In cooperation with the Fort Peck Tribes Office of Environmental Protection

Strontium Isotope Detection of Brine Contamination in the East Poplar Oil Field, Montana

Open-File Report 2010–1326

U.S. Department of the Interior
U.S. Geological Survey

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By Zell E. Peterman, Joanna N. Thamke, Kiyoto Futa, and Thomas A. Oliver

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KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2010

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Strontium Isotope Detection of Brine Contamination in the East Poplar Oil Field, Montana

Zell E. Peterman,[1] Joanna N. Thamke,[2] Kiyoto Futa,[1] and Thomas A. Oliver[1]

U.S. Geological Survey

[1]Denver, Colorado, [2]Helena, Montana

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Background

- Brine contamination was documented in the East Poplar oil field as early as the mid-1980s by the U.S. Geological Survey (Levings, 1984; Thamke and Craigg, 1997; Thamke and Midtlyng, 2003).
- The City of Poplar’s three public water-supply wells (COP-1, COP-2, and COP-3) are completed in the shallow aquifers downgradient from contaminated aquifers (S.S. Papadopulos & Associates, Inc., 2008).
- Data from the North Dakota Department of Health in 1985 and Energy Laboratories, Inc., in 2009 indicate that chloride concentrations in water from COP-3 exceed the secondary maximum contaminant level of 250 mg/L, as established by the U.S. Environmental Protection Agency (2010).

Background (cont'd)

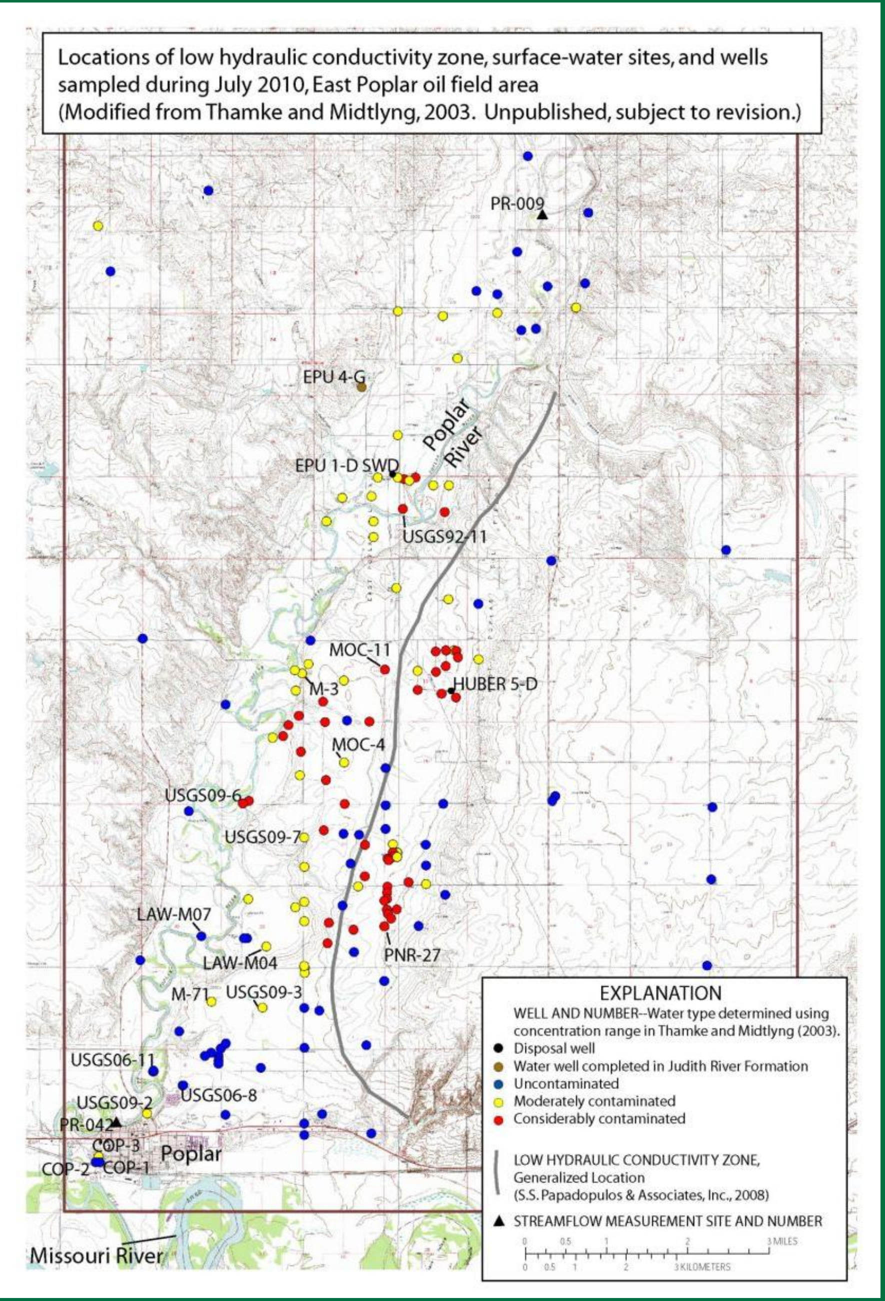
- In April 2010, representatives from Federal, State, and city agencies; energy companies; and private consultants were invited to discuss investigations of chloride (Cl) concentrations and possible sources in groundwater near the City of Poplar.
- Sample design and approach were discussed in June 2010 by the above, and water samples were collected by the U.S. Geological Survey (USGS) during July 2010.

Approach

- Groundwater samples were collected by the USGS Montana Water Science Center under the direction of Joanna Thamke and the Fort Peck Office of Environmental Protection under the direction of Christa Tyrrell.
- The analyses were conducted in the USGS Yucca Mountain Project Branch Geochemistry Laboratory in Denver, Colo.
  - Strontium isotopes were measured by thermal ionization mass spectrometry (TIMS).
  - Anion and cation concentrations were determined by ion chromatography (IC) and trace-metal concentrations by inductively coupled plasma-mass spectrometry (ICP–MS).

Locations of Sample Sites

- Wells, Poplar River, and disposal sites that were sampled during July 2010 are labeled in map.
- Samples were analyzed for strontium isotopes, dissolved ions, and trace metals.



Strontium Isotopes as Groundwater Tracers

- Strontium (Sr) is an alkaline-earth element that closely follows calcium (Ca) in geochemical and hydrological cycles.
- Sr is composed of four isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr, all of which are stable (nonradioactive).
- Fractionation of Sr isotopes in nature is extremely small and inconsequential in tracer studies.
- Some ^{87}Sr forms from the beta decay of ^{87}Rb with a half-life of 48.8 billion years.
  - Rocks with different ages and Rb/Sr ratios have different $^{87}Sr/^{86}Sr$ ratios.

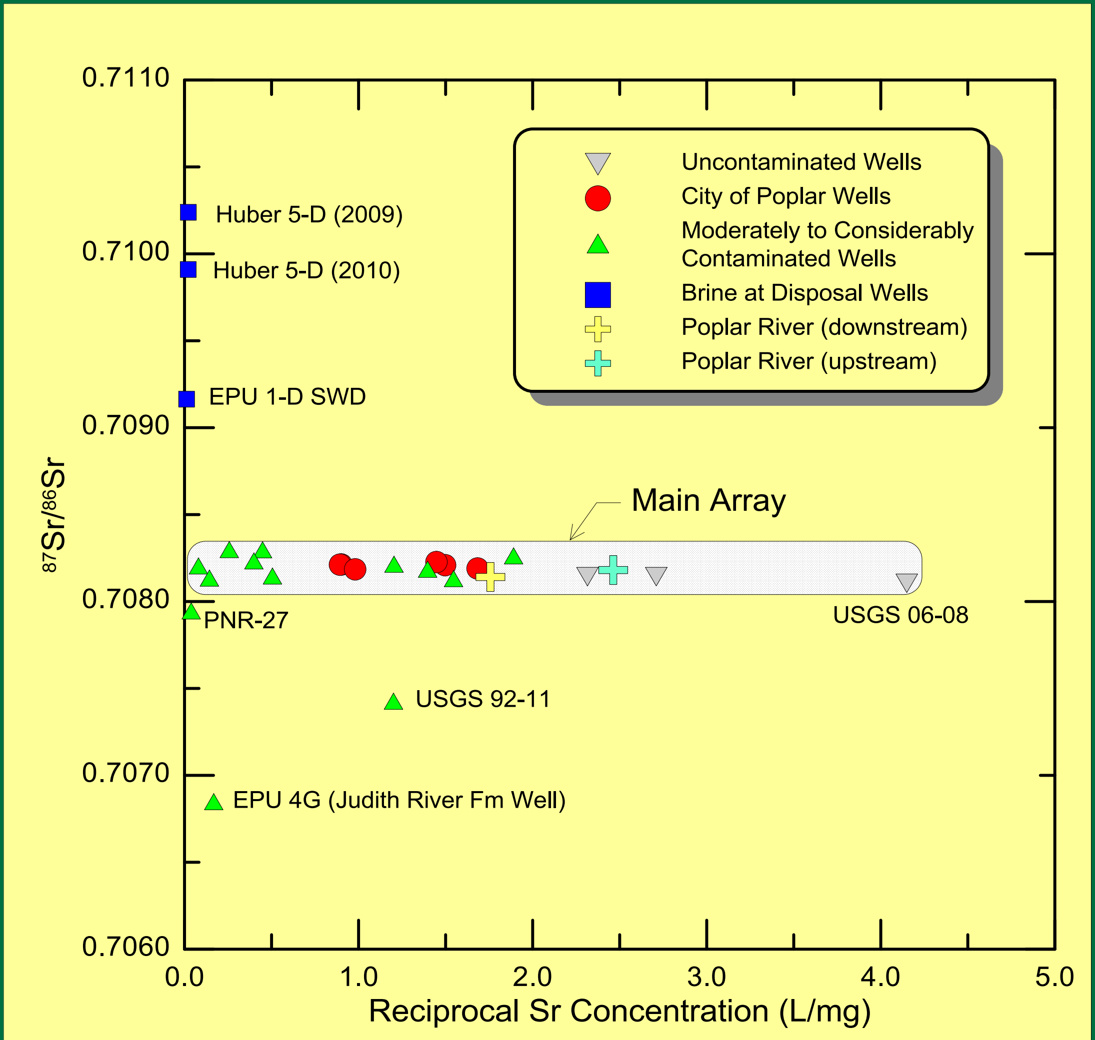
Strontium Isotopes as Groundwater Tracers (cont'd)

- $^{87}Sr/^{86}Sr$ ratios and Sr concentrations in groundwater are useful for detecting mixing of waters of different origins.
- Sr isotopes have been used near Goose Lake Waterfowl Protection Area to assess the impact of brine from oil-field operations on shallow groundwater within the Prairie Pothole Region (*http://steppe.cr.usgs.gov/*), and in the Weyburn field in Saskatchewan, Canada, to characterize the produced water from the Madison Group formations (Quattrocchi and others, 2006).

Mixing of Brines and Freshwater

- Sr concentrations of freshwater and brine differ by two to three orders of magnitude.
- Mixing of waters with different $^{87}Sr/^{86}Sr$ ratios and reciprocal Sr concentrations will produce linear trends, from which end-member compositions and mixing proportions can be calculated (Faure, 1998).

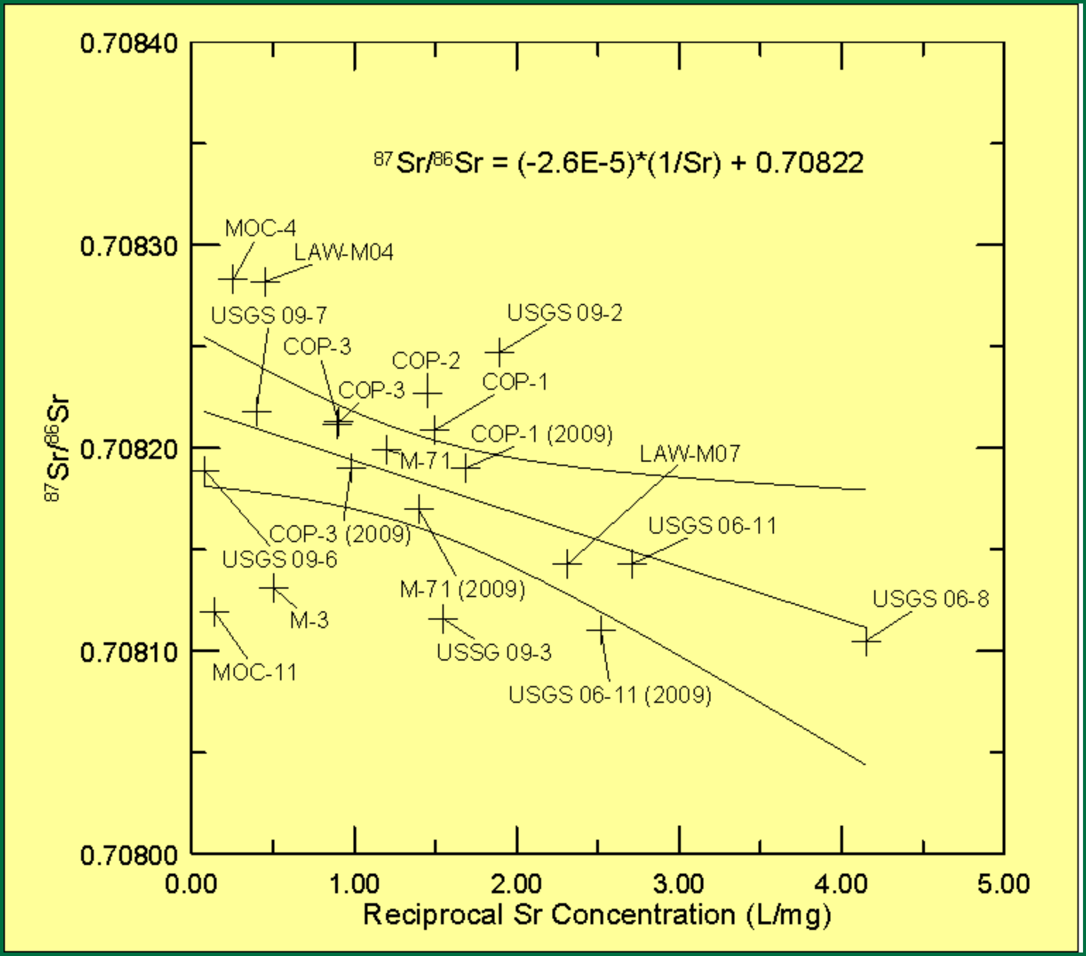
$^{87}Sr/^{86}Sr$ versus 1/Sr (Sr in mg/L)



- Two sigma uncertainty in the $^{87}Sr/^{86}Sr$ ratio is 1.3E-5.
- Two sigma uncertainty of Sr concentration is 5 percent of the value or less.

USGS

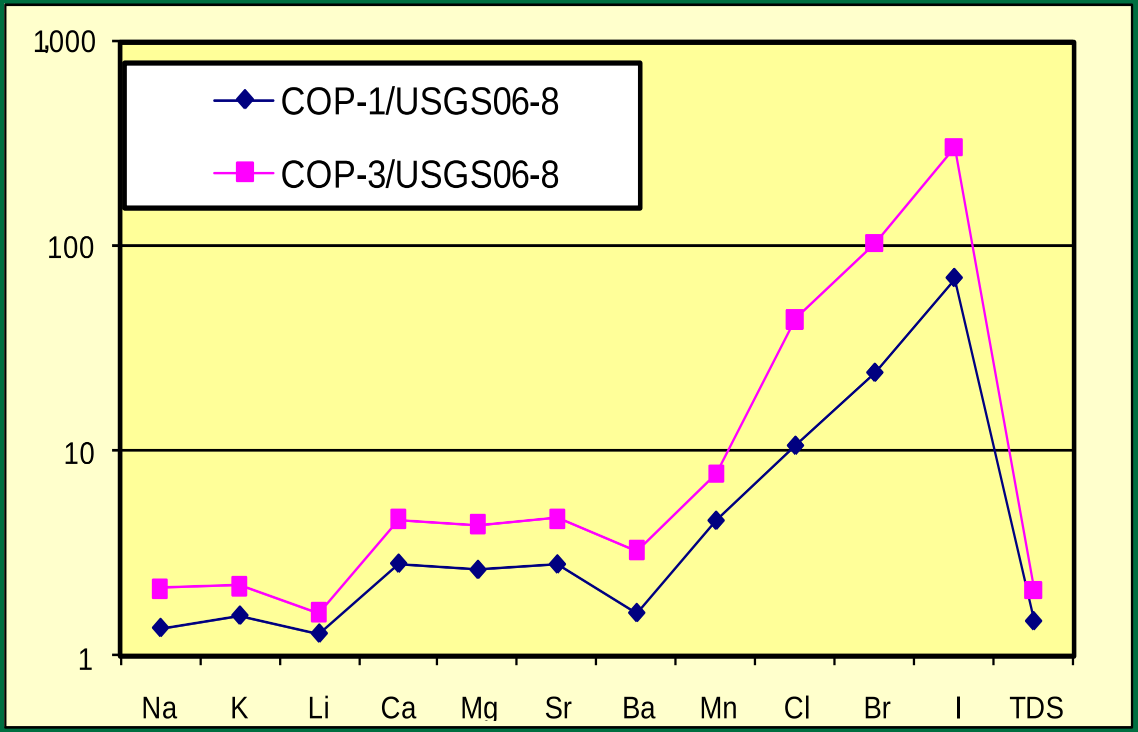
$^{87}Sr/^{86}Sr$ versus 1/Sr (Sr in mg/L)—(cont'd)



- Expansion of the Sr isotope axis of main array shows variability in $^{87}Sr/^{87}Sr$ and Sr concentrations
- The Y intercept is likely the mean Sr isotope ratio of the contaminant that produced the main trend.

USGS

Spider Diagram for COP-1 and COP-3



- Spider diagrams display ratios of concentrations of elements.
- COP-1, COP-2, and COP-3 are enriched in anions and cations that are abundant in brine.
- COP-2 is not shown because concentrations are similar to COP-1.

Conclusions

- The main array is a contamination trend produced by mixing low Sr and low Cl waters ($^{87}Sr/^{86}Sr$ ratio of about 0.7081) with brine ($^{87}Sr/^{86}Sr$ ratio averaging 0.70822).
- Water samples from the COP wells plot along the main array and are enriched in constituents that are present in oil-field brines at high concentrations.

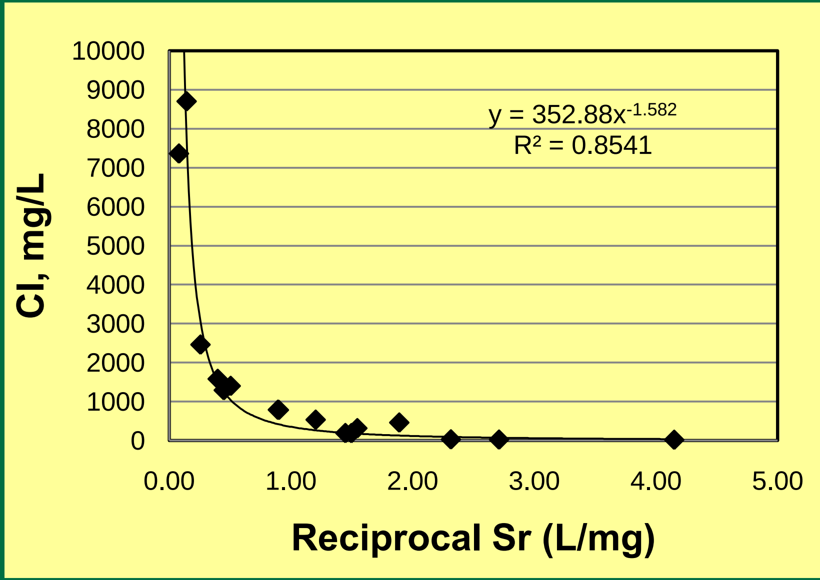
Conclusions (cont'd)

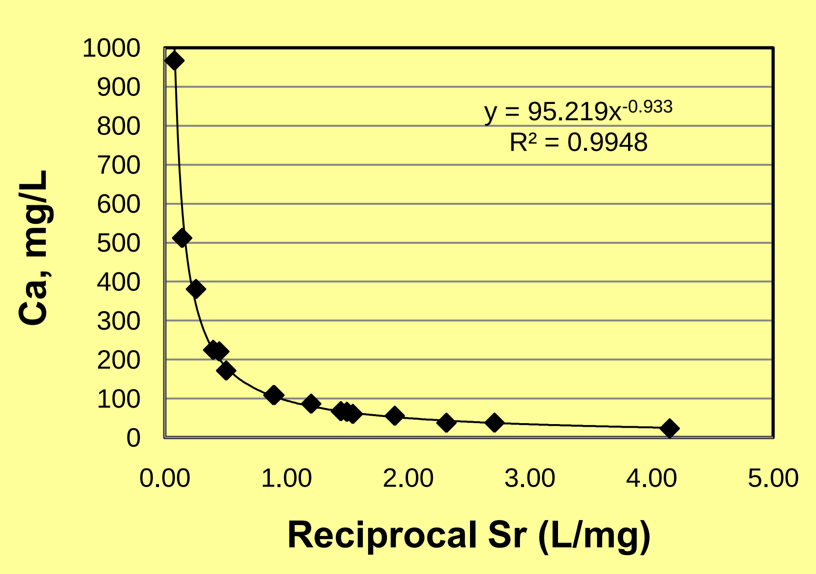
- **The brine that caused the main array is similar in $^{87}Sr/^{86}Sr$ to brines produced from the Madison Group elsewhere:**
  - **0.70802 at Goose Lake in northeast Montana (Peterman and others, 2010).**
  - **0.70811 ± 0.00013 at the Weyburn Field in southern Saskatchewan (Quattrocchi and others, 2006).**
- **The $^{87}Sr/^{86}Sr$ for water from the Judith River Fm indicates that upwelling is not likely to have affected the main array.**

Supplemental Slides

- Ca and Cl as a function of 1/Sr
- Sample collection information and field measurements
- Major dissolved-ion concentrations
- Trace-metal concentrations
- Sr isotopes and Rb and Sr concentrations
- References

1/Sr is an Index of Brine Contamination in the Main Array





Sample Collection Information and Field Measurements

Lab ID	Station ID	Station Name	Sample Date	Sample Time	Field pH	Field SC
FPT-001	480849105102301	LAW-M04	7/20/2010	1730	7.3	4,680
FPT-002	481328105072702	USGS 92-11	7/20/2010	1930	7.9	6,360
FPT-003	480634105121501	COP-3	7/21/2010	1445	7.4	3,280
FPT-004	480634105121501	COP-3	7/22/2010	1440	7.4	3,280
FPT-005	480631105122101	COP-2	7/21/2010	1410	7.6	1,930
FPT-006	480630105121601	COP-1	7/21/2010	1330	7.6	1,900
FPT-007	480656105120001	Poplar River PR-R-PR-042	7/21/2010	1100	8.7	1,790
FPT-008	480855105103901	LAW-M07	7/21/2010	1715	7.7	1,210
FPT-009	481448105080001	EPU 4-G	7/22/2010	0915	--	36,400
FPT-010	481132105064801	Huber 5-D	7/22/2010	0830	--	122,400
FPT-011	481352105073401	EPU 1-D SWD	7/22/2010	0900	--	158,800
FPT-012	481143105090301	M-3	7/22/2010	1200	7.6	5,120
FPT-013	481146105074401	MOC-11	7/22/2010	1515	6.9	25,000
FPT-014 A	PNR-27	PNR-27	7/22/2010	1705	6.5	34,900
FPT-014 B	PNR-27	PNR-27	7/22/2010	1705	6.5	34,900
FPT-015	481635105051301	Poplar River PR-R-PR-009	7/21/2010	0930	8.9	1,480
FPT-016	481020105100201	USGS 09-6	7/20/2010	1600	6.9	20,100
FPT-017	480958105090301	USGS 09-7	7/20/2010	1430	7.3	5,510
FPT-018	481046105082301	MOC-4	7/20/2010	1130	7.2	8,748
FPT-019	481046105082301	Field Blank coll. at MOC-4	7/20/2010	1135	--	--
FPT-020	480701105113201	USGS 09-2	7/20/2010	930	7.4	2,400
FPT-021	480720105105602	USGS 06-8	7/19/2010	1430	7.5	1,190
FPT-022	480729105112403	USGS 06-11	7/19/2010	1130	7.7	1,250
FPT-023	480809105094301	USGS 09-3	7/19/2010	1630	7.4	2,160
FPT-024	480814105102901	M-71	7/19/2010	1800	7.3	2,450

Major Dissolved Ion Concentrations

Sample		Charge Balance	Lab pH	Lab Specific Conductance	Na	Mg	K	Ca	F	Cl	HCO_3	SO_4	NO_3	Br	I
	Lab ID	percent		µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Minimum Reporting Limit					**0.02**	**0.05**	**0.02**	**0.15**	**0.005**	**0.09**	**1.2**	**0.02**	**0.02**	**0.005**	**0.005**
LAW-M04	FPT-001	-0.2	7.4	4,640	556	153	12.6	221	0.18	1290	378	278	0.04	0.342	0.044
USGS 92-11	FPT-002	-1.1	8.1	6,330	1400	12.7	7.65	36.0	0.48	1730	614	309	0.08	0.643	0.057
COP-3	FPT-003	0.1	7.4	3,230	518	56.0	8.20	109	0.28	783	516	105	<0.02	7.80	6.02
COP-3	FPT-004	-0.2	7.4	3,280	524	54.3	8.17	109	0.30	788	525	106	<0.02	7.82	6.10
COP-2	FPT-005	0.3	7.7	1,934	338	33.6	5.94	67.8	0.38	190	594	277	0.02	1.81	1.37
COP-1	FPT-006	-0.1	7.6	1,926	337	32.6	5.87	66.0	0.38	189	600	271	0.11	1.81	1.38
Poplar River PR-R-PR-042	FPT-007	0.8	8.7	1,779	331	50.3	9.08	28.9	0.42	120	642	287	<0.02	0.128	0.019
LAW-M07	FPT-008	-0.5	7.8	1,211	223	22.4	4.57	38.1	0.39	28.1	540	194	<0.02	0.082	0.017
EPU 4-G	FPT-009	-0.3	6.5	18,490	4190	19.5	9.56	100	0.57	6610	214	2.67	2.9	66.2	50.3
Huber 5-D	FPT-010	-1.2	7.0	116,400	32200	143	438	854	5.71	51800	274	1700	0.67	10.3	0.605
EPU 1-D SWD	FPT-011	-1.4	7.0	150,000	42800	213	691	1460	5.05	70600	242	1350	<0.80	23.0	1.78
M-3	FPT-012	-0.9	7.6	5,130	773	139	12.7	172	0.21	1400	543	315	<0.03	0.494	0.079
MOC-11	FPT-013	-0.9	7.0	24,990	5180	274	26.0	512	0.21	8700	480	1250	<0.12	17.9	9.40
PNR-27	FPT-014 A	-0.8	6.7	34,900	5160	1320	61.9	1610	0.16	12900	722	2060	201	3.41	0.047
PNR-27	FPT-014 B	-1.8	6.8	34,900	5070	1310	59.0	1610	0.16	13000	723	2070	201	3.46	0.046
Poplar River PR-R-PR-009	FPT-015	0.7	8.8	1,499	297	40.0	8.33	19.0	0.45	11.8	669	279	<0.02	0.079	0.012
USGS 09-6	FPT-016	-1.3	6.5	19,810	2310	778	33.2	967	0.10	7360	243	376	<0.10	3.08	0.451
USGS 09-7	FPT-017	-1.0	7.4	5,480	718	174	12.9	225	0.16	1580	421	327	<0.03	0.367	0.043
MOC-4	FPT-018	-0.6	7.2	8,690	1200	282	17.3	381	0.15	2460	443	928	0.05	1.33	0.272
Field Blank coll. at MOC-4	FPT-019	-27.0	6.5	1.4	0.04	0.092	<0.02	0.43	<0.005	0.023	3.2	<0.02	<0.02	<0.005	<0.005
USGS 09-2	FPT-020	-0.7	7.6	2,388	445	26.2	5.70	56.0	0.39	460	580	110	<0.02	4.83	3.80
USGS 06-8	FPT-021	-0.1	7.7	1,166	248	12.5	3.76	23.6	0.43	18.0	558	165	<0.02	0.076	0.020
USGS 06-11	FPT-022	0.0	7.6	1,246	239	20.9	4.22	38.3	0.41	22.1	605	172	0.06	0.096	0.024
USGS 09-3	FPT-023	-0.8	7.7	2,147	374	34.1	6.02	60.7	0.26	315	487	272	3.7	0.150	0.034
M-71	FPT-024	-0.5	7.4	2,428	364	49.4	6.55	87.0	0.25	533	401	146	<0.02	0.134	0.018

Trace-Metal Concentrations

Sample		Li	Be	B	Al	Cr	Mn	Co	Ni	Cu	Zn	As	Sr	Rb	Mo	Ag	Cd	Sb	Cs	Ba	Pb	Th	U
	Lab ID	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Minimum Reporting Limit		**0.5**	**0.2**	**10**	**5**	**0.9**	**0.15**	**0.25**	**3**	**0.5**	**3**	**0.6**	**1**	**0.1**	**0.1**	**0.7**	**0.2**	**0.2**	**0.2**	**3**	**0.18**	**0.03**	**0.03**
LAW-M04	FPT-001	153	<2.0	550	<50	<9.0	1180	<2.5	<30	<5.0	<30	8.3	2230	<1.0	2.1	<7.0	<2.0	<2.0	<2.0	142	<1.8	<0.30	0.90
USGS 92-11	FPT-002	183	<1.0	756	<25	<4.5	143	<1.3	<15	<2.5	<15	3.5	833	0.8	5.5	<3.5	<1.0	<1.0	<1.0	42	<0.90	<0.15	1.95
COP-3	FPT-003	127	<1.4	609	<34	<6.1	890	<1.7	<20	<3.4	<20	8.5	1110	2.7	8.0	<4.7	<1.4	<1.4	<1.4	89	<1.2	<0.20	1.35
COP-3	FPT-004	122	<1.4	587	<34	<6.1	867	<1.7	<20	<3.4	<20	8.5	1120	2.7	8.6	<4.7	<1.4	<1.4	<1.4	91	<1.2	<0.20	1.35
COP-2	FPT-005	98	<0.8	623	<20	4.3	526	<1.0	<12	<2.0	<12	6.5	691	2.1	11	<2.8	<0.8	<0.8	<0.8	44	<0.73	<0.12	1.24
COP-1	FPT-006	97	<0.8	633	<20	4.1	507	<1.0	<12	<2.0	<12	8.3	668	2.0	11	<2.8	<0.8	<0.8	<0.8	45	<0.73	<0.12	1.17
Poplar River PR-R-PR-042	FPT-007	106	<0.8	1100	<20	4.7	3.7	1.1	<12	<2.0	<12	4.6	569	1.6	2.8	<2.8	<0.8	<0.8	<0.8	65	<0.73	<0.12	2.07
LAW-M07	FPT-008	75	<0.5	604	<13	4.1	147	<0.6	<7.5	<1.3	<7.5	10	432	0.6	5.7	<1.8	<0.5	<0.5	<0.5	36	<0.45	<0.08	0.71
EPU 4-G	FPT-009	411	<2.0	4450	<50	<9.0	85	<2.5	<30	<5.0	396	17	5960	8.4	<1.0	<7.0	<2.0	<2.0	<2.0	6930	2.36	<0.30	<0.30
Huber 5-D	FPT-010	4040	<4.9	14300	<123	<22	130	<6.1	<74	<12	<74	73	47300	974	<2.5	<17	<4.9	<4.9	82	564	<4.4	<0.74	<0.74
EPU 1-D SWD	FPT-011	6000	<5.8	32200	<146	<26	62	<7.3	<87	<15	<87	92	83000	1580	<2.9	<20	<5.8	<5.8	139	1120	<5.2	<0.87	<0.87
M-3	FPT-012	159	<2.0	741	<50	<9.0	400	<2.5	<30	<5.0	<30	10	1980	1.2	2.7	<7.0	<2.0	<2.0	<2.0	104	<1.8	<0.30	1.08
MOC-11	FPT-013	736	<2.0	676	<50	<9.0	1240	3.0	<30	<5.0	<30	29	6990	2.6	2.9	<7.0	<2.0	<2.0	<2.0	49	<1.8	<0.30	2.64
PNR-27	FPT-014 A	973	<2.0	502	<50	<9.0	107	<2.5	<30	7.4	<30	29	26000	6.8	<1.0	<7.0	<2.0	<2.0	<2.0	52	<1.8	<0.30	76.5
PNR-27	FPT-014 B	958	<2.0	494	<50	<9.0	105	<2.5	<30	7.4	<30	31	26000	6.9	<1.0	<7.0	<2.0	<2.0	<2.0	52	<1.8	<0.30	77.4
Poplar River PR-R-PR-009	FPT-015	99	<0.7	1070	23	4.9	2.7	1.3	<10	<1.7	<10	4.6	406	1.5	2.7	<2.4	<0.7	<0.7	<0.7	47	<0.60	<0.10	1.81
USGS 09-6	FPT-016	369	<2.0	598	<50	<9.0	5150	<2.5	<30	<5.0	<30	24	12500	3.4	<1.0	<7.0	<2.0	<2.0	<2.0	321	<1.8	<0.30	1.07
USGS 09-7	FPT-017	172	<2.0	662	<50	<9.1	1030	<2.5	<30	<5.0	<30	9.4	2510	1.1	1.5	<7.0	<2.0	<2.0	<2.0	159	<1.8	<0.30	0.68
MOC-4	FPT-018	225	<1.0	632	<25	<4.5	2290	<1.3	<15	<2.5	<15	11	3890	1.6	1.6	<3.5	<1.0	<1.0	<1.0	60	<0.91	<0.15	1.95
Field Blank coll. at MOC-4	FPT-019	<0.5	<0.2	<10	<5	<0.9	0.9	<0.3	<3	<0.5	<3	<0.6	<1.0	<0.1	<0.1	<0.7	<0.2	<0.2	<0.2	<3	<0.18	<0.03	<0.03
USGS 09-2	FPT-020	83	<1.0	545	<25	<4.6	206	<1.3	<15	<2.5	<15	8.3	529	1.3	10	<3.6	<1.0	<1.0	<1.0	49	<0.91	<0.15	1.66
USGS 06-8	FPT-021	76	<0.5	552	<13	4.3	112	<0.6	<7.5	<1.3	<7.5	8.2	241	0.9	11	<1.8	<0.5	<0.5	<0.5	28	<0.45	<0.08	0.76
USGS 06-11	FPT-022	75	<0.5	522	<13	4.7	269	<0.6	<7.6	<1.3	<7.6	9.3	369	1.0	11	<1.8	<0.5	<0.5	<0.5	31	<0.45	<0.08	1.90
USGS 09-3	FPT-023	101	<1.0	631	<25	<4.5	386	<1.3	<15	<2.5	<15	11	647	0.8	3.9	<3.5	<1.0	<1.0	<1.0	112	<0.91	<0.15	1.10
M-71	FPT-024	115	<1.0	533	<25	<4.6	725	<1.3	<15	<2.5	<15	8.2	831	0.7	3.8	<3.6	<1.0	<1.0	<1.0	73	<0.92	<0.15	0.79

Sample		Sr	Rb	$^{87}Sr/^{86}Sr$
	Lab ID	µg/L	µg/L	Atom ratio
Minimum Reporting Limit		**1**	**0.1**	NA
LAW-M04	FPT-001	2,230	<1.0	0.70828
USGS 92-11	FPT-002	833	0.8	0.70741
USGS 92-11 (Sr dup)	FPT-002			0.70741
COP-3	FPT-003	1,110	2.7	0.70821
COP-3	FPT-004	1,120	2.7	0.70821
COP-3 (2009)		1,020	<5	0.70819
COP-2	FPT-005	691	2.1	0.70823
COP-1	FPT-006	668	2.0	0.70821
COP-1 (2009)		594	2.3	0.70819
Poplar River PR-R-PR-042	FPT-007	569	1.6	0.70814
LAW-M07	FPT-008	432	0.6	0.70814
EPU 4-G	FPT-009	5,960	8.4	0.70683
Huber 5-D	FPT-010	47,300	974	0.70991
Huber 5-D (2009)		45,700	1080	0.71024
EPU 1-D SWD	FPT-011	83,000	1580	0.70916
M-3	FPT-012	1,980	1.2	0.70813
MOC-11	FPT-013	6,990	2.6	0.70812
PNR-27	FPT-014 A	26,000	6.8	0.70793
PNR-27 (Sr dup)	FPT-014 A			0.70795
PNR-27	FPT-014 B	26,000	6.9	---
Poplar River PR-R-PR-009	FPT-015	406	1.5	0.70818
USGS 09-6	FPT-016	12,500	3.4	0.70819
USGS 09-7	FPT-017	2,510	1.1	0.70822
MOC-4	FPT-018	3,890	1.6	0.70828
Field Blank coll. at MOC-4	FPT-019	<1.0	<0.1	---
USGS 09-2	FPT-020	529	1.3	0.70825
USGS 06-8	FPT-021	241	0.9	0.70811
USGS 06-11	FPT-022	369	1.0	0.70814
USGS 06-11 (2009)		397	1.2	0.70811
USGS 09-3	FPT-023	647	0.8	0.70812
M-71	FPT-024	831	0.7	0.70820
M-71 (2009)		716	<5	0.70817

Sr Isotopes and Rb and Sr Concentrations

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