4th Annual
Midwest Soil Improvement Symposium: 2014
Research and Practical Insights into Using Gypsum

KANSAS STATE UNIVERSITY ALUMNI CENTER, AUGUST 13, 2014

GYPSOIL BRAND GYPSUM | KARA

4th Annual
Midwest Soil Improvement Symposium: 2014
Research and Practical Insights into Using Gypsum

History of Gypsum Use and Research Results On Crop Performance

Warren Dick, PhD
Soil Scientist and Professor
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The Ohio State University

AUGUST 13, 2014

GYPSOIL BRAND GYPSUM | KARA

Background, Role and Potential Crop Benefits in Using Gypsum

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College of Food, Agricultural, and Environmental Sciences

What is Gypsum?

Gypsum is a very soft mineral composed of calcium sulfate dihydrate, with the chemical formula $CaSO_4 \cdot 2H_2O$. The word gypsum is derived from a Greek word meaning "chalk" or "plaster". Because the gypsum from the quarries of the Montmartre district of Paris has long furnished burnt gypsum, this material has often been called plaster of Paris. Gypsum is moderately water-soluble. The source of gypsum is both mined and synthetic.

History of Gypsum in Agriculture

- Early Greek and Roman times
- Fertilizer value discovered in Europe in last half of 18th century
  - Germany (1768) – Reverend A. Meyer
  - France (date?) – Men working with alabaster (plaster of paris) noted better grass growth in areas they shook dust from clothing
- Extensive use in Europe in 18th century

Early History

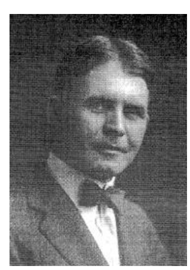
Benjamin Franklin

“This hill has been land plastered”

Early History

Doctor William Crocker was born in Medina County, OH on January 27, 1876. He received his A.B. degree in 1902 and an A.M degree in 1903 from the University of Illinois. From 1904 - 1906 he was a Fellow at the University of Chicago from which he obtained his PhD.

Early History



History of the Use of Agricultural Gypsum. 1922. Gypsum Industries Association, Chicago, IL (p. 7-36)

I. The Early Use of Gypsum as a Fertilizer

II. Recent Studies on the Function and Quantity of Calcium and Sulphur in Crops and the Supply of Sulphur in our Agricultural Soils.

III. Calcium in the Nutrition of Plants

Early History

History of the Use of Agricultural Gypsum. 1922. Gypsum Industries Association, Chicago, IL (p. 7-36)

IV. Gypsum as a Stimulant

V. Gypsum as Specific for Black Alkali

VI. Gypsum as a Preserver of Manure

VII. Effect of Gypsum on the Nitrogen Available for Crops

VIII. Gypsum Not a Substitute for Agricultural Lime

History of Gypsum in Agriculture

Gypsum as a Preserver of Nitrogen – In pioneering work by Heiden:

"Gypsum has great power in preserving the volatile nature of manure. It does this in large part by transforming the volatile ammonium carbonate into the non-volatile ammonium sulfate with the formation of calcium carbonate."

Further work on this topic was done by Ames and Richmond at The Ohio State Agricultural Experiment Station (Soil Science, 4:78-89, 1917). Using gypsum to preserve nitrogen for a 20 cow herd could provide $152 benefit in one year.

Gypsum Sources

- Mined Gypsum
- FGD gypsum - 24% of total U.S. gypsum in 2005
- Phosphogypsum – phosphoric acid production
  - 4.5 tons gypsum for each ton of phosphoric acid produced
- Titanogypsum – TiO_2 production
- Citrogypsum – citric acid production
- Biotech gypsum

Summary of Gypsum Benefits in Agriculture

- Ca and S source for plant nutrition
- Source of S and exchangeable Ca to ameliorate subsoil acidity and Al^{3+} toxicity
- Flocculate clays to improve soil structure and reclaim sodic and high magnesium soils
- Ca-humate and $CaCO_3$ formation in soil
- Treat liquid manure to enhance use efficiency
- Reduce phosphorus runoff from farm fields

Benefit #1

- **Ca and S source for plant nutrition**
- Source of S and exchangeable Ca to ameliorate subsoil acidity and Al^{3+} toxicity
- Flocculate clays to improve soil structure and reclaim sodic and high magnesium soils
- Ca-humate and $CaCO_3$ formation in soil
- Treat liquid manure to enhance use efficiency
- Reduce phosphorus runoff from farm fields

Relative Numbers of Atoms Required by Plants

Mo	1	P	60,000
Cu	100	Mg	80,000
Zn	300	Ca	125,000
Mn	1,000	K	250,000
B	2,000	N	1,000,000
Fe	2,000	O	30,000,000
Cl	3,000	C	35,000,000
S	30,000	H	60,000,000

Sulfur in Plant Physiology

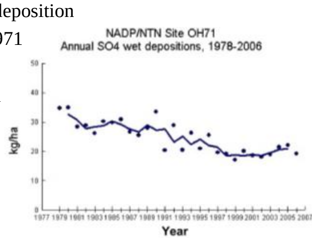
- Amino acids methionine and cysteine
  - Proteins
  - Precursors of other sulfur-containing compounds
- Sulfolipids (fatty compounds) in membranes, especially chloroplast membranes
- Nitrogen-fixing enzyme (nitrogenase)
  - 28 S atoms in active site

Causes of Sulfur Deficiencies in Crops

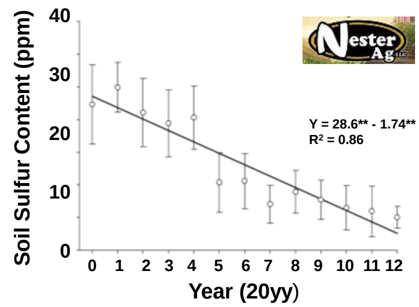
- Shift from low-analysis to high-analysis fertilizers
- High-yielding crop varieties use more S
- Reduced atmospheric S deposition
- Decreased use of S in pesticides
- Declining S reserves in soil due to loss of organic matter (erosion and tillage), leaching, and crop removal

Reduction in Atmospheric S Deposition

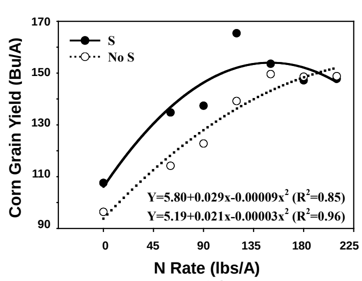
- Increasing in importance as cause for crop S deficiencies
- Loss of soil organic matter
- Reduced annual sulfate deposition
  - 34 kg sulfate/ha in 1971 (10 lb S/A)
  - 19 kg sulfate/ha from 2000 onward (5.7 lb S/A)



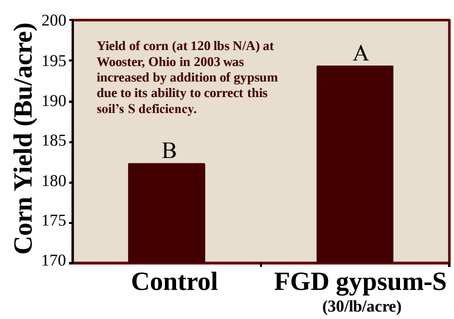
Soil Test Values - Sulfur



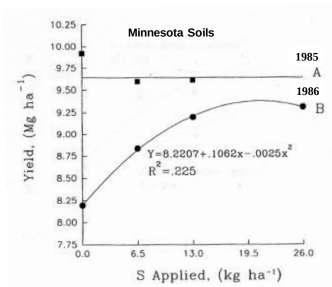
Average Corn Yields from 2002 to 2005 (Ohio)



Corn Yields in 2003 (Wooster, Ohio)

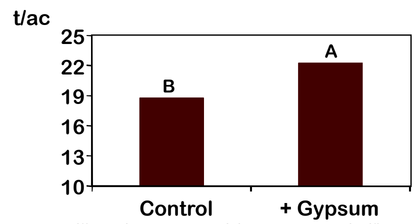


Corn (Sulfur Nutrition)



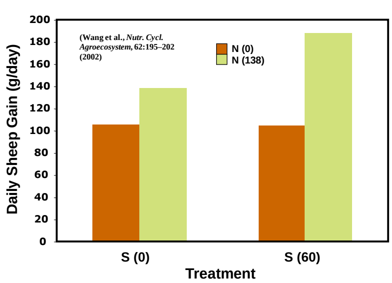
(Rehm, *Commun. Soil Sci. Plan Anal.*, 24:285-294, 1993)

Effect of Gypsum on Cumulative Alfalfa Yields at Wooster, OH (2000 - 2002)



Different letters over each bar represent a significant difference at $p \leq 0.05$.

Forage Quality and Fertilizer N Interaction



Calcium in Plant Physiology

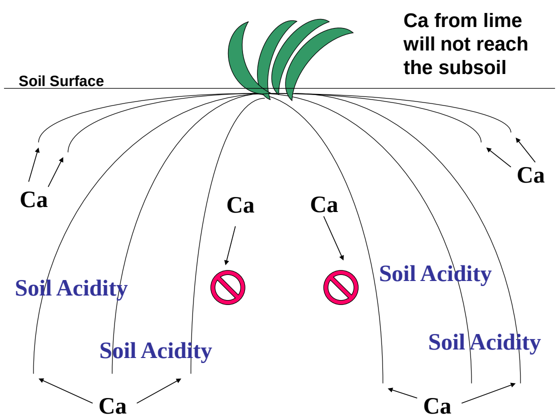
- Required for proper functioning of cell membranes and cell walls
- Needed in large amounts at tips of growing roots and shoots and in developing fruits
- Relatively little Ca is transported in phloem
  - Ca needed by root tips comes from soil solution

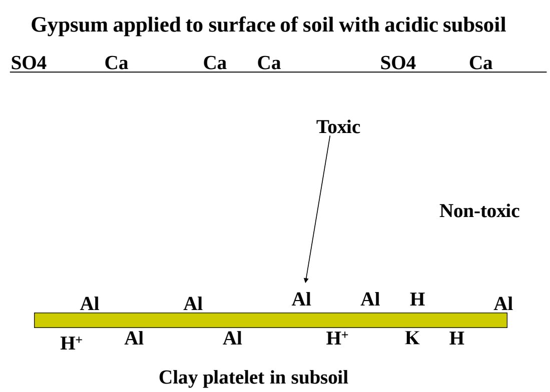
Benefit #2

- Ca and S source for plant nutrition
- **Source of S and exchangeable Ca to ameliorate subsoil acidity and Al^{3+} toxicity**
- Flocculate clays to improve soil structure and reclaim sodic and high magnesium soils
- Ca-humate and $CaCO_3$ formation in soil
- Treat liquid manure to enhance use efficiency
- Reduce phosphorus runoff from farm fields

Amelioration of Subsoil Acidity and Al^{3+} Toxicity

- Surface-applied gypsum leaches down to subsoil
- Ca^{2+} exchanges with Al^{3+}
- SO_4^{2-} complexes with Al^{3+} ion to form $AlSO_4^+$
- $AlSO_4^+$ is not toxic to plant roots
- Results in increased root growth in the subsoil

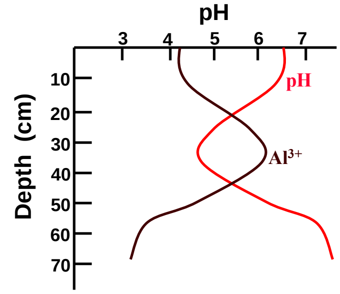




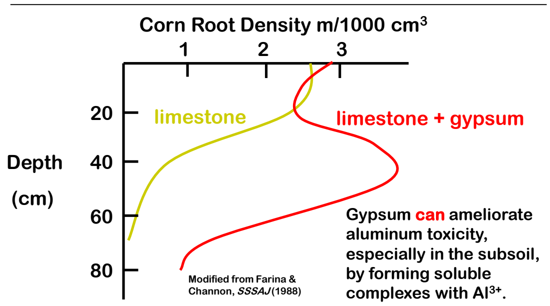
Increased Root Growth into Subsoil

- Increased water absorption
- Increased recovery of N from subsoil
  - Demonstrated in Brazilian soils
  - Improved N-use efficiency, Ohio, USA

Typical pH profile for a Blount soil

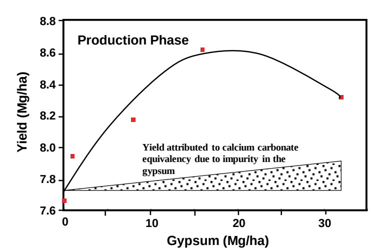


$CaSO_4 + Al^{3+} \longrightarrow Al(SO_4)^{+} + Ca^{2+}$
(toxic) (non-toxic)



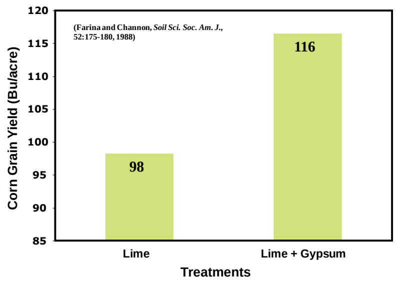
Gypsum can ameliorate aluminum toxicity, especially in the subsoil, by forming soluble complexes with Al^{3+}.

Forages (Subsoil Acidity)

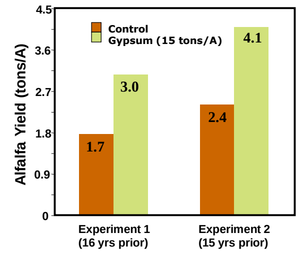


(Ritchey and Snuffer, *Agron. J.*, 94:830–839 (2002)

Increased Root Growth into Subsoil



Forages (Long-Term Effect)



Toma et al., *Soil Sci. Soc. Am. J.*, 63:891-895, 1999)

Conclusions

- **Benefits for corn and forages are associated with increased sulfur nutrition and reduced subsoil acidity.**
- **Benefits of gypsum use may persist for several years after application to soil.**
- **Inappropriate use of high rates of gypsum can decrease yield (due to nutrient imbalances).**

Benefit #3

- Ca and S source for plant nutrition
- Source of S and exchangeable Ca to ameliorate subsoil acidity and Al^{3+} toxicity
- **Flocculate clays to improve soil structure and reclaim sodic and high magnesium soils**
- Ca-humate and $CaCO_3$ formation in soil
- Treat liquid manure to enhance use efficiency
- Reduce phosphorus runoff from farm fields

Benefit #3

Soil Crusts

Gypsum applied to surface of sodic soil

$SO4$ Ca^{2+} Ca^{2+} Ca^{2+} $SO4$ Ca^{2+}

Na^{+} Na^{+} H^{+} Na^{+} Mg^{2+} K^{+} Al^{3+}

Clay platelet in sodic soil

Gypsum and Sodic Soil Reclamation (Colorado)

Print this fact sheet

no. 0.504

Managing Sodic Soils

by J.G. Davis, R.M. Waskom, and T.A. Bauder* (5/12)

Quick Facts...

- Sodic soils are poorly drained and tend to crust.
- Sodic soils respond to continued use of good irrigation water, good irrigation methods, and good cropping practices.
- Sodic soils are often reclaimed by adding a calcium-based soil amendment.

Gypsum and Sodic Soil Reclamation (China)

Comparison of field with (background) and without (foreground) FGD by-product gypsum

Benefit #4

- Ca and S source for plant nutrition
- Source of S and exchangeable Ca to ameliorate subsoil acidity and Al^{3+} toxicity
- Flocculate clays to improve soil structure and reclaim sodic and high magnesium soils
- **Ca-humate and $CaCO_3$ formation in soil**
- Treat liquid manure to enhance use efficiency
- Reduce phosphorus runoff from farm fields

Benefit #4

$$CaSiO_3 + 2CO_2 + 3H_2O = Ca^{2+} + 2HCO_3^- + H_4SiO_4$$

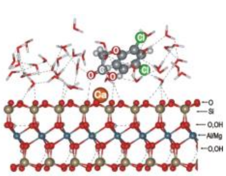
$$Ca^{2+} + 2HCO_3^- = CaCO_3 + H_2O + CO_2$$

NET: $CaSiO_3 + CO_2 + 2H_2O = CaCO_3 + H_4SiO_4$

Passive Sequestration of Atmospheric CO_2 Through Coupled Plant-Mineral Reaction in Urban Soils. Manning and Renforth, *Environ Sci. Tech*, 47:135-141, 2012.

Benefit #4

The cationic bridging effect of the calcium ion (Ca^{2+}) and the flocculating ability of clay and organic matter are crucial in the formation and stability of soil aggregates. (Wuddivira and Camps-Roach, Eur. J. Soil Sci., 2006).



The stability of microaggregates is enhanced by multivalent cations which act as bridges between organic colloids and clay. (Oades, Plant & Soil, 1984)

Benefit #5

- Ca and S source for plant nutrition
- Source of S and exchangeable Ca to ameliorate subsoil acidity and Al^{3+} toxicity
- Flocculate clays to improve soil structure and reclaim sodic and high magnesium soils
- Ca-humate and $CaCO_3$ formation in soil
- **Treat liquid manure to enhance use efficiency**
- Reduce phosphorus runoff from farm fields

Benefit #5

Calcium for precipitating organic matter when measuring enzyme activity in soil

Benefit #5

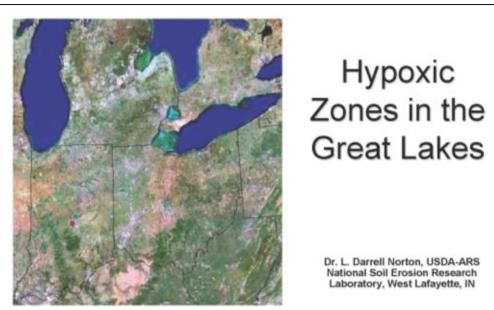
Precipitating liquid manure solids

Benefit #6

- ❑ Ca and S source for plant nutrition
- ❑ Source of S and exchangeable Ca to ameliorate subsoil acidity and Al^{3+} toxicity
- ❑ Flocculate clays to improve soil structure and reclaim sodic and high magnesium soils
- ❑ Ca-humate and $CaCO_3$ formation in soil
- ❑ Treat liquid manure to enhance use efficiency
- ❑ **Reduce phosphorus runoff from farm fields**

2014 All Ohio Chapter of the Soil & Water Conservation Society (Columbus, OH)

Water Quality - The Great Lakes



2014 All Ohio Chapter of the Soil & Water Conservation Society (Columbus, OH)

Water Quality - The Great Lakes

WATER QUALITY ...

Algae may spur new limits on fertilizers

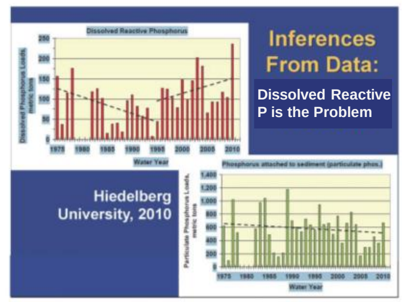
Are existing laws enough to protect Ohio from algae blooms?

PUBLISHED ON AUGUST 5TH, 2014

Toledo Mayor D. Michael Collins drinks tap water after his city lifted a water-use ban. (Paul Sancya, Associated Press)

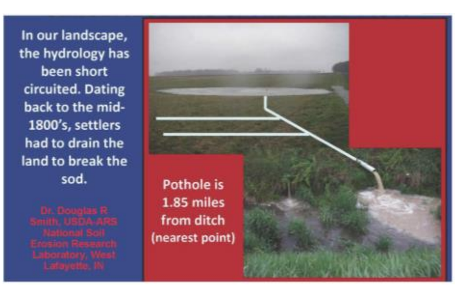
2014 All Ohio Chapter of the Soil & Water Conservation Society (Columbus, OH)

Water Quality - Lake Erie



Dr. Douglas R. Smith, USDA-ARS National Soil Erosion Research Laboratory, West Lafayette, IN

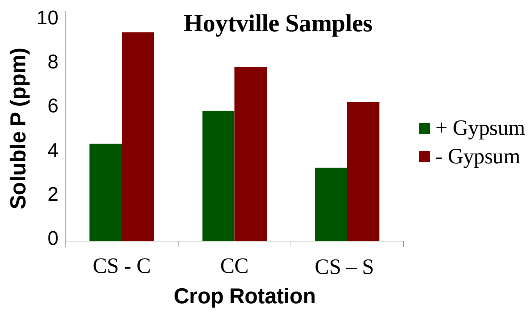
Water Quality - Agriculture



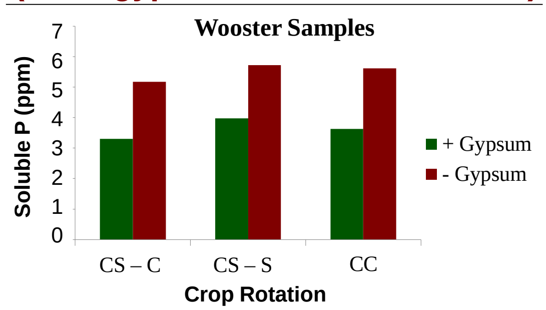
Phosphorus and Soil Management

Tillage System	Total P (0 - 12 in)	Reactive P (0 - 0.5 in)
	--------- mg/kg ----------	
Plow Till	580 (Wooster) 867 (Hoytville)	45 (Wooster) 38 (Hoytville)
No Till	609 (Wooster) 868 (Hoytville)	160 (Wooster) 282 (Hoytville)

Water Soluble P in 0.5 in soil layer (4 T/A gypsum, 1:3 w/v soil:water)

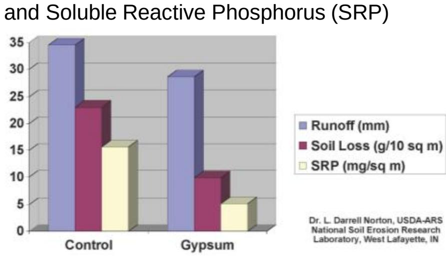


Water Soluble P in 0.5 in soil layer (4 T/A gypsum, 1:3 w/v soil:water)



Water Quality Benefits

Effect of Gypsum on Water Runoff, Soil Erosion and Soluble Reactive Phosphorus (SRP)



Dr. L. Darrell Norton, USDA-ARS National Soil Erosion Research Laboratory, West Lafayette, IN

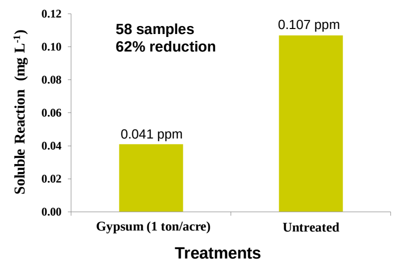
Tile Drain

Samples were collected from the Rolland Wolfrum Hale Farm (Hicksville, OH) on December 20, 2012.

Tile Drainage Samples (1)

Samples collected from the Ken Hahn Farm (Antwerp, OH) on January 6, 2013.

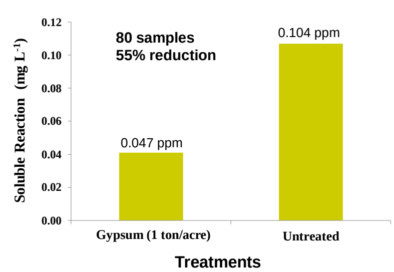
Conservation Innovation Grant (2011-July 2013)



Tile Drainage Samples (2)

Rolland Wolfrum farm samples 20 months after gypsum application

Conservation Innovation Grant (2011-present)



Summary of Results (to Date)

1. 43 total sampling events (126 total samples) from May 2012 through April 2014. P reductions in tile drainage water persist at least 20 months after gypsum treatment.
2. Reduction in P concentrations for individual gypsum-treated areas varied from 0 to 69%.

Summary of Results (to Date)

3. Average reductions for all gypsum-treated areas combined was 37%, with median reduction of 46% and a range from 0 to 93%.
4. P concentrations (mg/L) in drain water for individual sampling events ranged from 0.01 to 0.11 (mean = 0.042) in gypsum-treated areas and from <0.01 to 0.43 (mean = 0.085) in areas without gypsum.

Other Comments

Effects of Gypsum on Trace Metals in Soils and Earthworms

Special Section – Sustainable Use of FGD Gypsum for Agricultural Uses

Journal of Environmental Quality 43:263-272 (2014)

10 papers – all focused on gypsum use and in this case primarily, but not exclusively, environmental impacts.

Heavy Metal Impacts

Table 4. Concentrations of mercury, arsenic, and selenium in soils (0–10 cm layer).†

Location	Gypsum	Gypsum rate	Time‡	Hg	As	Se§
		Mg ha⁻¹	mo	µg kg⁻¹	mg kg⁻¹	
Ohio	FGD¶	20	5	65.8	11.2	0.473a
	mined	20	5	61.1	9.79	0.400b
	control	0	5	56.7	10.6	0.390b
Ohio	FGD	20	18	56.3	12.8	0.128
	mined	20	18	52.5	15.2	0.136
	control	0	18	52.2	13.0	0.100
Indiana	FGD	2.2	6	54.0	9.12	0.447
	mined	2.2	6	38.9	10.3	0.514
	control	0	6	44.7	9.40	0.410
Alabama	FGD	20	11	26.2	3.88	0.230
	mined	20	11	24.7	3.50	0.220
	control	0	11	26.7	3.53	0.216
Wisconsin	FGD	9.0	4	48.9 a	6.77	0.162
	mined	9.0	4	29.1 b	6.98	0.189
	control	0	4	29.5 b	7.75	0.187

† Values are means of four replications. Within a study site and element, means followed by no letters or the same letters are not significantly different at $p = 0.05$ using the LSD test.

‡ Length of time from gypsum application to soil sampling.

§ Selenium was measured after digestion using hydride generation atomic absorption spectrometry.

¶ Flue gas desulfurization.

Bioaccumulation Factors

Table 10. Bioaccumulation factors for mercury, arsenic, selenium, cadmium, zinc, copper, and molybdenum for nondepurated earthworms collected from soils.†

Location	Gypsum	Rate	Time‡	Bioaccumulation factors						
				Hg	As	Se	Cd	Cu	Mo	Zn
		Mg ha⁻¹	mo							
Ohio	FGD§	20	5	16.6	0.61	75.6	16.7	1.28	0.81	7.54
	mined	20	5	15.9	0.81	126	19.5	1.30	0.70	6.04
	control	0	5	13.9	0.53	78.4	11.1	1.02	0.42	4.41
Ohio	FGD	20	18	22.8	0.44	215	9.45	0.56	0.80	4.11
	mined	20	18	21.2	0.51	242	8.62	0.71	0.80	3.30
	control	0	18	19.5	0.39	271	9.50	0.66	1.02	4.19
Indiana	FGD	2.2	6	9.64	0.53	48.5	9.97	1.22	1.19	5.06
	mined	2.2	6	12.6	0.39	40.1	7.87	1.04	0.97	4.35
	control	0	6	11.7	0.44	35.8	6.82	1.13	1.55	4.11
Alabama	FGD	20	11	6.34	1.11	38.4	5.68	5.73	1.31	19.1ab
	mined	20	11	5.37	1.71	38.3	6.63	4.33	2.04	19.3a
	control	0	11	4.36	1.67	32.2	4.00	2.73	2.21	13.7bc
Wisconsin	FGD	9.0	4	3.70b	0.51	36.0	1.61	0.58	1.18	2.90
	mined	9.0	4	5.79a	0.59	31.2	1.87	0.55	1.61	3.08
	control	0	4	5.28a	0.51	23.5	1.81	0.58	1.22	3.22

† The bioaccumulation factor in this table was calculated as the ratio of the concentration of an element in a nondepurated earthworm to the concentration in the soil containing the earthworms. Values are means of four replications. Within a study site and element, means followed by no letters or the same letters are not significantly different at $p = 0.05$ using the LSD test.

‡ Length of time from gypsum application to soil sampling.

§ Flue gas desulfurization.

Amending Soil Properties With Gypsiferous Products

CONSERVATION PRACTICE STANDARDS (DRAFT)

NATURAL RESOURCES CONSERVATION SERVICE
AMENDING SOIL PROPERTIES WITH GYPSIFEROUS PRODUCTS

(Ac.)

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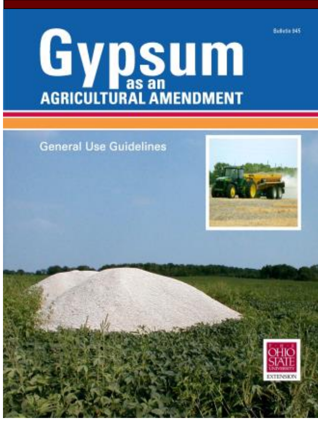


http://ohioline.osu.edu/b945/b945.pdf

Development of Network for FGD Gypsum Use in Agriculture

http://www.oardc.ohio-state.edu/agriculturalfgdnetwork

Workshop sponsored by:

Combustion ByProducts Recycling Consortium (CBRC)

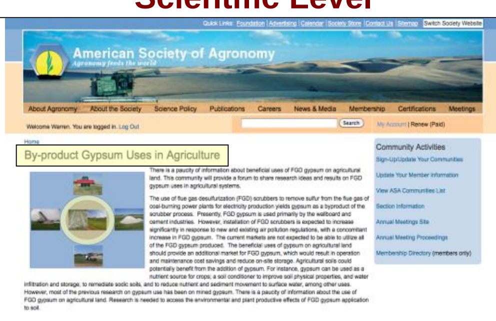
Electric Power Research Institute (EPRI)

The Ohio State University

U.S. Department of Energy/National Energy Technology Laboratory

November 4 (afternoon), Pittsburgh, PA
https://www.acsmeetings.org/

Increasing National Interest at the Scientific Level



THANK YOU!