WFC 2015 – Technical Innovation for a Sustainable Tropical Agriculture

USE OF NONCONVENTIONAL PHOSPHATE FERTILIZERS IN TROPICAL AGRICULTURE

Dr. Luís Ignácio Prochnow
IPNI Brazil Program Director

Dr. S. H. Norman Chien
Fertilizer Specialist – Formerly with IFDC

APATITE

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INTRODUCTION

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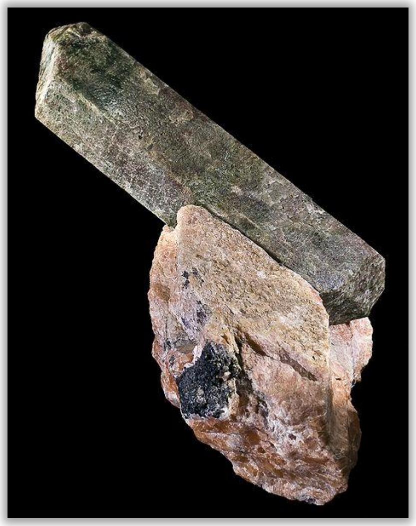
P in Agriculture =
Related to Apatite =
Deceiving Mineral



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 [a]
Kaiyang, China	9.372	$Ca_{9.98}Na_{0.01}Mg_{0.01}(PO_4)_{5.94}(CO_3)_{0.06}F_{2.02}$
Hahotoe, Togo	9.351	$Ca_{9.79}Na_{0.15}Mg_{0.06}(PO_4)_{5.39}(CO_3)_{0.61}F_{2.24}$
Pesca, Colombia	9.346	$Ca_{9.76}Na_{0.18}Mg_{0.07}(PO_4)_{5.28}(CO_3)_{0.72}F_{2.29}$
El-Hassa, Jordan	9.339	$Ca_{9.68}Na_{0.23}Mg_{0.09}(PO_4)_{5.12}(CO_3)_{0.88}F_{2.35}$
Gafsa, Tunisia	9.328	$Ca_{9.59}Na_{0.30}Mg_{0.12}(PO_4)_{4.90}(CO_3)_{1.10}F_{2.44}$
North Carolina, USA	9.322	$Ca_{9.53}Na_{0.34}Mg_{0.13}(PO_4)_{4.77}(CO_3)_{1.23}F_{2.49}$

How to Optimize the use of P Resources in Agriculture?

Two important Aspects:

- ✓ How we Produce?
- ✓ 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 soilid)
- 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:

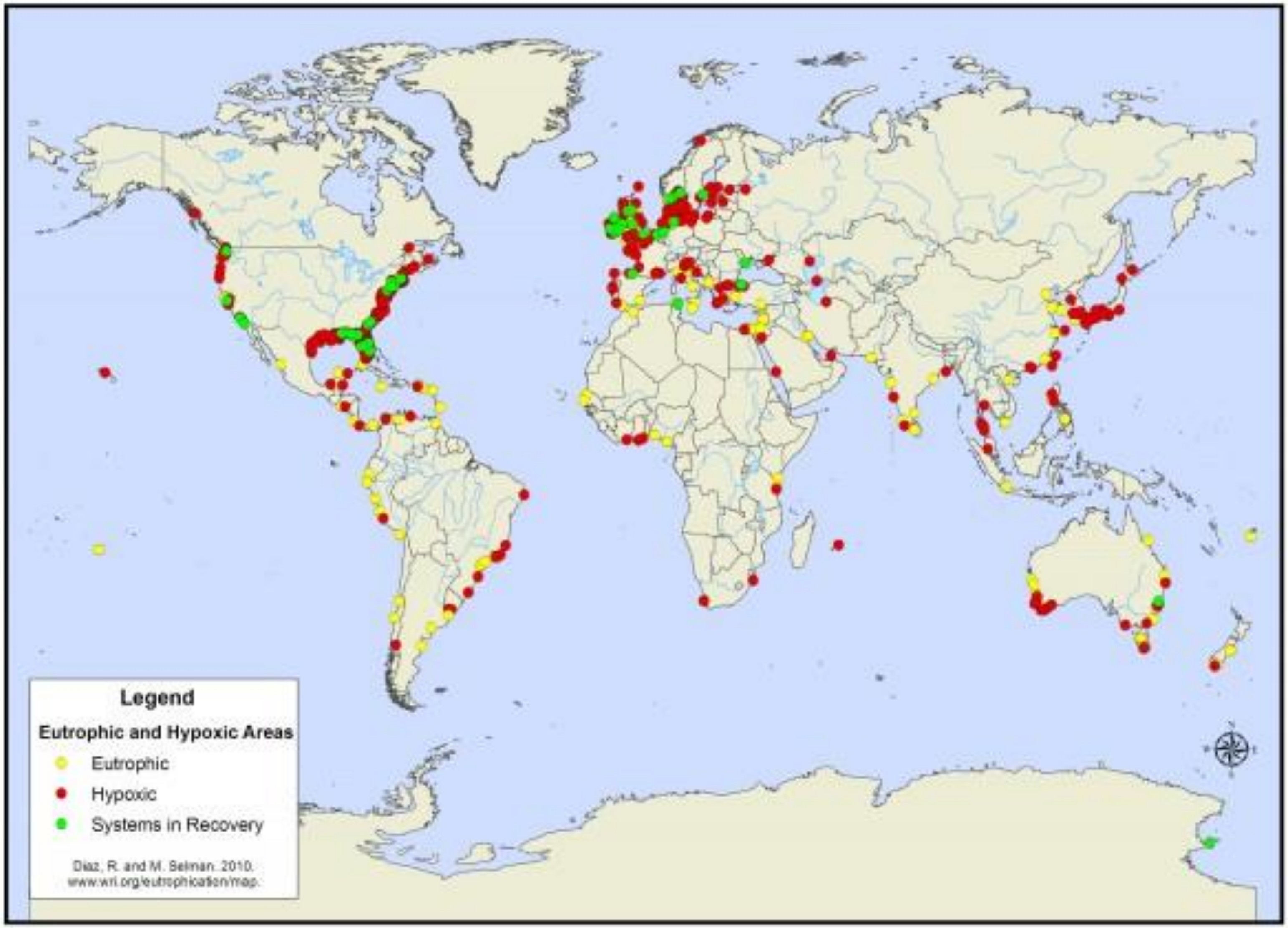
- Solubility.
- Hygroscopicity.
- “Metalling”/Caking.
- Salinity.

FACTORS INFLUENCING THE AGRONOMIC EFFECTIVENESS OF P SOURCES

- ✓ Fertilizer Properties.
- ✓ **Crop.**
- ✓ Soil Properties.
- ✓ Fertilizer and Soil Management.

- ✓ Crop.
- ✓ **Cropping System/Rotation.**

World Hypoxic and Eutrophic Coastal Areas



Source: Diaz & Selman. (2010).

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Phosphorus Initiatives

from « militant scientists » to institutional platforms

United Nations Environment Programme

GPNM 2014 ?

Nutrient Platform NL — 2010

VNP — 2012

European Sustainable Phosphorus Platform — 2013

NAPPs 2015

Ontario

CCME — 2013

Deutsche Phosphor Plattform — 2013

SERA-17 — 2003

Global Phosphorus Research Initiative — 2008

2009

Global Phosphorus Network — 2010

SPS — 2011

INEMAD — 2012

NSF P-RCN 2013

Global Phosphorus Forum — 2007

Phosphorus Recycling Promotion Council — 2008

2010

2011

P-REX — 2012

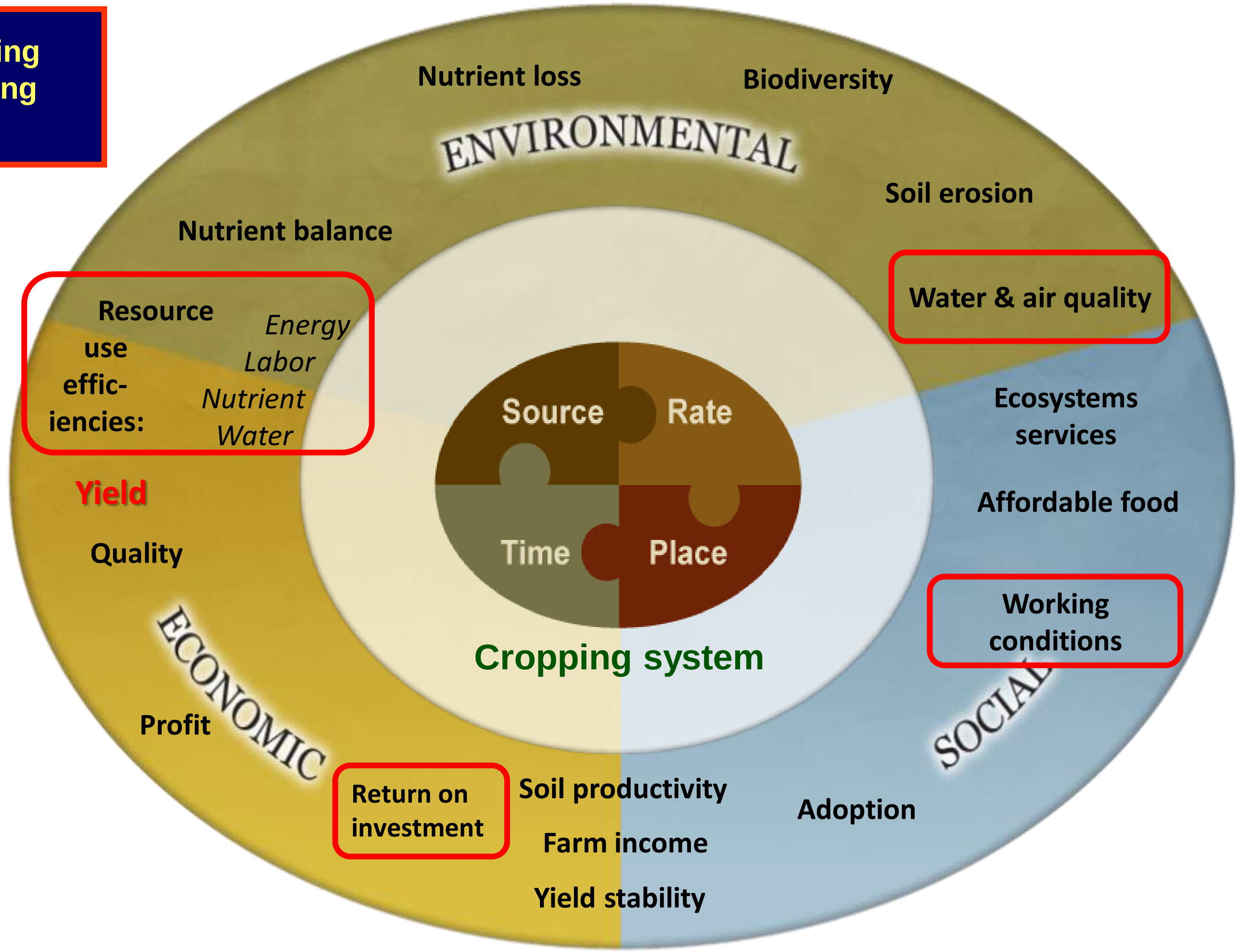
SCOPE NEWSLETTER — 1990

- ✓ **Planet Boundaries 2.0**
- ✓ **Global P Governance**

Source: Thorton, C.

4R Nutrient Stewardship Program

There is a need for integrating knowledge and for measuring performance indicators



APPLICATION OF THE RIGHT NUTRIENT SOURCE AT THE RIGHT RATE, TIME, AND PLACE

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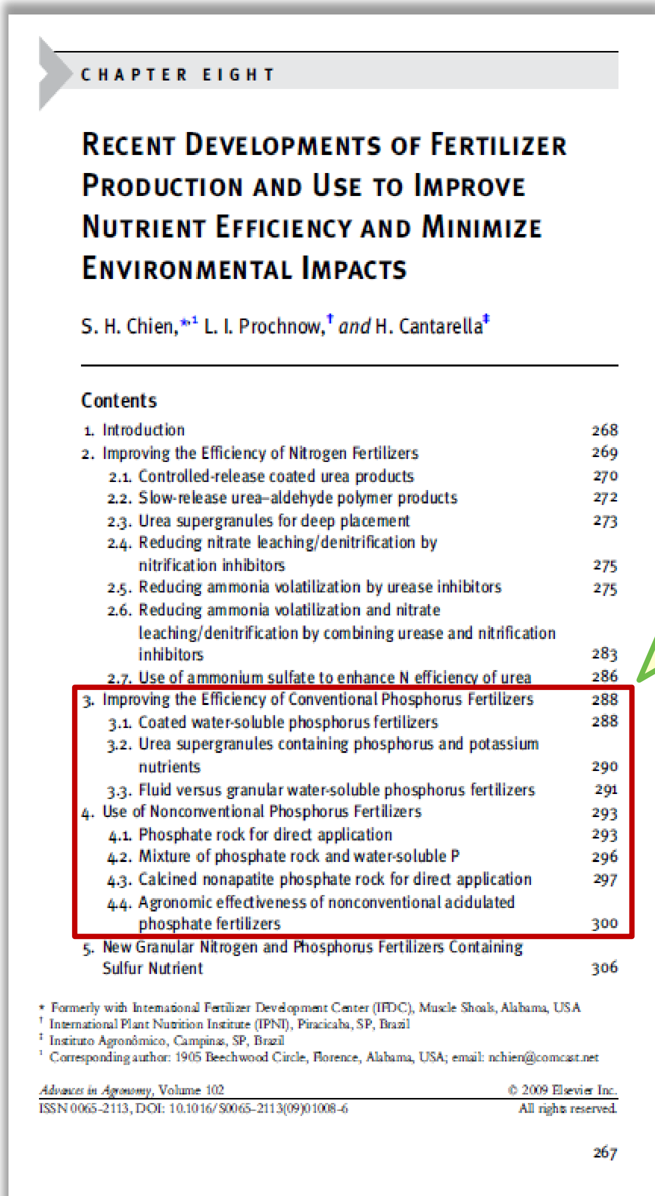
USE OF NONCONVENTIONAL PHOSPHATE FERTILIZERS IN TROPICAL AGRICULTURE

WHAT IS NONCONVENTIONAL ?

WHAT IS CONVENTIONAL ?

- High WSP Sources
(SSP, TSP, MAP, DAP, etc)



CHAPTER EIGHT

Recent Developments of Fertilizer Production and Use to Improve Nutrient Efficiency and Minimize Environmental Impacts

S. H. Chien,*[1] L. I. Prochnow,[†] and H. Cantarella[‡]

Contents

* Formerly with International Fertilizer Development Center (IFDC), Muscle Shoals, Alabama, USA
[†] International Plant Nutrition Institute (IPNI), Piracicaba, SP, Brazil
[‡] Instituto Agronômico, Campinas, SP, Brazil
[1] Corresponding author: 1905 Beechwood Circle, Florence, Alabama, USA; email: nchien@comcast.net

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Not all possilities of nonconventional are covered in my presentation. Other speechs focus on some other possibilities. Ex.: nanotechnology, organomineral, etc.

Use of Non-Conventional Phosphorus Fertilizers

Phosphate Rock for Direct Application

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Phosphate Rock for Direct Applicaton

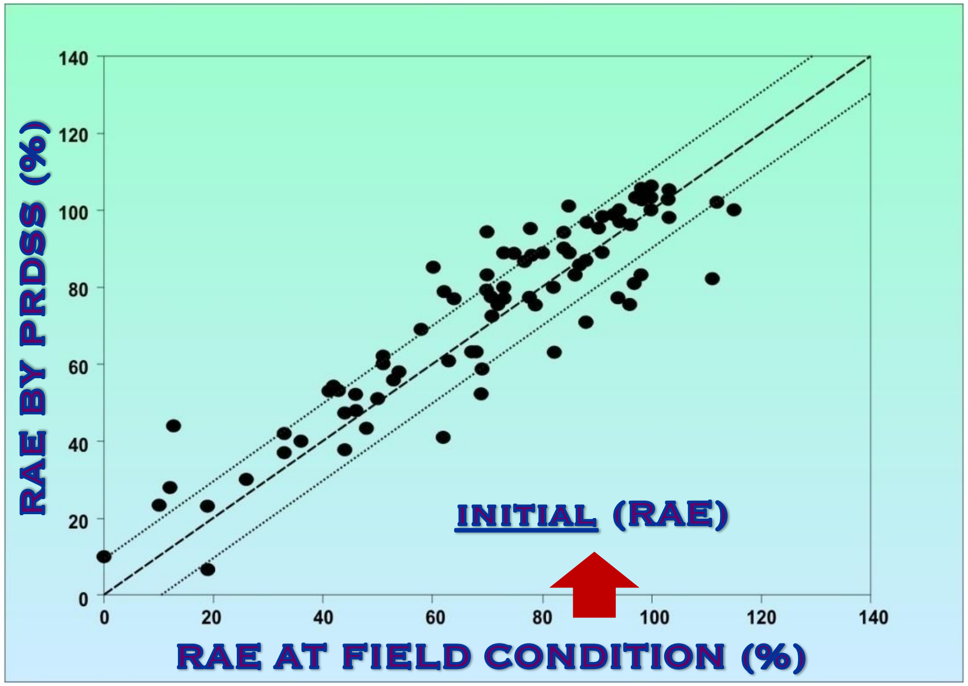
- ✓ Direct application of phosphate rock (PR) can be an effective agronomic and economic alternative to the use of more expensive WSP, especially in acid soils of the tropics.
- ✓ Several in depth reviews exists (Khasawenh and Doll, 19787; Hammond et al., 1986; Chien and Menon, 1995; Rajan et al., 1996; Chien, 2003; Truong, 2004; Rajan et al., 2004).
- ✓ Discussion only of the most recent developments on PR use: PRDSS, Environmental Aspects and Organic Agriculture.

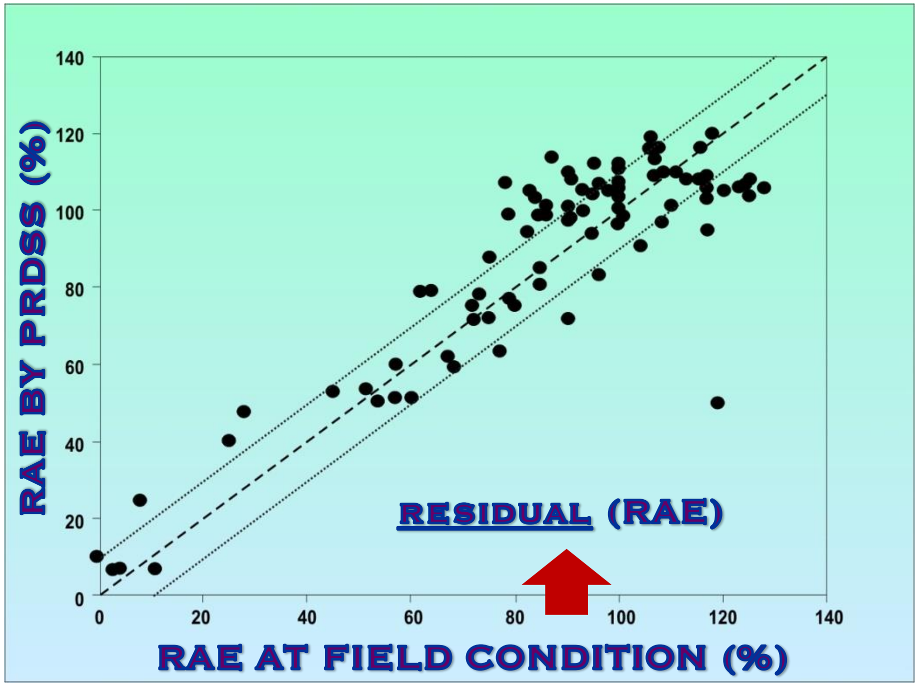
PRDSS

AE PR = f (PR Properties, Soil Properties, Management Practices and Crop Species)

- ✓ There is a need to integrate all the factors in a comprehensive system.
- ✓ PRDSS = Phosphate Rock Decision Support System (Smalberger et al., 2006).
- ✓ IAEA Website = www.iswam.iaea.org/dapr/srv/en/resources.
- ✓ Minimum dataset needed = PR solubility, soil pH and crop.
- ✓ RAE of PR as related to WSP sources.

Phosphate Rock Decission Support System (PRDSS)





Comparison of observed and predicted relative agronomic effectiveness (RAE) for the initial application of PR and WSP.

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http://www-iswam.iaea.org/dapr/srv/en/home

PR and the Environment

- ✓ Eutrophication of aquactic environments caused by excessive P runoff has led to the requirement to mitigate the P pollution problem (Cheseapeak Bay and Gulf of Meximo).
- ✓ Use of PR effectively can help (Hart et al., 2004; Shigaki et al., 2006; Shigaki et al., 2007)
- ✓ More field work is necessary.

Cumulative losses of dissolved reactive and total P of surface runoff from three soils

Soils	P sources		
	Control	PR	TSP
	Cumulative dissolved reactive P (DRP) loss, kg ha^{-1}		
Alvira	0.28	0.52	32.2
Berks	0.18	0.39	14.5
Watson	0.23	0.43	16.2
Average[a]	0.23c	0.45b	20.9a
	Cumulative total P loss, kg ha^{-1}		
Alvira	0.35	0.83	33.2
Berks	0.30	0.68	15.5
Watson	0.31	0.72	19.6
Average[a]	0.32c	0.74b	22.7a

[a]Average DRP and total P losses followed by the different letters are significantly different ($P<0.05$).

Source: (Shigaki et al., 2007).

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PR and Organic Farming

- ✓ PR has been increasingly used for organic farming worldwide.
- ✓ Still PR has to have high reactivity. Many misconceptions:
  - ➢ Ex. 1: Claims PR with high P content as good/efficient.
  - ➢ Ex. 2: Highly reactive PR to be used in crops grown on alkaline soils.
- ✓ Factors are the same except for composting.

Use of Non-Conventional Phosphorus Fertilizers

Mixture of Phosphate Rock and Water-Soluble P

- ✓ **Compacted**
- ✓ **PAPR**

Mixture of PR and WSP

- ✓ Under certain conditions PR effectiveness may be poor (e.g.: low PR reactivity, high soil pH, short-term crop growth).
- ✓ Mixing of PR an WSP can be feasible and improve the effectiveness of the PR (partial acidulation or compaction).
- ✓ For example, the agronomic effectiveness of a low-reactive Patos PR compacted with SSP at 50:50 ratio was as good as SSP in DMY of wheat and ryegrass (Prochnow et al., 2004).

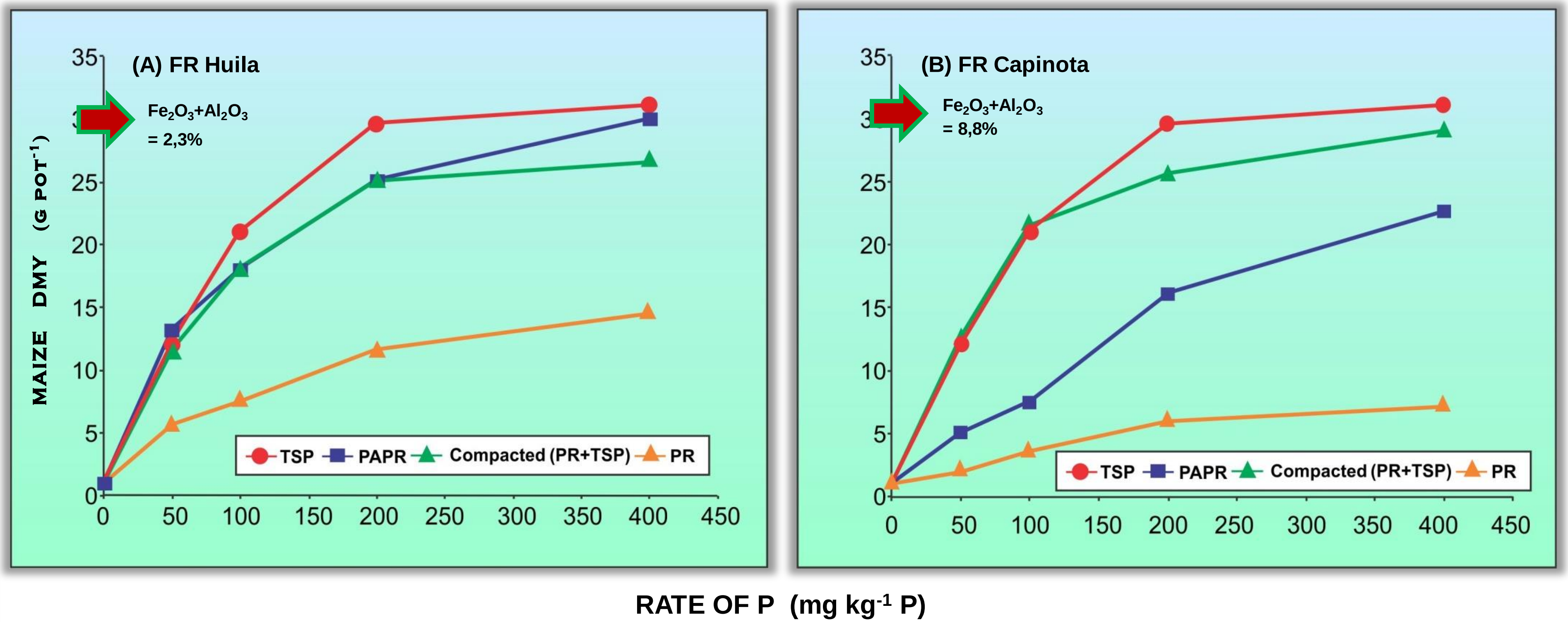
RAE OF ALTERNATIVE SOURCES OF P AS RELATED TO REGULAR HIGH WSP SSP

Fonte de P	EAR			
	Trigo		Rye Grass	
	MS	P acumulado	MS	P acumulado
SSP (padrão)	100	100	100	100
FR PM	1	1	30	15
LG SSP PM	91 ←	87	99 ←	95
FR + SSP (C)	99 ←	88	95 ←	77
FR + SSP (M)	69	57	86	72

WSP can provide initial available P to plants that result in a better root development that in turn may utilize PR more effectively and also because the acid reaction of WSP that can help to dissolve the PR.

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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More information on the use of mixtures of PR and WSP in terms of production, soil chemistry, and AE can be found in several reviews:

Hammond et al., 1986;

Chien and Hammond, 1989;

Chien and Menon, 1995;

Menon and Chien, 1996;

Chien, 2003.

Use of Non-Conventional Phosphorus Fertilizers

Calcined Non-Apatite Phosphate Rock for Direct Application

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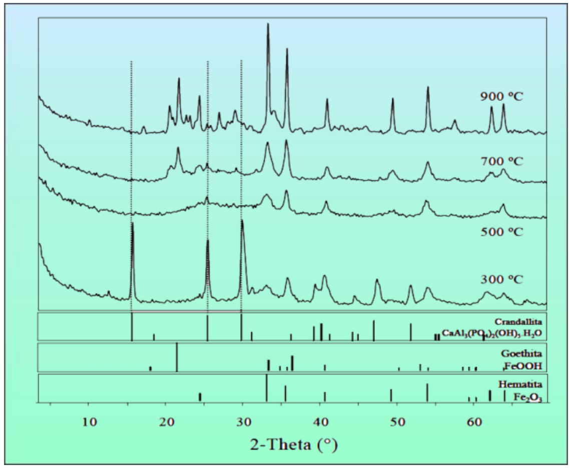
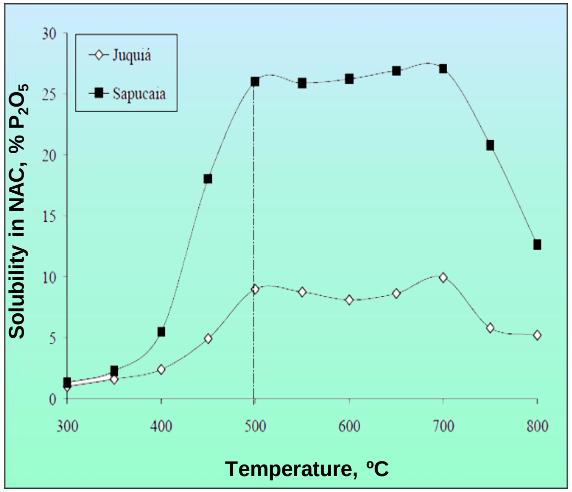
Calcined Non–Apatite Phosphate Rock for Direct Application

- ✓ Most PR used for chemical acidulation process or direct application contain Ca – P minerals in the form of apatite.
- ✓ Some deposits contain Ca – Fe – Al – P minerals in the form of crandallite.
- ✓ Not suitable for conventional P sources and also for direct application.
- ✓ The reactivity can be significantly increased upon calcination at temperatures ranging from 450 to 700ºC.

Crandallite (Al-P), $(X)(Al,Fe)_3(PO_4)_2(OH)_5.H_2O$, where (X) = (Ca, Ba, Sr, Pb, and/or other rare earth elements)



X-Ray diffractograms of crandallite submitted to 300, 500, 700 e 900ºC thermal treatments for 2 h



Effect of thermal treatment to varying temperatures in the NAC solubility of two crandallite based minerals

RAE (% basis) of crandallite P based sources as compared to TSP for upland rice

P Source	Grain Yield	P Uptake
	pH 5,4	
TSP	100	100
Juquiá (P-Al 1)	89	80
Sapucaia (P-Al 2)	83	80
Gafsa	95	106
	pH 7,0	
TSP	100	100
Juquiá (P-Al 1)	49	68
Sapucaia (P-Al 2)	49	62
Gafsa	0	1

Source: (Francisco et al., 2007)

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Use of Non-Conventional Phosphorus Fertilizers

Nonconventional Totally Acidulated Phosphate Fertilizers

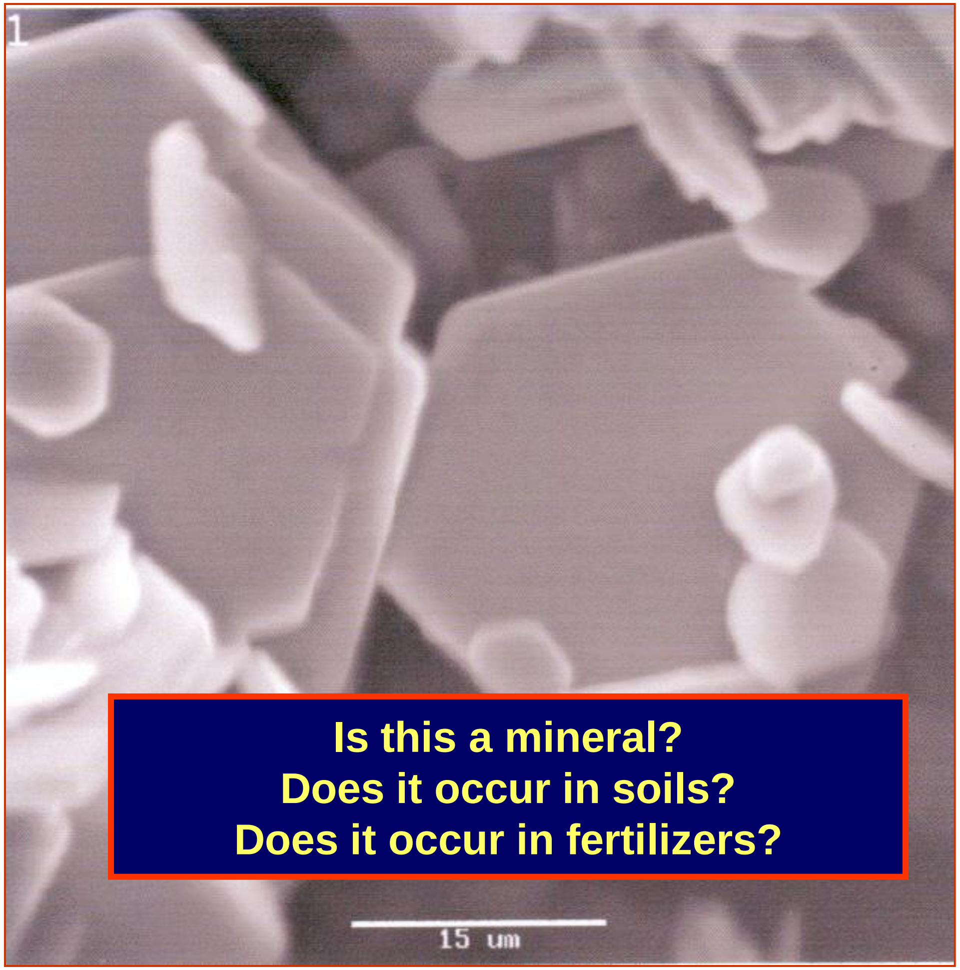
INITIAL CONSIDERATION

- ✓ Slides ahead challenge researchers and the nutrient stakeholders to think differently regarding P sources.

WHAT IS THIS?

Is this a mineral?
Does it occur in soils?
Does it occur in fertilizers?

WHAT IS THIS?



Is this a mineral?
Does it occur in soils?
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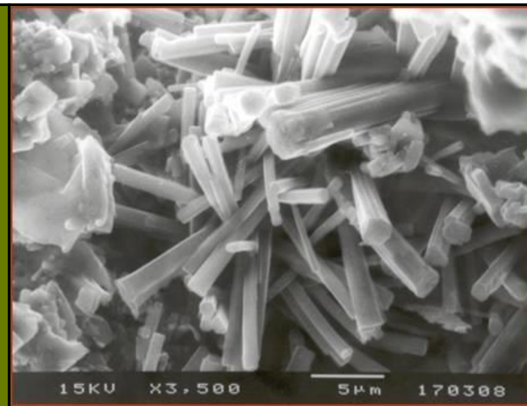

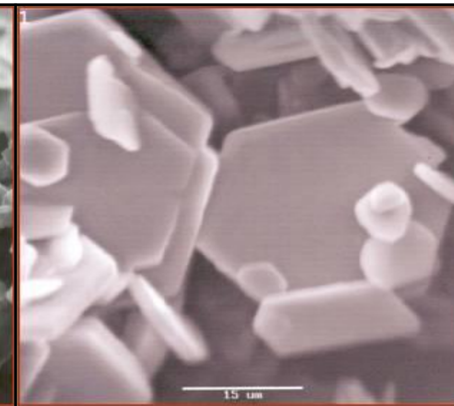

QUESTION/ COMPOUND CHARACTERIZATION		
Chemical Formula	$Fe_3KH_8(PO_4)_6.6H_2O$	$Fe_3KH_{14}(PO_4)_8.4H_2O$
Is it a mineral?	No	No
Where does it precipitate?	P Fertilizer, Generally in SSP	P Fertilizer, Generally in TSP
Total P (TP)	20.4	23.8
NAC Soluble P (CSP)	19.3	22.8
Water Soluble P (WSP)	0.03	0.2
(WSP/CSP) * 100	0.2	0.9
RAE(MCP; Upland Rice)	33	73
RAE (MCP; Flooded Rice)	75	104

Both compounds are much avoided because of their low water solubility. Does science prove this to be always necessary?

BACKGROUND INFORMATION

- ✓ **Totally acidulated P fertilizers (SSP, TSP, MAP, DAP) have high water solubility (WSP).**
- ✓ **Premium Grade PR to produce such fertilizers is decreasing worldwide.**
- ✓ **High amounts of energy and money are spent in order to always produce P fertilizers with high contents of WSP.**
- ✓ **To produce high WSP P sources part of the apatite concentrates are discarded, which means lost and potential environmental problems.**
- ✓ **Is it really necessary for totally acidulated P sources (not PAPR) to always have high water solubility?**
- ✓ **Interest and momentum exist to consider maybe such requirement is not necessary, leading to a better use of PR?**

Residues from the production of concentrated apatite - Catalão, GO

Photo: Francisco (2004).

STUDY 1

Characterization and agronomic evaluation of single superphosphates varying in iron phosphate impurities

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

46% of WSP

N.	Compound	SSP1	SSP2	SSP3
1	Fe3KH8(PO4)6	0.4	0.4	0.6
2	Fe3NaH8(PO4)6	5.02	3.35	6.36
3	Fe3H9(PO4)6	0.4	6.19	12.34
4	Na2SiF6	0.25	0.41	0.33
5	Ca10(PO4)6OH0.97F1.03	2.82	2.6	3.09
6	Ca4SiAISO4F13	2.18	0.4	2.1
7	SiO2	0	0	0.73
8	CaF2	0.25	1.44	0
9	MgSO4	0.35	0.4	0.45
10	SrSO4	1.53	1.32	1.17
11	ZnSO4	0.07	0.1	0.15
12	Ti2(SO4)3	0.92	1.4	1.88
13	BaSO4	1.92	1.14	1.28
14	Al2(SO4)3	0.25	1.27	1.08
15	Ba(H2PO4)2	0.19	0.41	0.28
16	CaSO4	49.15	49.7	46.87
17	Ca(H2PO4)2	34.19	19.08	12.81
	TOTAL	99.89	89.61	91.52

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 = (bi/bMCP)*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.

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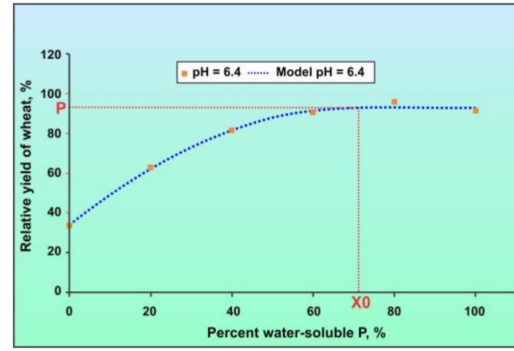
STUDY 2

Plant Availability of Phosphorus in Four Superphosphate Fertilizers Varying in Water-Insoluble Phosphate Compounds



Fonte de P[a]	pH	Modelo de regressão segmentada			Dose (mg kg-[1] P) requirida para alcançar [b]		WSP (%) requerido para alcançar [c]	
		Equação quadrática (R^2)	SE[d]	Plateau	Plateau	90% do plateau	Plateau	90% do plateau
					----- mg P kg^{-1} ------		------------- % -----------	
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.

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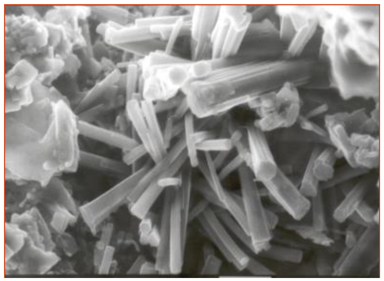
STUDY 3

Synthesis, characterization and agronomic evaluation of iron phosphate impurities in superphosphates

$Fe_3KH_8(PO_4)_6.6H_2O$

SEM



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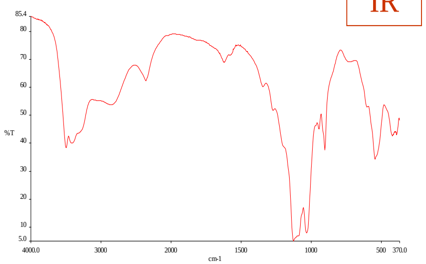
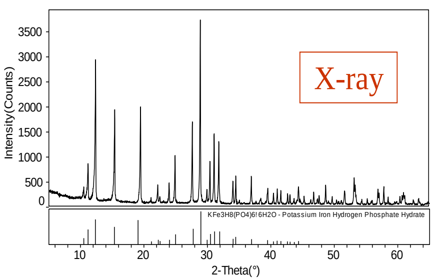




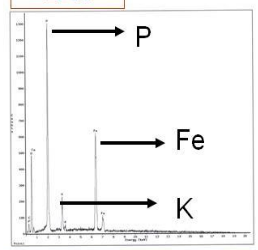
Chemical Analysis for total P, Fe, K, S and water of hydration

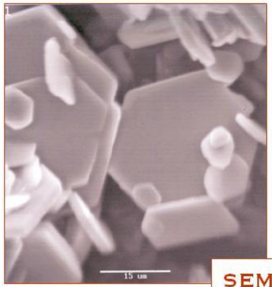
<u>Calculated Formula</u>:

$Fe_{2.8}K_{1.1}H_8(PO_4)_6!6.1H_2O$

$Fe_3KH_{14}(PO_4)_8.4H_2O$

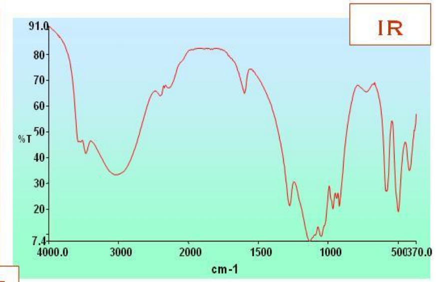
EDX



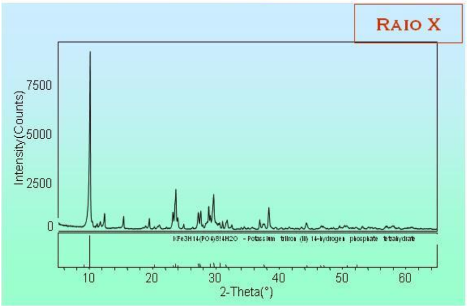


SEM

IR



RAIO X



Análise química para P total, Fe, K, S e água de hidratação

<u>Fórmula calculada</u>:

$Fe_{3.0}K_{0.9}H_{14}(PO_4)_{8.}4.3H_2O$

Source: PROCHNOW, L.I.; CHIEN, S.H.; et al. <u>Soil Science Society of America Journal</u>. 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	$Y=7.81+0.28X-6.2x10^{-3}X^2$	1.59	35.3	66.6	42.7
H14-syn	Upland Rice	$Y=22.83+0.398X-2.8x10^{-3}X^2$	2.36	36.9	70.9	34.6
H8-syn	Flooded Rice	$Y=14.52+1.168X-20.0x10^{-3}X^2$	2.15	31.6	29.3	16.7
H14-syn	Flooded Rice	$Y=25.08+0.299X-3.8x10^{-3}X^2$	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.

Source: PROCHNOW, L.I.; CHIEN, S.H.; et al. Soil Science Society of America Journal. 67:1551-1563, 2003.

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DOESN'T IT SOUND FUNNY ?

The fertilizer industry spends energy and money to transform phosphate rock, which has very low water solubility, in highly soluble P sources, like SSP, TSP, MAP, DAP, and then, because it is too soluble, many try to somehow protect it for lower water solubility ?

Isn't there another possibility in some cases ?
Isn't there a more logical possibility in certain circunstances?

WHAT IS THE PRACTICAL MEANING OF HAVING TOTALLY ACIDULATED P FERTILIZERS WITH LOWER WSP BUT WITH HIGH AGRONOMIC EFFECTIVENES ?

- ✓ Decrease in disposal of part of certain P resources.
- ✓ Lower WSP sources = lower potential environmental problems.
- ✓ Higher efficiency.
- ✓ Optimization in the use of P Resources.
- ✓ Anyone interested?

Statistical Group Experiment Analysis
- 16 Field Experiments -

Treatment	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

Source: PROCHNOW, L.I. Unpublished. Scientific Report.

GENERAL CONCLUSIONS

- ✓ Research has showed not to be necessary to always have high water-solubility in fully acidulated phosphate fertilizers. Data obtained indicated that the WSP requirement should be related to the soil system, the crop and the chemical composition of the fertilizer.
- ✓ Some Fe-P compounds, now avoided by the industry, can be good sources of P in some circuntances and can be agronomically more effective as a source of P under flooded soil systems than for upland crop systems.
- ✓ This all translates into possibilities for specific sources for different agro-climatic conditions, with a better use of P Resources.

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.

QUESTION

Some have been repeating the same message, now with more data, that Lehr stated decades ago. Why no action to optimize the use of PRs by producing, in some cases, alternative totally acidulated P fertilizers with lower water solubility ?

- ✓ **No credibility.**
- ✓ **More studies needed.**
- ✓ **People resist to change.**

I invite you to think about this possibility

Use of Non-Conventional Phosphorus Fertilizers

<u>Other P Sources</u>
(not in our Adv. Agron. paper)

RELATIVE AGRONOMIC EFFECTIVENESS, TSP = 100, CORN

P Source	EqTSP (%)	
	1º Ano	2º Ano
Triple Superphosphate	100	100
Mg Termophosphate	106	103
Gafsa PR	58	92
Patos de Minas PR	1	6

Problems related to thermophosphates:
(1) price, (2) obtaining the specific raw material they need (very specific size), and (3) being powder makes difficult to blend.

Source: Coutinho et al. (1991).

- NEW PRODUCTS -
SEVERAL POSSIBILITIES BUT FEW WITH GOOD PUBLISHED RESEARCH DATA

- ✓ **Many good opportunities in literature that could translate into new products. Need for final field research with results published by prestigious Journals.**
- ✓ **Need for advanced techniques applied in fertilizer research.**
- ✓ **Some opportunity to adapt plants to soil (genetic studies).**

FINAL COMMENTS

SOME PROPOSED CHANGES IN THE WAY WE THINK ABOUT PHOSPHORUS IN AGRICULTURE

- ✓ **P: From a concept of an inefficient nutrient in the soil system to a concept of, if utilized properly, an efficient nutrient.**
- ✓ **Consider P as a whole and not just agronomically. We need to also think about the economic, social and environmental aspects.**

CROP – GRASS
SYSTEMS OF CULTIVATION

Santa Fé: Maize with Brachiaria

SOME NEEDS IN TERMS OF P RESEARCH

- ✓ Need to define P localized x P broadcasted (literature review and if necessary new work at field condition).
- ✓ Establish most adequate cropping systems in different agroclimatic regions (not just about P but also about P).
- ✓ Need to define a better use of P by crop rotation of plants with morphological versus physiological adaptation to soils low in P.
- ✓ Basic and applied research published related to new technologies for new P products.
- ✓ Studies about P recycling.

Denes GÁBOR/Hungary

Nobel Prize 1973 - Holography

"THE FUTURE CAN NOT BE PREDICTED.

THE FUTURE CAN ONLY BE INVENTED."

THANKS FOR YOUR ATTENTION!

IPNI International Plant Nutrition Institute

@IPNIBrasil

IPNIBrasil

http://brasil.ipni.net/news.rss

Website: http://brasil.ipni.net
Telephone/fax: 55 (19) 3433-3254