

**SEMINAR: DISPONIBILIDADE E MANEJO DE FÓSFORO NO SOLO /  
ESALQ-USP**

**USING PHOSPHATE RESOURCES AS EFFICIENTLY  
AS POSSIBLE WITH CURRENT PRODUCTION AND  
AGRONOMIC USE TECHNOLOGIES**

**DR. LUÍS IGNÁCIO PROCHNOW  
IPNI BRAZIL PROGRAM DIRECTOR**



**APATITE**



**RESPONSE TO P**



INTERNATIONAL PLANT NUTRIT

# INTERNATIONAL PLANT NUTRITION INSTITUTE (IPNI)

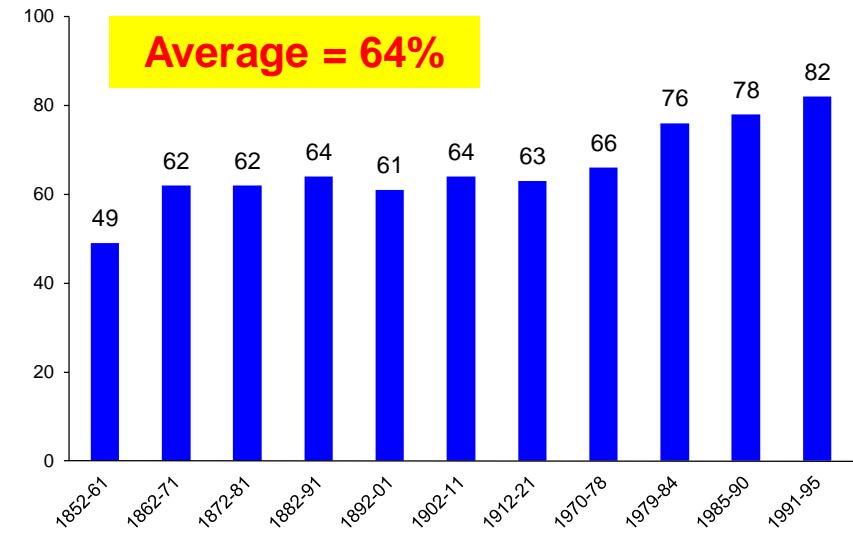
✓ Not-for-profit organization dedicated to research and education for the responsible management of plant nutrients for the benefit of the human family.

“We train the trainers and influence the influencers”

Dr. Terry Roberts - President IPNI

# Rothamsted, England

## Wheat Experiment, 1852-1995



- ✓ Oldest agronomic experiment in the world. Started in 1843.
  - ✓ Effect of fertilizer on crop production.



Source: Murrell, 2009

# **AMONG OTHER SEVERAL ACTIVITIES IPNI AWARDS**

## **IPNI INTERNATIONAL:**

- ✓ **IPNI SCIENCE AWARDS**
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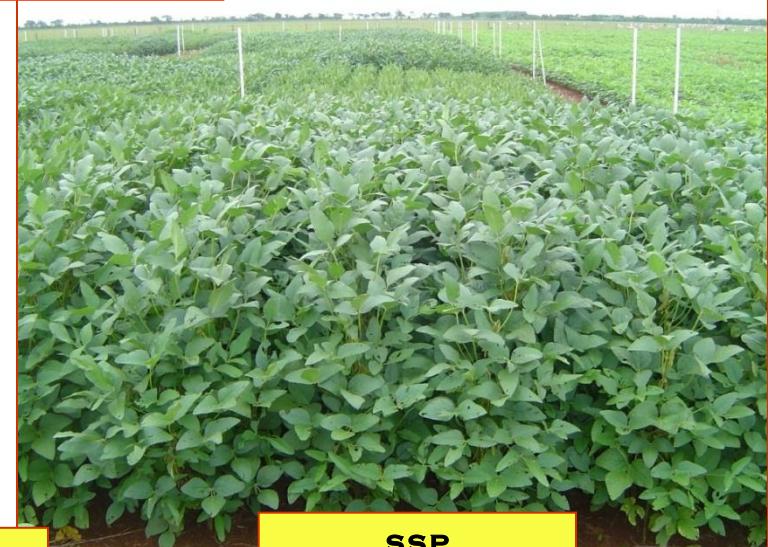
**USING PHOSPHATE RESOURCES AS EFFICIENTLY  
AS POSSIBLE WITH CURRENT PRODUCTION AND  
AGRONOMIC USE TECHNOLOGIES**

## **1. INTRODUCTION**

**SOYBEAN P RESPONSE**  
**ITIQUIRA, MT**



**CONTROL**



**SSP**

**120 KG/HA OF  $P_2O_5$**



**ARAXA**



**GAFSA**



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## HOW TO OPTIMIZE THE USE OF P RESOURCES?



GLOBAL  
TraPs

TRANSDISCIPLINARY PROCESSES FOR SUSTAINABLE PHOSPHORUS MANAGEMENT



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# GLOBAL TRAPs - LEADERS



**DR. ROLAND W. SCHOLZ**  
ETH



Eidgenössische Technische Hochschule Zürich  
Swiss Federal Institute of Technology Zurich



**DR. AMIT H. ROY**  
IFDC



## GLOBAL TRAPS – GENERAL INFORMATION

- ✓ **MISSION:** LEAD TO IMPROVED RESOURCE UNDERSTANDING AND AWARENESS, FUNNELING INTO SUSTAINABLE P MANAGEMENT AND STEWARDSHIP.
- ✓ **GUIDING QUESTION:** “*WHAT NEW KNOWLEDGE, TECHNOLOGIES AND POLICY OPTIONS ARE NEEDED TO ENSURE THAT FUTURE PHOSPHORUS USE IS SUSTAINABLE, IMPROVES FOOD SECURITY AND ENVIRONMENTAL QUALITY AND PROVIDES BENEFITS FOR THE POOR?*
- ✓ **VISION:** (1) LEADING GLOBAL LEARNING FORUM FOR SUSTAINABLE P USE IN A TRANSDISCIPLINARY (JOINT, EYE-LEVEL, TRANSPARENT), COMPLEMENTARY AND NON-POLITICIZED AREA, (2) TO DEFINE THE CURRENT STATE OF KNOWLEDGE, (3) TO DEFINE NEW TECHNOLOGIES WHICH ARE NEEDED TO BETTER PROCESS, USE AND RE-USE PHOSPHORUS, (4) TO DEFINE MOST VALUABLE AREAS FOR POLICY INTERVENTION TO ENSURE SUSTAINABLE P USE IN THE FUTURE.



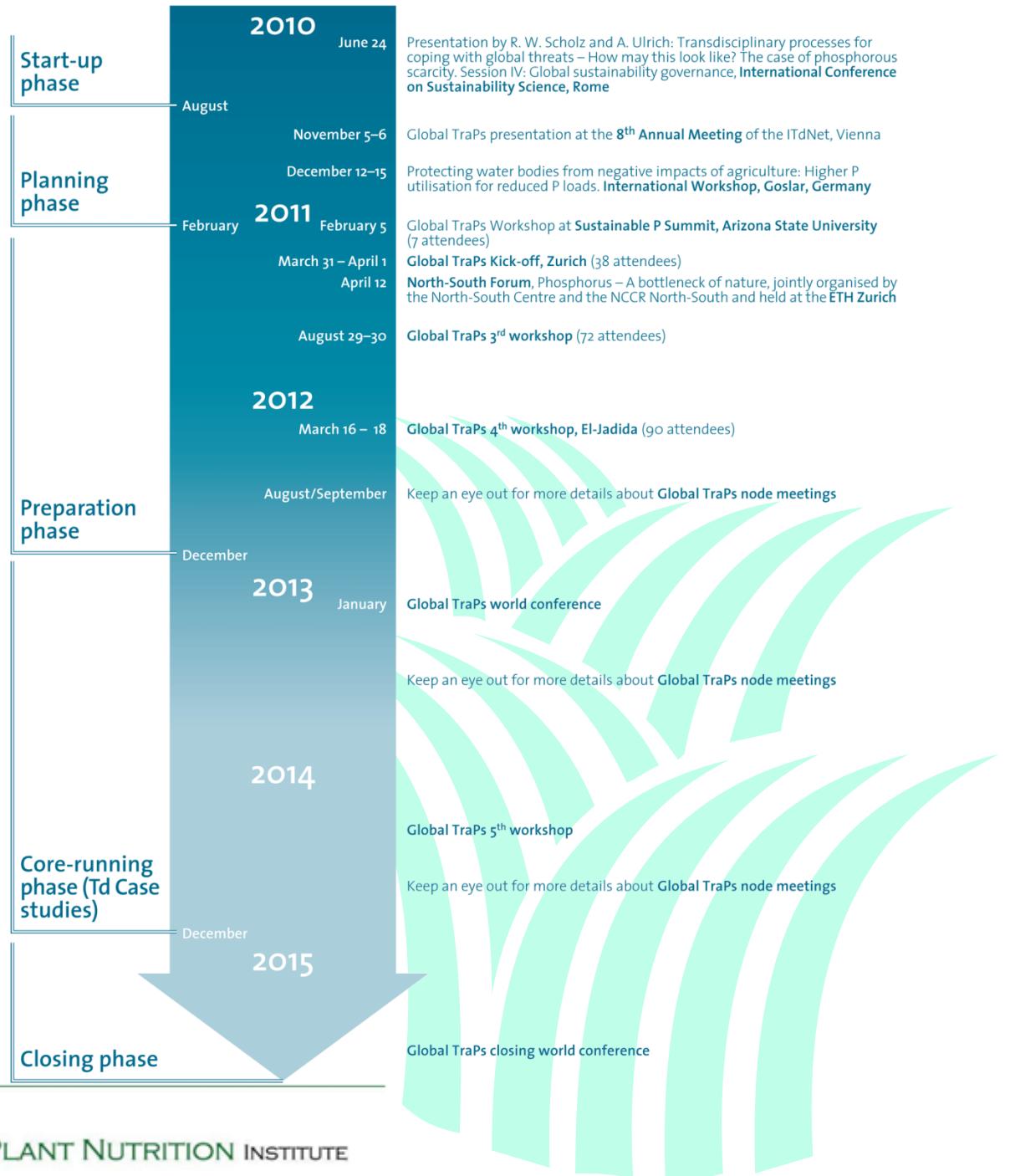
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# GLOBAL TRAPS – WORKSHOP IV

## EL-JADIDA, MARC 16–18 2012

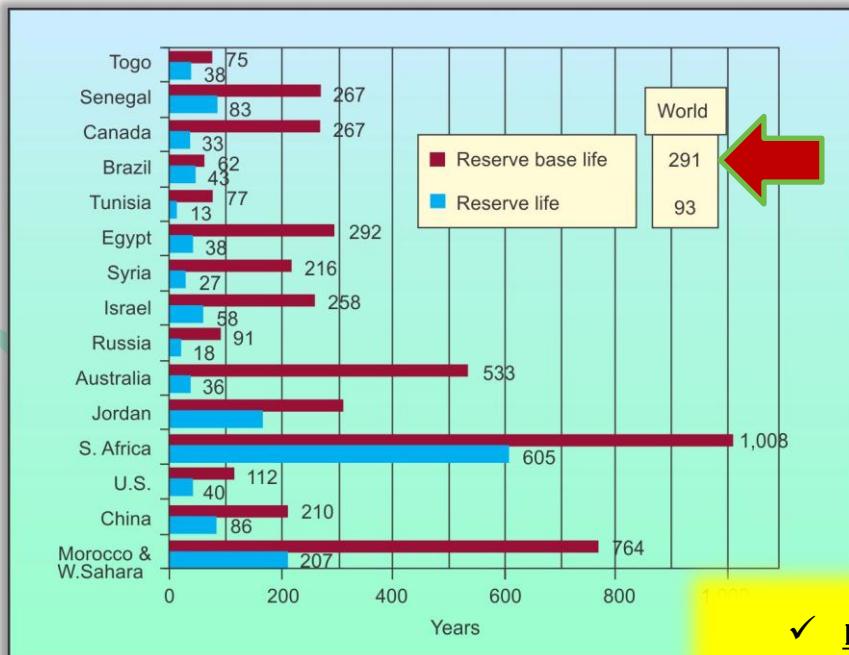


# GLOBAL TRAPS: PROJECT TIMEFRAME



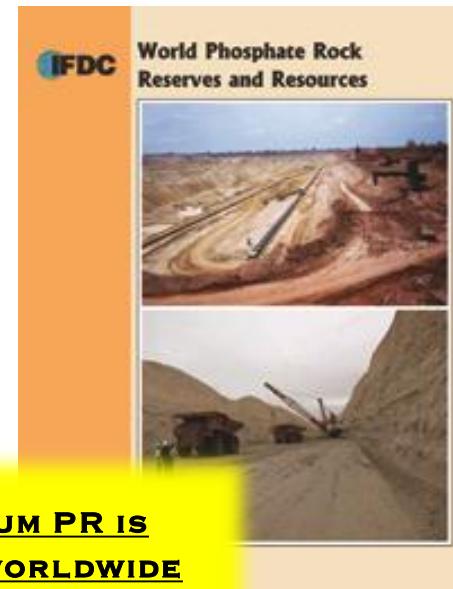
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# PHOSPHATE MINE RESERVE LIFE AND RESERVE BASE LIFE



SOURCE: USGS, 2009; ADAPTED FROM FIXEN, 2009.

New IFDC Report Indicates World Reserves of Rock Phosphate Are Adequate to Meet Demand



✓ **HIGH PREMIUM PR IS  
DECREASING WORLDWIDE**



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# **HOW TO OPTIMIZE THE USE OF P RESOURCES IN AGRICULTURE?**

**EMPHASIS IN TWO IMPORTANT ASPECTS:**

✓ **HOW WE PRODUCE?**

➡ ✓ **HOW WE UTILIZE (AGRONOMICS)?**

## **2. HOW WE UTILIZE? AGRONOMICS**



# FACTORS INFLUENCING THE AGRONOMIC EFFECTIVENESS OF P SOURCES

✓ FERTILIZER PROPERTIES.

✓ CROP.

✓ SOIL PROPERTIES.

✓ FERTILIZER AND SOIL

MANAGEMENT.

✓ PHYSICAL PROPERTIES:

- STATE (FLUID OR SOLID)
- PARTICLE SIZE.
- CONSISTENCY/HARDNESS.
- FLUIDITY.
- DENSITY.
- MIXTURES WITH OTHER NUTRIENT SOURCES.

✓ CHEMICAL PROPERTIES:

- ➡ CHEMICAL COMPOSITION (COMPOUNDS PRESENT).
- CONCENTRATION.
  - OTHER COMPOUNDS PRESENT (DESIRABLE OR NOT)/OTHER NUTRIENTS.
  - REACTION IN SOIL(S): ACIDITY OR BASICITY LEVEL.

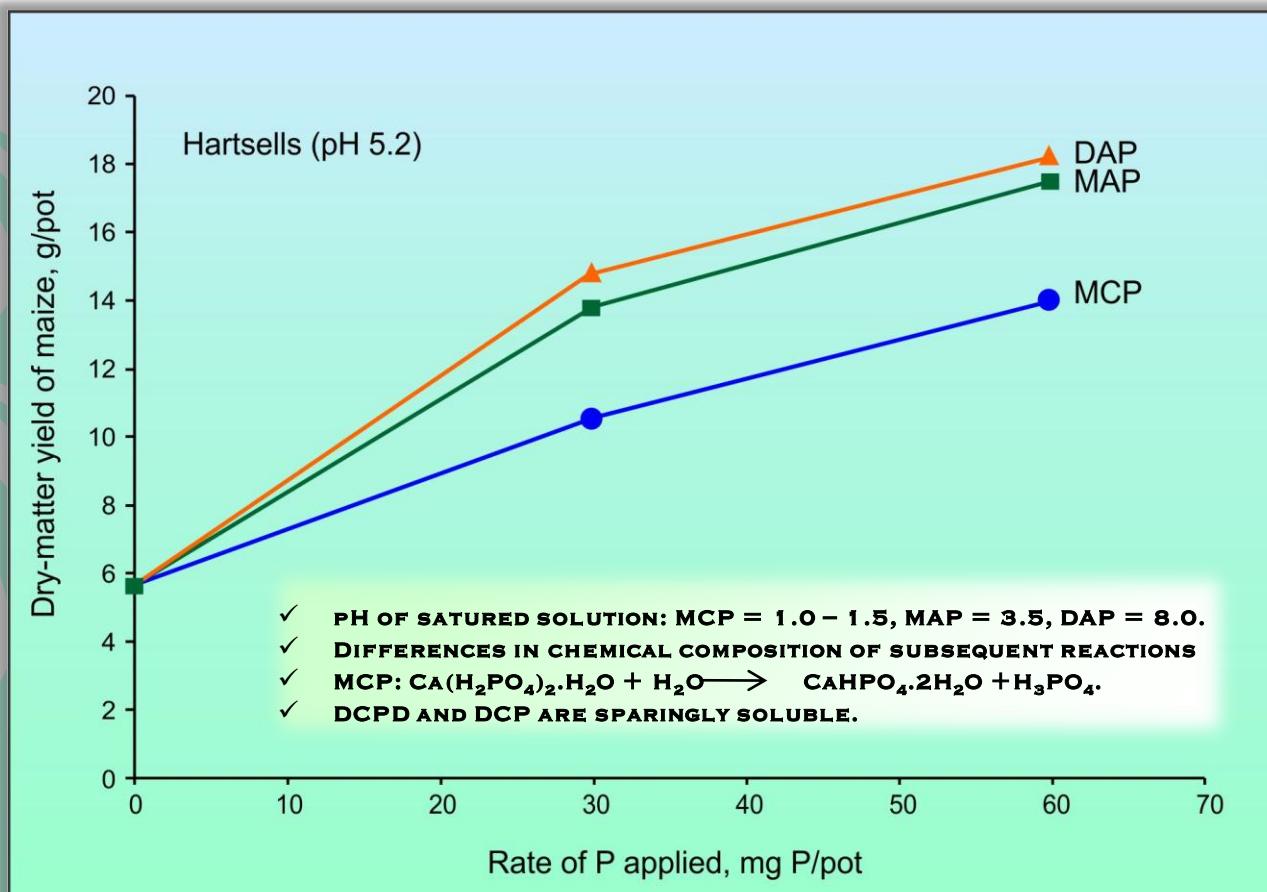
✓ PHYSICAL-CHEMICAL PROPERTIES:

- SOLUBILITY.
- HYGROSCOPICITY.
- “METALLING”/CAKING.
- SALINITY.



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# DRY-MATTER YIELD OF MAIZE (6 WEEKS) OBTAINED WITH DIFFERENT P SOURCES ON AN ACID HARTSELLS SOIL (PH 5.2)

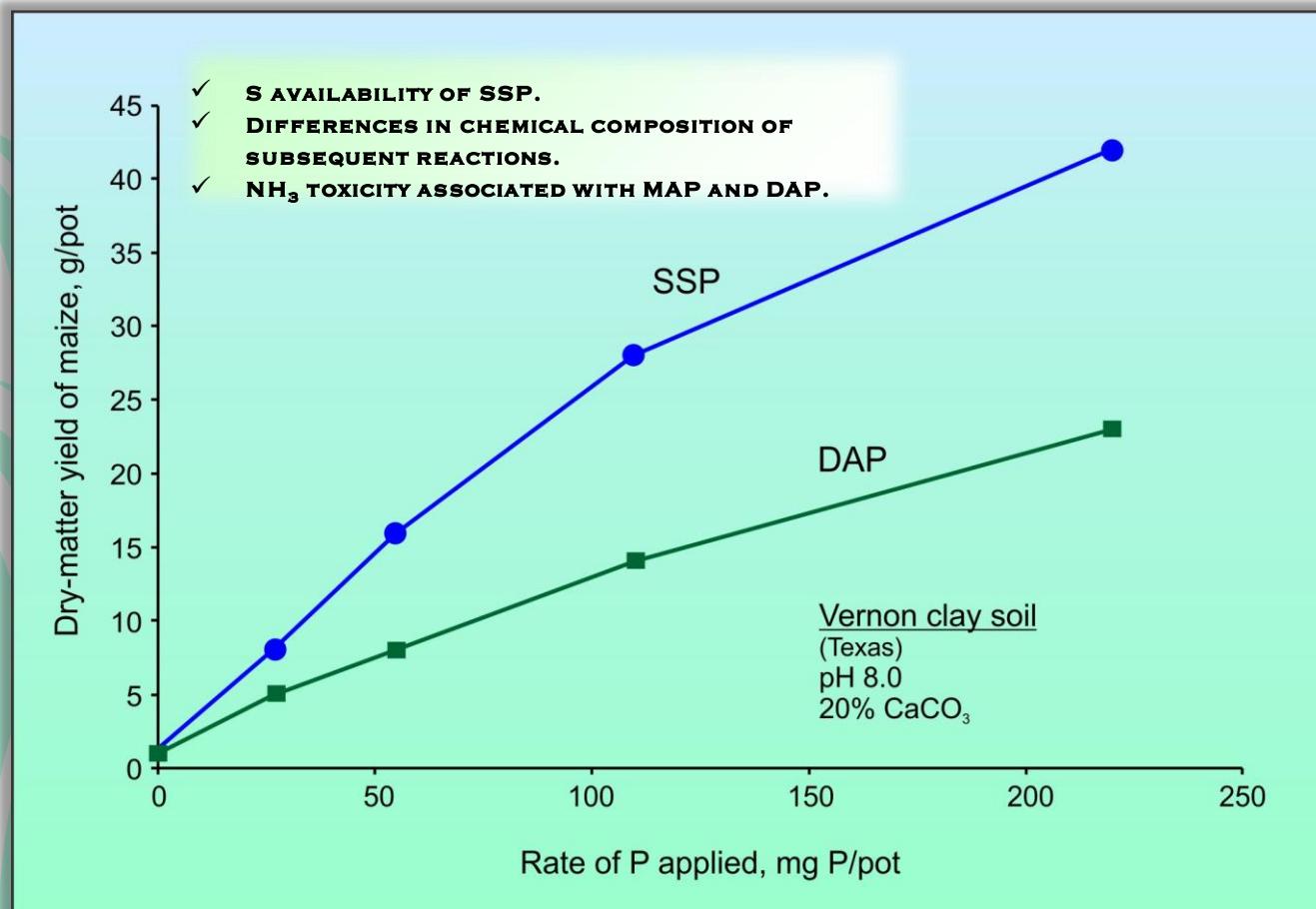


SOURCE: BOULDIN AND SAMPLE (1959).



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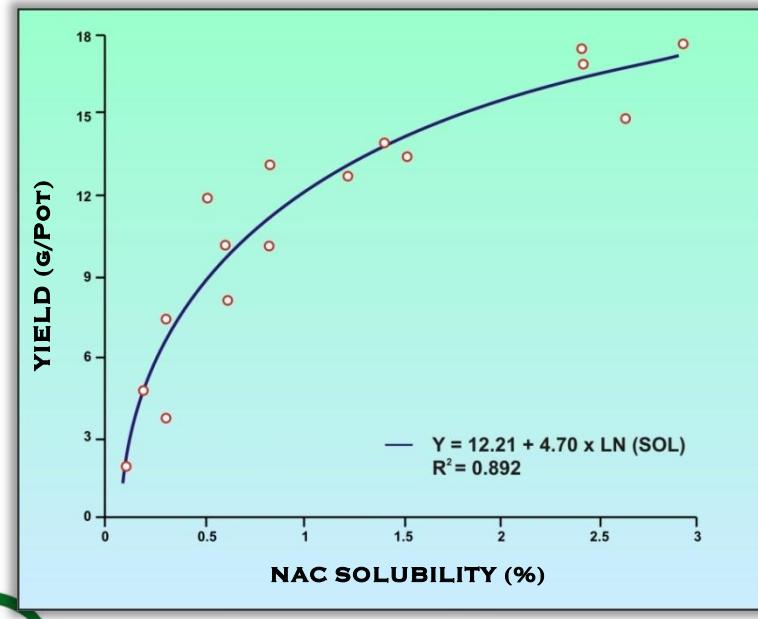
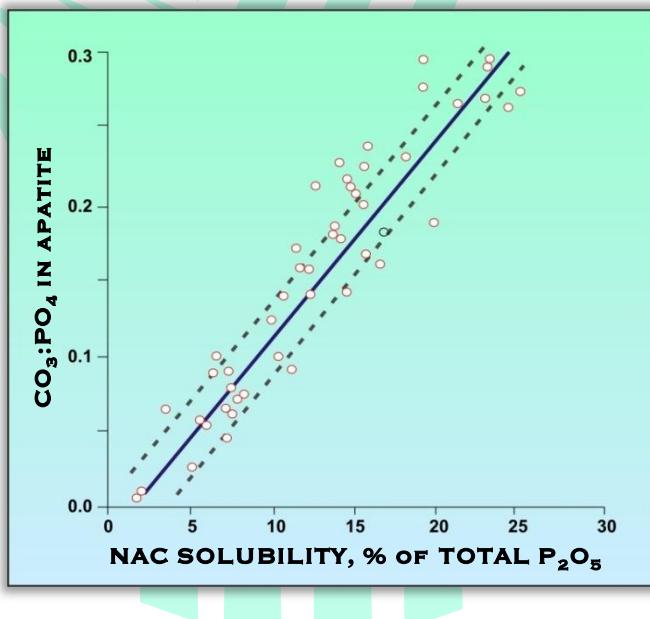
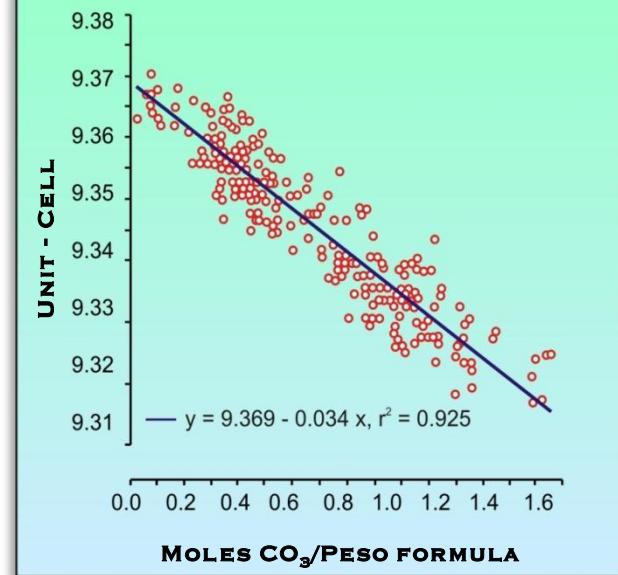
## DRY-MATTER YIELD OBTAINED WITH SSP AND DAP WHEN P WAS BROADCAST TO A CALCAREOUS SOIL



SOURCE: LU ET AL., (1987).

# FROM THE PR TO ITS AGRONOMIC EFFECTIVENESS

PR	COMPRIMENTO DO EIXO A (Å)	FORMULA DA APATITE <sup>a</sup>
KAIYANG, CHINA	9.372	$\text{Ca}_{9.88}\text{Na}_{0.01}\text{Mg}_{0.01}(\text{PO}_4)_{5.94}(\text{CO}_3)_{0.08}\text{F}_{2.02}$
HAHOTOE, TOGO	9.351	$\text{Ca}_{9.79}\text{Na}_{0.15}\text{Mg}_{0.08}(\text{PO}_4)_{5.39}(\text{CO}_3)_{0.61}\text{F}_{2.24}$
PESCA, COLOMBIA	9.346	$\text{Ca}_{9.78}\text{Na}_{0.18}\text{Mg}_{0.07}(\text{PO}_4)_{5.28}(\text{CO}_3)_{0.72}\text{F}_{2.28}$
EL-HASSA, JORDAN	9.339	$\text{Ca}_{9.69}\text{Na}_{0.23}\text{Mg}_{0.08}(\text{PO}_4)_{5.12}(\text{CO}_3)_{0.88}\text{F}_{2.35}$
GAFSA, TUNISIA	9.328	$\text{Ca}_{9.58}\text{Na}_{0.30}\text{Mg}_{0.12}(\text{PO}_4)_{4.80}(\text{CO}_3)_{1.10}\text{F}_{2.44}$
NORTH CAROLINA, USA	9.322	$\text{Ca}_{9.55}\text{Na}_{0.34}\text{Mg}_{0.13}(\text{PO}_4)_{4.77}(\text{CO}_3)_{1.23}\text{F}_{2.49}$



SOURCE: HAMMOND ET AL., (1986).



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# FACTORS INFLUENCING THE AGRONOMIC EFFECTIVENESS OF P SOURCES

- ✓ FERTILIZER PROPERTIES.
- ✓ CROP.
- ✓ SOIL PROPERTIES.
- ✓ FERTILIZER AND SOIL MANAGEMENT.

- ✓ CROP.
- ✓ CROPPING SYSTEM/ROTATION.

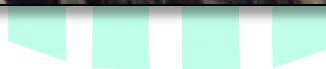


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# CROP – GRASS SYSTEMS OF CULTIVATION



SANTA FÉ: MAIZE WITH BRACHIARIA



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# P RECOVERY OXISOL, 22 YEARS

SSP	P RECOVERY	
	ANNUAL CROPS <sup>1</sup>	ANNUAL + GRASS <sup>2</sup>
KG/HA DE P <sub>2</sub> O <sub>5</sub>	----- % -----	
100	44	85
200	40	82
400	35	70
800	40	62

<sup>1</sup> A ÁREA FOI CULTIVADA POR DEZ ANOS COM SOJA, SEGUIDA DE UM PLANTIO COM MILHO E QUATRO CICLOS DA SEQÜÊNCIA MILHO-SOJA, DOIS CULTIVOS DE MILHO E UM DE SOJA.

<sup>2</sup> A ÁREA FOI CULTIVADA POR DOIS ANOS COM SOJA, SEGUIDA DE NOVE ANOS COM BRAQUIÁRIA MAIS DOIS ANOS COM SOJA E DOIS CICLOS DA SEQÜÊNCIA MILHO-SOJA, E CINCO ANOS COM BRAQUIÁRIA.

SOURCE: SOUSA ET AL., 2007.

# FACTORS INFLUENCING THE AGRONOMIC EFFECTIVENESS OF P SOURCES

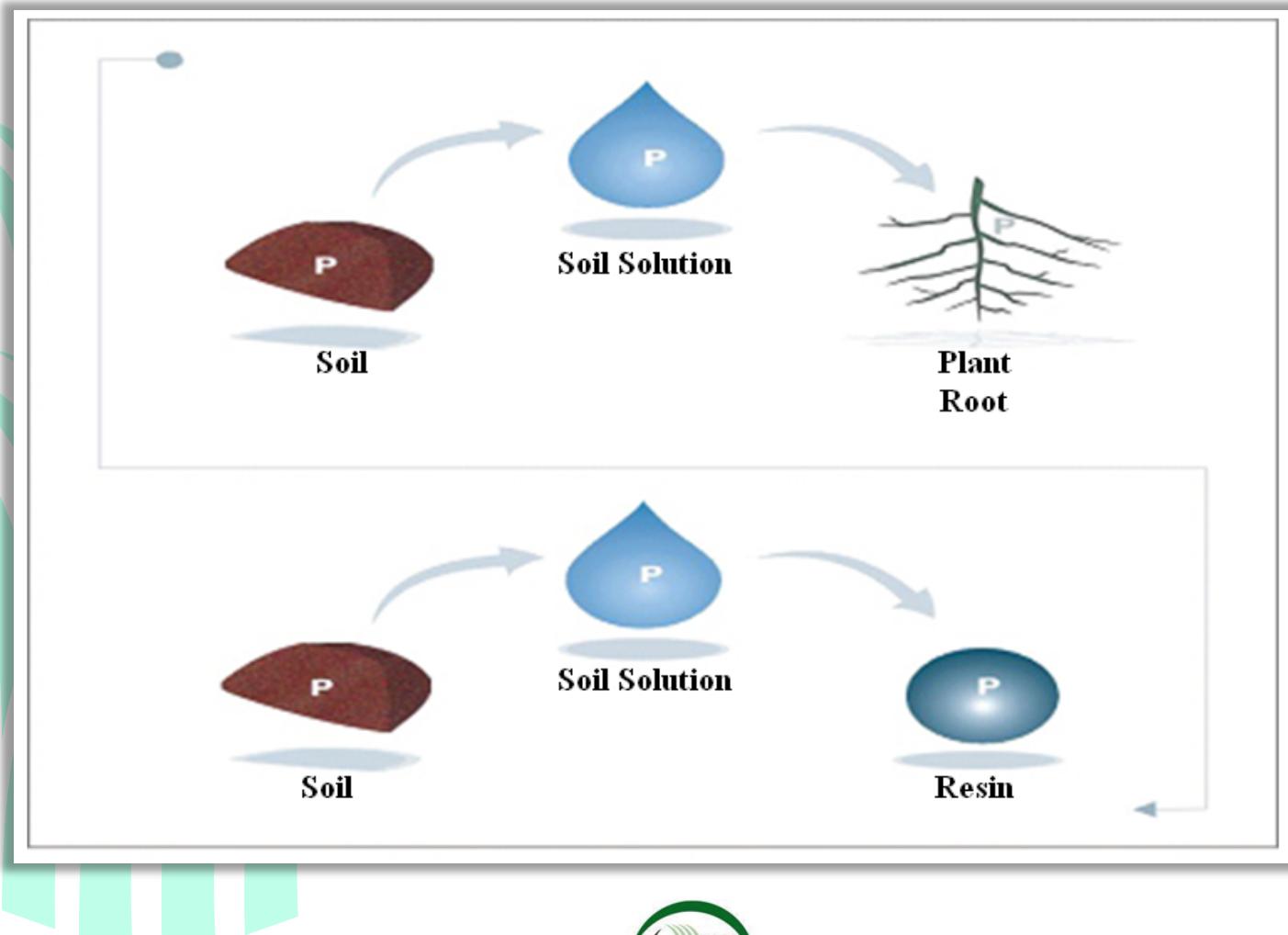
- ✓ FERTILIZER PROPERTIES.
- ✓ CROP.
- ✓ SOIL PROPERTIES.
- ✓ FERTILIZER AND SOIL MANAGEMENT.

- ✓ SOIL P AVAILABILITY.
- ✓ SOIL PH.
- ✓ SOIL P FIXATION (PRECIPITATION AND SPECIFIC ADSORPTION).
- ✓ SOIL MINERALOGY.
- ✓ SOIL GRANULOMETRY.
- ✓ SOIL OM.
- ✓ MYCORRHIZAES.



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# SCHEMATIC DEMONSTRATION OF P EXTRACTED FROM SOILS BY ION EXCHANGE RESIN



SOURCE: BETTER CROPS/VOL. 93 (2009, N° 1).

# EFFECT OF SOIL pH IN THE AMOUNT OF P IN PLANT LEAF AND SOIL P BY DIFFERENT METHODOLOGIES

CROP AND LOCATION	PH CACI <sub>2</sub>	LEAF P (g Kg <sup>-1</sup> )	SOIL P (mg dm <sup>-3</sup> )			
			MEHLICH 1	BRAY 1	OLSEN	RESINA
BEANS PARIQUERA-ÁCU	3.8 D *	2.44 B	17 A	20 A	41 A	33 B
	4.2 C	3.21 A	18 A	21 A	33 B	36 AB
	4.7 B	3.25 A	18 A	20 A	26 C	38 AB
	5.1 A	3.26 A	19 A	18 A	19 D	43 A
	5.2 A	3.25 A	20 A	19 A	21 D	43 A
SUNFLOWER MOCOCA	4.3 C	2.79 C	12 B	24 A	17 A	22 B
	4.6 C	3.27 B	12 B	22 A	17 A	26 AB
	5.3 B	3.81 A	16 A	25 A	16 A	33 AB
	5.5 AB	3.87 A	15 A	20 A	12 A	35 A
	5.7 A	3.80 A	16 A	20 A	12 A	37 A
SOYBEAN MOCOCA	4.3 A	1.85 C	6 A	15 A	10 A	13 C
	4.8 D	2.06 BC	7 A	16 A	11 A	16 C
	5.5 C	2.44 AB	5 A	13 A	7 A	17 BC
	6.1 B	2.26 A	7 A	17 A	8 A	22 AB
	6.4 A	2.55 A	7 A	15 A	8 A	27 A
SOYBEAN RIBEIRÃO PRETO	4.5 D	2.35 B	9 A	20 A	18 A	16 C
	4.9 C	2.69 AB	8 A	22 A	15 AB	19 BC
	6.1 B	2.88 A	8 A	20 A	13 AB	23 B
	6.6 A	2.85 A	10 A	24 A	12 B	34 A

SOURCE: RAIJ AND QUAGGIO (1990).

# FACTORS INFLUENCING THE AGRONOMIC EFFECTIVENESS OF P SOURCES

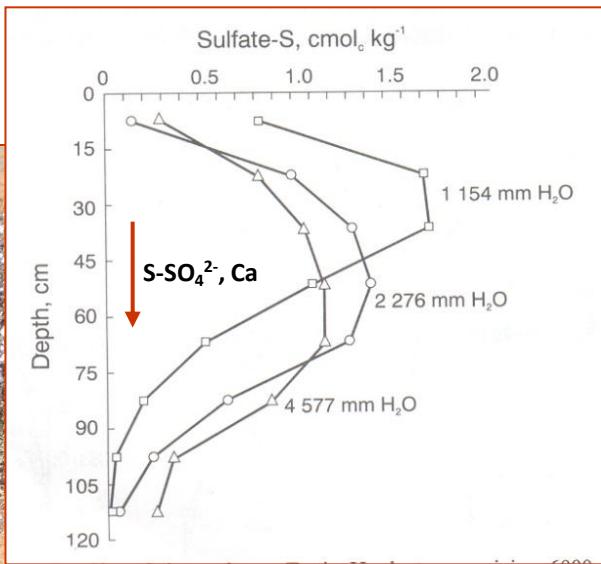
- ✓ FERTILIZER PROPERTIES.
- ✓ CROP.
- ✓ SOIL PROPERTIES.
- ✓ FERTILIZER AND SOIL MANAGEMENT.

- ✓ PLACEMENT.
- ✓ MANAGEMENT OF OTHER NUTRIENTS.
- ✓ WATER MANAGEMENT.
- ✓ MANAGEMENT OF OTHER LIMITING FACTORS.



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# PHOSPHOGYPSUM



EXPERIMENT: EMBRAPA CERRADO.  
PHOTO: IPNI.



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# NUTRIENT ABSORPTION BY BARLEY AS A FUNCTION OF LIMING AND PHOSPHOGYPSUM APPLICATION

TRATAMENTO	N	P	K	CA	MG	S
<b>G.KG<sup>-1</sup></b>						
<b>LIME</b>						
NO LIME	107,4	6,9	185,4 B	23,2	15,6	12,9
LIME ON SOIL SURFACE	128,8	8,2	207,7 AB	32,7	13,3	15,6
LIME MIXED TO THE SOIL	138,9	7,2	237,6 A	32,3	16,1	17,2
F VALUE	6,03NS	4,23NS	7,59*	3,82NS	4,48NS	1,87NS
CV (%)	18,1	18,2	14,5	35,0	16,0	36,1
<b>PHOSPHOGYPSUM, T.HA<sup>-1</sup></b>						
0	109,3	5,4	192,3	26,6	14,4	5,7
3	115,5	7,8	178,1	25,0	15,2	11,7
6	141,6	7,9	227,9	30,6	15,6	20,6
9	133,8	8,6	242,7	35,3	14,9	22,8
EFFECT	L**	L**	L**	L**	NS	L**
CV (%)	18,9	29,2	17,1	24,2	23,9	27,6

MÉDIAS SEGUIDAS POR LETRAS IGUAIS NAS COLUNAS NÃO DIFEREM SIGNIFICATIVAMENTE PELO TESTE DE TUKEY AO NÍVEL DE 5%. L: EFEITO LINEAR POR REGRESSÃO. NS: NÃO SIGNIFICATIVO A 5%, \*\*:SIGNIFICATIVO A 1%.

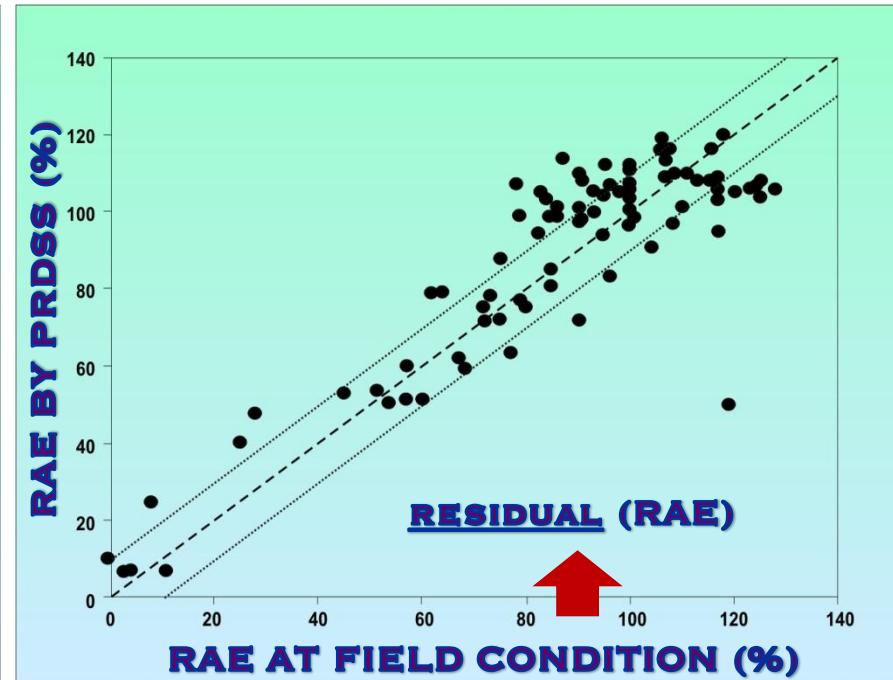
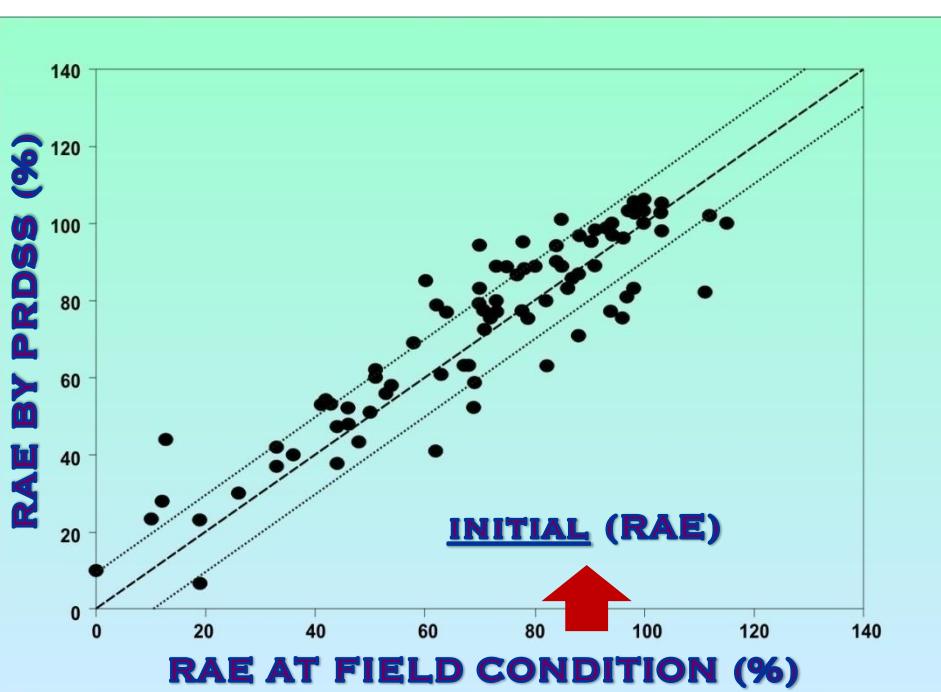
EXTRACTED FROM E.F. CAIRES ET AL.

SOURCE: BRAGANTIA, CAMPINAS, 60(3), 213-223, 2001.



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# PHOSPHATE ROCK DECISION SUPPORT SYSTEM (PRDSS)



[HTTP://WWW-ISWAM.IAEA.ORG/DAPR/SRV/EN/HOME](http://WWW-ISWAM.IAEA.ORG/DAPR/SRV/EN/HOME)

SOURCE: U. SINGH & S. H. CHIEN (2008), UNPUBLISHED DATA.

### **3. POTENTIAL NEW P SOURCES**



## RECENT DEVELOPMENTS OF FERTILIZER PRODUCTION AND USE TO IMPROVE NUTRIENT EFFICIENCY AND MINIMIZE ENVIRONMENTAL IMPACTS

S. H. Chien,<sup>\*†</sup> L. I. Prochnow,<sup>†</sup> and H. Cantarella<sup>‡</sup>

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\* Formerly with International Fertilizer Development Center (IFDC), Muscle Shoals, Alabama, USA

<sup>†</sup> International Plant Nutrition Institute (IPNI), Piracicaba, SP, Brazil

<sup>‡</sup> Instituto Agronômico, Campinas, SP, Brazil

<sup>\*</sup> Corresponding author: 1905 Beechwood Circle, Florence, Alabama, USA; email: nhchien@comcast.net



# RAE OF ALTERNATIVE SOURCES OF P AS RELATED TO REGULAR HIGH WSP SSP

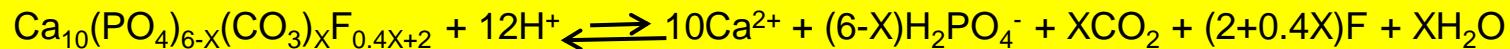
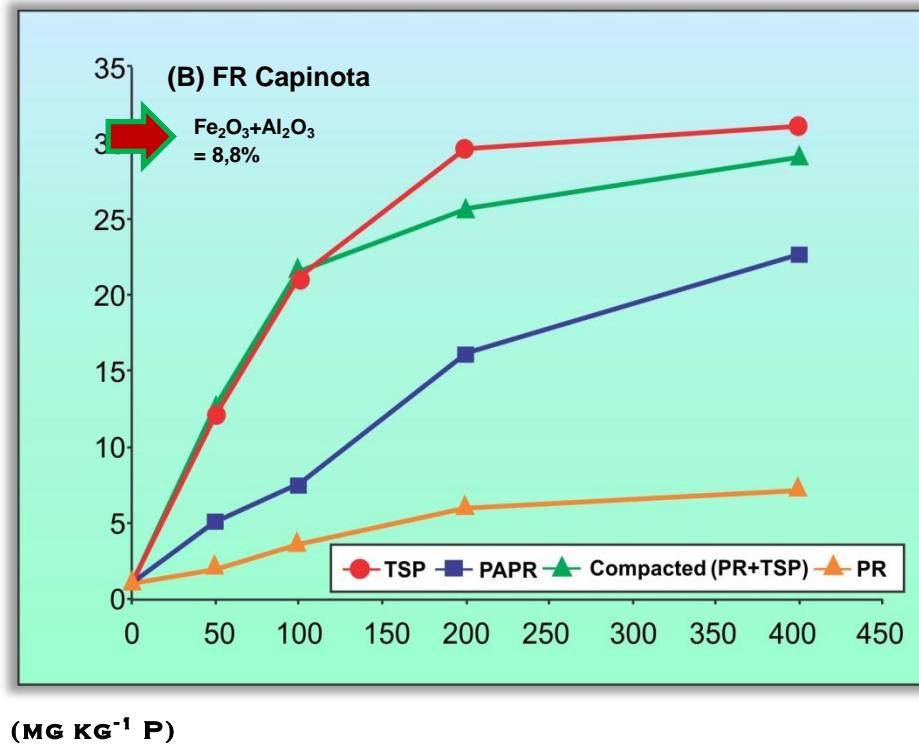
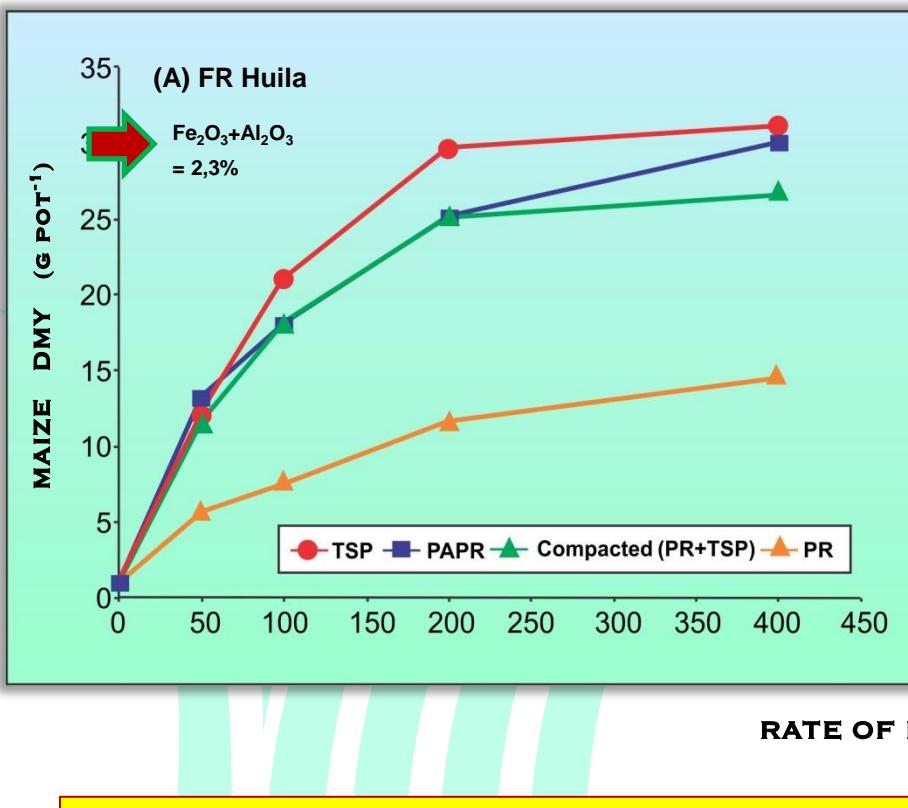
P SOURCE	RAE			
	WHEAT		RYEGRASS	
	DMY	P UPTAKE	DMY	P UPTAKE
SSP (STANDARD)	100	100	100	100
PM PR	1	1	30	15
LG PM SSP	91	87	99 ↙	95
PM PR + SSP (C)	99 ↙	88	95 ↙	77
PM PR + SSP (M)	69 ↙	57	86 ↙	72

6,0% CAALH(HPO<sub>4</sub>)<sub>2</sub>F<sub>2</sub>

SOURCE: PROCHNOW ET AL. (2004).

# MAIZE DMY WITH ALTERNATIVE SOURCES OF P

## (A) FR HUILA AND (B) FR CAPINOTA



SOURCE: MENON AND CHIEN (1990).



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## **4. PRODUCTION OF REGULAR FULLY ACIDULLATED P SOURCES**

**NOT PAPR**

## BACKGROUND INFORMATION

- ✓ IN SOME COUNTRIES, INCLUDING BRAZIL, ACIDULATED P FERTILIZERS HAVE TO HAVE HIGH WATER-SOLUBLE P (WSP; 90%) IN THE NEUTRAL AMMONIUM CITRATE (NAC) + H<sub>2</sub>O SOLUBLE P FRACTION (LEGISLATION).
- ✓ PREMIUM GRADE PR IS DECREASING WORLDWIDE.
- ✓ HIGH AMOUNTS OF ENERGY AND MONEY ARE SPENT IN ORDER TO ALWAYS PRODUCE P FERTILIZERS WITH HIGH CONTENTS OF WSP.
- ✓ PART OF THE APATITE CONCENTRATES ARE DISCARDED.
- ✓ IS IT REALLY NECESSARY FOR TOTALLY ACIDULATED P SOURCES TO ALWAYS HAVE HIGH WATER SOLUBILITY?



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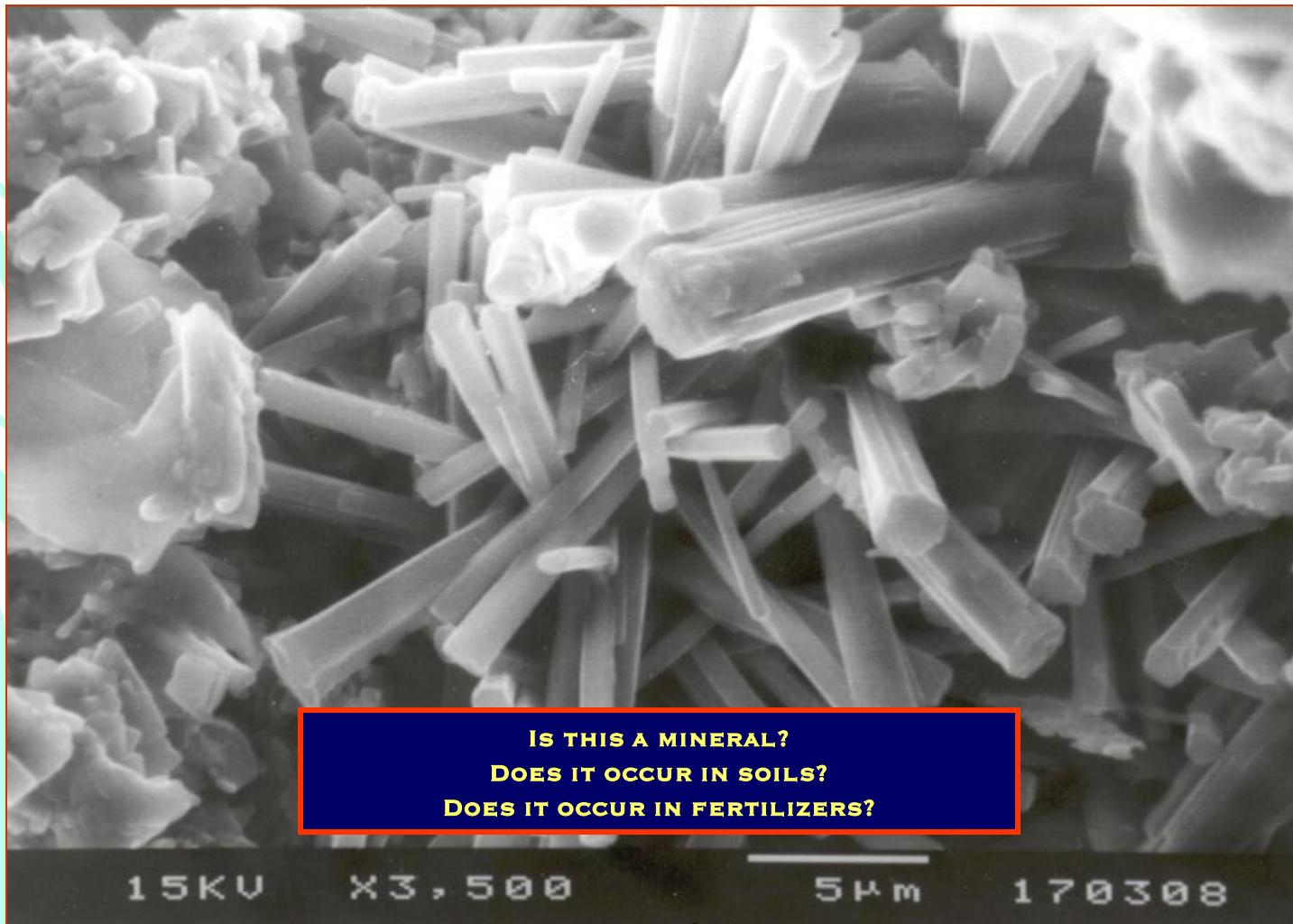
**LEHR (1980)**

**ARE WATER-INSOLUBLE PHOSPHATES TO BE AVOIDED AT  
ALL COST?**

**THE NEED FOR A MORE REALISTIC SET OF PRODUCT  
SPECIFICATIONS IS ONE OF THE MOST IMPORTANT  
PROBLEMS CONFRONTING PHOSPHATE PRODUCERS TO  
SEEK RELIEF FROM UNNECESSARY AND COSTLY  
PURIFICATION STEPS. ONLY AGRONOMIC RESEARCH CAN  
**PROVIDE THE NECESSARY GUIDANCE.****

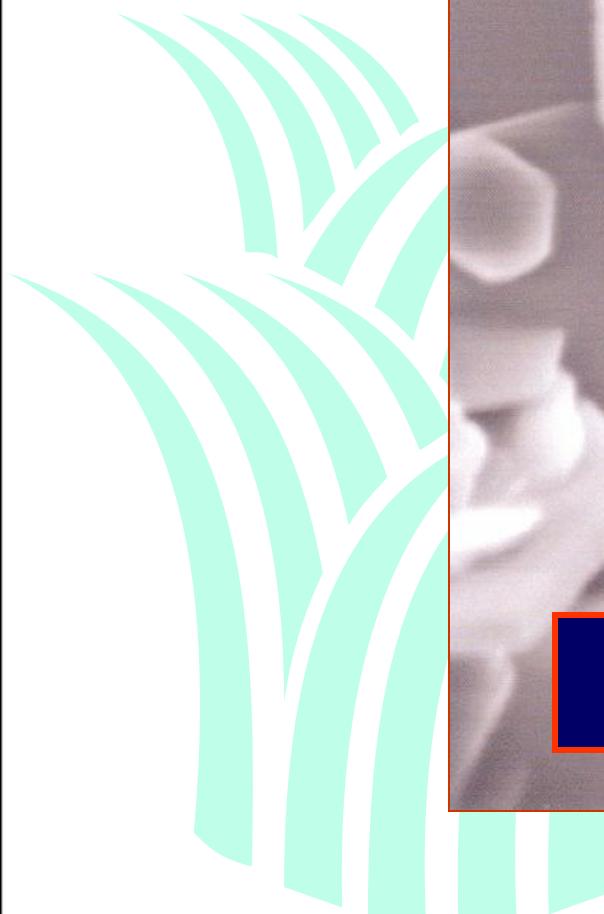
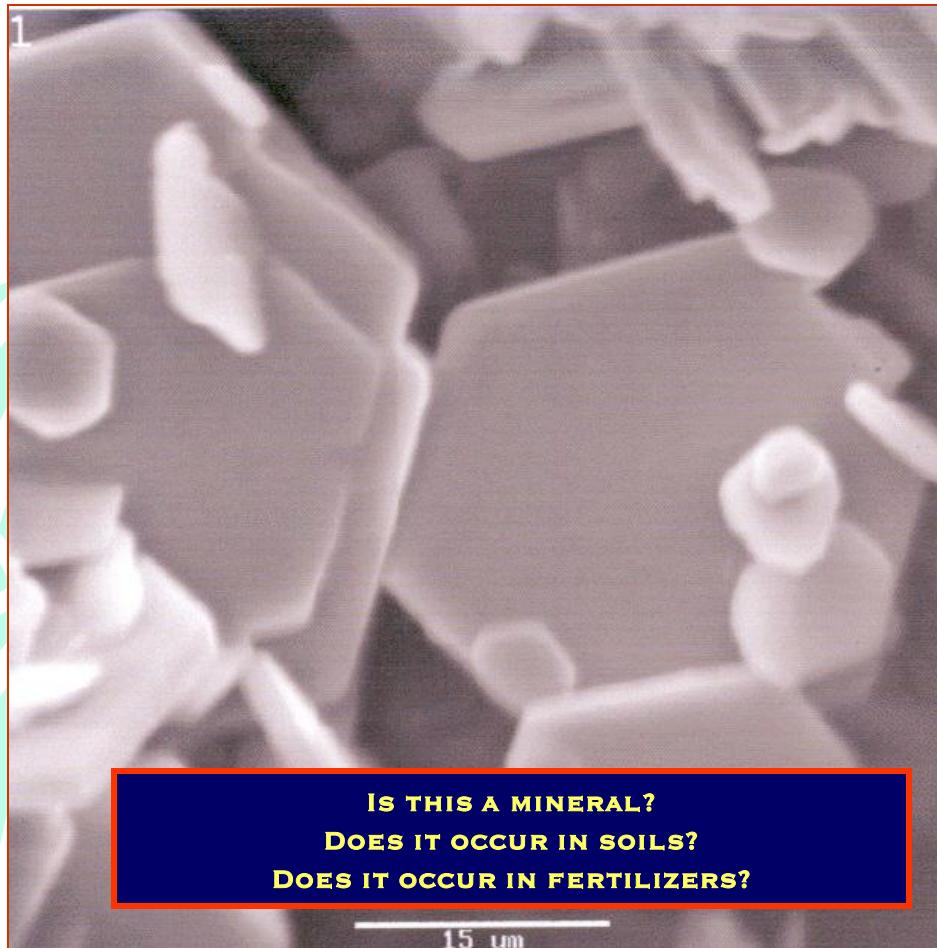


# WHAT IS THIS?

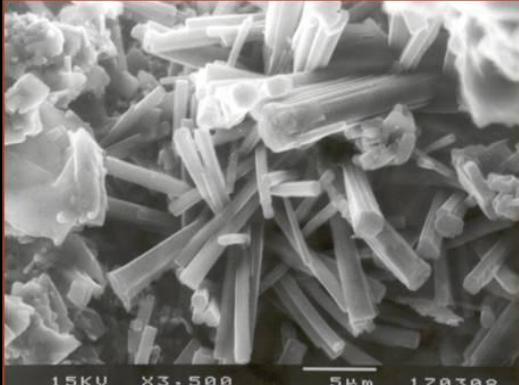
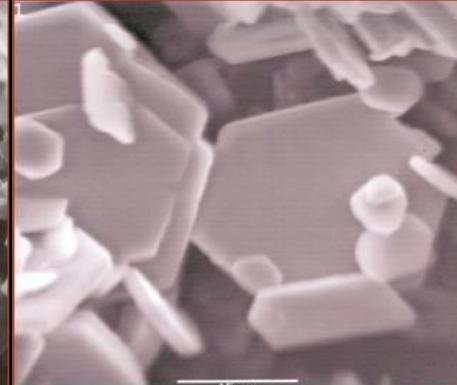


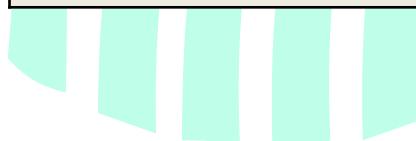
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# WHAT IS THIS?



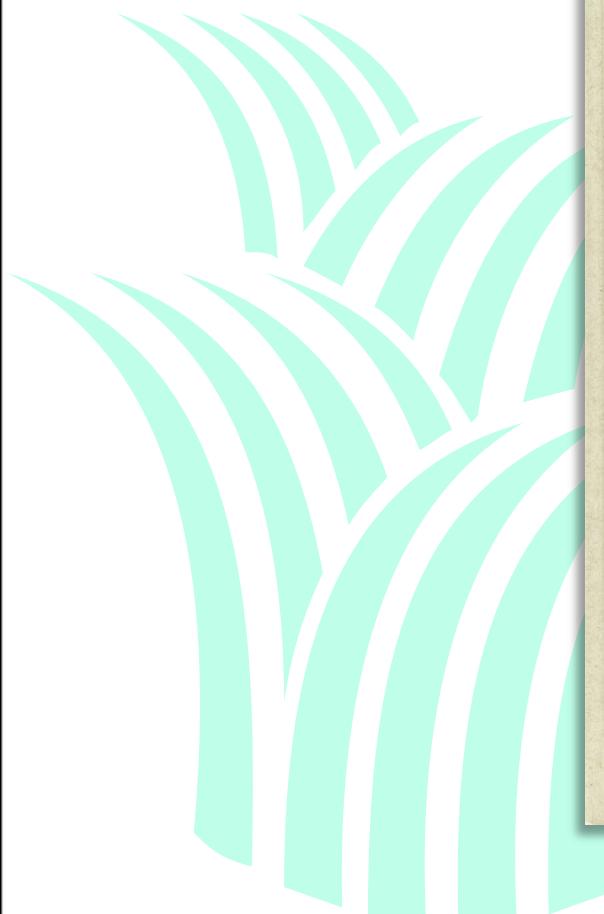
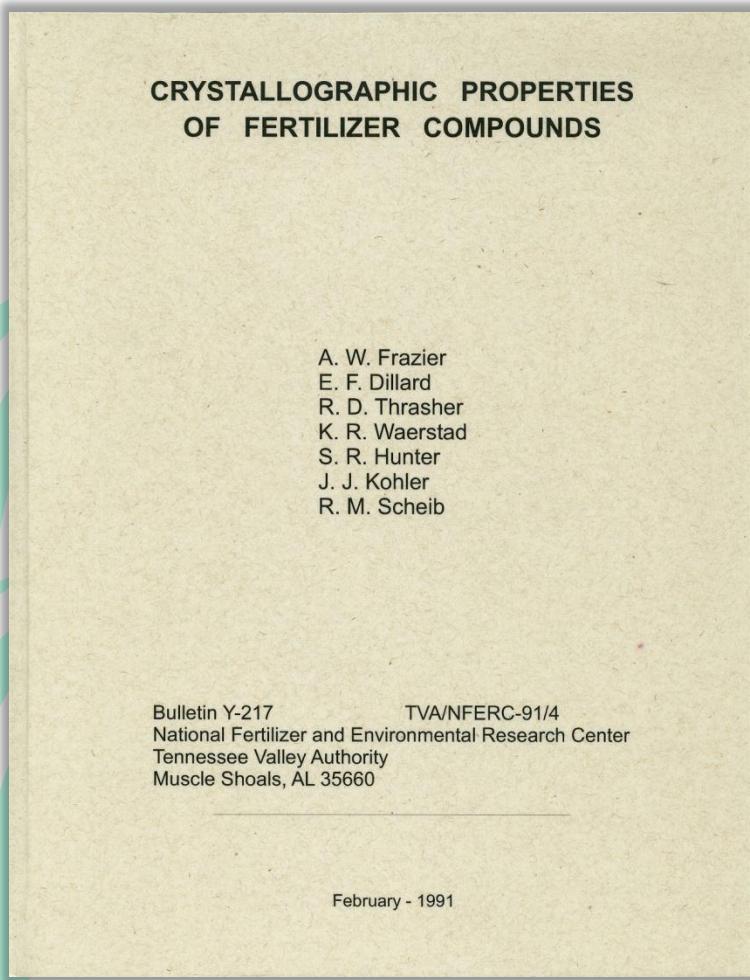
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QUESTION/ COMPOUND CHARAC.		
CHEMICAL FORMULA	$\text{Fe}_3\text{KH}_8(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$	$\text{Fe}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$
IS IT A MINERAL?	NO	NO
WHERE DOES IT PRECIPITATE?	P FERTILIZER, GENERALLY IN <u>SSP</u>	P FERTILIZER, GENERALLY IN <u>TSP</u>
TOTAL P (TP)	20.4	23.8
NAC SOLUBLE P (CSP)	19.3	22.8
WATER SOLUBLE P (WSP)	0.03	0.2
(WSP/CSP) * 100	0.2	0.9
RAE(MCP; UPLAND RICE)	33	73
RAE (MCP; FLOODED RICE)	75	104



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# BOOK ON FERTILIZER COMPOUNDS



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# CALCIUM DIHYDROGEN PHOSPHATE, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

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## CALCIUM DIHYDROGEN PHOSPHATE HYDRATE

Common Synonyms: Monocalcium phosphate, superphosphate  
Structural Formula:  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$   
CAS Number: 7758-23-8

### Environmental Data

DOT Number:                    EPA Number:                    RQ Number:  
Hazard Classification:  
Comments:

### Occurrence

Important constituent of superphosphate made by acidulation of phosphate rock with  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , or  $\text{HNO}_3$ . Hydrolysis product of vitreous calcium polyphosphate.

### Preparation

Add  $\text{Ca}(\text{OH})_2$  or  $\text{CaO}$  to concentrated  $\text{H}_3\text{PO}_4$ ; recrystallize product from hot 50%  $\text{H}_3\text{PO}_4$  solution with slow cooling and constant stirring. Wash crystals with dry acetone and dry in vacuum.

### Properties

Stable in air. Dissolves incongruently in  $\text{H}_2\text{O}$  to leave residue of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  or  $\text{CaPO}_4$ . Dehydrates above 108° C. to  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , or to calcium acid pyrophosphate.  $\text{F}_1$ ,  $\text{Cl}$ , and  $\text{Br}$  readily substitute in fattice, with slight changes in properties.

### References

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## CALCIUM DIHYDROGEN PHOSPHATE HYDRATE

### Optical Data

Crystal System, Class, and Habit:  
Triclinic, I. Crystallizes as colorless (010) plates elongated on c. Modifying forms include {100}, {001}, {110}, {011}, {111}, and the pair (101) and (101). Polysynthetic twinning (albite law) with (010) as the composition plane. Carlsbad twinning

### Refractive Indices:

$\alpha$ : 1.496                     $\beta$ ,  $\omega$ , or mean: 1.515                     $\gamma$ : 1.529                    d: 0.000

### Optical Properties:

Biaxial (-),  $2V=(81.5^\circ)$ . Z is ppd. to (010) and is inclined to the a-axis by  $2^\circ 40'$  in acute  $\beta$ ; the X-Y plane is ppd. to (010), with X and OAP inclined to (010) by  $37^\circ$  in obtuse  $\alpha$ . r > v, very weak.  $\beta=118.5^\circ$ ,  $d=2.22(2.23)$

### Unit Cell Data

Unit Cell Contents:  $2[\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}]$   
Crystal System: Triclinic                    Calculated Density: 2.190  
Lattice Constants:  
 $\alpha$ : 99°50'                     $\beta$ : 118°31'                     $\gamma$ : 83°9'  
 $a$ : 5.670                     $b$ : 11.920                     $c$ : 6.510  
Probable Space Group: PI

### X-ray Data (D-Spacings and Intensities)

11.740	75	5.850	9	5.660	15	5.340	1	4.940	9	4.900	20
4.650	3	4.420	15	4.320	9	4.160	13	3.880	100	3.690	90
3.580	13	3.400	5	3.350	15	3.190	15	3.180	13	3.150	9
3.080	7	2.996	25	2.952	30	2.935	9	2.833	11	2.788	9
2.728	9	2.688	13	2.677	5	2.669	25	2.652	3	2.640	1
2.585	11	2.560	20	2.537	1	2.473	7	2.452	15	2.422	7
2.406	9	2.392	9	2.347	3	2.323	3	2.296	3	2.266	1
2.240	3	2.211	3	2.158	7	2.147	7	2.124	5	2.097	3
2.081	9	2.046	3	2.021	9	1.996	20	1.958	7	1.942	11
1.934	9	1.925	7	1.881	1	1.872	3	1.863	1	1.854	1
1.845	3	1.831	5	1.792	11	1.780	3	1.762	7	1.745	7
1.722	3	1.703	9								

Infrared Absorption Bands ( $\text{cm}^{-1}$ )  
(VS=Very Strong, S=Strong, M=Medium, W=Weak, B=Broad, H=Shoulder)

3450	S	3100	S,B	2400	W,B	2280	W,B	1653	M	1234	S	1145	S
1100	SH	1080	VS	952	VS	910	SH	880	M	852	M	670	M
571	M	547	M	503	VS	395	M						



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# FE<sub>3</sub>KH<sub>14</sub>(PO<sub>4</sub>)<sub>8</sub>·4H<sub>2</sub>O

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## POTASSIUM TRIALUMINUM 14-HYDROGEN PHOSPHATE TETRAHYDRATE

### Common Synonyms:

Structural Formula: KAl<sub>3</sub>H<sub>14</sub>(PO<sub>4</sub>)<sub>8</sub>·4H<sub>2</sub>O

CAS Number: 66451-30-7

### Environmental Data

DOT Number:

EPA Number:

RQ Number:

Hazard Classification:

Comments:

### Occurrence

A major sludge phase in merchant-grade wet-process H<sub>3</sub>PO<sub>4</sub>. Considerable Fe substitution for Al is usual. Forms in wet-process H<sub>3</sub>PO<sub>4</sub> (28 to 32% P<sub>2</sub>O<sub>5</sub>) prepared from ores containing acid-soluble K minerals when concentrated beyond 35% P<sub>2</sub>O<sub>5</sub>.

### Preparation

Add soluble K salt to wet-process H<sub>3</sub>PO<sub>4</sub> (54% P<sub>2</sub>O<sub>5</sub>) containing Al at temps. from 25 to 100° C.

### Properties

Insoluble in H<sub>2</sub>O; dissolves incongruently in dilute H<sub>3</sub>PO<sub>4</sub>, but is relatively insoluble in H<sub>3</sub>PO<sub>4</sub> over concentration range 35 to 60% P<sub>2</sub>O<sub>5</sub>; solubility increases with temperature. The Na analog is known. Substitution of Na for K increases its solubility and makes it hygroscopic. Forms an isomorphous series in which Fe replaces Al and NH<sub>4</sub> or Na replaces K. Citrate soluble; equivalent to concentrated superphosphate (49% P<sub>2</sub>O<sub>5</sub>) as P source for growing plants; can be dehydrated at 100° C. without affecting agronomic value.

### References

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## POTASSIUM TRIALUMINUM 14-HYDROGEN PHOSPHATE TETRAHYDRATE

### Optical Data

#### Crystal System, Class, and Habit:

Monoclinic, 2/m. Pseudohexagonal plates, tabular on (001), sometimes elongated along b and modified by (100) and (110).

#### Refractive Indices:

α: 1.500 β, ω or mean: 1.528 γ: 1.531 ε: 0.000

#### Optical Properties:

Biaxial (-), 2V=36°, X<sub>WC</sub>, Y<sub>WA</sub> and Z=b. d=2.35 g/cc.

### Unit Cell Data

#### X-ray Data (D-Spacings and Intensities)

9.710	2	8.770	100	4.350	7	3.760	4	3.730	8	3.710	11
3.260	6	3.200	4	3.040	6	2.990	11	2.930	14	2.820	2
2.710	1	2.390	2	2.380	2	2.150	1	1.944	2	1.916	1
1.795	2	1.759	1								

#### Infrared Absorption Bands (cm<sup>-1</sup>) (VS=Very Strong, S=Strong, M=Medium, W=Weak, B=Broad, H=Shoulder)

3564	M	3445	M	3100	S,B	2400	W,B	1600	W	1196	S	1215	S
1144	VS	1088	VS	1070	SH	1045	SH	960	S	930	S	730	W,B
591	S	538	S	510	S	446	W						



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## GENERAL CONCLUSIONS FOR ENTIRE RESEARCH PROJECT

- ✓ WHEN WORKING WITH ALTERNATIVE TOTALLY ACIDULATED P FERTILIZERS IT IS FUNDAMENTAL TO ACCESS ITS CHEMICAL COMPOSITION (COMPOUNDS PRESENT IN THE WIPF).
- ✓ Fe-P COMPOUNDS CAN BE AGRONOMICALLY MORE EFFECTIVE AS A SOURCE OF P UNDER FLOODED SOIL SYSTEMS THAN FOR UPLAND CROP SYSTEMS.
- ✓ RESEARCH HAS SHOWED NOT TO BE NECESSARY TO ALWAYS HAVE HIGH WATER-SOLUBILITY IN FULLY ACIDULATED PHOSPHATE FERTILIZERS. DATA OBTAINED SUGGEST THAT THE WSP REQUIREMENT SHOULD BE RELATED TO THE SOIL SYSTEM, THE CROP AND THE CHEMICAL COMPOSITION OF THE FERTILIZER.



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# STUDY 1

## CHARACTERIZATION AND AGRONOMIC EVALUATION OF SINGLE SUPERPHOSPHATES VARYING IN IRON PHOSPHATE IMPURITIES

N.	COMPOUND	SSP1	SSP2	SSP3
1	Fe <sub>3</sub> KH <sub>8</sub> (PO <sub>4</sub> ) <sub>6</sub>	0.4	0.4	0.6
2	Fe <sub>3</sub> NAH <sub>8</sub> (PO <sub>4</sub> ) <sub>6</sub>	5.02	3.35	6.36
3	Fe <sub>3</sub> H <sub>9</sub> (PO <sub>4</sub> ) <sub>6</sub>	0.4	6.19	12.34
4	Na <sub>2</sub> SiF <sub>6</sub>	0.25	0.41	0.33
5	Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> OH <sub>0.97</sub> F <sub>1.03</sub>	2.82	2.6	3.09
6	Ca <sub>4</sub> SiAl <sub>2</sub> O <sub>8</sub> F <sub>13</sub>	2.18	0.4	2.1
7	SiO <sub>2</sub>	0	0	0.73
8	CAF <sub>2</sub>	0.25	1.44	0
9	MgSO <sub>4</sub>	0.35	0.4	0.45
10	SrSO <sub>4</sub>	1.53	1.32	1.17
11	ZnSO <sub>4</sub>	0.07	0.1	0.15
12	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.92	1.4	1.88
13	BaSO <sub>4</sub>	1.92	1.14	1.28
14	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.25	1.27	1.08
15	BA(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	0.19	0.41	0.28
16	CASO <sub>4</sub>	49.15	49.7	46.87
17	CA(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	34.19	19.08	12.81
	TOTAL	99.89	89.61	91.52

P SOURCE	P				Fe	FI
	TOTAL	AVAILABLE	WATER	2% C.A.		
%						
MCP	55.8	55.3	54.6	54.3	1.3	99
SSP1	20.8	19.6	16.8	17.6	2.2	86
SSP2	17.2	16.1	12.8	14.1	4.3	80
SSP3	17.7	16.4	7.5	10.2	5.8	46

P SOURCE	DRY-MATTER YIELD	P UPTAKE
UPLAND RICE		
MCP	100	100
SSP1	98	88
SSP2	96	93
SSP3	88	76
FLOODED RICE		
MCP	100	100
SSP1	97	91
SSP2	111	110
SSP3	102	85

MCP: STANDARD SOURCE OF P  
RAE =  $(\beta_i / \beta_{MCP}) * 100$ , I = OTHER SSP

SOURCE: PROCHNOW, L.I.; CHIEN, S.H.; TAYLOR, R.W.; CARMONA, G.; HENAO, J. & DILLARD, E.F. AGRONOMY JOURNAL. 95:293-302, 2003.

## STUDY 2

### PLANT AVAILABILITY OF PHOSPHORUS IN FOUR SUPERPHOSPHATE FERTILIZERS VARYING IN WATER-INSOLUBLE PHOSPHATE COMPOUNDS

✓ **MODEL:**  
SEGMENTED (QUADRATIC AND LINEAR)

✓ **RY = (DMY S<sub>I</sub>/DMY S<sub>J</sub>) \* 100**

S<sub>I</sub>: HIGHEST DMY

✓ **PLATEAU:**

■  $Y = A + BX + CX^2$  IF  $X < X_0$  AND  $Y = P$  IF  $X > X_0$

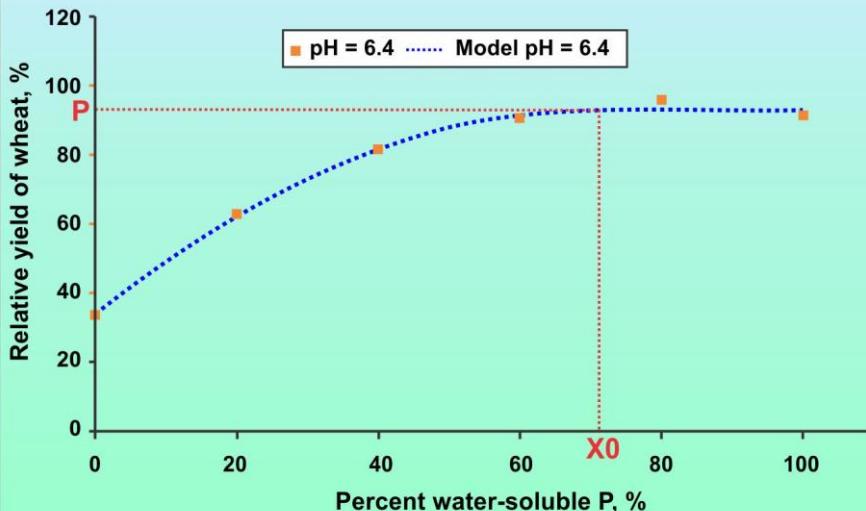
■ TWO SECTIONS MUST MEET AT  $X_0$

■ THE CURVE MUST BE SMOOTH (FIRST DERIVATIVE WITH RESPECT TO X ARE THE SAME AT  $X_0$ )

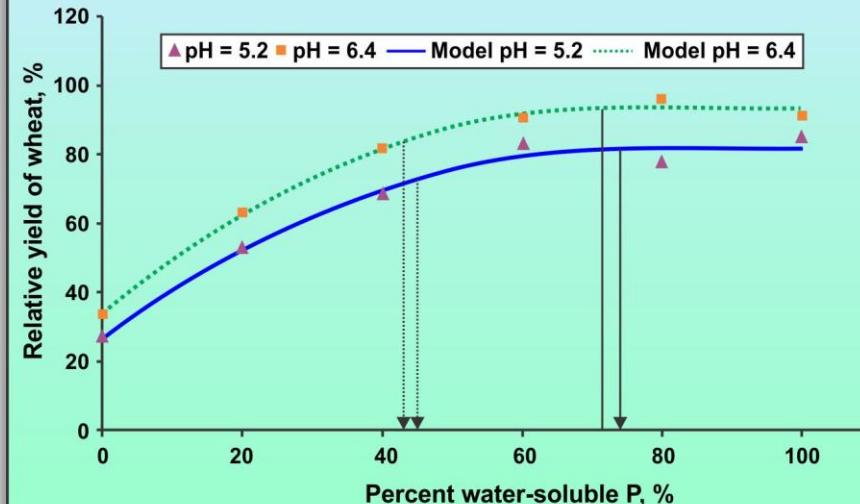
■ THESE CONDITIONS IMPLY THAT:

■  $X_0 = -B/2C$  AND  $P = A - B^2/4C$ .

Conceptual conditions for the segmented model



SSP – Relative yield



SOURCE: PROCHNOW, L.I.; CHIEN, S.H.; CARMONA, G.; HENAO, J.; DILLARD, E.F.; AUSTIN, E.R. SOIL SCIENCE SOCIETY OF AMERICA JOURNAL, 72:462-470, 2008.



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## STUDY 2

### PLANT AVAILABILITY OF PHOSPHORUS IN FOUR SUPERPHOSPHATE FERTILIZERS VARYING IN WATER-INSOLUBLE PHOSPHATE COMPOUNDS

COMPOUND	P SOURCE			
	%			
$\text{Fe}_3(\text{K}, \text{Na}, \text{H})\text{H}_8(\text{PO}_4)_6$	4.7		19.3	4.3
$\text{Fe}_3\text{KH}_{14}(\text{PO}_4)_8$		1.6		
$\text{CaAlH}(\text{HPO}_4)_2\text{F}_2$				6.0
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{F})$	5.0	3.4	3.1	6.4
$\text{SiO}_2$	0.7		0.7	18.7
$\text{CaSO}_4$	3.1		46.9	40.3
$\text{Ca}(\text{H}_2\text{PO}_4)$	81.8	87.9	12.8	16.7
<b>TOTAL</b>	<b>95.3</b>	<b>92.9</b>	<b>82.8</b>	<b>92.4</b>

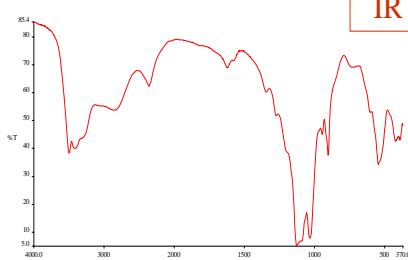
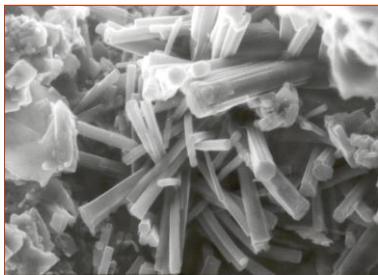
FONTE DE P <sup>A</sup>	PH	MODELO DE REGRESSÃO SEGMENTADA			DOSE (MG KG <sup>-1</sup> P) REQUERIDA PARA ALCANÇAR <sup>B</sup>			WSP (%) REQUERIDO PARA ALCANÇAR <sup>C</sup>	
		EQUAÇÃO QUADRÁTICA (R <sup>2</sup> )	SE <sup>D</sup>	PLATEAU	PLATEAU	90% DO PLATEAU	PLATEAU	90% DO PLATEAU	
MCP-DMY	5,2	$Y = 0,94 + 0,957x - 8,8 \times 10^{-3}x^2$ (0,98)	1,25	26,9	54,3	36,8			
MCP-RY	5,2	$Y = 3,27 + 3,337x - 30,0 \times 10^{-3}x^2$ (0,97)	4,37	93,9	54,3	36,8			
MCP-DMY	6,4	$Y = 0,70 + 1,447x - 19,3 \times 10^{-3}x^2$ (0,97)	1,45	27,8	37,4	25,4			
MCP-RY	6,4	$Y = 2,44 + 5,047x - 67,4 \times 10^{-3}x^2$ (0,95)	5,05	96,9	37,4	25,4			
TSP 1-RY	5,2	$Y = 35,44 + 1,249x - 7,9 \times 10^{-3}x^2$ (0,97)	1,57	84,9				79	46
TSP 1-RY	6,4	$Y = 34,13 + 1,830x - 15,3 \times 10^{-3}x^2$ (0,96)	2,66	88,8				60	36
TSP 2-RY	5,2	$Y = 47,98 + 0,745x - 3,9 \times 10^{-3}x^2$ (0,97)	2,14	83,5				95	49
TSP 2-RY	6,4	$Y = 42,97 + 1,161x - 6,8 \times 10^{-3}x^2$ (0,96)	5,04	92,9				86	48
SSP 1-RY	5,2	$Y = 17,93 + 1,705x - 11,4 \times 10^{-3}x^2$ (0,97)	3,62	81,6				75	48
SSP 1-RY	6,4	$Y = 24,42 + 1,897x - 13,1 \times 10^{-3}x^2$ (0,97)	2,21	93,2				72	46
SSP 2-RY	5,2	$Y = 58,76 + 0,683x - 4,7 \times 10^{-3}x^2$ (0,96)	4,02	83,7				73	31
SSP 2-RY	6,4	$Y = 60,97 + 0,926x - 6,9 \times 10^{-3}x^2$ (0,95)	5,24	92,1				67	31

SOURCE: PROCHNOW, L.I.; CHIEN, S.H.; CARMONA, G.; HENAO, J.; DILLARD, E.F.; AUSTIN, E.R. SOIL SCIENCE SOCIETY OF AMERICA JOURNAL, 72:462-470, 2008.

## STUDY 3

### SYNTHESIS, CHARACTERIZATION AND AGRONOMIC EVALUATION OF IRON PHOSPHATE IMPURITIES IN SUPERPHOSPHATES

SEM



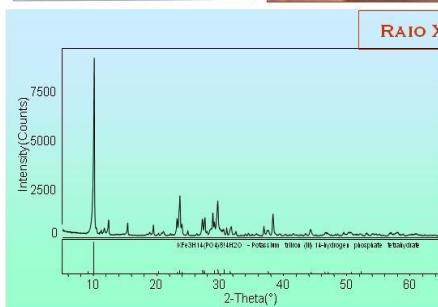
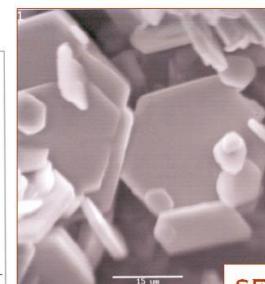
X-ray

Chemical Analysis for total P, Fe, K, S and water of hydration →

Calculated Formula:



EDX



IR

ANÁLISE QUÍMICA PARA P TOTAL, FE, K, S E ÁGUA DE HIDRATAÇÃO

FÓRMULA CALCULADA:



SOURCE: PROCHNOW, L.I.; CHIEN, S.H.; ET AL. SOIL SCIENCE SOCIETY OF AMERICA JOURNAL. 67:1551-1563, 2003.



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## STUDY 3

### SYNTHESIS, CHARACTERIZATION AND AGRONOMIC EVALUATION OF IRON PHOSPHATE IMPURITIES IN SUPERPHOSPHATES

P SOURCE	CROP	SEGMENTED REGRESSION MODEL			WSP (%) REQUIRED TO REACH §	
		QUADRATIC EQUATION	SE†	PLATEAU	PLATEAU	90% OF PLATEAU
H8-SYN	UPLAND RICE	$Y=7.81+0.28X-6.2\times10^{-3}X^2$	1.59	35.3	66.6	42.7
H14-SYN	UPLAND RICE	$Y=22.83+0.398X-2.8\times10^{-3}X^2$	2.36	36.9	70.9	34.6
H8-SYN	FLOODED RICE	$Y=14.52+1.168X-20.0\times10^{-3}X^2$	2.15	31.6	29.3	16.7
H14-SYN	FLOODED RICE	$Y=25.08+0.299X-3.8\times10^{-3}X^2$	1.45	30.9	39.1	10.6

† STANDARD ERROR FOR COMPARING PREDICTED VALUES.

§ PERCENTAGE WATER-SOLUBLE P NEEDED TO OBTAIN THE PLATEAU OR 90% OF THE PLATEAU OF THE SEGMENTED MODEL.

# STATISTICAL GROUP EXPERIMENT ANALYSIS

## 16 FIELD EXPERIMENTS

TRATAMENT	P SOURCE	AVERAGE RAE	
1	SSP GCA (HIGH WSP)	96.1	A
2	SSP RCA (Low WSP)	95.3	A
3	SSP GCA/RCA	94.5	A
4	SSP PATOS (Low WSP)	95.5	A

C.V. = 10.4; DMS = 4.2.

1 CONJUNTO DE DADOS = EXPERIMENTOS 01 SULCO, 01 LANÇO, 02 SULCO, 02 LANÇO, 04 SULCO, 04 LANÇO, 07 GRANULADO, 07 PÓ, 08-01 RSP, 08-01 RCP, 08-02 RSP, 08-02 RCP, 11, 12 M1, 12 M2, 12 M3.



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**IT IS BELIEVED THAT IT WILL BE POSSIBLE TO UTILIZE PR IN THE FUTURE IN A MORE COST-EFFECTIVE WAY BY:**

- ✓ BEING ABLE TO ACCESS THE WEIGHT PERCENT CHEMICAL COMPOUNDS OF THE FERTILIZERS (MODAL ANALYSIS),
- ✓ UNDERSTANDING THE BEHAVIOR OF THE IMPURITY COMPOUNDS IN SOILS AND AS A P SOURCE FOR DIFFERENT PLANT SPECIES,
- ✓ HAVING MORE ACCURATE PROCESSES OF CONTROLLING THE IMPURITIES FORMED IN THE PRODUCTION OF ACIDULATED P FERTILIZERS.



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## ACKNOWLEDGEMENTS

- ✓ **PREVIOUS RESEARCHERS:**  
**G. MULLINS, F. SIKORA, B. GILKES.**
- ✓ **UNIVERSITY OF SÃO PAULO.**
- ✓ **IFDC:**  
**N. CHIEN, G. CARMONA, R. AUSTIN & E. DILLARD.**

## 5. FINAL COMMENTS

1. **TECHNICAL (SPEECH WRAP UP)**
2. **POLYTICAL/PHILOSOPHICAL:**
  - 2.1. SIR FRANCIS BACON AND THE MISTAKES OF THE HUMAN MIND**
  - 2.2. THE FUTURE**



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**1º. FINAL COMMENT**  
**TECHNICAL**  
**(SPEECH WRAP UP)**

## **HOW TO OPTIMIZE THE USE OF P RESOURCES?**

- ✓ **MORE ADEQUATE AGRONOMIC PROCEDURES.**
- ✓ **MORE ADEQUATE AND REALISTIC PRODUCTION OF P FERTILIZERS.**
  
- ✓ **MANY FACTORS INTERACTING.**
- ✓ **FROM RESEARCH TO PRACTICE.**



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# P IN AGRICULTURE = RELATED TO APATITE = DECEIVING MINERAL



APATITE GETS ITS ODD NAME FROM THE GREEK WORD MEANING “TO DECEIVE” BECAUSE ITS VARIED FORMS AND COLORS CAUSED EARLY MINERALOGISTS TO CONFUSE IT WITH A HALF DOZEN OTHER MINERALS (ZIM ET AL., ROCKS AND MINERALS, 1957)

FOSFATO DE ROCHA	COMPRIMENTO DO EIXO A (Å)	FORMULA DA APATITE ^
KAIYANG, CHINA	9.372	$\text{Ca}_{9.98}\text{Na}_{0.01}\text{Mg}_{0.01}(\text{PO}_4)_{5.94}(\text{CO}_3)_{0.06}\text{F}_{2.02}$
HAHOTOE, TOGO	9.351	$\text{Ca}_{9.79}\text{Na}_{0.15}\text{Mg}_{0.06}(\text{PO}_4)_{5.39}(\text{CO}_3)_{0.61}\text{F}_{2.24}$
PESCA, COLOMBIA	9.346	$\text{Ca}_{9.76}\text{Na}_{0.18}\text{Mg}_{0.07}(\text{PO}_4)_{5.28}(\text{CO}_3)_{0.72}\text{F}_{2.29}$
EL-HASSA, JORDAN	9.339	$\text{Ca}_{9.68}\text{Na}_{0.23}\text{Mg}_{0.09}(\text{PO}_4)_{5.12}(\text{CO}_3)_{0.88}\text{F}_{2.35}$
GAFSA, TUNISIA	9.328	$\text{Ca}_{9.59}\text{Na}_{0.30}\text{Mg}_{0.12}(\text{PO}_4)_{4.90}(\text{CO}_3)_{1.10}\text{F}_{2.44}$
NORTH CAROLINA, USA	9.322	$\text{Ca}_{9.53}\text{Na}_{0.34}\text{Mg}_{0.13}(\text{PO}_4)_{4.77}(\text{CO}_3)_{1.23}\text{F}_{2.49}$



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## APATITE AND IPNI MISSION

- ✓ **APATITE IS A LIMITED RESOURCE.**
- ✓ **AMOUNTS OF HIGH QUALITY PR/APATITE IS DECREASING.**
- ✓ **APATITE IS DECEIVING.**
- ✓ **USING APATITE WISELY IS DIRECTLY RELATED TO IPNI MISSION,**  
I.E.,

**“TO DEVELOP AND PROMOTE SCIENTIF INFORMATION ABOUT THE  
RESPONSIBLE MANAGEMENT OF PLANT NUTRITION FOR THE  
BENEFIT OF THE HUMAN FAMILY”**



# VALOR DO SERVIÇO: COMO AVALIAR?

- ✓ UM TÉCNICO É CHAMADO POR UMA EMPRESA PARA AVALIAR O PROBLEMA EM UM COMPUTADOR EXTREMAMENTE VALIOSO.
- ✓ APÓS ESTUDO DETALHADO DO CASO O TÉCNICO DESLIGA O COMPUTADOR, ABRE UM COMPARTIMENTO ESPECÍFICO E DÁ UMA VOLTA E MEIO EM UM PARAFUSO.
- ✓ RELIGA ENTÃO A MÁQUINA QUE PASSA A FUNCIONAR PERFEITAMENTE.
- ✓ O DONO DA EMPRESA LHE DÁ OS PARABÉNS E PERGUNTA QUANTO É O SERVIÇO.
- ✓ FICA FURIOSO AO TER CONHECIMENTO QUE O VALOR COBRADO É DE R\$ 5.000. DIZ QUE NÃO VAI PAGAR A MENOS QUE O TÉCNICO ENVIE UMA FATURA ESPECIFICANDO TUDO O QUE FOI FEITO.
- ✓ O TÉCNICO BALANÇA A CABEÇA E VAI EMBORA SATISFEITO.
- ✓ NO OUTRO DIA A FATURA É ENVIADA E APÓS LEITURA O DONO DA EMPRESA – PESSOA DE BOM SENSO – DECIDE PAGAR DE IMEDIATO OS R\$ 5.000.
- ✓ A FATURA ESPECIFICAVA:
  - APERTAR UM PARAFUSO ..... R\$ 10,00
  - SABER QUAL PARAFUSO APERTAR ..... R\$ 4.990,00



**LUCIANO PIRES**  
**O MEU EVEST**

**POETA ESPANHOL**  
**ANTONIO MACHADO**

**CAMINANTE, NO HAY CAMINO.  
SE HACE LO CAMINO AL CAMINAR.**

**THANKS FOR YOUR ATTENTION WITH GREAT WISHES OF:**

- (1) SUSTAINABLE USE OF P RESOURCES AND  
(2) ENORMOUS SUCCESS TO ALL OF YOU AND TO AGRICULTURE**



INTERNATIONAL  
**PLANT NUTRITION**  
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**PLEASE DON'T FORGET:  
APATITE =  
DECEIVING MINERAL**

