Fluid Fertilizer Technology Workshop 2008

Session B: Fluid Sulfurs

Soil Amendments

Tom Fairweather

Tessenderlo Kerley

Western Fertilizer Handbook

Commonly Used Materials and Their Equivalent Amendment Values (Table 10-4)

Material 100% Basis	Chemical Formula	Tons of Amendment Equivalent to:	
		1 Ton of Pure Gypsum	1 Ton of Soil Sulfur
Gypsum	$CaSO_4 \cdot 2H_20$	1.00	5.38
Soil Sulfur	S	0.19	1.00
Sulfuric acid (conc.)	H_2SO_4	0.61	3.20
Ferric sulfate	$Fe_2(SO_4)_3 \cdot 9H_2O$	1.09	5.85
Lime sulfur 22% S	CaS_x	0.68	3.65
Aluminum sulfate	$AL_2(SO_4)_3 \cdot 18H_2O$	1.29	6.94
Ammonium polysulfide	$(NH_4)_2S_x$	0.37	1.95

NH_4 in APS is assumed to neutralize 1.8 lbs of $CaCO_3$ when a crop is present.

From "Water Penetration Problems in California Soils"

Soil Amendments

Chemical Name	Trade Name/ composition	Tons equal to one ton sulfur	Lbs required per acre to replace 1 meq/100g of Na in 6" of soil	Pounds required per acre foot of water to obtain 1 meq/L of calcium	Chemical reaction in calcareous soils
Elemental sulfur	100 % sulfur	1.00	321	43.6	$2S + 3O_2 + 2 CaCO_3 + 4NaX = 2CaX_2 + 2NaSO_4 + 2 CO_2$
Gypsum	100% $CaSO_4 \cdot 2H_2O$	5.37	1720	234	$CaSO_4 + 2NaX = CaX_2 + Na_2SO_4$
N-Phuric	10% N 55% Sulfuric acid	3.40 5.56	1090 1780	148	$H_2NCONH_2 \cdot H_2SO_4 + CaCO_3 + 2NaX = CaX_2 + H_2NCONH_2 + Na_2SO_4 + CO_2 + H_2O$
Ammonium Thiosulfate	Thio-Sul 12-0-0-26S	2.52 7.70	807 2470	110 336	$(NH_4)2S_2O_3 + 2O_2 + CaCo_3 + 2NaX = CaX_2 + (NH_4)2SO_4 + Na_2SO_4 + CO_2$
Ammonium polysulfide	Nitro-Sul 20-0-0-40S	1.59 3.13	510 1000	69.1 136	$(NH_4)_2S_5 + 8O_2 + 4CaCO_3 + 8NaX = 4CaX_2 + (NH_4)_2SO_4 + 4CO_2$
Sulfuric acid	100% H_2SO_4[a]	3.06	981	143	$H_2SO_4 + CaCO_3 + 2NaX = CaX_2 + Na_2SO_4 + CO_2 + H_2O$

Modified from Table 4.1

Purpose of Soil Amendments

- Reduce the amount of sodium in the soil
- Improve water infiltration
- Softens the soil
- Release other nutrients; P, Zn, etc.
- Indirectly provides S nutrition
  - Improves crop quality
  - Improves nitrogen utilization
  - Reduces plant stress

Comparison of Soil Amendments

Elemental Sulfur oxidation

$$\mathbf{S + 1.5\ O_2 + H_2O \xrightarrow{\text{Thiobacillus}} H_2SO_4}$$

32 **98**

1 lb of S will produce 3.06 lbs of sulfuric acid in the soil.

Comparison of Soil Amendments

- **H_2SO_4 + $CaCO_3$ $\longrightarrow$ $CaSO_4$ + H_2O + CO_2**

  98 100

- 1 lb of sulfuric acid will neutralize 1.02 lbs of $CaCO_3$
- 1 lb of elemental S will neutralize 3.125 lbs of $CaCO_3$
- 3.06 X 1.02 = 3.125 lbs

Ammonium - NH_4

- $NH_3 + H_2O \longrightarrow NH_4 + OH^-$
- $NH_4 + 3/2O_2 \xrightarrow{\text{Nitrosomonas}} NO_2 + H_2O + 2H^+$
- $NO_2 + 1/2O_2 \xrightarrow{\text{Nitrobacter}} NO_3$
- $2H^+ + OH^- \longrightarrow H_2O + H^+$

Net products: $NO_3^- + H^+ + 2H_2O$ or 1 H^+/1 N

Ammonium will neutralize 3.6 lbs of $CaCO_3$ per lb of N

From: “Fluid Fertilizer Science and Technology” by Palgrave

Urea

- $(NH_2)_2CO + H_2O \xrightarrow{\text{urease}} (NH_4)_2CO_3$
- $(NH_4)_2CO_3 + 2H_2O \longrightarrow 2NH_4^+ + 2OH^- + CO_2 + H_2O$
- $2NH_4^+ + 3O_2 \longrightarrow 2NO_2^- + 2H_2O + 4H^+$
- $2NO_2^- + O_2 \longrightarrow 2NO_3^-$
- $2OH^- + 4H^+ \longrightarrow 2H_2O + 2H^+$

Net products: $2NO_3^- + 2H^+ + 5H_2O$ or 1 H^+/ 1N

Urea will neutralize 3.6 lbs of $CaCO_3$ per lb of N

From: "Fluid Fertilizer Science and Technology" by Palgrave

Comparison of Soil Amendments

- 1 lb of N as Ammonium (NH4) will neutralize 3.6 lbs of $CaCO_3$
- 1 lb of N as Urea will neutralize 3.6 lbs of $CaCO_3$
- 1 lb of elemental sulfur will neutralize 3.12 lbs of $CaCO_3$
- 1 lb of sulfuric acid will neutralize 1.02 lbs of $CaCO_3$

Comparison of Soil Amendments

Product	Lbs $CaCO_3$ Neutralized	Lbs of Sulfuric acid
1 lb of N as NH_4	3.6	
1 lb of N as urea	3.6	
1 lb of elemental S	3.12	
1 lb of sulfuric acid	1.02	
1 lb of S will produce		3.06

Comparison of Soil Amendments
Sulfuric acid

- 1 ton of 93% sulfuric acid has 1860 lbs of acid
- 1860 lbs X 1.02 lbs of $CaCO_3$ = 1897 lbs $CaCO_3$ neutralized

Comparison of Soil Amendments N-Phuric 15/49

- N-Phuric is 15% N as urea with 49% sulfuric acid
- 2000 lbs X .49 = 980 lbs of sulfuric acid
- 980 lbs of acid X 1.02 lbs $CaCO_3$ = 1000 lbs $CaCO_3$ neutralized
- 300 lbs N as urea X 3.6 lbs $CaCO_3$ = 1080 lbs of $CaCO_3$
- Total = 2080 lbs of $CaCO_3$ plus the value of the nitrogen

15/49 VS Sulfuric Acid

- 15/49 will neutralize 2080
- Sulfuric acid will neutralize 1897
- The difference is in the value of the nitrogen

Comparison of Soil Amendments N-Phuric 10/55

- N-Phuric is 10% N as urea with 55% sulfuric acid
- 2000 lbs X .55 = 1100 lbs of sulfuric acid
- 1100 lbs of acid X 1.02 lbs $CaCO_3$ = 1122 lbs $CaCO_3$ neutralized
- 200 lbs N as urea X 3.6 lbs $CaCO_3$ = 720 lbs of $CaCO_3$
- Total = 1842 lbs of $CaCO_3$ plus the value of the nitrogen

Comparison of Soil Amendments

Lime Sulfur

6.0% Ca and 22% S

- **440 lbs S/ton X 3.12 lbs $CaCO_3$ = 1375 lbs of $CaCO_3$ neutralized per ton of product**
- **Contains 6.0% calcium equivalent to 300 lbs of calcium carbonate**
- **Total = 1675 lbs of $CaCO_3$**

APS

20-0-0-40S

- 800 lbs S X 3.12 lbs = 2,500 lbs of $CaCO_3$ neutralized.
- One pound of N as ammonium will neutralize 3.6 lbs of $CaCO_3$ = 400 X 3.6 = 1440 lbs.
- 2,500 + 1440 = 3,940 pounds of $CaCO_3$ neutralized per ton of product.

APS vs Sulfuric acid

- One ton of APS will neutralize 3,940 pounds of $CaCO_3$ (lime).
- One ton of 93% sulfuric acid will neutralize 1,897 pounds of $CaCO_3$.
- 3,937 / 1,897 = 2.074 tons: It will take this much sulfuric acid to equal the acidity developed by APS.

APS vs Sulfuric Acid

Product	Sulfuric Acid 93%	APS 20-0-0-40S
Lbs/gal	**15.3**	**9.4**
Gal/ton	**130.7**	**212**
Amount of calcium carbonate neutralized/ton	**1,897 lbs**	**3,940 lbs***
Lbs of $CaCO_3$ neutralized/gal	**14.5**	**18.5**
Lbs nitrogen/gal	**0**	**1.9**

- One pound of ammonium is assumed to neutralize 3.6 lbs of CaCO3 when no crop is present.
- One pound of elemental sulfur will produce 3.125 pounds of sulfuric acid.

APS vs Sulfuric acid

- One ton of APS is equal to the acidity of 2.074 tons of 93% acid.
- Sulfuric acid at $___ /ton X 2.074 = $______
- One ton of APS contains 400 pounds of ammonium nitrogen (NH4) at $___ /lb or $ _____ /ton.
- One ton of APS is equal to $ _____worth of sulfuric acid plus $ ___.00 of nitrogen.

Comparison of Soil Amendments Potential Acidity

Product	Lbs of $CaCO_3$ neutralized/ ton	Lbs of $CaCO_3$ neutralized / gal	Lbs $CaCO_3$ neutralized / 100 lbs of product	N	Lbs/ton N	Application	Comments
1.) Sulfuric acid 93%	1897	14.5	95	No	0	Drip, flood	Fast acting
2.) N-Phuric 15/49	2080	13.2	104	Yes	300	Drip, flood	Fast acting plus the value of the nitrogen
3.) N-Phuric 10/55	1842	11.8	92	Yes	200	Drip, flood	Relatively fast acting plus value of the nitrogen
4.) Lime Sulfur 22% S	1675*	8.9	84	No	0	Flood	Relatively fast acting within 2 to 3 weeks plus soluble calcium
5.) APS 20-0-0-40S	3940	19	197	Yes	400	Flood	Relatively fast acting within 2 to 3 weeks plus the value of the nitrogen

* Corrected for soluble calcium content

Soil Amendments

- Are good products for what they are intended
- They are not liquid jack hammers or liquid plows
- Restricted layer – should use mechanical method to first break up the layer then use a soil amendment
- Time the application to take advantage of any fertilizer value

Soil Amendments

- 1% $CaCO_3$ in the soil is equivalent to 20,000 lbs of lime in 6 inches of soil
- Soil amendments will help flush out sodium and/or free up other nutrients
- Phosphorus and zinc are often precipitated on calcium carbonate crystals in the soil.

Myths

- Gypsum lowers soil pH.
- Gypsum does not lower soil pH. All of the sulfur in gypsum is already oxidized to the sulfate form – SO_4.

Myths

- The sulfur in sulfuric acid is the element that lowers the soil pH.
- Sulfuric acid: All of the acidity in sulfuric acid is due to the hydrogen ions and not the sulfur – H_2SO_4.

Acid Forming Fertilizers

Some Commonly used fertilzers

- UAN 32
- Ammonium sulfate
- Ammonium thiosulfate
- Potassium thiosulfate
- Calcium thiosulfate
- Ammonium nitrate

Ammonium sulfate

$$(NH_4)_2SO_4 + H_2O \longrightarrow 2NH_4 + SO_4 + H_2O$$

$$2NH_4 + 3O_2 \longrightarrow 2NO_2 + 2H_2O + 4H^+$$

$$2NO_2 + O_2 \longrightarrow 2NO_3$$

Since there is no hydroxyl produced there is a net production of $2H^+$ per unit of N.

So, one lb of N as ammonium sulfate will neutralize 7.2 lbs of $CaCO_3$.

Acid Forming Fertilizers
Potential Acidity

Fertilizer	Lbs $CaCO_3$ neutralized / ton	Lbs $CaCO_3$ neutralized / gal	Lbs $CaCO_3$ neutralized / 100 lbs product
UAN 32[1]	2304	12.7	115
NH_4NO_3 (dry) 34% N	2448		122
Ammonium sulfate (dry) 21-0-0-24S	3024[4]		151
Ammonium thiosulfate 12-0-0-26S	1680[2] 2480[3]	9.3 13.7	84 124
Potassium thiosulfate 0-0-25-17S	531	3.2	27
Calcium thiosulfate 6% Ca, 10%S	313	1.6	16

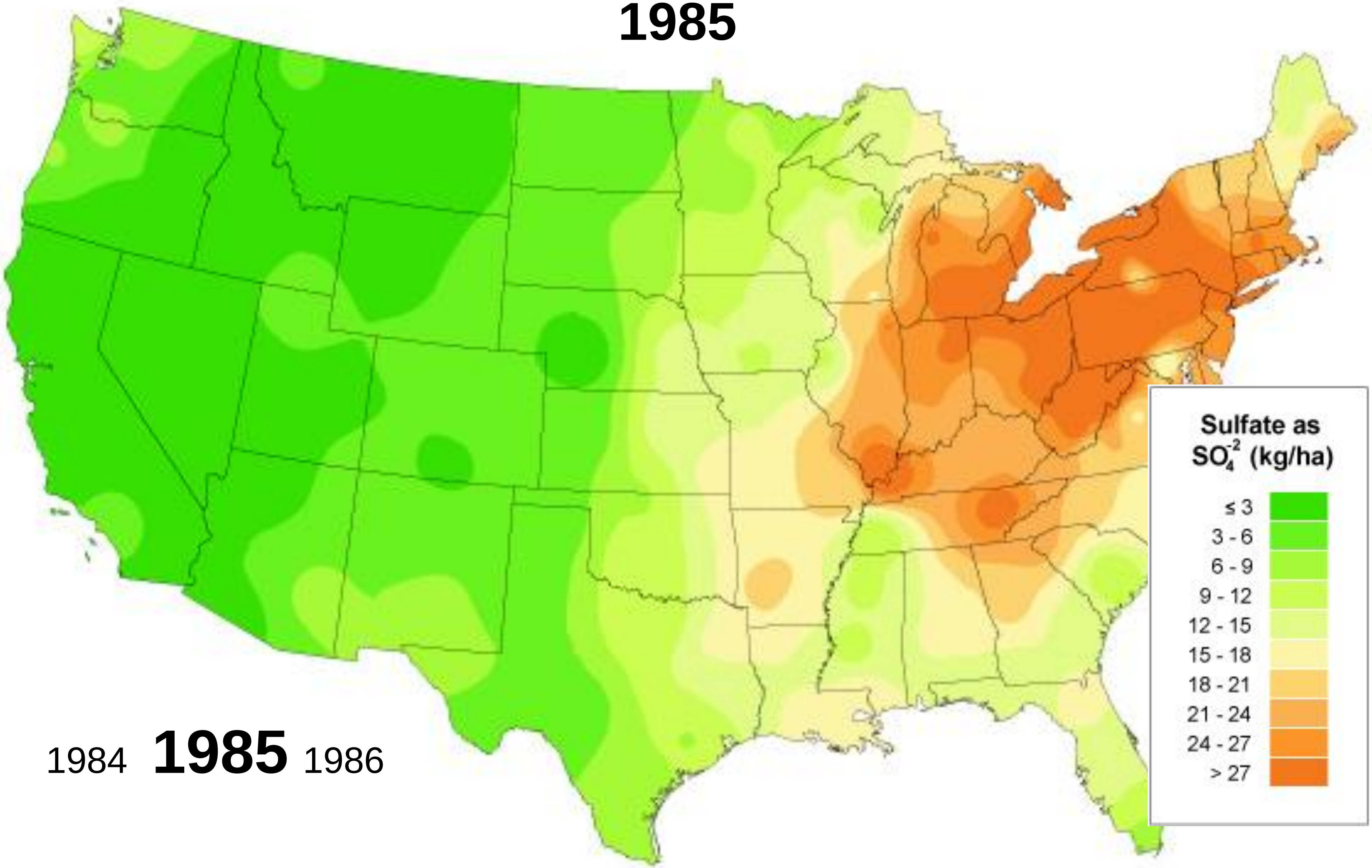
1, 2. From "Fluid Fertilizer Science and Technology" pp:437-438

3. From "Water Penetration Problems in California Soils"

4. Ammonium sulfate does not form hydroxide (OH) so 1 lb of N will neutralize 7.2 lbs of CaCO3.

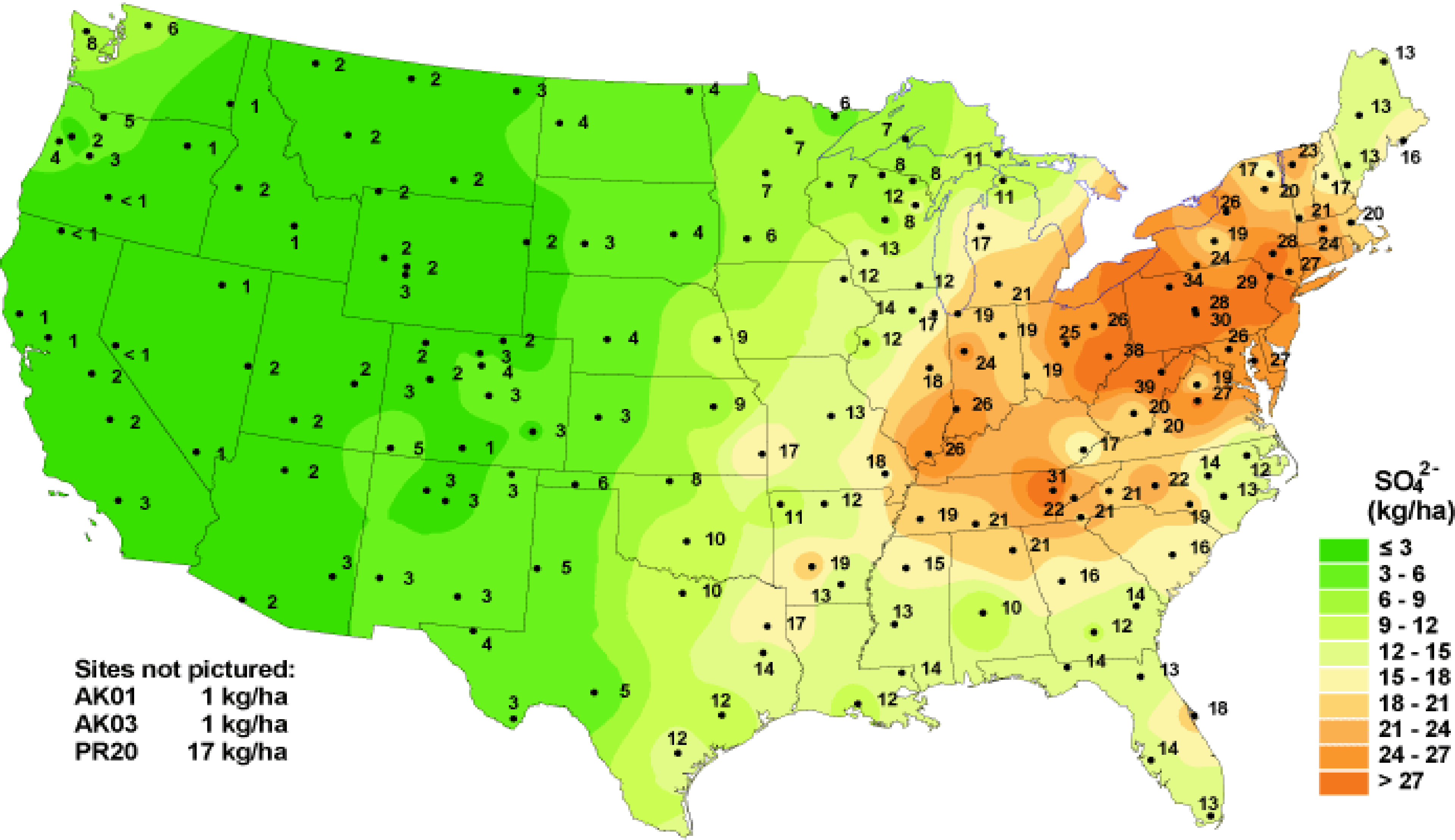
Sulfur Deficiency in California?

Sulfate Ion Wet Deposition
1985



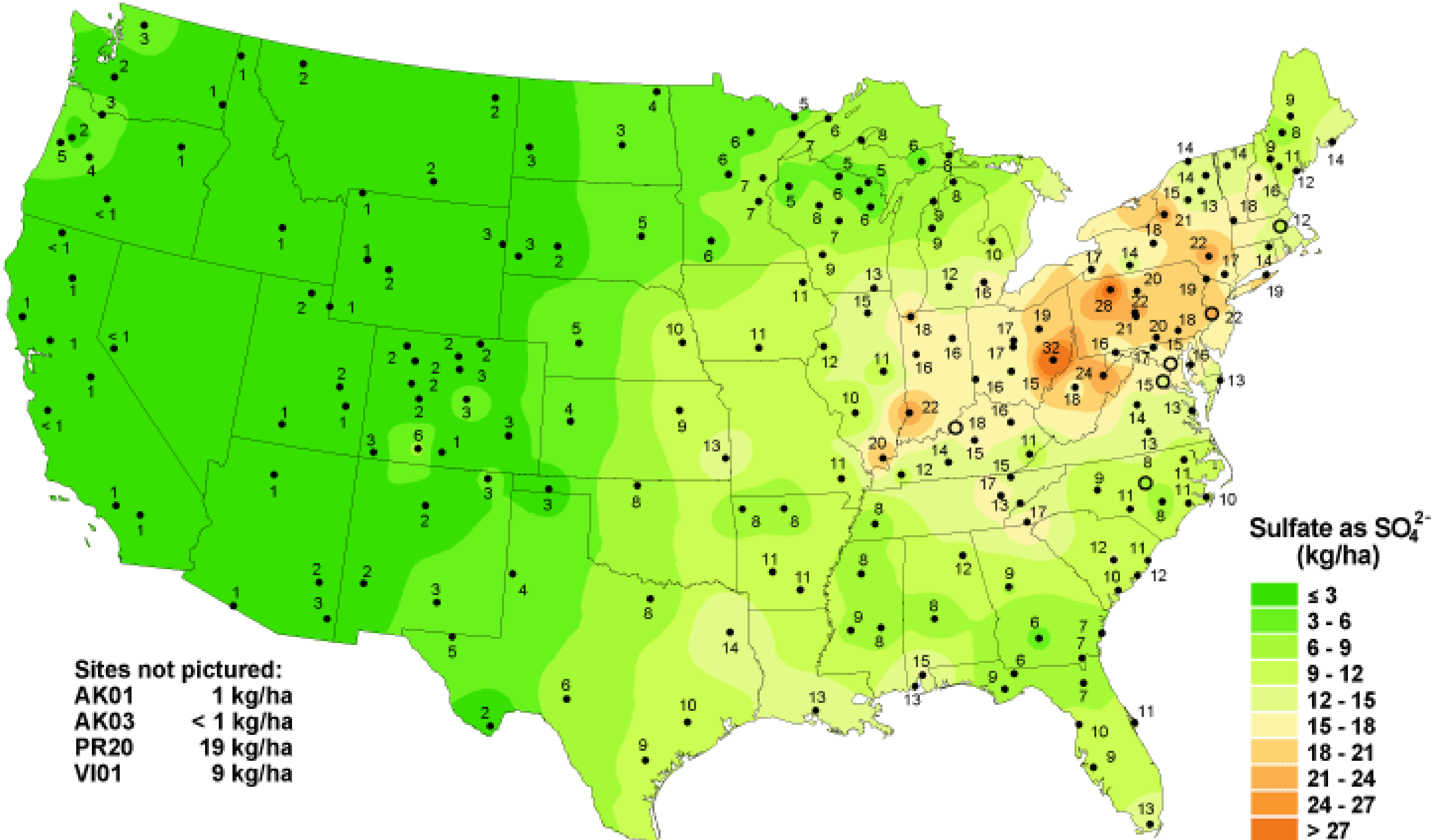
1984 **1985** 1986

Sulfate ion wet deposition, 1994



National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Sulfate ion wet deposition, 2007



National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

- Sulfur emissions from industrial activities has been reduced considerably, the fact still remains that 70% of the total S compounds in the atmosphere are not man made.

Estimate of Available Sulfur from Various Manures

	Sulfur Content			
	Solid		Liquid	
Manure	Total Lbs/ton	Available Lbs/ton	Total Lbs/1000 gal	Available Lbs/1000gal
Beef	1.8	1.0	4.8	2.6
Dairy	1.5	0.8	4.2	2.3
Swine	2.7	1.4	7.6	4.0
Poultry	3.3	1.8	9.0	5.0

From: Crop and Soils 4-1

Sulfur Requirement

- **Sulfur is required by crops such as beans, corn, wheat and potatoes in amounts about the same as phosphorus**
- **Alfalfa, cabbage and turnips contain larger amounts of S than P in their tissue**
- **N/S ratio in plant tissue ranges from 10:1 to 15:1 for many crops**

Sulfur Nutrition

- **Is essential for chlorophyll synthesis (but not a part of it)**
- **Enters into the composition of vitamins (co-enzyme A, Biotin, Thiomin in Vit B1)**
- **Is required for some lipids in membranes**
  - **Important for storage onions**
- **Has a key role in stress resistance**
- **Aids in protein formation and seed production**
- **Promotes nodulation for N fixation by legumes**
- **All plant enzymes require S, including the one for fixing CO2**
  - **In one study, alfalfa leaves fixed CO_2 at a rate 25% greater than from S deficient plants**

Sulfur in the Plant

- **Sulfur deficiency decreases stem and root diameter**
- **Sulfur deficiency delays maturity of the plant**
- **Essential in Nitrogen Utilization in the plant**

Effects of Sulfur Applied in Furrow Irrigation on Cotton Yield

Treatment		Rate/ac	Yield	Increase over check	Increase Value
1)	Check		1294		
2)	S	10 lbs	1366	+72	$37.00
3)	S	20 lbs	1394	+100	$52.00
4)	S	30 lbs	1477	+183	$95.00

Cotton pricing: $0.52/lb

Application timing: Starting at second irrigation – May 28th, 2 weeks later, 2 weeks later.

Research: Dr. Bill Weir, U.C. Davis

Balanced nutrition

- Plants need a balanced ratio of nutrients
- Rates depend on the type of plant, it's specific nutrient needs, and the stage of growth the application is being made


Would you ring this door bell?

Acid Soils in California

- Soil surface has become acidic in some areas
  - East side of the San Joaquin Valley
  - Under drippers and micro-sprinklers
  - Near drip tube emitters

- Basic type of fertilizers can be used when the problem is not severe

- Lime is the only cost effective method for correcting low pH soils
  - Must be incorporated to be effective
  - May have an effect on nitrogen fertilizer application

- Soil sampling:
  - 0-3 inch sample
  - 3-12 inch sample