

Arsenic Concentrations in Quaternary Drift and Quaternary-Tertiary Buried Channel Aquifers in the Athabasca Oil Sands (In Situ) Area, Alberta



Alberta Energy and Utilities Board Alberta Geological Survey



# Arsenic Concentrations in Quaternary Drift and Quaternary-Tertiary Buried Channel Aquifers in the Athabasca Oil Sands (In Situ) Area, Alberta

T.G. Lemay

Alberta Geological Survey

July 2003

©Her Majesty the Queen in Right of Alberta, 2003

The Alberta Geological Survey and its employees and contractors make no warranty, guarantee or representation, express or implied, or assume any legal liability regarding the correctness, accuracy, completeness, or reliability of this publication. Any digital data and software supplied with this publication are subject to the licence conditions. The data are supplied on the understanding that they are for the sole use of the licensee, and will not be redistributed in any form, in whole or in part, to third parties. Any references to proprietary software in the documentation, and/or any use of proprietary data formats in this release does not constitute endorsement by the Alberta Geological Survey of any manufacturer's product.

When using information from this publication in other publications or presentations, due acknowledgment should be given to the Alberta Geological Survey/Alberta Energy and Utilities Board. The following reference format is recommended:

Lemay, T.G. (2003): Arsenic concentrations in Quaternary drift and Quaternary-Tertiary buried channel aquifers in the Athabasca Oil Sands (in situ) Area, Alberta; Alberta Energy and Utilities Board, Alberta Geological Survey, Geo-Note 2002-04.

#### Published July 2003 by:

Alberta Energy and Utilities Board Alberta Geological Survey 4<sup>th</sup> Floor, Twin Atria Building 4999 – 98<sup>th</sup> Avenue Edmonton, Alberta T6B 2X3

Tel: (780) 422-3767 (Information Sales) Fax: (780) 422-1918 E-mail: EUB.AGS-Infosales@gov.ab.ca

Web site: www.ags.gov.ab.ca

# Contents

Acknow	ledgments	v
Abstract	t	vi
1 Intro	duction	1
2 Study	y Area	1
3 Arsei	nic Geochemistry	1
4 Obse	rvations and Preliminary Interpretations	4
4.1 (	Groundwater Chemistry	4
2	4.1.1 Error, Accuracy and Precision	
2	4.1.2 Groundwater arsenic concentrations	
	4.1.2.1 Observations	
	4.1.2.2 Preliminary Interpretations – Quaternary Intertill-Intratill Aquifers	28
	4.1.2.3 Preliminary Interpretations – Quaternary-Tertiary Buried Channel Aquifer	32
5 Sumi	mary	33
6 Refer	rences	34
<b>Tables</b> Table 1	Quaternary intertill-intratill and Quaternary-Tertiary buried channel aquifer water	
14010 1	chemistry	5
Table 2	Ouality assurance-quality control data	10
Table 3	Summary statistics of elemental concentrations in Quaternary intertill-intratill	
14010 5	aquifer water samples	27
Table 4	Summary statistics of elemental concentrations in Quaternary-Tertiary buried	
14010	channel aquifer water samples compared to Quaternary intertill-intratill aquifer	
	water samples	30
Table 5	Summary statistics of saturation indices in Quaternary intertill-intratill aquifer	
	water samples	31
Table 6	Summary statistics of saturation indices in Quaternary Tertiary buried channel	
	aguifer water samples compared to Quaternary intertill_intratill aguifer water samples	32
	aquiter water samples compared to Quaternary intertin-intratin aquiter water samples	
Figures		
Figure 1	Study area location.	2
Figure 2	Table of Quaternary to Devonian stratigraphic units in the Athabasca Oil Sands	
	(in situ) Area, Alberta.	9
Figure 3	Quaternary and Quaternary-Tertiary aquifer Eh-pH values in the As-O <sub>2</sub> -H <sub>2</sub> O	
-	system at 7.1°C and 1 bar total pressure: a) overview; and b) detailed view with	
	sample points.	22
Figure 4	SEM images of: a) pyrite and clay mineral within Quaternary till; and b) pyrite	
C	surrounding bacterially eroded Fe-oxide laths.	23
Figure 5	SEM images of: a) original framboidal pyrite of bacterial origin oxidized to	
U	Fe-oxide; and b) Fe-oxide grain coating, carbonate and evaporite mineral.	24
Figure 6	Ca-phosphate fragment (possibly fish scale) found in Quaternary till	25
Figure 7	Concentration relationships between: a) As and Al; b) As and Mn; c) As and	
0 - 1	Fe; and d) As and P in water from Quaternary intertill-intratill aguifers in the	
	Athabasca Oil Sands (in situ) Area of northeastern Alberta	26
Figure 8	Relationship between As and pH in water from Ouaternary intertill-intratill	
	aquifers in the Athabasca Oil Sands (in situ) Area of northeastern Alberta	27

Figure 9	Concentration relationships between: a) As and Ca; b) As and Mg; c) As and Sr; and	
	d) As and SO <sub>4</sub> in water from Quaternary-Tertiary buried channel aquifers in	
	the Athabasca Oil Sands (in situ) Area of northeastern Alberta.	
Figure 10	Relationships between: a) As and P; b) As and HCO <sub>3</sub> ; and c) As and Eh in	
	water from Quaternary-Tertiary buried channel aquifers in the Athabasca Oil	
	Sands (in situ) Area of northeastern Alberta	29

## Acknowledgments

This project was funded jointly by the Government of Alberta through the Energy and Utilities Board and by the Government of Canada through the Ministry of Western Economic Diversification under the Western Economic Partnership Agreement. This Geo-Note is one in a series of Geo-Notes detailing the results of the work completed as part of this project.

Norwest Labs completed the water analyses for major, minor and trace elements. Dr. John Duke of the University of Alberta's SLOWPOKE Nuclear Reactor Facility completed the neutron activation analysis for chloride, bromide and iodide in the water samples.

## Abstract

Sampling of selected wells from Quaternary drift aquifers and Quaternary-Tertiary buried channel aquifers, in the Athabasca Oil Sands (in situ) Area, was conducted between the summer of 1999 and the spring of 2001. The purpose of the sampling program was to obtain high-quality water samples that could be used to better define baseline groundwater chemistry in these geological units.

Twenty-one water samples were collected from Quaternary intertill-intratill aquifers. Three water samples were collected from Quaternary-Tertiary buried channel aquifers. For each of the samples collected, field determinations of pH, oxidation-reduction potential, temperature, conductivity, dissolved oxygen and total alkalinity were determined. Samples were collected by the Alberta Geological Survey and analyzed by various laboratories for concentrations of major, minor and trace elements, organic compounds, as well as stable and radiogenic isotopes. One of the elements included in the water-sample analysis is arsenic.

The majority of the Quaternary intertill-intratill aquifer water samples have arsenic concentrations below the analytical detection limit. Four of the water samples have arsenic concentrations that exceed the analytical detection limit of 0.01 mg/L. Arsenic concentrations appear to be controlled by a combination of the following mechanisms: 1) adsorption to oxide and clay minerals; 2) competition between arsenic species and phosphorus ions for adsorption sites; 3) release of arsenic brought about by changes in pH; and 4) proximity to bedrock.

All three samples from the Quaternary-Tertiary buried channel aquifer contained arsenic concentrations above the analytical detection limit. Arsenic concentrations in the Quaternary-Tertiary buried channel aquifer appear to be controlled by a combination of the following mechanisms: 1) competition between arsenic species and phosphorus or bicarbonate ions for adsorption sites; 2) release of arsenic brought about by changes in Eh; 3) dissolution of carbonate or evaporite minerals releasing associated arsenic; and 4) proximity to bedrock.

## 1 Introduction

Between 1999 and 2001, the Alberta Geological Survey conducted a groundwater-sampling program in the Athabasca Oil Sands (in situ) Area of northeastern Alberta. The purpose was to document baseline groundwater conditions in advance of oil sands development in the area. This project was funded jointly by the Government of Alberta, through the Energy and Utilities Board, and by the Government of Canada, through the Ministry of Western Economic Diversification, under the Western Economic Partnership Agreement. This Geo-Note is one in a series of Geo-Notes detailing the results of the project work completed. The purpose of this document is to present and discuss the observed concentrations of arsenic in groundwater in northeastern Alberta.

Twenty-one water samples were collected from Quaternary intertill-intratill aquifers and three were collected from a Quaternary-Tertiary buried channel. The wells were selected on the basis of geographic area, penetration of a horizon of interest, well-completion quality, water production history and, where available, verification of completion interval using geophysical logs. Field measurements were made and the water samples were analyzed by various laboratories to determine concentrations of total dissolved solids, major, minor and trace elements, extractable silica and silicon, radionuclides, as well as stable and radiogenic isotopes. Seven blank samples, six duplicate samples, six split samples and one trace metal standard were submitted along with the samples. The protocols used for field determinations, sampling and quality control were developed based on those defined by the Geological Survey of Canada, the United States Geological Survey, the United States Environmental Protection Agency and the universities of Alberta, Calgary and Saskatchewan. The protocols are documented in Lemay (2002).

## 2 Study Area

The study area is located in the northeastern portion of Alberta, bounded on the west by the Athabasca River, to the north by the Athabasca and Clearwater rivers, to the east by the Alberta/Saskatchewan border and to the south by the Mostoos Upland (Figure 1). The study area extent (aside from the provincial boundary) was selected to represent natural hydraulic boundaries. The Athabasca and Clearwater rivers are natural drainage boundaries. The Mostoos upland was selected because it forms the hydraulic divide between the Cold Lake – Beaver River drainage basin to the south and the Athabasca River – Clearwater River drainage basin to the north. The study area encompasses the southeast portion of the Energy and Utilities Board (EUB)-designated Athabasca Oil Sands Area.

## 3 Arsenic Geochemistry

Arsenic is a Group 15, Period 4 element generally classed as a chalcophile and, therefore, tends to concentrate in sulphide minerals and ores. Arsenic possesses five valence states: +5, +3, +1, 0 and -3. In natural water, however, arsenic is generally present only in the +5 (arsenate or As(V)) and/or +3 (arsenite or As(III)) state(s) as an oxyanion with the general form(s)  $H_nAsO_4^{3-n}$  and/or  $H_nAsO_3^{3-n}$ , respectively (Welch et al., 1988). Arsenic speciation is thought to be controlled by both pH and Eh. However, the determination of arsenic speciation between arsenite and arsenate is complicated by the fact that speciation is not necessarily predictable from field Eh measurements nor from calculated Eh values based on other measured redox couple concentrations (Welch et al., 1988). Both Cherry et al. (1979) and Yan et al. (2000), however, have correlated field measured Eh with calculated Eh values from arsenite and arsenate concentrations. The following general statements about arsenic speciation with respect to pH and Eh (Smedley and Kinniburgh, 2002) can be made.



Figure 1. Study area location.

Under oxidizing conditions

- under highly acidic conditions, H<sub>3</sub>AsO<sub>4</sub> may be present as the dominant species;
- $H_2AsO_4^-$  is the dominant species at pH values below approximately 6.9;
- at pH values greater than 6.9,  $HAsO_4^2$  becomes dominant; and
- under highly alkaline conditions,  $AsO_4^{3-}$  may be present as the dominant species.

Under reducing conditions

- at pH less than about 9.2, H<sub>3</sub>AsO<sub>3</sub> will predominate;
- at pH greater than 9.2 and less than approximately 12,  $H_2AsO_3^-$  will be dominant;
- at pH greater than approximately 12,  $HAsO_3^{2-}$  becomes dominant; and
- under highly alkaline conditions, AsO<sub>3</sub><sup>3-</sup> may be present.

Sources of arsenic are varied and include minerals, rocks, sediments, soil, anthropogenic sources and the atmosphere. Because of its ionic radii in both the As<sup>3+</sup> and As<sup>5+</sup> forms, arsenic can substitute for Si<sup>4+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup> Ti<sup>4+</sup> and S in numerous minerals (Smedley and Kinniburgh, 2002). Common mineral types include arsenates, sulphides, sulphosalts, arsenides, arsenites, oxides and native arsenic. Two of the most abundant arsenic-bearing minerals are arsenopyrite (Smedley and Kinniburgh, 2002) and arsenian pyrite (Nordstrom, 2000). Anthropogenic inputs of arsenic to the environment include: 1) agricultural application of pesticides; 2) use of arsenic as a wood preservative; and 3) use of arsenic in glass manufacturing operations. Arsenic is released into the atmosphere through sources such as volcanic gases and geothermal vents, as well as through the burning of fossil fuels and releases from industrial operations.

Processes that can lead to release of arsenic into the groundwater system include

- arsenic-bearing mineral dissolution;
- desorption of arsenic from soil material;
- chemical transformation of arsenic through redox or other processes;
- ion exchange between arsenic and other elements;
- release of arsenic through biological activity;
- release of arsenic through anthropogenic activity; and
- wet or dry deposition of atmospheric arsenic.

Important factors affecting these processes include

- pH and Eh;
- solution composition;
- competing and complexing ions concentrations;
- aquifer mineralogy;
- reaction kinetics;
- rate of diffusion of gases through the sediment;
- rate of sedimentation; and
- hydraulics of the groundwater system.

Arsenic is removed from the aqueous system through a number of mechanisms, including

- adsorption or co-precipitation by or with oxides of Fe, Al and Mn;
- adsorption onto clay, carbonate and phosphate minerals;
- adsorption onto organic material;

- co-precipitation with sulphide minerals; and
- oxidation of the more mobile As(III) to the less mobile As(V) by Mn(IV) with subsequent adsorption to oxide or clay minerals.

## 4 Observations and Preliminary Interpretations

The water chemistry data are presented in Table 1. Exact locations are not provided; only township and range. The approximate sample locations are plotted on Figure 1. A stratigraphic chart for the region is presented in Figure 2.

#### 4.1 Groundwater Chemistry

#### 4.1.1 Error, Accuracy and Precision

In an effort to ensure error, accuracy and precision could be estimated and quantified, quality assurance/ quality control (QA/QC) samples were collected during water sampling activities. These QA/QC samples included standard, sample-split replicates, sample duplicates and blank samples. A rigorous analysis of error, accuracy and precision has not yet been completed and therefore no comments have been made regarding this topic. However, strict, careful and detailed protocols were followed during sampling activities. Preliminary examination of the data indicates that the care taken during sampling is reflected in a high quality dataset. The QA/QC data are presented without comment in Table 2. Standard analysis methods were conducted on the water samples and, as such, low concentrations of arsenic were not resolved absolutely and are presented as being less than the detection limit.

#### 4.1.2 Groundwater Arsenic Concentrations

#### 4.1.2.1 Observations

Plotting the field-measured Eh against the field-measured pH in an Eh–pH diagram of the aqueous species of arsenic (Figure 3) indicates that the dominant arsenic species in solution, at the average aquifer temperature, would be  $HAsO_4^{2^-}$ . Arsenic in solution is likely in the As(V) arsenate form.

A preliminary examination of the water chemistry data shows that only seven of the 24 water samples collected have arsenic concentrations that are above the analytical detection limit of 0.01 mg/L. Two samples have arsenic concentrations of 0.01 mg/L (samples 15 and 35). Four of the samples have arsenic concentration of 0.02 mg/L (samples 17, 21, 33 and 34). One of the samples has an arsenic concentration of 0.03 mg/L (sample 10). This last concentration exceeds the interim maximum acceptable concentration for arsenic in drinking water of 0.025 mg/L as set out in the Summary of Guidelines for Canadian Drinking Water Quality (Federal-Provincial Subcommittee on Drinking Water of the Federal-Provincial-Territorial Committee on Environmental and Occupational Health, 2001).

Samples 15, 17 and 21 were collected from wells completed in Quaternary intertill-intratill aquifers. Sample 10 was collected from a piezometer installed by the Alberta Geological Survey (AGS) and is completed in an aquifer interpreted to be a terrace deposit of the Wiau Channel (Andriashek pers. comm., 2002). This terrace deposit sits directly on top of bedrock (Andriashek, pers comm., 2002). Samples 33, 34 and 35 are all completed within the Wiau Channel aquifer system.

Scanning electron microscope (SEM) analysis of till samples from the study area indicated the presence of minerals that are associated with arsenic. These minerals include pyrite, iron oxides, evaporites and carbonates (Figures 4a, 4b, 5a and 5b). The analysis also revealed the presence of clay minerals, Caphosphate minerals and of micro-organisms (Figures 4a, 4b, 5a and 6). Arsenic is known to adsorb to clay

Table 1. Quaternary intertill-intratill and Quaternary-Tertiary buried channel aquifer water chemistry.

							Field Pa	rameters					
ID	Township	Range	Ground Elevation (masl)	Formation	Completion Midpoint Depth (m)	Sample Date	Temperature (°C)	рН	Conductivity (μS/cm)	ORP (mV)	Standard half cell potential at field T (mV)	Eh (mV)	DO (mg/L)
1	085	09W4	763.5	Quaternary	12.1	July 11, 1979	7.0	7.20					
2	087	09W4	429.8	Quaternary	7.8	August 3, 2000	6.4	9.02	1513	-271	257	-14	0.8
3	077	15W4	662.5	Quaternary	6.7	June 22, 2001	6.4	7.07	402	-71	257	186	0.3
4	074	09W4	666.8	Quaternary	12.4	May 9, 2001	6.3	6.81	651	127	257	384	0.8
5	074	09W4	667.1	Quaternary	39.5	May 8, 2001	6.2	7.44	349	-155	257	102	0.0
6	074	09W4	667.0	Quaternary	73.9	May 8, 2001	7.0	7.48	424	-152	256	104	0.1
7	074	09W4	666.9	Quaternary	118.8	May 9, 2001	5.6	7.48	382	-154	257	103	0.1
8	075	05W4	648.2	Quaternary	14.3	May 11, 2001	6.6	7.08	506	69	257	326	0.2
9	075	05W4	648.3	Quaternary	78.1	May 11, 2001	8.3	7.17	1100	-49	255	206	0.1
10	075	05W4	648.2	Quaternary	157.0	May 10, 2001	7.1	7.67	594	-136	256	120	0.0
11	071	14W4	566.9	Quaternary	43.6	July 11, 2000	8.3	7.13	778	-141	255	114	2.0
12	070	17W4	566.9	Quaternary	44.2	July 12, 2000	10.4	7.44	912	-59	254	195	1.9
13	071	17W4	548.6	Quaternary	27.5	July 12, 2000	6.8	7.18	655	-190	256	67	1.2
14	071	17W4	562.4	Quaternary	28.8	July 13, 2000	7.2	7.15	610	-152	256	104	0.2
15	076	15W4	569.4	Quaternary	67.2	July 13, 2000	6.4	7.28	346	-145	257	111	2.8
16	084	10W4	652.0	Quaternary	19.2	July 18, 2000	6.5	7.28	391	-124	257	132	0.1
17	082	12W4	742.2	Quaternary	57.6	July 18, 2000	6.5	7.43	413	-170	257	86	0.1
18	070	04W4	672.2	Quaternary	65.9	July 24, 2000	7.6	7.40	542	-174	256	82	0.1
19	070	04W4	672.3	Quaternary	70.0	July 24, 2000	6.9	7.36	557	-148	256	108	0.2
20	076	07W4	571.2	Quaternary	49.6	July 26, 2000	7.2	7.29	427	-157	256	99	0.2
21	071	10W4	662.9	Quaternary	66.3	July 27, 2000	8.3	7.36	818	-105	255	150	0.2
22	069	12W4	585.2	Quaternary	50.7	March 21, 1989							
23	070	17W4	560.8	Quaternary	34.3	September 26, 1991							
24	070	17W4	570.0	Quaternary	26.9	September 13, 1990							
25	077	15W4	617.2	Quaternary	113.2	August 24, 1983							
26	070	17W4	557.8	Quaternary	19.9	September 8, 1992							
27	070	17W4	560.8	Quaternary	12.4	August 12, 1988							
28	070	17W4	570.0	Quaternary	9.9	September 13, 1990							
29	084	11W4	641.9	Quaternary	21.6	November 20, 1990							
30	086	18W4	529.0	Quaternary	50.5	January 27, 1987							
31	089	09W4	246.0	Quaternary	17.8	August 9, 1989							
32	085	09W4	764.1	Quaternary	35.7	August 4, 2000	5.1	8.09	297	-168	258	90	0.1
33	077	15W4	662.4	Quaternary	229.1	May 24, 2001	6.0	7.72	492	-171	257	86	0.1
34	073	06W4	713.2	Quaternary	280.1	July 25, 2000	8.6	7.99	593	-208	255	47	0.0
35	073	07W4	728.8	Quaternary	295.0	April 26, 2001	7.6	7.90	689	22	256	278	2.3

Table 1. Quaternary intertill-intratill and Quaternary-Tertiary buried channel aquifer water chemistry.

			Laboratory I	Parameter	S											
	P-Alk	T-Alk (ma/l)	Temperature	nH	Conductivity	P-Alk (mg	T-Alk (mg	Ca (mg/l )	Mg (mg/l )	Na (mg/L)	K (mg/l.)	HCO <sub>3</sub>	CO <sub>3</sub>	CI (mg/l)	CI by NAA	Br by NAA
	(iiig/L)		(0)	7 20				(IIIg/L)	(IIIg/L)	(IIIg/L)	(iiig/L)	(iiig/L)	(iiig/L)	(IIIG/L)	(ug/iiic)	(ug/iiiL)
1	-0	020		1.10	800.0	0.4	067	11.0	30.00	61.0	2.5	340	0	100.0		
2	<2	030		0.00 7.04	2170.0	04	2007	0.0	3.45	01/0	2.5	202	101	120.0	10.50	0.02
3	~2	666		7.24	1020.0	<5	601	168.0	50.60	4.0	2.4	393	10	9.4	0.03	0.02
4	<2	370		7.09	551.0	<5	311	82.0	24.40	4.5	3.6	370	<0 <6	<0.5	0.93	0.03
6	<2	570		7.55	645.0	<5	313	74.4	24.40	/8.0	0.0 0.0	381	<0 <6	11.0	12.80	0.01
7	<2	/12		7.65	601.0	<5	336	81.5	20.20	24.2	5.5	/10	<6	5.0	1 83	0.01
8	<2	472		7.00	770.0	<5 <5	398	104.0	38.40	24.2	2.8	485	<0 <6	15.0	18 70	0.01
9	<2	676		7.00	1540.0	<5	662	101.0	48.50	167.0	5.8	807	<6	82.7	88.00	0.36
10	<2	522		8 14	896.0	<5	453	32.9	11 20	182.0	4.7	552	<6	54	6.87	0.06
11	<2	418		7.31	1050.0		100	125.0	40.30	75.7	4.8	529	<6	15.3	15.10	0.08
12	<2	480		7.60	1160.0			72.5	26.80	202.0	4.7	656	<6	34.2	44.60	0.17
13	<2	436		7.32	875.0			120.0	36.50	41.6	4.5	537	<6	3.6	3.38	0.03
14	<2	410		7.22	848.0	<5	424	125.0	35.50	23.7	4.4	517	<6	4.4	2.25	0.02
15	<2	236		7.19	467.0	<5	260	68.6	18.90	11.6	3.2	317	<6	1.2	0.28	0.01
16	<2	286		7.32	559.0	<5	294	75.3	19.00	26.3	4.2	359	<6	0.9	0.63	< 0.02
17	<2	298		7.37	596.0	<5	316	76.2	18.90	34.2	6.6	385	<6	0.8	0.18	<0.04
18	<2	500		7.62	735.0	<5	428	85.5	25.00	66.0	4.6	521	<6	3.2	2.94	0.04
19	<2	510		7.63	765.0	<5	454	85.5	25.30	74.5	5.0	554	<6	2.8	3.39	0.05
20	<10	1200		7.58	603.0	<5	353	84.0	26.90	24.6	4.0	431	<6	<0.5	0.72	<0.04
21	<2	540		7.54	1140.0	<5	529	112.0	42.40	120.0	10.6	645	<6	4.8	4.33	<0.05
22				7.50	690.0			68.0	24.00	69.0	3.0	460		6.0		
23				7.66	990.0		468	78.0	24.00	123.0	5.1	571		8.0		
24				7.55	912.0		439	121.0	38.00	38.0	4.8	535		1.0		
25				8.40	660.0		385	63.0	18.00	85.0	5.5	459	5	<2		
26				7.44	882.0		439	139.0	32.00	10.0	3.4	535		0.8		
27				7.60	875.0		401	109.0	34.00	52.0	3.2	489		12.0		
28				7.50	675.0		372	95.0	32.00	6.0	2.6	453		1.0		
29				7.33	378.0		172	55.0	11.00	7.0		210		16.0		
30		_		8.70	1670.0		844	<1	<1	415.0	1.8	944	42	58.0		
31				7.68	784.0		310	79.0	22.00	58.0	3.1	378		46.0		
32	<2	310		7.91	440.0	<5	239	68.8	13.60	9.8	25.5	291	<6	< 0.5	1.84	< 0.012
33	<2	406		7.77	744.0	<5	395	64.8	18.70	98.9	5.4	482	<6	<0.5	0.44	0.01
34	<2	480	40.0	8.13	/87.0	<5	425	25.2	8.56	1/1.0	3.2	518	<6	35.1	44.00	0.29
35	<2	564	18.2	8.36	832.0	<5	495	7.4	3.47	215.0	2.0	603	<6	16.5	15.80	0.08

ID	l by NAA (ug/mL)	SO₄ (mg/L)	Hardness (mg/L CaCO <sub>3</sub> )	TDS (mg/L)	Charge Balance Error (%)	Acetic acid (mg/L)	Butyric acid (mg/L)	Formic acid (mg/L)	Propionic acid (mg/L)	As (mg/L)	AI (mg/L)	Sb (mg/L)	Ba (mg/L)	Be (mg/L)	Bi (mg/L)	B (mg/L)	Cd (mg/L)	Cr (mg/L)
1		36.60		596	2.2													
2		226.00	291.00	1440	-1.4	<0.2	<0.3	<0.1	221.0	<0.01	0.031	<0.005	0.0227	<0.0005	<0.007	3.700	<0.0005	<0.0008
3	0.01	7.84	341.00	342	1.6					<0.01	0.031	<0.005	0.2830	<0.0005	<0.007	0.060	<0.0005	<0.0008
4	0.01	6.87	628.00	591	2.5					<0.01	<0.008	<0.005	0.1570	<0.0005	<0.007	0.037	<0.0005	<0.0008
5	<0.01	5.11	305.00	313	2.9					<0.01	<0.008	<0.005	0.1720	<0.0005	0.008	0.088	<0.0005	<0.0008
6	<0.01	30.20	269.00	381	3.6					<0.01	0.011	<0.005	0.1750	<0.0005	<0.007	0.116	<0.0005	<0.0008
7	<0.01	6.08	304.00	348	2.0					<0.01	0.010	<0.005	0.2440	<0.0005	<0.007	0.158	<0.0005	<0.0008
8	<0.01	28.00	418.00	448	1.7					<0.01	<0.008	<0.005	0.1610	<0.0005	0.007	0.066	<0.0005	<0.0008
9	0.46	138.00	452.00	941	-5.7					<0.01	0.012	<0.005	0.0301	<0.0005	<0.007	0.330	<0.0005	<0.0008
10	0.03	54.20	128.00	562	1.3					0.030	0.012	<0.005	0.0718	<0.0005	<0.007	0.487	< 0.0005	<0.0008
11	0.02	188.00	479.00	710	-0.2	<0.2	<0.3	<0.1	0.5	<0.01	0.081	<0.005	0.0468	<0.0005	0.112	0.405	< 0.0005	<0.0008
12	0.03	108.00	291.00	771	2.7	<0.2	<0.3	<0.1	157.0	<0.01	0.039	<0.005	0.0785	<0.0005	0.019	0.517	<0.0005	<0.0008
13	0.01	103.00	449.00	573	-0.6	0.3	<0.3	0.4	176.0	<0.01	0.052	<0.005	0.0965	<0.0005	<0.007	0.214	0.0010	<0.0008
14	0.00	101.00	457.00	547	-1.9	0.4	<0.3	0.6	155.0	<0.01	0.057	<0.005	0.0880	<0.0005	<0.007	0.208	0.0009	<0.0008
15	<0.01	21.50	249.00	281	-1.0	0.2	<0.3	0.2	105.0	0.010	0.033	<0.005	0.0826	<0.0005	<0.007	0.099	0.0013	<0.0008
16	0.01	20.50	266.00	323	1.8	<0.2	<0.3	<0.1	107.0	<0.001	0.008	<0.005	0.0731	<0.0005	<0.007	0.186	< 0.0005	<0.0008
17	<0.01	21.00	268.00	347	1.8	0.3	<0.3	0.3	113.0	0.020	0.030	<0.005	0.1750	<0.0005	<0.007	0.308	< 0.0005	<0.0008
18	0.03	19.80	316.00	461	1.5					<0.01	0.017	<0.005	0.0800	<0.0005	<0.007	0.168	< 0.0005	<0.0008
19	0.03	18.40	318.00	484	0.9	0.2	<0.3	0.4	147.0	<0.01	0.017	<0.005	0.0965	< 0.0005	<0.007	0.176	< 0.0005	<0.0008
20	0.01	8.26	320.00	360	2.3	0.2	<0.3	0.2	126.0	<0.01	0.038	<0.005	0.1400	<0.0005	<0.007	0.122	< 0.0005	<0.0008
21	0.04	178.00	453.00	785	0.5	<0.2	<0.3	0.2	163.0	0.020	0.028	<0.005	0.0251	<0.0005	<0.007	0.209	< 0.0005	<0.0008
22		24.00		440	1.4													
23		80.00		600	0.4													
24		95.00		561	0.8													
25		34.00		439	1.2													
26		62.00		511	0.0													
27		65.00		516	4.3													
28		12.00		372	0.0													
29		2.00		231	0.2													
30		<5		988	2.8													
31		48.00		443	-0.8													
32	<0.01	17.50	228.00	278	4.5	<0.2	<0.3	<0.1	95.2	<0.01	0.044	<0.005	0.1260	<0.0005	<0.007	0.073	< 0.0005	<0.0008
33	<0.01	38.10	239.00	463	2.9					0.020	<0.080	< 0.005	0.0966	<0.0005	<0.007	0.360	< 0.0005	<0.0008
34	0.18	10.60	98.30	509	-1.1					0.020	0.036	<0.005	0.1560	< 0.0005	<0.007	0.333	< 0.0005	<0.0008
35	0.06	3.80	32.70	544	-1.8	<0.2	<0.3	<0.1	164.0	0.010	0.021	0.005	0.1360	0.0005	0.007	0.438	0.0005	0.0008

	1																		
		1	1	1		1	1			1	1		1	1	1	1			1
	Co	Cu	Fe	Pb	Li	Mn	Ηα	Мо	Ni	Р	Se	Si	Αα	Sr	s	ті	Ti	v	Zn
ID	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mq/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1	<b>\ U</b> /	( <b>U</b> /	,	( 0 /	,	( <b>U</b> /	,	( 0 /	( <b>U</b> /	\ <b>U</b> /	( <b>U</b> /	· · · /	\ <b>U</b> /	\ <b>U</b> /	( <b>U</b> )	· · · /	,	,	,
2	0.0025	0.111	0.007	< 0.002	0.081	0.005	< 0.0001	<0.001	0.073	0.64	< 0.004	2.920	<0.001	0.2740	75.300	< 0.004	< 0.0004	< 0.001	0.0017
3	0.0033	0.002	0.051	0.005	0.023	1.300	< 0.0001	< 0.001	0.004	< 0.03	< 0.004	8.510	0.001	0.4120	2.610	< 0.004	< 0.0004	< 0.001	0.0055
4	0.0010	< 0.001	0.094	< 0.002	0.020	0.025	< 0.0001	< 0.001	0.003	< 0.03	< 0.004	10.700	< 0.001	0.1570	2.290	< 0.004	< 0.0004	0.001	0.0011
5	0.0007	0.002	0.056	< 0.002	0.032	0.377	< 0.0001	< 0.001	< 0.001	< 0.03	< 0.004	11.000	< 0.001	0.3900	1.700	< 0.004	< 0.0004	<0.001	0.0010
6	0.0017	0.002	0.048	< 0.002	0.034	0.791	< 0.0001	0.010	< 0.001	< 0.03	< 0.004	9.340	<0.001	0.4070	10.100	< 0.004	< 0.0004	<0.001	0.0009
7	<0.0007	0.002	0.057	< 0.002	0.040	0.121	< 0.0001	<0.001	<0.001	< 0.03	0.004	11.800	<0.001	0.5540	2.030	< 0.004	< 0.0004	< 0.001	0.0006
8	0.0009	0.002	0.071	< 0.002	0.030	0.091	< 0.0001	0.001	<0.001	< 0.03	< 0.004	11.700	<0.001	0.2690	9.330	< 0.004	< 0.0004	0.004	0.0017
9	0.0024	0.001	0.081	< 0.002	0.062	0.077	< 0.0001	0.002	<0.001	0.11	< 0.004	11.000	<0.001	0.6030	46.000	< 0.004	< 0.0004	0.002	0.0008
10	0.0017	0.004	0.024	< 0.002	0.048	0.127	< 0.0001	0.034	0.002	0.39	< 0.004	14.900	<0.001	0.3140	18.100	< 0.004	0.0009	< 0.001	0.0006
11	0.0012	0.004	6.900	< 0.002	0.094	0.367	< 0.0001	<0.001	<0.001	0.49	< 0.004	8.480	<0.001	0.9200	62.700	< 0.004	< 0.0004	0.003	0.0139
12	0.0018	0.005	0.531	< 0.002	0.080	0.047	<0.0001	<0.001	0.004	0.25	<0.004	7.570	<0.001	0.7910	36.100	< 0.004	< 0.0004	0.003	0.0651
13	0.0009	0.004	7.800	< 0.002	0.060	0.266	< 0.0001	<0.001	<0.001	0.59	< 0.004	9.720	<0.001	0.7470	34.500	< 0.004	< 0.0004	0.002	0.0032
14	0.0008	0.004	7.330	< 0.002	0.066	0.138	<0.0001	<0.001	<0.001	0.58	<0.004	10.900	<0.001	0.9000	33.500	< 0.004	< 0.0004	0.002	0.0044
15	0.0007	0.004	11.200	<0.002	0.033	0.576	<0.0001	0.003	<0.001	0.76	<0.004	10.100	<0.001	0.3700	7.160	< 0.004	< 0.0004	<0.001	0.0048
16	0.0018	0.002	0.761	< 0.002	0.045	0.266	<0.0001	0.006	0.004	0.25	< 0.004	9.920	<0.001	0.4890	6.840	< 0.004	< 0.0004	0.002	0.0180
17	0.0014	0.002	4.200	< 0.002	0.049	0.259	<0.0001	0.015	<0.001	0.47	< 0.004	10.300	<0.001	0.7490	6.990	< 0.004	< 0.0004	<0.001	0.0163
18	0.0011	0.005	0.014	< 0.002	0.050	0.149	<0.0001	0.003	0.005	0.06	< 0.004	12.900	0.001	0.5140	6.620	< 0.004	< 0.0004	<0.001	0.0049
19	<0.0007	0.004	0.019	<0.002	0.053	0.134	<0.0001	0.003	<0.001	0.05	< 0.004	12.800	<0.001	0.5470	6.130	< 0.004	< 0.0004	<0.001	0.0027
20	0.0007	0.004	0.019	< 0.002	0.029	0.194	<0.0001	<0.001	<0.001	0.04	< 0.004	11.300	0.001	0.4120	2.750	< 0.004	< 0.0004	<0.001	0.0041
21	0.0015	0.003	0.027	< 0.002	0.064	0.794	<0.0001	0.005	<0.001	0.03	<0.004	9.280	0.001	0.5940	59.300	< 0.004	< 0.0004	0.001	0.0176
22																			
23			0.160																
24			4.480																
25			2.400																
26			5.310																
27			0.760																
28			4.190																
29			3.930																
30			0.100																
31			0.770																
32	<0.0007	0.008	0.013	< 0.002	0.054	0.282	<0.0001	0.002	0.006	< 0.03	<0.004	11.300	<0.001	0.6940	5.840	< 0.004	< 0.0004	<0.001	0.0039
33	0.0011	0.002	0.051	< 0.002	0.064	0.099	<0.0001	0.009	<0.001	0.17	<0.004	11.600	<0.001	0.4970	12.700	< 0.004	< 0.0004	<0.001	0.0007
34	0.0007	0.003	0.205	< 0.002	0.032	0.044	< 0.0001	0.014	<0.001	0.65	< 0.004	7.630	<0.001	0.3060	3.540	< 0.004	< 0.0004	0.002	0.0017
35	0.0024	0.003	0.133	< 0.002	0.018	0.013	< 0.0001	0.038	0.002	2.03	< 0.004	7.670	< 0.001	0.1050	1.270	< 0.004	0.0005	< 0.001	0.0041





ID Sample Name	Sample Type	Sample Date	Al-s	AI	Sb-s S	As-s	As	Ba-s	Ba	Be-s
1 Tubing and Filter Blank	System Blank	20000711	+	0.028	< 0.0	)5 <	0.01	+	0.0022	<
2 Tubing and Filter Blank	System Blank	20000718	+	0.029	< 0.0	)5 <	0.01	+	0.0075	<
3 Tubing and Filter Blank	System Blank	20000724	+	0.011	< 0.0	)5 <	0.01	+	0.0014	<
4 System Blank	System Blank	20000802	<	0.008	< 0.0	)5 <	0.01	+	0.0004	<
5 11-130 duplicate	Serial Duplicate	20000803	+	0.024	< 0.0	)5 <	0.01	+	0.0466	<
6 11-130a split	Split Sample	20000803	+	0.020	< 0.0	)5 <	0.01	+	0.0465	<
7 11-130b split	Split Sample	20000803	+	0.020	< 0.0	)5 <	0.01	+	0.0461	<
8 PW1CAQ1	Serial Duplicate	20000824	+	0.920	< 0.2	)0 <	0.50	+	24.40	<
9 PW1CAQ2	Split Sample	20000824	+	0.900	< 0.2	)0 <	0.50	+	24.30	<
10 PW1CT	Serial Duplicate after 1 week	20000831	+	0.750	< 0.1	)0 <	0.20	+	25.70	<
11 PW1ST	Standard Analytical Results	20000914	+	0.361	+ 0.0		0.04	+	0.3530	+
12 Trace Metals Sample	Standard Analytical Results from Manufacturer	20000914	+	0.300	+ 0.0	20 +	0.04	+	0.3000	+
13 PWIHB	HPLC Grade Water Blank	20000915	+	0.052	< 0.0	)5 <	0.01	+	0.0018	<
14 PWAQ23	System Blank	20010123	+	0.023	< 0.0	)5 <	0.01	+	0.0169	<
15 PWAQ24	Distilled Water Blank	20010123	+	0.033	< 0.0	)5 <	0.01	+	0.0085	<
16 PWAQ25	Serial Duplicate	20010124	+	0.130	< 0.0	50 <	0.10	+	12.30	<
17 PWAQ26	Split Sample	20010124	+	0.190	< 0.0	50 <	0.10	+	12.30	<
18 PWAQ27	Serial Duplicate	20010206	+	0.014	< 0.0	)5 <	0.01	+	2.02	<
19 PWAQ28	Split Sample	20010206	+	0.012	< 0.0	)5 <	0.01	+	2.02	<
20 System Blank	System Blank	20010427	<	0.008	< 0.0	)5 <	0.01	+	0.0002	<
21 WR 99-1-230-Duplicate	Serial Duplicate	20010524	<	0.008	< 0.0	)5 +	0.02	+	0.0959	<
22 WR 99-1-230-Split	Split Sample	20010524	<	0.008	< 0.0	)5 +	0.02	+	0.0958	<

ID	Sample Name	Sample Type	Be	Bi-s	Bi	B-s	В	Cd-s	Cd	Cr-s	Cr	Co-s	Co
1	Tubing and Filter Blank	System Blank	0.0005	<	0.007	+	0.009	<	0.0005	<	0.0008	<	0.0007
2	Tubing and Filter Blank	System Blank	0.0005	<	0.007	+	0.011	<	0.0005	<	0.0008	<	0.0007
3	Tubing and Filter Blank	System Blank	0.0005	<	0.007	+	0.008	<	0.0005	<	0.0008	<	0.0007
4	System Blank	System Blank	0.0005	<	0.007	+	0.019	<	0.0005	<	0.0008	<	0.0007
5	11-130 duplicate	Serial Duplicate	0.0005	<	0.007	+	1.02	<	0.0005	<	0.0008	+	0.0012
6	11-130a split	Split Sample	0.0005	<	0.007	+	1.02	<	0.0005	<	0.0008	+	0.0011
7	11-130b split	Split Sample	0.0005	<	0.007	+	1.01	<	0.0005	<	0.0008	+	0.0013
8	PW1CAQ1	Serial Duplicate	0.0300	<	0.400	+	4.78	<	0.0300	<	0.0400	+	0.0850
9	PW1CAQ2	Split Sample	0.0300	<	0.400	+	4.76	<	0.0300	<	0.0400	+	0.0650
10	PW1CT	Serial Duplicate after 1 week	0.0100	<	0.100	+	5.60	<	0.0100	<	0.0200	+	0.0420
11	PW1ST	Standard Analytical Results	0.0410	<	0.007	+	0.298	+	0.0348	+	0.5560	+	0.8840
12	Trace Metals Sample	Standard Analytical Results from Manufacturer	0.0400			+	0.250	+	0.0300	+	0.5000	+	0.7500
13	PWIHB	HPLC Grade Water Blank	0.0005	<	0.007	+	0.009	+	0.0014	<	0.0008	<	0.0007
14	PWAQ23	System Blank	0.0005	<	0.007	+	0.009	+	0.0006	+	0.0008	<	0.0007
15	PWAQ24	Distilled Water Blank	0.0005	<	0.007	+	0.007	<	0.0005	+	0.0014	+	0.0008
16	PWAQ25	Serial Duplicate	0.0050	+	0.070	+	9.12	<	0.0050	+	0.0080	<	0.0070
17	PWAQ26	Split Sample	0.0050	+	0.075	+	9.11	+	0.0055	+	0.0170	+	0.0110
18	PWAQ27	Serial Duplicate	0.0005	+	0.007	+	3.05	<	0.0005	<	0.0008	+	0.0026
19	PWAQ28	Split Sample	0.0005	+	0.007	+	3.05	<	0.0005	<	0.0008	+	0.0026
20	System Blank	System Blank	0.0005	<	0.007	+	0.005	<	0.0005	+	0.0009	<	0.0007
21	WR 99-1-230-Duplicate	Serial Duplicate	0.0005	<	0.007	+	0.361	<	0.0005	<	0.0008	+	0.0013
22	WR 99-1-230-Split	Split Sample	0.0005	<	0.007	+	0.360	<	0.0005	<	0.0008	+	0.0009

ID	Sample Name	Sample Type	Cu-s	Cu	Pb-s	Pb	Li-s	Li	Mo-s	Мо	Ni-s	Ni	P-s	Ρ
1	Tubing and Filter Blank	System Blank	+	0.004	<	0.002	<	0.001	<	0.001	<	0.001	<	0.03
2	Tubing and Filter Blank	System Blank	+	0.005	</td <td>0.002</td> <td>+</td> <td>0.002</td> <td>+</td> <td>0.001</td> <td><!--</td--><td>0.001</td><td>&lt;</td><td>0.03</td></td>	0.002	+	0.002	+	0.001	</td <td>0.001</td> <td>&lt;</td> <td>0.03</td>	0.001	<	0.03
3	Tubing and Filter Blank	System Blank	+	0.002	<	0.002	<	0.001	<	0.001	<b>^</b>	0.001	<	0.03
4	System Blank	System Blank	<	0.001	<	0.002	<	0.001	<	0.001	<b>^</b>	0.001	<	0.03
5	11-130 duplicate	Serial Duplicate	<	0.001	</td <td>0.002</td> <td>+</td> <td>0.076</td> <td>&lt;</td> <td>0.001</td> <td>+</td> <td>0.001</td> <td>+</td> <td>0.03</td>	0.002	+	0.076	<	0.001	+	0.001	+	0.03
6	11-130a split	Split Sample	<	0.001	<	0.002	+	0.076	<	0.001	<b>^</b>	0.001	+	0.05
7	11-130b split	Split Sample	<	0.001	<	0.002	+	0.076	<	0.001	<b>^</b>	0.001	+	0.09
8	PW1CAQ1	Serial Duplicate	<	0.050	<	0.100	+	2.61	<	0.050	<b>^</b>	0.050	+	2.70
9	PW1CAQ2	Split Sample	<	0.050	<	0.100	+	2.61	<	0.050	<	0.050	+	2.50
10	PW1CT	Serial Duplicate after 1 week	+	0.022	<	0.040	+	2.72	<	0.020	<b>^</b>	0.020	+	2.20
11	PW1ST	Standard Analytical Results	+	0.396	+	0.349	<	0.001	+	0.110	+	0.231	<	0.03
12	Trace Metals Sample	Standard Analytical Results from Manufacturer	+	0.350	+	0.300			+	0.100	+	0.200		
13	PWIHB	HPLC Grade Water Blank	+	0.008	<	0.002	<	0.001	<	0.001	<	0.001	<	0.03
14	PWAQ23	System Blank	+	0.018	<	0.002	+	0.004	<	0.001	+	0.002	<	0.03
15	PWAQ24	Distilled Water Blank	+	0.023	<	0.002	+	0.004	<	0.001	+	0.002	<	0.03
16	PWAQ25	Serial Duplicate	+	0.011	<	0.020	+	3.56	<	0.010	<	0.010	<	0.30
17	PWAQ26	Split Sample	<	0.010	<	0.020	+	3.54	<	0.010	+	0.021	<	0.30
18	PWAQ27	Serial Duplicate	<	0.001	<	0.002	+	1.22	<	0.001	+	0.002	+	0.29
19	PWAQ28	Split Sample	<	0.001	<	0.002	+	1.21	+	0.002	+	0.002	+	0.27
20	System Blank	System Blank	<	0.001	<	0.002	<	0.001	<	0.001	+	0.001	<	0.03
21	WR 99-1-230-Duplicate	Serial Duplicate	+	0.002	<	0.002	+	0.065	+	0.009	<	0.001	+	0.18
22	WR 99-1-230-Split	Split Sample	+	0.001	<	0.002	+	0.065	+	0.008	<	0.001	+	0.19

ID	Sample Name	Sample Type	Se-s	Se	Si-s	Si	Ag-s	Ag	Sr-s	Sr	S-s	S	TI-s	TI
1	Tubing and Filter Blank	System Blank	<	0.004	+	0.03	<	0.001	+	0.001	+	0.10	<	0.004
2	Tubing and Filter Blank	System Blank	+	0.006	+	1.07	<	0.001	+	0.002	+	13.60	<	0.004
3	Tubing and Filter Blank	System Blank	<	0.004	+	0.03	<	0.001	+	0.001	+	0.23	<	0.004
4	System Blank	System Blank	<	0.004	+	0.01	<	0.001	+	0.000	+	0.08	<	0.004
5	11-130 duplicate	Serial Duplicate	<	0.004	+	6.11	<	0.001	+	0.609	+	10.50	<	0.004
6	11-130a split	Split Sample	<	0.004	+	6.15	<	0.001	+	0.606	+	10.50	<	0.004
7	11-130b split	Split Sample	<	0.004	+	6.10	<	0.001	+	0.606	+	10.40	<	0.004
8	PW1CAQ1	Serial Duplicate	+	0.910	+	2.71	<	0.050	+	55.7	+	1.50	<	0.200
9	PW1CAQ2	Split Sample	+	0.250	+	2.43	<	0.050	+	55.8	+	1.90	<	0.200
10	PW1CT	Serial Duplicate after 1 week	<	0.080	+	2.90	<	0.020	+	56.9	+	2.91	<	0.080
11	PW1ST	Standard Analytical Results	+	0.112	+	0.43	+	0.057	+	0.315	+	0.02	+	0.146
12	Trace Metals Sample	Standard Analytical Results from Manufacturer	+	0.100			+	0.050	+	0.300			+	0.100
13	PWIHB	HPLC Grade Water Blank	+	0.015	+	0.06	<	0.001	+	0.002	+	0.05	+	0.006
14	PWAQ23	System Blank	<	0.004	+	2.76	<	0.001	+	0.073	+	24.40	<	0.004
15	PWAQ24	Distilled Water Blank	<	0.004	+	2.75	+	0.001	+	0.070	+	24.70	<	0.004
16	PWAQ25	Serial Duplicate	<	0.040	+	2.13	+	0.011	+	22.7	+	0.22	<	0.040
17	PWAQ26	Split Sample	+	0.071	+	2.20	+	0.012	+	22.6	+	0.13	+	0.067
18	PWAQ27	Serial Duplicate	<	0.004	+	3.04	<	0.001	+	2.240	+	2.77	<	0.004
19	PWAQ28	Split Sample	<	0.004	+	3.11	<	0.001	+	2.270	+	2.75	<	0.004
20	System Blank	System Blank	<	0.004	<	0.00	<	0.001	+	0.001	+	0.04	<	0.004
21	WR 99-1-230-Duplicate	Serial Duplicate	<	0.004	+	11.70	<	0.001	+	0.540	+	12.80	<	0.004
22	WR 99-1-230-Split	Split Sample	<	0.004	+	11.70	<	0.001	+	0.514	+	12.80	<	0.004

ID	Sample Name	Sample Type	Ti-s	Ti	V-s	۷	Zn-s	Zn	Hg-s	Hg	SiEx-s	SiEx
1	Tubing and Filter Blank	System Blank	<	0.0004	+	0.002	+	0.001	<	1E-04		
2	Tubing and Filter Blank	System Blank	<	0.0004	+	0.001	<	0.001	<	1E-04		
3	Tubing and Filter Blank	System Blank	<	0.0004	<	0.001	+	0.004	<	1E-04		
4	System Blank	System Blank	<	0.0004	<	0.001	+	0.003	<	1E-04		
5	11-130 duplicate	Serial Duplicate	<	0.0004	<	0.001	+	0.001	<	1E-04		
6	11-130a split	Split Sample	<	0.0004	<	0.001	<	0.001	<	1E-04		
7	11-130b split	Split Sample	<	0.0004	<	0.001	<	0.001	<	1E-04		
8	PW1CAQ1	Serial Duplicate	<	0.0200	<	0.050	+	0.040	<	1E-04	+	3.27
9	PW1CAQ2	Split Sample	<	0.0200	<	0.050	<	0.030	<	1E-04		
10	PW1CT	Serial Duplicate after 1 week	<	0.0080	+	0.042	+	0.074	<	1E-04	+	2.85
11	PW1ST	Standard Analytical Results	+	0.0215	+	0.388	+	0.833				
12	Trace Metals Sample	Standard Analytical Results from Manufacturer			+	0.350	+	0.750	+	0.014		
13	PWIHB	HPLC Grade Water Blank	+	0.0007	+	0.002	+	0.005				
14	PWAQ23	System Blank	<	0.0004	<	0.001	+	0.009	<	1E-04	+	2.35
15	PWAQ24	Distilled Water Blank	<	0.0004	<	0.001	+	0.012	<	1E-04	+	2.34
16	PWAQ25	Serial Duplicate	<	0.0040	<	0.010	+	0.025	<	1E-04	+	1.95
17	PWAQ26	Split Sample	<	0.0040	<	0.010	<	0.006	<	1E-04		
18	PWAQ27	Serial Duplicate	<	0.0004	+	0.002	+	0.002	<	1E-04	+	2.56
19	PWAQ28	Split Sample	<	0.0004	<	0.001	+	0.003	<	1E-04		
20	System Blank	System Blank	<	0.0012	+	0.001	+	0.007	<	1E-04		
21	WR 99-1-230-Duplicate	Serial Duplicate	<	0.0004	<	0.001	<	0.001	<	1E-04	+	3.73
22	WR 99-1-230-Split	Split Sample	<	0.0004	<	0.001	+	0.006	<	1E-04		

ID	Sample Name	Sample Type	SIO2Ex-s	SIO2Ex	AA-s	Acetic Acid	BuA-s	<b>Butyric Acid</b>	FA-s
1	Tubing and Filter Blank	System Blank							
2	Tubing and Filter Blank	System Blank							
3	Tubing and Filter Blank	System Blank							
4	System Blank	System Blank							
5	11-130 duplicate	Serial Duplicate							
6	11-130a split	Split Sample							
7	11-130b split	Split Sample							
8	PW1CAQ1	Serial Duplicate	+	6.99	<	0.20	<	0.30	<
9	PW1CAQ2	Split Sample							
10	PW1CT	Serial Duplicate after 1 week	+	6.10	<	0.20	<	0.30	<
11	PW1ST	Standard Analytical Results							
12	Trace Metals Sample	Standard Analytical Results from Manufacturer							
13	PWIHB	HPLC Grade Water Blank							
14	PWAQ23	System Blank	+	5.02	+	0.20	<	0.30	<
15	PWAQ24	Distilled Water Blank	+	5.00	+	0.30	<	0.30	<
16	PWAQ25	Serial Duplicate	+	4.18	<	4.00	<	6.00	<
17	PWAQ26	Split Sample							
18	PWAQ27	Serial Duplicate	+	5.47	+	1.10	<	2.00	<
19	PWAQ28	Split Sample							
20	System Blank	System Blank							
21	WR 99-1-230-Duplicate	Serial Duplicate	+	7.99					
22	WR 99-1-230-Split	Split Sample							

ID	Sample Name	Sample Type	Formic Acid	PA-s	Propionic Acid	pH-s	рΗ	Cond-s	Cond	Ca-s
1	Tubing and Filter Blank	System Blank				+	6.00	+	2.90	<
2	Tubing and Filter Blank	System Blank				+	8.16	+	187.00	<
3	Tubing and Filter Blank	System Blank				+	6.29	+	3.80	<
4	System Blank	System Blank				+	8.27	+	2.70	+
5	11-130 duplicate	Serial Duplicate				+	7.80	+	1080.00	+
6	11-130a split	Split Sample				+	8.07	+	1060.00	+
7	11-130b split	Split Sample				+	8.06	+	1060.00	+
8	PW1CAQ1	Serial Duplicate	0.10	+	13	+	6.92	+	47200.00	+
9	PW1CAQ2	Split Sample				+	7.12	+	46400.00	+
10	PW1CT	Serial Duplicate after 1 week	0.10	+	18	+	7.16	+	45900.00	+
11	PW1ST	Standard Analytical Results								+
12	Trace Metals Sample	Standard Analytical Results from Manufacturer								
13	PWIHB	HPLC Grade Water Blank								+
14	PWAQ23	System Blank	0.10	+	64	+	8.34	+	397.00	+
15	PWAQ24	Distilled Water Blank	0.10	+	64	+	8.23	+	386.00	+
16	PWAQ25	Serial Duplicate	2.00	+	153	+	7.62	+	30300.00	+
17	PWAQ26	Split Sample				+	7.67	+	29600.00	+
18	PWAQ27	Serial Duplicate	0.50	+	798	+	8.08	+	9880.00	+
19	PWAQ28	Split Sample				+	8.16	+	9980.00	+
20	System Blank	System Blank				+	6.34	+	1.60	<
21	WR 99-1-230-Duplicate	Serial Duplicate				+	7.78	+	747.00	+
22	WR 99-1-230-Split	Split Sample				+	7.98	+	740.00	+

ID Sample Name	Sample Type	Ca	Mg-s	Mg	Na-s	Na	K-s	K	Fe-s	Fe	Mn-s	Mn
1 Tubing and Filter Blank	System Blank	0.20	<	0.05	+	0.4	<	0.40	+	0.018	+	0.0006
2 Tubing and Filter Blank	System Blank	0.20	+	0.06	+	46.6	<	0.40	+	0.010	+	0.0011
3 Tubing and Filter Blank	System Blank	0.20	+	0.06	+	1.0	+	0.80	<	0.003	+	0.0006
4 System Blank	System Blank	0.30	+	0.25	+	0.5	<	0.40	<	0.003	+	0.0008
5 11-130 duplicate	Serial Duplicate	47.30	+	16.40	+	210.0	+	2.90	+	0.044	+	0.0385
6 11-130a split	Split Sample	46.90	+	16.30	+	209.0	+	3.00	+	0.148	+	0.0390
7 11-130b split	Split Sample	46.80	+	16.40	+	210.0	+	2.30	+	0.146	+	0.0388
8 PW1CAQ1	Serial Duplicate	536.00	+	253.00	+	11000.0	+	50.00	+	0.350	+	0.7300
9 PW1CAQ2	Split Sample	536.00	+	253.00	+	10900.0	+	50.00	+	0.360	+	0.7100
10 PW1CT	Serial Duplicate after 1 week	529.00	+	265.00	+	12200.0	+	53.00	+	0.140	+	0.7960
11 PW1ST	Standard Analytical Results	0.20	<	0.05	+	0.4	<	0.04	+	0.251	+	0.5590
12 Trace Metals Sample	Standard Analytical Results from Manufacturer								+	0.200	+	0.5000
13 PWIHB	HPLC Grade Water Blank	0.20	<	0.05	+	0.6	<	0.40	+	0.011	+	0.0005
14 PWAQ23	System Blank	9.00	+	7.26	+	66.5	<	0.40	<	0.003	+	0.0012
15 PWAQ24	Distilled Water Blank	9.10	+	7.32	+	66.9	<	0.40	<	0.003	+	0.0008
16 PWAQ25	Serial Duplicate	228.00	+	128.00	+	7570.0	+	40.10	<	0.030	+	0.8480
17 PWAQ26	Split Sample	227.00	+	128.00	+	7460.0	+	40.90	<	0.030	+	0.8400
18 PWAQ27	Serial Duplicate	21.90	+	23.50	+	2610.0	+	21.90	+	0.004	+	0.0765
19 PWAQ28	Split Sample	22.00	+	23.40	+	2550.0	+	21.80	+	0.003	+	0.0762
20 System Blank	System Blank	0.20	<	0.05	<	0.4	<	0.40	+	0.003	+	0.0003
21 WR 99-1-230-Duplicate	Serial Duplicate	65.60	+	19.10	+	99.8	+	5.40	+	0.056	+	0.0956
22 WR 99-1-230-Split	Split Sample	65.20	+	18.90	+	99.9	+	5.40	+	0.057	+	0.0961

ID	Sample Name	Sample Type	Cl-s	CI	CINAA-s	CI by NAA	BrNAA-s	Br by NAA	INAA-s
1	Tubing and Filter Blank	System Blank	<	0.50					
2	Tubing and Filter Blank	System Blank	+	2.40					
3	Tubing and Filter Blank	System Blank	<	0.50					
4	System Blank	System Blank	<	0.50					
5	11-130 duplicate	Serial Duplicate	+	74.70					
6	11-130a split	Split Sample	+	74.20					
7	11-130b split	Split Sample	+	73.90					
8	PW1CAQ1	Serial Duplicate	+	17100	+	20200	+	68.20	+
9	PW1CAQ2	Split Sample	+	18000					
10	PW1CT	Serial Duplicate after 1 week	+	19700					
11	PW1ST	Standard Analytical Results							
12	Trace Metals Sample	Standard Analytical Results from Manufacturer							
13	PWIHB	HPLC Grade Water Blank							
14	PWAQ23	System Blank	+	1.70	+	3.58	<	0.01	<
15	PWAQ24	Distilled Water Blank	+	1.30	+	3.44	+	0.01	<
16	PWAQ25	Serial Duplicate	+	11800	+	12800	+	38.50	+
17	PWAQ26	Split Sample	+	11800					
18	PWAQ27	Serial Duplicate	+	2120	+	2460	+	5.85	+
19	PWAQ28	Split Sample	+	2130					
20	System Blank	System Blank	<	0.50					
21	WR 99-1-230-Duplicate	Serial Duplicate	<	0.50					
22	WR 99-1-230-Split	Split Sample	<	0.50					

ID Sample Name	Sample Type	I by NAA	NO3+NO2-s	NO3+NO2	SO4-s	SO4	OH-s	OH	CO3-s
1 Tubing and Filter Blank	System Blank		<	0.006	+	0.31	<	5	<
2 Tubing and Filter Blank	System Blank		+	0.272	+	40.70	<	5	<
3 Tubing and Filter Blank	System Blank		<	0.006	+	0.68	<	5	<
4 System Blank	System Blank		+	0.014	+	2.05	<	5	<
5 11-130 duplicate	Serial Duplicate		+	0.010	+	31.50	<	5	<
6 11-130a split	Split Sample		+	0.009	+	31.50	<	5	<
7 11-130b split	Split Sample		<	0.006	+	31.20	<	5	<
8 PW1CAQ1	Serial Duplicate	10.60	+	0.660	+	4.60	<	5	<
9 PW1CAQ2	Split Sample		<	0.300	+	5.70	<	5	<
10 PW1CT	Serial Duplicate after 1 week		<	0.300	+	8.74	<	5	<
11 PW1ST	Standard Analytical Results				+	0.07			
12 Trace Metals Sample	Standard Analytical Results from Manufacturer								
13 PWIHB	HPLC Grade Water Blank				+	0.16			
14 PWAQ23	System Blank	0.01	+	0.304	+	73.20	<	5	<
15 PWAQ24	Distilled Water Blank	0.01	<	0.328	+	74.10	<	5	<
16 PWAQ25	Serial Duplicate	7.94	<	0.100	+	0.66	<	5	<
17 PWAQ26	Split Sample		<	0.100	+	0.38	<	5	<
18 PWAQ27	Serial Duplicate	1.34	<	0.060	+	8.30	<	5	<
19 PWAQ28	Split Sample		<	0.060	+	8.25	<	5	<
20 System Blank	System Blank		<	0.006	+	0.12	<	5	<
21 WR 99-1-230-Duplicate	Serial Duplicate		<	0.006	+	38.30	<	5	<
22 WR 99-1-230-Split	Split Sample		<	0.006	+	38.30	<	5	<

ID Sample Name	Sample Type	CO3	HCO3-s	HCO3	P-Alk-s	P-Alk	T-Alk-s	T-Alk	TDS-s	TDS
1 Tubing and Filter Blank	System Blank	6	<	5	<	5	<	5	<	1
2 Tubing and Filter Blank	System Blank		+	60	<	5	+	50	+	120
3 Tubing and Filter Blank	System Blank	6	<	5	<	5	<	5	+	2
4 System Blank	System Blank	6	<	5	<	5	<	5	+	3
5 11-130 duplicate	Serial Duplicate	6	+	599	<	5	+	491	+	677
6 11-130a split	Split Sample	6	+	602	<	5	+	494	+	678
7 11-130b split	Split Sample	6	+	608	<	5	+	498	+	680
8 PW1CAQ1	Serial Duplicate	6	+	124	<	5	+	102	+	28900
9 PW1CAQ2	Split Sample	6	+	121	<	5	+	100	+	29800
10 PW1CT	Serial Duplicate after 1 week	6	+	128	<	5	+	105	+	32800
11 PW1ST	Standard Analytical Results									
12 Trace Metals Sample	Standard Analytical Results from Manufacturer									
13 PWIHB	HPLC Grade Water Blank									
14 PWAQ23	System Blank	6	+	164	<	5	+	135	+	239
15 PWAQ24	Distilled Water Blank	6	+	161	<	5	+	132	+	238
16 PWAQ25	Serial Duplicate	6	+	206	<	5	+	169	+	19900
17 PWAQ26	Split Sample	6	+	206	<	5	+	169	+	19800
18 PWAQ27	Serial Duplicate	6	+	3550	<	5	+	2910	+	6550
19 PWAQ28	Split Sample	6	+	3530	<	5	+	2900	+	6480
20 System Blank	System Blank	6	<	5	<	5	<	5	<	1
21 WR 99-1-230-Duplicate	Serial Duplicate	6	+	477	<	5	+	391	+	463
22 WR 99-1-230-Split	Split Sample	6	+	480	<	5	+	394	+	464

ID	Sample Name	Sample Type	Hard-s	Hard
1	Tubing and Filter Blank	System Blank	<	0.7
2	Tubing and Filter Blank	System Blank	+	0.2
3	Tubing and Filter Blank	System Blank	+	0.2
4	System Blank	System Blank	+	1.7
5	11-130 duplicate	Serial Duplicate	+	186.0
6	11-130a split	Split Sample	+	184.0
7	11-130b split	Split Sample	+	184.0
8	PW1CAQ1	Serial Duplicate	+	2380.0
9	PW1CAQ2	Split Sample	+	2380.0
10	PW1CT	Serial Duplicate after 1 week	+	2410.0
11	PW1ST	Standard Analytical Results	+	0.6
12	Trace Metals Sample	Standard Analytical Results from Manufacturer		
13	PWIHB	HPLC Grade Water Blank	+	0.6
14	PWAQ23	System Blank	+	52.4
15	PWAQ24	Distilled Water Blank	+	52.8
16	PWAQ25	Serial Duplicate	+	1100.0
17	PWAQ26	Split Sample	+	1090.0
18	PWAQ27	Serial Duplicate	+	152.0
19	PWAQ28	Split Sample	+	151.0
20	System Blank	System Blank	<	0.7
21	WR 99-1-230-Duplicate	Serial Duplicate	+	242.0
22	WR 99-1-230-Split	Split Sample	+	241.0



a)

b)

Figure 3. Quaternary and Quaternary-Tertiary aquifer Eh-pH values in the As-0<sub>2</sub>-H<sub>2</sub>0 system at 7.1°C and 1 bar total pressure: a) overview; and b)detaled view with sample points.







Figure 5. SEM images of: a ) original framboidal pyrite of bacterial origin oxidized to Fe-oxide; and b) Fe-oxide grain coating, carbonate and evaporite mineral.



Figure 6. Ca-phosphate fragment (possibly fish scale) found in Quaternary till.

minerals. Micro-organisms can catalyze or otherwise enhance reactions that lead to the release of arsenic. Phosphorus species can compete with arsenic for adsorption sites on minerals.

In the Quaternary intertill-intratill aquifer water samples (10, 15, 17 and 21), the following relationships were observed through examination of the chemistry data table (Table 1). Concentrations of Al, Fe, Mn and P in solution decrease as concentrations of arsenic increase in solution (Figure 7a, b, c and d). Concentrations of As increase as pH increases (Figure 8). Aside from the observed trends in the arsenic vs. aluminum and arsenic vs. pH plots, sample 21 does not appear to follow the same trends as the other arsenic-bearing Quaternary intertill-intratill aquifer water samples. A table of summary statistics (Table 3) shows that the water samples that contain arsenic concentrations above the analytical detection limit have approximately the same average Al concentration, higher average Fe, Mn and P concentrations, as well as a higher average pH value than the water samples that have arsenic concentrations below the detection limit.



Figure 7. Concentration relationships between: a) As and Al; b) As and Mn; c) As and Fe; and d) As and P in water from Quaternary intertill-intratill aquifers in the Athabasca Oil Sands (in situ) Area of northeastern Alberta.

In the Quaternary-Tertiary buried channel aquifer samples (33, 34 and 35), the following general relationships were observed through analysis of the chemistry data table. Arsenic concentrations in solution increase as concentrations of Ca, Mg, Sr and SO<sub>4</sub> in solution increase (Figure 9a, b, c and d). Arsenic concentrations increase as concentrations of HCO<sub>3</sub> and P decrease in solution (Figure 10a and b). Arsenic concentrations increase as Eh decreases (Figure 10c). A table of summary statistics (Table 4) shows that the water samples from the Quaternary-Tertiary buried channel aquifers have lower average values of calcium, magnesium, sulphate, strontium and arsenic than water samples collected from Quaternary intertill-intratill aquifers, whereas concentrations of bicarbonate and phosphorus are greater in the Quaternary-Tertiary buried channel aquifers than in the Quaternary intertill-intratill aquifers.

Relationships between As and Ca, Mg, Sr,  $SO_4$ ,  $HCO_3$  and Eh were not observed in the Quaternary intertill-intratill aquifer water samples. Relationships between As and Al, Fe, Mn and pH were not observed in the Quaternary-Tertiary buried channel aquifers.



Figure 8. Relationship between As and pH in water from Quaternary intertill-intratill aquifers in the Athabasca Oil Sands (in situ) Area of northeatern Alberta.

All Quaternary Intertill	-intratili ad	quiter water sa	ampies			
	As	Al	Fe	Mn	Р	рН
Average value	0.020	0.031	2.05	0.304	0.336	7.40
Minimum value	< 0.010	< 0.008	0.007	0.005	< 0.03	6.81
Maximum value	0.030	0.081	11.2	1.30	0.760	9.02
Standard deviation	0.008	0.019	3.04	0.320	0.255	0.440
Number of values	4	18	30	21	14	22
Quaternary intertill-int	ratill aquif	er water samp	oles with arse	enic concentrat	ion above the d	letection limit
	As	AI	Fe	Mn	Р	pН
Average value	0.020	0.026	3.86	0.439	0.412	7.44
Minimum value	0.010	0.012	0.024	0.127	0.030	7.28
Maximum value	0.030	0.033	11.2	0.794	0.760	7.67
Standard deviation	0.008	0.009	5.273	0.303	0.300	0.170
Number of values	4	4	4	4	4	4

Table 3. Summary statistics of elemental concentrations in Quaternary intertill-intratill aquifer water samples.



Figure 9. Concentration relationships between: a) As and Ca; b) As and Mg; c) As and Sr; and d) As and S0<sub>4</sub> in water from Quaternary-Tertiary buried channel aquifers in the Athabasca Oil Sands (in situ) Area of northeastern Alberta.

#### 4.1.2.2 Preliminary Interpretations – Quaternary Intertill-Intratill Aquifers

Based on the Eh-pH diagram (Figure 3), if present, arsenic in the various aquifers is likely to be in the less mobile arsenate or As(V) form.

Since the majority of the samples have arsenic concentrations below the arsenic detection limit of the analytical procedure utilized (0.01 mg/L), arsenic may not be present at all in groundwater, suggesting that some mechanism must either exclude arsenic from solution or not allow it to enter solution, or arsenic is present in groundwater, but below detection limits. This suggests that at the majority of the locations one or a combination of the following is true: 1) arsenic is not being introduced into the groundwater system through natural or anthropogenic sources; 2) mechanisms for removal of arsenic, such as adsorption to oxyhydroxides or clay minerals, are very effective; 3) the exchange of other ions for arsenic in solution is not an effective means of releasing arsenic given aquifer conditions; 4) groundwater flow through the aquifers in question has flushed the majority of the arsenic out of the system already; 5) Eh-pH conditions within the aquifers are not conducive to the release of arsenic; 6) arsenic is simply not



Figure 10. Relationships between: a) As and P; b) As and HC)3; and c) As and Eh in water from Quaternary-Tertiary buried channel aquifers in the Athabasca Oil Sands (in situ) Area of northeastern Alberta.

present within these Quaternary sediments; 7) the analytical detection limit was too high to detect the arsenic in solution.

In four samples arsenic was detected. Trends in elemental concentrations of Al, Fe, Mn and P could help explain why.

Saturation indices (Table 5) indicate that the water within the Quaternary intertill-intratill aquifers is supersaturated with respect to gibbsite  $(Al(OH)_3)$ , amorphous  $Fe(OH)_3$ , goethite (FeOOH) and hematite  $(Fe_2O_3)$ . The same water samples are undersaturated with respect to amorphous  $Al(OH)_3$ , hausmannite  $(Mn_3O_4)$ , manganite (MnOOH), pyrolusite  $(MnO_2)$  and pyrochroite  $(Mn(OH)_2)$ . These values may indicate oxides of Fe and potentially Al are forming within the Quaternary sediments. Scanning electron microscope (SEM) analysis of till samples confirms the presence of iron oxide minerals (Figure 4a, 5a and 5b). The major minerals binding arsenic in sediments are the metal oxides, particularly those of Fe, Al and Mn (Smedley and Kinniburgh, 2002). However, arsenic concentrations increase as concentrations of Al, Fe and Mn decrease (Figure 7a, b and c). The inverse relationship between arsenic and Fe, Al and

Table 4. Summary statistics of elemental concentrations in Quaternary-Tertiary buried channel aquifer water samples compared to Quaternary intertill-intratill aquifer water samples.

All Quaternary intertill-intratill aquifer water samples											
	As	Ca	Mg	Sr	Р	HCO,	Eh				
Average value	0.020	88.3	26.9	0.529	0.336	504	133				
Minimum value	< 0.010	<1	< 1	0.157	< 0.03	210	-14.4				
Maximum value	0.030	168	50.6	0.920	0.760	944	384				
Standard deviation	0.008	31.3	11.0	0.212	0.255	163	90.1				
Number of values	4	31	31	21	14	32	21				
Quaternary intertill-intratill aquifer water samples with arsenic concentrations above the detection limit											
	As	Ca	Mg	Sr	P	HCO <sub>3</sub>	Eh				
Average value	0.020	72.4	22.8	0.507	0.412	475	117				
Minimum value	0.010	32.9	11.2	0.314	0.030	317	86.4				
Maximum value	0.030	112	42.4	0.749	0.760	645	150				
Standard deviation	0.008	32.4	13.5	0.202	0.300	150	26.4				
Number of values	4	4	4	4	4	4	4				
Quaternary-Tertiary	buried cl	nannel aquif	er water samp	les							
	As	Ca	Mg	Sr	P	HCO <sub>3</sub>	Eh				
Average value	0.017	32.5	10.2	0.303	0.950	534	137				
Minimum value	0.010	7.40	3.47	0.105	0.170	482	47.0				
Maximum value	0.020	64.8	18.7	0.497	2.03	603	278				
Standard deviation	0.005	29.4	7.75	0.196	0.966	62.1	124				
Number of values	3	3	3	3	3	3	3				

Mn concentrations seems to contradict the possibility that arsenic is being adsorbed to the oxyhydroxide minerals. The trend between phosphorus and arsenic concentrations however may help explain this inverse relationship.

Arsenic concentrations increase as concentrations of P decrease (Figure 7d). Phosphorus is known to compete with arsenic for adsorption sites on oxyhydroxide surfaces (Smedley and Kinniburgh, 2002). The competition for adsorption sites can result in the release of arsenic into solution. SEM images reveal the presence of calcium phosphate fragments within Quaternary sediments (Figure 6). Therefore, since oxide minerals are present, as are potential sources of phosphorus, competition with arsenic for adsorption sites may be occurring, resulting in the release of arsenic into solution. The average P concentration in the four water samples that contain arsenic is greater than the average concentration of P in the water samples that have arsenic concentrations below the analytical detection limit. Intuitively, a greater concentration of competing ion should result in a greater release of ion previously adsorbed.

Another possible explanation for the observed arsenic concentrations relates to the solution pH. Arsenic is unique among heavy metalloids and oxyanion-forming elements in its sensitivity to mobilization at the pH values typically found in groundwater under both oxidizing and reducing conditions (Smedley and Kinniburgh, 2002). Oxyanions of arsenate tend to become less strongly sorbed as pH increases (Dzombak and Morel, 1990), even at near-neutral pH values (Smedley and Kinniburgh, 2002). Figure 8 contains a plot of arsenic vs. pH and shows that the concentration of arsenic increases as pH increases. The pH of the solution may, therefore, be a factor controlling arsenic concentration in Quaternary intertill-intratill aquifers. Combined with the fact that P adsorption to oxide minerals increases as pH increases, it suggests

All Quaternary inter	till-intratill a	quifer water s	amples						
	AI(OH), a	AI(OH) <sub>3</sub>	Fe(OH), a	FeOOH	Fe,O,	Mn <sub>3</sub> O <sub>4</sub>	MnOOH	MnO,	Mn(OH),
Average value	-1.08	1.76	1.79	7.68	16.64	-15.06	-5.09	-11.90	-6.36
Minimum value	-2.37	0.50	0.26	6.15	13.18	-18.97	-7.72	-13.83	-8.39
Maximum value	-0.20	2.65	3.43	9.33	19.15	-8.99	-2.78	-8.73	-4.78
Standard deviation	0.65	0.69	0.89	0.89	1.80	2.85	1.08	1.63	0.75
Number of values	18	18	30	30	30	21	21	21	21
Quaternary intertill-	intratill aqui	fer water sam	ples with arse	nic concentra	tions above t	he detection li	mit.		
	AI(OH), a	AI(OH) <sub>3</sub>	Fe(OH), a	FeOOH	Fe,O,	Mn <sub>3</sub> O <sub>4</sub>	MnOOH	MnO,	Mn(OH),
Average value	-0.94	1.93	2.37	8.27	17.09	-15.14	-4.66	-12.31	-5.95
Minimum value	-1.46	1.40	0.94	6.83	14.32	-15.60	-4.80	-12.73	-6.04
Maximum value	-0.62	2.25	3.43	9.33	19.15	-14.55	-4.48	-11.89	-5.82
Standard deviation	0.36	0.37	1.25	1.25	2.43	0.53	0.15	0.38	0.10
Number of values	4	4	4	4	4	4	4	4	4

Table 5. Summary statistics of saturation indices in Quaternary intertill-intratill aquifer water samples.

Note: Al(OH)<sub>3</sub> a and Fe(OH)<sub>3</sub> a correspond to amorphous Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub> respectively.

that pH may be affecting both the mobilization of arsenic and the exchange of arsenic for phosphorus.

Stratigraphic position might also help explain the observed arsenic concentrations. Based on a recent drift thickness map of northeastern Alberta (Andriashek, unpublished map), samples 10, 15, 17 and 21 appear to be completed to depths within 15 m of the estimated bedrock depth at their respective locations. The remaining water samples appear to be completed to depths that may be 30 or more metres above the estimated bedrock depth at their respective locations. Sample 10 has the highest arsenic concentration and was collected from an aquifer sitting above bedrock. The La Biche Formation makes up bedrock in the area (Figure 2) and consists of shale and silty shale with ironstone partings and concretions. Shale contains some of the highest arsenic concentrations in sedimentary rocks (Smedley and Kinniburgh, 2002). Transport of fluids from the shale through either advection or diffusion may contribute arsenic to the Quaternary intertill-intratill aquifers. No direct evidence to support this hypothesis exists however.

Sample 21 does not appear to follow the same trends as the other Quaternary intertill-intratill aquifer water samples. The reason may be its location. Sample 21 is located to the south of the Mostoos Upland, whereas samples 10, 15 and 17 are located to the north of the Mostoos Upland (Figure 1). This may suggest that different factors are controlling arsenic concentrations on either side of these highlands.

In the last five paragraphs, three different mechanisms controlling arsenic concentration have been proposed. What makes the arsenic-bearing water samples different from the non arsenic-bearing water samples, and does one of the above mechanisms explain that difference? An examination of the water chemistry data table shows that elemental concentrations and pH values in arsenic-bearing and non arsenic-bearing groundwater samples are not significantly different. In addition, saturation indices for Fe-, Al- and Mn-oxide minerals are not significantly different either. The possibility of one mechanism controlling arsenic concentration is, therefore, unlikely. This suggests that arsenic concentration is likely controlled by multiple factors. The nature of this mechanism is not immediately obvious, but is likely a combination of pH, competition between arsenic and other anions for adsorption sites on minerals, and potentially transport of arsenic from bedrock.

#### 4.1.2.3 Preliminary Interpretations – Quaternary-Tertiary Buried Channel Aquifer

In all three Quaternary-Tertiary buried channel aquifer water samples, arsenic was detected above the analytical detection limit of 0.01 mg/L. Conditions must, therefore, exist within the Quaternary-Tertiary buried channel aquifer that allow arsenic to enter into solution or impede its removal from solution.

Certain trends in elemental concentrations hint at the means of arsenic introduction. Arsenic concentrations in solution increase as concentrations of Ca, Mg and Sr (three carbonate mineral components) and Ca and SO<sub>4</sub> (components of evaporite minerals) in solution increase. Arsenic is associated with both these mineral types (Smedley and Kinniburgh, 2002). Based on field and laboratory analysis of till core samples, carbonate minerals are ubiquitous (Andriashek, pers. comm., 2001). Saturation indices indicate the water samples are slightly oversaturated to slightly undersaturated with respect to carbonate minerals, such as calcite, aragonite and dolomite (Table 6). The saturation indices indicate the water samples are undersaturated with respect to evaporite minerals, such as gypsum and anhydrite (Table 6). Carbonate and evaporite minerals have been identified through SEM analysis (Figure 5b). This suggests the possibility that as carbonate or evaporite minerals are dissolved, and the Ca, Mg, Sr and SO4 enter solution, the arsenic associated with the carbonate or evaporite minerals also enters into solution. If carbonate minerals were being dissolved, an increase in HCO<sub>3</sub> concentrations would also be expected. However, arsenic concentrations increase as HCO<sub>3</sub> concentrations in solution decrease. Bicarbonate will compete with arsenic oxyanions for adsorption sites on clay minerals or oxyhydroxides. The increase in arsenic concentrations and the observed decrease in HCO<sub>2</sub> may indicate that such a competition is occurring and that HCO<sub>3</sub> is out-competing arsenic for the available adsorption sites.

All Quaternary intertill-intratill aquifer water samples												
	CaCO <sub>3</sub> (Calcite)	CaCO <sub>3</sub> (Aragonite)	CaMg(CO <sub>3</sub> ) <sub>2</sub> (Dolomite)	CaSO <sub>4</sub> (Gypsum)	CaSO <sub>4</sub> (Anhydrite)							
Average value	0.19	0.04	0.06	-2.10	-2.34							
Minimum value	-0.37	-0.51	-1.09	-3.33	-3.55							
Maximum value	0.69	0.53	1.22	-1.21	-1.47							
Standard deviation	0.24	0.24	0.55	0.50	0.49							
Number of values	31	31	31	31	31							
Quaternary intertill-intratill aquifer water samples with arsenic concentrations above the detection limit												
	CaCO <sub>3</sub> (Calcite)	CaCO <sub>3</sub> (Aragonite)	CaMg(CO <sub>3</sub> ) <sub>2</sub> (Dolomite)	CaSO <sub>4</sub> (Gypsum)	CaSO <sub>4</sub> (Anhydrite)							
Average value	0.13	-0.03	-0.20	-1.98	-2.24							
Minimum value	-0.14	-0.30	-0.79	-2.23	-2.48							
Maximum value	0.38	0.22	0.42	-1.29	-1.55							
Standard deviation	0.21	0.21	0.50	0.46	0.46							
Number of values	4	4	4	4	4							
Quaternary-Tertiary	buried channel aq	uifer water samples										
	CaCO <sub>3</sub> (Calcite)	CaCO <sub>3</sub> (Aragonite)	$CaMg(CO_3)_2$ (Dolomite)	CaSO <sub>4</sub> (Gypsum)	CaSO <sub>4</sub> (Anhydrite)							
Average value	0.19	0.03	0.00	-3.00	-3.25							
Minimum value	-0.22	-0.37	-0.69	-3.95	-4.20							
Maximum value	0.42	0.26	0.34	-2.05	-2.31							
Standard deviation	0.35	0.35	0.59	0.95	0.95							
Number of values	3	3	3	3	3							

Table 6. Summary statistics of saturation indices in Quaternary-Tertiary buried channel aquifer water samples compared to Quaternary intertill-intratill aquifer water samples.

As in the Quaternary drift aquifers, water samples from the Quaternary-Tertiary aquifers show an increase in the concentration of arsenic as P concentrations decrease. This may indicate that anions, such as P anions, are out-competing arsenic for adsorption sites resulting in the release of arsenic into solution.

A possible relationship exists between As concentration and Eh (Figure 10c). Arsenic concentration decreases as Eh increases. Relative to the other oxyanion-forming elements, arsenic is distinctive in being relatively mobile under reducing conditions (Smedley and Kinniburgh, 2002). This may imply that arsenic concentrations in solution are controlled to a certain extent by Eh.

There may also be a relationship between proximity to bedrock and arsenic presence. The Wiau Channel cuts into the La Biche Formation shale units and in some places through the La Biche Formation into the Pelican Formation sandstone and Joli Fou Formation shale (Figure 2). As previously noted, high arsenic concentrations are associated with shale (Smedley and Kinniburgh, 2002).

As with the Quaternary intertill-intratill aquifers, no single control over arsenic concentration in the Quaternary-Tertiary buried channel aquifers appears likely. A combination of carbonate and evaporite mineral dissolution reactions, competition between anions and arsenic for adsorption sites on clay and oxyhydroxide minerals, changes in Eh, and advection or diffusion of arsenic from bedrock may be contributing arsenic into solution.

## 5 Summary

Seventeen of the 21 water samples collected from Quaternary intertill-intratill aquifers in the Athabasca Oil Sands (in situ) Area of Alberta have arsenic concentrations below the analytical detection limit of 0.01 mg/L. One of the samples has an arsenic concentration of 0.01 mg/L. Two of the water samples have arsenic concentrations of 0.02 mg/L. One of the water samples has an arsenic concentration of 0.03 mg/L. This last water sample arsenic concentration exceeds the interim maximum allowable concentration for arsenic of 0.025 mg/L. The water sample was collected from an AGS installed piezometer completed in a terrace deposit of the Wiau Channel. All three water samples collected from the Quaternary-Tertiary buried channel aquifers have arsenic concentration of 0.01 mg/L, whereas two water samples have arsenic concentrations of 0.02 mg/L. Based on Eh and pH values, arsenic appears to be predominantly in the less mobile arsenate form.

The majority of water samples from Quaternary intertill-intratill aquifers have arsenic concentrations below the analytical detection limit. This suggests that analytical detection limits are too low to detect arsenic in solution, arsenic is not being introduced into solution, or that arsenic is effectively being removed from solution through water-rock interactions. In four samples, arsenic concentrations meet or exceed the analytical detection limits. Arsenic concentrations appear to be controlled by a combination of the following mechanisms: 1) adsorption to oxide and clay minerals; 2) competition between arsenic species and phosphorus ions for adsorption sites; 3) release of arsenic brought about by changes in pH; and 4) proximity to bedrock. At least two distinct geochemical systems may exist within the study area as indicated by the differences in the trends of elemental concentrations versus arsenic concentrations. One distinct system may be located to the north of the Mostoos Upland, whereas the second may be located to the south of the Mostoos Upland.

Arsenic concentrations in the Quaternary-Tertiary buried channel aquifers appear to be controlled by a combination of the following mechanisms: 1) competition between arsenic species and phosphorus or bicarbonate ions for adsorption sites; 2) release of arsenic brought about by changes in Eh; 3) dissolution of carbonate or evaporite minerals releasing associated arsenic; and 4) proximity to bedrock.

## 6 References

- Cherry, J.A., Shaikh, A.U., Tallman, D.E. and Nicholson, R.V. (1979): Arsenic species as an indicator of redox conditions in groundwater; Journal of Hydrology, v. 43, no. 1-4, p. 373-392.
- Dzombak, D.A. and Morel, F.M.M. (1990): Surface complexation modelling hydrous ferric oxide; John Wiley, New York, New York. 416 p.
- Federal-Provincial Subcommittee on Drinking Water of the Federal-Provincial-Territorial Committee on Environmental and Occupational Health, (2001): Summary of guidelines for Canadian drinking water quality; Health Canada. 8 p.
- Lemay, T.G. (2002): Sampling of groundwater from wells in the Athabasca Oil Sands (in situ) Area, Alberta, 1999-2001 – A compilation of protocols and methods; Alberta Energy and Utilities Board, EUB/AGS Geo-Note 2002-10, 52 p.
- Nordstrom, D.K. (2000): An overview of arsenic mass poisoning in Bangladesh and West Bengal, India; *in* Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Sc, Te, and Bi, C. Young (ed.), Society for Mining Metallurgy and Exploration, p. 21-30.
- Smedley, P.L. and Kinniburgh, D.G. (2002): A review of the source, behaviour and distribution of arsenic in natural waters; Applied Geochemistry, v. 17, p. 517-568.
- Welch, A.H., Lico, M.S. and Hughes, J.L. (1988): Arsenic in groundwater of the western United States; Ground Water, v. 26, no. 3, p. 333-347.
- Yan, X.-P., Kerrich, R. and Hendry, M.J. (2000): Distribution of arsenic(III), arsenic(V) and total inorganic arsenic in porewaters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada; Geochimica et Cosmochimica Acta, v. 62, no. 15, p. 2637-2648.