Flue Gas Desulfurization Gypsum Materials in Agriculture

Gypsum as a soil amendment and fertilizer for the production of commercial crops

Warren Dick
School of Environment and Natural Resources
The Ohio State University, Wooster, OH
dick.5@osu.edu; 330-263-3877
We are entering a time of chronic food scarcity, one that is leading to intense competition for control of land and water resources—in short, a new geopolitics of food.

—Lester R. Brown
Crop Surpluses?

- In the past, the world had two safety cushions in case of harvest shortfall:
  - idled U.S. cropland
  - large stocks of grain

- Now, we have lost those two safety cushions
  - U.S. abandoned cropland set aside programs
  - grain stocks have fallen dangerously low

World Grain Stocks as Days of Consumption, 1990-2012
Increased Food Prices

- Rising demand and tightening supply raise world food prices to new heights.
- For consumers who spend 50–70% of their income on food, higher prices mean eating less.
New Uses of Crops

- U.S. corn is largest crop of any grain worldwide, critical to world supplies
- Close to 1/3 of U.S. grain now going to ethanol
Plateauing of Crop Yields

- Farmers in France, Germany, and the United Kingdom (the three leading wheat producers in Western Europe) appear to have reached upper biological limits, exhausted the backlog of agricultural technology.
Worsening Soil Erosion

Overplowing, overgrazing, and deforestation make soil vulnerable to wind and water erosion

Roughly 1/3 of the world’s cropland is now losing topsoil faster than it can be re-formed

Topsoil loss reduces productivity, eventually leading to lower yields and higher prices
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
What is Gypsum?

Gypsum is a very soft mineral composed of calcium sulfate dihydrate, with the chemical formula CaSO$_4$·2H$_2$O. 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.
Gypsum Benefits in Agriculture

Arthur Wallace (1994)

“Use of gypsum on soil where needed can make agriculture more sustainable”

Lists 30 benefits from use of gypsum but there is some overlap of functions

We have also conducted a review on this topic.
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<sup>3+</sup> toxicity
- Flocculate clays to improve soil structure and reclaim sodic and high magnesium soils
- Growth media component for mushroom production - approximately 60 kg/ton compost
- Ca-humate and CaCO<sub>3</sub> formation in soil
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
## Relative Numbers of Atoms Required by Plants

<table>
<thead>
<tr>
<th>Element</th>
<th>Required (Atoms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>1</td>
</tr>
<tr>
<td>Cu</td>
<td>100</td>
</tr>
<tr>
<td>Zn</td>
<td>300</td>
</tr>
<tr>
<td>Mn</td>
<td>1,000</td>
</tr>
<tr>
<td>B</td>
<td>2,000</td>
</tr>
<tr>
<td>Fe</td>
<td>2,000</td>
</tr>
<tr>
<td>Cl</td>
<td>3,000</td>
</tr>
<tr>
<td>S</td>
<td>30,000</td>
</tr>
<tr>
<td>P</td>
<td>60,000</td>
</tr>
<tr>
<td>Mg</td>
<td>80,000</td>
</tr>
<tr>
<td>Ca</td>
<td>125,000</td>
</tr>
<tr>
<td>K</td>
<td>250,000</td>
</tr>
<tr>
<td>N</td>
<td>1,000,000</td>
</tr>
<tr>
<td>O</td>
<td>30,000,000</td>
</tr>
<tr>
<td>C</td>
<td>35,000,000</td>
</tr>
<tr>
<td>H</td>
<td>60,000,000</td>
</tr>
</tbody>
</table>
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 S deposition
  - 34 kg/ha in 1971 (30 lbs/A)
  - 19 kg/ha in 2002 (17 lbs/A)

Graph: NADP/NTN Site OH71 Annual SO4 depositions, 1978-2001


Amount: 0 10 20 30 40 50 kg/ha
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
Amelioration of Subsoil Acidity and $\text{Al}^{3+}$ Toxicity

- Surface-applied gypsum leaches down to subsoil
- $\text{Ca}^{2+}$ exchanges with $\text{Al}^{3+}$
- $\text{SO}_4^{2-}$ complexes with $\text{Al}^{3+}$ ion to form $\text{AlSO}_4^{+}$
- $\text{AlSO}_4^{+}$ is not toxic to plant roots
- Results in increased root growth in the subsoil
Ca from lime will not reach the subsoil

Soil Acidity

Ca

Soil Acidity

Ca

Soil Acidity

Ca

Soil Acidity

Ca
Gypsum applied to surface of soil with acidic subsoil

Clay platelet in subsoil

SO₄  Ca  Ca  Ca  SO₄  Ca

H⁺  Al  Al  Al  H⁺  K  H  Al

Toxic

Non-toxic
Typical pH profile for a Blount soil
CaSO$_4$ + Al$^{3+}$ (toxic) \[ \rightarrow \] Al(SO$_4$)$^+$ + Ca$^{2+}$ (non-toxic)

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

Increased Root Growth into Subsoil

- Increased water absorption
- Increased recovery of N from subsoil
  - Demonstrated in Brazilian soils
  - Improved N-use efficiency, Ohio, USA
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
Gypsum applied to surface of sodic soil

<table>
<thead>
<tr>
<th>SO₄</th>
<th>Ca²⁺</th>
<th>Ca²⁺</th>
<th>Ca²⁺</th>
<th>SO₄</th>
<th>Ca²⁺</th>
</tr>
</thead>
</table>

Clay platelet in sodic soil
Gypsum and Sodic Soil Reclamation in China

Comparison of field with (background) and without (foreground) FGD by-product gypsum
Corn/Wheat Production and Gypsum
Increased Root Growth into Subsoil

Yield of corn (at 120 lbs N/A) at Wooster, Ohio in 2003 was increased by addition of gypsum due to its ability to correct this soil’s S deficiency.
Average Corn Yields from 2002 to 2005 (Ohio)

Yield = 5.80 + 0.029x - 0.00009x^2 (R^2=0.85)

Yield = 5.19 + 0.021x - 0.00003x^2 (R^2=0.96)

S
No S

Corn Grain Yield (Bu/A)

N Rate (lbs/A)
Corn (Sulfur Nutrition)

[Graph showing the relationship between sulfur applied (kg ha⁻¹) and yield (Mg ha⁻¹) for Minnesota Soils in 1985 and 1986. The line equation is Y = 8.2207 + 0.1062x - 0.0025x² with R² = 0.225.]

Corn (Sulfur Nutrition)

Wheat (Sulfur Nutrition)

Grain yield was significantly influenced by applied S as CaSO$_4$ in six of 14 site-years.

(Hennessey Site (1998))

(Girma et al., *J. Plant Nutr.*, 28:1541–1555 (2005))
Forages Production and Gypsum
Effect of CFB and ag-lime in farmer’s field

Dry Weight of Alfalfa (tons/A)

Treatment

Control CFB Ag-lime

Different letters over each bar represent a significant difference at \( p \leq 0.05 \).
Alfalfa (Sulfur Nutrition)

(Mitchell and Ball, *Alabama Agri. Exp. Station*, Spring, 1972)
Forage Quality and Fertilizer N Interaction

Forages (Subsoil Acidity)

(Black and Cameron, New Zealand J. Agric. Res. 27:195-200, 1984)
Corn Silage (Sulfur Nutrition)

(Kless et al., Grass and Forage Science, 44:277-281, 1989)
Forages (Comparison of Gypsum Sources)

Soluble Al content in the 45-60 cm soil layer was decreased 43% by treatment regardless of gypsum source.


Coal Combustion Products Utilization and Management Workshop (Lexington, KY: 8-9 September 2012)
Forages (Long-Term Effect)


Experiment 1 (16 yrs prior)
- Control: 1.7 tons/A
- Gypsum: 3.0 tons/A

Experiment 2 (15 yrs prior)
- Control: 2.4 tons/A
- Gypsum: 4.1 tons/A

Coal Combustion Products Utilization and Management Workshop (Lexington, KY: 8-9 September 2012)

Forages (Gypsum from Wallboard)

Forages (Subsoil Acidity)

Yield attributed to calcium carbonate equivalency due to impurity in the gypsum

Grasslands in the humid southern USA are utilized primarily for grazing on improved pastures, most of which were developed since the 1930s and 1940s. Future areas of emphasis in improvement of these grasslands may include: (a) greater use of grazing-tolerant grasses and legumes; (b) stress-tolerant tall fescue with "friendly" non-toxic endophytes; (c) feed antidotes to the toxins of endophyte-infected tall fescue; (d) use of herbicide-and pest-resistant biotechnology genes in forage plants; (e) use of gypsum to alleviate subsoil acidity and improve rooting depth of aluminum-sensitive forage cultivars; (f) greater use of computers in information access and decision making by livestock producers; (g) greater use of forages for wildlife food; (h) breeding of pasture plants with greater winter productivity; (i) development of a perennial grass biomass energy industry for electrical generation and liquid fuel production.
Conclusions

- The scientific literature contains numerous examples of corn grain yield and forage yield benefits associated with use of gypsum.
- Benefits for corn and forages are often associated with increased sulfur nutrition and reduced subsoil acidity.
- Treating sodic soils with gypsum increases productivity of the soil for crop production.
- 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).
Water Quality Benefits

Offsite Water Quality Problems

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

Eutrophication in Lake Erie

This glass of water came from this Microsistis bloom

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

Hypoxic Zones in the Great Lakes

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

In our landscape, the hydrology has been short circuited. Dating back to the mid-1800’s, settlers had to drain the land to break the sod.

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

Pothole is 1.85 miles from ditch (nearest point)
Water Quality Benefits

Inferences From Data: No-Till is the Problem

Hiedelberg University, 2010

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

Effect of Gypsum on Erosion

- Runoff (mm)
- Soil Loss (g/10 sq m)
- SRP (mg/sq m)

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

Gypsum Effect on N and P

Dr. L. Darrell Norton, USDA-ARS National Soil Erosion Research Laboratory, West Lafayette, IN
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/
Gypsum as an Agricultural Amendment

General Use Guidelines

http://ohioline.osu.edu/b945/b945.pdf
Increasing National Interest at the Scientific Level

From: Ann Wolf <amw2@psu.edu>
Date: December 6, 2010 1:24:18 PM EST
To: sssa_s4s8@acs-net.soils.org
Subject: 2011 S8 Symposia Topics

To: S4/S8 members (Soil Fertility and Plant Nutrition/Soil Management and Soil & Plant Analysis)

Thanks to all of you who provided input on symposia topics for the 2011 annual meeting. Based on the feedback provided, S8 will be sponsoring the two symposia listed below. Ann Wolf (S8 Division Chair)

NOTE: One related to sulfur is shown below.

-----------------------------

Development of Soil-Test Based Recommendations: Historical Perspectives, Current Issues and Future Directions

Can Sulfur Still Be Ignored? Crop Responses, New Management Strategies, and Improved Methods for Assessing Sulfur Needs

Organizer: John Kovar (john.kovar@ars.usda.gov) ; Co-sponsored with the Canadian Soil Science Society

During the past ten years, sulfur deficiencies and crop responses to sulfur fertilizer have been reported with increasing frequency worldwide. This symposium will focus on crop species and soils most vulnerable to sulfur problems in today's high-yield production systems, new strategies for managing sulfur inputs, and recent improvements in assessing sulfur availability and crop sulfur status.
Increasing National Interest at the Scientific Level
Increasing National Interest at the Scientific Level

By-product Gypsum Uses in Agriculture

There is a paucity of information about beneficial uses of FGD gypsum on agricultural land. This community will provide a forum to share research ideas and results on FGD gypsum uses in agricultural systems.

The use of flue gas desulfurization (FGD) scrubbers to remove sulfur from the flue gas of coal-burning power plants for electricity production yields gypsum as a byproduct of the scrubber process. Presently, FGD gypsum is used primarily by the wallboard and cement industries. However, installation of FGD scrubbers is expected to increase significantly in response to new and existing air pollution regulations, with a concomitant increase in FGD gypsum. The current markets are not expected to be able to utilize all of the FGD gypsum produced. The beneficial uses of gypsum on agricultural land should provide an additional market for FGD gypsum, which would result in operation and maintenance cost savings and reduce on-site storage. Agricultural soils could potentially benefit from the addition of gypsum. For instance, gypsum can be used as a nutrient source for crops; a soil conditioner to improve soil physical properties; and water infiltration and storage; to remediate sodic soils; and to reduce nutrient and sediment movement to surface water, among other uses. However, most of the previous research on gypsum use has been on mined gypsum. There is a paucity of information about the use of FGD gypsum on agricultural land. Research is needed to access the environmental and plant productive effects of FGD gypsum application to soil.

View the By-product Gypsum Uses in Agriculture Community Leadership Roster
Thanks for the information. I sent an email to schedule a meeting with him.

Also, on our call for Thursday we would like to discuss how we figure how many tons per acre need to be applied. Our consulting company develops a lot of Nutrient Management Plans, we take the soil test with the manure analysis and establish the application rate through spreadsheets that we have developed. We would like to establish a similar process to show how many tons of gypsum should be applied to a cropfield, soil type, projected yield goal, gypsum analysis and soil test. We will have to document this type of information back to the regulatory authorities here in .

Let me know your thoughts. Thanks.
THANK YOU!