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IC Analysis of FRC Water Samples for Organic Anions

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Water samples from the Field Research Center (FRC) have been routinely screened for total organic carbon (TOC) and for specific organic compounds that are of potential concern from a regulatory perspective (e.g., chlorinated solvents). Comparison of the values from the two analyses indicated that only a small percentage of the TOC in FRC waters was positively identified. There are no records of organic compounds disposed in the former S-3 ponds. However, prior to their closure 19 years ago the ponds were treated by *in situ* biodenitrification. As part of that process, the ponds were amended with large amounts of acetate. Thus, acetate became a prime candidate as a constituent of some of the TOC in FRC well water. We sought a general method for the analysis of organic anions in these samples. This brief report describes the results of these efforts.

Selection of analytical method.

Several analytical techniques are available for the quantification of the organic compounds of interest in aqueous samples including: liquid chromatography (LC) or liquid chromatography coupled with mass spectrometry (LC/MS), gas chromatography (GC), capillary electrophoresis (CE), and ion chromatography (IC). Recognizing that no method would be ideal for all investigators, we hoped to identify a method that was reasonably straightforward and required equipment that was generally available in analytical labs. However, the method must also be compatible with the complex nature of samples from the FRC (e.g., total dissolved solids (TDS) ranging up to brines, pH ranging from 3.5 to 6.5, nitrate (NO_3^-) up to 41,800 mg/L (674 mM), up to several hundred mg/L each of alkali and alkaline earth metals, high concentrations of transition metals). These characteristics are generally incompatible with LC, LC/MS, and GC. Diluting samples to eliminate known or potential interferences would dilute organic compounds below detection limits. Several sample cleanup procedures or compound derivation methods were suggested to make samples amenable to LC, LC/MS, or GC but these would have added substantially to analysis time, difficulty, and the unit cost of analysis. Ion chromatography was selected as the most promising analytical method to pursue.

Results.

Specifics of the method are provided in Table 1. Initially, standards were prepared in deionized water (DIW). The method showed good ability to separate organic anions (Fig 1A). Linear calibration functions were obtained for the compounds shown over a range from 10 µM up to 1000 µM. Calibrations for

Table 1: Isocratic elution of organic anions in FRC samples by ion chromatography.

Sample loop volume:	50 µL
Analytical column:	Dionex IonPac ICE-AS6 Analytical Column
Eluant:	0.4 mM Heptafluorobutyric acid
Eluant flow rate:	1 mL/min
Detection:	Suppressed conductivity
Suppressor:	Dionex Anion-ICE MicroMembrane Suppressor
Regenerant:	5 mN Tetrabutylammonium hydroxide
Regenerant flow rate:	~ 5 mL/min
Background conductivity:	20-22 µS
Backpressure:	~500 psi

lactate and acetate were generally reproducible from day to day but citrate showed greater variability requiring more frequent calibration. Rigorous determination of detection limits has not been done but approximate detection limits for these three organic anions was in the micromolar (μM) range in our lab. Detection limits for lactate and acetate are not affected by the presence of NO_3^- whereas large amounts of inorganic anions will interfere with citrate.

According to the manufacturer, inorganic anions are not retained by the resin used in the analytical column. In our experience, it may be more accurate to say that strong acid anions (e.g., NO_3^-, Cl^-) are not retained by the resin. Conjugate bases of weak polyprotic inorganic acids (e.g., HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}) do seem to be retained by the resin. Phosphate elutes soon after NO_3^-, HCO_3^- elutes after acetate. We did not check specifically for SO_4^{2-} but it may also be retained by the resin. Given the high concentrations of NO_3^- in some FRC waters, separate peaks for these compounds are usually not resolved, with the exception of HCO_3^-, as described below. Consequently, the quantification of citrate is complicated when large amounts of NO_3^-/inorganic anions are present in samples as it elutes as a tailing peak on the NO_3^- signal (Fig 1B). The peak area for citrate decreased by 27% for the same standard prepared in 1% HNO_3 versus DIW (cf. Fig 1A and 1B). Lactate and acetate were not affected by the presence of NO_3^-. Similar effects are seen if the NO_3^- is added as $NaNO_3$, indicating that the pH change that accompanied the HNO_3 addition was not the cause for the change in peak area for citrate. The NO_3^-/inorganic anion content of FRC samples varies with location and time, so correcting for this NO_3^- interference may be sample-specific.

Samples from the FRC were analyzed using the same method and several compounds have been tentatively identified based on comparison to authentic standards and the response to standard addition treatments. Peaks that are consistent with citrate and acetate appear in samples from well FW100, a multilevel well at the Criddle/ Jardine field plot in Area 3 (Fig 1C). Other major constituents in the same sample are given in Table 2. In this sample, acetate accounts for 49% of the DOC, and citrate accounts for an additional 8%. Note that the sample was injected straight onto the column without dilution or pretreatment. Filtration is recommended to protect the analytical column where large amounts of suspended particulate matter are in the sample.

Table 2: Composition of sample FW100, 35' depth, sampled 15 Jan 02 (Figure 1C). All units are mg/L except pH or where indicated.

	mg/L
pH	4.16
Sp. Cond.	13.3 mS
Na	702
Mg	258
Al	183
K	56.7
Ca	1560
Mn	95.5
Fe	19.3
Ni	8.01
U	16.8
NO_3^-	8462
Cl^-	222
SO_4^{2-}	2286
DOC	66.3

The large peak following acetate (Figure 1C) was tentatively identified as bicarbonate based on the ability to generate similar peaks in standards prepared in $NaHCO_3$. When standards prepared in $NaHCO_3$ were acidified, the peak disappeared while there was no change in the peaks of the organic anions other than those noted above for citrate.

The presence of large amounts of bicarbonate in samples may interfere with acetate quantification. Due to the interaction of the highly acidic wastes with carbonate-bearing strata underlying the FRC, the groundwater is highly charged with inorganic carbon; some samples effervesce when brought to the surface.

A portion of the sample shown in Fig 1C was acidified from an initial pH of 4.1 to pH 1.5 with concentrated HNO_3 (10 μL acid added to 5 mL sample). The acidified sample was left open to the lab atmosphere with intermittent vigorous shaking and analyzed periodically. The peak believed to be bicarbonate decreased by 90% within the first 15 minutes post-acidification (cf. Fig 2A and 2B). Peak loss continued to decrease by 98% and 99.4% after 35 and 120 minutes, respectively (Fig 2C and D). Accompanying loss of the HCO_3^- peak , the acetate peak increased by 10% within 15 minutes and showed no significant change thereafter. Citrate peak areas decreased significantly with acidification (Fig 2). The decrease was apparently unique to this field sample as similar changes were not observed in acidified standard samples prepared in DIW. The decreased peak area cannot be attributed to an increase in the inorganic anion peak (Fig 2A and B). Peak areas for citrate continued to exhibit significant increases over time. These variations in peak area

may pose a problem for quantification of citrate in FRC samples.

A depth profile of organic anion concentration was developed for well FW100 using *unacidified* samples from two separate sampling dates (Fig 3). Note that at the later sampling date samples were not collected from all depths. Citrate was masked by a massive inorganic anion peak in the sample from the 50' depth collected 13 Feb 02. The fraction of organic carbon accounted for in these samples, as well as for two wells from Area 1 (FW016 and FW021, in the vicinity of the Istok field site) are provided in Table 3.

Table 3: Organic anion concentrations and fraction of DOC for several FRC samples.

Well	Area	Depth (ft)	Sample date	DOC (mM)	Acetate (μM)	Citrate (μM)	Fraction DOC
FW100	Area 3	20	15 Jan 02	2.99	9	43	0.09
FW100	Area 3	25	15 Jan 02	3.43	323	53	0.28
FW100	Area 3	30	15 Jan 02	5.15	851	110	0.46
FW100	Area 3	35	15 Jan 02	5.52	1360	73	0.57
FW100	Area 3	40	15 Jan 02	8.28	1821	38	0.47
FW100	Area 3	45	15 Jan 02	9.04	1700	28	0.39
FW100	Area 3	50	15 Jan 02	4.15	420	57	0.28
FW016	Area 1	--	13 Feb 02	--	3	36	--
FW021	Area 1	--	13 Feb 02	--	796	22	--

Equilibrium speciation calculations for the water composition shown in Table 2 (Fig 2 and 3) indicate that about 85% of the U(VI) is present as UO_2^{2+} or complexed with sulfate (Fig 4). Complexation by organic anions identified accounts for about 9% of the U(VI) in solution (5.5% U-citrate, 3.4% U-Acetate). Assumptions made for the purposes of the calculations: T = 25°C; P_{CO2} = 20%. Uranium speciation shows a strong pH-dependence; as the pH used in the calculation is increased, U-citrate complexes dominate U aqueous speciation over the pH range 4.6-6.6.

data for U(VI) inorganic complexes: Grenthe, I, J Fuger, RJM Konings, RJ Lemire, AB Muller, CNT Cregu, and H Wanner. 1992. Chemical Thermodynamics of Uranium. North-Holland.

data for U(VI)-Acetate complexes: Shock, E.L., and C. M. Koretsky. 1993. Metal-organic complexes in geochemical processes: Calculation of standard partial molal thermodynamic properties of aqueous acetate complexes at high pressures and temperatures. Geochim. Cosmochim Acta. 57:4899-4922.

data for U(VI)-citrate complexes: Rajan, K., and A. Martell. 1965. Inorg. Chem. 4:462.

Figure 1

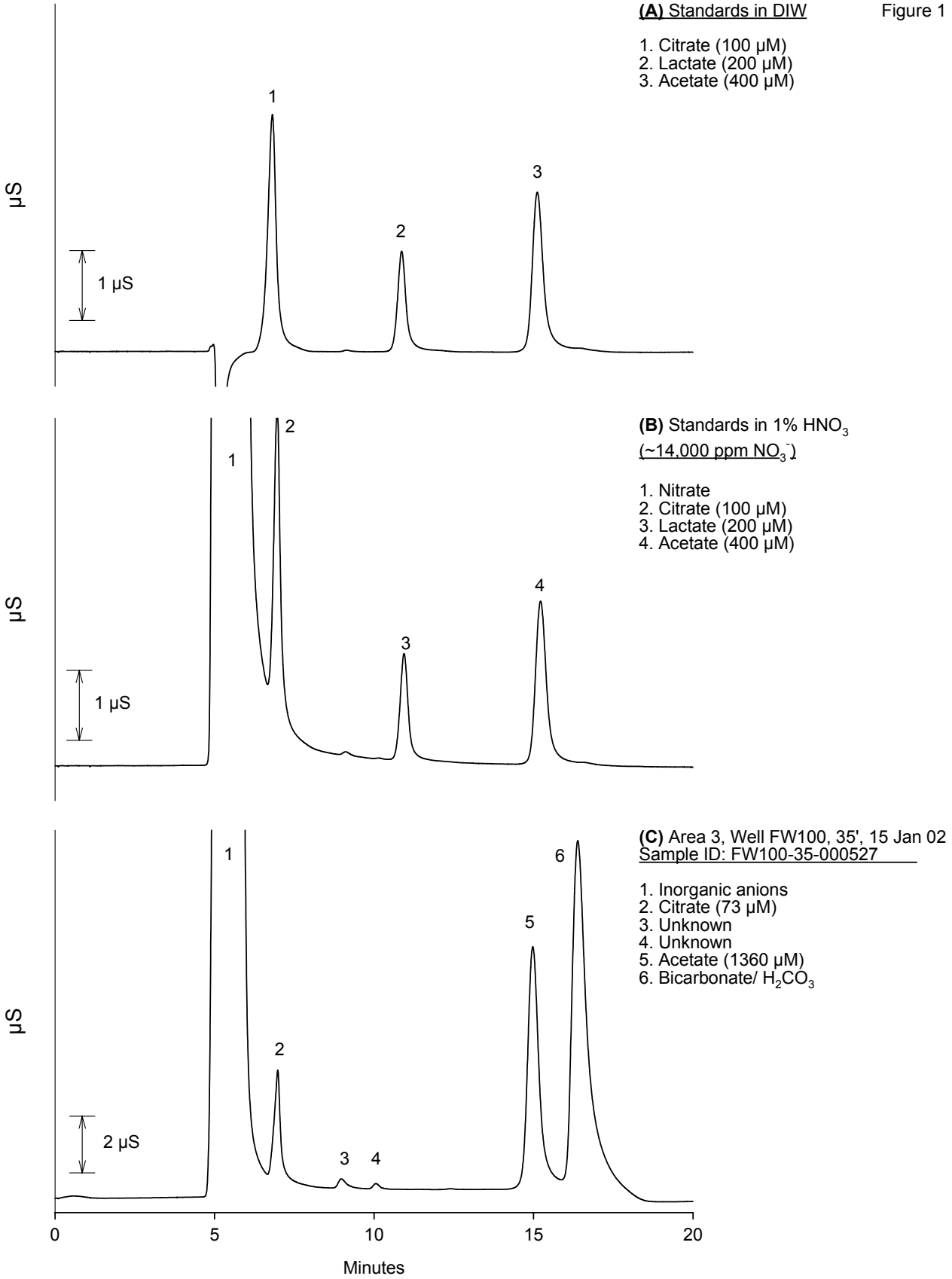
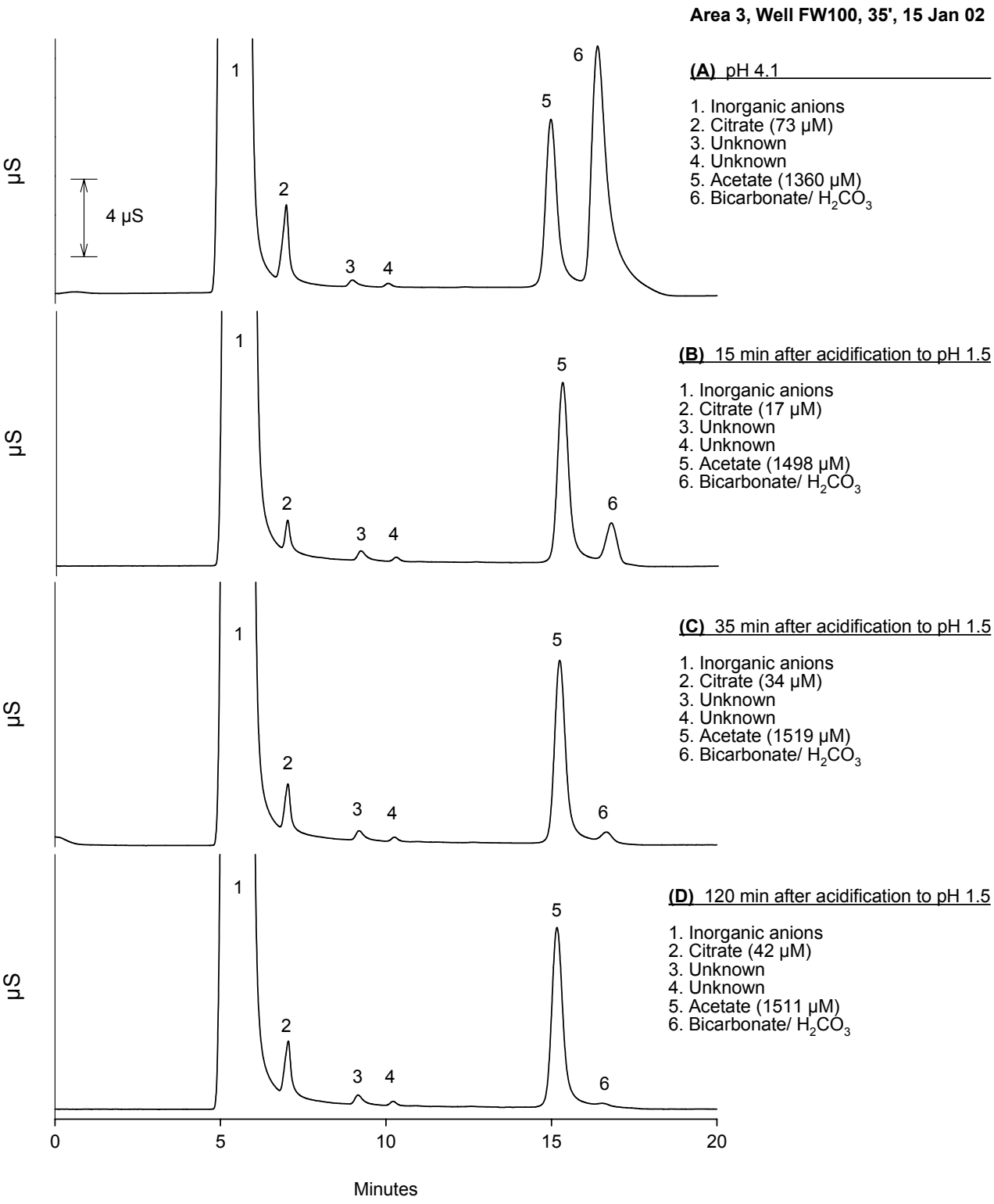

(A) Standards in DIW
1. Citrate (100 µM)
2. Lactate (200 µM)
3. Acetate (400 µM)
µS
1 µS
1
2
3
(B) Standards in 1% HNO3
(~14,000 ppm NO3-)
1. Nitrate
2. Citrate (100 µM)
3. Lactate (200 µM)
4. Acetate (400 µM)
µS
1 µS
1
2
3
4
(C) Area 3, Well FW100, 35', 15 Jan 02
Sample ID: FW100-35-000527
1. Inorganic anions
2. Citrate (73 µM)
3. Unknown
4. Unknown
5. Acetate (1360 µM)
6. Bicarbonate/ H2CO3
µS
2 µS
1
2
3
4
5
6
0
5
10
15
20
Minutes

Figure 2


Area 3, Well FW100, 35', 15 Jan 02
(A) pH 4.1
1. Inorganic anions
2. Citrate (73 µM)
3. Unknown
4. Unknown
5. Acetate (1360 µM)
6. Bicarbonate/ H_2CO_3
(B) 15 min after acidification to pH 1.5
1. Inorganic anions
2. Citrate (17 µM)
3. Unknown
4. Unknown
5. Acetate (1498 µM)
6. Bicarbonate/ H_2CO_3
(C) 35 min after acidification to pH 1.5
1. Inorganic anions
2. Citrate (34 µM)
3. Unknown
4. Unknown
5. Acetate (1519 µM)
6. Bicarbonate/ H_2CO_3
(D) 120 min after acidification to pH 1.5
1. Inorganic anions
2. Citrate (42 µM)
3. Unknown
4. Unknown
5. Acetate (1511 µM)
6. Bicarbonate/ H_2CO_3
µS
4 µS
0
5
10
15
20
Minutes

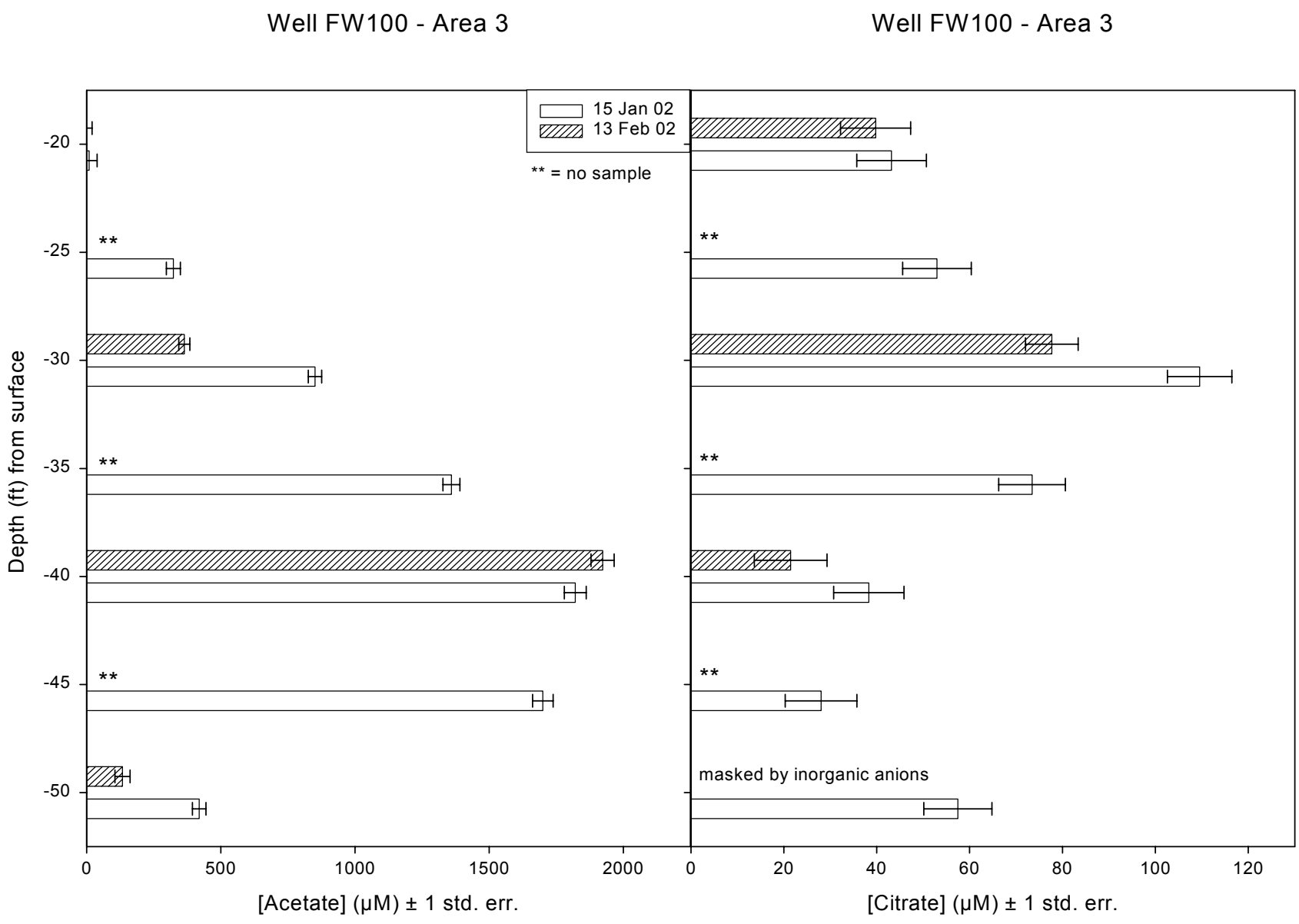
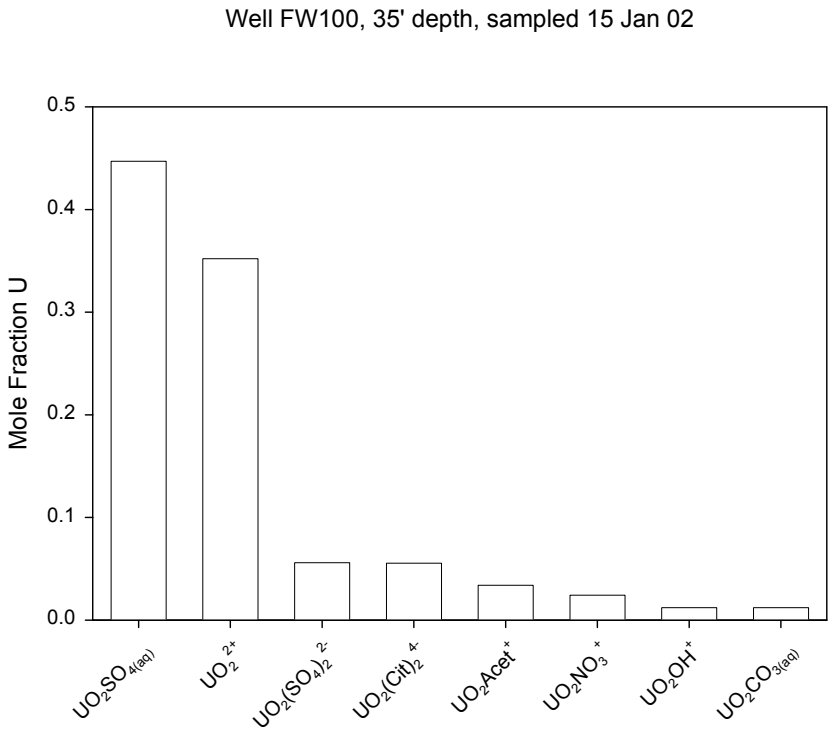

Well FW100 - Area 3
Well FW100 - Area 3
15 Jan 02
13 Feb 02
** = no sample
Depth (ft) from surface
-20
-25
-30
-35
-40
-45
-50
**
masked by inorganic anions
0
500
1000
1500
2000
[Acetate] (µM) ± 1 std. err.
0
20
40
60
80
100
120
[Citrate] (µM) ± 1 std. err.

Figure 3

Figure 4


Well FW100, 35' depth, sampled 15 Jan 02
Mole Fraction U
0.5
0.4
0.3
0.2
0.1
0.0
$UO_2SO_{4(aq)}$
UO_2^{2+}
$UO_2(SO_4)_2^{2-}$
$UO_2(Cit)_2^{4-}$
UO_2Acet^+
$UO_2NO_3^+$
UO_2OH^+
$UO_2CO_{3(aq)}$