UNITED STATES DEPARTMENT OF THE INTERIOR

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IMPACT OF THE LOWER ALAMOSA RIVER WATER ON ALFALFA, SOUTHWESTERN SAN LUIS VALLEY, COLORADO— 1995 FOLLOW-UP STUDY OF EFFECTS FROM THE SUMMITVILLE MINE

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HIGHLIGHTS

Three alfalfa fields irrigated by water from the Terrace Reservoir on the lower Alamosa River and sampled in June 1993, were resampled in July 1995. The purpose of the sampling was to evaluate possible metal uptake in plants caused by upstream water contamination. Alfalfa from the Terrace-irrigated fields was compared with three control fields that were irrigated from the Rio Grande or ground water. Alfalfa samples were also collected prior to each of the three cuttings in 1994 from two fields irrigated by Terrace water. Soils from all fields are either mapped as the same series or are physically similar. Water samples were collected from center-pivot sprinkler-irrigated fields to evaluate differences between the Terrace water and the control water. We also wanted to test possible changes between 1993 and 1995.

In July 1995, the pH in the irrigation water below Terrace Reservoir, about 5.5, was comparable to that measured in 1993. Concentrations of copper and manganese—two metals linked closely to contamination from the Summitville mine Superfund site—were also similar to those measured from the same irrigation water in 1993. In addition to copper and manganese, concentrations of zinc, cobalt, nickel, and the rare-earth elements lanthanum, cerium, neodymium, and yttrium were markedly higher in the Terrace waters compared to the control waters.

Copper levels in alfalfa have been the main focus over this 3-year study because anomalous concentrations of copper and, to a lesser extent, manganese in the lower Alamosa River and Terrace Reservoir (which stores water for down-stream irrigation in the San Luis Valley) have been traced to contamination from the Summitville mine farther upstream. Unlike the initial results from 1993, no statistically significant differences were found in 1995 for copper in alfalfa irrigated by the two water sources, in large measure because concentrations of several metals—copper, zinc, and barium—were appreciably higher in alfalfa collected from one of the three control fields. Yet concentrations of manganese in alfalfa from the two affected fields were double the concentrations in the samples from the control fields; the differences were statistically significant at the 90 percent confidence level. Of 15 elements tested, only the concentrations of one other element—cobalt—were statistically different (at the 95% level), but alfalfa from the affected fields contained only slightly higher concentrations of the 13 other elements than the control samples.

The manganese concentrations in alfalfa have increased markedly over the 3-year period. In the short term, this should not affect the nutritional value of this important livestock feed. The highest concentration reported, 150 ppm, is still well below the 1,000 ppm maximum tolerable level given for cattle and sheep. However, this exceeds the upper limit of the sufficient manganese requirement range for ***alfalfa***. These concentrations are higher than those found in alfalfa from several other producing areas in the West.

The 1995 study also included a small subset of samples in which sample splits were washed to test the effect of possible dust contamination. A Student's t-test of the unwashed versus washed samples revealed that washing significantly reduced the concentrations of aluminum (most likely aluminosilicates) by a third. Such a "dust" effect served only to cause a slight dilution of trace metals. The washing effect on 14 other elements was nonsignificant. Thus, washing alfalfa samples was relatively unimportant. Moreover, alfalfa hay is usually fed to livestock as harvested, or at least is not washed. This suggests that most of the metals reside in the plants themselves, not on the plants.

The maximum copper concentration in an unwashed sample of alfalfa irrigated by Terrace water—21 ppm—is considered nutritionally ideal for high-production dairy ration. On the other hand, a ***washed*** sample of alfalfa from one of the control fields contained 26 ppm copper, the lower end of the 26–38 ppm range considered deleterious for sheep feed. The published maximum tolerance level for beef cattle is 115 ppm. Sheep are therefore much less tolerant of copper than cattle, although the copper tolerance varies with breed.

A two-way analysis-of-variance tested, separately, the year-to-year (temporal) differences in the element composition of the test group alfalfa and the control group. The test group samples showed higher concentrations of copper, manganese, cobalt, nickel, and phosphorus in the 1995 cuttings. Unexpectedly, the control group alfalfa also revealed significantly higher concentrations for almost the same suite of metals—copper, manganese, nickel, phosphorus, and zinc—in samples from the 1995 cuttings. On average, the copper concentrations in alfalfa irrigated by the two different water sources were nearly the same.

This assessment of the importance of seasonality and even longer-term effects due to climate or management practices on tissue loading of metals serves to underscore the critical importance of long-term monitoring rather than a single point-in-time sampling, at least where crops are concerned. Results from this repeat sampling of alfalfa suggest that baselines which ignore the vagaries of time may be unreliable.

INTRODUCTION

Recent open-pit mining and the abandonment of the Summitville gold mine in the San Juan Mountains in late 1992 have led to serious problems with acid-mine drainage (Environmental Protection Agency, 1993). Contamination from the high-sulfidation epithermal gold mine (Plumlee and others, 1995a, b; White and Hedenquist, 1995) has raised concerns over the effects of low pH and metal-laden—particularly copper—surface waters carried down the Alamosa River. High sulfidation deposits commonly contain copper-arsenic minerals, especially easily weathered sulfosalts (Stoffregen, 1987; Hedenquist and others, 1994). Estimated copper loadings from the main drainage adit (now plugged) at the mine site into the Wightman Fork of the Alamosa River were 143,000 pounds per year (Williams, 1995). Previous studies of water-quality of the Alamosa River and Wightman Fork showed that the Summitville site on Wightman Fork has been the predominant source of aluminum, copper, iron, manganese, and zinc discharged into the Alamosa River during most of the year (Walton-Day and others, 1995; Mueller and Mueller, 1995). Water-quality data collected by the U.S. Geological Survey during 1995 indicate that Wightman Fork was the dominant source of copper and manganese that year (Pat Edelmann, written commun., 1996). These waters enter the Terrace Reservoir (fig. 1), which provides irrigation water to approximately 45,000 acres of farmland in the southwestern part of the San Luis Valley (Environmental Protection Agency, 1993). Approximately 85 percent of cropland acreage in the San Luis Valley is irrigated.

Following abandonment of the mine in December 1992, which drew the focus of extensive public attention, numerous studies were begun at the mine site and downstream at Terrace Reservoir and in the San Luis Valley. Many of the results were discussed and published at a forum on Summitville in early 1995 (Posey and others, 1995). Summitville is the first of the modern, heap-leach gold mines to be abandoned and require cleanup under the EPA's Superfund program (Williams, 1995).

An initial study of the effects of Summitville on alfalfa was conducted in June 1993. Those results, based on alfalfa sampled from Terrace-irrigated fields and control fields, were detailed in a report by Erdman and others (1995a). They concluded that, although the metal concentrations of the irrigation water from the reservoir were anomalously high, 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 affected by both water sources (i) met published nutritive requirements for cattle, (ii) were far below maximum tolerable levels reported for cattle, and

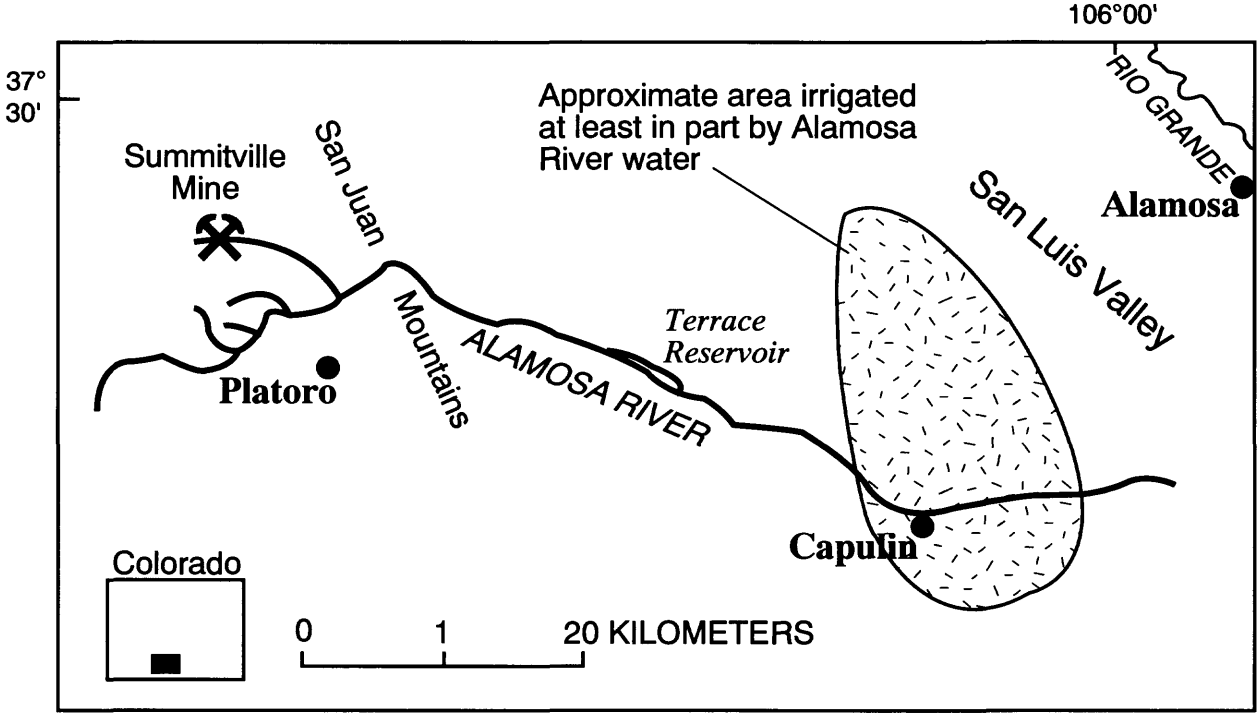


Figure 1. Index map showing location of Summitville mine and Terrace Reservoir with respect to farmlands irrigated with water from the reservoir.

(iii) were comparable to concentrations in alfalfa found in other parts of the country. In looking at the nutritional needs of alfalfa, Erdman and others (1995a) found that the Terrace Reservoir waters seemed to have enhanced the bioavailability of copper and manganese to optimum levels.

Agriculture underpins much of the economy of the San Luis Valley. In 1992 the combined market value of crops and livestock produced in the valley was approximately $173 million with the crop valuation amounting to $135 million of that total (data from 1992 Census of Agriculture, U.S. Department of Commerce, 1995, compiled by Brian Townley, Resource Analysis Section, Colorado Department of Agriculture, written commun., 1996). Negative publicity resulting from contamination of Alamosa River water irrigating even a small part of the valley might have had a ripple effect throughout the region. This possibility was averted through a brief report and accompanying press release shortly after the 1993 alfalfa results were available (Erdman and Smith, 1993).

In the 1994 irrigation season, unexpectedly large seasonal fluctuations 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 more than 100-fold from a nearly neutral 6.6 to a pH of 4.7. In the same period, copper concentrations increased 7-fold, manganese doubled, and zinc tripled. Although the profound chemical changes in the irrigation water between the first and second cuttings were not anticipated, plans to sample the three cuttings of alfalfa from two adjacent fields irrigated by Terrace Reservoir water throughout the growing season were already in place. The alfalfa sampled from two adjacent fields irrigated by Terrace Reservoir water reflected changes in irrigation-water chemistry, although not to the extent found in the waters sampled (Erdman and others, 1995b).

The study of alfalfa and associated irrigation water in 1995 was conducted to test whether water from the Terrace Reservoir still affects the quality of alfalfa as an important livestock feed. An added purpose was to compare these results with previous studies conducted in 1993 and 1994.

METHODS

Irrigation-Water Collection and Field Methods

Irrigation water was sampled at eight locations on July 26 and 27, 1995. These locations correspond to the alfalfa fields discussed in this report. Water from the control fields (C1, C2, and C4) was sampled on July 26, and the locations with irrigation water originating from Terrace Reservoir (T1, T2, T3, F1, and S1) were sampled on July 27. Center-pivot sprinkler-irrigation systems normally use ground water. In the area we studied, surface water and ground water are often stored in small reservoirs, then pumped to the sprinklers. An attempt was made to sample irrigation water directly from the first or second sprinkler heads at the center pivot (or from the ditch in the case of field F1). However, it was not possible to sample from the sprinkler system at fields C4 and T3 due to the presence of cut hay in the field or to the hay-cutting schedule. Therefore, water samples were collected from the storage reservoirs at fields C4 and T3. A duplicate sample was collected at field T3.

Irrigation-water samples were collected in unused 1-L polyethylene bottles. Each bottle was rinsed three times with the sample water prior to sample collection. Water temperature was measured at the time of sample collection. The sample was well-shaken in the 1-L bottle, and then portions were removed for pH and specific conductivity measurements. The pH equipment was calibrated with two pH buffers, and the value of an additional buffer was checked to verify the pH calibration. The 1-L bottles were then placed into a chilled cooler and transported to a central location for processing within ten hours of collection. Chain-of-custody protocol was followed for water-sample collection, transport, storage, and analysis. Table 1 lists sample information and data for the various sample locations.

Irrigation-Water Laboratory and Analytical Procedures

During processing, the chilled 1-L sample bottles were well-shaken and a portion of each sample was transferred to a 125-mL acid-cleaned polyethylene bottle and acidified with concentrated Ultrex nitric acid to a pH < 2. This sample will be referred to as the UA (unfiltered-acidified) sample. An unused 60-cc plastic syringe was rinsed three times with the sample water and then used to filter a portion of the sample through a 0.45 µm filter into a 125-mL acid-cleaned polyethylene bottle. This subsample was also acidified with concentrated Ultrex nitric acid to a pH < 2 and will be referred to as the FA (filtered-acidified) sample. The filter was prerinsed with approximately 10 cc of sample water. The UA bottle was prerinsed three times with sample water and the FA bottle was prerinsed three times with filtered sample water prior to use.

To address QA/QC concerns, a procedural blank was prepared to detect contamination from sample collection or processing. Also, blanks were prepared of the Ultrex acid used to preserve the water samples. Randomly-selected, blind analytical duplicates were prepared for two samples. Two additional samples were also run in duplicate at the time of analysis. Triplicate portions of a USGS water-quality standard were integrated into the data set for analysis. A duplicate sample was collected at field T3.

Irrigation-water samples, standards, and analytical duplicates were submitted for analysis together in a randomized sequence to reduce the effect of any systematic errors. Blank samples were submitted separately to prevent any cross-contamination. Element concentrations in irrigation water were determined for the UA and FA samples by inductively coupled plasma-mass spectrometry (ICP-MS) in the analytical laboratories of the U.S. Geological Survey, Denver, Colorado. Chain-of-custody protocol was followed for water-sample collection, transport, storage, and analysis.

Alfalfa Field and Laboratory Procedures

Sampling was conducted July 25–27, 1995, prior to the second cutting of alfalfa. Early-bud stage alfalfa was collected from six center-pivot, sprinkler-irrigated fields. Three of these fields were irrigated by water from Terrace Reservoir and three control fields were irrigated by water from other sources that included Rio Grande water and ground water. All fields selected had similar soils, either mapped as Graypoint series or physically comparable units (Pannell and others, 1973; Yenter and others, 1980; and Pannell and others, 1980). Sampling was conducted according to an unbalanced, four-level nested analysis-of-variance design (fig. 2), the term "unbalanced" reflecting only limited analytical duplicates at the bottom level. The term ***analysis-of-variance*** refers to a statistical technique "whereby the total variation is being analyzed or divided into meaningful components" (Walpole and Myers, 1978).

Because of mixed irrigation sources revealed from the 1995 water analyses, the sampling design for 1995 was scaled down from four fields irrigated by Terrace water and four control fields sampled in June of 1993. Four alfalfa samples were collected from the same sites in each of the fields sampled in previous years to minimize possible within-field variation. These samples were composited from approximately ten points within a 1-m radius of the center of the sample site. Separate samples from the first two sites in each field were collected and later washed to compare the analytical results with those from unwashed samples.

Table 1. Sample information and data for irrigation water at each sample location

[Cond. refers to the specific conductivity and temp. refers to the temperature, both measured at the time of sampling]

Sample location	Water source	Sample source	Onsite pH	Cond. (µS/cm)	Temp. (°C)
C1	Rio Grande	Sprinkler	8.8	176	22
C2	Ground water	Sprinkler	8.1	254	25
C4	Rio Grande	Reservoir at inlet	10.0	72	26
T1	Terrace Res.	Sprinkler	5.6	139	18
T2	Terrace Res.	Sprinkler	5.5	140	17
T3	Terrace Res. and Cat Cr.	Reservoir near pump intake	6.6	130	22
T3 Field dup.	Terrace Res. and Cat Cr.	Reservoir near pump intake	6.6	129	22
F1	Terrace Res.	Ditch	5.7	138	18
S1	Terrace Res.	Sprinkler	5.4	138	23

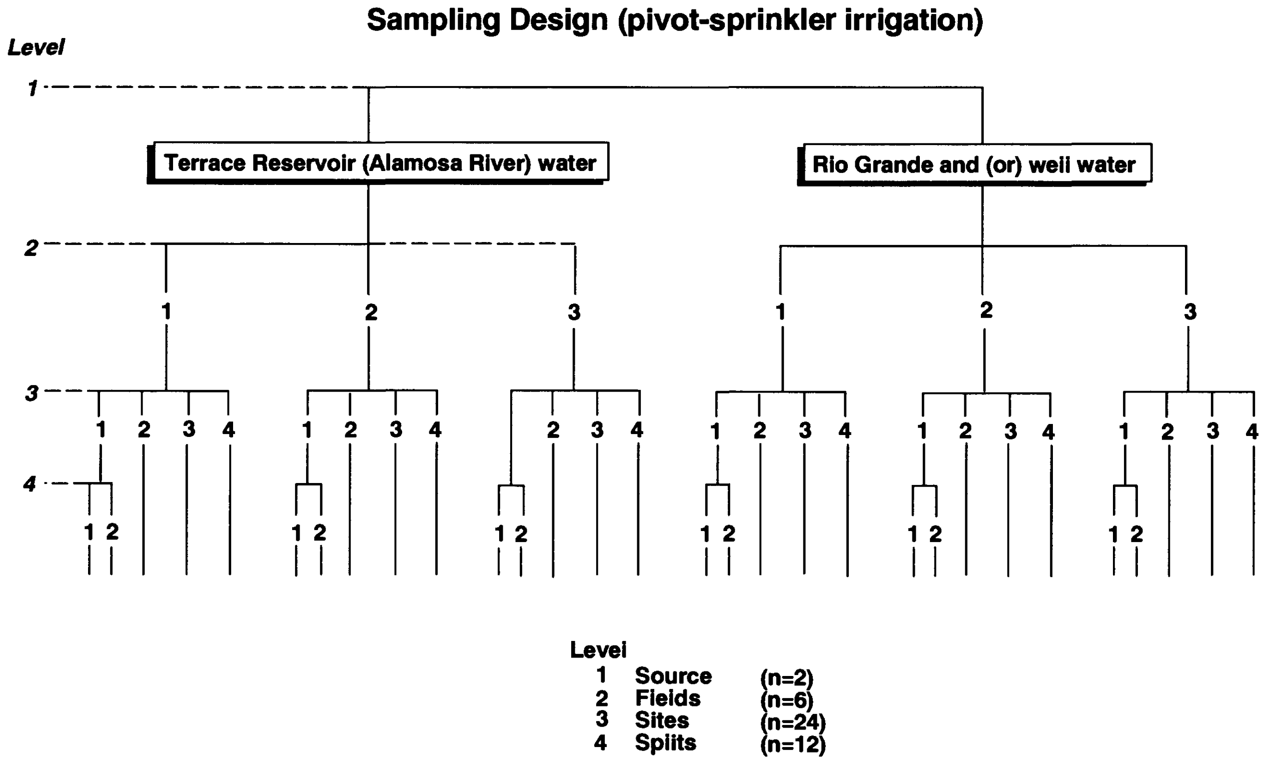


Figure 2. Four-level sampling design for alfalfa irrigated by Terrace Reservoir and control waters, July 1995.

At the urging of the Environmental Protection Agency, we conducted a small ancillary study to test the possible differences in tissue loading of alfalfa that is flood-irrigated and sprinkler-irrigated. Two adjacent fields were selected that had the same soil series. An alfalfa sample was a composite either from several sites at each of seven adjacent borders in the flood-irrigated field (more correctly termed "border-dike irrigation") or from randomly selected sites in the center-pivot sprinkler irrigated field. The simple two-level analysis-of-variance design is shown in figure 3.

The alfalfa samples were oven-dried in paper bags to constant weight at ~40°C and ground in a Wiley mill to pass a 2-mm sieve. Two additional samples from each field were washed in tap water followed by rinsing in distilled water. Except for these special samples, all other alfalfa samples analyzed in this study were ***not*** washed, because they were meant to represent hay as fed to livestock. A portion of each dried sample was ashed at ~500°C through two cycles in a muffle furnace, split to estimate the reproducibility of duplicate analyses, digested in a mixed-acid solution, and analyzed by ICP-AES (Briggs, 1990). The ash yield was calculated in order to convert the later analytical results to a dry-weight basis (Peacock, 1992) used in nutritional studies.

Two samples of the Standard Reference Material 1547, Peach Leaves (National Institute of Standards and Technology), were included with the alfalfa samples submitted for analysis. All samples—including duplicates and NIST standards—were submitted in a randomized sequence to convert any systematic error that might occur in either sampling or analysis into random error. The results for the two peach-leaf standards showed that the analyses compared closely with the published certified values (NIST Certificate of Analysis, January 22, 1992) and were reproducible.

Samples were handled according to prescribed quality assurance/quality control (Arbogast, 1990) and chain-of-custody protocol.

Statistical Methods

The limited number of water samples precluded a statistical analysis of the water data. Moreover, the strong differences in the character of water from the two source areas are so clear that such a test is unnecessary.

The alfalfa data were first converted to a logarithmic basis because geochemical data are often logarithmically distributed; for the 1995 results only aluminum, iron, and sodium concentrations showed positively skewed frequency distributions. For all elements, however, the results of the analysis-of-variance (Grundy and Miesch, 1988) on both the raw data and the transformed data were similar. The chromium and molybdenum data were not included in the ANOVA because a number of samples had concentrations reported to be below the lower limits of determination.

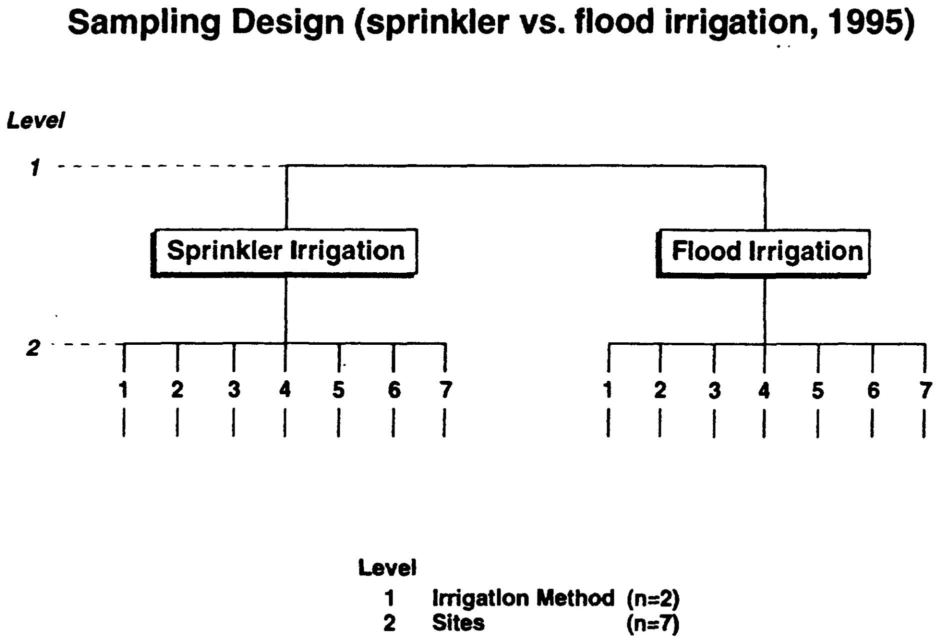


Figure 3. Sampling design to test effects of sprinkler versus flood irrigation on alfalfa irrigated with Terrace Reservoir (lower Alamosa River) water, July 1995.

RESULTS AND DISCUSSION

Irrigation Water

Analytical data for unfiltered-acidified (UA) and filtered-acidified (FA; 0.45 µm) samples are listed in table 2. The Colorado Surface-Water Standard for Agricultural Use for both copper and manganese is 200 µg/L (CDH, 1995). Sample values that exceed this standard for copper and manganese are shaded in table 2. The Agricultural Use classification refers to surface waters suitable or intended to become suitable for irrigation of crops usually grown in Colorado and that are not hazardous as drinking water for livestock (CDH, 1995). These standards are stated as total recoverable metals, which is the concentration of metals in an unfiltered water sample following acidification with nitric acid and subsequent heating with hydrochloric acid. The sample is then filtered and the volume adjusted (EPA, 1979). Our data for metal concentrations in unfiltered water are roughly comparable to Agricultural Use Standards that are based on total recoverable metals, but our samples were not heated with hydrochloric acid and filtered. Specific conductivity, pH, and temperature are given in table 1.

The irrigation water originating from Terrace Reservoir contains substantially higher concentrations of copper, manganese, zinc, cobalt, and nickel than water from the other sources. Field T3 was irrigated by a mixed water source (Terrace Reservoir and Cat Creek water) until July 4 after which Terrace water was used exclusively (anonymous cooperator, oral commun., October, 1995). Accordingly, the water sampled later that month has somewhat lower concentrations of several metals compared with samples from fields T1 and T2. (For this reason, we deleted the alfalfa results from field T3 in this report.) Data for field C4 seem to be noticeably different from fields C1 and C2, even though fields C1 and C2 are from different sources (Rio Grande and ground water, respectively). Field C4 was collected from the inlet of a storage reservoir rather than from a pivot sprinkler. The water in the field C4 reservoir appeared to be somewhat stagnant. With the exception of the unfiltered water from field C4, the Terrace Reservoir irrigation water also contains higher concentrations of aluminum, cerium, iron, lanthanum, neodymium, and yttrium. The control irrigation water tends to contain higher concentrations of arsenic, molybdenum, rubidium, scandium, strontium, uranium, and vanadium. Several of the elements that are more concentrated in the control irrigation water, such as arsenic, molybdenum, and vanadium, tend to be more mobile at higher pH.

As detailed by Smith and others (1995), there is an apparent relationship between the pH of the irrigation water and some metal concentrations in the water; generally, as the water becomes more acidic (lower pH), metal concentrations for copper, manganese, and zinc increase. Figure 4 shows the pH of irrigation water originating from Terrace Reservoir during the period from June, 1993 to July, 1995. Figure 5 shows the relationship between copper concentration and pH over the same time period. Figure 6 shows similar information for manganese. Irrigation-water samples collected in July, 1995 fall within the trend seen for previous sampling periods (figs. 5 and 6).

Water QA/QC

All values for the Ultrex nitric acid blanks and the procedural blank were below the limit of determination except for 1.4 ppb manganese in one of the acid blanks, 0.6 ppb manganese in the procedural blank, and 0.3 ppb copper in the procedural blank. Table 3 lists the average relative standard deviations by element for the four sets of analytical duplicates and for the duplicate collected at field T3. Table 4 gives the results for the USGS standards integrated into the analytical data set.

Table 2. Analytical results for unfiltered acidified (UA) and filtered acidified (FA; 0.45 μm) irrigation-water samples collected from alfalfa fields in the southwestern San Luis Valley, Colorado, during July 1995

[Data were determined by ICP-MS and all data are as ppb. Results for Ag, Au, Be, Bi, Cd, Cr, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, Nb, Pr, Sb, Sm, Sn, Ta, Tb, Te, Th, Tl, Tm, W, and Zr were below the limit of determination and are not included in this table. The Colorado Surface-Water Standard for Agricultural Use for elements listed in this table include: 100 μg/L arsenic, 200 μg/L copper, 100 μg/L lead, 200 μg/L manganese, 200 μg/L nickel, and 2000 μg/L zinc (all as total recoverable) (CDH, 1995). Shaded values are those that exceed Colorado Agricultural Use Standards]

Sample	Al	As	Ba	Ce	Co	Cu	Fe	La	Li	Mn	Mo	Nd	Ni	Pb	Rb	Sc	Sr	Ti	U	V	Y	Zn
Ag. Std.	5000	100	--	--	50	200	5000	--	2500	200	--	--	200	100	--	--	--	--	--	100	--	2000
C1 (FA)	24	0.8	22	0.1	< 0.1	0.88	70	< 0.1	2	1.2	0.6	< 0.1	2	< 0.3	3.6	8.0	180	1	0.5	1.8	< 0.1	8
C1 (UA)	48	0.9	24	0.2	< 0.1	0.5	100	< 0.1	2	2.3	0.6	0.1	2	0.5	3.5	7.0	170	2	0.5	1.6	< 0.1	3
C2 (FA)	12	1	29	< 0.1	0.2	0.4	< 40	< 0.1	3	0.9	1.2	< 0.1	4	< 0.3	4.0	10	230	< 1	0.3	3.9	< 0.1	6
C2 (UA)	11	1	31	< 0.1	0.1	0.8	< 40	< 0.1	3	8.5	0.80	< 0.1	3	< 0.3	4.0	9.1	230	2	0.3	3.5	< 0.1	< 2
C4 (FA)	27	1	12	0.1	0.2	1.2	50	< 0.1	2	2.8	< 0.2	< 0.1	1	0.4	1.2	1.9	58	< 1	< 0.1	1.5	< 0.1	3
C4 (UA)	240	0.8	15	0.9	0.3	1.2	290	0.3	3	23	< 0.2	0.5	1	2.2	1.5	2.7	64	5.0	< 0.1	2.0	0.3	12
T1 (FA)	110	< 0.5	21	1.1	10	340	250	0.6	1	500	< 0.2	0.6	16	0.6	0.96	2.5	120	1	0.1	< 0.1	0.6	140
T1 (UA)	130	< 0.5	22	1.0	10	350	310	0.5	2	500	< 0.2	0.5	17	< 0.3	0.97	2.7	120	1	< 0.1	< 0.1	0.7	170
T2 (FA)	78	< 0.5	21	1.0	8.7	290	150	0.5	1	410	< 0.2	0.4	13	< 0.3	1.0	2.4	110	< 1	< 0.1	< 0.1	0.6	140
T2 (UA)	120	< 0.5	21	1.1	9.5	330	280	0.4	2	460	< 0.2	0.6	14	< 0.3	0.84	2.4	110	2	< 0.1	< 0.1	0.6	160
T3 (FA)	8	< 0.5	25	0.1	4.8	78	< 40	0.1	2	300	< 0.2	< 0.1	9.2	< 0.3	0.95	2.0	110	< 1	< 0.1	< 0.1	< 0.1	110
T3 (UA)	76	< 0.5	25	0.6	4.8	140	230	0.3	2	310	< 0.2	0.5	12	< 0.3	1.2	2.2	110	< 1	< 0.1	0.1	0.4	100
F1 (FA)	78	< 0.5	22	0.8	8.4	290	160	0.4	1	420	< 0.2	0.4	14	< 0.3	0.87	1.9	110	1	< 0.1	< 0.1	0.5	150
F1 (UA)	96	< 0.5	22	1.0	8.1	290	240	0.5	< 0.9	410	< 0.2	0.5	11	< 0.3	0.91	2.0	110	< 1	< 0.1	< 0.1	0.6	150
S1 (FA)	68	< 0.5	21	0.3	10	270	170	0.2	2	500	< 0.2	0.2	14	< 0.3	0.98	2.8	120	2	< 0.1	< 0.1	0.3	150
S1 (UA)	140	< 0.5	24	0.6	10	300	370	0.3	2	530	< 0.2	0.3	16	< 0.3	1.0	3.1	120	1	< 0.1	0.2	0.4	160

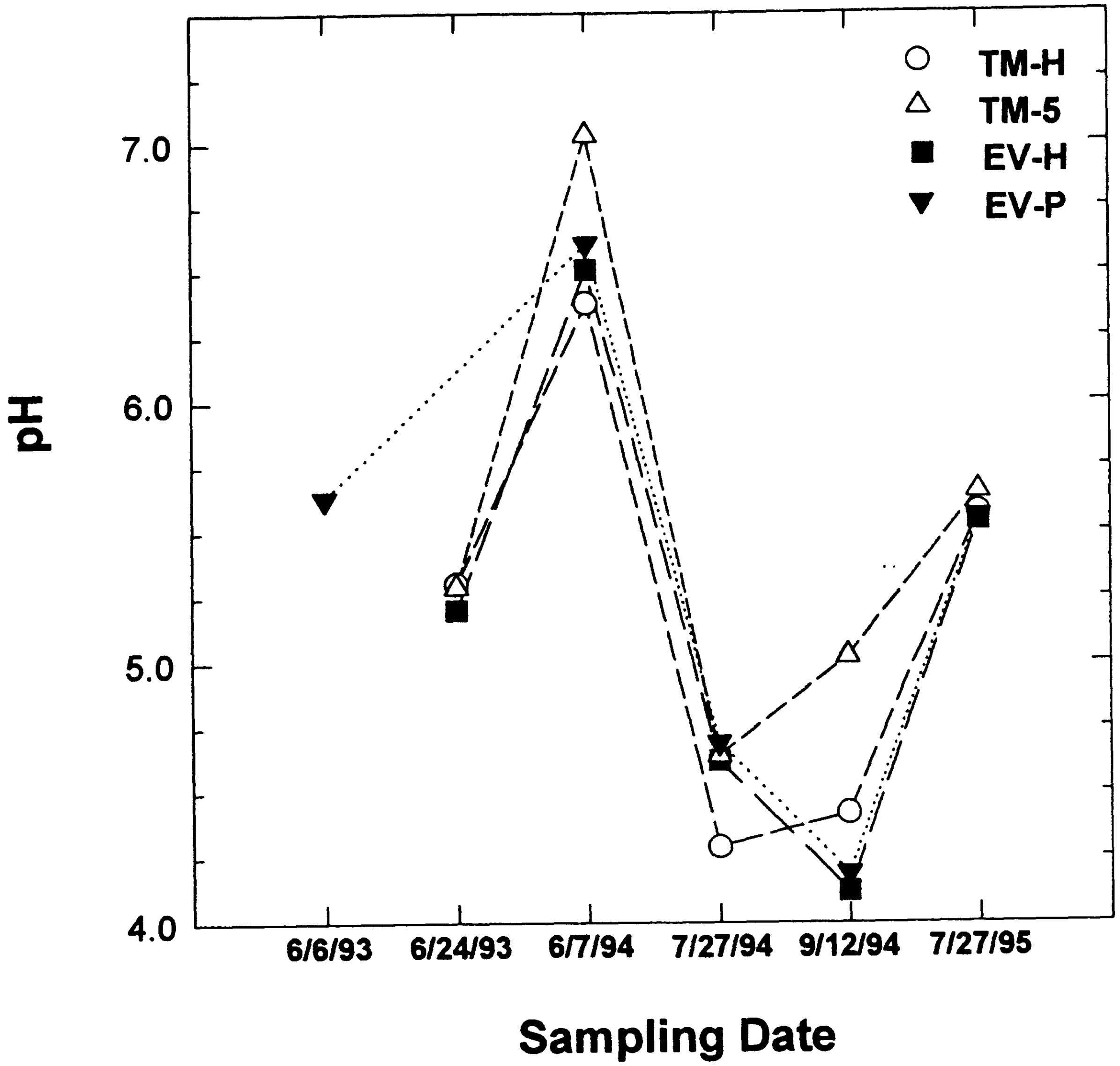


Figure 4. Plot of pH data for irrigation water originating from Terrace Reservoir for the period from June 1993 to July 1995. TM-H is the Terrace Main Canal headgate on the Alamosa River, TM-5 is a site on the Terrace Main Canal approximately 15 km from the headgate, EV-H is the El Viejo Ditch headgate on the Alamosa River, and EV-P is a storage pond on the El Viejo Ditch approximately 7 km from the headgate. Fields T1 and T2 in this study are irrigated with water from EV-P.

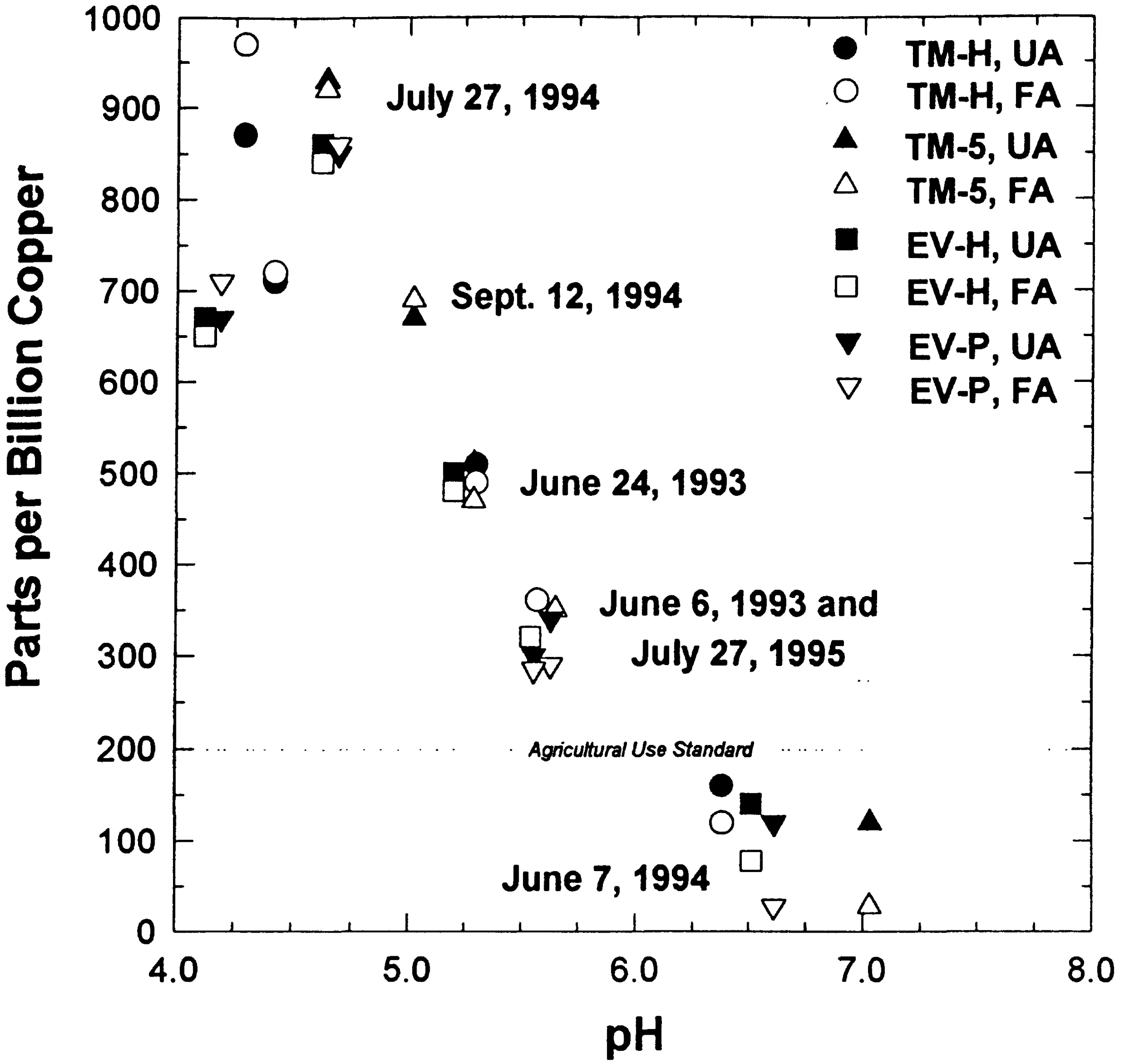


Figure 5. Plot of copper concentration as a function of pH for irrigation water originating from Terrace Reservoir for the period from June 1993 to July 1995. TM-H is the Terrace Main Canal headgate on the Alamosa River, TM-5 is a site on the Terrace Main Canal approximately 15 km from the headgate, EV-H is the El Viejo Ditch headgate on the Alamosa River, and EV-P is a storage pond on the El Viejo Ditch approximately 7 km from the headgate. UA refers to unfiltered acidified water samples and FA refers to filtered (0.45 μm in 1993 and 1995, and 0.2 μm in 1994) acidified water samples. Fields T1 and T2 in this study are irrigated with water from EV-P.

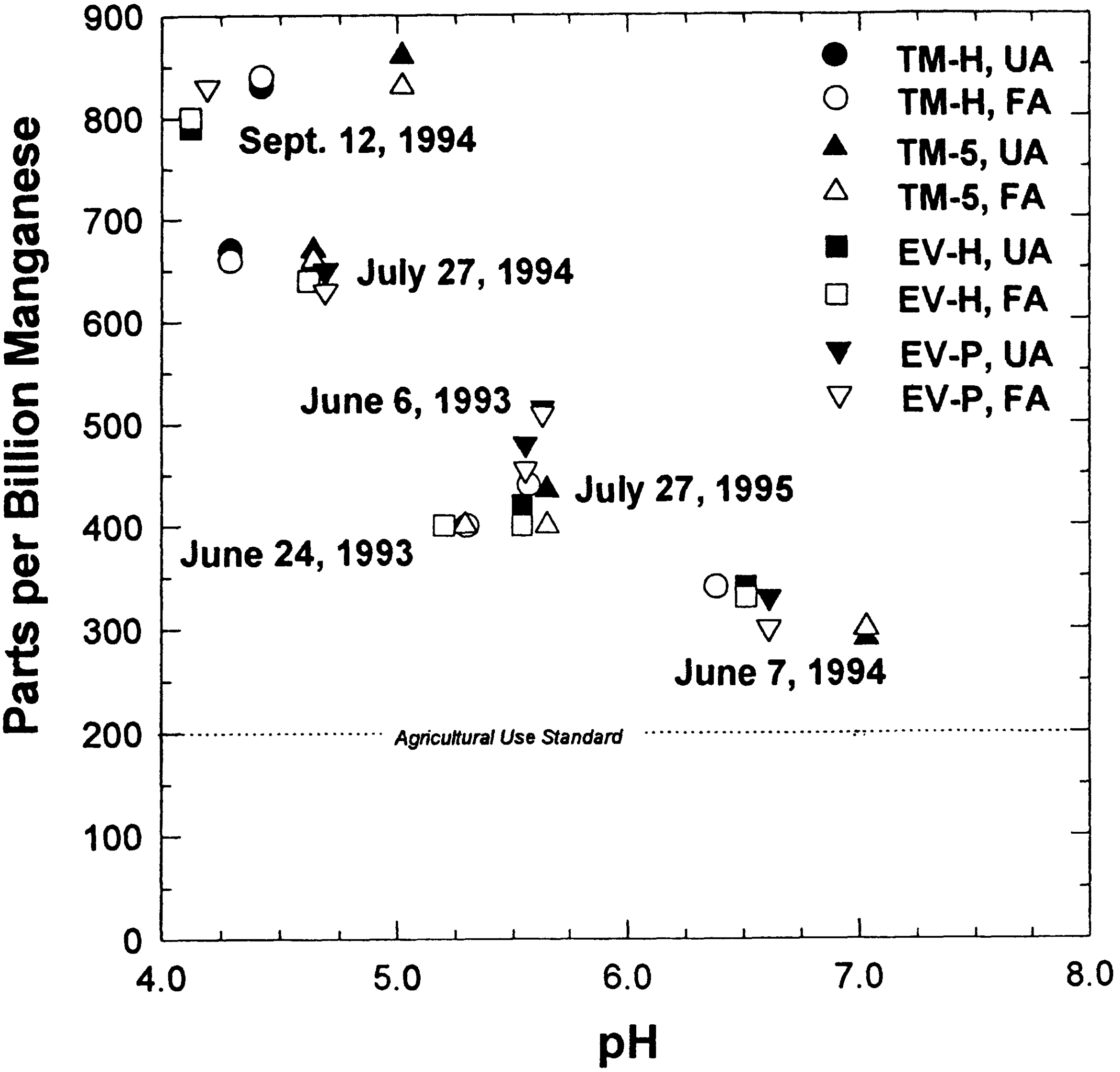


Figure 6. Plot of manganese concentration as a function of pH for irrigation water originating from Terrace Reservoir for the period from June 1993 to July 1995. TM-H is the Terrace Main Canal headgate on the Alamosa River, TM-5 is a site on the Terrace Main Canal approximately 15 km from the headgate, EV-H is the El Viejo Ditch headgate on the Alamosa River, and EV-P is a storage pond on the El Viejo Ditch approximately 7 km from the headgate. UA refers to unfiltered acidified water samples and FA refers to filtered (0.45 µm in 1993 and 1995, and 0.2 µm in 1994) acidified water samples. Fields T1 and T2 in this study are irrigated with water from EV-P.

Table 3. Average relative standard deviations (RSD) for four sets of analytical duplicates and one field duplicate (both unfiltered and filtered water; at field T3) integrated into the study

[RSD values are as percent, and are based on analyses by ICP-MS. "ND" = not determined, when data pairs contained less-than values or when the values were less than 10x the limit of determination, the RSD was not determined]

	Average RSD	
Constituent	Analytical. Dups.	Field Dup.
Al	4.8	2.8
As	ND	ND
Ba	2.8	1.4
Ce	ND	ND
Co	6.6	2.2
Cu	3.4	0.0
Fe	ND	3.1
La	ND	ND
Li	ND	ND
Mn	1.0	4.8
Mo	ND	ND
Nd	ND	ND
Ni	5.4	ND
Pb	ND	ND
Rb	8.8	ND
Sc	5.4	ND
Sr	1.1	0.0
Ti	ND	ND
U	ND	ND
V	2.0	ND
Y	ND	ND
Zn	11	3.4

Table 4. Results for triplicate analyses of USGS Standard Reference Water Sample T-85, which were randomly distributed throughout the data set

[Triplicate analyses are by ICP-MS. Shaded values are those that fall outside of the accepted concentration range for the standard]

Constituent	Standard Value (µg/L)	Triplicate Analyses by ICP-MS (ppb)		
Al	35 ± 17	33	31	30
As	6.2 ± 2.5	5.0	5.7	6.8
Ba	36 ± 7	37	35	37
Co	2.3 ± 0.5	2.1	2.2	2.6
Cu	54.1 ± 4.2	50	55	55
Fe	188 ± 14	170	170	200
Li	29.2 ± 6.7	27	27	30
Mn	96.7 ± 5.6	90	92	98
Mo	5.13 ± 4.02	3.9	3.6	4.4
Ni	10.5 ± 7.6	9.7	13	11
Pb	4.4 ± 2.4	4.3	3.9	4.0
Sr	1196 ± 84	1100	1100	1200
Zn	103 ± 7	72	79	85

Alfalfa

1995 Study: Of 15 elements that were compared in the alfalfa from fields irrigated by both Terrace and control waters, only the concentrations of manganese and cobalt are significantly different at the 90 percent and 95 percent confidence levels, respectively (table 5). On average, manganese concentrations in alfalfa from the Terrace fields were twice those in alfalfa from the control fields. Manganese is taken up and translocated rapidly within plants. Results for Ag, As, Au, Be, Bi, Cd, Ce, Eu, Ga, Ho, La, Nb, Nd, Pb, Sc, Sn, Ta, Th, Ti, U, V, Y, and Yb were below the limit of determination and therefore are not included in the table.

Surprisingly, levels of copper differed very little, on average, in alfalfa irrigated by the two water sources. Results of the one-way analysis of variance (table 6) show that none of the variability in concentrations of 12 elements—including copper—occurs at the water-sources level, despite the large variation in water quality. The estimate of the variance due to analytical error, based on six pairs of duplicate samples, is generally low for all elements except lithium. Virtually all the variance (98.2%) is analytical imprecision, as can be seen from the data given in table 7. Nickel was reported to be significantly higher in alfalfa from the Terrace fields sampled in 1993 compared to alfalfa collected from the control fields (Erdman and others, 1995a). Although a high percentage of the total variance was found at the source level (table 6), the twice-fold differences in average concentrations (table 5) are not significant.

The molybdenum results for samples from the Terrace fields and control fields (table 7) show clear differences that can be attributed to the different molybdenum levels of the two source waters (table 2), or possibly soil pH. The pH for soils that were sampled from these fields in June 1993, ranged from 6.3–6.7 for the two Terrace fields and from 7.1–8.4 for the three control fields. Fields of malting barley were sampled in 1993 (Stout and Emerick, 1995) and the soil pH (5.9–7.9) of those fields irrigated with Terrace water was significantly lower than soils from the control fields (7.7–8.5). Under oxidizing alkaline conditions, molybdenum is relatively mobile. As discussed by Smith and others (in press) the "availability of molybdenum to plants is greatest under alkaline conditions and least under acidic conditions." The level of molybdenum in alfalfa thus may be effected by two factors—molybdenum in the water and soil pH.

How do these increased concentrations of copper and manganese compare with those reported for alfalfa collected in other parts of the West, or for the nutrient status requirement of alfalfa? The copper results compare favorably; none of the levels found in any alfalfa samples from the 1995 study exceed the maximum for alfalfa from the San Joaquin Valley, California (Severson and others, 1991), the Casper, Wyoming area (Severson and others, 1989), or the Uncompahgre River Valley, Colorado (Crock and others, 1994). Nor does the maximum concentration of 26 ppm (sample C422, table 7) exceed the copper levels of 7–30 ppm given as nutritionally sufficient for alfalfa (Jones and others, 1991, p. 152).

In contrast to copper, all the alfalfa collected from the Terrace fields contained manganese in excess of levels reported for the three other areas given above. The sufficient manganese levels required for alfalfa productivity (Jones and others, 1991) range from 31–100 ppm. Most unwashed samples from Terrace field 2 samples (table 7), therefore, exceed that sufficiency range and fall in the lower end of the high range of 100–250 ppm. These concentrations are still well below the maximum tolerable level of 1,000 ppm for cattle (National Research Council, Subcommittee on Beef Cattle Nutrition, 1984) and sheep feed (National Research Council, Subcommittee on Sheep Nutrition, 1985), but they seem borderline high when matched against the nutrient needs of alfalfa.

Table 5. Basic statistics for elements in alfalfa (*Medicago sativa* L.) collected from fields irrigated with water from the lower Alamosa River (Terrace Reservoir Fields) or other water sources (Control Fields), southwestern San Luis Valley, Colorado

[Analyses on ash by inductively coupled plasma atomic emission spectrometry converted to dry-weight basis; AM, arithmetic mean; GM, geometric mean]

	Terrace Reservoir Fields				Control Fields			
Element	Minimum	Maximum	AM	GM	Minimum	Maximum	AM	GM
Ca, %	1.7	2.4	2.1	2.1	1.8	2.2	2.0	2.0
K, %	3.0	4.6	3.9	3.8	3.2	4.7	4.0	4.0
Mg, %	.29	.43	.35	.35	.31	.37	.34	.34
P, %	.53	.64	.59	.59	.46	.78	.57	.56
Al, ppm	13	140	47	38	24	200	86	68
Ba, ppm	18	38	29	29	9.5	49	25	22
Co, ppm**	.52	.72	.63	.62	.26	.65	.49	.47
Cu, ppm	16	21	18	18	10	21	15	15
Fe, ppm	78	200	120	110	65	300	160	140
Li, ppm	1.3	3.7	2.2	2.1	.96	3.1	1.9	1.8
Mn, ppm*	68	150	99	96	33	73	49	47
Na, ppm	300	910	480	450	290	710	500	480
Ni, ppm	1.6	3.9	2.5	2.4	.52	1.9	1.2	1.1
Sr, ppm	92	170	130	130	98	160	130	130
Zn, ppm	27	45	36	35	20	57	36	34

** Differences between water sources significant at the 95 percent confidence level.
 * Differences between water sources significant at the 90 percent confidence level.

Table 6. Distribution of variance for elements measured in alfalfa sampled July 1995, southwestern San Luis Valley, Colorado

	Percentage of variance:			
Element	Water sources	Fields	Sites	Analyses
Ca, %	0.0	55.5***	38.2**	6.3
K, %	0.0	35.2**	53**	11.8
Mg, %	0.0	58.5**	40.5***	1
P, %	0.0	63.2**	35***	1.8
Al, ppm	0.0	40.2**	50**	9.8
Ba, ppm	0.0	89.4***	10.3***	0.3
Co, ppm	44.3**	0.0	40	15.8
Cu, ppm	0.0	76***	12.5	11.5
Fe, ppm	0.0	43.2**	35.6	21.2
Li, ppm	0.0	1.8	0.0	98.2
Mn, ppm	68.2*	25.1	6	0.8
Na, ppm	0.0	40**	18.5	41.5
Ni, ppm	44.7	46.3***	5.2	3.9
Sr, ppm	0.0	77.8***	21.6***	0.6
Zn, ppm	0.0	94.6***	5**	0.4

*** Differences statistically significant at the 99 percent confidence level.
 ** Differences statistically significant at the 95 percent confidence level.
 * Differences statistically significant at the 90 percent confidence level.

Table 7. Analytical results for alfalfa collected from two fields irrigated with water from the Alamosa River (Terrace Fields) and from three fields irrigated with other water sources (Control Fields)

[Concentrations expressed on a dry-weight basis; first two samples in each block are analytical duplicates; the third and fifth row in each block are washed splits of the first- and fourth-row samples, respectively]

Sample No.	Ca %	K %	Mg %	P %	Al ppm	Ba ppm	Co ppm	Cr ppm	Cu ppm	Fe ppm	Li ppm	Mn ppm	Mo ppm	Na ppm	Ni ppm	Sr ppm	Zn ppm
Terrace Field #1																	
T1111 (U)	1.9	4.0	0.34	0.57	39	26	0.65	<.26	16	91	1.7	68	0.5	400	1.6	110	27
T1112	1.9	4.0	0.34	0.58	52	26	0.65	0.26	16	130	1.9	66	0.7	430	1.6	110	27
T112 (W)	2.1	3.9	0.34	0.58	26	27	0.52	0.39	16	160	1.3	77	0.7	340	1.9	110	29
T121 (U)	1.7	4.3	0.31	0.53	39	25	0.52	<.26	16	78	1.8	88	0.8	300	1.6	100	30
T122 (W)	1.8	4.4	0.34	0.53	26	26	0.65	0.39	17	78	2.2	99	0.7	390	1.8	110	30
T13	2.1	4.6	0.32	0.60	28	25	0.70	0.28	18	140	2.4	84	<.55	340	2.0	120	29
T14	1.8	4.2	0.29	0.53	13	18	0.65	<.26	16	78	2.7	73	<.52	380	1.7	92	30
Terrace Field #2																	
T2111 (U)	2.2	3.6	0.37	0.60	36	32	0.60	0.36	19	110	1.3	108	<.5	410	3.4	140	43
T2112	2.2	3.4	0.37	0.59	60	34	0.60	0.24	17	110	2.0	101	<.5	500	3.5	140	42
T212 (W)	2.5	3.5	0.38	0.62	65	35	0.39	<.26	17	140	2.7	87	<.52	790	3.3	170	40
T221 (U)	2.4	3.0	0.37	0.64	48	37	0.72	0.36	19	130	3.7	98	<.46	910	3.2	160	42
T222 (W)	2.2	3.6	0.38	0.64	60	40	0.72	0.36	20	120	2.2	110	<.46	800	3.0	160	42
T23	2.4	3.1	0.43	0.62	36	34	0.60	0.36	17	110	1.9	120	<.47	610	3.0	160	40
T24	2.4	4.1	0.39	0.63	140	38	0.56	0.28	21	200	2.1	154	<.54	520	3.9	170	45
Control Field #1																	
C1111 (U)	2.2	3.4	0.32	0.65	36	23	0.48	0.36	12	130	1.2	64	3.7	580	1.7	110	37
C1112	2.0	3.5	0.32	0.64	36	23	0.48	0.36	11	110	2.4	64	3.7	710	1.6	110	37
C112 (W)	2.0	3.7	0.31	0.64	12	22	0.36	<.25	11	110	1.4	58	3.6	440	1.7	110	32
C121 (U)	2.2	4.5	0.31	0.57	200	17	0.56	0.56	14	280	1.7	66	2.8	560	1.1	130	36
C122 (w)	2.1	4.9	0.31	0.60	98	18	0.42	0.42	15	110	1.7	53	2.5	460	1.1	130	32
C13	2.2	3.2	0.37	0.65	130	23	0.48	0.36	12	230	3.1	73	2.2	710	1.2	130	36
C14	1.9	4.0	0.31	0.64	180	20	0.52	0.39	16	300	2.5	52	4.0	490	1.4	120	36
Control Field #2																	
C2111 (U)	2.0	3.6	0.32	0.46	24	13	0.36	0.24	12	110	1.0	40	1.1	290	0.7	98	20
C2112	1.9	4.1	0.32	0.43	36	14	0.24	0.24	14	72	2.4	42	1.0	480	0.5	100	19
C212 (W)	1.8	4.3	0.32	0.44	12	13	0.48	<.24	14	96	1.2	43	1.0	310	0.6	97	19
C221 (U)	1.8	4.4	0.34	0.47	39	12	0.26	<.27	13	100	1.7	48	1.2	430	0.7	110	22
C222 (W)	1.9	4.2	0.34	0.48	13	12	0.52	<.27	13	78	1.8	44	1.2	490	0.9	120	22
C23	1.9	4.7	0.36	0.47	39	9	0.65	0.52	16	65	1.2	42	2.6	400	0.5	140	26
C24	1.9	4.2	0.35	0.51	26	18	0.65	0.39	10	120	1.8	51	1.3	680	1.0	130	22
Control Field #4																	
C4111 (U)	2.2	3.6	0.37	0.55	120	49	0.48	0.36	20	170	1.2	43	2.6	320	1.9	140	44
C4112	2.2	3.5	0.36	0.55	110	49	0.48	0.24	19	220	2.0	38	2.4	420	1.8	140	43
C412 (W)	2.2	3.5	0.36	0.59	36	44	0.60	0.48	18	130	0.7	41	2.0	170	2.2	140	44
C421 (U)	1.9	4.3	0.36	0.78	65	42	0.52	0.26	18	120	3.1	39	3.0	490	1.2	160	57
C422 (W)	1.9	4.4	0.35	0.74	39	43	0.39	0.52	26	120	2.1	40	2.7	490	1.6	160	57
C43	1.8	4.4	0.36	0.55	78	35	0.39	<.26	21	120	2.6	33	3.3	640	1.4	140	43
C44	1.8	3.7	0.32	0.50	96	36	0.48	0.36	20	130	1.8	34	3.5	410	1.2	140	46

The soils need not be the link between the irrigation water and alfalfa. Certain metals—especially copper, manganese, zinc, and iron—may be available to the leaves directly by foliar uptake (Kabata-Pendias and Pendias, 1984).

Temporal differences—alfalfa irrigated with Terrace Reservoir water (fig. 7): Concentrations of copper in alfalfa from two adjacent fields were compared over the 3-year period of sampling (fig. 8). Copper levels in the July cuttings from 1994 and 1995 are similar, on average, and differ markedly from the values given for the June 1993 and 1994 cuttings. Those differences are statistically significant when tested by a two-way analysis-of-variance. Copper concentrations, then, seem to have leveled off after having increased significantly from 1993 to 1994. Maximum concentrations from the last two cuttings in 1994 and the second cutting in 1995 have ranged from 20 to 22 ppm, levels considered ideal in total ration for dairy cows. Many dairymen try to feed—as total ration—their high-producing dairy herds at this 20 ppm level (Dr. Cheryl Nockels, Colorado State University, oral commun., December 1995). However, these concentrations approach the 26–38 ppm judged deleterious to sheep, which are much less tolerant of copper than are cattle.

On the other hand, concentrations of manganese have continued to climb since their lowest levels in June 1994 (fig. 9). Statistically, the differences between the June 1994 results and those for July 1995 are significant. Fortunately, cattle—and sheep—tolerate manganese well. The maximum tolerable level for both is 1,000 ppm (National Research Council, 1984, 1985). According to Cheryl Nockels (oral commun., 12/94), manganese is considered to be relatively non-toxic.

Significant increases in the concentrations of cobalt, nickel, and phosphorus also occurred in alfalfa sampled in 1995 compared with that sampled previously. Although the cobalt concentrations given in table 7 are considerably above the requirement range of 0.07–0.11 ppm in beef-cattle feed (National Research Council, Subcommittee on Beef Cattle Nutrition, 1984), they are still well below the maximum tolerable level of 5 ppm. Nutrient requirement standards for nickel in livestock feed were not found. Levels of phosphorus increased significantly through time in samples from the control fields as well (see below); such an increase does not seem to be attributable to the irrigation source waters.

Temporal differences—alfalfa irrigated with control water (fig. 10): Based on results from the 1993 and 1994 sampling, as reported by Erdman and others (1995a,b), the seasonal effects given above were anticipated. We did not expect to see the increases in concentrations of both copper and manganese in alfalfa collected from the control fields between cuttings taken in 1993 and 1995 (figs. 11, 12). The differences shown are statistically significant, as are the increased concentrations for nickel, phosphorus, and zinc. Later cuttings of alfalfa in the same growing season may be one explanation, but this unexpected complexity in the overall results of our data is still unresolved.

Effects of washing alfalfa: Alfalfa samples collected from the first two sites in each of the six fields were split at the site, one to remain unwashed and the other to be washed in the laboratory. The analytical data for the 12 pairs of samples were *log*-transformed and the differences were tested at the 95 percent confidence level, using the Student's *t* test. Such a transform serves to "pull in" extreme values in the data. (Data for samples from the five fields retained for the main 1995 study are given in table 7.)

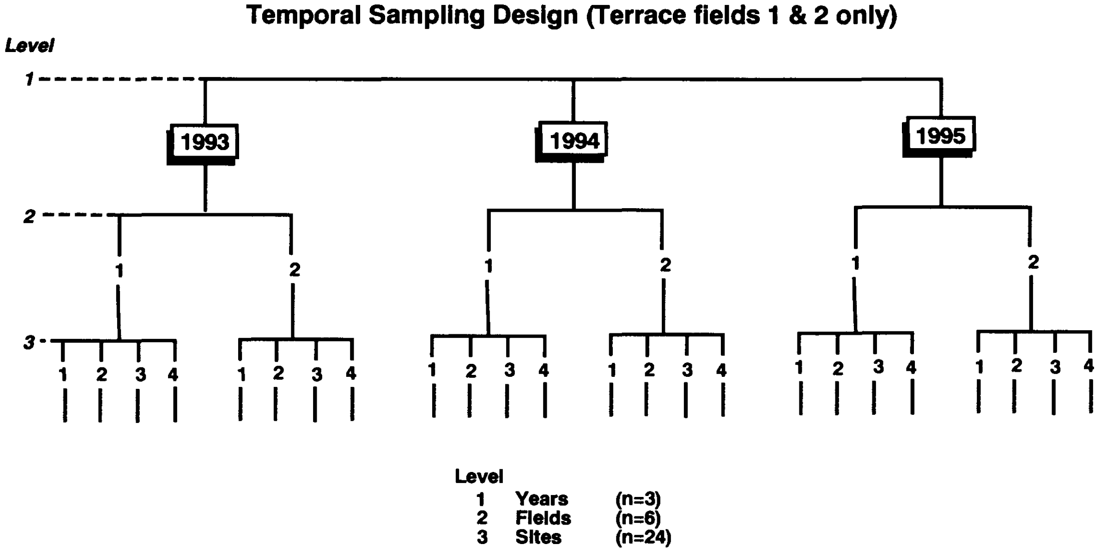
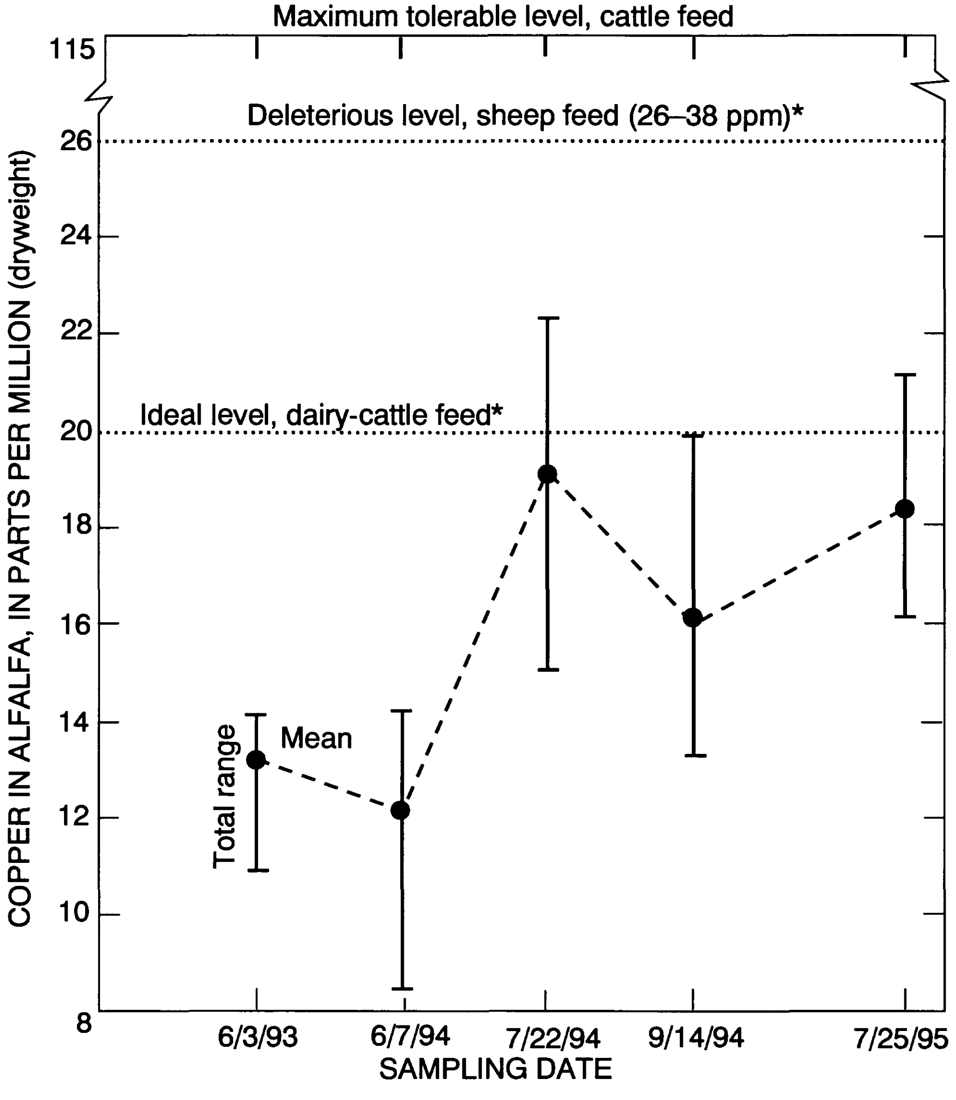


Figure 7. Three-level sampling design for alfalfa from two fields irrigated with Terrace Reservoir water over the 1993 through 1995 period.



*Cheryl Nockels, Specialist, Mineral Nutrition in Livestock, Colorado State University, oral commun., 1994.

Figure 8. Plot of copper levels in alfalfa irrigated with Terrace Reservoir water over the 1993 through 1995 period. (Analytical duplicates and washed samples given in table 7 are not included.)

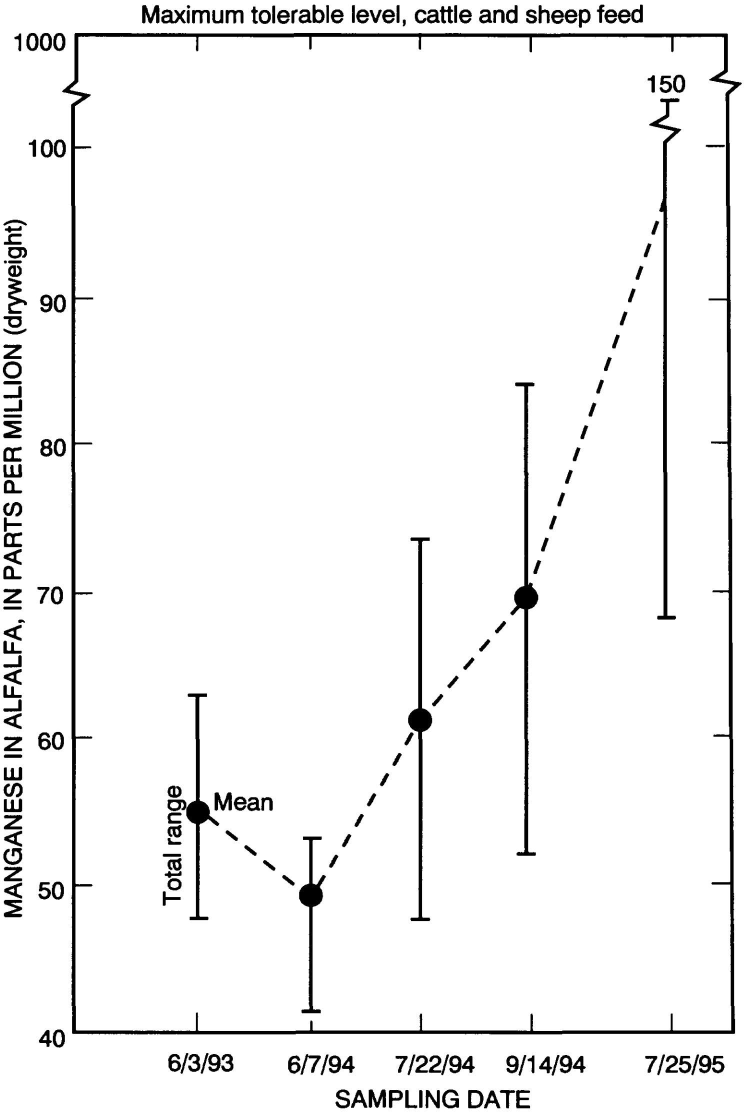


Figure 9. Plot of manganese levels in alfalfa irrigated with Terrace Reservoir water over the 1993 through 1995 period. (Analytical duplicates and washed samples given in table 7 are not included.)

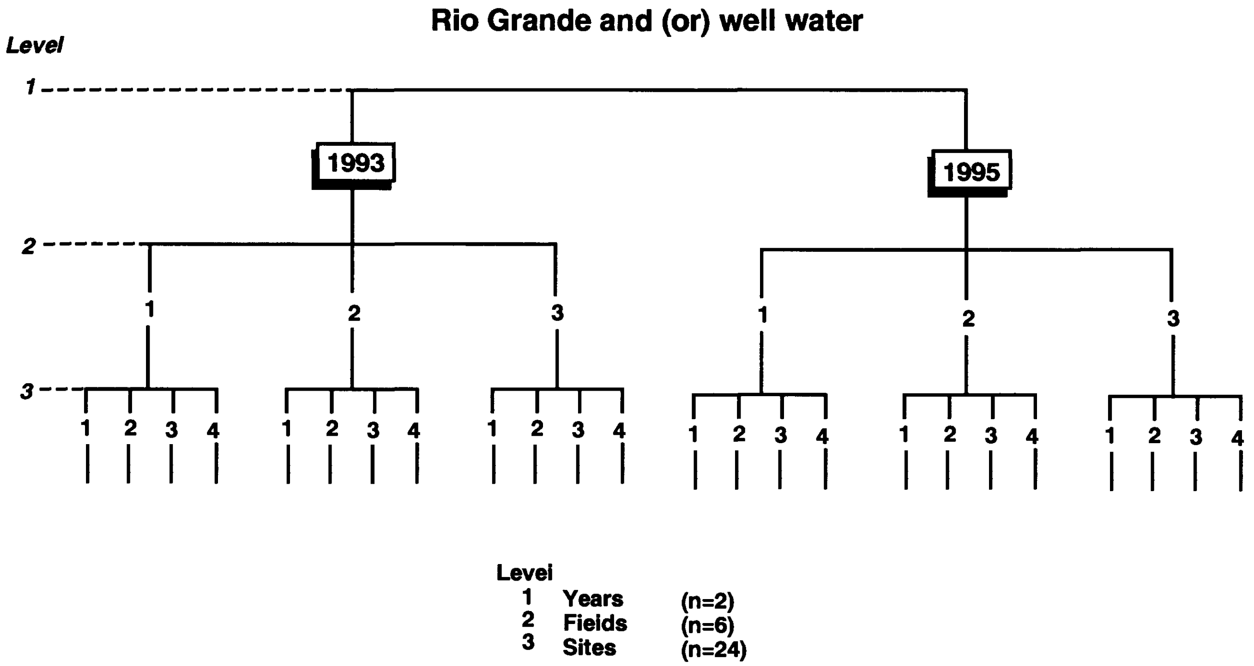
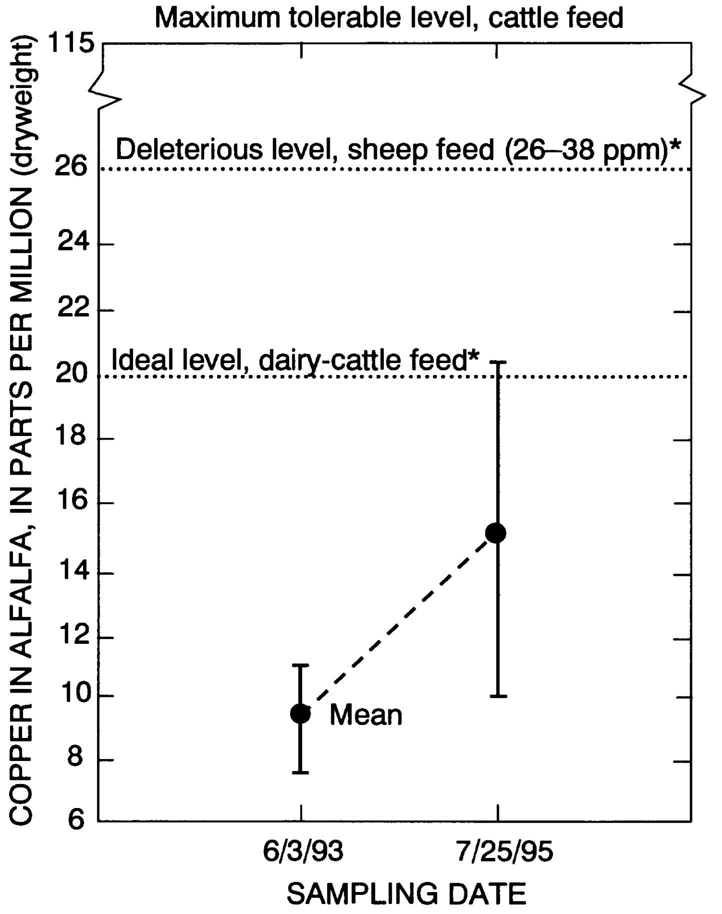


Figure 10. Three-level analysis-of-variance design for alfalfa sampled from three control-water fields, June 1993 and July 1995.



*Cheryl Nockels, Specialist, Mineral Nutrition in Livestock, Colorado State University, oral commun., 1994

Figure 11. Plot of copper levels in alfalfa from fields irrigated with control waters, June 1993 and July 1995 cuttings. Analytical duplicates and washed samples (table 7) not included.

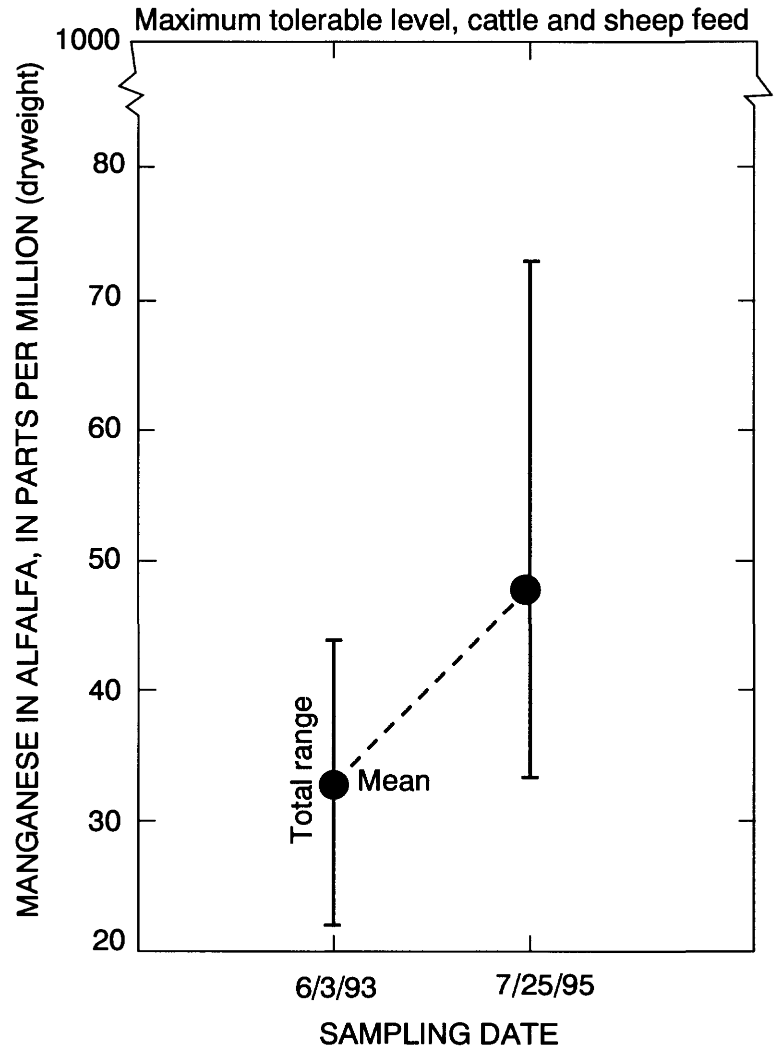


Figure 12. Plot of manganese levels in alfalfa from fields irrigated with control waters, June 1993 and July 1995 cuttings. Analytical duplicates and washed samples (table 7) not included.

Of 15 elements tested, only the concentrations of aluminum in the unwashed samples were significantly higher than those in the washed samples (differences were not significant where the ***raw*** data were used). In general, the levels were two to three times greater. Aluminum probably occurs as an aluminosilicate “dust” that, in theory, should serve as a diluent for other trace elements. Yet, for the other 14 elements tested, no significance could be attributed to rinsing this dust from the samples. Differences in copper concentrations between unwashed and washed samples, for example, were only one or two parts per million at an overall average of about 16 ppm.

Although washing alfalfa before analysis did decrease the aluminum content significantly, this procedure did not yield consistent decreases in ash after burning and seems unimportant with respect to the metals critical to this risk assessment. From a practical perspective, alfalfa as a livestock ration is not washed before feeding.

Comparison of flood-irrigated vs. sprinkler-irrigated alfalfa: As shown in table 8, significant differences were found, but the inconsistent results proved to be puzzling. Concentrations of copper, lithium, and sodium were statistically higher in the sprinkler-irrigated alfalfa. Those of barium, nickel, and zinc were higher in the flood-irrigated samples.

A tentative explanation can be offered for copper only. Root tissues have a strong capacity “to hold Cu against the transport to shoots under conditions of both Cu deficiency and Cu excess” (Kabata-Pendias and Pendias, 1984). Curiously, these authors also report that copper moves readily from the tops to the roots. Copper is taken up in soil solution in ionic or chelate forms that are present in very small quantities (Jones and others, 1991).

Foliar uptake from aerial sources, on the other hand, can be significant for copper as well as for other elements such as iron, manganese, and zinc (Kabata-Pendias and Pendias, 1984). The bioavailability of trace elements from aerial sources through the leaves has practical importance in foliar applications of fertilizers. The major route of foliar entry is by nonmetabolic cuticular penetration. This may explain the higher values in copper from the sprinkler-irrigated alfalfa, but fails to explain the higher values for zinc in the flood-irrigated alfalfa.

According to Jones and others (1991), “Zinc exists in the soil solution as the Zn^{+2} cation, as exchangeable Zn, and as organically complexed Zn,” forms that are taken up by plants. The availability of zinc is also affected strongly by soil pH, increasing with acidity.

These results add to the need to consider management practices when designing field-oriented agricultural studies.

CONCLUSIONS

- Consistent with pH measurements taken in 1993, the 1995 samples of irrigation water whose source was Terrace Reservoir were more acid (pH 5.4–5.7) than the samples of basic waters (pH 8.1–10) from the Rio Grande or ground water.
- The inverse relationship between water pH and metal content also has not changed. The 1995 irrigation water from the Terrace Reservoir contained substantially higher levels of copper, manganese, and zinc that are similar to those found in the 1993 samples. Concentrations of cobalt, nickel, and the rare-earth elements, cerium, lanthanum, and neodymium were also higher.
- Concentrations of copper and manganese in water from Terrace Reservoir continue to exceed Colorado’s Agricultural Use Standard, with one exception—the June 7, 1994 samples.

Table 8. Analytical results for alfalfa collected from single flood-irrigated and sprinkler-irrigated fields using Terrace Reservoir water

[Concentrations expressed on a dry-weight basis; **, treatment effects significantly different at the 99 percent confidence level; *, effects different at the 95 percent confidence level; shading indicates which treatment produced significantly higher concentrations]

Sample No.	Ca %	K %	Mg %	P %	Al ppm	Ba** ppm	Co ppm	Cr ppm	Cu** ppm	Fe ppm	Li* ppm	Mn ppm	Mo ppm	Na* ppm	Ni** ppm	Sr ppm	Zn** ppm
Flood-irrigated Field																	
F1	1.7	4.1	0.31	0.53	60	25	0.60	<.24	12	96	1.0	60	<.47	420	2.9	110	52
F2	1.8	3.4	0.30	0.51	55	26	0.77	0.22	12	120	2.4	56	0.6	590	2.8	110	54
F3	1.7	4.4	0.32	0.50	48	25	0.72	0.24	14	120	1.3	58	0.6	530	2.0	120	43
F4	1.7	4.0	0.31	0.58	48	29	0.72	0.24	14	130	1.3	62	<.47	370	2.5	110	53
F5	1.6	4.3	0.29	0.53	48	28	0.60	<.24	13	110	0.3	56	0.7	230	2.8	110	48
F6	1.8	4.0	0.31	0.54	48	28	0.60	0.24	12	130	0.3	56	1.3	250	2.4	120	47
F7	1.8	4.0	0.31	0.53	48	25	0.72	0.24	12	140	0.3	49	0.6	140	1.9	120	49
Sprinkler-irrigated Field																	
S1	1.8	4.4	0.29	0.52	52	14	0.39	<.25	14	130	1.3	47	2.1	360	1.4	110	36
S2	1.7	4.4	0.29	0.46	84	13	0.48	<.23	20	110	2.4	48	0.6	620	1.1	110	37
S3	1.9	3.7	0.28	0.53	48	13	0.72	<.24	18	180	1.4	66	<.47	470	1.7	110	46
S4	1.9	4.2	0.36	0.44	48	26	0.48	0.36	18	110	2.5	96	0.6	620	1.6	130	46
S5	1.8	3.5	0.28	0.41	66	18	0.55	<.22	15	150	0.9	48	0.6	510	1.1	110	34
S6	1.8	4.3	0.31	0.47	36	20	0.84	0.36	19	96	1.6	38	1.8	730	1.0	110	34
S7	1.6	4.1	0.29	0.58	48	13	0.48	<.23	16	130	2.5	77	<.46	730	1.9	90	42

- No significant differences in copper levels were found in alfalfa irrigated by the two water sources, but significantly higher concentrations for manganese and cobalt were found in alfalfa irrigated by Terrace Reservoir water.

- Copper and manganese concentrations in alfalfa irrigated by Terrace water have not fallen back to 1993 levels as they had in the water. Copper levels in samples from 1995 are significantly higher than in samples collected in the first cuttings of 1993 and 1994, but are similar to those taken from the succeeding two cuttings in 1994. Concentrations of manganese, however, have continued to increase.

- Unexpectedly, the levels of copper and manganese in alfalfa from the control fields also increased significantly when compared to those found in the 1993 samples. Although the average concentrations were lower than in those samples irrigated by Terrace water, these results underscore the complexity of trying to understand relationships in the natural landscape.

- The elevated concentrations of copper in the alfalfa affected by the Terrace waters continue to be nutritionally beneficial for cattle and dairy-herd feed. The levels are approaching the low end of the range of deleterious concentrations for sheep feed.

- Copper's nutrient status requirement by alfalfa continues to be slightly enhanced by irrigation water from the Terrace Reservoir.

- Unlike the copper results, manganese levels in alfalfa from the affected fields extend beyond the sufficient range required by alfalfa into the high range. They also exceed manganese concentrations found in alfalfa from several other producing areas in the West.

- A comparison of unwashed and washed alfalfa samples showed significantly higher levels of aluminum—probably as aluminosilicates in dust—in the former samples. But this apparent minor dusting of the samples did not affect, statistically, the concentrations of the other elements analyzed.

- The effects of sprinkler irrigation and flood irrigation from two alfalfa fields with the same soil series produced significant differences in concentrations of several elements. For copper, such an effect may be explained by foliar absorption and the known poor translocation of this metal within the plant.

- The results from the 1995 follow-up sampling have strengthened the need for multi-year studies of crops where environmental contamination and critical remediation efforts are inextricably linked.

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