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EPRI Project Manager
K. Ladwig

ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1338 ▪ PO Box 10412, Palo Alto, California 94303-0813 ▪ USA
800.313.3774 ▪ 650.855.2121 ▪ askepri@epri.com ▪ www.epri.com

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The Ohio State University
School of Environment and Natural Resources
The Ohio Agricultural Research and Development Center
1680 Madison Avenue
Wooster, OH 44691

Principal Investigators
W.A. Dick
D. Kost

Auburn University
Agronomy and Soils
259 Funchess Hall
Auburn, AL 36849

Principal Investigator
C.C. Mitchell

United State Department of Agriculture – Agricultural Research Service
National Soil Dynamics Laboratory
411 S. Donahue Drive
Auburn, AL 36832

Principal Investigators
D.B. Watts
H.A. Torbert

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ABSTRACT

Flue gas desulfurization (FGD) gypsum is an excellent source of gypsum ($CaSO_4 \cdot 2H_2O$) that can be beneficially used in agriculture. Research on FGD gypsum has been conducted as part of the Flue Gas Desulfurization Gypsum Agricultural Network program sponsored by the Electric Power Research Institute in collaboration with individual utilities, the USDA-ARS, the U.S. EPA, and universities. This report describes work that compared performance of FGD gypsum to that of commercial (mined) gypsum when growing cotton, Alabama's largest row crop, in terms of acreage and value. Most cotton producers rotate cotton with peanuts, a crop that is commonly fertilized with gypsum. A field experiment, established in 2009 on a Bama very fine sandy loam soil near Huxford, Alabama, was set up as a randomized complete block design with four blocks (replications) of nine soil amendment treatments. FGD gypsum and a commercially available agricultural (mined) gypsum were each applied at rates of 2.24, 4.48, and 8.96 Mg ha^{-1} (1.0, 2.0, and 4.0 tons $acre^{-1}$), and there was one control (that is, zero rate) treatment in each block. Two other treatments included agricultural lime at 2.24 Mg ha^{-1} applied alone or in combination with the low rate (2.24 Mg ha^{-1}) of FGD gypsum. There were no significant effects of gypsum treatments on cotton lint yield in 2009 (598 to 699 kg ha^{-1}) or 2010 (638 to 799 kg ha^{-1}). When measured after 5, 12, and 20 months, soil properties such as pH, lime test index, Bray-1 P, exchangeable cations (K, Ca, Mg, Na), base saturation of exchangeable cations, and loss on ignition (organic matter) were not affected by treatments. After 5 months, soil soluble salts (soil EC) and Mehlich-extractable S were greater for the high rates of FGD gypsum and mined gypsum versus the control treatment. There were no significant gypsum treatment effects on concentrations of As, Hg, or Se in soil, cottonseed, or vadose zone water. In summary, when FGD gypsum was applied at rates of 8.96 kg ha^{-1} (4.0 ton $acre^{-1}$) or less on land where cotton was being grown in Alabama, there appeared to be little effect on cotton lint yields or on soil, plant, or water quality.

Keywords
FGD gypsum
Agriculture
Cotton
Trace elements
Mercury
Alabama

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INTRODUCTION

Gypsum (calcium sulfate or CaSO4•2H2O) contains 23% calcium (Ca) and 19% sulfur (S) and is applied to agricultural fields to help improve soil chemical and physical properties and increase crop yields. Gypsum is moderately soluble in water (2.5 g per L) and approximately 200 times more soluble than lime (CaCO3). Many soils from semiarid to humid regions have an unstable structure, which makes them susceptible to erosion and difficult to manage. These soils have a tendency to disperse. As a result, they develop a more compacted structure, particularly at or near the soil surface, which results in crusting. Application of gypsum can reduce dispersion and brings about a better soil physical condition that increases water infiltration and percolation, thus reducing soil erosion and improving water quality. Gypsum also contains soluble Ca and S, essential plant nutrients that when applied to soils deficient in these elements can increase the growth, quality, and yields of crops grown on these soils.

Flue gas desulfurization (FGD) gypsum is a very pure form of gypsum that is a product from the combustion of coal for energy production. FGD gypsum is created during the removal of SO2 from the flue gas by reacting the SO2 with calcite (CaCO3) to form calcium sulfite (CaSO3•0.5H2O), which is further treated by forced oxidization to form calcium sulfate (gypsum, CaSO4•2H2O) (Laperche and Bigham, 2002). A study by the Electric Power Research Institute (EPRI, 2011) found FGD gypsum purity in 30 samples to be 90% or greater, and Bolan et al. (1991) reported purity greater than 99%.

The studies described herein were conducted as part of a broader Flue Gas Desulfurization Gypsum Agricultural Network sponsored by the Electric Power Research Institute working with individual utilities, the U.S. EPA, and USDA-ARS to develop the data and knowledge base needed to support the expanded use of FGD gypsum in agriculture by documenting its value and safety at a network of sites across the U.S. (EPRI, 2008). The objectives of the network were to:

- Determine the appropriate rates and technologies for FGD gypsum use in agriculture
- Evaluate the soil chemical and environmental effects of FGD gypsum when applied to different soil types for improving crop productivity
- Document the effectiveness of FGD gypsum for improving crop yield
- Compare the performance of FGD gypsum to that of commercial gypsum products

This report describes a field study on agricultural use of FGD gypsum in southern Alabama. In Alabama, agricultural gypsum is routinely recommended at rates of 560 to 1120 kg ha^{-1} (500 to 1000 lbs acre^{-1}) as a source of calcium for pegging peanuts, especially the large-seeded types and peanuts grown for seed. Although gypsum is a neutral salt, it has been found to reduce the toxic effects of aluminum in acid subsoils and improve surface soil structure (aggregation) in some situations.

The objectives of this research were (1) to evaluate the potential impacts of FGD gypsum application on soil, water, and plant quality, and (2) to determine the yield benefits associated with applying FGD gypsum to fields where cotton is being grown. The results of this research will be used to develop guidelines for applying FGD gypsum in conjunction with lime and other soil amendments for improving cotton production in the Southern Coastal Plain of the United States.

2

MATERIALS AND METHODS

2.1 Design and Establishment of the Field Study

This research was designed according to the protocol for the Flue Gas Desulfurization Gypsum Agricultural Network that is posted online at the following web address: http://www.oardc.ohio-state.edu/agriculturalfgdnetwork/Network%20files/Network%20Manual.pdf. The fundamental principle of the network is to compare FGD gypsum with mined (commercial) gypsum as soil amendments using the same rates in the same experiment.

A two-year field study, started in 2009, compared the agricultural use of FGD gypsum with a commercially available (mined) gypsum product and with agricultural lime. The field study site is located in Escambia County near Huxford, AL. The soil at the field site is Bama very fine sandy loam with 0-2% slopes (fine-loamy, siliceous, subactive, thermic Typic Paleudults). It is a very deep, well-drained, moderately permeable soil on high stream or marine terraces. Ultisols such as the Bama soil are characterized by an accumulation of clay in the subsoil and subsoil acidity. Depending on the specific location, the Bama soil varies from slightly acid to very strongly acid throughout the profile. Bama soils formed in thick beds of loamy sediments. This soil is found in extensive areas in the Southern Coastal Plain of Alabama, Florida, Mississippi, and Virginia. Pre-treatment soil samples (1 per replication) were collected in June 2009.

The experimental design was a randomized complete block design with four replications. In each replication, the treatments (n = 9) included the two gypsum products (FGD gypsum and the commercially available mined gypsum) applied at three rates and one control plot that received no gypsum. Two other treatments included agricultural lime (2.24 Mg ha^{-1} or 1.0 ton acre^{-1}) applied alone or combined with the low rate of FGD gypsum. Rates of gypsum applied to the soil on June 10, 2009, were 0, 2.24, 4.48, and 8.96 Mg ha^{-1} (0, 1.0, 2.0, and 4.0 tons acre^{-1}). Gypsum treatments were applied only at the beginning of the study and not in succeeding years. FGD gypsum was from the Lowman Power Plant of PowerSouth Energy Cooperative in Leroy, AL. Agricultural (mined) gypsum was from South Down, Inc., Easton, PA. Plots were 6 rows of cotton or 5.5 m by 7.6 m (18 ft by 25 ft) in size. Due to continuing rainfall, planting of cotton the first year (2009) was delayed until June. All treatments received 100-100-100 kg ha^{-1} (90-90-90 lb acre^{-1}) of N-P_2O_5-K_2O during the growing season.

Suction lysimeters for sampling vadose water were installed at 60 cm depth in the control (0 rate), high-rate FGD gypsum, and high-rate mined gypsum plots. One lysimeter was installed in each plot, but treatments were replicated four times. Water samples were collected on July 31 and October 27, 2009, May 5, 2010, and February 3, 2011. These dates for collecting water samples were approximately 2, 5, 11, and 20 months after gypsum application.

Post-treatment soil samples (0-20 cm depth) were collected from each plot on August 5 and November 2, 2009, June 9, 2010, and February 17, 2011. These dates for collecting soil samples were approximately 2, 5, 12, and 20 months after gypsum application. Cotton lint yield from all plots was measured in 2009 (October 26) and in 2010 (October 14) by harvesting the middle two rows of each plot. Cottonseed samples for chemical quality analysis were collected from all treatments during the harvest on October 26, 2009.

2.2 Sample Analyses

Analyses of gypsum, soil, water, and cottonseed samples were conducted in the STAR Laboratory of The Ohio State University (http://oardc.osu.edu/starlab/). Analyses of gypsum samples included total neutralizing power, lime test index, pH of a 1:1 gypsum:water ratio, and soluble salts (electrical conductivity, EC) of a 1:2 gypsum:water ratio (Sparks, 1996). Total N and total C were measured by combustion analysis. The gypsum samples were also digested using a modified microwave sample digestion (CEM Mars digestion unit) method based on EPA Method 3051a (U.S. Environmental Protection Agency, 1995). EPA Method 3051a provides a harsher extraction solution than the standard EPA 3051 method. The method was modified by treating 0.5 g soil with 9 ml of concentrated HNO_3 and 3 ml of concentrated HCl at 175 °C for 15 min, followed by heating at 200 °C for an additional 15 min. A suite of 28 elements in the microwave digest was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). This suite included the following elements: P, K, Ca, Mg, S, Al, B, Cu, Fe, Mn, Mo, Na, Zn, As, Ba, Be, Cd, Co, Cr, Li, Ni, Pb, Sb, Se, Si, Sr, V, and Tl. The ICP instrument was a Teledyne Leeman Labs Prodigy Dual View ICP. Finally, Hg was measured separately by cold vapor atomic fluorescence spectrometry using a CETAC M8000 analyzer. Samples for Hg analysis were digested in a 1:1 mixture of 72% perchloric acid and concentrated nitric acid for 3 h at 175 °C and 1 h at 210 °C.

Soil samples were analyzed for the same parameters using the same procedures as the gypsum materials except total neutralizing potential was omitted. Additional analyses performed for soil samples included available P by Bray-1 extraction, exchangeable bases (K, Ca, Mg, and Na) by ammonium acetate extraction, and calculation of cation exchange capacity and percent base saturation (Sparks, 1996). The analysis of 13 elements (P, K, Ca, Mg, S, Al, B, Cu, Fe, Mn, Mo, Na, and Zn) was also performed using ICP-AES after Mehlich-3 extraction (Mehlich, 1984). The Mehlich-3 extraction provides an estimate of the plant-available concentration rather than the total concentration of each element.

Cottonseed samples were analyzed for total N and total C by combustion analysis, for the suite of 28 elements by inductively coupled plasma-atomic emission spectroscopy after microwave sample digestion (EPA method 3051a), and for Hg by cold vapor atomic fluorescence spectrometry.

Soil water samples from the suction lysimeters were analyzed for pH, soluble salts, acidity, alkalinity, and the suite of 28 elements by inductively coupled plasma-atomic emission spectroscopy after filtering. Anions (fluoride, chloride, bromide, nitrate, phosphate, and sulfate) were measured by ion chromatography and Hg by cold vapor atomic fluorescence spectrometry.

2.3 Statistical Analyses

Data for soil chemistry, crop yield, and crop chemistry were subjected to ANOVA using JMP statistical software (SAS Institute, 2000). If the probability value for gypsum treatment in the ANOVA was less than 0.05, differences among means were tested by the LSD test. Data on gypsum chemistry were not analyzed statistically because there was no sample replication.

3
RESULTS

3.1 Gypsum Chemistry

There were a number of notable differences in chemical composition between the FGD gypsum and the mined gypsum (Table 3-1). The mined gypsum had much greater total neutralizing potential (% $CaCO_3$ equivalency), total C (%), and total N (%) than the FGD gypsum. The greater total C (%) for the mined gypsum may have been due to the presence of actual carbonates providing neutralizing power or to some C-containing organic binder used in forming the pellets of mined gypsum. The mined gypsum also had much greater Mg (44,000 mg kg^{-1} or 4.4%) than the FGD gypsum (1200 mg kg^{-1}). In terms of soil fertility and plant nutrition, the mined gypsum is a much larger source of Mg than the FGD gypsum. Applying high rates of gypsum that contains little Mg may result in the loss of Mg from soil. In some cases where Mg is naturally low in soils, a Mg-containing fertilizer may need to be included when high gypsum rates are applied (Ritchey et al., 2004). Generally, however, if the soils have 80% or less of the cation exchange sites occupied by Ca, gypsum applications should not cause nutrient imbalances. Sulfur was much higher in the FGD gypsum (15.0%) compared to the mined gypsum (8.67%), indicating the FGD gypsum is a higher-purity form of calcium sulfate.

The Hg concentration in the FGD gypsum (640 μg kg^{-1}) was 40 times greater than in the mined gypsum. The effect of this Hg on total soil concentrations and in cottonseed are described later in this report. Barium concentration was 5 times greater in FGD gypsum than in mined gypsum. Manganese concentration was 57 times greater in mined gypsum than in FGD gypsum, and Na was 92 times greater, and Fe, K, and Sr concentrations were 3.5 to 4.4 times greater in mined gypsum than in FGD gypsum. In both gypsums, concentrations of three elements measured by ICP-AES were below detection limits (mg kg^{-1}) and are not included in Table 3-1 (Be < 0.091, Pb < 0.774, and Tl <1.44).

Table 3-1
Chemical properties of the gypsum materials used in the cotton study at Huxford

Parameter[a]	FGD Gypsum	Mined Gypsum
pH	7.7	7.1
TNP[b] (% $CaCO_3$)	8.5	49.7
EC (dS m^{-1})	6.57	7.94
Total N (%)	0.008	0.161
Total C (%)	0.261	6.50
Microwave Digest and ICP Analysis (mg kg^{-1})		
Al	479	1370
As	<1.28	<1.28
B	7.2	12.0
Ba	299	61
Ca (%)	18.2	18.3
Cd	<0.074	0.13
Co	<0.146	0.31
Cr	5.0	6.5
Cu	<0.43	<0.43
Fe	637	2790
Hg[c] (µg kg^{-1})	640	15.8
K	183	800
Mg	1200	44000
Mn	2.9	164
Mo	1.0	1.3
Na	<13.0	1190
Ni	1.9	4.8
P	<0.25	<0.25
S (%)	15.0	8.67
Sb	10.9	8.2
Se	2.9	<2.3
Si	663	1350
Sr	257	907
Tl	<1.44	<1.44
V	4.7	8.1
Zn	18	33

[a] The following were analyzed but are not included in the table because they were always below detection: Be (<0.091 mg kg^{-1}), Pb (<0.774 mg kg^{-1}), Tl (<1.44 mg kg^{-1}).

[b] Total neutralizing potential as % calcium carbonate equivalency.

[c] Analysis of Hg by cold vapor atomic fluorescence spectrometry.

3.2 Soil Chemistry

There were few significant treatment effects on soil chemistry in 2009, and the significant effects mostly occurred for the November (five months after treatment application) rather than the August sample date (two months after treatment application) (Tables 3-2 through 3-5).

In terms of general soil chemical properties, there were no treatment effects on pH, lime test index, Bray-1 P, exchangeable cations (K, Ca, Mg, Na), base saturation of exchangeable cations, and loss on ignition (LOI) in 2009 or 2010-2011 (Table 3-2). Soluble salts as measured by electrical conductivity (EC) were greater for the high rate of FGD gypsum, the high rate of mined gypsum, and the lime+FGD gypsum treatments compared to the control and lime-only treatments in 2009. In 2011, several gypsum treatments also had greater EC compared to the lime-only treatment but not compared to the control treatment (Table 3-2). In all years, the increases in soluble salts due to treatments were not large enough to cause detrimental effects on plant growth.

Among the 13 elements measured using Mehlich-3 extraction, only S and Mn had significant treatment effects in 2009 (Table 3-3). Mehlich-extractable S was greater for the high rate of FGD gypsum, the high rate of mined gypsum, and the lime+FGD gypsum treatments versus the control and lime-only treatments. This is understandable because the gypsum materials used in this study contained 8.7 to 15.0 % S (Table 3-1). In 2010-2011, there were no significant treatment effects for S. The low rate of FGD gypsum (2.24 Mg ha^{-1}) had greater Mehlich-extractable Zn than all other treatments, but this could be considered an outlier when compared with all other Zn concentrations (Table 3-3).

Soil concentrations of plant essential elements were measured by combustion analysis (N, C) or by ICP analysis following a microwave-assisted, strong acid digestion. Soil Mn was the only nutrient significantly affected by treatments in 2009 (Table 3-4). However, these differences have little practical value in terms of crop growth or soil quality. There were no significant treatment effects for any plant essential elements in 2010-2011.

Soil concentrations of plant non-essential elements, including various trace elements, were also measured by ICP analysis after the microwave-assisted, strong acid digestion. Lead (Pb) was the only element with significant treatment effects in 2009 (Table 3-5). Concentrations of Pb were not statistically different for the high rate of FGD gypsum and the control treatments, but were statistically lower for the lime-only and lime+FGD gypsum. Silicon (Si) was the only non-essential element with significant treatment effects in 2010-2011, but the variability was great and no consistent pattern due to treatment could be observed. There were no significant treatment effects for soil Hg in any year, in spite of the 40X higher concentration of Hg in the FGD gypsum compared to the mined gypsum.

Table 3-2
Some standard chemical properties in the Huxford field for soil samples collected in August 2009 (2 months), November 2009 (5 months), June 2010 (12 months), and February 2011 (20 months) after gypsum treatments were applied

Parameter[b]	**Sample Date**	**Treatment Type and Rate (Mg ha^{-1})**[a]								
		Control	**FGD Gypsum**			**Mined Gypsum**			**Lime + FGD**	**Lime Only**
		0	**2.24**	**4.48**	**8.96**	**2.24**	**4.48**	**8.96**		
pH	Aug. 5, 2009	5.46	5.33	5.35	5.33	5.55	5.46	5.26	5.34	5.56
	Nov. 2, 2009	5.63	-[c]	-	5.53	-	-	5.56	5.63	5.56
	June 9, 2010	5.15	-	-	5.28	-	-	5.24	5.24	5.24
	Feb. 17, 2011	5.14	5.28	5.22	5.35	5.36	5.26	5.36	5.33	5.29
LTI	Aug. 5, 2009	63.6	64.1	65.1	64.6	65.4	65.3	56.8	64.1	64.4
	Nov. 2, 2009	63.6	-	-	64.2	-	-	64.8	64.8	64.2
	June 9, 2010	64.2	-	-	64.3	-	-	64.5	64.8	64.1
	Feb. 17, 2011	61.9	62.4	63.4	64.0	63.6	63.3	64.6	63.9	63.8
LOI (%)	Aug. 5, 2009	3.42	3.38	3.14	3.28	2.68	2.84	2.96	2.96	3.03
	Nov. 2, 2009	3.44	-	-	3.20	-	-	2.83	3.08	3.12
	June 9, 2010	3.40	-	-	3.23	-	-	2.92	2.94	3.32
	Feb. 17, 2011	3.54	3.46	3.28	3.10	2.91	3.00	2.94	3.24	3.23
EC (dS m^{-1})	Aug. 5, 2009	0.174	0.394	0.521	0.631	0.204	0.351	0.478	0.311	0.185
	Nov. 2, 2009	0.161 c	-	-	0.249 ab	-	-	0.286 a	0.219 b	0.156 c
	June 9, 2010	0.168	-	-	0.210	-	-	0.180	0.160	0.155
	Feb. 17, 2011	0.170 ab	0.165 b	0.195 ab	0.190 ab	0.158 c	0.162 bc	0.202 a	0.170 ab	0.148 c
P Bray-1 (mg kg^{-1})	Aug. 5, 2009	23.9	27.4	23.8	28.8	20.8	24.3	23.0	20.7	23.3
	Nov. 2, 2009	23.6	-	-	21.9	-	-	20.4	20.3	20.5
	June 9, 2010	31.2	-	-	30.6	-	-	30.9	28.1	28.1
	Feb. 17, 2011	29.6	28.8	27.0	30.2	29.2	29.3	30.5	26.8	28.0

[a] Within a parameter and sample date (row), means followed by no letters or by similar letters are not significantly different at $P < 0.05$ using the least significant difference (LSD) test.

[b] LTI = Lime test index, EC = electrical conductivity, CEC = cation exchange capacity.

[c] "-" = Not determined.

Table 3-2 (continued)
Some standard chemical properties in the Huxford field for soil samples collected in August 2009 (2 months), November 2009 (5 months), June 2010 (12 months), and February 2011 (20 months) after gypsum treatments were applied

Parameter	Sample Date	Treatment Type and Rate (Mg ha^{-1}) Control	FGD Gypsum			Mined Gypsum			Lime + FGD	Lime Only
		0	2.24	4.48	8.96	2.24	4.48	8.96		
CEC (cmol kg^{-1})	Aug. 5, 2009	11.7	11.5	10.8	12.0	9.4	10.1	20.7	11.1	10.6
	Nov. 2, 2009	11.8	-	-	11.1	-	-	10.4	10.2	10.4
	June 9, 2010	10.3	-	-	10.3	-	-	10.1	9.42	10.6
	Feb. 17, 2011	12.9	12.6	11.3	10.8	11.0	11.2	10.1	10.8	10.7
Exchangeable Bases (mg kg^{-1})										
Ca	Aug. 5, 2009	606	722	807	924	613	695	800	658	606
	Nov. 2, 2009	628	-	-	691	-	-	676	637	513
	June 9, 2010	496	-	-	570	-	-	544	491	520
	Feb. 17, 2011	489	551	563	586	529	496	567	544	503
K	Aug. 5, 2009	103	89.8	89.9	86.2	87.2	84.2	90.9	85.6	89.1
	Nov. 2, 2009	89.7	-	-	81.6	-	-	75.0	86.2	81.9
	June 9, 2011	93.9	-	-	78.8	-	-	82.4	80.8	90.2
	Feb. 17, 2011	83.4	86.3	77.7	77.6	78.0	76.6	75.1	79.8	81.6
Mg	Aug. 5, 2009	71.1	68.6	73.7	78.6	74.8	79.8	72.4	67.6	72.8
	Nov. 2, 2009	76.3	-	-	65.6	-	-	69.1	70.8	72.2
	June 9, 2010	69.7	-	-	56.1	-	-	67.7	64.5	75.0
	Feb. 17, 2011	59.9	59.6	48.4	60.3	65.8	64.8	62.9	65.2	69.6
Na	Aug. 5, 2009	74.7	69.3	74.0	83.8	74.8	69.4	77.8	79.2	74.2
	Nov. 2, 2009	58.2	-	-	58.1	-	-	56.0	58.7	55.6
	June 9, 2010	-	-	-	-	-	-	-	-	-
	Feb. 17, 2011	-	-	-	-	-	-	-	-	-

Table 3-2 (continued)
Some standard chemical properties in the Huxford field for soil samples collected in August 2009 (2 months), November 2009 (5 months), June 2010 (12 months), and February 2011 (20 months) after gypsum treatments were applied

Parameter	Sample Date	Treatment Type and Rate (Mg ha^{-1})								
		Control	FGD Gypsum			Mined Gypsum			Lime + FGD	Lime Only
		0	2.24	4.48	8.96	2.24	4.48	8.96		
Base Saturation (%)										
Ca	Aug. 5, 2009	27.2	31.7	37.6	38.2	33.2	34.7	28.0	29.6	28.7
	Nov. 2, 2009	27.9	-	-	31.6	-	-	32.6	31.4	24.5
	June 9, 2010	24.9	-	-	28.7	-	-	27.9	26.2	24.8
	Feb. 17, 2011	19.3	22.2	25.3	28.1	25.6	22.4	29.0	25.0	23.4
K	Aug. 5, 2009	2.28	2.00	2.15	1.85	2.40	2.18	1.62	1.98	2.18
	Nov. 2, 2009	1.95	-	-	1.92	-	-	1.88	2.18	1.98
	June 9, 2010	2.35	-	-	2.00	-	-	2.12	2.20	2.18
	Feb. 17, 2011	1.65	1.78	1.78	1.90	1.85	1.75	1.95	1.90	1.95
Mg	Aug. 5, 2009	5.35	5.05	5.72	5.48	6.72	6.58	4.00	5.08	5.88
	Nov. 2, 2009	5.62	-	-	5.02	-	-	5.55	5.80	5.82
	June 9, 2010	5.92	-	-	4.58	-	-	5.80	5.70	5.90
	Feb. 17, 2011	3.92	3.95	3.58	4.70	5.15	4.85	5.50	5.08	5.38

Table 3-3
Concentrations (mg kg^{-1}) of elements extracted from the Huxford field by Mehlich-3 for soil samples collected in August 2009 (2 months), November 2009 (5 months), June 2010 (12 months), and February 2011 (20 months) after gypsum treatments were applied

Parameter	Sample Date	Treatment Type and Rate (Mg ha^{-1})[a]								
		Control	FGD Gypsum			Mined Gypsum			Lime + FGD	Lime Only
		0	2.24	4.48	8.96	2.24	4.48	8.96		
Al	Aug. 5, 2009	909	904	854	861	825	844	868	889	921
	Nov. 2, 2009	946	-[b]	-	928	-	-	884	920	937
	June 9, 2010	896	-	-	891	-	-	878	886	913
	Feb. 17, 2011	922 ab	946 a	873 bc	856 cd	832 cd	879 bc	852 cd	896 abc	916 abc
B	Aug. 5, 2009	1.27	1.19	1.07	1.04	1.04	1.04	1.00	1.01	1.02
	Nov. 2, 2009	1.07	-	-	1.06	-	-	1.01	1.02	1.01
	June 9, 2010	<0.15	-	-	<0. 15	-	-	<0.15	<0.15	<0.15
	Feb. 17, 2011	<0.15	<0.15	<0.15	<0.15	<0.15	<0. 15	<0.15	<0.15	<0.15
Ca	Aug. 5, 2009	701	894	922	1040	719	823	990	755	759
	Nov. 2, 2009	703	-	-	767	-	-	742	710	595
	June 9, 2010	565	-	-	665	-	-	621	556	612
	Feb. 17, 2011	593	638	656	686	597	583	666	638	579
Cu	Aug. 5, 2009	0.60	0.59	0.56	0.60	0.53	0.53	0.57	0.55	0.57
	Nov. 2, 2009	0.63	-	-	0.63	-	-	0.54	0.56	0.53
	June 9, 2010	0.432	-	-	0.422	-	-	0.412	0.372	0.422
	Feb. 17, 2011	0.468	0.538	0.420	0.448	0.430	0.410	0.425	0.455	0.432
Fe	Aug. 5, 2009	66.4	61.9	59.5	66.3	55.0	60.1	63.6	60.1	58.7
	Nov. 2, 2009	71.8	-	-	69.0	-	-	62.7	61.1	58.9
	June 9, 2010	50.0	-	-	51.6	-	-	47.2	40.7	43.4
	Feb. 17, 2011	60.3	51.8	52.0	54.6	45.9	51.0	52.7	48.3	47.7
K	Aug. 5, 2009	92.0	81.0	79.7	78.3	77.8	77.0	82.7	76.1	78.0
	Nov. 2, 2009	80.4	-	-	75.8	-	-	67.2	77.6	74.5
	June 9, 2010	75.1	-	-	62.2	-	-	65.2	66.2	76.6
	Feb. 17, 2011	71.3	69.2	63.5	62.6	63.9	61.8	61.0	66.7	65.8

[a] Within a parameter and sample date (row), means followed by no letters or by similar letters are not significantly different at $P < 0.05$ using the least significant difference (LSD) test.

[b] "-" = Not determined.

Table 3-3 (continued)
Concentrations (mg kg^{-1}) of elements extracted from the Huxford field by Mehlich-3 for soil samples collected in August 2009 (2 months), November 2009 (5 months), June 2010 (12 months), and February 2011 (20 months) after gypsum treatments were applied

Parameter	Sample Date	Treatment Type and Rate (Mg ha^{-1})								
		Control	FGD Gypsum			Mined Gypsum			Lime + FGD	Lime Only
		0	2.24	4.48	8.96	2.24	4.48	8.96		
Mg	Aug. 5, 2009	87.2	87.7	88.9	95.0	91.1	100	92.8	82.0	92.1
	Nov. 2, 2009	92.7	-	-	80.2	-	-	85.8	87.2	90.2
	June 9, 2010	83.1	-	-	70.8	-	-	83.7	78.7	92.4
	Feb. 17, 2011	77.0	74.1	62.4	76.0	79.7	79.9	79.8	81.6	84.6
Mn	Aug. 5, 2009	45.0	42.9	51.1	54.0	44.2	41.3	47.1	44.7	41.8
	Nov. 2, 2009	48.5 ab	-	-	57.5 a	-	-	46.9 b	47.6 b	41.1 b
	June 9, 2010	27.3	-	-	32.8	-	-	30.9	26.9	26.7
	Feb. 17, 2011	36.8	30.6	34.1	38.2	30.1	28.0	34.4	31.3	31.4
Mo	Aug. 5, 2009	0.045	0.058	0.045	0.042	0.065	0.075	0.052	0.065	0.052
	Nov. 2, 2009	0.060	-	-	0.088	-	-	0.042	0.042	0.040
	June 9, 2010	0.475	-	-	0.588	-	-	0.482	0.095	0.138
	Feb. 17, 2011	0.520	0.685	0.245	0.635	0.645	0.320	0.308	0.642	0.395
Na	Aug. 5, 2009	53.7	56.4	61.4	65.5	55.5	57.5	66.2	57.2	61.0
	Nov. 2, 2009	19.7	-	-	17.9	-	-	2.54	5.85	2.84
	June 9, 2010	160	-	-	158	-	-	161	155	159
	Feb. 17, 2011	144	144	140	146	146	139	142	148	141
P	Aug. 5, 2009	23.0	26.8	23.2	29.6	20.9	24.3	23.3	20.4	23.1
	Nov. 2, 2009	22.2	-	-	20.5	-	-	19.8	18.7	18.1
	June 9, 2010	13.2	-	-	13.6	-	-	11.6	10.2	11.7
	Feb. 17, 2011	17.5	15.2	13.9	18.1	14.3	14.8	16.8	13.4	14.4
S	Aug. 5, 2009	62.8	178	211	320	75.8	167	302	130	71.0
	Nov. 2, 2009	62.7 b	-	-	107 a	-	-	117 a	94.0 a	66.4 b
	June 9, 2010	70.5	-	-	116	-	-	95.3	97.2	72.5
	Feb. 17, 2011	63.9	68.4	76.9	78.0	63.8	62.9	79.6	79.4	70.6
Zn	Aug. 5, 2009	1.00	1.32	1.00	1.46	1.84	1.36	1.39	1.60	0.80
	Nov. 2, 2009	2.07	-	-	0.80	-	-	1.14	1.05	0.73
	June 9, 2010	1.36	-	-	1.09	-	-	0.772	1.29	0.838
	Feb. 17, 2011	0.618 b	4.76 a	0.970 b	0.662 b	0.648 b	0.540 b	0.645 b	0.595 b	0.595 b

Table 3-4
Total concentrations of elements in the Huxford field for soil samples collected in August 2009 (2 months), November 2009 (5 months), June 2010 (12 months), and February 2011 (20 months) after gypsum treatments were applied

Parameter	Sample Date	Treatment Type and Rate (Mg ha^{-1})[a]								
		Control	FGD Gypsum			Mined Gypsum			Lime + FGD	Lime Only
		0	2.24	4.48	8.96	2.24	4.48	8.96		
C (%)	Aug. 5, 2009	1.56	1.54	1.41	1.44	1.25	1.30	1.35	1.36	1.40
	Nov. 2, 2009	1.50	-[b]	-	1.45	-	-	1.27	1.29	1.31
	June 9, 2010	1.22	-	-	1.24		-	1.06	0.974	1.15
	Feb. 17, 2011	1.37	1.42	1.27	1.30	1.16	1.21	1.26	1.24	1.21
N (%)	Aug. 5, 2009	0.102	0.100	0.095	0.094	0.086	0.087	0.090	0.088	0.091
	Nov. 2, 2009	0.092	-	-	0.086	-	-	0.080	0.081	0.080
	June 9, 2010	0.078	-	-	0.071	-	-	0.068	0.066	0.074
	Feb. 17, 2011	0.084	0.083	0.079	0.078	0.073	0.070	0.076	0.075	0.074
B (mg kg^{-1})	Aug. 5, 2009	3.70	3.34	2.99	3.18	3.05	4.20	2.87	3.05	3.47
	Nov. 2, 2009	3.48	-	-	3.24	-	-	3.35	3.39	3.17
	June 9, 2010	<0.015	-	-	<0.15	-	-	<0.15	<0.15	<0.15
	Feb. 17, 2011	<0.015	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15
Ca (mg kg^{-1})	Aug. 5, 2009	839	988	1040	1190	802	902	999	900	1030
	Nov. 2, 2009	856	-	-	936	-	-	896	840	716
	June 9, 2010	639	-	-	777	-	-	673	635	679
	Feb. 17, 2011	690	754	755	781	671	689	764	711	636
Cu (mg kg^{-1})	Aug. 5, 2009	5.56	5.48	5.17	5.03	5.36	5.25	31.6	5.70	5.91
	Nov. 2, 2009	5.03	-	-	4.95	-	-	5.11	5.46	6.08
	June 9, 2010	7.63	-	-	6.68	-	-	7.49	8.29	8.34
	Feb. 17, 2011	7.08	6.93	6.92	6.49	5.74	6.61	6.23	7.40	6.87
Fe (mg kg^{-1})	Aug. 5, 2009	20100	19500	15600	15300	14300	13500	14300	15300	16800
	Nov. 2, 2009	19200	-	-	16900	-	-	14300	16900	17400
	June 9, 2010	19391	-	-	17440	-	-	16441	18405	17912
	Feb. 17, 2011	17891	17213	16957	16263	15332	14233	13794	15767	16792
K (mg kg^{-1})	Aug. 5, 2009	634	618	624	578	620	596	598	596	663
	Nov. 2, 2009	592	-	-	550	-	-	551	554	586
	June 9, 2010	504	-	-	447	-	-	474	502	521
	Feb. 17, 2011	458	512	442	411	469	490	418	441	448

[a] Within a parameter and sample date (row), means followed by no letters or by similar letters are not significantly different at $P < 0.05$ using the least significant difference (LSD) test.

[b] "-" = Not determined.

Table 3-4 (continued)
Total concentrations of elements in the Huxford field for soil samples collected in August 2009 (2 months), November 2009 (5 months), June 2010 (12 months), and February 2011 (20 months) after gypsum treatments were applied

Parameter	Sample Date	Treatment Type and Rate (Mg ha^{-1})								
		Control	FGD Gypsum			Mined Gypsum			Lime + FGD	Lime Only
		0	2.24	4.48	8.96	2.24	4.48	8.96		
Mg	Aug. 5, 2009	587	578	576	559	580	609	606	577	674
	Nov. 2, 2009	595	-	-	573	-	-	598	584	629
	June 9, 2010	593	-	-	538	-	-	578	608	635
	Feb. 17, 2011	544	536	506	500	520	538	529	530	561
Mn	Aug. 5, 2009	288	258	258	285	240	237	265	269	267
	Nov. 2, 2009	290 ab	-	-	324 a	-	-	243 b	242 b	227 b
	June 9, 2010	174	-	-	211	-	-	177	169	181
	Feb. 17, 2011	230	211	202	222	178	187	216	201	191
Mo	Aug. 5, 2009	0.755	0.670	0.640	0.718	0.588	0.742	0.585	0.638	0.662
	Nov. 2, 2009	0.675	-	-	0.650	-	-	0.608	0.685	0.692
	June 9, 2010	0.678	-	-	0.515	-	-	0.642	0.630	0.658
	Feb. 17, 2011	0.645	0.698	0.575	0.542	0.645	0.660	0.525	0.695	0.600
Ni	Aug. 5, 2009	12.9	13.2	12.1	12.0	12.4	12.4	12.1	12.9	13.6
	Nov. 2, 2009	13.2	-	-	12.5	-	-	12.3	13.9	14.6
	June 9, 2010	19.3	-	-	18.5	-	-	18.4	21.0	20.4
	Feb. 17, 2011	13.9	19.2	13.6	13.0	15.3	14.5	13.0	15.2	15.2
P	Aug. 5, 2009	322	310	278	298	258	252	264	260	278
	Nov. 2, 2009	314	-	-	282	-	-	240	255	260
	June 9, 2010	267	-	-	238	-	-	221	227	242
	Feb. 17, 2011	292	279	259	261	234	228	240	250	244
S	Aug. 5, 2009	267	363	406	528	237	314	374	306	246
	Nov. 2, 2009	214	-	-	258	-	-	249	232	195
	June 9, 2010	183	-	-	232	-	-	202	200	177
	Feb. 17, 2011	184	185	188	183	159	165	187	187	173
Zn	Aug. 5, 2009	30.1	25.6	23.3	23.5	23.6	22.7	23.1	22.3	25.0
	Nov. 2, 2009	23.4	-	-	21.7	-	-	22.5	22.6	23.8
	June 9, 2010	24.0	-	-	21.7	-	-	23.3	24.7	24.9
	Feb. 17, 2011	24.4	23.5	22.7	21.5	20.3	22.1	21.3	22.4	21.8

Table 3-5
Total soil concentrations (mg kg^{-1}) of non-essential plant elements in the Huxford field for soil samples collected in August 2009 (2 months), November 2009 (5 months), June 2010 (12 months), and February, 2011 (20 months) after gypsum treatments were applied

Parameter	Sample Date	Treatment Type and Rate (Mg ha^{-1})[a]								
		Control	FGD Gypsum			Mined Gypsum			Lime + FGD	Lime Only
		0	2.24	4.48	8.96	2.24	4.48	8.96		
Al	Aug. 5, 2009	28400	29000	26300	25800	26500	26100	26000	27500	28800
	Nov. 2, 2009	28700	-[b]	-	27300	-	-	26200	29200	30800
	June 9, 2010	31300	-	-	28900	-	-	30000	32900	32300
	Feb. 17, 2011	28100	28800	26900	25900	26900	26600	25500	28400	29200
As	Aug. 5, 2009	8.39	7.21	7.44	7.03	7.00	7.09	7.29	6.61	7.70
	Nov. 2, 2009	8.19	-	-	7.98	-	-	6.62	7.35	7.65
	June 9, 2010	8.21	-	-	7.11	-	-	7.63	7.39	7.51
	Feb. 17, 2011	8.15	7.72	8.20	7.14	6.83	6.52	6.90	7.46	7.58
Ba	Aug. 5, 2009	52.8	52.1	50.8	50.2	48.4	48.5	50.9	49.7	52.4
	Nov. 2, 2009	54.0	-	-	53.3	-	-	51.0	49.8	50.4
	June 9, 2010	51.8	-	-	50.7	-	-	51.9	50.2	51.8
	Feb. 17, 2011	50.0	47.7	49.2	45.9	42.6	45.4	46.0	45.8	46.9
Cd	Aug. 5, 2009	1.41	1.29	1.02	1.03	0.896	0.964	0.875	0.980	1.05
	Nov. 2, 2009	0.959	-	-	0.856	-	-	0.722	0.864	0.831
	June 9, 2010	0.702	-	-	0.604	-	-	0.550	0.624	0.590
	Feb. 17, 2011	0.634	0.633	0.589	0.580	0.608	0.480	0.442	0.539	0.542
Co	Aug. 5, 2009	3.34	3.13	3.06	3.12	2.94	2.94	3.09	3.03	3.18
	Nov. 2, 2009	3.34	-	-	3.39	-	-	3.01	3.06	3.18
	June 9, 2010	3.59	-	-	3.54	-	-	3.49	3.61	3.61
	Feb. 17, 2011	3.51	3.33	3.13	3.28	3.11	3.09	3.20	3.15	11.2
Cr	Aug. 5, 2009	32.5	30.6	25.4	25.7	26.8	24.9	25.0	24.8	28.8
	Nov. 2, 2009	33.0	-	-	29.4	-	-	26.3	26.3	27.9
	June 9, 2010	30.9	-	-	27.9	-	-	31.0	29.4	28.6
	Feb. 17, 2011	31.1	28.2	32.5	29.1	26.2	29.1	25.0	26.7	33.0

[a] Within a parameter and sample date (row), means followed by no letters or by similar letters are not significantly different at $P < 0.05$ using the least significant difference (LSD) test.

[b] "-" = Not determined.

Table 3-5 (continued)
Total soil concentrations (mg kg^{-1}) of non-essential plant elements in the Huxford field for soil samples collected in August 2009 (2 months), November 2009 (5 months), June 2010 (12 months), and February, 2011 (20 months) after gypsum treatments were applied

Parameter	Sample Date	Treatment Type and Rate (Mg ha^{-1})								
		Control	FGD Gypsum			Mined Gypsum			Lime + FGD	Lime Only
		0	2.24	4.48	8.96	2.24	4.48	8.96		
Hg (µg kg^{-1})	Aug. 5, 2009	34.8	-[b]	-	32.0	-	-	29.1	28.9	28.8
	Nov. 2, 2009	36.9	-	-	34.1	-	-	42.6	32.6	32.8
	June 9, 2010	31.0	-	-	29.6	-	-	29.1	28.5	30.1
	Feb. 17, 2011	26.0	-	-	25.1	-	-	24.7	26.3	26.9
Na	Aug. 5, 2009	38.6	41.6	37.3	37.4	38.5	40.1	39.0	37.7	41.4
	Nov. 2, 2009	37.0	-	-	33.6	-	-	29.7	31.4	33.5
	June 9, 2010	63.8	-	-	64.1	-	-	76.0	68.1	68.0
	Feb. 17, 2011	63.7	76.0	70.2	71.1	47.1	75.4	65.2	74.2	45.6
Pb	Aug. 5, 2009	7.33	5.97	5.24	5.95	4.10	4.73	4.82	4.64	4.65
	Nov. 2, 2009	6.54 ab	-	-	7.06 a	-	-	4.87 bc	4.18 c	4.12 c
	June 9, 2010	4.20	-	-	4.59	-	-	3.57	2.41	3.03
	Feb. 17, 2011	6.20	3.78	5.58	6.00	3.05	4.00	5.05	4.04	3.84
Se	Aug. 5, 2009	1.73	2.44	1.79	1.56	2.52	2.80	3.43	2.69	2.44
	Nov. 2, 2009	1.53	-	-	1.54	-	-	2.49	1.40	2.74
	June 9, 2010	5.58	-	-	5.17	-	-	6.71	6.00	4.27
	Feb. 17, 2011	4.92	4.73	6.50	3.93	4.53	3.73	2.88	4.40	5.30
Si	Aug. 5, 2009	76.6	64.5	69.1	70.6	82.7	73.2	93.7	105	72.4
	Nov. 2, 2009	62.3	-	-	57.9	-	-	58.5	51.7	52.0
	June 9, 2010	478 bc	-	-	1260 a	-	-	230 c	1140 ab	544 bc
	Feb. 17, 2011	646	166	182	182	201	170	225	231	282
Sr	Aug. 5, 2009	5.28	5.48	5.57	5.62	5.42	5.86	6.00	5.10	5.90
	Nov. 2, 2009	5.43	-	-	6.35	-	-	5.56	5.10	5.09
	June 9, 2010	4.77	-	-	5.02	-	-	4.82	4.74	4.88
	Feb. 17, 2011	4.61	4.59	4.52	5.01	4.43	4.84	5.16	4.42	4.44
V	Aug. 5, 2009	51.8	51.5	43.3	43.4	42.5	41.5	42.0	44.0	47.6
	Nov. 2, 2009	50.8	-	-	47.3	-	-	42.2	46.7	48.9
	June 9, 2010	54.0	-	-	48.8	-	-	49.1	53.2	52.0
	Feb. 17, 2011	51.1	48.8	48.4	45.2	45.0	47.7	42.9	47.2	49.1

3.3 Cotton Lint Yield

There were no significant treatment effects on yield of cotton lint in 2009 or 2010 (Table 3-6). During both years, the control (0 rate) treatment ranked first or second in lint yield.

Table 3-6
Cotton lint yields at the Huxford field in 2009 and 2010

Treatment Applied in 2009	Gypsum Rate Applied in 2009	Cotton Lint Yields[a] 2009	Cotton Lint Yields[a] 2010
	Mg ha^{-1}	----------------kg ha^{-1}	-----------------
Control	0	694	799
FGD gypsum x	2.24	627	638
FGD gypsum 2x	4.48	676	728
FGD gypsum 4x	8.96	683	728
Mined gypsum x	2.24	641	683
Mined gypsum 2x	4.48	598	672
Mined gypsum 4x	8.96	699	762
Lime (2.24 Mg ha^{-1}) + FGD gypsum x	2.24	674	672
Lime only (2.24 Mg ha^{-1})	0	643	694

[a] There were no significant effects of treatment on cotton lint yields in 2009 or 2010.

3.4 Cottonseed Chemistry

Measurements of cottonseed chemistry were made at harvest in the first growing season (October 2009) (Table 3-7). Concentrations (mg kg^{-1}) of Be (<0.091), Cd (<0.074), Co (<0.146), Se (<2.32), and Tl (<1.44) were at or below the detection limits and are not included in Table 3-7.

There were significant treatment effects on cottonseed concentrations only for Ba and Sr. Both gypsums caused decreases in cottonseed Ba compared to the control treatment. Strontium in cottonseed was decreased by the intermediate and high rates of FGD gypsum, but increased by the low rate of mined gypsum. These cottonseed responses were observed even though there were no treatment effects on extractable Ba and Sr in the soil in 2009 (Table 3-5). The effect of gypsum on plant Ba is readily understandable because barium sulfate is quite insoluble. Thus gypsum applications to soil would make the Ba unavailable for plant absorption, but this would not cause any decrease in total soil Ba as measured by microwave digestion. Although Mehlich-extractable S was increased in soil by the gypsum treatments (Table 3-3), there was no significant effect of gypsum on S in cottonseed. There was no statistical difference in mercury concentrations among the treatments.

Table 3-7
Element concentrations (mg kg^{-1}) in cottonseed at harvest in October 2009

Parameter[b]	Treatment Type and Rate (Mg ha^{-1})[a]								
	Control	**FGD Gypsum**			**Mined Gypsum**			**Lime + FGD**	**Lime Only**
	0	**2.24**	**4.48**	**8.96**	**2.24**	**4.48**	**8.96**		
Al	1.01	0.348	0.740	0.835	1.25	0.030	0.978	0.092	2.27
As	0.239	0.173	0.006	0.250	0.015	0.139	0.020	0.082	0.006
B	10.3	10.0	9.79	10.4	10.0	9.93	9.86	9.48	9.46
Ba	2.39 ab	1.97 cd	1.58 e	1.53 e	2.17 bc	2.08 cd	1.79 de	2.06 cd	2.53 a
C (%)	49.5	49.6	50.4	49.8	49.8	49.5	49.8	49.8	49.9
Ca	1250	1320	1200	1210	1390	1240	1230	1260	1210
Cr	0.180	0.240	0.212	0.183	0.198	0.144	0.183	0.179	0.240
Cu	0.300	0.250	0.061	0.224	0.091	0.001	0.001	0.001	0.053
Fe	54.2	55.3	51.6	52.1	55.3	49.0	53.5	53.5	51.0
Hg (μg kg^{-1})	11.3	-[c]	-	13.2	-	-	11.0	21.8	10.2
K	9490	9790	9220	9390	9380	9300	9400	9450	9450
Mg	3420	3480	3350	3400	3400	3250	3330	3360	3410
Mn	12.1	11.9	11.1	11.6	11.8	11.6	11.6	11.6	11.7
Mo	0.378	0.355	0.372	0.325	0.552	0.390	0.468	0.250	0.438
N (%)	4.25	4.36	4.45	4.28	4.36	4.26	4.25	4.32	4.31
Na	1820	1890	1570	1650	1810	1840	1810	1800	1630
Ni	0.846	0.820	0.834	0.674	0.804	0.732	0.739	0.854	0.940
P	5190	5350	5210	5310	5250	4880	5110	5160	5290
Pb	0.038	0.095	0.003	0.178	0.022	0.004	0.168	0.141	0.036
S	2940	3090	3000	2960	3040	2910	2940	3290	3060
Sb	0.462	0.588	0.480	0.534	0.503	0.298	0.300	0.266	0.370
Si	10.9	10.7	10.6	10.7	11.7	10.4	10.6	10.7	10.6
Sr	1.46 b	1.53 ab	1.23 c	1.23 c	1.66 a	1.45 b	1.41 b	1.46 b	1.56 ab
V	0.778	0.790	0.708	0.743	0.778	0.804	0.740	0.813	0.818
Z	30.1	30.6	29.5	29.5	30.8	27.3	28.5	28.7	30.7

[a] Within a parameter and sample date (row), means followed by no letters or by similar letters are not significantly different at $P < 0.05$ using the least significant difference (LSD) test.

[b] The following were analyzed but are not included in the table because they were always below detection: Be (<0.091 mg kg^{-1}), Cd (<0.074 mg kg^{-1}), Co (<0.146 mg kg^{-1}), Se (<2.32 mg kg^{-1}), and Tl (<1.44 mg kg^{-1}).

[c] "-" = Not determined.

3.5 Vadose Zone Water Characteristics

Physical and chemical characteristics of vadose water (60 cm depth) in the cotton study are listed in Table 3-8. In 2009, water concentrations of six elements measured by ICP-AES were below the detection limits (mg L^{-1}) for all measurements: Al (0.0099), As (0.0064), Be (0.00046), Co (0.0073), Se (0.012), and Tl (0.0072). Concentrations of Cu (0.0022), Fe (0.0018), Ni (0.0013), and Pb (0.0039) were below the detection limits for most measurements. In 2010-2011, concentrations of Al, As, Be, Cd, Co, Fe, Pb, and Se were below the detection limits for all measurements, and Cu, P, and Tl were below the detection limits for most measurements. The anions F^-, Br^-, and PO_4^{3-} were below the detection limit (0.10 mg L^{-1}) of the ion chromatograph for all years. Data for these elements are not included in Table 3-8.

In 2009, the volume of water that could be collected from the lysimeters was limited. Preference was given to using the small sample volumes for ICP analysis rather than for other analyses. Values of pH, alkalinity, acidity, Cl^-, NO_3^-, and SO_4^{2-} for July and EC for October are based on 1 or 2 samples only per treatment. Thus, although mean values for several parameters showed increases for the high-rate FGD or mined gypsum treatments compared to the control, the increases were not statistically significant (Table 3-8). These included NO_3^- and SO_4^{2-} in October, Ca and S on both sample dates, Sr in July, and Hg in October. There were statistically significant treatment effects for Cr, Mg, Mo, Sb, Sr, and V for the October date. Molybdenum (Mo) and V were statistically greater for mined gypsum than the control. Chromium (Cr), Mg, and Sb were statistically greater for the high rate FGD gypsum treatment than mined gypsum or the control. Strontium was statistically greater for the high rate FGD gypsum treatment than the control.

In 2010-2011 there were four replications for all treatments on both sample dates, except only three replications for the high rate of FGD gypsum in 2011. For the May 2010 samples, EC, SO_4^{2-} by ion chromatography, Ca, Cr, S, and Sr were greater for the high-rate FGD gypsum treatment than the control treatment, with mined gypsum being intermediate (Table 3-8). Also in May 2010, Mg and Sb were greater for both high-rate gypsum treatments compared to the control, and V was greater for mined gypsum compared to the other two treatments. There were strong trends for EC, SO_4^{2-}, Ca, Cr, Mg, S, Sb, and Sr to show treatment effects in the February 2011 samples, but the differences were not significant. The only significant treatment effect for the February 2011 samples was greater Ni for mined gypsum compared to FGD gypsum and the control treatment. There were no significant gypsum effects on Hg concentrations in vadose water in 2010 or 2011.

Table 3-8
Chemical properties of vadose zone water from 60 cm depth extracted from the Huxford field soil in July 2009 (2 month), October 2009 (5 months), May 2010 (11 months), and February 2011 (20 months) after gypsum application at rates of 0 (control) or 8.96 Mg ha^{-1}. Unless indicated otherwise, the units of concentration for the elements are mg L^{-1}.

Parameter[b,c]	Sample Date	Treatment Type and Rate[a]		
		Control	FGD Gypsum	Mined Gypsum
pH	July 31, 2009	7.16	7.19	6.95
	Oct. 27, 2009	6.77	6.78	6.77
	May 5, 2010	6.75	6.48	6.89
	Feb. 3, 2011	6.21	6.46	6.86
EC (μS cm^{-1})	July 31, 2009	138	-[d]	-
	Oct. 27, 2009	104	603	154
	May 5, 2010	165 b	554 a	389 ab
	Feb. 3, 2011	176	425	342
Alkalinity (mg L^{-1})	July 31, 2009	26.4	29.7	19.1
	Oct. 27, 2009	19.0	20.0	17.8
	May 5, 2010	19.5	18.3	19.5
	Feb. 3, 2011	15.3	22.0	17.8
Acidity (meq L^{-1})	July 31, 2009	0.10	0.05	0.00
	Oct. 27, 2009	0.017	0.092	0.105
	May 5, 2010	0.105	0.078	0.050
	Feb. 3, 2011	0.102	0.140	0.065
Anions				
Cl^-	July 31, 2009	5.44	6.40	7.96
	Oct. 27, 2009	5.88	8.32	7.20
	May 5, 2010	11.5	9.81	12.4
	Feb. 3, 2011	8.60	12.0	10.6
NO_3^-	July 31, 2009	25.4	63.8	47.4
	Oct. 27, 2009	37.7	94.9	60.3
	May 5, 2010	20.4	12.6	10.0
	Feb. 3, 2011	43.9	33.6	33.7
SO_4^{2-}	July 31, 2009	16.7	326	11.1
	Oct. 27, 2009	17.0	139	14.5
	May 5, 2010	25.9 b	241 a	139 ab
	Feb. 3, 2011	20.0	151	100

[a] Within a parameter and sample date (row), means followed by no letters or by similar letters are not significantly different at $P < 0.05$ using the least significant difference (LSD) test.

[b] EC = electrical conductivity.

[c] The following were analyzed but are not included in the table because they were always or mostly below detection: Al (<0.0099 mg L^{-1}), As (<0.0064 mg L^{-1}), Be (<0.00046 mg L^{-1}), Br (<0.10 mg L^{-1}), Co (<0.0073 mg L^{-1}), Cu (<0.0022 mg L^{-1}), F (<0.10 mg L^{-1}), Fe (<0.0018 mg L^{-1}), Ni (<0.0013 mg L^{-1}), Pb (<0.0039 mg L^{-1}), PO_4 (<0.10 mg L^{-1}), Se (<0.012 mg L^{-1}), Tl (<0.072 mg L^{-1}).

[d] "-" = Not determined.

Table 3-8 (continued)
Chemical properties of vadose zone water from 60 cm depth extracted from the Huxford field soil in July 2009 (2 month), October 2009 (5 months), May 2010 (11 months), and February 2011 (20 months) after gypsum application at rates of 0 (control) or 8.96 Mg ha^{-1}. Unless indicated otherwise, the units of concentration for the elements are mg L^{-1}.

Parameter	Sample Date	Treatment Type and Rate		
		Control	FGD Gypsum	Mined Gypsum
Concentrations of elements after filtering				
B	July 31, 2009	0.063	0.038	0.041
	Oct. 27, 2009	0.064	0.042	0.035
	May 5, 2010	0.104	0.058	0.062
	Feb. 3, 2011	0.027	0.024	0.032
Ba	July 31, 2009	0.039	0.068	0.068
	Oct. 27, 2009	0.050	0.072	0.058
	May 5, 2010	0.053	0.053	0.041
	Feb. 3, 2011	0.056	0.076	0.072
Ca	July 31, 2009	17.5	85.8	31.3
	Oct. 27, 2009	16.0	66.7	18.4
	May 5, 2010	18.3 b	86.2 a	57.0 ab
	Feb. 3, 2011	19.8	64.6	50.0
Cd	July 31, 2009	<0.00037	0.00051	<0.00037
	Oct. 27, 2009	<0.00037	0.00043	0.00042
	May 5, 2010	<0.00037	<0.00037	<0.00037
	Feb. 3, 2011	<0.00037	<0.00037	<0.00037
Cr	July 31, 2009	<0.00097	0.0020	0.0012
	Oct. 27, 2009	0.0010 b	0.0025 a	0.0011 b
	May 5, 2010	0.0010 b	0.0022 a	0.0012 b
	Feb. 3, 2011	0.0010	0.0020	0.0012
Hg (μg L^{-1})	July 31, 2009	45.5	94.5	46.5
	Oct. 27, 2009	65.0	179	143
	May 5, 2010	-	-	-
	Feb. 3, 2011	-	-	-
K	July 31, 2009	1.16	2.27	2.25
	Oct. 27, 2009	1.12	1.64	1.52
	May 5, 2010	1.84	2.85	3.20
	Feb. 3, 2011	2.13	2.18	2.15
Mg	July 31, 2009	1.91	5.34	2.25
	Oct. 27, 2009	1.96 b	4.59 a	2.06 b
	May 5, 2010	2.03 b	7.46 a	5.55 a
	Feb. 3, 2011	1.98	5.55	5.30
Mn	July 31, 2009	0.0010	0.0052	0.0034
	Oct. 27, 2009	0.0161	0.0200	0.0051
	May 5, 2010	0.0067	0.132	0.0064
	Feb. 3, 2011	0.041	0.020	0.0063
Mo	July 31, 2009	0.0026	0.0041	0.0037
	Oct. 27, 2009	0.0021 b	0.0039 ab	0.0053 a
	May 5, 2010	0.0012	0.0020	0.0025
	Feb. 3, 2011	0.0015	0.0020	0.0015

Table 3-8 (continued)
Chemical properties of vadose zone water from 60 cm depth extracted from the Huxford field soil in July 2009 (2 month), October 2009 (5 months), May 2010 (11 months), and February 2011 (20 months) after gypsum application at rates of 0 (control) or 8.96 Mg ha^{-1}. Unless indicated otherwise, the units of concentration for the elements are mg L^{-1}.

Parameter	Sample Date	Treatment Type and Rate		
		Control	FGD Gypsum	Mined Gypsum
Na	July 31, 2009	5.42	9.37	5.13
	Oct. 27, 2009	3.64	9.03	3.67
	May 5, 2010	5.29	5.98	3.21
	Feb. 3, 2011	4.31	6.35	2.55
P	July 31, 2009	<0.016	<0.016	<0.016
	Oct. 27, 2009	<0.016	<0.016	<0.016
	May 5, 2010	<0.016	<0.016	<0.016
	Feb. 3, 2011	<0.016	<0.016	<0.016
S	July 31, 2009	6.59	69.3	18.5
	Oct. 27, 2009	4.29	45.6	4.81
	May 5, 2010	9.78 b	74.8 a	46.2 ab
	Feb. 3, 2011	7.24	48.4	35.6
Sb	July 31, 2009	0.015	0.022	0.018
	Oct. 27, 2009	0.015 b	0.022 a	0.017 b
	May 5, 2010	0.008 b	0.017 a	0.015 a
	Feb. 3, 2011	0.009	0.016	0.014
Si	July 31, 2009	1.32	0.950	1.21
	Oct. 27, 2009	0.840	0.930	0.968
	May 5, 2010	2.18	2.07	2.30
	Feb. 3, 2011	2.14	2.24	2.48
Sr	July 31, 2009	0.011	0.167	0.076
	Oct. 27, 2009	0.042 b	0.140 a	0.061 ab
	May 5, 2010	0.040 b	0.198 a	0.133 ab
	Feb. 3, 2011	0.041	0.144	0.124
V	July 31, 2009	0.022	0.036	0.031
	Oct. 27, 2009	0.0043 c	0.0131 b	0.0205 a
	May 5, 2010	0.0052 b	0.0061 b	0.011 a
	Feb. 3, 2011	0.0047	0.0052	0.0061
Zn	July 31, 2009	0.084	0.222	0.053
	Oct. 27, 2009	0.058	0.048	0.033
	May 5, 2010	0.030	0.054	0.062
	Feb. 3, 2011	0.144	0.148	0.159

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DISCUSSION

Application of gypsum to soils has been hypothesized to provide several soil and crop benefits. This study reports on the effects of applying to soil either FGD gypsum or mined gypsum alone or in combination with lime. Cotton was the test crop, and cotton lint yield and cottonseed chemistry were also evaluated.

The rates of FGD gypsum or mined gypsum were as high as 8.96 Mg ha^{-1} (4.0 tons $acre^{-1}$), which is approximately 2-4 times higher than normally recommended for soils for peanut production, a crop commonly rotated with cotton in Alabama. The mined gypsum had much higher concentrations of Al, C, Fe, and Mg than the FGD gypsum and lower concentrations of Hg and S (Table 3-1). This indicated the mined gypsum was less pure (except for Hg) and contained substantial amounts of mineral material and lime ($CaCO_3$). The much higher pH and total neutralizing potential of the mined gypsum, compared to the FGD gypsum, also supports this claim.

Neither FGD gypsum nor agricultural gypsum had an effect on cotton lint yields (Table 3-6). This was attributed to the soil having sufficient S to meet crop needs. Soil pH remained at or below about 5.6 for all treatments, with the lime treatments improving pH values above the control only little or not at all. Gypsum is not a liming agent, but can sometimes counteract the negative effects of low pH by binding toxic Al^{3+}. There did not seem to be any negative effects of pH on cotton lint yields observed in this study.

The Hg concentration in the FGD gypsum (640 μg kg^{-1}) was 40 times greater than in the mined gypsum and about 20 times greater than in the background soil (Tables 3-1 and 3-5). However, because of the large volume of soil compared to the volume of FGD gypsum applied, there were no significant differences in plant uptake, as determined by measuring Hg in the cottonseed, or in the soil due to the high rate (8.96 Mg ha^{-1}) of FGD gypsum applied. Similarly, Hg concentrations in the vadose zone water were not statistically affected at the $P < 0.05$ level of significance, although the mean Hg concentrations for the plots with the high rate of FGD gypsum were always the highest (Table 3-8) and were approaching being significantly different compared to the control or the high rate of mined gypsum treatments.

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CONCLUSIONS

When gypsum, either FGD gypsum or mined gypsum, was applied at rates up to 8.96 Mg ha^{-1} (4.0 tons $acre^{-1}$) there were no effects on cotton lint yield observed compared to an untreated control, or where gypsum and lime were both applied at a 2.24 Mg ha^{-1} rate or lime was applied alone at the same rate. There were also few significant differences in the extractable or total concentrations of elements in soil or cottonseed due to gypsum treatment. Although Hg was higher in the FGD gypsum than in the soil or mined gypsum, we did not find the FGD gypsum addition increased Hg in soils and cottonseeds, but there were trends toward higher Hg concentrations in shallow soil water at the high rate (8.96 Mg ha^{-1}) of FGD gypsum application. Overall, FGD gypsum was found to be a suitable substitute for mined gypsum as a soil amendment in fields where cotton is being grown, including when in a rotation following peanuts.

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A

BASELINE SOIL SAMPLES

Table A-1
Baseline soil samples before gypsum treatments were applied. One composite soil sample was collected from each replication (block) of the study.

							Exchangeable Bases				Base Saturation		
Replication	**pH**	**OM**[a]	**LTI**[b]	**EC**[c]	**Avail P**[d]	**CEC**[e]	**Ca**	**K**	**Mg**	**Na**	**Ca**	**K**	**Mg**
		%		dS m^{-1}	mg kg^{-1}	cmol kg^{-1}	-------------- mg kg^{-1} --------------				--------------- % ---------------		
1	5.40	3.40	64.2	0.122	19	10.0	490	81	50	39	24.4	2.1	4.1
2	5.78	3.03	65.1	0.122	24	10.0	644	107	70	43	32.3	2.8	5.8
3	5.72	2.77	65.5	0.128	26	8.9	548	90	67	46	30.7	2.6	6.2
4	5.36	2.99	63.9	0.128	33	10.1	426	86	54	49	21.0	2.2	4.5

	Total		**Mehlich 3 Extractable**												
	C	N	Al	B	Ca	Cu	Fe	K	Mg	Mn	Mo	Na	P	S	Zn
	------ % ------		------ mg kg^{-1} ------												
1	1.57	0.09	868	0.91	597	0.79	55.3	73.5	65.5	30.0	0.03	9.36	11.6	54.6	4.45
2	1.56	0.09	801	0.88	782	1.03	51.6	96.4	96.1	47.1	0.04	6.59	22.1	46.3	2.64
3	1.40	0.08	834	0.90	692	1.18	46.8	80.8	94.8	39.1	0.08	19.9	22.5	48.8	5.07
4	1.47	0.09	908	0.83	489	3.19	54.4	74.8	72.9	37.2	0.04	11.0	28.2	45.0	5.06

[a] OM = organic matter.

[b] LTI = Lime Test Index

[c] EC = electrical conductivity

[d] Available P was determined by weak Bray (P1) extraction.

[e] CEC = cation exchange capacity.

Table A-1 (continued)
Baseline soil samples before gypsum treatments were applied. One composite soil sample was collected from each replication (block) of the study.

	EPA 3051 Extended Microwave Digestion												
Replication	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg
	mg kg^{-1}												
1	28500	7.82	4.85	53.3	<0.091	680	0.791	3.13	32.8	4.69	19500	588	543
2	22500	6.71	3.69	46.3	<0.091	835	0.723	2.73	55.7	1.66	17100	489	489
3	24006	5.62	4.44	49.4	<0.091	770	0.461	2.90	25.0	3.81	12300	600	557
4	24500	6.06	4.59	52.9	<0.091	574	0.406	3.19	25.3	3.97	12300	674	582

	EPA 3051 Extended Microwave Digestion												
	Mn	Mo	Na	Ni	P	Pb	S	Sb	Se	Si	Sr	V	Zn	Hg
	mg kg^{-1}													µg kg^{-1}
1	221	0.76	33.2	14.4	288	6.64	174	<1.05	<2.32	214	5.42	53.6	28.3	38.4
2	282	0.46	25.5	12.9	297	3.81	151	<1.05	<2.32	213	4.56	47.4	20.5	32.0
3	276	0.40	26.9	12.9	274	2.82	156	<1.05	<2.32	271	5.12	40.2	27.2	31.0
4	253	0.53	34.1	14.1	271	4.31	142	<1.05	<2.32	680	5.26	40.7	28.4	36.1

B

STAR LABORATORY QA/QC SAMPLES AND STANDARDS

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http://oardc.osu.edu/starlab/t08_pageview3/Home.htm

Quality assessment is the systematic measurement and documentation of bias, accuracy, and precision. It is used to determine if an analytical process is in statistical control and otherwise in compliance with QA program guidelines. There are several types of check samples used by STAR Laboratory personnel to assess laboratory performance internally. The type, purpose, frequency of use, and expected results and acceptance criteria for the different quality assurance/quality control samples used by the STAR Laboratory are described below.

B.1 Description of Quality Assurance/Quality Control Procedures

B.1.1 Assessing Bias and Contamination

STAR Laboratory includes at least one reagent blank in each set of samples analyzed. Blanks are run every 20 samples in sets larger than 30 samples. The frequency of use is intended to be at or near 5%. Each blank starts as an empty container and is carried through the entire procedure including reagent addition and subsequent processing, whether it be shaking and extraction or digestion and filtering. The blanks are diluted as samples and analyzed with the samples.

When analysis by ICP-AES is used, reagent blanks are generally below instrument detection limits for major- and micro-nutrients. When analyzing for trace elements, blanks are more likely to exhibit significant concentrations. If the blank values are consistent and cannot be eliminated, the blank value will be subtracted from the sample values.

B.1.2 Assessing Accuracy

Reference samples, used to assess precision and accuracy of analytical results, will constitute no less than 5% of the total number of samples. STAR Laboratory uses an array of standard reference materials (SRMs) to document the accuracy of analytical results. Table B-1 lists the SRMs and the certified elements used by STAR Laboratory. An SRM that is similar, but not exactly the same matrix as samples being analyzed, is selected and analyzed as an unknown sample.

Table B-1
Suitable standard reference materials (SRMs) for different types of samples

Company or Agency	Material ID	Analytes
SCP Science 348 Route 11 Champlain NY 12919-4816 800-361-6820 www.scpscience.com	CP-1 Compost	N P K Mg Ca Cu Fe Mn Zn Na pH
US Dept of Commerce National Institute of Standards & Technology Building 202, Room 204 Gaithersburg MD 20895 301-975-6776 www.nist.gov	SRM 2781 – Domestic Sludge	As Cd Cu Pb Hg Mo Ni Se Zn
	SRM 2782 – Industrial Sludge	Ca Fe Mg P K Na
	SRM 2704 – Buffalo River Sediment	Al Ca C Fe Mg P K Si Na S Ti Sb As Ba Cd Cr Co Cu Pb Li Mn Hg Ni Se Sr V Zn
	SRM 2709 – San Joaquin Soil	Al Ca Fe Mg P K Si Na S Ti Sb As Ba Cd Cr Co Cu Pb Mn Hg Ni Se Ag Sr V Zn
	SRM 1567a – Wheat Flour	Ca Mg P K S Al Cd Cu Fe Mn Mo Se Na Zn
	SRM 1633b – Coal Fly Ash	Al Ca Fe Mg K Si Na S Ti As Ba Cd Cr Cu Pb Mn Hg Ni Se Sr V
	SRM 1547 – Peach Leaves	Ca Mg P K N Al As Ba B Cd Cl Cu Fe Pb Mn Mo Ni Se Na Sr V Zn
	SRM 1570a – Spinach Leaves	Ca P K Na Al As B Cd Co Cu Mn Ni Se Sr V Zn
	SRM 1575 – Pine Needles	Ca P K Al As Cu Cr Fe Mn Ni Pb Sr

To supplement purchased SRMs, STAR Laboratory is enrolled in proficiency testing (PT) programs. In these programs, identical samples are sent to all cooperating laboratories, which analyze them according to specified methods and protocols. Accuracy of analytical results for testing methods, which may not be available from purchased SRMs, can be obtained in this way. Typically, median and mean absolute deviation (MAD) statistics are reported for each analyte and for each method, based on the data returned by participating labs. Any results from a contributing lab that are outside acceptable control limits are flagged on the report to that laboratory. While median values from PT reports do not constitute a certified or guaranteed analysis, values obtained from several laboratory sources can be considered closer to the "true" values than results derived solely from one laboratory.

STAR Laboratory is enrolled in two PT programs. The Compost Analysis Proficiency testing program (CAP) is available through the U.S. Composting Council (contact: USU Analytical Lab, Utah State University, Logan UT 84322 or http://tmecc.org/cap/contact.html). The North American Proficiency Testing program (NAPT) for soil and plant analysis is an activity of the Soil Science Society of America (contact: USU Analytical Lab, Utah State University, Logan UT 84322 or http://www.naptprogram.org).

Samples from PT programs are of high quality and can be stabilized by refrigeration as necessary. Median values can be used in lieu of certified content and any remaining sample used as a surrogate SRM to document accuracy. This is especially useful where no purchased SRM of similar matrix and/or concentration range is available.

Accuracy of solution analysis is documented using a quality control check sample (QCCS). A QCCS is a solution of known content, which is derived from a source separate from, or independent of, the source for the calibration standards. QCCS solutions are made in-house using separate stock solutions from a different scientific supply vendor. The contents of a QCCS should be within the normal range of sample unknowns for all analytes. It serves as an independent verification of the calibration standards and is also used as a check of calibration drift or stability. Accuracy control limits for a QCCS are set as a fixed range of percent recovery of known content for each analyte. The frequency of use of a QCCS is at or near 10% of the number of samples analyzed.

The Lowest Detection Limits (LDLs) for various types of samples are provided in Table B-2. The LDLs are a function of dilution and instrument capabilities. For water, the LDLs are 200 times less than for plants, soil, or other types of solid tissues because of the need for chemical digestions, which leads to dilution effects prior to analysis by ICP-AES. The Limits of Quantitation are calculated values and are given as three times the LDLs for each element and each sample type.

B.1.3 Assessing Precision

STAR Laboratory uses a variety of check samples to monitor method precision. Check samples or internal reference samples are large, stabilized (dried or refrigerated) samples. These check samples have been thoroughly ground and mixed to homogenize them. Subsamples of check samples are run with each batch of sample unknowns. STAR Laboratory analyzes at least one check sample with every sample set. Frequently, they are analyzed along with SRMs and the samples. Check samples are selected not only to match the type of sample but also to provide a range of results on a specific element or analysis. Precision control limits are derived from the standard deviation from the mean of these repeated measurements. Many of the check samples have data covering ten or more years and hundreds of analyses. Proficiency testing samples are also used as check samples. Acceptance limits are calculated for each check sample and used to check precision. If check sample data fall outside the 2 standard deviation limits, then reasons for the failure are determined and corrective actions taken. The frequency of use of SRMs and PT samples combined is at or near 5% of the number of samples analyzed.

B.2 Statistical Control and Control Charts

Accuracy is measured in terms of the deviation or relative deviation of a measured value from the known or certified value. Precision is presented in terms of standard deviation (SD) from the mean of repeated measurements on the same sample or in terms of relative percent difference (RPD) between replicate analyses of the same sample. Together, accuracy and precision document the systematic and random errors that constitute analytical uncertainty in all laboratory results.

Accuracy and precision statistics are the performance criteria used to determine if a methodology is in “statistical control”—that is, whether method control limit standards are being met daily and over the long term. Check sample statistics can also be used by technicians and managers as daily decision-making tools during sample analysis to determine if expected results are being generated and if the analytical system is functioning properly at any given time. Determining that a problem exists at the time it is happening can save a great deal of lost time in running samples over again at a later date (Delavalle, 1992).

B.2.1 X-Charts

Quality assessment statistics can be presented graphically, through control charts, for ease of interpretation. STAR Laboratory uses X-charts to present both accuracy and precision data. Repeated measurements of external or internal reference samples are graphed on a time line. A minimum of seven measurements is needed, although 15 are recommended for valid statistical calculations (Taylor, 1987). Included with the individual results is the cumulative mean (in the case of an internal reference sample) or the known content (in the case of an external SRM or PT sample). Upper and lower warning limits (UWL and LWL) are calculated as +/- 2 SD, and upper and lower control limits (UCL and LCL) are calculated as +/- 3 SD. In a normally distributed sample population, +/- 2 SD represents a 95% confidence interval (CI) and +/- 3 SD corresponds approximately to a 99% CI.

An individual value between UWL and UCL or LWL and LCL is considered acceptable, although two or more in a row are unacceptable. A single value outside UCL or LCL is considered unacceptable. If statistical control is considered unacceptable, based on either standard, all routine sample unknowns run since the last check sample are rerun. Check sample results that fall within the warning limits, but that are exhibiting a trend toward the UWL or LWL, can signal a potential problem in the process that needs to be addressed (Delavalle, 1992). X-charts are especially useful as a day-to-day tool to monitor ongoing or emerging problems.

Accuracy and precision statistics are documented and updated when the check or reference samples are analyzed.

Table B-2
Lowest Detection Limits and Limits of Quantitation for water, soil, and plant samples. Samples were digested using a modified EPA 3051A method before elements were quantified using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

		Lowest Detection Limits		Limit of Quantitation[b]	
Element	Wavelength nm	Water mg L^{-1}	Soils and Plants[a] mg kg^{-1}	Water mg L^{-1}	Soils and Plants mg kg^{-1}
Ag	328.070	0.001765	0.353000	0.00530	1.05900
Al	308.215	0.009942	1.988400	0.02983	5.96520
Al	396.152r	0.034925	6.985600	0.10478	20.9568
As	189.042	0.006421	1.284100	0.01926	3.85230
B	208.956	0.000762	0.152300	0.00229	0.45690
Ba	455.403r	0.000815	0.163000	0.00245	0.48900
Be	234.861r	0.000455	0.091000	0.00137	0.27300
Ca	422.673r	0.031016	6.203200	0.09305	18.60960
Cd	214.441	0.000371	0.074200	0.00111	0.22260
Co	228.615	0.007310	0.146200	0.02193	0.43860
Cr	267.716	0.000970	0.194000	0.00291	0.58200
Cu	324.754	0.002160	0.432000	0.00648	1.29600
Fe	259.940	0.001824	0.364800	0.00547	1.09440
Fe	263.132	0.011655	2.331000	0.03497	6.99300
Hg[c] (ng g^{-1})	-	0.001000	0.200000	0.00300	0.60000
K	766.491	0.180597	36.11940	0.54179	108.358
Li	670.784	0.000382	0.076400	0.00115	0.22920
Li	670.784	0.006393	1.278600	0.01918	3.83580
Mg	285.213r	0.003314	0.662800	0.00994	1.98840
Mn	257.610	0.001019	0.203800	0.00306	0.61140
Mo	277.540	0.001125	0.222500	0.00338	0.66750
Na	589.592r	0.065200	13.04100	0.19560	39.1230
Ni	231.604	0.001272	0.254400	0.00382	0.76320
P	178.283	0.027917	5.583400	0.08375	16.75020
P	214.914	0.016640	3.328000	0.04992	9.98400
Pb	220.353	0.003870	0.774000	0.01161	2.32200
S	180.731	0.025885	5.177000	0.07766	15.53100
Sb	206.833	0.005237	1.047300	0.01571	3.14190
Se	196.090	0.011605	2.321000	0.034815	6.96300
Si	288.158	0.003424	0.684800	0.01027	2.05440
Sr	407.771	0.000204	0.040800	0.00061	0.12240
V	310.230	0.001485	0.297000	0.04455	0.89100
Zn	206.200	0.001561	0.312200	0.00468	0.93660
Cs	894.347	0.131678	26.335600	0.39503	79.00680
Sn	283.999	0.004593	0.918600	0.01378	2.75580
Tl	190.864	0.007205	1.441000	0.02161	4.32300

[a] To account for dilutions and other analytical steps, the lowest detection limit for water must be multiplied by 200 to obtain the lowest detection limit for soil and plant samples on a mass basis.

[b] The Limit of Quantitation is defined as three times that of the Lowest Detection Limit.

[c] See Materials and Methods (Section 2 of this report) for details of soil digestion and analysis for Hg.

B.3 Data Collection and Reporting

Electronic data files are kept for all sample analyses. When possible, instrument data are transferred to client files electronically so that transcription errors are avoided. All data from STAR Laboratory's ICP-AES, ion chromatograph (IC), and N/C Analyzer are transferred electronically. All original files generated by instruments are maintained in the instrument computer as well as being backed up on a portable memory device.

Sample files are generated for each sample set and filed according to the sample log number and principle investigator's name—e.g., 1234 Doe. Periodically, all sample data files are compiled and saved on CDs.

Client notification and sample results are transmitted electronically except when the client specifically requests otherwise. Accuracy and precision statistics are reported only on demand when the client desires the results.

B.4 References

Delavalle, N.B. 1992. Handbook on Reference Methods for Soil Analysis. Quality Assurance Plans for Agricultural Testing Laboratories: 18-32. Soil and Plant Analysis Council, Inc. Athens, GA.

Taylor, J.K. 1987. Quality Assurance of Chemical Measurements. Lewis Publishers, Inc. Chelsea, MI.

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3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 USA
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