U. S. DEPARTMENT OF THE INTERIOR

U. S. GEOLOGICAL SURVEY

Impact of the lower Alamosa River water on alfalfa, southwestern San Luis Valley, Colorado—1994 follow-up study

By

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Open-File Report 95-43

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1995

Highlights

Two of four alfalfa fields irrigated by lower Alamosa River water and sampled just before the June 1993, cutting were resampled in 1994. Water and alfalfa samples were collected when the alfalfa was harvested in early June, late July, and mid-September 1994, to determine (i) if any metal concentrations had changed appreciably between crop years and (ii) if important seasonal differences occurred between the three 1994 cuttings. The results for standard reference materials and duplicate samples showed that the analyses were accurate and reproducible. The exellent reproducibility (precision) assures that the variability found between cuttings was due to natural conditions rather than analytical error.

The pH of the irrigation water changed 100 fold from an almost neutral 6.6 in early June to quite acid conditions—4.7—by late July. During that same interval, the copper level in the unfiltered water increased seven-fold from 120 to 850 parts per billion (ppb; $\sim\mu g/L$). On average, these changes in the water quality caused the copper levels in the alfalfa to almost double, from about 12 parts per million (ppm) to 20 ppm in the dry material. Copper levels in alfalfa generally dropped to about 15 ppm in the alfalfa sampled just before the fall cutting, which corresponded to a drop in copper concentrations in the irrigation water from 850 to 670 ppb. These results suggest that the copper content in alfalfa responds remarkably to short-term changes in the copper levels of the irrigation water.

A copper concentration of 20 ppm in alfalfa is ideal for dairy-cattle feed. Many dairy operators reportedly try to feed at this level. However, sheep are much less tolerant of copper than cattle, although the copper tolerance varies with breed. The maximum tolerance level of copper for sheep is 25 ppm compared to 115 ppm for beef cattle.

Concentrations of copper and manganese in alfalfa collected from the first cuttings of 1993 and 1994 were nearly the same despite a tenfold increase in the pH of the irrigation water between those two periods. However, a marked increase in the concentrations of these two metals did occur in the alfalfa between the first and second cuttings in 1994, which corresponded to a sharp increase in acidity and levels of copper and manganese in the water.

INTRODUCTION

Contamination from the Summitville gold mine in the San Juan Mountains, Colorado, has raised concerns about the potential environmental effects of low pH and metal-laden—particularly copper—surface waters carried down the Alamosa River. These waters enter the Terrace Reservoir, which provides irrigation water to the southwestern part of the San Luis Valley.

An initial study of the effects of Alamosa River waters on alfalfa was conducted in June 1993. Those results, based on alfalfa sampled from Terrace-irrigated fields and control fields irrigated with water from other sources, were detailed in a report by Erdman and others (1995). They concluded that, although the metal concentrations of the irrigation water from the reservoir were anomalous, the waters had only a minor effect on the total soil chemistry. Significantly higher concentrations of copper, manganese, and nickel were found in alfalfa from the Terrace-irrigated fields. More importantly, concentrations of these metals in alfalfa irrigated with water from both sources (i) met published nutritive requirements for cattle, (ii) were far below maximum tolerable levels reported for cattle, and (iii) were comparable to concentrations in alfalfa found in other parts of the country. In focussing on the nutritional needs of alfalfa, Erdman and others (1995) found that the Terrace Reservoir waters seemed to have enhanced the bioavailability of copper and manganese to optimum levels.

In the 1994 irrigation season, unexpectedly large seasonal differences for pH and metal concentrations occurred in water from the Alamosa River (Smith and others, 1995). Between early June and late July 1994, acidity increased 100 fold from a nearly neutral 6.6 down to a pH of 4.7. In the same period, copper concentrations increased sevenfold, manganese doubled, and zinc tripled (see Table 1). The pH further dropped to 4.2 by September; concentrations of copper decreased slightly while manganese continued to rise. As described below, alfalfa sampled from two adjacent fields irrigated by Terrace Reservoir water reflected those changes but not to the degree found in the waters sampled.

METHODS

Sample Collection and Field Methods

The sampling design for 1994 was scaled down considerably from the June 1993 sampling plan, which included four fields irrigated by Alamosa River water and four control fields irrigated by water from other sources (Erdman and others, 1995). Two adjacent center-pivot irrigation fields that receive water from the same storage pond were selected, and sampling was conducted according to the same balanced, four-level nested analysis-of-variance design used previously. Sampling dates were June 6, July 22, and September 14, 1994.

Four alfalfa samples were collected from each of the two fields and at the same sites as the previous year to minimize the effects of possible within-field variation. These samples were composited from ten points within a 1-m radius of the center of the sample site.

Irrigation Water Collection and Field Methods

On June 6, 1993, and June 7, July 27, and September 12, 1994, water quality samples were collected from an irrigation storage pond that serves the two alfalfa fields sampled for this study. Specific conductivity, pH, and temperature were measured on site, and both filtered (0.2 μm) and unfiltered water samples were collected. Chain-of-custody protocol was followed for water-sample collection, transport, storage, and analysis.

Laboratory and Analytical Procedures

Samples were handled according to prescribed quality assurance/quality control (Arbogast, 1990). Chain-of-custody procedures followed for alfalfa in the 1993 study were not used in the smaller 1994 study.

Splits of filtered and unfiltered irrigation water samples were acidified with concentrated nitric acid (to pH <2) for subsequent metal analysis. Portions of the filtered (unacidified) water were saved for anion and alkalinity determinations. Samples for anion and alkalinity determinations were refrigerated prior to analysis. Element concentrations were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) in the analytical laboratories of the U.S. Geological Survey (USGS), Denver. USGS water standards, samples, and duplicates were submitted in a randomized sequence for analysis.

The alfalfa samples—four from each of two fields, eight from each cutting—were oven-dried and homogenized in a Wiley mill to pass a 1.3-mm sieve. They were *not* washed, since they were meant to represent hay as fed to livestock. A portion of each sample was ashed at ~500°C in a muffle furnace, then split to estimate the reproducibility of duplicate analyses. These 48 samples plus two reference standards were digested in a mixed-acid solution and analyzed by ICP-AES. Ash yield was calculated to allow conversion to the dry-weight basis used in nutritional studies (Peacock, 1992). All samples were submitted in a randomized sequence.

RESULTS AND DISCUSSION

Water

As shown in Figure 1, the pH of the storage pond increased from 5.6 in early June 1993, to nearly neutral (pH 6.6) in early June 1994 (see Table 1). However, acidity of the storage pond water increased 100 fold between early June and late July 1994, when the pH dropped substantially to 4.7 by late July 1994, and continued to drop between late July and mid-September 1994, when the pH was measured at 4.2.

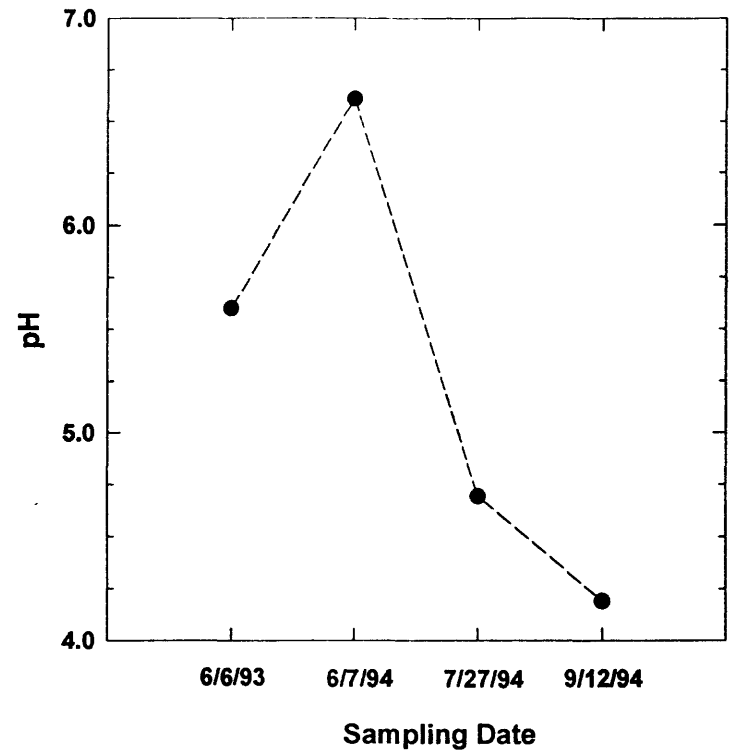

Figure 1. Plot of the irrigation storage-pond water pH data for the period from June 1993 to September 1994.

As detailed by Smith and others (1995), there is an apparent relationship between the pH of the irrigation water and the metal concentrations in the water; generally, as the water becomes more acid (lower pH), metal concentrations increase. Figures 2 and 3 illustrate total copper and manganese concentrations, respectively, in the storage-pond water at the different sampling dates. The Colorado Surface-Water Standard for Agricultural Use is 200 μg/L for both total copper and manganese (CDH, 1993). Total copper concentrations were three times higher and total manganese 1.5 times higher in early June 1993, than in early June 1994. However, between early June and late July 1994—the same period during which the water pH dropped 100 fold—the total copper concentration rose seven times and total manganese concentration doubled. Between late July and mid-September, 1994, the total copper concentration decreased slightly and total manganese continued to increase. This decrease in total copper concentration and increase in manganese concentration corresponds to trends for copper and manganese concentrations in alfalfa from the third cutting (see Table 2). Water quality data for unfiltered (UA; total) and filtered (FA) samples are listed in Table 1.

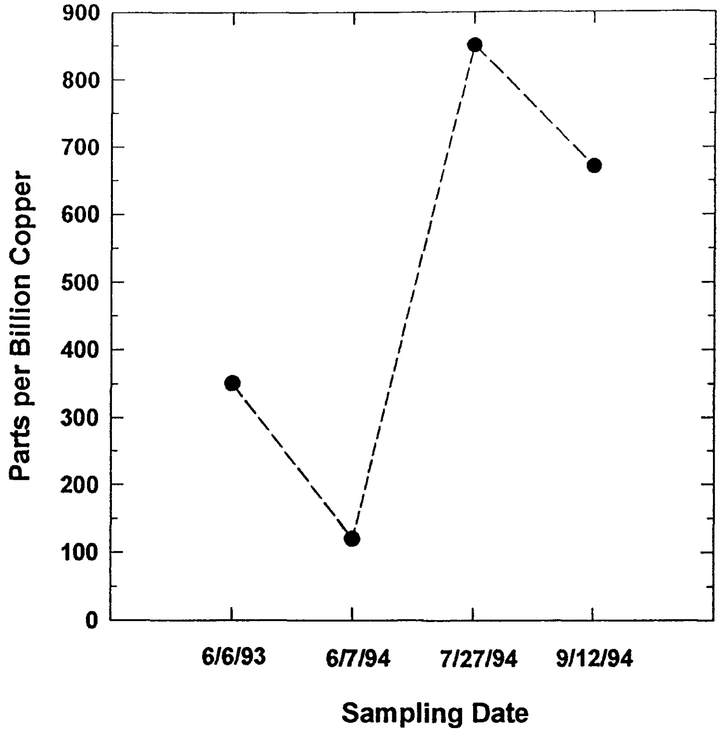

Figure 2. Plot of irrigation storage-pond water total-copper concentration for the period from June 1993 to September 1994. Data shown are for unfiltered acidified water samples.

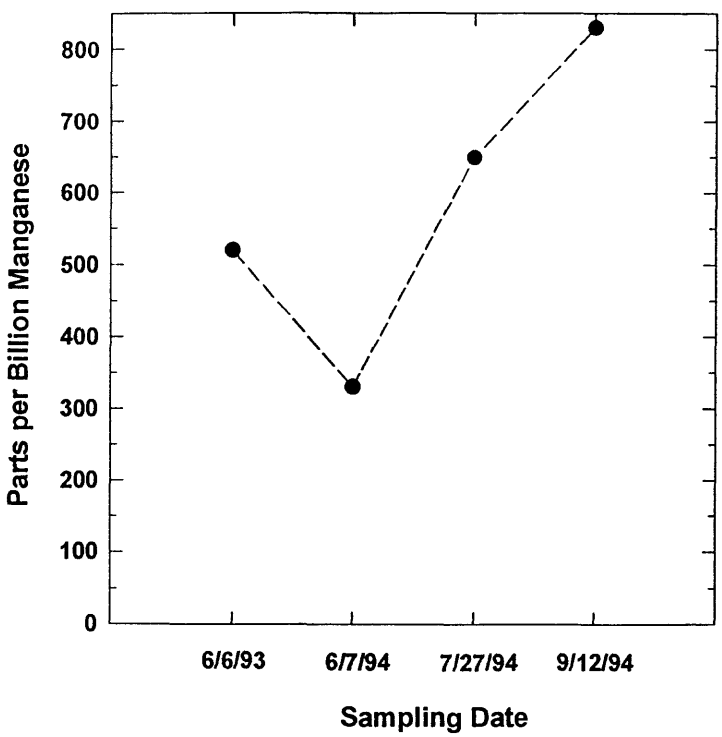

Figure 3. Plot of irrigation storage-pond water total-manganese concentration for the period from June 1993 to September 1994. Data shown are for unfiltered acidified water samples.

Alfalfa

The concentrations of copper and manganese in alfalfa from the first cuttings of 1993 and 1994 were quite similar (Figures 4 and 5) despite the disparity in the water pH. However, the changes in the quality of the irrigation water within the 1994 growing season were strongly reflected in the three cuttings of alfalfa. The copper levels in alfalfa nearly doubled between the first and second cuttings (Figure 4); unexpectedly, those levels decreased in samples from the last cutting. For dairy-grade alfalfa hay, concentrations of 20 ppm are ideal, and many dairymen try to feed their dairy herds at this level (Cheryl Nockels, Animal Science Department, Colorado State University, oral commun., 1994). But sheep are less tolerant of copper than cattle; maximum tolerance levels for sheep and beef cattle are 25 ppm and 115 ppm respectively (National Research Council, 1984, 1985).

As shown in Figure 5, concentrations of manganese rose in the alfalfa sampled through the 1994 season. Unlike the pattern for copper, however, manganese concentrations continued to increase in the fall cutting, tracking concentrations of manganese in the irrigation waters. Fortunately, cattle and sheep tolerate manganese well. The maximum tolerable level for both animals is 1,000 ppm (National Research Council, 1984, 1985). Concentrations of zinc and nickel, discussed in the earlier report by Erdman and others (1995), were virtually unchanged among cuttings (Table 2). Enrichment of arsenic in the drainage water below Summitville reflect the abundance of arsenic-bearing enargite and tennantite in the ores (Plumlee and others, 1995), and has raised some concerns about its impact downstream. None of the alfalfa we sampled contained arsenic above the lower limit of determination— ~2 ppm, dry-weight basis—well below the 50 ppm maximum tolerable level reported for beef cattle (National Research Council, 1984, table 5).

In conclusion, irrigation-water quality diminished markedly over the course of the 1994 irrigation season. The decrease in pH and increases in concentrations of copper and manganese in the waters caused a marked increase in the copper and manganese concentrations in alfalfa. Changes in the concentrations of zinc in the water did not trigger any similar change in the alfalfa. Nutritional needs in cattle were not compromised. However, concentrations of copper in alfalfa that are ideal for dairy cattle tend to approach levels that may not be tolerated by sheep.

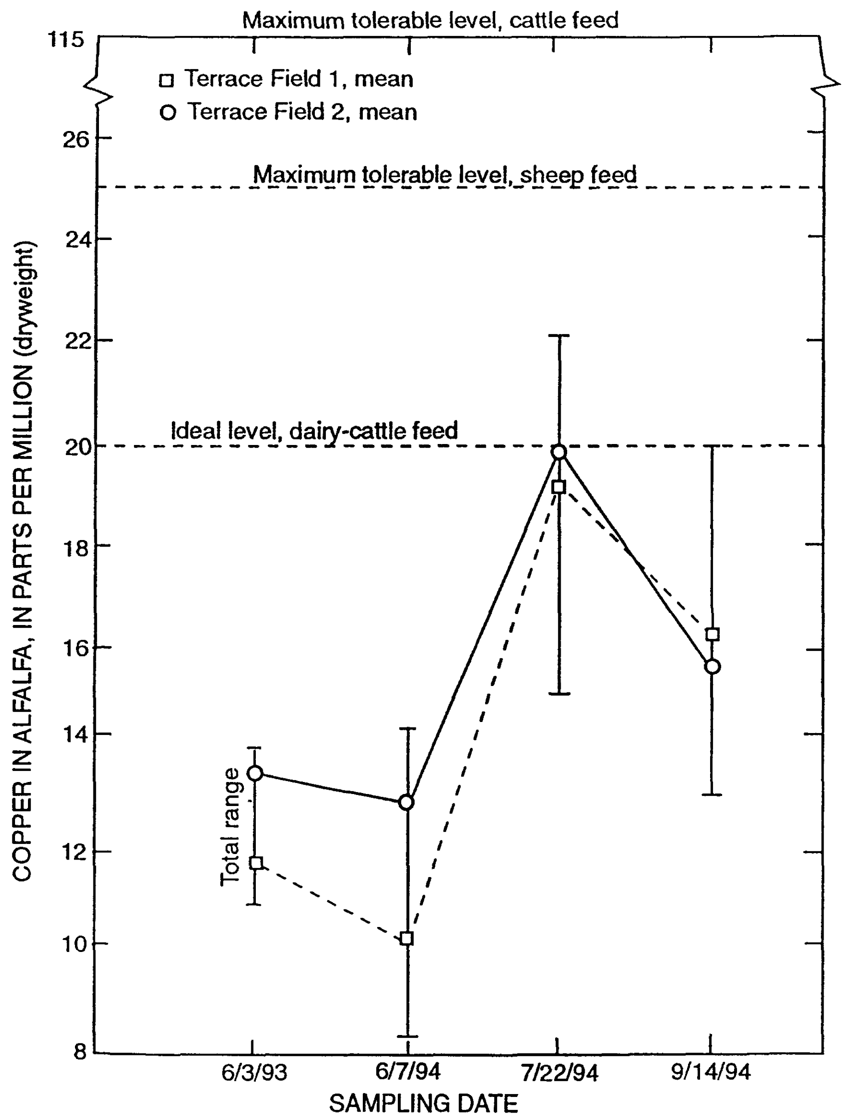

Figure 4. Plot of copper levels in alfalfa for the 1994 seasonal study, including the first-cutting sampling June 1993.

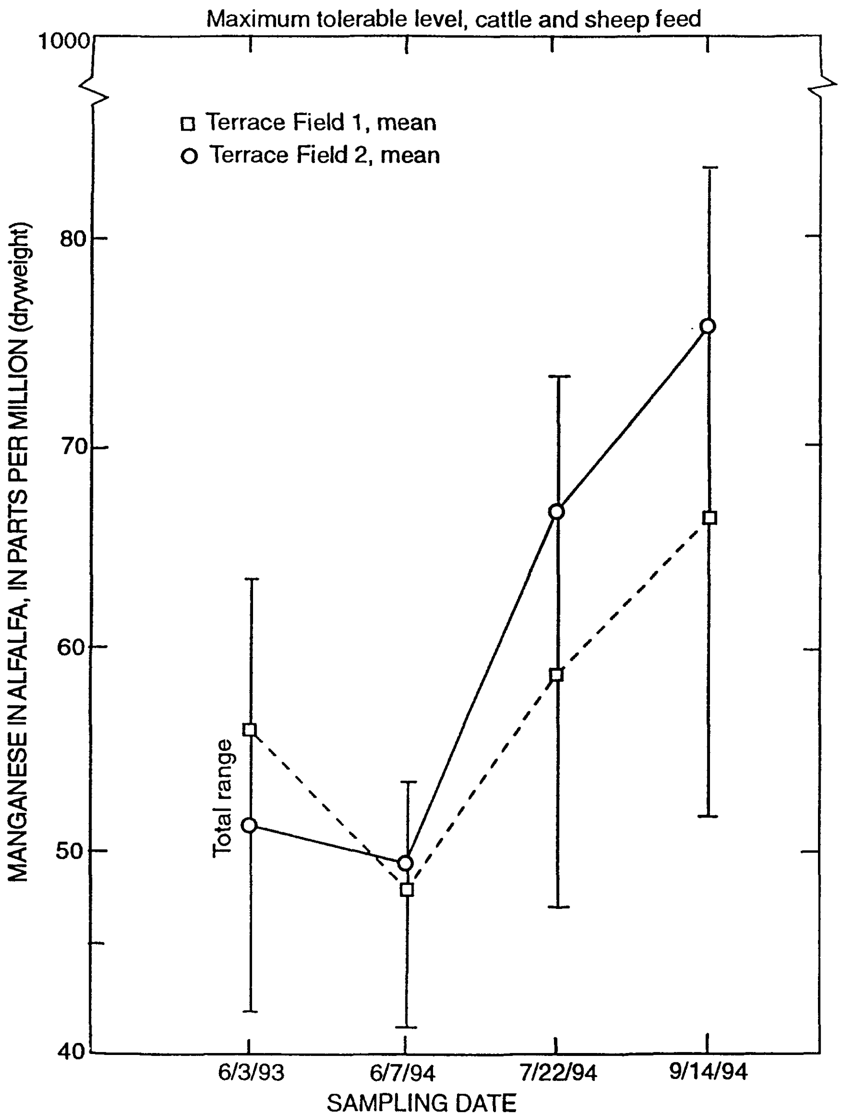

Figure 5. Plot of manganese levels in alfalfa for the 1994 seasonal study, including the first-cutting sampling June 1993.

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Table 1. Water-quality data for major and minor element concentrations determined for unfiltered acidified (UA; total) and filtered (0.2 μm) acidified (FA; "dissolved") irrigation storage pond samples by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

	Date							
	6/6/93		6/7/94		7/27/94		9/12/94	
Type	UA	FA	UA	FA	UA	FA	UA	FA
Field pH	5.6		6.6		4.7		4.2	
Al (ppm)	<1	<1	<1	<1	0.5	0.6	<0.5	<0.5
Ba (ppb)	<40	<40	28	21	34	31	36	35
Ca (ppm)	15	15	15	14	25	26	32	33
Cu (ppb)	350	290	120	<40	850	860	670	710
Fe (ppm)	1	<1	1.8	<1	<0.5	<0.5	<0.5	<0.5
K (ppm)	<1	<1	<1	<1	1.7	1.5	1.6	1.6
Mg (ppm)	2	2	2.5	2.5	4.3	4.4	5.2	5.3
Mn (ppb)	520	510	330	300	650	630	830	830
Na (ppm)	4	4	3.8	4.1	9.1	9.5	11	11
Si (ppm)	4	4	5.0	4.3	6.8	6.7	7.6	7.6
Sr (ppb)	120	120	120	120	190	200	240	250
Zn (ppb)	190	180	94	76	280	290	280	300

Table 2. Analytical results for alfalfa collected from two fields irrigated with lower Alamosa River (Terrace Reservoir) water, southwestern San Luis Valley, Colorado, 1993-1994
[Concentrations expressed on a dry-weight basis; paired samples are analytical duplicates; element symbols for copper and manganese, shaded owing to their importance]

Sample No.	Ca %	K %	Mg %	P %	Al ppm	Ba ppm	Co ppm	Cr ppm	Cu ppm	Fe ppm	Mn ppm	Na ppm	Ni ppm	Sr ppm	Zn ppm
FIRST CUTTING, 1993															
Terrace Field #1															
1111	2.1	3.4	0.27	0.52	37	27	0.62	0.25	11	98	63	529	1.2	118	27
1112	2.1	3.5	0.29	0.55	39	27	0.52	0.26	11	104	60	520	1.3	117	30
1121	2.0	3.9	0.25	0.51	53	27	0.53	<0.27	11	93	61	213	1.5	114	32
1122	1.9	4.0	0.25	0.52	53	27	0.67	0.40	11	106	60	213	1.3	113	33
1131	1.9	4.1	0.27	0.49	53	23	0.67	0.40	13	120	57	213	1.2	98	28
1132	1.6	4.3	0.25	0.45	50	23	0.50	0.38	12	113	46	200	1.0	94	26
1141	1.8	3.6	0.27	0.48	111	27	0.49	0.37	12	148	52	135	1.1	100	28
1142	1.8	3.8	0.28	0.49	175	28	0.50	0.38	13	175	49	113	1.1	98	30
Terrace Field #2															
1211	2.2	3.1	0.30	0.43	132	32	0.48	0.36	13	156	54	228	1.7	156	34
1212	2.0	3.2	0.31	0.42	118	34	0.59	0.35	13	177	52	224	1.2	153	33
1221	2.1	3.1	0.31	0.44	118	33	0.59	0.35	14	165	58	236	1.4	153	34
1222	2.0	3.1	0.30	0.44	115	32	0.23	<0.23	14	161	52	230	1.5	150	35
1231	1.9	3.5	0.29	0.47	36	24	0.48	0.24	13	96	48	156	1.4	120	36
1232	1.7	3.5	0.27	0.44	34	24	0.45	0.23	12	90	42	147	1.4	113	34
1241	2.1	2.8	0.29	0.43	88	30	0.55	0.22	14	143	51	176	1.2	132	31
1242	1.9	3.0	0.29	0.42	77	31	0.55	<0.22	14	132	47	176	1.2	132	31
FIRST CUTTING, 1994															
Terrace Field #1															
TA111	2.1	2.7	0.32	0.39	109	26	0.44	0.22	12	120	51	578	1.3	120	26
TA112	2.1	2.7	0.32	0.39	98	26	0.33	0.22	12	131	51	578	1.3	120	26
TA121	2.2	2.4	0.30	0.41	97	27	0.43	<0.22	10	130	49	616	1.1	130	24
TA122	2.2	2.3	0.31	0.41	97	27	0.43	0.22	10	130	49	616	1.1	130	25
TA131	2.1	3.2	0.31	0.41	81	24	0.46	0.35	10	151	45	429	1.0	116	24
TA132	2.1	3.2	0.31	0.41	93	24	0.46	0.23	10	139	45	429	0.9	116	24
TA141	1.7	2.6	0.25	0.45	46	21	0.35	<0.23	8	92	41	196	1.0	99	20
TA142	1.8	2.8	0.26	0.46	46	22	0.35	<0.23	9	92	43	196	0.8	104	21
Terrace Field #2															
TA211	2.4	2.2	0.40	0.42	100	33	0.44	<0.22	14	133	53	577	1.6	178	29
TA212	2.4	2.1	0.40	0.42	100	32	0.44	<0.22	14	155	53	577	1.4	178	29
TA221	2.2	2.2	0.37	0.43	105	30	0.42	0.21	13	168	45	693	1.4	158	29
TA222	2.2	2.3	0.37	0.43	126	30	0.53	0.32	14	168	46	693	1.5	158	29
TA231	2.3	2.5	0.33	0.43	57	31	0.45	0.34	12	215	51	542	1.6	158	33
TA232	2.3	2.7	0.34	0.43	68	32	0.45	0.34	12	362	52	565	1.7	158	35
TA241	2.1	2.9	0.34	0.43	89	28	0.56	0.44	12	133	47	522	1.4	144	32
TA242	2.1	2.7	0.33	0.44	78	28	0.56	0.33	12	144	47	511	1.6	144	32

Table 2. Continued

Sample No.	Ca %	K %	Mg %	P %	Al ppm	Ba ppm	Co ppm	Cr ppm	Cu ppm	Fe ppm	Mn ppm	Na ppm	Ni ppm	Sr ppm	Zn ppm
SECOND CUTTING, 1994															
Terrace Field #1															
TB111	2.1	2.4	0.25	0.45	42	27	0.62	0.21	20	73	63	385	1.0	125	28
TB112	2.1	2.5	0.25	0.45	31	27	0.52	0.31	20	73	63	374	1.1	125	28
TB121	2.1	2.4	0.27	0.41	31	29	0.52	<0.21	20	73	73	437	1.0	125	26
TB122	2.1	2.6	0.27	0.41	31	30	0.42	0.21	20	73	72	437	1.0	125	26
TB131	1.9	2.9	0.24	0.41	22	22	0.44	<0.22	22	78	48	222	0.8	111	21
TB132	1.9	2.4	0.24	0.40	22	21	0.44	0.22	22	67	47	211	0.8	111	21
TB141	1.7	3.0	0.23	0.38	21	30	0.42	0.21	15	85	49	127	0.5	102	18
TB142	1.7	2.5	0.23	0.38	21	29	0.32	<0.21	15	64	49	138	0.5	103	18
Terrace Field #2															
TB211	2.0	2.3	0.27	0.42	41	27	0.52	<0.21	20	93	56	258	1.2	144	27
TB212	2.0	2.2	0.27	0.42	31	28	0.41	<0.21	21	72	57	258	1.2	144	27
TB221	2.0	2.4	0.29	0.38	40	35	0.61	0.20	20	91	64	364	1.2	152	26
TB222	2.1	2.4	0.29	0.41	30	36	0.51	0.20	21	71	64	374	1.1	152	27
TB231	2.0	2.6	0.28	0.44	21	28	0.53	0.42	18	84	70	294	1.6	126	28
TB232	1.9	2.2	0.29	0.44	21	27	0.53	<0.21	18	74	70	284	1.4	126	28
TB241	1.9	2.8	0.26	0.41	62	30	0.52	0.31	20	104	72	250	1.7	135	28
TB242	1.9	3.0	0.26	0.40	73	29	0.42	0.31	20	114	73	239	1.8	135	29
THIRD CUTTING: 1994															
Terrace Field #1															
TC111	2.1	2.5	0.24	0.43	32	28	0.64	<0.21	17	106	80	392	1.4	117	29
TC112	2.1	2.5	0.24	0.43	32	29	0.53	<0.21	16	95	81	392	1.3	127	29
TC121	2.1	2.8	0.24	0.42	42	31	0.42	0.32	20	95	81	435	1.1	127	28
TC122	2.0	2.4	0.24	0.42	42	30	0.64	<0.21	20	138	80	424	1.1	127	27
TC131	1.2	1.8	0.16	0.34	124	26	0.51	0.29	15	139	52	168	0.9	88	22
TC132	1.2	1.8	0.17	0.34	117	25	0.51	<0.15	15	146	53	168	0.9	88	23
TC141	1.3	2.3	0.19	0.33	162	27	0.49	0.24	13	146	51	162	0.8	89	21
TC142	1.3	2.5	0.19	0.32	146	28	0.49	0.24	13	146	51	154	0.7	89	21
Terrace Field #2															
TC211	1.8	2.2	0.24	0.39	75	26	0.38	0.19	15	122	69	301	1.3	122	28
TC212	1.8	2.0	0.24	0.39	85	25	0.38	<0.19	15	113	70	301	1.3	132	28
TC221	1.6	2.7	0.24	0.41	58	32	0.49	0.29	16	116	82	340	1.6	116	27
TC222	1.7	2.2	0.24	0.44	58	31	0.58	<0.19	16	116	83	340	1.4	126	28
TC231	1.8	1.9	0.26	0.38	46	25	0.46	<0.18	17	109	69	419	1.3	118	27
TC232	1.8	2.0	0.26	0.38	46	25	0.46	0.27	16	100	70	419	1.4	118	27
TC241	1.7	2.3	0.21	0.39	58	25	0.38	<0.19	15	106	77	278	1.2	125	28
TC242	1.7	2.0	0.21	0.39	48	25	0.48	0.19	15	106	78	269	1.2	115	28