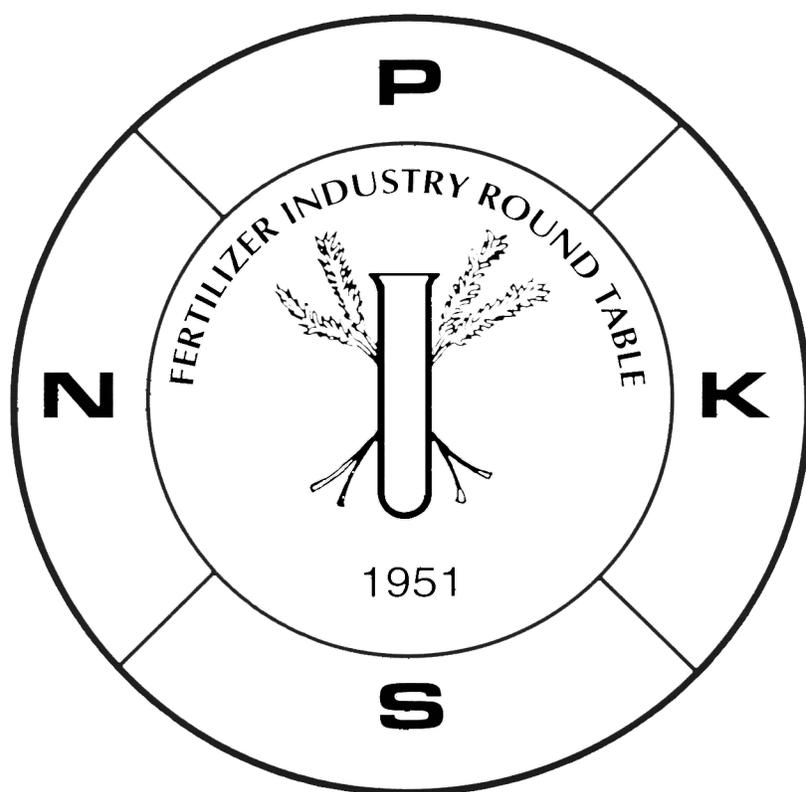


**PROCEEDINGS  
OF THE 51st ANNUAL MEETING  
THE FERTILIZER INDUSTRY  
ROUND TABLE  
2001**



**October 22, 23, & 24, 2001  
TradeWinds Resort  
St. Pete Beach, Florida**



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The next annual meeting is: October 28, 29, and 30, 2002  
Embassy Suites  
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# Monday, October 22, 2001

## Session I Moderator:

**Donald Day**

### **Opening Remarks** *Donald Day*

Good Morning Ladies and Gentlemen:

On behalf of the Board of Directors, welcome to the 51<sup>st</sup> annual meeting of the Fertilizer Industry Round Table. It is a pleasure to be meeting again in St. Pete Beach under the beautiful sky, which also covers the central Florida phosphate industry. However, there are many dark clouds, which hang not only over the phosphate industry but the fertilizer industry in general. Our outlook speakers this morning will address if these dark clouds are the storm “a coming” or the storm which has “just passed”.

I do not have to remind this audience that the world population is constantly increasing at the same time the amount of arable land is constantly decreasing. This simply means we must produce more food, natural fibers, and animal livestock feed through increased crop yields.

There is no question biotechnology will play a key role in increasing crop yields. I am confident that we will have in the very near future our traditional grass/cereal crops such as corn, wheat, rice, etc.,

extracting nitrogen from the atmosphere just as their cousins the legume crops presently do. However, the other three major crop nutrients – phosphorus, potassium, and sulphur – and the trace or micronutrients cannot be extracted or mined from the atmosphere. These essential plant nutrients must be mined, processed, and applied to the soil with conventional, or yet to be developed methods, in order for crops to grow and achieve higher yields. If we think of biotechnology as the fuel for the rocket ship which will take us to the unknown world of plant yields not yet achieved, then fertilizers will be the cargo or payload carried by that rocket.

I am pleased to see each of you here in light of the economic conditions facing the fertilizer industry and the worldwide war on terrorism. Both are responsible for our drop in attendance this year. The latter is responsible for the cancellation of our Tuesday afternoon trip to the Florida Power & Light Facility. I will address the revised Tuesday afternoon schedule later today.

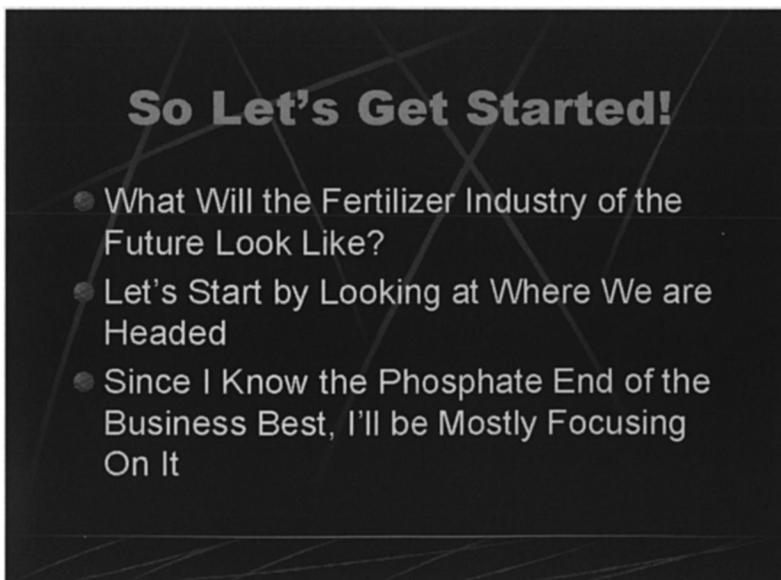
I do not want to take any more time away from our Keynote and Outlook speakers on this morning’s program. Thanks for your attendance and support of The Fertilizer Industry Round Table and again welcome to St. Pete Beach and the 51<sup>st</sup> annual meeting of The Fertilizer Industry Round Table.

**Keynote Address**  
**The Future of the Fertilizer Industry**  
*Regis Stana*  
**University of Florida**

*Slide 1*



*Slide 2*

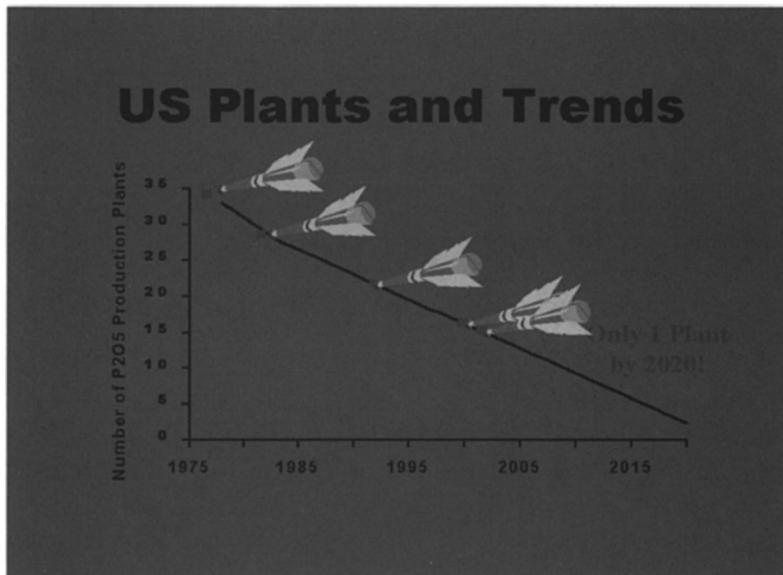


Slide 3

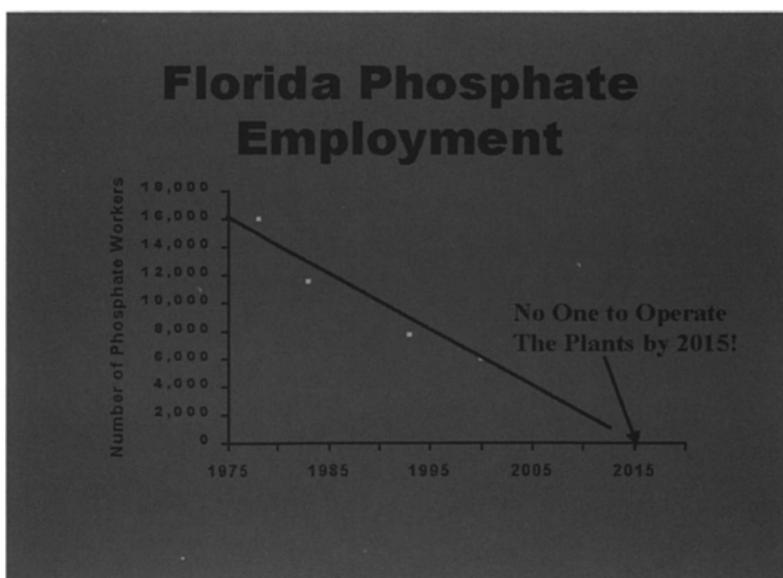
**In 1994, I Attended a Local AiChE Meeting in Which a Farmland Marketing Manager Gave the Following Information on the US Phosphate Industry**

- In 1978, 33 Plants Produced 9,825,000 Tons of  $P_2O_5$
- In 1983, 28 Plants Produced 11,220,000 Tons of  $P_2O_5$
- In 1993, 21 Plants Produced 12,140,000 Tons of  $P_2O_5$

Slide 4



Slide 5

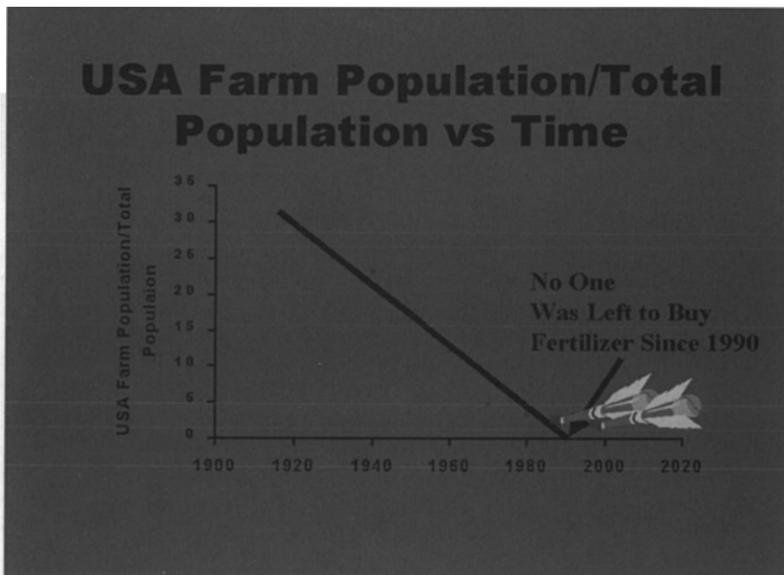


Slide 6

## Now Let's Look at the US Farm Situation

- How About a Graph of the Percentage of People Living on Farms vs Time!

Slide 7



Slide 8

### There Are Some Conclusions that We Could Drawn From These Graphs

- Both Farm and Fertilizer Production Productivity has Increased Dramatically!
- For at Least 30 Years I Have Seen Predictions of Robots Doing All Our Work in "Just a Few Years"
- We Must be Finally Entering the Age of the Robot!

*Slide 9*

## **July 2000, Smithsonian**

- Robots are Being Developed That Will Pick Bugs from Crops and Use Them as Fuel to Power Themselves

*Slide 10*

## **But Perhaps We Should Look at What is Driving These Graphs Downward**

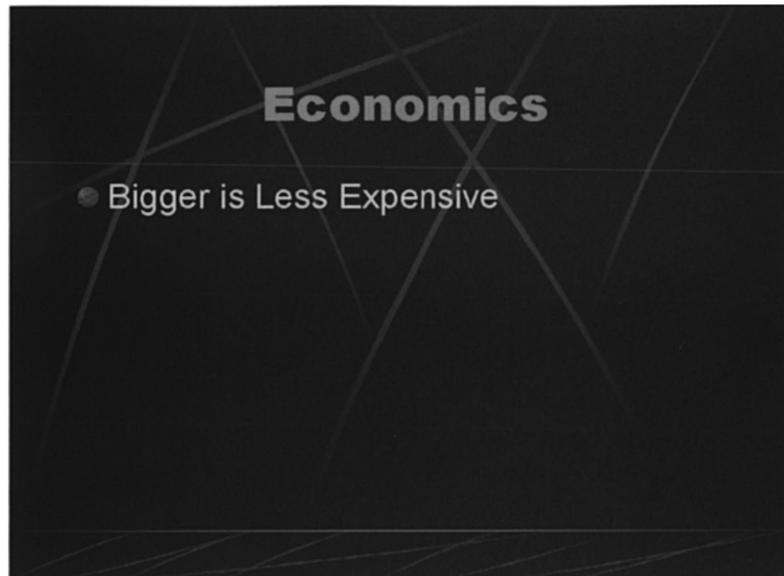
- I Think Both Have Been Driven Down With Ease

*Slide 11*

## **What Are the E's**

- Economics
- Efficiency
- Environment

Slide 12

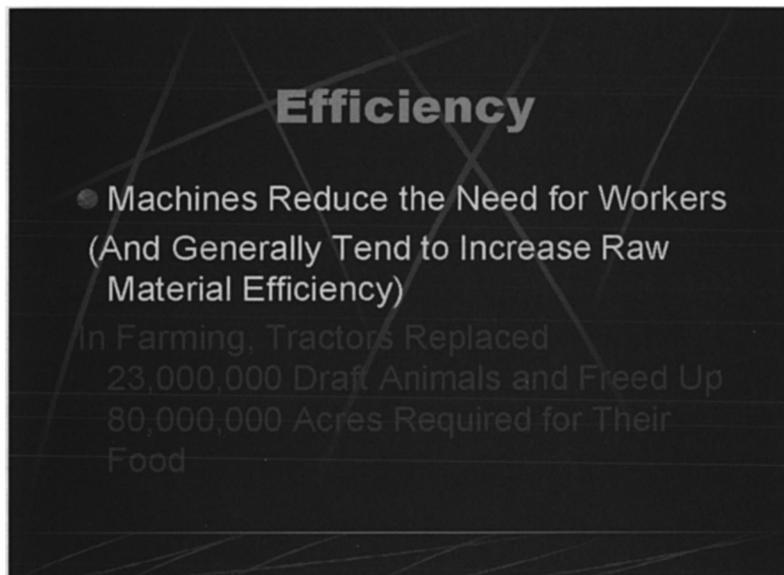


**Economics**

- Bigger is Less Expensive

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Slide 13



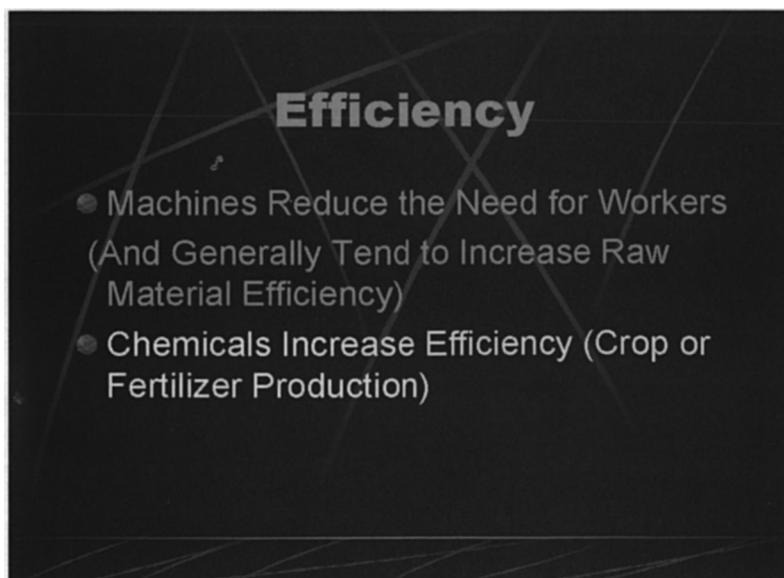
**Efficiency**

- Machines Reduce the Need for Workers (And Generally Tend to Increase Raw Material Efficiency)

In Farming, Tractors Replaced 23,000,000 Draft Animals and Freed Up 80,000,000 Acres Required for Their Food

The slide features a dark background with a faint, light-colored geometric pattern of intersecting lines forming a grid-like structure.

Slide 14



**Efficiency**

- Machines Reduce the Need for Workers (And Generally Tend to Increase Raw Material Efficiency)
- Chemicals Increase Efficiency (Crop or Fertilizer Production)

The slide features a dark background with a faint, light-colored geometric pattern of intersecting lines forming a grid-like structure.

Slide 15

## Efficiency

- Machines Reduce the Need for Workers (And Generally Tend to Increase Raw Material Efficiency)
- Chemicals Increase Efficiency (Crop or Fertilizer Production)
- New Processes/Crops Are More Efficient

Slide 16

## July 8, 2001 Associated Press

Genetically Engineered Crops in the USA

Year	2000	2001
Soybeans	54%	68%
Cotton	61%	69%

Slide 17

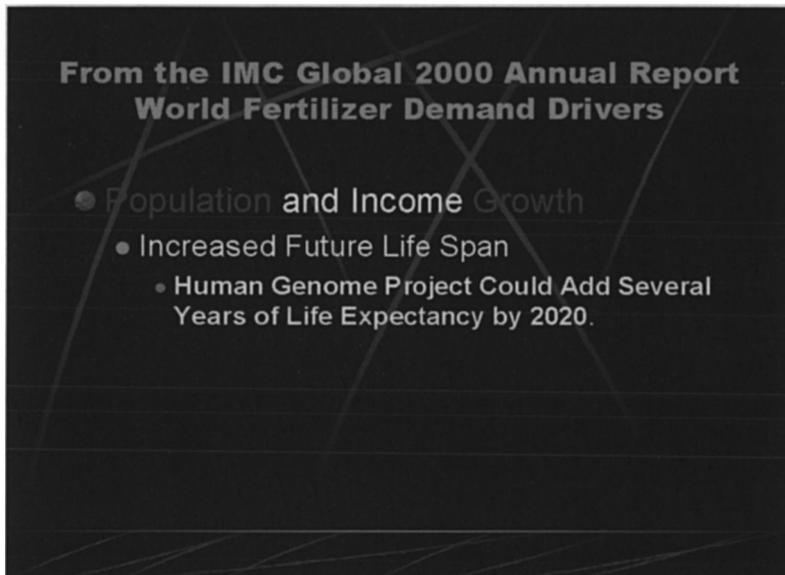
## Environment

- Though We All Complain How Environmental Laws Have Driven Up Our Costs, In Most Cases They Have Actually Helped Improve Efficiency and Long Term Costs

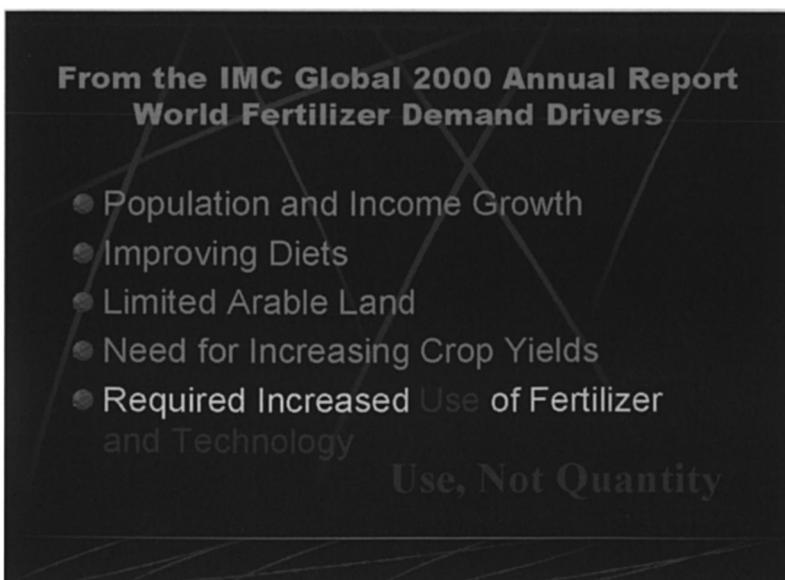
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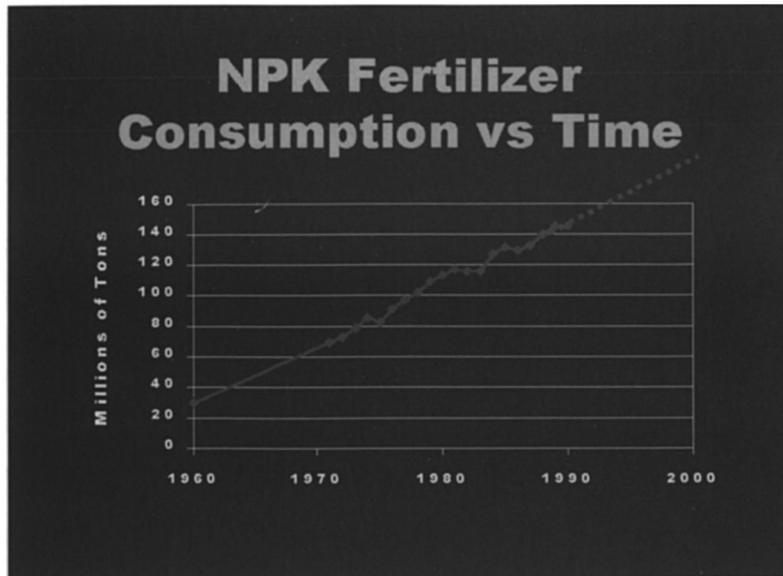
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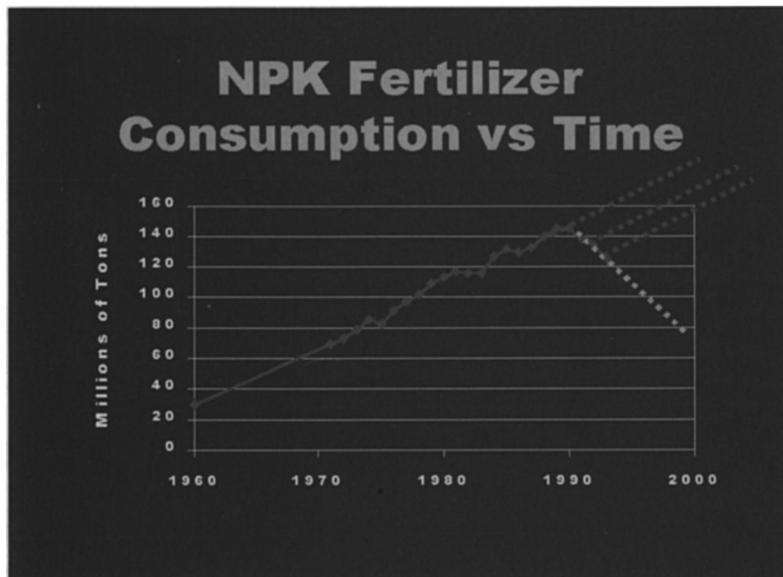
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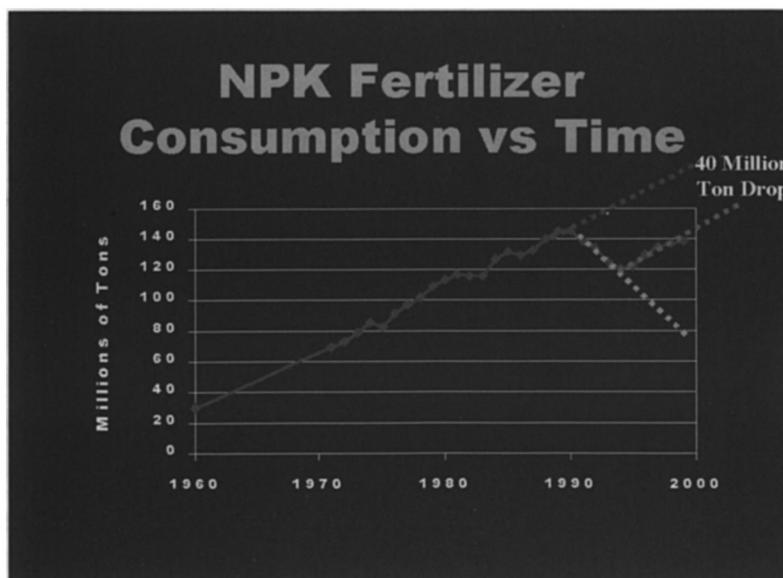
Slide 21



Slide 22



Slide 23

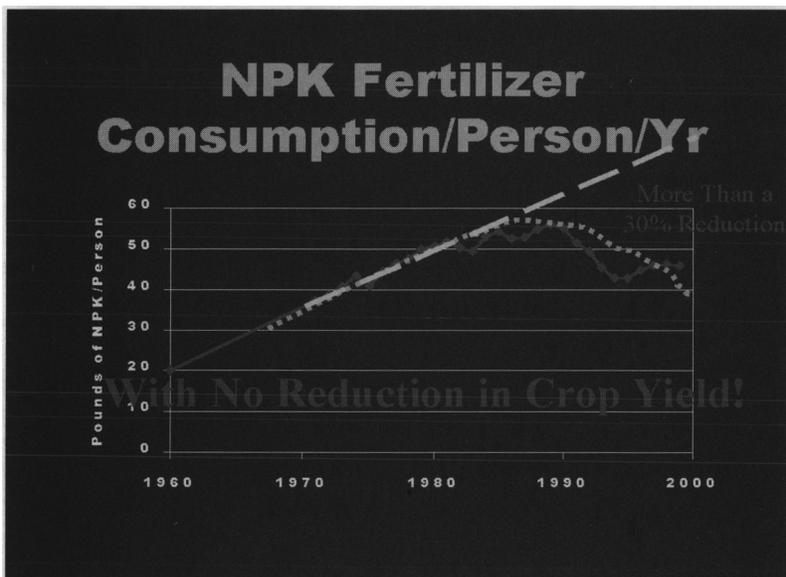


Slide 24

## 40 Million Ton Drop?

- And Crop Yields Kept on Improving!
- Perhaps We Should Graph the Data Differently
- Let's Look at it as Pounds of Nutrients/Person/Year

Slide 25



Slide 26

## Does This Suggest that the Use of Fertilizer Nutrients is Becoming More Efficient?

- Is the Demand for Fertilizer Being Driven Down With E's?
- Certainly, Economics has Always Been a Driving Force
- And One Only Has to Pick Up Just About Any Newspaper to See That Environmental Forces are There
- If Fertilizer Use is Becoming More Efficient, How Much More Improvement Could There Be?

*Slide 27*

**Which Major Nutrient Has the Lowest Efficiency?**

- Nitrogen
- Phosphate
- Potassium

*Slide 28*

**But Is It Nitrogen?**

*Slide 29*

**According to the Book "Fertilizer Technology and Application"  
Published in 1999**

- Crop Use Efficiency of Most Nitrogen Fertilizers is 50-70%
- Crop Use Efficiency of Phosphate Fertilizers is 20-40%
- Crop Use Efficiency of Potassium Fertilizers is 30-50%
- Crop Use Efficiency of Micronutrient Fertilizers is 5-10%.

Slide 30

### **According to Jerry H Stoller in Language of the Plant: Foliar Nutrition**

- Crop Use Efficiency of Nitrogen Fertilizers is 50%
- Crop Use Efficiency of Phosphate Fertilizers is 15%
- Crop Use Efficiency of Potassium Fertilizers is 25%
- Crop Use Efficiency of Sulfur is 50%.

Slide 32

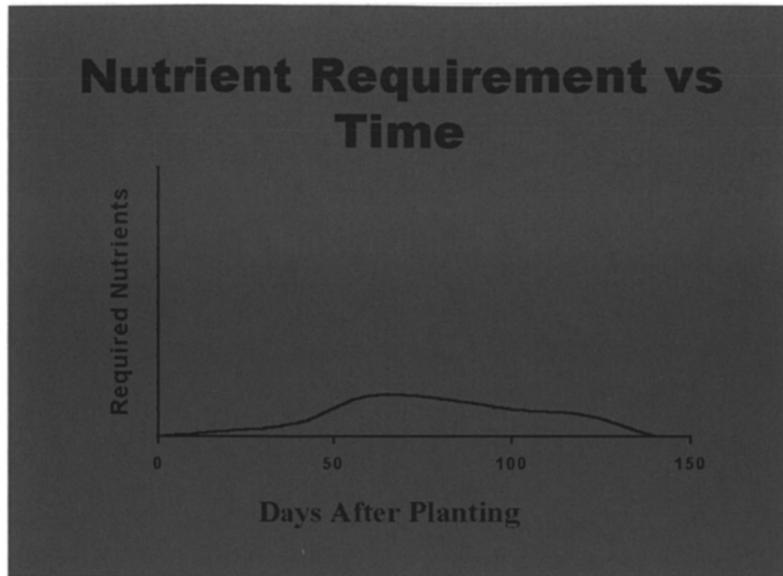
### **Fertilizer Efficiency**

- According to the Fertilizer Handbook, Published by TFI in 1982  
Loss of Plant Nutrients in the past 50 Years in the US from Erosion and Runoff Have Exceeded Nutrient Removal by Crops  
The Mississippi River Alone Carries 9.6 Million tons of NPK to the Gulf Each Year

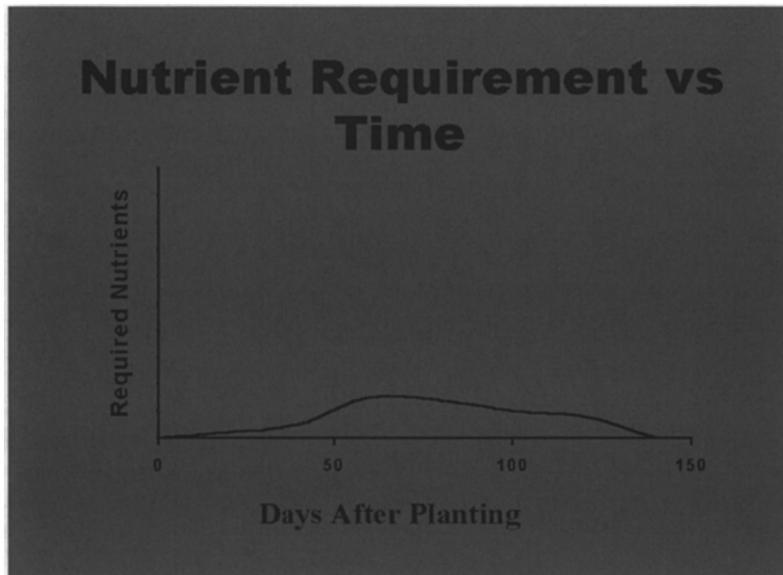
Slide 32

### **Why So Low?**

Slide 33



Slide 34



Slide 35

### But This is Only the Efficiency of the Plant

- What About
  - Crop Losses to Insects and Blight
  - Fertilizer Loss to Weeds
  - Crop Losses in Harvesting

Slide 36

## Crop Losses to Insects

- According to a Program on the History Channel on Modern Farming Technology  
Insects Currently Destroy 20-40% of the Major Crops in the USA

Slide 37

## Fertilizer Efficiency

- According to Raun and Johnson , In 1996, 49,743,804 Metric Tons of N Fertilizer Were Applied World-Wide for Cereal Production.
- Of that, 16,572,232 Metric Tons of N Were Removed in the Harvested Grain
- This Gives a Nitrogen Utilization Efficiency of 33%

Slide 38

## Fertilizer Efficiency

- If the Same Drop from Crop Efficiency to Harvest Efficiency (50 to 33%) is Applied to the Other Major Nutrients Then the Harvest Efficiency is:
  - Nitrogen 33%
  - Phosphorous 10-27%
  - Potash 17-33%

Slide 39

## Fertilizer Efficiency

- But We're Not Done Yet!
- How About Losses and Spoilage in Shipment and Storage?
- How About Losses (Spoilage) in Our Homes?  
(Spoilage Can be Significantly Reduced by More Wide Spread Chemical Treatment or Irradiation)
- Then There's the Food Left on Our Plates!

Slide 40

## Fertilizer Efficiency

- It is Quite Likely That the Overall Efficiency of the Major Fertilizer Nutrients is:
  - Nitrogen <20%
  - Phosphorous <10%
  - Potash <15%

Slide 41

## As a Crude Balance on Phosphate

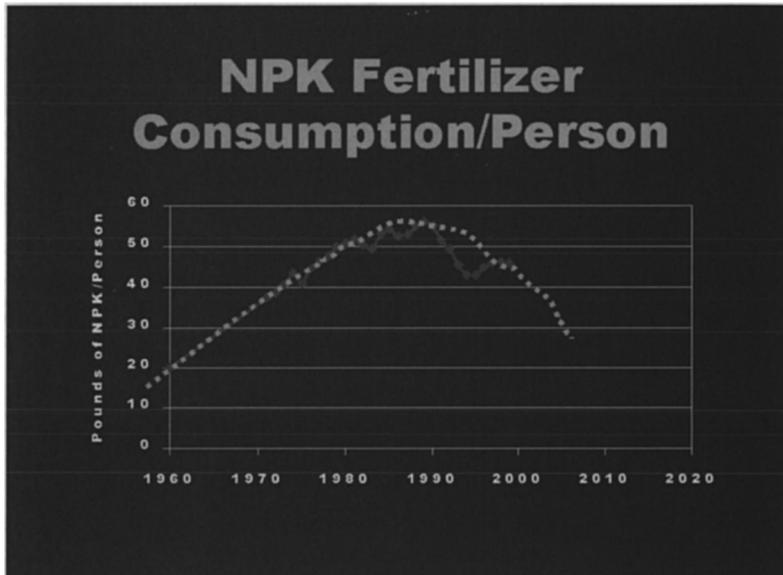
- The Dietary Requirement for Phosphate is 800 mg/Day
- The Annual Requirement as  $P_2O_5$  is Less than 900,000 Tons
- At Least 30,000,000 Tons of  $P_2O_5$  is Applied Each Year
- You do the Math

Slide 42

## So If Efficiency is Improving

- Future Demand for Fertilizer Could Drop Very Significantly

Slide 43

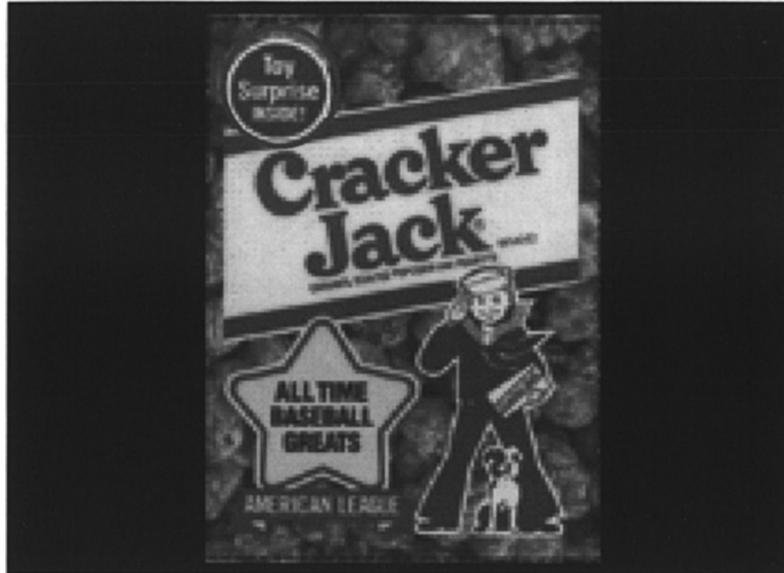


Slide 44

## If Fertilizer Demand Drops, How Will the Industry Survive?

- Perhaps We Should Try a New (Old) Marketing Approach
- How About a Cracker Jack Idea?

Slide 45



Slide 46

### **What “Toy” Could We Add to Fertilizer to Make it Sell Better?**

- What Does the Market Need?

Slide 47

### **A Successful Farmer Only 60 Years Ago**

- May Have Owned as Little as 100 Acres
- May Have Owned a Tractor and a Few Attachments
- Learned What he Needed to Know “on the Farm” From his Father in a Few Years
- Spent Much of his Time in the Field, Tilling, Weeding etc.

Slide 48

## Today's Successful Farmer

- Needs to be an Expert in
  - Agriculture
  - Entomology
  - Statistics
  - Soil Sampling
  - Economics
  - Mathematics
  - Weather
  - Government Programs
  - Etc

Slide 49

## Today's Successful Farmer

- Must Make Numerous Decisions Correctly
  - What to Plant
  - When to Plant
  - What Fertilizer/When
  - Herbicide/Pesticide/Genetically Modified
  - When to Water (if Option)

Slide 50

## Today's Successful Farmer

- Farms at Least Several Thousand Acres
- Has a Large Investment in Equipment
- Spends More Time on Computer Than in Field
- Has on Staff or has Access to Experts or PhD's in Just About Every Aspect of Farming
- Is Still at the Mercy of the Weather, and World Economics

*Slide 51*

## **However, Today's Typical "World Wide" Farmer"**

- Farms Few Acres
- Has Few Tools
- Knows Little About Fertilizer, Herbicides and Pesticides
- Plants Own Seeds or Seed Provided by Government
- Has Little Education
- May be Illiterate

*Slide 52*

## **How Can We Upgrade the "World Wide Farmer"?**

- Clearly the "World Wide Farmer" Needs Education
- In Fact, to Join the Ranks of the Successful Farmers, He Needs a PhD!

*Slide 53*

## **How do We Efficiently Educate the "World Wide Farmer"?**

- Put a Scholarship in Every Bag of Fertilizer!
- (UF Would Like That, Particularly if They Can Play Football)

*Slide 54*

**What can the Fertilizer Industry do to Help the Less than Knowledgeable Farmer**

- We need to Produce Fertilizer with a PhD

*Slide 55*

**How Do We Produce Fertilizer With a PhD?**

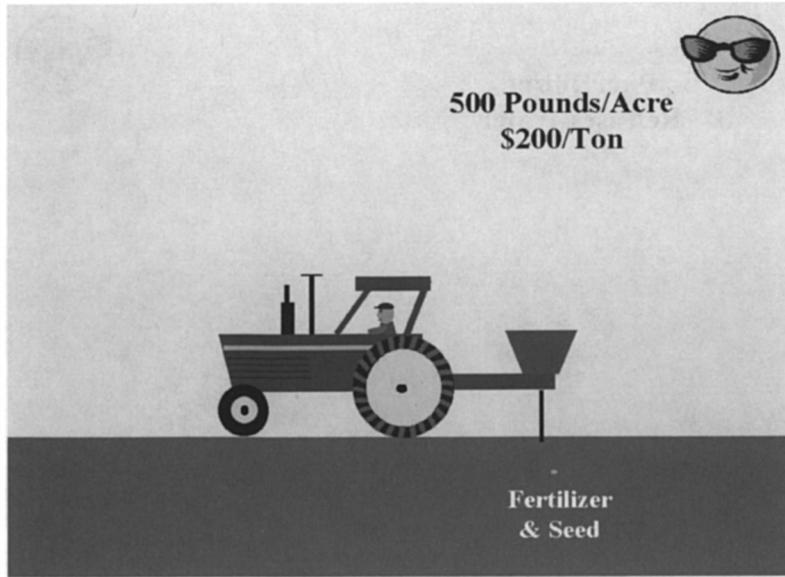
- Simple!!  
(So Simple, Maybe We Should Patent it!)
- We Just Make PherDilizer

*Slide 56*

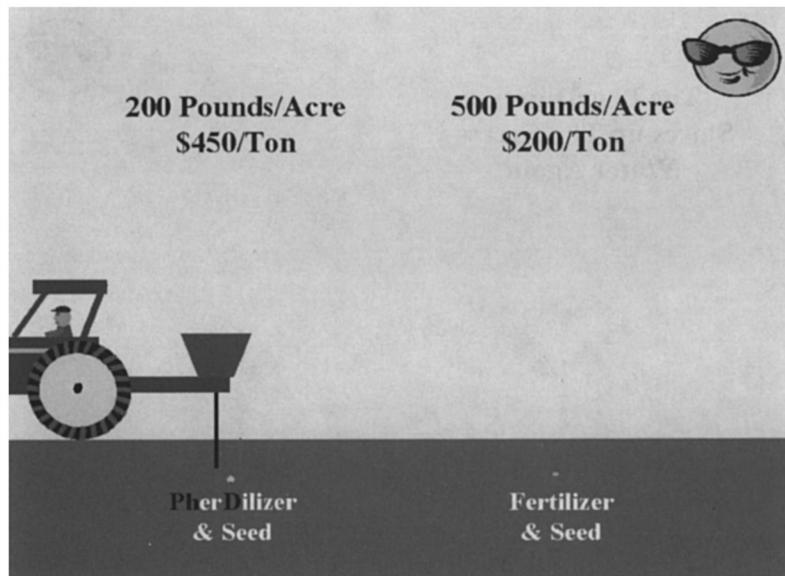
**What is PherDilizer?**

Well, Here's one Concept

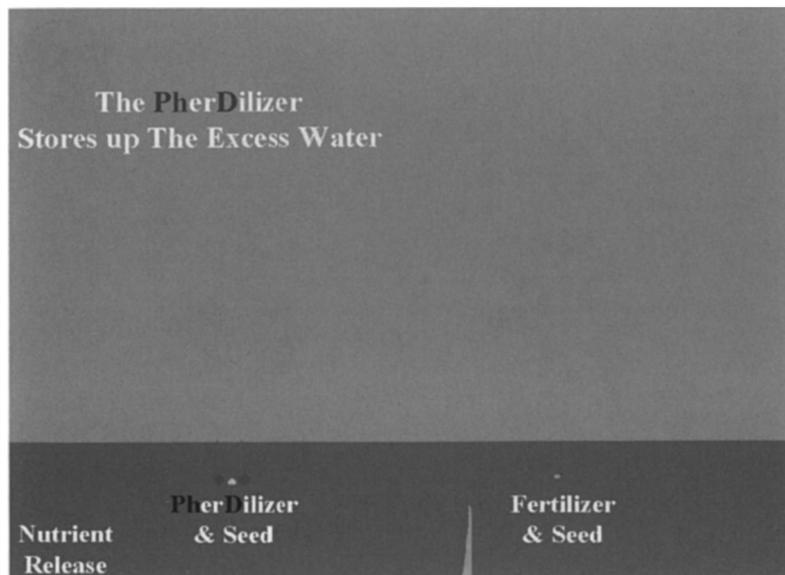
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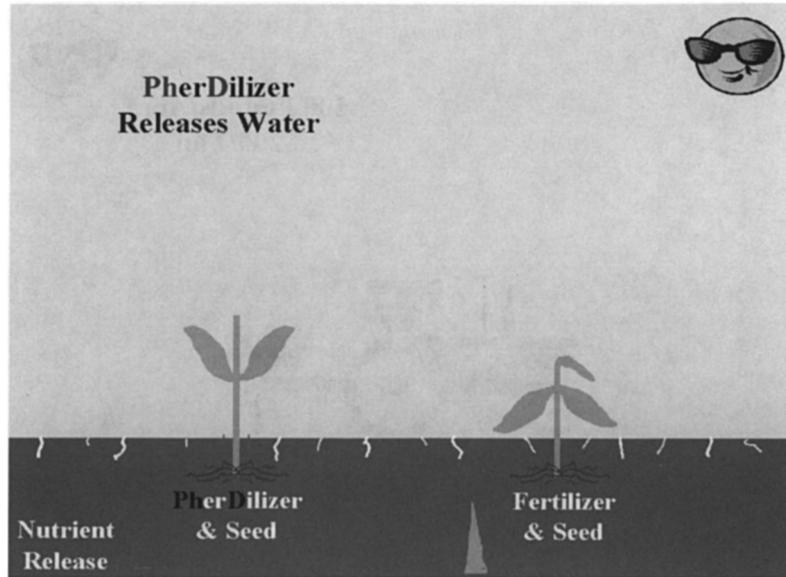
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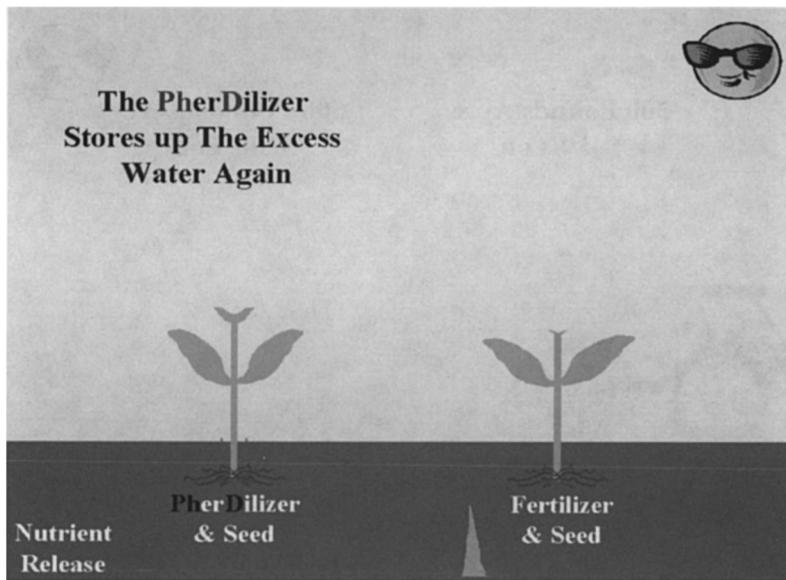
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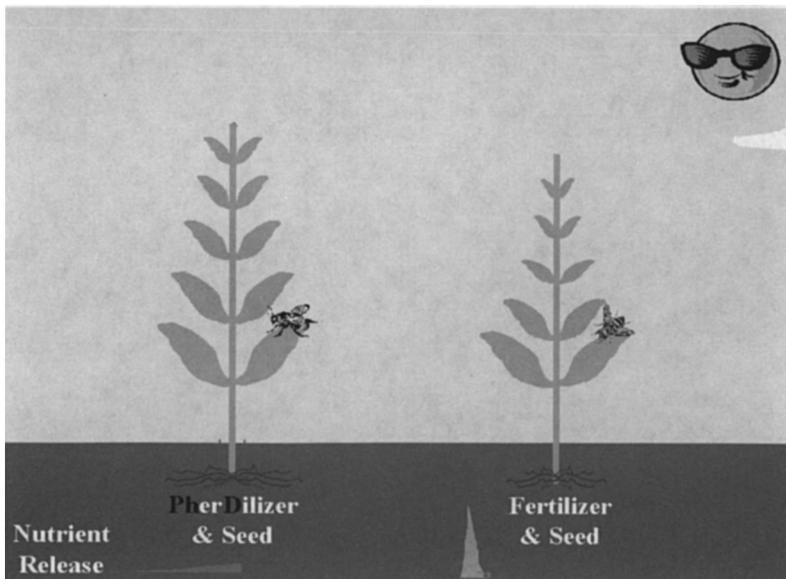
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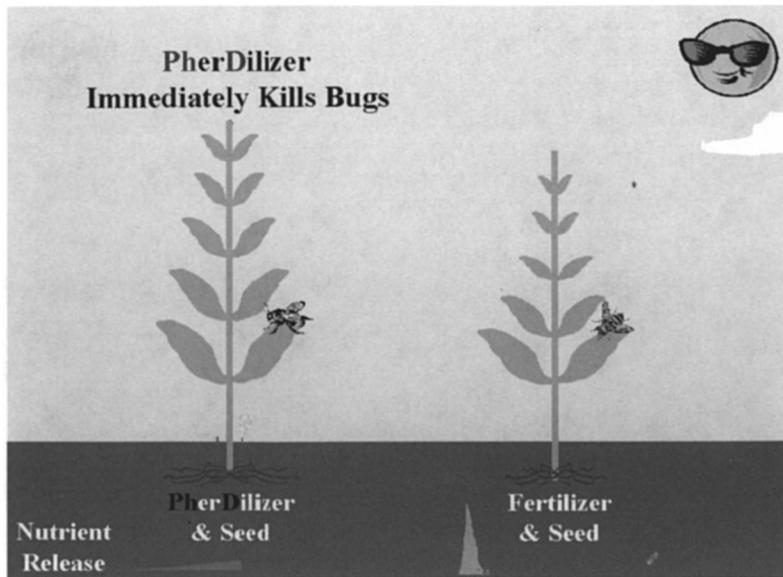
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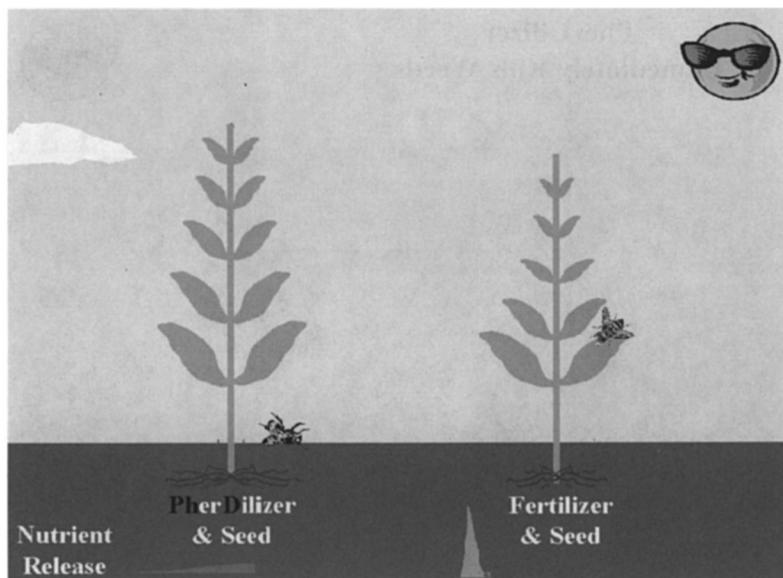
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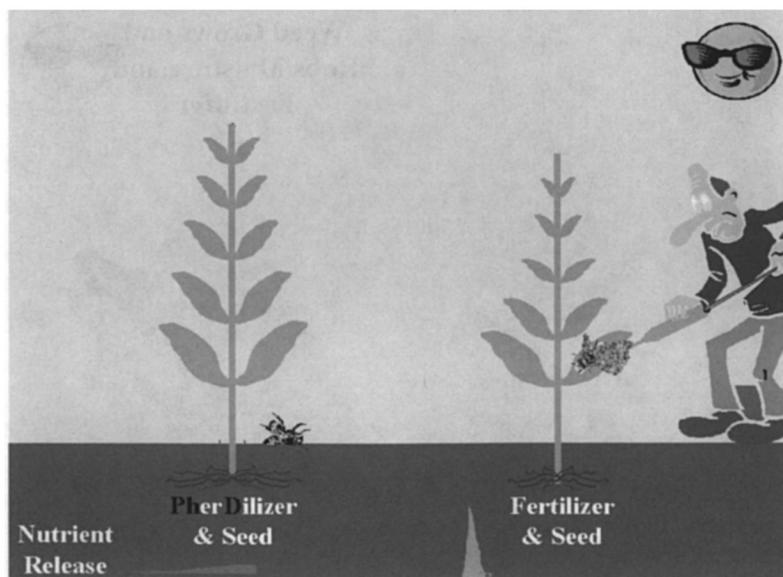
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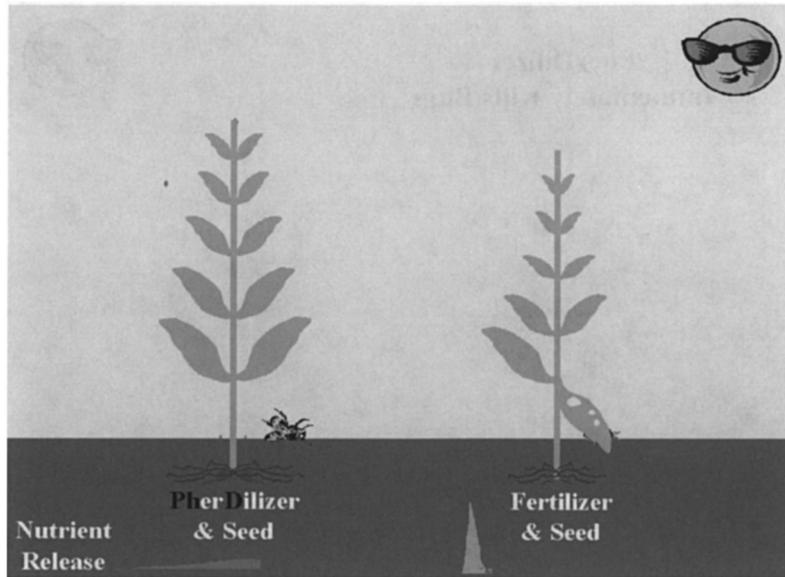
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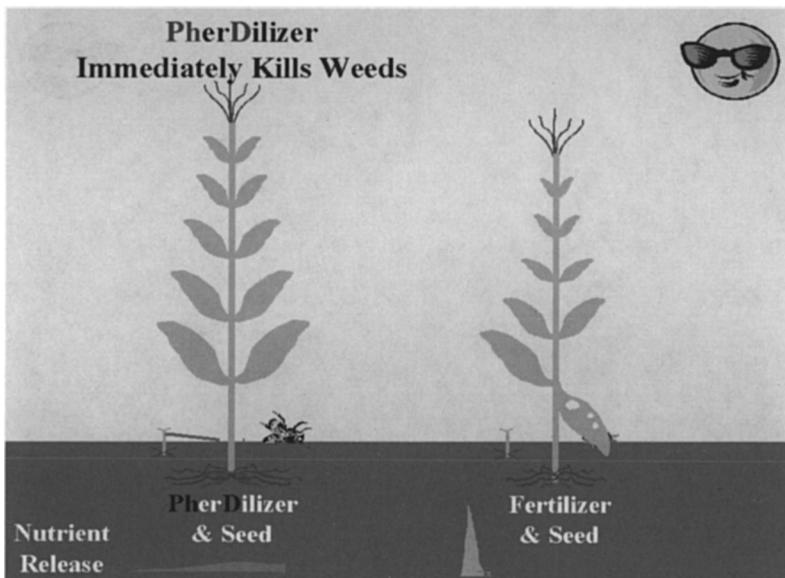
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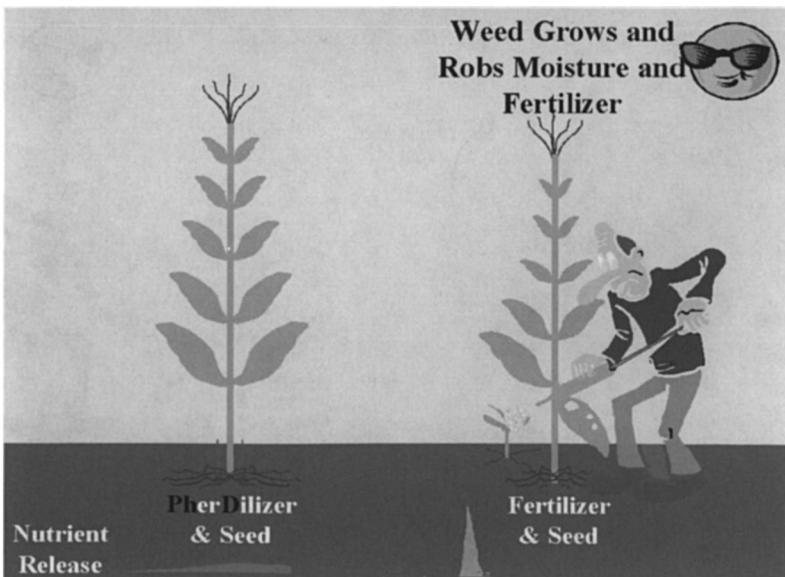
Slide 66



Slide 67



Slide 68





Slide 72

## Will it Happen?

- On Oct 1<sup>st</sup>, I Made the Following Internet Searches Using Excite

Search	Hits
● "Efficient Fertilizer"	282
● "Smart Fertilizer"	7
● "Intelligent Fertilizer"	1
● "Fertilizer with a PhD"	1 (Bogus)
● "PherDilzer"	0

How Many "Hits" will There Be a Year from Now?

Slide 73

## Will it Happen?

- Most of the Technology Exists (Most Developed in the Last 5 Years) (In Fact There are Several Alternatives)
- Just 40 Pounds/Acre of the Same Material Used in Disposable Diapers Could Store 15% of the Total Water Needed for a Crop

**Unless You'd Rather See Someone Else Produce A Herbicide or Pesticide With a PhD!**

- The Economics Are There
- Perhaps it Will Happen With Ease!

# It's Really Up to You

Slide 74

# The End

## Outlook for Nitrogen

Al Mulhall

### Potash Corporation

#### Presentation Summary:

- 1) Introduction:
- 2) US nitrogen consumption past FY, this FY, next FY
- 3) Natural gas
  - a) World reserves 60 years
  - b) US reserves 7 years
  - c) US & Europe have 42% consumption
  - d) Recent gas history
    - Prices
    - Gas drilling rig activity
    - Gas inventory level changes
    - Series of NYMEX futures prices
    - Explanation why the future ain't what it used to be
    - Graph of winter temperatures
    - Gas consumption reduction - mostly economic slowdown, partially weather related & change to alternate fuels
  - a) Effect of gas price on ammonia price
  - b) Global gas price comparison to US
  - c) Nitrogen imports FY 99/00 vs 00/01 ammonia, urea, AN, solution, N
  - d) Nitrogen monthly imports
  - e) Control of US nitrogen inventories
- 4) LNG - US Market share
  - a) LNG economic decision point from Venezuela/Trinidad <\$2.50 gas
  - b) LNG economic decision point from further afield approx \$3.00 gas
- 5) Cost of US ammonia imports vs US ammonia produced from \$2-3 gas

- 6) FY 99/00 vs FY 00/01 nitrogen import volumes for ammonia, urea, AN, solutions
- 7) Monthly nitrogen import volumes FY 99/00 vs 00/01 vs 01 to date
- 8) Nitrogen import projection for '01/02
- 9) US TFI nitrogen inventory levels
- 10) Impact on shipping of the War on Terrorism
- 11) World ammonia export growth
- 12) World urea export growth
- 13) World capacity utilization growth for ammonia & urea
- 14) Environment  
Fertile Minds approach

#### The Nitrogen Outlook

1) Screen opening slide.  
2) **Title Slide:** Thank you, and good morning, everyone. It's my pleasure to be here with you. I was lucky to get here in time to tour St. Petersburg. What a gorgeous part of the world! I particularly enjoyed watching the setting sun turn the green-blue waters of the Gulf to gold.

#### 3) **Bullet points on presentation content:**

In examining the nitrogen outlook, I'm going to start with the a projection for next fertilizer year's demand in the U.S. Shifting gears to natural gas, which is so important in the U.S. nitrogen market, I'll explore the effect of the global and U.S. gas markets on nitrogen. Next will be a look at nitrogen supply/demand and international trade, and I'll close with a few words about the environment.

#### 4) **N Consumption:**

First, the U.S. nitrogen outlook. We all know that application was low in fertilizer year 2000/2001. High nitrogen prices and a wet, cold spring combined with a reduction in acres planted to corn and an increase in soybean plantings to pull nitrogen consumption down. All the facts and figures are not yet in, so opinions differ on the depth of the reduction. My estimate comes down on the more pessimistic side, indicating a reduction of 6% compared to the 1999/2000 fertilizer year. How-

ever, my outlook for 2001/2002 agrees with several other estimates in anticipating a recovery to close to 1999/2000 consumption levels. The combination of more corn acres and farmers' need to replace mined soil nutrients will be bolstered by the high farm income in 2001. This is estimated at about \$61 billion, with government payments providing a big assist. I think we can look forward to a nice 5.5% increase in nitrogen consumption compared to the last fertilizer year.

#### **5) *Natural Gas:***

Now let's look at the impact that changes in the global gas picture are having on the nitrogen industry.

#### **6) *World Gas Reserves:***

Global gas reserves are sufficient to meet world needs for 60 years. Almost 75%, shown in yellow, are in Eastern Europe, the former Soviet Union and the Middle East. In striking contrast, North America and Western Europe -- in blue -- have a very small share of reserves, with a combined total of 7%.

#### **7) *World Gas Consumers:***

That gets turned around on the consumption graph.. The U.S. and Western Europe, both developed regions, are shown in blue. They use about 42% of the gas consumed worldwide each year. This is very disproportionate to their share of reserves.

#### **8) *North American Reserve Life:***

Current U.S. natural gas reserve life is approximately seven years. New reserves can be identified by exploration, but compared to the world average, we don't have a lot of gas left in the tank.

#### **9) *Gas Price Graph Price increasing:***

When gas reserves are low, production rates marginal and consumption high as we had with last winter's hot economy and cold weather, the supply-demand ratio pushes gas prices up. They rocketed to levels over \$10/MMBtu.

#### **10) *Gas drilling rigs:***

Those prices spurred tremendous drilling interest, and the number of active rigs climbed to over 1050. This was the highest level of drilling activity in history, and was sustained for the longest period.

**11) The high demand for natural gas didn't continue, as the yellow line indicating this year's inventory shows. The cold November/December was followed by a mild January/February, and the summer air conditioning demand was reasonable. A deepening economic downturn further reduced demand. The combined effect of slow demand and plenty of drilling activity quickly pushed up the natural gas inventory. After being at a historically low point at the beginning of the year, the inventory turned the corner in April, and is now at 90% of the capacity of the storage caverns.**

#### **12) *Natural gas price curve again with the down-side:***

The inventory rise eliminated worries about shortages, and natural gas prices continued to plunge. The recent levels of around \$2/MMBtu have not been seen since early 1999. What is the outlook for the future?

#### **13) *NYMEX futures prices:***

Well, as Yogi Berra once said, "The future ain't what it used to be." This graph shows recent NYMEX futures market prices for natural gas, with the gold line representing the price six months ago and the blue line illustrating a few days ago. The price has come down substantially but is not expected to remain at the current level. A couple of factors play a role in this expectation of higher prices.

#### **14) *Winter Temperatures 1895-2000:***

The first factor is winter temperature. We'll use this chart from 1895-2000 to see why. The graph indicates the average U.S. winter temperature for December to February. Six consecutive warm winters before 2000 gave us a false sense of security about the necessary levels of natural gas production. When last winter hit, the 24<sup>th</sup> coldest

of the 105 winters shown here, gas consumption soared, production was unable to keep up, and the gas inventory plunged. The long-term winter outlook projection from weather forecasters based on ocean surface temperatures says “the party’s over, guys.” We’ve moved into a period of colder than average winters, though the one ahead is not expected to be quite as cold as last winter.

#### **15) Gas drilling graph again:**

We need to go back to the gas well drilling graph to explain the second factor. Since prices fell, the number of active drilling rigs has dropped from 1050 to 953. Current estimates say \$3 gas is required to keep the rig number high enough to sustain production at a level equal to demand. At current gas prices production rates are not expected to be able to stay ahead of demand as the economy begins to return to normal growth.

#### **16) LNG Market Share:**

Until recently, liquefied natural gas, or LNG, has played a very small role in U.S. gas markets, due to the high capital cost of production and the costly transportation. The bar on the left shows that it currently makes up only 0.6% of U.S. consumption. However, technological advances in cryogenics have brought these costs down. LNG imports to the U.S. from nearby gas fields such as Venezuela and Trinidad are now considered viable at gas prices as low as \$2.50/MMBtu. Together with this advance, the \$3/MMBtu gas cost for sustainable drilling is projected to result in LNG filling an estimated 70% of the growth in gas demand over the next five years. Thereafter LNG will have to come from farther afield, and is expected to be roughly competitive with \$3 gas drilling costs.

#### **17) Global map with gas prices:**

At the near-term futures price of \$3/MMBtu, the U.S. and Western Europe are regions of high-priced natural gas. Low-priced gas from such regions as Venezuela, Trinidad and the Middle East can be converted to nitrogen products and transported and sold in the U.S. at prices that put substantial pressure on Gulf producers.

#### **18) Slide of nitrogen production plus shipping costs to the US:**

This slide shows the cost of shipping ammonia from various offshore points to the Gulf compared to the cost of producing it in the US with gas at \$2/MMBtu and \$3/MMBtu. Trinidad and Venezuelan suppliers are competitive down to \$2, while imports from other offshore producers would be expected to taper off between these levels.

#### **19) Nitrogen imports:**

Let’s look at the impact of last year’s high gas and consequent high nitrogen prices on U.S. nitrogen imports on a fertilizer year basis.

#### **20) Ammonia imports:**

Ammonia imports for the fertilizer year ending this past June were up close to 30% compared to the previous fertilizer year.

#### **21) Urea imports:**

For urea, the increase was 55%.

#### **22) AN imports:**

Ammonium nitrate imports rose 9%.

#### **23) N solution imports:**

Nitrogen solutions showed the largest increase on a percentage basis, a cool 248%.

#### **24) Monthly nitrogen imports:**

Next we’ll look at monthly import levels to see how the reduction in gas prices is affecting imports. Ammonia for the current fertilizer year, shown by the red line, shows a sharp downward movement.

25) Urea, again in red, is also below last year’s levels, in green.

26) Ammonium nitrate is substantially below last year’s levels.

27) And UAN imports are also showing a downward trend.

28) Now let's look at the origins of these higher imports, Ammonia imports were up from all suppliers except Canada. Canadian imports were down due to curtailments taken during periods of high gas prices during the year.

29) Urea imports are up from all suppliers except Canada, and Western Europe.

30) For UAN, the major jump was in imports from Eastern Europe, the Ukraine and Russia.

31) After seeing what happened to imports recently, what can we expect for next year? Imports are projected to be lower than those we have just seen, but higher than in fertilizer year 1999/2000. Overall, U.S. nitrogen imports in fertilizer year 2000/2001 were up 41% compared to FY 1999/2000. A 22% drop is projected for the current fertilizer year.

32) Now let's look at imports' effect on nitrogen inventories as reported by TFI. Ammonia, in red, was not affected significantly, remaining close to the black 5-year average line.

33) The urea inventory bulged in the spring, when local production came back in addition to the high rate of imports. After the spring season, curtailments in imports brought the inventory back below the 5-year average.

34) UAN, which surged for the same reasons, is also currently below the 5-year average.

**35) Slide indicating war on terrorism:**

Let's look now at the outlook for regional imports. The war on terrorism has added a premium for war risk insurance to shipping rates from the Arabian Gulf region. It's been only approximately \$1-2 to date, but could increase. Insurers are reported to be refusing to provide a war risk insurance rate until the arriving vessel is four days from port, to take into account any escalation in hostilities. Furthermore, the devastating terrorist attack at the World Trade Center is reported to have cost insurance companies over \$50 billion, and may have

an impact on future rates. (*\$55 billion quoted in discussions with insurers*)

**36) Ammonia Exports:**

On the export front, FSU exports should be reduced during the next five years as a result of increased consumption within the FSU. Exports from the low-cost gas regions of Trinidad, the Middle East and Asia, and to a lesser extent from new South American projects, will be higher. In total, trade is projected to grow by about 3% annually from now until 2006, from the current 12% of world production.

**37) Urea Exports:**

Because of its popularity, exports of urea are projected to grow more quickly than those for ammonia. FSU exports will drop, while higher production from the low-cost gas regions in South America, the Middle East and Asia will push exports up by close to 5% annually from 2001 to 2006.

**38) % Capacity Utilization:**

Global capacity utilization for both ammonia and urea is projected to grow, but this growth will be tempered in the international trade market by new export-oriented projects coming on stream. Whether these produce a supply overhang in the international trade market or not will depend on the level of industry rationalization over the next few years.

**39) Environment:**

My final remarks will deal with the environment, an area that concerns us all as nitrogen and other fertilizers are being unfairly blamed for everything from hypoxia in the Gulf to deformed frogs. At the same time, the fertilizer industry is coming under more scrutiny. Some of our critics are entering government and becoming ever more influential. Their lack of understanding of fertilizer's beneficial dual role feeding the world while conserving the environment poses a threat to our ability to manage our assets effectively.

**40)** For the most part, people who express such concern do so with the best of intentions. Unfortunately, we have not kept them properly informed about our industry's vital role in the modern world. In mature fertilizer markets, people began to take food for granted during the 1980s, even as environmentalism flourished.

**41)** The identification of the fertilizer industry as evil is the precautionary principle at work, shifting the onus from proving something is harmful to proving it has absolutely no risk. It's the 'better safe than sorry' concept. Little attention is paid to fertilizer's benefits, and our most outspoken foes may not even be aware of them. Many people have no concept of the link between the food in their supermarket and the farmers who produce it, by using fertilizer to improve both nutritional quality and availability of that food.

**42)** Remember that line from the movie, *Cool Hand Luke*, starring Paul Newman: "What we have here is a failure to communicate." When communication breaks down, conflict often follows. Our world cannot afford a communications breakdown about the link between fertilizer and food, for the worst-case scenario of reduced fertilizer use would quickly result in conflict over the declining quantities of food. We must make sure the world knows about our vital contribution to improved diets for people everywhere and their hopes for an even better standard of living.

**43)** At PotashCorp, we've taken the first step. We launched our Fertile Minds educational campaign in July with ads in Washington, DC editions of national U.S. magazines. We were inspired to act by a survey we did of staff members of U.S. senators and congressmen who sit on committees affecting our business. The results showed that 70 percent didn't know the source of either nitrogen or potash, and 61 percent had no idea about phosphate's origin. When we asked 150 lawmakers to rate organic and conventional fertilization methods, organic fertilizers sailed past N, P and K.

**44)** This worries us, for these people draw up and vote on laws affecting the production and application of crop nutrients. We could be angry with them for not being as well versed on our industry as we would like, but in many ways we have only ourselves to blame. We can no longer afford the luxury of simply focusing on the noble profession of feeding the world in anonymity. As an industry spanning the globe, we've got to trumpet the news of our great products worldwide.

**45)** It's up to all of us to tell this story. This entire industry needs to start speaking with one voice as consistently and as passionately as our detractors do. The effort has begun, but we have much work to do.

# Outlook for Nitrogen

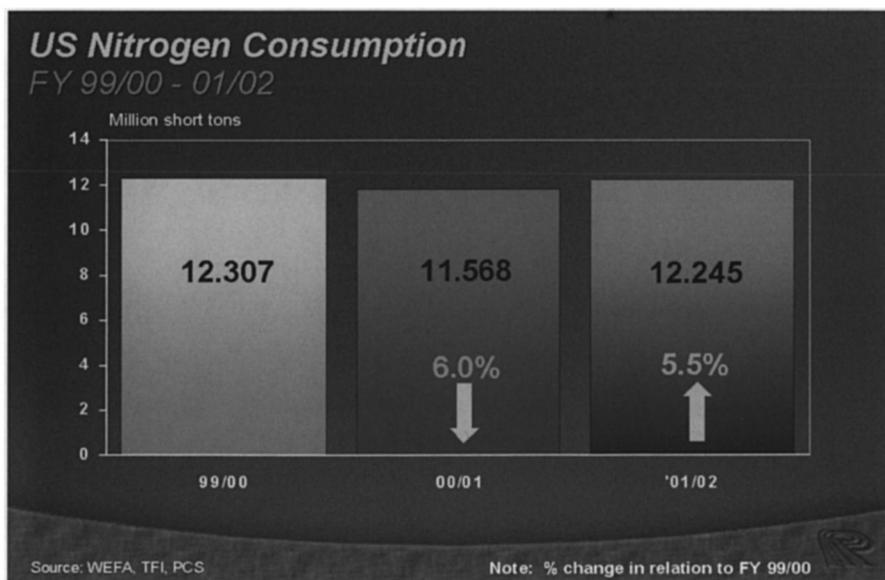
*Al Mulhall*  
Potash Corporation

Slide 1

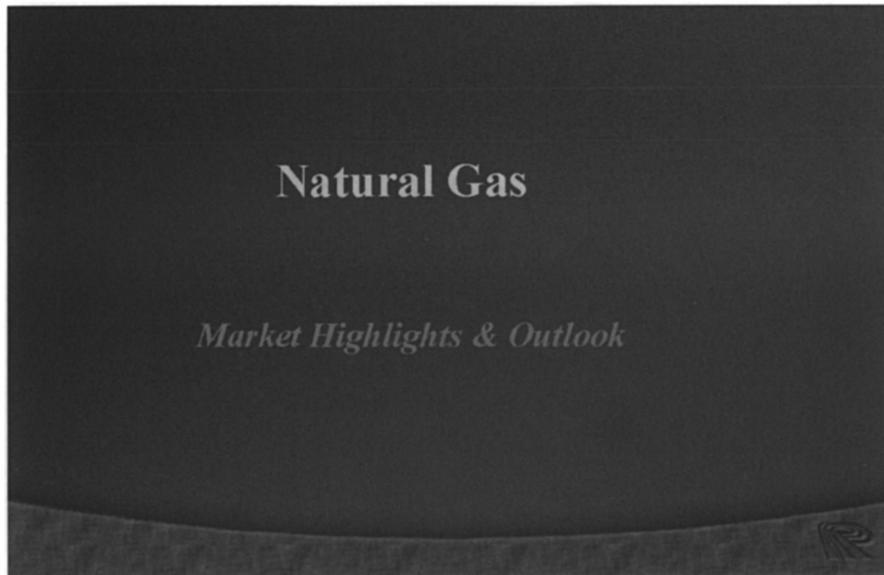
### TFI Outlook - Nitrogen

- ▶ Outlook for US N consumption
- ▶ Impact of US and world gas markets on nitrogen
- ▶ Nitrogen - supply/demand & international trade
- ▶ Nitrogen & the environment

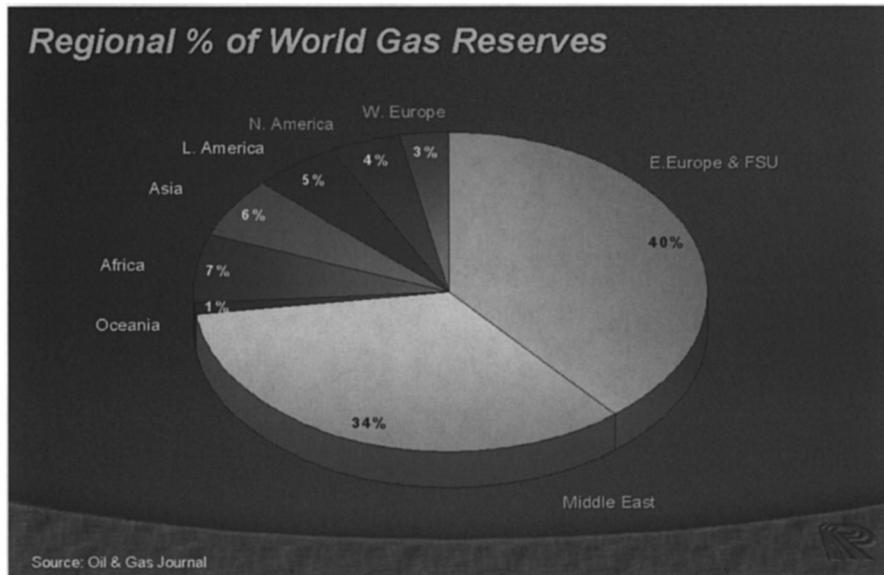
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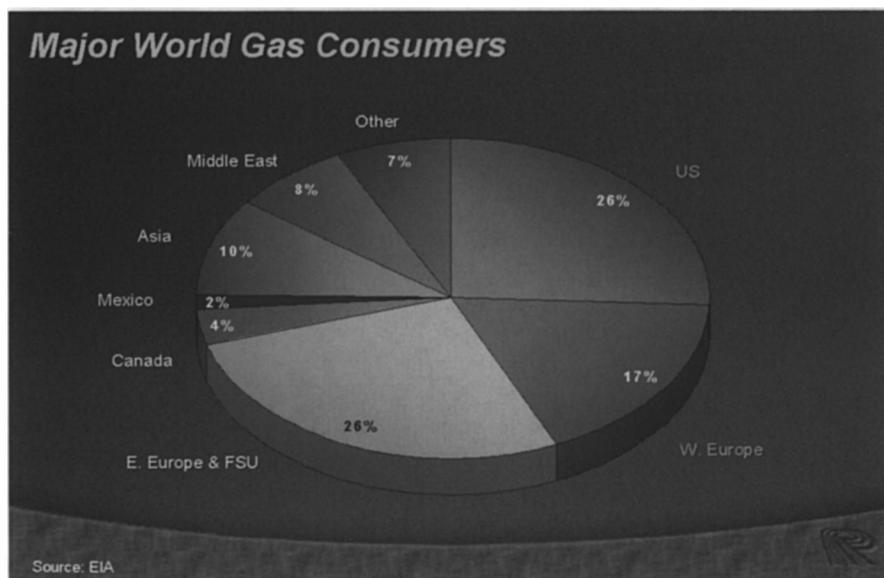
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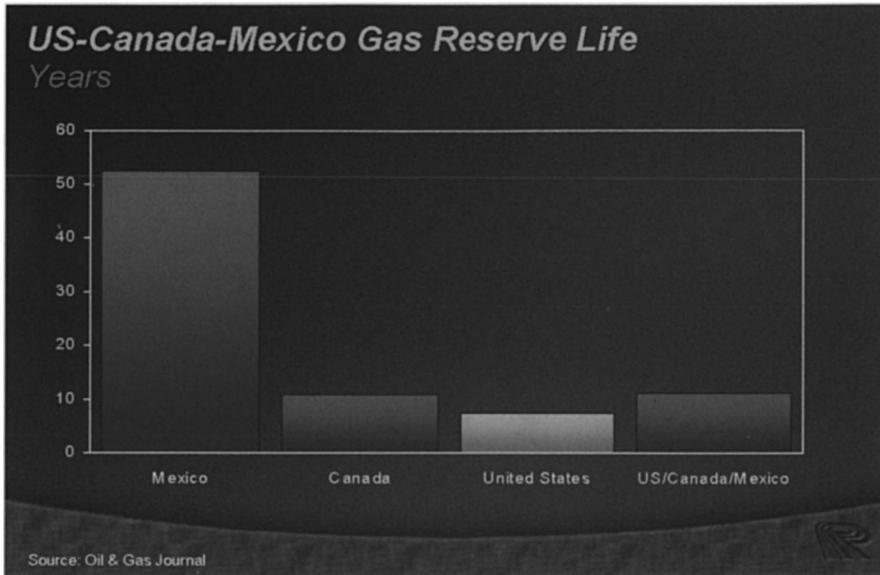
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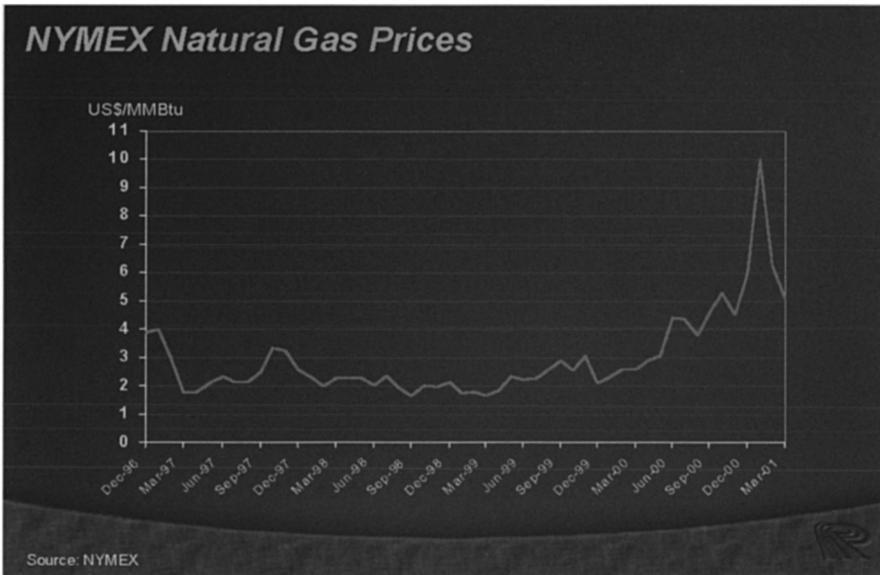
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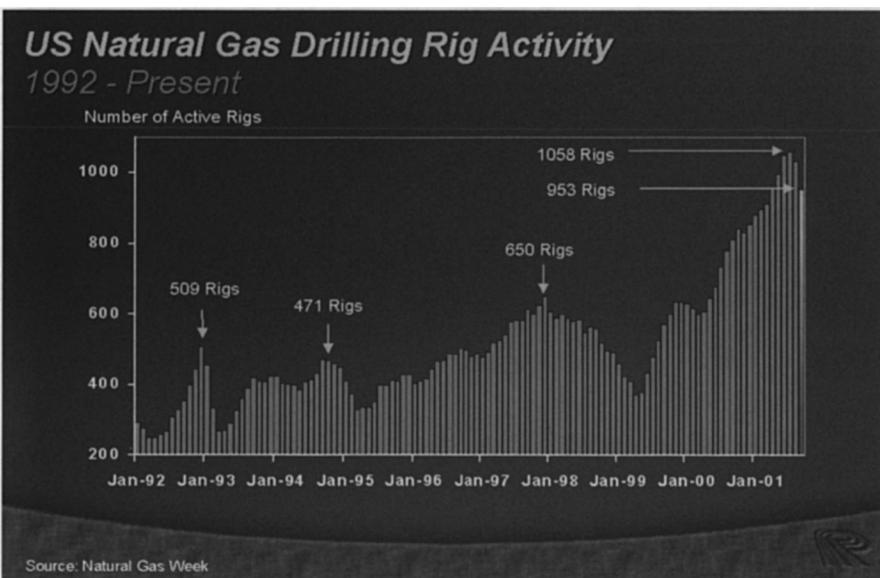
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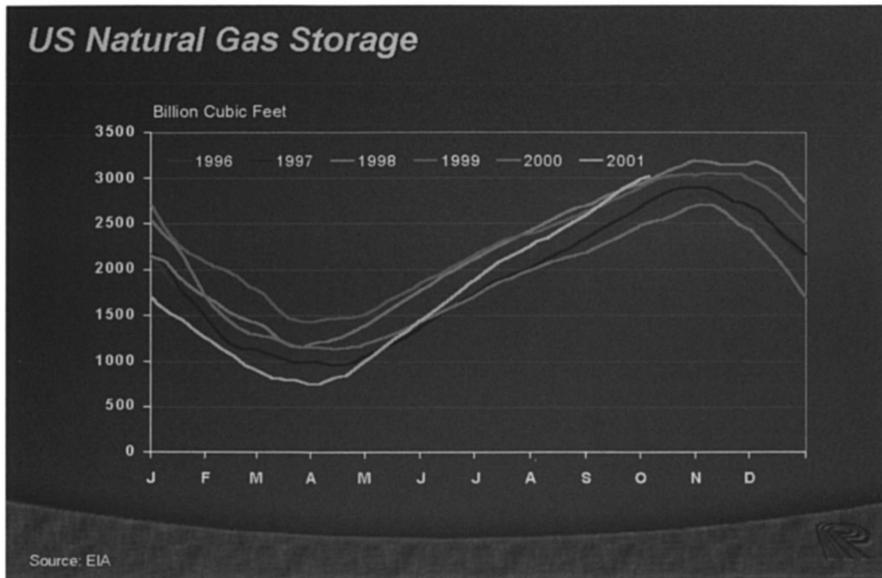
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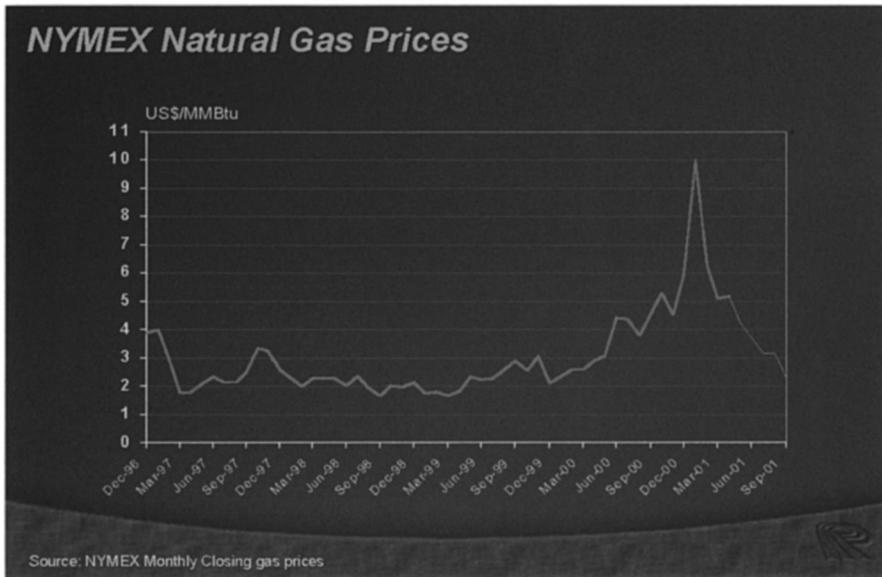
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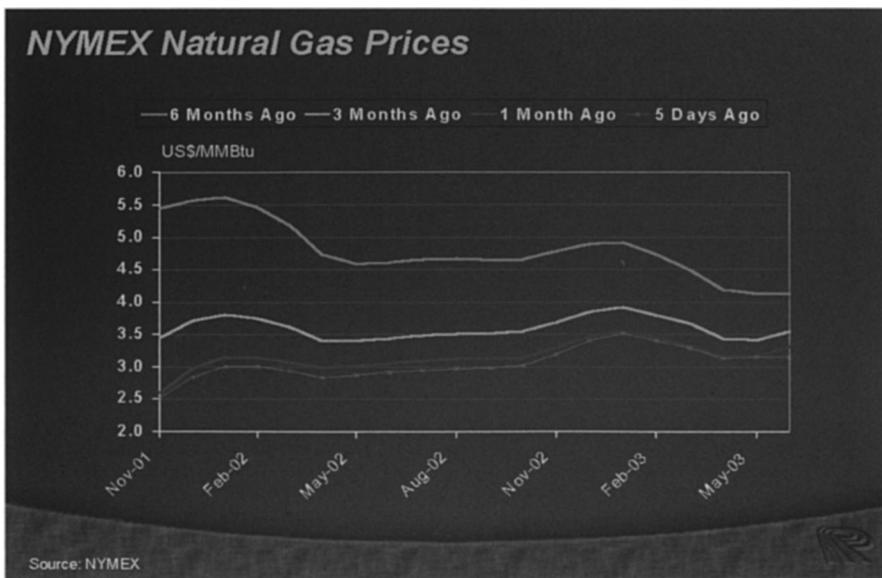
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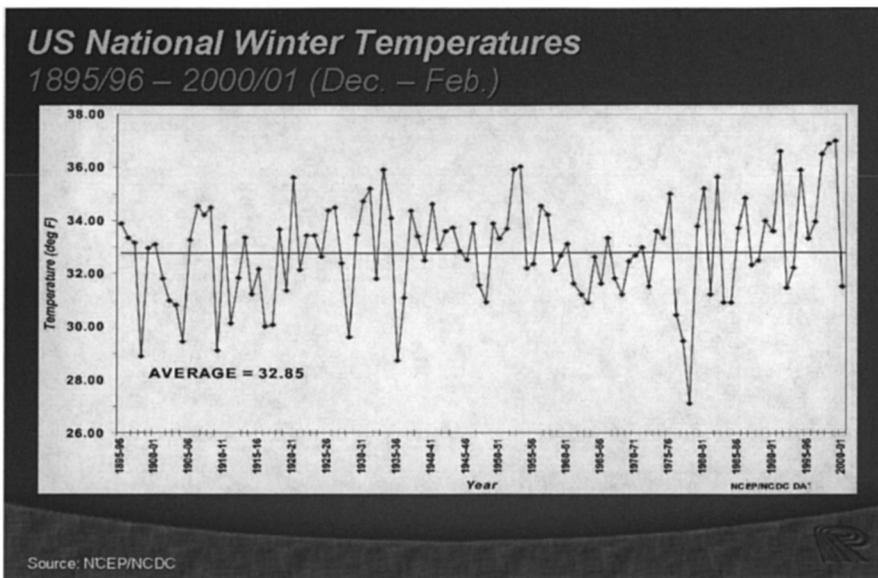
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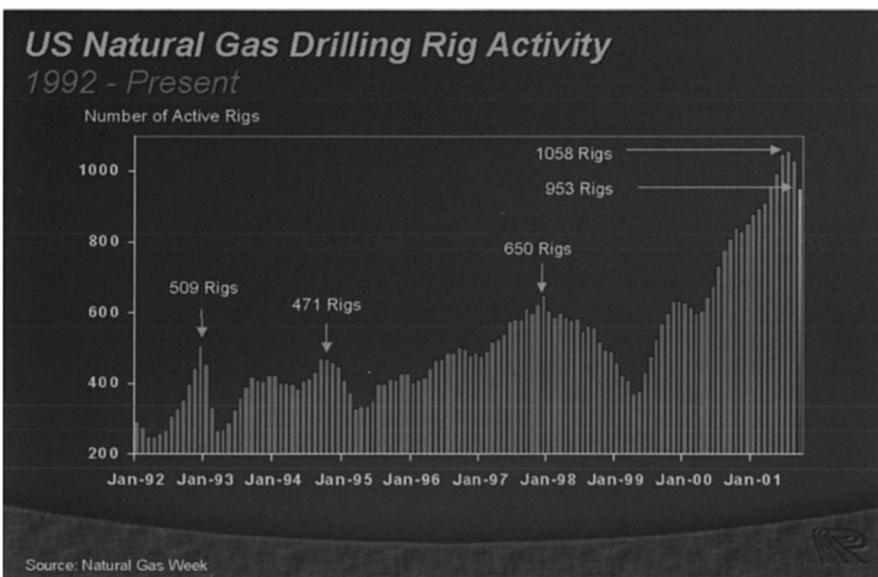
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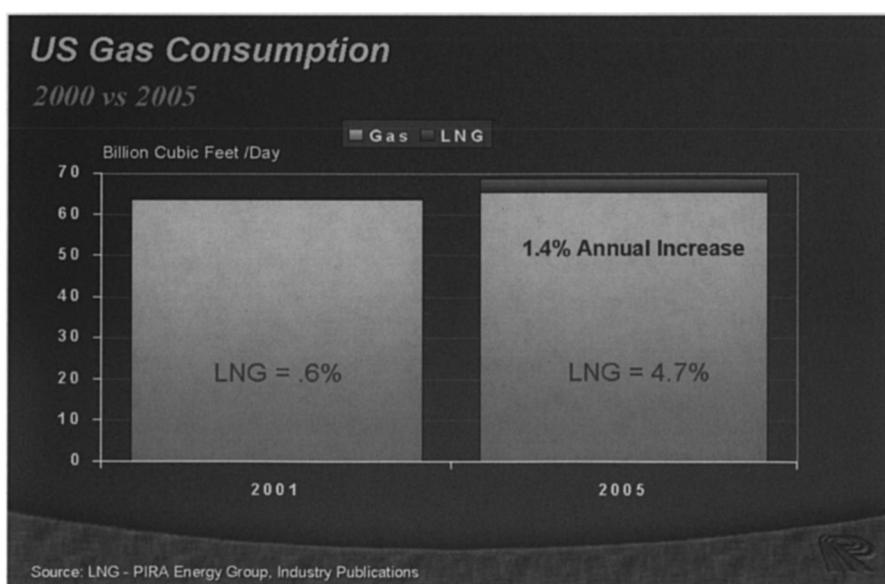
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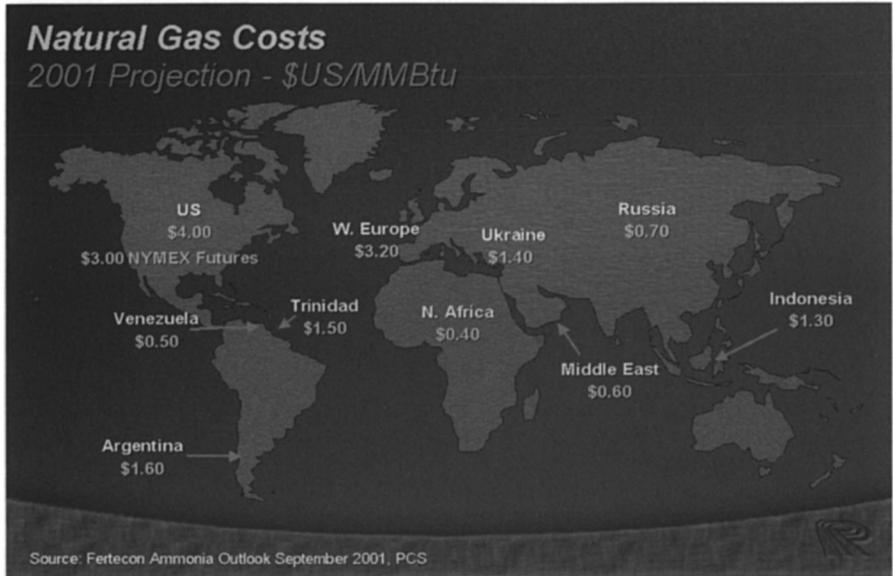
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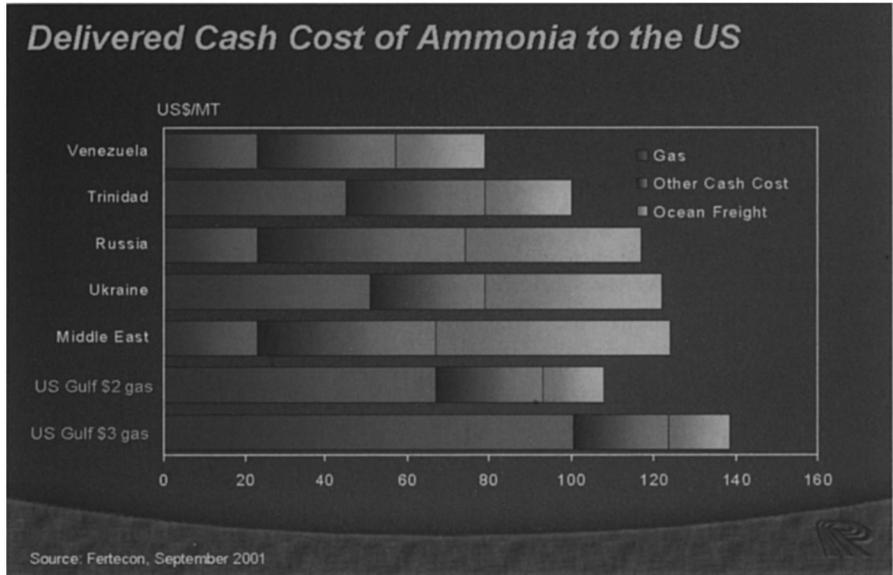
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Slide 15



Slide 16

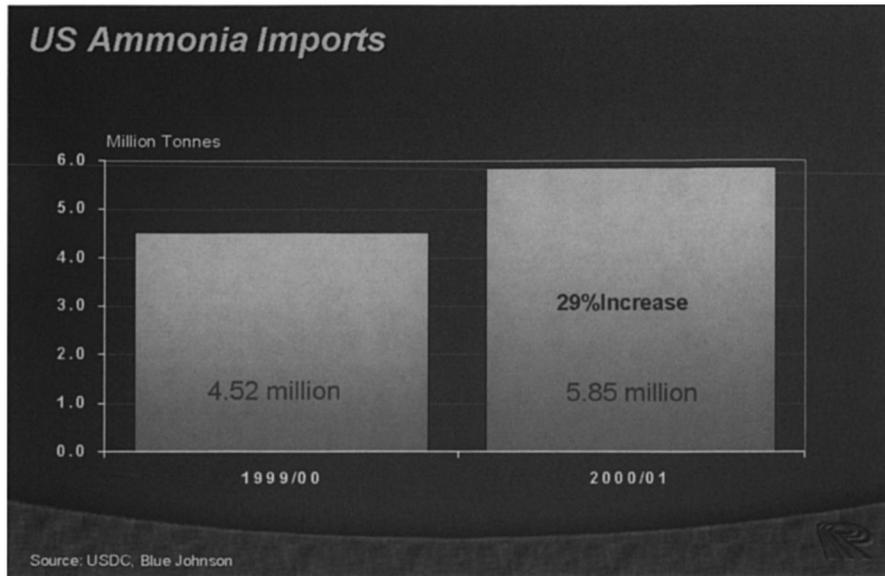


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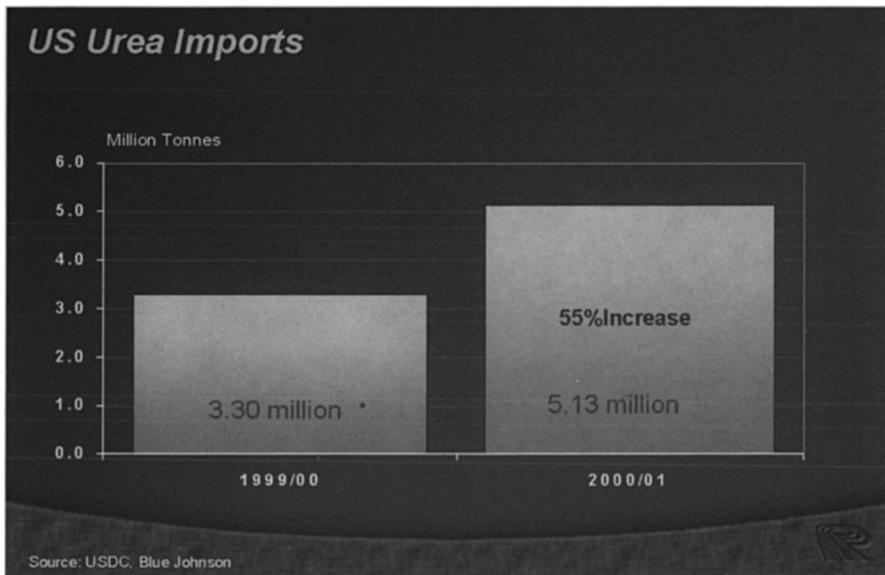
# Nitrogen Imports

Market Highlights & Outlook

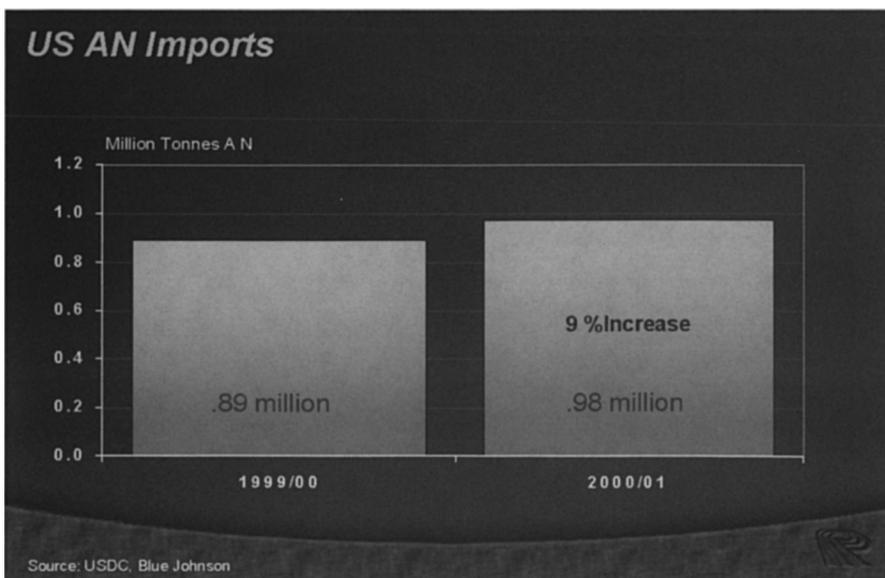
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Slide 19



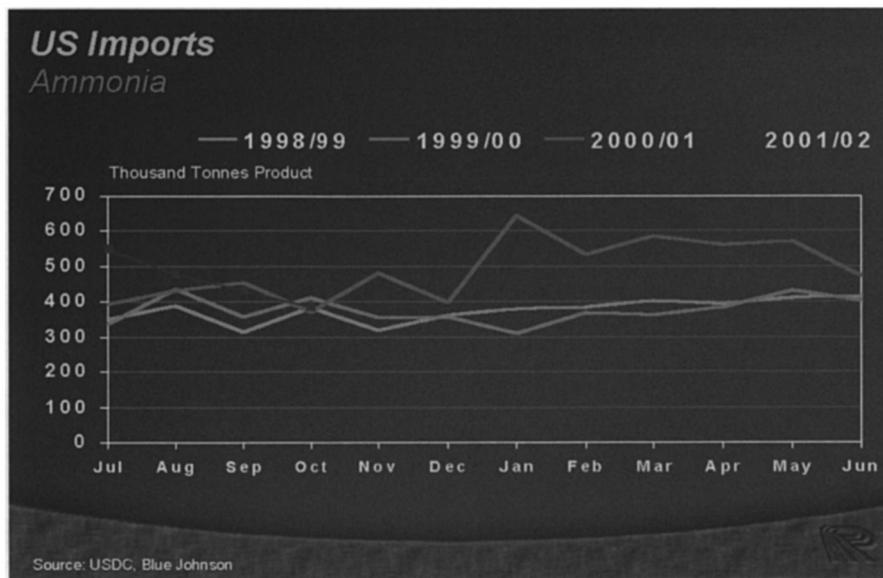
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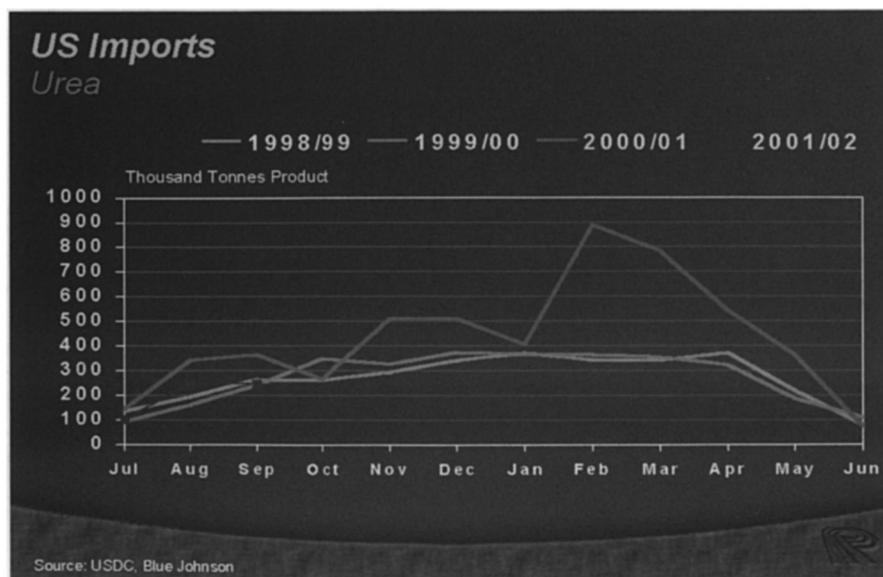
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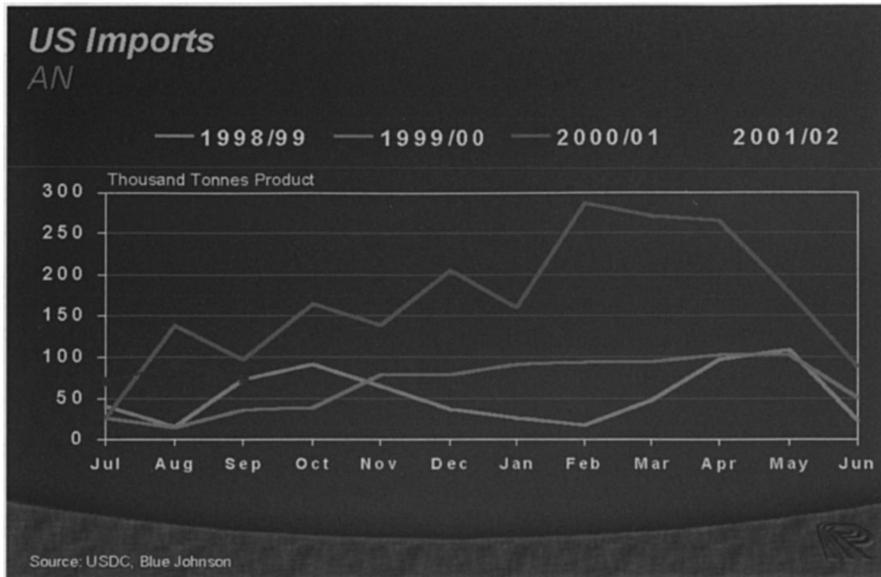
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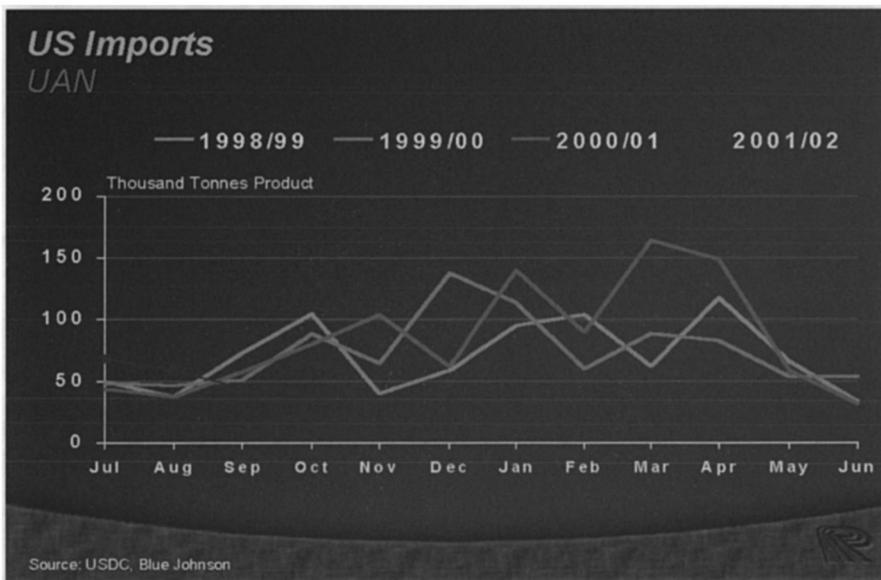
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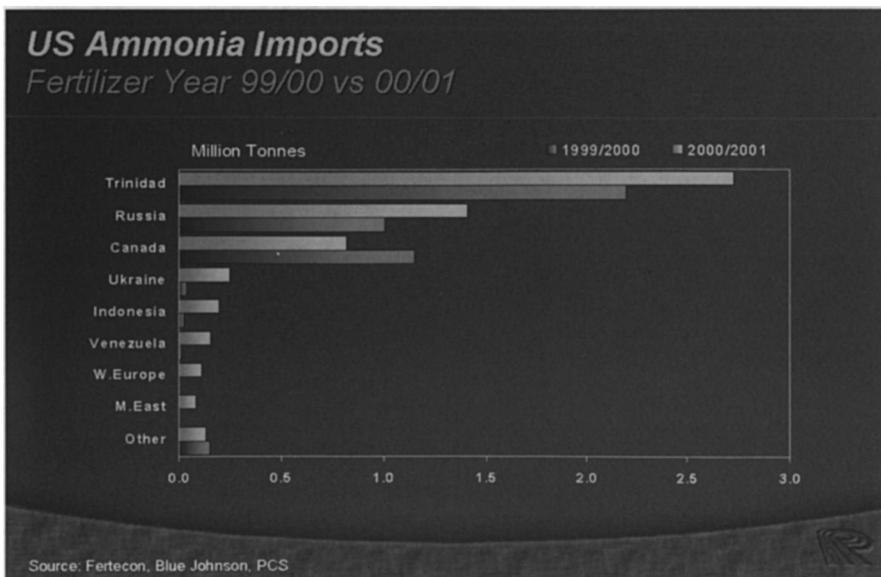
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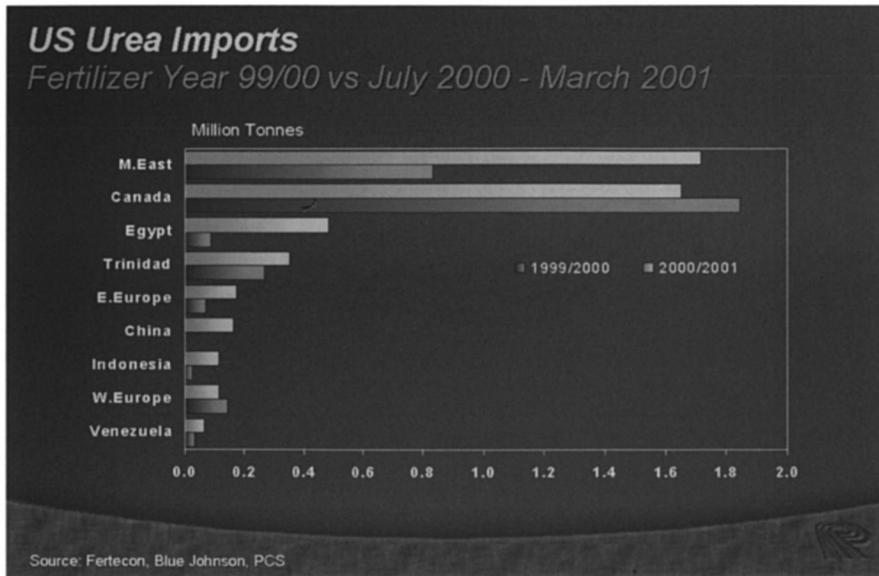
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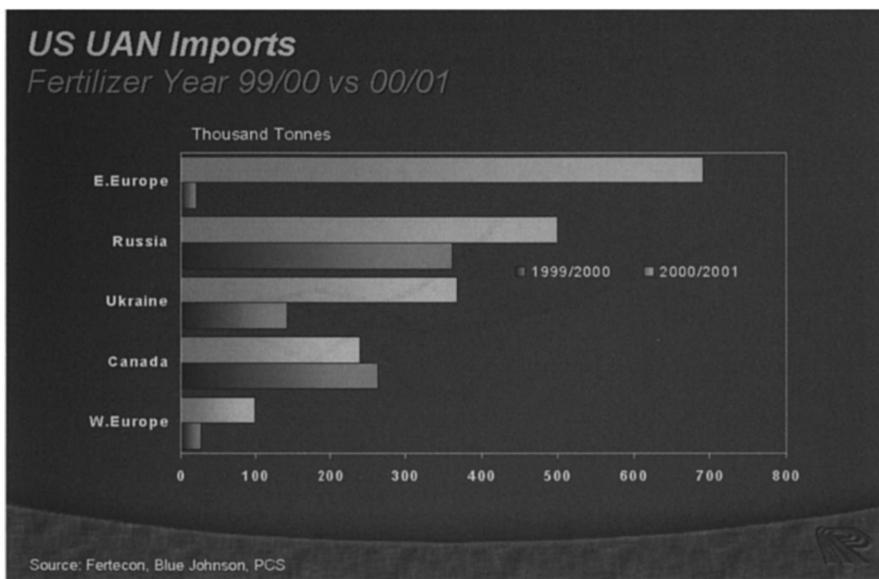
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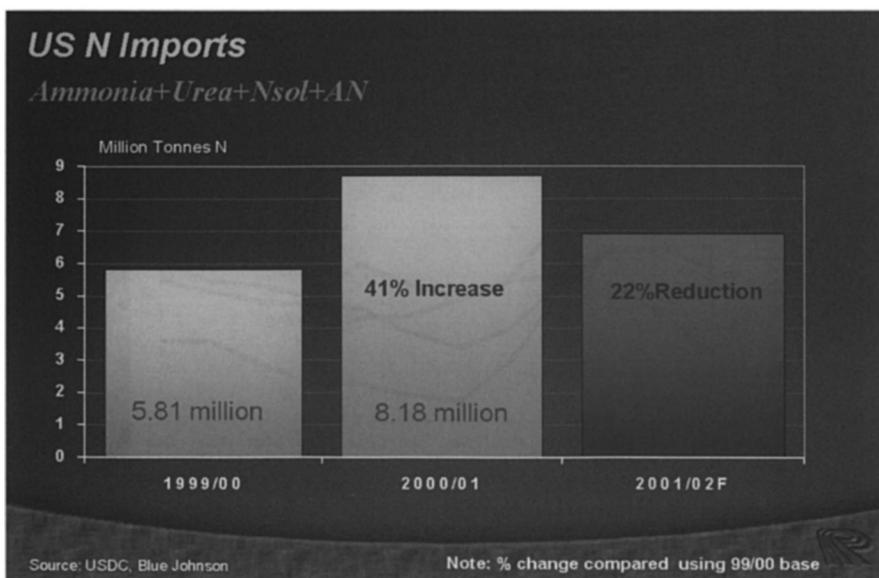
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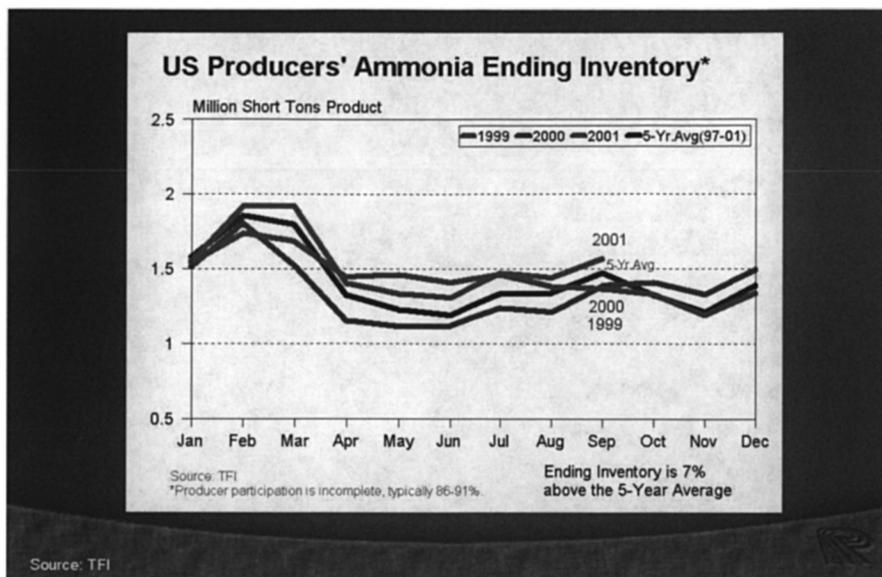
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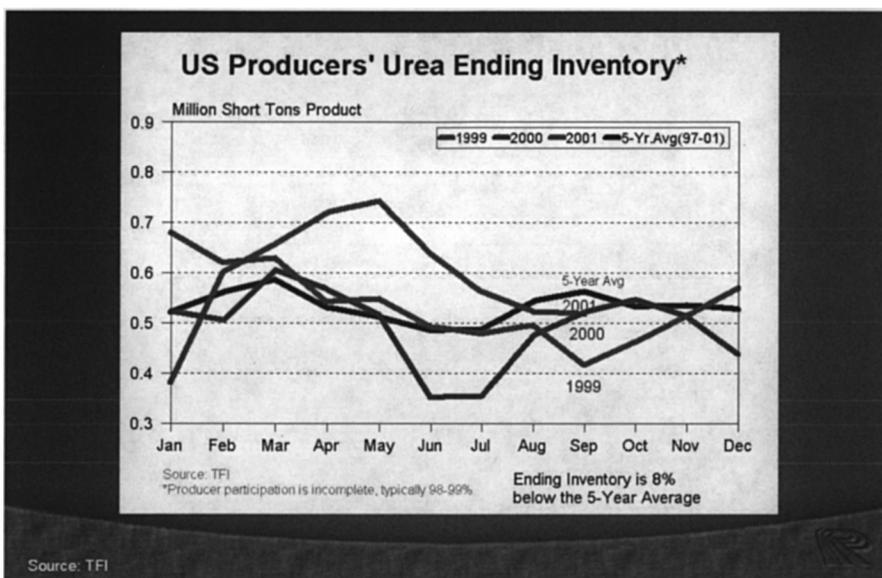
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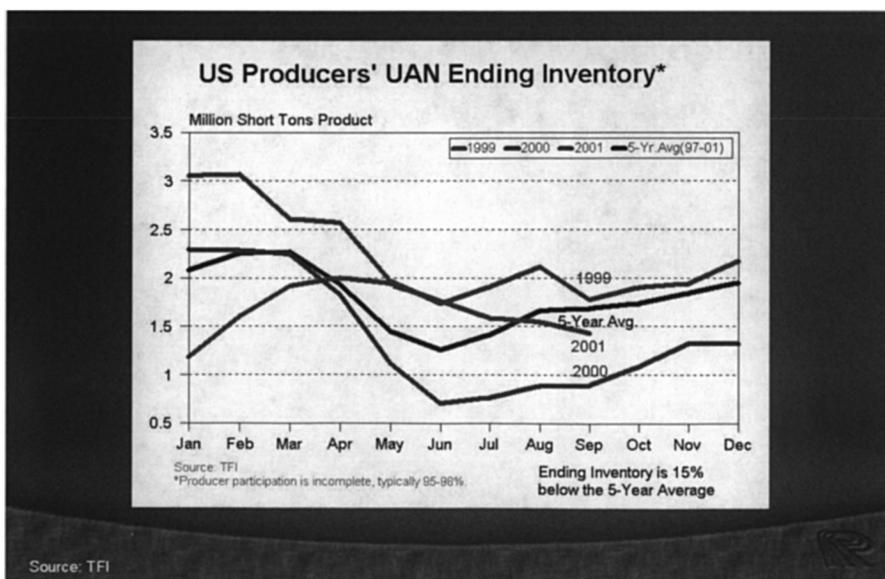
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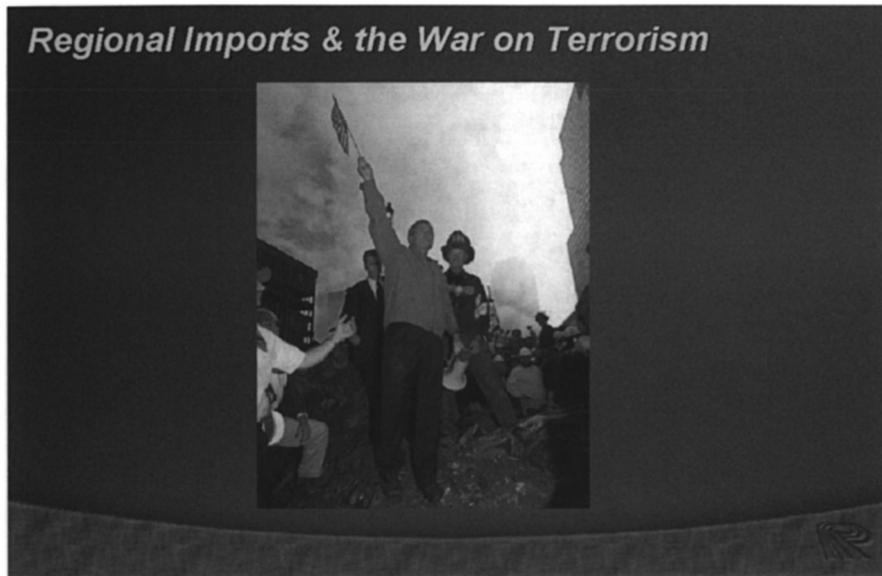
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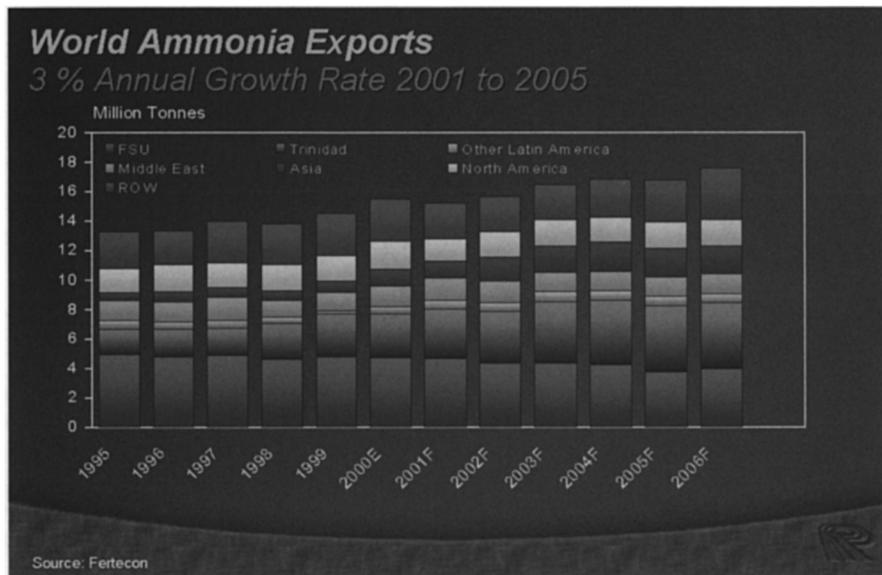
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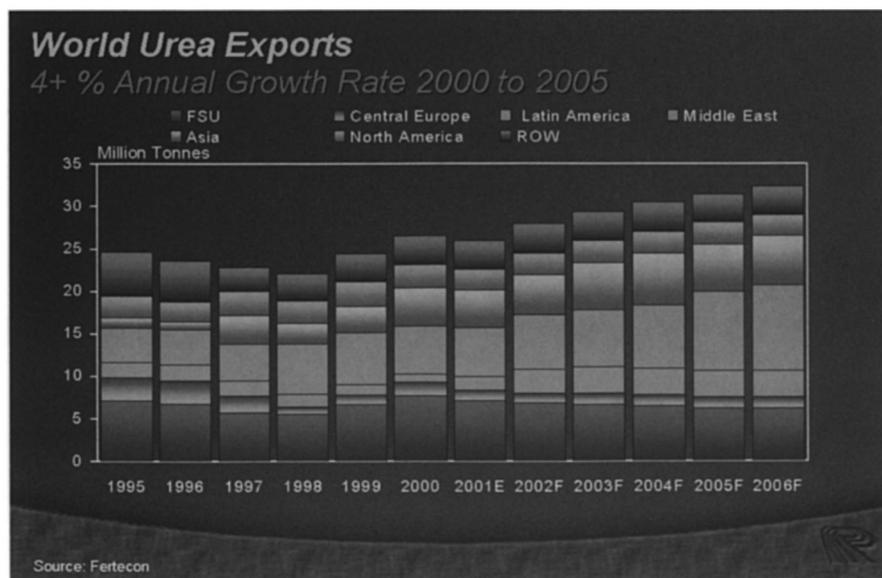
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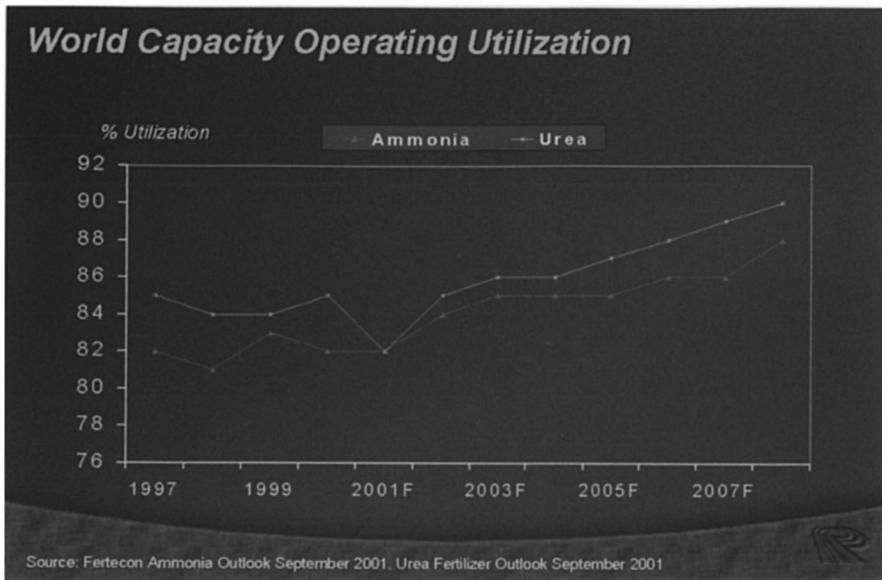
Slide 34



Slide 35



Slide 36



Slide 37



Slide 38



Slide 39

### Fertilizer on Trial

**Fertilizer is Evil**

- Lack of Knowledge
- "Better Safe than Sorry"

**Fertilizer is Essential**

- Feeds 1/3 of World
- Conserves Habitat
- Conserves Wildlife

Slide 40

### Failure to Communicate

Link: Fertilizer – Food - Environment

- Conflict often follows communications breakdown
- Result of reduced fertilizer use is declining quantities of food
- World must know about our vital contribution to improved diets and better standard of living

Slide 41

### Educating the Lawmakers

Fertile Minds

- 70% unaware of origin of nitrogen or potash
- 61% unaware of origin of phosphate
- Organic fertilizer ranked ahead of manufactured

Slide 42



Slide 43

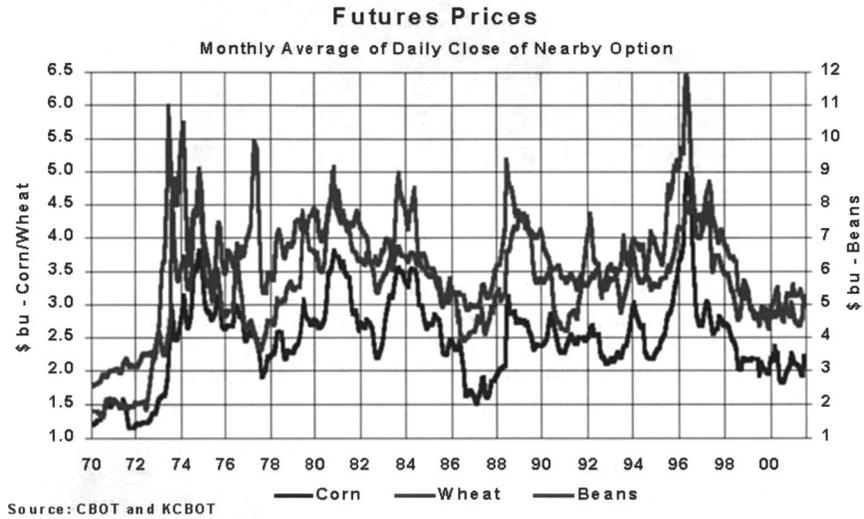


# The Near Term Phosphate Outlook

Corrine Ricard  
Cargill Fertilizer, Inc.

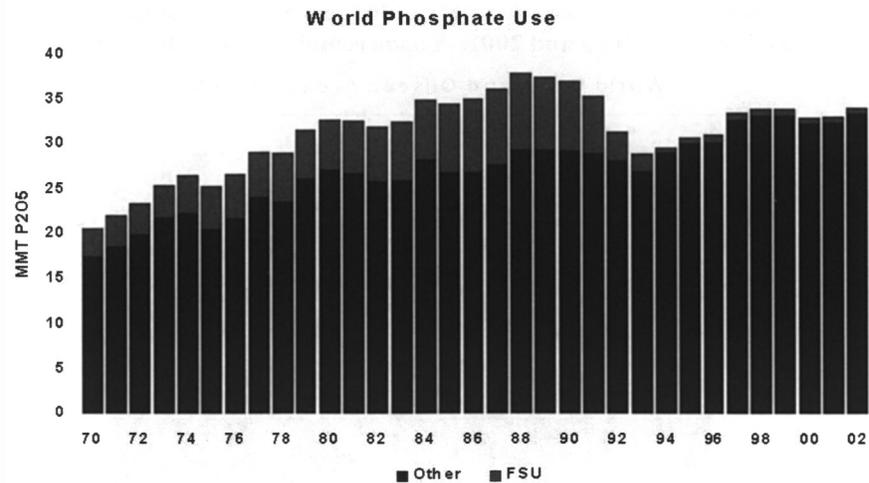
Slide 1

## Grain and oilseed prices remain at low levels



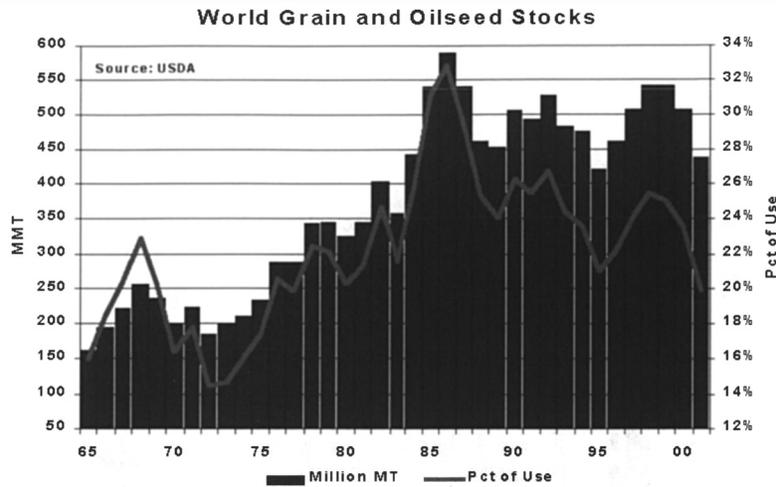
Slide 2

## Low grain and oilseed prices have dulled phosphate demand growth during the last few years



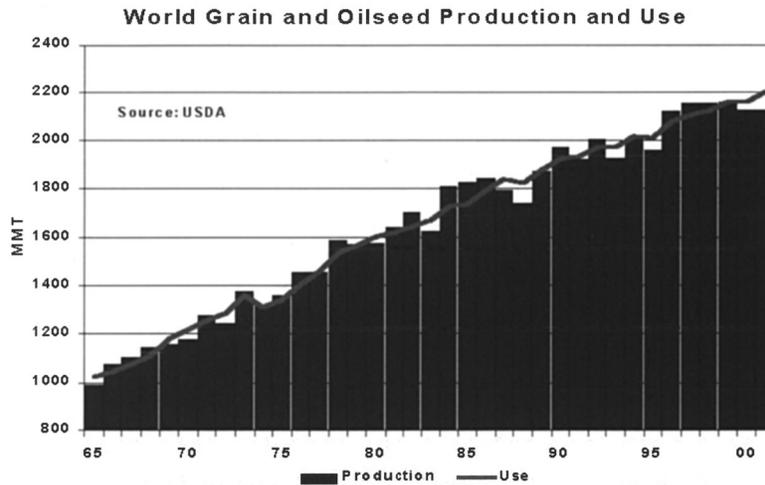
Slide 3

**World grain and oilseed stocks are projected to decline 71 mmt to 438 mmt or 19.9% of use during the 2001/02 crop year**



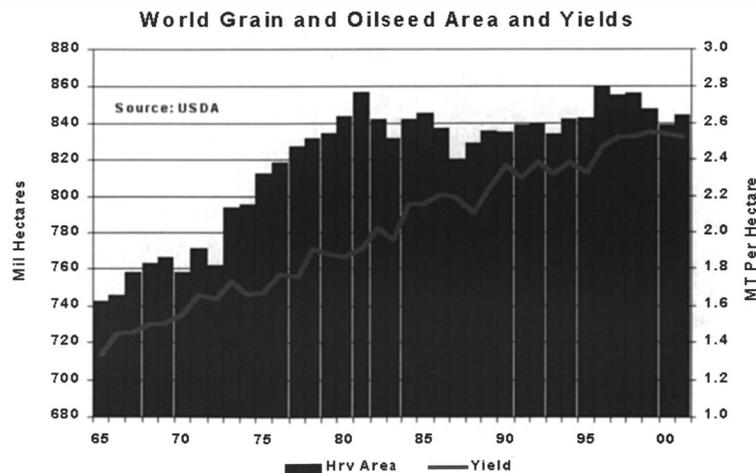
Slide 4

**The projected decline in grain and oilseed stocks is the result of the demand in consumption - demand at a record 2.20 bmt in 2001/02**



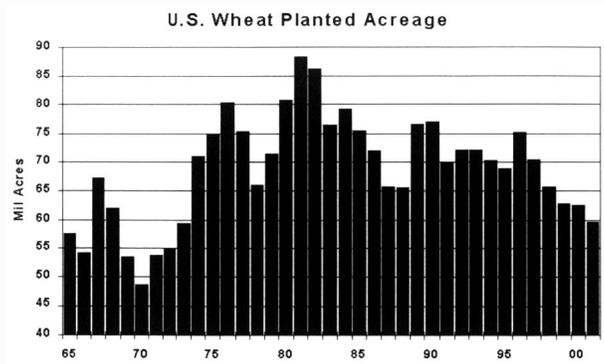
Slide 5

**Low prices have forced reductions in harvested area worldwide. The drop in harvested area accounted for the drop in world grain and oilseed production in 2000 and 2001. Yields remained flat at high levels last year.**



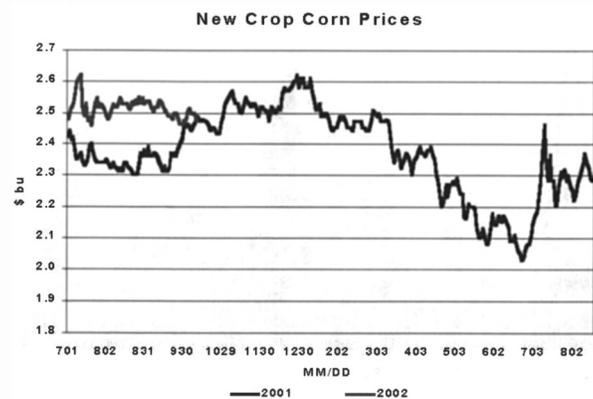
Slide 6

**U.S. wheat acreage dropped to less than 60 million acres in 2001, the lowest level since 1973**



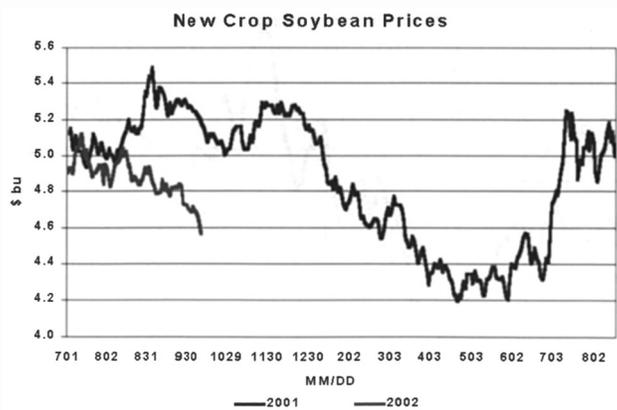
Slide 7

**New crop corn has remained stable at the \$2.5 per bushel range**



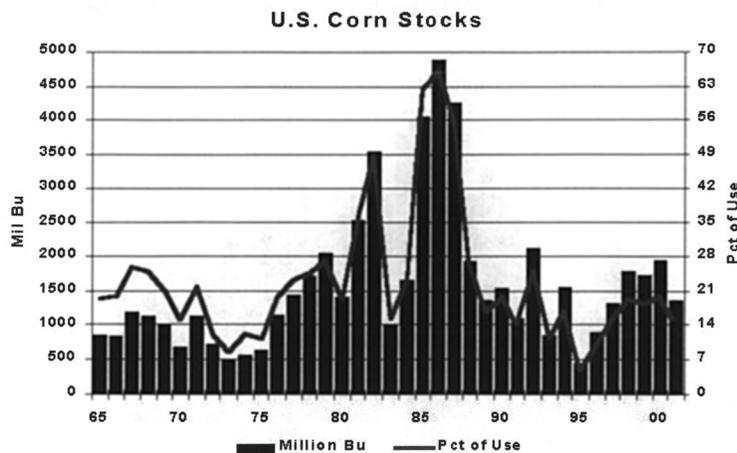
Slide 8

**New crop bean has dropped more than 40 cents since September**



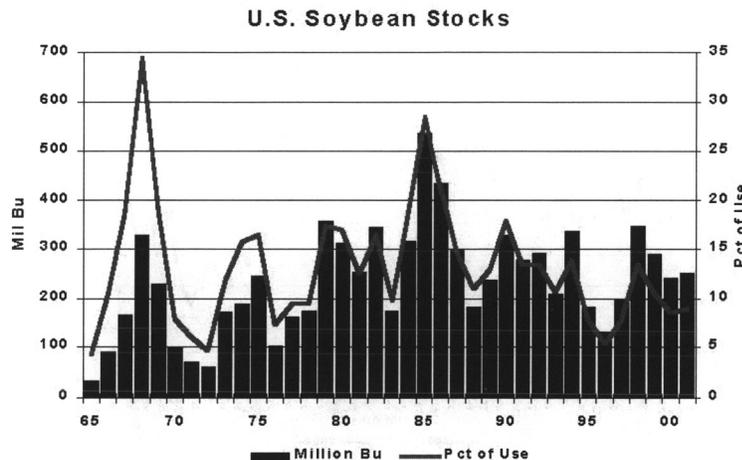
Slide 9

**Corn stocks are projected to decrease to less than 1.36 billion bushels at the end of 2001/02 - a drop of about 30% from 2000/01.**



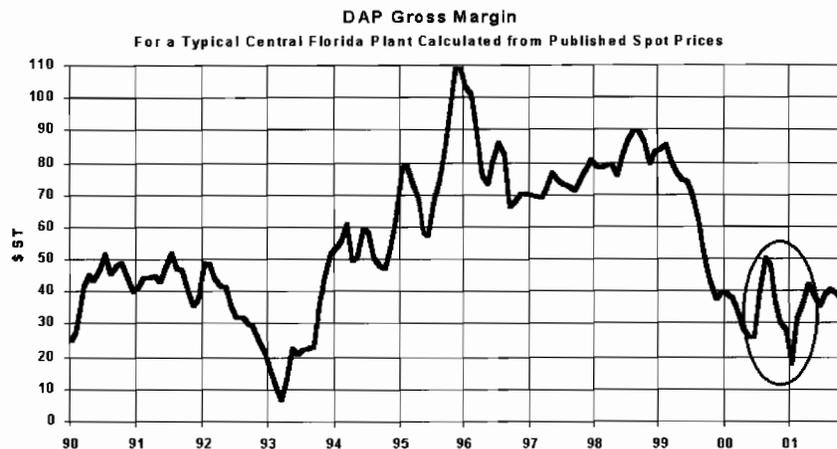
Slide 10

**Soybean stocks are projected to increase to more than 250 million bushels by the end of the 2001/02 crop year.**



Slide 11

**The surge in ammonia prices severely squeezed DAP margins last winter. Breaks in raw materials costs coupled with higher DAP prices have pulled gross margins to the upper-\$30 st range.**



Source: Fertecon, Green Markets, TFI and Cargill Forecasts

Slide 12

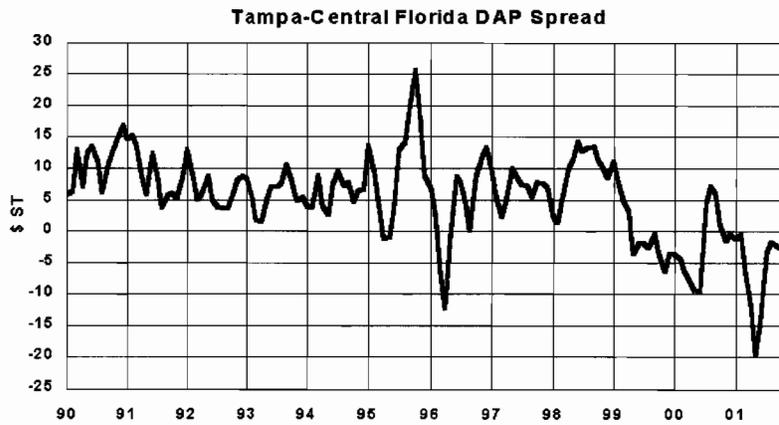
**DAP prices have dropped to the lowest level since 1993.**



Source: Fertecon

Slide 13

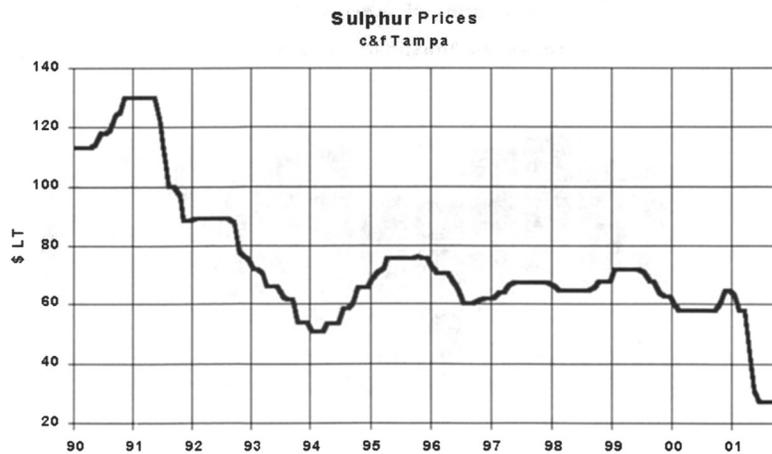
**Tampa vessel prices have traded at a large discount to Central Florida rail prices.**



Source: Fertecon and Green Markets

Slide 14

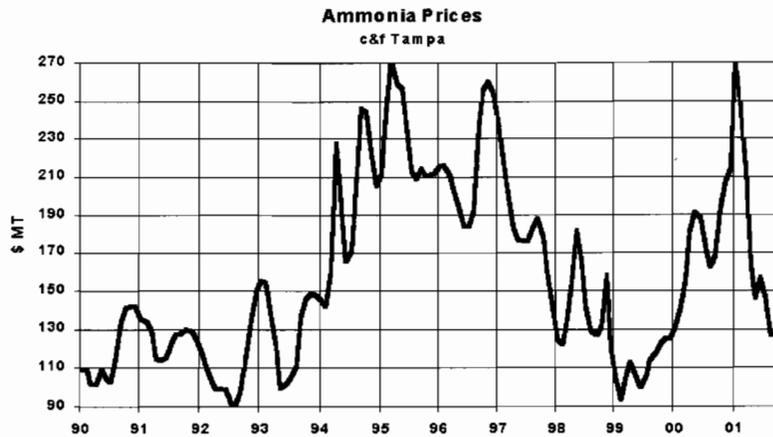
**Sulphur prices have dropped to record lows as a result of depressed phosphate operating rates and increases in recovered**



Source: Green Markets

Slide 15

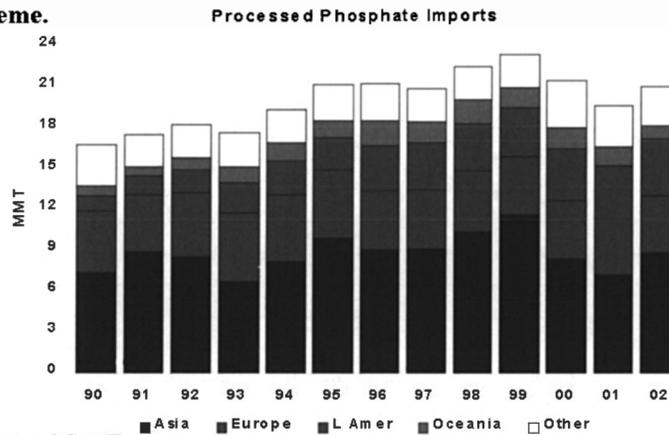
Surging gas costs caused ammonia prices to spike to more than \$260 mt c&f Tampa last winter.



Source: Fertecon

Slide 16

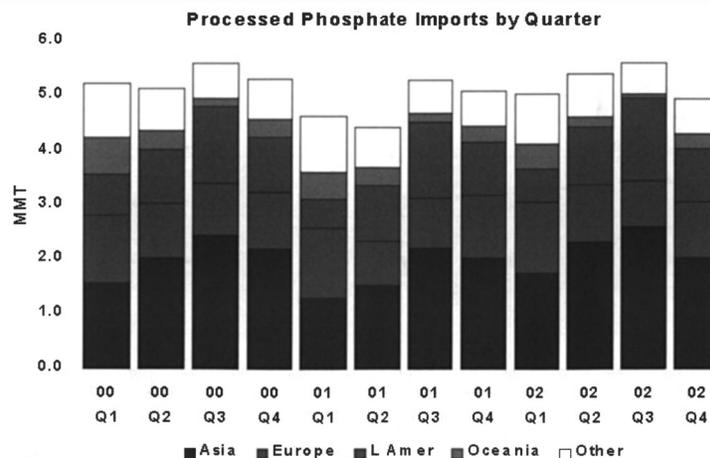
Processed phosphate import demand is forecast to decline to 19.4 mmt in 2001, the lowest level since 1993 and a drop of 16% or 3.8 mmt from the 1999 peak. Demand is forecast to recover to 20.9 mmt in 2002, but that assumes China enters the WTO this year and India reforms its DAP subsidy scheme.



Source: Fertecon and Cargill

Slide 17

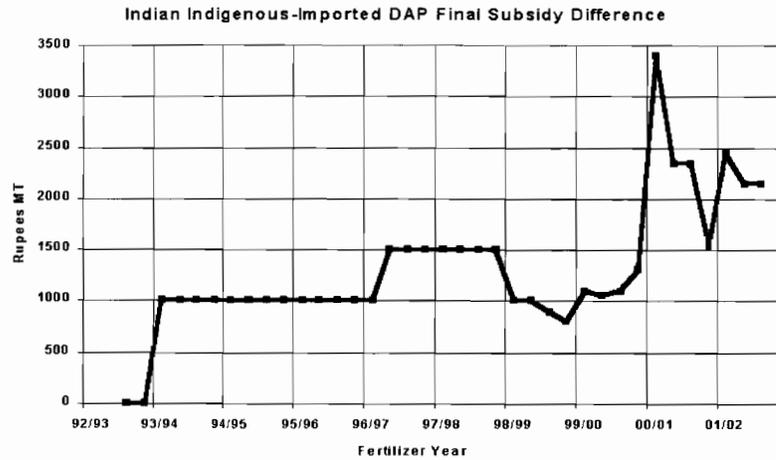
Processed phosphate imports during the first half of 2001 dropped to extremely low levels as a result of weak Asian demand. A moderate recovery is forecast for the second half of 2001 and 2002.



Source: Cargill

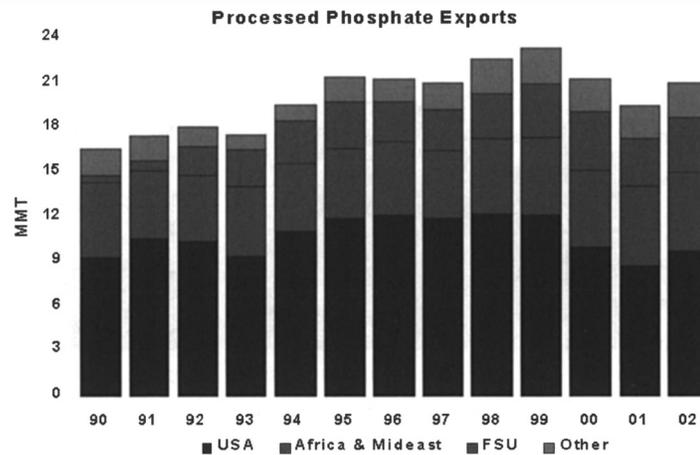
Slide 18

**India provides a higher subsidy to domestic DAP producers than importers. The differential violates WTO rules and stimulates the construction of inefficient capacity.**



Slide 19

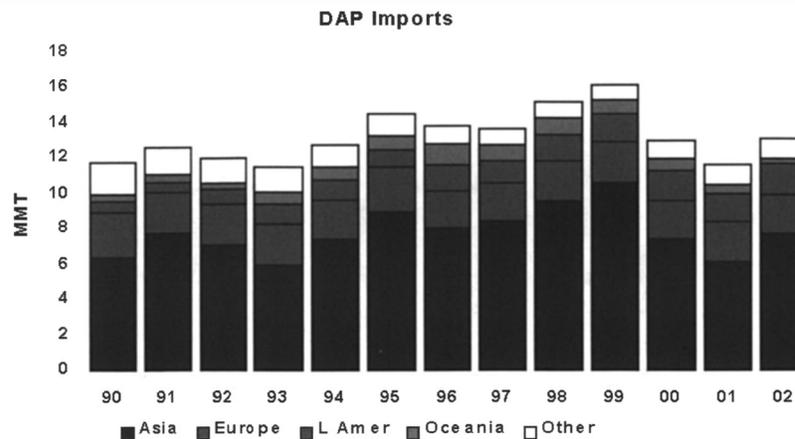
**The United States accounted for all of the supply adjustments in 2000 and further reductions -- particularly during the first half of the year -- are required to balance projected demand in 2001**



Source: Fertecon and Cargill

Slide 20

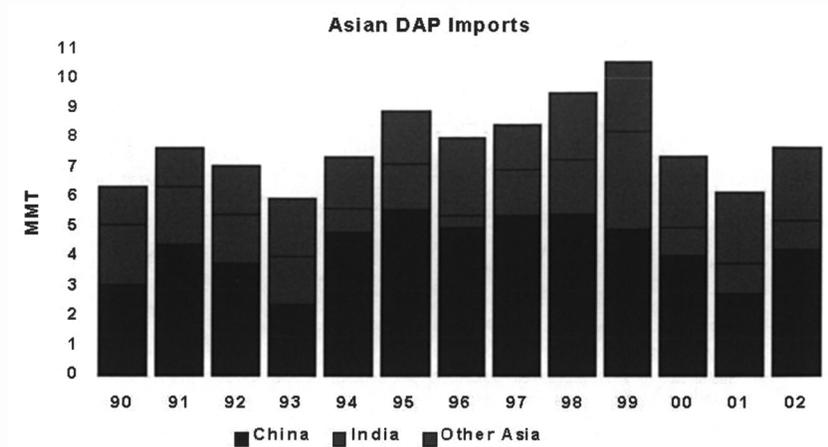
**After climbing to a record 16.1 mmt in 1999, DAP trade dropped 20% or more than 3.0 mmt to less than 13.0 mmt in 2000. Import demand is forecast to drop further to 11.6 mmt in 2001**



Source: Fertecon and Cargill

Slide 21

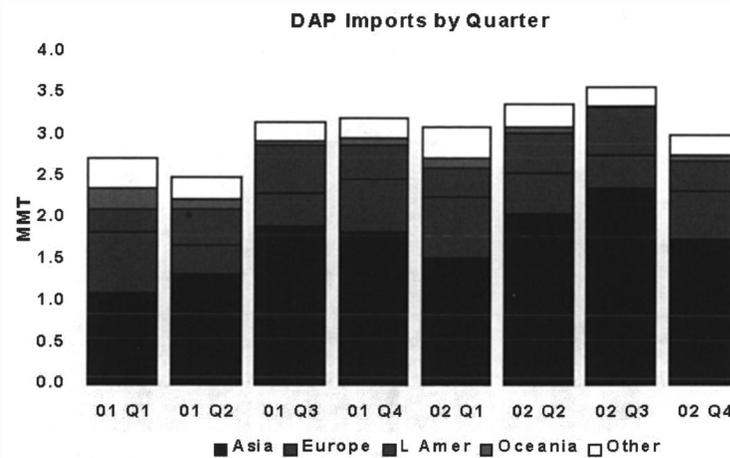
**China and India accounted for all of the decline in DAP shipments to Asia last year. Shipments to China are expected to drop further this year.**



Source: Fertecon and Cargill

Slide 22

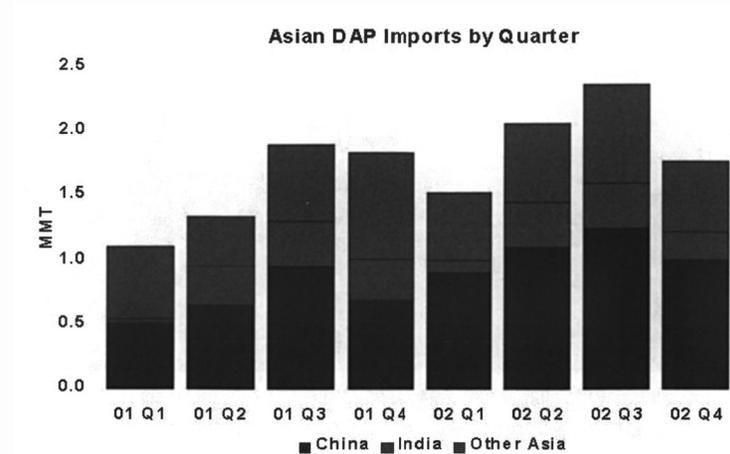
**DAP import demand dropped to extremely low levels during the first half of 2001 as a result of ...**



Source: Cargill

Slide 23

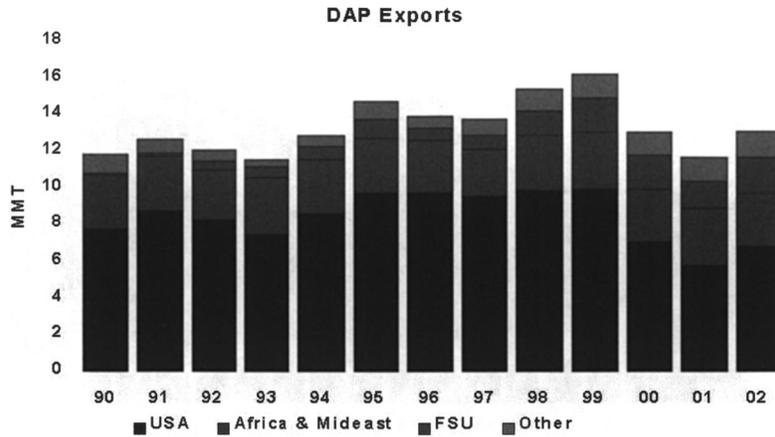
**... very small purchases by India and much lower than normal shipments to China during the first half of 2001**



Source: Cargill

Slide 24

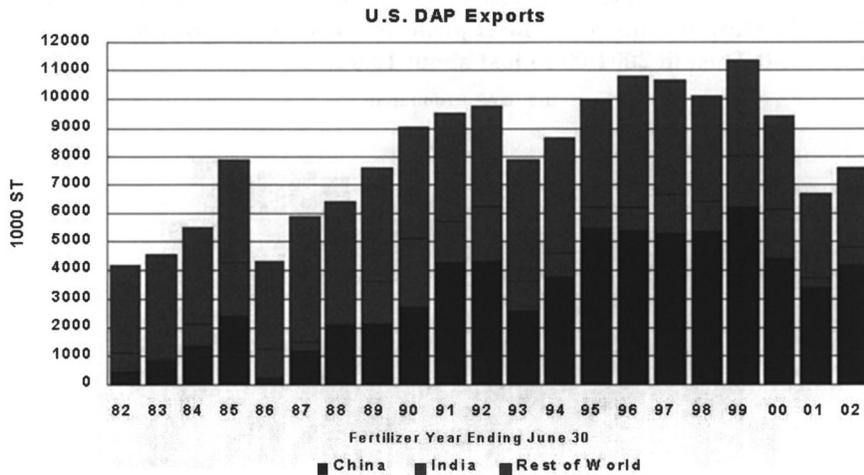
The United States accounted for nearly all of the DAP supply adjustments in 2000 and 2001



Source: Fertecon and Cargill

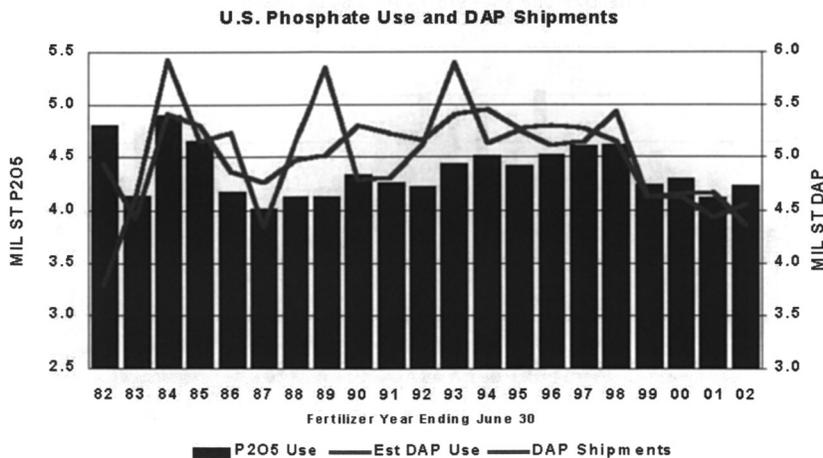
Slide 25

U.S. DAP exports in 2000/01 dropped to the lowest level since 1987/88.



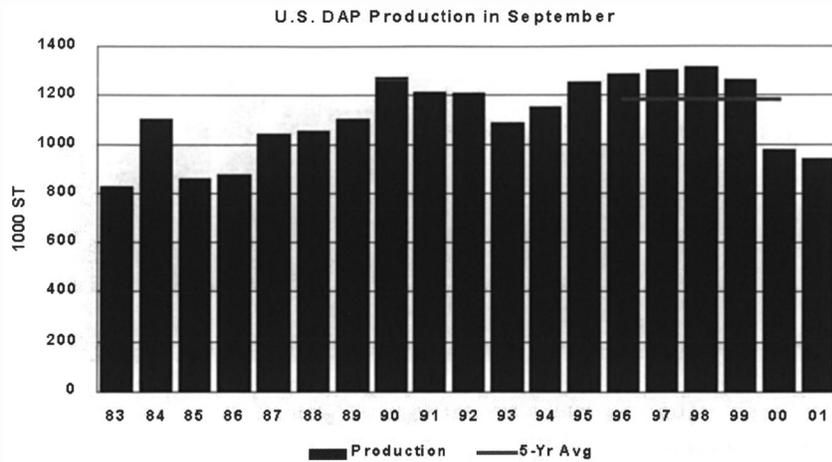
Slide 26

U.S. phosphate demand declined 4+% in 2000/01. DAP pipeline stocks increased roughly 228,000 st. Small increases in domestic use are forecast for 2001/02, but shipments will decline due to high stocks.



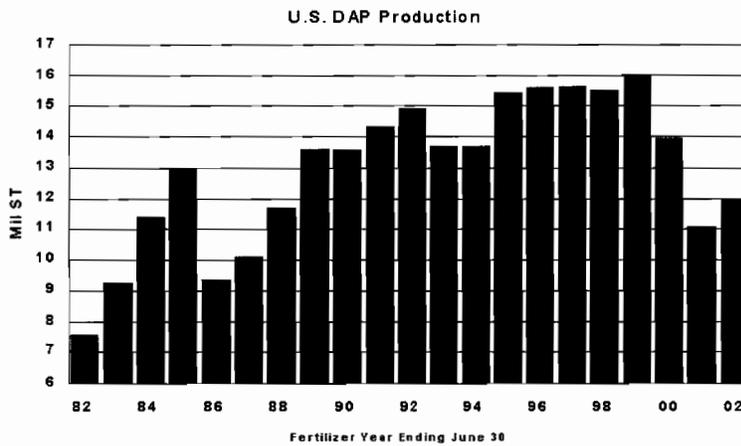
Slide 27

**U.S. DAP plants are running at the very low rates**



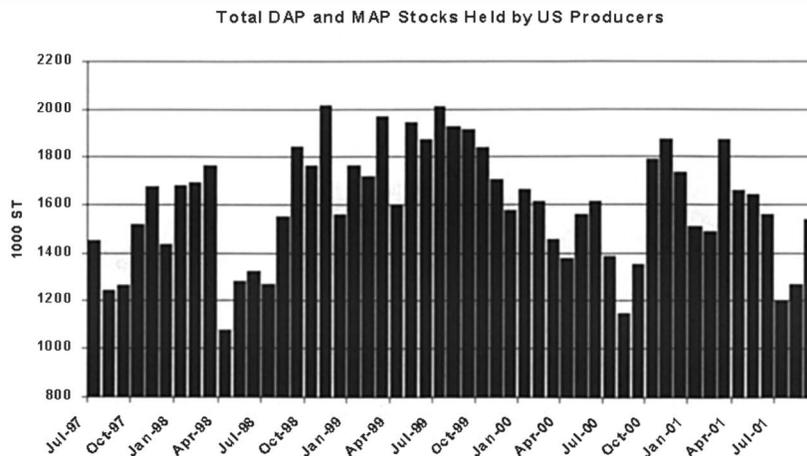
Slide 28

**U.S. DAP production for the 2000/01 fertilizer year (Jul-Jun) dropped 2.9 mst from the lower level of 1999/00 and 5.0 mst from the record level of 1998/99. Output required to meet projected demand is forecast to increase 0.9 mst in 2001/02 to just about 12.0 mst.**



Slide 29

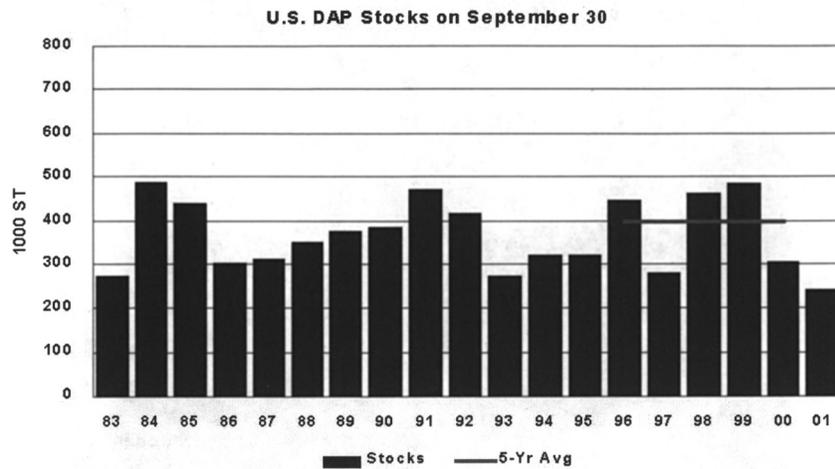
**U.S. producers are expected to hold relatively high level of stocks because of low export**



Source: TFI

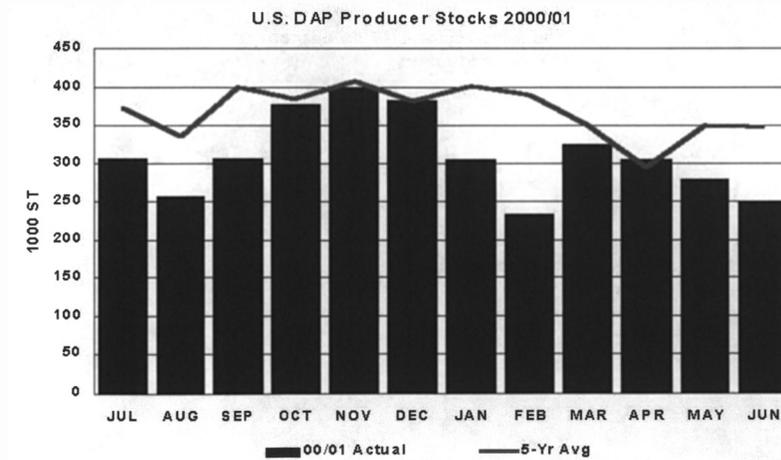
Slide 30

**DAP stocks held by U.S. producers at on-site facilities were lower than the 5-year average level on September 30**



Slide 31

**U.S. DAP stocks settled at levels much lower than the 5-year average by the end of last fertilizer year**

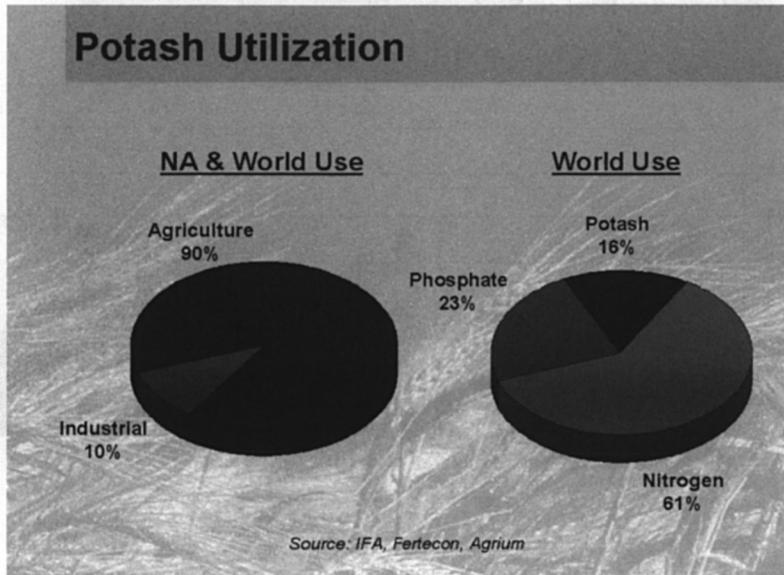


# Outlook for Potash

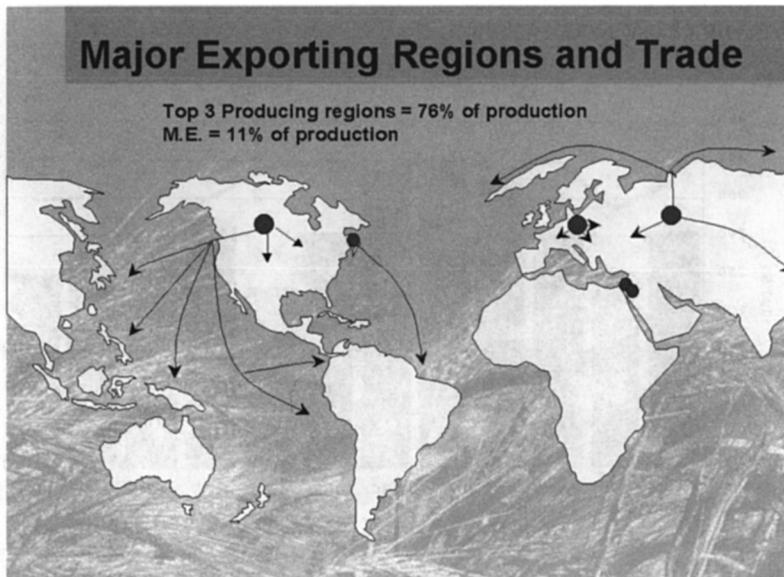
Richard Downey

Agrium, Inc.

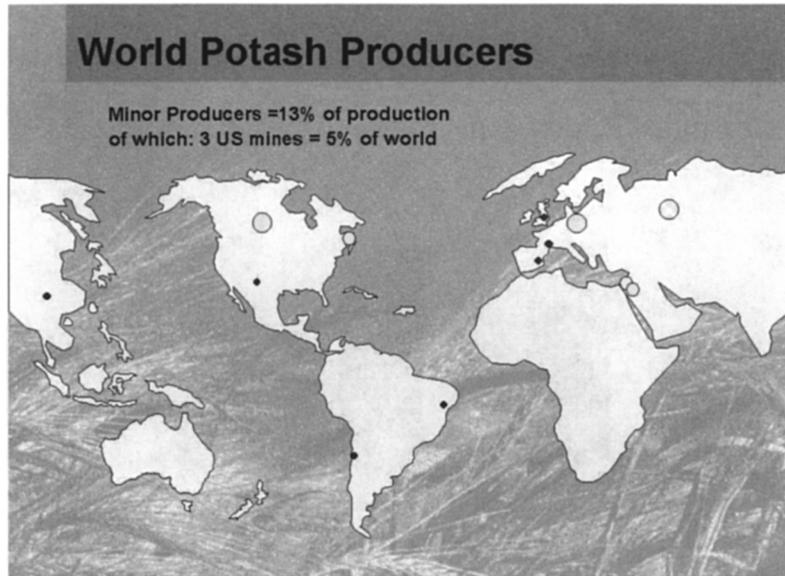
Slide 1



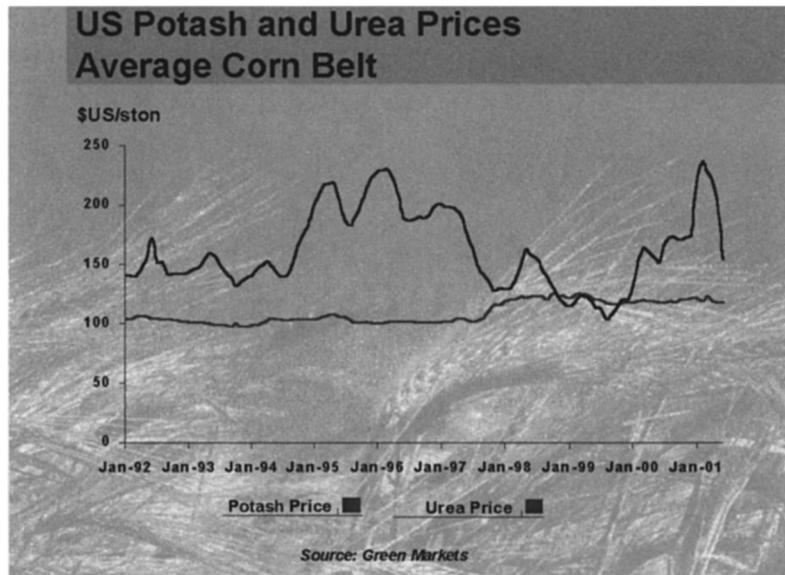
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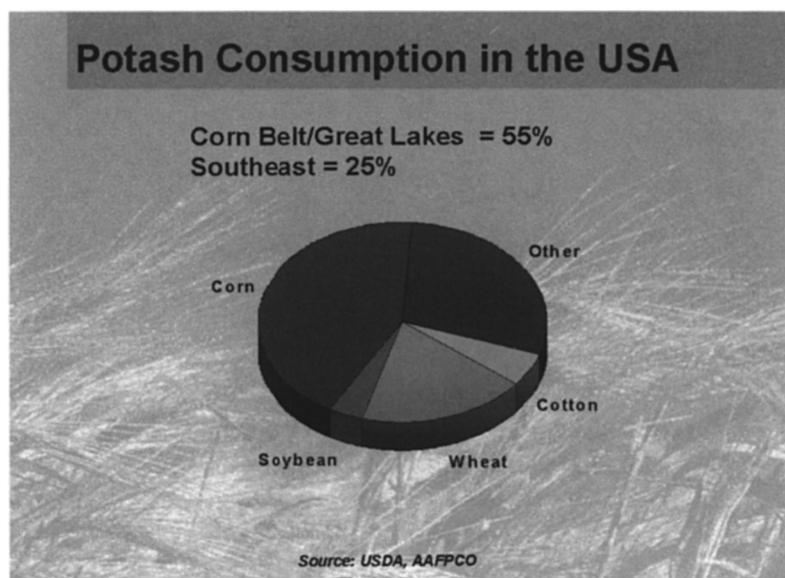
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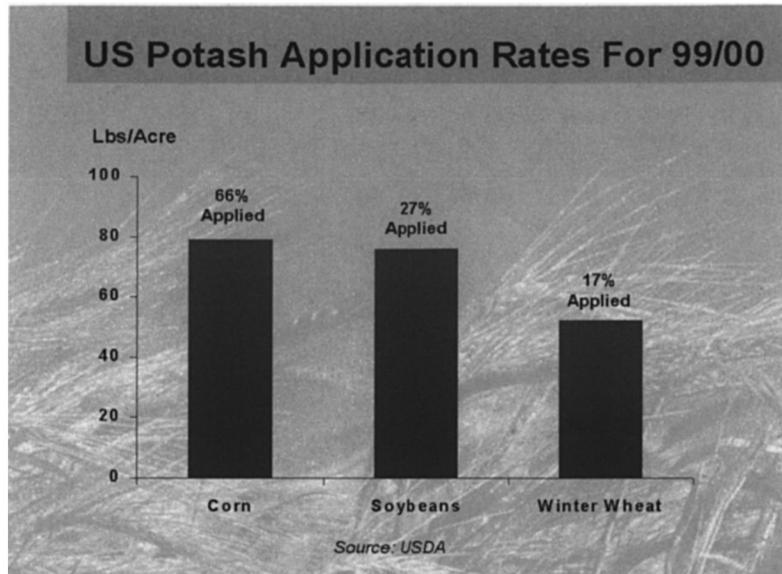
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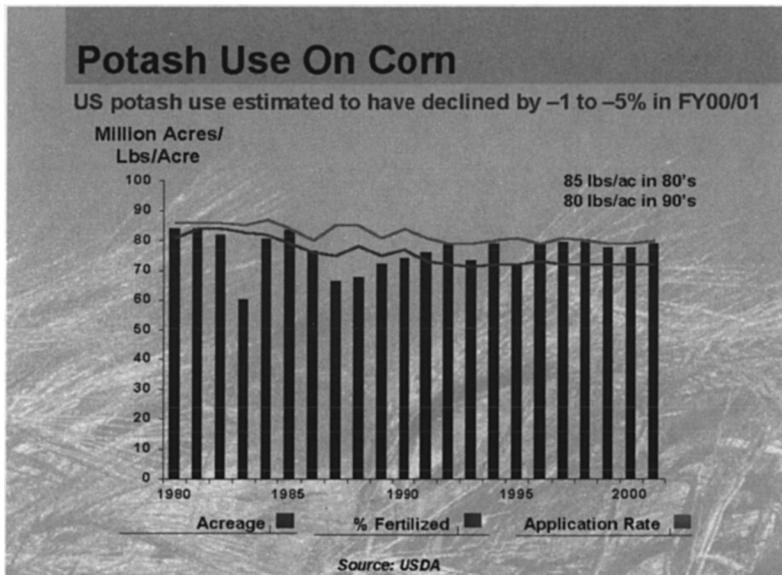
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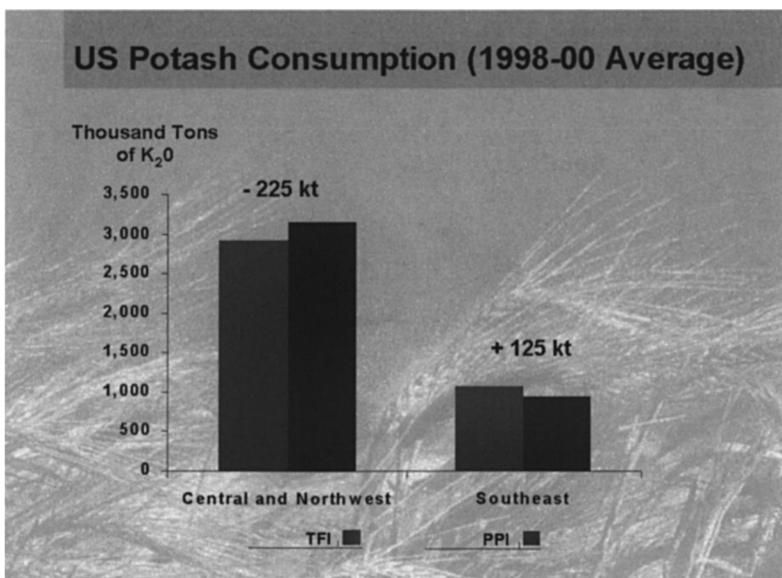
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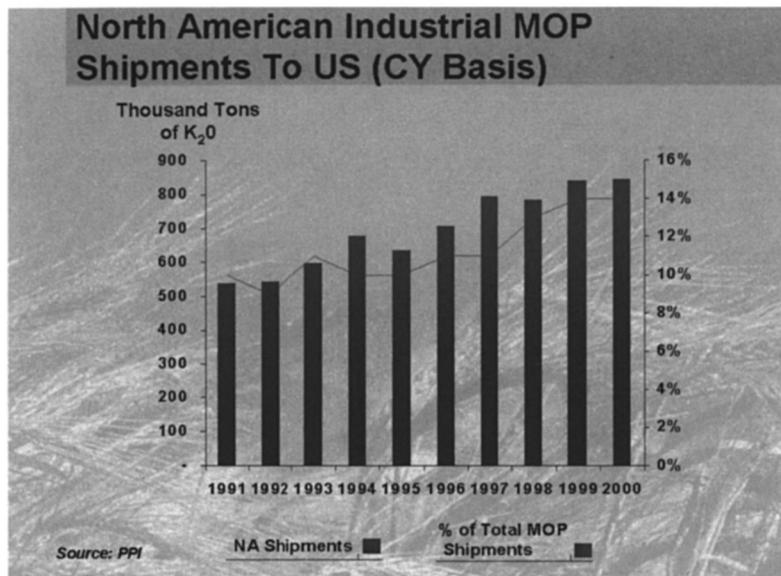
Slide 7



Slide 8



Slide 9



Slide 10

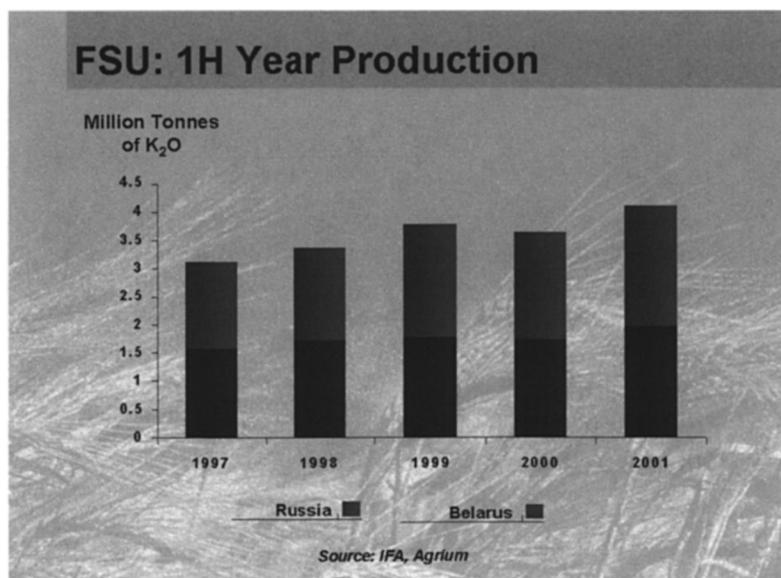
### 2001 Potash Situation

High NA inventories due to:

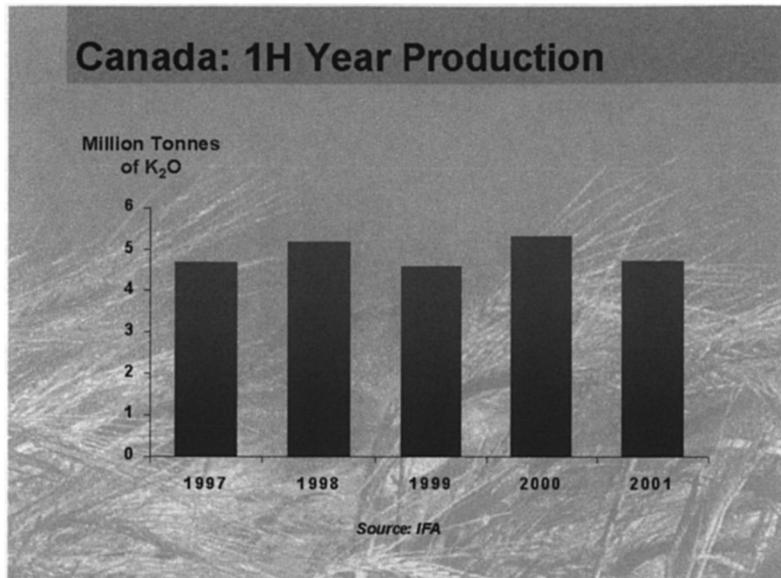
- lower NA demand (1-5%), and
- Canadian offshore exports (-17%).

Saskatchewan potash mine sales to NA for Jan-Sept. 2001 are -7%.

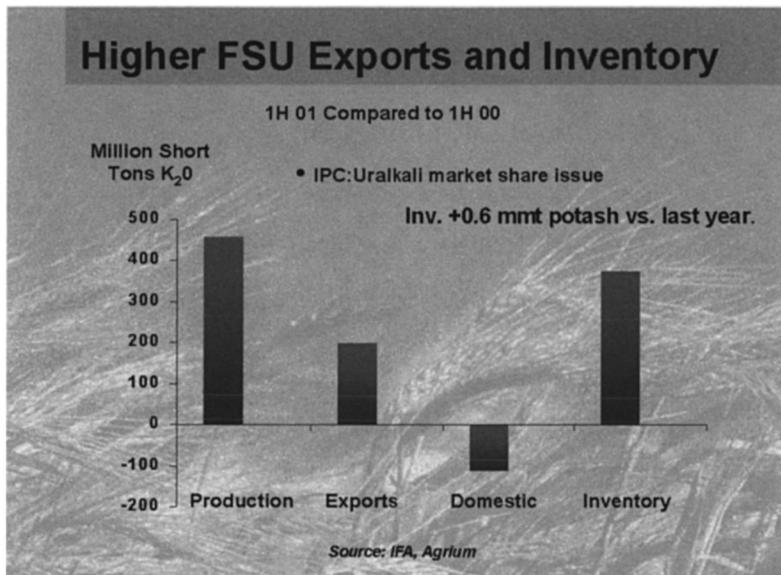
Slide 11



Slide 12



Slide 13



Slide 14

### Canadian & CIS Potash Operating Rates

	1998	1999	2000	2001(f)
(million tonnes K <sub>2</sub> O)				
<b>Canada</b>				
Capacity	13.4	13.4	13.4	13.4
Production	9.1	8.2	9.2	8.3
Operating Rate	68%	61%	69%	62%
<b>FSU</b>				
Capacity	11.9	11.9	11.9	11.9
Production	6.9	7.7	7.2	7.4
Operating Rate	58%	65%	60%	62%

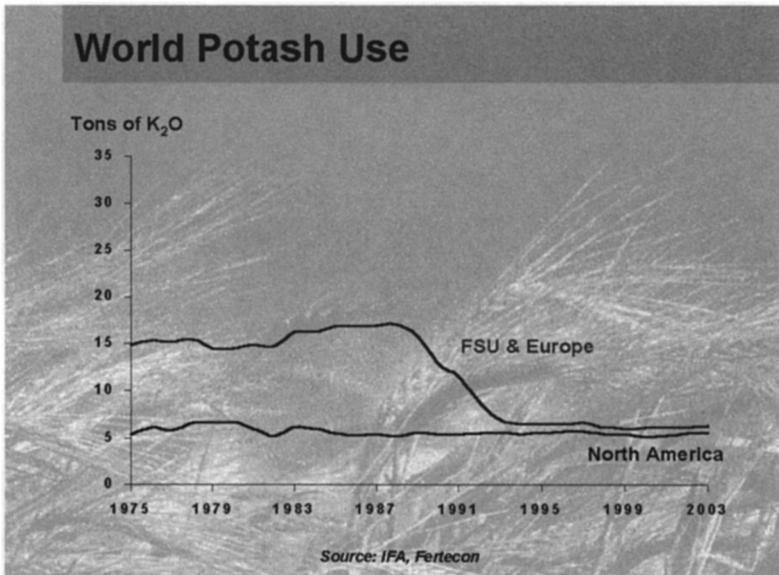
Source: IFA, Fertecon, Natural Resources Canada, British Sulphur, PPI, Agrim

Slide 15

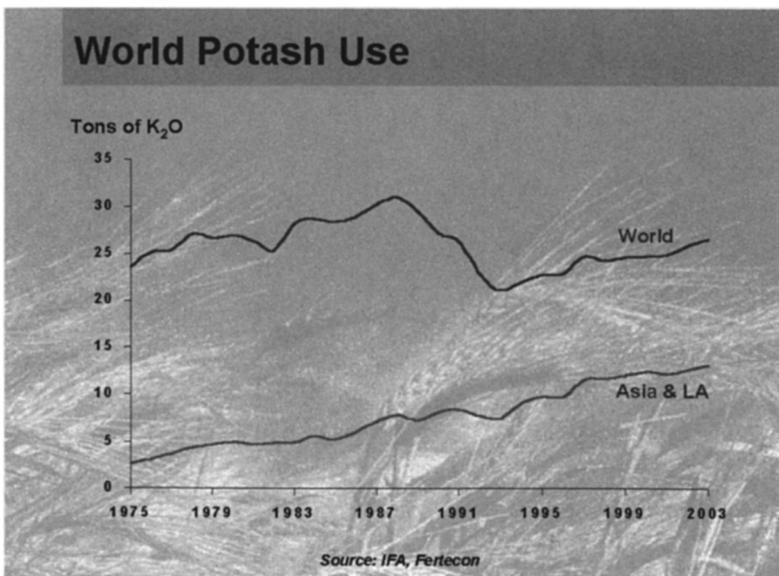
### Operating Capacity

- FSU capacity numbers are substantially overstated.
- Not all muriate of potash is created equal. World demand & capacity vary by grade, standard versus premium product.
- Those facilities that have large compaction capacity for premium product have advantage.

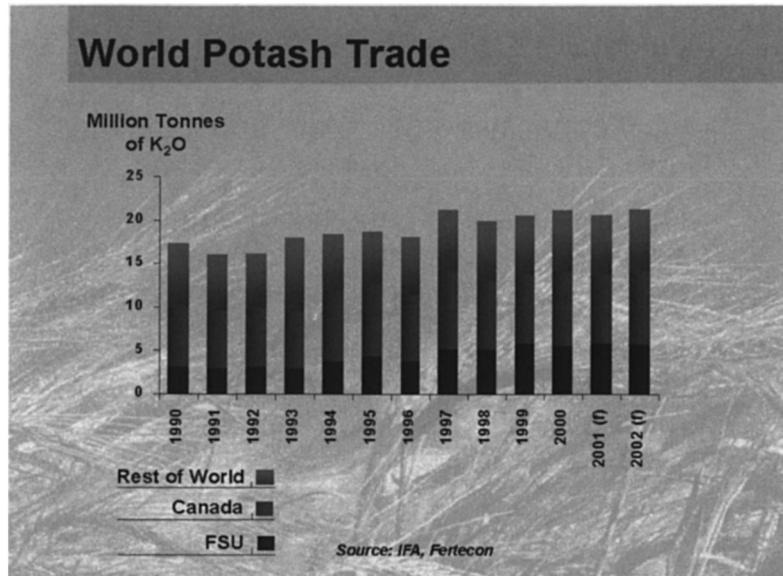
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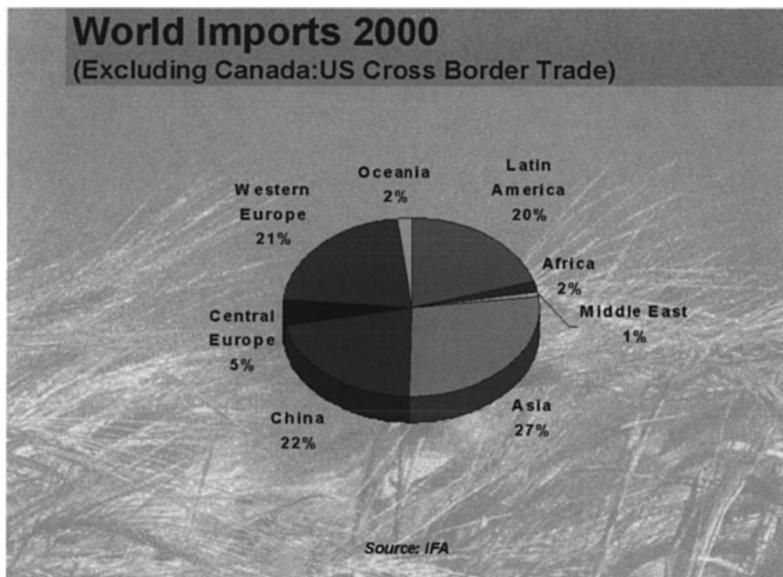
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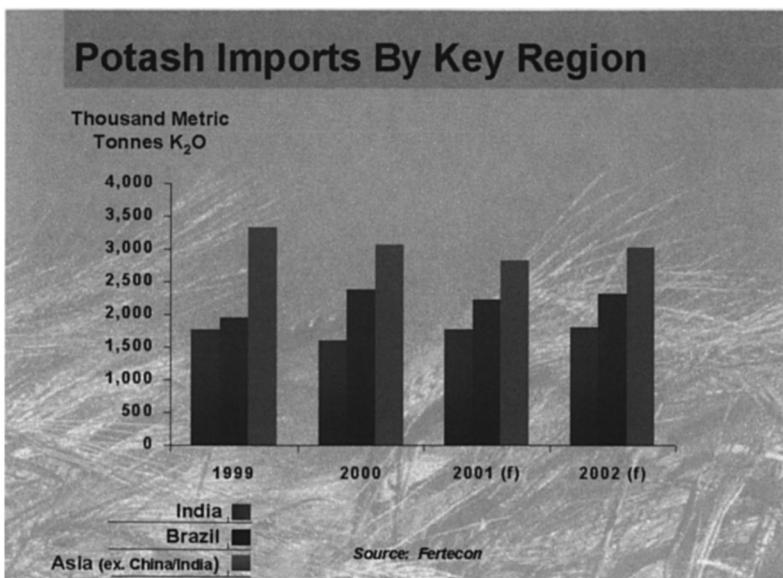
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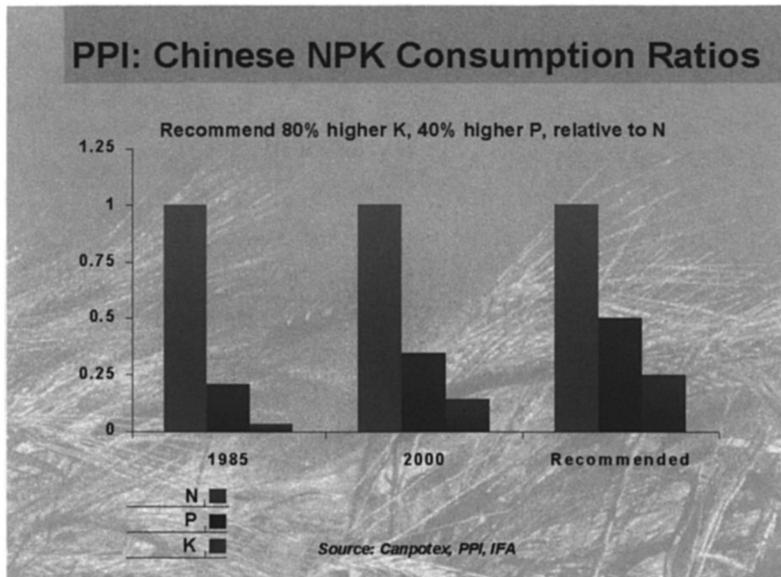
Slide 19



Slide 20



Slide 21



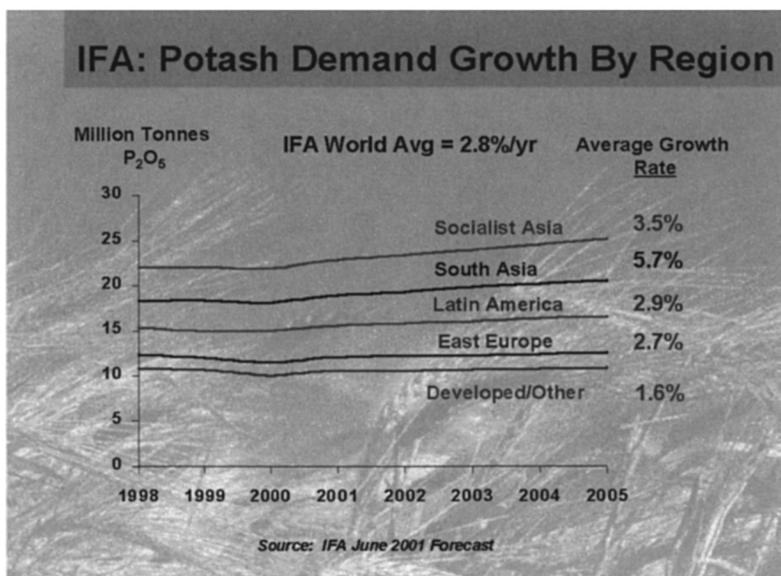
Slide 22

### Asian Demand Growth Based On Improved NPK Balance

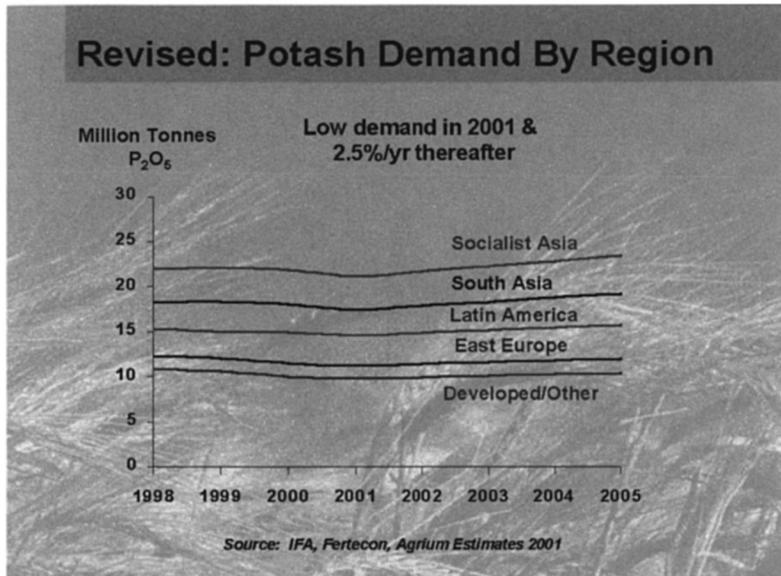
- Chinese potash use in 2000 = 5.3 MMT.
- 10 MMT is recommended at “optimal rates”.
- Chinese accession to WTO in 2002:
  - quotas will be eliminated, but government still controls imports,
  - limited impact of WTO accession on imports.

Same rationale for D growth in SE Asia.

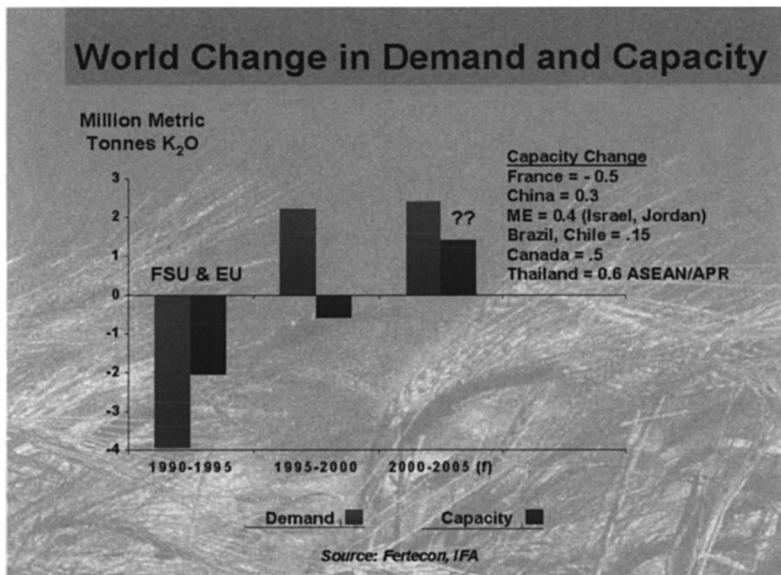
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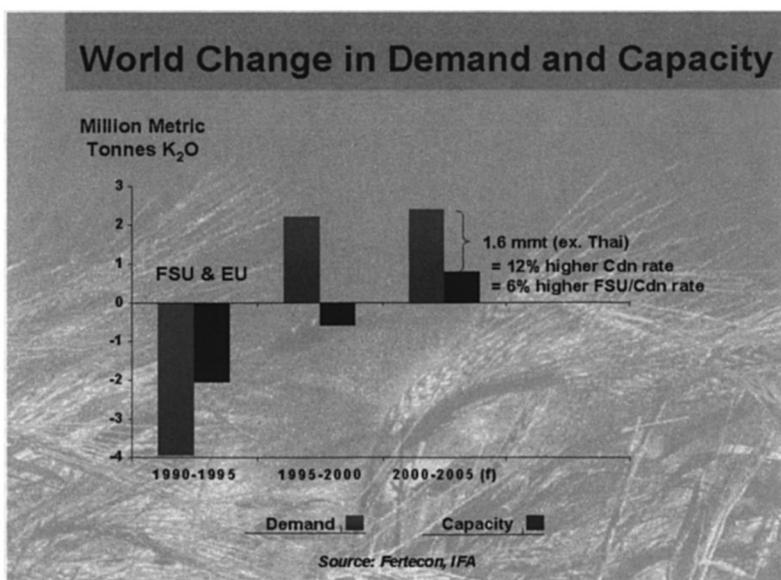
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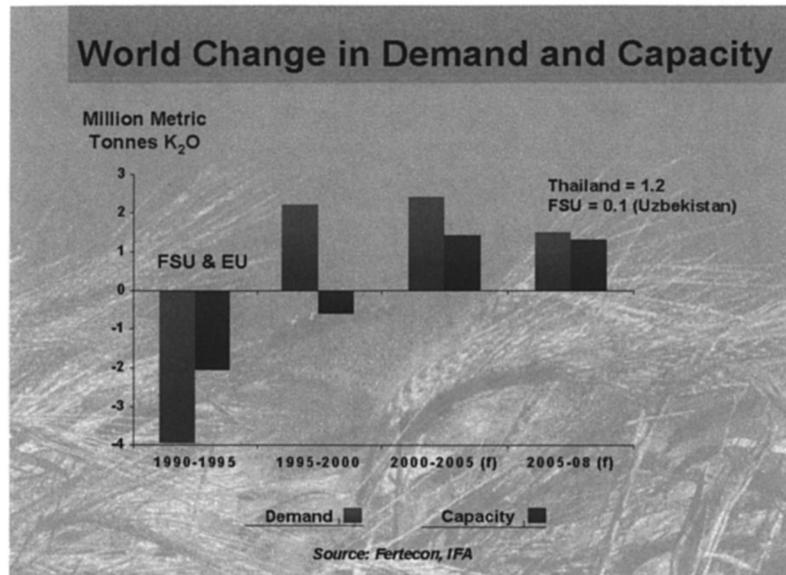
Slide 25



Slide 26



Slide 27



Slide 28

### Potential Capacity Changes Beyond 2005

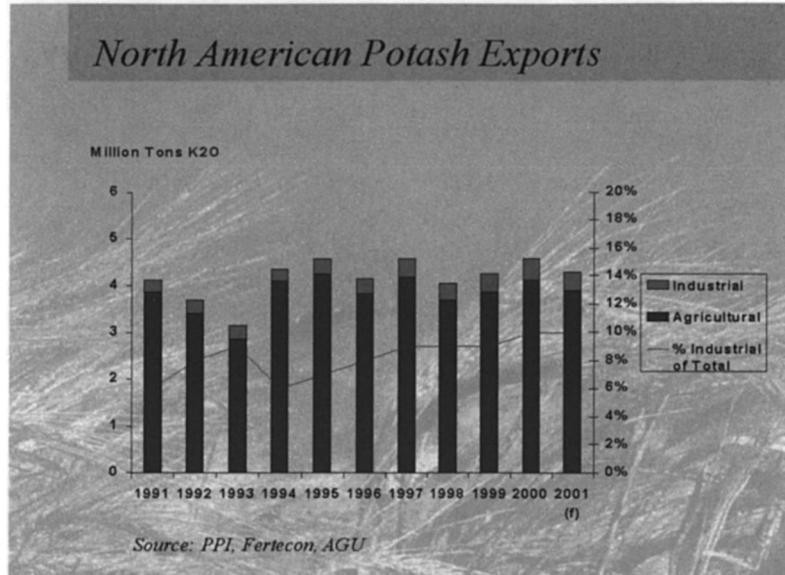
- Canada/FSU (more an issue of operating rate).
- New mine at Belaruskali, no capacity change (ore depletion at mine), will use existing mills.
- Long term: Thailand (ASEAN, APR), Brazil.
- Long shots: Thailand (?), Argentina, Manitoba, Congo, Tunisia.
- Potential environmental or ore quality issues in some regions: England, other W. Europe, US.

Slide 29

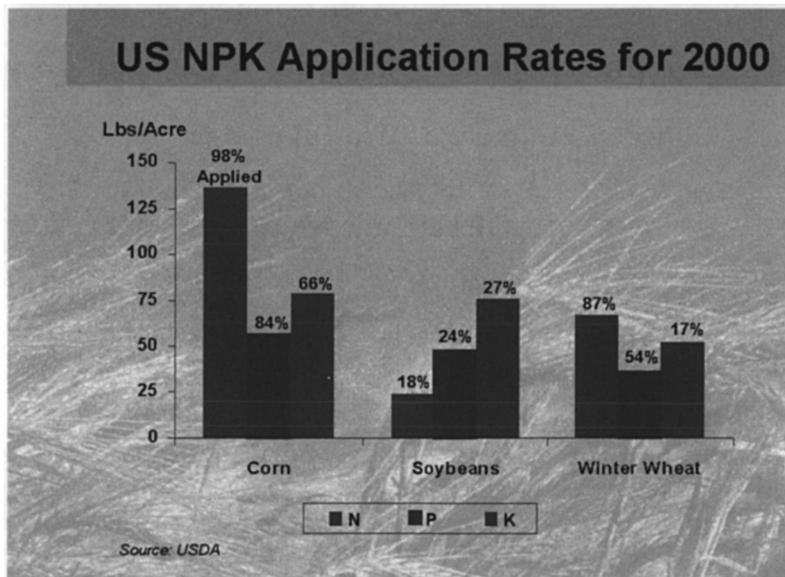
### Future Bright for Potash

- Still uncertainty over growth rates in world supply & demand.
- Overall picture for potash is for steady improvement.
- Always potential for a few surprises: operating rates, new mine, mine closures (flooding/ore), unexpected shifts + or - in import demand or consumption.

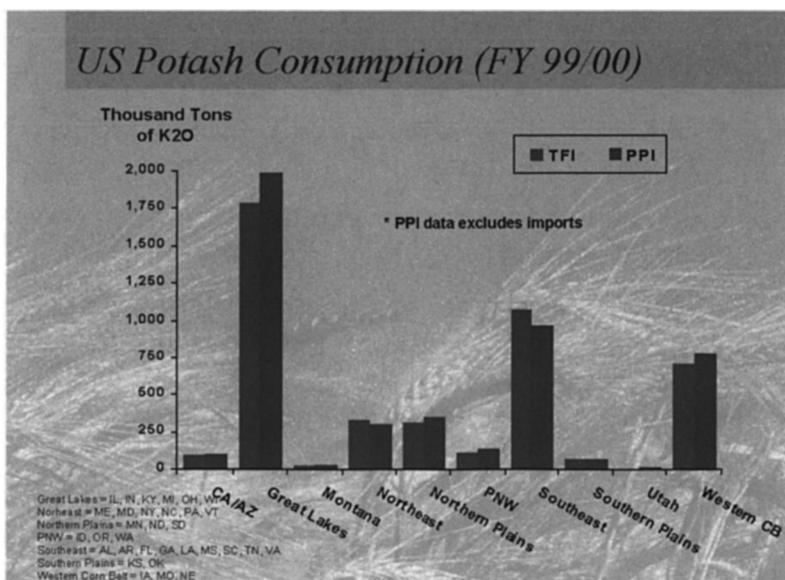
Slide 30



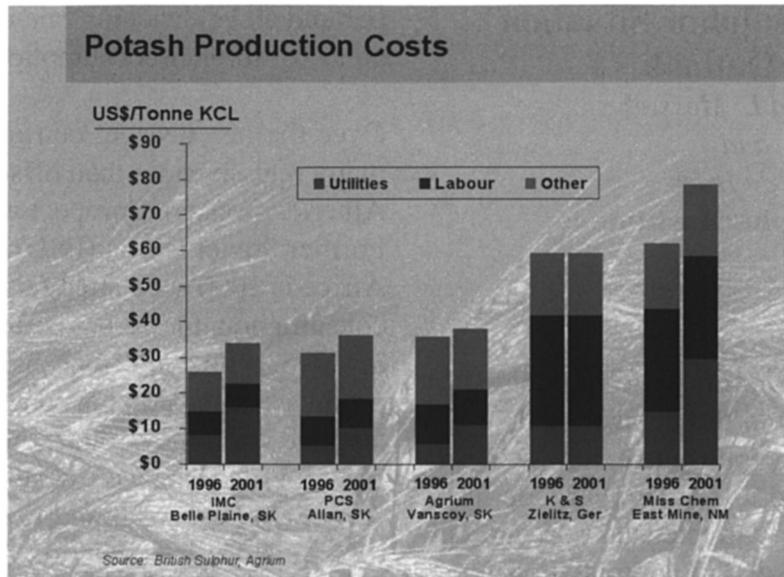
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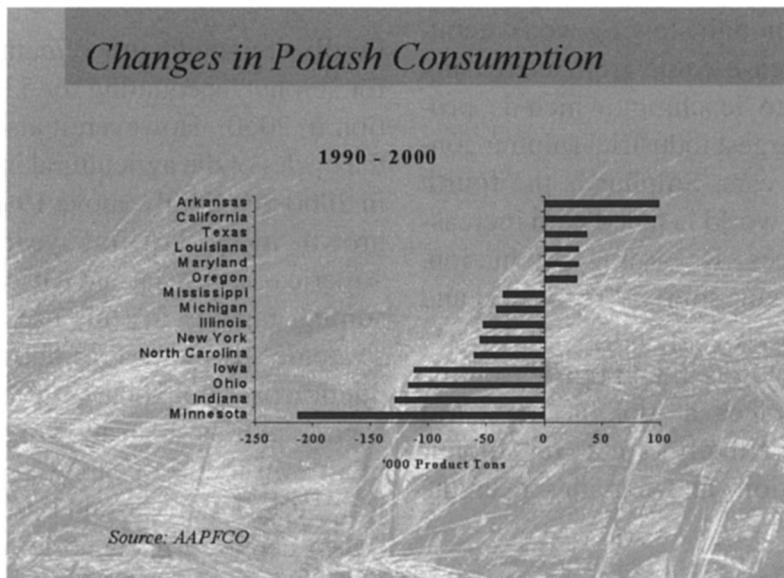
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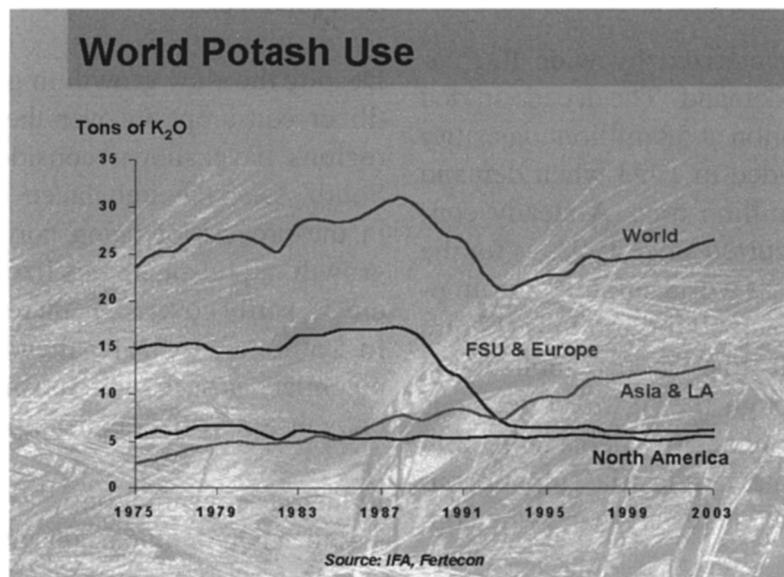
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# The Global Sulphur Situation and Outlook

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*and*

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**The Sulphur Institute**

## Introduction

The sulphur industry continues to be molded by changing events on both the demand and supply side. Consumption for phosphate fertilizer production, the major end use of sulphur, continued to face difficult times, affected by soft agricultural commodity markets. In contrast, non-fertilizer consumption enjoyed relatively strong growth, spurred by a healthy though slowing world economy; part of the increase came from increasing non-ferrous metals ore leaching, which is projected to become the largest industrial sulphur consumer over the next years. Sulphur is the fourth plant nutrient, and the world is faced with increasing nutrient imbalances. Regarding production, non-discretionary sulphur sources "recovered and smelter acid" continue to expand, with discretionary output sources "Frasch and pyrites" on the decline. This paper takes a look at the latest developments and their likely effects on sulphur consumption, production, and logistics over the coming decade.

## Sulphur Consumption

### *Recent Past*

The 1990s were characterized by wide fluctuations in world sulphur demand. The decade started with sulphur consumption at 58 million tons, after which a decline extended to 1993 when demand bottomed out at 50 million tons. A steady consumption recovery occurred since 1993, as for the seventh consecutive year world sulphur consumption rose in 2000 to reach 60 million tons (Figure 1), very close to the all-time record established in the late 1980s. Although the fertilizer sector is the largest market segment, it remains subject to cyclical swings. The rate of industrial sulphur consumption has accelerated in recent years, with cop-

per and nickel leaching one of the largest growth areas for sulphur consumption. (See Figure 1).

Over the last decade, consumption increases in many regions more than offset declines in North America, Western Europe, Eastern Europe and the Former Soviet Union (FSU). North America and Africa in 2000 accounted for 44% of total sulphur consumption for fertilizer use "down from 51% in 1995, with more than half of output used to produce processed phosphates for exports. In the last five years the strongest increases in total sulphur consumption were posted by East Asia, Latin America, West Asia, and South Asia, more than offsetting declines in North America and Eastern Europe (See Figure 2).

Fertilizer manufacture remains the largest end use for sulphur, accounting for 53% of total consumption in 2000. However, it also remains subject to the cycles of the agricultural industry, with demand in 2000 marginally above 1999 and showing slow growth in the last four years (Figure 1). North America, East Asia, and Africa are the largest consuming regions for this use. These regions hold strategic advantages for phosphate fertilizer production based on their large reserves of phosphate rock, with East Asia showing the fastest development over the last years. Except for North America, Western Europe, and Eastern Europe, all other areas increased phosphoric acid production over the last five years. Oceania became a phosphoric acid producer.

Despite the slow growth in global phosphate fertilizer consumption over the last years, specific regions have shown considerable increases. In South Asia, the imbalance in NPK nutrition is in the process of being corrected with a strong growth in phosphate fertilizer consumption (Figure 3), partly covered by increased regional output. In Latin America, the region's vast agricultural potential has been more fully realized by increased phosphate fertilizer consumption (See Figure 4).

Industrial consumption of sulphur makes up for less than half of global consumption, with a variety

of end uses, led by fibers and metallurgical processing. This vast sector accelerated its growth rate in the last half of the 1990s (See Figure 1), in part as a result of the increased use of sulphuric acid for non-ferrous metals ore leaching, particularly copper in Latin America, and to a lesser extent nickel.

By end use, regional changes in sulphur consumption were marked by sharp discrepancies over the last decade. In the fertilizer sector, East Asia, West Asia, and Africa showed the largest increments of growth (Figure 5), highlighting a trend in phosphate fertilizer production towards the developing world. In contrast, the FSU, Western Europe, North America, and Eastern Europe had the largest declines. In the non-fertilizer sector, East Asia and Latin America led the increases; the former was largely represented by the burgeoning Chinese economy. A fair indication of China's growing importance as a sulphur consumer, for both its fertilizer and non-fertilizer sectors, is the sharp increase in imports over the last years (See Figure 6), becoming the world's largest importer in 2000. Latin American increases in consumption indicate mostly higher ore leaching by the copper sector, particularly in Chile. The regions with the largest declines for industrial sulphur use included the FSU and Eastern Europe, whose economies were yet to turn around by the end of the decade.

### **The Future**

World total sulphur consumption is projected to increase by an annual growth rate of about 2.0%, depending on a number of factors. Regionally, the largest incremental growth is expected to originate in East Asia, Oceania, and Africa (See Figure 7).

Africa and East Asia are jointly expected to account for over half of the increment in sulphur use for phosphate fertilizer, with East Asia in the course of this decade surpassing North America as the largest consumer. In contrast, North American consumption patterns are expected to show the characteristics of a residual supplier, with marginal increments from debottlenecking of its fertilizer plants. Global non-phosphate fertilizer consump-

tion will climb as deficits of plant nutrient sulphur generalize in many regions. Oceania, East Asia, and Latin America will jointly account for much of the increment in non-fertilizer use, mostly in copper and nickel leaching. Start-up problems encountered with the high-pressure acid leach nickel process are expected to be overcome in the short term, with the technology becoming mainstream over the coming decade.

### **Sulphur Production**

#### *Recent Past*

Sulphur is produced from four major sources: brimstone (elemental sulphur) recovered predominantly as a by-product of natural gas and oil refining; brimstone mined from natural deposits mostly through the Frasch process; sulphur in other forms (SOF), consisting mainly of sulphur recovered as sulphuric acid from the smelting of non-ferrous metals; and mined pyrites, which are processed to produce sulphuric acid. World sulphur production in all forms increased in 2000 for the seventh consecutive year to 62 million tons, up 1% from 1999 and over 9 million tons above the low of over 52 million tons reached in 1993. Increases in non-discretionary sulphur "recovered and SOF" were partially offset by strong declines in discretionary sulphur "Frasch and pyrites" (See Figure 8).

Brimstone production continues to account for an increasing share of total output, climbing to over two-thirds of total production in 2000. This was all on account of increased recovered which climbed to 40 million tons. In contrast, brimstone from Frasch and native sulphur production decreased to over 2 million tons. Sulphur produced as sulphuric acid accounted for the remaining third of output. Sulphuric acid produced from the smelting of non-ferrous metals (SOF) rose in 2000 to close to 14 million tons. Sulphuric acid derived from pyrites declined to over 5 million tons.

North America remains the largest sulphur-producing region (See Figure 9), mostly from gas-recovered in Canada and petroleum refining operations in the United States. Production in 2000 was down from five years earlier, mostly from the cessation

of Frasch output in the U.S., the major production highlight of 2000, and reductions in smelter acid. East Asia, largely represented by China and Japan, was the second-largest sulphur-producing region, and was down from 1995. Declining pyrites output in China, in part the result of TSI-led initiatives to foster the consumption of more cost-effective brimstone, was more than offset by rising SOF and recovered production. The FSU became the third largest sulphur producer in 2000, surpassing Western Europe, mostly from gas-recovered. Most of the recent increments in world sulphur output originated in the FSU, West Asia, and Latin America, in all cases coming from recovered sources.

### **The Future**

World sulphur production is projected to climb steadily over the decade. Non-discretionary sulphur is projected to continue gaining output share through 2010. In contrast, discretionary sulphur production is projected to continue declining.

North America will remain the largest sulphur producer, increasing output over the decade (See Figure 10), but with a declining share of global output, in part the result of ceased Frasch output. Most North American increases will come from Canadian gas and oilsands, and American oil-recovered. West Asia, Latin America, East Asia, and the FSU are expected to show strong increases in production, from recovered and SOF. An issue which may gain relevance in future recovered production is the re-injection of sour gas streams, particularly in remote areas, which hinges, in part, on the development of new technology.

### **Sulphur Logistics and Inventories**

The shift in production to non-discretionary sources has brought to the forefront the increasing importance of the logistical chain for the orderly marketing of both sulphur and sulphuric acid. The cessation of Frasch production followed by the decline in phosphate fertilizer production in the U.S. over the last year, resulted in some North American logistical imbalances and market turmoil. Similarly, evolving smelter acid production in selected regions coupled with uneven demand

growth, namely in Europe, East Asia, North America, Oceania, and Latin America, impacted regional acid markets. The development of adequate and flexible logistical chains to match evolving production and consumption is paramount to the sulphur marketplace. International and intra-regional trade of brimstone and acid will increasingly contribute to matching supply and demand. Brimstone inventories, which have risen steadily over the last years (See Figure 11) are expected to play an increasingly important role in world sulphur markets. The discretionary sulphur producer is being replaced by non-discretionary sulphur suppliers with vatted sulphur facilities, where permitted. Canada, West Asia, and the FSU are expected to maintain the bulk of world brimstone inventories.

### **Plant Nutrient Sulphur**

The use of sulphur fertilizer continues to expand worldwide. Intensification of agricultural production results from increasing world food demand facing a fixed and even declining new land base. Fertilization with N, P, and K fertilizers increased accordingly, though P and K use lagged behind N. Nutrient imbalances are increasingly common in many regions, and include sulphur, dubbed the 4<sup>th</sup> nutrient. Empirical studies demonstrate that adequate sulphur supplies are essential to ensure efficient N and P utilization. The increased trend to use high-analysis fertilizers containing little or no sulphur, and declining levels of soil organic matter have reduced soil sulphur availability to levels that are limiting production. Last but not least, tightened environmental regulations principally in Western Europe and North America, but also increasingly in developing countries, have decreased atmospheric sulphur deposition. Over 10 million tons of sulphur are applied to soils worldwide through fertilizers, 75% of which are in the form of single superphosphate (SSP) and ammonium sulphate. These products continue to be important sources, particularly where their sulphur benefit is recognized. However, the decline in SSP consumption, particularly in parts of Asia, will exacerbate the need for alternative sources of sulphur. Ongoing research and development

is producing new materials which continue to gain market share. The current potential plant nutrient sulphur market is estimated to require an additional 8 million tons. With increased food production raising sulphur requirements, the unfulfilled requirement for sulphur fertilizers is projected to grow to close to 11 million tons by 2010 (See Figure 12).

A regional breakdown of world sulphur deficits is shown in Figure 13. Asia indicates the greatest shortfalls. Intensified agricultural production, pressured by food self-sufficiency goals and limited land resources in China and India, the two most populous nations, created a sulphur nutrient imbalance. This imbalance could be accentuated with the declining trend in the use of SSP in both countries. China's current deficit of about 1.3 million tons is expected to grow to 2.1 million tons. India's deficit is projected to increase from 1.3 million tons to 2.0 million tons by the end of the decade.

An ever increasing array of field trial data point to sulphur deficiencies affecting agricultural productivity in China and India. More than 30% of soils in the major agricultural regions of China and India are sulphur deficient, according to experimental results carried out by TSI and other parties. In China, it includes vast swathes of eleven provinces. In India, soil sulphur deficits were detected at different locations in at least ten states.

In Europe, the intensive nature of Western European agriculture and the significant drop in sulphur dioxide emissions since the 1970s, plus the use of sulphur-free fertilizers, made sulphur deficiency a major nutritional problem. A well-developed agricultural extension system facilitates farmers' response to the deficit. The PNS market is projected to expand moderately from the current level of over 400,000 tons to 500,000 tons in 2010, as the increased need for sulphur, particularly in the North, is partially offset by efficiency gains in fertilizer application. Sulphur deficiencies are expected to expand further in line with anticipated reductions in sulphur dioxide emissions. In East-

ern Europe, still a dormant market for sulphur fertilizers, additional commercial opportunities are expected as several countries join the European Union, which are likely to lead to intensification of agriculture and reduced sulphur dioxide emissions. The current Eastern European sulphur deficit of 300,000 tons is expected to rise by at least 100,000 tons by the end of the decade.

In North America, sulphur deficiencies are driven by the reduction in sulphur dioxide emissions combined with intensification. Recent EPA estimates indicate sulphur dioxide emissions were reduced by 4 million tons between 1995 and 1999, following the 8 million ton reduction from 1970 to 1993. Most sulphur deficiencies occur in temperate regions, where the sulphur contributions from precipitation and irrigation water are low and soils predominate from moderately- to highly-weathered parent materials. Both conditions exist in major portions of the U.S. north-western states and in Canada's western provinces. The sandy soils of the Southeast, Mid-Atlantic, and the Corn Belt are also noted for their increasing sulphur deficiencies. The North American deficit for sulphur fertilizers is expected to increase from the current 1.2 million tons to 1.5 million tons by 2010.

Latin America is a growth market for plant nutrient sulphur. Agricultural production increased significantly over the last decade, which combined with rising use of high-analysis fertilizers leads to increasing instances of sulphur deficits, particularly in the larger markets of Brazil and Argentina. Unlike most of the world, expansion of new lands, particularly in Brazil, will contribute to increased output. The current increased market opportunity is estimated at 600,000 tons, and is projected to rise to at least 900,000 tons by the end of the decade.

There is a wide array of sulphur sources for plant nutrient sulphur. In China and India, as well as in Latin America, SSP is the most common source, (although it has declined in the two former countries), followed by ammonium sulphate and potassium sulphate, the last particularly suited for

acid-sensitive crops. Other fertilizers of mostly regional importance include gypsum, phosphogypsum, and elemental sulphur. The use of elemental sulphur as fertilizer is increasing mostly in the developed world. Two features of elemental sulphur highlight its use as a controlled-release granular fertilizer for permanent pastures and crops. First, it is the most concentrated sulphur form, which lowers transport and application costs. Secondly, it offers reserve availability. Elemental sulphur is converted to sulphate over time. Thus, availability is a function of this process, which depends on the specific source and environmental factors. Elemental sulphur fertilizers are now manufactured in Oceania, North America, Western Europe and West Asia. In Western Europe, ammonium sulphate is the most popular source, used both as a direct-application material and in blends. New formulations of elemental sulphur-based fertilizers are being introduced. In North America, ammonium sulphate is the major sulphur source, with different formulations adapted to different regions and crops. Increasingly, innovative elemental sulphur based fertilizers have established their market presence, including ammonium thiosulphate (ATS), which has become the most important liquid sulphur fertilizer.

Plant nutrient sulphur consumption is on a growth path, and is increasingly becoming mainstream. The generalization of PNS fertilization, particularly in developing countries, will impact future overall sulphur demand. The decision on which

product to use will depend on availability, management and economics, but all have a place in modern agriculture. The demand forecast includes a conservative estimate for plant nutrient sulphur consumption of 10.7 million tons by the end of the decade.

### Concluding Remarks

Global sulphur supply or demand forecasts could swing by several million tons in either direction, with a shift in any of several economic or other variables during the next decade. While sulphur demand in both the fertilizer and non-fertilizer sectors is currently projected to continue increasing through the decade, production gains, primarily as recovered sulphur and SOF, are expected to outpace increasing demand. Stronger economic indicators could expand sulphur consumption and production, especially if these included the still dormant FSU. Healthier agricultural market conditions could lessen the projected sulphur surplus, particularly if plant nutrient sulphur deficits are adequately addressed. New technological breakthroughs, such as the non-ferrous ore leaching processes, or the re-injection of sulphur in oil and gas fields, could likewise alter sulphur demand and supply conditions. Nevertheless, sulphur supplies should be ample for the fertilizer industry from growing involuntary sulphur production, inventories, and, if necessary, available discretionary sources. Exciting and challenging times lie ahead for sulphur markets.

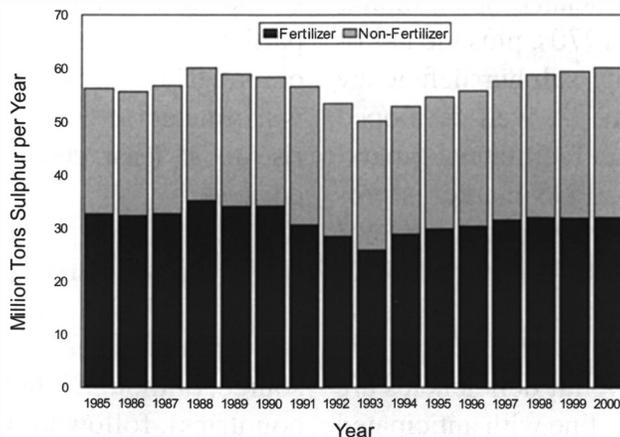


Figure 1. World Sulphur Consumption by End User

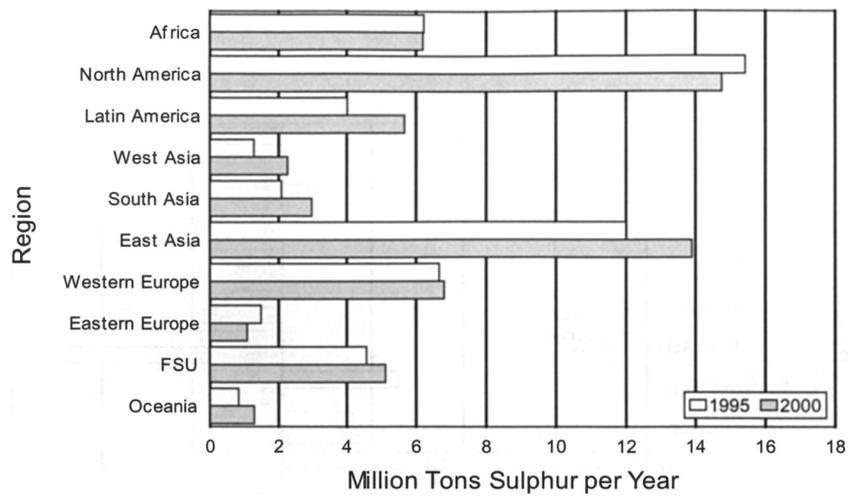


Figure 2. Regional Sulphur Consumption

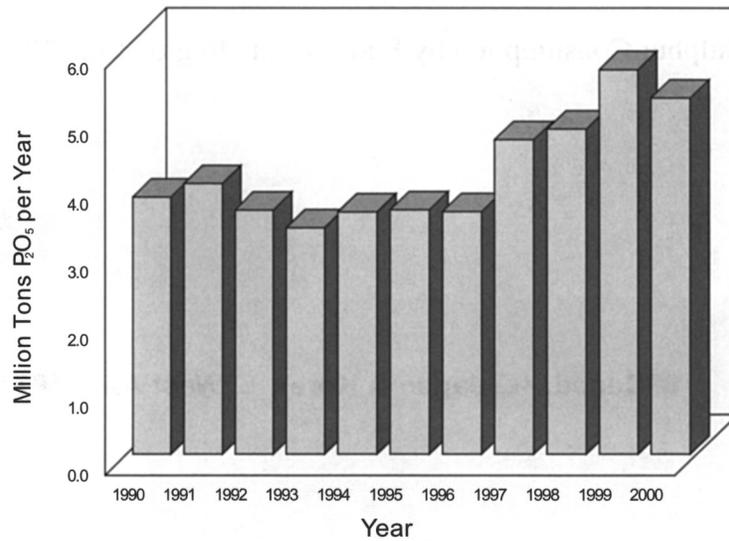


Figure 3. South Asian Phosphate Fertilizer Consumption

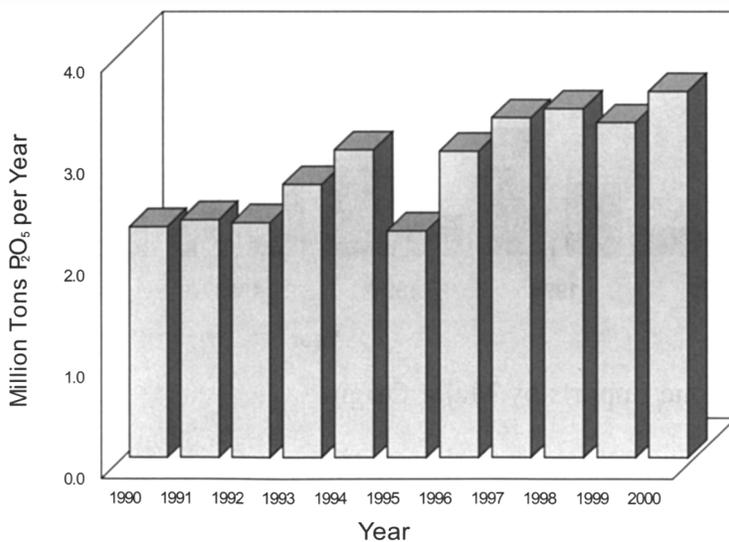


Figure 4. Latin American Phosphate Fertilizer Consumption

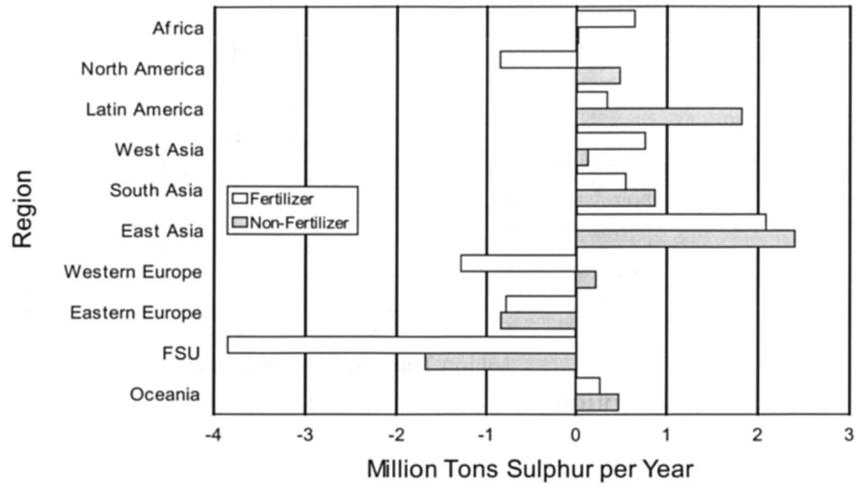


Figure 5. Incremental Sulphur Consumption by End Use and Region from 1990 to 2000

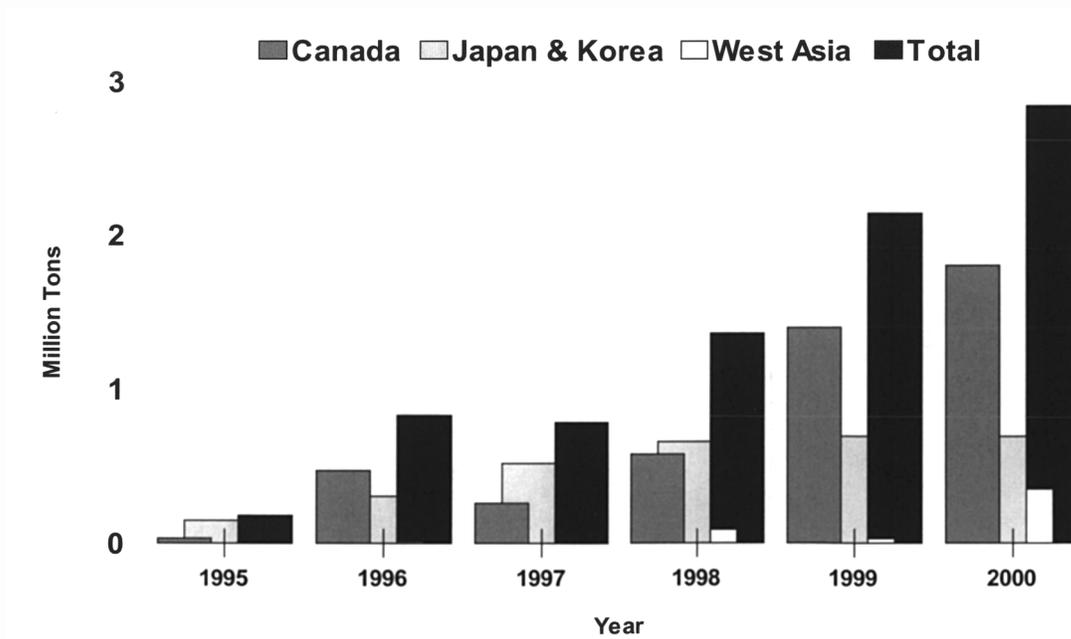


Figure 6. Chinese Brimstone Imports by Major Origin

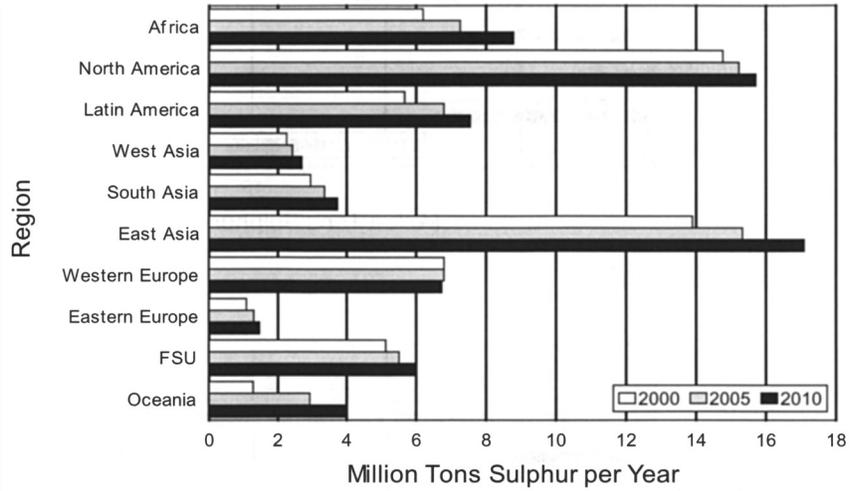


Figure 7. Region Sulphur Consumption Forecast

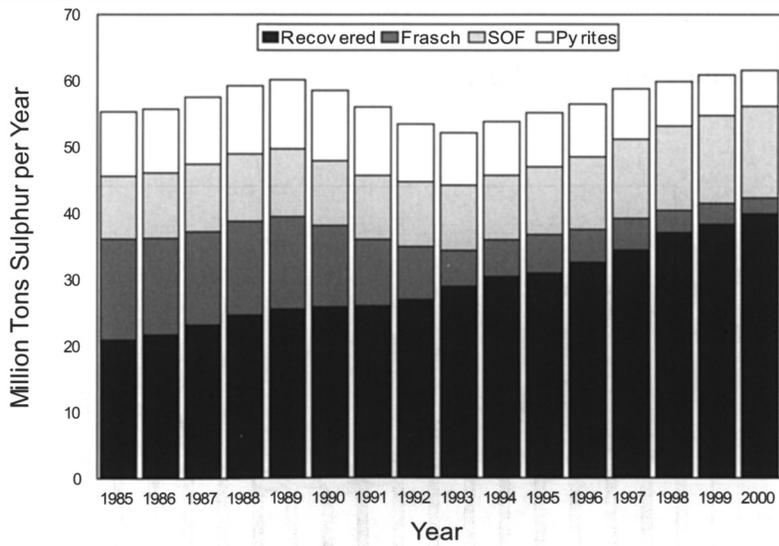


Figure 8. World Sulphur Production by Type

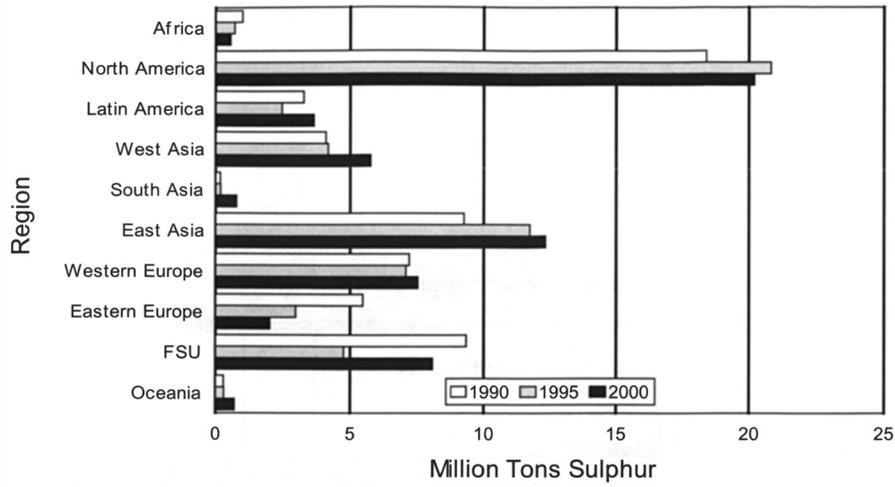


Figure 9. Regional Sulphur Production

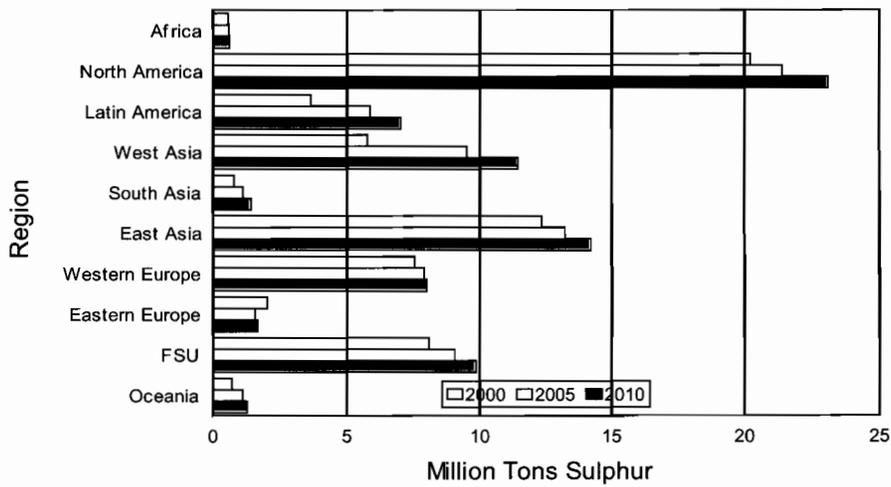


Figure 10. Regional Sulphur Production Forecast

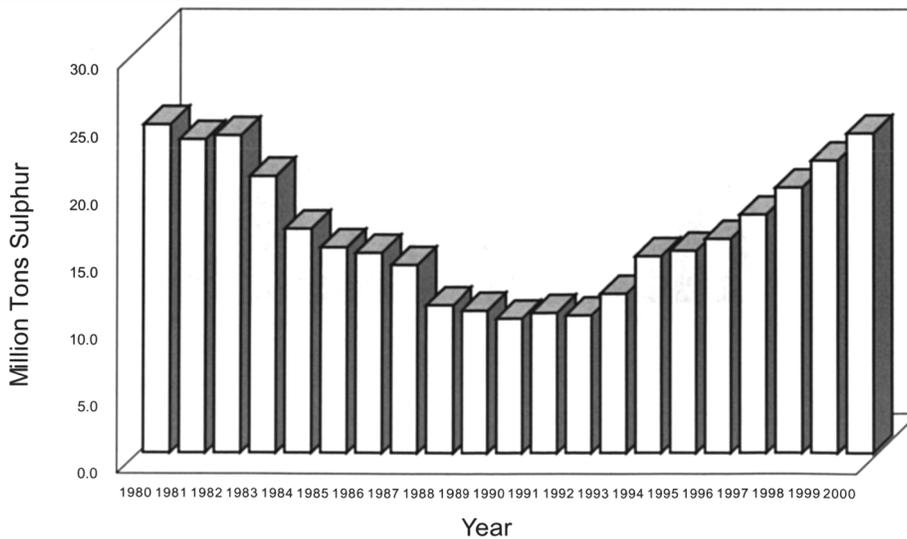


Figure 11. Brimstone Inventories

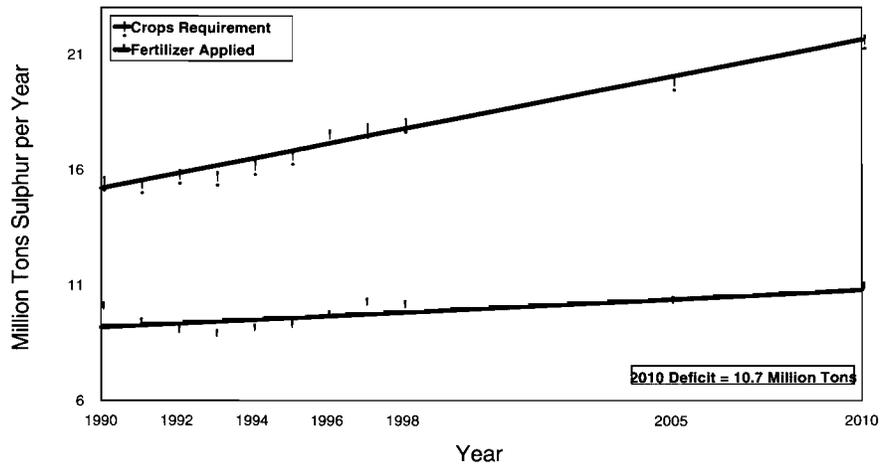


Figure 12. World Plant Nutrient Sulphur Balance

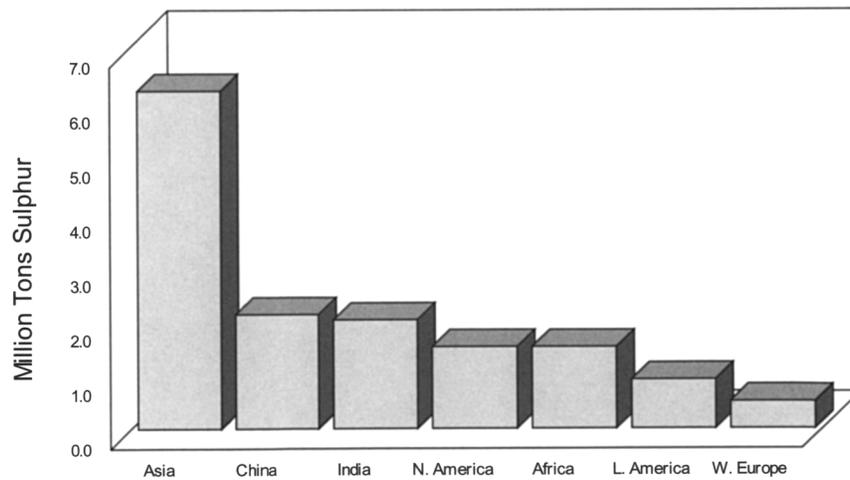


Figure 13. Plant Nutrient Sulphur Deficit in 2010



# Monday, October 22, 2001

Session II

Moderator:

**William L. Hall**

**Fertilizer is Safe**  
*Kathy Mather*  
**The Fertilizer Institute**

Good afternoon and thanks for the kind invitation to join you here today. This is my first trip out of Washington following the terrorist events of September 11<sup>th</sup>, the day all of our lives were forever changed. I usually like to open up these presentations with a short joke or a story, and at this time, a story seems more appropriate.

On the morning of September 11<sup>th</sup>, I was in Chicago at TFI's World Fertilizer Conference. For those of you who are unfamiliar – this conference usually draws almost a thousand delegates from all over the world. I had just left an early morning meeting at the World Conference and I had gone down the ballroom to listen to the general session speakers. News that a plane had just hit the World Trade Center filtered down to everyone attending the conference. It was unbelievable – and so was the news that a second plane had hit in New York and then another in Washington. Everyone was stunned including our general session speakers who were so shaken they could not go on with their presentations.

In the days following the attacks, we struggled with what all this meant to the U.S. We knew our lives were changed, but none of us had any idea of how. In the weeks following September 11<sup>th</sup>, we started to wonder how this new world might impact our industry.

About the only thing that has been certain for us is: There are lots more questions than answers! Like most all American businesses, our perception of the vulnerabilities we face has changed

immensely. And so too has the speech I had planned to give. Fertilizers are Safe! Has now turned into “Are we Keeping Fertilizers Safe?”

Since September 11<sup>th</sup>, we have heard from the following government agencies:

- I. The FBI
- II. The Bureau of Alcohol Tobacco and Firearms
- III. The Department of Transportation
- IV. The Department of Agriculture
- V. States – including Florida
- VI. EPA

Since September 11<sup>th</sup>, we have been interviewed on safety issues by the following:

- I. The Wall Street Journal
- II. The BBC
- III. The Associated Press
- IV. CNN
- V. Fox News

It's safe to say the pressure is on us as an industry to show our products are not going to be a part of the next weapon used by terrorists.

In the wake of the Oklahoma City bombing – where fertilizers were used with criminal intent, we worked with the Bureau of Alcohol Tobacco and Firearms to develop a program to increase awareness of the potential for criminal misuse of our products. That program – “Be Aware for America” encouraged retailers to:

- I. Know their customers;
- II. Protect their product, and

III. Make the right call – by using a toll free number to report suspicious activity

Just this past summer, TFI worked with the Bureau of Alcohol Tobacco and Firearms to develop a companion program called “Be Secure for America.” This program stressed the importance of vigilance on security issues and reminded anyone handling ammonium nitrate to check locks, fences and rail cars to ensure product can’t be stolen.

Both “Be Aware for America” and “Be Secure for America” have been successful programs, but in the wake of the September 11 attacks, we are under enormous pressure – both internal and external – to do more. *If ammonium nitrate fertilizer is used as a part of any terrorist activity, there will be enormous pressure to ban the product.* Already, we are under pressure to implement some kind of registration program to regulate the sale of ammonium nitrate. In the past we’ve been opposed to this kind of regulation, but the climate has changed and certainly everyone’s idea of what is possible has changed.

In order to better understand the challenges we face, TFI is working with its members to assess vulnerabilities on several fronts:

- I. Production;
- II. Use;
- III. Transportation; and
- IV. Storage of our products.

We have already been attacked on the distribution of ammonium nitrate.

A recent article in the Wall Street Journal told readers ammonium nitrate is too easy to buy: Under the headline: “Fertilizer Used in Oklahoma City is Still Sold with No Restrictions” the article read:

“Ammonium nitrate, the main ingredient of the truck bomb used by Timothy McVeigh to blow up the Alfred P. Murrah Federal building six years ago is still easier to get than beer in rural America.”

So, what is the answer – or do we really need a government program in place of or in addition to the awareness programs we’ve developed with federal law enforcement officials?

Beyond that, what is our responsibility on manufacturing stewardship issues? How can fertilizer manufacturers do a better job of protecting manufacturing and large storage assets from the evil a terrorist might do? Right here in the Tampa area, we have large storage facilities which are receiving additional attention, but what about production plants? Is plant security and product security such a site-specific issue that there is no role for a national trade association?

**Here is my answer:**

While security has its site-specific components, we believe there are still opportunities to share information and act as an industry. For this reason, we’ve asked the members of our Executive Committee to recommend individuals within their companies who can participate on a new Homeland Security Task Force we’re forming. The group will:

- I. Allow for information exchange within the industry;
- II. Allow for information exchange with the appropriate government agencies;
- III. Allow for information exchange with other industries and associations; and
- IV. Develop policy recommendations as necessary.

The group’s first meeting is a conference call tomorrow afternoon. This initial meeting will focus on information exchange, and it is likely that future meetings will feature input from federal law enforcement officials, regulators and private security firms. I hope we can find a common ground from which we can establish the security of all of our products so they can be used in the beneficial way we intend.

Without some kind of action on the industry's behalf, we would probably see successful yet misguided efforts to regulate our products. That isn't to say, every effort to regulate is misguided, just that our input is necessary to make sure any regulations are effective and workable.

Now I would like to move for a few minutes to update you on some of the issues the conference organizers here probably had in mind when they assigned "Fertilizers are Safe," as a title for this presentation.

I will review some of TFI's new work on metals in fertilizers and then provide a look at some of the public relations challenges surrounding those issues and provide you with a view of our intended destination.

Past risk assessment work conducted by TFI, EPA and the State of California which has been reported in more detail to this group has established that the naturally occurring levels of metals in fertilizers generally pose no threat to human health or the environment. These studies looked at the most sensitive populations – farm families and farm workers – and *still* came to the conclusion that fertilizers are indeed safe.

Following up on that work and as part of our continuing effort to show fertilizers are safe, TFI is currently funding work at North Carolina State University to conduct chemical analysis of the major fertilizer source materials. The goal of the work is to obtain estimates of the mean concentration of metals in "lots" of materials produced at a facility during a particular time period. The following source materials are being evaluated:

- I. DAP
- II. MAP
- III. Ammonium Sulfate
- IV. Potassium chloride
- V. Phosphate rock
- VI. Triple Superphosphate
- VII. Single Superphosphate
- VIII. Urea (both granular and prill)

- IX. Ammonium nitrate
- X. Potassium/Magnesium Sulfate
- XI. UAN, and
- XII. Ammonia

While this work is ongoing, I am showing you this chart as a point of reference on the DAP and MAP composite samples:

While this work has been slowed significantly by plant shutdowns which have made successful sample collection difficult, it is the type of information we'll find useful as we're called to defend our products in the future. I should take a minute to thank those of you in the room who have worked with Dr. Robarge on this project.

Another study on the safety of fertilizer products is the TFI product testing program.

The TFI Product Testing program is a two-year testing program that culminates in the preparation of Health & Environmental Safety Data Summary Documents for each of 23 high production volume fertilizer materials.

The first phase of the testing, acute toxicity, is completed and the results shared with the member companies. The second and third phases of testing, gene toxicity and chronic testing, will be completed by the end of the year. We are very pleased with the results to date. These results we have so far are available to TFI members on a CD and will ultimately be summarized and published by TFI.

So what about this destination I spoke of earlier? That's where I'll conclude by talking a few moments about the need to communicate about our commitment to the safety of our products for farmers and consumers. There is still much work to be done to assure the public about the safety of our products. We have collected a significant amount of data on our fertilizer products and our challenge for the future will be to communicate about this safety data.

It's not unlikely we will face future challenges which are going to require new science. As an

industry we have to be willing to continue to generate and identify the science which shows our products are safe.

In the near term, we have taken a few steps to move us closer to that destination. Most notably we've entered into a formal relationship with North Carolina State University to hire an extension associate to help us identify and gather the science we will need to defend the use of our products. This Masters level associate came on board in August and is acting as a liaison between TFI and the academic community at NC State.

She has already been helpful to us on several fronts including our preparation for last week's International Nitrogen Conference.

Another challenge we've faced on the safety of our products came from a huge New York publishing company. This fall, Harper Collins released a book written by Duff Wilson – the Seattle Times newspaper reporter who had written the 1997 series, "Fear in the Fields," The book alleged collusion amongst the fertilizer industry to keep the public from knowing what was in fertilizer products. The book made some of us -- not me! – famous for a day and created quite a buzz in our industry before September 11<sup>th</sup>. Duff was scheduled to be interviewed on NBC's Today Show during the week following the terrorist attacks. It never happened and, of course it's hard to say how things might have shaped up for us if he had actually appeared on the Today Show.

As of this date, the "Fateful Harvest" book tour has been cancelled and I would be surprised to see much more of Duff Wilson mixing within our industry.

Then again, he does still own the "Fatefulharvest.com" web address! In our preparation for the book's release, we worked with our members to write a background paper on metals in fertilizer. The paper is available from TFI – just leave me your business card and I will e-mail you a copy. The paper stresses the following message points:

- I. The industry is committed to the safety of its products for use by both farmers and consumers;
- II. The industry is committed to science-based standards for regulation of its products;
- III. The fertilizer industry is committed to responsible recycling of secondary materials for the benefit of the environment.

While the Duff Wilson book hasn't hit the best-seller list, there is still some activity on the issues related to heavy metals in fertilizers. As a result of a request by the Washington Toxics Coalition, EPA is holding a hearing on its waste derived fertilizer rule. This hearing, originally scheduled for September, is now scheduled for November 29<sup>th</sup>.

This hearing may very well turn into the media event the Toxics Coalition has in mind. Our messages on the hearing will be consistent with the messages in our background paper.

Whether its in the form of a book, a hearing or something else, we are going to continue to be challenged to defend our products and their safety to the public. We have done so much work to generate data about the safety of our products, it's now important to put the same kind of energy and resources into communicating about that safety. All of you in the room here are key to that work. I encourage you to be a part of that effort.

# Heavy Metals and Other Trace Elements in Phosphate Rock and Fertilizers

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## Introduction

Worldwide public awareness and concern regarding protecting the environment have increased, and the global fertilizer sector is subject to increasing scrutiny and accountability. Among the primary environmental issues confronting fertilizer producers, marketers, promoters, and users are concerns over the presence of heavy metals and other trace elements (potentially hazardous elements) in phosphate rock and phosphate fertilizers.

Almost all phosphate fertilizers are produced from phosphate rock. "Phosphate rock" is a general term used to describe naturally occurring rocks that contain significant amounts of phosphate minerals. The term is also used to describe naturally occurring ores or beneficiated concentrates that can be used for fertilizer production and chemical processing.

About 16 elements associated with phosphate rock and fertilizer are potentially hazardous to human health. The more common potentially hazardous elements found in phosphate rocks include arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), selenium (Se), mercury (Hg), uranium (U), and vanadium (V). In sufficient concentrations arsenic, cadmium, lead, mercury, and uranium are considered highly toxic when ingested and/or inhaled [Lewis, 1993]. All inorganic and many organic compounds of mercury are considered highly toxic. Selenium fumes are considered toxic and some compounds of selenium and vanadium are considered toxic. Chromium is a suspected carcinogen. When phosphate rocks are used as fertilizer (direct application) or as feedstocks to produce fertilizers, these potentially hazardous elements are entrained in processes and may be redistributed in products and byproducts. Ultimately, all or part of these elements are applied to the soil or must be

managed as wastes, such as phosphatic tailings and phosphogypsum.

Of the more common potentially hazardous elements associated with phosphate rock and fertilizers, cadmium is certainly the element of most concern at the present time. Cadmium naturally occurs at trace levels in a broad spectrum of rock types that comprise the crust of the earth. Cadmium is particularly enriched in some coal, zinc, and phosphate rock deposits. The cadmium content of the original phosphate rock, type of processing, and any secondary processing within a specific process dictate the redistribution of cadmium to products, byproducts, and wastes.

While cadmium is the element of most concern in phosphate rock and fertilizers at the present time and will be the main focus of this paper, the contents of several other potentially hazardous elements in phosphate rock and fertilizers are also the cause of concern. In the author's experience, the other elements generating the most concern are uranium, arsenic, and lead.

## The Heavy Metals Issue

The heavy metals in fertilizer issue mainly centers around the element cadmium. Cadmium is recognized by the World Health Organization (WHO) as a carcinogen by inhalation; no evidence exists to link cadmium to cancer by oral ingestion, and there is no evidence of genotoxicity [Anonymous, 2001a]. Cadmium accumulates in the kidneys with a half-life of 10-35 years. According to WHO, the critical concentration of cadmium in the renal cortex that would produce a 10% prevalence of low-molecular weight proteinuria in a general population is about 200 mg/kg and would be reached after a daily dietary intake of about 175 g/person for 50 years. The provisional tolerable weekly intake (PTWI) has been set at 7 g/kg of body weight. Cadmium has no known function in the human body.

Itai-itai disease is a well-known health hazard induced by cadmium in cadmium-polluted areas in the Jinzu River Basin in Toyama Prefecture, Japan.

Citizens of the area consumed rice grown on the floodplain of the river downstream of a lead-zinc mine, which disposed of its wastes in the river basin. Exposure of the citizens began in the early 20<sup>th</sup> century. Recognition of cadmium as the prime factor in the disease did not occur until the mid-20<sup>th</sup> century due to collaboration between Japanese and European scientists. The main clinical features of Itai-itai disease are osteomalacia accompanied with osteoporosis and multiple proximal renal tubular dysfunctions.

Cadmium poisoning is also known from industrial environments, primarily in zinc mining and processing, both in Europe and North America. For an overview of the history and other aspects of the cadmium issue, the reader is referred to the abstracts and proceedings of the SCOPE Workshop on “Environmental Cadmium in the Food Chains: Sources, Pathways, and Risks” [Anonymus, 2001b; Syers and Gochfield, 2001].

Just as cadmium tends to build up in the human body with continued exposure, cadmium concentrations can build up in the soil. Cadmium exposure and buildup in agricultural soils are of extreme concern, particularly in Europe, and member states in the European Union (EU) have instituted mandatory and/or voluntary limits on the cadmium contents of fertilizers and/or limits on cadmium inputs to soils (**Table 1**) [Hutton and de Meeûs, 2001].

While fertilizers are certainly not the only source of cadmium in the environment, fertilizers are a significant source that is most assuredly viewed as a source of cadmium that can be controlled. Similar to Europe, cadmium concentrations in fertilizers have become an issue in the United States, particularly in California, Texas, and Washington. The California Department of Food and Agriculture (CDFA) has performed a risk assessment and is establishing safe screening levels for arsenic, cadmium, and lead in fertilizer products [Anonymus, 2001c].

Cadmium is produced commercially as a byproduct of the zinc industry; there are no mineral deposits that are mined exclusively for cadmium. In 1999 world cadmium production was estimated at 19,900 mt [USGS, 2000]. Cadmium metal prices have been falling since 1995 (US \$4.05/kg) to a price of US \$0.55/kg in 1999 (average New York dealer price for 99.95% purity in 5 short ton lots).

Like zinc, cadmium is almost always divalent in stable compounds. The ionic radius of cadmium in the +2 state is 0.97 angstroms. This ionic radius is very similar to calcium; in the +2 state the ionic radius of calcium is 0.99 angstroms. Cadmium may substitute for calcium in calcium-bearing compounds and minerals.

Cadmium is widely dispersed in the rocks that comprise the earth's crust at levels generally less than 1 ppm [Adriano, 1985; Carmichael, 1982; Turekian, 1972; Turekian and Wedepohl, 1961]. Among the various igneous rock types, basalts contain the highest average cadmium contents (0.22 ppm). Among the general types of sedimentary rocks, shales and pelitic rocks have relatively higher cadmium contents (up to 1.4 ppm). Because cadmium naturally occurs in the minerals comprising the bedrock of the earth, cadmium naturally occurs in soils.

Relatively high cadmium contents are associated with zinc, copper, and lead sulfide ores. The cadmium content of such ores is usually dispersed within the mineral sphalerite (ZnS), and zinc sulfide deposits are the most cadmium enriched of the various metal sulfide ores. The cadmium content of sphalerite samples can range from less than 100 ppm to several thousand ppm. The USGS [USGS, 2000] estimates that world resources of cadmium are  $6 \times 10^6$  million mt based on zinc resources containing about 3,000 ppm cadmium.

Cadmium is concentrated and/or removed at several stages in the processing of sulfide ores. In modern facilities most of the cadmium reporting to gaseous emissions and dust will be contained.

The potential to disperse cadmium in the environment exists in sulfide mining, processing, and waste storage (mining and processing).

Coal formation is generally recognized to result from a rapid burial of plant material in coastal marsh or deltaic environments. Absorption processes and ion exchange during the life of the plants and later during decay results in the concentration of several elements including cadmium. While many coals have cadmium contents on the order of <1 to 3 ppm, high cadmium content coals (Western Interior, United States; New South Wales, Australia) may contain 20-30 ppm cadmium [Wixson, 1977].

The potential to redistribute cadmium in the environment exists in coal mining, processing, waste storage (mining and processing), and the burning of coal. Although there are several sources of cadmium in the environment, zinc ores and coal are probably the most significant sources. Wixson [1977] indicates the primary atmospheric sources of cadmium probably rank as follows: smelter > incineration of plastics and pigments > fossil fuel, including coking > steel mills > metallurgical.

Cadmium naturally occurs in soils at levels up to about 20 ppm [Wixson, 1977]. The cadmium content of soils is undoubtedly influenced by the cadmium content of the parent bedrock, and cadmium often appears to be enriched in the overlying soil [Adriano, 1985]. Cadmium contents of soils can be enriched in soils over zinc and lead deposits and particularly enriched in soils with a high organic content near zinc sulfide deposits [Meyer and Evans, 1973].

While not specifically addressed by this paper, much of the concern over several other of the potentially hazardous elements in fertilizers such as lead and arsenic appears to be, in part, from their presence in micronutrient additives. Micronutrient sources can be derived from base metal (zinc, copper, and lead) primary processing or secondary recovery operations. Of course, high levels

of cadmium can be present in zinc micronutrient sources.

### **World Production and Resources of Phosphate Rock**

World production of phosphate rock concentrate and unbeneficiated phosphate rock for chemical processing and direct application was estimated to be 145.5 million mt ( $145.5 \times 10^6$ ) (Table 2) in 1999 [USGS, 2000], the last year for which firm figures are available. Over the last 20 years, 80%-90% of world phosphate rock output has been delivered to the world fertilizer industry. The remaining production is mainly directed to the animal feed and chemical industries. Prior to the breakup of the former Soviet Union (FSU) in the late 1980s, world production of phosphate rock was over  $160 \times 10^6$  mt.

Twelve countries dominate world phosphate rock production. The production of other countries ( $9.6 \times 10^6$  mt) is approximately 6.6% of the world total. Of the total 1999 production of the top 12 countries ( $135.9 \times 10^6$  mt), approximately  $18.5 \times 10^6$  mt (13.6%) came from igneous phosphate rock deposits in Russia, Brazil, and the Republic of South Africa. The remaining production ( $117.4 \times 10^6$  mt or about 88%) of the top 12 producers originated from sedimentary deposits.

The exact amount of phosphate rock reserves for each deposit and the world is rather uncertain; these types of data are often privileged information and can often only be obtained indirectly. The reserve data in Table 2 were derived mostly from a United States Geological Survey (USGS) source [USGS, 2000]. Where USGS data were not available for a particular deposit, other sources were used and it was assumed that the quoted reserves were producible under current technical and economic conditions.

Moroccan and Western Saharan reserves ( $5.7 \times 10^9$  mt) amount to approximately 50% of total world reserves ( $12 \times 10^9$  mt). At first glance, the Republic of South Africa reserves are quite substantial ( $1.50 \times 10^9$  mt) according to USGS [2000]. However, the

amount of phosphate rock concentrate that may be ultimately recoverable is a matter of speculation. The 1999 USGS estimate indicates that the Russian reserve base is about  $1.5 \times 10^8$  mt from both sedimentary and igneous sources. Production of phosphate rock in Russia at this time is mainly igneous rock. The amount of phosphate rock concentrate that will be eventually economically producible is a matter of speculation. U.S. reserves are estimated at  $1.0 \times 10^9$  mt of concentrate. This includes producible rock in the Florida, North Carolina, and Western U.S. deposits. The reserves of phosphate rock in China are quoted by the USGS [2000] as  $500 \times 10^6$  mt. Information on Chinese reserves is difficult to obtain; reserves may be larger. The remaining 7 of the top 12 phosphate rock producers are Jordan, Brazil, Tunisia, Israel, Togo, Syria, and Senegal. Reserve estimates for some of these countries may be accurate, while others may be questionable.

### **Potentially Hazardous Elements in Sedimentary and Igneous Phosphate Rocks**

Almost all phosphate fertilizers are produced from naturally occurring phosphate rock. Phosphorus occurs in trace amounts in nearly all rock types but is concentrated in association with certain basic and ultrabasic igneous intrusions, igneous carbonatites, sedimentary phosphorites, and insular deposits.

The most prevalent phosphate minerals in igneous and sedimentary phosphate rocks that are commercially produced are species of the apatite family. In igneous phosphate deposits the three primary species of apatite that are found are chlorapatite, hydroxylapatite, and fluorapatite. Igneous apatites are commonly substituted with strontium and rare earth elements. Sedimentary apatites are found as two species. Carbonate-fluorapatite (francolite) is the most abundant species and is found in association with a broad spectrum of marine and freshwater deposited sedimentary rocks. The hydroxyl-containing sedimentary apatites or hydroxyl-fluor-carbonate apatites are typically associated with insular or cave deposits where bird

or bat guano may have contributed to formation [Van Kauwenbergh, 1995].

Whatever their origin, igneous or sedimentary, apatites can be highly substituted and have variable compositions. More than 25 elements are known or proposed to substitute in the apatite structure [McClellan, 1980]. The more common potentially hazardous elements found in phosphate rocks include arsenic, cadmium, chromium, mercury, lead, selenium, uranium, and vanadium. The exact residence of these elements may be speculative. Often the only indication of an association is a positive correlation with varying phosphate contents. These elements may be substituting within the apatite structure, substituting in other minerals associated with phosphate deposits, or may be adsorbed on the surface of apatite and other minerals. Divalent calcium (Ca) may be substituted in the apatite structure by divalent cadmium, mercury, or lead or by other cations such as vanadium, chromium, or uranium if compensating substitutions take place. Phosphorus ( $P^{+5}$ ) may be substituted by arsenic or vanadium and chromium if compensating substitutions take place. Work by Sery et al. [1996] utilizing fluorescence-yield extended x-ray absorption fine-structure (EXAFS) spectroscopy indicates cadmium atoms are located within the apatite framework at both Ca crystallographic sites and are not adsorbed at mineral surfaces or grain boundaries.

Some of these elements may be enriched in the weathered portions of phosphate deposits. Leaching, secondary uptake, and enrichment of uranium are known from the Florida deposits [Altschuler et al., 1958]. McArthur [1980] worked with samples of unweathered and weathered Moroccan and Queensland (Australia) phosphate rock and noted that elements such as uranium and rare earth elements (REE) are generally removed during weathering, and secondary enrichment and element retention are common features in weathered samples. Lucas et al. [1980] noted increases in vanadium, chromium, zinc, lead, and other elements from nonweathered to weathered facies in the Moroccan phosphate deposits. Selective leach-

ing of the carbonate component of carbonate-containing phosphate rock beds downdip of the highly weathered ore zone in the Togo deposit suggests a portion of the cadmium content (approximately 25%) is associated with the calcite component [Van Kauwenbergh, 1997]. Phosphate and cadmium become more concentrated with leaching of the carbonate-containing bed and removal of calcite.

In **Table 3**, the results of an IFDC study by Van Kauwenbergh [1997] are compared with the results of a similar study by Altschuler [1980] that compared the trace element compositions of sedimentary phosphorites with an average shale. Shales are the most abundant sedimentary rocks. Sedimentary rocks constitute about 8% of the volume of the crust of the earth, and shales are estimated to constitute about 53% of the total volume of sedimentary rocks [Carmichael, 1982].

Altschuler [1980] compared the trace element compositions of phosphorites with an average shale through the use of concentration and depletion factors. When the average concentration of an element determined for a phosphate rock group (sedimentary or igneous) is greater than the values given for standards (shales in the case of sedimentary phosphate rocks; basalts, granites, and crustal abundance in the case of igneous phosphate rocks), the average concentration of the element for the phosphate rock group is divided by the concentration of the standard; the resulting value is termed the enrichment factor. When the concentration given for an element in a standard is greater than the average concentration determined for a particular phosphate rock group, the concentration of the element in the standard is divided by the average value determined for the phosphate rock group; the resulting value is termed the depletion factor.

The phosphate rock data used by Altschuler [1980] are not strictly analogous to the data used in the Van Kauwenbergh [1997] study. Altschuler used data from sedimentary phosphorite deposits from 18 sedimentary basins. Many of these samples

were unprocessed ores and contained relatively low amounts of  $P_2O_5$ . The data used in the Van Kauwenbergh [1997] study were obtained mainly from processed concentrates with relatively high  $P_2O_5$  contents.

Altschuler [1980] considered an element in phosphorites enriched or depleted if the enrichment or depletion factor compared with an average shale is greater than two. Using these criteria, Altschuler considered arsenic, chromium, and vanadium to have normal abundances in phosphorites when compared with an average shale. Mercury was considered depleted. Cadmium, lead, selenium, and uranium were considered enriched. Cadmium and uranium had the highest enrichment factors of 60 and 32, respectively.

The enrichment and depletion factors determined in the Van Kauwenbergh [1997] study are similar to those of Altschuler [1980]. A slightly different shale was used for comparative purposes [Carmichael, 1982]. Using these criteria that depletion or enrichment factors of less than two are normal abundances, chromium, mercury, and vanadium are considered in normal abundance in sedimentary phosphate rocks when compared with an average shale. Lead is the only element considered depleted in sedimentary phosphate rocks. The depletion of lead (2.4) and normal abundance of mercury (1.0) are the two most significant differences between the previous study of Altschuler [1980] and the Van Kauwenbergh [1997] study.

The Van Kauwenbergh [1997] study indicates arsenic, cadmium, selenium, and uranium are considered enriched in sedimentary phosphate rocks. Arsenic is only slightly enriched with an enrichment factor of 2.0. The enrichment factor of selenium (8.0) is only slightly more than the value (7.7) found by Altschuler [1980]. Cadmium and uranium are the most enriched potentially hazardous elements in sedimentary phosphate rocks and show enrichment factors of approximately 69 and 30, respectively.

Eighty-five percent of the sedimentary phosphate rock deposits surveyed exhibit arsenic concentrations below 20 ppm (85%). Chromium concentrations are generally below 300 ppm (97%).

Mercury data indicate that 90% of the sedimentary phosphate rock deposits surveyed have concentrations of <400 ppb. Lead data indicate a maximum number of deposits at <2 ppm with concentrations ranging up to 26 ppm.

More detailed chemical data for the cadmium contents of 35 sedimentary phosphate deposits in 20 countries are given in **Table 4**. Most of the data available are for countries that are among the top 12 world producers of phosphate rock. However, little data are available for the Chinese sedimentary deposits, and there were no data available for sedimentary deposits in the FSU.

Concentrations of cadmium in sedimentary phosphate rocks from specific mines or ores are plotted in **Figure 1** with respect to the number of deposits on which data were available. Fifteen of the sedimentary phosphate rock deposits surveyed (42.8%) exhibit concentrations of <10 ppm cadmium. Nine deposits exhibit concentrations of 10-19 ppm cadmium. Phosphate rocks from three deposits have between 20 and 29 ppm cadmium, and four deposits exhibit cadmium concentrations between 30 and 39 ppm. Only four deposits in the data set exhibited cadmium concentrations that were greater than 50 ppm.

From the data in **Table 4**, it is apparent that cadmium concentrations in sedimentary phosphate rocks can vary widely between deposits within a particular country. Concentrations of cadmium can also vary widely within a particular deposit area. The overall average of the sedimentary deposits surveyed is 20.6 ppm cadmium with a range of 0.5-150 ppm cadmium.

Data on the potentially hazardous element contents of igneous phosphate rocks are summarized in **Table 5** and compared with the crustal abundances and abundances of the chosen elements in

granitic and basaltic rocks. Granites and basalts are two of the most common igneous rocks that form the crust of the earth.

Compared with crustal abundance, mercury and lead are considered in normal abundance in igneous phosphate rocks. Chromium and vanadium are considered depleted in igneous phosphate rocks when compared with crustal abundance. Arsenic, cadmium, selenium, and uranium are considered enriched in igneous phosphate rock when compared with crustal abundance and the compositions of granites and basalts. Arsenic and selenium are the most enriched elements. However, it should be noted that the samples in the data set from Kiruna and Grangesburg (Sweden) have very high arsenic values (up to 1,300 ppm) and have a profound influence on the data. It should also be noted that there are only five selenium values for igneous phosphate rocks within the entire data set.

Arsenic data indicate phosphate rocks from 80% of the igneous deposits surveyed contain less than 100 ppm. Ninety percent of the igneous phosphate deposits exhibit chromium concentrations below 40 ppm. The cadmium concentrations of all the deposits were below 2.5 ppm. The data indicate 72% of the igneous phosphate deposits surveyed have mercury concentrations below 60 ppb. Lead concentrations range up to 36 ppm. Eighty percent of uranium concentrations are below 50 ppm. Selenium concentrations range from about 2 to 5 ppm. Vanadium concentrations may be over 175 ppm, but 91% of the values are below 100 ppm.

More detailed chemical data for the cadmium contents of 11 igneous phosphate rock deposits in nine countries are shown in **Table 6**. The average cadmium concentrations of all the igneous deposits were below 2.5 ppm. While igneous phosphate rocks have much lower cadmium contents than sedimentary phosphate rocks, they are still enriched in cadmium. Based on a worldwide average of 1.5 ppm cadmium, igneous phosphate rocks exhibit an enrichment factor of 7.5 compared with crustal abundance [**Van Kauwenbergh, 1997**].

### **Future World Production**

Some generalities can be made concerning world phosphate reserves and future world production of phosphate rock with respect to potentially hazardous element contents. Of the current top twelve producers of phosphate rock, nine produce from sedimentary deposits; six of these nine sedimentary producers are export oriented.

The present world production mix for the top 12 producing countries of approximately 86% sedimentary phosphate rock and 14% igneous phosphate rock is in response to several factors. Sedimentary phosphate rock is simply more abundant than igneous phosphate rock. Many of the sedimentary deposits can be mined by low-cost surface methods. Major sedimentary deposits are often located near a coast, increasing the economic viability of export. Development of sedimentary deposits near coasts will continue to be more favorable than deposits that are far inland, a category that includes many igneous phosphate deposits. The use of igneous phosphate rocks that contain lower concentrations of cadmium and other potentially hazardous elements may be a desirable alternative; however, substantially increased world production of igneous phosphate rock is not foreseen to be a viable option to replace the use of sedimentary rock.

With the notable exceptions of arsenic and lead, sedimentary rocks simply contain more potentially hazardous elements from igneous phosphate rocks (Table 7). In absolute terms, igneous phosphate rock potentially contains more arsenic and lead.

The low content of cadmium and other potentially hazardous elements may be one factor to stimulate increased production and/or development of phosphate deposits. However, it is suggested that established producers have a distinct advantage in terms of capital investment and expertise, and those established sedimentary phosphate rock producers with ample reserves would continue to supply most of the phosphate rock to the world market.

### **Manufacture of Phosphate Fertilizers and Potentially Hazardous Elements Contents**

At the present time, nearly all phosphatic fertilizers are manufactured from naturally occurring phosphorus-containing minerals. Phosphate rock must generally be treated to convert the phosphorus to water-soluble or plant-available forms. There are various methods to process phosphate rock (**Figure 2**); the most important methods are described in the following sections. For more detailed information concerning the cadmium content of phosphate products produced from specific phosphate rock sources, see Van Kauwenbergh [2001].

#### **Single Superphosphate**

Single superphosphate (SSP), also called simple, ordinary, or normal superphosphate, is the simplest and oldest of manufactured phosphate fertilizers. Ground phosphate rock is treated with sulfuric acid in a comparatively simple plant to produce a product usually containing about 18%  $P_2O_5$ . The importance of SSP has steadily declined, having dropped far behind high-analysis ammonium phosphates and triple superphosphate (TSP) in world production due to the comparative cost advantage of shipping high-analysis phosphate fertilizers.

Sulfuric acid is not usually a raw material that carries trace elements or heavy metals [UNIDO, 1978]. If sulfuric acid from zinc or lead sulfide smelting is used for manufacturing SSP fertilizers, there is a potential of introducing lead, cadmium, and other impurities in the process.

All the potentially hazardous elements present in the phosphate rock will be transmitted to the SSP product. No byproducts or wastes are removed from the system.

#### **Wet-Process Phosphoric Acid**

Wet-process phosphoric acid (WPA) became important in fertilizer production in the early 1950s when TSP was established as an effective, economical, high-analysis fertilizer. WPA is usually produced in large complexes often near the phosphate rock deposits. A large part of the acid is used near the sites of rock production to produce

nongranular and granular TSP and granular ammonium phosphates.

The ground phosphate rock is reacted (digested) as a slurry with sulfuric acid in multiple-reaction tanks or in a compartmented single tank. Slurry from the reaction system is filtered to remove the calcium sulfate that is precipitated in the reaction. The dihydrate WPA process results in the precipitation of byproduct calcium sulfate as the dihydrate form (gypsum). Other WPA processes are operated at higher temperatures resulting in the precipitation of calcium sulfate in the hemihydrate or the anhydrite form. The filter cake is washed to recover the  $P_2O_5$  as phosphoric acid at a concentration usually ranging from 28% to 30%  $P_2O_5$  for the dihydrate process or 40% to 50%  $P_2O_5$  for the hemihydrate and anhydrite processes.

The filter acid is concentrated to 52%-54%  $P_2O_5$  (merchant grade) for shipping and for use in producing phosphate fertilizers. For ammonium phosphate production at the site, a concentration of about 40%-45%  $P_2O_5$  is sufficient. Wet-process superphosphoric acid, used mainly in preparation of liquid fertilizers, is prepared by concentration to 68%-72%  $P_2O_5$  content.

In Florida, the calcium sulfate that is removed from the reaction slurry in production of WPA usually is disposed of by storage in huge piles (stacks). Large areas of land are required for storage. Central Florida-produced gypsum must be stacked because the radioactivity of the material exceeds 10 picocuries/g, the United States Environmental Protection Agency (EPA) limit for gypsum; gypsum-exhibiting radioactivity above these levels cannot be used for agricultural or other purposes and it must be contained at controlled locations. North Carolina gypsum falls below the 10 picocuries/g limit and some of this gypsum is used for agricultural purposes; the bulk of the gypsum is slurried with tailings and used to back fill the mine. In many locations, gypsum is disposed of by dumping into rivers or the ocean. In Japan and a few other locations, the calcium sulfate hemihydrate is processed to the dihydrate form and used

in the production of wallboard and other similar building materials.

The radioactivity associated with phosphogypsum is related to the partitioning of uranium and daughter elements with shorter half lives during processing. Becker [1983] indicates 85%-95% of the uranium goes into the phosphoric acid solution. Most of the radium reports to the phosphogypsum (Table 8). Radium-226 is a long-lived alpha emitter with a half-life of 1,622 years and is a gamma radiation source when accompanied by radon-222 and its progeny. Radon-222 is a noble gas and a continuous production source of radon progeny, including polonium-218, lead-214, bismuth-214, and polonium-214. Further decay results in the formation of lead-210, bismuth-210, and polonium-210. These radon-222 progenies include alpha, beta, and gamma emitters.

When producing phosphoric acid, cadmium in the phosphate rock will report to both the acid product and to the calcium sulfate byproduct. When using a dihydrate process, approximately 55%-90% of the cadmium originally contained in the rock is transmitted to the phosphoric acid [IFDC, unpublished data] (Table 9). Becker [1983] indicates about 80% of the original cadmium in the phosphate rock is found in the filter acid when using the dihydrate process, and only 50% of the original cadmium is found in the filter acid using hemihydrate systems.

Cadmium concentrations are also an issue in gypsum disposal. Target limits for cadmium in gypsum disposed of in the North Sea are 0.5 g cadmium/mt of phosphogypsum [Hutton and Meeûs, 2001].

Depending on the process used and the intended end use of the phosphoric acid, the acid may or may not be clarified and concentrated (or concentrated and clarified). Clarification may remove significant amounts of cadmium as sludge. Becker [1983] indicates rather high concentrations of cadmium are found in the sludge precipitated from 30%  $P_2O_5$  acid.

Depending on the phosphate rock source, degree of concentration, type and amount of clarification, and utilization of purification processes, phosphoric acids can have cadmium contents ranging from 1 ppm to over 130 ppm. In general, the use of high cadmium content rocks will result in high cadmium concentrations in the phosphoric acid products.

It is very important to note that many clarification or other purification processes will produce two acid streams. The cleaned acid stream will usually be used to produce diammonium phosphate (DAP), liquid fertilizers, or for other chemical products. The sludge- and impurity-containing stream will be utilized in applications that are more tolerant of impurities such as TSP, monoammonium phosphate (MAP), or ammonium phosphate sulfate (APS) production. These sludges/precipitates may have high  $P_2O_5$  contents, and high  $P_2O_5$  recovery may be essential to the economic viability of the entire processing scheme.

### **Triple Superphosphate**

Triple superphosphate (nominally 46%) is made by acidulation of phosphate rock with phosphoric acid. The phosphoric acid is usually produced from the same phosphate rock. Like SSP, TSP is a straight product of the reaction between acid and the rock where no byproducts are removed from the process (with the exception of fluorine). All potentially hazardous elements contained in the rock and in the acid will be present in the final product. Depending on the phosphate rock source, TSP can have from <10 ppm to over 100 ppm cadmium contents. Triple superphosphate is sometimes made by some commercial manufacturers of WPA to process sludge from the clarification of phosphoric acid.

### **Ammonium Phosphates**

Ammonium phosphates were first produced in significant quantities during the early 1960s. Ammonium phosphate became the leading form of phosphate fertilizers in the United States in 1971

and in the world by 1977. The main ammonium phosphate fertilizers are DAP, MAP, and APS.

Diammonium phosphate and MAP are produced by reacting WPA and ammonia. The standard DAP grade for international trade is 18-46-0 (18%  $P_2O_5$ , 46% N, 0% K). High impurity contents in the phosphoric acid can lead to the formation of impurity-phosphate compounds in the process so that the phosphate is not completely available for reaction with ammonia. Therefore, clarification/purification of phosphoric acid may be required to achieve the standard N grade. MAP is produced in a variety of grades. Unlike DAP there is no standard for international trade. A typical MAP grade is 11-52-0. Production of MAP can be very similar to that of DAP although several process variations are possible.

Ammonium phosphate-sulfate essentially consists of MAP and ammonium sulfate formed by the reaction of ammonia, phosphoric acid, and sulfuric acid, although solid ammonium sulfate can be used in place of sulfuric acid. The best known grade is 16-20-0.

In manufacturing ammonium phosphates, metal impurities precipitate upon ammoniation of WPA. The compositional form and relative abundance of these metal salts depend upon both acid composition and operative parameters during ammoniation and granulation. Cadmium is thought to precipitate along with other divalent metals as ( $M^{2+} NH_4 PO_4^{2-}$ ) compounds. These compounds are generally expressed as anhydrous compounds.

Depending on the phosphate rock source, phosphoric acid processing scheme, and use of any clarification/purification processes, DAP products can have cadmium contents ranging from 1 ppm to over 100 ppm. Monoammonium phosphate and APS products may contain over 200 ppm cadmium due to the fact that MAP and APS production are also used for sludge processing similar to the case of TSP. Monoammonium phosphate and APS production does not require that the sludge be sepa-

rated from the acid, and all the sludge is fed into the neutralization system.

### **NPK Fertilizers**

Numerous examples of the cadmium contents of NPK fertilizers are found in the literature. However, it is practically impossible to determine what phosphate sources and what production processes were used. NPKs can be produced by numerous methods, including bulk blending, steam granulation, and chemical granulation, in conjunction with nitrophosphate and APS production or by other processing schemes. The phosphate products discussed in the previous sections are used as raw materials in the production of NPKs by steam granulation, bulk blending, chemical granulation, and with APS production. It should be noted that NPK facilities are generally designed and run as zero effluent/waste facilities. That is, liquid effluents, solid spillage, etc., are integrated with production so that no waste is produced; some particulate matter may be carried from such sites, but the amount of this material is typically minimal. Any cadmium or other potentially hazardous elements in the raw materials are redistributed in the products.

Nitrophosphates are produced using several process variations, the most common being the Odda Process. Basically, phosphate rock is dissolved with nitric acid. The resulting phosphoric acid intermediate is generally utilized internally within the fertilizer complex to produce a number of multnutrient granular products. Calcium is removed from the system as calcium carbonate, calcium ammonium nitrate (CAN), or calcium nitrate. The level of calcium removal from the nitric/phosphoric acid solution controls the water solubility of the phosphate in the finished product. Insolubles (silica sand, etc.) are removed from the system and may be sold as construction materials. Any cadmium or other potentially hazardous elements present in the phosphate rock are redistributed to products and coproducts.

### **Removal of Potentially Hazardous Elements**

#### *Cadmium*

There are two main opportunities to remove cadmium prior to the production of fertilizers. Cadmium can be removed from the phosphate rock prior to processing, or it can be removed during or after the production of phosphoric acid.

Limited work at IFDC has indicated that neither common beneficiation techniques nor selective leaching are feasible methods to remove cadmium from phosphate rock. The only known method to effectively remove cadmium from phosphate rock is by calcination.

Removal of cadmium from phosphate rock by calcination is governed by the known physical properties of cadmium metal and cadmium oxide. Cadmium can be removed from phosphate rock by calcination most effectively at temperatures between approximately 850° and 1150°C under either an inert atmosphere or reducing conditions. The higher end of the temperature range is needed for the most effective cadmium removal.

Significant research has been performed in the area of calcination [Henin, 1984; Walker and Tuffley, 1974; Frankenfeld and Peter, 1985; Plas-sen and Baechle, 1983a, 1983b; Friedrich et al., 1983; Friedrich and Baechle, 1983; Plas-sen and Schimmel, 1987; Smidth, 1986; Smith, 1980], and several patents have been granted. To the author's knowledge the only facility that has been built in the world to remove cadmium was installed (75 mtph) on the Island of Nauru for Nauru Phosphate Corporation. The exact cost of calcination is not known, but in 1992 untreated Nauru phosphate rock sold for approximately US \$50/mt while calcined product sold for over US \$90/mt.

The exact costs for calcining phosphate rock by various methods to remove cadmium are not known; companies promoting this option at one time probably have good figures. The cost per metric ton of phosphate rock is probably in the US \$10-\$20/mt range, depending upon the scale

of operations and treatment of wastes. Interest and research in this area have waned due to economic considerations and because of results from research in other areas that indicated alternate routes might be more cost effective.

Cadmium can be removed from phosphoric acid that is produced with sulfuric acid-based processes by a variety of methods, including co-crystallization with anhydrite, precipitation with sulfides, removal by ion exchange resins or liquid ion exchange, removal by solvent extraction, and separation by membrane technology.

In a comprehensive study, Davister [1992] contacted all known research groups/companies then involved in cadmium removal technology, assessed the various technologies, and developed general/average costs for co-crystallization with anhydrite, precipitation, ion exchange resins, and solvent extraction (Table 10). The results of this study indicate the cost advantages of the co-crystallization route [Becker, 1994]. Precipitation, ion exchange resins, and solvent extraction were all much more expensive methods for removing cadmium.

In the Davister study, the potential values of the rejects were used to offset the costs of treatment. Some caution should be used in applying the value of the cadmium-containing rejects as a way to reduce the cost per metric ton of  $P_2O_5$  for the co-crystallization process. This part of the analysis was not as detailed as other aspects, and the value of cadmium and other elements to be recovered from the rejects and processed into marketable products may be highly variable. As mentioned in a previous section, in 1999 cadmium metal was worth a fraction of what it was worth 4 years earlier. If the reject material must be disposed of as a hazardous waste, overall costs may increase significantly.

In the co-crystallization with anhydrite process, concentrated phosphoric acid (50%-54%  $P_2O_5$ ), including sludges, is heated and further treated with calcium phosphate and sulfuric acid. Impuri-

ties are precipitated as anhydrite with phosphate and metal substitutions.

A very favorable aspect of the process is the small amount of reject generated; Davister [1992] indicates that about 70 kg of reject is generated per metric ton  $P_2O_5$ . It should be noted that a significant proportion of the cadmium will report to the calcium sulfate byproduct that is produced during the generation of the concentrated phosphoric acid that is fed to this coprecipitation process.

Baechle and Wolstein [1984] indicate it is more difficult to separate cadmium from solutions when the phosphate rock is digested with nitric acid. An extraction process used for the production of rare earths by Kemira Oy and a Czech process are mentioned as possible methods for cadmium separation. There were no examples or costs presented by Baechle and Wolstein.

A study conducted for the EU [Hutton and Meeûs, 2001] indicates the potential costs for various cadmium removal methods (Figure 3). The potential costs of decadmiation by calcination by neutral/reducing atmosphere and cocrystallization are similar to those given in this paper. It should be noted that the low costs associated with calcination under an oxidizing atmosphere may not be appropriate to further analyses; the method is not suitably effective in most cases (perhaps a 40%-50% reduction in cadmium contents) and may only be appropriate to reduce cadmium content in some cases to meet specific limits.

It should be stressed that the costs mentioned in this section and the EU study are only potential production costs; there have been no significant successful implementations of the technologies mentioned for fertilizer production to adequately assess all associated costs. The costs of processing or disposing of wastes are particularly uncertain. Furthermore, the production costs mentioned are not the added costs farmers will ultimately pay for product. Primary producers, secondary producers, brokers, distributors, etc., will expect to make a reasonable profit on their investments. If

US \$10-\$20/mt  $P_2O_5$  is added at the primary production level, the cost/metric ton  $P_2O_5$  could very easily double by the time the fertilizer reaches the consumer.

### Other Elements

There is no known method for economically removing uranium directly from phosphate rock. Uranium can be recovered from phosphoric acid. Commercial extraction of uranium from phosphoric acid has been mainly carried out by using the solvent extraction technique. An organic solvent, in which uranium preferentially collects, is added to the phosphoric acid. The uranium is extracted by recovering the organic solvent. The remainder of the process consists of stripping the uranium from the organic solvent, usually in the form of  $UF_4$  (green cake) and upgrading this product to form yellow cake. At the present time, uranium recovery from phosphoric acid is not economical in the United States. The last operating uranium from phosphoric acid unit, the IMC uranium plant at the New Wales fertilizer complex, was closed in 1992.

Arsenic can be removed from phosphoric acid by sulfide precipitation [Becker, 1983]. Many of the other potentially hazardous elements mentioned in this paper, if solubilized in phosphoric acid, can probably be removed by the various methods mentioned to remove cadmium. Similar to cadmium, most of these methods are probably economically unrealistic at the present time.

### Continuing Issues

European Union options under consideration to control cadmium contents in phosphate fertilizers include limits of 60, 40, or 20 mg cadmium/kg  $P_2O_5$  (Table 11); these limits would be phased in or voluntarily implemented by predetermined dates [Hutton and Meeûs, 2001]. The author is not aware of any scientific basis for these proposed cadmium levels; risk-based analysis techniques do not appear to have been used to select these cadmium levels. The proposed cadmium levels appear to be a phased approach to lowering cadmium levels in fertilizers by eventually using the lowest

cadmium content phosphate rocks available and/or using the best available techniques to lower cadmium contents to the lowest levels possible.

Use of low-cadmium raw materials has been determined to be the lowest cost option. The impact on the use of different rock sources can be seen in Table 11. Imposition of a 20 mg cadmium/kg  $P_2O_5$  limit would limit use to igneous phosphate rock sources and a very limited number of very low cadmium content sedimentary sources.

Cadmium removal is considered costly. The European outlook, from a cautious health perspective and due to environmental concerns, is that cadmium removal may be necessary. When the costs of cadmium removal are calculated to the individual consumer level in Europe, the costs do not seem excessive.

Cadmium charges (taxes) have also been considered. Cadmium taxes are already levied in Sweden. Management of the cadmium levels of soils and crops in the EU is also under consideration. Such management might focus on soils with high levels of cadmium and crops that preferentially uptake cadmium.

The U.S. EPA, CDFA, and The Fertilizer Institute (TFI) have undertaken evaluations of potential human health risks as a result of exposure to metals in fertilizers. The risk assessments by these organizations share much of the same underlying science and methodologies. Details of these studies are available from TFI [Anonymous, 2001d].

Collaboration among consultants working on behalf of TFI and CDFA resulted in a risk-based acceptable concentration (RBC) for cadmium of 10 ppm per 1%  $P_2O_5$  in NPK products and 83 ppm per 1% of micronutrient. The RBC is the estimated maximum safe level of a particular metal present in a phosphate fertilizer product at 1% of the nutrient level. This cadmium value and other metal values have been recommended by the Association of American Plant Food Control Officials (AAPFCO) Board of Directors to be incorporated into

the Statement of Uniform Interpretation and Policy (SUIP) #25, the fertilizer adulteration clause, and is the proposed AAPFCO standard (**Table 12**). Under this standard, any phosphate rock commonly available on the world market can be processed to phosphate fertilizer by conventional means to produce fertilizers with acceptable cadmium levels.

The State of California has further agreed to phase in additional restrictions on metals in phosphate fertilizers over a 2-year period [**Anonymous, 2001e**]. For each percent of available phosphate (water-soluble + neutral ammonium citrate [NAC]  $P_2O_5$ ) starting January 1, 2002, the allowable units will be 4 ppm arsenic, 6 ppm cadmium, and 20 ppm lead. Limits as of January 1, 2003 will be 3 ppm arsenic and 5 ppm cadmium; lead will remain at 20 ppm. On January 1, 2004, the limits will be lowered to final levels of 2 ppm arsenic, 4 ppm cadmium, and 20 ppm lead for each percent of available phosphate.

To contrast the proposed AAPFCO cadmium standard, the final California standard (4 ppm cadmium per 1%  $P_2O_5$ ) and proposed EU standards, an example of a 10-50-0 MAP product can be used. Under the AAPFCO standard, the RCB would be 500 ppm cadmium. The final California standard would allow 200 ppm cadmium in a 10-50-0 MAP product. Under the proposed EU limits of 60, 40, and 20 mg cadmium/kg  $P_2O_5$ , the limits would be 30, 20, and 10 ppm cadmium, respectively, in a 10-50-0 MAP product.

The differences in these maximum cadmium levels will undoubtedly spawn considerable debate. For one perspective on this issue, see the website of the California Public Interest Research Group [**Anonymous, 2001f**].

Even more basic to the cadmium issue is the considerable amount of debate within the medical research community concerning cadmium. Swedish researchers basically consider any cadmium intake unacceptable; any detection of proteinuria due to cadmium intake is indicated to eventually

lead to a decreased quality of life. Swedish researchers consider the renal effects of cadmium irreversible [**Friberg, 2001**].

Belgian research [**Bernard, 2001a; 2001b**] indicates that renal effects are reversible. Belgian research indicates that the effects of cadmium intake are more disturbing from the perspective of incorporation in bone and joint tissue.

U.S.-based research [**Chaney, Ryan, and Angle, 2001**] indicates the assessment of the ultimate bioavailability of cadmium in foods is very complex. Most livestock and wildlife have no increase of cadmium in tissue used as food even when crop cadmium is increased substantially as long as the cadmium:zinc ratio is near natural levels. Zinc inhibits cadmium absorption and/or retention in tissue, even liver and kidney. Feeding studies, which used cadmium salt additions to diets, are not relevant to risk assessment because zinc was not increased simultaneously. Many of the toxic effects of high cadmium doses (without normal increased zinc) result from cadmium-induced zinc deficiency and are not relevant to risk assessment.

Similarly, the U.S. researchers concluded that risk to the food chain of soil cadmium is very dependent on the cadmium:zinc ratio of the soil. Most plant species exclude cadmium relative to zinc during formation of grain fruits or storage roots. However, rice grown in flooded soils has an opposite pattern in which grain cadmium is substantially increased, while grain zinc remains at background levels. Worldwide use of rice-based studies has resulted in an overestimation of risk from soil and food cadmium. The U.S. researchers indicate the ultimate risk from bioavailable crop cadmium should be the basis for any limits developed for cadmium in crops or soils.

## Conclusions

Cadmium and other potentially hazardous elements naturally occur at trace levels in some soils and a broad spectrum of rock types that comprise the earth's crust. Cadmium is particularly enriched

in some coal, zinc, and phosphate rock deposits. Phosphate rock deposits provide the basis for most of the fertilizer production of the world. The bulk of phosphate rock mined in the world is used for the production of fertilizers. World production of phosphate rock is mainly based on sedimentary phosphate rock. World reserves of phosphate rock are dominantly sedimentary phosphate rock. World production and resources of igneous phosphate rock are located mainly in Russia, Brazil, and the Republic of South Africa.

Sedimentary phosphate rocks in general contain much higher concentrations of cadmium and several other potentially hazardous elements than igneous phosphate rocks. Igneous rocks are also enriched in cadmium; however, the average content of cadmium is much lower than that in sedimentary phosphate rocks. The concentration of cadmium in sedimentary phosphate rock can vary among the phosphate rock deposits of a given country and within a given deposit. Sedimentary phosphate rock will continue to supply most of the world's phosphate rock requirements in the future. The average amounts of cadmium in phosphate rock available on the world market may increase in the future. This statement assumes that most of the future world demand will be supplied by additional production from known sedimentary deposits. Several major undeveloped sedimentary deposits have low contents of cadmium. It is suggested that if low cadmium content products are mandated in specific regions of the world, demand and costs will increase for low cadmium igneous and sedimentary phosphate rocks.

While igneous phosphate rocks have much lower cadmium contents than sedimentary phosphate rocks, igneous rocks can contain higher concentrations of arsenic and lead. If arsenic and lead are a cause of concern, the screening and selection of igneous phosphate rocks is suggested; treatment may be required and treatment may not be economic.

Straight phosphate fertilizers, like SSP and TSP, contain cadmium and other potentially hazardous

elements that are directly derived from the phosphate rock source. The amount of potentially hazardous elements in the final products depends on the rock source. Because the production of SSP and TSP does not generate byproducts, all the potentially hazardous elements in the raw materials (phosphate rock and acids) are transmitted to the final product.

If very low cadmium contents for phosphate fertilizers are mandated, the use of igneous phosphate rocks, the lowest cadmium content sedimentary phosphate rocks, or treated phosphate rock will be required to produce SSP or TSP. The only effective way to treat phosphate rock to remove cadmium is by calcination under a neutral or reducing atmosphere; this type of treatment is very expensive. With treatment of the phosphate rock by calcination, production of SSP and TSP may become uneconomic relative to processes that totally dissolve the rock wherein cadmium can be removed by less costly methods.

Phosphoric acid is an intermediate raw material for the production of many phosphate fertilizers and a source of potentially hazardous elements. Although WPA may be treated to remove some elements and clarified for some products, a significant portion of the cadmium generally remains in the acid (liquid phase) and is transmitted to the final products. In addition, WPA production generates significant amounts of byproduct calcium sulfate, which contains a proportion of original cadmium derived from the rock source. Disposal of cadmium-containing phosphogypsum is an issue. Uranium preferentially reports to the WPA in processing. Disposal of uranium progeny-containing gypsum is also an issue.

Ammonium phosphates (MAP, DAP, and APS) will contain all of the potentially hazardous elements that are contained in the phosphoric acid source. If the phosphoric acid has been treated or clarified, less cadmium will be found in the final fertilizer products. Monoammonium phosphate and APS products may contain proportionally more cadmium because sludge, clarification

solids, and other WPA byproduct streams that are used for production of these fertilizers may contain high impurity levels. NPK products, whether formulated by use of finished phosphate products and/or intermediates or produced by nitrophosphate processes, will generally contain all of the potentially hazardous elements that are introduced with the raw materials.

There are several technologically feasible means that have been developed to remove naturally occurring cadmium from phosphate rock and phosphoric acid and thereby reduce cadmium levels in phosphate fertilizer products. The most cost-effective means appear to be those involving cadmium removal from concentrated phosphoric acid. The investment and production costs of cadmium removal are significant. Further study is needed to determine the exact costs of removal processes, treatment/disposal of byproducts/wastes, and eventual added cost to the consumer. Other potentially hazardous elements can potentially be removed by methods proposed to remove cadmium; further study is also needed in this area.

The issue of cadmium will continue to be debated from a fundamental medical research level, from the perspective of cadmium incorporation in foods, and at the policy/administrative level of various government entities. Maximum cadmium levels proposed for adoption by the EU are very restrictive practically mandating use of very lowest cadmium content phosphate rocks as raw materials and/or the implementation of processing strategies to remove cadmium. Proposed U.S. RCBs for cadmium are much higher and would not restrict the use of most commercially available phosphate rock for the production of phosphate fertilizers by conventional processing techniques. Production schemes, which utilize high impurity content phosphoric acid streams or sludges in the production of impurity tolerant products, may result in products that will not meet proposed U.S. or State of California standards.

There is no substitute for phosphorus in agriculture. There is no substitute for phosphate rock in

phosphate fertilizer production. There is a tradeoff in this scenario; the naturally occurring potentially hazardous elements found in phosphate rocks are simply inherent to the situation. Based on world demand for phosphate fertilizers and available resources/reserves, simply selecting sources of phosphate rock to avoid potentially hazardous elements or purchasing low potentially hazardous-element-containing products is not a viable solution in a world context. The necessity of removing or restricting the level of potentially hazardous elements in phosphate fertilizer products should be carefully considered with respect to the risk to human health and costs/benefits of the entire situation. U.S.-based organizations have taken a risk-based approach to this issue. While technologically advanced and affluent countries may be able to set high standards with respect to impurity levels in phosphate fertilizer products, less affluent countries may be forced to take a more pragmatic approach.

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(Footnotes)

<sup>1</sup> Paper presented at The Fertilizer Industry Roundtable, St. Pete Beach, Florida, October 22, 23, and 24, 2001.

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	Cd in Fertilizers (mg kg P <sub>2</sub> O <sub>5</sub> )	Cd Input to Agricultural Soil (g/ha/a)	Cd in Agricultural Soils (mg/kg dry soil)
Austria	75	10 <sup>a</sup> /5 <sup>b</sup>	1.0
Belgium/Luxembourg	90	150	1.0-3.0
Denmark	47		0.5
Finland	21.5	3	0.5
Germany	40-90 <sup>c</sup>	16.7 <sup>d</sup>	1.0
Netherlands			
Portugal	40-70 <sup>f</sup>		
Sweden	43 <sup>e</sup>	1.75 <sup>h</sup>	
United Kingdom		0.15 <sup>i</sup>	3.0 <sup>j</sup>

- a. Arable land.
- b. Grassland and vegetables.
- c. Based on a voluntary agreement between government and industry.
- d. Average over a period of 3 years.
- e. OECD [1994] mentions a limit of 40 mg/kg phosphorus (17 mg/kg P<sub>2</sub>O<sub>5</sub>). According to a spokesman of VKP, there is no limit for the Cd content in P fertilizers in the Netherlands. Instead a voluntary agreement is in preparation.
- f. Mentioned in OCED (1994); probably not a legal limit.
- g. A voluntary limit of 21.5 mg/kg P<sub>2</sub>O<sub>5</sub> has been introduced by the SLR.
- h. Average for 7 years; will lower to 0.75 g/ha/year as from 2000.
- i. With sewage sludge only.
- j. Soils with a pH of 5 and above, treated with sewage sludge.

Source: Hutton and de Meeûs [2001]. See original reference for further explanation of the table and references within footnotes.

Table 1. Limit Values for Cadmium in Fertilizers and in Soil in the EU Member States

Table 2. World Phosphate Rock Production and Reserves

Country	1999 Production <sup>a,c</sup>	Reserves <sup>a,c</sup>	Reserve Base <sup>d</sup>	Comments
	(tonnes x 000)			
United States	40,867	1,000,000	4,200,000	Combined North Carolina, Florida, and Western United States
Morocco and Western Sahara	21,986	5,700,000	21,000,000	Reserves may be much larger
China	30,754	500,000	1,200,000	Reserves may be much larger
Russia	11,219	150,000	1,000,000	Production mainly from igneous deposits, Anonymous [1999], indicates 3.2 x 10 <sup>9</sup> of reserves in Kola area
Tunisia	8,006	100,000	600,000	Combined production and reserves of several mines
Jordan	6,014	900,000	1,700,000	Savage [1987] indicated 790 x 10 <sup>6</sup> tonnes of measured reserves
Brazil	4,301	330,000	370,000	Production from igneous deposits
Israel	4,100	180,000	180,000	Savage [1987] indicated 150 x 10 <sup>6</sup> tonnes of proven reserves
Republic of South Africa	2,941	1,500,000	2,500,000	Verster and van Luitingh [1997] indicate a resource base of 2.31 x 10 <sup>9</sup> tonnes of concentrate @ 38% P <sub>2</sub> O <sub>5</sub>
Syria	2,084	60,000	100,000	
Togo	1,715	30,000	60,000	Hahotoe, Kpogame, and Dagbati areas
Senegal	1,879	50,000	160,000	Taiba 35 x 10 <sup>6</sup> tonnes product; Tobene 50 x 10 <sup>6</sup> tonnes product
All other countries	9,576	1,000,000	2,500,000	
<b>Total</b>	<b>145,472</b>	<b>11,877,000</b>	<b>33,760,000</b>	

a. Sources: Mew, 2000; IFDC unpublished data.

b. Data from USGS [2000].

c. Economically recoverable materials producible under present conditions.

d. May encompass those parts of resources that have a reasonable potential for becoming economically available within planning horizons beyond those that assume proven technology and current economics.

*Table 3. Potentially Hazardous Trace Element Abundances in Sedimentary Phosphorites, Sedimentary Phosphate Rock, and Average Shales*

Element	Altschuler [1980]			Van Kauwenbergh [1997]			
	Average Shale <sup>a</sup>	Average Phosphorite	Enrichment or (Depletion) Factor	Average Shale <sup>b</sup>	Sedimentary Average Phosphate Rock	Range	Enrichment or (Depletion) Factor
	(ppm)			(ppm)			
As	13	23	1.8	6.6	13.2	3-79	2.0
Cd	0.3	18	60	0.3	20.6	1-150	68.7
Cr	90	125	1.4	100	129.2	16-1,000	1.3
Hg	0.4	0.055	(7.3)	0.4	0.4	0.010-99	1.0
Pb	20	50	2.5	20	8.4	1-55	(2.4)
Se	0.6	4.6	7.7	0.6	4.8	2-42	8.0
U	3.7	120	32.4	3.2	96.1	10-390	30.0
V	130	100	(1.3)	130	129.6	2-1,737	1.0

a. Turekian and Wedepohl [1961].

b. Carmichael [1982].

Table 4. Phosphate and Cadmium Contents of Sedimentary Phosphate Rocks

Country	Deposit	No. of Samples	Average P <sub>2</sub> O <sub>5</sub>	Average Cd	Range Cd
			(wt %)	(ppm)	
Algeria	Djebel Onk	2	28.8	22.5	13-32
Algeria	Djebel Kouif	1		12	-
Australia	Duchess	4	31.2	4.17	0.5-5
Burkina Faso	Kodjari	3	29.2	2.5	2-3
China	Kaiyang	1	35.9	<2	-
Colombia	Media Luna	1	30.1	9	-
Colombia	Sardinata	2	35.4	12	12-19
Egypt	Abu Tartur	3	29.89	5.67	3-10.5
Egypt	Hamrawen	1	22.2	15	-
Egypt	West Makamid	1	26.5	6	-
India	Mussoorie	2	25.0	8	-
India	Rajasthan	1	33.3	1	-
Israel	Zin	6	31.13	30.77	20-40
Israel	Undifferentiated	4	32.8	24.25	20-28
Israel	Arad	3	32.4	14.33	12-17
Israel	Oron	1	33.62	5	-
Jordan	El-Hasa	5	31.9	5.42	3-12
Jordan	Shidyia	1	30.5	6	6
Mali	Tilemsi	1	28.8	8	8
Mataiva Island		1	35.6	9	
Morocco	Undifferentiated	6	32.7	25.98	10-45
Morocco	Bu Craa	2		37.5	32-43
Morocco	Khouribga	10	32.6	15.06	3-27
Morocco	Youssoufia	6	31.22	23.17	4-51
Nauru		4	36.65	85.15	70-100
Niger	Parc W	2	34.3	4	<2-4
Peru	Sechura	4	30.2	25	11-41
Senegal	Taiba	12	35.91	86.67	60-115
Syria	Khneifiss	1	31.9	3	-
Tanzania	Minjingu	1	28.6	1	-
Togo		19	36.7	58.41	48-67
Tunisia		4	29.95	39.5	30-56
United States	Central Florida	27	32.1	9.13	3-20
United States	North Florida	7	31.0	6.14	3-10
United States	Idaho	7	31.7	92.29	40-150
United States	North Carolina	14	29.8	38.21	20-51
Venezuela	Recieto	1	27.9	4	-
Overall Sedimentary Averages <sup>b</sup>			31.3	20.6	0.5-150

a. Full details and references can be found in Van Kauwenbergh [1997].

*Table 5. Potentially Hazardous Trace Element Abundances in the Crust, Granite, Basalt, and Igneous Phosphate Rocks<sup>a</sup>*

Element	Crustal Abundance <sup>b</sup>	Granite <sup>b</sup>	Basalt <sup>b</sup>	Igneous Phosphate Rock	Range	Enrichment or (Depletion) Factor Relative to Crust
	(ppm)					
As	1.8	1.5	2.0	121.4	3-1,300	67.4
Cd	0.2	0.2	0.2	1.5	1-5	7.5
Cr	100	4	200	26.9	1-100	(3.7)
Hg	0.08	0.08	0.08	0.06	1-500	(1.3)
Pb	20	5	20	15.0	4-36	(1.3)
Se	0.05	0.05	0.05	3.8	3-5	76
U	2.7	4.8	0.6	59.8	7-247	22.1
V	135	20	250	49.5	4-300	(2.7)

a. Van Kauwenbergh [1997].

b. Carmichael [1982].

Table 6. Phosphate and Cadmium Contents of Igneous Phosphate Rocks<sup>a</sup>

Country	Deposit	No. of Samples	Average P <sub>2</sub> O <sub>5</sub> (wt%)	Average Cd (ppm)	Range Cd
Brazil	Araxa	2	37	2.50	2-3
Brazil	Catalao	1	37.4	<2	
Burundi	Matongo	1	40.4	<2	
Finland	Siilinjarvi	1	39.50	<2	
S. Africa	Phalaborwa	5	38.6	1.3	1-1.6
Sri Lanka	Eppawala	3	36.43	2.17	0.5-5
Sweden	Kiiruna	2	35.3	0	<1-<5
Sweden	Grangessburg	2	37.85	1	-
Uganda	Sukulu Hills		38.6	1	-
Russia	Kola	5	39.2	1.25	0.3-2
Zimbabwe	Dorowa		33.1	1	1
Overall Igneous Averages			37.58	1.5	0.5-5

a. Full details and references can be found in Van Kauwenbergh [1997].

Table 7. Comparison of the Potentially Hazardous Trace Element Contents of Sedimentary and Igneous Phosphate Rocks<sup>a</sup>

	Sedimentary Phosphate Rock	Igneous Phosphate Rock
P <sub>2</sub> O <sub>5</sub> (wt %)	31.2	37.4
As (ppm)	13.2	121.4
Cd (ppm)	20.6	1.5
Cr (ppm)	129.2	26.9
Hg (ppb)	375.4	61.6
Pb (ppm)	8.4	15.0
Se (ppm)	4.8	3.8
U (ppm)	96.1	59.8
V (ppm)	129.6	49.5

a. Average of averaged data for each individual deposit.

Table 8. Radionuclide Redistribution in Phosphoric Acid Processing

	Radioactive Elements	
	U-238	Ra-226
	(pCi/g)	
Phosphate rock	32	37
Phosphoric acid	30	<1
Byproduct gypsum	<1	20

Source: Roessler, Smith, and Bolch [1979].

Table 9. Cadmium Distribution in Phosphoric Acid Production by the Dihydrate Process

Phosphate Rock	Cd Content (ppm)	Proportions Recovered (%) in	
		Acid <sup>a,b</sup>	Gypsum
Senegal <sup>c</sup>	78	75	25
Togo <sup>c</sup>	55	90	10
United States			
Central Florida <sup>d</sup>	5	67	33
North Florida <sup>d</sup>	8	60	40
North Carolina <sup>d</sup>	38	55	45
Western Region <sup>d</sup>	120	60	40

a. 28%-32% P<sub>2</sub>O<sub>5</sub> filter-grade acid.

b. Based on total amounts of cadmium removed in acid and gypsum cake.

c. IFDC [unpublished data].

d. Wakefield [1980].

Table 10. Potential Costs of Cadmium Removal From Phosphoric Acid<sup>a,b,c</sup>

Type of Treatment	Conditions	Investment (million US \$)	Cost /mt P <sub>2</sub> O <sub>5</sub> (US \$)
Co-crystallization with anhydrite	Without treatment of reject	3.30	8.65
	Without value of reject		5.65
	With value of reject	4.35	10.10
	With treatment of reject		5.65
Precipitation		4.25	20.00
Ion exchange resins	Partial treatment	6.20	25.00
Solvent extraction	Full treatment	6.30	27.00

a. Source: Davister [1992].

b. Capacity = 500 mt P<sub>2</sub>O<sub>5</sub>/24 h.

c. All costs in U.S. dollars, April 1, 1992.

*Table 11. Impact on Different Rock Deposits According to the Hypothetical Limits of Cadmium in Fertilizers Proposed for the EU*

Limit	Fertilizers	Deposits
	(mg Cd/kg P <sub>2</sub> O <sub>5</sub> )	(average in mg Cd/kg P <sub>2</sub> O <sub>5</sub> )
60		Algeria Djebel Onk (60) Morocco Khouribga (55) Israel Nhal Zin (61)
40		Florida (23) Israel Arad (35) Morocco Khouribga (37) Syria (22)
20		South Africa Phalaborowa (2.7) Russia Kola (2.8) Jordan El-Hassa (13) Egypt Abu Tartur (15)

Note: Above table based on average figures giving only a approximate values.

Source: Adapted from Hutton and Meeûs [2001].

*Table 12. Proposed AAPFCO Recommended Metal Limits in Phosphate Fertilizers and Micronutrient Sources*

Metals	ppm per 1% P <sub>2</sub> O <sub>5</sub>	ppm per 1% Micronutrients
Arsenic	13	112
Cadmium	10	83
Cobalt	3,100	23,000
Lead	61	463
Mercury	1	6
Molybdenum	42	300
Nickel	250	1,900
Selenium	26	180
Zinc	420	2,900

Source: Anonymous [2001g].

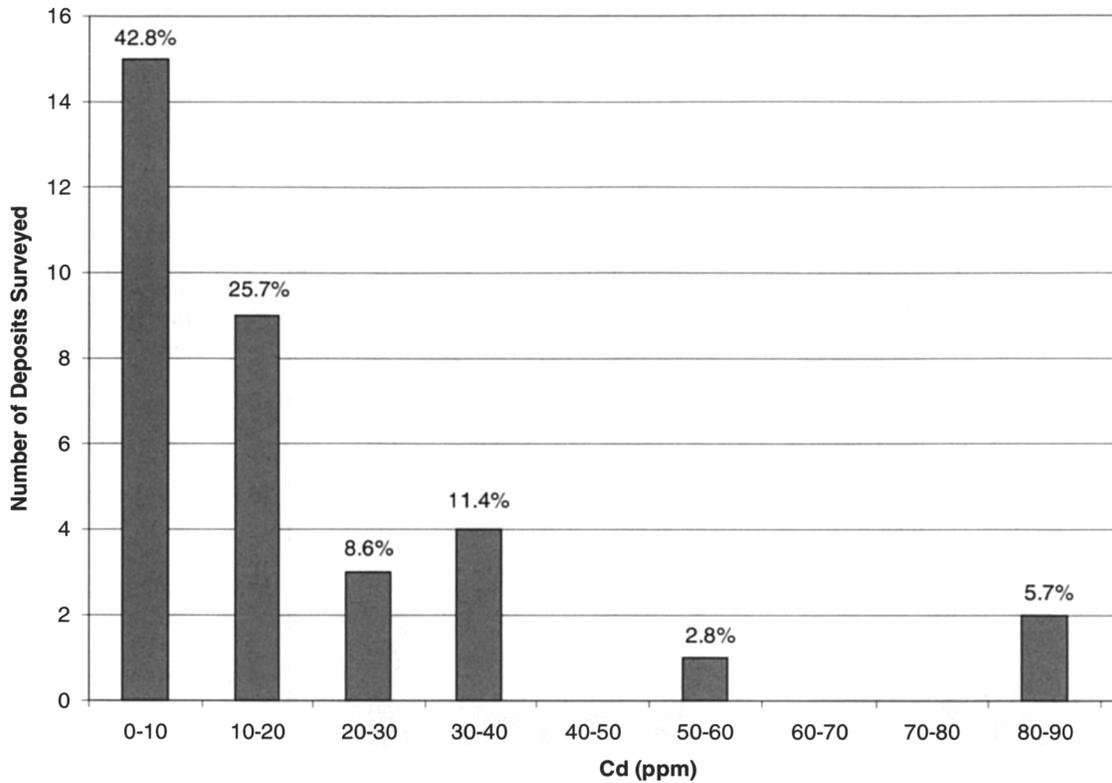


Figure 1. Concentrations of Cadmium in Sedimentary Phosphate Rocks Versus Number of Deposits Surveyed.

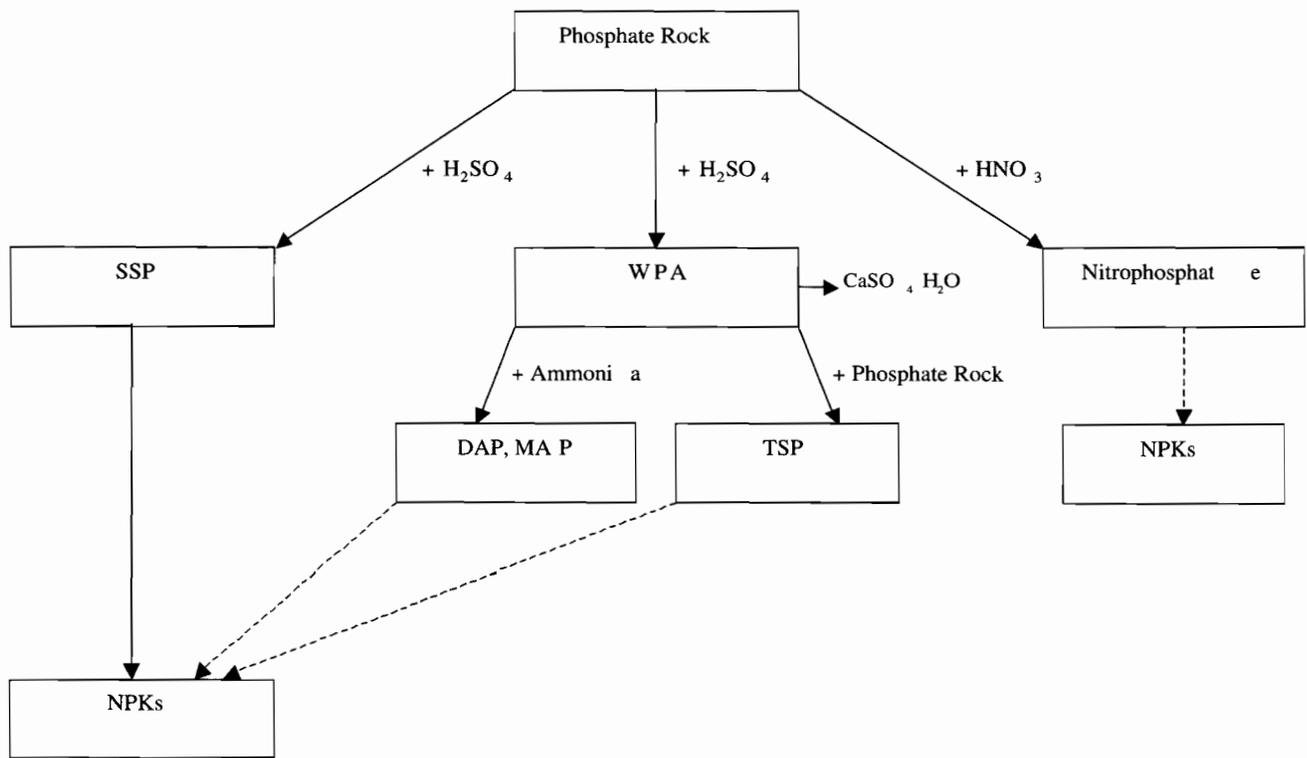


Figure 2. Relationship of Phosphate Rock and Phosphate Fertilizers

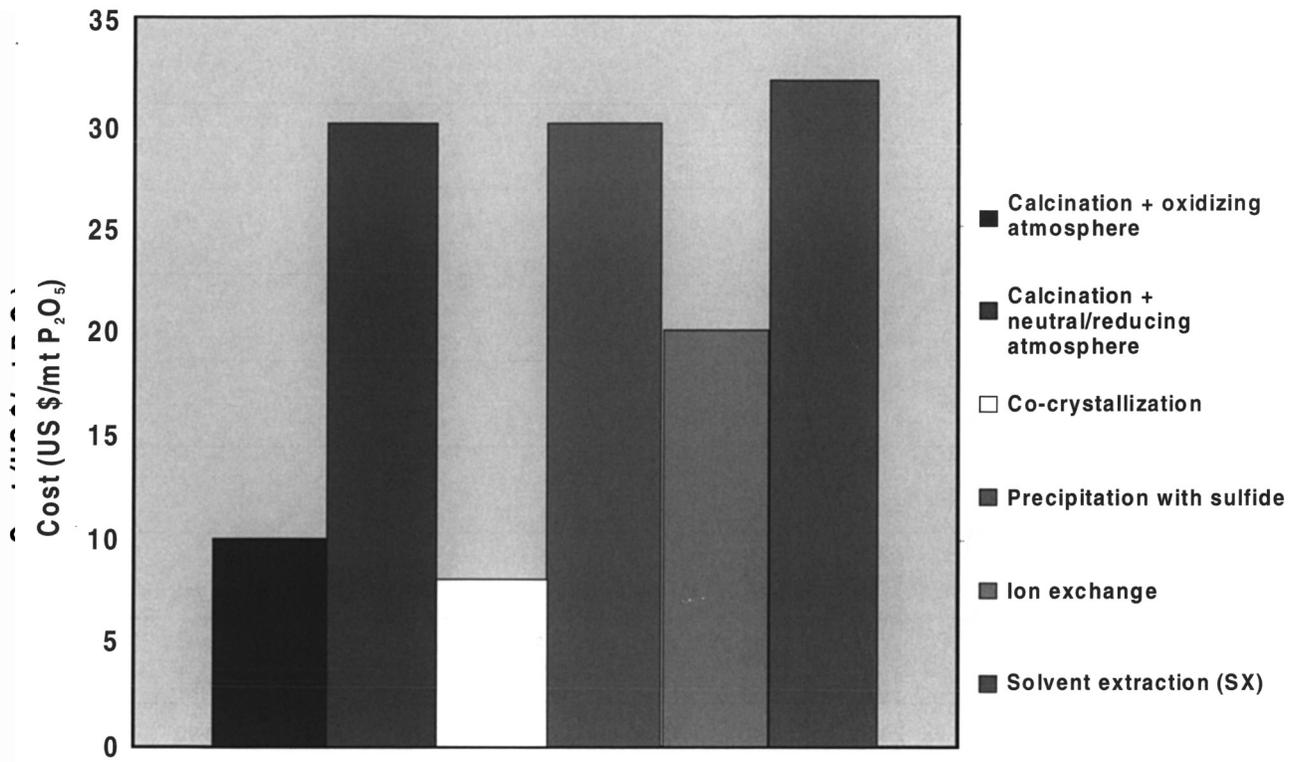


Figure 3. Cost of Various Decadmiation Methods (US \$/mt P<sub>2</sub>O<sub>5</sub>)

# **Comparative Methods for Metals in Fertilizers and Some Pitfalls to Avoid**

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The Association of Fertilizer and Phosphate Chemists (AFPC, formerly known as the Association of Florida Phosphate Chemist, has developed analytical methods to analyze state-regulated metals and other metals in fertilizers. These metals include Fe, Al, Mg, Ca, Na, K, Cd, As, Cu, Zn, Hg, Pb, Mn, Cr, Co, Mo, Ni, and Se. Fertilizers analyzed are diammonium phosphate (DAP), monoammonium phosphate (MAP) and granular triple superphosphate (GTSP), which are the three major phosphate concentrated fertilizers used in the United States. The study includes two different analytical methods developed by the AFPC and compares them with the EPA's method for analyzing metals in sludge (Solid Waste 846 Guidelines). The Association of Fertilizer and Phosphate Chemists has established a monthly check program for metals in fertilizer and has published the results on their web page <http://afpc.net>.

There are some pitfalls to avoid in the analyses of metals using either atomic absorption or inductive coupled plasma. Examples of the pitfalls to avoid with ways to correct the analytical values will be presented.

The discussion will include how we came to this point in regulation of metals in fertilizers by the State Agencies, such as State of Washington, State of California and others.

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## **Background**

In recent years there has been an increasing focus on metals in fertilizer and their potential health effects. Several states have adopted limits using

the Canadian Standards for metals in fertilizer. The Association of American Plant Food Control Officials (AAFPCO) has proposed similar limits on metals in fertilizers based on risk assessment developed by the State of California and The Fertilizer Institute (TFI). These metals include Cd, As, Ni, Zn, Hg, Pb, Co, Mo and Se.

Currently, no accepted analytical method for metals in fertilizer exist for these nine regulated metals. The EPA has an analytical method for metals in solid waste and State of Washington recommends the use of the EPA method for metals analyzed for the State. The AFPC recognized a need to establish uniform methods for fertilizers because accurate uniform methods are important in state regulations. The AFPC's mission statement calls for uniformity in analytical methods.

During the early 1990's the AFPC began studying elements such as chromium, lead and mercury to be included with other metals such as cadmium, iron, aluminum, calcium and magnesium in the official analytical methods of the Association. The Association's procedure includes collaboration of methods within its membership and outside its membership using the AFPC Check Sample

The AFPC has conducted extensive studies on analytical methods for analyzing metals in fertilizer. Since the AFPC conducts a check sample program, which includes DAP, MAP and GTSP fertilizers, different methods used by members can be evaluated by the Methods Committee. In 1997, the AFPC added these metals to their existing check sample program for DAP, MAP and GTSP fertilizer samples.

## **Purpose:**

The purpose of this paper is to discuss valid analytical methods for analyzing metals in fertilizer and some of the pitfalls found when using Inductively Coupled Plasma and Atomic Absorption. Data collected since 1997 by the AFPC are used in this presentation. The methods used in this study by the AFPC include Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Cou-

pled Plasma Atomic Emission Spectroscopy (ICP AES) and EPA's method for metals in sludge.

**Discussion:**

Two AFPC analytical methods for determining metals in fertilizer are compared to EPA's method for determining metals in solid waste. Method one uses inductively coupled plasma mass spectrometer, fitted with aluminum cones and a Meinhard Type C concentric nebulizer with microwave digestion using ultrapure nitric acid. The second method uses an inductively coupled plasma atomic emission spectrophotometer with a radial torch, cyclonic spray chamber and a \*Noordermeer V Groove Nebulizer using a mixture of ultrapure nitric and hydrochloric acid digestion. One member of the AFPC used the EPA procedures using an atomic absorption for metal determination with a graphite furnace for Mo, hydride generation for As and Se, and cold vapor for Hg. The digestion method for the EPA protocol uses nitric acid and hydrogen peroxide digestion.

*\*A Noordermeer V Groove Nebulizer is used for high dissolved solids.*

**Results:**

Analytical results for the nine metals can be found in Tables 1 - 3 for DAP, MAP and GTSP. The three analytical methods used by the AFPC are shown with an overall average and standard deviation in ppm from all participating laboratories in the AFPC Check Sample Program. Note: Between 10-15 laboratories participated in the AFPC Metals Check Sample Program. The following nine metal averages from Tables 1 - 3 for DAP, MAP and GTSP products are shown below:

*Average Values in Fertilizer from AFPC Check Program in ppm*

Metals	DAP/MAP/GTSP
Cd	6
As	13
Zn	61
Hg	<0.5 (est. 0.02 )
Pb	4

Co	4
Mo	10
Ni	18
Se	<5

The above metal concentrations found in 20 DAP & MAP and 4 GTSP fertilizers meet all the regulations from the risk assessment of EPA, State of California and The Fertilizer Institute. The fertilizer products of DAP, MAP and GTSP are considered *SAFE*.

**Pitfalls:**

Studying a micronutrient from the Magruder Check Sample Program reveals some of the "pitfalls" of analyzing different matrix fertilizers by Inductive Coupled Plasma (ICP) or Atomic Absorption (AA). The sample Magruder 2001 04B was used because its matrix was complexed with high iron (37.57 ± 5.24%) and manganese (22.04 ± 1.85%) backgrounds. There are several questions that need to be answered. What types of standards are to be used when analyzing different fertilizer matrix? Would a matrix-matched standard eliminate interference or can you use a pure standard matrix?

Digestion of the sample can be a pitfall in determining metals in fertilizers. Most fertilizers are digested with nitric and hydrochloric acid, but in the case of Magruder Sample 2001-04B an additional acid was added - hydrofluoric acid. This problem of digestion was apparent after reviewing the Magruder results as published. We found higher levels of As, Co, Ni, Pb and Se with the HCl/HNO<sub>3</sub>/HF digestion.

Using pure standards vs matrix matched standards, after complete digestion using HCl, HNO<sub>3</sub> and HF acids, the resulting values for all the metals using an internal standard were *NOT* the same. Internal standards must be used in the analyses of DAP/MAP/GTSP. If an internal standard is not used matrix matching will need to be used. This will require additional time to prepare standards. Scandium is used for an internal correction on all samples and is important for obtaining accurate and

precise data, allowing for drift and corrects to differences in viscosity effects on the nebulizer. The actual sample of scandium is injected and mixed prior to the nebulizer rather than adding it to every sample. Not using the proper internal standard or matrix match standards can be more pitfalls in determining metals in fertilizers.

The metal cadmium as reported by Magruder Average was  $28 \pm 35$  ppm. One, two and three standard deviations were 35, 70 and 105 ppm, respectively. The CFII result found approximately 36 ppm using pure standards and <1 ppm using matrix-matched standards. In reviewing scans of different wavelengths for Cd for this micronutrient sample we found no interference, but noticed an unusual shift in the concentration peak from the normal line at wavelengths 214.438 and 226.502. After contacting the instrument manufacture about this unusual shift we found a weak iron line at this wavelength, but with the high concentration of iron it caused an iron peak overlapping the Cd peak. So how do we correct for the iron peak? In high concentrations of metals such as iron and manganese interference may be found. Wavelength lines picked to analyze metals need to be researched for possible overlap as in this case and change to another wavelength. If this is not possible, the iron peak must be subtracted, leaving the remaining Cd peak. The true Cd value is <1 ppm using ICP-AES and 0.25 ppm as furnished by IMC- New Wales using ICP-MS.

	*CFII Pure Standards	*CFII Matrix Standards	Magruder Average
As	46	47	12
Cd	35	<1	28
Co	116	110	79
Cr	77	79	121
Cu	87	91	79
Mo	8	9	4
Ni	80	81	54
Pb	77	88	31
Se	82	89	12

\*Both sets of data from CFII used the internal standard, scandium. Samples digested with HCl, HNO<sub>3</sub> and HF.

The use of a standard such as an NIST certified standard is necessary for determining metals in fertilizers. The AFPC has developed a certified standard of a phosphate rock standard called Check Rock #22. The standard has been under development for the past several years for a metal standard. Studies have been included techniques of Neutron Activation, ICP-MS, ICP-AES and AA. Samples of Check Rock #22 have been submitted to NCSU for Neutron Activation and submitted to the AFPC Check Program four times and the Magruder Check Sample Program once. Data was tabulated for the metals with the result below:

	Check Rock #22 Average Value with Std
As	8 +/- 1
Cd	6 +/- 1
Co	3 +/- 1
Cr	57 +/- 2
Cu	8 +/- 2
Mo	9 +/- 4
Ni	10 +/- 5
Pb	20 +/- 3
**Hg	0.1 +/- 0
**Se	1.9 +/- 1

\*\* Not certified, but still under consideration. Future values and updates for the Check Rock # 22 can be found on the web site of the AFPC. (<http://afpc.net>)

Additional standards such as DMR QA 21 Check Sample in ppb can be used to help with quality control measures. Performance of the IRIS Advantage can be reviewed (See Table A):

### Conclusion:

1. The two methods (ICP-MS and ICP-AES) used by the AFPC were validated using the AFPC Check Sample Program. Results comparing the ICP-MS and ICP-AES data from the check samples were compared on 20 DAP and MAP samples and 4 GTSP samples on nine different metals. The results

from the two different methods compared with each other and with the overall averages for each metal.

2. The two analytical methods for metals used by the AFPC were comparable to EPA's metals in solid waste. The results from the check sample program were compared on 20 DAP and MAP samples and 4 GTSP samples on nine different metals. The results between the three methods, (ICP-MS, ICP-AES, and EPA's sludge method) compare with each other and with the overall averages for each metal. See tables 1-3 for actual results.

3. The metal data from this study of methods for fertilizer production of DAP, MAP and GTSP are below the nine metal concentrations used in the Canadian Standards, the State of California Risk Assessment and TFI's Risk Assessment.

4. EPA, California's Risk Assessment and TFI's Risk Assessment come to the same conclusion, "Fertilizers are Safe!"

5. Most pitfalls in determining metals in fertilizer can be avoided by understanding the complexity of your samples and using the proper digestion methods. Using matrix-matching standards and internal standard are a must and using an internal standard such as \*\*\*scandium will eliminate viscosity interference. Research multiple wavelengths to help eliminate spectral interference from other metals.

*\*\*\* Yttrium or Beryllium may be used provided they are not present in your samples. CFII is using scandium because of cost and safety concerns.*

#### *Outline of Slides Used in Presentation:*

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Title

Slide 2-7

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Slide 8

TFI's Risk Assessment of Metals

Slide 9-12

State of California's Limits on Metals in Fertilizer

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Limits on DAP and MAP

Slide 15

Hypothetical for DAP and MAP

Slide 16

Caution

Buyer Beware!

Slide 17

Examples of Caution

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Background for Metal Study

Slide 19

No Acceptable Methods for Metals in Fertilizer

Slide 20

Need for Acceptable Methods

Slide 21-22

AFPC Organization

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Methods Used in Study

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Digestion Methods Used in Methods

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Samples Used in Study

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Cd and As Examples in Study

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Overall Results for DAP, MAP and GTSP

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Compare Results to Risk Assessment

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Fertilizers Are Safe

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Study of Mix Fertilizer Magruder 2001-04B

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Matrix of Samples in Study

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Averages and STD of Dominant Metals Present

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Results as Published by Magruder for 2001-04B

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Cd Results for Magruder 2001-04B

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Correct Value for Cd

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CFII's First Results for Magruder 2001-04B

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CFII's Second Digestion on Magruder 2001-04B

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Pure vs Matrix Matched Standards

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Pure vs Matrix Matched Results Compared to Magruder 2001 4B Results

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Finding from Study

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AFPC Average Results for Cd, As and Pb

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Cd Averages and STD on Magruder 2001-03

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As, Pb, Hg and Se Results for Magruder 2001-03

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Development of AFPC Standard

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Methods Used in Development

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Detection Limits for ICP-AES

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Conclusion

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8<sup>th</sup> Edition of the AFPC Methods Manual

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Website of the AFPC (<http://afpc.net>)

*Table A*

<b>Parameter</b>	<b>IRIS Adv. ICAP Value ug/l</b>	<b>Certified Value ug/l</b>	<b>Performance Acceptance Limits ug/l</b>
<b>Sb</b>	<b>466</b>	<b>477</b>	<b>358 - 563</b>
<b>As</b>	<b>696</b>	<b>698</b>	<b>524 - 824</b>
<b>Ba</b>	<b>199</b>	<b>193</b>	<b>158 - 228</b>
<b>Cd</b>	<b>75</b>	<b>77</b>	<b>62.9 - 90.5</b>
<b>Co</b>	<b>403</b>	<b>394</b>	<b>323 - 465</b>
<b>Cr</b>	<b>761</b>	<b>792</b>	<b>649 - 935</b>
<b>Cu</b>	<b>778</b>	<b>785</b>	<b>644 - 926</b>
<b>Hg</b>	<b>23</b>	<b>26.8</b>	<b>20.1 - 33.5</b>
<b>Mn</b>	<b>2000</b>	<b>2030</b>	<b>1660 - 2400</b>
<b>Mo</b>	<b>402</b>	<b>406</b>	<b>333 - 479</b>
<b>Ni</b>	<b>2269</b>	<b>2230</b>	<b>1830 - 2630</b>
<b>Pb</b>	<b>495</b>	<b>478</b>	<b>392 - 564</b>
<b>Se</b>	<b>226</b>	<b>214</b>	<b>161 - 253</b>
<b>V</b>	<b>4680</b>	<b>4770</b>	<b>3910 - 5630</b>
<b>Zn</b>	<b>672</b>	<b>643</b>	<b>527 - 759</b>

**TABLE 1****Mo in DAP, MAP & GTSP**

All results in ppm

	Jun-99	Nov-99	Dec-99	Jan-00	Feb-00	Mar-00	May-00	Jun-00	Jul-00	Sep-00	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	May-01	Avg.
ICP-AES	17	11	12	12	7	7	7	12	9	9	10	10	9	10	10	10	11	10
EPA	10	10	10	12	10	7	8	13	12	7	10	9	6	12	9	9	12	10
ICP-MS	15			12	10	10		13	10	8	11	13			11	10	11	11
Average	14	11	10	13	9	8	9	11	10	8	12	10	10	11	9	10	11	10
1 std	7	2	2	1	1	1	6	1	1	1	5	2	1	1	2	1	1	2

**Cd in DAP, MAP & GTSP**

All results in ppm

	Mar-97	Dec-97	Jan-98	Jul-98	Mar-99	May-99	Jun-99	Nov-99	Dec-99	Jan-00	Feb-00	Mar-00	May-00	Jun-00	Jul-00	Sep-00	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	May-01	Avg.
ICP-AES	4	5	9	5	4	2	7	2	6	5	6	4	5	5	4	38	8	2	3	3	5	5	2	6
EPA	4	3	4	4	3	2	8	2	5	4	5	5	3	6	4	35	7	2	3		4	4	2	5
ICP-MS	5	4	5	9			8		6	4	6	5		6	4	39	7	2	4	3	5	5	2	7
Average	4	4	6	6	4	2	7	3	6	5	6	5	3	6	4	36	7	2	4	4	5	5	2	6
1 std	0.4	1	2	2	1	0.4	2	1	2	1	1	1	3	1	1	4	1	1	2	2	2	1	0	1

**As in DAP, MAP & GTSP**

All results in ppm

	Mar-97	Dec-97	Jan-98	Jul-98	Mar-99	May-99	Jun-99	Nov-99	Dec-99	Jan-00	Feb-00	Mar-00	May-00	Jun-00	Jul-00	Sep-00	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	May-01	Avg.
ICP-AES					12	8	13	12	15	18	3	11	9	12	18	2	10	14	11	19	11	14	9	12
EPA	12	13	16	13	10	11	12	12	13	18	9	10	10	13	25	2	11	17	13		15	14	9	13
ICP-MS		13	14	28	10		13			17	9	12		13	18	3	12	13		19	12	14	10	14
Average	13	13	15	20	10	12	14	10	14	16	8	9	12	9	16	3	18	13	12	16	12	13	10	13
1 std	1	0	1	7	1	2	3	2	1	4	4	2	10	6	6	1	17	3	3	6	2	2	1	4

**TABLE 2**

**Pb in DAP, MAP & GTSP**

All results in ppm

	Mar-97	Dec-97	Jan-98	Jul-98	Mar-99	May-99	Jun-99	Nov-99	Dec-99	Jan-00	Feb-00	Mar-00	May-00	Jun-00	Jul-00	Sep-00	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	May-01	Avg.
ICP-AES					4	2	9	2	4	3	4	1		7	4	2	8	2	3	3	10	3	1	4
EPA	1	2	3	3	1	2	6	1	2	3	5	1		6	9	2	5			2	6	1	1	3
ICP-MS		2	3	6	1		5			3	4	1		6	2	2	6	1			10	2	1	3
Average	4	2	3	4	2	2	15	5	2	5	5	3		9	4	1.3	8	2	2	1	11	1	2	4
1 std	2		0	2	2	1	9	5	2		2	4		6	2	0.6	9	2		1	7	1	1	3

**Co in DAP, MAP & GTSP**

All results in ppm

Method	Mar-97	Dec-97	Jan-98	Jul-98	Mar-99	May-99	Jun-99	Nov-99	Dec-99	Jan-00	Feb-00	Mar-00	May-00	Jun-00	Jul-00	Sep-00	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	May-01	Avg.
ICP-AES					4		4	2	5	6	6	4	2	5	4	6	5	3	4	3	5	4	2	4
EPA		5	5	5	5		5	5	5	5	5	5	5	5	5	5	5	5			5	5	5	5
ICP-MS				5	3		3			6	3	3		3	4	1	4	2		4	4	4	2	3
Average		5	5	5	5		5	5	5	6	5	5	3	4	5	3	3	3	4	3	4	4	2	4
1 std							5			1			3	2		2	2	1	1	0	3	1	1	2

Note: All 5 ppm for EPA was actually < 5 ppm Co

**Ni in DAP, MAP & GTSP**

All results in ppm

	Dec-97	Jan-98	Jul-98	Mar-99	Jun-99	Nov-99	Dec-99	Jan-00	Feb-00	Mar-00	May-00	Jun-00	Jul-00	Sep-00	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	May-01	Average	
ICP-AES				16	16	12	20	20	21	15	10	15	16	29	20	13	14	14	18	14	10	15	
EPA	10	9	9	14	15	9	16	18	13	14	8	13	16	29	15	10			15	13	6	16	
ICP-MS			23	16	19			19	15	16		16	17	36	24	13		18	21	21	9	21	
Average	11	9	16	13	18	14	22	21	17	16	11	17	17	32	19	12	14	14	17	17	9	18	
1 std	1		10	2	4	4	2	2	5	3	4	3	2	3	4	1	1	3	3	4	1	3	

**TABLE 3**

**Se in DAP, MAP & GTSP**

All results in ppm

	Jan-98	Jul-98	Mar-99	Jun-99	Dec-99	Jan-00	Feb-00	Mar-00	May-00	Jun-00	Jul-00	Sep-00	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	May-01
ICP-AES						0.2			1.9	4	nd	<3	<3	<3	<3	<3	0.9	<3	0
EPA	<0.25	<0.25	<0.5	<0.25	<0.25	0.03	nd	<0.25	<0.25	<0.25	<0.25	<0.25	0.5	<0.25	<2.5	1		<0.25	<0.25
ICP-MS				<5	<5		<5	<5		<5	<5	<5	<5	<5			0.8	<1	<1
Average	<0.25	<0.25	<0.5	<5	<5	<5	<5	<5	<1.9	<5	<5	<5	3	<5	<3	<3	3	<3	<2
1 std													8				3		

**Hg in DAP, MAP & GTSP**

All results in ppm

	Dec-97	Jan-98	Jul-98	Mar-99	Jun-99	Nov-99	Dec-99	Jan-00	Feb-00	Mar-00	May-00	Jun-00	Jul-00	Sep-00	Oct-00	Nov-00	Jan-01	Feb-01	Mar-01	May-01	Average
ICP-AES																		0.2			
EPA	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	0.05	0.04	1	0.02	<0.02	<0.02	0	nd		0.04	0.04	0.03	
ICP-MS			<0.5	<0.5	<0.5		<0.5		<0.5			<0.5	<0.5	<0.5	0.04	<0.02	<0.1	<0.01	<0.01	<0.01	
Average	0.02	<0.02	<0.5	<0.5	<0.5	<0.03	<0.5	0.05	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.1	0.1	<0.05	<0.05	<0.02
1 std								0.02										0.09			

**Zn in DAP, MAP & GTSP**

All results in ppm

	Dec-97	Jan-98	Jul-98	Mar-99	Jun-99	Nov-99	Dec-99	Jan-00	Feb-00	Mar-00	May-00	Jun-00	Jul-00	Sep-00	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	May-01	Average
ICP-AES	58	81	68	70	55	30	75	40	52	61	45	70	34	577	87	40	42	31	61	71	46	82
EPA	48	78		47	53	35	69	37	67	64	48	60	44	542					66	56	41	88
ICP-MS		83	91	106	88		88		77	66		67	53	595	99	49		49	56	69	46	109
Average	59	82	80	74	65	35	71	40	68	66	55	66	46	575	89	51	50	42	65	63	43	87
1 std	12	3	16	30	20	5	9	5	14	15	25	6	10	35	11	11	9	8	6	9	3	13

**COMPARATIVE METHODS  
FOR METALS IN FERTILIZERS  
AND  
“SOME” PITFALLS TO AVOID**

By  
**J. Harold Falls, Sanford Siegel, John  
Longest and Barton Boggs**  
CF Industries, Inc.  
Plant City Phosphate Complex



Slide 1

**Lead in “My”  
French Fries**

Seattle Times  
D.W.  
Pb Lead  
Atomic Number: 82  
Atomic Mass: 207.20

“This fertilizer  
contains 20-20-20.  
What is the  
remaining 40%?”



Slide 2

Duff Wilson  
Finalist for the Pulitzer Prize

**FATEFUL HARVEST**

THE TRUE STORY  
OF A SMALL TOWN,  
A GLOBAL INDUSTRY,  
AND A TOXIC SECRET



Slide 3

<b>Hg</b> Mercury Atomic Number: 80 Atomic Mass: 200	<b>Pb</b> Lead Atomic Number: 82 Atomic Mass: 207.20
<b>Zn</b> Zinc Atomic Number: 30 Atomic Mass: 65.39	<b>As</b> Arsenic Atomic Number: 33 Atomic Mass: 74.92
<b>Co</b> Cobalt Atomic Number: 27 Atomic Mass: 58.93	<b>Cd</b> Cadmium Atomic Number: 48 Atomic Mass: 112.41
<b>Cr</b> Chromium Atomic Number: 24 Atomic Mass: 52	<b>Ni</b> Nickel Atomic Number: 28 Atomic Mass: 58.69
	<b>Cu</b> Copper Atomic Number: 29 Atomic Mass: 63.55
	<b>Mn</b> Manganese Atomic Number: 25 Atomic Mass: 54.94



Slide 4

**Metals  
and the  
Periodic  
Chart**

**Perchlorates  
Dioxins**



Slide 5

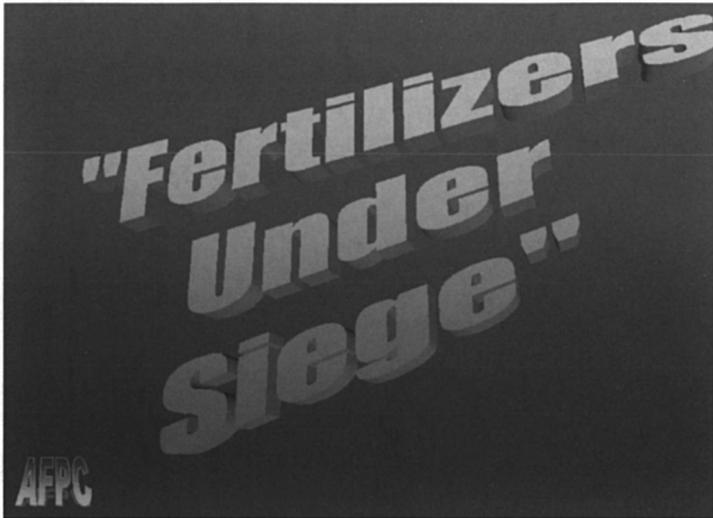
“However, it does not entirely lay the question of perchlorates in fertilizer to rest because it begs the issue of past practices, according to Kevin Mayer, EPA’s Region 9 coordinator for perchlorate issues.”

As Mayer wrote in a recent EPA memo, “The distribution of perchlorate detections in the environment seems to be directly related to the effort put forth in searching for perchlorate.”

Taken from ES&T -Science News - July 12, 2001



Slide 6



Slide 7

**TFI RISK ASSESSEMENT LIMITS**

Metal	ppm per	ppm per 1%
	1% P <sub>2</sub> O <sub>5</sub>	Micronutrient
Arsenic	13	112
Cadmium	10	83
Cobalt	3100	23000
Lead	61	463
Mercury	1	6
Molybdenum	42	300
Nickel	250	1900
Selenium	26	180
Zinc	420	2900

AFPC

Slide 8

**State of California Current**

Metal	ppm per	ppm per 1%
	1% P <sub>2</sub> O <sub>5</sub>	Micronutrient
Arsenic	13	13
Cadmium	12	12
Lead	140	140

AFPC

Slide 9

**State of California 2002**

Metal	ppm per	ppm per 1%
	1% P <sub>2</sub> O <sub>5</sub>	Micronutrient
Arsenic	4	20
Cadmium	6	30
Lead	20	100

AFPC

Slide 10

**State of California 2003**

Metal	ppm per	ppm per 1%
	1% P <sub>2</sub> O <sub>5</sub>	Micronutrient
Arsenic	3	15
Cadmium	5	25
Lead	20	100

AFPC

Slide 11

**State of California 2004**

Metal	ppm per	ppm per 1%
	1% P <sub>2</sub> O <sub>5</sub>	Micronutrient
Arsenic	2	10
Cadmium	4	20
Lead	20	100

AFPC

Slide 12

Diammonium Phosphate Limits		
Metal	All in ppm except as noted.	
	Maximum Amount Allowed by TFI Risk Assessment	Maximum Amount Allowed by State of California
Arsenic	598	92
Cadmium	460	184
Cobalt	14.26%	
Lead	2806	920
Mercury	46	
Molybdenum	1932	
Nickel	11500	
Selenium	1196	
Zinc	19320	

Slide 13

Monoammonium Phosphate Limits			
Metal	All in ppm except as noted.		
	Maximum Amount Allowed by TFI Risk Assessment	Maximum Amount Allowed by State of California	Current Level in Florida Based DAP/MAP/GTSP
Arsenic	676	104	13
Cadmium	520	208	6
Cobalt	16.12%		4
Lead	3172	1040	4
Mercury	52		<0.5
Molybdenum	2184		10
Nickel	13000		18
Selenium	1352		<5
Zinc	21840		61

Slide 14

**Production of 18-46-0  
Would be Restricted to  
14-36-0**

**Production of 11-52-0  
Would be Restricted to  
9-41-0**

Slide 15

**Caution: Foreign  
Sources of  
Fertilizers**

Slide 16

**Found 12% Cadmium in  
a Shipment of 35% Zinc.**

**Other Shipments Found  
High Levels of Lead (Pb)**

**One Zinc Shipment  
Contained 875 ppm Cd and  
5501 ppm Pb**

Slide 17

**Background**

**Increased focus on Metals in Fertilizers**

**Potential Health Effects**

**Several States Adopted Limits on Metals in  
Fertilizer**

**Metals include Cd, As, Ni, Zn, Hg, Pb,  
Co, Mo and Se**

Slide 18

# No Accepted Analytical Method

AFPC

Slide 19

Need to Establish Analytical  
Method for Metals in Fertilizers

EPA - Established Method for  
Metals in Solid Waste

“Need Uniformity of Methods”

AFPC

Slide 20

## Association of Fertilizer and Phosphate Chemists

Organized in 1920 (81 years young)

Currently 17 Member Companies

Published 7 Method Manuals

New Publication No. 8 - November 2001

AFPC

Slide 21

AFPC Conducted Extensive Studies on  
Analytical Methods for Metals -  
used a traceable NIST standard

Use the AFPC Check Sample  
Program for Evaluation

DAP, MAP and GTSP in  
Program

AFPC

Slide 22

### Methods Used:

Inductively Coupled Plasma - Mass  
Spectrometry (ICP-MS)

Inductively Coupled Plasma -  
Atomic Emission Spectrometry  
(ICP-AES)

EPA's Solid Waste Method uses an  
Atomic Absorption with a graphite  
furnace for Mo, hydride generation for  
As and Se, and cold vapor for Hg

AFPC

Slide 23

### Digestion Methods:

ICP-MS used microwave digestion with  
ultrapure nitric acid

ICP-AES used a mixture of ultrapure  
nitric and hydrochloric acid

EPA's Method used a mixture of  
ultrapure nitric acid and hydrogen  
peroxide

AFPC

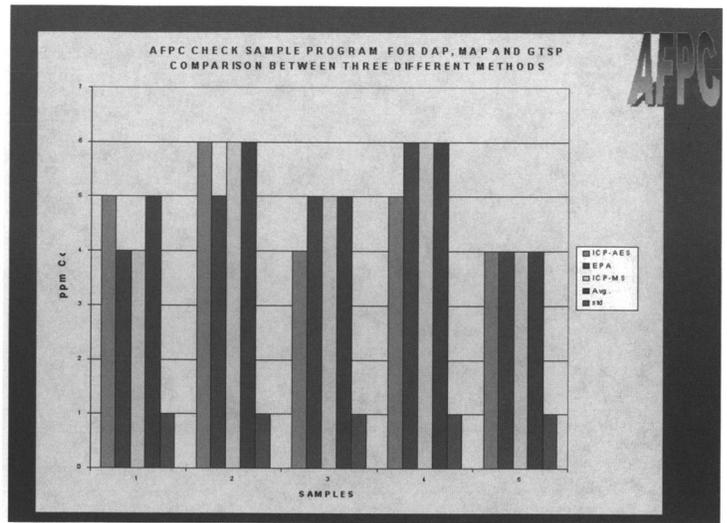
Slide 24

Analyzed 20 DAP and MAP samples and 4 GTSP samples in the AFPC Check Sample Program

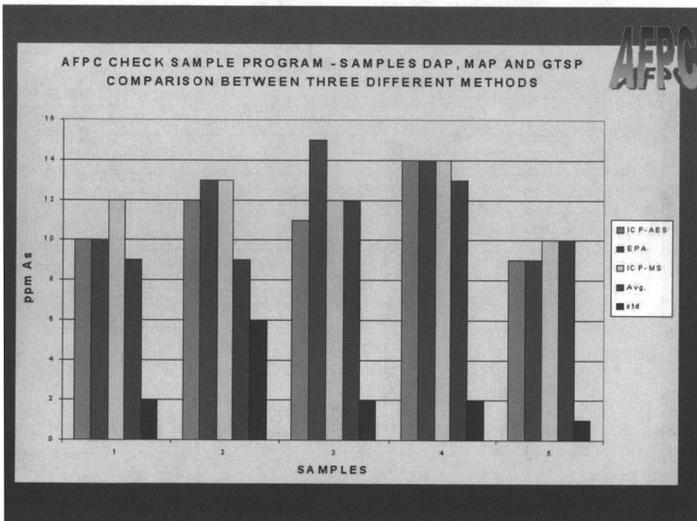
Compared results from the ICP-MS, ICP-AES and EPA's Method for Solid Waste with the Overall Average Results



Slide 25



Slide 26



Slide 27

**Average Values in Fertilizer from AFPC Check Sample Program in ppm**

Metal	Average
Cd	6
As	13
Mo	10
Pb	4
Co	4
Ni	18
Zn	61
Se	< 5
Hg	< 0.5

Slide 28

Metal Data in DAP, MAP & GTSP from the study:

“Below”

Canadian Standards

State of California Risk Assessment

“New” State of California Risk Assessment

TFI's Risk Assessment



Slide 29

**Fertilizers  
are  
Safe!**

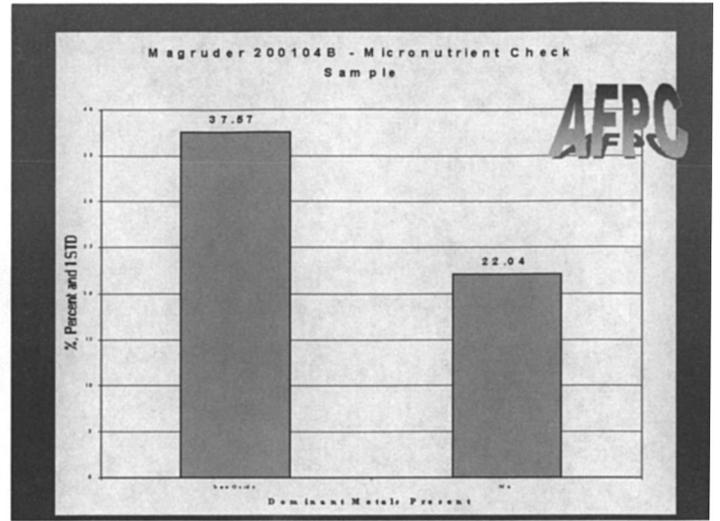


Slide 30

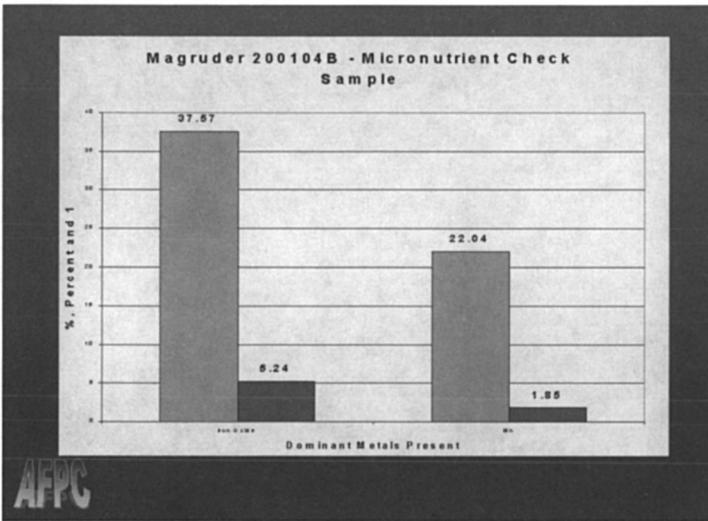
# Study of Magruder Check Sample 2001-04B Micronutrient

AFPC

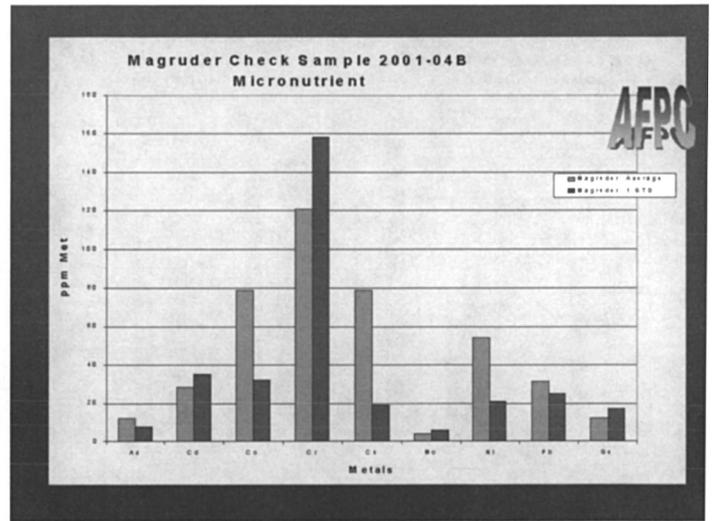
Slide 31



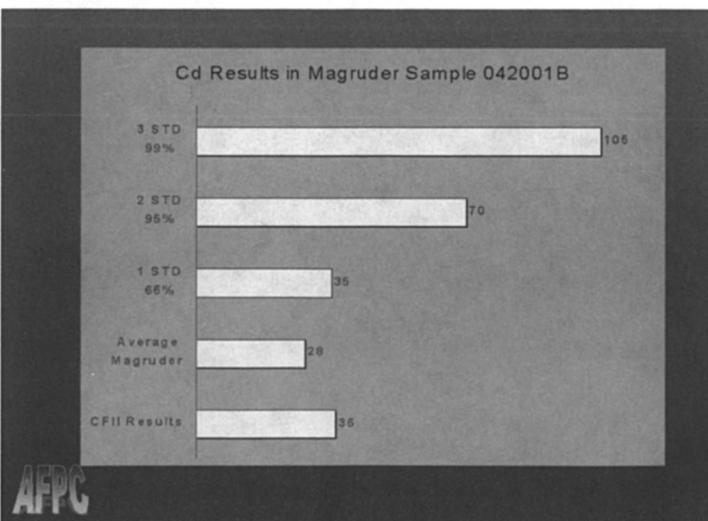
Slide 32



Slide 33



Slide 34



Slide 35

## Value for Cd Incorrect

Cd value is 0.25 ppm.

AFPC Furnished by IMC-Global at New Wales

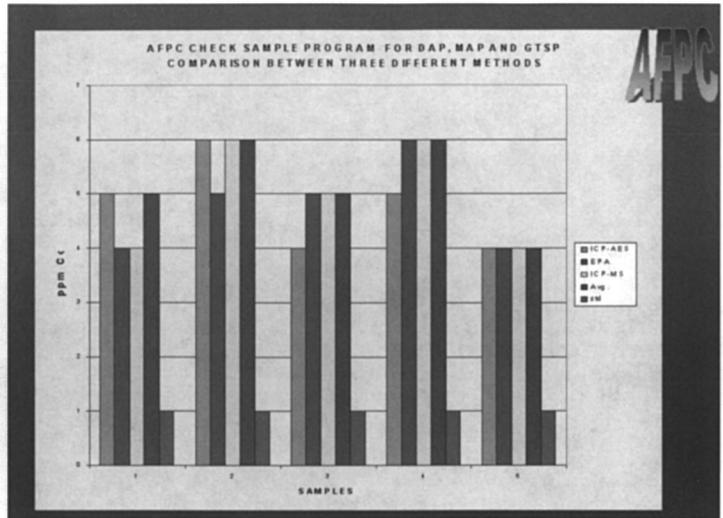
Slide 36

Analyzed 20 DAP and MAP samples and 4 GTSP samples in the AFPC Check Sample Program

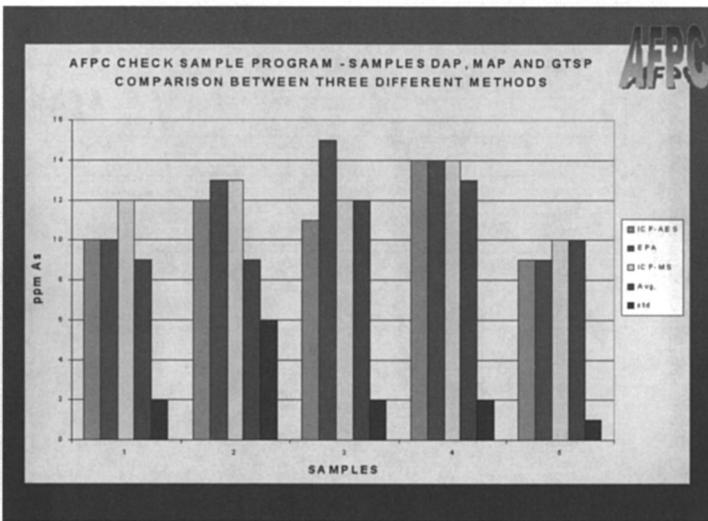
Compared results from the ICP-MS, ICP-AES and EPA's Method for Solid Waste with the Overall Average Results



Slide 37



Slide 38



Slide 39

**Average Values in Fertilizer from AFPC Check Sample Program in ppm**

Metal	Average
Cd	6
As	13
Mo	10
Pb	4
Co	4
Ni	18
Zn	61
Se	< 5
Hg	< 0.5

Slide 40

Metal Data in DAP, MAP & GTSP from the study:

“Below”

Canadian Standards

State of California Risk Assessment

“New” State of California Risk Assessment

TFI's Risk Assessment



Slide 41

**Fertilizers  
are  
Safe!**

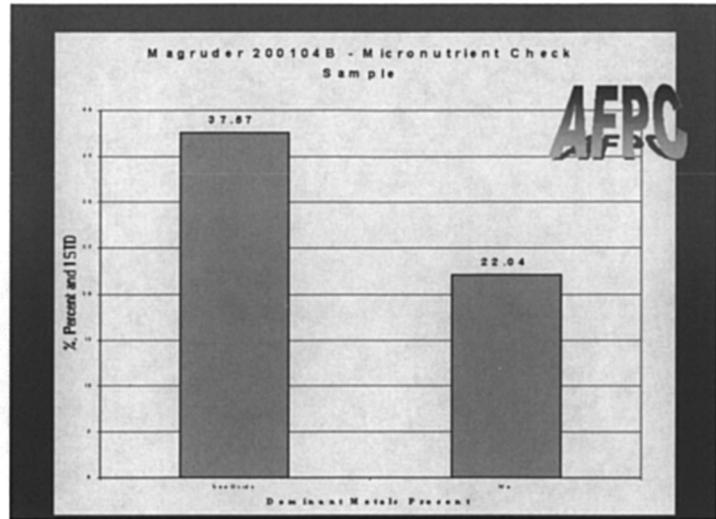


Slide 42

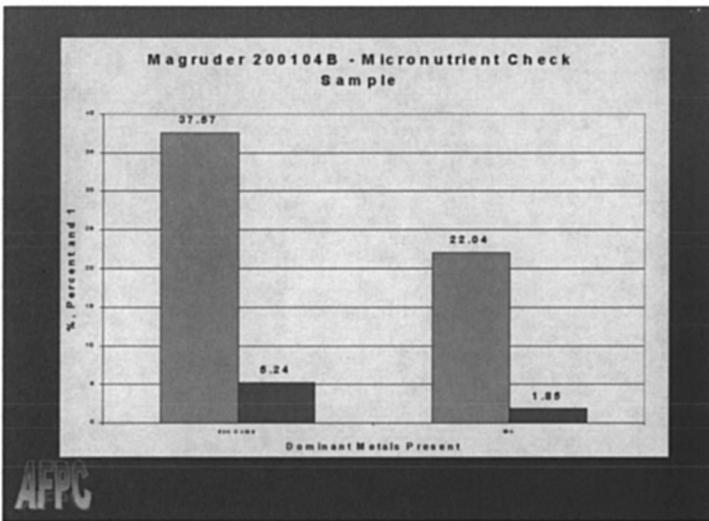
Study of Magruder  
Check Sample  
2001-04B  
Micronutrient

AFPC

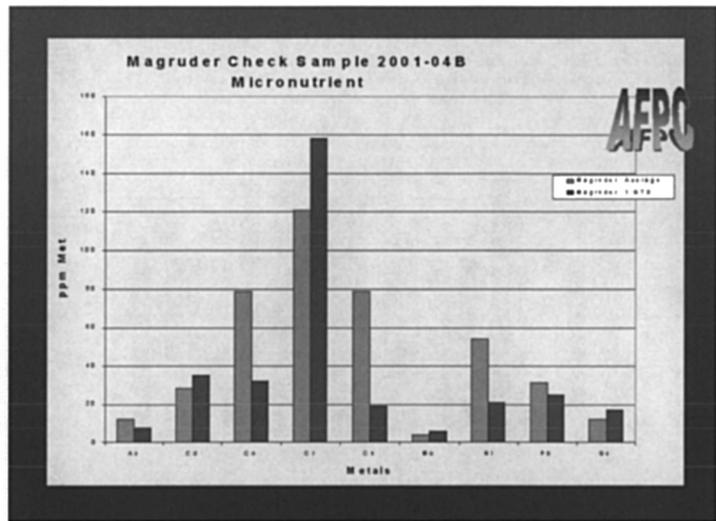
Slide 43



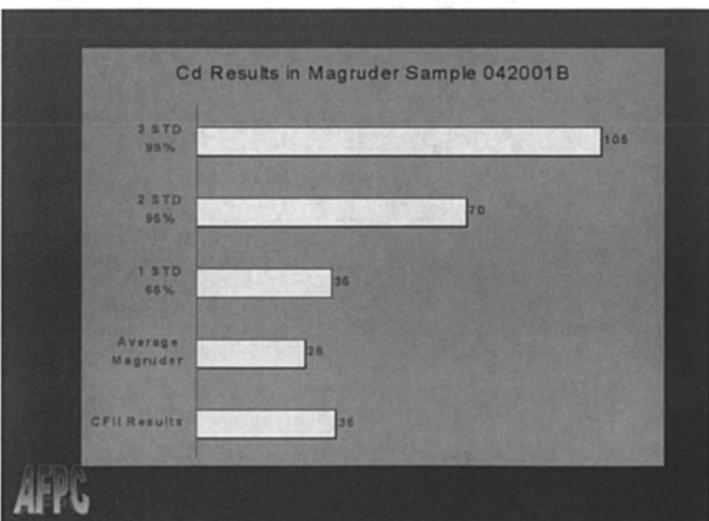
Slide 44



Slide 45



Slide 46



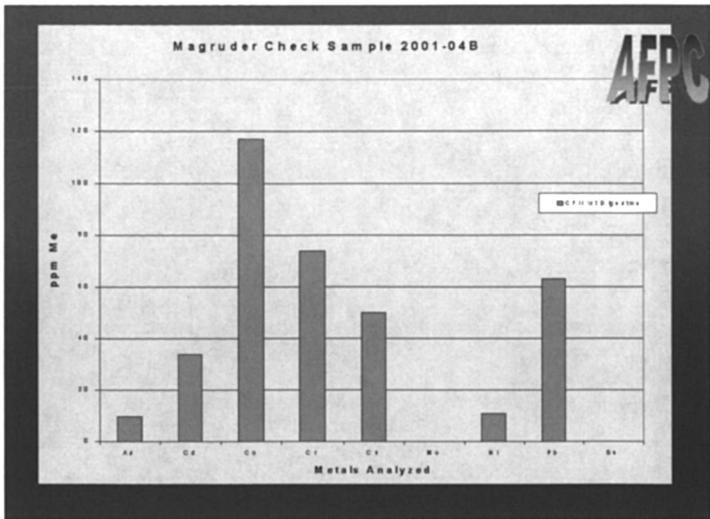
Slide 47

**Value for Cd  
Incorrect**

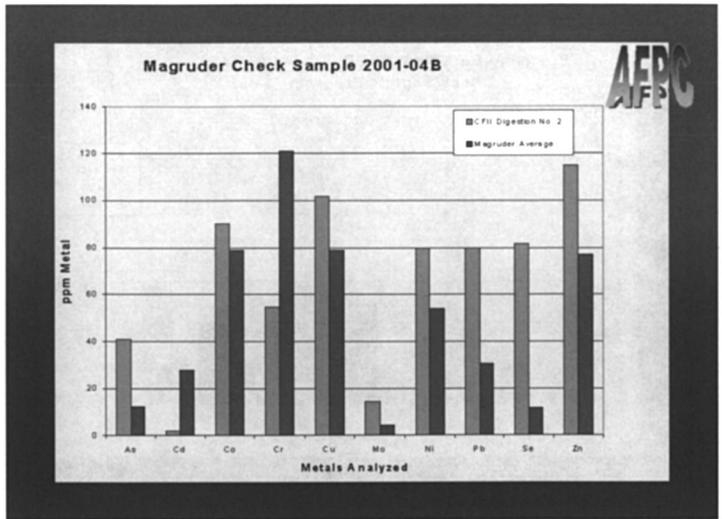
**Cd value is 0.25 ppm.**

AFPC Furnished by IMC-Global at New Wales

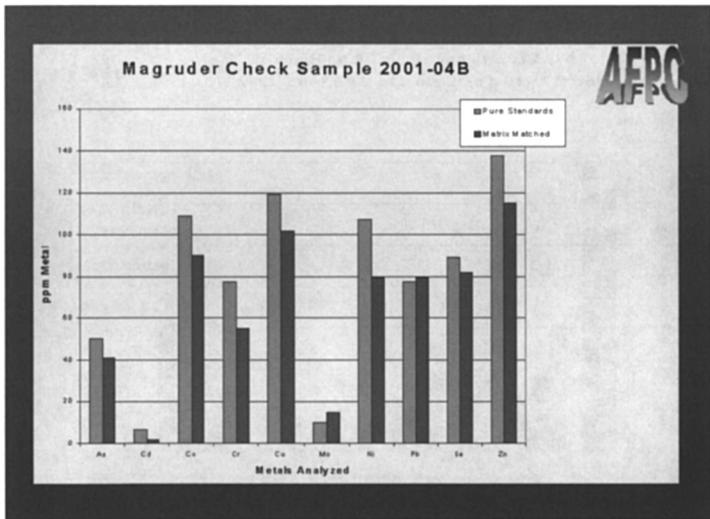
Slide 48



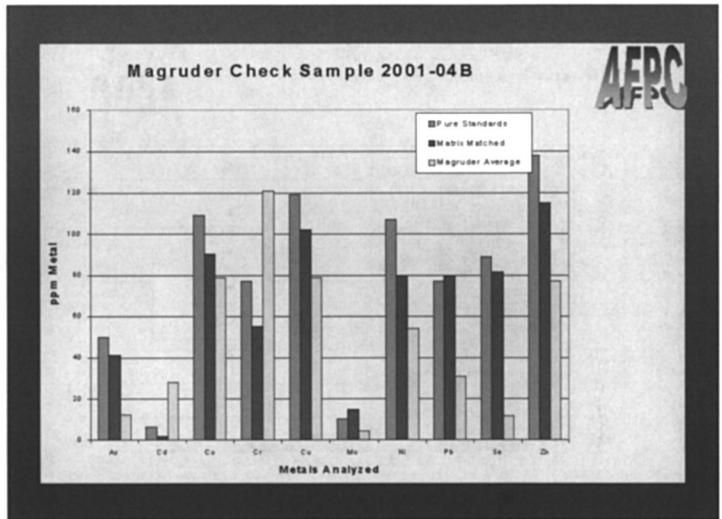
Slide 49



Slide 50



Slide 51

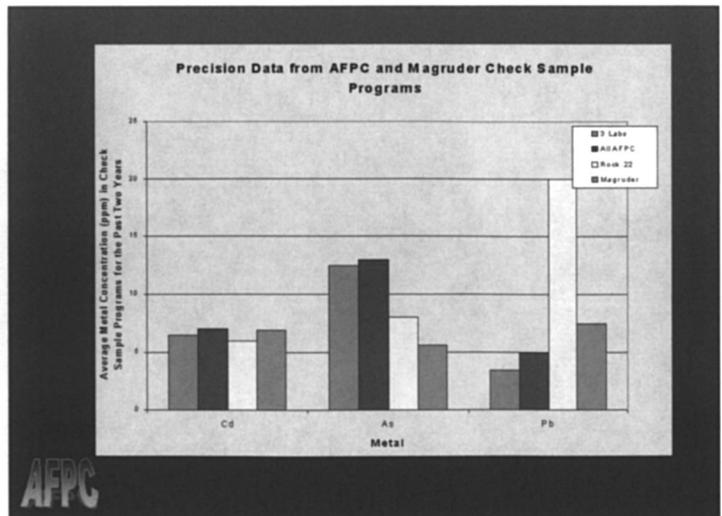


Slide 52

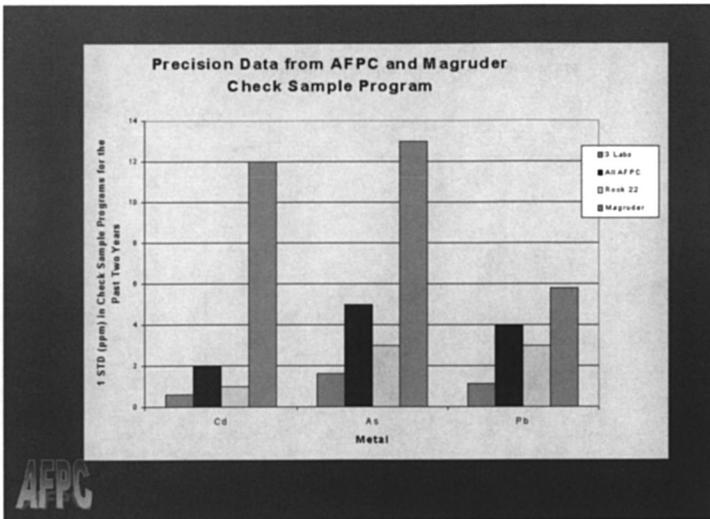
Pure Standards vs Matrix Matched Standards are “Not” the same when using an Internal Standard for all metals analyzed.

Digestion Differences using Different Digestion Acids

Slide 53



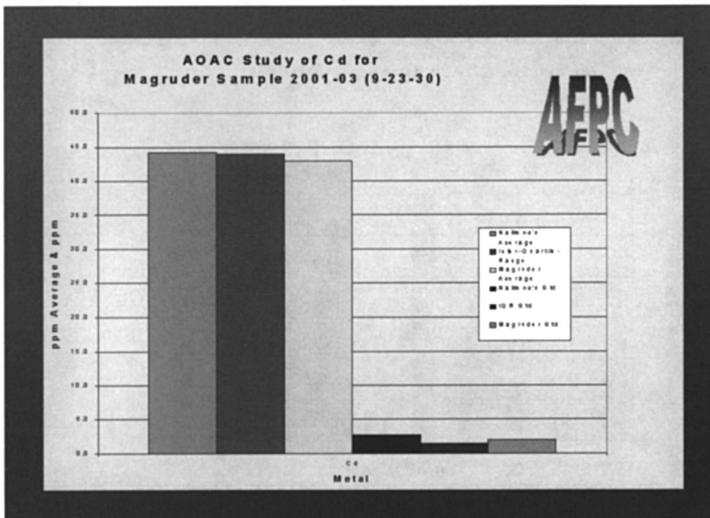
Slide 54



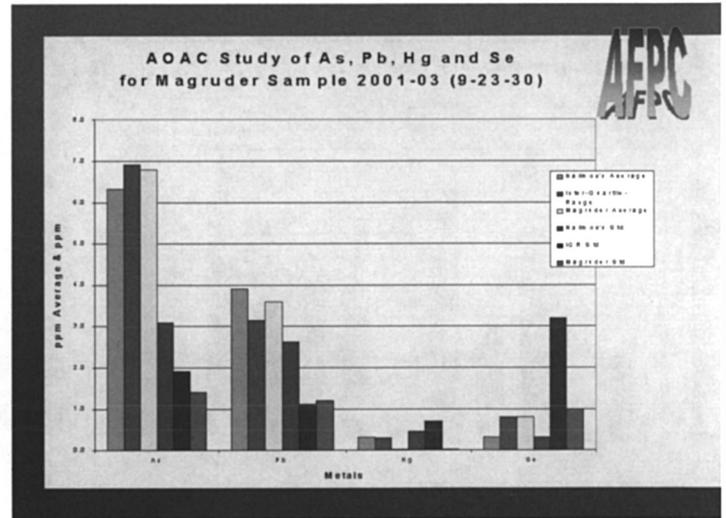
Slide 55

# AOAC Metal Study of Magruder Sample 2001-03

Slide 56



Slide 57



Slide 58

Development of a Known Standard such as AFPC Check Rock # 22

Slide 59

## AFPC Check Rock #22

Cd	6	1
As	8	1
Cr	57	2
Co	3	1
Cu	8	2
Pb	20	3
Hg	0.1	0
Mo	9	4
Ni	10	5
Se	1.9	1
Zn	59	11

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AFPC Check Phosphate Rock Standard No. 22

Analyzed by:

ICP - MS

ICP -AES

AA - EPA Protocol for Sludge

Neutron Activation - NCSU

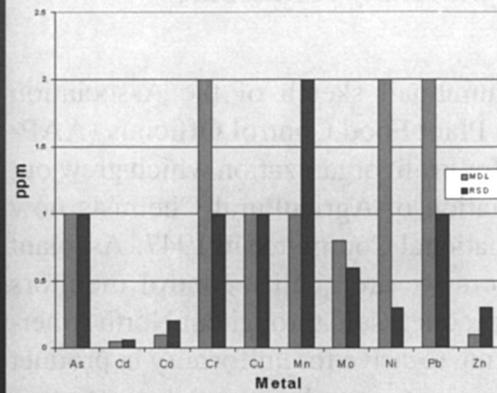
Submitted to AFPC Check Rock Programs 4  
different times

Submitted to Magruder Check Program



Slide 61

ICP-AES Detection Limits



Slide 62

Avoid the following pitfalls in  
determining metals in fertilizers  
when using ICP-AES:

1. Understand the complexity of your samples.  
Use the proper digestion methods .
2. Use matrix matching in standards.
3. Use an internal standard correction.
4. Use multiple wavelengths with no  
interference's from other metals.



Slide 63

Conclusion:

ICP-MS compares with  
ICP-AES

Both ICP Methods Compare with  
EPA's Solid Waste Method

ICP-AES Compares with Neutron  
Activation



Slide 64

8th Edition of the  
AFPC Methods Manual



Slide 65

Web Site for AFPC

<http://afpc.net>



Slide 66

## **AAPFCO Update**

*Joseph Slater*

**University of Missouri**

Here is a thumbnail sketch of the Association of American Plant Food Control Officials (AAPFCO), a not for profit organization which grew out of an Association of Agricultural Chemists now AOAC International Committee in 1947. As plant food regulators we are quality control monitors for fertilizer products sold throughout North America, cooperating to strive for uniformity in product labeling, definitions, sampling procedures, testing methods, model legislation and tonnage reporting. Our phrase "Uniformity by Consensus" exemplifies our cooperative nature with each other, and the industry that we regulate.

Our Association structure is made up of twelve standing committees dealing with specific areas of interest, accepting input from voting regulatory members and non-voting industry liaison members. Items hammered out in committee are sent to the Board for consideration before going to the general membership for further action. All items voted and passed by the membership are placed in tentative status for further consideration with referral back to the Board of Directors. Our Board then takes up the item at the midyear meeting to make recommendations on the future of the topic. Once voted out of the Board the second time, the item is voted on by the entire Association, at which time it can be raised to Official status or remain tentative for another year. Items can remain Tentative indefinitely, but require the above procedure each year of their life. Once raised to Official, it takes a vote by the Association to change an adopted document.

### **Education and Information**

Final edits and review of the AAPFCO Operating Manual are expected at this midyear meeting. This manual will provide definition and the scope of AAPFCO Committee structure to the casual outsider seeking additional information about the Association. The committee is working to update

the current Association brochures: The Standard Label and Uniformity by Consensus. New brochures planned, but as not yet titled include: Duties and Responsibilities of Liaisons and Standard Format and Supporting Documentation Needed by a Committee to adequately discuss an agenda item. Further discussion was given to the dissemination of this information, whether to publish or simply to place the information on the Association Web-Site, (<http://www.aapfco.org/>).

### **Environmental Affairs**

Environmental Affairs currently works through two Sub-committees: Nutrient Management and By-Products and Recycled Materials.

Nutrient Management is discussing how various states are handling nutrient management issues, sharing both positive and negative experiences. Industry members have discussed how regulations affect daily operations for fertilizer manufactures and crop advisors.

By-Products and Recycled Materials continue to discuss SUIP #25 Metals in Fertilizers. The complete text of this Tentative Statement of uniform Policy is attached. Updates were presented by several states and Canada on procedures adopted to deal with non-nutritive metals contained in fertilizer. Two additional topics presented for further oversight are: Effects of urban development will have on fertilizers and their use; and the perception that nitrogen and phosphorous application on land for crop or other uses is as bad as any contaminant contained in fertilizer products.

A presentation was given by a representative of the US EPA regarding the current state of rule making governing fertilizers made from recycled hazardous waste. The new standards are likely to include:

1. Metals and dioxins in hazardous waste zinc derived fertilizers, with the concentration limits likely to be based on those achievable using good manufacturing practices.

2. The likely elimination of the current exemption from contaminant standards for KO61 derived fertilizers.
3. Relief from RCRA hazardous waste regulations will be proposed for waste generators and zinc fertilizer manufacturers to remove current obstacles to legitimate recycling of zinc-bearing wastes.
4. A discussion of fertilizers made from mining wastes was also addressed.

The industry is working on refining analytical methods for metals in fertilizers. There are concerns that the EPA method used by many states is performance based, however, in many cases there are interference's that enhance or lower the results. There is a need to standardize a method for everyone to use. A two day workshop is planned in conjunction with our mid-year meeting in Lakeland, FL to discuss standardization of methods.

### **Good Manufacturing Practices**

This committee is devoting considerable activity to the development of a Fluid Fertilizer Blend Manual paralleling the format of the Bulk Blend Fertilizer Manual with similar language directed to the plant operator. It is anticipated to require two more edits before being ready for the final printing, and should be available sometime next year.

Two bulk blend workshops have been conducted in 2001. One held in February in Wisconsin and one in Martins Ferry, OH. Forty-nine workshops have been conducted to date; however, there are none currently planned.

The committee is working on four definitions, "Blending", "Application", "Blender" and "Custom Blend" for insertion into the Model Fertilizer Bill.

An environmental checklist is being developed for use in conjunction with Bulk Blend Workshop, as the committee is trying to move in the direction of a whole plant concept in this training session.

### **Laboratory Services**

Discussions and activities of this committee centered around a presentation given at our annual meeting, "Comparative Methods for Metals in Fertilizers and Some Pitfalls to Avoid", by Harold Falls. Members recognized that there is a need for standardization in testing methods for heavy metals. For organizations that normally follow AOAC International procedures for analysis, there are no AOAC approved methods for analysis of heavy metals in fertilizer. Therefore, the committee members suggest the need for collaborative study to identify appropriate methods. Some of the areas of concern are: the need to run inter-elemental corrections; commercially purchased standards may produce low results; matrix matched standards are a requirement to produce reliable values; quantification must be done on internal standards, examining in-house procedures for determining resolution of instrumentation using NIST certified standards for baselines (NIST western ore #194 was suggested). It was generally accepted that EPA SW-846 methods are appropriate for analysis and should be the basis used for the collaborative study.

A preliminary report of results was presented, Bill Hall discussing a heavy metal study being conducted on Arsenic, Cadmium, Lead, Mercury, and Selenium, by 29 participating laboratories. Early results indicate that methods of analysis for cadmium are reliable, lead is probably worth doing, arsenic and selenium produce results which are scientifically questionable, and ICP or AA analysis of mercury is an exercise in futility which should not be done. The cold vapor AA method for mercury appears to be the most reliable at this time. Further refinement on digestion procedures was suggested to eliminate variability and an evaluation of how EPA 3051 and variations would work with fertilizer matrixes to validate reference instrumental method(s) as a standard to measure other instrumental techniques.

The committee is also proceeding with work on the Fertilizer Sample Prep manual which is intended

to outline procedures for proper handling of samples prior to the chemical analysis.

### **Labeling and Definitions**

There has been concern for the last several years by some of our members about new requirements in their laws requiring materials to be listed in a derived from statement. This has come about primarily through the consumer right to know and also concerns over the last several years about inclusion of non-nutritive metals that may be contained in some products. Therefore, many states are requiring valid AAPFCO definitions before allowing the inclusion of materials on product labels. This has been the cause for a rapid influx of newly authorized terms and definitions that were generally accepted from other sources, i.e. chemical handbooks and such.

Four new phosphate definitions: Potassium Polyphosphate, Monopotassium Phosphate ( $\text{KH}_2\text{PO}_4$ ), Dipotassium Phosphate ( $\text{K}_2\text{HPO}_4$ ), Tripotassium Phosphate ( $\text{K}_3\text{PO}_4$ ); a definition for dried whey sludge have been proposed. While 77 micronutrient definitions have been raised to official.

A sub-committee was formed to investigate chelating agent definitions. Another sub-committee was formed to develop a definition for "Humus". The sub-committee on phosphate was instructed to prepare a final consideration at the next meeting.

### **Magruder Check Sample**

The Magruder Check sample program has identified 14 samples to be analyzed for the coming year. Participation fee has increased to \$150.00 annually to cover additional costs for sample preparation, handling and postage, and also the additional of two samples, normally the program sends out 12 per year. Most of the approved sample will also go with a request to perform heavy metal analysis. Also subscribers will be asked to provide information on the methods of analysis used to determine the heavy metal content. This information will be used to assist in the preparation for recommendations on standardizing methods of analysis.

### **Seminars**

Continuing education is important to our association; therefore, we sponsor traveling workshops. Our administrator seminar exposes new and old administrators to varying perspectives on the same problems. It is an intense three days of problem solving and personal development. While the number of participants is limited to about 30 the size is manageable for serious group participation and no one gets left out. This seminar is moved around the country to encourage increased participation.

We also sponsor inspector training workshops. Recently, these workshops have been combined with the feed group, because in most instances the inspector may have this dual responsibility in their job description. Arrangements for this seminar are made by a state agreeing to host, then a trained staff of instructors conducts the three day training which includes both classroom and hands-on in field work. There were two training sessions held in the past year one in Granville, OH and one in Great Falls, MT.

### **Uniform Bills**

This committee worked on and passed additions to the Model Fertilizer Bill and Rules adding a labeling requirement for "Directions for Use Statement" and "Directions that are specific enough for a consumer to be able to properly apply the product". Fertilizers that are purchased in bulk should have similar information or the buyer is supplied an application rate per acre.

The committee has been asked to prepare a model bill for compost products similar to the Model Fertilizer Bill, and they are proceeding through the final revisions and discussions before submitting it to the board.

A new sub-committee has been formed to propose pre-emptive language for inclusion in to the Model Fertilizer Bill. The provisions have been requested by industry representatives to help keep regulation at the state level, rather than having to deal with a myriad of local municipalities.

## Uniform Reports

The committee approved an upgrade to the Uniform Fertilizer Tonnage Reporting System (UFTRS) several years ago. The upgrade moved the product from a DOS based database to a Windows based database. We are currently in Version 4.04. The companion software for industry reporting has also been upgraded and is available on our website.

AAPFCO continues to prepare Commercial Fertilizers with the assistance of TFI.

Commercial Fertilizers 2000 was published in April and is available in several formats. Contact Dr. David Terry, Association Secretary, if you are interested. ([dterry@ca.uky.edu](mailto:dterry@ca.uky.edu))

We are also working on a standard registration form to assist companies in registering their small packaged products. This system is being developed in an Excel format.

## Task Force

### *Slow Release Task Force*

Laboratory analysis continues on methods to test the slow release characteristics of fertilizer material claims. Field correlation of the results has begun and this work is being conducted initially in Florida by Dr. Jerry Sartain, other sites around the country are being sought to help validate the methods.

### *Sampling Task Force*

Work has concluded on a sampling method for mini-bulk bags and a technique has been developed. The new method extracts 4 Missouri "D" cores from each of three bags, which are composited to make up the official sample. This procedure was validated by stream cutting the bags on filling. The analysis verified the two samples were statistically the similar. The procedure has been forwarded to AOAC International for consideration as an Official Method.

## SUIP 25. Metals in Fertilizers

Federal, state and industry sponsored risk-based assessments have been completed and the results demonstrate that metals in fertilizer generally do not pose harm to human health or the environment. Except as otherwise provided below, as a guide<sup>1</sup> for implementation of Section 12(a) of the Uniform State Fertilizer Bill, fertilizers that contain guaranteed amounts of phosphates and/or micronutrients are adulterated when they contain metals in amounts greater than the levels of metals established by the following table:

	<u>Metals</u>	ppm per 1% P <sub>2</sub> O <sub>5</sub>	ppm per 1% Micro nutrients <sup>2</sup>
1.	Arsenic	13	112
2.	Cadmium	10	83
3.	Cobalt	3,100	23,000 <sup>3</sup>
4.	Lead	61	463
5.	Mercury	1	6
6.	Molybdenum	42	3003
7.	Nickel	250	1,900
8.	Selenium	26	1803
9.	Zinc	420	2,9003

### To use the Table:

Multiply the percent guaranteed P<sub>2</sub>O<sub>5</sub> or sum of the guaranteed percentages of all micronutrients (Iron, Manganese, Zinc, etc. ) in each product by the value in the appropriate column in the Table to obtain the maximum allowable concentration (ppm) of these metals. The minimum value for P<sub>2</sub>O<sub>5</sub> utilized as a multiplier shall be 6.0. The minimum value for micronutrients utilized as a multiplier shall be 1. If a product contains both P<sub>2</sub>O<sub>5</sub> and micronutrients multiply the guaranteed percent P<sub>2</sub>O<sub>5</sub> by the value in the appropriate column and multiply the sum of the guaranteed percentages of the micronutrients by the value in the appropriate column. Utilize the sum of the two resulting values as the maximum allowable concentrations.

Biosolids, and all compost products<sup>4</sup>, shall be adulterated when they exceed the levels of metals permitted by the United States Environmental Protection Agency Code of Federal Regulations, 40 CFR Part 503. Dried biosolids and manure, as well as manipulated manure products either separately or in combination, shall also be deemed adulterated when they exceed the levels of metal

permitted by the United States Environmental Protection Agency Code of Federal Regulations, 40 CFR Part 503. Hazardous waste derived fertilizers (as defined by EPA) shall be adulterated when they exceed the levels of metals permitted by the United States Environmental Protection Agency Code of Federal Regulations, 40 CFR Parts 261, 266 and 268.

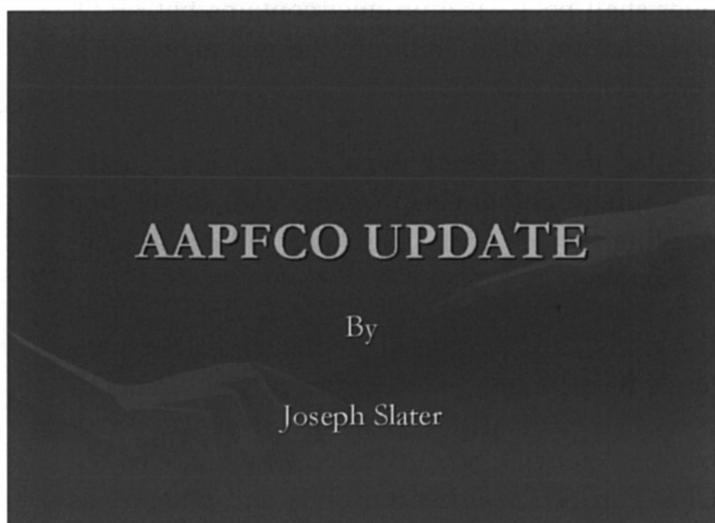
**Footnotes:**

<sup>1</sup> These guidelines are not intended, to be used, to evaluate horticultural growing media claiming nutrients but may be applied to the sources of the nutrients added to the growing media.

<sup>2</sup> Micronutrients (also called minor elements) are essential for both plant growth and development and are added to certain fertilizers to improve crop production and/or quality. These micronutrients are iron, manganese, zinc, copper, molybdenum and boron. In addition, cobalt and selenium can also be considered micronutrients.

<sup>3</sup> Only applies when *not guaranteed*.

<sup>4</sup> Includes all compost products separately or in combination with biosolids, manure or manipulated manure, even those registered as fertilizers (making nutrient claims).



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## Task Forces

- Sampling
- Slow Release Fertilizer

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## Education & Information

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- AAPFCO Operating Manual
- Proposed Brochures

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  - State Perspectives
  - Effects of Urban Development
  - Misperception about Nitrogen and Phosphorus
- By-Products and Recycled Material
  - SUIP #25 Metals in Fertilizers
  - EPA Update on Zinc Bearing Wastes

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## Good Manufacturing Practices

- Fluid Fertilizer Bulk Blend Manual
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- New Definitions

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## Laboratory Services

- Heavy Metal Analysis
- Needed AOAC Collaborative Study on Heavy Metals Analysis Methods
- Possible Sources of Standards
- Preliminary Results on Arsenic, Cadmium, Lead, Mercury and Selenium by 29 Labs
- Sample Preparation Manual

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## Labeling & Definitions

- New Definitions
- Phosphite
- Organic
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## Magruder Check Sample

- Fourteen Samples Approved
- Participation Fee set at \$150.00
- Heavy Metal Analysis

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## Seminars

- Fertilizer Administrators
- Fertilizer Inspectors
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## Uniform Bills

- Directions For Use
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## Uniform Reports

- UFTRS Version 4.04
- Commercial Fertilizers
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## Task Forces

- Sampling
- Slow Release Nitrogen

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## Controlling Reactions in The Microenvironment

Larry Sanders

Larry Murphy

Michael Kimmerely

Specialty Fertilizer Products, Inc

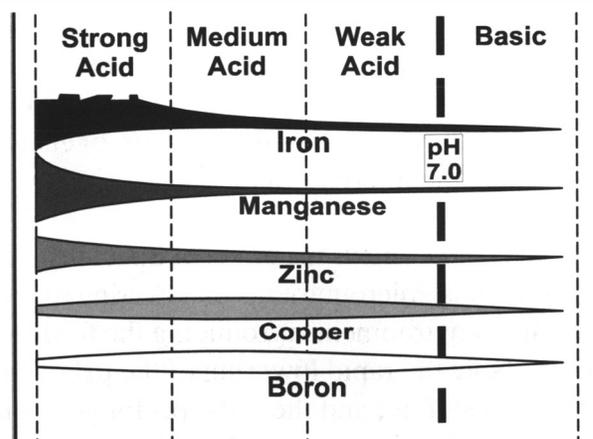
### Introduction

The microenvironment surrounding a fertilizer granule is subject to a series of primary and secondary reactions. Influencing or controlling these reactions is of primary importance due to their influence on fixation and the subsequent availability of the nutrients involved.

In the past, agriculture has used a “fertilize the acre” concept. Now, there is the opportunity to focus on enhancing fertilizer availability in microenvironments to increase nutrient use and efficiency. This concept applies more to the non-mobile nutrients, but certainly has applications to nutrients that exist as either anions or cations (ie. nitrogen). Products have been developed and are being used, that affect nitrogen use efficiency by influencing reactions in the microenvironment. Examples of these products are N-Serve, DCD and Agrotain. With phosphorus, biologicals have been utilized to enhance availability in the microenvironment around the granule.

### Micronutrients - The Problem

Historically, micronutrient availability has been poor. Negative interactions from liming, and/or higher pH soils have typically reduced micronutrient availability. In general plants absorb micronutrients (Zn, Fe, Mn, Cu and B) better in acid pH soils. Unfortunately, that is not the most favorable pH for maximum plant growth, and use of macronutrients (N, P and K). The chart below illustrates the effect of pH on micronutrient availability. It is interesting to note that micronutrient availability decreases significantly before pH 7.0. In fact, above pH 5.5 most micronutrients lose significant availability, and continue to become less available as pH is increased.



The availability of Mn, Cu, Zn and Fe to plants generally decreases as the soil pH increases. Sharp yield depressions often observed when strongly acid soils are limed to pH 6.0, or above, probably result from deficiency of one or more micronutrients. *Fertilizer Technology and Use*. Foy, et al.

### Micronutrients

#### The Solution

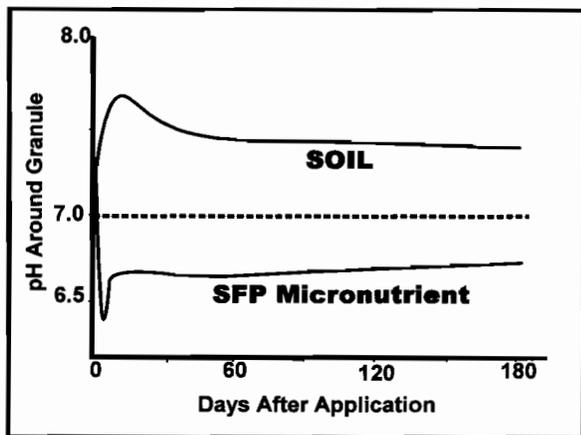
Since most micronutrients are immobile, or move very little in the soil, developing a micronutrient pH treatment to affect their availability theoretically becomes a practical solution. For years farmers have attempted to acidify soils to increase availability of micronutrients. From an economic standpoint, acidification of the soil by the acre has been too costly and impractical.

Other approaches have been developed using ammonium sulfate or sulfur in row applications to influence the pH and availability. Ammonium sulfate as an acidifying agent is short lived in a calcareous soil, and elemental sulfur is unreliable due to its dependence on environmental factors to oxidize and produce sulfuric acid. Spatial differences between particles have also caused these approaches to be mostly ineffective.

Different sources of micronutrients have been developed (sulfates, oxysulfates and chelates). Research has not shown that there is one source that is superior under all conditions. Specialty Fertilizer Products, LLC has developed a patented source of micronutrients that provide enhanced

availability (Pat. No. 6,132,485 and Pat. No. 6,210,459B). These products utilize the acidity produced from both ammonium sulfate and elemental sulfur co-granulated in a homogeneous granule with the micronutrients.

The graph below shows the effect of Specialty Fertilizer Products' micronutrients on lowering the pH in the microenvironment surrounding the fertilizer granule. Note the rapid lowering of the pH due to ammonium sulfate; and then, the prolonged control of the pH by elemental sulfur oxidation. Even on alkaline soils (pH above 7.0) the soil around the granule drops below pH 7.0 and stays there for over 180 days.



The ability to influence or control reactions in the microenvironment around the fertilizer granule significantly improves:

- economics
- crop yields
- environmental issues.

The practical application of this technology is verified by Bohn, et al. in *Soil Chemistry*.

Because of the small quantities of micronutrients required for plant growth, adequate amounts can be taken up from small portions of the root zone, if such regions are sufficiently acidic.

Also, note that total quantities of micronutrients in soils are suggested to be far less important than plant-available nutrients that can be enhanced by use of this technology. From an agricultural point of view, the plant-available micronutrient contents of the soils are more important than the

total contents. The total amount of micronutrients, their spatial distribution, and the chemical form in which they occur are generally not directly related to the availability of micronutrients in soils. For example, calcareous soils may be high in total Fe and Mn, but the availability is usually low because of the high pH in these soils and the low solubility of the oxides and absorbed forms of these elements under those conditions. Hence, in calcareous soils, particularly if they are low in organic matter, deficiencies of Fe and Mn as well as Zn and Cu may occur irrespective of the total contents of these elements. *Micronutrients in Tropical Food Crop Production*. Velek.

The benefits of this technology can have a tremendous impact on micronutrient use in fertilizer programs. With increased flexibility and less tie-up and fixation, consider the following:

- broadcast vs. banding micronutrients with protected microenvironments can now be broadcast.
- fall application with a liming program Acid microenvironments that last over 180 days allow for fall applications without tie-up.
- application in variable rate fertilization micronutrients with protected microenvironments can be broadcast with lime or over soils with varying pHs and still have enhanced availability.

#### Zinc

- Zn availability progressively diminishes with increasing lime rates. It becomes a practical problem for Zn-sensitive crops on low Zn soils when they are limed to pH 6.0 or more. *Soil Acidity and Liming*. Adams.
- the availability of Zn in soils may become critical at pH values as low as 5.3. *Fertilizer Technology and Use*. Olson, et al.

University of Maryland data show that Specialty Fertilizer Products zinc produced significant yield increases above the sulfate source.

### Maryland Corn

Treatment Applied	Yield Bu/Acre
Check	130bc
3 Lbs/Ac Zinc Sulfate	103a
6 Lbs/Ac Zinc Sulfate	117ab
9 Lbs/Ac Zinc Sulfate	129bc
3 Lbs/Ac SFP Zinc	153d
6 Lbs/Ac SFP Zinc	138c
9 Lbs/Ac SFP Zinc	143cd

Zinc Broadcast Preplant, Low Zinc Soil Test, Soil pH=7.3

Fall broadcast applications of Specialty Fertilizer Products zinc on a soil pH of 7.7 in Texas were much more effective than zinc sulfate, emphasizing the importance of microenvironments in maintaining zinc availability.

### Texas Corn

Treatment Applied	Grain Yield Bu/Acre
Check Treatment	134
SFP Zinc, 3 lbs per acre	167
SFP Zinc, 6 lbs per acre	197
SFP Zinc, 9 lbs per acre	183
Average, all rates of SFP Zinc	182
Zinc Sulfate, 3 lbs per acre	158
Zinc Sulfate, 6 lbs per acre	150
Zinc Sulfate, 9 lbs per acre	168
Average, all rates of Zinc Sulphate	159

Zinc Soil Test = 0.2 ppm, VL Soil pH=7.7

### **Iron**

The significance of high pH on iron availability is obvious when it is realized that Fe+3 and Fe+2 activities in solution decrease 1000-fold and 100-fold, respectively, for each unit increase in pH. *Soil Fertility and Fertilizers*. Tisdale, et al.

Banded Specialty Fertilizer Products iron was more effective for irrigated corn than oxysulfate iron on a pH 7.8 Texas soil.

### Texas Corn

Treatment Applied	Total CWT/Acre
Control	182
8 Lbs/Acre Oxysulfate Iron	205
8 Lbs/Acre SFP Iron	225

## **Manganese**

- Manganese availability is highly sensitive to soil pH changes. Liming these soils to pH 6.5 or more has induced striking Mn deficiencies *Soil Acidity and Liming*. Adams.

- The fixation of added Mn, converting it into the unavailable, nonexchangeable form in many neutral and alkaline soils, occurs rapidly after liming *Trace Elements in Agriculture*. Sauchelli.

- The acidified microenvironment in Specialty Fertilizer Products manganese formulations enhanced potato yields by 4 cwt. per acre over manganese sulfate.

### Idaho Potatoes

Treatment Applied	Total CWT/Acre
Check	304
Management Sulfate	325
SFP Manganese	329

## **Copper**

The mobility of copper in soil solutions often decreases with increasing pH And its supply to plants is correspondingly reduced because of greatly diminished solubility and increased adsorption onto mineral colloid surfaces. *Soil Fertility and Fertilizers*. Tisdale, et al.

Wheat yields were increased by about 3 bu/A over copper sulfate in Texas when Specialty Fertilizer Products copper was used on a limed soil.

### Texas Wheat

Treatment Applied	Total CWT/Acre
Control	29.8
1 Lbs/Acre Copper Sulfate	33.6
1 Lbs/Acre SFP Copper	36.2

## Boron

- Purvis and Davidson found that B deficiency was often lime induced, and Percival, et al. mentioned that concentrations of Cu were reduced in some forages with increased liming. *Soil Acidity and Liming*. Adams.
- Soil pH and liming strongly influence the availability of boron to plants. This element generally becomes less available to plants with increasing pH. There is often a dramatic drop in boron availability and plant uptake at pH levels greater than 6.3 to 6.5. *Soil Fertility and Fertilizers*. Tisdale, et al.
- Arkansas cotton data also emphasized the effectiveness of Specialty Fertilizer Products formulations. Yield responses from SFP boron consistently exceeded sodium borate.

### Arkansas Cotton

Treatment Applied	Plant B PPM	Total CWT/Acre
Control	80	1716
.05 Lbs Sodium Borate	91	1473
1.0 Lbs Sodium Borate	95	1711
2.0 Lbs Sodium Borate	144	1941
.05 Lbs SFP Boron	100	1743
1.0 Lbs SFP Boron	103	1886
2.0 Lbs SFP Boron	100	2193

Soil pH 6.2 Soil B:0.9 ppm Variety: SG 125 B/R

## Phosphate Fertilizers

### *The Problem*

It is well known that even under the best conditions that only 20-30% of fertilizer phosphate is taken up by the crop during the first cropping season. It is also known that at high pH levels phosphates are fixed by calcium and magnesium and at low pH levels by predominately iron and aluminum. Thus, the historical problem with the chemistry of phosphate fertilizers has been lack of availability.

The residual phosphorus that is not taken up by the crop (70-80%) becomes a potential environmental problem. Recently a number of studies have shown that soil erosion carrying increased loads

of fertilizer phosphorus has contributed to eutrophication of lakes, streams, rivers and the Gulf of Mexico. This focuses on the need to develop a phosphorus product that is more efficient, that produces greater crop responses and leaves less of an environmental footprint.

## Phosphate Fertilizers

### *The Solution*

Specialty Fertilizer Products has developed and patented a family of compounds that affects the availability of phosphate fertilizers. These compounds are biodegradable and highly water-soluble. The technology can be applied directly to granular phosphate fertilizers as a coating, or injected into liquids.

The mode of action appears to be simple, but effective. The table shows the effect of varying concentrations of the technology coated onto granular MAP which was placed in 100 ppm solutions of calcium, iron and aluminum. The resulting phosphorus concentrations in solution show that the compound sequesters the antagonistic ions out of solution leaving the phosphorus available and unfixed.

### Experimental Material Effects on MAP solubility

Treatment Applied % Experimental Coated	Cation ppm	Mgm P/Gram MAP	% of Total P in Solution
0.00	Al 100	236.9	45.5
0.25	Al 100	298.4	57.4
0.50	Al 100	284.5	54.7
0.75	Al 100	326.0	62.7
1.00	Al 100	309.4	58.9
0.00	Ca 100	251.5	48.4
0.25	Ca 100	295.8	56.9
0.50	Ca 100	314.1	60.4
0.75	Ca 100	310.4	59.7
1.00	Ca 100	308.2	59.3
0.00	Fe 100	289.9	55.8
0.25	Fe 100	316.7	60.9
0.50	Fe 100	303.5	58.4
0.75	Fe 100	329.2	63.3
1.00	Fe 100	305.2	58.8

The coating dissolves rapidly in the soil. It then sequesters the antagonistic ions that tie up phosphorus in the area surrounding the granule. Since phosphorus is immobile, once the dissolution area has been cleansed, the un-fixed phosphorus can be taken up by the plant without interference.

Phosphorus fertilization and its affect on plant growth and yields can be influenced by many factors. Some of these are:

- 1 Μετηοδος οφ Αππλιχατιον
- (2) Type of Crop
- 3 Σοιλσ
- A πΗ Λεωελσ
- B Σοιλ Τεστ Π
- 3 Πηοσπηατε Αππλιχατιον
- Ρατεσ

### Methods of Application

University of Arkansas wheat data shows that MAP coated with the compound out yielded ordinary MAP. Yields on banded, broadcast, and broadcast seeded were all significantly increased with a 1% coating. The largest increase was with banded applications where yields were increased 22 bushels per acre.

#### Arkansas Wheat

Treatment Applied	Yield Bu/Acre
Control	46.7
MAP Banded	54.7
MAP Broadcast	58.2
MAP + Exp. Product, Banded	76.9
MAP + Exp. Product, Broadcast	65.6
Broadcast Seeded, MAP	55.1
Broadcast Seeded, MAP + Exp.	68.3
LSD (0.05)	7.5

### Crops

Coated phosphate fertilizer at rates from 0.5% to 1.0% has produced increased phosphorus uptake and increased yields on a wide range of crops. Experiments with collards, grass, corn, wheat and potatoes have produced positive responses to the coated phosphate over regular phosphate. The table shows Auburn University data on collards. Both banded and broadcast applications of experi-

mental MAP increased yields over ordinary MAP by 6 and 21 percent, respectively.

#### Alabama Collards

Treatment Applied	Fresh Wt lbs/plot
Control	1.4
MAP Banded	5.2
MAP Broadcast	3.9
MAP + Exp. Product, Banded	5.5
MAP + Exp. Product, Broadcast	4.7

### Soils

Soil pH is a major factor affecting phosphorus availability. At pH levels below 5.5, iron and aluminum tie up phosphorus. At pH values above 7.0, calcium and magnesium influence phosphorus availability. This chemistry possesses the ability to protect fertilizer phosphates making P available to the crop.

#### pH Less Than 5.5

Kansas State University data on wheat showed enhanced yield response with the experimental phosphorus. Although these soils (pH 4.7) have a high P test, they also have a high fixation capacity.

#### Rice County Kansas Wheat

Treatment Applied	Total BU/Acre
Control	31.6
MAP	34.2
MAP + Experimental product	39.5
LSD (0.20)	7.2

Phosphate Banded at Planting

#### pH between 5.5-7.0

University of Missouri corn data show an example of a moderate pH and low P soil test combination

which should be very responsive to phosphate fertilizer. The data show no response to MAP, but a significant response to experimental MAP (20 bu/A).

### Missouri Corn

Treatment Applied	Yield bu/Acre
Control	132
MAP Banded	138
MAP Broadcast	135
MAP + Exp. Product, Banded	158
MAP + Exp. Product, Broadcast	152

### *pH above 7.0*

Experiments at soil pH's above 7.0 were conducted at the University of Arkansas and at SARDI in South Australia on wheat, and at the University Minnesota on corn. All three of these experiments showed significant positive responses to experimental MAP over MAP.

### Minnesota Corn

Treatment Applied	Yield Bu/Acre
Control	108
Broadcast Seeded, MAP	116
Broadcast Seeded, MAP + Exp.	122

### **Soil Test Phosphorous**

Although low P soils are very responsive, many soils have a medium to high P soil test and produce less yield response to applied P. An example from central Texas shows that wheat yields were not increased over the check with 25 and 50 pounds of untreated phosphate, but the experimental phosphate increased yields on these medium P test soils.

### Texas Wheat

Treatment Applied	Yield Lb/Acre
Control	30.1
MAP Untreated 25 P <sub>2</sub> O <sub>5</sub> Lbs/Acre	29.5
MAP Untreated 50 P <sub>2</sub> O <sub>5</sub> Lbs/Acre	32.4
MAP Treated 25 P <sub>2</sub> O <sub>5</sub> Lbs/Acre	37.6
MAP Treated 50 P <sub>2</sub> O <sub>5</sub> Lbs/Acre	37.8

Kansas Sate University plots on high P test soils also showed enhanced yield response on wheat with the experimental phosphorus. Although these soils are high test for P, they also have a high fixation capacity due to their low pH (4.7).

### **Phosphate Application Rates**

Wheat data from SARDI in South Australia show that experimental MAP out performed MAP at three different P rates. Yields were increased as much as 10% on these high pH soils [pH 8.3].

### Australia wheat

Treatment Applied	Grain Yield BU/Acre
MAP 4 Lbs/Acre	25
MAP 10 Lbs/Acre	29
MAP 20 Lbs/Acre	31
Enhanced MAP 4 Lbs/Acre	28
Enhanced MAP 10 Lbs/Acre	30
Enhanced MAP 20 Lbs/Acre	33
LSD (0,10)	2

Soil 70% Calcium Carbonate

### **Economic Solutions for the Farmer**

University of Idaho potato data also show the effects of the experimental MAP at varying rates over MAP compared to untreated MAP. Yields were increased at both the 60 and 120 pound P<sub>2</sub>O<sub>5</sub> rates by the experimental material. When experimental MAP was applied at both rates, significant increases in yields and returns resulted. The higher experimental MAP rate [120 lbs/A] gave the best yields and profits. The coated MAP increased US No. 1 yields by 14%, and gross returns by \$200 / A at the higher phosphate rate.

## **Idaho Potatoes**

Treatment Applied	Yield CWT/Acre
Control	
MAP Untreated 60 P <sub>2</sub> O <sub>5</sub> Lbs/Acre	330
MAP Untrated 120 P <sub>2</sub> O <sub>5</sub> Lbs/Acre	345
MAP Treated 60 P <sub>2</sub> O <sub>5</sub> Lbs/Acre	339
MAP Treated 120 P <sub>2</sub> O <sub>5</sub> Lbs/Acre	369

### **Conclusion**

Influencing or controlling reactions in the micro-environment around the fertilizer granule has a tremendous effect on the fate of the nutrient. The objective of agriculture has always been to provide the quantity of available nutrients to achieve the maximum economic yield for crops' genetic potential. By modifying the microenvironment around fertilizer particles, it has been shown that both macronutrient and micronutrient absorption and utilization by crops can be improved using normal fertilization rates. This will not only improve crop yields which impacts farmers' profits, but it also leaves less residual nutrient in the soil, lowers nutrient loads in runoff, and produces a significant positive environmental effect by reducing the environmental foot print from fertilizer use.

### **Production of a Fortified Organic Fertilizer**

*Vernon Meacham*

**Harmony Products**

*Brent Cummings*

**FEECO International, Inc.**

### **Abstract**

Through the use of innovative technology several steps have been combined in the variant of a traditional granulation plant to yield a highly salable fortified organic based fertilizer product, while reducing or eliminating odors from the process plant floor and air emissions and utilizing a non-traditional heat source that eliminates side waste streams and yields additional fertilizer ingredients.

## **1. Background In Virginia**

1.1 The spotlight on the reuse of organic waste streams in VA has focused on the intensive poultry farming practices in the state. There are many large entities that have seen that the ideal climatic conditions exist in the Delmarva region that are conducive to the production of poultry both chicken and turkey.

1.2 Historically in the region, as in many other agricultural regions of the US, and indeed the world, the waste streams from these intensive-farming operations have been utilized locally. However, this has lead to under utilization of many of the nutrients in the waste stream, primarily nitrates and phosphates. These nutrients have run-off from the soils and are now a major source of water pollution, and are coming under more regulatory review.

1.3 Compiling this problem is the continued use of chemical based fertilizers. Many growers in the region that have utilized the poultry litter as a source of N and P also hedge their bets with the use of chemical fertilizer based on the agronomic need of the crop and soil tests. The use of the chemical based fertilizer sometimes was done with no credit for N or P being given to the land applied organics, therefore resulting in an over application of chemical fertilizer.

1.4 Industrial sources also contribute to the runoff that is detected in the state waterways.

1.5 Other intensive livestock farming practices also impact the runoff either through the land application of solids or the uncontrolled runoff from the containment areas.

1.6 While it is felt that there are many sources of pollutant resulting in the degradation of the states waterways it is the poultry

industry that is bearing the brunt of the initial regulatory review.

## **2. Background II**

### **2.1 Pressure to Find Solutions**

**2.1.1 Population Density** - has increased across the US. In order to provide cost effective supplies of food for this rising population, there has been a transformation in the way that food is farmed in agricultural areas such as the Delmarva Peninsula and Shenandoah Valley in Virginia. No longer are there small "mom and pop" farmers in these areas, they have been replaced by the corporate farmer. The corporate farmer can produce a larger quantity of food at a lower price over the traditional farmer. However, this does have a price, the resulting intensive farming practices result in a concentration of livestock and the resulting waste residuals that must be removed.

**2.1.2 Urban Areas Expanding** - has become a major cause for finding solutions to the current methods of manure and litter disposal. Historic use of the land has been in farming and cropping and now this is being eroded by urban sprawl. Many areas that use to grow the food for the local city have now become the subdivisions that house the workers of those same cities. These new residents are not as familiar with farming practices and certainly less tolerant of traditional manure disposal methods.

**2.1.3 Government Regulations** have become more stringent on the methods that wastes from intensive farming practices have been disposed of. New regulations look to lower the threshold by which farms are classified. These classifications will dictate the method by which the farm can dispose of wastes generated, these same classifications will force the consolidation of many smaller producers due to the expense and necessity of record

keeping, waste removal, treatment and disposal. While we have seen many industries consolidate we will see many more in the farming sector.

### **2.2 The Solution Has Been Around For Years**

**2.2.1 Plant Food** has been the historic use of poultry litter and other manures, the difference now is that the pollution that has been caused by excessive fertilizer use has come under the regulatory view. The solution can be found in moving the manure from its current water shed to an area where there is a shortage of organic materials and where cropping is more intensive.

**1.1.2 Modernized Methods** are a necessity for the best utilization of the manure produced by intensive farming practices. These methods include the containment and collection of the manure, the transformation of the materials into a useful, transportable and reusable form.

**1.1.3 Selecting A Method That Makes Sense** is key to the successful transformation of a waste stream into a value added product. The use of a granulation, fortification and drying technology, accomplish this goal. The form of the final product meets the needs of the end-user in that it reflects the physical properties of a chemical based fertilizer so that it can be applied with the same equipment, it does not break down in shipping and attrition is minimal.

The Harmony process results in a Bridge product, where by the product is a uniform granulated fertilizer with each granule having the guaranteed chemical analysis. This uniformity of product allows the organic based fertilizer to be utilized in the same manner as a chemical based fertilizer.

The analysis of the final product is custom designed to meet the end users specification

while also adding the value of an organic. The granulated fertilizer is in a dry form thereby reducing the volume that is transported to other markets, this alone results in a tremendous saving to the growers that traditionally would have to move up to 50% water with their non granulated / dried manure.

## **2. Background II**

### **2.1 Nationwide Issues**

2.1.1 Municipal biosolids are becoming a greater disposal issue due to the same factors that are impacting the intensive livestock farms. However, traditionally the municipalities have been held to higher regulatory standards and have developed a process whereby biosolids can be converted into value added products. These products, assuming that they meet heavy metal, pathogen and bacterial standards are considered Class A biosolids and are used as a fertilizer, primarily land application to non humane consumption food crops.

Additional treatment that includes drying and granulation can turn these materials into exceptional quality (EQ) fertilizer. As an EQ fertilizer the end use of the fertilizer has a broad band of applications that requires no record keeping outside of that that is required for chemical fertilizers for the end user.

2.1.2 Many of the same issues that are promoting the regulation of intensive farming practices are the issues that brought about regulation of the municipal wastewater industry, application methods and areas, pollutant loading and application rates, fines for non compliance.

2.1.3 Heat drying and granulation is becoming one of the most popular alternatives for biosolids disposal since the same economic factors such as transportation, end users requirements and location in urban areas come into play.

## **3. Basic Problem**

3.1 Issues in the Shenandoah Valley have resulted from the production of 400,000 tons per year of poultry manure. Regulatory pressure is making the disposal of manure the key-limiting factor in survival and growth of the poultry industry.

## **4. Perspective**

4.1 400,000 tons per year of poultry manure with an average analysis of 3-4-2 would equal

- 12,000 tons N
- 16,000 tons P<sub>2</sub>O<sub>5</sub>
- 8,000 tons K<sub>2</sub>O

4.2 Fertilizer imports in the Shenandoah Valley, Virginia equal

- 300,000 tons per year imported
- Imports likely to exceed
- 42,000 tons N
- 24,000 tons P<sub>2</sub>O<sub>5</sub>
- 36,000 tons K<sub>2</sub>O

4.3 Net Fertilizer Needs

4.4 Poultry Manure Utilized at HSV

## **6. The Harmony Products Process Plant**

6.1 The Harmony Process utilizes several new concepts in the production of an organic based fertilizer in addition to the proprietary granulation method.

6.1.1 Primary Heat Source. The primary source of energy for the drying operation is a close coupled gasifier. The fuel for the unit is the oversized particles from the manure conditioning process. Oversized material that cannot be used as a fertilizer input is metered into the gasification unit. The initial stage of gasification converts the organic materials into a combustible gas. The gas is then combusted to supply the heat for the dryer operation.

tion. The gases leave the gasifier in a range of 2000 deg. F to 2100 deg. F. The residuals from the gasifier are high in phosphate and potassium and are incorporated into the granulated product as a nutrient source. The total residuals from the gasification process are approximately 25% by weight of the incoming fuel.

The use of the gasifier reduces another side stream from that operation that otherwise would need to be disposed of.

### 6.1.2 Air Pollution Control and Odor Abatement

The challenge of the air pollution control and odor abatement system resulted in the combination of two key pieces of technology;

1. A blend chamber that combined the off-gases of the gasifier and the recycled gases from the dryer operation resulting in a single piece of equipment that heated the process gases while at the same time burning out VOC and particulate. The ash created is either directed back to the dryer system where it becomes part of the agglomerate or is drawn into the exhaust gas stream where the particulate would be removed in the scrubber system.

An auxiliary burner is also available to operate while the gasifier is being maintained. A constant temperature burner is utilized to

maintain the operating temperature in the blend chamber at various firing rates.

2. The scrubber system combines a quenching system with a packed tower to eliminate the particulate in the exhaust gases. The scrubber also is maintained at a pH of 4.5 to remove any free ammonia that may have not been reacted in the granulation stage. The liquor from the scrubber is used to the granulator as a binding agent.

### 6.1.3 Product Cooling

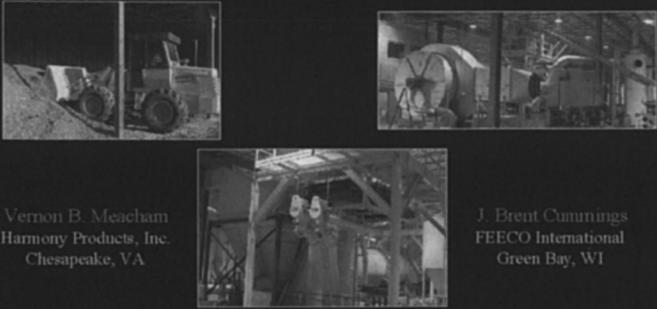
The HSV plant utilizes the patented FEECO International, Inc. dynamic cooling hood. This results in a space saving footprint and a reduction in moving components in the plant. Material is cooled from 160 deg. F to 120 deg. F utilizing only approximately six feet of floor space.

The dynamic cooling hood utilizes a fluidized bed concept that cools the material as it is discharged from the dryer. The cooler utilizes ambient air but can also have an auxiliary coolant coil added.

### Conclusion

The Harmony Shenandoah Valley plant utilizes innovative technology to produce the most consistent fortified organic fertilizer in the marketplace. The development of the key process stages has allowed for a consistent operation at the highest plant outputs.

## Production of a Fortified Organic Fertilizer



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Fertilizer Industry Round Table  
St. Petersburg, FL  
October 2001

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Slide 1

## Background in VA

Spotlight is on the Poultry Industry

Problems in the Waterways

- Run-off from Poultry Manure

But Also-

- Chemical Fertilizers
- Industrial Sources
- Other Livestock

The Poultry Industry is a Convenient Target

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Slide 2

## Background II

The Pressure is On to Find Solutions

- Population Density
- Urban Areas Expanding
- Government Regulations

The Solutions Have been Around for Years

- PLANT FOOD
- Modernize Methods
- Select Ones that Make Sense

The World is 'Discovering' Organics

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## Background III

Nationwide Issues

- Municipal - Movement from Class B Biosolids to Class A
- Biological Concerns - Pathogen and Bacterial Kill
- Value of Organic Based Fertilizer
- Material Handling Ease
- Fines
- Location of Organic's

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## Basic Problem

- 400,000 Tons per year of poultry manure are produced in the Shenandoah Valley
- Regulatory Pressure makes manure disposal a key limiting factor in survival and growth of the poultry industry.

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Slide 5

## Perspective

- 400,000 Tons per year of poultry manure with an average analysis of 3-4-2 would equal
  - 12,000 tons N
  - 16,000 tons P<sub>2</sub>O<sub>5</sub>
  - 8,000 tons K<sub>2</sub>O

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### Fertilizer Imports Into Virginia

- 300,000 tons per year of fertilizer are imported into the Valley
- Imports each year likely exceed
  - 42,000 tons N
  - 24,000 tons P<sub>2</sub>O<sub>5</sub>
  - 36,000 tons K<sub>2</sub>O

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### Chemical Fertilizer Needs

	Tons of Chemical	Tons in Litter	Still Needed as Chemical
Nitrogen	42,000	12,000	<b>30,000</b>
P <sub>2</sub> O <sub>5</sub>	24,000	16,000	<b>8,000</b>
K <sub>2</sub> O	36,000	8,000	<b>28,000</b>

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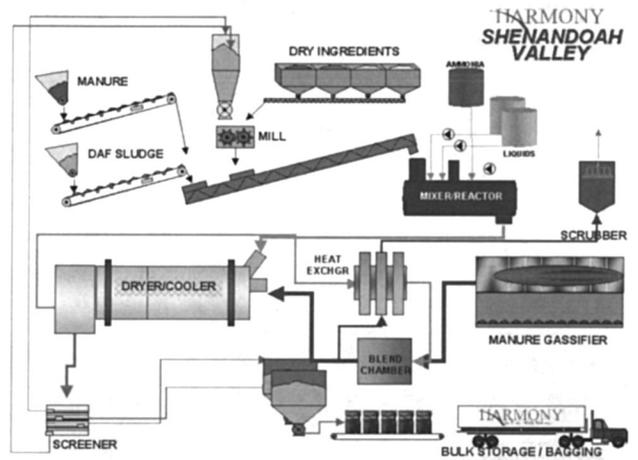
### Poultry Manure Utilized at HSV

	Tons Annually
Manure Used in Fertilizer	54,000
Manure Gasified	8,000
Total Manure Used at HSV	62,000
Total Manure Shipped out of Watershed as Fertilizer	43,400
Phosphorus (P) shipped out of Watershed as Fertilizer	602

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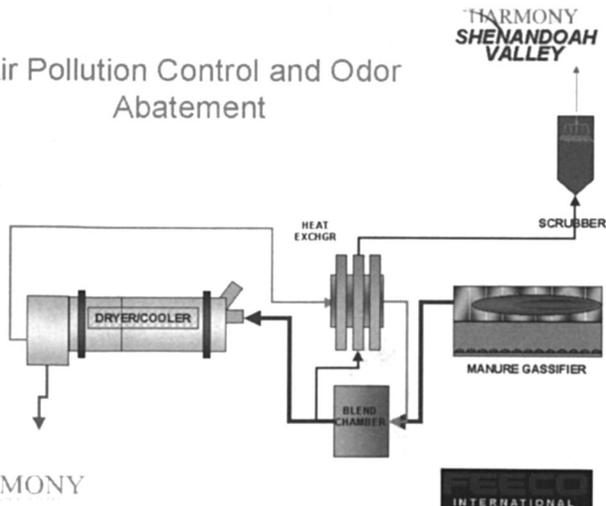


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### Air Pollution Control and Odor Abatement



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### Questions ?



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# Tuesday, October 23, 2001

Session III  
Moderator:

Paul Clifford

## Technology for Removing Dolomite From Phosphate

Glenn A. Gruber  
Jacobs Engineering

### Abstract

This paper describes the pilot scale demonstration of a flotation process developed by the China Lianyungang Design and Research Institute to treat waste pebble from Florida. The research project was primarily funded by the Florida Institute of Phosphate Research; however, IMC Phosphates was the project manager and a co-sponsor. Demonstration testing was performed at JACOBS pilot plant in Lakeland, FL.

Two low-grade pebble samples were treated by the flotation process to reduce the content of dolomitic and insoluble impurities. Pebble 1 contained little clay and the particles were relatively hard. Test results indicated that this sample could be upgraded from 51% to 65% BPL, with a phosphate recovery of 76%. The MgO content was reduced from 3.5% to 1.1%, while the insol content was lowered from 10% to 5%. Pebble 2 was soft and sticky because of substantial clay content. The process upgraded this sample from 42 to 63% BPL, while recovering 81% of the phosphate. The MgO content was reduced from 2.8% in the pebble to 0.8% in the concentrate. Similarly, the insol content was reduced from 27% to 9%. JACOBS preliminary engineering study indicated that the process is technically and economically feasible. The costs of flotation reagents for Pebble 1 and Pebble 2 pilot plant testing were \$4.39 and \$2.93 per ton of concentrate, respectively. All reagents, except the dolomite collector, are currently used in phosphate flotation.

**Keywords:** Phosphate, Dolomite Flotation, CLDRI Process.

### Introduction

Phosphate rock has been mined in Florida for more than a century. During the first 50 years exploitation schemes focused on easily recoverable river pebble and then on land pebble. For the last 50 years phosphate rock has been recovered from Florida ores by a combination of washing and flotation. The Southern Extension of the Central Florida Phosphate District (see map following please) generally has two ore zones. Upper zone ore characteristics are familiar to the Industry; however, the lower zone contains more magnesium impurities, generally in the form of dolomite (El-Shall and Bogan, 1994).

The problems in phosphoric acid production due to magnesium impurities have been investigated and described (Baumann, 1978; Blythe, 1992). As phosphate mining advances southward, the Industry relies on selective mining to maintain problematic magnesium impurities at a tolerable level. Selective mining is an expedient and proven technique to avoid phosphate contaminated by dolomite; however, resources are consequently wasted. An alternative method that solves rather than avoids the problem of removing dolomite from phosphate is needed. Sixty years ago the tonnage of phosphate rock that could be economically recovered from Florida resources was substantially increased by flotation technology that efficiently separated phosphate from quartz. New flotation technology to separate phosphate from dolomite would also increase the tonnage of economically recoverable phosphate rock. El-Shall (1994) reported on several dolomite flotation research programs funded by the Florida Institute of Phosphate Research (FIPR). Subsequent related research, sponsored by FIPR, has been reported by Leyshon (2000). The latter reference mentions

the CLDRI Process, which is the subject of this paper.

The FIPR Board of Directors approved a project, in October 1997, allowing IMC to subcontract with the China Lianyungang Design and Research Institute (CLDRI) to develop a flotation process to remove dolomite from high MgO Florida phosphate rock. CLDRI was chosen because of their demonstrated success in developing similar processes for Chinese phosphate ore. The results of that program were reported by Gu (1999), and were sufficiently encouraging for the FIPR Board of Directors to fund a pilot plant demonstration of the process. IMC subcontracted the pilot plant set-up and operation to JACOBS, with on site technical assistance from CLDRI process engineers.

#### **Methods and Materials CLDRI Process**

The CLDRI flotation process for low-grade pebble utilizes anionic reagents to remove dolomite from phosphate with the subsequent (optional) use of cationic reagents to remove quartz from phosphate. To liberate phosphate from the gangue minerals and to produce dolomite grains at an optimum size for flotation, it is necessary to grind the pebble to more than 60% passing 200 mesh (74 microns). One unique aspect of the process is that no desliming takes place after grinding. Consequently, desliming losses of phosphate are avoided.

JACOBS designed and erected the pilot plant based on a process diagram and parameters provided by CLDRI. The pilot plant is designed to process low-grade pebble at a controlled feed rate using either tap water or beneficiation plant process water from tanker trucks. The pilot plant flow-sheet is illustrated on Figure 1, which also shows equipment items identified by prefix E and sample points identified by prefix S. Five process streams exit the pilot plant, two of which are concentrates and three of which are wastes.

See Figure 1. Flow Diagram for JACOBS Pilot Plant

#### **Materials**

JACOBS collected the required quantities of high-MgO pebble samples, beneficiation plant water, and all pilot plant flotation reagents except the dolomite collector, from local producers. The proprietary PA-31 was provided by CLDRI. The samples collected for pilot plant testing are listed below:

- Pebble 1: 30 tons from the Four Corners mine
- Pebble 2: 20 tons from Hardee Complex II
- Kingsford plant water: 3 tanker trucks (15,000 gallons)
- New Wales phosphoric acid: 60 gallons @ 52%  $P_2O_5$
- Kingsford plant reagents:
- Sulfuric acid: 30 gallons of 98% solution
- Soda ash: 100 gallons of plant solution
- Amine: 5 gallons
- No. 2 Diesel Oil (No. 2 D.O.): 5 gallons

Reagents utilized in the CLDRI dolomite flotation process are described below in order of the sequence of addition.

#### **Sulfuric and Phosphoric acids.**

These reagents were added to the first dolomite-conditioning tank to adjust the slurry pH and to depress the phosphate mineral during the subsequent dolomite flotation step. The  $P_2O_5:SO_4$  ratio, an important process variable, was examined over the range of 1:0 to 0:1. For the pilot plant operation 98% sulfuric acid and 52% phosphoric acid were mixed at the desired ratio, diluted with tap water to about 20%, and metered with a single pump.

**PA-31.** This proprietary reagent has been developed by CLDRI. FIPR, IMC, and JACOBS have signed confidentiality agreements concerning PA-31. This reagent is added to the dolomite conditioning tanks and to the dolomite flotation cells as a 7% solution. This dolomite collector developed by CLDRI is currently in commercial use in China. Its raw materials are vegetable fatty acids

and a surfactant, which are available at reasonable prices in the US market.

**Soda ash.** This reagent (at 15% solution) is added to the coarse concentrate prior to the first silica conditioning tank. The soda ash solution adjusts the slurry to neutral pH for silica flotation.

**Amine.** Amine solution (at 2% solution) is added to the first silica-conditioning tank. Amine is a collector for silica (quartz).

**No. 2 D.O.** The diesel oil is utilized as an extender for amine, and is added to the first silica-conditioning tank.

### Methods

Formal test runs were normally on Mondays and Wednesdays, allowing sample preparation, chemical analyses, and data review to be performed Tuesdays and Thursdays. In this way it was possible to establish the conditions for each test knowing the results of the previous test. CLDRI process engineers operated the dolomite and silica flotation cells. JACOBS personnel maintained the supplies of low-grade pebble, water, and reagents required for testing, and operated all equipment except the flotation cells.

The sampling program involved manually cutting samples at twelve (12) pilot plant sampling stations. Sample numbers in Figure 1 locate the sampling stations listed below.

Sample No.	Sample Type	Description	Classification
S1	Input	Log Washer Feed	Damp Solids
S2	Output	Log Washer O'flow	Slurry
S3	Internal	Rod Mill Discharge	Slurry
S4	Internal	Mill Classifier O'size	Slurry
S5	Internal	Mill Classifier Feed	Slurry
S6	Internal	Dolomite Flot Feed	Slurry
S7	Output	Dolomite Tails	Slurry
S8	Internal	Dolomite Flot Concen	Slurry
S9	Output	Fine Concentrate	Slurry
S10	Internal	Silica Flotation Feed	Slurry
S11	Output	Silica Flotation Tails	Slurry
S12	Output	Silica Flot Concen	Slurry

Measured flow rates, chemical analysis, and sieve analysis data for process streams were transmitted to IMC for input to their Matbal program. Matbal is used by IMC to statistically convert measured data into a coherent data set, so that output is exactly equal to input for each parameter at each step of the process. Measured data include sampling and analytical errors that usually preclude perfect closure of all parameters in a material balance. The Matbal program provides an unbiased method of correcting the data to arrive at 100% closure for all parameters.

A second advantage of the Matbal program is that the magnitude of adjustment required to arrive at 100% closure for all parameters is evident. Large adjustments indicate biased data or that process conditions were not at equilibrium. Small adjustments indicate reliable sample data. Therefore the confidence in test results may be high if the Matbal output shows only small adjustments to the measured data.

Matbal input for each formal test run comprised measured parameters for key streams. The 12 key streams are identified as S1 through S12 in Figure 1, and are described above. Streams S1, S2, and S3 had inputs for solids rate and chemical analysis only. Streams S4 through S12 had inputs for solids rate, chemical analysis, and particle size analyses.

### Results

#### Performance

Eleven formal pilot plant runs were performed with Pebble 1. The target parameters for each run were specified by CLDRI. Parameters examined during these runs included reagent dosage, dolomite flotation cell agitator speed, dolomite flotation cell froth paddle speed and clearance, mesh of grind, and flotation with tap water and plant water. The ground flotation feed ranged from 77 to 57% passing 200 mesh. Dolomite flotation was performed with dosages of PA-31 that ranged from 3.00 to 5.58 lb./ton of pebble feed to the pilot plant. The yield of combined wastes ranged from 33 to 51% of the pebble weight; however, the phosphate

content of the combined wastes was relatively uniform at 30 to 35% BPL. The yield of combined coarse and fine concentrates ranged from 49 to 67% of the pebble weight. At the low yield the concentrate contained 64.5% BPL and 1.06% MgO. At the high yield the concentrate contained 62.1% BPL and 1.25% MgO. Results from run 18, the formal demonstration run for Pebble 1, are summarized on Table 1. The combined coarse and fine concentrate from Pebble 1 had an MER of 0.125 and a CaO/P<sub>2</sub>O<sub>5</sub> ratio of 1.558. The reagent cost for run 18 was \$4.39 per ton of concentrate.

Pebble 2 was log washed twice because it was heavily contaminated with clay. The first pass through the log washer was made before the formal testing to remove sticky clay that would subsequently cause choking problems in the pilot scale equipment. The first stage of log washing rejected 22% of the pebble weight as a low-grade waste product. No scavenger screen was used to recover low-grade feed from the log washer over flow. The second log washing was performed as a pre-treatment during formal testing, and rejected only about 3% weight.

Eight formal pilot plant runs were performed with Pebble 2. Parameters examined during these runs included reagent dosage, mesh of grind, and flotation with tap water and plant water. In addition to PA-31, dolomite collector FA-#4, prepared from American feedstock, was tested on Pebble #2. The target parameters for each run were specified by CLDRI. The ground flotation feed ranged from 72 to 44% passing 200 mesh. Dolomite flotation was performed with dosages of PA-31 that ranged from 1.78 to 4.35 lb./ton of pebble feed to the pilot plant. The yield of combined coarse and fine concentrates ranged from 28 to 54% of the pebble weight. At the low yield the concentrate contained 61.8% BPL and 0.51% MgO. At the high yield the concentrate contained 63.4% BPL and 0.81% MgO. Results from run 9B, the formal demonstration run for Pebble 2, are also summarized on Table 1. The combined coarse and fine concentrate had an MER of 0.116 and a CaO/P<sub>2</sub>O<sub>5</sub> ratio of 1.550. The reagent cost for run 9B was \$2.93 per ton of concentrate.

### **Reagent consumption and cost**

Reagent cost details for runs 18 and 9B are presented on Table 2. The price of PA-31 was estimated at \$0.30 per pound. The other reagents are in the range of costs experienced currently.

The test data indicated that the use of plant water did not impact flotation performance, provided that the collector dosage was adjusted. For dolomite flotation the impact was minimal; however, in silica flotation amine consumption had to be increased about 25% to achieve the same concentrate % Insol. Reagent FA-#4, the dolomite collector made from American feedstock, was less effective than PA-31.

### **Preliminary study**

Using CLDRI's process concept and performance, JACOBS developed estimates of capital and operating costs for the battery limits plant with a design waste pebble rate of 300 tph. The battery limits are defined as follows:

- Ore Supply: A 600-ton pebble surge bin. (conveyor system to bin provided by others).
- Water Supply: 900-gpm (low-pressure water provided by others).
- Concentrate Dispatch: Two agitated tanks having about 8 hours capacity each are provided for thickened concentrate slurry. (The concentrate pumping system and slurry pipeline is by others).
- Tailings disposal: A general mill tailing pump, a return water pump, and associated pipelines are included. The tailing pond construction is excluded from the capital cost, but is included as an annual accrual of \$850,000 to the operating cost estimate.

The process elements within the battery limits are listed below:

- Pebble pretreatment (desliming)
- Closed circuit grinding
- Dolomite flotation and reagent supply
- Silica flotation and reagent supply, preceded by two stage classification

- Thickening of coarse and fine concentrates with water recycle
- Disposal of clay, dolomite, and silica wastes with water recycle

### Cost Estimates

The components of JACOBS operating cost estimate for the battery limits plant are presented on Table 3. The estimated variable (production rate dependent) costs are \$12.52/ton of concentrate. Fixed costs, which include labor, overhead, depreciation, operating supplies, taxes, and insurance, total an estimated \$3.10/ton of concentrate. Total operating costs, which are the sum of variable and fixed costs, are \$15.62/ton of concentrate. The raw materials cost item on Table 3 is an allowance by JACOBS to cover the cost of retrieving and transporting waste pebble to the battery limits plant surge bin. Electric power is based on the connected motor Hp and a unit price of \$0.04 per kW.h.

JACOBS estimate of the battery limits plant constructed cost is 32 million dollars. This estimate includes all the equipment plus construction materials, construction labor, subcontracts, field indirect costs, engineering and procurement services, and an allowance of 10% for unforeseen costs. Excluded from the estimate are land costs, soil testing and major site preparation, working capital, start up expenses, and escalation.

The battery limits plant includes silica flotation, which reduces the concentrate insol. from 19 to 6%. Capital and operating cost savings would be obtained if the phosphoric acid plant could tolerate the higher level of inert material. Excluding the silica flotation circuit would save about 14% of the constructed cost (4.5 million dollars) and 10% of the operating cost (\$1.50 per ton of concentrate).

### Conclusions

The measured pilot plant data were analyzed by IMC's Matbal program to obtain material balances with 0% closure errors. Comparisons of measured and Matbal adjusted data showed that the required adjustments were typically small and within allow-

able error for sampling and analysis. The test data obtained by this project are therefore considered to be reliable and provide a sound basis for evaluation.

The possible overall phosphate recovery, taking into account desliming, dolomite flotation, and silica flotation is about 85% for Pebble #2 and 75% for Pebble #1. The possible overall dolomite rejection is about 82% for Pebble #1 and 86% for Pebble #2. Roughly speaking, the CLDRI Process can reduce MgO content by two thirds and maintain acceptable recoveries. The concentrates produced are at the high limit of CaO:P<sub>2</sub>O<sub>5</sub> for rock accepted by phosphoric acid plants, and exceed the MER limit for DAP production. For both concentrates the high MER is caused by elevated levels of MgO and I&A. Elevated I&A is particularly a problem for Pebble #2. The CLDRI Process, similar to other dolomite flotation schemes, does not specifically reject iron oxides and alumina. Herein lies a problem, because low-grade pebble often contains elevated levels of I&A.

Estimates of constructed cost and operating cost for a 300-tph plant utilizing the CLDRI Process indicate economic feasibility, relative to a grass roots mine with the same capacity. The battery limits plant would cost about 32 million dollars and produce about 1.58 million tons of concentrate annually. The estimated production cost of \$15.62 per ton of concentrate is less than the industry average operating cost of about \$20 to \$22 per ton.

### Acknowledgements

The author appreciates the opportunity to present this paper to the Fertilizer Industry Round Table. JACOBS successful pilot plant demonstration of the CLDRI Process was due in large part to the exceptional participation of process engineers from CLDRI and the cooperation, assistance, and guidance provided by FIPR and IMC. CF Industries greatly assisted with the collection of Pebble 2.

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**Table 1. CLDRI Process Demonstrated Performance**

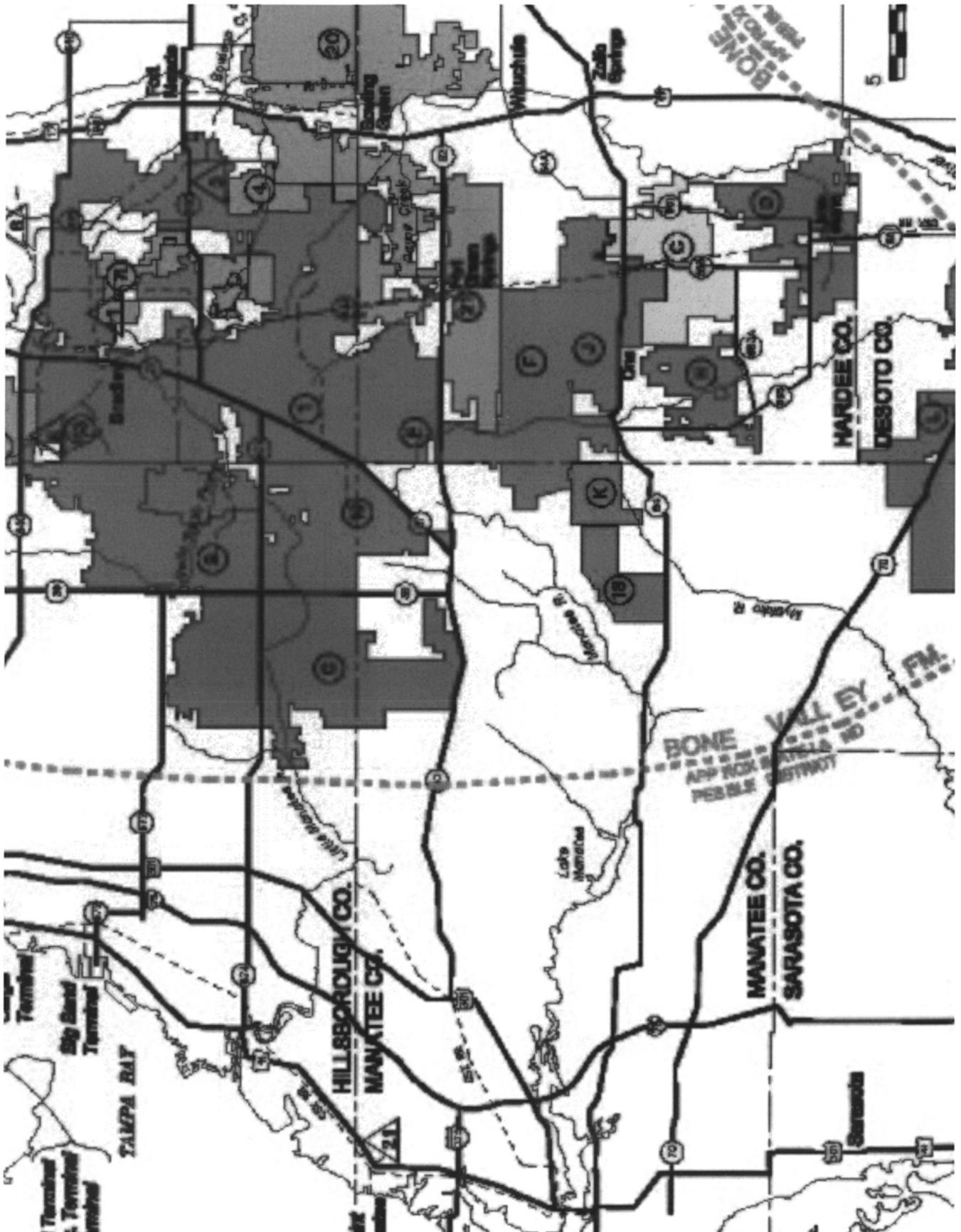
	Pebble 1, Run 18				Pebble 2, Run 9B			
	% Wt.	% BPL	% MgO	% Insol	% Wt.	% BPL	% MgO	% Insol
Washings	0.0	n/a	n/a	n/a	22.0	11.4	5.86	51.0
Clay O'flow	4.7	36.2	7.71	6.8	2.7	30.2	7.95	13.1
Dolomite Tail	27.2	32.9	9.07	4.0	9.8	32.0	8.66	9.8
Silica Tail	7.8	17.4	0.29	74.0	11.4	10.3	0.13	83.9
<b>Combined Conc.</b>	<b>60.3</b>	<b>64.9</b>	<b>1.14</b>	<b>4.6</b>	<b>54.1</b>	<b>63.4</b>	<b>0.81</b>	<b>9.3</b>
Composite	100.0	51.2	3.54	9.9	100.0	41.9	2.81	27.2
<b>% Recovery to Concentrate</b>	<b>60.3</b>	<b>76.5</b>	<b>19.4</b>	<b>27.8</b>	<b>54.1</b>	<b>81.8</b>	<b>15.6</b>	<b>18.6</b>

<b>Table 2. Reagent Usage and Cost</b>				
Flotation Reagent	Pebble 1, Run 18		Pebble 2, Run 9B	
	lbs/t	\$/t	lbs/t	\$/t
H <sub>2</sub> SO <sub>4</sub>	0.69	0.01	3.03	0.05
P <sub>2</sub> O <sub>5</sub>	12.09	1.09	5.98	0.54
PA-31	4.22	1.27	2.16	0.65
Na <sub>2</sub> CO <sub>3</sub>	0.57	0.04	1.16	0.08
Amine	0.91	0.23	1.07	0.27
Diesel Oil	0.19	0.01	0.13	0.01
\$ per ton of pebble		<b>2.64</b>		<b>1.59</b>
\$ per ton of concentrate		<b>4.39</b>		<b>2.94</b>

<b>Table 3. Estimated Operating Costs</b>			
<b>Variable Costs</b>	<b>\$/year</b>	<b>\$/ton pebble</b>	<b>\$/ton concentrate</b>
Raw Materials	5,925,000	2.50	3.75
Electric Power	1,699,185	0.72	1.08
Reagents	5,040,985	2.13	3.19
Consumables	2,261,481	0.95	1.43
Severance Tax	2,564,719	1.08	1.62
Dam Building	850,000	0.36	0.54
Contract Maintenance	791,580	0.33	0.50
Services	649,096	0.27	0.41
<b>Subtotal</b>	<b>19,782,046</b>	<b>8.34</b>	<b>12.52</b>
<b>Fixed Costs</b>	<b>4,917,992</b>	<b>2.08</b>	<b>3.10</b>
<b>Total Cost</b>	<b>24,700,038</b>	<b>10.42</b>	<b>15.62</b>



Map Southern Extension Central Florida Phosphate District



# **Rail Veyor Bulk Material Transport System**

*Mike Dibble*  
**Rail-Veyor Technologies, Inc**

## **Abstract**

The phosphate industry has traditionally used slurry pipelines to move phosphate matrix from the mine site to the processing plant. As phosphate matrix grade decreases and transport distances increase the transport cost per ton of product has significantly increased. These increased costs are forcing alternative matrix transport methods to be evaluated.

The Rail-Veyor represents a possible replacement for slurry pipelines by combining the best features of a railroad, trucks and overland conveyors without the high capital cost requirements. The Rail-Veyor system can move phosphate matrix at a much higher percent solids in its static environment rather than the dynamic environment of a pipeline.

The demonstration Rail-Veyor system operated successfully as it was able to load, transport, and dump phosphate debris in a very efficient manner. The system was able to operate continuously with only one set of stationary drive units in physical contact with the 42 car 168 foot open trough train at any time. The system operated at about 588 feet/minute with energy required of about 0.3 KWH per ton-mile.

The Rail-Veyor met the objectives of the project and offers potential as a cost effective, environmentally attractive, bulk material transport system.

## **INTRODUCTION**

The Florida phosphate industry has historically produced the lowest cost phosphate rock in the world. Favorable ratios of overburden to matrix and concentration of matrix had made the Bone Valley Member of central and south Polk County

the most cost effective source of rock. The substantial presence of "pebble", coarse rock plus 1.0 MM that did not require beneficiation, also contributed to the cost effectiveness of these large reserves.

The success of the American agricultural industry has been profoundly influenced by the presence of these low cost reserves. The phosphorus element is the one component of fertilizer that there is no substitute for. Fertilizer represents "cheap land" as it allows continuous use of the land even after the exhaustion of the natural components. By providing very efficient farmland utilization, fertilizer has allowed the agricultural sector of the United States to feed the rest of the country with less than 5% of the labor force. This proportion is unprecedented in the world.

Historically, water was readily available at the central Florida Bone Valley deposits. Since the process steps to both size and clean phosphate sands required a low percent solids slurry, the transport system evolved because it was more efficient to dilute the matrix at the mine site and transport a slurry in a pipeline to the process plant. The slurry was elevated to a washer where the pebble and clay were removed. The water separated from the clays after settling and the flotation tailings were recycled to slurry new matrix.

As with all good things, high grade Bone Valley phosphate rock is a thing of the past. The present phosphate resources are now southern extensions from the Bone Valley and are primarily from the lower grade Hawthorn Extension. The present rock sources now have minimal or noncommercial pebble rock, significantly lower grade flotation feed grades, and higher percentages of the minus 100 micron clays requiring larger disposal areas.

To remain competitive, the Florida phosphate mining industry needs to explore all avenues to improve efficiency in producing a cost effective rock product. Beneficiation methods have been optimized to the point where recovery improvements are indicated in tenths of a percent. A great

deal of future effort is not expected to produce significant improvements in product recovery.

There are three areas however, that represent significant potential to improve production costs of phosphate rock. These areas are listed as follows:

With the increased overburden to matrix ratios dragline efficiency is an area that offers potential cost savings. A study developed by FIPR in 1988 indicated that a dragline could improve its mining efficiency by 30% by windrowing matrix rather than spot loading a matrix slurry well.

Windrowed phosphate matrix allows the dragline to operate independent of the process plant. Avoiding the short-term cyclic changes of feeding a plant from a multiple of draglines, the plants operational efficiency will significantly improve. Both the dragline and the process plant can then improve maintenance efficiency by utilizing preventative maintenance.

The movement of phosphate matrix in a very dynamic environment, such as a slurry pipeline in combination of 60 to 70% water, is not energy efficient over long distances. By moving the matrix at high solids (70 to 80%) from windrowed matrix with no friction, other than a metal wheel on a steel track, very significant energy savings are evident.

The Rail-haul system developed by Agrico Chemical Co. demonstrated that moving phosphate matrix at high solids from a windrowed pile was successful. Conventional open - top, bottom - dump railroad cars were filled with front-end loaders from the windrowed matrix piles, then transported to the process plant where high-pressure water washed the matrix through a grizzly screen into a conventional slurry washing system. There were mechanical problems in the loader motor systems used that caused problems in reliability. The process concept proved to be sound however. In addition to the rail-haul system an attempt to move phosphate matrix by use of an overland conveyor was considered a failure, primarily because of design problems rather than concept.

The economic advantages of moving windrowed matrix are evident. The selection of the optimum transport method to move this material is, at present, under intense study. The Rail-Veyor concept proposed to FIPR combined the best features of the rail-haul system and the overland conveyor. An economic study comparing a conventional slurry pumping system and a Rail-Veyor system indicated that the Rail-Veyor system would have significantly less capital (+/-25%) as well as operating cost (for a six-mile haul distance).

A proposal was made to FIPR to build a semi-works scale Rail-Veyor system using a 1/4 mile track, with 8 equally spaced drive stations (165 feet apart) moving a 4 foot long by 20 inch wide open trough car in a 42 car train. The resulting 168-foot train was to always be in contact with a drive station. Included with the proposed system was an outside loop dumping station and car loading hopper. Cargill Fertilizer Co. generously provided us a site adjacent to the Cargill Bartow Chemical Plant.

### **Methodology**

The Rail-Veyor design presented to FIPR incorporated the use of light rail (25 #/yard) without ballast and 3 inch wide rail spacer plates every four feet. The rail bed selected was scrapped and smoothed with a motor grader. No ballast or sleepers were used or required.

The drive stations consisted of a fixed plate that provided for two opposing drives, each of which consisted of a 10 HP 480 volt motor driving a 21:1 SM-cyclo gear reducer. This motor/drive was mounted on a vertical post, which allowed rotational movement in a horizontal dimension. A drive tire was attached to the vertical shaft of the reducer that could provide horizontal pressure on the train. The tire selected had a low durometer (62) surface that provided excellent traction. This tire was filled with foam and was 26.5 inches in diameter. The opposing drive was identical to the first drive with the exception that the rotational direction was reversed. Two additional posts were mounted on the fixed plate that provided the force,

by use of a jack, to rotate the drive unit to provide car side pressure.

Each drive station with two motors had an inverter control system that allowed for forward or reverse rotation and full load starting torque. These inverters provided for controlled deceleration or acceleration. The integration of drive controls permitted overall management of the entire system from a central point.

The 42 cars were designed and fabricated with a single set of wheels at the rear of each car with a single blade clevis connection at the front of each car and a double blade clevis at the back. The clevis connection was designed to allow movement in three dimensions, 15-degree twist, 5 degree of bend between cars, and 45 degrees in a vertical plane. Each car had a 3/16-inch thick trough rolled into a semi-circle with a 10- inch radius. Each trough was 47 inches long, which formed a 1-inch gap between cars. A 3/8-inch thick urethane sheet was attached to the front of each car and overlapped the forward car covering the one-inch gap during operation as well as the increase space which opened during the outside loop dumping cycle. These urethane sheets sealed the gaps between cars and prevented any material leakage.

The car wheels were 7-7/8 inch diameter steel wheels with a single inside flange. Each wheel had dual thrust bearings that proved to be very successful. An early attempt to use bronze bushings proved to be a failure as no thrust forces could be provided and wear was significant.

A set of side plates were attached to each car, outside the wheels. The side plates measure 6 inches wide by 48 inches long 1/2 inch thick. The leading and trailing edges of these plates were cut to allow relative movement between cars while maintaining continuity of contact with the drive station. The initial openings were too close to allow car rotational twisting after dumping so they were widened, which did not cause the expected roughness of transfer of cars through the drive stations.

The car configuration called for the drive plate to be symmetrical to the wheel allowing operation in the inverted position with dual rails. The dumping system consisted of dual parallel rails rolled to a 12-foot diameter loop. The vertical spacing between rails was 8 inches or 1/8 inch wider than the wheel and 1-1/2 inch less than the flange. This dual track system encapsulated the wheels allowing rotation in an outside loop. With the completion of the loop and the cars in the inverted position, a rotational twist was then applied which was 10 degrees per 4 foot car length or 72 feet of the 168 foot train to return to the up right position. Space limitations required that the rotational phase be completed in the 72-foot distance with a 120-foot radius turn. This limitation forced the modification of the cars to prevent metal-to-metal contact of the drive plates and car frames during rotation. One-inch diameter steel rods were substituted for rail during this rotational phase.

The train was operated at 588 feet/minute  $((1,780/21) \times (26.5 \times 3.14/12))$ . The 42 cars, when full, contained about 8 tons of material. At 588 feet/minute with a 168-foot train the loading time was only 17 seconds. This required a loading system that had the incremental capacity of 1,686 tons per hour to fully load the train operating at design speed. The proximity of the dumping station to the loading station did not allow speed reduction, as the dumping speed could not be reduced in the space available to operate the loading system at lower train speeds. Although the track was built to a length of 1/4 mile, the effective dumping/loading system would have only been 1/8 of a mile. The cycle time for the train was 2.27 minutes or 26.5 trips per hour.

## **Results**

The Rail-Veyor train functioned very well with smooth consistent operation. The variability of side pressure by the opposing drive stations reduced any slippage during startup to a minimum. The cycle time for the train was extremely consistent. The individual drive stations had light sensor controls that started that station just prior to the train arrival and shut down the drive after the

train had passed. The feed hopper conveyor had the same control system so that the feeder started as the first car passed and shut down after an adjustable time interval just prior to the passing of the last car.

A test was conducted to determine tire drive plate traction under adverse conditions. A high viscosity phosphatic clay was smeared on both the drive plates and tires on a fully loaded train. The low durometer drive tire literally squeezed the clay from the drive plate and startup was comparable to normal dry tire/plate environment. This test was repeated several times.

The full train effectively could carry 8 tons of material at 26.5 trips per hour or 212 tons per hour. By expanding this track to 2 miles the capacity would be reduced to 26.5 tons per hour. The consistency of the drives and the controls built into the system would allow several trains to be operated on this same track. Each drive station is myopic and only recognizes the train in immediate contact. After the passing of a train it is immediately ready to accept a new train through its drive sensor system.

The dumping phase was very successful as the urethane sheets acted as individual chutes on each car allowing the carried material to slide forward and be projected outward by tangential forces. The impact point of the ejected material was very consistent and could have been removed by a relatively small hopper over a radial stacker.

The drive stations with a loaded train only operated from 30 to 45 % of the torque load. The drive units had the capacity of over 200% of full torque load during startup but rarely used more than 80% of full torque load during this phase. The energy consumed to operate this system indicated that the car and load of 16.5 tons was moved by 8.29 Kilowatts of energy (at 50% torque load). By moving 26.5 tons/hour of load @ 8.29 KWH gave an incremental rate of 0.31 KWH per ton-mile. By increasing the load relative to the car weight, by enlarging the cars, this rate will decrease.

## **Conclusions and Recommendations**

The Rail-Veyor semi works scale plant engineered, built and operated for FIPR met all of the objectives of the original proposed program. The system proved the efficiency of the stationary drive stations and their ability of being controlled through the inverter system allowing the drives to start from dead stop through maximum RPM with a fully loaded train. This function performed well even when a heavy load of clay had been smeared on both the tires and side plates. The controls also allowed power-off standby with rapid sensor controlled startup and shutdown as the train entered the station and left the station. Energy was only required when the train was in contact with the drive unit.

The lightweight rail (25 #/yard) did not require either sleepers or ballast and proved to be easy to move when required. The 3-inch wide spacer plates used to maintain rail spacing installed every 4 feet seems to be totally adequate for a train of this size. Angle iron anchors were provided and did supply some lateral support. Larger trains and rails subject to extensive use will require some type of anchor and possibly some sleeper support dependent upon the ground conditions that would be site specific.

The open trough cars, when incorporating a urethane spill flap proved to be virtually leak proof when filled with wet sandy as well as dry fine material. After many loading and dumping cycles over a period of seven months there was no evidence of any spillage between the rails. The load pressed the flap against the tail end of the forward car effectively forming a seal. The elasticity of the urethane allowed flexing and twisting of cars without loss of sealing integrity. During the dumping cycle the flap acted like a spout overextending the forward car. All of the car contents were projected forward beyond the forward car as the outside loop continued and no material fell on the forward car. This extension of the flap also allowed the flushing of any material trapped between the flap and the car from the tangential forces resulting from the outside loop.

The ratio of the wheel diameter and the side plate, 7-7/8 inch and 6 inches was too low for the degree of twist to rotate back to the upright position. The degree of twist, 10 degrees per car length of four feet, was too tight because of space limitations of the site but was corrected by a field modification of the side plates. The test site would not be a typical installation because under normal conditions the loading and dumping sites would be at opposite ends of the track system.

The conclusions drawn from the test program are that there does not appear to be any limit as to the capacity of a site-specific design Rail-Veyor system. A hypothetical material handling system was cost estimated to handle 600 TPH of wet sand over a two-mile (11,000 foot) distance. The system selected for this illustration was a 30-inch diameter car that was six feet long and consists of three 128-car trains. The cost of the fixed components such as track, drive stations, controls, loading and dumping stations was estimated at \$2,250,000. Each of the 128 car trains (768 foot each) was estimated to cost \$445,000 and could each move 200 TPH. Three of these trains could move the required 600 TPH at a capital cost of \$1,335,000. This cost combined with the fixed cost estimate of \$2,250,000 represents a total capital cost in dollars / TPH capacity of \$5,975. If we were to increase capacity of the system to 2,000 TPH (incorporating 10 trains) then this cost would be reduced to \$3,350 /TPH capacity. (see graph in Appendix)

It is very conceivable that this system of 29 drive stations could support nearly as many trains as drive stations less reasonable open spaces between trains (room for slowdown at loading stations). Assuming that only 1/2 of the track was utilized then a system of 14 trains could handle 2,800 TPH at about \$3,030 per installed TPH capacity (for a two mile distance).

One of the very important aspects of a multi-train system is the effect on the loading system. The greater the percentage of time that loading is conducted relative to a fixed time frame the lower the incremental loading rate can be. The loading sta-

tion feed rate in the 600 TPH case indicated above @ 400 FPM = 16.7 minutes/hour for loading. This would require an incremental loading rate of 2,200 TPH. As long as all trains are loaded at this rate it will remain consistent regardless of the number of trains. Because of only handling 8 tons per load in 17 seconds for a 168-foot train our demonstration plant needed a loading rate of almost 1,700 TPH.

The above cost analysis indicates the enormous capacity range the Rail-Veyor system offers over other material handling systems. All systems are directly affected by speed. The speed of the Rail-Veyor is a function of the motor speed, gear ratio and drive tire diameter. The gear reduction limitation is a direct function of torque. The higher the ratio, the lower the shaft speed and higher the torque. The lower the ratio the greater the shaft speed with a lowering of the torque. By developing an optimum combination of gear reduction and tire diameter to allow full load start up in cases of power failure, the train speed can be fixed. Once the proper combination is developed then system capacity is only a function of the number of trains operating in the system.

The slurry pipeline for moving phosphate matrix is limited by the fluid dynamics of velocity as it affects friction loss, which directly relates to energy consumption. Increased percent solids of the transported slurry can help improve capacity but have limitations as to pumping efficiencies. Overland conveyors have limits as to the cross sectional area of the material on the belt before unacceptable spillage losses can occur. Increasing speed of conveyors to increase capacity also has limitations because of increased friction and energy losses. Capacity increases in established slurry pipelines or overland conveyors are relatively small increments of the design capacity while the Rail-Veyor can represent increases of many multiples.

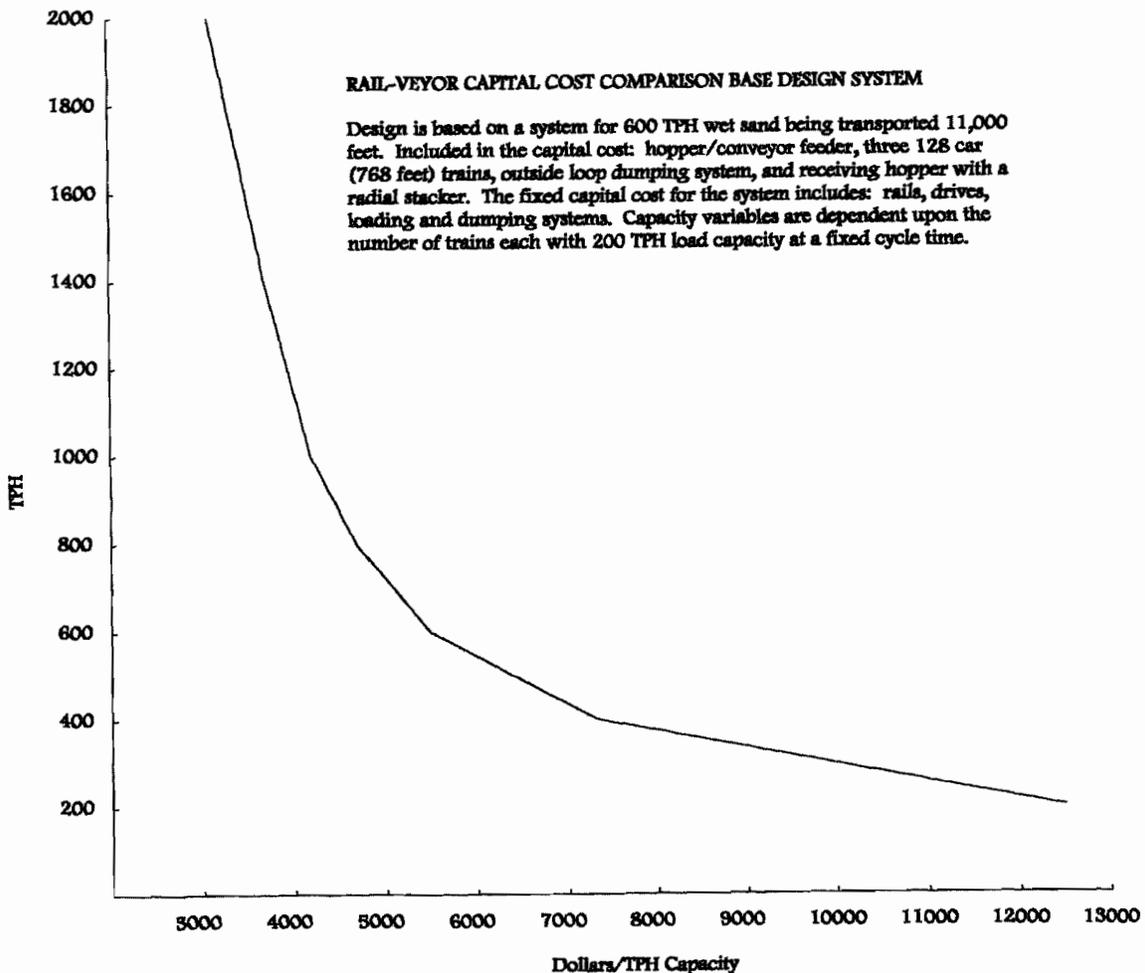
The Rail-Veyor system was designed to be as simple as possible. The cars are simple, the rails are conventional and obviously simple, and the drives are effectively motor gearboxes that are an off the

shelf type item. It is only the combination of these features that makes the Rail-Veyor system unique. The ease of replacing key elements in case of failure would indicate that the operating factor would well exceed 90%

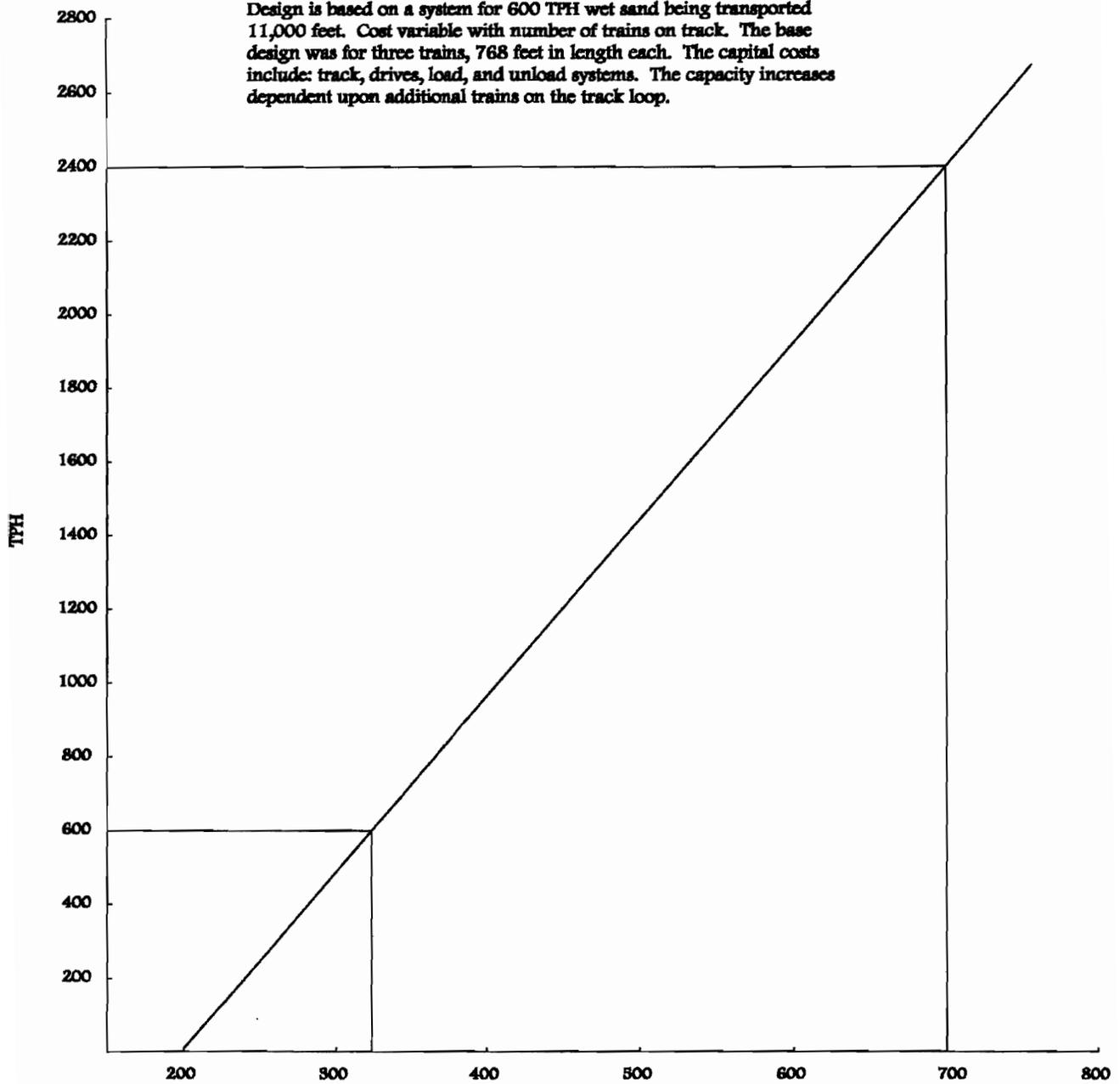
There does not appear to be any limitation as to the capacity of a Rail-Veyor system. The drive efficiencies are all relative to the pressure of the contact footprint of the drive tire and the drive plate. Groups of drives can be packaged in multiples of two to keep units as standardized as possible. In the case of phosphate matrix transport from a windrow there does not appear to be any limit of car diameters. The selection of car widths is influenced by the size of the carried material and transport distance. To simplify the drive controls the number used is influenced by the length of unit trains selected. The live volume contained within

a train and total loop time from loading to unloading and return all will impact the car size. The cross sectional shape of a car can also influence its capacity. The possibility of a large multi-lobed loop serving several dragline windrows is also a possibility with alternate trains picking up loads at different locations and dumping at a plant site. This would significantly influence plant efficiencies and operating factors because of the blending and feed rate control advantages offered.

The simplicity, capital and operational costs indicate that the Rail-Veyor system offers an alternative to conventional material handling systems. Although the thrust of our program was toward the movement of phosphate matrix, There did not appear to be any reason it could not be used to transport concentrate, tailings, dried gypsum or any other bulk material.



**RAIL-VEYOR CAPITAL COST COMPARISON - \$ PER FOOT INSTALLED**  
 Design is based on a system for 600 TPH wet sand being transported 11,000 feet. Cost variable with number of trains on track. The base design was for three trains, 768 feet in length each. The capital costs include: track, drives, load, and unload systems. The capacity increases dependent upon additional trains on the track loop.



Dollars per foot installed cost from load to dump (1/2 loop) on 11,000 foot system

## Uses of Phosphogypsum

*G. Michael Lloyd, Jr.*

### Florida Institute of Phosphate Research

#### Uses of Phosphogypsum

Almost from its inception FIPR has had the goal of eliminating the phosphogypsum stacks in Florida. In order to achieve this goal the following three prong research plan of action was formulated to investigate and demonstrate:

1. Use as a chemical raw material
2. Agricultural uses.
3. Construction uses.

The primary driving force behind all this interest was an annual production rate of 30 million tons and a then on ground inventory of 600 million tons. In addition it just did not seem to make good sense to ignore a 600 million ton readily available raw material supply that had the potential for solving so many problems. Later on we became even more convinced that the negative environmental impacts associated with leaving it in the stack greatly exceeded any negative environmental impacts associated with using it.

Using phosphogypsum as a chemical raw material offered two opportunities:

1. Sulfur recovery.
2. Ammonium sulfate manufacture.

The economics of ammonium sulfate manufacture were not too appealing and in addition there was the problem of what to do with the byproduct calcium carbonate that would be produced in amounts almost as great as the phosphogypsum that was consumed. We did develop processes for recovering the sulfur as either sulfur or sulfur dioxide for sulfuric acid manufacture. By the time the sulfur recovery processes were proven the price of sulfur had dropped from \$156/lb to less than \$100/lb and with the present price of \$25/lb it is somewhat unlikely that sulfur recovery from phosphogypsum will become very popular in the immediate future.

With the exception of sulfur recovery there does not appear to be any single use that might easily consume all the phosphogypsum produced each year. There are multiple agricultural uses that have the potential to achieve this goal and these uses fall into two classes:

1. Soil conditioning
2. Calcium and/or sulfur fertilization

Florida does not have a sodic soil problem but subsoil acidity syndrome is a problem in some areas that can be controlled by surface applications of phosphogypsum to reduce aluminum toxicity. Another research program demonstrated that phosphogypsum could be used to reduce rain water runoff and the resulting loss of soil due to erosion. Surface applications of phosphogypsum increased the rate of water infiltration and reduced runoff even in the most extreme rainfall events. With all the concern today about fertilizer runoff into streams and rivers, it would seem that phosphogypsum could offer a simple and easy solution to this problem.

The beneficial advantages from using phosphogypsum for fertilization has been demonstrated on almost any crop that is raised in Florida with the best known use as a calcium source for peanuts. However, the application that has the greatest potential to use large quantities of phosphogypsum, estimated to be as much or more than the entire annual production, is pasture fertilization. Forage grasses need sulfur and with the proper sulfur fertilization the protein content of the grass is at the highest level and the grass is more digestible resulting in increased weight gain for livestock. Demonstrations around the world have shown that a 20% increased weight gain for livestock is not uncommon when grass has optimal sulfur content. This use of phosphogypsum could have a major and decided favorable affect on Florida agriculture.

Another application that would be extremely beneficial for Florida is road building. We have demonstrated that phosphogypsum makes a superior

road base at a significantly lower cost than conventional road base materials. When a secondary road in Polk County Florida, Parrish Road, was paved using a phosphogypsum base the University of Miami Industrial Engineering Department prepared a cost analysis of Parrish Road and two other Polk County roads, Tanner Road and Windy Hill Road, that were constructed during the same general time period.

Road	Tanner	Windy Hill	Parrish
Costs per mile			
Materials	\$35,009	\$ 47,719	\$ 0
Labor	28,912	38,408	9,511
Equipment Use	34,418	43,193	13,974
Total	98,339	129,320	23,485

When it rains during traditional road building in Florida it is normal to shut the job down and send the workers home while the limestone base dries to the point that it can be worked again. When using phosphogypsum the job was shut down when it rained and started back when the rain stopped. The zero raw material cost for Parrish Road is because the phosphate industry had agreed to give the phosphogypsum to either the counties or the state for road building.

A very critical part of all these studies and demonstrations was the evaluation of the environmental impacts of using phosphogypsum. We were satisfied that the uses we had investigated would not create any significant adverse environmental impacts.

At this time the EPA elected to get into the act. In October 1989 EPA proposed a rule that would ban:

1. All chemical uses
2. All agricultural uses
3. All construction uses
4. All research involving phosphogypsum

The EPA bans were based on radiation exposure, primarily radon and the possibility of increased cancer risks. The ban on research created quite a stir even among people who were not particularly interested in phosphogypsum. Here you have

EPA using multiple pages in the Federal Register to describe the problems associated with phosphogypsum use and deciding that the solution to the problem is "to do nothing".

EPA adopted a final rule in June 1992 that:

1. Banned all chemical uses.
2. Permitted agricultural uses of any phosphogypsum containing less than 10 pCi of radium.
3. Banned all construction uses.
4. Allowed research as long as you used less than 700 pounds phosphogypsum for any one project.

I will not go into all the details of our lengthy discussions with EPA but I would like to describe one thing that happened. EPA had developed a computer model to calculate risks, PATHRAE-EPA and we asked them to provide us with a copy in order that we could use the same methodology that EPA was using to calculate risks. When our consultant started evaluating EPA's results that had been reported in the Federal Register and used as the basis for banning use of phosphogypsum, they found they could not duplicate EPA's results. When we asked EPA for a copy of their actual work sheets we were advised that it could not be found at EPA, at EPA's contractor or at the subcontractor who made the actual calculations. After almost six months EPA called a meeting where they advised us that they were unable to determine how these calculations had been made but they were not made using PATHRAE-EPA or by any of the other PATHRAE programs. By law these results must be retained by all three of the parties involved for a minimum of seven years.

In February 1999 EPA issued a revised research rule that permitted the unlimited use of phosphogypsum for research as long as you had no more than 7000 pounds in your laboratory at one time. In the original rule EPA allowed you to have only 700 pounds in a three story laboratory building having nine labs in total. Under the new rule you could have 7000 pounds in each of the nine labs

for a total of 63,000 pounds in the building and still not have a significant risk to the researcher.

I would like to quote one of EPA's justifications for the rule change as reported in the Federal Register of February 3, 1999:

"Third, EPA revised the assumption on the number of hours a researcher spends in the laboratory from 4000 hours down to 1000 hours per year. The value of 4000 hours that was used in the 1992 rulemaking exceeded by 100% the typical occupational year of 2000 hours. The value of 1000 hours was judged to be a more realistic estimate." This will give you some idea of our level of confidence in EPA's risk estimates.

We have continued to do phosphogypsum research despite the EPA's rule and have determined that there are a number of applications that could be quite beneficial.

One that is most interesting is the use of phosphogypsum in municipal solid waste landfills to speed the decomposition of the waste. In many landfills decomposition slows or stops entirely soon after the waste is covered because the anaerobic bacteria quit working because they do not have an energy source. These bacteria are capable of decomposing either nitrate or sulfate to obtain the energy they need to work at optimum speed. By replacing the soil used as cover material at the end of each day with phosphogypsum it is possible to create ideal conditions for bacterial growth in the landfill.

Bench and pilot plant scale testing have been completed and a full scale demonstration is planned at the Brevard County landfill to start as soon as the EPA grants an exception to the rule. Using phosphogypsum in this manner enables the landfill operator to recover at least 40% of the volume of the landfill within five years or to put it another

way, you would have to build half as many landfills in the future. A secondary benefit is that the landfill leachate contains no heavy metals because they are precipitated as insoluble sulfides. The Florida DEP has put their seal of approval on this project but the EPA has yet to grant an exemption to the rule after more than a year. You would think that the regulators would encourage efforts that offer so much benefit but it never seems to work that way. Another demonstration project is now planned at PCS at White Springs. This project will produce glass from phosphogypsum with sulfur dioxide as a by product. The glass will be used for structural products such as tile, roofing tile, etc. Risk analysis for these products show that even when using Bone Valley derived phosphogypsum tiles, you could use tiles on the floor, all walls and the ceiling in a room and the risk would be far less than the maximum risk EPA considers acceptable.

Louisiana State University has been investigating using a mixture of phosphogypsum, fly ash, and cement to produce a solid material that could be used in marine environments as riprap, oyster culch, etc. The oyster culch is a hard solid material, like coarse aggregate that the young oysters can attach to and begin to grow. In the past oyster shells were used for this purpose but regulations have restricted the use of shells. LSU has demonstrated that using phosphogypsum in his manner does not introduce any undesirable contaminants into the marine environment or into the marine food chain. If this material can be produced at a competitive price, it could find wide spread marine applications.

There is no doubt that there are many practical and economical uses for phosphogypsum and that there is an amply supply on hand to last for a very long time. We will continue our efforts to have it recognized as a valuable raw material asset for the state of Florida and we hope to be able to offer you a more encouraging report the next time this subject comes up for discussion.

# Uses of Mined Phosphate Lands to Treat Surface and Waste Water

Peter J. Schreuder  
Schreuder, Inc.

## Abstract

This project involves the purification of reclaimed and excess surface waters by treatment through natural processes on reclaimed lands previously mined by phosphate mining companies. As a result of the mining process, the phosphate companies leave behind open mine pits, clay settling areas (CSA) and tailing sand deposits (TSD). The companies are required to reclaim the mined areas as land and lakes, wetlands, and/or pasture and agricultural lands. The basis for this project is the assumption that the natural systems, in particular wetlands created on reclaimed CSA\*s followed by tailing sand filtration, will remove any organic, inorganic and microbiological contaminants in surface waters and waste waters, resulting in water that will meet drinking water standards. To store the water, the project envisions recharge to the underlying Floridan Aquifer, a regionally extensive limestone confined ground-water system, capable of storing and transmitting large quantities of water. The projects in support of this concept have been funded by the Florida Institute of Phosphate Research. Studies have been completed on the radiological and microbiological aspects of the percolation of water through tailing sand deposits. This paper will describe in detail the ongoing pilot project now being tested at a site owned and operated by Florida Power Corporation and will present the results of the studies conducted so far.

Additional Keywords: Water supply development, natural treatment, surface water diversion, ground water recharge.

## Description of the Basic Concept

The project involves the purification of reclaimed and surface waters by treatment through natural processes on reclaimed lands previously mined by phosphate mining companies. As a result of the

mining process, the phosphate companies leave behind open mine pits, clay settling areas (CSA) and tailing sand deposits (TSD). The companies are required to reclaim the mined areas as land and lakes, wetlands, and/or pasture and agricultural lands.

Mined lands can provide a surface water storage area to receive and mix the water prior to a controlled release to a CSA wetland. The release of the water from the storage reservoir is controlled by the treatment capacity of the wetland to remove nutrients and organic and inorganic contaminants. From the treatment wetland, the water flows by gravity into recharge basins, created on the top of an area containing mine cuts filled with a deposit of tailing sands. From the recharge basins, the water can percolate vertically downward to a series of horizontally placed filter pipes installed in the lower part of the filled-in mine cut. The water exfiltrating from the TSD's is expected to meet drinking water standards. This water can then be recharged into the underlying Floridan Aquifer, which are the water-bearing zones in a highly permeable limestone formation, for storage, subsurface conveyance and later recovery. A detailed schematic diagram of the concept of the natural purification of surface waters is presented in Figure 1.

## Prior Research

There is a practical example in the area of the capacity of wetlands on CSA's to improve water quality. A Waste Water Treatment Plant (WWTP) on the south end of the City of Lakeland is discharging advanced secondarily treated waste water to a CSA on the Bonnie Lake mine property. Data have been collected on the concentrations of the NPDES parameters at the inflow and outflow stations for several years. The results indicate a reduction in total nitrogen, phosphorus, and biochemical oxygen demand (BOD) of 95, 75, and 85 percent respectively. Tailing sand is the result of an industrial process, and therefore may impart chemicals to the water percolating through it. Schreuder, Inc. conducted a 7.5 month long bench test investigation into the degree of dissolution of radio-nuclides

from the residual phosphatic minerals into the water in contact with the tailing sand during the filtration phase (Schreuder and Dumeyer 1998). Another concern was the capability of the tailing sand filter to remove bacterial and viral microorganisms. A second bench test investigation was conducted to evaluate that capability (Schreuder, Dumeyer and Stark 1998).

### **Location of the Study Area**

The area in which the concept could be implemented is within the boundaries of the Bone Valley Phosphate Mining District located in the middle of the Florida peninsula along the Gulf Coast. Florida Power Corporation (FPC), a subsidiary of Progress Energy Corporation, has purchased 8,800 acres of previously mined land from IMC Phosphates, Inc. and the Estech Corporation, just to the south to southwest of the City of Bartow in Polk County (Figure 2). The site is known as the Hines Energy Complex (HEC). FPC is planning to build a total of 6 units of 500 megawatt electric power generating facilities. At present the first unit is operational and preparations are underway for the construction of the second unit, Powerblock #2. The pilot project has been built at the FPC's HEC property.

### **Description of Pilot Project**

The Boards of Directors of the Florida Institute of Phosphate Research (FIPR) and the Southwest Florida Water Management District (SWFWMD) approved funds to build a pilot project and conduct tests for two years on the effectiveness of the proposed water treatment system. In the pilot study, water from three distinctly different sources will be pumped into a wetland on one side, the water will be then pumped from the other side of the wetland onto a tailing sand deposit and the filtered water will be extracted from the tailing sand deposit through a set of horizontal drains. One source will be treated effluent from the WWTP of the City of Bartow; another source will be storm water collected in FPC's water cropping areas which are reclaimed CSA's on their property; the third source will be water from FPC's power plant cooling pond.

A schematic diagram of the construction is shown in Figure 3. The wetland will be an area along two ditches which are connected on the west side. The northern ditch was formerly part of the Noralyn mine recirculation system. The southern ditch is shallower and collects toe drain water from the SA-8 CSA. A sand tailing filter has been constructed in tailing sand that was deposited in the northwest corner of the SA-8 CSA. A schematic cross sectional diagram of the construction of the tailing sand filter basin is shown in Figure 4.

### **Water Quality Testing Program**

The project design calls for a continuous rate of flow of 135 gallons per minute. During the first stage of the project, the filtered water will be discharged back to the cooling pond. At a later stage of the project the filtered water will be used during the testing phase of the installation of an aquifer recharge well at the site. The testing phase of the project began in May 2001 and will operate continuously for two years during which time water samples will be collected on a weekly and quarterly basis as shown in Figure 5. The samples will be analyzed for all the chemical, physical and microorganism parameters listed in rule number 62-550 [Florida Department of Environmental Protection (FDEP)]. A summary of the parameters is listed in Table 1.

### **Goals and Objectives of the Study**

The goal of the study is to assess the practicality of the natural treatment concept and the feasibility of implementing large scale projects. The SWFWMD is considering including this concept in their long term regional water-resources management plan, which calls for the diversion, treatment and recharge of surface water during high flow periods for storage in and conveyance through the underlying Floridan (predominantly limestone) Aquifer. In addition the immediate objective of the pilot study is to gather the necessary water-quality information to obtain a permit from the FDEP for the installation of a well to recharge the filtered water directly into the underlying Floridan Aquifer. If this phase of the research is successful, FPC will proceed in constructing a much larger sys-

tem to treat and recharge up to 5 million gallons per day into the Floridan Aquifer for storage until needed as water to make-up for water losses from the cooling pond system during low rainfall periods.

### Initial Results

The initial results focus on two important areas: 1) physical performance of the system; and 2) water quality. What is of particular interest is the performance of the filter basin. In the design phase Schreuder, Inc. took great care in attempting to eliminate or at least minimize the concentrations of suspended solids in the water pumped from the wetland, in particular the presence of algae. The suspended solids will reduce percolation efficiency in the tailing sand filter basin. To suppress these concentrations, we designed and built the wetland pump intake system in such a manner as to minimize the penetration of sunlight into the water. To date it appears that the construction of the wetland pumping station is meeting its goal of minimizing total suspended solids (TSS).

### Physical Performance of the Natural Treatment System

*Flow Measurements:* Between the start of the test on May 3<sup>rd</sup> and our last field measurement on October 11<sup>th</sup> a total of 34 million gallons (MG) was pumped from the filter basin (FB) to the cooling pond (CP), at an average rate of 161 gallons per minute (GPM). Similarly, a total of 30 MG was pumped from the wetland to the FB at an average rate of approximately 140 GPM, which is very close to the design rate of 135 GPM.

*Filter Basin Percolation Performance:* During each field visit, Schreuder, Inc. personnel take photographs of each of the quadrants in the filter basin. These photographs are taken from the same location to enable comparisons from one time period to another. The purpose of this photographic record is to obtain a qualitative record of the expanding wetted area on the surface of the filter basin as an indication of the clogging potential of the sand surface. The total surface of the actual wetted areas

was found to be 8,700 feet<sup>2</sup>. The average water application rate is 140 gallons per minute. Thus, the actual average vertical hydraulic conductivity (Kv) is calculated to be 3.1 feet/day. Using this vertical hydraulic conductivity rate, the “theoretical” percolation over the entire 49,400 feet<sup>2</sup> surface area of the filter basin could be as high as 1.1 million gallons per day or 0.98 million gallons per day per acre.

### Water Quality Testing

The sampling program began on May 3<sup>rd</sup>, 2001 with a complete analysis at the cooling pond, wetland, and sand filter basin. The complete analysis included all the parameters in the following groups: Primary Inorganic Compounds, Volatile Organic Compounds, Pesticides and PCB's, Secondary Drinking Water Standards, Group I, II, and III Unregulated Organic Contaminants, Gross Alpha, Turbidity, Fecal and Total Coliform, Unionized Ammonia, and Total Phosphorus. In addition, *Cryptosporidium* and *Giardia* were sampled on May 7<sup>th</sup>, 2001 at the sand filter basin. No *Cryptosporidium* or *Giardia* were detected in the filter basin, however, heavy debris, rare algae, and nematodes were noted. After this, a performance analysis was performed weekly in May and June; and biweekly in July and August.

*Field Parameters:* During every visit to the site, field parameters were measured including pH (Figure 6), Temperature (Figure 7), Specific Conductivity (Figure 8), Iron, and Turbidity. The field results for Iron have remained fairly constant with about 1.5 to 2.5 ppm in the filter basin (with one exception) and about 0.5 ppm in the wetland and the cooling pond. Field turbidity has also remained fairly constant at about 0-5 JTU in the filter basin and the wetland (except for one reading of 15 JTU in the wetland), and about 25-35 in the cooling pond.

*Sample Analyses:* The results for the chemical analyses of the water samples from the cooling pond (the source), the wetland and the filter basin included Total Nitrogen (Figure 9), Total Phosphorous (Figure 10), and Sulphate (Figure 11). The performance analyses included Iron (Figure

12), Manganese (not shown), Fluoride (Figure 13), Total Alkalinity (not shown), Total Suspended Solids (not shown), Gross Alpha (not shown), and Total and Fecal Coliform (Figures 14 and 15).

### Observations

The pilot filtration system is currently in the first eight-month cycle of the operational and testing phase. Water from the cooling pond is being used to supply the linear wetland system during the first cycle. Subsequent cycles will use water from the effluent supply and the storm water source. Because we are at the beginning of a two year sampling program, no solid conclusions can be drawn. Some observations, however, are appropriate. It is encouraging that the filtration capacity of the filter basin has remained so high. Because the tailing sand contains a fair amount of iron associated with the sand, it is not surprising to see the iron concentrations that have been observed. The reduction in nutrients is encouraging. The concentration of fluoride above standards is quite likely associated with the tailing sand deposits. The presence of detectable total and fecal Coliform bacteria in certain samples likely reflects the introduction of organic matter into the vertical stand pipes by bird activity. The annular spaces at the top of the stand pipes have since been sealed to prevent further introduction of microbial contaminants. Of interest is the reduction of the concentrations of sulphate. "Sulphur" smells have been noted at the wetland pumping stations leading to the question if a desulphurization process is at work in the wetland system. The reduction in specific electrical conductivity as well as the reduction in sulphate could also be caused by the onset of the rainy season.

In closing it can be concluded that the value of the pilot project lies in the continued monitoring of the water quality. Initial results are, however, very encouraging.

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1) Paper presented at: THE FERTILIZER INDUSTRY ROUND TABLE CONFERENCE; held at the Trade Winds Resort in St. Petersburg Beach on October 22 through 24, 2001.

II. Peter J. Schreuder, M.Sc., Certified Professional Geologist and President of Schreuder, Inc., a Water-Resources & Environmental Consulting Firm, 110 West Country Club Drive, Tampa, Florida 33612. (813) 932-8844; schreuder@worldnet.att.net

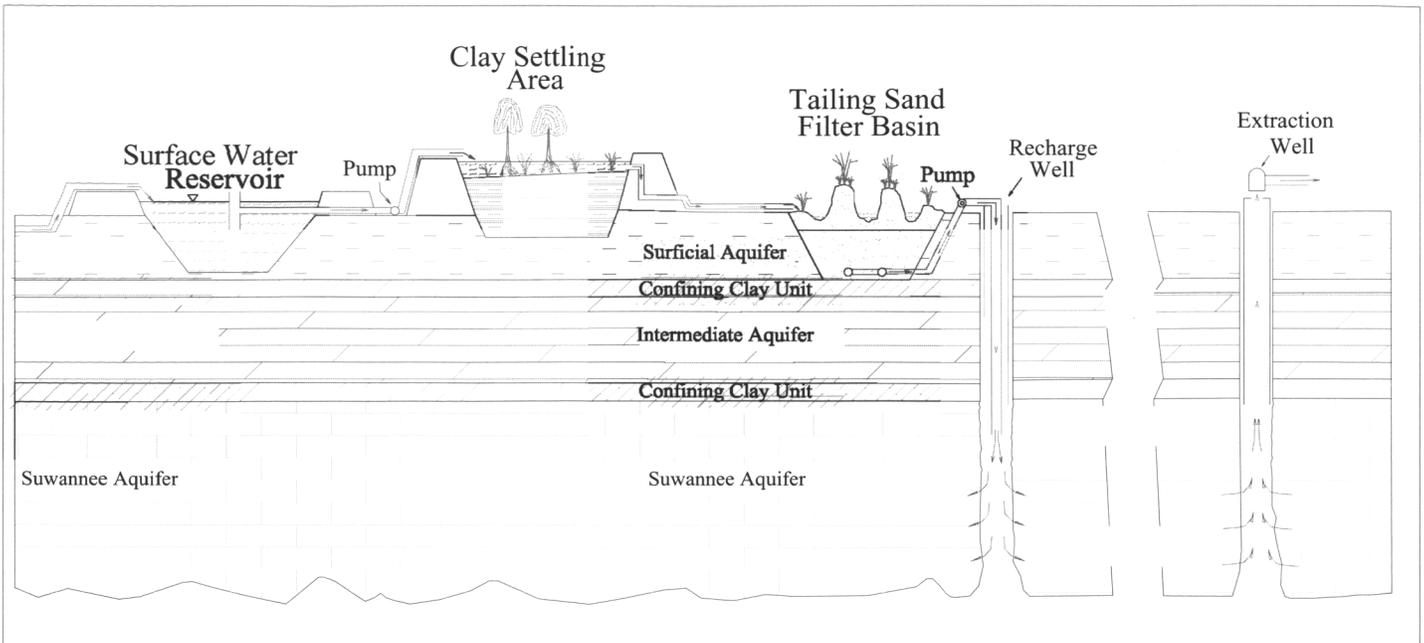


Figure 1. Schematic Diagram of the Integrated Wetland Treatment, Sand Tailing Filtration, and Aquifer Recharge Concept.

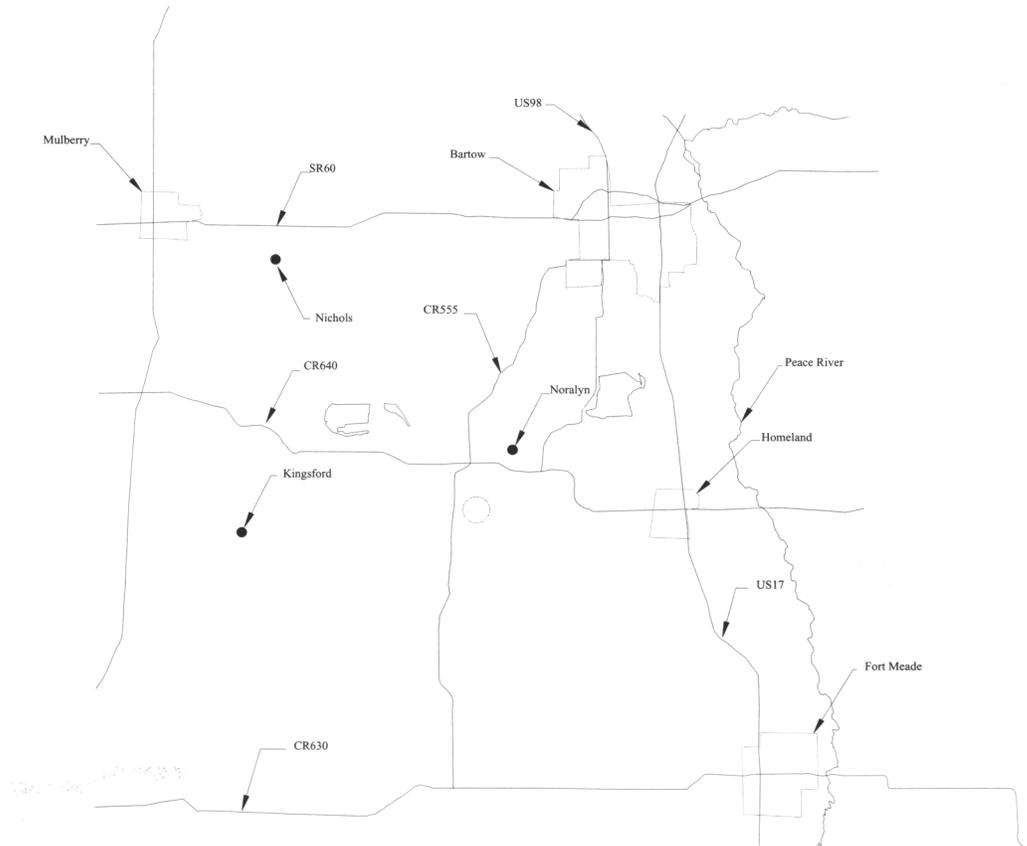


Figure 2. Project Location

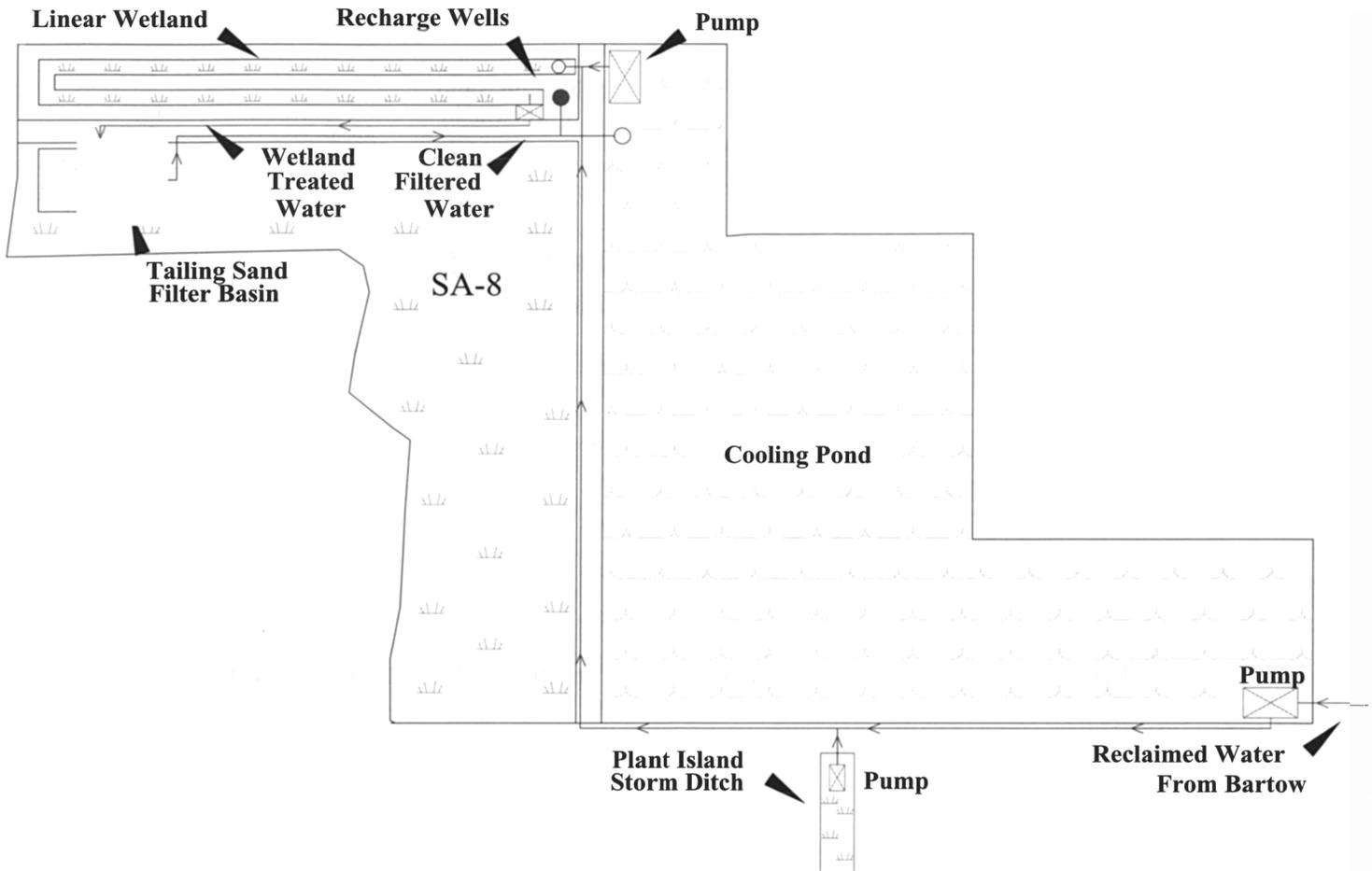


Figure 3. Schematic Construction Diagram of Pilot Project.

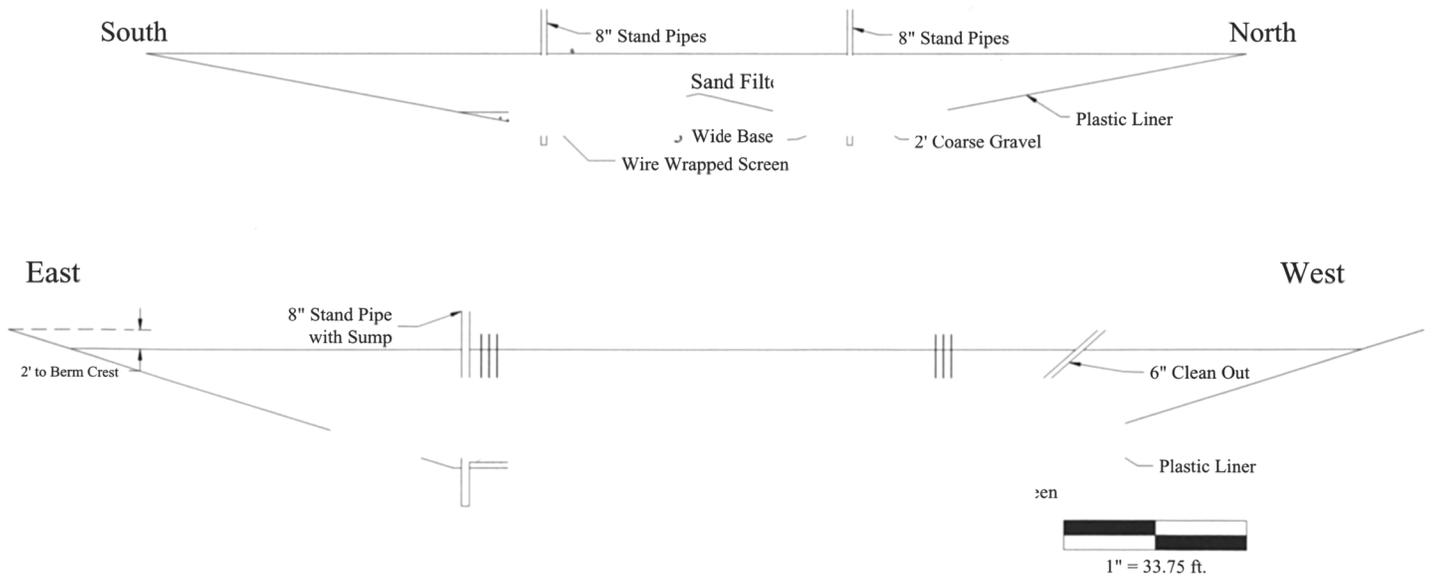
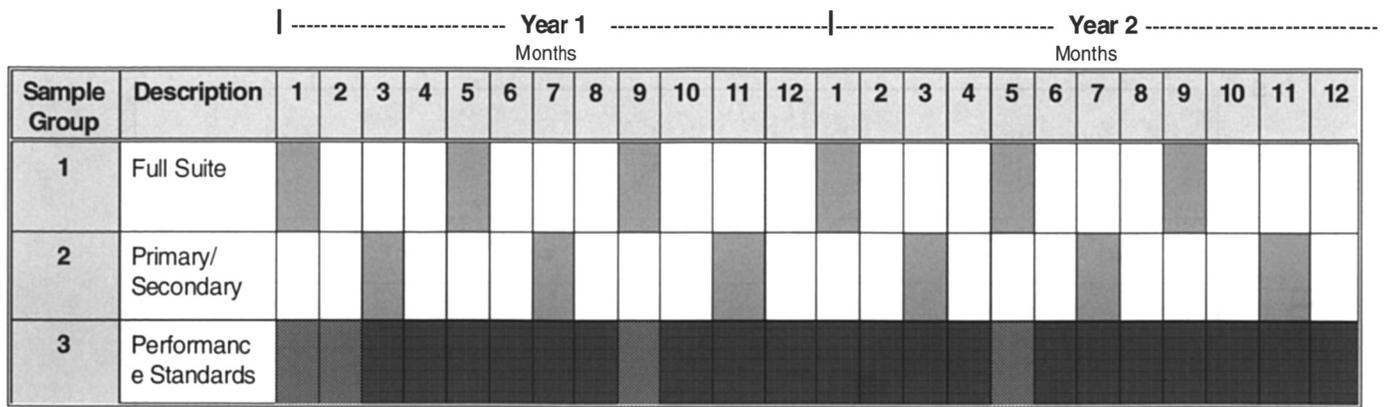


Figure 4. Cross Section of Tailing Sand Basin Construction.



Sampling Cycle/Water Source: | #1 - Cooling Pond | #2 - Storm Water | #3 - Effluent |

Legend	
█	one sample in indicated month
█	weekly sampling
█	bi-weekly sampling

Figure 5. Schedule of Water Quality Testing Program.

### Bi-Weekly

- Primary Drinking Water Standards
- Secondary Drinking Water Standards
- Gross Alpha
- Turibity

### Quarterly

- Pesticides
- Group I, II, and III Unregulated Organic Contaminants
- Volatile Organic Compounds
- Trihalomethanes
- Cryptosporidium
- Giardia

Table 1. Water Quality Sampling Program Parameters

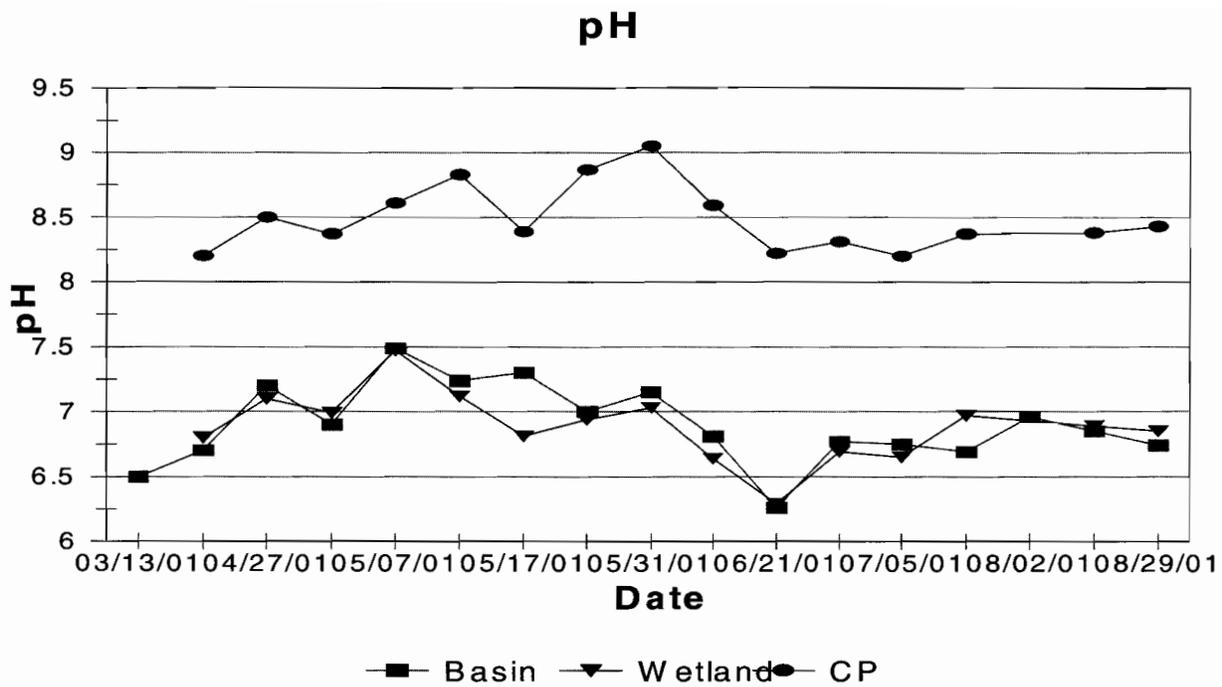


Figure 6. pH of the Basin, Wetland, and Cooling Pond Waters.

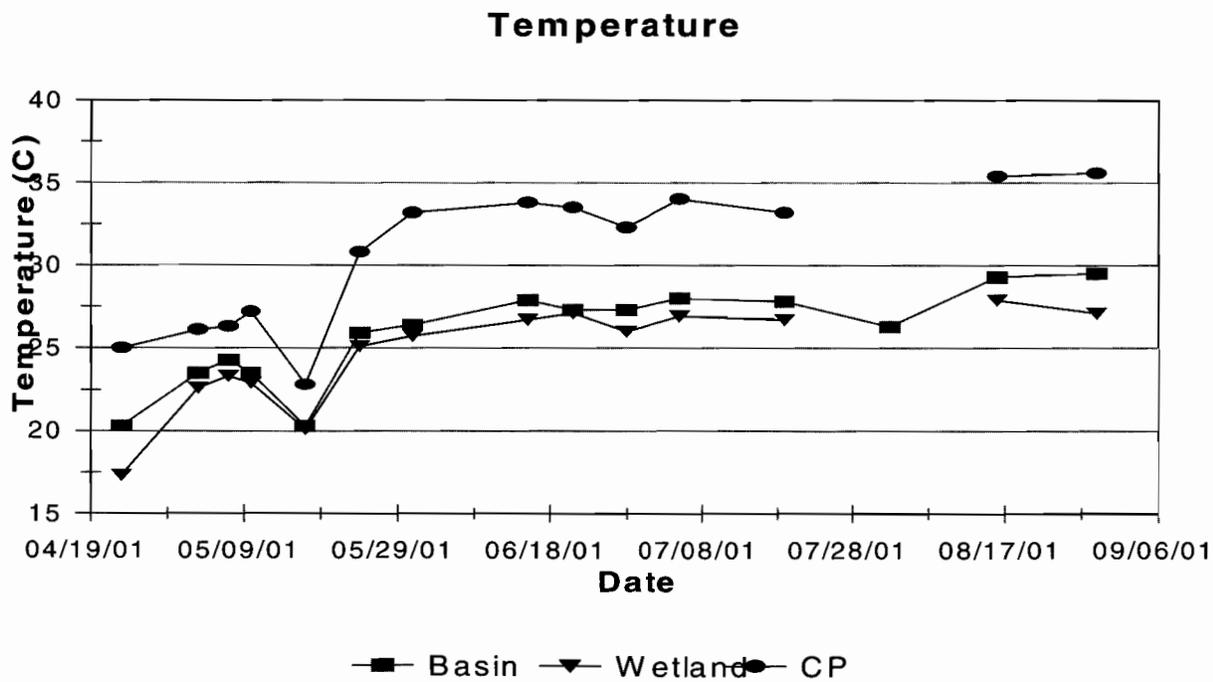


Figure 7. Temperature of the Basin, Wetland, and Cooling Pond Waters

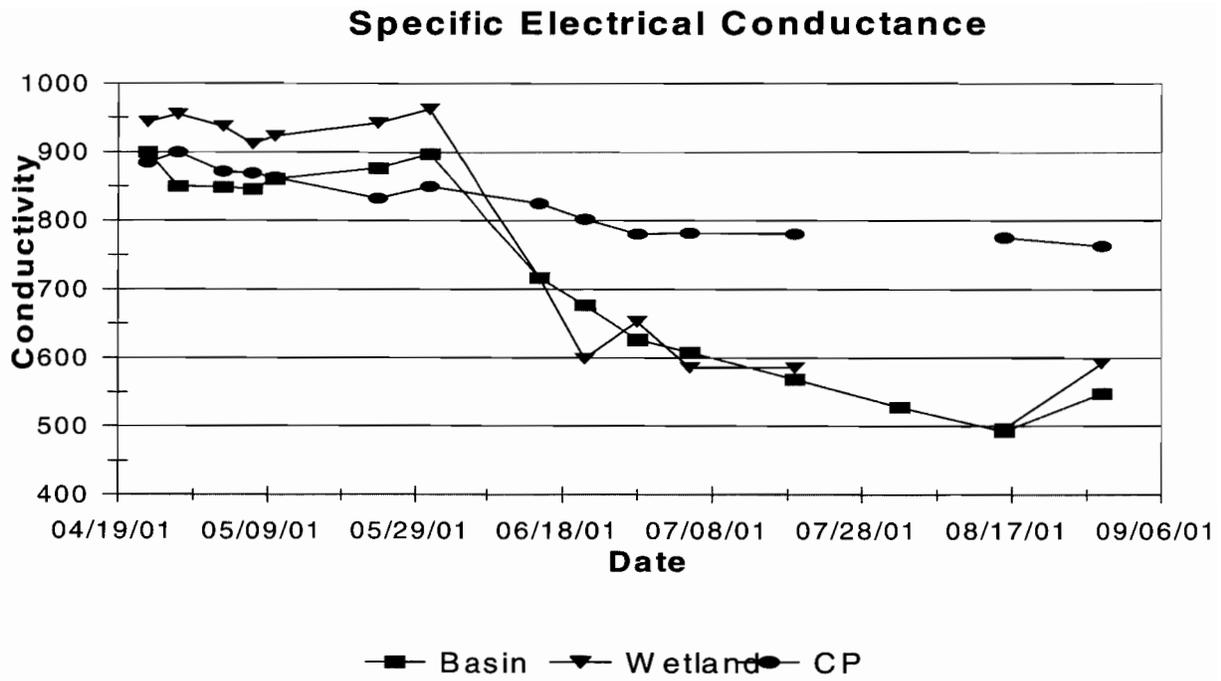


Figure 8. Specific Electrical Conductance of Basin, Wetland, and Cooling Pond Waters.

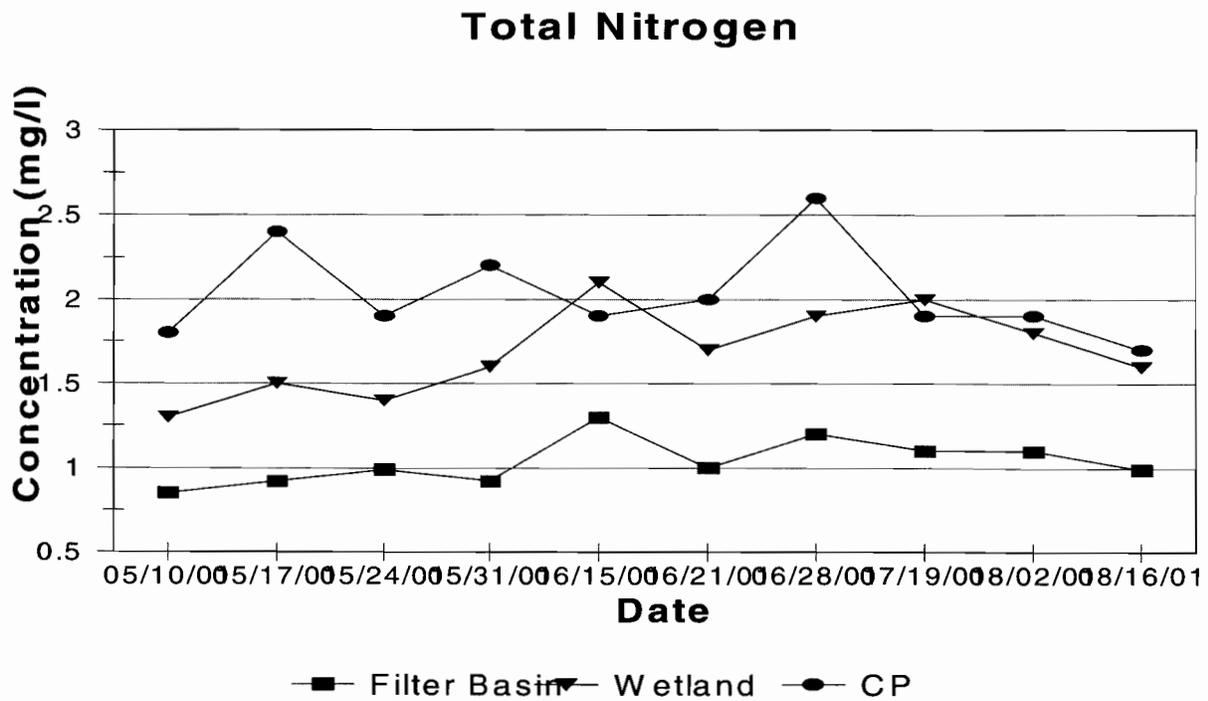


Figure 9. Concentrations of Total Nitrogen in the Basin, Wetland, and Cooling Pond Waters.

### Total Phosphorus

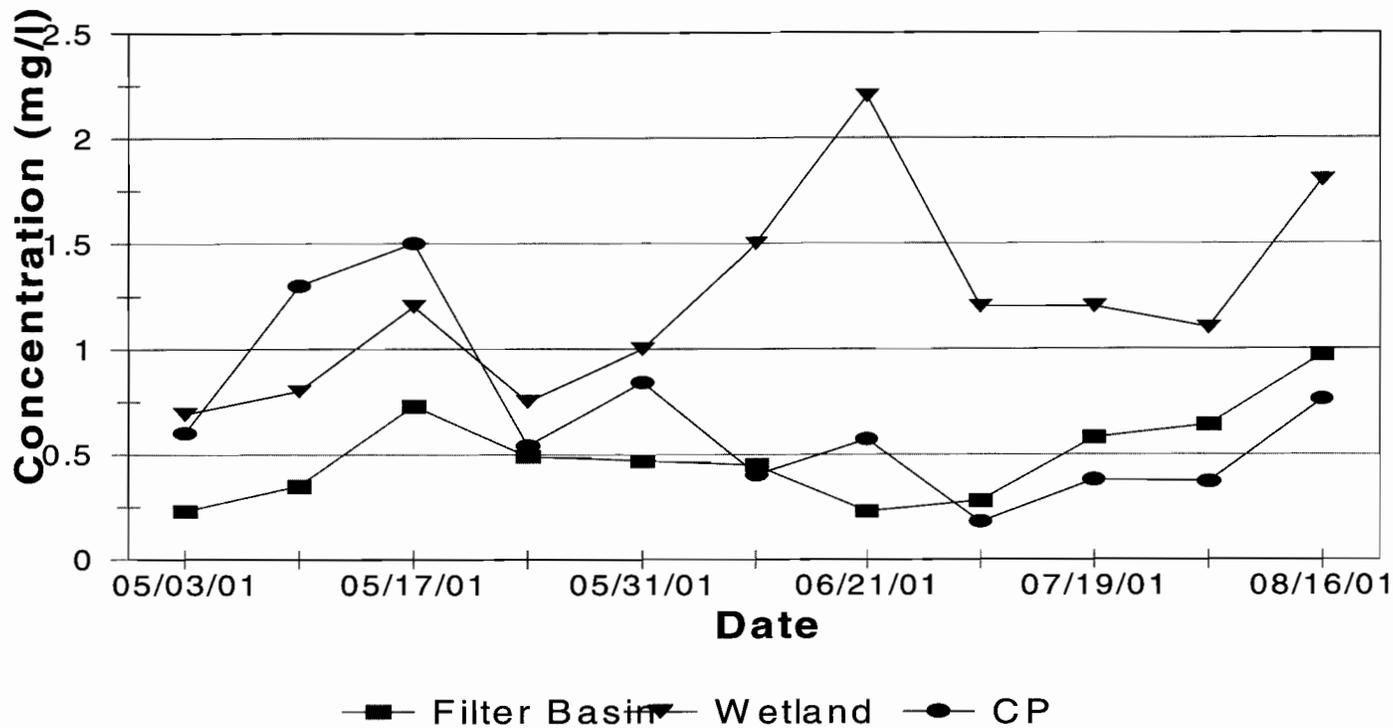


Figure 10. Concentrations of Total Phosphorus in the Basin, Wetland, and Cooling Pond Water.

### Sulfate

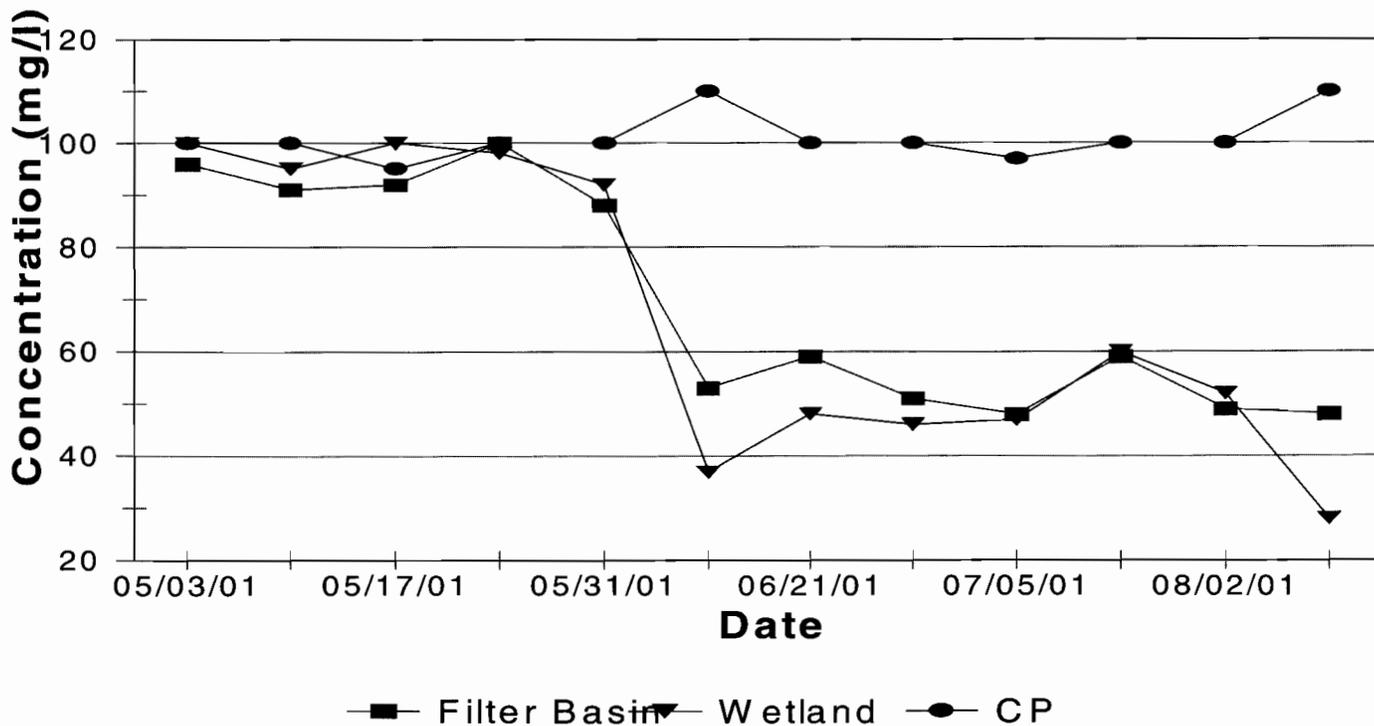


Figure 11. Concentrations of Sulfate in the Basins, Wetland, and Cooling Pond Waters.

## Iron

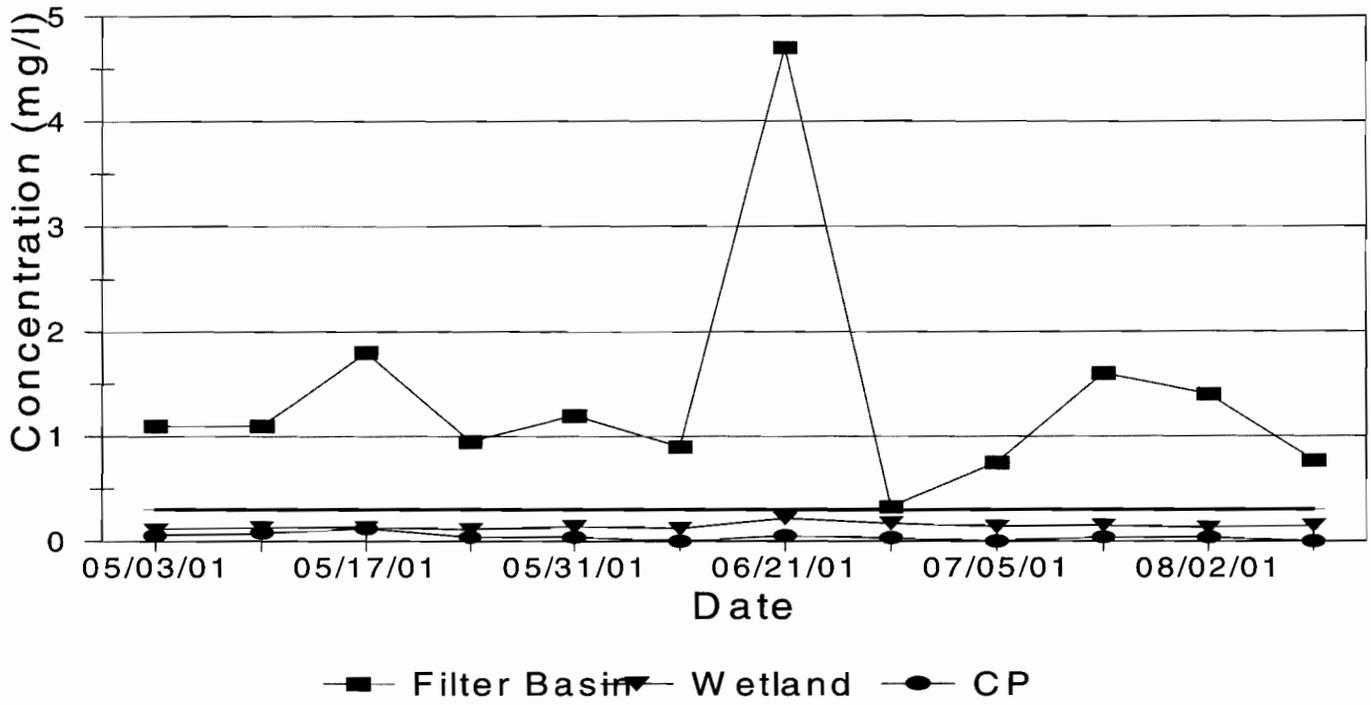


Figure 12. Concentrations of Iron in the Basin, Wetland, and Cooling Pond Waters.

## Fluoride

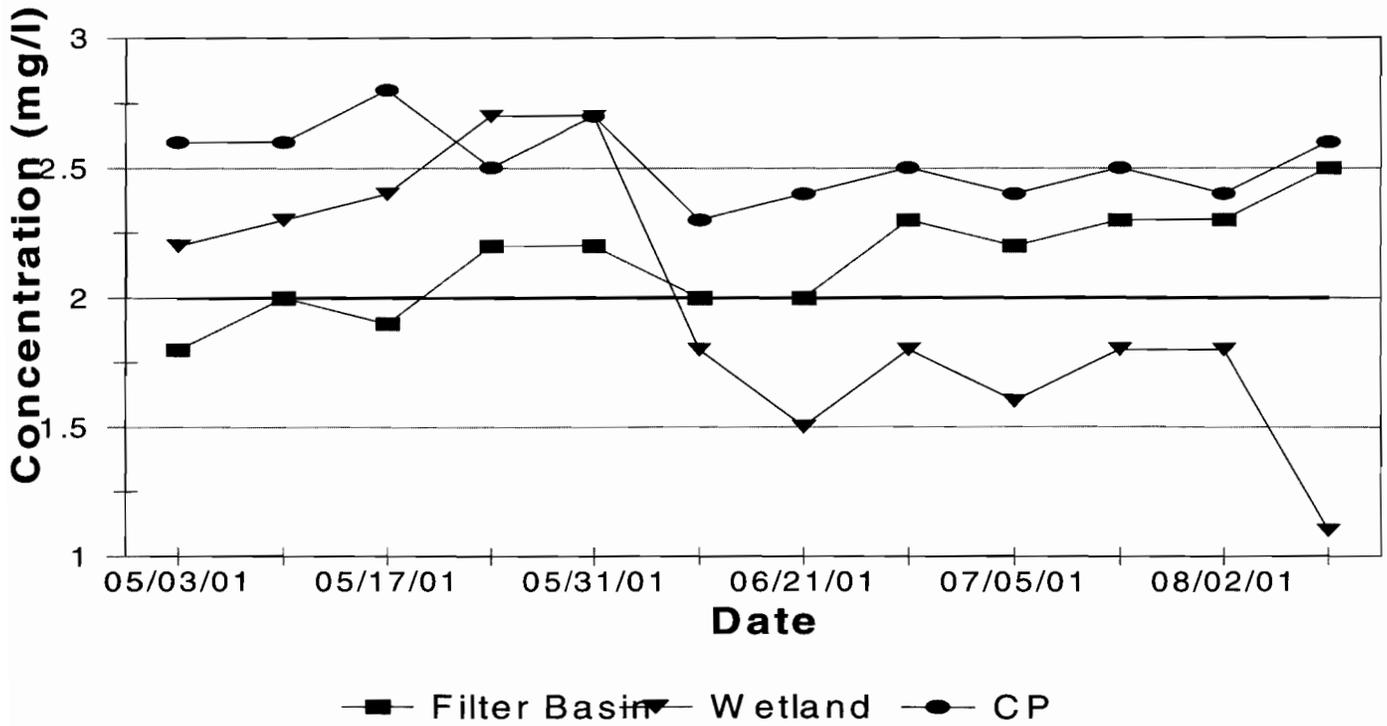


Figure 13. Concentrations of Fluoride in the Basin, Wetland, and Cooling Pond Waters.

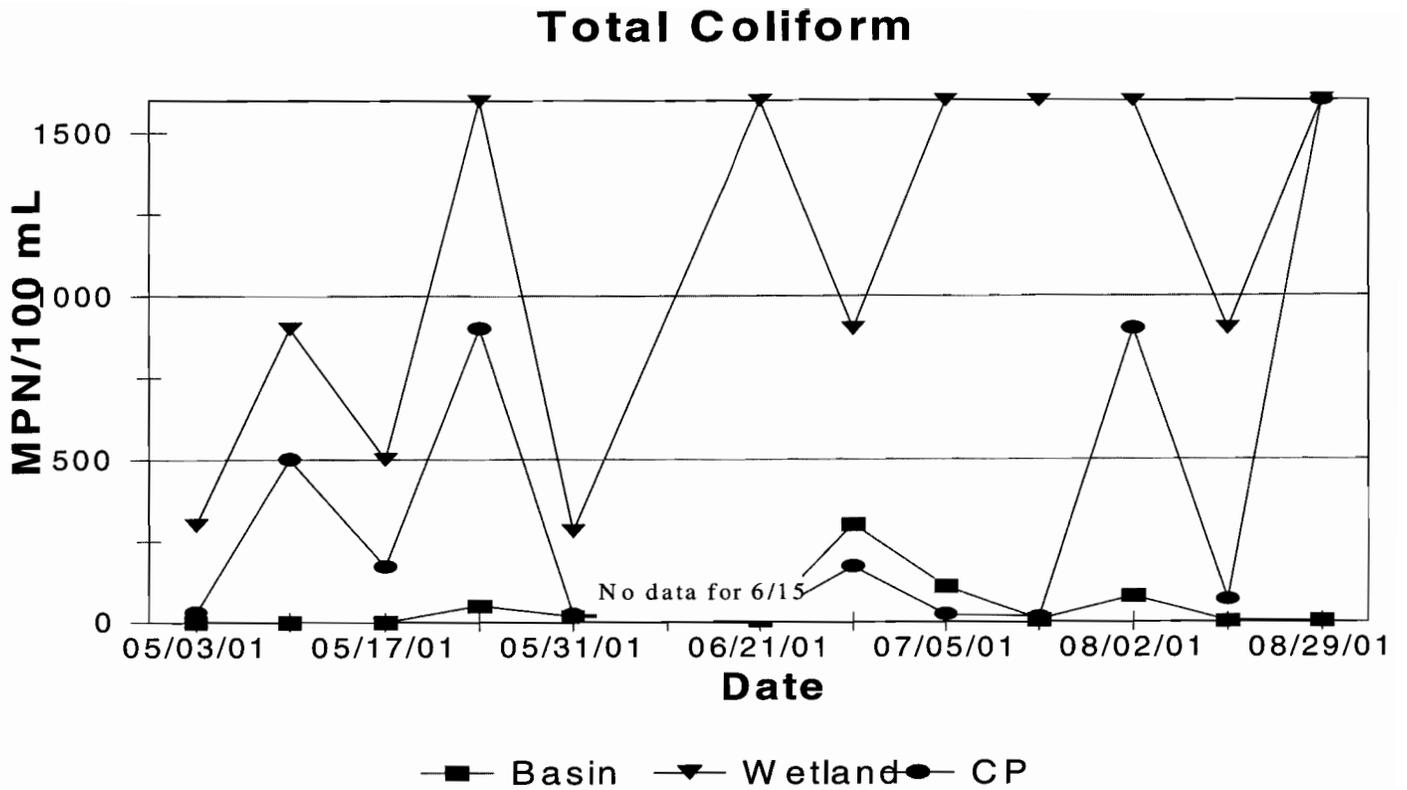


Figure 14. Total Coliform Concentrations in the Basin, Wetland, and Cooling Pond Waters.

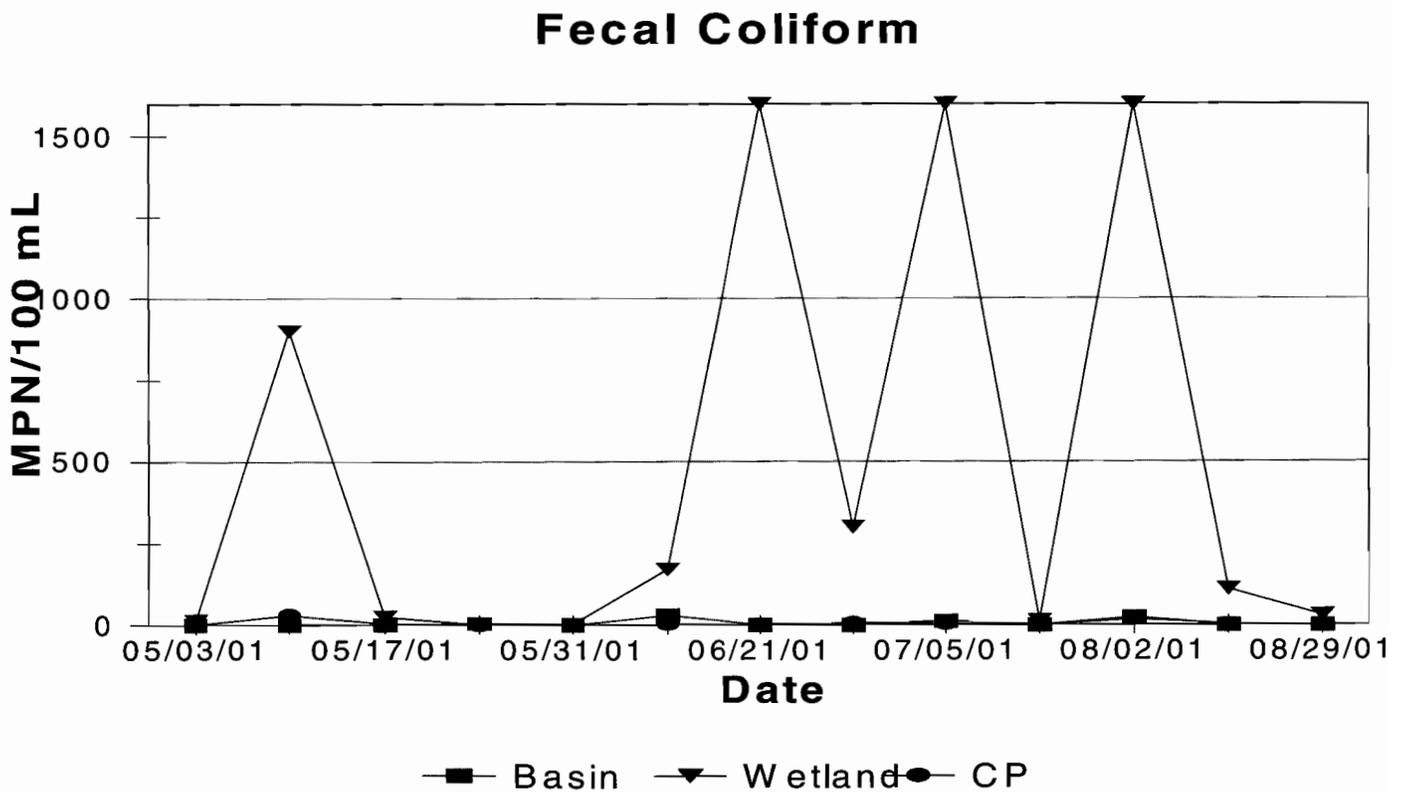


Figure 15. Fecal Coliform Concentrations in the Basin, Wetland, and Cooling Pond Waters.

**Select Radionuclide (Ra-226, Pb-210)  
and Metals (Cd, Hg, Pb) Dose Potential  
from Consumption of Central Florida  
Phosphate Mineralized Region  
Freshwater Fish Protein**

*Brian Kent Birky*

**Florida Institute of Phosphate research**

Mining of the Central Florida phosphate mineralized region has resulted in the creation of many reclaimed and unreclaimed lakes used heavily by local citizens for recreational fishing as well as a small commercial fishery for Tilapia. The Florida Institute of Phosphate Research authorized this study in order to determine if there was an elevated risk of exposure to radionuclides or toxic metals as a result of consuming local fish from lakes on previously mined lands. The study lakes comprised four unreclaimed lakes, two reclaimed lakes, three natural lakes (control lakes), and one man-made reservoir. Since this study was targeted to determine human dose potential, only edible portions of legal size fish were utilized. Six species, largemouth bass (*Micropterus salmoides*), bluegill (*Lepomis macrochirus*), shellcracker (*Lepomis microlophus*), speckled perch (*Pomoxis nigromaculatus*), catfish (*Ictalurus sp.*), and tilapia (*Tilapia sp.*), were sampled. Over 430 data points were collected for each analyte group. Metals (cadmium, lead, and mercury) were digested and analyzed by inductively coupled plasma mass spectroscopy and cold vapor atomic absorption spectroscopy. Radionuclides (lead-210 and radium-226) were determined by direct emanation spectroscopy.

Cadmium was observed sporadically and at low levels. Cadmium appears to be an insignificant contaminant for this area. Mean lead levels were generally an order of magnitude below the U. S. Fish and Wildlife 1984-1985 study observation of 0.110 g/g. Only 20% of all samples exhibited measurable levels. Of these 87 samples almost half (45%) were confined to two lakes (one impacted and one natural). Lead in fish flesh is thus not a widespread or significantly elevated

problem within the study group. Mercury was widely distributed above 0.005 g/g. At 84% positive results, all lakes were affected by mercury to some degree. Natural lakes exhibited a higher trend for mercury than impacted lakes. Bass and bluegill from one natural lake were the most impacted species with a potential for elevated risk to above average consumers, particularly subsistence fishers and pregnant women. Radionuclide data did not exhibit significant differences between natural or impacted lakes. Values observed were within historical expectations and do not appear to indicate an elevated risk from consumption.

### **Introduction**

#### *Background and Statement of the Problem*

During the late 1990s, public sector officials within Central Florida (Polk County Health Department – Radiological Health, Florida Fish and Wildlife Conservation Commission) and researchers (Florida Institute of Phosphate Research) observed an increasing public concern, both at public meetings and through individual inquiries, regarding the risk of health effects from heavy metals and radionuclides consumed from locally harvested freshwater fish. Local citizens are aware of the role of radionuclides in local mining. Thus, while extensive research on local agricultural and range food products was performed in the 1980s and early 1990s, radionuclide consumption data for finfish from local sources was very limited. Concurrently, numerous other studies were focusing on the growing problem of toxic metals (particularly mercury) in both fresh and saltwater finfish from around the world. As interest grew in the subject of toxic metals contamination of consumable fish, local interest in local data also grew.

### **Literature Review**

One of the earliest studies on the subject of radionuclides in finfish from the study area was *Radium-226 in Central Florida Aquatic Organisms* by Upchurch, and others, from the University of South Florida Geology Department (Upchurch, 1981). Upchurch noted then in his literature search that there was a paucity of literature regarding radionuclides in freshwater indigenous species. He also noted most exposure studies

focused on artificial isotopes from the nuclear industry rather than on naturally occurring isotopes. The Upchurch study focused on the effects of radium-226 uptake on the local ecology. The study was not designed to evaluate human risk from consumption.

In 1985, FIPR Publication No. 03-018-029, *Ecological Considerations of Reclaimed Lakes in Central Florida's Phosphate Region* (Boody IV, and others) was an extensive ecological study of sixteen lakes, natural and impacted. This study greatly expanded the radium-226 work of Upchurch, 1981. However, with the exception of *Micropterus salmoides*, most of the fish species observed were of less than 5 samples per lake. Both studies observed radium bioaccumulation but no biomagnification in fish. With the exception of *Micropterus* in Boody IV, and others, 1985, both studies suffered from low sample numbers (average < 5) per species. Neither study looked at toxic metal accumulation in fish flesh.

FIPR has funded several studies that have collected significant data on local lake sediment and water column metals. Boody IV, and others, 1985, and its follow up study, FIPR Publication No. 03-046-052, *Water Quality in Central Florida's Phosphate Mineralized Region*, 1987, quantified cadmium, lead and mercury levels in sediments and waters of sixteen lakes, four of which are also the focus of this study. Mercury was found in the water column and sediments of all the study lakes; cadmium and lead were observed to a much lesser extent.

## Methodology

### *Sampling and Sample Handling Methodology*

The overwhelming majority of sampling employed electroshock methods. The Florida Fish and Wildlife Conservation Commission provided a vessel, electroshock equipment, and manpower to collect the samples. Gill nets, cast nets and hook and line were also utilized. Captured fish were immediately placed into iced coolers and kept iced until prepared for final shipment to the test laboratories. Not all species were available at the lakes. Speck-

led perch (*Pomoxis nigromaculatus*) was particularly difficult to obtain.

The panfish specimens too small to fillet (approximately 80%) were scaled, finned, beheaded and butterflied. Thus, most of the panfish did include some bone material. This was not considered an undesirable positive bias for these fish since many people enjoy deep-frying and eating these fish whole. The small bones fry crunchy and are fully edible.

## The Study Area

Ten lakes in a four county area were observed for this study. These central Florida counties are Hillsborough, Polk, Hardee and Manatee. Since the primary purpose of the study was to determine potential risk by human consumption of popular fish, efforts were concentrated to locate lakes that were:

- (a) generally accessible to the public,
- (b) previously studied for metals and/or radionuclides, and
- (c) likely to contain the fisheries of interest.

Of the ten lakes selected, four are considered "control" lakes. These are either natural or impoundments with no recent (< 25 years) history of mining in a mix of rural and urban settings. The remaining six lakes are a mix of mined reclaimed or unreclaimed lakes in rural and urban settings. These were considered to be "impacted lakes."

## Metals Analysis Methodology

### *Sample Preparation*

Fish tissue was digested using USEPA Method 200.11 (EPA 1991). This preparation uses a strong base, tetramethylammonium hydroxide (TMAH), to solubilize the tissues overnight at 60°C. The following day nitric acid addition and digestion at 100°C is performed to complete the process and provide an acidic digest for analysis. These digests are diluted to appropriate volume prior to analysis.

## Sample Analysis

Elemental analysis for cadmium and lead was performed by Inductively Coupled Plasma Mass Spectrometry (ICP/MS) and followed EPA Method 200.8 (EPA 1994). Mercury analysis was performed by cold vapor atomic adsorption following EPA Method 245.6 (Modified). The method modification consisted of using EPA Method 200.11 as the technique for the digestion of the tissue samples. This modification was validated by demonstration of appropriate recovery of mercury from standard reference materials. In each case, instruments were calibrated against a commercial standard (Inorganic Ventures, Lakewood, NJ) serial dilution to produce a multipoint calibration. The calibration was evaluated for linearity and then verified against a secondary commercial standard (Environmental Resource Associates, Arvada, CO). Sample analysis proceeded batchwise with quality control samples including segmenting batches at 10% frequency.

Routine quality control analyses were applied to assure data quality. Quality control samples included blanks, sample spikes, sample duplicates, continuing calibration checks and the analysis of a standard reference material: DORM-2, Dogfish Muscle Tissue (National Research Council of Canada, Ottawa, Ontario). Data collected from the various quality control samples indicated that data quality is acceptable.

## Radioactivity Analysis Methodology

### *Sample Preparation*

The majority of the samples were filleted and sealed in 500 ml Marinelli beakers by the field crew at the time of sampling (shock system). These sealed samples (vinyl electrical tape used to seal lids to beakers) were marked with the date collected, a lake code, a species code and the net weight of the fish filets. The samples were then transported to the radiation laboratory in the Environmental Engineering Sciences Building at the University of Florida; and were kept cool for the two weeks equilibrium build-up time.

## Sample Analysis

The EG&G Ortec Gamma Analysis program was used to analyze the gamma spectra produced by each sample. The program reported results of peak analysis for seven distinct peaks of interest: three short lived radon daughter peaks (295, 353, and 609 keV) that are reflective of the radon-222 in equilibrium with radium-226, the characteristic peak for Pb-210 at 46 keV, and the characteristic peak for Cs-137 at 662 keV. Once the standard and background runs were available, a spreadsheet calculation for these radionuclides with all appropriate efficiencies, time of counting, net weight, etc. was developed and used for the entire set.

## Statistical Analysis

### *Methodology*

The Analysis of Variance (ANOVA) was utilized to test the normal distribution and evaluate the homogeneity of sample variance. Student's T-test was used to compare the difference between pairs of samples. Two levels of significance were tested. Significant difference at  $p = 0.99$  was utilized to provide maximum protection against concluding there were differences where none exist (error type I, where  $p < 0.01$ ) and significant difference at  $p = 0.95$  was utilized to prevent missing more subtle differences (error type II, where  $p < 0.05$ ).

Data transformations were limited to assigning a value of zero to metals results less than the instrument detection capability and assigning a value of one-half the MDC for radionuclide negative counts (non-detects). Radionuclide data for thorium-234, potassium-40, and cesium-137 was collected but not analyzed within the scope of the study.

## Results

Cadmium was found in only a few fish samples (8 out of 436) in two of the ten lakes (Table 2). No significant differences were observed between natural and impacted lakes.

Lead was present in all tested fish species from all tested lakes. Bluegill, bass, shellcracker, and speckled perch did not exhibit significant differences between lakes. Catfish from two impacted

lakes were higher than in other lakes. Tilapia from one natural and two impacted lakes were higher than in other lakes. Catfish and tilapia exhibited significantly higher lead quantities (at  $p > 0.95$ ) than the other species. Two impacted lakes were significantly lower (at  $p > 0.99$ ) and another impacted lake significantly higher (at  $p > 0.95$ ) than the other lakes. No significant differences were noted for natural vs. impacted or urban vs. rural.

Mercury was present in all species in all lakes. Tilapia are lowest (at  $p > 0.99$ ), speckled perch and bass are highest (at  $p > 0.99$ ) in mercury between species. A natural lake was lowest (at  $p > 0.99$ ) and another natural lake was highest (at  $p > 0.99$ ) between all lakes. Natural lakes are significantly higher (at  $p > 0.99$ ) than impacted lakes. Rural lakes were significantly higher than urban lakes (at  $p > 0.99$ ).

Radium-226 was found in all species in all lakes as expected from a ubiquitous naturally-occurring radionuclide. Radionuclide data was analyzed with non-detects given as one-half the MDC. This is a conservative approach designed to prevent a negative bias from levels too low for a practical count in the time available. Thus for radium the caveat is given that 215 of the 434 samples (50%) were below detection. At  $p < 0.99$ , bluegills were highest from two impacted and one natural lake, and catfish were highest from a natural lake. At  $p > 0.95$ , tilapia from two natural and one impacted lake were lowest. Between lakes, one natural lake was lower (at  $p > 0.99$ ) than the others. Bass were the lowest species (at  $p > 0.95$ ) while shellcracker and bluegills were the highest (at  $p > 0.99$ ).

Lead-210 was found in all species in all lakes, again, as expected. Lead-210 is a daughter product of gaseous radon-222 decay and precipitates from the ambient atmosphere. For lead-210 the caveat is given that 232 of the 434 samples (53%) were below detection. Bluegill from three impacted lakes were higher than from the other lakes (at  $p > 0.99$ ). Catfish from two impacted lakes were higher than from the other lakes (at  $p > 0.99$ ). Bass were significantly lower (at  $p > 0.95$ ) than the other

species. When all data were considered, no significant differences (at  $p > 0.99$ ) were observed between natural and impacted or urban and rural lakes. (See Table 2)

## **Consumption Dose Assessment**

### *Cadmium*

The Agency for Toxic Substances and Disease Registry (ATSDR) has derived a minimum risk level (MRL) for a chronic oral exposure to cadmium. It is based on a NOAEL (no observed adverse effect level) of 2.1 g/kg/day using an uncertainty factor of 10 for variability in the human population. The MRL is 0.2 g/kg/day or 14 g/day for 70 kg person (ATSDR 1997). Since the current average dietary cadmium intake for adults in the U.S. is about 0.4 g/kg/day (Gartrell and others 1986), Americans currently do not have a good margin of safety with respect to cadmium intake.

Eating fish from the study lakes will not add substantially to this dietary cadmium intake or related health risk. In the two lakes where a total of eight fish were collected with measurable cadmium concentrations, four of the eight were catfish. The catfish also had the highest cadmium level detected in this study. Based on the FDA Pennington Diet fish consumption rate for the average adult of 20.6 g/day, an adult eating catfish from this lake only (maximum individual) would add 0.33 g/day dietary cadmium intake. This is about 2% of the minimum risk level for a 70 kg (154 pound) person.

### **Lead**

The principal adverse health effects of lead can be related to concentrations of lead in the blood. Correlation of data on blood lead concentrations and various health effects define those effects that begin to become apparent in human populations with blood lead concentrations in the range of 10-15 g/dL. More pronounced effects are seen as blood lead concentrations increase above this range. The Centers for Disease Control and Prevention (CDC) considers children to have

an elevated level of lead if the amount in the blood is 10 g/dL or more (ATSDR 1997).

Consider the adult consuming tilapia, the study species with the maximum lead concentration from Lake Hunter, the study lake where the maximum mean concentration occurred. The blood lead contribution from this source is 0.05 µg/dL. The risk of adverse health effects is minimal for blood lead levels less than 10 µg/dL.

Under these conservative constraints, only children eating tilapia at nearly the adult consumption rate might be at risk for exceeding the limits. This by itself would not be sufficient to increase the risk of adverse health effects. This table assumes a typical rate of lead ingestion from other sources. It is not applicable when elevated lead ingestion from other sources is known or suspected.

### **Mercury**

The EPA has advised states to use the screening value of 0.6 ppm mercury in fillets as a criterion to evaluate their fishable waters (EPA 1995). Even though the mercury concentration in some fish collected exceeded this EPA screening value of 0.6 ppm (g/g), the average level for fish from each study lake did not exceed this level. Largemouth bass collected from Lake Walk-in-Water had the highest mean mercury concentration with a value of 0.575 g/g.

The Florida Department of Health is the state agency with the responsibility for health advisories related to mercury concentrations in fish flesh. A health advisory may be issued for a lake by the State Health Officer if testing demonstrates a mean mercury level above 0.5 ppm in the fish flesh. The mean mercury concentration for bass collected from Lake Walk-in-Water during this study meets this threshold. Since we have only this data set, and several of the higher values were qualified, additional data sets should be collected to determine if a health advisory is warranted.

Consumption of largemouth bass, the study species with the maximum mercury concentration,

from Lake Walk-in-Water, the lake where the maximum mean concentration occurred, will result in a mercury intake of 11.85 g/day. This is well below the minimum risk level of 18 g/day (evaluated for the 60 kg woman). The consumption of fish from the impacted study lakes results in a lower mercury intake than from the natural study lakes.

### **Radionuclides**

A recommended limit of 0.25 mSv (25 mrem) per year for specific human-made sources is now widely regarded as necessary for protection of public health (for example, NCRP 1993). Another way to evaluate dose is the dose constraint concept, in which it is assumed that doses which are equivalent to or less than background doses are less than the variation in background doses and are appreciably less than standards will make an undetectable and acceptable contribution to total risk. The annual average total effective dose equivalent from natural sources is frequently estimated at 300 mrem/year. Of this value approximately 16 mrem is estimated from the average diet.

Even under worst-case comparison, the dose difference between natural lakes in the phosphate mineralized region and phosphate mining impacted lakes in the region is a fractional number (less than one mrem). Dose attributable to fish from mined lakes versus natural lakes is, therefore, insignificant in this data set.

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**Table 1. Sampled fish.**

Common Name(s)	Scientific Name(s)
Bass	<i>Micropterus salmoides</i>
Bluegill	<i>Lepomis macrochirus</i>
Catfish (channel catfish, white catfish)	<i>Ictalurus punctatus</i> <i>Ictalurus catus</i>
Shellcracker (Red Ear Sunfish)	<i>Lepomis microlophus</i>
Speckled Perch (Black Crappie)	<i>Pomoxis nigromaculatus</i>
Tilapia	<i>Tilapia aurea</i>

**Table 2. Fish flesh concentrations by species and contaminant.**

	<b>Total No. Fish Sampled</b>	<b>No. Lakes Above DL<sup>1</sup></b>	<b>Maximum • g/g wet weight</b>	<b>Mean • g/g wet weight</b>	<b>Standard Deviation</b>
<b>Cadmium</b>					
Bass	100	0/10	BDL <sup>2</sup>	NA	NA
Bluegill	100	1/10	0.018	<0.001	0.002
Catfish	75	2/10	0.102	0.004	0.017
Shellcracker	20	0/2	BDL	NA	NA
S. Perch	59	1/7	0.029	0.001	0.005
Tilapia	82	1/9	0.029	<0.001	0.003
<b>Lead</b>					
Bass	100	5/10	0.048	<0.001	0.006
Bluegill	100	5/10	0.077	0.002	0.010
Catfish	75	8/10	0.140	0.010	0.021
Shellcracker	20	1/2	0.094	0.007	0.023
S. Perch	59	3/7	0.055	0.002	0.008
Tilapia	82	7/9	0.378	0.019	0.060
<b>Mercury</b>					
Bass	100	10/10	0.762	0.192	0.165
Bluegill	100	10/10	0.164	0.034	0.035
Catfish	75	10/10	0.225	0.028	0.040
Shellcracker	20	2/2	0.116	0.033	0.026
S. Perch	59	7/7	0.711	0.114	0.164
Tilapia	82	8/9	0.022	0.005	0.006
<b>Ra-226</b>					
Bass	100	10/10	0.100	0.015	0.016
Bluegill	100	10/10	0.332	0.046	0.056
Catfish	74	9/9	0.392	0.029	0.054
Shellcracker	20	2/2	0.065	0.030	0.020
S. Perch	60	7/7	0.193	0.029	0.033
Tilapia	80	9/9	0.223	0.022	0.003
<b>Pb-210</b>					
Bass	100	10/10	0.500	0.105	0.082
Bluegill	100	10/10	0.950	0.188	0.161
Catfish	74	9/9	1.740	0.187	0.258
Shellcracker	20	2/2	0.160	0.086	0.039
S. Perch	60	7/7	1.100	0.189	0.238
Tilapia	80	9/9	1.235	0.144	0.160

I. Number of lakes above the instrument detection level (DL) over the number of lakes where fish samples were obtained. DL (• g/g or ppm): Cd = 0.018, Pb = 0.007, Hg = 0.005

II. BDL = Below Detection Level



# Tuesday, October 23, 2001

## Session IV Moderator:

Walter J. Sackett, Jr.

### Modern Regional Granulation in Eastern Europe

*Charles Formisani*

A.J. Sackett & Sons Company

### Introduction-granulation In The Usa

The development and construction of regional granulation facilities, capable of 10 to 20 tons per hour production, occurred during the period of 1900 to 1950 when fine or powder form and liquid fertilizer ingredients became available in the market place. i.e. standard Potash, ammoniating solutions, run-of-pile Single Super Phosphates, Sulfuric Acid, Ammonium Sulfate etc. In order to safely handle and apply these amorphous or non-granular materials to crop fields, they had to be combined into a dry, granular product that allowed for efficient and uniform spreading on crop lands. Regional drum granulation facilities were the answer for combining the non-granular raw materials available into a safe, dry, granular and thus spreadable material.

These early granulation plants typically produced Single Super Phosphate for use as the phosphorus source material in the granulator. Powder or run-of-pile Single Super Phosphate, standard grade Potash, Sulfuric Acid and ammoniating solutions were the normal raw materials used for making a granular homogeneous NPK in a drum granulator. Most of the small regional plants produced granulated NPKs of relatively low analysis. Triple 8 or Triple 10 were generally the maximum 1:1:1 ratio concentrations possible. Grades such as 3-9-18, 8-8-8, 4-12-12 etc. were common.

1:1:1 ratio granular fertilizer was typically used as a "shotgun cure-all" when soil requirements had

not been precisely identified by soil or tissue testing. Flexible, precision formulation in very small batches was not practical. Early regional granulators typically produced only 3 or 4 grades and these grades were expected to cover all crop requirements.

The 1960s saw the beginning of and rapid adoption of the mechanical blending industry. It was only possible to produce a uniform product with mechanical blending when high quality, granular ingredients were readily available. Granular DAP and MAP, granular Potash, prilled Ammonium Nitrate and granular Ammonium Sulfate were typical ingredients used to make blended fertilizers. Later granular urea became readily available and today is the most common nitrogen used in blended fertilizers.

As mechanically blended fertilizers increased in popularity, the regional granulators that were making lower analysis products began to disappear or became manufactures of specialty product needed in niche applications. By the 1980s, broad agriculture was predominantly served by mechanically blended fertilizers or by straight materials.

Low analysis, homogeneous ammoniated products were relegated to specialty applications, lawn and garden products and in markets needing bagged fertilizers etc. Homogeneous NPKs could not compete with the flexibility of grades and the lower unit cost of blended fertilizers, particularly against the large volumes used in broad agriculture such as is typical in the midwest and in the Plains States.

Few regional granulation plants still exist in the USA today. Most are located east of the Missis-

sippi river and serve specific needs in a regional geography. These granulation plants exist together with mechanical blending plants. Many grind and granulate limestone and otherwise serve “niche” type markets or requirements, particularly for bagged fertilizers.

### **Europe**

Granulation of NPKs developed in Europe several years before granulation developed in the USA and continues even today as the most common form of fertilizers used in Europe. The European granulated fertilizer business was developed by major companies that build large facilities compared with the regional plants that were built in the USA. Names like BASF, Norsk Hydro, Kemira Oy, Grand Paroisse built granulation facilities capable of producing over a million tonnes per year. Today granulation facilities exist in Western Europe that produce 250,000 tonnes to 2 million tonnes per year.

Mechanical blending is growing in Western Europe but not to the extent that it developed in the USA in the 1970s and 1980s. Europe in general prefers to have all the nutrients and micronutrients contained in each granule. Western Europe has little or no phosphate rock and therefore phosphoric acid and high quality, granular DAP has to be imported from Morocco, the USA, Tunisia or from some factories in Russia. Western Europe has much greater access to uniform sized Ammonium Nitrate, Calcium Ammonium Nitrate, Urea, Potash and DAP or MAP for making blended fertilizers, but acceptance at the farm level has yet to develop. Also, Western Europe prefers NPKs that have at least 1/2 of the nitrogen in the nitrate form. Therefore nitrophos based NPKs are the preferred NPKs. Urea is produced in Europe and particularly in Eastern Europe but ammonium nitrate and calcium ammonium nitrate continue to be the preferred nitrogen whether used as a straight material or in NPKs as the nitrogen source.

Mechanical blending will continue to grow slowly in Western Europe and eventually in Eastern Europe, but not likely to the extent that blending has come to dominate the USA fertilizer industry.

Western Europe has access to the high physical quality ingredients needed for producing quality blends but nonetheless, homogenous products are and will remain the preference. The small cost advantage that exist today in Western Europe between blends and NPKs is not enough to change the attitude of the farmer-consumer.

Eastern Europe has yet to develop much of a mechanical blending following due mainly to the lack of competitively priced, readily available, good physical quality ingredients necessary for producing uniform quality blends. Additionally, the tradition in Eastern Europe is for homogenous materials. As an example, not one granular urea plant exists in Eastern Europe and finding good physical quality ammonium nitrate or calcium ammonium nitrate is nearly impossible. High quality DAP and MAP are available but expensive for local consumers since the export market pays a premium for these ammoniated phosphates relative to what local demand can afford. Additionally large sophisticated spreading equipment common in the USA does not exist in Eastern Europe therefore homogeneity of nutrients in each granule becomes an absolute necessity when used in small or poorly functioning mechanical spreading equipment.

### **Realistic Problems Facing The Fertilizer Industry In Eastern Europe**

When discussing the possibility of incorporating modern techniques of the fertilizer industry into the developing countries of Eastern Europe, several hurdles must be overcome. By modern techniques I am referring specifically to techniques surrounding the manufacture and application of NPK fertilizers. These problems root from a history of very limited formulations, which parallels the limited knowledge of agronomy and soil sampling.

In recent years, technology transfer has allowed developing countries, like Lithuania in Eastern Europe, to open their minds to the possibility of providing optimum nutrients to their soils and crops. The problems they face are based around the

ever-changing infrastructure of their government, economy and trade. The availability of raw materials can change from month to month. Many raw materials in this region come from Russia which bare the burden and influence of it's own internal changes. In addition to the moving target of raw materials, the knowledge of the production of homogeneous NPK fertilizers also complicates the advancement of fertilizer technology. For the purpose of this paper I am using as an example a modern regional granulation plant built in Lithuania by The A.J. Sackett & Sons Company in 2000.

### **Solution**

The ever present need to incorporate homogeneous NPK fertilizers and micro-nutrients into the farming practices of developing countries revisits the need for regional granulation plants which represent several unique features and challenges. The design basis for a plant of this nature is simple. The requirement is a granulation plant which thrives on the uncertainty of the raw material market and the asset of the finished goods. This plant I am describing is one that lives and breathes flexibility while epitomizing simplicity. With the incorporation of modern controls with age-old rotary granulation technology, a level can be met that optimizes both these important traits.

### **Variables For The Granulation Plant**

The idea of flexibility is rooted in the variables that are constantly faced by the fertilizer plant. At the front end of the granulation plant these variables consist of availability, composition and cost of dry raw materials and liquid chemicals. Within plant operation, the knowledge and experience of personnel and management is diverse. The back end involves market needs and storage. All these variables are considered in the design of what we are calling a Modern Regional Granulation Plant.

### **Incorporation Of Design Parameters**

Incorporation of these variables into the process and plant design is a difficult chore. The three main key points in the design are numerous granulation methods, automation, and simplicity. There

are three types of granulation, that when all accessible, can allow for the granulation of almost any combination or single raw material. These types are chemical granulation, steam granulation, and binder granulation.

When chemicals like sulfuric or phosphoric acid are available, chemical granulation can be used with dry raw materials to make several formulations of high analysis fertilizers. This method of granulation has been around since the 1900's and is very well known. Steam granulation can be used to achieve a very favorable product with the right raw materials and when chemicals may not be available. It is also sometimes incorporated into chemical granulation for process reasons. The limitations faced with steam granulation are the agglomeration problems associated with different combinations. By this I mean that there are only so many combinations of NPKs that will bond properly with steam as the binder.

The final and most inclusive type of granulation is that by which a specific binder is used. I am referring to an inorganic binder process, patented by The A.J. Sackett & Sons Company that holds the ability to bind NPK fertilizers as well as single raw materials and organics. This method requires no heat for bonding, i.e. no chemicals or steam. With the availability of these three methods of granulation, variations in raw materials pose no threat for the plant and maximum flexibility is obtained.

### **Automation**

When introducing a new technology into a region, operation of the facility and process can be one of the biggest challenges. With the advancement of control systems in recent years, it is in the best interest of the plant owner to utilize automation in the control of the plant. As with the case study in Lithuania, it was important to automate the basic functions of the granulation plant. Basic functions refer to dosing of liquid and dry materials, monitoring and adjustment of recycle, coating application, and safety. This automation is possible through the use of a PLC (Programmable Logic Control) system with a PC (Personnel computer)

or equivalent type HMI (Human Machine Interface). Because of the nature of this new technology, a complete manual back up parallels the PLC and PC.

### **Simplicity**

As previously mentioned, simplicity is achieved through plant design from basic granulation technology. This technology, uses rotary equipment for agglomeration, drying and cooling, vibrating screens for separating and combines with a standard recycle loop to define the granulation process. A basic process description is as follows:

### **Process Description**

The first step in the process involves loading the raw material hoppers. This is done with a front-end loader into a continuous elevator. The elevator is preceded by a material conditioner to ensure no large lumps enter the system. Depending on the requirements of the blend, the time may be short; therefore bin level indicators are displayed to the driver.

The next step is metered feeding of raw material into the system. Each hopper feeds onto a feeder belt, which will supply each material at the specified rate. The material that requires grinding will be ground at this point. The material is then feed into the screw conveyor, which will feed the main elevator. The elevator will carry the material to such a level that the granulation plant can make optimum use of gravity in its process flow.

From here the material is conveyed into a Pug Mill mixer where water, steam, and binder can be added. At this point, the recycle is added back into the system. Thorough mixing is achieved and seeds are formed prior to granulation. The material is then fed to the granulator through a feeder screw.

The granulator is a rotating drum designed to increase the size of the incoming seed by adding layers during the rolling motion. In this process, densification and roundness also take place. Sparger pipes are located in the granulator for

spraying liquid ingredients and additional binding agents onto or into the bed of material.

From the granulator, the material drops into a rotary dryer where the moisture is evaporated due to convection heat transfer to the material from high temperature co-current air-flow. Generally, incoming material contains up to 15% moisture, which is reduced to a target of 0.5% by the exit. Flights are used in the dryer to induce a curtain motion of the material for better air-flow; hence better drying.

From the dryer, the material drops onto a transfer belt conveyor where it is discarded into a chain elevator and then onto 2 single deck shaker screens. Here, the fines drop out into the recycle screw where they are returned back to the main elevator and to the Pug Mill.

The majority of the material is fed to the cooler via a screw conveyor. The cooler is a rotating drum similar in design to the dryer. The flights allow for proficient cooling by ambient air resulting in an outlet material temperature close to 100°F. Outlet material temperature will vary with the conditions of the air used for cooling.

The cooler discharges into an elevator which discharges onto a final shaker screen where the product and over-size are screened. The on-size material is fed into a coating drum and then onto a belt conveyor and discharged as a final product. The over-size material is coarsely ground and returned to the double deck screen where the fines are returned as recycle and the over-size repeats the process. This balance has been proven to work very effectively for the granulation process.

### **Pc Screen- Flow Diagram**

When running the process through the PC, the Process Flow Diagram appears on the screen where all data can be accessed. The screen appears as follows: (See Figure 1)

In order to start the process equipment, it is necessary to move the mouse over the corresponding

equipment to initialize the stop/start button. There is also a screen with the stop/start buttons for all the equipment. The buttons are interfaced this way to simplify the order of start-up while following the flow diagram.

Upon successful start-up of all process equipment, it is important to focus on the front end of the system. The system used here is a series of hoppers and automatic weigh feeder belts that are controlled from the PLC. The schematic for this system that appears on the computer screen is shown below. (See Figure 2)

Shown here are six hoppers and weigh belts for the main ingredients and two hoppers and weigh belts for micro-ingredients. A cage mill is located below two of the main hoppers for materials that need to be crushed prior to granulation. Before starting the process, the operator will access the Recipe screen to choose which formula will be made. Multiple recipes can be stored and easily modified if assay is off. With a recipe chosen the loader driver can fill the hoppers accordingly. The Recipe screen is shown below. (See Figure 3)

### **Continuous Feed System**

There are several advantages to the automatic feed system and the Recipe function. These advantages include quick throughput change, formula adjustment, and formula change. It is possible to make these changes while the plant is in operation. This entails opening the Recipe Builder screen, making the necessary changes, and updating the system. The PLC will automatically send all new set points out to the corresponding weigh belt controllers and liquid controls. It is also possible to make adjustments by putting an individual loop, like the steam controller, into manual mode and controlling it from the screen separately.

The system is also setup to continuously monitor the plant recycle ratio. This information can be used by the PLC to make automatic adjustments in the amount of liquids fed to the granulator or mixing device. The operator can also input a maximum amount of recycle before the PLC will automatically reduce the amount of raw materials.

The coating system for the final product is also PLC driven. The PLC reads the product flow rate from a weigh device on the product belt conveyor. This signal is put through a formula to determine the necessary amount of coating agent for the production rate at that instant. This result is sent to a control device on the coating supply line to control the flow rate of the coating liquid according to the updated set point. This system is continuous and has proven reliability and cost savings.

### **Plant Monitoring**

The PLC, in addition to its other functions, serves as an overall plant monitoring system also. Information is continuously collected from various points in the process and interpreted by the PLC. Examples are motor amps, burner system parameters, dust collector differential pressures, dry material and liquid flow rates. These parameters can be programmed to alarm, shut down equipment, make adjustments, etc. while at the same time storing trends of raw material usage and manufactured product. (See Figure 4)

### **Operation**

Utilizing the PLC control of the granulation process with a simple interface like a PC or touch screen, the operation of the plant is significantly simplified. The basic operation sequence is:

- Start-up of equipment
- Choose/start recipe
- Keep bins full (level indicators)
- Monitor granulation

With modern control of regional granulation plants, developing countries, like Lithuania, can produce optimum fertilizers unique to their requirements while dealing with the uncertain nature of raw materials. This process gives them the flexibility that makes homogeneous manufacture of fertilizer possible for these countries. Modern controls allow for inexperience in process operation to not destroy the possibility of a manufacturing facility. Lastly, controls enable the plant

to minimize wasted materials and track all trends to make constant improvements.

### **Conclusion**

Available in Eastern Europe are the basic non-granular raw materials necessary for making NPKs in regional type drum granulation systems. Anhydrous ammonia or ammonium nitrate solution, sulfuric acid, standard potash, phosphoric acid, standard ammonium sulfate, powder Map and various types of micronutrient source compounds are available at relatively low prices. i.e. low relative to prices paid for imports or for high quality products that get good prices on the export market. In this environment, Regional Granulation plants make good economic sense. They can serve a very desirable and economic function by converting the non-granular raw materials into a homogeneous, granular NPK that can be used by any farmer regardless of the type of spreading equipment employed (even if spread by hand).

High quality blends are possible only if there is economic access to high physical quality granular materials such as granular DAP, granular Urea, granular Ammonium Nitrate and granular Potash. To a farmer in the old East Bloc, this would be luxury. Regional compound granulation driven by local labor costs and economics can serve the

needs more effectively and cheaper than having to pay the price for high physical quality from of shore or from great distances. Using more localized non-granulated and liquid fertilizer ingredients that are relatively cheap on a “per unit nutrient basis” makes better economic sense for the Eastern European Regional Granulation Plant.

### **References:**

The modern regional granulation plant I have been referencing is currently in its first year of operation in Lithuania and is successful with several formulations of NPK and PK fertilizers sold in the region. Over 30,000 tons have been sold to an ever-expanding market. Examples of sold products are show below.

### **Production Fertilizer**

15-15-15 for Lithuania  
17-9-14 for Lt, Denmark, Germany  
12-11-22 +Na, B for Lithuania  
8-20-30 for Lt, Poland, Latvia  
8-20-30 +B for Poland  
13-10-15 for Lithuania  
8-24-24 for Lithuania  
13-7-22 for Latvia  
17-6-14 – Experimental- Good So Far  
16-20 (P-K) for Denmark and Germany

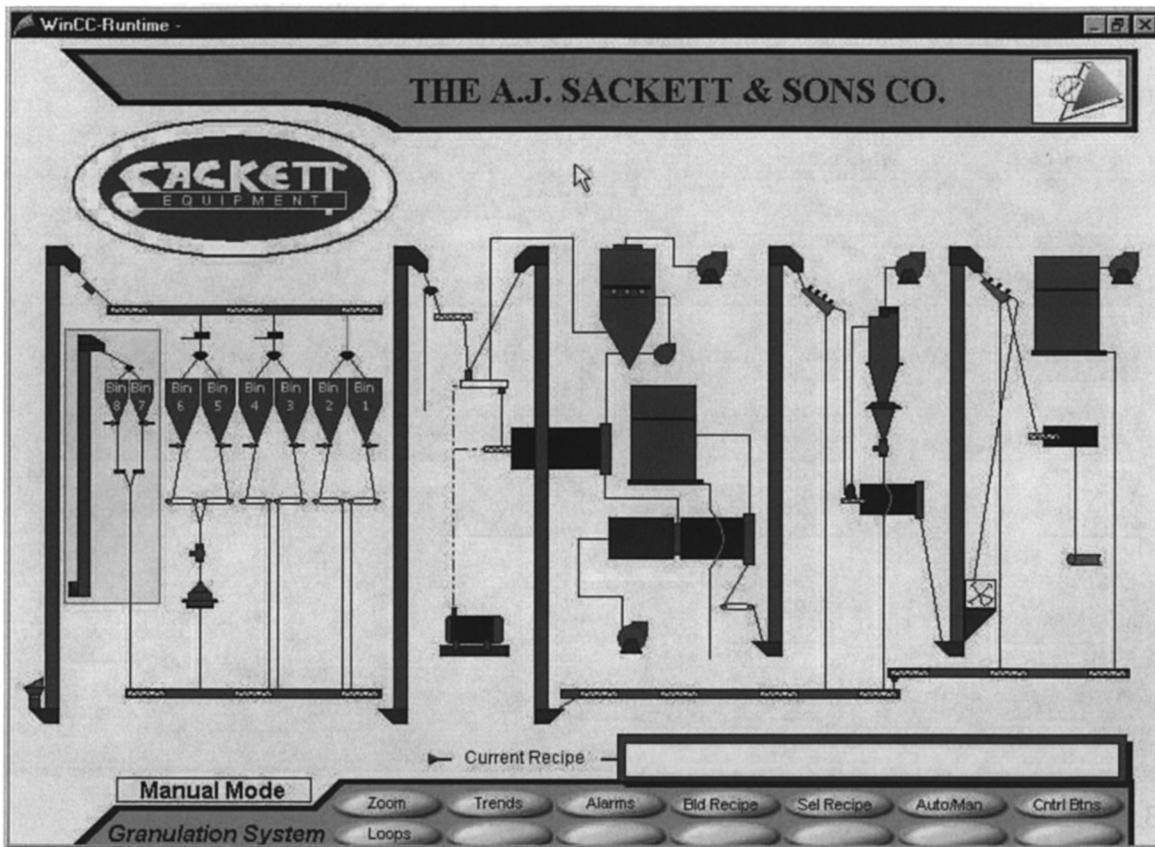


Figure 1.

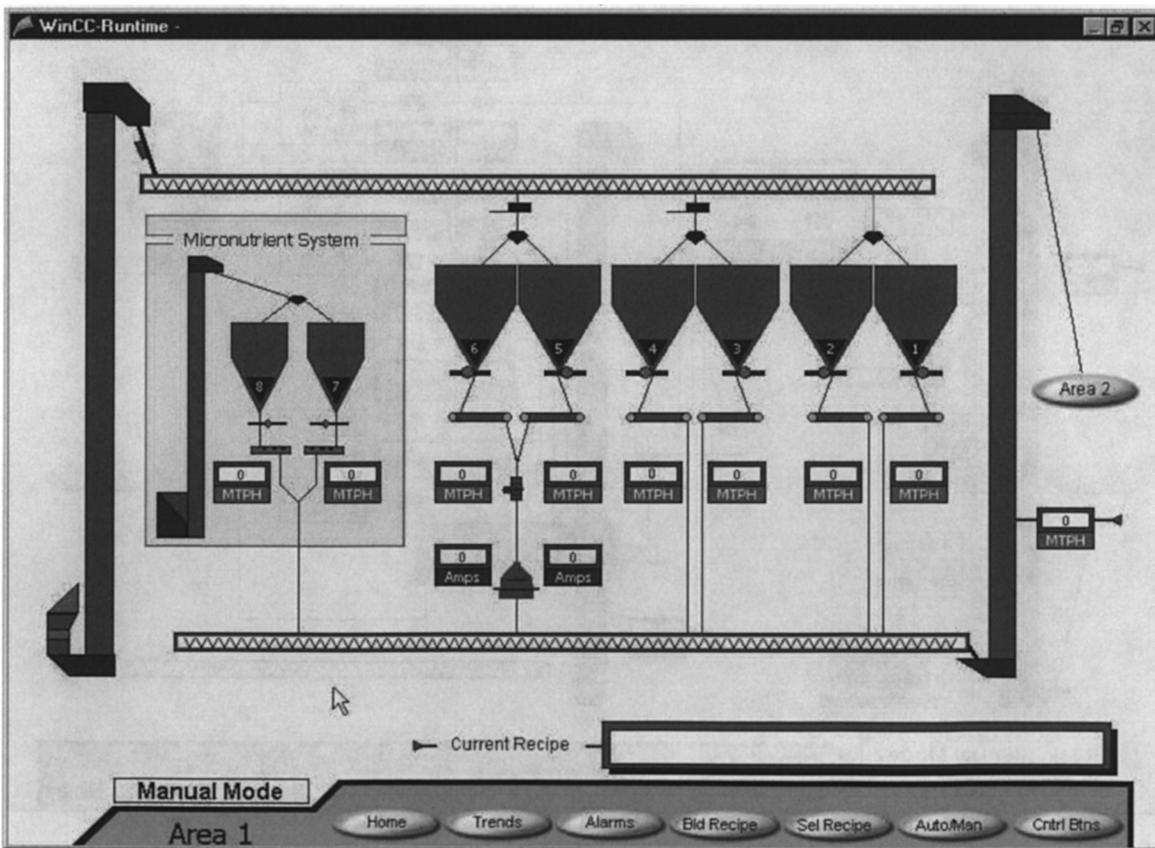


Figure 2.

### RECIPE BUILDER

Return To HMI Tons per hour

Recipe Number  Recipe Name  Go to Recipe Number

Recipe load result

Hopper 1 Product <input type="text" value="Ingredient1"/> Weigh Belt 1 Feed Rate SP <input type="text" value="1.1"/>	Hopper 2 Product <input type="text" value="Ingredient2"/> Weigh Belt 2 Feed Rate SP <input type="text" value="2.2"/>	Hopper 3 Product <input type="text" value="Ingredient3"/> Weigh Belt 3 Feed Rate SP <input type="text" value="3.3"/>	Hopper 4 Product <input type="text" value="Ingredient4"/> Weigh Belt 4 Feed Rate SP <input type="text" value="4.4"/>
Hopper 5 Product <input type="text" value="Ingredient5"/> Weigh Belt 5 Feed Rate SP <input type="text" value="5.5"/>	Hopper 6 Product <input type="text" value="Ingredient5"/> Weigh Belt 6 Feed Rate SP <input type="text" value="6.6"/>	Hopper 7 Product <input type="text" value="Ingredient7"/> Weigh Belt 7 Feed Rate SP <input type="text" value="7.7"/>	Hopper 8 Product <input type="text" value="Ingredient1"/> Weigh Belt 8 Feed Rate SP <input type="text" value="8.8"/>

Mixer Water Amount <input type="text" value="1.200"/>	Acid Amount <input type="text" value="3.400"/>	Granulator Water Amount <input type="text" value="5.600"/>	Dryer Temp SP <input type="text" value="88"/>
Mixer Steam Amount <input type="text" value="2.300"/>	Ammonia Amount <input type="text" value="4.500"/>	Granulator Steam Amount <input type="text" value="6.700"/>	Dryer Alarm Dev % <input type="text" value="9"/>
			Max Reclaim Tons/hour <input type="text" value="10.10"/>

Figure 3.

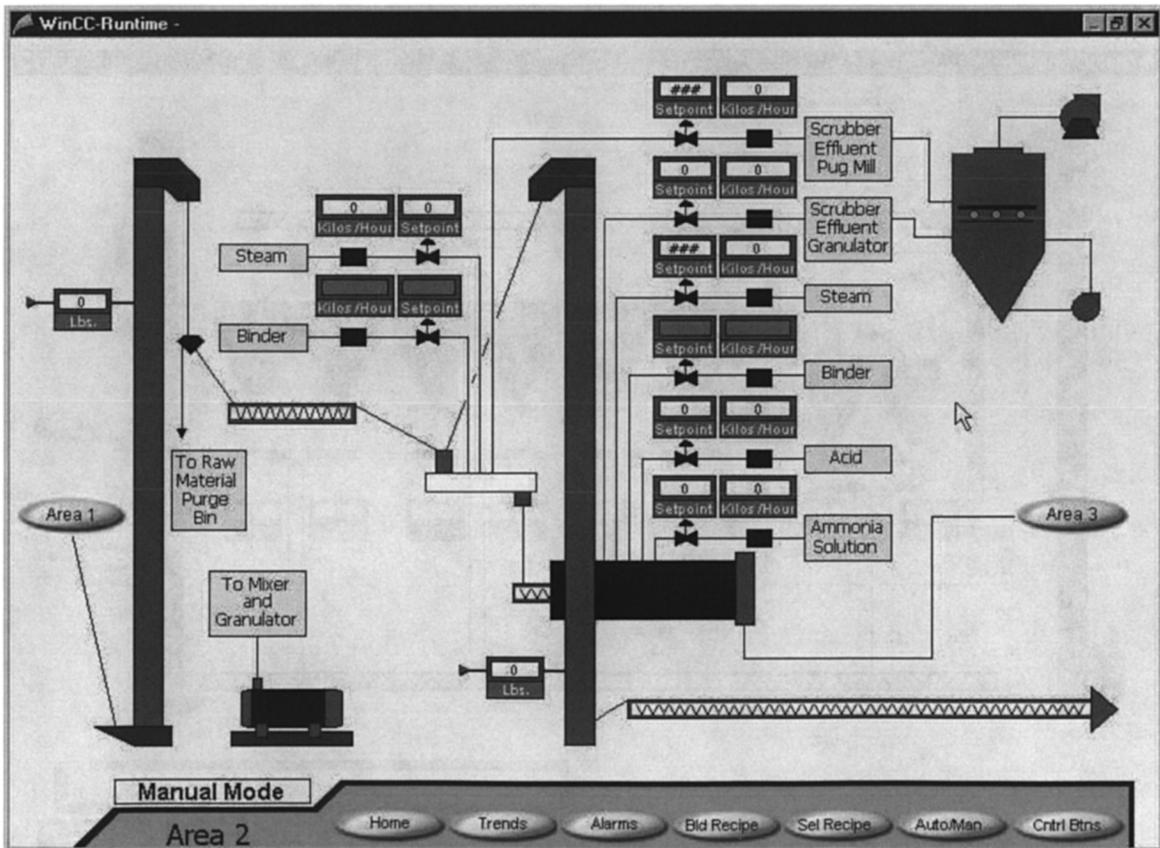


Figure 4.

## MODERN REGIONAL GRANULATION IN EASTERN EUROPE

BY CHARLES FORMISANI  
THE A.J. SACKETT & SONS CO.



*Slide 1*

## PAST GRANULATION IN THE USA

- ❖ INTRODUCTION OF REGIONAL GRANULATION PLANTS IN THE EARLY 1900'S
- ❖ AVAILABILITY OF STANDARD GRADE FERTILIZER MATERIALS AND LIQUID INGREDIENTS
- ❖ NEED FOR HOMOGENEOUS MIXTURE THAT COULD BE EASILY HANDLED AND SPREAD
- ❖ DRUM GRANULATION ANSWERED THESE NEEDS
- ❖ PRODUCTION RUNS OF LOW ANALYSIS GRADES SUCH AS TRIPLE 8, 3-9-18, AND 4-12-12
- ❖ MID-1960'S GRANULAR MATERIALS SUCH AS MAP AND DAP BECAME READILY AVAILABLE
- ❖ BULK BLENDING DOMINATED GRANULATION

*Slide 2*

## Europe



*Slide 3*

## WESTERN EUROPEAN MARKET

- ❖ LARGE DEMAND FOR HOMOGENEOUS NPK FERTILIZERS
- ❖ LARGE SCALE GRANULATION PLANTS DEVELOPED BEFORE GRANULATION IN THE USA AND CONTINUE TODAY
- ❖ FACILITIES PRODUCING UP TO 2 M TONS OF NPKS PER YEAR
- ❖ VERY LARGE PRODUCTION RUNS WITH NO ECONOMIC DRIVE TO MEET NICHE MARKETS
- ❖ SLOWLY INCREASING BULK BLENDING MARKET

*Slide 4*

## EASTERN EUROPEAN MARKET

- ❖ LITTLE DEVELOPMENT OF BULK BLENDING DUE TO LACK OF AVAILABILITY OF GOOD PHYSICAL QUALITY INGREDIENTS OR EFFICIENT SPREADING EQUIPMENT
- ❖ TRADITION FOR HOMOGENEOUS FERTILIZERS
- ❖ HIGH PRICED EXPORT MARKETS FOR ANY QUALITY GRANULAR INGREDIENTS
- ❖ AVAILABILITY OF BASIC NON-GRANULAR MATERIALS
- ❖ RELATIVELY INEXPENSIVE ON A "PER UNIT NUTRIENT BASIS"
- ❖ GRANULAR NPKS FROM REGIONAL GRANULATION PLANTS MORE ECONOMICAL

*Slide 5*

## ADDITIONAL NEEDS OF EASTERN EUROPEAN FERTILIZER MARKET

- ❖ SPECIFIC FORMULATIONS MEETING NEEDS OF NICHE MARKETS
- ❖ MICRO-INGREDIENTS
- ❖ COST EFFECTIVE

*Slide 6*

## SOLUTION

- ❖ INTRODUCTION OF A REGIONAL GRANULATION PLANT
- ❖ INCORPORATE MAXIMUM FLEXABILITY
- ❖ MEET THE NEEDS OF NICHE MARKETS
- ❖ SIMPLICITY OF OPERATION WITH AUTOMATIC CONTROL

*Slide 7*

## VARIABLES FOR THE GRANULATION PLANT

- ❖ DRY RAW MATERIALS
- ❖ LIQUID CHEMICAL AVAILABILITY AND TYPE
- ❖ MARKET NEEDS
- ❖ OPERATOR EXPERIENCE

*Slide 8*

## HOW DO YOU INCORPORATE THESE VARIABLES

- ❖ NUMEROUS GRANULATION METHODS
- ❖ AUTOMATION
- ❖ SIMPLICITY

*Slide 9*

## GRANULATION METHODS

- ❖ CHEMICAL GRANULATION
- ❖ STEAM GRANULATION
- ❖ BINDER GRANULATION

*Slide 10*

## AUTOMATION

- ❖ PLC WITH PC INTERFACE
- ❖ COMPLETE MANUAL BACKUP
- ❖ AUTOMATIC LIQUID AND DRY DOSING FROM RECIPE
- ❖ MONITORING AND ADJUSTMENT FOR RECYCLE RATE
- ❖ AUTOMATIC COATING APPLICATION
- ❖ ADVANCED ALARM AND INTERLOCK SYSTEM

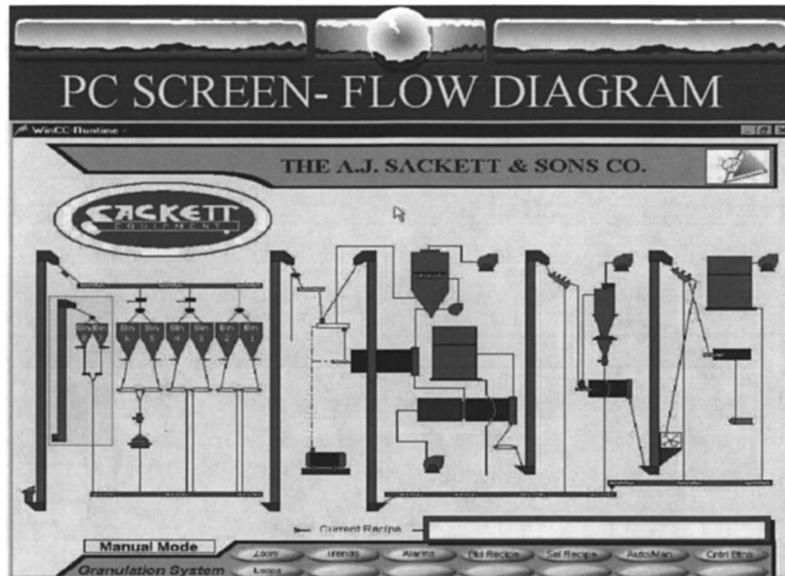
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## SIMPLICITY

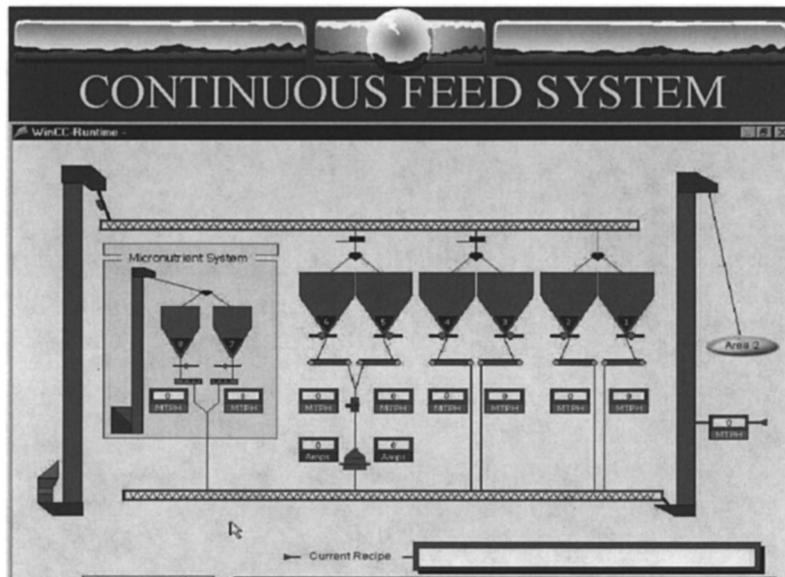
- ❖ DRUM GRANULATION
- ❖ ROTARY DRYING/COOLING
- ❖ VIBRATING SCREENS
- ❖ STANDARD RECYCLE LOOP

*Slide 12*

Slide 13



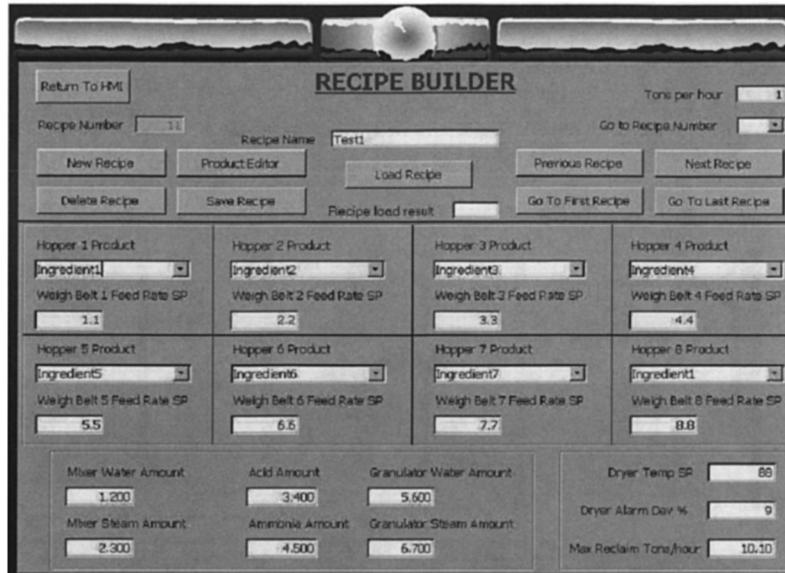
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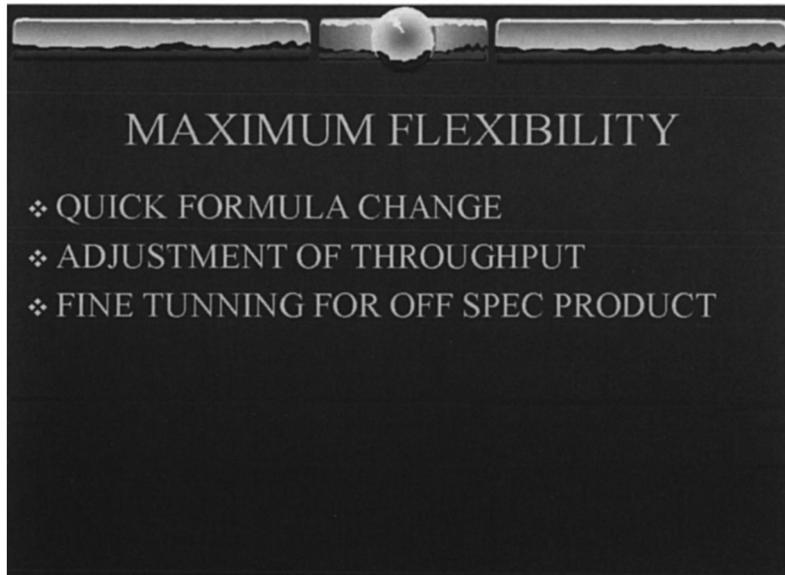
Slide 15

- ## BENEFITS
- ❖ AUTOMATIC CONTROL OF DRY INGREDIENTS
  - ❖ HIGHLY ACCURATE
  - ❖ COMPUTER MONITORING OF FLOW TRENDS
  - ❖ DATABASE STORAGE OF MATERIALS
  - ❖ PROCESS ALARMS

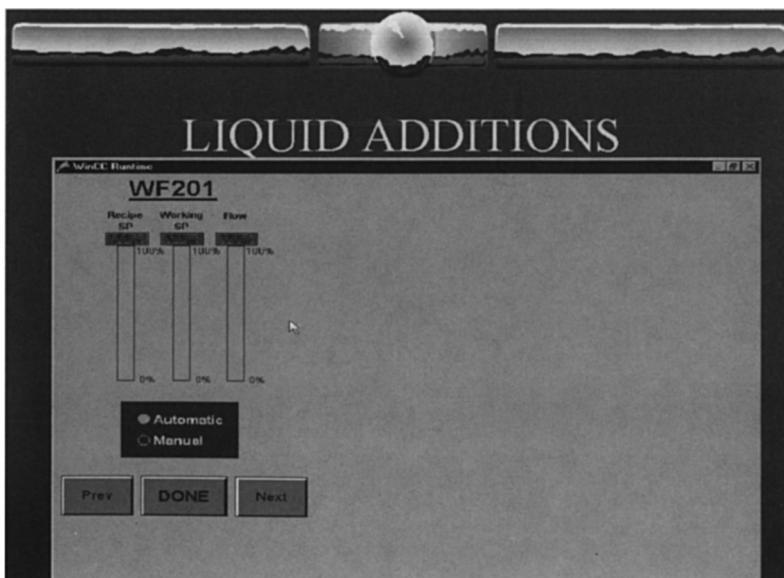
Slide 16



Slide 17



Slide 18



## RECYCLE SYSTEM

- ❖ CONTINUOUSLY MONITORED RECYCLE RATE
- ❖ AUTOMATIC ADDITION OF STEAM AND WATER
- ❖ AUTOMATIC PLANT TURNDOWN

*Slide 19*

## COATING SYSTEM

- ❖ CONTINUOUS MONITORING OF PRODUCT RATE
- ❖ LOGIC TO CONTROL COATING AGENT BASED ON % OF PRODUCT RATE
- ❖ INSURE CORRECT DOSAGE

*Slide 20*

## PLANT MONITORING

- ❖ CRITICAL MOTOR AMPS/OVERLOADS
- ❖ BURNER SYSTEM
- ❖ INTERLOCK EMERGENCY SHUTDOWN
- ❖ DIFFERENTIAL PRESSURES FOR DUST COLLECTORS AND SCRUBBERS
- ❖ ALL DRY MATERIAL AND LIQUID FLOW RATES
- ❖ TRENDS

*Slide 21*

## CONCLUSION

- ❖ MODERN GRANULATION PLANTS CAN OVERCOME THE PROBLEMS ASSOCIATED WITH FERTILIZER MARKETS IN DEVELOPING COUNTRIES
- ❖ HIGH QUALITY HOMOGENEOUS FERTILIZER WITH MAXIMUM FLEXIBILITY
- ❖ MODERN CONTROL MINIMIZES NECESSARY EXPERIENCE
- ❖ CONTROLS MINIMIZE WASTED MATERIAL
- ❖ RESULT IS SIMPLE, ECONOMICAL, AND PRODUCTIVE OPERATION OF A REGIONAL GRANULATION PLANT THRIVING IN TODAY'S NICHE MARKET

*Slide 25*



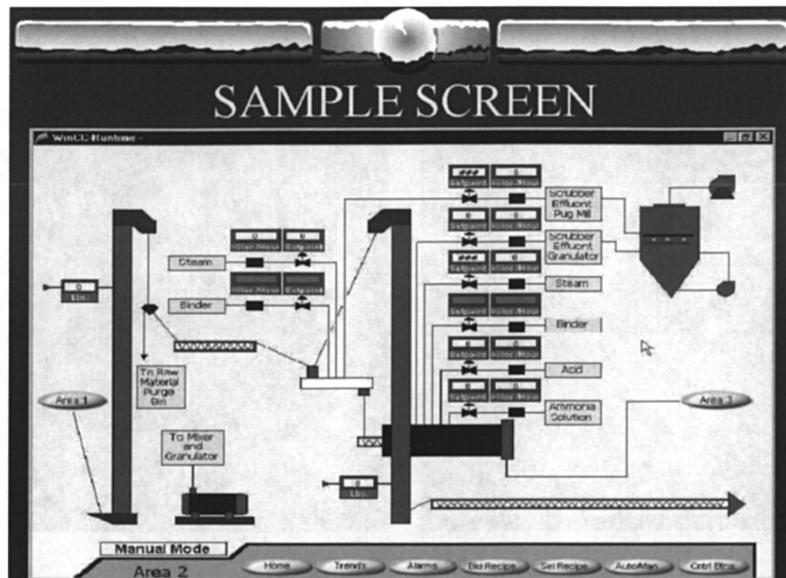
*Slide 26*

## FERTILIZER PRODUCED

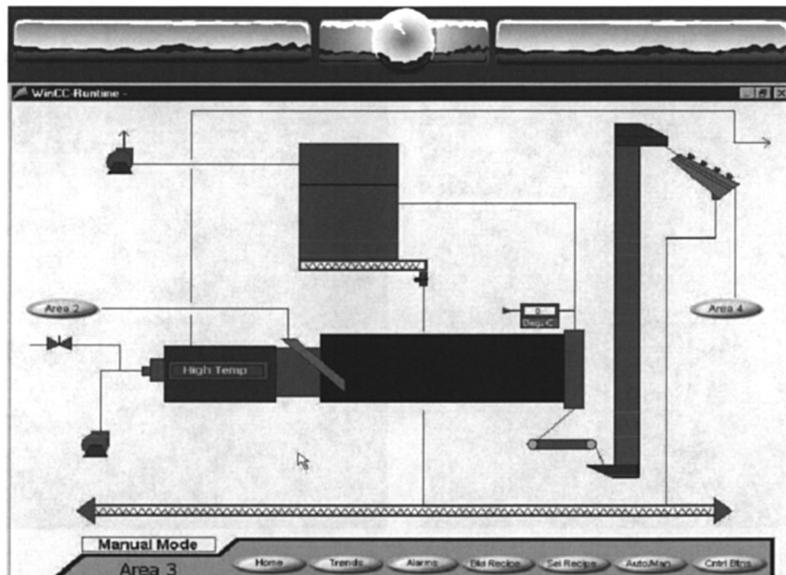
- ❖ 15-15-15 FOR LITHUANIA
- ❖ 17-9-14 FOR LT, DENMARK, GERMANY
- ❖ 12-11-22 +Na, B FOR LITHUANIA
- ❖ 8-20-30 FOR LT, POLAND, LATVIA
- ❖ 8-20-30 +B FOR POLAND
- ❖ 13-10-15 FOR LITHUANIA
- ❖ 8-24-24 FOR LITHUANIA
- ❖ 13-7-22 FOR LATVIA
- ❖ 17-6-14 – EXPERIMENTAL- GOOD SO FAR
- ❖ 16-20 (P-K) FOR DENMARK AND GERMANY

*Slide 27*

Slide 22



Slide 23

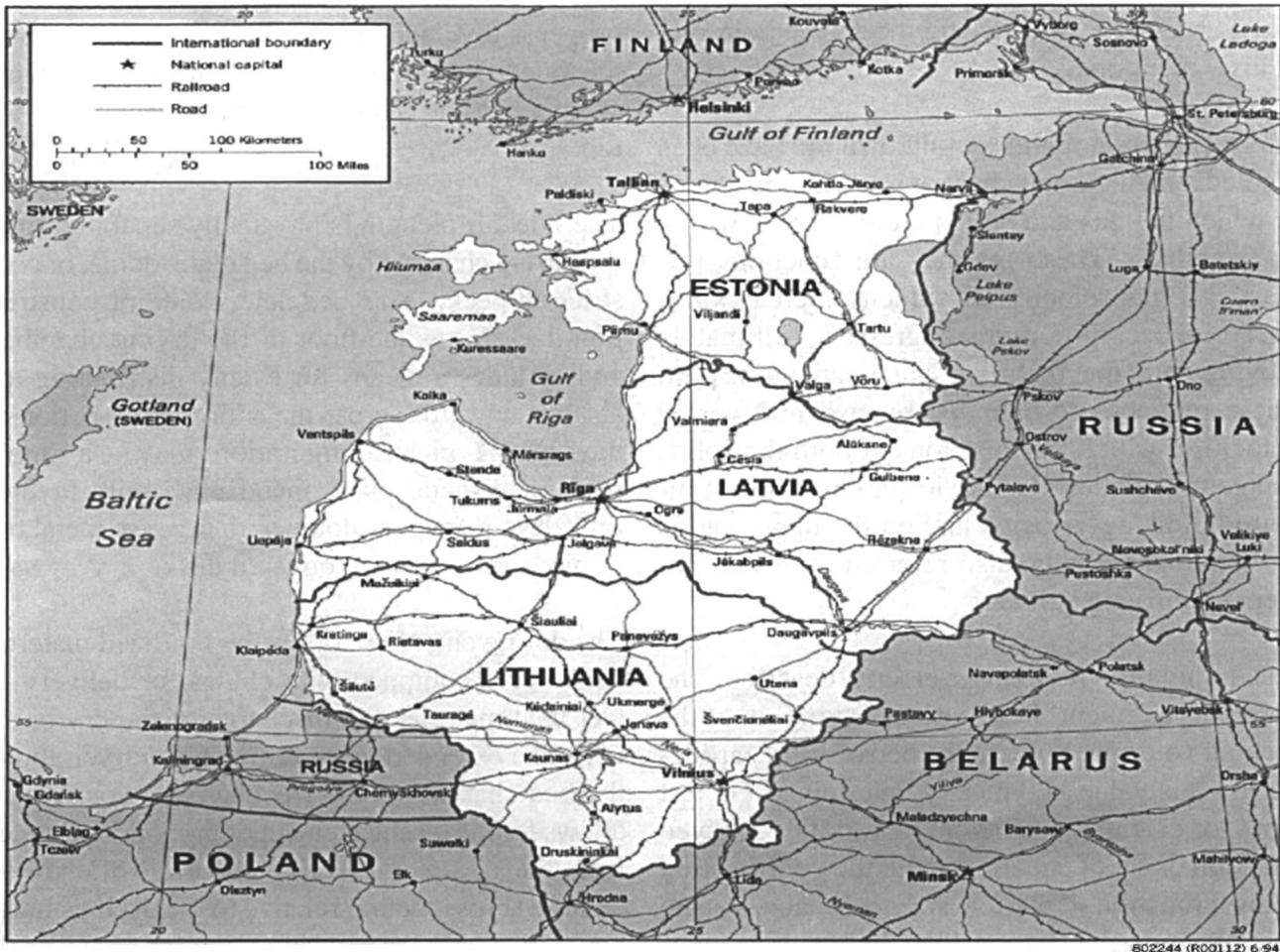


Slide 24

### OPERATION

- ❖ START-UP OF EQUIPMENT
- ❖ CHOOSE/START RECIPE
- ❖ KEEP BINS FULL(LIVEL INDICATORS)
- ❖ MONITOR GRANULATION

## The Baltic States



## Innovative Fluid Bed Process

*Frank Fisher*

**Heyle & Patterson**

### Introduction

Fluidized bed technology has long been of common practical usage in the bulk solids processing industries. Common applications include drying, roasting or calcining, chemical reactions, combustion, conveying and classifying. Heyl & Patterson, through its Renneburg Division, is a manufacturer primarily of drying equipment, with a fairly extensive resume in the fertilizer industry, among others. As such, the focus of this paper will be on fluid bed drying. We will discuss briefly the theoretical basis of fluid bed technology, the configuration and operation of typical pneumatic fluid bed dryers, and two variations on the basic fluid bed drying process which may be of some interest in the fertilizer industry.

### Theoretical Basics

Fluidization refers to the conversion of a stagnant mass, or bed, of particulate solids to an expanded, suspended bed by the introduction of a flow of gas through the solid particulate material. The drag force exerted by the flowing gas on the individual particles causes them to move and separate from one another to the extent that the particles are free to move at random through the bed. When sufficiently fluidized, the bed of particulate solids exhibits several properties of true fluids, such as:

- zero angle of repose;
- solids mass seeks its own level;
- solids mass takes the shape of the vessel in which it is contained.

In this state, the particles are free to intimately interact with the fluidizing gas over virtually the entire surface of the particle. It is this intimate and

extensive solids/gas contact which makes fluidized beds particularly attractive for the applications previously mentioned.

Several different regimes of fluidization have been defined, and these are characterized by the degree to which the gas and solids are dispersed within one another. These regimes are functions primarily of gas velocity; as velocity increases fluidization becomes more aggressive, ultimately moving into the realm of pneumatic transport. These regimes are bounded by two noteworthy velocities, which are functions of both the solids and gas properties. On the lower end is the minimum fluidizing velocity, and on the upper end is the terminal velocity, also referred to as entrainment or carrying velocity.

The minimum fluidizing velocity describes the point of incipient fluidization, taking into the account void space within the bed of solid particulates. This value is typically determined via test work, or calculated using an empirically-derived equation or set of equations with the void fraction being a function of particle size and shape. As the void fraction achieves unity, the fluid/particle interaction becomes independent of the other particles, and terminal velocity is achieved.

The terminal velocity is thus defined as the gas velocity at which the drag force imposed by still air on a falling particle balances gravitational force, and thus the particle experiences no acceleration and falls at a constant, or terminal speed. Conversely, and more appropriate for this analysis, we consider the particle to be still and the fluid to be moving. At the terminal velocity, the particle remains suspended motionless in the rising fluid stream. Exceeding this velocity will result in movement of the particle with the fluid stream, thus moving from the realm of fluidization to that of pneumatic transport.

### **The Fluid Bed Dryer**

The typical pneumatic fluid bed dryer consists of the dryer proper, fluidizing blower, air heater, dust

collection equipment, and exhaust fan. The dryer proper is divided horizontally into three sections; the inlet air plenum on the bottom, the drying chamber in the middle, and the freeboard at the top.

The inlet air plenum is physically separated from the drying chamber by the bed plate, dome, or constriction deck. This bedplate, dome or constriction deck forms the floor of the drying chamber, and includes a means for evenly distributing the air flow upwards across the entire cross section of the dryer. Typical configurations may be a simple perforated metal plate, metal plate with tuyeres (nozzles), refractory dome with tuyeres, metal bar or pipe grid, or metal louvered deck.

The drying chamber houses the fluidized material bed, and is equipped with chutes for delivery of wet feed material and discharge of the dry product. The extended top section of the dryer above the bed chamber is the freeboard section, which allows for the disengagement of the solids particles from the air stream. The freeboard is often of an enlarged cross section relative to the drying chamber, to decrease the gas velocity prior to exit from the dryer. The moisture-laden exhaust air stream is vented from the top of the freeboard, and through the dust collection equipment, prior to release to atmosphere through the exhaust fan.

The hot fluidizing air stream is provided by the fluidizing blower and the air heater, which can be direct-fired or steam-heated. The hot air is forced through the heater and into the inlet plenum section of the dryer, for distribution through the drying chamber. The dryer operates under a combination forced/induced draft, with the null point ideally at the top of the material bed. The fluidizing blower exerts the positive pressure through the air heater, inlet plenum, bedplate and fluidized bed, and the exhaust fan pulls the draft through the dryer freeboard and dust collection equipment. Proper fan balancing will allow the dryer to operate without airlocks on the feed and discharge chutes, although these are oftentimes employed anyway.

## Applications

The design of a conventional pneumatically-fluidized fluid bed dryer is based on employing a velocity which is high enough to fluidize the largest particles, yet low enough so as to avoid or minimize the entrainment of the smaller particles. Maintaining the dynamic state of the fluidized bed is also a critical design aspect, thus limiting the ability of the dryer to handle lumpy, sticky, agglomerated material. Typically, then, fluid bed dryers usually find their best usage when handling a material with the following characteristics:

- **Relatively Narrow Particle Size Range**  
The narrower the size range, the more likely that there will exist a velocity which satisfies both of the desired conditions, i.e. a velocity which is greater than the minimum fluidizing velocity of the largest particle, and less than the terminal velocity of the smallest particle. Uniformity of particle shape also matters in this regard, as particle shape affects the surface area presented to the gas flow, and void fraction within the bed.
- **Particle Size, Weight and Shape**  
Even if a very tight range of particle size exists, some materials are too fine, too light, or too irregularly-shaped for a fluid bed dryer to be practical. To suit these materials, the dryer must operate at such a low air velocity that it makes the size of the equipment ungainly, and may also make uniform upward air flow difficult to achieve or maintain. Conversely, some materials may be too large and heavy, requiring a velocity which results in an undesirable pressure drop through the system.
- **Material Dispersion**  
The typical feed material for a fluid bed dryer is free flowing, non-sticky, with no large lumps or agglomerates. The material must be able to disperse easily and completely in the dryer.

Conventional fluid bed dryers may thus be limited in their application by materials which exhibit properties contrary to any one or a combination of the characteristics outlined above. For instance, filter cakes are not typically suitable feed material for fluid bed dryers, as they usually occur as relatively high-moisture, lumpy materials. Even if the individual particle sizes are small, typically the cake will be compacted such that very large lumps up to several inches in size are present. In a pneumatically fluidized bed dryer, these lumps would quickly amass on the bedplate, and restrict the air flow through the dryer, rendering it inefficient at best, and more than likely, totally inoperable.

There is probably no more irksome experience for plant operations personnel than having to enter a confined vessel, shovel in hand, and manually dig out a large quantity of material.

## The Media Fluid Bed Dryer

The media fluid bed dryer has been developed to address such situations. This dryer is a unique hybrid of a fluid bed and flash dryer, utilizing the desirable features of each, while eliminating the major problems of the conventional types of these dryers.

The media dryer utilizes a fluidized bed of inert material, or media, to disperse and assist in heat transfer to the process material. The media resides in the drying chamber of the dryer, and the heated air stream is forced upward through the inert bed mass, creating a vigorously fluidized condition in the fashion of a conventional fluid bed dryer. The wet process material is fed directly into the fluidized bed, where it is thoroughly broken down and dispersed into its individual particulate form by the vigorous roiling action of the fluidized media. As the material is broken down in and dispersed throughout the fluidized bed, it is dried by the hot fluidizing air, and swept out of the dryer with the exhaust air, to be collected in a cyclone in the manner of a flash dryer. The media is well-oversized relative to the process material, so it is not carried

out of the dryer with the dry-product-laden exhaust air stream. What results is a uniformly-dry, totally-lump-free product stream.

This drying technique was originally developed and instituted decades ago in the drying of mineral concentrates, however, as far as we know, it has not been widely applied outside of this particular usage. Within the past two decades, we ourselves have designed and manufactured several of these media dryers for mineral concentrates, but had not until recently made the efforts to apply this technology in other applications. Over the past several years, however, this has changed. We have expanded the applicability of this technology to other processes where other types of dryers are, for various reasons, either undesirable or outright unsuitable.

As is the case with conventional fluid bed dryers, the basic design methodology for the media dryer starts with determining the proper air velocity. As the entire product stream is to be carried out of the dryer with the exhaust air, the exhaust air velocity must be greater than the terminal velocity of the largest particle. Once the air velocity is set, the media is then selected. The media must be of the appropriate size and density combination such that the velocity employed in the dryer is above the minimum fluidizing velocity for the media.

Selection of the proper media for any particular application is a point of interest which must be carefully considered, as there is no across-the-board type of media which will be serviceable in every application. The media may be a naturally-occurring product, such as flint, or an engineered manufactured product, such as alumina milling media. The selection of the proper media will be governed by many factors, such as:

- ***Particle Size and Weight***

It is easy to imagine that the larger a particle, or the denser a particle, the higher the velocity will have to be to fluidize or entrain it. It is desirable to

have a sufficiently large disparity between the critical velocities of the process material and those of the media. If the media particles are not sufficiently greater in size and/or weight than the process material particles, the potential for carry-over of the media with the product stream may be realized.

- ***Compatibility with Process Environment***

The media must not be affected by the temperatures employed in the normal drying operation. It is wise to consider possible excursion temperatures as well, as these will occur. Typically, a dryer will be equipped with a high-temperature limit automatic shutdown. If it is possible to use a media which will withstand this temperature with no adverse effects, it is wise to do so. The media must not be affected by the moisture present in both the process material and as vapor in the airstream. Corrosion of the media, or of the dryer because of the media, is another factor to be considered.

- ***Product Purity Requirements***

It is important to consider the degradation of the media in the selection process. While it may be possible to utilize a material with an extremely high resistance to impact, abrasion, fracturing or other degradation mechanisms, it should be understood that virtually all materials will eventually break down over time. It is almost inevitable that some introduction of foreign material into the product stream by the media will result, however small in concentration. This foreign material must be either 1) able to be sufficiently separated from the product via screening or other techniques; or 2) tolerable in the product stream from all pertinent aspects including, but perhaps not limited to concentration, chemistry, particle size, morphology, etc.

- **Economics**

Once all of the preceding issues have been addressed, the selection of the media will be governed by economics. We have employed materials as pedestrian as a "pea gravel" with unspecified chemistry and little-controlled size distribution, which can be had for literally a few dollars per ton. Conversely, we have considered materials costing as much as \$15 per pound. Depending on the size of the dryer, the media charge could be from perhaps 3-4 cu. ft. on the small end, up to perhaps 300 cu. ft. on the larger dryers. In conjunction with the actual material cost, it is necessary to consider the frequency of the need for additional or replacement media, the expense associated with media addition or replacement, disposal costs, and availability of the material. These factors must be considered within the context of plant budgets, regulations, resources and philosophies to arrive at the best choice.

The media fluid bed drying technique has been successfully employed by Heyl & Patterson in various commercial applications and in laboratory testing on a number of different materials. Low product moistures can be achieved using relatively low air temperatures, due to the rapid and complete dispersion of the product. As no product can exit the dryer until it achieves sufficiently small size, the product stream is completely free of lumps which are only surface-dried. As with a conventional fluid bed, the thermal efficiency is high compared to other types of convection dryers due to the intimate material/gas contact. The relatively high air velocity also allows for a reduction in the physical size of the dryer compared to a conventional fluid bed dryer. The agitation by the fluidized bed enables the media fluid bed dryer to handle wet, sticky, lumpy material, without a dry product recycle or other means to decrease the feed moisture or improve its material-handling characteristics. The media fluid bed is thus well suited for applica-

tions which would otherwise be unsuitable for conventional fluid bed or flash drying systems.

### **Fluid Bed Drying/granulation Systems**

Another variation on fluid bed drying technology is combined drying and granulating systems, which employ the use of a liquid stream of the process material. This application is useful in the processing of inorganic salts, tanning products, and pharmaceuticals. Target particle sizes in the 4 to 40 mesh range are typical for these applications.

The basic premise of this operation involves a direct spray of a solution, suspension or melt onto a fluidized bed of solid seed crystals. The introduction of the wet spray results in particle growth through two possible mechanisms: 1) the sticking together of two or more particles, which when dried, remains bound by the bridge of the dried solid constituent of the spray; and/or 2) repeated layering of the surface of the seed crystal by the dried solid constituent of the spray.

The configuration of the dryer/granulator for these operations is basically unchanged from a typical fluid bed dryer, with the additional feature of the spray systems for the liquid feed. As the growth of the particles in the dryer/granulator occurs randomly, the dried, granulated discharge stream will consist of varying particle sizes. Typically, a fairly tight final product size range is desired, so screening of the discharge stream is performed. The oversize particles may be milled back down and recycled around to the seed crystal feed stream, along with the undersized particles. The portion of the product stream which is of the proper size is directed to further processing, packaging or storage.

The design of these systems must be carefully and properly performed. The achievement of a steady-state operation at optimal process conditions can be difficult due to the interdependence of the various aspects of the process. Typically, lab testing must be performed to determine the optimum operating conditions for a given process. The test work is performed to study the aspects

which are unique to this type of operation, compared to a straight drying application. Among the areas of study during such lab tests may be:

- ***Spray System***

It is imperative to employ a uniform spray of the appropriately-sized droplets. The correct droplet size and number, location and type of nozzles must be employed for optimal performance. The liquid spray may be applied on the top of the bed or submerged in the bed.

Improper liquid application may lead to an undesirable granulation pattern, inefficient or ineffective dryer operation, and plugging or caking in the dryer.

- ***Solids/Liquid Feed Ratio***

As the dryer operates with a recycle of the undersized product, the rate of liquid addition must be in proper proportion to maintain the equilibrium of the system. If the spray rate is too low, the product stream becomes heavier in the smaller sizes, thus increasing the rate of solids feed and diminishing the effectiveness of

the system. If the spray rate is too high, the effectiveness of the granulation will most likely deteriorate, plugging may occur, and the dryer discharge may not be sufficiently dry.

- ***Residence Time***

In contrast to a straight drying application, the granulation aspect adds an additional consideration in that excessive retention time may lead to excessive particle growth, which could adversely affect the fluidity of the bed.

With proper design, the granulating fluid bed dryer can offer several advantages when compared to separate drying and granulating processes. As there is only one process unit, the equipment capital and installation costs are typically lower. Maintenance costs are also reduced, due to the reduction in equipment scope, coupled with the fact that the fluid bed system is stationary. The fluid bed system is also more compact, thus requiring less space, and lending itself more readily to installation where space restrictions are present.

# Wednesday, October 24, 2001

## Session V

### Moderator:

Walter J. Sackett, Jr.

### **The Foliar Application of Nitrogen, Phosphorus and Potassium**

*Ed Norris*

#### **The Andersons**

Foliar fertilization of nutrients is anything but a new concept. In 1844, Gris applied iron to the leaves of pin oak trees to try to cure "chlorosis sickness". The treatment worked and thus began foliar fertilization.

The use of micronutrients in foliar applications to help overcome the effects of adverse soil or environmental conditions is a common practice throughout the world today. In fact some crops such as pineapple and banana rely heavily on foliar applications for their total nutrient needs. Micronutrients such as manganese and iron are applied to soybeans in many areas of the mid-west to either improve or to maintain yield.

The foliar application of the major nutrients is ticklish business. Temperature, humidity, the amount of stress on the plant, and the form of fertilizer all play an important part in the success of the treatment. Foliar applications of the urea form of nitrogen to corn under very wet conditions have been a very successful "bail out" for the plant until more favorable conditions arrive. Forty pounds per acre of nitrogen applied as a low-biuret urea can do wonders for a plant slowly starving to death for nitrogen.

The quick green-up from foliar applied urea nitrogen is consistent with the results reported by Don Johnson, retired agronomist for Allied Chemical company. The leaves will absorb about thirty percent of the nitrogen in one hour, and absorb almost all of it in six hours. It takes twenty-four hours for

the leaves to absorb the potassium and seventy-two hours for the phosphate. Timing becomes critical so that there is optimum weather for uptake without becoming too hot and dry during the day. If the water evaporates from the surface of the leaves, fertilizer salt is left behind that will damage the leaves to the point of no further absorption. The optimum time to apply the major nutrients to the plant is during times of high humidity and low temperature early morning and late evening.

Timing can cause another problem. Often when corn and soybean plants are small, stress can all but stop growth. It is at this time that foliar applications can be very desirable. Unfortunately, leaves are small and not much of the fertilizer solution actually gets on the leaves. Hoefl, et al, estimates that only five percent of the spray solution actually gets on the leaves of six-inch corn and only about twenty percent is retained on twenty-four inch corn. The general rule is that more than one application is needed to try to supply what the plants needs. This is what John Hanway, Iowa State University found out in the mid-seventies with his soybean foliar fertilization study. Three to four sprays of nutrient solution were required between the R5 and R8 stages of soybeans to produce the desired effect. When the conditions were right, Dr. Hanway's nitrogen, phosphate, potassium and sulfur fertilizer did wonders for soybean yields. (See Table 1)

A nine-bushel per acre yield increase in soybean yield is certainly worth the attention it got at that time. The secret was using urea nitrogen, potassium phosphate, and potassium sulfate as the fertilizer sources and using 40 gallons per acre of total spray solution. The difficulty was dry weather following the application. The sulfur would burn the

leaves enough to reduce further photosynthesis so that the final effect was no response.

Foliar fertilization won't replace good soil fertility. Most growers have soils that are not perfect and a well-timed foliar application can be very beneficial. Working with a low phosphate, high pH soil, Kansas State University in the 1960's showed the effect of foliar applying phosphate.

Just moving the plant into the leaf and into the rest of the plant requires that we know a little about the differences in absorption and mobility of different nutrients in the plant. Wittwer, in his work on foliar applications found the following to be true.

Urea nitrogen and potassium are readily absorbed into the plant and are very mobile when inside. Phosphorus, however, is mobile on the inside but only moderately absorbed. Phosphorus presents the problem of maintaining the leaf in a high absorptive state for 24 hours after application. The applicator has no control of that, but the use of a

safe surfactant will increase the leaf area in contact with the phosphate solution.

**Summary:**

Foliar applications of the major nutrients can be beneficial under stress conditions when the plant is having difficulty meeting it's nutrient requirements from the soil. To avoid leaf burn, a low-biuret urea form of nitrogen is necessary and the total salt concentration on the leaf should be no higher than 0.3 to 0.5 percent.

Application should be made during the early morning and late evening when the temperature is low and the humidity is high to prevent leaf burn. The form of phosphate and potassium must be taken into consideration to avoid damage.

Foliar fertilization will not take the place of a sound soil fertility program. When the conditions are stressful, foliar applications can be of help to a struggling plant.

N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	S	Yield
Lb/A	Lb/A	Lb/A	Lb/A	Bu/A
0	0	0	0	44
0	16	26	4	42
71	0	26	4	43
71	16	0	4	42
71	16	26	0	49
71	16	26	4	53

Table 1. The effect of foliar fertilizer of nitrogen, phosphate, potassium, and sulfur on soybeans. 1975-1977.

P <sub>2</sub> O <sub>5</sub> (lb/A)	Yield (Bu/A)
0	98
5	113
10	114
20	130

Table 2. The effect of a foliar application of phosphate on corn yields in Kansas. Soil P1 test = 7 pounds per acre, soil pH = 7.9.

Absorption rank:	Mobility Rank:
<i>Rapid:</i>	<i>Mobile:</i>
Urea Nitrogen	Urea Nitrogen
Potassium	Potassium
Zinc	Phosphorus
	Sulfur
<i>Moderate:</i>	<i>Partially Mobile:</i>
Calcium	Zinc
Sulfur	Copper
Phosphorus	Manganese
Manganese	
<i>Slow:</i>	<i>Immobile:</i>
Magnesium	Magnesium
Copper	Calcium
Iron	

Table 3. Absorption and mobility ranking of selected plant nutrients, Wittwer. 1969.

## Placing Fluid Fertilizers in a Band

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Placing fertilizers in concentrated regions near the seed is a concept perhaps as old as farming itself. Research from the recent past suggests that concentrated nutrient zones overcome chemical and biological mechanisms that render nutrients unavailable. Research from the last decade verifies the improved efficiency gained from banding fertilizers. In this paper we survey supporting research on a variety of crops. The research cited is representative of current agronomics but is not intended to be exhaustive. Much of the research was conducted with fluid fertilizers. Fluid fertilizers are used widely by growers in all parts of the country due to their superior handling qualities and practical efficiencies.

Optimum placement of fertilizers has been of interest to farmers for decades. As early as 1600, Squanto recommended to the Pilgrims the placing of a fish in a hill of corn. Now, over 400 years later, correct fertilizer placement is still of interest because of economic, environmental, and production requirements.

Four objectives are usually involved in the placement of fertilizers. These are 1) to increase the efficiency of fertilizer use to the plants, 2) to prevent or reduce environmental contamination, 3) to prevent fertilizer salt injury to plants, and 4) to provide an economical and convenient operation. Many factors come into play to achieve all of these objectives. To a large extent, environmental conditions dictate whether precision placement of nutrients will be successful or not. Other factors include soil cation exchange capacity, soil conditions (pH, texture, organic matter content, cation exchange capacity, moisture content, and nutrient soil test levels). Generally, producers are more interested in final yield than crop cultural characteristics. However, the increased early growth experienced with precise placement is an advantage to maintain an even crop, and help strengthen young plants against early season stresses brought about by numerous factors including tillage and environmental.

The early literature usually worked with soils low in phosphorus. More recently, there has been interest in the effects of reduced or no-tillage practices on nutrient uptake. Researchers have investigated

the effects of band placement even on high testing soils. Nutrient combinations have an effect even under high soil test conditions. The three greatest elements of interest are nitrogen, phosphorus, and potassium. Nitrogen is important because of its environmental impact and its tendency to revert to nitrate and be lost through leaching. Phosphorus and potassium are important because they are relatively immobile in the soil. These factors are quite important as they relate to the crop and its rooting pattern, the concentration and closeness of fertilizer to the seed, and soil test levels. Fertilizer placement methods range from applying and incorporating fertilizer into a large volume of soil, commonly called broadcasting, to methods where the fertilizer is applied to very restricted zone or banded in the soil or on the surface of the soil. How much of the soil needs to be fertilized has been a research topic since the mid 1950s. Miller and Ohlrogge (1958) showed that placement of nitrogen fertilizer caused a relative increase in the feeding power of the root system on band placed phosphorus. Nitrogen had a greater influence when mixed with the phosphorus, than when placed in a band 3 to 4 inches from the phosphorus band. The influence was nearly independent of the soil phosphate level when the nitrogen was mixed with the banded phosphorus, but it was not independent of the soil phosphate level when the nitrogen was separated from the phosphorus band. They, in effect, showed that if nitrogen and phosphorus are placed in the band together in close proximity to the root system the plant was better able to take up both nutrients. Later Duncan and Ohlrogge (1958) demonstrated that root development in a concentrated nutrient zone was greater than outside the concentrated nutrient zone. The authors quantified observations by others that root proliferation was greater in a fertilizer band than outside the band.

### **Corn**

In the mid 70s, Barber (1974) proposed that only a small proportion of the soil, about 10-30 percent, needed to be fertilized. The advantage of this was demonstrated in research trials that showed strips of fertilizer laid on the surface of the soil produced

nine extra bushels of corn in a soil testing 21 ppm P. Anghinoni and Barber (1980) described a model that predicted the observed effects of P placements and reasonably predicted phosphorus uptake by corn. In this study, plants were grown in three-liter pots in a controlled climate chamber using two soil types. Added phosphorus was mixed with 100, 50, 25, and 12.5 percent of the soil. The total amount of P added to each pot did not change, so that the P rate per unit of fertilized soil increased as the fertilized fraction of the soil decreased. After 18 days, plants were harvested. Roots from the fertilized and unfertilized fractions were harvest separately. Results indicated that the relative proportion of total root weight and length was greater in the P-treated soil (See Table 1).

Kovar (1995) concluded that a localized concentration of N and/or P effects root morphological development and, as a consequence, root distribution in the soil. Phosphate, ammonium, and nitrate stimulate development of the first order and the second order of lateral roots. This effect has been characterized for barley, as well as other agronomic species. Therefore, when P or N fertilizer is placed in some fraction of the rooting zone, root distribution between the fertilized fraction and unfertilized fraction can be described mathematically. The relation applies to corn, soybean, and wheat when the amount of available P in the unfertilized soil is low. A similar effect has been reported for ammonium placement, although it was assumed that a NxP interaction did not effect the relation.

Kovar and Barber (1987) theorized that phosphorus and potassium recovery was greatest when the volume of soil was fertilized between 1.7 and 20 percent. Placement had a greater effect on P recovery the lower the P soil test value. The increase in efficiency due to K placement was less than that for P placement. However, the size of the fertilized soil fraction that gave the greatest K uptake was similar to those for P. Kovar and Barber (1990) investigated the relative increases in both solution K and soil exchangeable K in multi-element fertilizer additions. They used 33 surface soils equilibrated for moisture. High rates of application were

used to simulate a band K application. The characterization of changes in solution potassium and soil exchangeable K after addition of K provided information useful for determining the effectiveness of K placement.

Commensurate with the explosion of information about the movement of banded phosphorus, potassium, and nitrogen was the increased adoption of reduced tillage. The adoption of conservation tillage proceeded rapidly between 1990-1998, but has since reached a plateau. The no-till soybean acreage adoption in the US continued to rise to the current 21.1 million acres in crop year 2000. No-till corn adoption in the US has been approximately level since 1994 whereas no-till adoption in all crops in the US continued to rise to 50.7 million acres in crop year 2000. (Figure 1). Managing nutrient application under no-till is a challenging task. No-till generally creates stratification of non-mobile elements such as phosphorus and potassium. At the same time, the root proliferation near the surface is greater under no-till conditions. Stratification results from a minimal mixing of broadcast materials or shallow band application, as well as from cycling of nutrients from deep to shallow soil layers. These factors create a more favorable environment for root activity near the soil surface. However, nutrient uptake and root activity are affected by weather conditions. As the soil surface layers become dryer, root development in deeper portions of the soil profile increases. When this happens in a reduced-till field or where there is significant nutrient stratification, the portion of root system actively taking up nutrients can be below the zone of highest nutrient concentration. Conversely, under more moist conditions, the surface residue will keep the soil surface wetter and cooler. These conditions can inhibit root growth and nutrient uptake early in the season. Therefore, proper placement of fertilizer potassium and phosphorus may be critical for optimizing yields in no-till systems. (See Figure 1.)

A study describing the results of stratification was conducted by Iowa State University researchers. Bordoli and Mallarino (1998) compared broadcast,

deep banded, and planter band P and K placements for no-till corn. Long term P and K trials were established 1994 in five Iowa research centers and were evaluated for three years. Eleven short-term P, K trials were established in farmers' fields during the same period. Treatments were various P and K rates broadcast, banded with a planter 2 inches beside and below the seed, and deep banded at the 7 to 9 inch depth before planting. Phosphorus increased yield only in soils testing low or very low and there was no response to P placement at any sight. Potassium, on the other hand, increased yields in several soils that tested optimum or higher in soil test potassium and, yields were higher where K was deep banded. Higher rates of broadcast or planter-banded K did not offset the advantage of deep-banded K. Responses were better related with deficient rainfall in late spring and early summer than with soil test K. They concluded that current soil test P interpretations in P fertilizer recommendations based on chisel plow tillage are appropriate for most Iowa soils managed with no tillage. However, further work is needed to better characterize and predict deep-banded K. Because the yield response was small, cost effectiveness of deep-band K will be determined largely by application cost. Mallarino and Murrell (1998) reporting on the same experiments show that when only when the responsive sights were considered, broadcasted K applications increased yields by about 5 bushels per acre (Table 2). However, deep-banded K increased yields by approximately 13 bushels per acre. Yield increases were also observed on soils testing in the optimum and high categories (See Table 3).

Similar observations were made by Yibirin et al. (1993). They investigated the yield potential of corn as it relates to soil exchangeable potassium and placement of potassium fertilizer in a no-till system. Potassium was either broadcast or banded at the rate of 41 pounds per acre over three mulch rates (zero, normal, double mulch) and five initial soil exchangeable potassium concentrations. Increasing mulch rate increased ear leaf potassium concentration at all soil exchangeable potassium concentrations and yield at soil exchangeable potassium levels below 90 ppm. Increasing soil

exchangeable potassium increased yield in the zero and normal mulch treatments, but not in the double mulch treatments. Banding K increased ear leaf potassium concentration and yield only at the low soil exchangeable potassium concentration. The effect of banding on yield was observed only in the zero mulch treatments. The lack of increased yield with banding in the mulch treatments was attributed to greater root growth in the 0- to 2-inch depth, which may have allowed for more efficient use of the broadcast K fertilizer. The soil exchangeable potassium concentration decreased with depth and distance from the row in all treatments. Results indicated that the yield benefit of banding K, increasing soil exchangeable concentration, or both decreases with increasing rates of mulch.

The effect of tillage and moisture was demonstrated by Vyn et al. (1999). In Ontario studies, no-till corn did not respond to banded potassium. However, zone till and mulch-till systems achieved the highest yields with deep-banded potassium. In one site, starter K increased corn grain yield more in the no-till than in corn following the fall mold board plow. This site soil test ranged from 65-90 parts per million K which would fall into the responsive range. The extra response at the no-till site suggests that no-till corn had a greater need for added K.

Work on corn and nitrogen replacement usually concentrates on volatilization characteristics of urea based fertilizers. Stecker et al. (1993) investigated the interactive effects of fertilizer application time and placement method by applying urea ammonium nitrate (UAN) solution in no-till corn. Eight site-years of data were collected from central, northeast, and northwest Missouri. The experimental design was a complete factorial of an application time (pre-plant and side-dress), placement method (knife, dribble, and broadcast) and rate (60, 120, and 180 pounds N per acre). Knife injected N increased yields relative to broadcast and dribble N in five of eight site years. Yields from knife N ranged from 4 to 20 percent more than dribble and 5 to 40 percent more than broad-

cast (Figure 2). Ear Leaf N concentration and grain N uptake were increased from knife injected N in six of the eight site-years. Dribble and broadcast UAN performed similarly in most site-years for grain yield, ear leaf, and grain and uptake. In two site-years sidedress resulted in lower grain yields and application time had no effect on grain yield. No interaction of application time was apparent, as knife injection was superior to broadcast and dribble at both application times. This suggested that N loss associated with surface application of urea based N sources was similar for pre-plant and side-dress application times. (See Figure 1.)

They attributed higher yields from injected N relative to broadcast and dribble N were likely due to reduced ammonia volatilization and immobilization losses. Dribble N on the soil surface did not result in a marked improvement in grain yield, leaf N concentration, or grain N uptake compared to broadcast. While others have shown improved grain yields from dribbling UAN onto the soil surface relative to broadcast, data from this study did not indicate any consistent improvement in crop performance from this placement method.

### **Soybean**

While it is common to see responses by corn to starter or deep band placed N, it is less common for research to show a band application advantage in soybean. This was demonstrated by Buah et al. (2000) who studied no-tillage soybean response to both banded and broadcast potassium and phosphorus fertilizer. The Iowa study evaluated the response of soybean to fertilizer P or K rates and placement as well as residual and direct fertilization from 1995 through 1996. Two K and two P experiments were established on farmers' fields with ten year histories of no tillage. An additional P experiment was conducted on one of Iowa State University's research farms. Treatments on farmers' fields included two rates of P (0 and 40 pounds  $P_2O_5$  per acre) or K (0 and 55 pounds  $K_2O$  per acre), placement of fertilizer, surface broadcast or sub-surface band (two inches beside and two inches below the seed), and time of fertilizer applica-

tion. Treatments on the research farm were similar except the P rates were applied as 0, 40, 80, and 160 pounds  $P_2O_5$  per acre. The researchers found P and K levels were stratified. High nutrient concentrations were in the upper zones of the soil. Fertilizer placement on farmers' fields did not affect the concentration of the fertilizer nutrient in the leaf at early bloom. In nine of eleven site years, control treatments were not significantly different from the fertilized treatments. Little or no response to added P or K fertilizers occurred when the soil test levels were optimum or higher. This suggests that P and K levels on farmers' fields, although stratified, were sufficient to meet the nutritional requirements of soybean. Where the soil tests phosphorus was below optimum, soybean responded to P fertilizer in the year of application more frequently than to residual P fertilizer applications. These observations indicate that applications of a given quantity of P in similar or smaller annual applications may be more effective than larger semi-annual applications. Residual and direct K fertilization resulted in similar grain yields at both K sites. The researchers found that soybean responded to broadcast P or K applications as well as or better than band applications despite the stratification of nutrients. Therefore, there is probably no yield advantage in banding P or K for no-tillage soybean when soil tests are optimum or above. Adequate surface soil moisture may have kept root systems active in the high nutrient zone.

### **Wheat**

The effects of banding phosphorus on wheat have been studied for years. Seed and knifed P applications, both of which are banding methods, have usually performed similarly in Nebraska on winter wheat. These methods of P application have also been found to be two or three times more effective than broadcast applications. Fiedler et al. (1989) showed that in low P soils, seed applications of P fertilizer to winter wheat doubled the profits compared to broadcast application, even though optimum P rates were slightly higher for seed application than for broadcast.

Adverse environmental conditions can sometimes delay winter wheat seeding causing a reduction in grain yield. Studies have shown that seed placed P can reduce some of the negative effects of late planting. Sander and Eghball (1999) studied the effect of planting date and phosphorus fertilizer placement on winter wheat. They studied seed and knife banding methods of applying P to winter wheat. Their study was conducted to determine the effect of optimal and delayed date of wheat planting on performance on seed applied and knifed P on grain yield, P uptake, and yield components. Four rates of P were seed and knife applied on two different soil types in 1986-1987. There were two planting dates in 1986 and three in 1987. All soils had soil P tests levels of low to very low. While seed and knife application performed similarly with an optimum planting date, seed application was a superior P application method in terms of grain yield and P uptake when planting was delayed. The primary reason for the superiority of seed P application was its ability to stimulate tillering and head formation at the later planting dates. The difference in performance between the two methods of P application was probably related to quicker root access to fertilizer P in the fall soon after planting.

Banded applications are also suited for one pass seeding operations at varied landscape positions. The difficulty with applying fertilizers at seeding is the danger of seed germination damage due to high salt effects. Matus et al. (1999) studied the use of anhydrous ammonia in single pass seeding operations and found that both side-band and sweep wing tip openers performed equally well in improving grain yields and protein content in spring wheat. They did not experience crop damage even at the highest N rate of 93 pounds of N per acre. Anhydrous ammonia performed as well as granular urea and ammonia nitrate in the study. Johnston, et al. (1997) found that anhydrous ammonia did not adversely effect grain yield in spring wheat, but did show a reduction in grain yield with canola at one of the five trial sites in their study. The lower canola yield reflects the N loss when anhydrous ammonia is applied on

clay soils. Loss of anhydrous ammonia on clay and silty clay soils, which were wet at application, resulted in reduced crop N uptake and lowered N use efficiency relative to urea at one wheat and two of the canola trial locations. The results of the trial indicated that, given adequate seed fertilizer separation, partially liquefied anhydrous ammonia can be safely applied at seeding in a precision side band application. Soil conditions that are known to cause N loss on application of anhydrous ammonia, in particular wet clay and silty clay soils may benefit more from an alternative N source such as solution N or granular urea. They advised producers interested in adopting this technology to pay close attention to the type of opener and field topography for best results.

Reduced tillage and one pass seeding operations create special opportunities for banding of phosphorus on wheat. Drought conditions also create unique risk management opportunities. A study by Travis Miller (1998) in Texas showed that deep placing phosphorus provided an additional risk management tool for winter wheat in the Southern Great Plains. In the Southern Great Plains, wheat is a dual-purpose crop, with winter pasture and grain production both being of great importance to farmers and ranchers. Therefore, fertilizer management to enhance early forage production is of near equal importance to practices that optimize grain yield. Late August through early October is typically a high rainfall period so wheat is planted early to optimize vegetative growth. This rapid early growth tends to deplete surface moisture. Conventional fertilizer applications present a problem because of the concentration of nutrients on the surface. As the soil dries out, root activity decreases in the surface and access to non-mobile elements such as phosphorus is limited due to the reduced root growth. Beef cattle production is the largest agricultural enterprise in the Southern Great Plains and the potential for enhanced forage yields and the resultant increase in current capacity under drought conditions have very large implications. Approximately ten million acres of wheat are grazed annually in this production region. The economic potential for a system to improve yields

in high risk or dry years is enormous with respect to farmers, ranchers, and the agricultural industry as a whole. Nitrogen and phosphorus were injected six to eight inches deep on eight to ten inch centers. Fifty pounds of N and 40 pounds of  $P_2O_5$  were used per acre. Wheat was planted from mid September to early October on ten-inch centers. The results showed forage dry matter yield response was greatest with deep-banded P relative to surface incorporated P or the untreated check in the dry years. (See Table 4).

In five of the eight site year comparisons in the Texas rolling plains, deep banded P resulted in forage yield 50 percent greater than wheat treated with the same rate of surface incorporated P and 45 percent greater than wheat treated with same rate of N but no P fertilizer. In four of the five sites, fall weather was abnormally dry. Two clear effects were noted: the first is that P placement significantly improved forage yields; the second is that surface incorporated P use efficiency, with respect to forage yield, was nil in dry fall weather. In six trials where valid comparisons of grain yield were made between P placement techniques, three yielded significantly higher with deep placed P, with the yield average of deep banded P being 8.4 and 10.5 bushels per acre greater than the surface incorporated treatment and the untreated check, respectively. This represents a yield increase of 57 and 83 percent under the very dry conditions. In two trials, there was no difference between P placement techniques with respect to grain yield. In one trial during a very wet growing season, wheat fertilizer with the surface incorporated P yielded more than deep-banded treatment. Averaged over six sites, deep-banded P resulted in grain yields of 2.0 and 9.9 bushels per acre greater than the surface incorporated P and the untreated check, respectively. In two sites where drought drastically limited grain yields, no response was obtained to N fertilizer alone or N fertilizer with surface incorporated P. Significant yield response was obtained with N and deep banded P (See Table 5).

### **Vegetable Crops**

Phosphorus placement in relation to root proximity is important to vegetable crops as well as grain

crops. Hegney and McPharlin (1999) studied the effects of broadcasting and band placing phosphate fertilizers on potatoes on the coastal sands of Australia. They concluded that for both broadcast and banded methods of application, potato yield responded significantly to applied P on the soil studied. Higher levels of applied P were required to achieve maximum yield in the broadcast compared with the banded method of application. However, maximum yield was between 13 and 17 tons per hectare higher when the P was broadcast compared to banded. The higher yield potential of broadcasting was associated with significantly higher petiole P concentrations. They attributed the difference between the two methods to possible toxic effects of high levels of P fertilizers banded close the potato seed piece at planting. They also theorized that the differences between the potential yield of potatoes when P fertilizers is broadcast and banded are likely to decrease as the P absorption capacity of the soil increases. Lastly, they suggested that placement of P fertilizer needs to be close to the primary roots of the potato and not where the tuber seed piece is.

Hip (1970) demonstrated the importance of fertilizer placement on yield of tomatoes. He examined the effectiveness of both broadcast P and band placed P for direct seeded tomatoes on three different soils common to south Texas and Northern Mexico. He found that broadcast P was ineffective in producing high yields even when soil P levels were low enough that a P response should have been obtained. Phosphorus concentrations in young tomato plants were much higher in band P than broadcast P treatments. Final distance of P placement from the seed row was critical in obtaining maximum early tomato growth. Broadcast P on a Harlingen clay soil was ineffective in creating a yield increase. P placed directly beneath the seed yielded a two-fold increase over the no P check. There was a sharp increase in yield of tomatoes grown on an Adelo silty clay loam when P was supplied in a band underneath the seed. Maximum yields were obtained when P was applied in a band at the rate of 100 pounds  $P_2O_5$  per acre. These data suggest that if soil P level was low enough to

obtain a response from P then P should be placed in a band below the seed for high yields.

Mortley, et al. (1991) studied the effects of fertilizer placement on tomato growth, fruit yield, and elemental concentrations. They found that banding significantly increased yields and nutrient uptake over broadcast treatments. Fertilizer was applied broadcast at two rates or banded in two bands at two widths or at four bands or applied in combinations of side dressing or broadcasting plus banding of N, P, and K at rates of 50, 100, or 200 pounds per acre of each. Total fruit yield for the 100 pounds per acre banded treatment was 24 percent higher than that for the same rate broadcast and similar to the yield for the 200 pounds per acre broadcast (See Table 6). Treatments involving combined placements, wider bands, or four bands produced similar yields to that for the 100 pound per acre banded rate, but the 50 pound per acre banded with two 50 pound per acre side dressing had the highest yield. Leaf concentrations and plant contents of N, P, and K (in percentage of recovery of quantities applied) were generally higher in treatments involving banding or side dressing when compared to broadcasting.

Tomato may be more sensitive to Nitrogen form than placement of Nitrogen. Motis, et al. (1998) found that total season yields were greater with ammonium nitrate than polymer-coated urea but were not affected by placement of N. Increasing the percentage of drip or band applied N resulted in leaf N concentrations that were inconsistent with trends in marketable fruit production; however, trends in leaf K concentration early in the season were similar to those of early-season large fruit yields.

Sanchez (1991) examined the relative efficiency of broadcast or banded phosphorus for sweet corn produced on histosols. Histosols account for more than half of the fresh sweet corn marketed in the USA from October to July. Smaller amounts of sweet corn are also produced during the summer months on Histosols in New York, several mid-western states, and in Canada. Because histosols used for crop production are often hydrologically

linked to environmentally sensitive wetlands, it's important that management strategies improve the efficiency of P fertilization. Furthermore, sweet corn produced on the Florida histosols is grown in rotation with sugarcane, which responds negatively to high P. To that end studies were conducted across six site seasons during 1988 and 1989 to evaluate the relative efficiency of broadcast and banded P for sweet corn. Broadcast and banded P rates were 0, 12 ½, 25, 37, and 50 pounds P<sub>2</sub>O<sub>5</sub> per acre. Phosphate was surface applied and disked into the soil before planting. Banded P was applied approximately one inch below the corn seeds in bands mixed with the soil in approximate diameter of about two inches. Sweet corn responded to P when soil test P levels were less than optimum. Total marketable yields, yield of US fancy, and quality parameters of sweet corn ears were increased by P rate and affected by placement in four of the six site seasons. Band placement reduced the amount of P required for a specified sweet corn yield and also appeared to result in a higher total yield. Relative efficiency of banded to broadcast P depended on soil test P level. The relative efficiency was greater than 3:1 (band over broadcast) when soil test P was less than 0.2 grams per cubic meter but approached 1:1 as soil test P increased to 1.2. Overall, results indicated that banding P is indeed a viable strategy to reduce the amount of P used for sweet corn production on histosols.

### **Forages**

Band placements in forages present special problems to growers. Simmons, et al. (1995) examined the effect of fertilizer placement on yield of established alfalfa stands. They used double disk openers to place P in a band in established alfalfa fields or broadcast P and K at the rate of 0, 4, 8, or 16 pounds P<sub>2</sub>O<sub>5</sub> per acre and 0, 40, or 80 pounds K<sub>2</sub>O per acre. The double disk was intended to penetrate to a depth of about two and a half inches but in practice this was difficult to achieve so the depth was between 1 and 2 ½ inches. Band spacing was approximately 8 inches. On the clay loam soil there was no yield difference between banded and broadcast fertilizer application. On the fine,

sandy loam soil, band application reduced yields slightly compared the broadcast application, particularly at first harvest following fertilizer application. Yield reduction was attributed to root interference with the band placement.

Recognizing deficiencies in earlier research Malhi (1997) investigated a special technique to increase the effectiveness of phosphorus fertilizer on alfalfa. He initiated a five-year experiment on existing alfalfa stands on a P deficient black soil in Ponoka, Alberta to compare surface broadcast with subsurface band applications of P. P bands were six inches apart, two inches deep using a coulter-type disk. All plots received an annual blanket application of potassium and sulfur. There was an excellent response to applied P in both the annual and single applications for both application methods. Forage yields increased three to four fold relative to the unfertilized check. On average, yield differences between the two application methods were greater at the lower application rates, but tended to disappear at higher application rates. Disk banding consistently produced greater forage yield than surface banding when averaged across P rates. Over the five year period, band application produced an average of about 836 pounds per acre per year more dry matter than the broadcast application when P was supplied annually and about 660 pounds per acre per year more dry matter when the P was supplied initially at the beginning of the study. Root activity and proximity to fertilizer placement was attributed to the higher yields experienced in subsurface band application. He cautions that equipment will influence the outcome. A hoe drill type of implement damages forage stands, causing injury to the superficial roots and loss of moisture by opening the soil, particularly in a dry year or in a relatively dry soil climate zone. He concluded that the coulter-type disk drill apparently does not cause disturbance to soil or plant roots.

Banded nitrogen on bromegrass has been shown to be effective both in improving nitrogen recovery (Malhi, 1995), but the grower must be careful that the bands are not spaced too far apart. Malhi and

Ukrainetz (1990) demonstrated that nitrogen bands further apart than 7 ½ inches may result in decreasing yield. Although tall fescue is one of the major cool season grasses used for animal feed in the USA, its often unfertilized or is top dressed with N alone. Additional fertilizer nutrients supplied with N may improve yield and quality. Subsurface placement of N has been shown to improve cool season grass production, so Sweeney, et al. (1996) began a field study to determine the effects of multi-nutrient fertilization and placement method on nutrient concentrations and yield of tall fescue. The nutrients examined were N, NP, NPK, NPKS-BZn, and PKZnSB without N. Placement methods included broadcast, dribble (surface banding), and knifing (subsurface banding). Nitrogen was the primary nutrient limiting fescue growth. Adding N doubled yields of samples that estimated early-grazing potential and tripled yields of hay. Supplementing N fertilization with additional nutrients increased tissue concentrations of the added nutrients, but increases in yield were small and often not significant. Broadcasting fertilizers resulted in greater yields in early-grazing samples and higher P and K concentrations than knifing; however, by hay harvest, knifing resulted in about 10 percent greater yields and 20 percent greater N concentrations. Dribble applications generally resulted in responses intermediate between those of broadcasting and knifing.

### **Band longevity**

Banded fertilizers have a tendency to stay around in the soil for a period of time after application. Eghball et al. (1990) studied the longevity of banded phosphorus fertilizers in three different soils. The calculated longevity of banded phosphorus fertilizer ranged from 2.6 years at 7 ½ pounds P<sub>2</sub>O<sub>5</sub> per acre in a Sharpsburg soil to 6 ½ years at 30 pounds P per acre on a Coly soil. The longevity of banded P fertilizer was shortest for the Sharpsburg soil with highest P adsorption capacity. It was the longest for the Coly soil with the lowest P adsorption capacity. They calculated the probability of P-affected soil being collected during soil sampling ranged from 11.7 percent at the 15 per pound rate to 25.9 percent at the

higher rate of 30 pound P per acre. Kitchen, et al. (1990) examined the problem of soil sampling under banded fertilizer conditions. They summarized that when the location of the P bands is unknown and less than 20 sub-samples are taken, paired sampling consisting of a completely random sample and a second sample 50 percent of the band spacing distance from the first sample yet perpendicular to the band direction reduced variability compared to a completely random sampling. The greatest variability or deviation from the true P soil tests occur when inadequate sampling includes, rather than excludes the band, and thus will underestimate P fertilizer needs. James and Hurst (1995) proposed that rapid collection of a single representative sample with equipment capable of taking a slice of soil across the fertilizer band and accurately weigh in-band and out-band soil test phosphorus by volume. They verified that there were two distinct categories of soil test phosphorus. The in-band category will overstate the amount of phosphorus available and understate the amount of fertilizer recommended. Out-band category will understate the amount of P available for crop growth and overstate the amount of fertilizer needed. They found that low starter fertilizer rates less than 10 pounds of P per acre could be ignored, but larger build-up rates cannot be ignored if the residual fertilizer effects are to be properly factored into the soil fertility management through diagnostic testing. Hence, they proposed that a portable power tool that can rapidly cut a slice of soil across the fertilizer band to a depth and length needed to weight the band in the bulk soil and simultaneously sub sample the slice at a point in the field should be developed. Repeating this process at 10 to 12 randomly selected sampling points should give an economical and reliable estimate of the overall soil P fertility in the band fertilized fields.

Band spacing not only effects soil test properties, but it also effects fertilizer distributions in the band. Eghball and Sander (2000) theorized that the greater the rate of application, the smaller becomes the distance between droplets in a liquid fertilizer band. Results of their study sug-

gested that lower analysis P fertilizers could be more effective than widely used 10-34-0 for pre-plant banding and row applied starter fertilizers. Mixing of 10-34-0 with UAN may have improved P use efficiency both through improved P distribution and through ammonium-N effects on P uptake and P fixation. In a 12-inch band spacing, P was delivered unevenly in spaced droplets. Droplet distances ranged from about 2 inches at a  $P_2O_5$  rate of 15 pounds per acre to a continuous band at 75 pound per acre of  $P_2O_5$ . Increasing band spacing decreased the distance between droplets at the same application rate. The smaller the band spacing the greater the distance between the droplets. With a band spacing of 12 inches, distance between droplets was 2, 0.75, 0.35 and 0.12 inches with  $P_2O_5$  application rates of 15, 30, 45, and 60 pounds per acre, respectively. Continuous bands were formed at band spacing of about 17, 22, and 31 inches with application rates of 60, 45, and 30 pounds per acre of  $P_2O_5$ , respectively. The discontinuous bands at the low P rates may be overcome through diluting the liquid fertilizer to form a continuous band. In a Kansas experiment, the authors report that the same amount of solution was applied for different phosphate rates, but the solution was diluted for rates of less the 50 pounds per acre  $P_2O_5$ . Knifed P resulted in higher grain yield than seed applied. The predicted distances between the droplets were 0 and 0.7 inches for knifed and seed applied P, respectively. The probability of root P contact is known to be very important to P efficiency. It appears that when roots contact a P droplet, root proliferation can be expected as well as an increase in root growth in that part of the soil. However, exhaustion of P in that soil area affected by the P droplet could be a limiting factor. Therefore, root droplet contact would have to be made with several droplets to ensure adequate P supply to the plants. They suggest that plant roots will follow a continuous band with only one root contact. However, with discontinuous bands, where fertilizers placed in droplets a new root contact may be needed for each droplet or particle. The benefit of adding UAN to starter fertilizers to produce about a one to one N to P ratio may be due in part to the improved distribution of P

reported in these studies from higher rates of P application. This does not diminish the importance of additional ammonium in P uptake or the possible effects of high ammonium on P fixation reactions, which may in turn keep more P in the available form. Better distribution, continued ammonium-N presence, and possible delay of P fixation reactions are added factors in approved P response and the benefits of band placement of fluid P fertilizers.

### **Starter Fertilizers**

The role of starters in productivity enhancement for the northern US was reviewed by Fixen and Lohry (1994). They summarized the state of technology at that time as the following: early season nutrition of corn and other crops is often inadequate in today's cropping systems causing an interest in fertilizer applied at planting time. Starter composition and rate can influence performance and should be based on local research. Data continued to support the two by two placement of starter as the ideal, however alternatives may be nearly equal in specific situations. Starter responses do occur in high soil test levels and factors leading to such response include conservation tillage, soils with restricted drainage, cool, wet conditions following planting, weather conditions favoring shoot growth over root growth, hybrids with high shoot to root ratios, and early or late spring planting. Soybean and sorghum are generally less responsive to starter than corn, cotton, sugar beats, or potatoes, although responses do occur especially at medium or lower soil test levels. In-furrow placed starter fertilizers should be used with caution especially on sandy soils or with salt sensitive crops. Local guidelines for maximum rates should be followed. Factors influencing injury are crop type, soil moisture content and texture, precipitation after planting, seedbed condition, total salt rate (N+K<sub>2</sub>O), and row spacing.

Kovar (1994) reviewed the role of starter fertilizer and productivity enhancement in the Southern US. His summary was that in general, starter fertilizers are quite effective if soil fertility is low; however, yield responses also have been observed on soils

with high levels of available nutrients. Research with cotton suggested that starter fertilizer will not turn a poor crop into a good crop, but can improve yields of good crops. Applications of starter fertilizers in a two by two band, in a three to four inch surface band over the seed furrow, and in-furrow at planting appeared to be most effective. In-furrow applications may require significantly lower fertilizer rates and should not be used on sandy soils. In most cases, starter mixers contain N and P, but often K, S, and several micronutrients are included. Starter composition should be based on local conditions. Finally, starter fertilizer use is often beneficial under reduced tillage or no-till management.

Hybrids may vary in their responsiveness to starter. Teare and Wright (1990) examined the value of placing small amounts of soluble fertilizers in close proximity to the seed at planting time amongst different corn hybrids. They used ammonium polyphosphate in a band on the soil surface at planting. Starter fertilizers significantly increased grain yields compared to no starter however hybrid by year and hybrid by starter treatment interactions were significant. Certain corn hybrids were identified as positive responders that consistently yielded more with starter than others which were identified as either non-changers or as negative-changers. Percent lodging generally was greater with no starter fertilizer. Certain corn hybrids consistently exhibited less lodging than the hybrid mean when fertilized with the starter. The management implication is that certain corn hybrids may be profitably fertilized with starter fertilizer but others may not since they either do not respond or respond negatively to starter fertilizer.

Part of the reason that certain hybrids may respond may have to do with the configuration of the root system. Rhoads and Wright (1998) studied root mass as a determinate of corn hybrid response to starter fertilizer. They noted that field experiments with approximately 25 hybrids over three seasons showed that some hybrids respond to row applied fertilizer with enhanced growth and yield increases while others did not respond. They compared root

and shoot growth of responsive and non-responsive corn hybrids and their uptake of nitrogen and phosphorus. Two glass house experiments were conducted with hybrids from the field studies found to be most and least responsive to row applied fertilizers. Time from seeding to harvest was 33 days for the first experiment, 41 days for the second. Root weight of the non-responsive hybrids was 31 percent higher than the responsive hybrid in the first experiment and 48 percent higher in the second. Each hybrid responded similarly to starter P with 62 to 78 percent increase in top growth. The responsive hybrid produced a significant increase in top and root weight due to starter N but the non-responsive hybrid did not respond to N placement. The lack of response to starter N was attributed to greater root growth in the non-responsive hybrid because its top and root weight with broadcast were about the same as those of the responsive hybrid with banded or starter N. The researchers noted that since the hybrids differed only in response to starter N, a convenient method to classify corn hybrids with respect to starter fertilizer response is to measure top growth at six weeks after planting with banded against broadcast N at planting.

Corn hybrid response to starter fertilizer in a no-till dry land environment was studied by Gordon, et al. (1997). This field experiment was conducted in the north Kansas experiment field near Belleville, Kansas on a Crete silt loam. Treatments consisted of five corn hybrids and two starter treatments. Fertilizer treatments were starter fertilizers (30 pounds N, 30 pounds  $P_2O_5$  per acre) or no starter fertilizer. Starter fertilizer was applied two inches to the side and two inches below the seed at planting. In all of the three years of the experiment, grain yield, maturity, and total P uptake were affected by a hybrid by starter fertilizer interaction. Starter fertilizer consistently increased yields, reduced the number of thermal units needed from the emergence to mid silk, and increased total P uptake of three hybrids but had no effect on two others. When averaged over the three years of the experiment, starter fertilizer increased grain yield of the responding hybrids by 13 bushels per acre.

Starter fertilizer increased V6 stage above ground dry matter production and N and P uptake of all hybrids evaluated. Ear leaf N and P concentrations were also increased by starter fertilizer, regardless of hybrid. Results of this work show that starter fertilizer can increase grain yield and be feasible for some hybrids whereas yields of other hybrids are not effected.

In contrast, a no-tillage corn hybrid and starter fertilizer study in Iowa (Buah, et al., 1999) showed no hybrid by starter interaction. In this study, starter fertilizer was applied two inches to the side and two inches below the seed at planting at four different locations in Iowa. Starter fertilizers increased early season growth significantly in four of eight site years and grain yield of seven of nine site years. Average grain yield increases ranged 4 bushels per acre to 18 bushels per acre in 1995. The results suggest that starter fertilizer will likely benefit no-tillage corn for most hybrids in the northern corn belt even on soils with adequate P and K.

A little studied area is in-furrow starter fertilization on early sweet corn. Swiader and Shoemaker (1998) conducted field studies to evaluate in-furrow starter fertilization of early sweet corn. In both years, three starter fertilizer treatments were applied ammonium polyphosphate (APP) with N and P at 11 and 38 pounds per acre, respectively, either banded two inches below and beside the seed or placed in-furrow, and a control with no starter fertilizer. Additionally in 1995 the rate of ammonium polyphosphate was increased to supply 23 pounds of N and 75 pounds of P per acre either in combination with either band two by two or in-furrow. Seedling in-furrow emergence was delayed whenever starter fertilizer was applied with the seed; however, significant reductions in plant stand occurred only at the high rate of in-furrow placement. In both years all starter treatments had a positive effect on seedling dry matter production, and hastened silking. In-furrow application increased marketable ear yields 34 percent in 1995 but had no effect in 1994. Lack of yield response to the high rate of in-furrow fertilizer in

1995 was primarily a function of reduced stand, as ear number and ear mass per plant, and average ear size were similar in the other starter treatments. Based on these results in-furrow APP appears to be an effective starter fertilization regime for early sweet corn, comparable in effect to the higher banded rate; however, high rates of in-furrow APP may reduce stands. Although significant yield response to in-furrow starter fertilizer may not always be realized, the increase early seedling growth may itself be a benefit, since fast growing seedlings are more likely to be tolerant of adverse environmental conditions than are other less vigorous plants.

Starter fertilization has been commonly thought of as a practice for northern corn producers. Scharf (1999) demonstrated that yield responses to starter fertilizer are fairly common even in the southern corn belt. But, producer skepticism about the applicability of small plot research to production situations is one reason for a lack of adoption. During a three year period, six replicated strip trials were conducted in production corn fields comparing no starter to three categories of starter fertilizer: traditional low N high  $P_2O_5$ , medium N medium  $P_2O_5$ , and N only. Significant positive yield responses to starter fertilizers were observed in all six experiments. Yield differences between the three categories of starter fertilizer were minimal and not statistically significant when averaged across location. The average of all starter categories at experiment locations showed that starter fertilizer increased yield of corn by 13 bushels per acre. Use of starter fertilizer for no-till corn appears to be a profitable practice under production field conditions in the southern corn belt. Nitrogen only starter was the most profitable because it had the lowest material cost and produced about the same yield as P containing starters.

Corn has become an important crop used in rotation with cotton in the mid south region of the US, but there has been little research about cultural practices for corn in this cropping system. Mascagni and Boquet (1996) examined planting dates

of mid March, early April, mid April, and late April or early May with and without ammonium polyphosphate starter. Yield response to planting date was not consistent across year: in two of the three years however planting later than early April decreased yield. Starter fertilizer was not consistent across years hybrids were planting dates. Starter fertilizer increase early season plant height by 2 to 36 percent and increased grain yield across planting dates from .5 from 1.4mg per hectare in 1991 and .4 to 1.0mg per hectare in 1993. There was no yield response to starter in 1992. Application of starter fertilizer, averaged across hybrids in years, reduced harvest grain moisture by 5 percent and days to silking by 3 to 5 days. In this mid south study, inferal NP starter fertilizer increased early season corn plant height and grain yield and decreased the number of days to silking of corn rotated with cotton.

Bednarz, et al. (2000) performed an agronomic and economic analysis of cotton starter fertilizers. They set out to examine if cotton grown on coastal plains soils in South Georgia would response to different starter fertilizer sources and also if use of starter fertilizers would result in an economic gain. Three different locations were employed with five starter fertilizers sources applied two inches beside and two inches below the seed drill at planting time. Lint yields were significantly increased for starter fertilizers at two of the locations in 1997 when the crop was exposed to an extended period of cool weather immediately after planting. The authors concluded that the most appropriate cotton starter fertilizer appeared to depend on soil type. Products employed were 10-34-0 plus 32-0-0, 10-34-0 alone, 32-0-0 alone, 2-0-0-5 and a treatment with calcium 9-0-0-11. The authors concluded that starter fertilizers would be an efficient method of sulfur application on the soils studied. Also, the economic analysis showed that there were greater dollar returns even though some of the yield increases were not statically significant. (See Table 9.)

### **Benefits of Banding Liquids**

Fluid fertilizers offer distinct advantages. They can be formulated to meet crop needs for macro- and micronutrients and every drop has the same analysis. Fluids are easily pumped from transport vehicle to application machinery. Tillage and planting equipment is easily modified to handle liquid applications. A variety of equipment is available to deliver liquid fertilizer in bands before, after, and at planting time. The nutrients are readily available to plants since they are predominantly in the soluble forms. Most important is that the delivery mechanisms are flexible enough to handle nearly every growing situation. In the final analysis liquids offer the greatest opportunity to improve nutrient efficiency.

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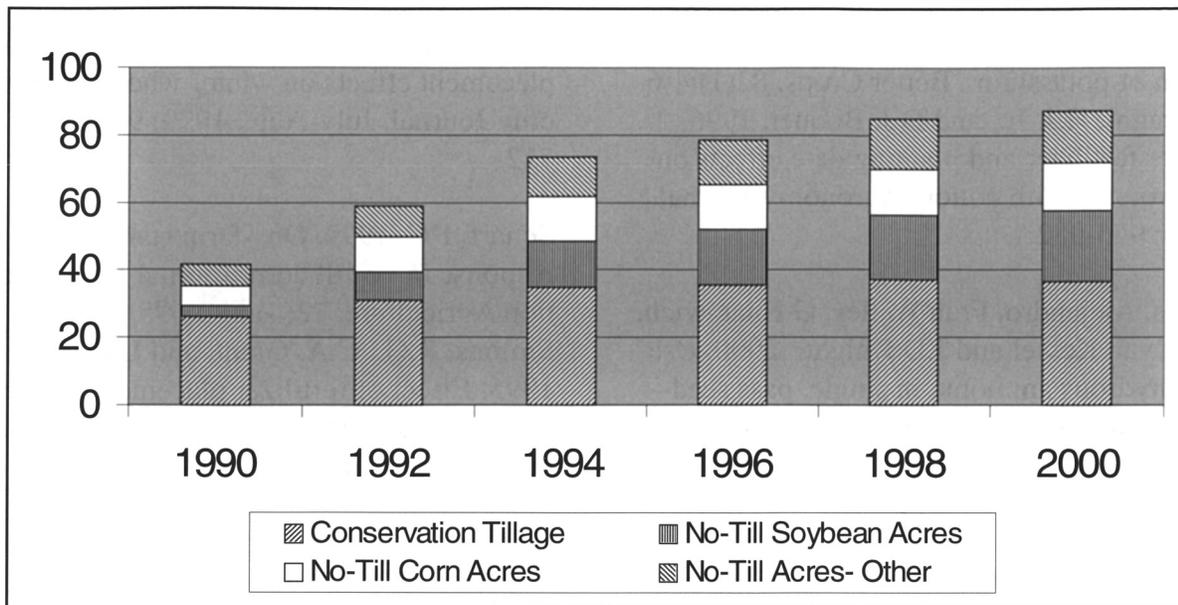


Chart 1. Change in reduced and conservation tillage acres. (CTIC, 2000)

Figure 1

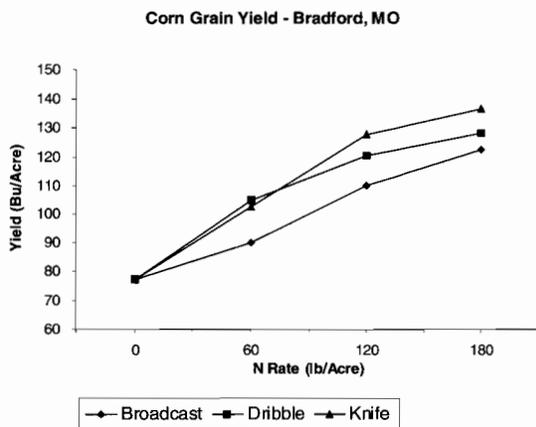


Table 1. Effect of phosphorus placement on root growth of 18-day-old corn grown in 3L pots in a controlled climate chamber.

Soil Type	Fraction of Plant Total		
	Soil Fraction Fertilized	Root Weight	Root Length
Raub sil	0.5	61.1	62.2
	0.25	36.5	36.2
	0.125	21.5	25.5
Wellston sil	0.5	60.3	66.0
	0.25	33.5	41.7
	0.125	17.8	20.5

Based on Anghinoni and Barber (1980).

Long-term research sites showing positive corn grain yield responses to banded applications of

Table 2.

K. Number of site-years showing corn grain yield increases in the following comparisons

Soil test K category	Soil test K range, ppm	Number of site-years in category	Deep banding compared to broadcast	Planter banding compared to broadcast	Deep banding compared to planter banding
Optimum	91-130	4	4	2	3
High	131-110	5	5	3	5
Very High	171+	6	4	2	4

Mallarino and Murrell, 1998

Short-term research sites showing positive corn grain yield responses to banded applications of

Table 3.

K

Soil test K category	Soil test K range, ppm	Number of short-term sites in category	Number of sites with an average corn grain yield increase from deep banding compared to broadcast
Optimum	91-130	4	3
High	131-170	3	3
Very High	171+	4	3

Mallarino and Murrell, 1998

Table 4.

Location	Year	Forage yield, lb/Acre				Check
		Deep P+N	Surface P+N	N only		
Runnels	1988	2,583a	1,595b	1,482b	-	
Wichita	1995	2,357a	1,238b	1,248b	1,199b	
Baylors	1994	2,552a	1,248b	1,568b	-	
Baylors	1995	4,295a	3,757b	3,615b	3,607b	
Abilene	1995	3,898b	4,770a	2,200c	-	
Abilene	1997	580a	483a	477a	259b	
Young	1997	1,050a	749bc	935b	598c	
Wichita	1997	1,003a	929a	912a	-	
Average		2,290	1,856	1,556		

\* Yields in the same row followed by the same letter are not different according to LSD(.05)

Response of wheat grain yield to fertilizer placement, Texas Rolling Plains.\*

Table 5.

Location	Year	Forage yield, lb/Acre				Check
		Deep P+N	Surface P+N	N only		
Runnels	1988	31.0a	25.8b	20.8c	-	
Baylors	1994	46.0a	47.0a	35.0b	-	
Baylors	1995	41.4a	39.2a	39.1a	27.9a	
Wichita	1995	16.4a	5.1b	4.8b	3.5b	
Abilene	1995	34.0b	48.5a	19.5c	-	
Abilene	1996	22.0a	13.2b	12.2b	7.7d	
Average		31.8	29.8	21.9		

\* Yields in the same row followed by the same letter are not different according to LSD(.05)

Table 6. Fertilizer placement effects on yield responses of 'Count 11' tomatoes (1986-88).

Treatment <sup>1</sup>	Total yield (Ton/Acre)	Fruit wt oz.	Large fruit oz.	Ripe fruit %	Vine wt (Ton/Acre)
Control	27.2c	4.2a	39.3a	31.9ab	3.6c
100 Br	27.4c	3.8b	28.1c	32.3ab	3.9be
100 Ba	33.9ab	4.0ab	29.8be	34.5a	4.2abc
200 Br	31.4b	3.8b	26.3c	32.8ab	4.5ab
50 Br/50 Ba	32.0ab	3.9ab	29.2be	34.6a	4.6ab
50 Ba/50Sd1	31.7ab	3.8b	26.1c	32.6ab	3.9be
50 Ba/50 Sd2	35.4a	4.0ab	25.7c	30.0b	4.7a
100 WBa	33.9ab	4.0ab	31.7be	31.9ab	4.4abc
100 4Ba	34.8ab	4.1ab	35.3ab	33.4ab	4.7ab
LSD <sup>2</sup>	3.9	0.4	6.7	4.4	0.8

1. N, P, and K rates (lb./acre). Br = broadcast, Ba = banded, Sd = sidedressed once (1) or twice (2), WBa = wide bands, 4Ba = four bands, two on each side.

2. Mean separation within each column by Fisher's protected LSD test, P = 0.05.

Table 9.  
and Tifton, GA, in 1997 and 1998.

Treatment	Midville			Plains			Tifton		
	1997	1998	Avg.	1997	1998	Avg.	1997	1998	Avg.
	\$ per acre								
10-34-0 + 32-0-0	762	514	638	587	633	610	759	691	725
10-34-0	776	511	643	668	674	671	763	669	716
32-0-0	864	483	674	525	684	605	833	688	761
28-0-0-5 (S)	896	532	714	535	682	608	833	727	780
9-0-0-11 (Ca)	752	528	640	575	690	632	810	725	768
Untreated	672	442	557	549	678	613	798	675	737

Net return is cotton income (price times yield) minus ginning and warehousing and treatment costs. Treatment costs include starter fertilizer, additional labor and fuel in handling and hauling of starter fertilizer and application equipment, annual fixed costs of investment in application equipment, additional picking and hauling for difference in yield between the treatments and the untreated check, and interest on additional expenses. All costs except ginning and warehousing were zero for the untreated check.

# Calcium's Role in Plant Nutrition and Fertilizer Technology

*G. W. Easterwood*

**Hydro Agi North America, Inc.**

## **Abstract**

Topics addressed in this synoptic review of calcium's role in plant nutrition and fertilizer technology include: 1) the functions of calcium in the plant, 2) influence of timing of application, calcium and nitrogen fertilizer sources and calcium deficiency disorders, 3) crop response to calcium fertilization in terms of disease resistance and stress mitigation, and 4) calcium source and nitrogen use efficiency.

## **Introduction**

Calcium fertilization of many crops is frequently confused with lime or gypsum soil amendment applications. Many believe application of these minerals to their soils sufficiently supplies the calcium requirement of their crops. In short, the role of calcium in plant nutrition and fertilizer technology is often eclipsed by interest in macronutrients or specific micronutrients. Many times, calcium fertilization has been overlooked and is only considered when deficiency disorders influence the economic threshold of produce quality and value. However, we now know the following: 1) calcium is a multifunctional nutrient in the physiology of crop plants; 2) calcium source solubility influences availability and uptake; and 3) nitrogen use efficiency of urea-containing fertilizers is also increased with soluble calcium sources such as calcium nitrate.

## **Functions of Calcium in Plants**

If one reviews introductory level plant physiology texts, one finds that calcium is an immobile nutrient in plant tissue and aids in plant cell wall structure. Our focus in this short paper will primarily address the importance of calcium in cell wall structure and crop production. But, we are learning much more about the important functions of calcium in the plant that should be mentioned. Physiological processes associated with calcium

regulation in plants include abscission, ripening, and senescence when there is a deficiency and cell wall material secretion, tropism, spore germination, pollen tube growth, cytoplasmic streaming, chloroplast movement, cell division, leaf movements, tuberization, guard cell swelling, mitigation of freezing and heat stress and hormonal actions when there is a sufficiency (1). Plasma membrane structure and function and seed germination (1) are also dependent upon calcium activity. Without a steady supply of calcium taken up by the roots, many of these physiological processes will fail from calcium deficiency. Classical visual symptoms in calcium deficient plants include death of growing points, abnormal dark green foliage, premature shedding of blossoms and buds and weakened stems. Therefore, calcium fertilization must meet the demand of the rapidly growing fruit or vegetable crop. Calcium fertilizer source solubility is key.

## **Time of Application, Calcium Fertilizer Source, Deficiency Disorders and Nitrogen Form**

For most commercially grown vegetables, the time required from planting to market maturity ranges from 60 to 120 days. Plants grow rapidly after initial transplant. To support early growth, soluble calcium sources such as calcium nitrate are applied in the bed mix. For vegetables grown with plasticulture, most fertigation regimes are initiated during the second week after transplanting with liquid calcium nitrate or a liquid mixture of calcium nitrate and potassium nitrate. Nutrient injections will continue through fruiting to crop maturity (2). Many fruit and tuber crops such as apple and potato have a very narrow window for calcium uptake. Ninety per cent of the calcium taken up by potato tubers or apple fruit occurs within a four to six week period after bloom for apple or during bulking [tuber initiation and expansion] for potato.

The source of calcium fertilizer is important. Soluble calcium fertilizers such as calcium nitrate or calcium chloride are immediately available for uptake. Gypsum and lime require time and/or large quantities of water to dissolve and provide

available calcium (Table 1). With many rapidly growing crops, these insoluble sources will not provide adequate calcium fertility. Calcium inadequacies are also manifest through soil testing. Many states utilize the Mehlich I (double acid) soil extractant for their soil tests. Soil exchangeable calcium as well as insoluble calcium minerals in the soil are dissolved. Abnormally high soil test calcium results often give a grower false security that he has adequate calcium in the soil that is available for his crop when he does not. Calcium deficiencies and plant disorders can result. (See Table 1) Cell wall strength and thickness is increased by calcium addition. Calcium is a critical part of the cell wall that produces strong structural rigidity by forming cross-links within the pectin polysaccharide matrix. With rapid plant growth within a short period of time, the structural integrity of stems that hold flowers and fruit as well as the quality of the fruit produced is strongly coupled to calcium availability.

Calcium deficiency disorders of the cell wall go by many names. In leafy vegetables, it is known as tipburn of lettuce, cabbage, broccoli and cauliflower, blackheart of celery and internal browning of Brussels sprouts. In fruit or other storage organs, calcium deficiency is known as internal brown spot or rust spot of potatoes, cavity spot of carrots and parsnips, bitter pit and cork spot in apples, alfalfa greening in pears and blossom end rot of tomatoes, squash, cucumbers, melons and peppers. In other crops, calcium deficiency disorders may be expressed as cracking or splitting of cherries and strawberries, decreased firmness of strawberries and red raspberries and increased mortality of peach and citrus trees. These calcium deficiency disorders greatly reduce marketable yield and produce quality. A continuous supply of calcium and water must be supplied during bloom and after fruiting to prevent deficiency (3).

Plants require more nitrogen than any other nutrient. The form of nitrogen available to plant roots also influences the uptake of other nutrients. Ammonium nitrogen ( $\text{NH}_4^+$ ) is positively charged, a cation. Nitrate nitrogen ( $\text{NO}_3^-$ ), an anion, is nega-

tively charged. There is competition at the root surface between ions of like charge. Since ammonium is positively charged and preferentially taken up by the root, its uptake can depress the accumulation of other nutrient cations like potassium ( $\text{K}^+$ ), calcium ( $\text{Ca}^{++}$ ) and magnesium ( $\text{Mg}^{++}$ ). Nutrients of opposite charge, such as nitrate and calcium, do not compete for uptake by plant roots. In fact, there is a synergistic effect of ions of opposite charge that enhances uptake for both nutrients. Studies with tobacco (4) and tomato (5) indicate that calcium uptake can be increased up to 3-fold with nitrate compared to ammonium nitrogen fertilization. Therefore, nitrate nitrogen fertilization is an important fertilizer management tool for crops susceptible to calcium deficiency disorders.

#### **Disease Reduction with Calcium Application**

As stated previously, calcium is an important component for the structure, stability and thickness of the plant cell wall and especially the middle lamella, the calcium pectate cell wall structure between cells. Many fungi and bacteria invade and infect plant tissue by producing enzymes that dissolve the middle lamella. Enzymes responsible for dissolving the middle lamella include polygalacturonases and pectolytic enzymes such as pectate traseliminase.

Increasing the tissue calcium content astonishingly lowers polygalacturonase and pectolytic enzyme activity from *Erwinia carotovora*, for example. *Erwinia* bacteria infect many vegetable crops and are also responsible for storage rot in potato tubers. Increasing the bean tissue calcium content from 1.6 to 3.4% (Table 2) greatly reduced *Erwinia carotovora* infection. Plants containing 1.6% calcium were completely destroyed within 6 days. Plants containing 3.4% calcium were healthy and possessed no symptoms of infection (Table 2.) (6). New research findings also indicate that soft rot or storage rot in potato tubers can be significantly reduced if the medullary tissue of the tuber contains at least 200 PPM Ca.

Fungal pathogenic infection is also reduced with increased calcium uptake by plants. A steady supply of available calcium delivered during fertigation by calcium nitrate reduces *Fusarium oxysporum* activity, the fungal pathogen that causes wilt and crown rot in tomatoes. Research indicates that tomato plants receiving low rates of calcium fertilization [5mM Ca in the xylem sap] were severely infected with *Fusarium oxysporum* compared to healthy plants receiving higher calcium rates with 25mM calcium in the xylem sap (7). Calcium fertilization also reduces Pythium blight and root rot of turf grass and citrus (8).

How effective is calcium fertilization in comparison to other nutrients? Research indicates that calcium uptake in plant tissue is superior to potassium in reducing the infection of the fungal pathogen *Botrytis* in lettuce (Table 3) (9). Increasing potassium concentration in lettuce from 1.44 to 4.89% did not deter *Botrytis* infection. However, decreasing tissue calcium concentration by half from 1.06% to 0.54% increased infection from a slight to moderate rating. (See Table 3)

A further decrease in calcium by one-half in the tissue (0.54 to 0.22%) resulted in severe *Botrytis* infection. It is apparent that strong healthy plants can defend themselves against pathogen attack, whereas weaker plants succumb to disease organisms. Enhanced cell wall structural integrity supplied by calcium fertilization is therefore important for plant health.

In summary, calcium reduces the pathogenic activity of several bacteria and fungi. It is apparent that the mechanism producing this benefit is increased cell wall thickness and/or reduction in effectiveness of pectolytic enzymes that break down host plant tissue. Readily available water-soluble calcium fertilizer sources appear to aid plants against pathogen attack

### **Heat Stress Mitigation by Calcium Application**

Intense heat during summer stresses many vegetable and grass crops. Plants try to reduce

heat damage to tissue through evapotranspiration. However, some plants within the same variety can effectively control heat stress while others have tissue damage. Research indicates that available calcium uptake during heat stress appears to be key in minimizing damage on potato. When nitrogen is applied to potato before or during heat stress, tissue damage reducing plant photosynthetic capabilities and tuber yield is observed. However, when calcium is applied with nitrogen during heat stress, tissue damage is greatly reduced and photosynthetic capabilities remain high to significantly increase tuber yield (See Table 4) (10). Higher stomatal conductance, providing regulation of the opening and closing of the stomates for better water use efficiency, was observed from the calcium treated plants. Calcium is an important nutrient for regulation of the H<sup>+</sup>-ATPase activity in the guard cells. Hence, it is highly probable that the energy for active transport of potassium into guard cells to close stomates is dependent on calcium availability and uptake into the leaf during heat stress. Similar findings have recently been observed with grasses. Heat stress significantly reduced quality in tall fescue and Kentucky bluegrass, but soluble calcium fertilizer treatment increased heat tolerance, turf quality and photosynthetic rate during the heat stress. Also, calcium treated grass maintained antioxidant activities and reduced the manufacture of leaf senescence enzymes, indicating that tissue damage was not as extensive with soluble calcium source fertilization (11).

We have reviewed the biochemical functions of calcium in plants, how calcium uptake is influenced by timing of application, nitrogen form and fertilizer source solubility and how available calcium reduces deficiency disorders, disease and heat stress. We will now review how soluble calcium in liquid fertilizers can increase the nitrogen fertilizer efficiency of surface applied urea fertilizers.

## **Calcium and Urea Nitrogen Fertilizer Efficiency**

Urea, in the presence of the enzyme urease, is converted to ammonium carbonate when applied to the surface of a moist soil. If the pH of the concentrated fertilizer solution is 8 or higher from the increased carbonate concentration during the urea conversion, a substantial quantity of ammonium-nitrogen can be volatilized as ammonia into the atmosphere. Nitrogen loss from ammonia volatilization of surface applied urea can approach 60-80% of the applied nitrogen, especially on higher pH soils (12).

Surface application of urea with soluble calcium fertilizer solutions reduces ammonia volatilization. The soluble calcium fertilizer source, either calcium nitrate or calcium chloride for example, precipitates the carbonate component from the solution as calcium carbonate. As a result, the concentrated fertilizer solution pH is decreased. Subsequently, less ammonia is lost. Water-soluble calcium fertilizer sources are key in this reaction. Calcium sources such as lime, gypsum and soil exchangeable calcium cannot reduce ammonia volatilization loss (13).

How much water-soluble calcium is required to minimize ammonia volatilization loss from surface applied urea? Research indicates that a ratio of 0.5 of pounds soluble calcium per pound of urea nitrogen is agronomically and economically optimal (13). Hence, if you apply 100 pounds of nitrogen from urea, you should apply 50 pounds of a soluble calcium source.

Recent field experiments with urea calcium ammonium nitrate ("UCAN" 21-0-0-4Ca with a calcium/urea ratio of 0.4), UAN solution and UAN plus Agrotain (urease inhibitor) were conducted at Kansas State University to determine nitrogen fertilizer efficiency of each source.

The test crop was corn. Results (See Table 5) indicate that within each fertilizer rate, UCAN produced the highest yields and had the highest nitrogen fertilizer efficiency. Subtracting the yield

of the control from the nitrogen treatment and dividing the remainder by the rate of nitrogen applied results in the nitrogen fertilizer efficiency within specific rates of N application. Using this method, one can determine the yield effectiveness of the nitrogen source applied. A three-fold increase in yield per pound of nitrogen applied was observed for UCAN-21 in comparison to surface applied UAN or UAN plus Agrotain at the 50 and 100 pound N application rates. UAN and UAN plus Agrotain approach the nitrogen fertilizer efficiency of UCAN-21 only when nitrogen was applied in excess (150 lbs. N/A). These findings suggest that the maximum economic crop yield can be achieved at lower rates of UCAN nitrogen application.

To test this hypothesis, a no-till fertilizer source and rate study was conducted at the University of Tennessee. Fertilizer sources were ammonium nitrate, UAN-32 and UCAN-23 (23-0-0-4Ca) applied at incrementally increasing rates of 30 pounds of nitrogen per acre. Wheat yield data is given in Table 6. It is very interesting to note that UCAN-23 performed as well as and often superior to ammonium nitrate, the preferred nitrogen source for no-till cultivation. UCAN-23 achieved optimal economic yield at 60 pounds of N/a. Ammonium nitrate and UAN required 90-120 pounds of nitrogen, respectively to produce similar yields. Minimally, nitrogen. (See Table 6)

Wheat Grain Yield (Bu/A) by N Fertilizer Source and Rate application rate could be reduced by 30 pounds of N per acre with UCAN-23 in this study and produce the same economic yield as other sources. Also, from an environmental point of view, judicious nitrogen management coupled with yield optimization is the goal of the fertilizer industry. Mixing two fertilizers to reduce nitrogen loss is very appealing. Calcium, therefore plays a vital role in urea nitrogen fertilizer efficiency.

## **Conclusions**

Calcium availability is essential in the biochemistry of plants and, as we are learning, in the nitrogen fertilizer efficiency of surface applied urea.

We should not be confused with the role of important soil amendment such as lime or gypsum and the requirements of soluble calcium by high value crops. Both are extremely important in soil fertility and plant nutrition and complement each other. However, fertilization with a soluble calcium fertilizer, such as calcium nitrate, to optimize plant uptake is extremely important for the production of high quality fruit and vegetables.

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Source	% Ca	Gal. H <sub>2</sub> O to Dissolve 1 Ton
Calcium Nitrate	19	235
Calcium Chloride	36	247
Calcium Sulfate (Gypsum)	23	80000
Calcitic Lime	40	80000
Dolomitic Lime	22	35100

Ca Content (%)	Polyglacturonase Activity	Pectate traseliminase	Severity of <i>Erwinia</i> Symptoms*
0.68	62	7.2	4
1.60	48	4.5	4
3.40	21	0	0

Table 2. Bean Tissue Calcium Content Effects Bacterial Pathogen Infection

\*4= Complete Decay of Plants in 6 Days; 0= No Symptoms

Table 3. Bean Tissue Calcium Content Effects Bacterial Pathogen Infection

\*0-5 Slight Infection; 6-10 Moderate Infection; 11-15 Severe Infection

%K	%Ca	%Mg	Botrytis Infection Rating*
1.44	1.06	0.32	4
2.38	0.54	0.41	7
3.42	0.22	0.47	13
4.89	0.18	0.42	15

Treatment	Tubers (g Fresh Wt.)	Foliage (g Fresh Wt.)	Tubers + Foliage (g Fresh Wt.)
Nitrogen (before stress)	612 b	318 a	930 b
Nitrogen (during stress)	700 b	325 a	1025 b
Ca + Nitrogen (during stress)	1000 a	381 a	1381 a

Table 5. Corn Grain Yield (Bu/A) and N Fertilizer Efficiency by N Source and Rate

\*N Fertilizer Efficiency as Bu/lb. N Applied; Control [No N] = 41 Bu/A

Fertilizer Source	50	100	150	50*	100*	150*
UAN	48 a	54 a	89 a	0.14	0.13	0.32
UAN +NBPT						
(Agrotain)	51 a	61 a	84 a	0.20	0.20	0.29
UCAN-21		62 a	80 b	97 a	0.42	0.39 0.37

**Table 6. Wheat Grain Yield (Bu/A) by N Fertilizer Source and Rate**

<b>Fertilizer Source</b>	<b>30</b>	<b>60</b>	<b>90</b>	<b>120</b>	<b>150</b>
Ammonium Nitrate	73 a	79 b	89 a	90 a	85 b
UAN-32	68 a	78 b	83 b	90 a	93 a
UCAN-23	67 a	86 a	92 a	92 a	93 a

**Back to Basics – Building Markets with Quality**

*Ray Hoyum*  
**IMC Global**

**Introduction**

IMC has historically provided soil fertility information to farmers and the industry at large. However, it has only been recently that IMC realized how much they needed to increase their educational efforts.

Field reports about two years ago indicated that nearly half of the nation’s soils tested medium or below for both phosphorus and potassium. Coupled with that, low commodity prices were causing many U.S. farmers to trim input costs including fertilizer applications. Identifying a critical need, IMC, with the support of the Potash and Phosphate Institute (PPI), implemented the Back-to-Basics program in the fall of 1999 to help growers nationwide rediscover the basic principles of proper soil fertility.

**Basic Principles Drive Back-to-Basics**

For a grower oriented educational initiative to be successful, it must focus on efforts to improve grower profitability. Successful farmers base input decisions on site-specific facts that help assure they will get optimum returns from dollars invested in inputs such as fertilizer. Most profitable farmers have lower costs per unit of production because they attain higher crop yields while controlling total costs. In an Iowa study, higher yields accounted for about 67 percent of increased profits among top farmers in a four-year survey.

Cost cutting contributed 21 percent toward higher profits.

Similar results were obtained in studies at Kansas State University and the University of Minnesota. In addition, they found that the most profitable growers also adopted technology faster, as well as spent more time gathering information, analyzing choices, planning activities and evaluating results. Therefore, since high yields are important for grower profitability, it is critical that growers understand those factors that influence yield and how to manage them effectively.

Since the mid-seventies, PPI has summarized every three to four years soil test results for P, K and pH from public and private laboratories across the United States and Canada. In general, soil test levels improved throughout the 70s and 80s. However, in the early 90s, the summaries started to show a reversed trend. Growers were not fertilizing adequately for the yields they were producing and were in effect mining the soils. In fact, the Illinois P budget went from a 20% surplus in the early 80s to basically balanced in the late 80s to a 20% deficit in the late 90s. Obviously, there was an urgent need to educate growers about the importance of proper nutrient management in high yield, profitable production.

**Narrowing the Yield Gap**

There is a large gap between the record-breaking yields that have been reported and the ones most growers actually obtain. Proper soil fertility management can help narrow the yield gap. Likewise, anything growers can learn from high yield

management systems can assist them in improving their own yields and profitability.

### **The Back-to-Basics Educational Initiative**

As a leader in the fertilizer industry, IMC delivered this important message to the marketplace. By targeting influencers (including the media, fertilizer dealers, crop consultants, county agents, university extension personnel, ag lenders and farm managers) as conduits to the end-user/grower, IMC also recognized the opportunity to reinforce its leadership position with its customers and others within the fertilizer industry.

So, while the ultimate message was grower directed, the campaign focused on re-acquainting influencers with the basic principles of proper soil fertility so that they could pass on the Back-to-Basics message to growers with whom they have contact.

While the campaign's name perhaps is not as important as the educational message it conveys, Back-to-Basics does illustrate a critical lesson. No matter what the economic or agronomic environment, farmers need to make the basics of a profitable crop production program a top priority. Proper soil fertility is the foundation on which high yields are built.

### **2000-2001 Campaign Components**

With each Back-to-Basics campaign component, IMC helped strengthen its leadership position in the fertilizer industry by providing information on proper soil fertility practices.

Direct marketing efforts allowed IMC to target its message specifically to the audiences that have the greatest impact on growers, such as fertilizer dealers, crop consultants, university extension personnel, ag lenders, and farm managers. A postcard promoting the *back-to-basics.net* web site was mailed to more than 19,000 people.

**A Spring 2001** Back-to-Basics informational kit also was mailed to the same audience. Kit components included: a teaser envelope that stated,

“Look inside for your new Back-to-Basics materials and FREE mousepad;” a personalized cover letter from Dr. Ray Hoyum; a mousepad promoting the [www.back-to-basics.net](http://www.back-to-basics.net); a folder that organized educational and promotional materials for use to promote a balanced soil fertility program; educational statement stuffers from PPI with order form; a *back-to-basics.net* homepage insert; and lastly, order forms for dealers and influencers to order ad slicks, radio scripts, statement stuffers and reminder postcards.

To generate even more awareness and to differentiate IMC as a leader in the fertilizer industry, advertising was placed in key trade publications highlighting the benefits of the Back-to-Basics program. A 4-color, 1-page ad (the boot ad) was created that promoted specifically the Back-to-Basics program to complement an ad (the hands ad) created in 2000. These ads were placed in key trade publications.

IMC created [www.back-to-basics.net](http://www.back-to-basics.net) to build understanding of all the resources available to growers and fertilizer dealers. The Web site is dedicated to providing growers and influencers with timely soil fertility information to help them make wise fertilizer decisions. The site includes information from PPI, a spring planning checklist, an on-line version of the Efficient Fertilizer Use Manual, environmental articles, AgriFacts, agronomic fact sheets, regional crop conditions and soil fertility updates, and article archives.

Tradeshows helped IMC impact key audiences with the Back-to-Basics message. More than 2000 growers at the 2001 Commodity Classic in San Antonio, Texas, heard the Back-to-Basics messages on proper soil fertility and the availability of the [www.back-to-basics.net](http://www.back-to-basics.net).

**A Fall 2001** Back-to-Basics informational kit was also mailed to the same audience as the Spring promotion. Additional emphasis was put on the development and use of the website.

## Results to Date

The integrated marketing communications campaign has had an overwhelmingly positive response. The balanced soil fertility message was timely and important to growers and influencers nationwide. IMC has discovered through dealer feedback that they are providing them with the resources and educational information they need to support their marketing efforts. The Back-to-Basics program helps dealers and other influencers respond to the current marketplace conditions with factual and professional information on the basics of proper soil fertility.

Since 1999, the educational and informative nature of the Back-to-Basics public relations effort has resulted in 18 feature articles in national agricultural publications, nationwide news releases placed in grassroots newspapers and regional publications, two segments on AgDay television, and a Noon Show and Saturday morning segment with Orion Samuelson of WGN.

The one-to-one personal nature of the direct mail campaigns served as an effective way to reach their target audience with great marketing materials. The Industry Average Response Rate is around 3%. The Back-to-Basics program came in at an impressive response rate of 13%. Of that 13%, Ag Dealers made up 30%; County Agents/University Extension personnel, 14%; Crop Consultants, 15%; and Farm Managers, 6%. Close to 70 percent of the respondents said they found the educational literature most helpful in promoting proper soil fertility. Visits to the Back-to-Basics web site jumped dramatically by the thousands as people logged on nationwide to view such things as the Efficient Fertilizer Use Manual and regional soil fertility information. PPI was pleased with the relationship building effort. The mailing resulted in over 1,500 requests for additional information from PPI.

Message frequency and message reinforcement are key components to building awareness and the trade advertising for Back-to-Basics did just that. Through fall 2000 and spring 2001, 17 ads were strategically placed in trade publications to keep the program message top-of-mind with their dealers. In addition, *Farm Chemicals* ran 8-page poster inserts in March and then again in September that dealers could hang on the wall of their dealership.

Results to date have shown that the Back-to-Basics program is a significant educational campaign that serves to increase visibility of IMC as a leader in the marketplace, and continues to provide growers and influencers with the information they need to make the best management decisions possible. Success can be measured in many ways and the positive response from all targeted audiences indicates that IMC delivered its message at the right time in a credible, professional way.

## What Role Will Back-to-Basics Play in the Future?

Even as high-tech agriculture continues to sweep through the industry, IMC's educational and support programs will stay focused on the agronomic fundamentals. New technologies have enabled IMC to deliver soil fertility messages more efficiently and effectively to agribusiness professionals and growers through their Back-to-Basics web site. At [www.back-to-basics.net](http://www.back-to-basics.net), users can engage in interactive educational activities that allow them to test their knowledge on soil fertility and conservation topics and access soil fertility information unique to their geographic region. The Back-to-Basics program will remain focused on helping growers maximize their profitability by learning that management literally starts at the ground level. Agribusiness professionals should be assured that no matter what the economic or agronomic environment, education and innovation will always play key roles in the way IMC helps them adapt to future challenges in developing quality and sustainable markets.

# ***THE FERTILIZER INDUSTRY ROUND TABLE***

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## **FINANCIAL STATEMENT OCTOBER 4, 2000 TO OCTOBER 22, 2001**

Cash Balance October 4, 2000		\$ 49,734.69
Income October 4, 2000 to October 22, 2001		
Registration Fees - 1999 Meeting & Cocktail Party & Coffee Break Receipts	\$ 8,238.86	
Sale of Proceedings	409.60	
Registration Fees - 2000 Meeting & Cocktail Party & Coffee Break Receipts	<u>17,930.00</u>	
Total Receipts October 27, 1999 to October 4, 2000		<u>26,578.46</u>
Total Funds Available October 27, 1999 to October 4, 2000		\$ 76,313.15
Disbursements October 4, 2000 to October 22, 2001		
1999 Meeting Expenses (Incl. Cocktail Party)	\$ 15,266.94	
Misc. Expenses Incl. Postage, Stationery, etc.	1,618.58	
1999 Proceedings	7,937.22	
2000 Meeting Preliminary Expense	1,528.23	
Directors' Meetings	2,645.60	
Secretarial Contract Expense	<u>10,000.00</u>	
Total Disbursements Oct. 4, 2000 to October 22, 2001		<u>38,996.57</u>
Cash Balance October 22, 2001		\$ 37,316.58

Respectfully submitted,

Paul J. Prosser, Jr.  
Secretary\Treasurer

PJPjr:ts

Meeting Attendance: 87