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OVERVIEW OF THE USE OF PHOSPHATE FERTILIZERS IN BRAZIL, A REVIEW

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ABSTRACT:
Brazilian agriculture has grown considerably in the last three decades, making the country one of the greatest agricultural powers in the world. All this growth demands a large amount of fertilizers. However, Brazil is a major importer of fertilizers about 75% of what is consumed comes from outside the country. Even though it is a subject of great importance for Brazilian agriculture, it is common for farmers, students and even agronomists not to know about the manufacturing process and the functioning of fertilizers, especially in relation to phosphate sources. P is a rare and non-renewable resource, so it is important to use it with quality and sustainability. Adding knowledge is fundamental, so it becomes necessary for agribusiness professionals to know about the fertilizer chain. To know the available sources, the manufacturing process, the performance of these materials in the field, and to learn about new technologies that can be used in order to optimize the use of this nutrient.

Keywords: fertilizer consumption, phosphorus reserves, slow release fertilizer, fertilizer production

PANORAMA DO USO DE FERTILIZANTES FOSFATADOS NO BRASIL, UMA REVISÃO

RESUMO:
A agricultura brasileira cresceu bastante nas últimas três décadas fazendo com que o país se tornasse uma das maiores potências agrícolas do mundo. Todo esse crescimento demanda grande quantidade de fertilizantes. No entanto, o Brasil é um grande importador de fertilizantes cerca de 75% do que é consumido vem de fora do país. Mesmo sendo um tema de grande importância para a agricultura brasileira, é comum o agricultor, o estudante e até mesmo profissionais da área agronômica não conhecer sobre o processo de fabricação e funcionamento dos fertilizantes, principalmente em relação às fontes fosfatadas. O P é um recurso raro e não renovável, por isso é importante seu uso com qualidade e sustentabilidade. Agregar conhecimento é fundamental, por isso torna-se necessário por parte dos profissionais do agronegócio conhecer sobre a cadeia de fertilizantes. Conhecer as fontes disponíveis, o processo de fabricação, desempenho desses materiais no campo e inteirar-se sobre novas tecnologias existentes que podem ser utilizadas no intuito de otimizar o uso deste nutriente.

Palavras-chave: consumo de fertilizantes, reservas de fósforo, fertilizante de liberação lenta, produção de fertilizantes

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INTRODUCTION

Brazil is one of the largest food producers in the world, currently in fourth place behind China, India and the United States. It is the world leader in the production of coffee, oranges, soybeans and sugarcane, and is also second in the production of meat, chicken, papaya and pineapple, while in the cultivation of beans and corn it is ranked as the third largest producer (Faostat, 2022).

The country has fantastic conditions for the cultivation of various species, and in some regions it is possible to grow three to four crops in a year, occupying the soil practically 12 months of the year. But it wasn't always like this. All this is the result of decades of research carried out by companies, universities and consultancies. This research has made it possible to better understand the soil in Brazil, identify its potential and, above all, develop techniques to improve farming conditions, especially in regions previously considered unproductive, such as the Cerrado.

One of the pioneering works that allowed the mapping of the potentialities of the Brazilian Cerrado was carried out by the professor and researcher Alfredo Sheid Lopes (1970). The work developed from the collection and analysis of more than 500 soil samples in 58 municipalities, in the states of MG, GO, DF and TO, being representative for more than 600 thousand square kilometres, which corresponds to more than 1/3 of the biome in central Brazil (Lopes & Guilherme, 2016).

The main conclusions were that the soils were extremely acidic, deficient in almost all nutrients, presented high Al^{3+} contents and a great capacity for fixing P, that is, with many restrictions to cultivation. In addition to the work of Lopes & Cox (1977), other publications (Braga & Defelipo 1972; Goodland & Polard 1973; Weaver 1974; Bahia Filho 1974; Almeida Neto & Brasil Sobrinho 1977; Yost et al. 1979) highlighted the problem of P in Cerrado soils. Besides being naturally poor in this element, the phenomenon of "P fixation" limits the availability of this element to plants. Even with these limitations, it was concluded that these soils could become suitable for cultivation if they went through a process of building fertility through liming, gypsum, corrective and maintenance fertilization practices.

Brazil has adapted to these difficulties and today is a protagonist in global food production. However, the use of P in agriculture is still a sensitive issue, since it is a finite resource and its efficiency is still very low. In addition to this, the policy adopted by the country makes it largely dependent on imported phosphate fertilizers.

In recent years, with the growing demand for phosphate fertilizers and the increase in prices, there has been an internal debate about alternative management practices to improve the P use efficiency, as well as of a national fertilizer policy, aiming to reduce external dependence on this important input. This review aims to present an overview of phosphate fertilizers in Brazil, addressing sources, their characteristics, and the domestic and foreign markets.

USE EFFICIENCY OF PHOSPHATE FERTILIZERS

The low efficiency of phosphate fertilizers in tropical soils is widely reported in the literature. Novais et al. (2007) describes that soils with an advanced degree of weathering, as is the case with soils in tropical regions, have an increased capacity to retain anions and this causes the soil to behave much more like a "drain" than a source of P. Of all the P applied to crops via fertilizers about 30% is utilized by the plants, and the rest is lost by adsorption/fixation in the argilominerais fraction of the soil (Novais & Smyth, 1999; Malhi et al, 2002; Johnston et al., 2014; Benício et al., 2020).

This low efficiency is described by Fageria et al. (2011). The authors cultivated soybean for three consecutive years on a Oxisol, testing sources and doses of P (simple superphosphate (SSP), Yoorin thermophosphate and Arad phosphate). At the end, besides the phytotechnical parameters, the authors evaluated indices of the efficiency of P use, among them the apparent recovery, which is basically the percentage that the plant withdraws from the soil in relation to what was applied. The results showed a recovery of 11,7 %; 11,5 % and 5,9 % for SSP, Yoorin and Arad respectively; this indicated that in the best case scenario, 90% of the P applied was still in the soil in some form.

Other studies on nutrient balance in Brazilian agriculture between 1988 and 2016 presented in Cunha et al. (2011, 2014, 2018) an index of fertilizer use was developed. The authors call it "offtake rate", this index corresponds to the percentage of nutrients removed from the system in relation to that applied. In these works the P offtake rate varies between 41 and 63% (Figure 1), an optimistic scenario regarding the use of P when compared to other works found in the literature. However, if confronted with the rates of N and K, the values are still far below what can be achieved.

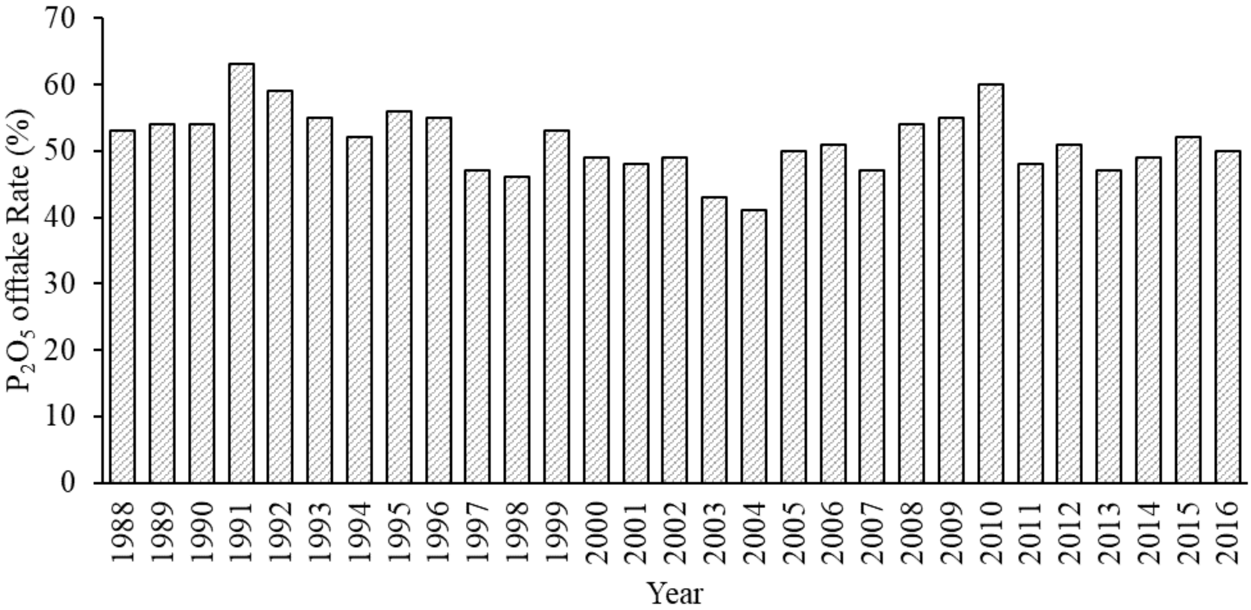

Figure 1. Annual nutrient offtake rate (P_2O_5) between the years 1988 and 2016 in Brazilian agriculture. *(Source: adapted from Cunha et al. 2011, 2014 and 2018)*.

This low efficiency of P has encouraged studies over the years that seek to raise the levels of P use. This is important both from an agronomic and economic point of view, besides contributing to more sustainable production. Many of these studies seek to implement management practices in agricultural systems and modes of use of phosphate fertilizers. Another strand of research more linked to industry and innovation sectors, seeks to develop new sources of P that are more efficient and economically feasible for the farmer.

FERTILIZER CONSUMPTION IN BRAZIL

Brazil currently ranks 4th in the world with around 8% of global fertilizer consumption, with potassium being the main nutrient used by national producers (38%). Next comes phosphorus, with 33% of total fertilizer consumption, and nitrogen, with 29% (Brazil 2020).

Brazil has increased its agricultural production considerably in the last decade, both in cultivated area and productivity, and this has reflected in the amount of fertilizers consumed by the country. In 2010, 24.5 million tons of fertilizers were delivered to Brazil, while in 2021, around 45.9 million tons would be delivered, a 53.3% increase over the period (Figure 2).

The speed of growth of Brazilian demand has exceeded the world's growth rate and its supply has occurred via increased imports. The country went from being a fertilizer exporter to a major importer between 1992 and 2020. Most of the fertilizer consumed by Brazil is of foreign origin, and only 15% of what is consumed is produced by the Brazilian industry.

When demand is segmented by nutrient (NPK), external dependence becomes even more evident, especially due to potassium consumption, since 94% of the nutrient consumed here in Brazil is of external origin (Figure 3).

Brazil is important in the world market not only because of the significant volume of inputs consumed domestically, but also because its demand is concentrated in the second half of the year, which gives the country relative bargaining power. The main suppliers of fertilizers to Brazil are Russia 22%, China 15%, Canada 10%, Morocco 7%, Belarus 6%, and the United States 4% (Comex Stat 2022).

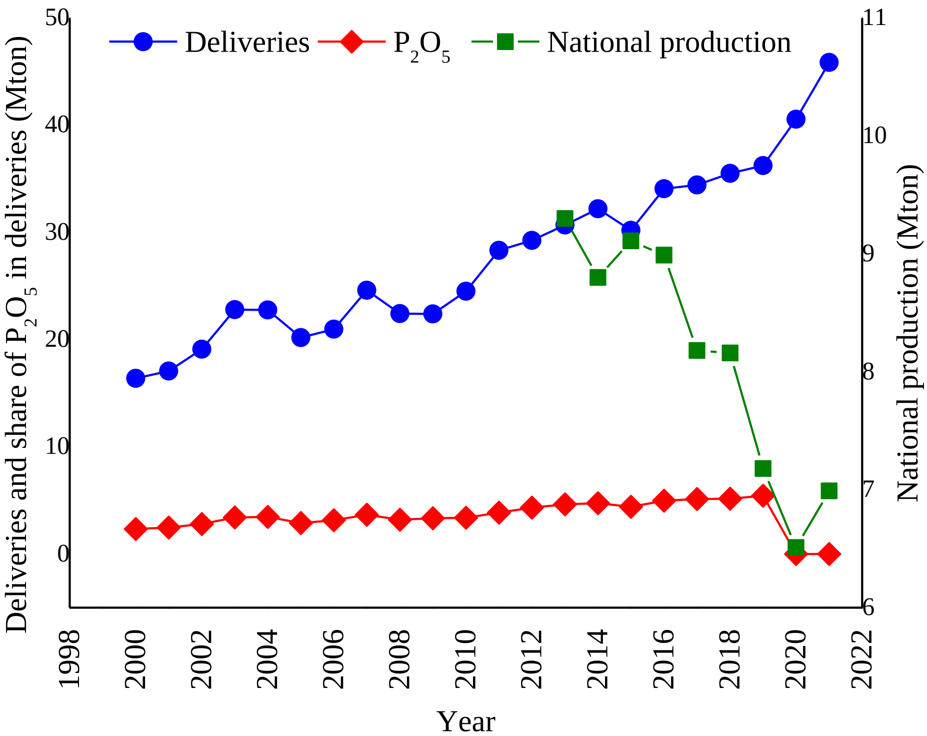

Figure 2. Fertilizer deliveries in Brazil and share of P_2O_5 between 2000 and 2021, and national fertilizer production between 2013 and 2021. *(Source: Anda 2021)*.

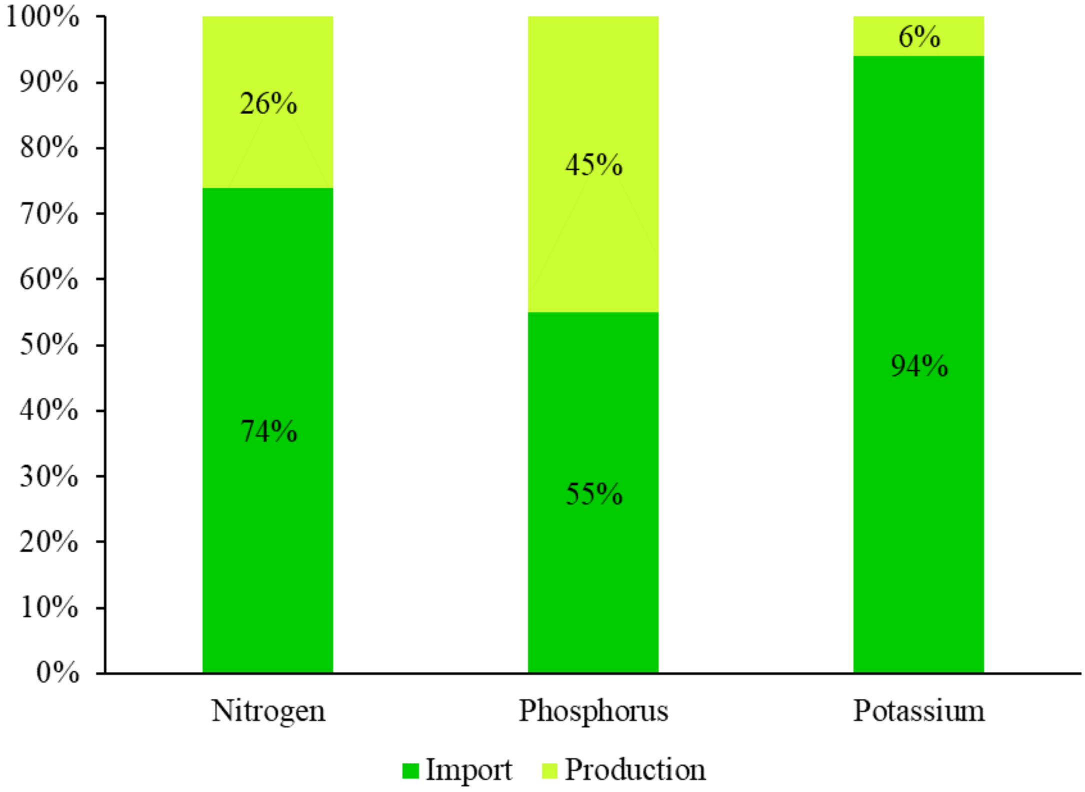

Figure 3. Fertilizer production and imports by nutrient *(Source: MAPA)*.

WORLD STOCKS OF P

Phosphate rocks is a term used to designate a mineral rock or salt containing one or more compounds of P. The great affinity of this element for oxygen means that it is widely distributed in the earth's crust, but never in an isolated form. Due to the various combinations and conditions of formation, different types of phosphate rocks can be found, from igneous rocks to sedimentary rocks of organic origin (Martins et al., 1975).

The main phosphate rock deposits occur as marine sediments (phosphorites), the largest sedimentary deposits are in North Africa, the Middle East, China and the United States. Currently phosphate rock deposits amount to more than 300 billion tonnes (USGS, 2021). Only five countries: Morocco, China, Egypt, Algeria and Saudi Arabia concentrate about 85% of known reserves (Table 1), with Morocco being the largest holder of these reserves (>70%).

Table 1. Main phosphate rock reserves (thousand cubic tons) in the world (Source: USGS, 2021).

Country	Reserve	Of world resources
Morocco	$5{,}00x10^7$	70,42%
China	$3{,}20\ x10^6$	4,51%
Egypt	$2{,}80\ x10^6$	3,94%
Algeria	$2{,}20\ x10^6$	3,10%
Brazil	$1{,}60\ x10^6$	2,25%
South Africa	$1{,}60\ x10^6$	2,25%
Saudi Arabia	$1{,}40\ x10^6$	1,97%
Australia	$1{,}10\ x10^6$	1,55%
United States	$1{,}00\ x10^6$	1,41%
Finland	$1{,}00\ x10^6$	1,41%
Jordan	$1{,}00\ x10^6$	1,41%
Russia	$6{,}00\ x10^5$	0,85%
Kazakhstan	$2{,}60\ x10^5$	0,37%
Peru	$2{,}10\ x10^5$	0,30%
Tunisia	$1{,}00\ x10^5$	0,14%
Usbequistao	$1{,}00\ x10^5$	0,14%
Israel	$5{,}30\ x10^4$	0,07%
Senegal	$5{,}00\ x10^4$	0,07%
Turkey	$5{,}00\ x10^4$	0,07%
India	$4{,}60\ x10^4$	0,06%
Mexico	$3{,}00\ x10^4$	0,04%
Togo	$3{,}00\ x10^4$	0,04%
Vietnam	$3{,}00\ x10^4$	0,04%
Other countries	$2{,}60\ x10^6$	3,66%
World Total	$7{,}10\ x10^7$	100,0%

Some countries have considerable reserves of phosphate rock, but they are not of sedimentary origin, and most of them are low quality material and, in some cases, low levels of P_2O_5, as is the case in Brazil. Other countries have significant reserves, but internal situations such as civil wars or trade embargoes mean that these countries are not represented on the world market, as is the case of Jordan.

There have been discussions about the depletion of phosphate reserves in a short space of time, but today there is a worldwide consensus that this is not an immediate threat. Today it is known that existing resources, at the current rate of exploitation, are expected to last for about 260 years, and can be altered for more or less through economic factors, geopolitics, legislation taxes and tariffs (Khabarov & Obersteiner 2017; Brownlie et al. 2021).

MAIN PHOSPHATE FERTILIZERS

Rock Phosphates

Phosphate rock, regardless of its origin, can be used directly as a source of P for plants, known as natural phosphates. Natural phosphate may be reactive (FNR) or not. Worldwide, FNR is characterized by having at least 27% of total P_2O_5, and at least 30% of the total soluble in citric acid 2%. These characteristics are found only in sedimentary phosphates (e.g. Morocco), hardly present in Brazil. The reactivity of the rock varies according to its origin and its physical-chemical characteristics. This reactivity directly influences its agronomic efficiency. In the world there are several phosphate rocks with different reactivity and agronomic efficiencies, as shown in Table 2.

Aiming to foster the use of Brazilian phosphates, in 2018 the legislation on the subject was changed, thus, currently in Brazil FNR is characterized by rocks containing at least 12% of total P_2O_5 and at least 30% soluble in citric acid 2% (MAPA, 2019). Even though most Brazilian phosphates are FNR, they are of inferior quality due to their lower reactivity and lower agronomic efficiency (Table 2).

Table 2. Agronomic efficiency and degree of reactivity of different phosphate rocks compared with triple superphosphate *(adapted from León et al. 1986).*

Phosphate	Source	Total P_2O_5 content (%)	Agronomic Efficiency Index (%)	Degree of Reactivity
North Carolina	United States	30	99	High
Bayovar	Peru	31	96	High
Gafsa	Algeria	30	96	High
Arad	Israel	35	85	High
Central Florida	United States	32	79	Average
Hulia	Colombia	20	76	Average
Pesca	Colombia	19	74	Average
Tenesee	United States	30	74	Average
Lobatera	Venezuela	19	67	Low
Sardinata	Colombia	20	59	Low
Patos de Minas	Brazil	24	58	Low
Araxá	Brazil	27	48	Low
Abaeté	Brazil	21	42	Low
Jacupiranga	Brazil	36	28	Very Low
Catalan	Brazil	35	22	Very Low
Tapira	Brazil	36	12	Very Low

The application of phosphate rock in agriculture has been studied for a long time and presents various results, which almost always vary depending on the type of soil, crop, management and rock type. For a better knowledge on the subject the reader can consult the works of Khasawneh & Doll (1979), Chien & Menon (1995), Rajan et al. (1996), and Chien et al. (2010).

Acidulated Phosphates

Besides natural phosphates, soluble sources (acidulous phosphates) are widely used in Brazilian agriculture. Among the main soluble phosphate fertilizers available on the market are simple superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP), diammonium phosphate (DAP) and NPS which is a kind of MAP enriched with S.

The phosphate fertilizers described above, the oldest are SSP and TSP which date from 1840 and 1872, respectively. They are products of the reaction of phosphate rock with sulphuric acid (SSP) and with phosphoric acid (TSP), and TSP has a higher concentration of P. MAP and DAP, on the other hand, are products generated through the neutralization of phosphoric acid with liquid ammonia. The difference between the two is the proportion of reactants in the reaction, where DAP needs a greater amount of ammonia, generating a product with a higher concentration of N. NPS is formed by adding elemental S or sulphuric acid during the MAP granulation process. Figure 4 shows a simplified flowchart of the production of the main phosphate fertilizers.

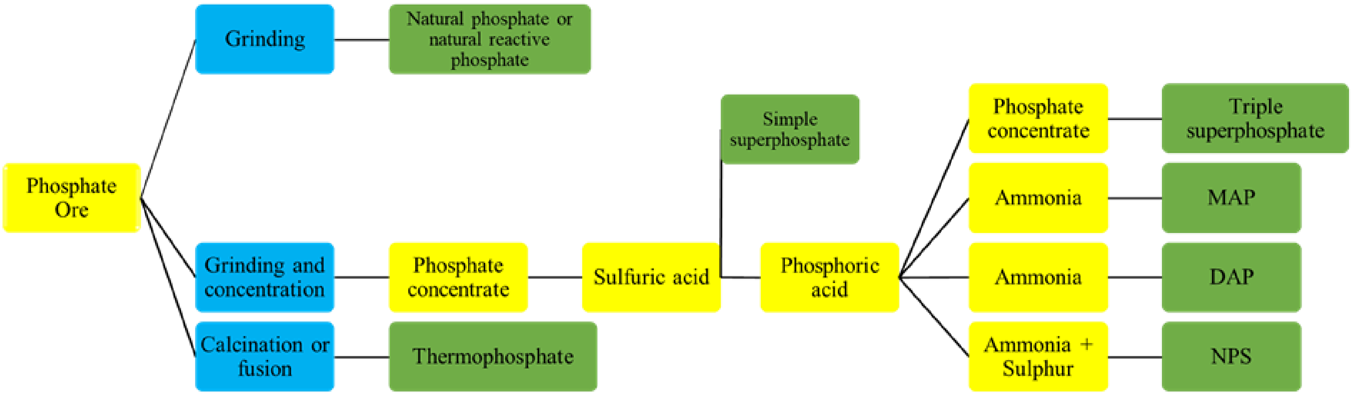

Figure 4. Flowchart of phosphate fertilizer production. In yellwo raw materials, blue points the process and green poits the final product.

Thermophosphates

Apart from rock phosphates and acidulous phosphates, there is also another class, thermophosphates, as shown in Figure 3. Thermophosphates are phosphate fertilizers whose production process is based on heating phosphate rock, which may be done by calcination (900 to 1200 °C) or fusion (1400 to 1500 °C). These phosphate fertilizers have low solubility in water, but are highly soluble in citric acid. This means that it is a source of phosphorus with gradual release fostered by the natural acidity of the soil solution or influence of the roots.

The sources of P described above are the most traditional on the market, all of which present the most varied results in the field, depending on conditions such as soil characteristics, the species cultivated, the intended productivity, the climate, among others. However, what is generally observed among all of them is the low efficiency of P use by the plants.

NEW TECHNOLOGIES IN PHOSPHTE FERTILIZERS

Many studies presenting "innovation" in phosphate fertilizer production can be found in the literature, several mechanisms for increasing P efficiency have been developed in recent years. Weeks Jr. & Hettiarachchi (2019) classify the mechanisms of increased efficiency of phosphate fertilizers in i) alternative P sources, ii) slow release mechanisms, iii) fixation blockers and iv) inducers of biochemical response.

In the present work we will emphasize fixation blockers and slow release mechanisms, as within these categories some "technologies" are already available in the Brazilian fertilizer market.

Fixation Lockers

The theory behind blockers is based on the idea of adding high molecular weight compounds with large amounts of negative charges (usually carbon based). These charges would be responsible for interacting with the cations that promote precipitation of P in the soil solution (Al^{3+}, Fe^{2+} and Ca^{2+}), so that most of the P added to the soil would be readily available since it would not undergo immediate precipitation.

Humic Substances

In the Brazilian fertilizer market, the main adsorption blocker used is humic substances (HS). The SH are formed from the organic matter humification. They are compounds rich in carbonyl and phenolic groups that promote both complexation and ionic exchange. They also have a great capacity for chemical interaction with soil minerals (Mikkelsen, 2005).

The use of SH in fertilizers is based on mixing SH-rich compounds into the fertilizer through pellets, adhesion to the fertilizer grain, or even capping the fertilizer granule with polymers and SH. The mechanism of P protection promoted by organic SH components is well described in Fink et al. (2016). The negatively charged functional groups of SH (e.g. phenols and carboxyls) have a higher electrical affinity with the surfaces of soil minerals (Fe and Al oxides), thus they are able to i) displace or desorb phosphates bound to minerals, ii) create cation bridges by changing the surface charges of minerals and iii) expand their surface area by occupying most of the mineral binding sites (Figure 5).

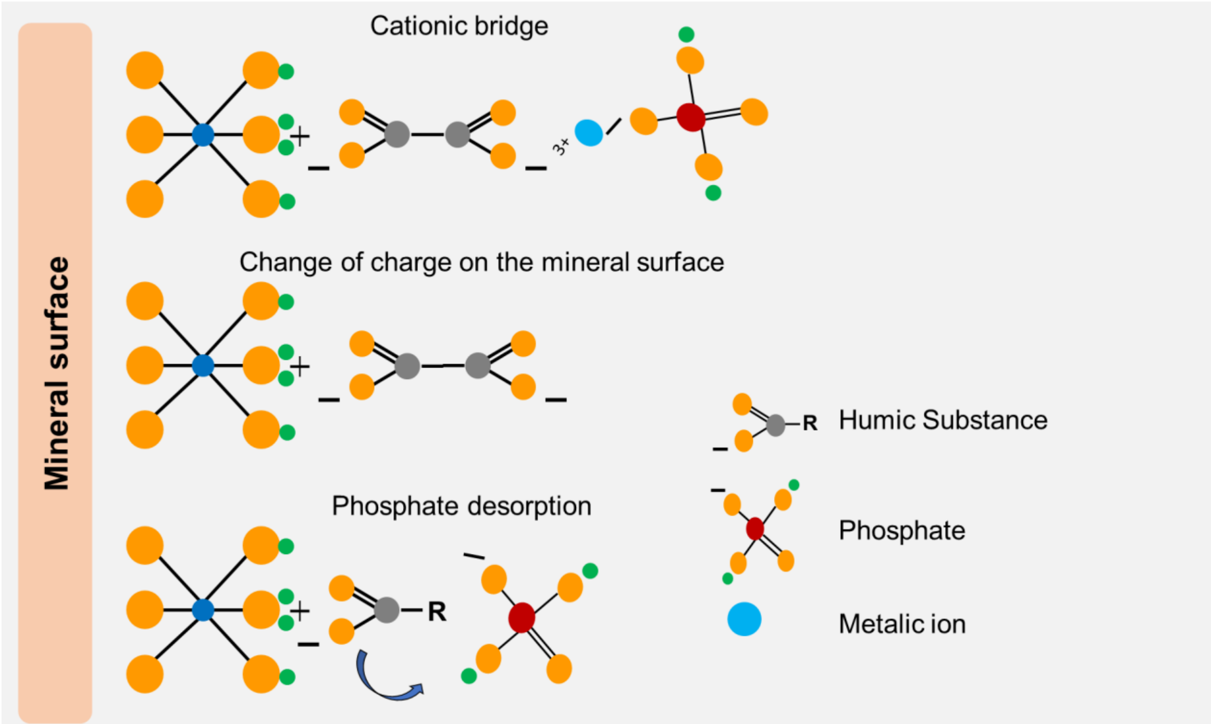

Figure 5. Effect of humic substances on phosphate adsorption by iron and aluminium oxyhydroxides in soils.

This possibility of interaction with the mineral fraction of the soil makes it widely tested as a blocker of P fixation in soils and several works can be found in the literature (Wang et al. 1995; Mayhew 2004; Cimrin & Yilmaz 2005; Quan-Xian et al. 2008; Rosa et al 2020; Purwanto et al. 2021; Jing et al. 2022).

The use of humic substances can be an important strategy to improve the levels of P in the soil and better nourish the plants, but it should be taken into account that the effect of humic substances together with fertilizers may change depending on variables such as soil texture, source of P and the dose used, according to Rosa et al. (2020). The authors, who used humic substances together with SSP, obtained efficiency results in a clayey soil, but in a soil with a texture average results were not satisfactory. These results make this type of technology interesting, since in most cases the fixation of P in soils is directly related to the increase in clay content.

Slow Release Mechanisms

The slow and/or controlled release mechanisms in fertilizers seek to release the nutrients in a way that delays their availability for uptake by the plants, or that extends their availability to the plant, so that the release of the nutrient is synchronized with the demand of the plant. This process means that the nutrient is less exposed to loss and is used with greater efficiency (Figure 6).

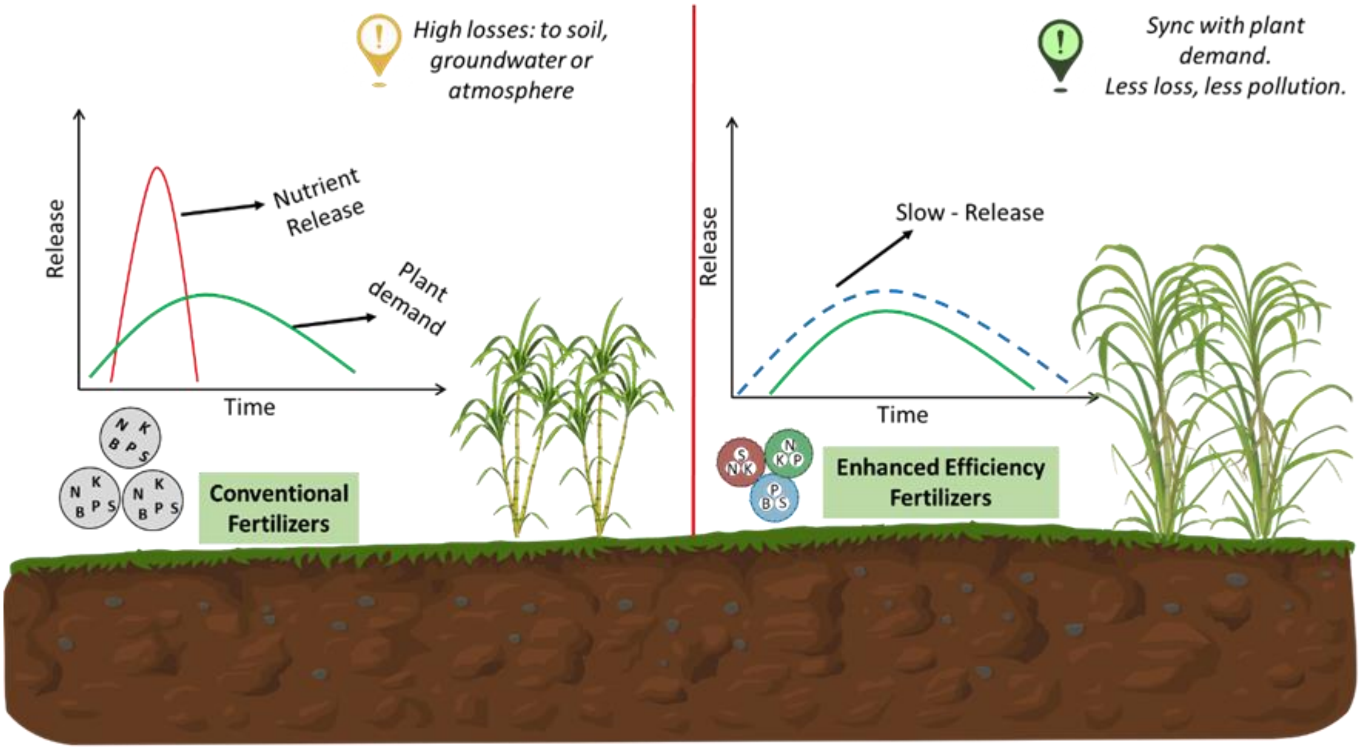

Figure 6. Comparison diagram between conventional fertilizers and slow-release fertilizers. (*Source: Benício 2020*).

The main form of producing these fertilizers is through the encapsulation of the raw material (MAP, DAP, TSP, SSP and etc.) with a material that is insoluble promoting a physical protection between the P of the fertilizer and the mineral phase of the soil. This protection is most of the time done with polymers that control the entrance of water in the "capsule" promoting then a control in the rate of dissolution of the nutrient, and the exit from inside the "capsule" occurs in a gradual way.

Polymer types to coat TSP and slow release fertilizers were proposed by Fertahi et al. (2020). The results were promising; the dissolution of P was delayed by approximately 30 days. Whereas dissolution of conventional TSP occurred in only 3 days where P was more exposed and consequently more likely to be adsorbed/fixed.

Even with a valid working premise, in practice this technology depends on the quality of the coating of the fertilizer granules. Incomplete coating due to the irregularity of the granules does not provide complete physical protection and the slow release mechanism ends up not working, while a very thick coating may delay the release of the nutrient, harming the plant. This is proven by Cruz et al. (2017), with different percentages of polymer in relation to the weight of the fertilizer (1.5%, 3%, 4.5%, 6%, 7.5% and 9%). The authors found that 3% or less of the granule coverage was incomplete and did not promote changes compared to conventional fertilizer, between 4.5% and 7% resulted in a moderate dissolution of the fertilizer, already 9% drastically limited the dissolution of the fertilizer.

At two types of polymers (polyvinyl alcohol and liquid paraffin) and ratios, Sarkar et al. (2020) obtained better results in both wheat yield and P use efficiency by the plant, the authors attributed these results to greater phosphorus protection reducing possible losses by fixation.

Many works are found around this theme and the results are diverse, this range of results is explained by Weeks Jr. & Hettiarachchi (2019). The authors state that the performance of slow release fertilizers, especially those coated with polymers, depend on the crop used, the soil properties and especially the quality and type of coating used.

The major disadvantage of this type of fertilizer is related to the cost of production, or even large-scale production. Besides the fact that some processes are difficult to implement, the coating material may be more expensive than the nutrient itself. Therefore, when developing these fertilizers, attention should be paid to the cost, so that they are attractive when compared to traditional fertilizers.

CONCLUDING REMARKS

Even with soils naturally poor in nutrients, today Brazil is one of the largest food producers in the world, and this is only possible through the use of fertilizers. Even though it has mastered agricultural practices like no other country, there is still room for improvement on many fronts, especially in increasing the efficiency of nutrient use, especially P, which is the greatest limiting factor for agriculture in Brazil. Today, with the management techniques of cultivation systems, it is possible to optimize the use of traditional sources of P. However, it is necessary to advance by seeking technologies that reduce the loss of P by fixation, improve the use of this element by the plants and, consequently, provide a financial return to the farmer. Besides the traditional sources, today the farmer already finds technologies that deliver better results. Many of these products have been on the market for a long time and are often not used because farmers are unaware of them or because of their cost. In this sense it is important not only to develop new phosphate fertilizers, but to disseminate these innovations and, above all, to seek to make their use economically viable.

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