

MBMG Open-File Report 215

Reclamation Techniques for Heavy Metal Contaminated Agricultural
Lands in Deer Lodge, Powell and Silver Bow Counties

by

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Table of Contents

	Page
Acknowledgments.	iii
Introduction	1
Laboratory Leaching Study Results.	2
Field Site Experimental Results.	7
Summary and Conclusions.	17
References Cited	18

List of Tables and Figures	Page
Table 1. Water chemistry from leaching columns.	3
Table 2. Analyses of amendment components	4
Table 3. Water chemistry from lysimeter samples	8
Table 4. Lysimeter sampling dates and rain gage data.	12
Figure 1. As concentration versus pore volumes for the gravity drained columns.	5
Figure 2. As concentration versus pore volumes for the pumped columns	5
Figure 3. Plot of average dissolved arsenic concentration from each lysimeter versus lysimeter depth	12
Figure 4. Plot of average pH from each lysimeter with pH values versus lysimeter depth.	11
Figure 5. Plot of average dissolved zinc concentration from each lysimeter versus lysimeter depth	14
Figure 6. Plot of average dissolved copper concentration from each lysimeter nest versus depth.	14
Figure 7. Plot of average specific conductance from each lysimeter nest versus depth.	16
Figure 8. Plot of average dissolved sulfate concentration from each lysimeter nest versus depth.	16

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INTRODUCTION

Trace element contamination of both heavy metals and arsenic in soils adjacent to Silver Bow Creek is a serious problem in the upper Deer Lodge Valley. The contamination is the result of milling processes in Butte, and smelter activity in Anaconda. The reduction of soil pH and associated heavy metals have caused the destruction of alfalfa crops and pasture vegetation. Soil erosion caused by the loss of covering vegetation has resulted in as much as two feet of denudation in the affected areas. These areas now are in a state of non-use or limited irrigated use.

In an attempt to reclaim these contaminated areas, the Mile High Conservation District and Headwaters RC&D have sponsored a study of amendment techniques. The study site is on the Spangler ranch where tailings-rich flood waters in about 1919 inundated an area that had been irrigated. The study's goals were two-fold: to develop a reclamation technique that is effective and economical for landowners; and, to determine whether such techniques will mobilize heavy metals and/or arsenic into the local groundwater system.

Three soil amendments were selected by Bill Schafer and Ted Dodge for the study: agricultural lime; a mixture of lime and agricultural phosphorus; and a mixture of lime, phosphorus, and manure. Each was applied and plowed into the soil to an average depth of 6 inches in the field plots. Several different grasses were then planted to evaluate their response to the various amendments. Three sets of field plots have subplots containing the three amendments, as well as, control subplots which have no amendment.

The original work plan was developed upon the results of Osborne, et al, (1986) and called for monitoring wells and stream seepage studies. These approaches were abandoned when drilling results showed the presence of a thick gravel layer at a depth of 27 to 30 inches. This appears to be the same gravel that is being quarried nearby. It has a considerable (15 to 20 feet) unsaturated thickness with water in its basal zone. The gravel provides an excellent medium for the lateral movement of groundwater to Silver Bow Creek. Consequently, any changes in the water chemistry resulting from the effects of such small experimental plots would probably be lost because of dilution by the groundwater flowing under the site. Thus the research scope was modified to provide a more intensive laboratory and field lysimeter sampling approach.

Two approaches were employed to evaluate the impact of the amendments on metal and arsenic mobility: lysimeter nests installed in the field study plots; and, laboratory leaching column experiments. The lysimeters were installed at depths of 8, 16, and 24 inches to collect soil moisture samples throughout the soil profile. Lysimeter nests were installed in subplots containing each amendment and a control (unamended) subplot. A regular sample collection schedule was established; however, because of near drought conditions during 1987 and 1988, fewer samples than expected were actually collected. A set of six leach columns were loaded with the different amended soils along with nonamended soils. Both gravity and pump driven volumes of distilled water were passed through the columns to leach soluble metals. Samples were collected at intervals of increasing leaching. All samples were analyzed by the Montana Bureau of Mines.

This report contains a summary of both field and laboratory data and an interpretation of the significance of the data.

LABORATORY LEACHING STUDY RESULTS

The leaching column experiments have been completed, and the reduced data have been assembled in Table 1. Only the lime and lime plus phosphorus (L+P) amendments were compatible with column studies; the lime, phosphorus, and manure (L+P+M) amendment, when saturated, was virtually impermeable in columns and has not been evaluated. A batch leaching experiment was to be performed to study this amendment and further column studies were to be conducted as a check on the initial results by the junior author, because of the relatively high pH values and low metals loads of the first column runs. Reduction of the data from the second phase of the work was not satisfactory. The reduced data will be provided if the junior author completes his thesis. Consequently, this section deals only with the results of the first suite of column studies. The amendment components were analyzed and the results are presented in Table 2; ug/g is the same as parts per million.

Data acquired from each of the six column studies include pre- and post-leaching bulk solid chemistries, periodic leachate chemistries, and regularly collected field parameters of the leachates.

Arsenic proved to be mobile in both amended and nonamended soils; however, the lime amended soil showed the smallest release of dissolved arsenic, whereas the L+P amendment showed the greatest release of dissolved arsenic. Diagrams plotting the dissolved arsenic concentration versus the number of pore volumes (the volume of water needed to saturate the pore spaces in a column) of leachate that had passed through the columns for all three gravity-drained columns are shown in Figure 1. These can be used to calculate the net mass flux of arsenic from the leaching column. The area under each of the curves is equal to the net mass of arsenic leached. As a result it was found that 5 to 10% of available arsenic had been mobilized when compared to pre-leached soil concentrations. The lime amended soils showed the smallest release of arsenic, and the L+P amendment showed the largest release of arsenic.

A similar plot for the pumped columns (Figure 2) was used to calculate the integrated mass flux. As with the gravity drained columns, the mass flux of leached arsenic was lowest for the lime amendment and highest for the L+P amendment; however, 20 to 30% of the arsenic was leached. Roughly twice the volume of water was moved through these columns, and the flow rate was about six times faster than gravity drained columns. It could be hypothesized that, kinetically, the arsenic release reactions are more rapid than secondary precipitation or sorption reactions and that this explains the higher concentrations released per unit volume of water; however, this is not completely consistent with the field data, when the limited number of second year samples are considered.

The initial concentrations were highest for the L+P amended soil. Phosphate and arsenate have been shown to be similar in physical and chemical behavior as they both exist in similar aqueous forms. This should result in competition between phosphate and arsenate molecules for adsorption sites and dissolved components needed to form both precipitates and soluble complexes. Because of this competition and the higher flux rate of water through the columns, the greater arsenic concentrations in the effluent from phosphorus amended soil may be understandable. However, the field data are more suggestive of a co-precipitation process.

Table 1. WATER CHEMISTRY FROM LEACHING COLUMNS; SPANGLER SITE SIMULATION DATA

A. GRAVITY DRIVEN COLUMNS

Amendment Column Number	<-----UNTREATED----->			<-----LIME----->			<-----LIME + PHOSPHATE----->		
	#2	#2	#2	#3	#3	#3	#5	#5	#5
# of Pore Volumes	1.98	10.25	55.86	1.83	10.88	50.33	1.18	10.64	50.91
mg/l									
Ca	82.8	63.2	8	176	34.4	16.7	152	39.5	17.7
Mg	21.5	15.6	1.5	43.8	8.1	3.5	38.9	9.4	3.4
Na	18.4	5.3	0.5	24.7	3.3	0.3	27.5	2.8	0.2
K	23.4	10.2	2.7	30.1	8.9	4.1	29.7	9.2	4.3
Al	<.03	<.03	0.06	<.03	<.03	<.03	<.03	<.03	<.03
Fe	<.002	0.02	0.052	0.006	0.02	0.025	0.037	0.003	0.015
Mn	0.021	2.05	0.17	0.061	0.81	0.32	0.2	0.87	0.38
SiO2	54.5	56.7	35	54.4	55.1	35.4	-	72.1	36.8
ug/l									
As	53	74	946	7	112	278	44	564	2310
Cu	56	44	24	21	5	2	58	<2	11
Zn	9	40	5	37	<1	<3	18	<3	3
pH	8.10	8.75	7.60	7.57	7.95	7.55	8.21	8.47	7.62

B. PUMPED COLUMNS

Amendment Column Number	<-----UNTREATED----->			<-----LIME----->			<-----LIME + PHOSPHATE----->		
	#9	#9	#9	#10	#10	#10	#11	#11	#11
# of Pore Volumes	1.03	11.27	102.	0.96	11.1	98.1	1.01	12.3	101
mg/l									
Ca	44.4	12.8	6.7	85.3	21.5	12.8	145	23.8	9.1
Mg	10.9	2.9	1.1	21.4	4.9	2.9	40.4	5.6	1.5
Na	13.3	1.5	0.1	14.3	0.9	1.5	21.7	1.1	0.1
K	22.5	7.5	1.9	27.7	9.1	7.5	40.7	13.6	1.2
Al	0.04	0.27	0.05	<.03	<.03	0.27	<.03	<.03	0.11
Fe	0.017	0.15	0.016	<.002	0.003	0.15	<.002	0.002	0.067
Mn	0.01	0.005	0.002	0.006	0.022	0.005	0.032	0.02	0.071
SiO2	32.4	30.5	9.3	40.8	27.4	30.5	132	33.6	8.8
ug/l									
As	35	1120	90	19	126	1120	5020	493	158
Cu	66	23	3	26	26	23	85	20	18
Zn	140	17	3	23	5	17	280	<3	<3
pH	8.03	8.22	7.90	8.01	8.00	7.91	6.35	7.88	7.71

Table 2. ANALYSES OF AMENDMENT COMPONENTS USED AT THE SPANGLER SITE

Element ug/g	Spangler Lime	Spangler Manure	Spangler Phosphate
Ca	361000	34000	126000
Mg	2000	9400	8700
Na	2300	9700	2900
K	360	20000	2200
Al	2000	27000	7800
Fe	930	9100	5600
Mn	100	220	240
Cd	25	3	130
Cr	56	32	560
Cu	50	85	14
Li	<2	9	4
Mo	<10	<10	10
Ni	<10	10	260
P	<100	4800	170000
Pb	130	<20	<20
Sr	26	340	260
Ti	70	770	140
V	60	20	830
Zn	50	110	1400
Zr	130	37	23
MBMG LAB NO.	87G 275	87G 276	87G 277

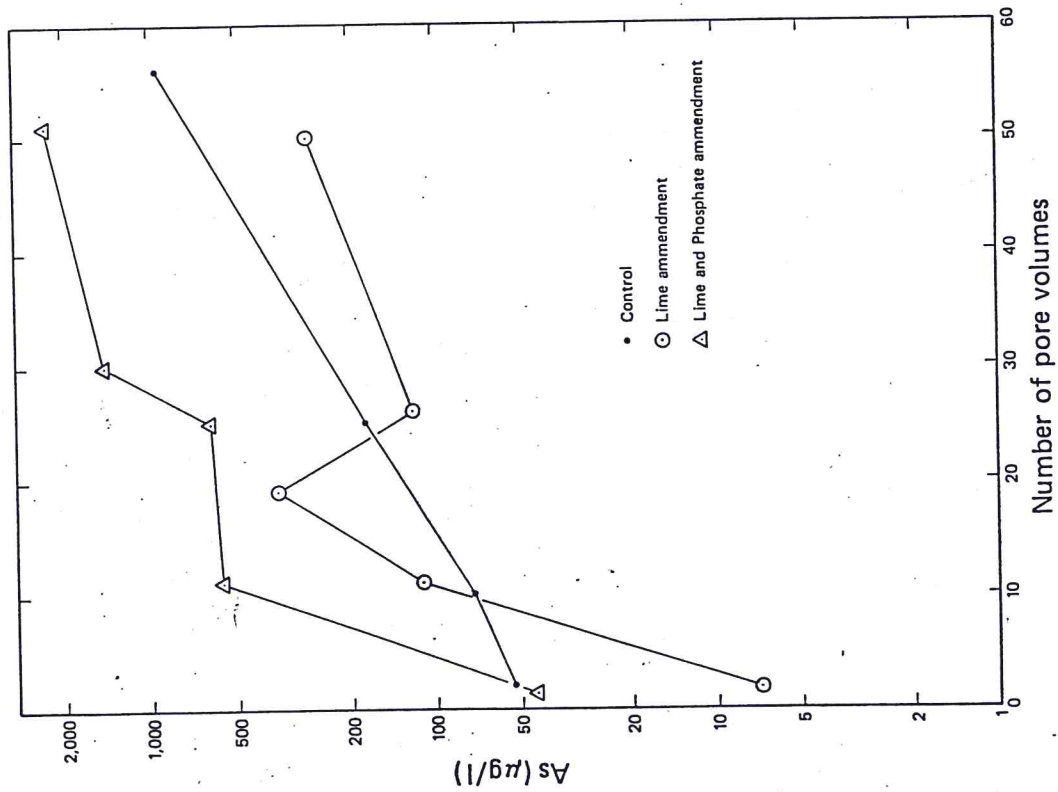


Figure 1. Arsenic concentration versus pore volumes for the gravity drained columns.

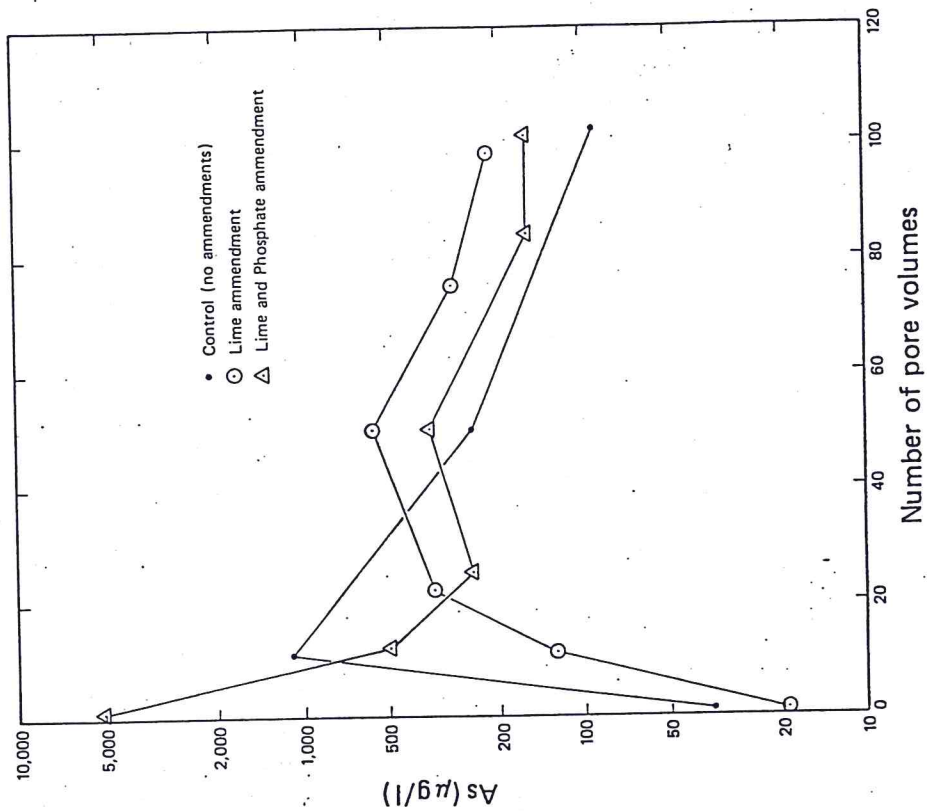


Figure 2. Arsenic concentration versus pore volumes for the pumped columns.

In many of these tests with gravity columns, dissolved arsenic displayed an inverse relationship with dissolved calcium. In other words, with increasing amounts of leaching, the dissolved calcium decreased while dissolved arsenic increased. The inverse relationship to calcium and the retention of arsenic with the addition of lime lead to the hypothesis that a calcium arsenate precipitate might be a major controlling phase in arsenic mobility. To test this, the geochemical computer codes WATEQ4F and MINTEQA2 were used to model the water chemistries. Neither laboratory nor field samples for the control (unamended) conditions or the amended conditions were found to be saturated with respect to any of the "ideal" arsenate phases present in these programs. A calcium carbonate-arsenate or calcium phosphate-arsenate phase may exist and be a solubility control, or possibly an amorphous iron hydroxide-arsenate is limiting dissolved arsenic concentrations. It should be emphasized that there is no direct evidence for this hypothesis.

If the arsenic concentrations from the gravity drained, lime amended soil columns could be thought of as representative of field concentrations, then the effectiveness of the lime seems to fail around 10 pore volumes. A failure here is the point at which calcium concentrations drop to 60 mg/l, or the arsenic concentration exceeds 50 micrograms per liter (ug/l). One pore volume is representative of approximately a one and a half years of infiltration in the field. Using this as a time frame for amendment effectiveness, every 10 to 15 years a reapplication of amendment to the soil would be required.

This however, would be a worst case. Since the field is only periodically saturated, the mobility of arsenic would likely be less than that seen in the leach column results. With a mixing factor in the groundwater of only 10 to 1, the concentration of leached arsenic would not exceed the EPA's drinking water standards until the calcium concentration in the soil water was reduced to about 40 mg/l.

FIELD SITE EXPERIMENTAL RESULTS

Introduction

Lysimeters were successfully sampled until the end of August 1987, after which the soil became too dry to obtain samples from the ceramic lysimeters installed at depths of 8, 16, and 24 inches. The "soil" materials became too coarse for deeper lysimeter installation; below about 27 inches gravels with interstitial sand and minor silt were encountered. Averaged results from samples of as many as seven lysimeter collected for chemical analysis of cations and arsenic or anions are presented in the following figures. In-plot lysimeters were installed on subplots 5, 6, 7, 8, 11, and 15, as depicted by Schafer and Associates (1988). It should be noted that replicate lysimeter nests were installed in two of the plots containing agricultural lime, L, (actually $1/3 \text{ Ca(OH)}_2$ and $2/3 \text{ CaCO}_3$, applied at the rate of six tons per acre) and agricultural lime plus phosphate, L+P, applied at the same lime rate plus 750 pounds of 45 percent P205 per acre (Schafer, W. M., 1987, written comm.). We were unable to obtain lysimeter samples from the lime plus phosphate plus green manure, L+P+M, plot at the 8-inch depth. One pair of lysimeters located off of the plot were sampled as a cross check; these data suggest some cross contamination of amendments or considerable variation in soil content of leachable sulfate, nitrate, and arsenic. The variation between results from the two L plots also suggests such variance.

Results from the lysimeter sampling are presented in Table 3. The lysimeter sample collection dates and rain gage data are presented in Table 4.

Arsenic

Figure 3 depicts the relationships between dissolved arsenic in the soil moisture and depth. The As concentrations from each lysimeter are plotted separately, although the value at each point is the arithmetic average of the results for samples collected from that lysimeter. The purpose of showing the individual lysimeter results is to emphasize the variability of the field data. The data spread indicates that variation in arsenic source concentrations and amendment mixing and concentration probably exists. The source concentration is probably the major factor in the variability. Two sets of soil samples analyzed for As content varied by a factor of eight. Had more extensive sampling from all three of the complete plot replications been feasible, a greater spread would have undoubtedly occurred. It is apparent that the field site results during the first year did not completely parallel the laboratory results. The lowest arsenic concentrations at depths of 8 and 16 inches were found in the samples from the control (untreated) plot. The replicated plot samples yield higher concentrations at the 16-inch depth for the L+P amendment, whereas at the 24-inch depth, the L amendment concentrations are higher than the L+P amendment concentrations. The largest value shown, 758 parts per billion (ppb), is an average of three samples collected from the 8-inch depth lysimeter of one of the L+P plots. The repetition of two 1,000+ ppb values indicates that it was not an analytical fluke. The pH values of 5.14 and 5.19 for the 1,086 and 127 ug/l samples, respectively, suggests that pH is not the controlling factor at a depth of eight inches in the L+P plot.

The L+P samples collected from a depth of 24 inches show the lowest dissolved arsenic concentrations. The 24-inch lysimeters are installed just above an

Table 3. WATER CHEMISTRY FROM LYSIMETER SAMPLES AT THE SPANGLER SITE

AMENDMENT	DEPTH	FIELD COLL #	FIELD pH	FIELD SC umho/cm	As ug/l	Cu ug/l	Zn ug/l	SO4 mg/l	NO3 mg/l as N
=====									
L+P+M (L4)	8-INCHES	NO SAMPLES SUCESSFULLY COLLECTED							
	16-INCHES	3						296	
	SITE 1	4	6.2	4275	202	680	10000		
		5		1160				318	
		6		4080	255	820	24500		
		8		6115				325	
		22	5.79		182	1310	37700	387	
	AVERAGE =		6.00	3908	213	937	24067	332	
	24-INCHES	1			944	150	150		
	SITE 1	2	6.82		737	790	190		
		5		3350				207	
		6			644	170	350		
		22	6.96		540	230	800	559	790
	AVERAGE =		6.89	3350	716	335	373	383	790

L+P (L3)	8-INCHES	1	5.19		127	86	7830		
	SITE 5	5		3000				1121	
		21	5.14	15200	1086	280	660	577	300
		22			1061	780	7260	555	
	AVERAGE =		5.17	9100	758	382	5250	751	300
	SITE 4	1			196	400	2740		
		2	5.6		178	230	2430		
		3	6.18	1740				127	
		4	6.01	1140	216	180	2540		
		5		1520				170	
		6		1140	328	290	4540		
		8		1494				149	
		19			175	490	10300		
		21	5.29	1375	235	360	5320	84.6	136
		22	5.95		279	290	5380	106	127
	AVERAGE =		5.81	1402	230	320	4750	127	132

L+P (L3)	16-INCHES	1			452	3720	18400		
	SITE 5	2	5.74		518	2770	14100		
	SITE 4	1			50	73	330		
		2	6.57		553	82	130		
		5		2350				230	
		6		2500	60	49	200		
		8		2394				258	
		21			56	140	1070	208	473
		22	6.99		49	76	640	198	480
	AVERAGE =		6.78	2415	154	84	474	224	477
	24-INCHES	2			72	300	1394		
	SITE 5	4			44	180	910		
		5						494	
		6			54	200	1820		
		8		2284				538	
	AVERAGE =			2284	57	227	1375	516	

Table 3 (continued)

AMENDMENT	DEPTH	FIELD COLL #	FIELD pH	FIELD SC umho/cm	As ug/l	Cu ug/l	Zn ug/l	SO4 mg/l	NO3 mg/l as N
	SITE 4	2	6.85		79	42	75		
		3						105	
		4	7.2	2025	106	22	36		
		5		1528				163	
		6		1700	84	25	19		
		8		1550				141	
		21	8.25		104	65	35	126	210
	AVERAGE =		7.43	1701	78	39	41	134	210

L	8-INCHES	1	5.74		97	120	1060		
(L2)	SITE 2	2	5.85		108	140	910		
		21	5.26	990	181	210	1190	39	102
		22	5.72		161	100	810		
		23	5.35	2930	74	230	11800		
		24	4.87	2679	77	320	15100	123	298
	AVERAGE =		5.47	2200	116	187	5145	81	200
	16-INCHES	1			145	120	970		
	SITE 2	3	6.56	1730				178	
		4	6.12	2150	191	100	1230		
		5		1575				204	
	AVERAGE =		6.34	1818	168	110	1100	191	

	L	16-INCHES	1			388	100	405	
(L2)	SITE 6	2	5.18		292	52	180		
		3	4.9	353				67.4	
		4	5.2	355	205	53	170		
		5		415				60.6	
		22			240	95	210	51.4	400
	AVERAGE =		5.09	374	281	75	241	60	400
	24-INCHES	1	5.83		83	180	1230		
	SITE 2	2	6.25		91	150	890		
		3	6.38	3000				330	
		4	5.97	3400	142	150	5260		
		5		2750				306	
		6		2050	124	150	4800		
		21	5.54	2490	84	200	7340	413	690
		22	5.86		86	140	5850		
	AVERAGE =		5.97	2738	102	162	4228	350	690
	SITE 6	1			241	43	370		
		2	5.11		196	23	180		
		3						93	
		4	5.38	545	187	44	150		
		5		500				142	
		6			121	46	220		
		23	6.05	1919	481	240	1260		
		25	6.51	2795	532	200	640		
	AVERAGE =		5.76	1440	293	99	470	118	

Table 3 (continued)

AMENDMENT	DEPTH	FIELD COLL #	FIELD pH	FIELD SC umho/cm	As ug/l	Cu ug/l	Zn ug/l	SO4 mg/l	NO3 mg/l as N	
CONTROL (L1)	8-INCHES SITE 3	1			138	470	2580			
		2			116	340	2040			
		5		875				161		
		6			101	260	1820			
		AVERAGE =			875	118	357	2147	161	
		16-INCHES SITE 3		1			106	600	6090	
		2	5.24		96	420	3880			
		3	4.77	1290				130		
		4	4.59	1100	79	230	2090			
		5		1085				255		
	6		1060	53	220	1850				
	8		910				219			
	24	5.57	951	119	140	730	114	63.4		
AVERAGE =		5.04	1066	91	322	2928	180	63		
CONTROL (L1)	24-INCHES SITE 3	1	4.02		196	400	2740			
		2	5.69		178	230	2430			
		3	4.38	1323				106		
		4	4.59	1180	216	180	2540			
		5		970				173		
		6		1140	328	290	4540			
		8		700				191		
		AVERAGE =		4.67	1063	230	275	3063	157	

	OFF-PLOT CONTROL									
8-INCHES SITE SP	21				343	1580	3240	28.3	21.4	
	23	5.86			466	753	2590			
	26				514	870	3000			
	29	5.85	400	433	190	560	25.2	25.4		
	30		325	570	680	2430	37.9	16.4		
	AVERAGE =		5.85	363	461	815	2360	30.5	21.1	
16-INCHES SITE SP	19				164	130				
	21	6.63	322	98	59	250	27.3	22		
	22			283	38	190	21.5	21.6		
	25	7.62	330	357	140	560	21.8	25.5		
	26	6.0	333	343	100	320	21.8	26.8		
	28	6.3	507	341	200	370	22.5	29.9		
	29	5.93	492	395	70	220	25.5	25.7		
	30			450	110	270	25.8	28.1		
	31			355	78	220	27.4	22.9		
	AVERAGE =		6.50	397	310	103	300	24.2	25.3	

Table 4. SAMPLING SEQUENCE NUMBERS WITH DATES AND PRECIPITATION DATA

Sequence Number	Date	Precipitation (inches since previous visit)
1	06/01/87	0.06
2	06/23/87	1.07
3	07/06/87	0.23
4	07/22/87	2.82
5	07/29/87	0.38
6	08/05/87	0.08
7	08/07/87	0.00
8	08/17/87	0.34
9	08/20/87	0.00
10	08/28/87	0.42
11	09/18/87	0.16
12	09/25/87	0.16
13	10/09/87	0.05
14	10/19/87	0.00
15	10/30/87	0.00
16	11/10/87	0.15
17	12/21/87	Frozen
18	02/26/88	0.93 cumulative since 11/10/87
19	04/19/88	0.95
*	04/20/88	0.32
*	04/21/88	0.29
*	04/27/88	0.44
20	04/28/88	0.00
21	05/03/88	0.22
22	05/18/88	0.70
*	05/23/88	0.18
*	05/28/88	0.04
23	06/01/88	0.98
24	06/02/88	0.05
*	06/07/88	0.01
25	06/13/88	0.20
26	06/21/88	0.065
27	06/23/88	0.06
28	07/10/88	0.40
29	07/12/88	0.00
30	08/05/88	0.17
31	09/20/88	1.00

* = precipitation measurement only, no attempt to sample.

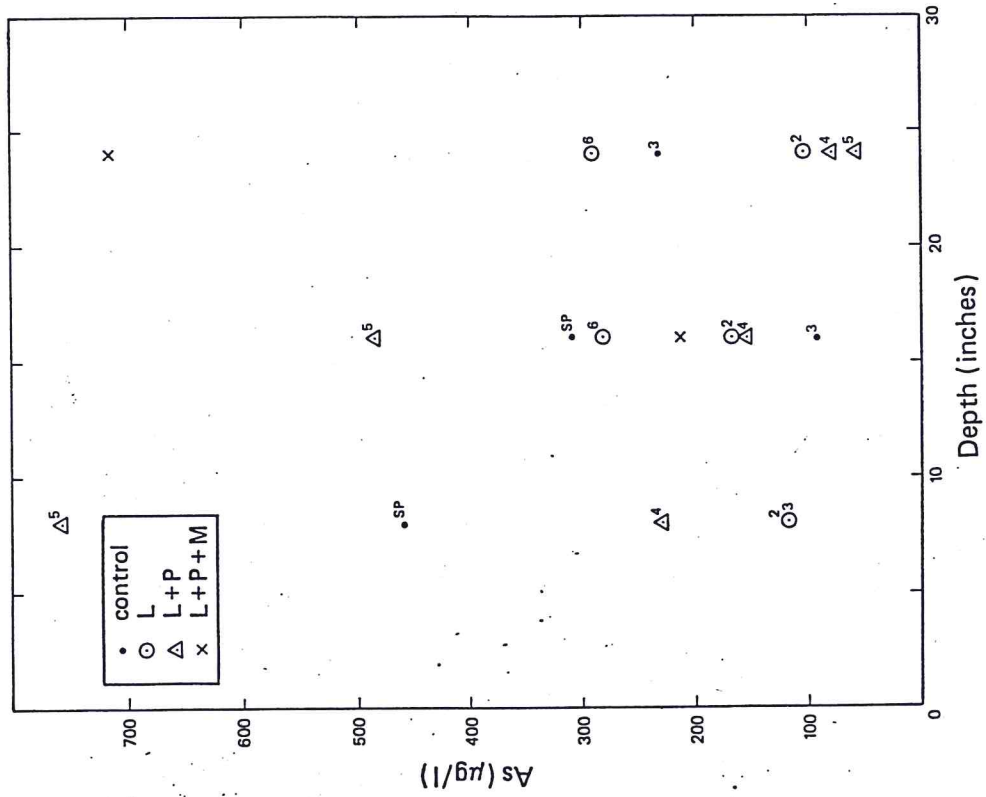


Figure 3. Plot of average dissolved arsenic concentration from each lysimeter versus lysimeter depth.

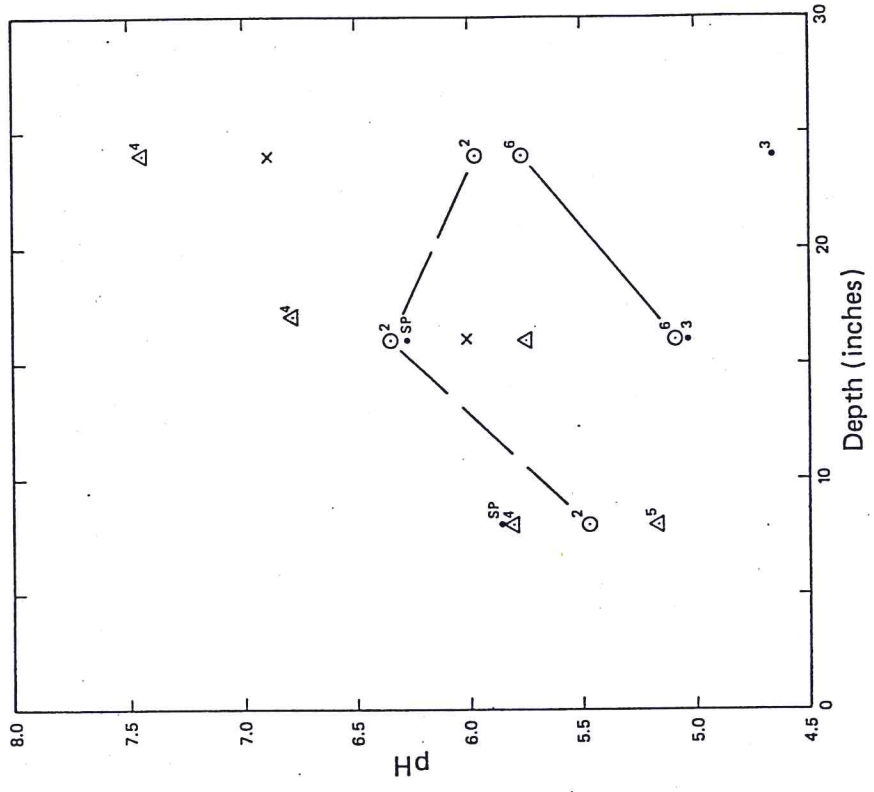


Figure 4. Plot of average pH from each lysimeter with pH values versus lysimeter depth.

underlying gravel zone. No further attenuation is expected once the gravels are reached. Hence, it appears that the lime plus phosphorous amendment provides the best solution for improving the soil while protecting the groundwater from arsenic release.

pH

The pH of soil solutions from amended plots ranged from 4.9 to 8.25, while most of the amended pH values were within 1/2 unit of 6.0. However, one of the L-plots had five pH values from the two deeper horizons; their range (from 4.9 to 5.38) suggests that a higher liming rate is needed at this site. Figure 4 shows the arithmetic average of the pH values for the solutions collected at the lysimeters. The trend in the amended plots is for pH to increase with depth. The one L-amended plot that had the best sampling record diverges from this pattern; it is indicated with a dashed line connecting the values for the three depths. Unfortunately, there was not an 8-inch depth pH value for the control plot and the off-site control only had 8- and 16-inch deep lysimeters. The two data points plotted show a trend of decreased pH with depth. Based upon zinc and copper concentrations, the pH of the 8-inch depth for the control plot is estimated to be 5.0.

The pH values for unamended plots on-site and off-site suggest that considerable variation in soil pH is to be expected within any reasonably sized area to be treated with amendments. The low pH values from the on-site control plot show that cross contamination with lime did not occur.

Zinc

Figure 5 depicts the relationship between dissolved zinc and the lysimeter depth. Because of the three order of magnitude range in zinc concentrations, this diagram had to be plotted with a logarithmic concentration scale. The most homogeneous data is from the off-site control plot at a depth of 16 inches. Eight samples range from 190 to 560 ppb. The on-site control plot show the most uniformity when all three depths are considered.

At the shallow, 8-inch depth, the unamended samples showed the lowest dissolved zinc concentrations (2 to 2.5 ppm). At a depth of 16 inches, the data show substantial spreading, and repeated analyses from the same lysimeter show similar spreads in some cases. The 24-inch deep data show extreme variation for the L and L+P replicate plots. These data make any interpretation treacherous, but show that there must be considerable variation in source concentrations of leachable zinc and suggest that the L+P amendment may be the preferred choice.

Copper

Figure 6 depicts the relationship between dissolved copper in the soil-water samples and lysimeter depth. The control plot again shows the greatest uniformity of analytical results for all three depths. The L amendment may outperform the L+P amendment as indicated by the scatter of averages for L+P at 24 inches; the L+P+M amendment actually resulted in higher Cu concentrations than those from the control plots.

The scatter between replicate plots strongly suggests that there is excessive variability in the experimental design. The L+P+M amendment does not appear to be helpful, however, because of the scatter the column simulations should probably be used to select between the L and L+P amendments. Those results

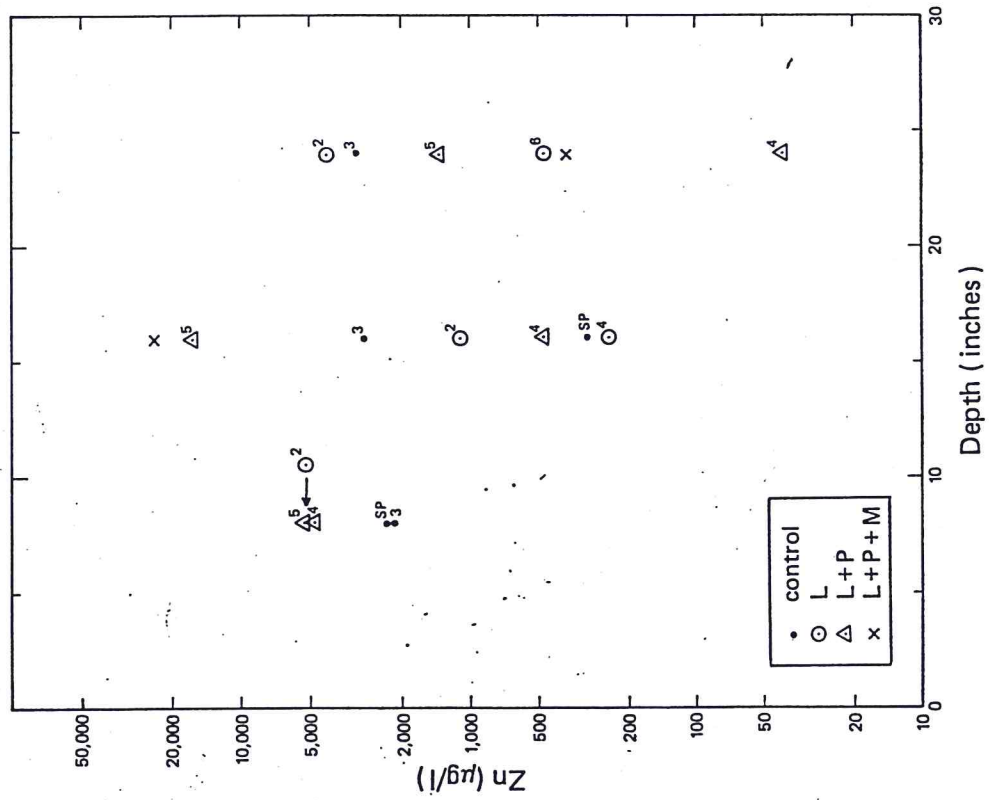


Figure 5. Plot of average dissolved zinc concentration from each lysimeter versus lysimeter depth.

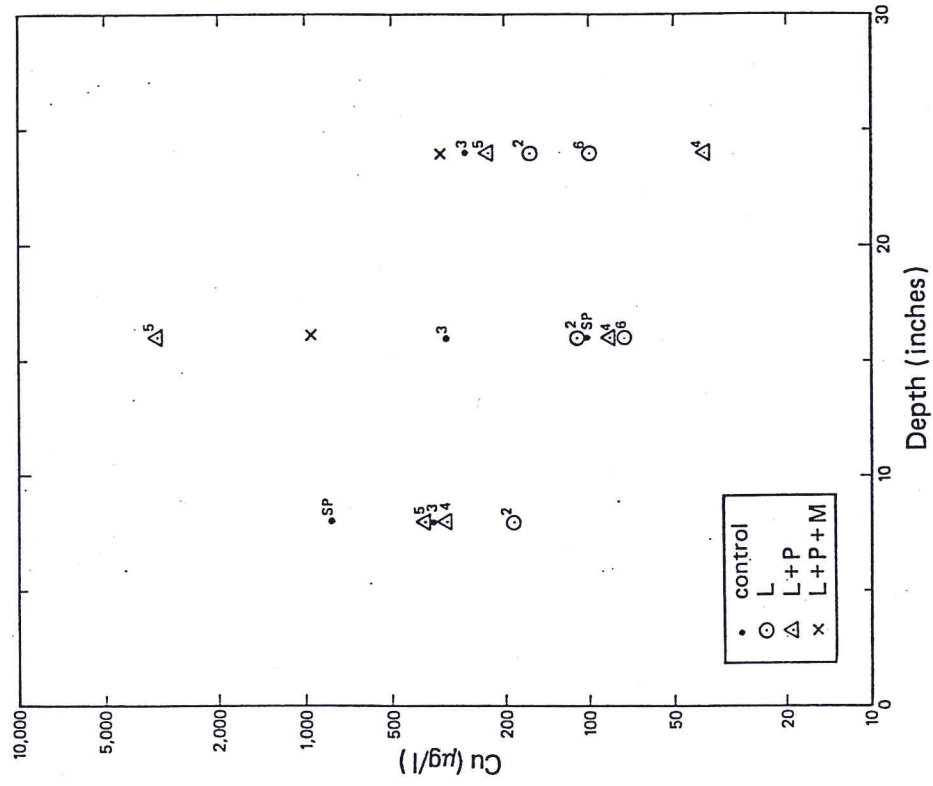


Figure 6. Plot of average dissolved copper concentration from each lysimeter nest versus depth.

suggest that the L amendment will release slightly less copper and zinc.

Specific Conductance

Specific conductance (SC) is a measure of the ability of the water to conduct electricity. It results from the presence of dissolved compounds which have positive and negative charges (cations and anions). Thus the specific conductance of the collected soil water indicates, in general, if changes are caused by the amendments. Figure 7 depicts these variations for the lysimeter samples. The data available are more limited (see Table 3) because it was the lowest priority sample, and frequently there simply was not enough water available for this field determination.

However, it is clear that, with the exception of the replicate lime plot (#6), the amount of dissolved ions increased because of the amendments; i.e., the amendments are being leached in the soil moisture and will be added to the groundwater. The sulfate discussion which follows and the nitrate values presented in Table 3 support this interpretation.

Sulfate

Analysis of sulfate required most or all of the water from a typical sample volume. There are two sources of sulfate, oxidation of sulfide minerals and impurities in the agricultural amendments. Of the two, sulfides in the tailings-damaged soils are thought to be far more significant. Figure 8 shows off-site control values to be less than 50 mg/l. All on-site sample values were higher than the highest off-site value. The difference between on-site replicates for L and L+P amendments are suggest a three-to-five fold variation in the soluble-sulfate source. The difference between the on-site and off-site control lysimeter samples is nearly as striking.

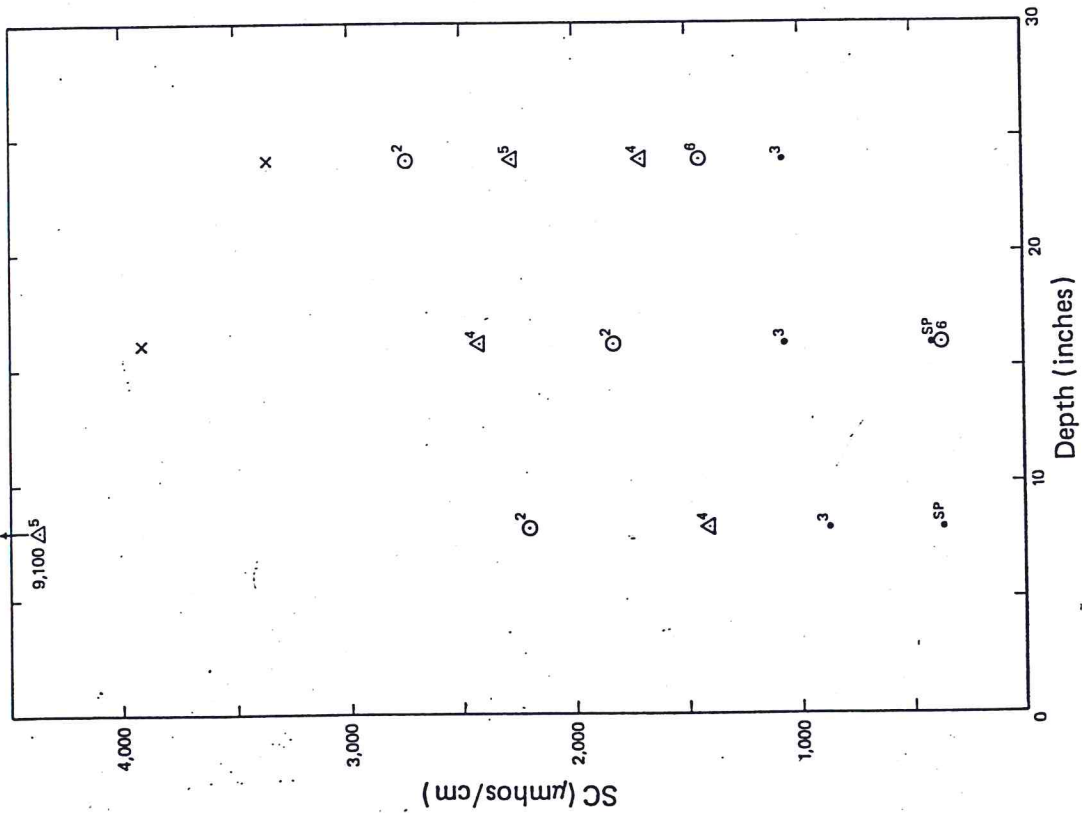


Figure 7. Plot of average specific conductance from each lysimeter nest versus depth.

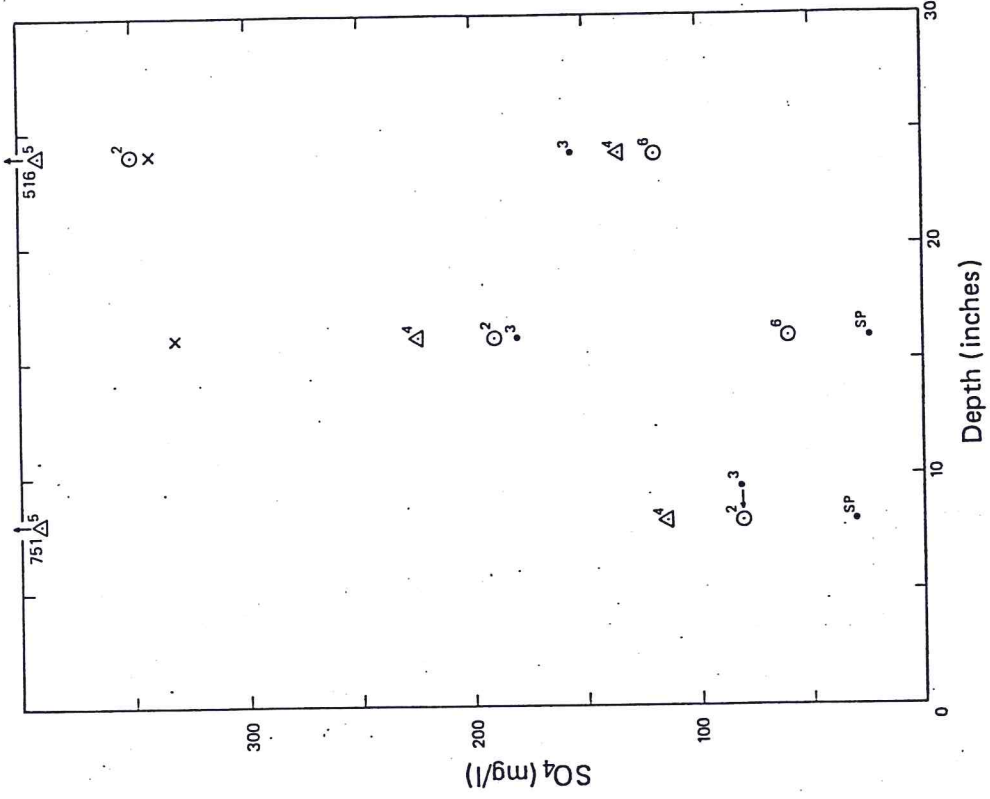


Figure 8. Plot of average dissolved sulfate concentration from each lysimeter nest versus depth.

SUMMARY AND CONCLUSIONS

The poor correlation between the laboratory bench tests and the field tests suggest that a non-representative soil sample may have been employed in the laboratory tests. The laboratory pH values for the column effluent from both the gravity and pumped unamended soil runs were slightly alkaline. Hence, the results of the field tests are given much greater weight in the summary and recommendations.

The 24-inch lysimeter results from the field are thought to be the most valid criteria for evaluating the effectiveness of the amendments at retaining arsenic to protect groundwater while increasing the soil pH to enhance vegetation growth and reduce erosion. Review of the field data suggests that the agricultural lime plus phosphate (L+P) is the preferable amendment approach for reducing arsenic release to the groundwater and for retaining copper and zinc in the soil.

The lime plus phosphorus plus manure (L+P+M) amendment resulted in excessive arsenic release. It also appears to produce excessive quantities of dissolved zinc which may be taken up by the vegetation at shallower depths; the average dissolved zinc concentration in samples from the 16-inch deep lysimeter was 24 mg/l.

The lime (L) amendment has slightly poorer results in minimizing the mobility of copper and zinc and was roughly one third less effective at retaining arsenic. Variability of the field conditions may be a significant factor causing some of this inconsistency. The variation between replicates is greater than the variation between the high-metals L and L+P plots or the low-metal L and L+P plots.

The relatively low pH values from some of the lysimeter nests may have resulted from soil variability or from the wind blowing away some of the amendment, either before it was incorporated or from failure to incorporate deeply enough. In standard agricultural practice, however, it would probably be necessary to increase the amendment rate to minimize the effects of metals source variability and/or wind losses.

Modeling of the chemical analyses from the 24-inch depth lysimeter samples provide permissive support for all of the proposed coprecipitation controls (calcium carbonate, calcium phosphate as any of the varieties of apatite, and ferric hydroxide) upon the solubility of arsenic in the soil water for the amended plots but not for the control plot. Apparently, the only viable precipitation-mechanism control upon dissolved arsenic concentration for the unamended plot is a coprecipitate with ferric hydroxide. However, such controls are strictly theoretical. Groundwater samples from aquifers in the lower Madison Valley near Three Forks (Sonderegger, et al, 1989) show no measurable attenuation of arsenic in waters with similar chemistry and arsenic concentrations but lower nitrate and sulfate concentrations and slightly higher pH values. More to the point, the progressively deeper lysimeter samples show reductions in dissolved arsenic which decrease its concentration to approximately the same range as those concentrations found near Three Forks. The similarity of dissolved arsenic concentrations suggests that some common control mechanism may exist.

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