L</b>
09-BC-KL	Well	3.9	<0.08	0.45
09-BC-PE	Spring	1.2	<0.08	0.22
09-BC-SC	Creek	2.6	<0.08	0.31
09-BC-SC-2	Spring	1.9	<0.08	< 0.10
09-BC-SM	Well	<0.05	<0.08	< 0.10
09-BC-CA	Creek	1.3	<0.08	1.2
09-BC-GO	Creek	2.8	<0.08	0.91
09-BC-KN	Well	2.5	<0.08	2.4
09-BC-LA-2	Well	1.0	<0.08	0.38
09-BC-LA	Spring	2.7	<0.08	0.25
09-BC-BA	Spring	0.90	<0.08	1.4
09-BC-WO	Spring	0.84	<0.08	0.54
09-BC-RA	Well	3.7	<0.08	0.14
09-BC-DE	Spring	1.9	0.75	0.21
09-BC-ME	Well	0.51	<0.08	0.33
EPA's Maximum Contaminant Level (MCL) for As and Cd; Action Level for Pb		10	5	15









**Map 2b**  
**CFR Reach A (South End)**  
**Domestic Well Sampling Locations**

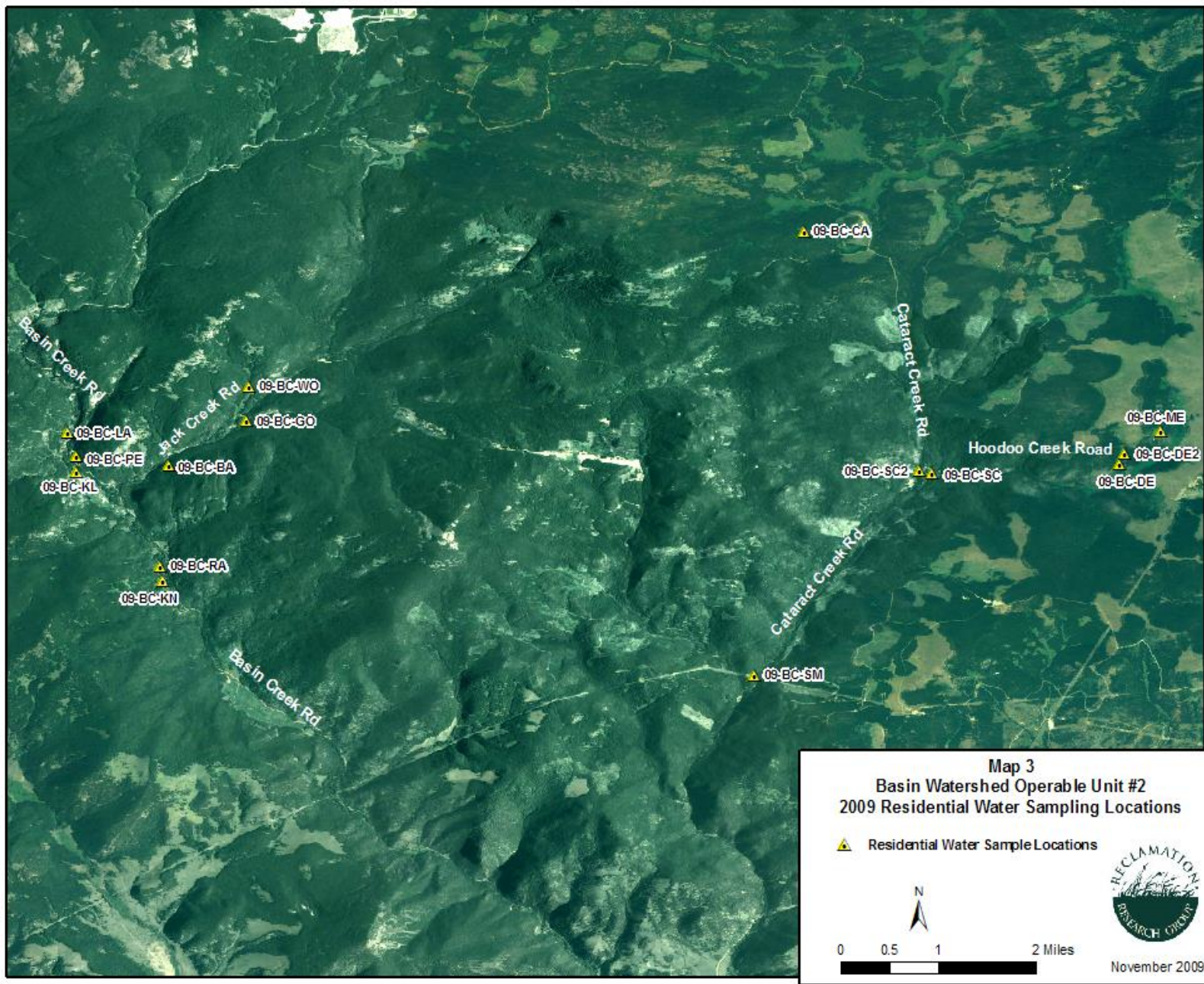
Wells  
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## Discussion and Conclusions

### Clark Fork River OU

Forty six (46) domestic water wells in Reach A were sampled and analyzed for total and dissolved concentrations of As, Cd, Cu, Pb and Zn. A total of 46 samples were obtained at 45 properties. Many of these wells were previously sampled in 1987 as part of a screening study. The findings from the 2007 sampling event are as follows:

- Total Pb concentration in well D-36 was determined on two separate occasions: June and November 2007, with values of 198 and 185 µg/L, respectively. It is speculated the well has been compromised by lack of use as a high sediment load was visually observed during sampling. After passing the water through a 0.45µ filter, it was clear. Dissolved Pb concentrations were measured at 4.7 µg/l and < 1.0 µg/L. [*see footnote for Table 1*].
- One other well, DW-47, exceeded the 15 µg/L action level for Pb with a reported concentration of 16.8 µg/L. The dissolved concentration of Pb in water from this well was 0.97 µg/L.
- Total and dissolved As concentrations in water drawn from Well 38 exceeded the MCL of 10µg/L. The well was sampled in June and again in November 2007. Results were as follows: total As 14.6 µg/L (June) and 15.0 µg/L (November); dissolved arsenic of 15.6 µg/L (June) and 15.0 µg/L (November). It was recommended the people living in the house not use their water for drinking or in food preparations.
- All other total concentrations for Cd, Cu and Zn, were less than MCLs, action levels, and secondary standards for drinking water.
- The two wells sampled during the 1987 screening study that had As levels above 10µg/L and were re-tested during the 2007 sampling event. These wells were identified as DW-16 and DW-25. Concentrations of total As were less in the 2007 sampling for both of these wells as follows:
  - DW-16—total As concentrations decreased from 42 µg/L (1987) to 3.7 µg/L.
  - DW- 25—total As concentrations decreased from 13 µg/L (1987) to 3.3 µg/L.

## Basin Creek Watershed OU

Of the 15 domestic water used as drinking water, the following conclusion can be made.

- All As, Cd, and Pb concentrations were below their respective regulatory levels of 10, 5 and 15 µg/L, respectively.
- The average As concentration in the drinking waters was 1.9 µg/L, ranging from at/or below 0.05 to 3.9 µg/L.
- All of the Cd concentrations were reported at the detection limit of 0.08 µg/L.
- The average Pb concentration in the drinking waters was 0.60 µg/L, ranging from at/or below 0.10 to 2.4 µg/L.

### Acknowledgements

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