UNIVERSIDADE DE BRASÍLIA
FACULDADE DE AGRONOMIA E MEDICINA VETERINÁRIA
PROGRAMA DE PÓS-GRADUAÇÃO EM AGRONOMIA

ESTRATÉGIAS DE ADUBAÇÃO FOSFATADA NO LONGO PRAZO: RESPOSTA DE CULTURAS, DISTRIBUIÇÃO ESPACIAL E ADSORÇÃO DE FÓSFORO

LUIZ EDUARDO ZANCANARO DE OLIVEIRA

TESE DE DOUTORADO EM AGRONOMIA

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TESE DE DOUTORADO SUBMETIDA AO PROGRAMA DE PÓS-GRADUAÇÃO EM AGRONOMIA, COMO PARTE DOS REQUISITOS NECESSÁRIOS À OBTENÇÃO DO GRAU DE DOUTOR EM AGRONOMIA

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“É bom lembrar: ‘Quem semeia pouco também colherá pouco, e quem semeia com largueza colherá também com largueza’”
2 Coríntios 9:6

RESUMO

O manejo da adubação fosfatada é especialmente sensível nos solos altamente intemperizados do Cerrado. Devido à elevada capacidade de adsorção de fósforo (P) destes solos em condições naturais, há receios com possíveis baixas eficiências das aplicações deste nutriente, especialmente na correção inicial dos baixos teores mas também nas adubações de manutenção por longo prazo. Este trabalho visou avaliar, em um experimento de longa duração, diferentes estratégias de adubação de correção e manutenção com P e seus impactos na produtividade das culturas, na distribuição espacial e nas propriedades de sorção deste nutriente no solo. Os níveis do fator correção foram: aplicação de 105 kg P total ha^{-1} como superfosfato triplo (SFT) ou fosfato natural reativo de Gafsa (FNR) incorporados ao solo antes do primeiro plantio, além do controle sem esta aplicação inicial. Dentro de cada uma das três estratégias de correção, o manejo de manutenção foi feito com 35 kg P total ha^{-1} aplicados na cultura de verão como SFT, FNR ou uma mistura de ambos em partes iguais, no sulco de plantio ou a lanço na superfície do solo. A aplicação corretiva de P resultou em ganhos elevados de produtividade logo nos primeiros anos, e ainda com prolongados efeitos residuais, enquanto que nos tratamentos apenas com a manutenção, elevadas produtividades só foram obtidas quando o P residual acumulado no solo alcançou níveis mínimos. Os estoques necessários para obtenção de 90% da produtividade referência foram 113,6 e 205,2 kg P ha^{-1} para SFT e FNR, respectivamente, considerando que destes, 35 kg P ha^{-1} referem-se à aplicação do fertilizante de manutenção do ano. A aplicação a lanço aumentou em cerca de 2,9% a produtividade das culturas nos anos finais do experimento, quando os estoques residuais de P no solo eram altos, na média de todos tratamentos adubados. A aplicação a lanço causou elevada concentração superficial de P total e Mehlich-1, gerando um maior volume total de solo corrigido com elevados teores desta fração lábil (>12 mg kg^{-1}). Em compensação, o volume de solo sob influência do fertilizante (>3 mg kg^{-1}) foi maior com a aplicação no sulco, devido ao posicionamento em maior profundidade do fertilizante e a distúrbios mecânicos como a abertura de sulcos. Observou-se um pequeno movimento vertical de P de aproximadamente 3 cm na aplicação a lanço entre o 8º e 16º anos de cultivo, e também um enriquecimento nas entre-linhas quando da aplicação no sulco. Foi constatada uma diminuição da capacidade de adsorção de P no solo nas regiões de aplicação do fertilizante fosfatado, especialmente nas camadas superficiais. Da mesma forma, observou-se que o SFT foi mais eficiente em reduzir esta capacidade de adsorção, provavelmente devido à pronta difusão de P para o interior das argilas, enquanto que nos solos onde houve aplicação da fonte pouco solúvel, o fertilizante permaneceu em parte como partículas não dissolvidas, aumentando em compensação seu efeito residual. Verificou-se uma necessidade de P menor do que a esperada por outros estudos em solos similares para redução da capacidade de adsorção a níveis adequados para a produção agrícola.

Palavras-chave: Latossolo, fósforo residual, adsorção, sistema plantio direto, distribuição de fósforo

ABSTRACT

Phosphate fertilization management is especially sensitive in highly weathered Cerrado soils. Due to the high phosphorus (P) adsorption capacity of these soils under natural conditions, there are concerns regarding the use efficiency of this nutrient, especially of the first high rate, corrective applications of P fertilizers, but also of the long-term maintenance applications. This work aimed to evaluate, in a long-term experiment, different correction and maintenance P fertilization strategies and their impacts on crop yields, and on the spatial distribution and sorption properties of this nutrient in the soil. The correction factor levels were: application of 105 kg P total ha^{-1} as triple superphosphate (TSP) or Gafsa reactive phosphate rock (RPR) incorporated in the soil before the first planting, in addition to the control without this initial application. Within each of the three correction strategies, maintenance management was carried out with 35 kg total P ha^{-1} applied to the summer crop as TSP, RPR or a mixture of both in equal parts, applied in the crop row (band) or broadcast on the soil surface. The corrective application of P resulted not only in high yield gains in the first few crops but also a prolonged positive residual effect. In the maintenance-only treatments, high yields were only obtained when minimum levels of residual P had been accumulated in the soil. Fertilizer P stocks needed to obtain 90% of the reference yield were 113.6 and 205.2 kg P ha^{-1} for TSP and RPR, respectively, considering that 35 kg P ha^{-1} of these are applied as fresh maintenance P fertilizer. Broadcast application increased crop yields by circa 2.9% in the final crops of the experiment, when residual P stocks in the soil were high, for the means of all fertilized treatments. A surface concentration of total and Mehlich-1 P was observed in broadcast application, resulting in larger volumes of soil with high levels of this labile fraction (>12 mg kg^{-1}). On the other hand, soil volumes under fertilizer influence (>3 mg kg^{-1}) were higher with band applications, due to the deeper positioning of the fertilizer and to mechanical disturbances such as the opening of furrows. A small vertical movement of P of approximately 3 cm was observed under broadcast application after the time period between the 8th and the 16th crops, while an enrichment of P between the crop rows was observed when P was band applied. A decrease in P sorption capacity was observed in the phosphate fertilizer application zones, especially in the surface layers. In addition, TSP was more effective in reducing sorption capacity, probably due to short-term P release from fertilizer and subsequent diffusion into the soil particles matrix; in soils where the sparingly soluble source was applied, fertilizer particles remained partly undissolved, what in turn increased its residual effect. P rates required for substantial reduction in sorption capacity were found to be lower than the expectations raised by other studies with similar soils of the Cerrado region, benefiting a sustainable agriculture in Oxisols.

Keywords: Oxisol, residual phosphorus, adsorption, no-tillage system, phosphorus distribution

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INTRODUÇÃO

A maior parte dos solos brasileiros, especialmente os do Cerrado, sob condições naturais, apresenta baixa disponibilidade de macro e micronutrientes. Assim, o atual sucesso do agronegócio nestas regiões ocorreu, inicialmente, devido à construção da fertilidade química do solo, a fim de suprir as necessidades nutricionais das culturas.

A adubação fosfatada, embora apresente longo efeito residual, é um dos investimentos iniciais mais onerosos para o produtor. Em geral, os solos da região do Cerrado apresentam baixa disponibilidade natural de fósforo (P), sendo necessário o fornecimento de fontes fosfatadas antes do início dos cultivos. Contudo, apesar de existirem recomendações sobre alguns aspectos do manejo destas aplicações, como doses de correção e manutenção (Sousa; Lobato, 2004), estudos de longo prazo podem contribuir para o refinamento destas estratégias de manejo, levando também em conta aspectos como a escolha da fonte e modo de aplicação. Devido à interação do P com os coloides do solo (Fink et al., 2016c), proporcionando elevado efeito residual (Oliveira et al., 2019), estas escolhas influenciarão a produtividade dos cultivos por longo período.

Devido à sua importância como macronutriente, sendo fundamental para diversas etapas do metabolismo das plantas, a mencionada forte interação de P com a fase sólida do solo pode tornar este nutriente um dos mais limitantes para a produção vegetal. Assim, a adubação fosfatada tem sido estudada desde o final do século XIX (Russell; Prescott, 1916; Johnston; Poulton, 2019), e com crescente importância, uma vez que o aumento da demanda e produção mundial de alimentos exige grande aporte de P aos agroecossistemas. Em 2019, essa demanda alcançou 20,5 milhões de toneladas de P no mundo, com expectativas que se alcance 21,8 milhões de toneladas em 2023 (USGS, 2020). No entanto, as reservas mundiais de rochas apatíticas conhecidas, matéria prima para a produção de fertilizantes fosfatados, têm previsão de acabarem em pouco menos de 300 anos, caso se mantenha o atual ritmo de consumo (USGS, 2020). Além disso, preocupações com a elevada capacidade de adsorção de P ao solo levam muitos agricultores a utilizarem doses elevadas de fertilizantes fosfatados (Riskin et al., 2013), tendo por consequência o surgimento de preocupações com o impacto ambiental gerado, principalmente na qualidade dos recursos hídricos (Dodd; Sharpley, 2015).

Desta forma, estratégias que visem aumentar a eficiência de uso das fontes fosfatadas pelas culturas têm recebido destaque nas pesquisas nos últimos anos, também devido ao aumento do custo relativo deste tipo de fertilizante principalmente quando aplicado em culturas de relativo baixo valor agregado, como a soja (Elser et al., 2014). Com baixas expectativas de que este cenário seja alterado (Elser et al., 2014), iniciativas como o conceito dos 4 “Cs”, que incentivam a aplicação da fonte certa do nutriente, na dose certa, e no momento e localização certos voltaram a ganhar o interesse da indústria e comunidade científica (Johnston; Bruulsema, 2014).

Muita atenção é dada atualmente ao estoque residual de P nos solos agrícolas, acumulado após um longo período sob cultivos com adições deste nutriente em quantidades superiores às exportadas pelas culturas. Isto é consequência de preocupações com a possibilidade de contaminação de rios e lençóis freáticos com P, o aumento do custo dos fertilizantes fosfatados e potencial economia gerada pela utilização deste estoque residual. Apesar disto, globalmente, 32% das áreas de cultivos anuais ou perenes e 43% das áreas de pastagens apresentam déficit na disponibilidade de P, especialmente no continente africano, onde esta deficiência cresce (Lun et al., 2018). Assim, a correção adequada dos níveis de P no solo ainda é de vital importância para o aumento da produção de alimentos, e também influencia a posterior eficiência de uso do P residual no solo.

Nesse contexto, o presente trabalho de tese visa avaliar os efeitos de diferentes estratégias de correção do solo e manejo da adubação fosfatada sobre a distribuição espacial e propriedades físico-químicas de P no solo, relacionando estes fatores à resposta produtiva das plantas cultivadas em um experimento conduzido por 16 anos em sistema de plantio direto (SPD) em um Latossolo argiloso. A tese foi dividida em três capítulos. O primeiro apresenta uma discussão sobre os efeitos de diferentes estratégias de correção do solo e manejo da adubação fosfatada de manutenção sobre a produtividade das culturas, desenvolvimento dos estoques e disponibilidade de P no solo. O segundo discute o efeito da fonte de manutenção e modo de aplicação sobre a distribuição espacial de diferentes frações de P no solo ao longo do tempo. O terceiro aborda a influência das mesmas estratégias de manejo discutidas no capítulo 1 sobre as características de interação deste nutriente com a fase sólida do solo.

1 REVISÃO BIBLIOGRÁFICA

1.1 SPD E ADUBAÇÃO FOSFATADA NO CERRADO

A adoção do SPD nos grandes cinturões produtores de grãos do Brasil tem promovido mudanças no perfil do solo nestas regiões. Além dos impactos diretos nas operações realizadas pelo produtor rural, como ausência de revolvimento do solo e economia de operações agrícolas, houve diversas consequências indiretas, como na distribuição e disponibilidade de nutrientes no perfil do solo e no acúmulo de matéria orgânica, entre outras alterações (Nunes et al., 2020; Tiecher et al., 2020).

Apesar do SPD apresentar características próprias, como a elevada estratificação da disponibilidade de nutrientes, de uma forma geral os benefícios da adoção deste sistema são muito grandes e amplamente estudados na literatura. Nunes et al. (2018), por exemplo, observaram diversas melhorias nas propriedades químicas, físicas e biológicas do solo com a adoção do SPD, com maiores níveis de matéria orgânica, proteínas, estabilidade de agregados e taxa de infiltração.

O abandono do preparo mecânico do solo, contudo, por si só não garante os benefícios possíveis de se obter com o SPD. Este envolve um conceito mais amplo, como a adoção do cultivo de plantas que propiciem uma elevada quantidade de resíduos vegetais no solo, com persistência suficiente para adequada cobertura do solo. Apesar de muitos produtores já terem abandonado o preparo mecânico do solo, a adoção de estratégias para aumentar a cobertura do solo é recente. Assim, a utilização de plantas de cobertura na entressafra ou consorciada com a cultura principal tem crescido nos últimos anos. Os benefícios diversos incluem a incorporação de carbono ao sistema, reciclagem e disponibilização de nutrientes às culturas principais (Calegari et al., 2013; Tiecher et al., 2017; Soltangheisi et al., 2020) estruturação do solo, e redução dos danos causados por nematoides (Neher et al., 2019). Ligado a estes conceitos está a eficiência geral do sistema e da adubação fosfatada, a qual depende de um bom manejo agronômico em todo o sistema de cultivo.

A necessidade da cobertura do solo e intensificação biológica do sistema deriva em parte da necessidade de elevados aportes de carbono ao sistema para manter os níveis de matéria orgânica no solo, especialmente em sistemas de plantio direto mais antigos, onde os teores se aproximam da capacidade máxima de estabilização de C no sistema (Corbeels et al., 2016). Em um Latossolo de Cerrado, por exemplo, Sousa et al. (2016) estimaram que são necessários pouco mais de 12 Mg ha^{-1} ano^{-1} de aporte de matéria seca ao solo para manter o teor inicial de 34,3 g kg^{-1} de matéria orgânica no solo, o que dificilmente é alcançado sem a utilização de plantas de cobertura ou consórcio. A manutenção de elevados teores de matéria orgânica possui estreita relação com a redução da energia de ligação de P com a fase sólida do solo (Barrow; Feng; Yan, 2015; Yang; Chen; Yang, 2019), impactando sobremaneira a eficiência de uso deste nutriente, inclusive reduzindo níveis críticos de P lábil no solo (Sousa et al., 2016).

Contudo, algumas particularidades precisam ser observadas. Em condições de baixa disponibilidade inicial de P no solo, o consórcio de milho safrinha com braquiária ruziziensis (*Urochloa ruziziensis*), reduziu a disponibilidade de P (Almeida et al., 2018, 2019) e a produtividade da cultura subsequente (Merlin; He; Rosolem, 2013; Almeida et al., 2018, 2019), possivelmente devido à incorporação de P inorgânico em formas orgânicas indisponíveis a curto prazo nos resíduos culturais. Assim, embora existam relatos de aumento da disponibilidade de P com o uso de plantas de cobertura (Tiecher et al., 2017), os efeitos benéficos da utilização destas plantas sobre a nutrição fosfatada das culturas principais aparentemente são mais relacionadas a efeitos sobre fatores que atuam indiretamente na capacidade das plantas de obterem P do solo. Por exemplo, como na redução da energia de ligação de P ao solo com o aumento do aporte de C ao sistema, como mencionado acima, e outros fatores como a redução da população de nematoides (Costa; Pasqualli; Prevedello, 2014; Amorim et al., 2019; Acharya; Yan; Berti, 2020), o que permite a manutenção de maior área radicular, volume de solo explorado e melhores níveis de indicadores de qualidade biológica do solo de forma geral (Lopes et al., 2018; Mendes et al., 2019, 2021).

O manejo da adubação fosfatada também tem passado por transformações ao longo do desenvolvimento do SPD na região do Cerrado. Por exemplo, em consequência de janelas de plantio curtas, com a finalidade de aproveitamento máximo do período de chuvas para maximizar a produtividade principalmente da segunda safra, seja de milho, sorgo ou algodão, muitos agricultores têm recorrido à adubação a lanço de P na safra principal. Esta operação gera ganhos operacionais em comparação à adubação no sulco de plantio, pela menor necessidade de reabastecimento das máquinas com fertilizante e possibilidade de uso de plantadeiras com elevado número de linhas de plantio. Assim, esta prática intensificou o já observado acúmulo de P e outros nutrientes nas camadas mais superficiais do solo sob SPD (Nunes et al., 2011; Calegari et al., 2013; Oliveira et al., 2020).

É importante observar que o sistema radicular das culturas tende a se adaptar em consequência desta estratificação da disponibilidade de nutrientes, criando uma concentração maior de raízes nos primeiros 10 cm de solo sob SPD (Li et al., 2017; Nunes et al., 2021). Mesmo assim, existe a tendência de se obter maior massa total radicular ao longo do perfil em comparação ao sistema convencional (Li et al., 2017). Também nota-se que o modo de aplicação do fertilizante fosfatado tem menor influência nesta forte estratificação do crescimento radicular, que é uma característica inerente ao SPD (Nunes et al., 2021).

Assim, como derivação da possibilidade de se realizar a adubação fosfatada a lanço, uma prática que começou a ganhar importância é a aplicação, de forma antecipada na cultura de cobertura, de fontes fosfatadas menos solúveis do que as fontes convencionalmente utilizadas. Desta forma, fosfatos naturais reativos (FNR) podem ser aplicados antes da safra principal, aumentando seu período de solubilização e possibilitando maior eficiência de uso de P na cultura principal, e possivelmente até proporcionando incremento de biomassa da própria cultura de cobertura (Collier et al., 2008; Ramos et al., 2010).

Outra mudança que vem acontecendo no campo é a intensificação do manejo biológico. Já estão bem estabelecidos os manejos de pragas que atacam a parte aérea das culturas e a inoculação de rizóbios fixadores de nitrogênio nas sementes, especialmente na cultura da soja. Porém ainda há intensa mobilização da pesquisa na utilização de novos microrganismos com objetivo de promover o crescimento vegetal, sendo que em alguns casos ainda existe o intuito de aumentar a eficiência da adubação, especialmente a fosfatada (Pereira et al., 2020; Rosa et al., 2020; Barrow; Lambers, 2022). Esta área provavelmente receberá cada vez mais atenção no futuro sendo que, no sentido de monitorar o status biológico do solo, pesquisa recente tem trabalhado na elaboração de níveis críticos de indicadores microbiológicos (Lopes et al., 2018), uma vez que nem sempre indicadores exclusivamente químicos refletem o potencial produtivo do solo. Tal fato é tão significativo que existe um esforço de incorporar tais avaliações na rotina comercial de análise de solo (Mendes et al., 2019).

1.2 INTERAÇÃO DE P COM O SOLO E SUA RELAÇÃO COM ADUBAÇÃO CORRETIVA DE P

Cerca de metade de todo P adicionado a áreas agrícolas produtivas no mundo tem sido mantido no solo devido à eficiência de uso média de P da ordem de 50% (Lun et al., 2018). Apesar disto, mais de um terço das áreas agrícolas no mundo apresentam baixa disponibilidade de P, especialmente no continente africano (Lun et al., 2018). Assim, a já grande variabilidade nos teores de P tende a crescer e está relacionada ao uso do solo, sistema de cultivo e fontes utilizadas, dentre outros (Lou et al., 2018). Como consequência, Kvakić et al. (2018) estimaram que a produtividade média mundial da cultura do milho poderia ser quase duas vezes maior que a atual se muitas áreas, especialmente na Ásia central e África, não apresentassem grande deficiência na disponibilidade de P no solo.

Segundo Barrow (1980; 2015), a adsorção de fosfato no solo acontece em duas etapas. Inicialmente, ocorre de forma específica e reversível, na superfície de óxidos e hidróxidos de Fe e Al. No longo prazo, através de reações lentas, ocorre a difusão no estado sólido deste fosfato para o interior das partículas adsorventes, o qual é de muito mais difícil acesso pelas plantas, caracterizando o P ocluso, pouco disponível. Este fato é provavelmente o responsável pelo pensamento tradicional de que a eficiência de uso de fósforo do solo é baixa, porém esta reação é necessária para permitir a eficiência de adubações fosfatadas posteriores (Barrow; Barman; Debnath, 2018). Teores crescentes de P no solo decrescem a capacidade tampão deste nutriente no solo, com eventual cessão do fluxo de difusão para o interior das partículas (Barrow, 2015). Também pela diminuição do número de pontos de adsorção não ocupados com P, aumenta-se a probabilidade de solubilização e difusão do P fracamente adsorvido ou precipitado para a solução do solo (Santner et al., 2015; Almeida et al., 2019). Assim, teores elevados podem aumentar a eficiência de utilização de P pelas plantas, especialmente daquelas menos eficientes na absorção deste nutriente.

Desta forma, é necessário um nível crítico de P no solo que proporcione produtividade satisfatória e a partir do qual pode-se adotar uma adubação que mantenha os teores disponíveis acima do nível crítico determinado. Assim, a adubação que eleva os níveis para o teor crítico é chamada adubação de correção, constituindo a base para a implementação de cultivos em solos com baixa disponibilidade inicial de P. Além do custo da adubação fosfatada, o receio de produtores com as reações de indisponibilização de P no solo pode ser uma limitação para a maior adoção da prática de correção.

1.2.1 Correção e reações iniciais de P no solo

É comum encontrar valores de P extraído por Mehlich-1 na ordem de 1,0 mg P kg^{-1} de solo virgem do Cerrado, ao passo que o nível crítico para um solo com teor de argila compreendido entre 36% e 60% é de 12 mg P kg^{-1} (Sousa; Lobato, 2004). Assim, a necessidade de elevar os teores de P lábil para níveis mínimos nos Latossolos da região central do Brasil é conhecida desde os primeiros passos da agricultura nesta região. A utilização de uma dose inicial elevada mais o uso de doses pequenas de P a cada cultivo, estratégias hoje conhecidas como adubação de correção e de manutenção, respectivamente, foram vistas como muito eficientes desde a década de 1970, como demonstrado por Yost (1977) em experimentos na Embrapa Cerrados, em Planaltina-DF. A aplicação inicial de correção, a lanço em área total com incorporação, serviria para ocupar sítios de adsorção com elevada afinidade por P, proporcionando bom efeito residual enquanto reduzindo a adsorção de novos aportes de P (Yost et al., 1979, 1981).

A correção gradual dos teores de P é uma opção viável quando o produtor não dispõe de recursos para aplicar as elevadas doses de P exigidas na correção total. Porém a melhor estratégia de manejo da adubação fosfatada quando se opta pela correção gradual depende do sistema de manejo de solo. No SPC, a aplicação em área total corrige um elevado volume de solo, mesmo que parcialmente. Com a dose de 35 kg P ha^{-1}, a aplicação desta forma gerou melhores respostas em produtividade do que a aplicação no sulco de semeadura enquanto os estoques de P no solo ainda eram baixos, uma vez que o maior volume de solo fertilizado na aplicação a lanço compensou a maior disponibilidade de P em uma faixa estreita como no caso da aplicação no sulco (Nunes, 2014).

Já no SPD, embora não seja aconselhável iniciar este sistema antes da adubação de correção (fosfatagem) com incorporação, a fim de se elevar os teores de P pelo menos na camada 0-20 cm, caso se opte pela correção gradual neste sistema é preferível que se realize a aplicação do fertilizante na linha de plantio (sulco de semeadura). Isto porque a aplicação em superfície e sem incorporação neste sistema limita a área de contato e reação de P com o solo, que é importante na fase de correção gradual, enquanto que a aplicação no sulco eleva os teores de P próximos às raízes e consequentemente a produtividade da cultura nesta fase inicial (Nunes, 2014). Esta estratégia de aplicação no sulco pode também ser adotada quando, por algum motivo, o produtor tenha permitido que os teores de P lábil tenham caído tanto no solo que seja necessária reposição de P no sistema, mas que se deseje preservar o SPD instalado na área (Kurihara et al., 2016).

Uma vez que um fertilizante é adicionado ao solo, uma série de reações ocorre entre o P liberado pela solubilização do fertilizante e componentes do solo. Estas reações incluem a precipitação que ocorre na região saturada em P próxima ao fertilizante, formando novos compostos de fase sólida a partir de íons em solução (Mclaughlin et al.,

2011) e a adsorção, que será abordada em detalhes no próximo tópico e que pode ser seguida pela penetração de P para dentro das partículas do solo.

Inicialmente, porém, é necessário que ocorra a solubilização dos grânulos de fertilizante. No caso de fertilizantes fosfatados compostos de sais de fosfato, como superfosfato simples (SFS) e superfosfato triplo (SFT), devido à alta capacidade higroscópica de fosfato monocálcico – FMC - ($Ca(H_2PO_4)_2.H_2O$) contido nestas fontes, o grânulo é capaz de absorver umidade mesmo em condições de baixa umidade do solo, como -1500 kPa (Lawton; Vomocil, 1954), devido à menor pressão de vapor na superfície do grânulo em relação ao solo adjacente. Ainda de acordo com esses autores, em 24 h, 20-50% do P do fertilizante já move-se para a solução do solo nestas condições, enquanto que em condições de umidade próximas à capacidade de campo, esta proporção é de cerca de 50-80%.

Após a absorção de água, reações de precipitação ocorrem dentro do próprio grânulo de fertilizante. Com a dissolução de FMC e o início da movimentação da solução para fora do grânulo, fosfato dicálcico dihidratado – FDCDH – ($CaHPO_4.2H_2O$) e fosfato dicálcico anidro – FDC – ($CaHPO_4$) precipitam na região do grânulo (Lehr; Brown; Brown, 1959; Sousa; Volkweiss, 1987a; Hedley; Mclaughlin, 2005). Esta reação é resultado do aumento do pH da solução fortemente ácida por ocasião da reação de ácido fosfórico residual com partículas residuais não aciduladas de apatita enquanto a solução é gradativamente diluída pela entrada de água do solo (Hedley; Mclaughlin, 2005). Após a dissolução completa dos grânulos, 27 a 34% do P presente inicialmente nos grânulos de SFS ou SFT principalmente como FMC foram precipitados como FDCDH ou FDC em um experimento conduzido em solos com diferentes teores de argila e pH, sendo que este valor foi reduzido para cerca de 25% sete meses após (Lehr; Brown; Brown, 1959). Valores semelhantes foram encontrados por Sousa e Volkweiss (1987a) em solos da região Sul do Brasil e Bouldin e Sample (1959) em solos dos EUA.

Após a solubilização, a textura do solo afeta a distância de migração de P a partir da partícula do fertilizante (Sousa; Volkweiss, 1987a). De acordo com estes autores, para um Latossolo Vermelho com 79% de argila, esta distância de migração foi de 10 mm a partir do centro do grânulo, 5 mm menos que em um Argissolo com 25% de argila, considerando-se grânulos de SFT entre 2,00 e 2,38 mm. A partir destes resultados, pode-se estimar o volume de solo ocupado com P advindo da reação de SFT em cada tipo de solo. Levando-se em conta o número de grânulos necessários para uma adubação corretiva com 120 kg de P ha^{-1} e o volume ocupado por cada grânulo em cada tipo de solo, chega-se a um volume total de solo ocupado por P advindo da reação de SFT como 216 m^3 no solo argiloso e 730 m^3 no solo arenoso, o que representa cerca de 11% e 37% do volume de solo em um hectare na camada 0-20 cm, desde que não exista sobreposição de regiões de difusão de P. Para obtenção dos mesmos 216 m^3 ocupados por P no solo argiloso, seria necessária uma dose de apenas 35 kg P ha^{-1} no solo arenoso. Esta é parte da justificativa das menores doses de correção recomendadas em solos arenosos.

O efeito da textura do solo sobre o raio de migração de P, porém, é menos intenso do que o efeito do tamanho do grânulo de fertilizante (Sousa; Volkweiss, 1987a). Devido à concentração de P ao redor dos grânulos com maior diâmetro ser elevada e abastecida pela dissolução de FMC, a difusão para regiões mais afastadas é facilitada (Sousa; Volkweiss, 1987a). Por exemplo, após 121 dias de incorporação de grânulos de SFT entre 2,00 e 2,38 mm de diâmetro em um Argissolo com 25% de argila, a migração de P chegou a um raio de 15 mm para fora do grânulo a partir do centro da partícula de fertilizante enquanto que para grânulos entre 5,66 e 6,35 mm, o raio de migração chegou a 30 mm. É interessante considerar que para uma determinada dose de adubo fosfatado, a quantidade de grânulos aplicada depende diretamente de seu tamanho médio, uma vez que a densidade dos grânulos é a mesma independentemente de seu diâmetro. Logo, quanto maiores os grânulos, menor quantidade destes é aplicada por área para uma determinada dose. Mas até que ponto a maior migração de P a partir dos grânulos maiores compensa a menor quantidade de grânulos aplicados? De acordo com o cálculo do volume da esfera, um aumento x no raio de uma partícula de fertilizante ocasiona um aumento de x^3 em seu volume. Sendo a densidade constante, isto implica em uma redução cúbica na quantidade de grânulos para uma mesma dose, e o mesmo raciocínio vale para a variação do volume adubado em função do raio de migração de P a partir do centro de cada grânulo. Assim, desde que o aumento do diâmetro do grânulo de fertilizante (por exemplo, de 2,00 mm para 4,00 mm, ou 2x) seja igual ao aumento do raio de migração de P no solo (de 15 mm para 30 mm, ou 2x), a redução da quantidade de grânulos para uma mesma dose seria perfeitamente compensada pelo aumento do raio de migração, caso não haja sobreposição das esferas ocupadas com P em nenhum dos casos. Como no exemplo do solo com 25% de argila descrito acima foi necessário um aumento de mais de duas vezes do diâmetro do grânulo (de 2,00 mm para 5,66 mm, ou 2,83x) para que o raio de migração dobrasse (de 15 mm para 30 mm), a redução do número de grânulos aplicados seria o efeito mais significativo e ocasionaria uma redução do volume total corrigido com P. Para os outros solos estudados por Sousa e Volkweiss (1987a), com 79% e 19% de argila, este efeito de compensação também não parece perfeito, porém pode ser devido às dificuldades de avaliação inerentes a este tipo de estudo.

Na região de migração de P próxima ao grânulo, ocorre predominância de reações de precipitação, devido ao elevado teor deste nutriente na solução do solo, uma vez que a capacidade de adsorção do solo nesta região é inferior à capacidade de liberação de P pelo grânulo de fertilizante (Hedley; Mclaughlin, 2005). Esta alta concentração excede a constante de produto solubilidade de íons fosfato e determinados cátions comuns nos solos, ocasionando a precipitação de compostos de P. As reações específicas, contudo, dependem de algumas características principais da solução saturada de P na região próxima ao grânulo: concentração e especiação do íon fosfato, forma e concentração do cátion acompanhante e pH da solução (Hedley; Mclaughlin, 2005). O SFT caracteristicamente produz uma reação ácida intensa com a dissolução de FMC no solo (pH 1,0 a 1,5) (Lindsay; Frazier; Stephenson, 1962), com alta concentração de cátions de Ca. O baixo pH resultante provoca a dissolução de hidróxidos de Fe, Al e aluminosilicatos, dentre outros compostos (Lindsay; Frazier; Stephenson, 1962), ocasionando um aumento da concentração de Fe, Al, Mn, Si, Ca, Mg e K na solução saturada de P. Isto leva à precipitação de fosfatos de Fe e Al amorfos complexos de fórmula química (Fe, Al, X) $PO_4.nH_2O$, onde X representa um cátion que não Fe ou Al, e de FDCDH. As quantidades mobilizadas de Ca, Fe e Al na zona de precipitação, por mol de P adicionado como SFT, foram quantificadas como respectivamente 0,34 mol, 0,14 mol e 0,56 mol (Sousa; Volkweiss, 1987b). Acredita-se que a precipitação com Ca seja preferível, uma vez que pode proteger P de reações com os demais cátions para os quais os compostos formados apresentam maior estabilidade (Sousa et al., 2016). Contudo, formas cristalinas de fosfatos de Fe e Al como variscita e estrengita não foram identificados como produtos desta reação (Golden et al., 1991) e são improváveis de serem formados (Wang; Harris; Yuan, 1991).

Conforme discutido, as reações de precipitação podem ser mais ou menos intensas conforme a natureza da dissolução do grânulo no solo. Como a solução concentrada da reação de fosfato diamônio (DAP) ($(NH_4)_2HPO_4$) possui pH 8,0 (Lindsay; Frazier; Stephenson, 1962), o fosfato dissolvido pode atingir distâncias maiores em solos ácidos, ocasionando maior volume de solo adubado, uma vez que as reações de precipitação próximas ao grânulo são reduzidas em relação a uma partícula de SFT (Bouldin; Sample, 1959).

Se por um lado um solo ácido tende a dissolver fosfatos de cálcio, como pode-se observar na maior eficiência da adubação com fosfatos de rocha nestes solos em relação a solos calcários, o baixo pH do solo pode potencializar a reação ácida do fertilizante e a precipitação com cálcio na zona de reação do grânulo. Evidência disto foi encontrada em análise espectroscópica onde a maior presença de P associado a cálcio foi observada no solo mais ácido estudado (Beauchemin et al., 2003). Por outro lado, em solos calcários, mesmo fontes de reação menos ácida que SFT e que não contenham Ca, como fosfato monoamônio (MAP) ($NH_4H_2PO_4$, pH da solução saturada = 3,5), a insolubilização de P pode ocorrer, com formação de compostos de apatita e fosfato octacálcico ($Ca_8H_2(PO_4)_6.5H_2O$) (Lombi et al., 2006).

1.2.2 Reações de sorção de P no solo

As propriedades de adsorção e desorção de P pelo solo são frequentemente estudadas através das chamadas "curvas de sorção" (do inglês "sorption curves"), onde avalia-se a quantidade de P adsorvida em uma pequena amostra de solo (geralmente 1 g) após agitação em soluções contendo diferentes concentrações iniciais de P. Estas curvas são muitas vezes também denominadas "isotermas de adsorção", uma vez que a temperatura tem um importante papel na velocidade da interação de P com o solo (Barrow, 2015), sendo, portanto, necessária uma temperatura constante ao longo da realização do experimento. Os pontos da curva são função das diferentes concentrações finais de P na solução (c) e quantidade calculada de P proveniente da solução adsorvida na amostra de solo (S). Diferentes modelos não lineares podem então ser ajustados, sendo os mais utilizados os de Langmuir, Freundlich e Tempkin (Barrow, 2008). Similarmente, o estudo da dessorção pode ser feito através da agitação dos solos interagidos com as diferentes soluções de P com solução de $CaCl_2$ 0,01 M, porém não contendo P.

A maioria dos trabalhos recentes que estudam a dinâmica de adsorção e dessorção de P no solo ajustam a equação de Langmuir (Zhang et al., 2009; Fink et al., 2016a, 2016b; Yan et al., 2017), uma vez que se pode facilmente derivar índices relativos ao comportamento da adsorção como a capacidade máxima de adsorção (S_{max}), a energia de ligação de P com o solo (k) e a capacidade tampão máxima (*MBC – maximum buffering capacity*). A equação de Langmuir pode ser descrita como:

$$S = \frac{S_{max}kc}{1 + kc}$$

Onde: S indica a quantidade total de P sorvida (mg P kg^{-1} solo), S_{max} representa a capacidade máxima de adsorção de P (mg P kg^{-1} solo), k indica a energia de ligação de P com o solo (L mg^{-1}) e c a concentração final de P na solução (mg L^{-1}).

A quantidade total de P sorvida (S) consiste na quantidade adsorvida de P proveniente da solução (S') mais a quantidade inicial de P adsorvida (S_0), que pode ser determinada de acordo com Zhang et al. (2009), porém pode ser negligenciada se for muito pequena (Olsen; Watanabe, 1957).

Barrow (2008), contudo, questiona a adequação do modelo de Langmuir por principalmente dois motivos: o modelo não leva em consideração o efeito de alteração do potencial elétrico das superfícies dos coloides do solo pela adição de fosfato e também devido ao fato de que o modelo de Langmuir leva em conta reação com superfícies homogêneas, o que dificilmente seria o caso de solos. Segundo este autor, a equação de Freundlich pode ser derivada considerando-se que a reação ocorre com uma superfície heterogênea para a qual o log da constante de energia de ligação é reduzida à medida que a quantidade de P adsorvida ao solo aumenta. A equação de Freundlich pode ser descrita como abaixo:

$$S = ac^b + q$$

Onde: S indica a quantidade de P sorvida (mg P kg^{-1} solo), c representa o teor de P final na solução (mg P L^{-1}), b é um coeficiente adimensional; a representa a constante de energia de adsorção de Freundlich (mg P^{1-b} kg $solo^{-1}$ L^b), e q um parâmetro que representa o intercepto, especialmente importante em solos que contenham maiores quantidades de P. Este parâmetro q representa quanto P poderia ser dessorvido se a concentração deste nutriente na solução pudesse ser mantida em zero.

As limitações do modelo de Langmuir são especialmente importantes devido à observação de que o poder tampão de P no solo diminui à medida em que mais fosfato interage com a superfície dos coloides do solo, o que ocorre por dois motivos (Barrow, 2015). Inicialmente, em solos pobres em P com elevado teor de óxidos de ferro e alumínio, após atração eletrostática de fosfato, carregado negativamente, às superfícies das partículas do solo, ocorre penetração dos ânions fosfato para o interior destas partículas. Em segundo lugar, esta reação não ocorre indefinidamente, uma vez que a crescente carga negativa previne que mais fosfato seja absorvido ou mesmo adsorvido com elevada força de atração.

Um fato que se deve atentar ao ajustar o modelo de regressão escolhido é que as variáveis da curva de sorção (*c* e *S*) não são independentes, uma vez que a quantidade de P sorvida (*S*) é calculada a partir da diferença de concentração inicial e final (*c*) de P na solução. Isto contraria o princípio de independência das teorias de regressão. Embora trivial, dificilmente se vê um trabalho em que este problema é endereçado. Segundo Barrow (2008), este problema pode ser resolvido através da solução simultânea, para cada ponto da curva, de duas equações que determinam sorção: o modelo não linear escolhido (Freundlich, Langmuir ou Tempkin) e um modelo linear em função da relação solo:solução e da diferença inicial e final de P na solução.

Desde os primeiros trabalhos nesta linha de pesquisa, identificou-se que as curvas de sorção e dessorção frequentemente não seguem o mesmo percurso. Isto acontece pelo fato de que a reversibilidade do processo de adsorção é dificultada pela penetração difusiva de fosfato para dentro dos coloides do solo (Barrow, 2015). Este efeito é chamado de histerese, e é especialmente notável em solos com baixo *status* inicial de P e elevados teores de óxidos de Fe e Al de carga variável (Okajima; Kubota; Sakuma, 1983), ocasionando elevado poder tampão de sorção de fosfato. Através de um estudo recente em diferentes solos europeus com a técnica de gradiente de difusão em filme fino (*diffusive gradients in thin films* – DGT), não se observaram indicativos de que uma fração com liberação lenta de P possa existir no curto prazo, apenas de sítios de rápida dessorção (Santner et al., 2015), o que corrobora as observações acima.

A razão de histerese de um solo pode ser obtida através da divisão do índice de poder tampão de dessorção dividido pelo índice de poder tampão de adsorção (Barrow; Debnath, 2014). Estes índices, por sua vez, podem ser calculados pela multiplicação dos parâmetros *a* e *b* da equação de Freundlich descrita acima para as curvas de dessorção e sorção, respectivamente. Quando este índice é próximo de um, há baixo efeito de histerese, sendo, portanto, esperado dessorção de fosfato dos coloides do solo na mesma velocidade em que este foi previamente adsorvido. Este efeito ocorre em solos com mais elevados teores de P ou que receberam doses altas deste nutriente, pela saturação dos sítios de adsorção onde ocorreu penetração de P para dentro dos coloides (Barrow; Debnath, 2014; Barrow, 2015; Barrow; Barman; Debnath, 2018). Esta observação é visualizada facilmente em situações de campo e está incorporada nas recomendações de adubação corretiva de solos pobres em P. Sousa e Lobato (2004) recomendam inicialmente elevadas doses de P para correção de solos do Cerrado pobres em P, a fim de elevar os teores de P lábil nos solos. Esta adubação corretiva terá doses tanto mais altas de P quanto maior o teor de argila do solo, uma vez que este está intimamente relacionado à capacidade tampão do solo, especialmente de P. Uma vez estabelecido um teor adequado de P lábil para o cultivo das culturas, basta repor a exportação de P na forma de produtos colhidos com adubações de manutenção (Sousa; Lobato, 2004; Barrow; Debnath, 2014). Isto se dá pela eficiência gradualmente aumentada das aplicações sucessivas de P a um mesmo solo, onde a dessorção acontece mais facilmente (Barrow, 2015; Barrow; Barman; Debnath, 2018; Mumbach et al., 2020).

Os efeitos de práticas de manejo na capacidade de sorção de P no solo ainda são pouco estudados. A maior parte dos esforços da comunidade científica são relacionados a estudos das propriedades de substâncias purificadas como minerais de argila encontrados em solos, em alguns casos buscando replicar as condições de campo com a aplicação de compostos encontrados no campo, como ácidos fúlvicos e húmicos (Guppy et al., 2005; Antelo et al., 2007). Também existem diversos estudos que visam comparar as características da sorção de P em solos de diferentes características (Okajima; Kubota; Sakuma, 1983; Alovisi et al., 2020; Dunne et al., 2020). No entanto, poucos trabalhos têm focado no efeito do sistema de manejo do solo. Fink et al. (2016a) estudaram a sorção de P em amostras indeformadas de solo submetidas ao SPD e SPC, não obtendo diferenças na capacidade de adsorção, porém observaram uma maior capacidade de dessorção de P no sistema conservacionista, a qual foi creditada à menor energia de ligação de fosfato com as superfícies dos minerais devido à maior concentração de matéria orgânica no SPD. No entanto, ao contrário do que normalmente se observa, a adição de resíduos orgânicos a solos sujeitos a alagamento pode aumentar os teores de Fe e Al amorfos, causando aumento da capacidade de adsorção de P (Yan et al., 2017).

Parte dos efeitos do manejo do solo sobre a capacidade de adsorção de P pode ser relacionada a sua influência nas características e acúmulo de matéria orgânica. Muitos trabalhos atribuem uma reduzida capacidade de adsorção de fosfato aos coloides do solo quando ocorrem elevados teores de matéria orgânica no solo à competição entre radicais de ácidos orgânicos carregados negativamente e fosfato por cargas positivas dos coloides (Fink et al., 2016c). Contudo, trabalhos mais recentes tem creditado a maior disponibilidade de P em solos com elevados teores de matéria orgânica não tanto à reduzida capacidade de adsorção, mas principalmente ao aumento da capacidade de dessorção (Barrow; Feng; Yan, 2015; Guedes et al., 2016; Yang; Chen; Yang, 2019). Na adsorção de um ânion fosfato (inorgânico), a carga negativa deste íon é transferida para dentro dos coloides no processo de adsorção, causando uma redução da capacidade tampão de P do solo. Por outro lado, na adsorção de compostos fosfatados orgânicos, a carga negativa dos grupos fosfato é transferida para a parte externa do complexo molécula orgânica-partículas de solo, causando um menor efeito feedback de repulsão eletrostática. Assim, a adsorção de moléculas fosfatadas orgânicas apresenta uma menor capacidade de diminuir o poder tampão de P do solo em relação à adsorção de moléculas inorgânicas, pouco influenciando na eficiência de adubações fosfatadas posteriores (Barrow; Feng; Yan, 2015), porém facilitando a liberação e mineralização do composto orgânico contendo P. Estas observações ajudam a justificar trabalhos iniciais onde se constatou que a matéria orgânica atrasa mas não impede a adsorção de P no solo (Afif; Barrón; Torrent, 1995).

A mineralogia do solo também exerce um papel primário no comportamento da sorção de P. Roy et al. (2017) acreditam que décadas de fertilização com balanço positivo de P no sistema sejam necessárias para compensar a elevada capacidade de adsorção de P nos solos do Mato Grosso por eles estudados, devido ao elevado teor de argila, dominada principalmente por oxi-hidróxidos de Fe e Al. Óxidos de Fe, especialmente goetita, tem sido identificados como tendo grande influência no aumento da capacidade máxima de adsorção de P (Fink et al., 2016b), muito embora tem sido observada importância crescente dos argilominerais neste processo (Gérard, 2016; Fang et al., 2017; Antonangelo et al., 2020)

O efeito do pH na capacidade de sorção de fosfato no solo é um assunto muito controverso no meio científico. Tradicionalmente, acredita-se que a faixa ideal de disponibilidade de P situa-se em torno de pH 5,5 a 6,5, uma vez que abaixo destes valores ocorreria predominância da ligação de fosfato a óxidos e hidróxidos de Fe e Al carregados positivamente, e em valores mais elevados de pH ocorreria precipitação de P na forma de fosfatos de cálcio, reduzindo sua disponibilidade na forma aniônica que é a absorvida pelas plantas. Porém, o tema é complexo pois o pH influencia tanto na capacidade de adsorção como na de dessorção de P pelo solo, inclusive com intensidades diferentes e às vezes com efeitos opostos ao longo da faixa de pH encontrada no solo (Barrow, 2017; Barrow; Debnath; Sen, 2018), sendo impossível definir um comportamento generalista, ainda mais entre diferentes tipos de solo.

Schmitt et al. (2017) procuraram entender se as propriedades de adsorção do solo conseguidas a partir do estudo das curvas de adsorção, como S_{max} e *MBC*, estão relacionadas às frações em que se encontra o P adsorvido após a conclusão destes estudos. Para isto, os autores aplicaram o fracionamento sequencial clássico de Hedley (Hedley et al, 1982) aos resíduos de solo obtidos após sua agitação em soluções de P de diferentes concentrações, de acordo com a metodologia mais utilizada no estudo das propriedades de adsorção de P (Nair et al., 1984). Os autores observaram que a maior parte do P estava presente em frações de elevada labilidade de acordo com a metodologia de Hedley, mesmo em solos onde o poder tampão de P era calculado como elevado pelas isotermas de adsorção. Isto levou os autores a considerarem que os parâmetros de sorção poderiam superestimar a capacidade de retenção de P do solo. Isto, contudo, poderia ser explicado pela lenta absorção de P para o interior dos coloides do solo após adsorção específica superficial (Barrow, 1980).

Desde os primeiros estudos da química da sorção de P no solo, observou-se que uma parte das reações aconteciam rapidamente após a exposição dos coloides a fosfato e uma parte reagia mais lentamente. Isto pode ocorrer devido a presença de sítios de adsorção com propriedades distintas, levando a reações mais ou menos rápidas, ou devido a um efeito de cinética química em que a reação se tornasse mais lenta com o passar do tempo. Volkweiss (1973) chegou a identificar até três populações diferentes de sítios de adsorção em solos do Rio Grande do Sul através do ajuste de modelos de Langmuir com diferentes inclinações. Mais recentemente, contudo, acredita-se que o efeito de penetração de fosfato para o interior dos coloides promove um aumento do potencial negativo em seu interior conforme visto anteriormente (Barrow, 2015; Barrow; Barman; Debnath, 2018), levando a uma reação cada vez mais lenta e menos intensa de mais fosfato com este coloide, justificando a redução da inclinação da curva de adsorção observada por Volkweiss (1973).

1.3 ACÚMULO DE P NO SOLO

Devido à forte interação de P com solo vista nos tópicos acima, este nutriente apresenta uma elevada capacidade de se acumular nos solos agrícolas, proporcionando elevado efeito residual. Assim, o impacto do manejo de solo e adubação fosfatada nas frações de acúmulo ou de uso de P residual do solo tem sido de grande interesse da comunidade científica, onde usualmente aplica-se a metodologia original de Chang e Jackson (1958) ou o método modificado por Hedley et al. (1982). Resultados de mais de 100 trabalhos deste tipo foram sumarizados em um trabalho de revisão (Negassa; Leinweber, 2009).

Deve-se considerar, contudo, que a maior parte do P presente no solo se apresenta em um contínuo de disponibilidade, e não em frações discretas de diferentes graus de solubilidade (Barrow et al., 2020), com as exceções sendo constituídas pelas frações orgânicas e pelos compostos formados nas regiões de alta concentração de P, como próximo ao fertilizante, discutido acima. Apesar disso, o fracionamento sequencial pode dar indicativos categóricos da disponibilidade de P no solo. Por exemplo, em um Latossolo argiloso do Distrito Federal cultivado com adições anuais de P, os mais elevados incrementos aconteceram nas frações inorgânicas moderadamente lábeis (Nunes et al., 2020).

Um aspecto geralmente pouco observado que afeta o efeito residual do fertilizante é a granulometria das partículas, uma vez que esta característica física tem efeito imediato sobre a velocidade das reações de P no solo, influenciando sua eficiência de uso futura. Por exemplo, em comparação à utilização do fertilizante em pó, a granulação de SFT proporciona maior efeito residual quando o solo não é revolvido (Sousa; Volkweiss, 1987b). Isto porque a granulação é uma forma de localização do fertilizante, diminuindo a interação deste com o solo, o que possibilita maior efeito residual, desde que estas regiões ricas em P no entorno do grânulo não sejam destruídas pelo preparo mecânico do solo (Oliveira et al., 2019).

Apesar da distribuição química de labilidade de P no solo ser influenciada por diversos fatores, a distribuição espacial depende basicamente do manejo de solo e adubação, uma vez que por sua forte interação com o solo, este nutriente apresenta pouca mobilidade no perfil.

1.3.1 Distribuição espacial de P no solo em função de manejos de solo e adubação

Pela própria natureza do SPD, pela ausência de revolvimento do solo, e pela baixa mobilidade de P no perfil, ocorre acúmulo deste nutriente nas camadas superficiais, gerando forte gradiente de concentração em profundidade (Tiecher et al., 2017), principalmente no caso da adubação a lanço (Nunes et al., 2011; Tiecher et al., 2012; Tiecher; dos Santos; Calegari, 2012; Calegari et al., 2013). No SPC, além da redistribuição de P ao longo do perfil que ocorre com o preparo de solo, a redução da disponibilidade é intensificada nas camadas superficiais devido a interação com a fase sólida (Rheinheimer et al., 2019). A estratificação vertical (ao longo do perfil do solo) da distribuição de P pode variar não só com o sistema de preparo e o modo de aplicação mas também conforme a dose aplicada, com maior gradiente de disponibilidade em doses elevadas, devido aos elevados teores criados superficialmente em função da baixa mobilidade de P no perfil (Messiga et al., 2012; Li et al., 2019).

A princípio, este acúmulo de P nas camadas superficiais significa um menor volume de solo com níveis adequados de P que pode ser explorado pelas raízes. Este fato é principalmente importante em áreas novas em solos naturalmente pobres em P, quando não se tem teores corrigidos com este nutriente. Deste modo, o preparo convencional do solo nos primeiros anos para incorporação de P em profundidades é recomendável (Nunes, 2014).

Em muitos trabalhos, contudo, observa-se produtividades semelhantes nas adubações de manutenção feitas a lanço ou no sulco de plantio (Nkebiwe et al., 2016; Rosendo dos Santos et al., 2018; Preston; Ruiz Diaz; Mengel, 2019). Em uma meta-análise avaliando o efeito do modo de aplicação de diversos fertilizantes em 40 experimentos de campo, Nkebiwe et al. (2016) observaram uma tendência de semelhantes produtividade e biomassa média da parte aérea entre aplicações a lanço e localizadas. A observação de ineficiência da aplicação a lanço normalmente está relacionada a baixa disponibilidade inicial de P (Nunes, 2014), o que caracterizaria a necessidade de adubação de correção com incorporação (Sousa; Lobato, 2004).

Desta forma, pressupõe-se que, a despeito das desvantagens apresentadas, exista algum benefício na adubação a lanço para que a eficiência desta forma de aplicação possa ser tão alta quanto a localizada. Um possível efeito benéfico da localização restrita e superficial de P no solo é que sua maior concentração promova ocupação de maior quantidade de sítios de adsorção, de modo que a menor quantidade de sítios não ocupados seja um menor impeditivo à solubilização e difusão do P fracamente adsorvido ou precipitado para a solução do solo (Santner et al., 2015; Almeida et al., 2019).

A variabilidade horizontal da distribuição de P no solo também pode ocorrer principalmente devido ao modo de aplicação, com maior concentração na zona de aplicação (linha de plantio), especialmente quando o espaçamento entre-linhas é grande (Fernández; Schaefer, 2012), como comumente utilizado na cultura do algodão (76 cm). Este fato é tão significativo que metodologias de amostragem são desenvolvidas com o objetivo de levar esta variabilidade em consideração, procurando melhor ponderar a heterogeneidade espacial (Nicolodi; Anghinoni; Salet, 2002; Fernández; Schaefer, 2012). Quando o balanço entre entradas e saídas de P do sistema é reduzido (alta eficiência de uso de P), tal variabilidade é reduzida (Cambouris et al., 2017), porém se torna significativo quanto mais positivo o aporte de P.

Recentemente, um modelo de simulação foi desenvolvido objetivando descrever a dinâmica da distribuição espacial em duas dimensões de P lábil (concentração de íon ortofosfato em solução) em um solo manejado sob SPD, levando em consideração uma grande variedade de fatores que afetam esta movimentação, em especial parâmetros da cinética de sorção-desorção de P, biomassa e distribuição de raízes, balanço de P e deposição de resíduos na superfície (Li et al., 2019). Os autores conseguiram boa assertividade na previsão da distribuição vertical e horizontal de P no solo após 23 anos de manejo do solo quando levaram todos estes fatores em consideração, mais a incerteza da exata sobreposição das linhas de plantio ano após ano e a possibilidade de movimentação de P no perfil através da atividade de anelídeos.

2 HIPÓTESES E OBJETIVOS

2.1 OBJETIVO GERAL

O objetivo geral deste trabalho foi compreender os efeitos do manejo da adubação de correção e manutenção com fósforo na produtividade de grãos, distribuição espacial e propriedades de adsorção de fósforo no solo.

2.2 OBJETIVOS ESPECÍFICOS

a) Avaliar a eficiência da adubação fosfatada de correção em Latossolo com muito baixo teor inicial de fósforo e sua interação com a fonte fosfatada de manutenção e seu modo de aplicação.
b) Relacionar o manejo da adubação fosfatada de manutenção com a distribuição espacial de fósforo no solo e caracterizar seu comportamento ao longo do tempo.
c) Avaliar os efeitos da adubação fosfatada na capacidade de adsorção de fósforo no solo, em função das estratégias de adubação e tempo de cultivo.

2.3 HIPÓTESES

a) A correção de um solo com baixa disponibilidade inicial de fósforo eleva rapidamente a produtividade das culturas, especialmente com a fonte solúvel, sendo que o modo de aplicação e o tipo de fosfato aplicado na manutenção não afetam a produtividade.
b) A aplicação a lanço do fertilizante fosfatado de manutenção aumenta os teores de fósforo disponível nas camadas superficiais do solo, enquanto que na aplicação no sulco há maior diluição em camadas subsuperficiais, independentemente da fonte utilizada. A movimentação de fósforo no perfil do solo sob plantio direto é muito baixa.
c) O acúmulo de fósforo residual no solo reduz a capacidade de adsorção deste nutriente, especialmente nas zonas de aplicação do fertilizante, independentemente da fonte.

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CHAPTER I

LONG-TERM PHOSPHATE FERTILIZATION STRATEGIES EVALUATION IN A BRAZILIAN OXISOL

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4 CHAPTER 1. LONG-TERM PHOSPHATE FERTILIZATION STRATEGIES EVALUATION IN A BRAZILIAN OXISOL

4.1 ABSTRACT

There are concerns related to the application of phosphate fertilizers to weathered soils that present low soil test phosphorus (STP) due to P adsorption in iron oxyhydroxides. Furthermore, long-term trials are needed to evaluate crop response to corrective P fertilization and its interaction with different maintenance P fertilization strategies in these soils. An experiment involving the combination of three initial corrective P fertilization schemes (control without P correction or with the application of 105 kg P ha^{-1} as triple superphosphate- TSP, or reactive rock phosphate- RRP), four P maintenance strategies (a control without the application of maintenance P, or 35 kg P ha^{-1} year^{-1} as TSP, RRP or a mix of both) and two application methods was cultivated during 16 years at the Embrapa Cerrados experimental station in Planaltina, DF, Brazil. Corrective P fertilization promoted an early crop yield response. In contrast, high crop yields were only obtained in control treatments with no corrective P fertilization after soil P stocks were increased to a minimum level. With increasing P stocks, broadcast application resulted in slightly better yields. The required residual P stocks in soil to obtain high yields were estimated as equivalent to 113.6 kg P ha^{-1} and 205.2 kg P ha^{-1} for TSP and RRP, respectively. These values allow for STP contents to increase to critical levels, whose value for TSP of 4.1 mg kg^{-1} Mehlich-1 P is below that recommended for the region, possibly due to the contribution of organic P forms in the long-term no-tillage system.

Abbreviations list: NT, no-tillage system; RRP, reactive rock phosphate; R*tsp*, residual TSP; R*rrp*, residual RRP; RY, relative yield; STP, soil test P; TSP, triple superphosphate.

4.2 INTRODUCTION

Due to concerns related to the depletion of finite apatite reserves, the main raw material for production of phosphate fertilizers, much has been discussed about the use of residual phosphorus (P) (or legacy P) that accumulated in agricultural soils after decades of phosphate fertilization (Liu et al., 2014; Menezes-Blackburn et al., 2018). The build-up of legacy P occurs with the addition of larger amounts of P to the soil than the quantity exported in the harvested crop parts and some possibly lost in erosion processes.

This P accumulation occurs mainly in weathered and acidic soils, in which the real need to raise the initial P levels, together with the widespread belief that soil has an indefinite P adsorption capacity, leads to high P fertilization rates.

High P rates occur in developing countries that have intense agricultural exploitation, such as midwestern Brazilian (Roy et al., 2016) and East Asia (Lou et al., 2018). Therefore, in these places, and in developed countries, there are already great possibilities for exploiting residual P, which is highly valuable (Rowe et al., 2016; Menezes-Blackburn et al., 2018). On the other hand, in agricultural frontiers where STP is naturally low, different strategies to correct and maintain P levels in soil are adopted which can reduce the accumulation and use of residual P over the years. In addition, about 32% of the world's agricultural area and 43% of that under pasture still show deficient P levels (Lun et al., 2018), requiring corrective P fertilization to raise STP to critical levels, and thus allow for adequate crop growth.

Despite the need to address this question in soils such as Oxisols present in central Brazil, there is very little information on the subject in literature. Decades ago, some studies flirted with the idea of evaluating methods and application doses for P correction of Oxisols (Yost et al., 1979, 1981). However, there are few long-term evaluation trials which assess slow processes in soils, such as solubilization of poorly soluble fertilizers. Sousa and Lobato (2004) developed recommendation tables for corrective and maintenance P fertilization, which make up the current reference for the region, based on internal experiments at the Embrapa Cerrados experimental station.

Maintenance P fertilization management studies, including the evaluation of sources, doses and application methods have been widely explored, as well as the development of several methods for analyzing the availability and fractionation of soil P (Bray and Kurtz, 1945; Olsen et al., 1954; Hedley et al., 1982). However, there are few long-term studies that assess the impacts of different phosphate sources and application methods on crop responses under tropical conditions, in soils containing high levels of Fe and Al which have a high adsorption capacity (Fink et al., 2016a). Experiments of this type have already shown great value in other regions, as detailed in a review of long-term experiments at the Rothamsted experimental station, England (Johnston and Poulton, 2019).

Natural phosphates with medium solubility in citric acid, such as reactive rock phosphates (RRP), usually represent a small market-share although the P unit cost is less than that of soluble fertilizers. In addition, these sources present even greater residual effect in soil due to its slower solubilization (Silveira et al., 2018; Oliveira et al., 2019). On the other hand, highly soluble sources are able to rapidly release P to plants after dissolution in soil solution, but may have the adverse effect of prompting exposure of P to adsorption sites.

Broadcasting P fertilizers has been a growing practice in Brazil due to increases in operational efficiency in the field, which allows for the best timing at sowing. However, this practice has generated controversies regarding its efficiency due to the low mobility of P in soil. Short-term experiments usually support these controversies (Hansel et al., 2017b; Rosendo dos Santos et al., 2018; Lu et al., 2019), which contributes to further fuel the doubts of farmers. In long-term experiments, with adequate soil P levels and a well-established production system, results generally point to similar crop yields in both application methods (Nunes et al., 2011; Coelho et al., 2019; Preston et al., 2019). This variety of results is not surprising, since the efficiency of the P application method depends on many factors, such as the cultivation system, STP and phosphate source solubility (Nunes, 2014). Adding more complexity to the matter, there are still discussions related to the possibility of water course contamination (Dodd and Sharpley, 2015), reduced drought tolerance (Hansel et al., 2017a) and creation of a strong P availability gradient through the soil profile (Coelho et al., 2019) when P fertilizer is broadcast-applied. Thus, in the Cerrado region where the practice of broadcast spread P fertilization has been expanding, more long-term studies are needed to assess its viability.

One of the most important results encountered from long-term experiments at the Rothamsted station (England) is that P added to the soil is not irreversibly adsorbed (Johnston and Poulton, 2019) and can be recovered more than 100 years after its application. The P balance encountered in these different experiments and soil types can be highly correlated to Olsen P, indicating that it is possible to monitor total P status in soil via more practical STP methodologies. On the other hand, in Brazilian Oxisols there are doubts about the availability of residual P from fertilizers applied to low STP soils, since the total adsorption capacity remains high even after decades of fertilization (Roy et al., 2017).

This work sought to evaluate the effects of different soil P correction and maintenance fertilization strategies on the response of a soybean-corn rotation system, cultivated in an Oxisol in central Brazil managed under no-tillage system (NT).

4.3 MATERIALS AND METHODS

4.3.1 Characterization of the experimental area

The experiment was conducted in the experimental area of Embrapa Cerrados, in Planaltina, DF, Brazil (latitude 15º 36´S and longitude 47° 42´W). The climate is classified as Cwa according to the Köppen classification (Alvares et al., 2013), with annual precipitation and temperature means of 1570 mm and 21.3 °C, respectively. The elevation is 1014 m, with smooth undulating relief and the natural vegetation is that of Cerrado. Soil is characterized as a clayey Oxisol (Rhodic Haplustox) (USDA-NRCS, 2003), with 54% clay, whose mineralogical composition in the diagnostic horizon is dominated by kaolinite, gibbsite and hematite.

4.3.2 Experimental design and management

The experiment was installed in June 1999, where the effects of P sources and application methods were evaluated on a soybean-corn rotation system, with one main crop per year (during summer) followed by a cover crop in winter (millet). Before the first crop, three initial conditions of P in soil were defined: corrective P fertilization with TSP or RRP (both at the rate of 105 kg ha^{-1} of total P) and a control which had no P application (natural condition). From 1999 to 2014, maintenance P applications were conducted with 35 kg P ha^{-1} in each main crop as triple superphosphate (TSP), Gafsa reactive rock phosphate (RRP) or a mixture of both in equal P parts, plus controls without these maintenance applications. Maintenance phosphate fertilizers were evaluated under two application strategies: broadcast spreading of the fertilizer on the soil surface or band-applying it in the crop row furrow, about 5 cm below the seeds. Thus, the experimental design was a complete factorial (3x3x2 + controls) arranged in randomized blocks, with three replicates (Table 1).

RRP fertilizer particles were mostly between 0.5 and 2.8 mm in diameter and contained 12.3% total P, 44% of which was soluble in a 2% citric acid solution, considering a ground phosphate (<0.063 mm) to extraction solution of 1:100. TSP contained 20.8% total P, 92% of which was soluble in a 2% citric acid solution.

Table 1: Characterization of the experimental treatments at Embrapa Cerrados (Planaltina, DF, Brazil).

Treatment	Correction P source	Maintenance P source (35 kg P ha^{-1})	Application method	P applied (16 crops) (kg ha^{-1})*
1	-	-	-	0
2		TSP	Broadcast	560
3			Band-applied	560
4		RRP	Broadcast	560
5			Band-applied	560
6		TSP + RRP	Broadcast	560
7			Band-applied	560
8	105 kg P ha^{-1} as TSP	-	-	105
9		TSP	Broadcast	665
10			Band-applied	665
11		RRP	Broadcast	665
12			Band-applied	665
13		TSP + RRP	Broadcast	665
14			Band-applied	665
15	105 kg P ha^{-1} as RRP	-	-	105
16		TSP	Broadcast	665
17			Band-applied	665
18		RRP	Broadcast	665
19			Band-applied	665
20		TSP + RRP	Broadcast	665
21			Band-applied	665

*Not included total P applied as agricultural gypsum (9.7 kg P ha^{-1})

Before installing the experiment, samples were taken for soil analysis in 12 plots, 4 from each of the three blocks, with 20 subsamples per plot in the 0-20 cm layer (Table 2). Soil chemical deficiencies, except for P, were then interpreted and corrected for according to Sousa and Lobato (2004) with the application of dolomitic lime (65% RTNP) to raise cation exchange saturation to 50%, 75 kg ha^{-1} of K in the form of potassium chloride, 75 kg ha^{-1} of sulfur in the form of agricultural gypsum and 100 kg ha^{-1} of FTE BR-12 as a micronutrient source (Table 3).

The soil was plowed and harrowed to incorporate the fertilizers in the total experimental area to 20 cm deep at the end of 1998. Before planting the first crop in 1999, TSP and RRP (105 kg ha^{-1} of P) were applied to plots according to the treatments that would receive corrective P fertilization, then proceeding with another harrowing operation. After this last soil preparation, the experiment was then conducted under no-tillage (SPD).

Table 2: Chemical and texture characteristics of the soil prior to liming and fertilization of the experimental area in the 0-20 cm layer.

pH H_2O (1)	P (2)	K^+ (2)	Ca^{+2} (3)	Mg^{+2} (3)	Al^{+3} (3)	H + Al (4)	CEC
	mg kg^{-1}	----------------------------		cmol$_c$ kg^{-1}		--------------------------	
4.5	1.2	0.1	0.2	0.2	1.4	8.1	8.6

OM	V	Clay	Silt	Coarse sand	Fine sand
g kg^{-1}	----------------------------		%		----------------------------
2.8	5.6	54	5	12	29

1:2.5 soil solution ratio; (2) Mehlich-1; (3) KCl 1 mol L^{-1}; (4) calcium acetate 0,5 mol L^{-1} in pH 7.0; OM: organic matter by the Walkley-Black procedure; V: cation exchange saturation; CEC: cation exchange capacity

The annual maintenance dose of 35 kg of total P ha^{-1} was band-applied to the crop furrow or broadcast, depending on the treatments. The furrows were opened with a no-till planter to allow for manual application of fertilizers at about 5 cm deep. In treatments that received broadcast application, fertilizers were uniformly distributed by hand in the respective plots after planting all treatments.

Corn (*Zea mays*) was sown manually, using two seeds per position, to guarantee the germination of at least one plant. Plants were thinned when necessary to guarantee a plant population of 70,000 plants ha^{-1}. Soybeans (*Glycine max*) were sown using a portable machine, in order to establish 17 to 25 plants per meter, according to the variety used. For planting millet (*Pennisetum glaucum*), a traditional no-till planter was used, with a spacing of 0.20 m between rows, configured to distribute 20 kg seeds ha^{-1}.

As for maintenance fertilization with other nutrients, 67 kg K ha^{-1} were applied in the form of potassium chloride to every summer crop. To soybeans, cobalt and molybdenum were added as seed dressing. No application of N was necessary in the soybean crop due to inoculation of seeds with *Bradyrhizobium*. However, in corn 30 kg of N ha^{-1} were applied to the sowing furrow in addition to two top-dressing applications of 60 kg ha^{-1} each, always using urea as source. In order to amend the soil profile, 1 Mg ha^{-1} of agricultural gypsum (20% Ca; 15% S; 0.2% P) was applied annually between the fifth and seventh crops, totaling 3 Mg ha^{-1}, as indicated for soil correction up to 80 cm deep (Sousa and Lobato, 2004) (Table 3).

Agricultural gypsum reapplications for sulfur supply were as follows: 20 kg ha^{-1} of S in 2006 and 15 kg S ha^{-1} $year^{-1}$ from 2007 onward. Lime reapplications occurred in 2006 (975 kg ha^{-1} in order to reach 50% cation exchange saturation) and in 2014 (2158 kg ha^{-1}).

Table 3: Crop sequences and fertilizations in the experimental area.

	Season	Main crop	Cover crop	Lime¹	S (gypsum)	N (urea)	K (KCl)	Micronutrients (FTE BR-12)
						kg ha^{-1}		
1	1999/00	Soybeans	*Mucuna aterrimum*	3835	75	-	75+67	100
2	2000/01	Soybeans	Millet	-	-	-	67	-
3	2001/02	Soybeans	Millet	-	-	-	67	-
4	2002/03	Corn	Millet	-	-	30+60+60	67	-
5	2003/04	Soybeans	Millet	-	150	-	67	-
6	2004/05	Corn	Millet	-	150	30+60+60	67	-
7	2005/06	Soybeans	Millet	-	150	-	67	-
8	2006/07	Corn	Millet	975	20	30+60+60	67	-
9	2007/08	Soybeans	Millet	-	15	-	67	-
10	2008/09	Corn	Millet	-	15	30+60+60	67	-
11	2009/10	Soybeans	Millet	-	15	-	67	-
12	2010/11	Corn	Millet	-	15	30+60+60	67	-
13	2011/12	Soybeans	Millet	-	15	-	67	-
14	2012/13	Corn	Millet	-	15	30+60+60	67	-
15	2013/14	Soybeans	Millet	-	15	-	67	-
16	2014/15	Corn	Millet	2158	15	30+60+60	67	-

¹Equivalent in 100% total relative neutralizing power

The first three main crops were soybeans (1999/00, 2000/01 and 2001/02), followed by a rotation between corn and soybeans, always with millet as a winter cover crop, until the 16th and last crop (corn). Experimental plots measured 49.5 m² (11 x 4.5 m), and the inter-row distance was 0.45 m for soybeans, 0.70 m for corn and 0.20 m for millet. Supplementary sprinkler irrigation was performed when tensiometer readings installed at a depth of 20 cm in plots indicated a value greater than 45 kPa, aiming at maintaining the productive potential.

In order to better evaluate and discuss the effects of treatments, in some cases yields were calculated relative to the treatment most widely adopted by farmers in the Cerrado region, which is demonstrated in treatment 10 (Table 1): use of a soluble P source in corrective and maintenance fertilization, band-applying the fertilizer in maintenance applications. Therefore, crop yields for the different treatments were expressed as a percentage of the reference treatment.

4.3.3 Soil sampling and analysis

Soil samples were taken with a Dutch auger in the 0-20 cm layer. These samplings were carried out after harvesting the following crops: 2nd to 6th and 11th to 16th, in treatments fertilized exclusively with TSP or RRP. For plots with broadcast P fertilization, 20 sub-samples were taken randomly in the plot to make up the composite sample. For plots with band-applied P fertilizer, sampling was performed according to Nicolodi et al. (2002). This method involves sampling from 7 points across a crop row:

one right over the row, and 3 equally spaced to each side, to the center of the corn inter-row. Soil from each of the 7 positions in a given layer was then mixed to form one sub-sample per layer. This procedure was repeated in 3 crop rows to form 3 sub-samples per plot, which were mixed to form the plot composite sample. This methodology was adopted because it better considers the localized effects of band-applying P fertilizers.

STP was determined using a Mehlich-1 (0.05 M HCl + 0.0125 M H_2SO_4) and Bray-1 (HCl 0.025 M + NH_4F 0.03 M) (Bray and Kurtz, 1945) solutions, and the content was assessed by colorimetric analysis (Murphy and Riley, 1962).

4.3.4 Residual P stocks

The amounts of P applied to the soil before the first harvest can be separated into four groups: the control without any application of P (treatment 1); those without initial P correction but with annual maintenance inputs according to the different sources and modes of application, characterizing a gradual corrective fertilization (treatments 2 to 7); the controls with application of corrective fertilization using TSP or RRP, but without maintenance fertilization (treatments 8 and 15, respectively); and finally treatments with both corrective and maintenance fertilization (treatments 9 to 14 and 16 to 21, or treatments under total corrective fertilization). Thus, before the first crop 0, 35, 105 and 140 kg P ha^{-1}, respectively, were applied to these treatment sets (Table 1).

After the second crop harvest onwards, the residual P stocks in soil before each new crop were calculated from the difference between all P inputs via fertilizers or soil conditioners and export by the harvested grains up to that moment (P input-output budget). For this, the P content in the grains was evaluated by wet digestion with HNO_3 + $HClO_4$ (3:1, v:v) (Embrapa, 1999), and then multiplied by the grain yield to obtain the equivalent total of exported P per ha in the grains.

4.3.5 Statistical analysis

Data was subjected to analysis of variance (ANOVA) considering the fixed effects model and in case of significant differences, the means were compared using the Tukey test (P <0.05). Controls for each soil correction conditions were treated as additional treatments.

The following model was considered for the complete factorial (without control):

$Y_{ijkl} = \mu + B_l + C_i + M_j + A_k + CM_{ij} + CA_{ik} + MA_{jk} + CMA_{ijk} + \varepsilon_{ijkl}$, where μ = general average, B = block (l = 1, 2, 3), C = soil correction (j = 1, 2, 3), M = maintenance source (j = 1, 2, 3), A = mode of application (k = 1,2), ε = experimental error.

Assumptions of homoscedasticity and normality of the residues were verified by the Levene and Shapiro-Wilk tests, respectively. An ANOVA was also made in order to evaluate the yield development of soybeans and corn crops through the growing seasons, considering repeated measurements (Vivaldi, 1999). Regression analyzes were also performed between the relative yield and residual P stock present in the soil, adjusted to the Mitscherlich model via the "nls" function of the statistical package R version 3.5.2 (R Core Team, 2018).

In order to verify the statistical equality of these models for each cultivated crop, within each P source used and vice versa, the model identity analysis was performed (Regazzi and Silva, 2010). Four Mitscherlich nonlinear models were generated resulting from the relationship between residual in the soil (x) and relative productivity (y), given by:

$$y_i=\beta_1-\beta_2.e^{(\beta_3.x_i)}+\varepsilon_i$$

Where:

y_i: corresponds to the i-th value of the response variable, i = 1, 2, ..., N observations;

x_i: corresponds to the i-th value of the explanatory variable, i = 1, 2, ..., N observations;

β_k: corresponds to the parameter of the non-linear model, k = 1, 2, 3.

ε_i: corresponds to random errors.

The model identity analysis was used to verify the possibility of creating a unique model for each phosphate source, which involved the two different crops grown in the experiment (soybeans and corn). Similarly, the possibility of creating a model for each crop, involving the two P sources was also tested. Through the likelihood ratio test with approximation by the F statistic (Regazzi and Silva, 2010), it was determined if the parameters β_k are the same for each set of observations under comparison.

The regressions between the Mehlich-1 P and residual P in soil were adjusted to the Freundlich model using the "freundlichanalysis" command of the "PUPAIM" package present in the R statistical software version 3.5.2 (R Core Team, 2018). Regression between Bray-1 P and residual P was adjusted to the linear model through the “lm” command. All other statistical analyses mentioned above were also carried out in the R software.

4.4 RESULTS

4.4.1 Annual and total grain yield

Figure 1 shows crop yields obtained over the 16 experimental years, indicating a high yield potential, compatible with high technology systems. In the last soybean (15th) and corn (16th) crops, for example, the average yield of treatments that received maintenance fertilizer was 4.0 and 13.4 Mg of grain ha^{-1}, respectively. There is also growing crop yield potential over the years. In addition, there is a large initial dispersion of different treatment effects, which is reduced, but not eliminated, in later seasons of the experiment. For example, in the first harvest treatments that received correction fertilization produced on average 180% more grains than those that did not receive this initial P input, while in the last harvest this difference was reduced to 9%. Similarly, treatments that received maintenance fertilizer with TSP produced 29% more than those with RRP maintenance in the first harvest, an advantage that was reduced to 6.5% in the last crop.

The significance of the main effects and interactions of treatments on grain yield was summarized in Table 4. There is a consistent positive effect of soil correction, which lasted throughout the entire duration of the experiment, with the exception of the 15th crop (soybeans). The maintenance source also had effects on almost all crops, and many interacted with the correction factor. On the other hand, the P fertilizer application method was not significant in every season, but it did have a significant effect on the accumulated total yield.

Table 4: Analysis of variance of the different variation sources in the yield of the 16 crops. C: P correction source; M: P maintenance source; A: application method.

ANOVA	1999/00	2000/01	2001/02	2002/03	2003/04	2004/05	2005/06	2006/07	2007/08	2008/09	2009/10	2010/11	2011/12	2012/13	2013/14	2014/15
Factors	**1 (Soybeans)**	**2 (Soybeans)**	**3 (Soybeans)**	**4 (Corn)**	**5 (Soybeans)**	**6 (Corn)**	**7 (Soybeans)**	**8 (Corn)**	**9 (Soybeans)**	**10 (Corn)**	**11 (Soybeans)**	**12 (Corn)**	**13 (Soybeans)**	**14 (Corn)**	**15 (Soybeans)**	**16 (Corn)**
C	****	****	****	****	****	****	***	****	*	****	**	****	*	*	ns	**
M	****	****	****	****	**	****	****	****	****	****	**	**	ns	ns	ns	*
A	****	ns	*	ns	****	ns	ns	**	ns	ns	**	***	ns	*	ns	**
C x M	****	****	**	*	**	ns	ns	**	***	*	ns	ns	ns	*	ns	ns
C x A	ns	*	ns	ns	ns	ns	ns	ns	*	ns	*	ns	ns	ns	ns	**
M x A	ns	ns	ns	ns	ns	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	**
C x M x A	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns

	Phase 1	Phase 2	Phase 3	Phase 4	Total	Soybeans total	Corn total
C	****	****	****	****	****	****	****
M	****	****	****	ns	****	****	****
A	ns	ns	**	****	**	*	*
C x M	****	*	**	*	****	****	***
C x A	ns	ns	ns	ns	ns	ns	ns
M x A	ns	ns	ns	ns	ns	ns	ns
C x M x A	ns	ns	ns	ns	ns	ns	ns

ns: not significant; * $0.05>P>0.01$; ** $0.01>P>0.001$; *** $0.001>P>0.0001$; **** $P<0.0001$

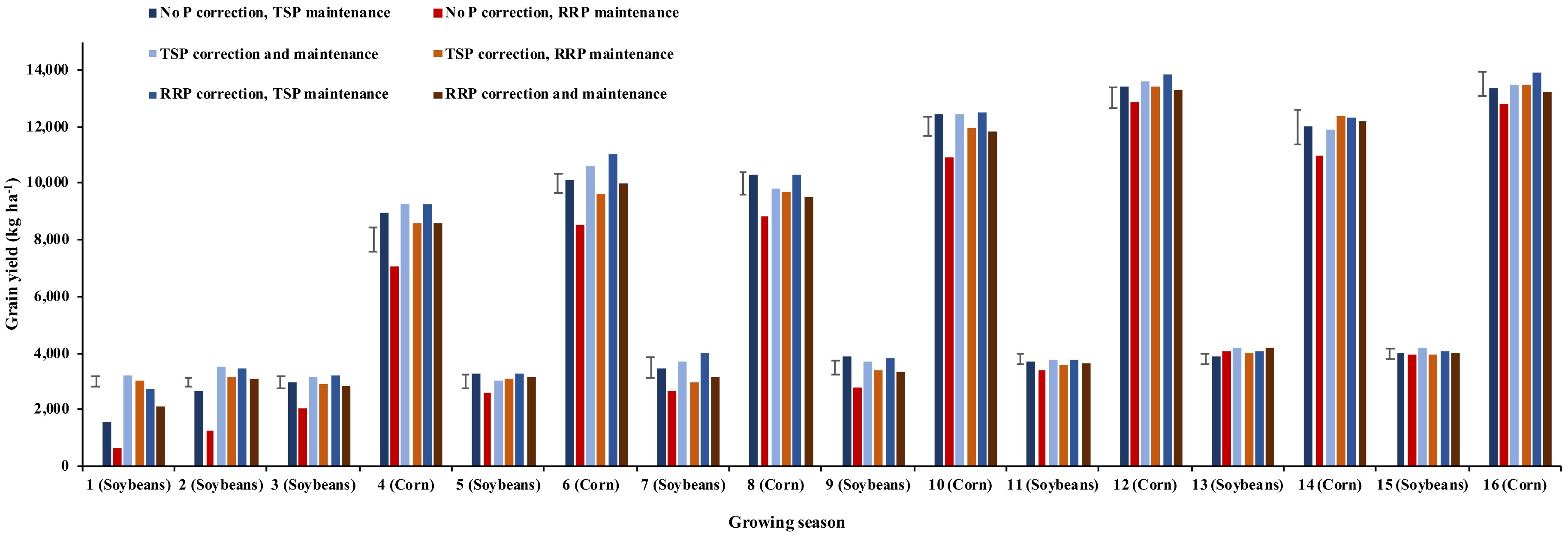

Figure 1: Annual soybean and corn yield in the 16 experiment growing seasons, started in 1999, in a clayey Oxisol with very low initial STP, in different soil correction and phosphate maintenance fertilization strategies. Values represent the means of the two application methods and three replicates (n = 6). Bars represent the HSD at 5% probability according to Tukey's test. Yields for the control treatment with no P fertilization (treatment 1) varied between 182.3 kg ha^{-1} and 392.2 kg ha^{-1} for soybeans and between 52.5 kg ha^{-1} and 1205.5 kg ha^{-1} for corn.

Table 5 shows the total relative accumulated yields at the end of the experiment. There was a significant effect of correction fertilization compared with the control, either with TSP or RRP, and there was no difference between the two sources for all maintenance conditions. The main difference observed between soil P correction strategies was in the control treatments, i.e., without annual P maintenance fertilization. In this case, a single corrective fertilization at the beginning of the experiment with 105 kg ha^{-1} of P allowed for production of about 27. 7% of the total produced in the reference treatment (correction and maintenance with TSP, with total production of 113,606.3 kg grains ha^{-1}), while no application of any P source limited the productivity to 5.6% of the total observed in the reference treatment. In relation to phosphate maintenance, the application of TSP resulted in higher crop yields compared to the sparingly soluble source (RRP), regardless of the correction condition ($P < 0.05$). Total yield with annual applications of TSP was especially higher when compared to the use of RRP when there was no corrective fertilization. In this case, 13% more grains were produced, whereas in the case of corrective phosphate fertilization, this difference was reduced to an average of 5.1% (Table 5). Use of the TSP and RRP mixture in equal P proportions generally showed an intermediate behavior between the results observed when these sources were applied separately. Therefore, this treatment was omitted from the subsequent figures, but always considered in the analysis of variance.

Table 5: Total yields after the 16 crops cultivated in the experiment, relative to the mean of treatments under correction and maintenance fertilization with TSP (100% = 113,606 kg ha^{-1}). Values represent the mean of the different application methods and replicates (n = 6), except for controls without application of maintenance P (n = 3, number of replicates).

		P correction					
		Control		TSP		RRP	
		------------------ *Relative yield (%)*---------------------					
P maintenance	Control	5.6	Bd	27.0	Ac	28.4	Ad
	TSP	97.0	Ba	100.0	Aa	101.9	Aa
	RRP	84.0	Bc	96.3	Ab	95.4	Ac
	TSP + RRP	92.4	Bb	99.2	Aa	98.1	Ab

Capital letters compare different soil correction strategies (treatments in the same row) and lower case letters compare those in the same column (maintenance sources) according to Tukey's test ($P < 0.05$).

Figure 2 shows time trends for the yield of soybeans (a) and corn (b) in different treatments subjected or not to maintenance P applications. Where P was applied as corrective fertilization in the beginning of the trial and no maintenance was made, crop yields dropped severely. This drop was more intense in the case of TSP correction in the soybeans crop.

Control treatment with no P application retained very low crop yields throughout the experiment. Treatments that received maintenance fertilization but not the initial dose of P showed the highest yield improvement, especially in the soybeans crop. By the end of the experiment, though, all treatments subjected to the annual P dose reached similar yields.

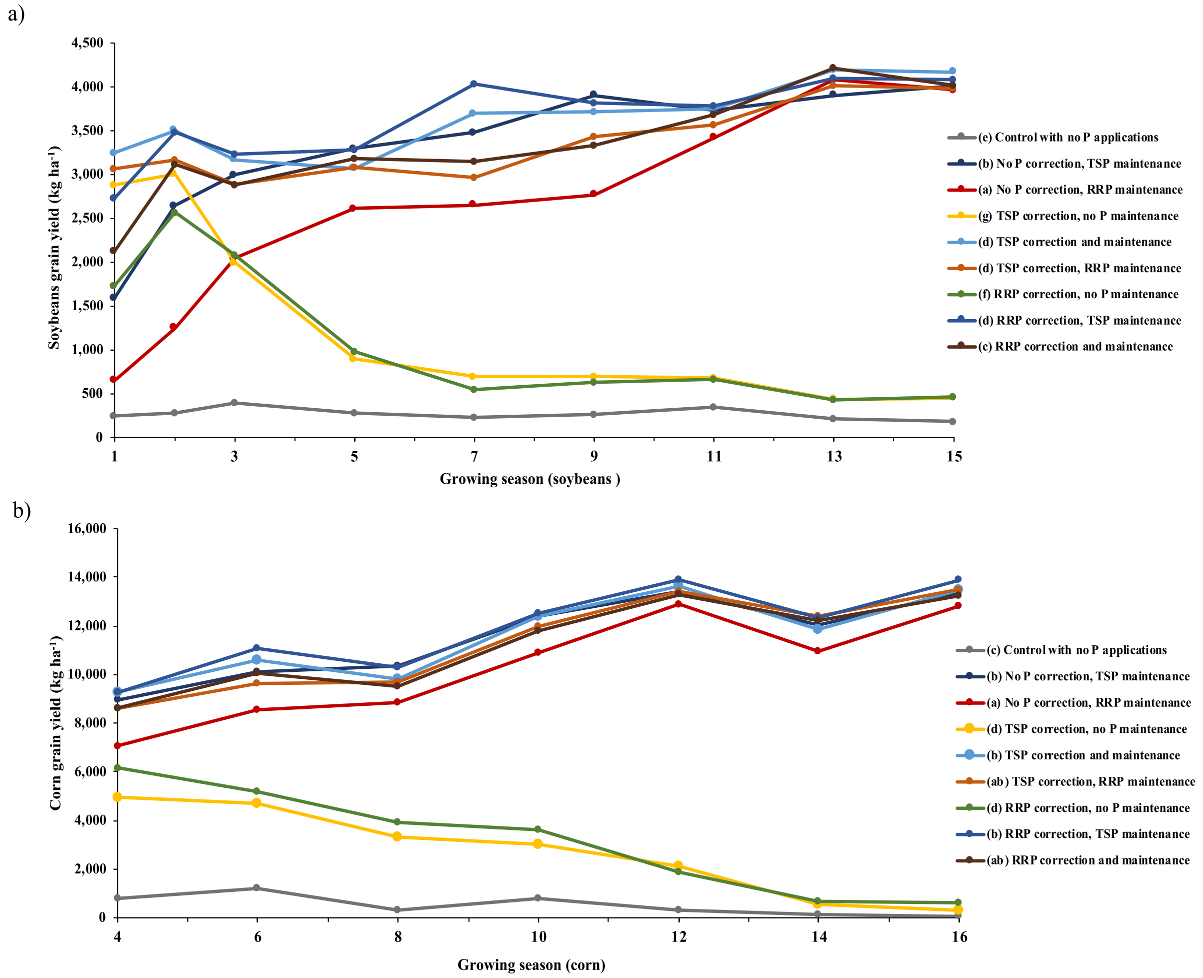

Figure 2: Soybeans (a) and corn (b) crop yields evolution through the growing seasons. Letters in parenthesis compare different time trends in yield development according to Tukey's test ($P<0.05$). Values represent the mean of the different application methods and replicates ($n = 6$), except for controls without application of maintenance P ($n = 3$, number of replicates).

4.4.2 Correction and maintenance P effects in different cultivation phases

Effects of the treatments on crop yields varied over the growing seasons. Thus, to facilitate the comprehension of these effects, the average relative yield of crops was grouped in 4-year phases. The reference treatment was that most similar to what is practiced by farmers in the region: corrective fertilization and maintenance with TSP, band-applying the maintenance fertilizer in the sowing furrow. Phase 1 is then composed of three soybean crops and only one corn crop, and phases 2 to 4 are composed of two growing seasons for each crop. Figure 3 explores the relative yields per phase for each crop.

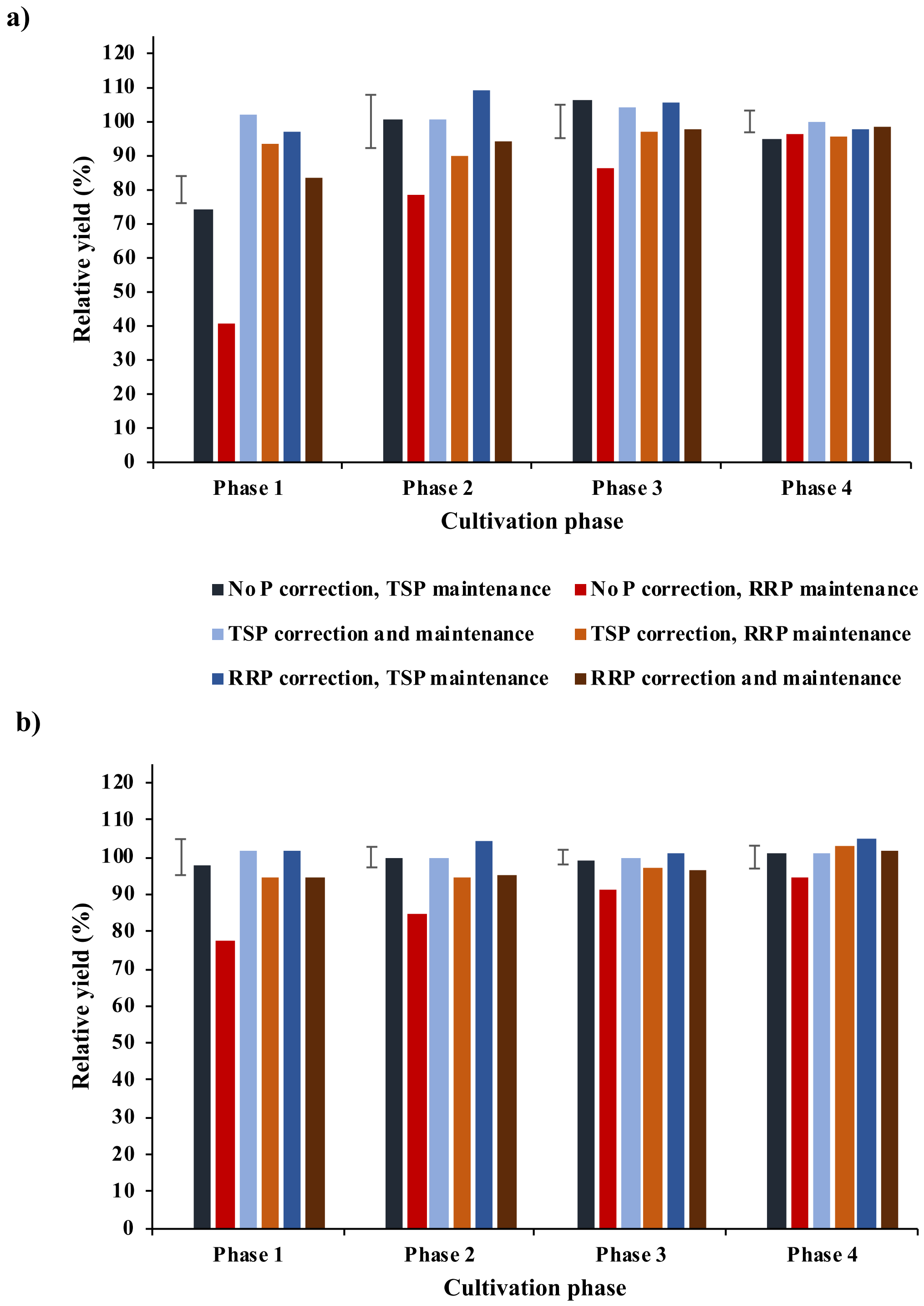

Figure 3: Relative yield of soybeans (a) and corn (b) in 16 consecutive years of cultivation, initiated in 1999, grouped by stages of cultivation (Phase 1: crops 1 to 4, Phase 2: crops 5 to 8; Phase 3: crops 9 to 12; Phase 4: crops 13 to 16). Values are relative to the treatment with correction and maintenance fertilization with band-applied TSP and represent the means of the two modes of application and three replicates (n = 6). Bars represent HSD at 5% probability according to Tukey's test.

In the soybean crop (Figure 3 a), the effect of soil correction with P was markedly noticed in the first analyzed phase, since this was the crop grown in the first three of the four years. In this phase, lack of a correction application with 105 kg of P ha^{-1} severely restricted plant growth, especially when the maintenance source used was RRP. In this case, yields were only 41% of that observed in the reference treatment, while in treatments with TSP application this value rose to 74%. In the other two correction conditions, the advantage of the soluble source used in maintenance, although less pronounced, was also significant. Comparing the two P sources in soil correction, there was no difference between them when using TSP for maintenance. On the other hand, when maintenance was performed with the sparingly soluble source, corrective fertilization with TSP produced 12.2% more grains than with RRP.

The second phase in the soybean crop was characterized by main correction effects, with treatments without corrective fertilization producing an average of 11.1% less than those with application of TSP or RRP, with no significant difference between the two sources. As a source of P for maintenance fertilization, TSP promoted higher yields than RRP ($P < 0.05$), with an average advantage of 536 kg ha^{-1} per crop or 18.3%. In the third phase, the absence of corrective fertilization was only significant when maintenance was performed with RRP. As for the source of P in maintenance, yields were similar between TSP and RRP when correction was made with the soluble source. However, when soil was not previously corrected or when it was corrected with RRP, maintenance fertilization with TSP provided greater yields. In the fourth phase, for soybeans, there was no significant difference between the different correction or maintenance strategies adopted in this study.

The effects of the treatments on corn yield were similar to those observed in soybeans (Figure 3 b). Crop production with RRP correction when maintenance was performed with TSP in the second phase was markedly greater (average of 464 kg ha^{-1} more per crop in relation to the TSP correction) and greater yields in the corrected treatments were observed until the third phase in all maintenance conditions. Also observed were lower yields when using RRP for maintenance in non-corrected soil in the last phase.

In general, maintenance with TSP, even in treatments with corrective fertilization, provided better crop responses than RRP up until the third cultivation phase. In the fourth phase, there was little influence of phosphate fertilization strategies on the soybean or corn yield response.

4.4.3 Effects of the application method

Band-applying P fertilizer significantly increased crop yields in the first (soybean) and eighth (corn) crops, respectively, by 10.4 and 4.3% when compared to broadcasting. In the ninth crop (soybeans), the advantage of band-application was revealed only when maintenance was done with RRP (8.4% more) (data not shown). In all other crops, broadcast fertilization proved to be as or more productive than the application of phosphate fertilizer in the planting furrow. When a longer evaluation period is considered, with grouping in growing phases, similar yields are observed between both methods of application in the two initial phases, while in the two final stages the best crop response was found under broadcast application (Figure 4). In the total accumulated production, broadcast application promoted 1.64% higher yields on average, a small but significant advantage.

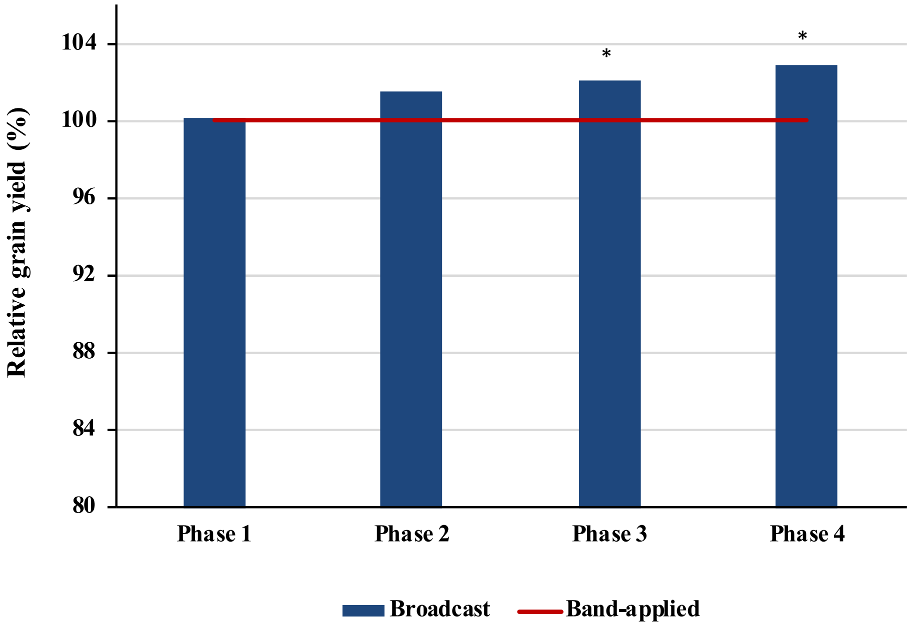

Figure 4: Average relative yield of broadcast P fertilizer application treatments in the 4 cultivation phases of the experiment, regardless of the form of soil correction and maintenance source (n = 27). Values relative to the average of treatments with band-applied fertilizer (100%). * Significant according to Tukey's test (P <0.05).

4.4.4 Residual P stocks

Due to the different amounts of P exported in the grains and that added or not as maintenance fertilization, a large variation in the residual P stocks in soil was created throughout the growing seasons (Figure 5). P stocks depletion was observed in the control treatments that received only the application of the initial corrective fertilization, due to the exportation of P in harvested grains and no annual replacement via maintenance fertilization. In treatments in which only maintenance fertilizer was applied, a gradual increase in soil P stocks can be observed, characterizing a gradual correction of P contents (Figure 5). Residual P values in these treatments approached those observed where soil was initially corrected and maintained with annual fertilization (treatments under total corrective fertilization). As a result, there was also an approximation in yields obtained in these two treatment groups (Figures 2 and 3).

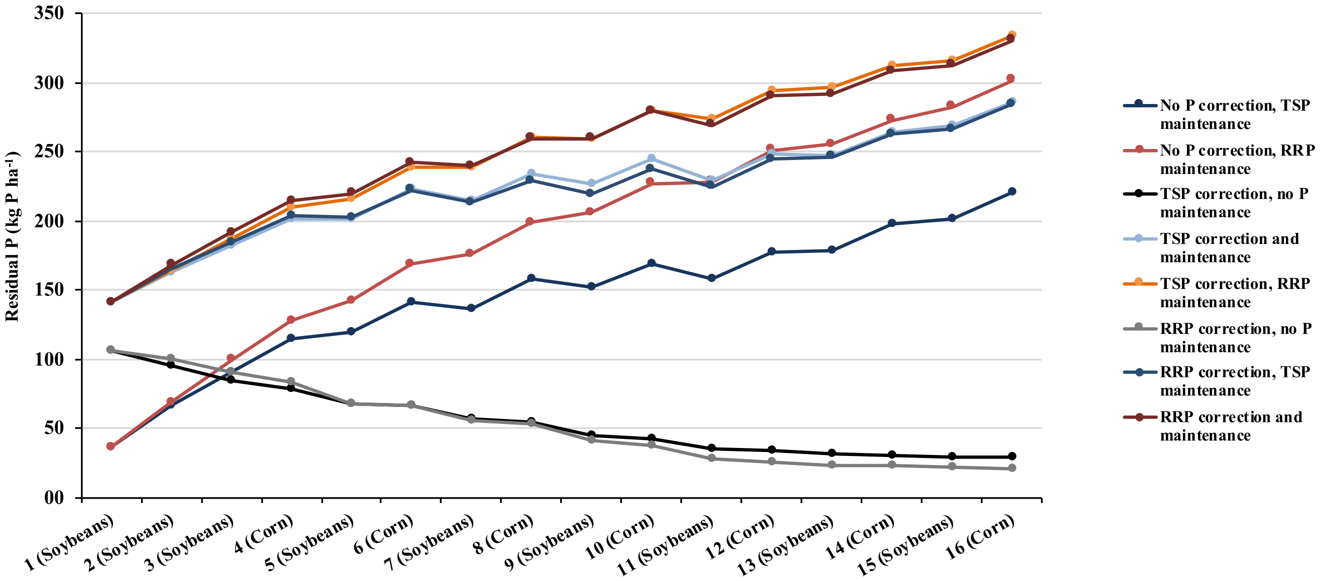

Figure 5: Residual fertilizer P in soil (kg P ha^{-1}) before each of the 16 cropping seasons, started in 1999. Values represent application method means for treatments with maintenance fertilization (n = 6) and replicate means for treatments without maintenance fertilization (controls, n = 3).

Due to the often-higher yields in treatments with maintenance fertilizer in the form of TSP (Figure 1), greater P offtake via the grains gradually resulted in reduced P accumulation in these treatments when compared to RRP. At the end of the 16 crops, total P stocks in soil of treatments maintained with RRP, regardless of the P correction and maintenance strategies, was on average 28.2% higher.

4.4.5 Critical residual and labile P levels

The P input-output balance in soil of the treatments fertilized exclusively with TSP or RRP, calculated from the difference between fertilizer inputs and P export in the grains during the 16 years of experimentation, allowed for establishment of critical residual P levels in soil based on its relationship with crop yield and STP (Figures 6 and 7).

Figure 6 shows regression models between residual P in soil and the relative yield of soybean and corn crops for each P source. In order to obtain 90% of the reference treatment yield, it was necessary to have 107.7 kg of residual P ha^{-1} in soil for the cultivation of soybeans and 126.6 kg of P ha^{-1} for the cultivation of corn, when the source used was TSP. The statistical comparison of these models showed that there is no difference between the response of soybeans and corn to the residual P in soil (P = 0.1611). Thus, these values are close to that recommended by Sousa and Lobato (2004) for corrective P fertilization according to the clay content and initial Mehlich-1 P found in the studied soil (130 kg of P ha^{-1}), valid for annual grain crops.

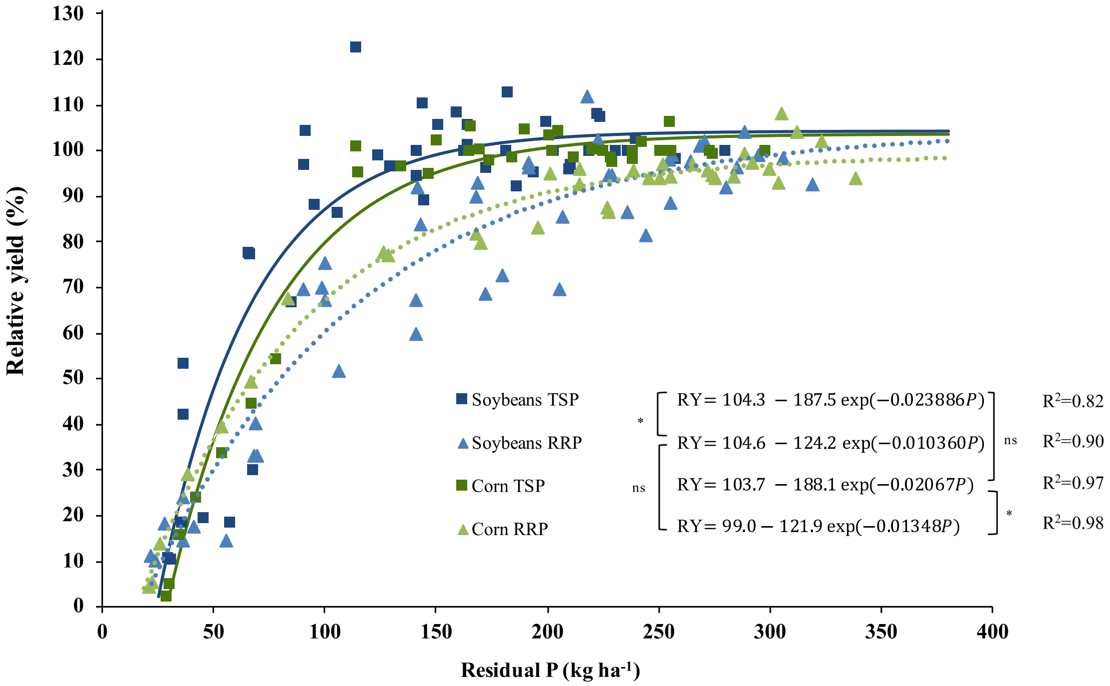

Figure 6: Relative yield as a function of the residual fertilizer P stock ha^{-1} present in the soil. Values are calculated as a percentage of the reference treatment yield (treatment 10, correction fertilization with TSP and maintenance with band-applied TSP). Data for treatments fertilized exclusively with TSP (treatments 2, 3, 8, 9 and 10) or RRP (4, 5, 15, 18 and 19). *P*: residual P in soil (kg ha^{-1}); *RY*: relative yield. All model coefficients were significant at 0.1% by the t-test, n = 45 for soybeans and n = 35 for corn. *: models differ statistically according to the F-test at 5% probability; ns: models do not differ according to the F-test at 5% probability.

When RRP was used there was a need for higher residual P doses in soil in relation to what was necessary with TSP in order to obtain 90% of the relative yield. This fact was significant for both soybean (P <0.001) and corn crops (P <0.001). These values were 206.9

and 193.2 kg P ha^{-1} for soybeans and corn, respectively. Comparing both crop responses when using the sparingly soluble source (RRP), there was no difference between the models (P = 0.3413).

By adopting a single model involving the two crops, a critical value of 113.6 kg of P ha^{-1} was found for residual TSP. For this residual value in soil, the critical Mehlich-1P level was 4.1 mg kg^{-1} (Figure 7a). This value is lower than that proposed by Sousa and Lobato (2004) to obtain 90% of the yield potential. For RRP, the residual critical value of P in the soil was 205.2 kg ha^{-1}, which provides 20.4 mg kg^{-1} of Mehlich-1 P (Figure 7a).

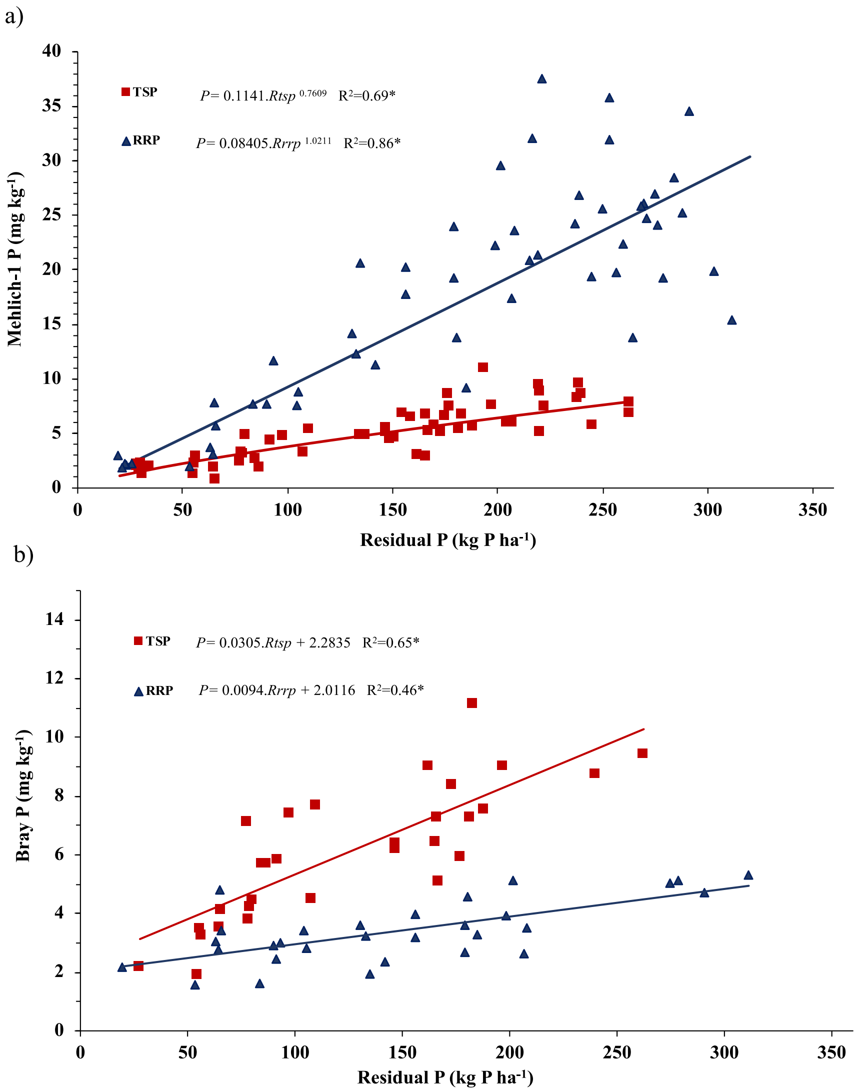

Figure 7: Mehlich-1 (a) and Bray-1 (b) labile P in the 0-20 cm layer according to the soil residual P stock. Data from sampling performed after the 2nd to 6th and 11th to 16th crop harvests in treatments fertilized exclusively with TSP (2, 3, 8, 9 and 10) or RRP (4, 5, 15, 18 and 19). R*tsp*: residual TSP (kg P ha^{-1}); R*rrp*: residual RRP (kg P ha^{-1}); P: labile P (mg kg^{-1}). * Significant at 0.1% according to the F-test, n = 55 for Mehlich-1 and n = 35 for Bray-1.

For the critical values of 113.6 kg P ha^{-1} in soil for residual TSP and 205.2 kg P ha^{-1} for RRP, expected Bray-1 P levels are 5.7 and 3.9 mg kg^{-1}, respectively (Figure 7b).

From the models that relate the residual contents of RRP and TSP in soil and their respective relative yields (Figure 6), considering the means of the two crops for each source, it was possible to establish an equivalence ratio between the two sources to obtain the same relative yield (Figure 8). Data indicates the need to apply higher P rates when using RRP in relation to application of TSP in order to obtain the same yields.

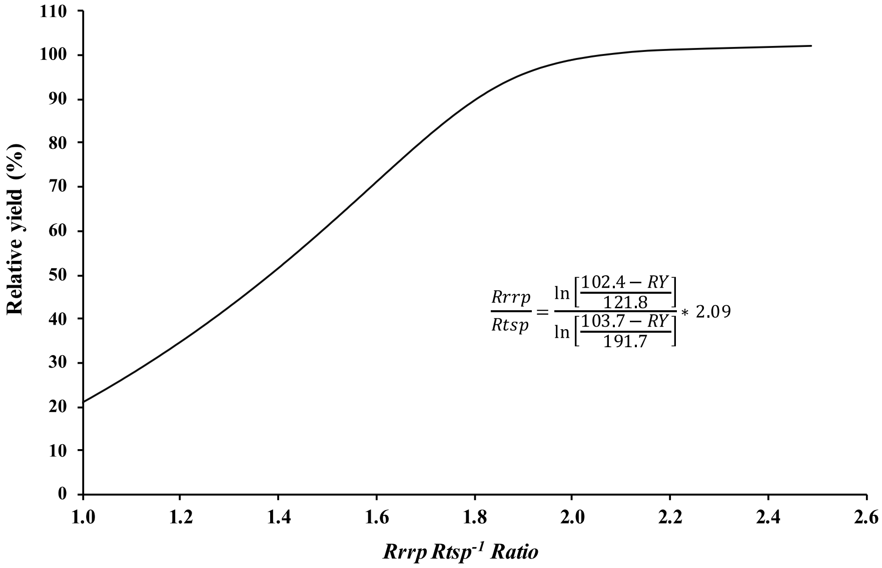

Figure 8: Relationship between the ratio of residual P stocks from TSP and RRP in the soil and relative yield (reference: correction and maintenance with band-applied TSP). R*rrp*: residual RRP (kg P ha^{-1}); R*tsp*: residual TSP (kg P ha^{-1}); *RY*: relative yield.

4.4.6 P Recovery

P recovery, calculated as the ratio between P offtake in the grains and all P inputs in the system (via fertilizers and conditioners) at the end of the experiment is shown in Figure 9. The highest values are observed for the control treatments where correction fertilization was applied, but no maintenance fertilization was made. It was possible to recover 75.8% and 83.1% of P applied in treatments with correction in the form of TSP and RRP, respectively.

Due to the higher total grain yield observed with broadcast fertilization, P recovery with this application method was also higher in relation to banding (6.2% more). As for the maintenance source, application of TSP allowed for the recovery of 18.7% more P on average than the application of RRP. Soil P correction, on the other hand, did not influence P recovery efficiency.

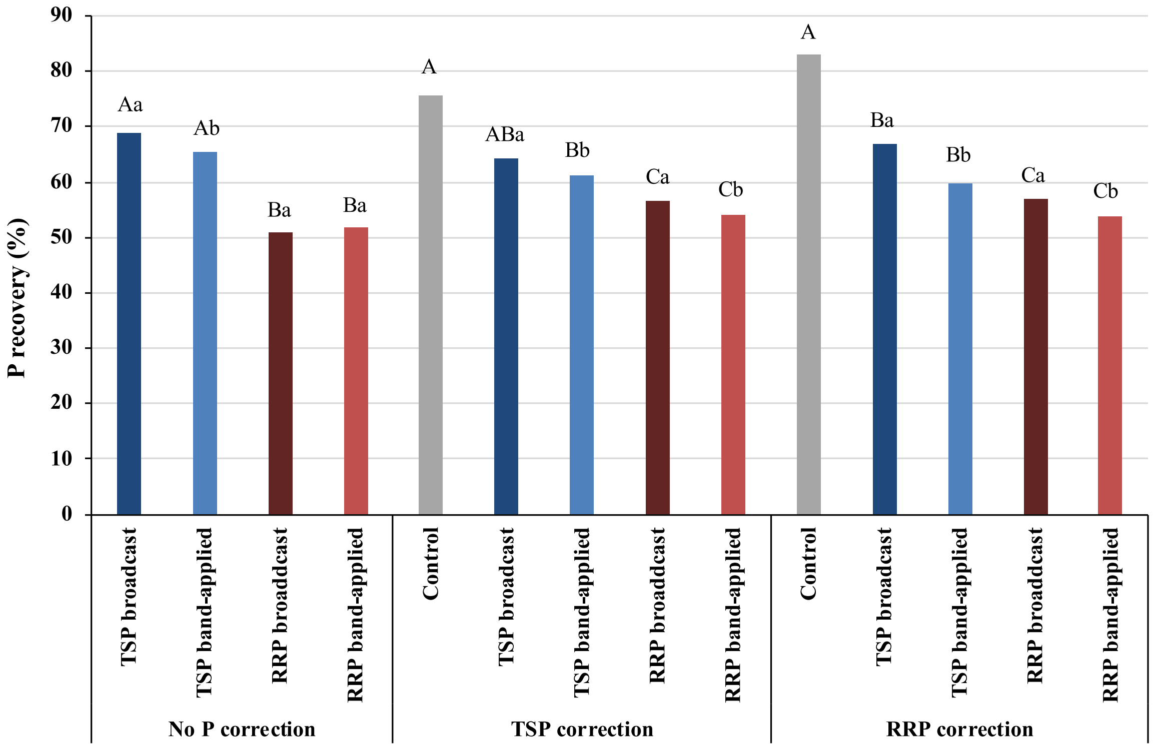

Figure 9: Total recovery of P contained in harvested products (grains), as a percentage of P applied as fertilizers and soil conditioners, after the end of the experiment. Uppercase letters compare controls and maintenance sources in each soil correction strategy, and lowercase letters compare application methods in a given correction and maintenance source. Means with the same letter do not differ according to Tukey's test ($P < 0.05$), n = 3. Total P exported in the control treatment (treatment 1) with no correction or maintenance phosphate fertilizer application, with P applied only as agricultural gypsum: 17.8 kg ha^{-1}.

4.5 DISCUSSION

4.5.1 Soil phosphorus correction is key

The remarkable effect of soil P correction on crop yield, especially in the first three crop cycles, was due to the need to raise STP to critical levels. Especially in this stage, there is a greater interaction of phosphate ions with the surface of positively charged Fe and Al oxides and hydroxides present in high concentrations in Oxisols and with high P adsorption capacity (Fink et al., 2016a). Over time phosphate ions penetrate into clay particles, decreasing the intensity of the positive outside charge (Barrow, 2015). As a result, there is less interaction of other phosphate ions with these oxy-hydroxides, reducing the soil P buffering capacity and increasing the efficiency of subsequent phosphate fertilizations (Barrow et al., 2018), hereinafter referred to as maintenance fertilization. This phenomenon is corroborated by the fact that in less clayey soils the need for P correction is reduced, which allows for high yields with modest maintenance P fertilizer applications, even with relatively low STP (van der Bom et al., 2019).

Due to the rapid solubilization, use of a soluble source such as TSP increases the proportion of labile P forms in soil (Nunes, 2014; Soltangheisi et al., 2018), and can quickly raise soil P contents to adequate levels which significantly increases crop yield in the first year of application (Figure 1). However, due to slow solubilization, as seen in the slow development of yield in treatments subject to correction and maintenance with RRP (Figure 2), the residual effect of applying a medium solubility source in soil, such as the RRP used, is prolonged (Oliveira et al., 2019). This is related to the fact that a decrease in the period of time that phosphate interacts with soil minimizes sorption (Barrow, 1980). This justifies the equivalent yields, several years after RRP application, to treatments where correction was made with TSP (Figures 1 and 3). Thus, in the accumulated result (Table 5) there was no difference between the sources used for soil P correction.

The similar relative yields approached by both P sources when residual P in soil is high (Figure 6) contrasts with the observation of reduced crop development when using different rock phosphates in more alkaline soils (Binh et al., 1978), where even high rates of this source are usually not effective. An explanation is that, according to Bolan and Hedley (1990) the dissolution of phosphate rocks diminishes with increasing pH, especially above pH 5.5.

A crucial aspect at the farm level is the economic return of corrective P fertilization. This was calculated as the average extra yield that treatments subjected to TSP correction gained over treatments with no corrective P application. Taking in account average soybeans and TSP prices in 2019 (World Bank Group, 2020), average extra yield totaled the equivalent to $1,821.55 per ha after the first three soybeans crops, a great return on the investment of $148.54 as TSP, not considering residual benefits in the following crops.

4.5.2 Maintenance with low solubility P sources requires attention

Maintenance with a soluble P source increased crop yields, especially in the first phases (Figure 3), since the low residual contents of this nutrient in soil were not yet sufficient to provide high relative yields, especially in treatments with RRP maintenance. This was due to the fact that for obtaining increasing relative potential yields there is a need of greater amounts of RRP in relation to TSP (Figure 8). To obtain the maximum yield potential (100%) with RRP, 351.8 kg P ha^{-1} in soil were needed, which is 181.8 kg P ha^{-1} more than when the source was TSP. This is in line with the proposal of Barrow (1985) for the evaluation of relative effectiveness between two fertilizer sources, which is given by the ratio of the partial differential for one fertilizer to another. For RRP and TSP these values were respectively 0.004858 and 0.010150, what gives 48% relative effectiveness for the sparingly soluble source, justifying the need for a P rate 2.09 times greater.

Up until the third phase, even in treatments under total corrective fertilization where the residual P (Figure 5) was sufficient to promote more than 90% relative yield (Figure 6), lower yields were observed with the use of RRP for maintenance compared to TSP (Figure 3). In the 4th and last studied phase, when the residual P content in soil previously treated with correction P fertilization approached values sufficient for 100% relative yield, there was no difference between the P maintenance sources. This indicates that for maintenance, due to the slow solubilization effect, the application of RRP is more suitable for soils where STP is not limiting. This benefit is observed in the longer term (Oliveira et al., 2019), in a manner similar to its use as a P correction source. In these situations, crop nutrition depends little on recently applied P fertilizer, where soil is the main provider of P to the plants (Mclaren et al., 2015).

Due to lower yields frequently observed with the use of RRP for maintenance, P recovery efficiency with the use of this source at the end of the experiment was lower than with the soluble source in all correction conditions. On the other hand, the control treatment grown only with corrective RRP fertilization at the beginning of the experiment exported 83.1% of the added P, whereas with TSP correction, this value was 75.8%. However, this difference was not significant.

Maintenance with the TSP and RRP mixture in equal P parts showed intermediate crop response between the separate application of these sources (Table 5), which is in line with expectations, with no synergetic effect that justifies its recommendation.

The regression models between relative yield and residual P in soil were the same between soybean and corn crops within each phosphate source (Figure 6). This is in accordance with the official recommendation for the region (Sousa and Lobato, 2004), which does not differentiate annual grain crops in terms of the recommendation for corrective or maintenance P fertilization.

4.5.3 P application method and grain yield in long-term NT

Increasing P stocks throughout the cropping seasons in treatments that received maintenance P caused STP values to rise (Figures 5 and 7). In phases 3 and 4, with adequate P stocks and STP values in soil, broadcast application increased yields by 2.1% and 2.9% on average over band-applied P fertilizer, respectively (Figure 4). This fact was also reflected in the greater P recovery under broadcast application (Figure 9).

There are probably three reasons for this. The P concentration in surface layers decreases the soil buffer capacity (Barrow et al., 2018), i.e., P biding intensity to soil colloids in surface layers is reduced since adsorption sites are quickly saturated. Because crop rows rarely overlapped perfectly for two or more growing seasons, the P concentration effect when from banding the fertilizer is reduced over the years. Although the fertilized soil volume extends to deeper layers in this case, this does not seem to counterbalance the effect of high P availability found in the superficial layers with broadcast application.

Although maximum P adsorption capacity is not affected by soil organic matter in highly weathered soils in Brazil (Fink et al., 2014), it can reduce the P binding energy intensity with soil colloids (Fink et al., 2016b). This means that uneven P distribution throughout the soil profile under broadcast P application, and its similarity with the distribution of C contents under NT, may be a positive factor. For example, Coelho et al. (2019) cited organic C accumulation in the 0-7.5 cm soil layer as a possible reason for the greater P use efficiency observed in broadcast P application.

The third possible justification for the higher observed P use efficiency under broadcast application may be related to the low organic C:P ratio found in NT superficial layers, which promotes high phosphatase enzyme activity (Sousa et al., 2019). A reduction of this ratio can be enhanced in broadcast application due to the even higher values of labile organic and inorganic P observed in the first 5 cm layer (Nunes, 2014). Thus, potential P supply from organic forms, not accounted for in the Mehlich-1 method, can be very significant when phosphatase enzyme activity is increased.

It should be noted, however, that there are doubts regarding the effect of prolonged droughts on P absorption in areas where P is mainly concentrated in shallow surface layers, as occurs in NT under broadcast P application due to the reduction of water availability in the narrow layer rich in P. Experimentally, however, there were no major yield losses when a water deficit was induced compared to P application at a depth of 5 cm (Hansel et al., 2017a). This might be related to the ability of some plants to raise soil moisture closer to the surface, although this is limited (Shen et al., 2011).

4.5.4 Critical STP levels in NT may be lower than expected

In order to obtain 90% yield potential in relation to the reference treatment, approximately 113.6 kg ha^{-1} of residual P from TSP was required in soil of which the expected

Mehlich-1 P content for this P stock was about 4.1 mg kg^{-1} (Figure 7); this is lower than that recommended for the Cerrado region by Sousa and Lobato (2004) for irrigated (12 mg kg^{-1}) and dryland production systems (8 mg kg^{-1}). This was probably related to the fact that the calibration curves adopted by these authors were based on the conventional tillage system (CT). In NT as in the present experiment, for reasons such as high organic matter content and less phosphate interaction with soil solid phase (Tiecher et al., 2017), critical levels were reduced (Sousa et al., 2010). This was probably due to the increase in organic P fractions that play an important role in crop nutrition, but whose availability is not considered by traditional STP methods, such as Mehlich-1 (Sousa et al., 2010).

Bray-1 and Olsen (0.5 M $NaHCO_3$) soil tests are often considered alternatives for the assessment of labile P in soils fertilized with phosphate rocks. In our results, however, it is noticeable an underestimation of labile P in soil fertilized with RRP when using the Bray-1 test, since STP values are considerably lower than that observed for TSP for a given residual P (Figure 7b). Even when considering that greater amounts of residual RRP P are necessary to obtain the same relative yields as TSP, as discussed above, Bray-1 P values are still low. For example, for the production of 90% relative yield, it is estimated the need for critical values of 113.6 kg residual TSP P ha^{-1} and 205.2 kg residual RRP P ha^{-1} in soil (Figure 6). The expected Bray-1 P levels for these respective amounts of residual P are 5.7 mg kg^{-1} for TSP and lower than that for RRP (3.9 mg kg^{-1}), despite the extra 91.6 kg P ha^{-1} (Figure 7b). Figure 7a also shows an opposite problem, an apparent overestimation of labile P when Mehlich-1 soil test is used to assess lability in RRP fertilized soils, which is due to solubilization of unreacted RRP particles by the acid extract.

The aforementioned problems were discussed by Oliveira et al. (2019) in the same soil type. The authors noticed similar underestimation between Bray-1 and Olsen tests and an overestimation of Mehlich-1 P when dealing with RRP fertilized soils. A series of similar results are also discussed by Zapata and Roy (2004). Despite these concerns, Oliveira et al (2019) affirm all these three methods can all adequately assess STP, provided that results are interpreted considering the respective P source.

More recently some studies have suggested that high yielding modern varieties would require a reassessment of soil P critical levels (Hopkins and Hansen, 2019). However, under well-established NT conditions not only STP critical levels appear to be adequate (Antonangelo et al., 2019), but also there are many areas receiving high P inputs compared to outputs in harvested products, what allows for opportunities for farmers to exploit residual P (Withers et al., 2018).

4.6 CONCLUSIONS

Corrective P fertilization promoted a rapid response in crop yields, with an equivalence between the P sources in most evaluated cultivation phases. Exceptions were the higher yields observed for TSP correction when maintenance was performed with RRP in the first phase of the soybean crop, and the higher yields obtained with RRP correction under TSP maintenance in the second phase of the corn crop. However, in the first crop harvest high TSP solubility was more efficient in supplying P to crops. In the uncorrected condition, high yields were only obtained when residual P in the soil was sufficient for its correction, especially when using RRP for maintenance. The application method did not influence average yields in the first two phases, however with accumulating P stocks in soil, broadcast application improved yields in phases 3 and 4. Estimated residual stocks of 113.6 kg of P ha^{-1} using TSP and 205.2 kg of P ha^{-1} in RRP equivalent were necessary to obtain 90% of the reference yield potential. These values permit that Mehlich-1 P is increased to critical levels, where the value of 4.1 mg kg^{-1} for TSP is lower than that recommended for the region and may be due to the contribution of organic P in NT, the fraction not accounted for in the Mehlich-1 method.

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SUPPLEMENTARY MATERIAL FOR CHAPTER I

Table S1: P content in harvested grains (soybeans or corn) in all experimental years according to P correction and P maintenance levels.

P correction	**P maint.**	**P content in grains (g kg^{-1})**															
		1999/00	**2000/01**	**2001/02**	**2002/03**	**2003/04**	**2004/05**	**2005/06**	**2006/07**	**2007/08**	**2008/09**	**2009/10**	**2010/11**	**2011/12**	**2012/13**	**2013/14**	**2014/15**
		Soybeans	**Soybeans**	**Soybeans**	**Corn**	**Soybeans**	**Corn**	**Soybeans**	**Corn**	**Soybeans**	**Corn**	**Soybeans**	**Corn**	**Soybeans**	**Corn**	**Soybeans**	**Corn**
-	**control**	2.96	3.02	2.81	3.48	2.94	2.60	4.23	4.12	3.89	3.14	2.53	2.05	2.76	2.06	2.34	1.85
	TSP	3.20	3.74	3.88	3.63	4.66	4.04	4.26	3.99	4.50	3.77	4.20	2.45	4.30	2.56	4.20	2.48
	RRP	3.61	3.57	3.36	3.18	3.93	3.54	4.69	3.09	5.07	3.13	3.53	2.39	4.33	2.32	4.07	1.92
TSP	**control**	3.62	3.60	3.29	2.60	3.05	2.59	4.66	2.65	4.83	2.23	2.68	1.54	2.72	1.71	2.32	2.53
	TSP	3.89	4.69	4.84	4.03	5.04	4.27	4.38	4.32	4.67	4.01	4.29	2.67	4.43	2.56	4.36	2.55
	RRP	3.78	4.01	4.10	3.59	4.71	3.81	4.66	3.69	4.55	3.45	4.01	2.45	4.82	2.49	4.42	2.44
RRP	**control**	3.72	3.57	3.33	2.89	3.29	2.58	4.36	3.18	5.23	2.89	2.71	1.51	2.41	1.68	2.42	2.23
	TSP	3.80	4.65	4.82	4.15	5.35	4.14	4.83	4.38	4.56	3.81	4.06	2.41	4.56	2.54	4.25	2.65
	RRP	3.72	3.78	4.12	3.63	4.73	3.93	4.84	3.69	4.70	3.82	3.92	2.51	4.40	2.53	4.23	2.22
		Standard deviation (g kg^{-1})															
-	**control**	0.21	0.40	0.08	0.19	0.09	0.45	0.54	0.43	0.23	0.46	0.30	0.16	0.20	0.23	0.06	0.30
	TSP	0.21	0.12	0.20	0.38	0.21	0.34	0.94	0.21	1.00	0.71	0.35	0.26	0.27	0.17	0.25	0.21
	RRP	0.30	0.23	0.11	0.34	0.30	0.30	0.50	0.36	0.37	0.28	0.64	0.28	0.44	0.45	0.30	0.19
TSP	**control**	0.30	0.43	0.23	0.14	0.08	0.29	0.58	0.21	0.71	0.27	0.15	0.04	0.22	0.18	0.03	0.34
	TSP	0.34	0.49	0.29	0.16	0.28	0.26	0.34	0.24	0.61	0.32	0.27	0.24	0.35	0.30	0.38	0.10
	RRP	0.17	0.29	0.24	0.17	0.28	0.17	0.36	0.16	0.66	0.41	0.40	0.33	0.37	0.32	0.27	0.33
RRP	**control**	0.07	0.34	0.05	0.14	0.11	0.18	0.50	0.17	1.06	0.05	0.37	0.12	0.15	0.11	0.03	0.12
	TSP	0.14	0.27	0.28	0.50	0.30	0.41	0.47	0.46	0.50	0.42	0.53	0.19	0.15	0.26	0.23	0.21
	RRP	0.15	0.10	0.15	0.30	0.46	0.28	0.46	0.24	0.65	0.62	0.38	0.33	0.24	0.49	0.37	0.19

CHAPTER II

SPATIAL DISTRIBUTION OF SOIL PHOSPHORUS FRACTIONS IN A CLAYEY OXISOL SUBMITTED TO LONG-TERM PHOSPHATE FERTILIZATION STRATEGIES

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5 CHAPTER 2. SPATIAL DISTRIBUTION OF SOIL PHOSPHORUS FRACTIONS IN A CLAYEY OXISOL SUBMITTED TO LONG-TERM PHOSPHATE FERTILIZATION STRATEGIES

5.1 ABSTRACT

Due to the strong interaction of phosphorus (P) with soil constituents, P fertilizer placement can significantly affect how crops take up this nutrient. Nonetheless, few studies address the spatial distribution of P at the row-interrow scale according to management strategies. In a 16-yr no-tillage (NT) field experiment involving two different P fertilizer application methods (broadcast or band application) and two P sources (triple superphosphate – TSP or reactive Gafsa phosphate rock-RPR), plus a control treatment, the spatial distribution of P fractions was assessed in two occasions: after the 8th and the 16th crops. This was done vertically to a depth of 30 cm and horizontally from the crop row to the center of the interrows. Broadcast treatments showed total and Mehlich-1 P accumulation at the soil surface while for band application this accumulation was in the crop row region. A small P movement down the soil profile was observed from the 8th to the 16th crop with broadcast application, whereas with band fertilizer this effect was more noticeable, showing increased soil volume under P fertilizer influence even without soil tillage; it is likely that this was partly due to biological P turnover and application at depth. After 16 crops, the soil volume under the influence of P fertilizer was greater under band application while the volume above Mehlich-1 P critical levels for the 0-20 cm layer in regional studies was higher under broadcast application, independent of the P source. Soil organic carbon (SOC) contents were not affected by P placement or source. However, a significant accumulation of SOC was seen from the soil surface downwards after the last eight crops. The spatial distribution of P and SOC was better correlated under broadcast treatments, with high values for both variables at the soil surface; this may explain similar yields to those obtained with band application, where P fertilizer is placed near the main roots in an attempt to reduce P adsorption to the soil solid phase.

Keywords: Phosphorus placement; total P; broadcast fertilization; no-tillage; P run-off; Soil sampling

Abbreviations list[1]

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[1] NT, no-tillage system; RPR, reactive phosphate rock; RY, relative yield; STP, soil test P; TSP, triple superphosphate; SOC, soil organic carbon; Po, organic P; BR, broadcast; BA, band-application.

5.2 INTRODUCTION

Phosphorus (P) usually presents low mobility in soils, especially in weathered tropical regions due to its strong interaction with soil mineral constituents (Calegari et al., 2013; Gérard, 2016). Therefore, phosphate fertilizer management is thought to greatly influence the degree of contact between P inputs and plant roots, especially according to P placement strategy. As a result, P fertilizer is more commonly applied to the crop planting furrow a few centimeters below the seeds, seeking to maximize initial crop development due to early root-fertilizer contact. This method is also referred to as band application. However, many farmers in Brazil have been moving towards broadcast P fertilization in high soil test P (STP) areas due to improved field logistics. This is especially the case when considering the possibility of using very large planters and flexibility to choose the P source, such as natural rock phosphates, and application timing, including early-season application to cover crops, months before crop drilling (Caires et al., 2017). Although selecting an application method appears to be a trivial decision by farmers, it largely impacts the spatial distribution of P in soil under a no-tillage system (NT) because this nutrient presents very low mobility due to interactions with the solid phase, which may impact P nutrition of crops.

Much interest has been given to P application methods in the past few decades but conflicting results have been commonly reported, and few trials have addressed the long-term effects in soils considered highly adsorptive for P (Costa et al., 2009; Coelho et al., 2019; Preston et al., 2019; Oliveira et al., 2020a). In a meta-analysis, band applications were found to improve the yields of various crops, especially when nitrogen (N) sources were associated with P (Nkebiwe et al., 2016). This application method is also generally recommended to reduce P contact and its adsorption by soil colloids (Novais & Smyth, 1999). In addition, there are concerns that surface applications of P fertilizer may restrict P uptake in the case of water deficit, especially in drier climate regions. This was thoroughly investigated by Hansel et al. (2017), who found that deep banding fertilizer at 20 cm deep induced root growth and drought resilience. Comparing broadcast fertilization and fertilizer banding at a more common depth (5 cm), however, revealed that broadcast fertilization coped better with water deficit.

Under NT, a spatially localized effect of P inputs may exist not only for band-application, but also for broadcast application (however in a different region) due to P accumulation on the soil surface. The buildup of residual P in a shallow layer near the surface in coexistence with a high organic matter content promotes P availability (Guedes et al., 2016; Yang et al., 2019); there is also the decrease of soil P buffering capacity due to the feedback effect of previous surface applications (Barrow, 2015a; Barrow et al., 2018a). These were hypotheses suggested to justify slightly higher crop yields under long-term broadcast P application in an Oxisol (Oliveira et al., 2020a). Yield and biomass increases observed with P inputs to low STP soils often consequently improve levels of soil organic carbon (SOC) and C sequestration (Coonan et al., 2019). A feedback effect benefiting P nutrition of subsequent crops may therefore be expected due to the competitive interaction of phosphate and organic compounds for sorption sites (Kreller et al., 2003; Kang et al., 2009; Fu et al., 2013; Fink et al., 2016), although this effect could be limited at the field scale considering organic acid concentrations normally found in soils (Guppy et al., 2005). Knowledge about the long-term behavior and spatial distribution of P fractions and SOC, as well as their interactions, may thus support management decisions that improve soil P absorption by crops.

Phosphate sources of medium solubility can be considered as slow-release P fertilizers. Applications of reactive phosphate rock (RPR) to low STP areas are often initially less effective than that of an equivalent total P dose of a water soluble phosphate source (Caires et al., 2017; Nunes et al., 2020). However, in the long-term the residual effect of RPR P inputs to soils is more pronounced than when a soluble source is used (Oliveira et al., 2019). As long as a minimum available P stock exists in the soil from previous applications, fertilization with RPR is able to match that obtained with triple superphosphate (TSP) (Oliveira et al., 2020a). Because soil-fertilizer contact is especially critical for RPR dissolution in acid soils, decision on the best fertilizer must consider the effects of different application methods. In NT systems, broadcast and band applications of RPR usually return similar crop yields (Nunes et al., 2020, 2021). Although high pH values can be found at the soil surface due to lime applications, limiting RPR dissolution, greater soil-fertilizer contact may compensate this limitation. Nonetheless, under limited STP conditions, RPR rates should be increased in either case to match the yield potentials with soluble sources (Oliveira et al., 2020a). As long as these observations are considered, RPR may be an excellent cost-effective source for tropical soil conditions (Sousa et al., 2014; Pavinato et al., 2017).

Weihrauch (2019) alerted that the importance of spatially characterizing P distribution has been underrated. Less than 16% of papers on soil P reviewed by this author involved a vertical soil sampling context and up to 90% of papers did not consider a lateral component in soil sampling for P assessments. Among studies that focus on spatial P distribution, many involve either the country scale (Pavinato et al., 2020), the macro landscape scale (Mallarino, 1996; Guérin et al., 2011; Cherubin et al., 2015; Chen et al., 2020) or the micro and fertilizer granule scale of P processes and reactions (Sousa and Volkweis, 1987; Beauchemin et al., 2003; Lombi et al., 2006). Recent efforts have been made towards the modelling of P spatial distribution in the long-term, according to parameters like soil characteristics, root growth and P balance (Li et al., 2019).

However, despite the probable significant effects of phosphate fertilization management strategies on soil P spatial distribution, few studies have addressed this matter, which occurs at the decimetric row-interrow scale. In a study involving a top-down view of the horizontal spatial distribution of P, Cambouris et al. (2017) found no effect of tillage or P fertilizer banding in the 0-5 cm layer distribution of Mehlich-3 P in the soil at a plot scale, which was possibly due to the low rates of P applied during the 20-yr soybean-corn rotation. On the other hand, long-term buildup of soil P may also reduce spatial P distribution variability at the field scale (Memiaghe et al., 2021). In Illinois-USA, after 3 years of precision planting corn and soybeans on the same crop rows positions, subsurface banding increased P levels at the point of application (10-20 cm below the crop row) while both surface (0-10 cm) and subsurface P levels between the crop rows were reduced (Fernández and Schaefer, 2012). This was considered an indication that crops take up P uniformly from the soil surface, irrespective of P placement, especially because there was no effect of banding on roots distribution (Farmaha et al., 2012; Fernández and Schaefer, 2012).

Knowledge on P management strategies in tropical soils is evolving rapidly and long-term experiments are essential for rational use of diminishing world phosphate rock reserves and increasing soil P stocks (legacy P) (Withers et al., 2018; Pavinato et al., 2020). Characterization of the spatial distribution of nutrients through the soil profile is especially important for P, due to its low mobility characteristics and dependence on management strategies. Nevertheless, most studies address only the vertical distribution of P fractions, and usually in short-term assessments. This study therefore aims to characterize both the vertical and horizontal distribution at the row-interrow scale of different soil P fractions and organic carbon (SOC) through the soil profile as a function of the P source (reactive rock phosphate [RRP] or triple superphosphate [TSP]) and P fertilizer application method (band-applied [BA] or broadcast on the soil surface [B]) in two occasions of a long-term no-tillage experiment. Evaluation of the spatial distribution and relationships between P fractions (and SOC) over time may shed light on how crops may adapt to absorb P according to different P application strategies and sources, and how the distribution of P fractions evolve over time.

5.3 MATERIALS AND METHODS

5.3.1 Characterization of the experimental area

The experiment was established in the experimental area of the research station of Embrapa Cerrados, Planaltina, DF, Brazil (latitude 15º 36´S and longitude 47° 42´W). The relief is smooth undulating, with a mean elevation of around 1014m, while original vegetation is classified as typical Cerrado. The climate is Cwa according to Köppen (Alvares et al., 2013), with annual precipitation and temperature averages of 1570 mm and 21.3 °C, respectively. The soil is characterized as a highly weathered, low nutrient content and naturally acidic clayey Oxisol (Rhodic; Soil Survey Staff, 1998) or as a Latossolo Vermelho Distrófico according to the Brazilian Soil Classification System (Embrapa, 2013). The clay fraction represents 540 g kg^{-1} of the soil weight, and is composed mainly by kaolinite, gibbsite, hematite and goethite. Table 1 presents initial attributes of the soil before the application of amendments necessary for crop cultivation.

After clearing the native vegetation, all soil chemical deficiencies, except P, were corrected according to Sousa & Lobato (2004). This involved application of dolomitic lime to increase cation exchange saturation to 50% (3835 kg ha^{-1} effective calcium carbonate equivalence (ECCE) of lime), 500 kg ha^{-1} of agricultural phosphogypsum (20% Ca, 15% S, 0.2% P), 75 kg ha^{-1} of K (as KCl) and 100 kg of FTE BR-12, a micronutrients source containing 9% Zn, 2.1% Mn, 1.8% B, 0.8% Cu and 0.1% Mo. The soil was then plowed and harrowed to incorporate fertilizers down to 20 cm.

Table 1: Chemical and physical characteristics of the soil in the 0-20 cm layer after clearing the native vegetation, before liming and fertilization for experiment establishment.

pH H_2O $^{(1)}$	P $^{(2)}$	K^{+} $^{(2)}$	Ca^{+2} $^{(3)}$	Mg^{+2} $^{(3)}$	Al^{+3} $^{(3)}$	H + Al $^{(4)}$	CEC
	mg kg^{-1}	--------------------------- cmol$_c$ kg^{-1} -------------------------					
4.5	1.2	0.1	0.2	0.2	1.4	8.1	8.6

SOC	V	Clay	Silt	Coarse sand	Fine sand
g kg^{-1}	--------------------------- g kg^{-1} ---------------------------				
16.2	5.6	540	50	120	290

(1) 1:2.5 soil solution ratio; (2) Mehlich-1; (3) KCl 1 mol L^{-1}; (4) calcium acetate 0.5 mol L^{-1} at pH 7.0; SOC: soil organic carbon by the Walkley-Black procedure; V: cation exchange saturation; CEC: cation exchange capacity at pH 7.0. Modified from Oliveira et al. (2020a).

5.3.2 *Experimental design and management*

This study complements research on selected treatments explored in our previous work (Oliveira et al., 2020a). Briefly, the experiment was installed in 1999 and was conducted for 16 years, cultivating soybeans [*Glycine max* (L.) Merr] and corn (*Zea mays* L.) in rotation as main summer crops, and as winter cover crops the mauritius bean [*Mucuna aterrimum* (Piper & Tracy) Holland] after the first main crop, and millet [*Pennisetum glaucum* (L.) R.Br] after all following main crops (Table 2). The selected treatments consisted of a complete bifactorial design involving annual application of a maintenance P source (triple superphosphate [TSP] or reactive rock phosphate [RRP]) in two different application methods: broadcast spreading the fertilizer over the soil surface or band applying it in the crop row furrow (approximately 5 cm below the seeds), totaling four fertilizer treatments. An additional control treatment was cultivated without any P inputs except for that contained in phosphogypsum. Treatments were arranged in a randomized block design containing 3 replicates.

Table 2: Crop sequences and fertilization in the experimental area[1].

	Season	Main crop	Cover crop	Lime[2]	Gypsum	N (urea)	K (KCl)
				kg ha^{-1}			
1	1999/00	Soybeans	Mauritius bean	3835	500	-	75+67
2	2000/01	Soybeans	Millet	-	-	-	67
3	2001/02	Soybeans	Millet	-	-	-	67
4	2002/03	Corn	Millet	-	-	30+60+60	67
5	2003/04	Soybeans	Millet	-	1000	-	67
6	2004/05	Corn	Millet	-	1000	30+60+60	67
7	2005/06	Soybeans	Millet	-	1000	-	67
8	2006/07	Corn	Millet	975	133	30+60+60	67
9	2007/08	Soybeans	Millet	-	100	-	67
10	2008/09	Corn	Millet	-	100	30+60+60	67
11	2009/10	Soybeans	Millet	-	100	-	67
12	2010/11	Corn	Millet	-	100	30+60+60	67
13	2011/12	Soybeans	Millet	-	100	-	67
14	2012/13	Corn	Millet	-	100	30+60+60	67
15	2013/14	Soybeans	Millet	-	100	-	67
16	2014/15	Corn	Millet	2158	100	30+60+60	67

[1]Modified from Oliveira et al., 2020a. [2]Effective calcium carbonate equivalence (ECCE).

Considering the initial soil test P (STP) and clay content in the experimental area (Table 1), regional recommendations suggest an application of 130 kg P ha^{-1} with incorporation to depth to increase STP (corrective fertilization) before planting crops (Sousa & Lobato, 2004). However, this set of treatments did not receive this kind of fertilization so the effect of maintenance P management could be better assessed . As a consequence, a gradual increase in soil P stocks was expected during the experimental growing seasons due to the application of 35 kg total P ha^{-1} annually as TSP or RRP, a rate expected to be slightly above the average offtake by crop harvests. P dynamics in the soil profile could then be a direct consequence of maintenance P management (source and placement), as well as crop growth and yield in the no-tillage system that was adopted after establishment of the first crop.

Characteristics of phosphate fertilizers used were as follows: TSP and RRP contained 20.8% and 12.3% total P, respectively. Solubility of P contained in fertilizers was analyzed using a 2% citric acid solution considering 1:100 fertilizer:solution ratio and ground RRP particles (<0.063 mm), resulting in 92% and 44% solubility for the P present in TSP and RRP, respectively. Nonetheless, the phosphate fertilizer rate was based on the total P content. Fertilizer treatments then received a total amount of 280 kg of total P ha^{-1} after the first 8 crops (first soil sampling) and 560 kg of total P ha^{-1} after 16 crops (last soil sampling), plus a total of 9.7 kg P ha^{-1} contained in phosphogypsum (the only P input also applied to the control treatment).

Experimental plots measured 49.5 m^2 (11 m long by 4.5 m wide). Soybeans were cultivated in a 45 cm row spacing while for corn this distance was 75 cm, in approximately the same positions every season. Different row spacing between soybeans and maize and small variations in the directions of the crops' lines may resemble what happens at a farm level using controlled traffic operations and when cultivating different crops, which is not a hamper to the characterization of P distribution according to the different application methods (broadcast or band-application). Soybeans were planted using a no-till drilling machine and the seed rate varied between 340,000 and 500,000 plants per ha, according to the variety used. Corn was manually sown using two seeds per position, in order to allow for subsequent thinning and optimal plant population in all plots (70,000 plants ha^{-1}). For both crops, maintenance fertilization was done according to Table 2, involving the application of K as KCl in every crop, N as urea in corn (30 kg ha^{-1} at planting and two 60 kg ha^{-1} dressings) and occasional applications of lime and gypsum in order to amend surface and subsurface soil acidity and provide sulphur (S). Liming was performed to maintain the soil cation exchange saturation (V%) near 50%, sufficient for Al neutralization and an adequate pH in water (around 5.5) for crop development. More details about crop cultivation can be obtained in our previous work (Oliveira et al., 2020b).

5.3.3 Soil sampling

Soil samples were taken on two occasions after corn cultivation: after the 8th and 16th crops, i.e., after the end of phases 1 (2007) and 2 (2015) of the experiment, respectively. On both occasions, soil samples were taken in 7 positions across a crop row, being one right over the row and three others equally spaced 12.5 cm to each side to the center of the corn interrows (Figure 1). In each position, soil was sampled in 5 layers after the 8th crop (0-2.5, 2.5-5, 5-10, 10-20 and 20-30 cm) and 4 layers after the 16th crop (0-5, 5-10, 10-20 and 20-30 cm). This procedure was repeated 6 times in each plot, including 3 locations in each of the two central crop rows of each plot in order to obtain the composite samples representative of the plot. A 5 cm diameter cylindrical soil core sampler (also used for soil density evaluations) was used to take samples down to 10 cm while a Dutch auger was used for deeper layers, thus minimizing possible contamination from upper layers. The first two layers collected after the 8th crop were merged into 0-5 cm samples for analysis, in order to obtain the same soil layers scheme used for sampling after the 16th crop. Composite samples totaled approximately 600 g. Therefore, final composite samples represent spatial distribution of soil properties in 4 depths at 7 positions across the crop row (Figure 1) for each plot, totaling 28 observations. After collection, soil samples were air dried and sieved (<2 mm). Samples taken after the 8th crop were analyzed for soil organic carbon (SOC) and Mehlich-1 P prior to storage in plastic bags at ambient temperature in the laboratory storage facility. The remaining analysis were then conducted concomitantly with the phase 2 samples.

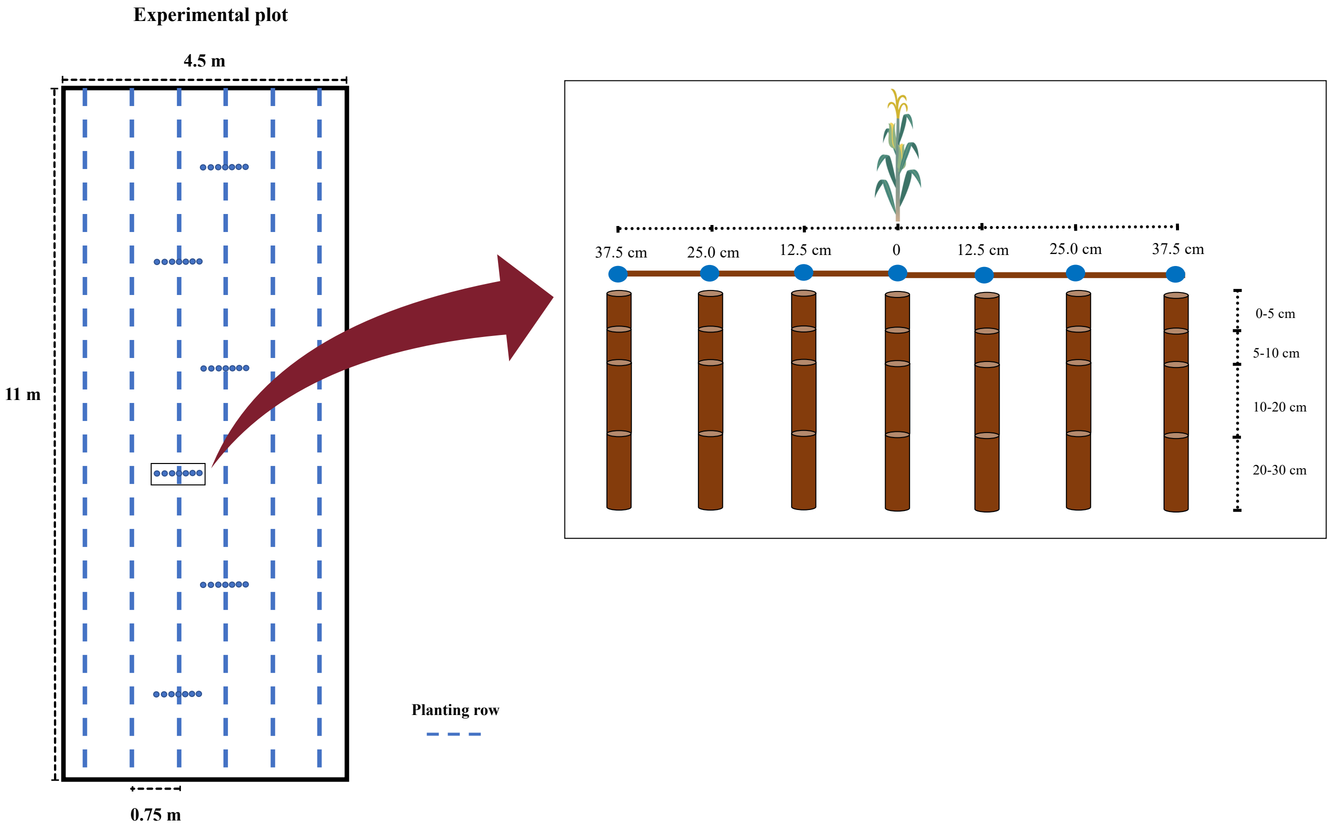

Figure 1: Diagram illustrating the six sampling locations used to compose the 28 composite samples (7 horizontal positions x 4 depths) for each experimental plot in order to characterize the vertical and horizontal distribution of P fractions and organic C. Considering that 5 cm diameter soil samples were taken at 7 different positions in a 75 cm interval (distance between interrows centers), approximately 47% of the soil volume was actually sampled in that interval (7 x 5 cm/75 cm = 47%).

5.3.4 Soil analysis

Labile P was determined according to the Mehlich-1 method (0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H_2SO_4), which is widely adopted in commercial laboratories throughout Brazil, while soil organic carbon (SOC) was determined according to Walkley & Black (1939).

Total P was determined by acid digestion with 18 mol L^{-1} H_2SO_4 (Merck®), a concentrated solution of $MgCl_2$ (Brookes and Powlson, 1981) and H_2O_2 (Merck®) under heating (Hedley et al., 1982). Briefly, 7.5 mL of H_2SO_4 and 1 mL of the saturated $MgCl_2$ solution were added to a 0.15 g soil sample (<2 mm) in a digestion tube. A small condensation funnel was placed at the top and the digestion block was heated to 200 ºC for 2 h. The temperature was then reduced to 100 ºC to allow for two additions of H_2O_2 (2 mL each) in 1-

hour intervals, after which digestion proceeded for 2 more hours at 150 ºC. The following day, ambient temperature extracts were diluted to 50 mL, filtered in quantitative filter papers and P was determined according to the molybdenum blue method (Murphy and Riley, 1962; Nagul et al., 2015).

Total organic P (Po) was determined according to the ignition method (Hance & Anderson, 1962; Olsen & Sommers, 1982) with the modification of increasing the H_2SO_4 concentration to 2.0 mol L^{-1}. Two sets of soil samples were weighed, and one was submitted to ignition at 550 ºC for 1.5 h and the other not. All samples were then submitted to extraction using 2.0 mol L^{-1} H_2SO_4 under horizontal shaking at 220 rpm for 16 h at a 1:8 soil:solution ratio (w/v). After filtration, the P content in the acid extracts was determined according to the molybdenum blue method (Murphy and Riley, 1962; Nagul et al., 2015). Po was calculated as the difference between P contents in the ignited and non-ignited samples.

All analysis were performed on the complete set of 420 samples per sampling year, consisting of 5 treatments, 3 field replicates, 7 horizontal positions and 4 depths. Field replicate results were averaged to perform the geostatistical analysis described below.

5.3.5 P offtake and residual fertilizer P stocks

Residual P stocks in soils were estimated by the difference between P inputs (P fertilizers and gypsum) and P offtake as harvested grains. To obtain the P offtake, the P content in grains was assessed by wet digestion with HNO_3 and $HClO_4$ (3:1, v:v) (Embrapa, 1999), while crop yield was assessed by harvesting 7 meters of the central 4 corn rows and 6 soybean rows, expressing yields at a 130 g kg^{-1} moisture content. After the evaluations, the main crop residues (all plant parts except grains) were then returned to the respective plots. Yield and P content in grains were evaluated in all 16 main crops, so that the P input-output balance could be calculated after any given main crop harvest.

5.3.6 Dry-matter production and P turnover estimations

Above-ground dry-matter production of the main crops was estimated based on harvest indexes obtained in similar experiments located at the Embrapa Cerrados research center (35% for soybeans and 55% for corn). For cover crops, the above-ground dry-matter production was evaluated annually by cutting the shoots delimited in two square frames measuring 1 m^2 each in each plot. For both main and cover crops, in order to account for total dry-matter production (above + below ground dry-matter), root contributions were added considering that it accounts for approximately 30% of the crop total dry-matter production (Bolinder et al., 2007). Above-ground P turnover was then estimated based on the above-ground dry-matter production multiplied by P concentrations estimated for the same crops in similar experiments at the Embrapa Cerrados research center for corn and millet, and according to Bargaz et al. (2017) for soybeans. All cover crop plant residues were returned to the plots and maintained on the soil surface after evaluations.

5.3.7 Statistical and geostatistical analysis

2-D geostatistical analyses were performed on the horizontal (lateral) and vertical distribution of SOC and soil P fractions in the different treatments. Semivariograms were calculated to predict the spatial dependence of SOC and P fraction contents on the different sampling points in the 0.75 m × 0.3 m soil sections for each treatment, allowing for the estimation of contents at non-sampling points by ordinary kriging. Experimental semivariograms were calculated using the package 'gstat' (Pebesma, 2004; Gräler et al., 2016) in the software R (R Core Team, 2018), according to the following equation:

$$\gamma(h) = \frac{1}{2n}\sum_{i=1}^{n}\{Z(x_i) - Z(x_i + h)\}^2 \qquad \text{eq (1)}$$

Where $\gamma(h)$ represents the semivariance of the lag distance h; n is the number of pairs of data separated by the respective lag distance h; $Z(x_i)$ represents the value of a given soil attribute (C or P fraction content) at a specific i_{th} location while $Z(x_i+h)$ is this given attribute value at the $(i+h)_{\mathrm{th}}$ location.

Directional semivariograms were constructed to evaluate anisotropy. Due to few observations per map (28), all possible data pairs were considered (cutoff = maximum distance). Most maps showed a greater spatial continuity in the horizontal direction. Different models were tested and adjusted to these horizontal search semivariogram plots according to the least squares fitting criterion. The models selected were all linear or spherical with or without significant nugget effect. A cross-validation was performed to evaluate the effectiveness of the kriging parameters, and a linear regression between observed values and the cross-validation estimates was made. Interpolated maps were created using the program Surfer® version 16 (Golden Software, LLC).

The spatial distribution correlation between different variables was assessed via the global bivariate Moran Index, because a simple linear regression does not take into account the spatial dependence between observations. This was calculated using the GeoDa™ software version 1.20.0. The significance of the correlation was assessed by Monte Carlo simulations with 999 permutations.

Yield, residual P and P offtake data were subjected to analysis of homoscedasticity and normality of the residues by the Levene and Shapiro-Wilk tests, respectively. After confirming these assumptions, a two-way analysis of variance was used to identify possible differences between treatments, adopting Tukey's test to compare the means where the F test was significant ($P<0.05$).

5.4 RESULTS

5.4.1 Crop yields and residual fertilizer P in the soil

Mean soybean and corn grain yields in the first 8 crops and in the following 9th to 16th crops and the overall 16-yr mean for each crop are presented in Figure 2. In all cases, under TSP treatments both crops yielded more than when RPR was used, while there was no statistical difference between application methods; when considering a more complete set of treatments in the same experiment, though, broadcast fertilization yielded statistically more grains than band application (Oliveira et al., 2020a). While in phase 1 RPR yielded 17% and 34% lower than TSP treatments, in phase 2 this difference was reduced to 7% and 8%, for corn and soybean, respectively.

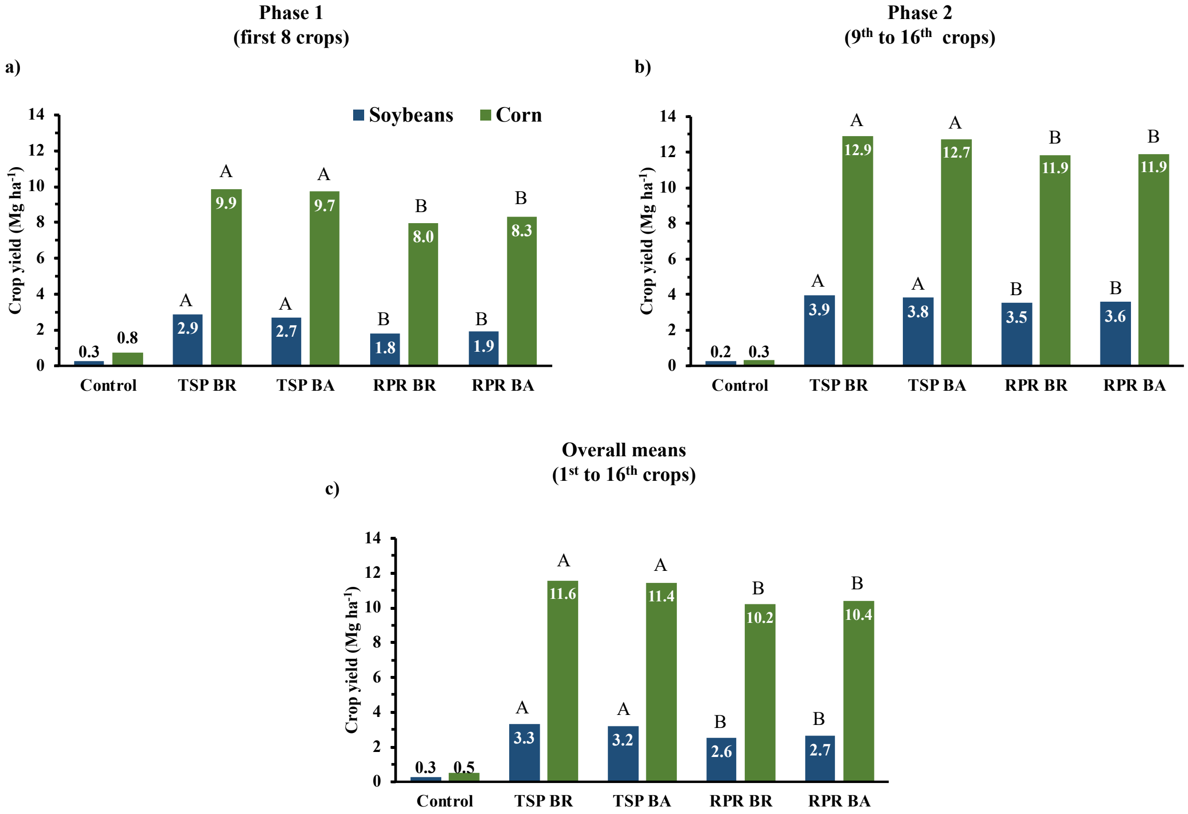

Figure 2: Average soybeans and corn yields during phase 1 (1st to 8th crops) (a), phase 2 (9th to 16th crops) (b) and overall average (c). Letters compare treatments in each crop according to Tukey's test ($P<0.05$). In all cases the control treatment without any P inputs yielded less grains than the average of fertilized treatments, according to orthogonal contrast ($P<0.05$). TSP: triple superphosphate; RPR: reactive phosphate rock; BR: broadcast application; BA: furrow band application.

P offtake by crop harvests and residual fertilizer P calculated to be present in soil after 8 and 16 crops are presented in Figure 3. P offtake was greater with the use of TSP, resulting in approximately 33% lower residual P stocks in soils under these treatments on average after 16 crops. Although non-significant statistically, residual P after 16 crops under TSP broadcast fertilization was 10% lower than under band-application, due to slightly better yields (Figure 2) and greater P content in grains; on average these were 3.4 g P kg^{-1} in broadcast and 3.2 g P kg^{-1} in band application for corn grains, while for soybeans both application methods averaged 4.1 g P kg^{-1}. Residual P stocks built-up approximately 60% from the end of phase 1 to the end of phase 2 in all fertilized treatments. In absolute values, RPR allowed for the accumulation of over 100 kg P ha^{-1} in the final 8 crops, while TSP treatments gained 70 kg P ha^{-1} on average.

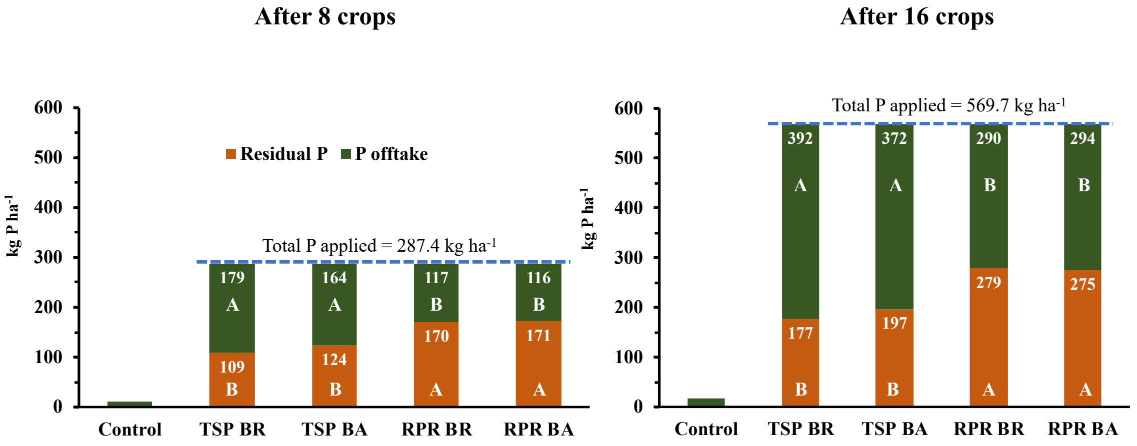

Figure 3: Residual fertilizer P in soil and P offtake by crop grains after 8 (a) and 16 (b) growing seasons/crops. Letters compare treatments according to Tukey's test (P<0.05). In all cases the control treatment without any P inputs differed significantly from the group of fertilized treatments, according to orthogonal contrast (P<0.05). Residual P in the control treatment after phases 1 and 2 were, respectively, -3.6 and -8.1 kg P ha^{-1}, indicating a small utilization of naturally occurring P. TSP: triple superphosphate; RPR: reactive phosphate rock; BR: broadcast application; BA: furrow band application.

5.4.2 Spatial distribution of P fractions and organic C

Linear regressions between the observed and the ordinary kriging estimates showed significant correlations ($r^2 > 0.9$, $P < 0.05$), characterizing adequate local estimations (Table S1). Cross-validation r^2 results are also shown in Table S1 and illustrate the effectiveness of the kriging parameters, especially in broadcast treatments ($r^2 > 0.37$, $P < 0.05$) despite the low number of observations per map (28).

The spatial distribution of total P contents through the soil profile in the four fertilized treatments and both sampling occasions is shown in Figure 4, down to 25 cm deep and horizontally to 37.5 cm on each side of the crop row (i.e, up to the center of the corn interrows). Broadcast P application treatments present a horizontal pattern of total P distribution while band-application concentrated P near the crop row, as expected based on fertilizer field distribution. In accordance with the calculated residual P stocks (Figure 3), RPR fertilized soils presented higher total P contents than TSP soils, especially in the application zone of each placement strategy. The development of P accumulation is observed in all treatments when comparing both sampling occasions, with a noticeable deepening of the 300 mg kg^{-1} total P concentration frontier. In addition, the effect of band-application is less intense after the 16 crops when compared to the previous sampling occasion, especially in the RPR treatment. The control treatment showed relatively small but unexpected average P gains in the plotted 1,875

cm^2 soil profile (25 x 75 cm), gaining 47.6 mg P kg^{-1} in the last 8 crops from the 213.2 mg kg^{-1} determined after the initial 8 crops (Table S2).

Different from total P, the distribution of SOC showed less pronounced effects of phosphate fertilization management (Figure 5). A slight accumulation of SOC in all treatments was observed at the crop row, especially at the first sampling, after the 8th crop. Nonetheless, the most evident effect on SOC contents was the effect of time, with great gains in SOC contents mainly in the 0-5 cm soil layer in the last eight growing seasons. The average volume occupied by contents greater than 19.8 g kg^{-1} in the 0-25 cm layer was 4.6% after 8 crops and increased to 24.6% after 16 crops. Carbon content gains down the soil profile were also evident, with values below 15.2 g SOC kg^{-1} starting from about 7.5 cm deep after 8 crops and about 12.5 cm deep after 16 crops. In TSP treatments, gains were on average 2.85 g C kg^{-1} between both sampling occasions, while for RPR the average was 1.85 g C kg^{-1} (Table S2). Considering estimations of both above-ground (Table S5) and root dry-matter production (30% of the total above ground dry-matter), and an average content of 40% total C in plant tissue dry-matter (Lovato et al., 2004; Costa et al., 2008), the average conversion of C inputs via crops residues into SOC in the 0-25 cm layer varied between 6.9% and 9.7%.

Similar to SOC, the last 8 crops contributed to increase Po contents near the soil surface (Figure 6). However, in deeper layers contents lower than 75 mg Po kg^{-1} occupied a greater soil volume after 16 crops, revealing diminished Po contents below 15 cm. Differences in Po concentration distributions between treatments at each sampling occasion did not follow a well-defined pattern, in contrast to what was observed in other variables.

The labile inorganic P fraction, represented by Mehlich-1 P contents, showed a similar spatial distribution to that observed in total P (Figure 7). The effects of P placement were well marked, with the highest values observed in the crop row region in band-applied P fertilizer treatments, with point estimates up to 74.6 mg kg^{-1} with TSP and 162 mg kg^{-1} with RPR after 16 crops. A point maximum of 2.9 mg kg^{-1} Mehlich-1 P was observed in the control treatment after 16 crops (Figure S1). Band-application treatments revealed a significant deepening of the 3 mg kg^{-1} frontier (Figure 7) while broadcast treatments, on the other hand, presented a higher soil profile volume occupied by Mehlich-1 P contents greater than 12 mg kg^{-1}, the critical level recommended for the region with the use of water soluble P sources (Sousa & Lobato, 2004; Oliveira et al., 2019). After 16 crops, that volume was 21.4% under broadcast fertilization while under band-application 14.7% of the volume surpassed this level in evaluations down to 25 cm deep with TSP applications. The average Mehlich-1 P contents down to 20 cm were 1.2

mg kg^{-1} for the control, and 7.7 mg kg^{-1} and 9.3 mg kg^{-1} for TSP broadcast and band applications, respectively (Table S3).

Broadcast treatments showed higher Moran's bivariate index values for the correlation between the spatial distribution of SOC and P fractions in both sampling occasions and for both P sources (Table S4). This association was strengthened after the last 8 crops. Though weaker, correlations were also significant for band-application treatments. Po and SOC also showed high levels of correlation in both occasions and in all treatments.

Table S5 indicates 17.8% lower dry-matter production and 14.2% lower estimated P turnover means for treatments under RPR fertilization in relation to those under TSP after 16 crops. This is in accordance with increased average SOC contents under TSP after the second phase of the experiment, although contents were similar after the first phase (Table S3). Po contents were similar between both P sources in both phases (Table S3), despite reduced estimated P turnover in RPR treatments (Table S5).

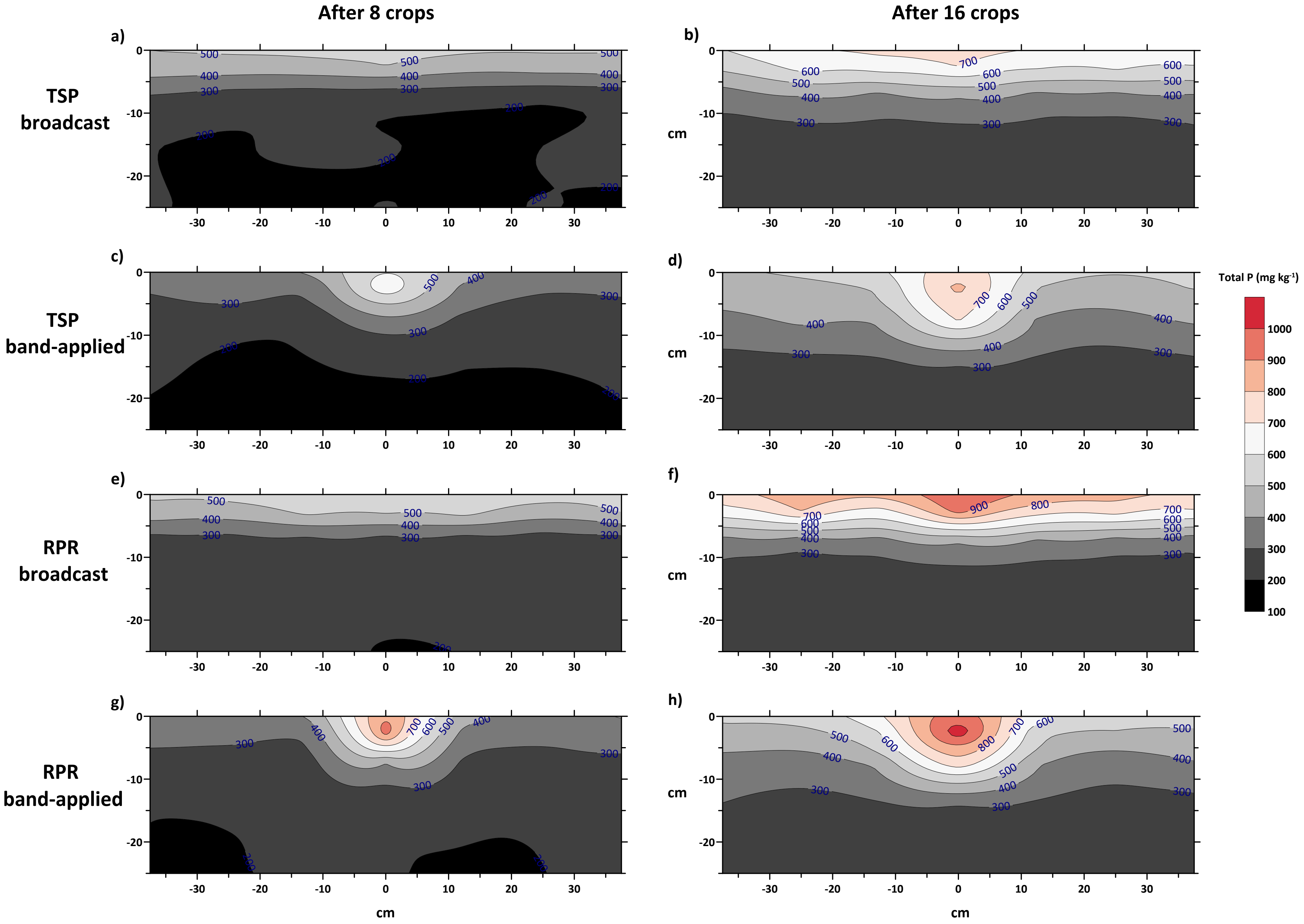

Figure 4: Spatial distribution of total P (mg P kg^{-1} soil) in the soil profile vertically down to 25 cm and horizontally to 37.5 cm on each side of the corn crop row, i.e, up to the center of the interrow. TSP: triple superphosphate; RPR: reactive phosphate rock.

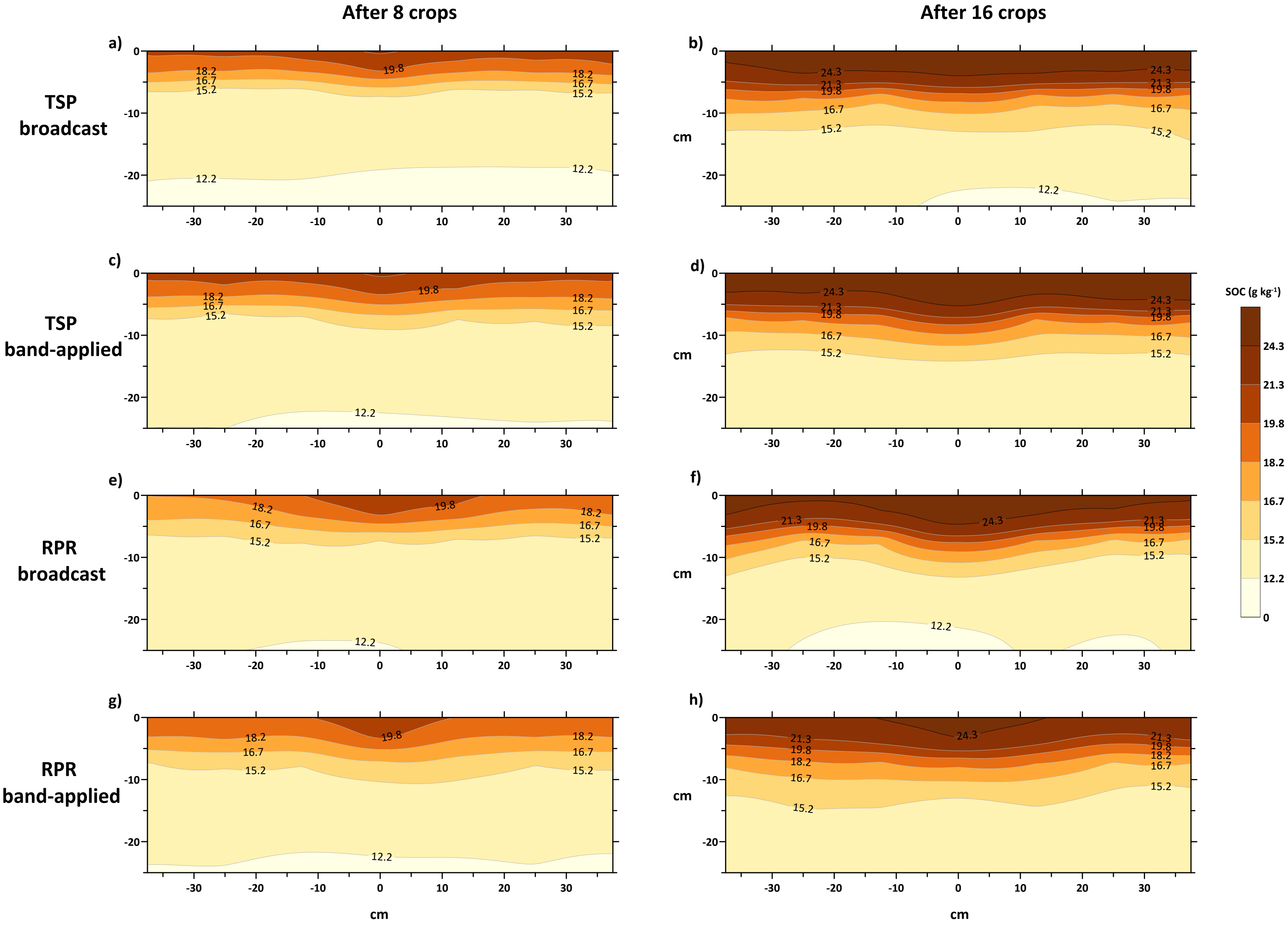

Figure 5: Spatial distribution of soil organic C (SOC) (g kg^{-1} soil) in the soil profile vertically down to 25 cm and horizontally to 37.5 cm on each side of the corn crop row, i.e, up to the center of the interrow. TSP: triple superphosphate; RPR: reactive phosphate rock.

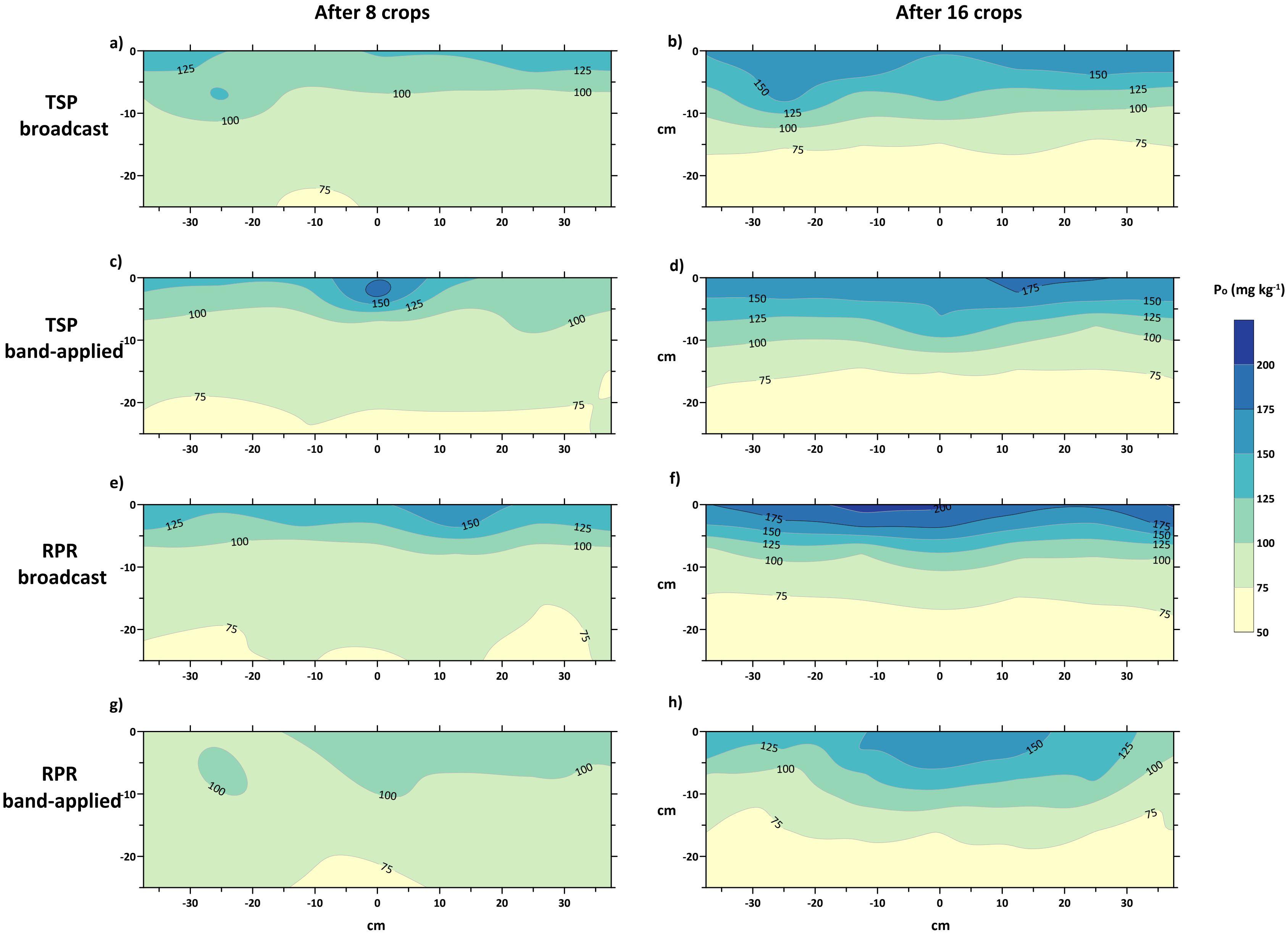

Figure 6: Spatial distribution of total organic P (mg kg^{-1} soil) in the soil profile vertically down to 25 cm and horizontally to 37.5 cm on each side of the corn crop row, i.e, up to the center of the interrow. TSP: triple superphosphate; RPR: reactive phosphate rock.

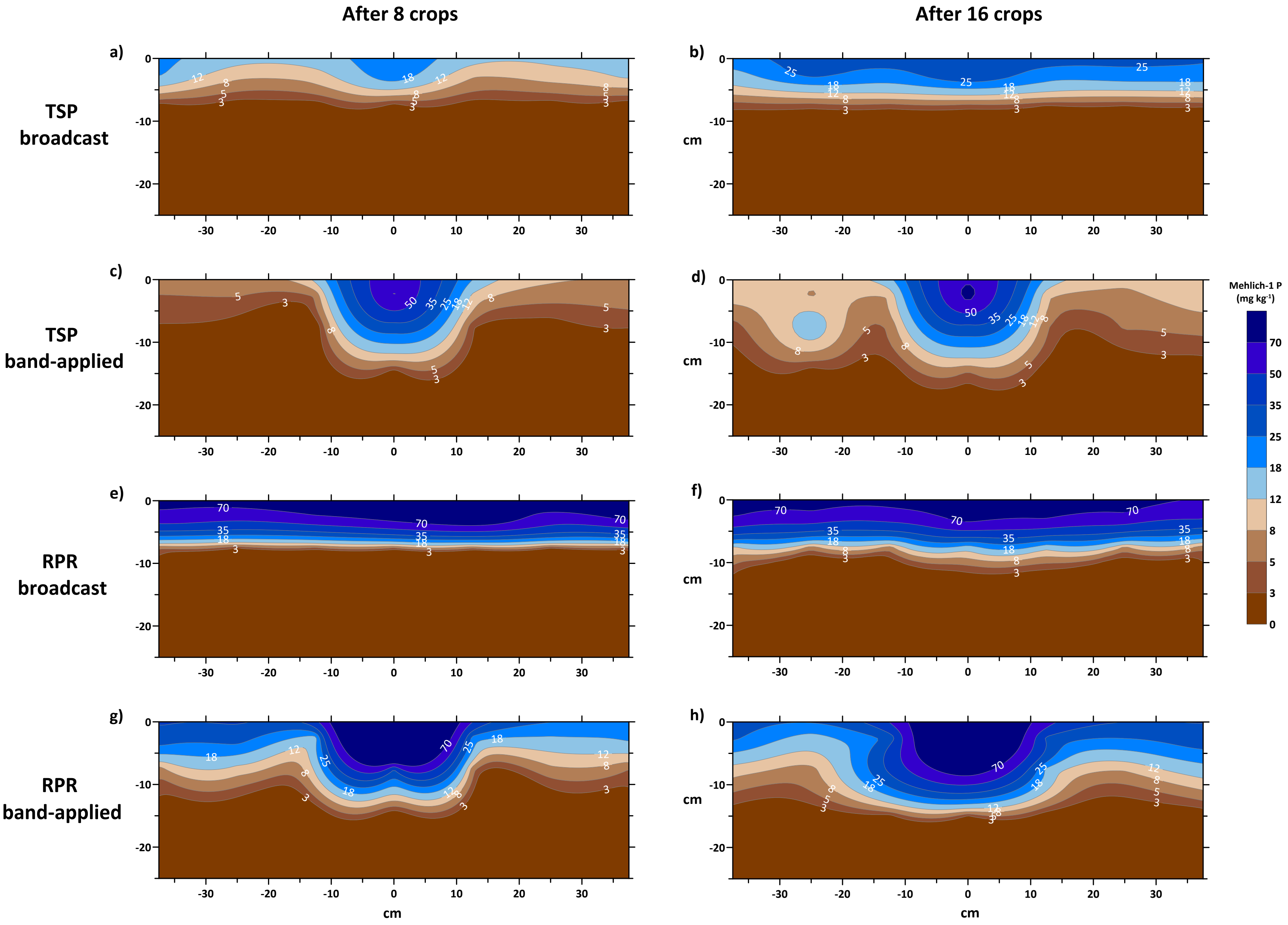

Figure 7: Spatial distribution of Mehlich-1 P (mg kg^{-1} soil) in the soil profile vertically down to 25 cm and horizontally to 37.5 cm on each side of the corn crop row, i.e, up to the center of the interrow. TSP: triple superphosphate; RPR: reactive phosphate rock.

5.5 DISCUSSION

5.5.1 The evolution of yields and P and SOC spatial distributions

The less pronounced differences in crop yields between the four fertilized treatments in phase 2, after 8 crops (Figure 2), is due to the increased soil P stocks in all fertilized treatments. These results are part of a set of treatments evaluated in our previous work, which also involved treatments under corrective P fertilization before the establishment of the first crop (Oliveira et al., 2020a).

Comparisons between both sampling occasions illustrate the slow but effective movement of P down the profile of a clayey Oxisol, especially in the levels of total P and Mehlich-1 P (Figures 4 and 7), that could not be identified by previous long-term studies (Calegari et al., 2013; Tiecher et al., 2017). When fertilizer is broadcast, P movement down might be supported by root growth and death in the subsoil and mesofauna biological activity, which is consistent with the increase of SOC and Po down the soil profile (Figures 5 and 6), although this seems to be limited. When band-applied, soil disturbance in the planting process and placement about 5 cm below the soil surface is the major driver to increasing P levels in depth, which adds to the naturally occurring processes as in broadcast application. Phosphate derived from RPR was able to move as far down as that derived from TSP, probably because of its lower solubility, with part of applied P remaining as rock phosphate particles, less prone to P adsorption (Prochnow et al., 2006). Phosphate descent in the soil profile would thus be mainly related to mechanical movement of those particles and biological activities rather than P leaching, which is normally only seen at very high P concentrations (Heckrath et al., 1995).

Gains in SOC were related to the positive balance between C inputs via plant tissues and losses via microbial mineralization, a well-known phenomenon in conservationist systems (Jerke et al., 2012; Coonan et al., 2019). Calculated SOC gains between sampling occasions are in accordance with Sá et al. (2014) and Nunes et al. (2011), who estimated that 8.2% of the total C added via crop residues in a no-till system with millet as cover crop was incorporated into the soil organic matter. Gains in SOC were thus probably related to both the gradual establishment of the NT system and the boosted crop yields in the second phase of the experiment (Figure 2, Table S5), due to increased P stocks (Figure 3). According to regional studies, average SOC contents higher than 19.8 g kg^{-1} in the 0-20 cm layer are well correlated with maximum grain crop yields, because high yielding crops allow high amounts of residue inputs to the soil and consequently SOC maintenance and buildup (Sousa & Lobato, 2004; Lopes et al., 2013; 2018).

Both spatial distribution evaluations of the soil attributes were performed after the corn crop (i.e, after the 8th and 16th crops). Because the experiment consisted of a rotation between soybeans and corn crops, planted with different row spacings (0.45 m and 0.75 m, respectively), the horizontal 75 cm width evaluated in this study necessarily comprehended two soybeans crop rows from the previous soybeans growing seasons (i.e, the 7th and 15th crops), since the planting direction was always the same (perpendicular to the terrain slope). Nevertheless, this was only noticeable in the distribution of Mehlich-1 P contents in the TSP band-applied treatment after 16 crops, where an increased P content is found about 25 cm to the left of the corn row, which is probably related to residual fertilizer applied at the soybean row in the 15th experimental crop. The other soybean row should thus be localized 20 cm to the right of the corn row, but no increased P level was verified. None of the two soybeans rows could be identified in the RPR band-applied treatments either, despite the longer residual effect of this source (Oliveira et al., 2019). Possible hypotheses are that: 1) soil sampling did not incorporate the previous soybean crop furrow, although 6 subsamples were taken in each plot for each composite sample and that sampling comprised 47% of the horizontal distance, since 5 cm diameter cylindrical soil core samplers were used down to 10 cm in the 7 sampling positions (Figure 1); 2) that the effect of the previous soybean row was diluted due to the shorter row spacing used in this crop (less fertilizer per length unit); 3) that the operations of opening furrows gradually disturbed the previous season's band-applied fertilizers; 4) that small variations in the direction of crops' furrows also diminished a possible pronounced effect of locally applying the previous crop's fertilizer; 5) and that the 6 subsamples taken to compose each "depth-row distance" combination composite sample in each plot (Figure 1), plus the effect of averaging soil analysis results across the 3 field replicates for geostatiscal interpolation, resulted in a dilution of the effect of the previous soybeans rows. However, the effect of the corn row was preserved in all cases due to easy visual identification and sample collection over the row briefly after the crop harvest. If the effect of not detecting the previous soybeans rows proved to be mainly due to the first hypothesis (insufficient soil sampling), other consequences may apply, for instance, not representing the actual dimensions of the high P concentrations found near the crop rows.

5.5.2 Fertilizer management effects on P spatial distribution

Band-application treatments were characterized by the P intensity factor, showing the highest values of labile P (Mehlich-1) observed, specifically in the crop row region where the fertilizer was applied; however, this effect was partly reduced with time. Zones with Mehlich-1 P equal or higher than 3 mg kg^{-1} in fertilized treatments were considered under the influence of P derived from fertilizer since the maximum content found in the control was 2.9 mg kg^{-1}. Therefore, band-application also showed increased soil volumes under the influence of P fertilizer, due to increased labile P contents in deeper layers, especially after all 16 crops. As a result, the effect of P placement became less pronounced after planting many crops as in the case of total P; this is probably related to constant P turnover in the main and cover crops (Table S5) as well as the different row spacing crops and the soil disturbance caused by these operations. Nevertheless, the band region was still clearly marked after 16 crops, which differs from Cambouris et al. (2017) who could not detect the fertilizer application zone in NT; this was attributed to the P balance being close to zero in that experiment.

Critical labile P levels are defined for specific soil layers (e.g., 0-20 cm or 0-10 cm), averaging a whole set of spatially irregular intensity distribution. Therefore, critical levels for specific soil regions or distribution patterns are hard to define. We then used local references based on critical levels in the different soil layers as a means of comparing availability across treatments. It should be noted that the Mehlich-1 method overestimates P availability in soils fertilized with rock phosphates in comparison with those that received soluble P sources, so a direct comparison is not possible; however, results can nonetheless be used to analyze P distribution in the soil and incipient results including a response curve for soils fertilized exclusively with RPR have already been obtained (Oliveira et al., 2019). That said, broadcast applications showed a greater soil volume occupied with high, above critical levels, labile P contents for both sources. Using the same RPR as in this study, Oliveira et al. (2019) obtained a critical Mehlich-1 STP level of 26.7 mg kg^{-1} with the use of this sparingly soluble source and results show that 24.4% of the soil volume under broadcast fertilization and 20.4% of that under band-application were found above this critical level in these treatments (Figure 7). A similar pattern was found for TSP, described above. This maintenance of high levels of P availability under broadcast fertilization may be related to the feedback effect of previous applications being more intense in this application method, because fertilizer is applied constantly (every crop) at the same place (soil surface). This increases the negative potential of surface soil particles (Barrow, 2015b, 2021) and consequently the effectiveness of newly added fertilizer (Barrow et al., 1998)

Phosphorus absorption has been suggested to occur predominantly from surface layers down to approximately 10 cm deep in NT, even when P is band-applied (Fernández and Schaefer, 2012; Oliveira et al., 2020b). There is evidence to conclude that plants can admirably manage different horizontal and vertical soil P distribution patterns and then produce similar yields with different application methods (Figure 2). This is consistent with the fact that plants grow roots towards a nutrient rich region when competing neighbors are present (Cahill et al., 2010), although when the bulk soil volume already presents sufficient P levels, roots may not respond to localized P applications (Farmaha et al., 2012). Thus, the long-term P fertilizer broadcast applications in the present study resulted in a probable beneficial spatial distribution of inorganic P fractions for crop absorption, with high contents in the 0-10 cm layer which coincides with roots development and high SOC contents, a possible direct and indirect promoter of P availability (Fink et al., 2016). Nonetheless, many crops respond well to band-applications, especially if nitrogen is also provided to non N fixing crop species (Novais and Smyth, 1999; Nkebiwe et al., 2016). It is worth noting that soil tillage, mechanically incorporating P down the soil profile, has a much greater effect on root growth at depth than the choice of P placement in NT (Nunes et al., 2021). Before establishing NT, it is thus recommended to increase P levels at depth with the incorporation of P fertilizer at the appropriate rate (Oliveira et al., 2020a); nonetheless, this was not done in the present study so that the effects of treatments on P and SOC spatial distributions could be better assessed.

Since inorganic P exists in the soil in a lability degree continuum, and not in discrete categories of different availabilities (Barrow et al., 2018, 2020), total P and the labile fraction Mehlich-1 showed high spatial correlations (Table S4), in a probable equilibrium between phosphate diffused into the mineral phase and that still adsorbed onto surface charges. Mainly as a constituent of the soil organic matter, the distribution of Po was highly correlated with that of SOC (Table S4). Despite limitations of the ignition method used to assess Po, especially in highly weathered soils where an overestimation is expected (Turner et al., 2005), these would have affected all treatments equally, probably not compromising the characterization of the spatial distribution of this P fraction. Nevertheless, Po represented only around 30% of the total soil P (Table S2), less than circa 50% found in the south region of Brazil (Tiecher et al., 2012).

5.5.3 Considerations on P run-off risks and soil sampling strategies

Phosphorus accumulation at the soil surface in broadcast treatments represents a potential risk of water contamination and eutrophication due to water run-off in cases where crop residues at the soil surface are sparse and/or field slope is high (Dodd and Sharpley, 2015; Gatiboni et al., 2020). Also, the effect of water shortage must be investigated as P concentration near the surface might negatively affect P uptake and crop growth, although that was not the case in the study of Hansel et al. (2017) with no-till soybeans submitted to different water stress conditions. These authors compared TSP broadcast application with banding the fertilizer 5 cm deep and 5 cm to the side of the crop row, placement strategies similar to those used in the present study.

The present study results may help the decision-making process of defining soil sampling strategies to be adopted in a field, according to the P fertilization management adopted. Nonetheless, no single numerical result is able to represent the spatial irregularities of a field. Band (row) spacing, P rate and soil adsorption capacities are factors influencing the ideal ratio of between-bands and in-band sampling locations (Kitchen et al., 1990). Based on this study, the weighed soil profile for the Mehlich-1 mean contents of the different layers using 7 horizontal positions, consisting of one in the crop row for every 6 between-bands (Figure 1), provided significant correlations with the kriged soil profile means for band-application. For example, weighed Mehlich-1 means in the 0-20 cm layer for TSP and RPR band-applied treatments after 16 crops were 8.2 mg kg^{-1}and 19.0 mg kg^{-1}, respectively, while the interpolated map means for the same soil section were, respectively, 9.3 mg kg^{-1} and 21.7 mg kg^{-1} (Table S3).

5.6 CONCLUSIONS

P application methods significantly affected the distribution of P fractions through the soil profile, with total and labile P accumulation in the application zone, i.e, at the soil surface in broadcast applications and at the crop row in banding, irrespective of the P source. The main effect of the P source was on increased labile Mehlich-1 P contents when RPR was used, but that was mainly related to the acidic characteristic of the extraction solution, and the contents must be interpreted accordingly.

A positive P input-output balance (soil P build-up) was reflected in increased soil P fraction contents after the last eight crops and allowed a vertical enrichment of inorganic P down the soil profile under band application. Under broadcast application, P movement down the soil profile was more discrete, and a more detailed sampling in depth would be required to better understand this migration.

Soil volumes with high contents of Mehlich-1 P (>12 mg kg^{-1}) were higher under broadcast than under band application. This was probably related with the feedback effect of constantly applying P fertilizer at the same place during broadcast treatments (at the soil surface), saturating adsorption sites and allowing more phosphate from fertilizer to remain in labile forms. On the other hand, soil volumes under the influence of P fertilizer (>3 mg kg^{-1}) were higher under band application than under broadcast. This must be mainly due to application at depth in sowing operations.

The increases in SOC that occurred in the last 8 crops were in accordance with regional estimates of the conversion efficiency of C present in plant residues into SOC. The P management strategy was not related to SOC spatial distribution, i.e, a uniform horizontal distribution and pronounced vertical content gradient was found irrespective of P placement or source for this attribute.

The similar spatial distributions of SOC and Mehlich-1, and total P fractions when fertilizer was broadcast (i.e, horizontally uniform and decreasing rapidly with depth) may be beneficial for P use efficiency, because SOC is considered a promoter of P availability. However, this spatial coincidence cannot be considered a cause-effect relationship, but instead a fortunate coincidence that may improve P nutrition under broadcast application, allowing these treatments to match yields obtained under band application, a method considered to improve P nutrition. As a result, irrespective of P placement, cultivated crops were able to adapt very effectively to the irregularly distributed soil P and achieve high yields, especially with TSP.

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SUPPLEMENTARY MATERIAL FOR CHAPTER II

Table S1: Coefficient of determination (r^2) of the linear regression between the observed values and kriging estimates, and between the observed values and the cross-validation estimates. All values for observed x kriging estimates were significant in the F test ($P < 0.01$).

	Total P		**SOC**		**Total Po**		**Mehlich-1 P**	
	After 8 crops	**After 16 crops**	**After 8 crops**	**After 16 crops**	**After 8 crops**	**After 16 crops**	**After 8 crops**	**After 16 crops**
				Observed x Estimates				
Control	0.9998	0.9999	0.9999	0.9999	1.0000	0.9998	0.9335	0.9999
TSP Broacast	0.9998	0.9998	0.9999	1.0000	0.9999	0.9999	0.9998	0.9985
TSP Band-applied	0.9997	0.9996	1.0000	0.9999	0.9996	0.9999	0.9998	0.9990
RPR Broadcast	0.9999	0.9999	0.9999	1.0000	0.9998	0.9999	0.9985	0.9985
RPR Band-applied	0.9997	0.9994	1.0000	1.0000	0.9999	0.9999	0.9985	0.9988
				Observed x Cross-validation estimates				
Control	0.2138	0.6529	0.7874	0.8533	0.9015	0.6402	0.5173	0.6374
TSP Broacast	0.8929	0.8973	0.8525	0.9160	0.7324	0.8495	0.3741	0.7855
TSP Band-applied	0.5495	0.7789	0.9066	0.8955	0.4602	0.9058	0.4962	0.1922
RPR Broadcast	0.7459	0.8095	0.8667	0.8955	0.6809	0.8354	0.8264	0.7295
RPR Band-applied	0.3373	0.7465	0.9042	0.8894	0.5502	0.7625	0.5585	0.4300

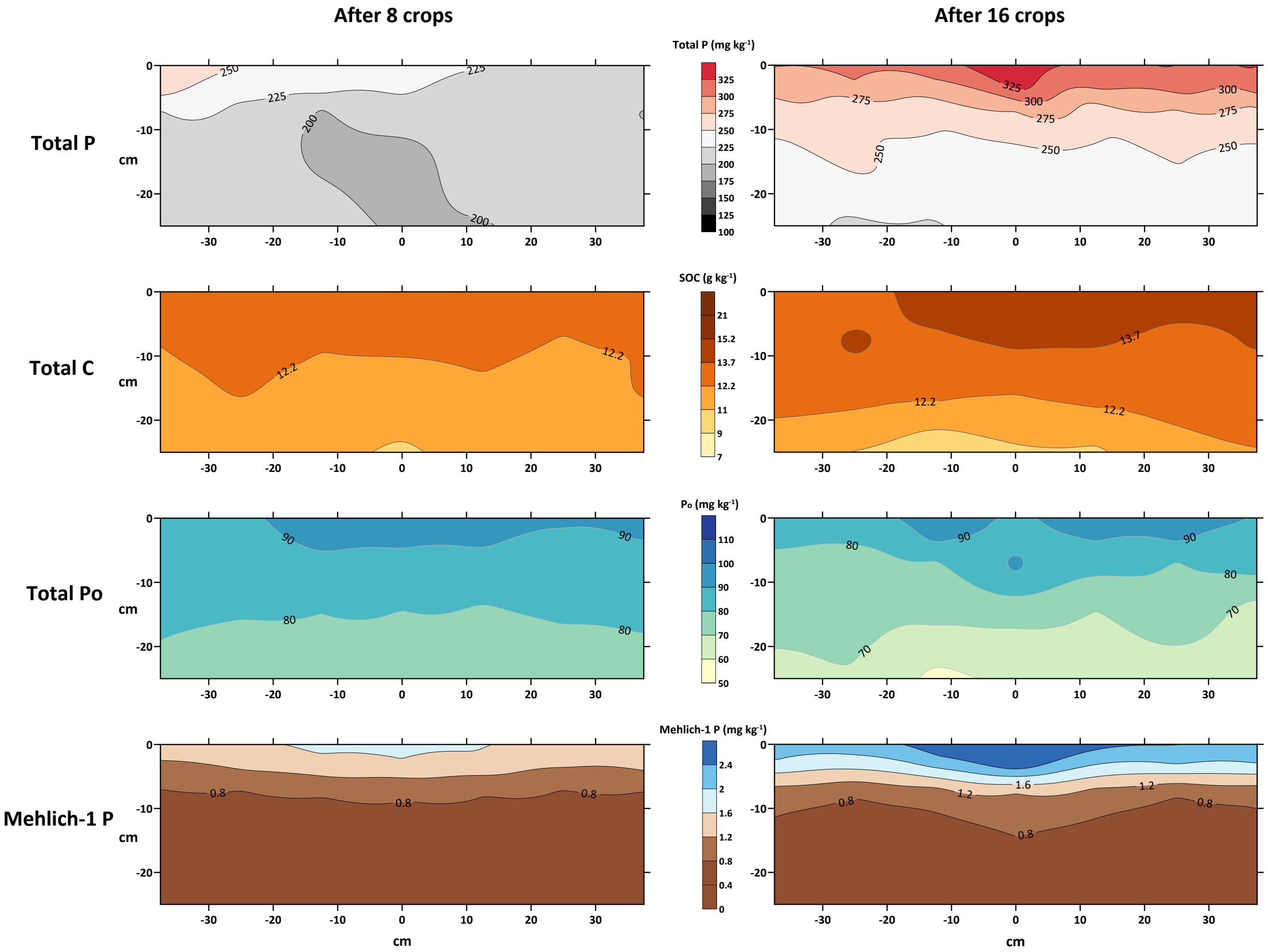

Figure S1: Spatial distribution of different soil P fractions and total SOC in the control treatment with no P applications after 8 and 16 crops. Total Po: total organic P.

Table S2: P fractions and SOC mean contents and standard deviations (SD) in the evaluated soil profile, considering the ordinary kriging estimates in 13,600 grid nodes in the 75 x 25 cm soil section.

		Total P		**SOC**		**Total Po**		**Mehlich-1 P**	
Treatment	**After**	**mg kg^{-1}**	**SD**	**g kg^{-1}**	**SD**	**mg kg^{-1}**	**SD**	**mg kg^{-1}**	**SD**
Control	**8 crops**	213.2	12.8	12.1	0.5	82.9	5.2	0.8	0.3
	16 crops	260.8	27.2	12.9	1.0	76.0	8.7	1.0	0.6
TSP broadcast	**8 crops**	262.9	104.5	14.2	2.7	93.0	17.7	3.6	4.9
	16 crops	356.3	150.8	17.1	4.7	101.2	34.1	6.4	9.3
TSP band-applied	**8 crops**	254.5	88.2	14.8	2.6	90.8	20.9	5.8	11.1
	16 crops	360.7	136.1	17.6	5.0	101.4	35.8	7.7	11.8
RPR broadcast	**8 crops**	281.4	112.5	14.7	2.2	92.7	23.2	16.7	29.0
	16 crops	381.6	198.9	16.5	4.6	102.1	40.5	17.1	26.7
RPR band-applied	**8 crops**	277.6	116.4	14.9	2.4	89.9	11.1	16.2	34.9
	16 crops	372.0	168.8	16.8	3.4	97.4	29.8	17.5	28.2

Table S3: P fractions and SOC mean contents and standard deviations (SD) in the evaluated soil profile, considering the ordinary kriging estimates in 13,600 grid nodes in the 75 x 20 cm soil section.

		Total P		**SOC**		**Total Po**		**Mehlich-1 P**	
Treatment	**After**	**mg kg^{-1}**	**SD**	**g kg^{-1}**	**SD**	**mg kg^{-1}**	**SD**	**mg kg^{-1}**	**SD**
Control	**8 crops**	215.1	13.6	12.3	0.4	84.6	4.5	0.9	0.4
	16 crops	267.2	26.9	13.3	0.7	78.6	7.7	1.2	0.7
TSP broadcast	**8 crops**	279.4	110.1	14.9	2.7	97.1	17.8	4.4	5.4
	16 crops	386.1	152.9	18.2	4.7	109.5	33.4	7.7	9.8
TSP band-applied	**8 crops**	270.0	93.0	15.4	2.6	95.2	21.4	7.1	12.0
	16 crops	390.8	135.0	18.7	5.0	110.0	35.4	9.3	12.4
RPR broadcast	**8 crops**	300.5	120.1	15.2	2.2	97.2	24.3	21.0	31.5
	16 crops	418.9	209.2	17.6	4.5	111.0	41.3	21.1	28.2
RPR band-applied	**8 crops**	296.4	123.9	15.6	2.2	93.0	10.3	20.3	38.1
	16 crops	404.9	172.1	17.6	3.4	104.7	29.0	21.7	30.0

Table S4: Global bivariate Moran's index, representing the spatial correlation between the distribution of two variables, in different treatments and phases of the experiment and the associated significance of the correlation.

		Moran's *I* after 8 crops			**Moran's *I* *p*-value after 8 crops**		
		Total P	**SOC**	**Po**	**Total P**	**SOC**	**Po**
Control	**SOC**	0.53			0.001		
	Po	0.54	0.94		0.001	0.001	
	Mehlich-1 P	0.67	0.73	0.69	0.001	0.001	0.001
TSP broadcast	**SOC**	0.96			0.001		
	Po	0.87	0.90		0.001	0.001	
	Mehlich-1 P	0.76	0.74	0.65	0.001	0.001	0.001
TSP band-applied	**SOC**	0.72			0.001		
	Po	0.51	0.68		0.001	0.001	
	Mehlich-1 P	0.17	0.23	0.18	0.016	0.008	0.005
RPR broadcast	**SOC**	0.90			0.001		
	Po	0.95	0.93		0.001	0.001	
	Mehlich-1 P	0.94	0.87	0.89	0.001	0.001	0.001
RPR band-applied	**SOC**	0.59			0.001		
	Po	0.55	0.86		0.001	0.001	
	Mehlich-1 P	0.13	0.23	0.17	0.006	0.005	0.043

		Moran's *I* after 16 crops			**Moran's *I* *p*-value after 16 crops**		
		Total P	**SOC**	**Po**	**Total P**	**SOC**	**Po**
Control	**SOC**	0.66			0.001		
	Po	0.82	0.75		0.001	0.001	
	Mehlich-1 P	0.88	0.65	0.77	0.001	0.001	0.001
TSP broadcast	**SOC**	0.97			0.001		
	Po	0.96	0.98		0.001	0.001	
	Mehlich-1 P	0.88	0.87	0.77	0.001	0.001	0.001
TSP band-applied	**SOC**	0.77			0.001		
	Po	0.82	0.97		0.001	0.001	
	Mehlich-1 P	0.23	0.26	0.29	0.017	0.007	0.003
RPR broadcast	**SOC**	0.89			0.001		
	Po	0.96	0.96		0.001	0.001	
	Mehlich-1 P	0.90	0.86	0.88	0.001	0.001	0.001
RPR band-applied	**SOC**	0,72			0.001		
	Po	0.58	0.78		0.001	0.001	
	Mehlich-1 P	0.25	0.36	0.30	0.013	0.002	0.004

Table S5: Total above-ground plant tissue dry-matter production and corresponding P turnover in crops tissues in different phases of the experiment, averaged between P application methods in fertilized treatments.

Treatment	**Above ground dry-matter production (kg ha^{-1})**								
	1st to 8th crops (sum)			**9th to 16th crops (sum)**			**Total**		
	Soybeans	**Corn**	**Cover Crop**	**Soybeans**	**Corn**	**Cover Crop**	**1st to 8th crops**	**9th to 16th crops**	**Overall total**
Control	2,735.4	1,886.7	3,986.3	1,885.9	1,035.8	2,330.0	8,608.4	5,251.7	13,860.1
TSP	26,596.1	24,103.4	40,423.5	29,552.3	42,001.9	56,883.5	91,123.0	128,437.7	219,560.8
RPR	17,492.8	20,071.9	25,363.4	27,039.8	38,987.3	51,502.3	62,928.1	117,529.4	180,457.5
	P turnover (kg P ha^{-1})								
	1st to 8th crops (sum)			**9th to 16th crops (sum)**			**Total**		
	Soybeans	**Corn**	**Cover Crop**	**Soybeans**	**Corn**	**Cover Crop**	**1st to 8th crops**	**9th to 16th crops**	**Overall total**
Control	6.8	0.8	3.2	4.7	0.4	1.9	10.8	7.0	17.9
TSP	66.5	12.1	39.9	73.9	21.2	56.1	118.5	151.2	269.7
RPR	43.7	8.5	31.3	67.6	16.6	63.6	83.6	147.8	231.5

CHAPTER III

SOIL PHOSPHORUS SORPTION AFTER SIXTEEN YEARS OF PHOSPHATE FERTILIZATION MANAGEMENT

6 CHAPTER 3. SOIL PHOSPHORUS SORPTION AFTER SIXTEEN YEARS OF PHOSPHATE FERTILIZATION MANAGEMENT

6.1 ABSTRACT

Crop nutrition with phosphate in highly weathered soils has been thoroughly investigated in the past decades. However, the effects of phosphorus (P) accumulation on the efficiency of newly applied P fertilizers have had little attention, and may vary according to management practices. The sorption properties of soil samples taken after the 8th and 16th crops of a long-term experiment involving the application of either a soluble or a sparingly soluble P source at the crop row or broadcast were therefore assessed via sorption curves and related to soil total P. Although P application significantly reduced P sorption capacity of natural soils, the effects of clearing the native vegetation for crop production with the application of soil conditioners as lime had the largest impacts on reducing P sorption capacity. The effects of P fertilization management also showed significant differences on P sorption, though on a smaller scale. Reduced sorption capacity was found in the region of fertilizer application (i.e, on the crop rows in band application) and in the 0-5 cm soil layer of all treatments. Triple superphosphate (TSP) showed greater capacity to reduce P sorption of soils in comparison to the less soluble source (Gafsa reactive phosphate rock - RPR), even with circa 33% lower accumulated residual fertilizer P stocks. On the other hand, extended residence time as RPR fertilizer particles in soil prevented P adsorption up to the time of crop needs, improving RPR residual effects and benefiting yields by 3% even 16 years after application, in relation to TSP. A reduction in sorption capacity between the 8th and 16th crops was probably related to gains in residual fertilizer stocks in soil. It was also found that, despite the extremely high P sorbing capacity of the studied weathered soil, relatively low P doses, equivalent to 191 mg P kg^{-1} soil, were needed to significantly reduce sorption indexes, benefiting a sustainable use of phosphate fertilizers in these soils.

6.2 INTRODUCTION

The study of the phenomenon of P sorption in soils is dated from long ago (Russell and Prescott, 1916; Olsen and Watanabe, 1957). This can be explained by concerns regarding initial observations of the high affinity of phosphate to clay minerals, which, on the one hand, drastically reduces the possibility of leaching losses, however, on the other hand, can compromise P absorption by plants. Therefore, numerous studies have sought to relate the adsorption capacity of P to several characteristics of different soils, such as clay content, mineralogy, organic matter (OM) content and P balance and source (Roy et al., 2017; Yan et al., 2017; Yang et al., 2019; Alovisi et al., 2020).

Excessive P inputs to low sorbing soils in temperate zones have caused increased concerns regarding environmental problems, such as the eutrophication of water bodies (Haque, 2021) and the destination of P-rich manures and P mining efforts (Vandermoere et al., 2021). Not only inorganic P but also organic sources have caused concerns (Dodd and Sharpley, 2015); in addition, some tropical and subtropical soils also became a point of attention (Fischer et al., 2018; Gatiboni et al., 2020). Despite that, in central Brazil, one of the largest grain production regions in the world, P adsorption and consequently reduced P utilization efficiency by crops is still a concern (Roy et al., 2016, 2017). Roy et al. (2017) state that even after decades of P fertilization, the remaining P adsorption capacity was still very high and P saturation index, low, so that P application rates could probably not be envisaged in the short-term.

The preferential accumulation of P in “moderately labile” and “non-labile” forms (as said such) in highly weathered soils (Rodrigues et al., 2016), and the presence of fast P-reacting sites with high hysteresis levels (Guedes et al., 2016) support the view that most phosphate applied may become irreversibly adsorbed in these soils. Some argue that low solubility compounds are formed, but the presence of discrete phosphate fractions of differing solubilities in soils is questionable (Barrow et al., 2020b). Nonetheless, it has become widely accepted that once applied to a soil, solid-state diffusion of P into the interior of soil colloids reduces the electric potential of the surface and thus its affinity to new additions of phosphate, improving the efficiency of following P fertilizers applications (Barrow et al., 1998; Barrow and Debnath, 2014). It means that although a “P tax” (Roy et al., 2016) may indeed have to be paid to soils, it does not come without a positive feedback.

The effects of P fertilizer management on sorption capacity have received little attention, though. Most studies involving P source are related to organic fertilizer applications (Yan et al., 2017), while studies involving spectroscopy of P species in soil have found that clay minerals (e.g kaolinite) can adsorb as much P or even more than Fe and/or Al oxides (Antonangelo et al., 2020), corroborating a review study by Gérard (2016); these constituents are present in large amounts in tropical soils. In highly concentrated fertilizer bands, the decrease in pH may solubilize soil Al, leading to an initial precipitation of Al-P minerals and therefore reduced P availability (Meyer et al., 2021).

No-tillage soil management is often considered a promoter of P availability, what may be related to the reduction of soil P sorption capacity (Fink et al., 2016a; b), especially due to the effects of OM accumulation on diminishing P affinity for soil colloids or due to competition between organic anions and phosphate for sorption sites (Fink et al., 2016c). On the other hand, it has been suggested that OM breakdown may account for increased P levels in the soil solution that have not been considered in sorption experiments (Guppy et al., 2005), while at the same time maximum P sorption capacity might not be affected by soil tillage (Pavinato et al., 2010), once there are indications that OM delays but does not prevent adsorption o P by soils (Afif et al., 1995).

The objective of this study was to evaluate the soil P sorption properties as a function of phosphate fertilization management factors, such as P source, application method and P balance. Other soil attributes related to phosphate nutrition of crops, such as labile and total P, were also analyzed as possible rulers of P sorption capacity. The hypotheses are that the accumulation of P in soil reduces P sorption potential, increasing the efficiency of subsequent applications of this nutrient, and that this reduction occurs mainly in the regions of P application in the soil, according to fertilizer management.

6.3 MATERIALS AND METHODS

6.3.1 Characterization of the experimental area

A field trial involving the evaluation of low soil P correction strategies with phosphate and the management of maintenance phosphate fertilization with different P sources and methods of application was used as the basis for this study. This trial was installed in 1999 at the experimental station of Embrapa Cerrados, Brasília- Brazil, and was cultivated for 16 years with a rotation between soybeans and corn as main crops. The soil is classified as a dystrophic Red Latosol, with clay, silt and sand content of, respectively, 540, 50 and 120 g kg $^{-1}$ soil. There is a predominance of kaolinite, gibbsite and hematite in the clay fraction, and long and intense weathering processes are responsible for this soil's high natural acidity and low availability of macro and micronutrients. The region climate is classified as a Cwa according to Köppen's classification system (Alvares et al., 2013).

6.3.2 Experimental design

The experiment was designed as a three factors factorial involving P correction strategy, P maintenance source and fertilizer application method. The three P correction levels were: no P correction application or the application and incorporation in the soil of 105 kg P ha^{-1} as TSP (triple superphosphate) or as RPR (Gafsa reactive phosphate rock) before the first crop, in 1999. The four maintenance P source levels were: no P maintenance, or the application of 35 kg P ha^{-1} in every main crop (annual applications) of TSP, RPR or a mix in equal P parts of TSP and RPR (i.e, 17.5 kg P ha^{-1} of each). All P doses were based on total P contents. The third factor, application method, involved the following levels: broadcast surface application of the P fertilizer or band application at the crop row at the sowing occasion. Table 1 describes all factor levels combinations studied in the experiment.

Table 1: Description of the experimental treatments evaluated at the Embrapa Cerrados experimental station (Brasília, DF, Brazil) between 1999 and 2015. TSP: triple superphosphate; RPR: reactive phosphate rock; BR: broadcast; BA: band application.

Treatment	**P correction (105 kg ha^{-1})**	**P maintenance (35 kg ha^{-1})**	**Application method**	**Total P applied**	
				After 8 crops	**After 16 crops**
1	-	-	-	0	0
2	-	TSP	BR	280	560
3	-	TSP	BA	280	560
4	-	RPR	BR	280	560
5	-	RPR	BA	280	560
6	-	TSP+RPR	BR	280	560
7	-	TSP+RPR	BA	280	560
8	TSP	-	-	105	105
9	TSP	TSP	BR	385	665
10	TSP	TSP	BA	385	665
11	TSP	RPR	BR	385	665
12	TSP	RPR	BA	385	665
13	TSP	TSP+RPR	BR	385	665
14	TSP	TSP+RPR	BA	385	665
15	RPR	-	-	105	105
16	RPR	TSP	BR	385	665
17	RPR	TSP	BA	385	665
18	RPR	RPR	BR	385	665
19	RPR	RPR	BA	385	665
20	RPR	TSP+RPR	BR	385	665
21	RPR	TSP+RPR	BA	385	665

Not included P applied as that contained in gypsum: 7.4 kg ha^{-1} total up to the 8th crop and 2.3 kg ha^{-1} more between the 8th and 16th crops.

More details on crop cultivation and fertilizer characteristics can be obtained in Oliveira et al. (2020b) and Oliveira et al. (2022).

6.3.3 Soil sampling

All treatments

Samples were taken from all treatments after the last maize crop (16th crop, 2015), in the layers 0-10 cm, 10-20 cm and 20-30 cm, using a Dutch auger. For plots with broadcast fertilization, 20 subsamples were randomly taken to compose the composite sample of the respective plot. In the plots with fertilization in the crop row, directed samples were taken based on the orientation of the planting line, comprising one point over the crop row and another three equally spaced to each side of the row, up to the center of the interrows (Nicolodi et al., 2002). This procedure was repeated at three different locations in each plot in order to obtain the composite sample representative of the plot. This method was adopted since it better considers the effects of fertilizer placement and concentration on the planting row. The number of composite samples evaluated consists of 21 treatments, 3 soil layers and 3 field replicates, totaling 189 samples.

For P sorption analysis

For a more detailed evaluation of the P adsorption capacity as a function of fertilization management, the 5 treatments without application of corrective P fertilization were selected for stratified sampling considering both sampling position and soil layer. Positions were: at the previous crop row or in the middle of the interrows, while soil layers comprised the 0-5 cm and 5-10 cm depths. Composite samples were formed from subsamples taken from six different locations in each plot. A 5 cm diameter soil core sampler, also used for soil density evaluations, was used for these layers down to 10 cm. Sampling was performed both after 8 crop harvests (2007) and after 16 harvests (2015), totaling 2 sampling occasions, 5 fertilizer treatments, 2 soil layers, 2 sampling positions and 3 field replicates, giving 120 samples.

Natural vegetation soil

Three areas near the experiment and preserved with the original Cerrado vegetation were also sampled. A total of 20 subsamples were taken randomly in each of these areas to compose three composite samples. The evaluated layers were 0-5 cm, 5-10 cm, 10-20 cm and 20-30 cm. All soil samples were sieved to <2 mm and air dried and stored up to the occasion of soil analysis.

6.3.4 Soil analysis

Total P (Pt)

Soil Pt was determined by acid digestion in the presence of an oxidizing agent under heating in a digestion block (Brookes and Powlson, 1981; Hedley et al., 1982). Briefly, 7.5 ml of 18 M H_2SO_4 and 1 ml of a saturated solution of $MgCl_2$ were added to a digestion test tube containing 0.15 g of a sieved soil sample (<2 mm). The mixture was then heated for 2 hours in a digester block for 2 h at 200 °C. After this period, the temperature was reduced to 100 ºC in order to add 2 mL of H_2O_2 to each tube in two moments, with a slight agitation, at intervals separated by 1 hour. One hour after the last addition of the oxidizing agent, the temperature was increased to 180 °C for another 2.5 h, and the block was then switched off until the following day, when the dilutions were made and the P in the extract was determined colorimetrically (Murphy and Riley, 1962).

Total organic and inorganic P (Total Pi and Po)

The ignition method was used, although care must be taken in interpretation once it potentially overestimates Po in highly weathered soils (Turner et al., 2005). For every field sample, soil was weighed in duplicates containing 2 g each. One was submitted to ignition at 550 ºC for 1.5 hours (Pt_{ign}) in porcelain crucibles, while the other duplicate was maintained at room temperature. Both samples were then submitted to extraction for 16 hours with H_2SO_4 2.0 mol L^{-1}, in a soil:solution ratio of 1:8. The Po was therefore obtained by the difference in the P content of the two acid extracts (Hance and Anderson, 1962; Olsen and Sommers, 1982), analyzed by spectrophotometry at 820 nm (Murphy and Riley, 1962). Total Pi was obtained by the difference between Pt determined by acid digestion and Po obtained by this ignition method.

Mehlich-1 and Bray P

Mehlich-1 P was determined after extraction with a solution of H_2SO_4 0.0125 mol L^{-1} + HCl 0.05 mol L^{-1} in a soil:solution ratio of 1:10, followed by stirring for 5 minutes. After 16 hours of settling, the colorimetric method (Murphy and Riley, 1962) was used to determine the P content by spectrophotometry at 820 nm. For Bray P analysis, 5 g of soil was mixed for 1 min with 40 mL of a solution containing 0.025 mol L^{-1} HCl + 0.03 mol L^{-1} NH_4F (Bray and Kurtz, 1945). After filtration on quantitative filter paper, 5 mL of the filtrate were mixed with 5 mL of distilled water and 15 mL of a reducing solution (0.88 g of ascorbic acid + 10 mL of ammonium molybdate solution + 300 mL of deionized H_2O), and then P contents were determined by spectrophotometry at 680 nm wavelength.

Remaining P (P rem)

P rem was determined as the concentration of P remaining in solution after 5 min gentle mixing a soil sample in a solution containing initially 60 mg P L^{-1} (Embrapa, 2009). The background electrolyte of the solution was $CaCl_2.2H_2O$ at a concentration of 0.01 mol L^{-1}, and the soil:solution ratio was 1:10. After mixing, the solution was left to settle for 16 h before quantification of P in solution. The spectrophotometer used for all colorimetric readings was the Shimadzu UV-1800, owned by the Embrapa Cerrados Soil Chemistry Laboratory.

Sorption curves

The samples selected to evaluate the P adsorption capacity were stirred with 6 solutions containing different P concentrations (0, 5, 10, 20, 30 and 60 mg P L $^{-1}$), prepared out of a concentrated KH_2PO_4 solution and $CaCl_2$ at 0.01 mol L^{-1} as background electrolyte. Mixing was carried out in 40 mL centrifuge tubes, in a soil:solution ratio of 1:10, with 2.0 g of soil and 20 mL of solution, in addition to 2 drops of chloroform to inhibit biological activity (Nair et al., 1984). Stirring was performed on an orbital shaker at 120 rpm for 24 h at 25 °C. The samples were then centrifuged at 320,000 g, and the supernatant was separated for P content determination according to the colorimetric method (Murphy and Riley, 1962).

6.3.5 Residual P balance

The P input – output balance after each crop could be calculated based on all P inputs via fertilizers and soil conditioner (agricultural phosphogypsum) minus P offtake via harvested products (grains). The later was calculated based on yields and P concentrations in grains, which were analyzed via wet digestion with HNO_3 and $HClO_4$ (3:1, v:v) (Embrapa, 2009).

6.3.6 Leaf sampling and foliar P determination

Corn leaf samples were taken at the time of flowering (VT growth stage) in the useable area of the plots, subjected to drying at 60 ºC and then milled for P content analysis according to Embrapa (2009). Thirty leaves immediately below the corn cob insertion were taken from each plot to compose the representative sample. Determination of P in leaves was done by wet digestion, similarly to the grain P analysis described above.

6.3.7 Statistical analysis

The sorption curve models were fitted to the Freundlich model using the Simplex algorithm, implemented in the Basic language in the QB64 program, in order to find the coefficients of the models that provide the lowest residual sum of squares of the differences of the logs of observed and predicted final P concentrations in solution. The Freundlich equation used is described as follows:

$$S = ac^{b} - q \quad \text{(Eq. 1)}$$

Where S is the amount of P sorbed (mg kg^{-1} soil), c the final concentration of P in the solution (mg L^{-1}), and a, b and q coefficients estimated by the algorithm. According to Barrow (2021), the coefficient a is related to the amount of reacting surfaces in the soil sample and their affinity for phosphate. According to this author, it can be an important measure of soil P buffering capacity, giving indications of composition and previous reactions with phosphate. The b coefficient reflects the heterogeneity of the reacting surfaces and is expected to be somewhat stable for a given soil type irrespective of P fertilization; mathematically, it represents the curvature of the model. The q parameter is equal to the amount of P that could be desorbed if solution concentration could be maintained at zero. After initial evaluations, the b coefficient was found to be best if fixed as 0.26 for the surface 0-5 cm soil layer and as 0.29 for the 5-10 cm layer, with the other model coefficients freely estimated by the program. These values gave the lowest residual sum of squares, while the resulting total sum of squares of all soil samples models was not significantly greater than when there were individual values of the b coefficient for each soil sample. A sorption index was then calculated as the product a x b, in an attempt to describe the sorption properties of soils as a single value, instead of a curve (Barrow, 2000, 2008). This index is equal to the instantaneous slope of the sorption curve at the solution concentration of 1.0 mg P L^{-1}, and is therefore influenced by the curve fitted to all observations (Barrow and Debnath, 2014).

It must be noted that once sorption curves relate two variables that are not independent (S in the y-axis is calculated from c in the x-axis), traditional non-linear regression approaches should not be used, once the main principle of independence of the variables of regression theory is not met (Barrow, 2008). That way, the resolution of two simultaneous equations must be considered, being the sorption equation (Eq. 1) and the soil:solution equation (S= soil: solution ratio times (initial concentration – final observed concentration)) (Barrow, 2008). The coefficients of the sorption curve models were compared based on the model identity test (Carvalho et al., 2010; Regazzi and Silva, 2010).

A 3-way analysis of variance (ANOVA) was also used to compare the effects of treatments on several soil attributes and production components of the last (corn) crop cultivated in the experiment. The normality and homoscedasticity of the residuals were checked according to the Shapiro-Wilk and Bartlett tests, respectively ($P<0.05$). When the F test noted significant differences between treatments, the Tukey test was used to compare the means ($P<0.05$).

In addition, a multivariate analysis was performed on variables related to both soil and crop attributes. With the software XLSTAT (Adinsoft, 2013), total P, Pi and Po, residual P, Mehlich-1 and Bray P, and also yield, foliar P and P rem were subjected to a Principal Component Analysis (PCA) in order to identify the variables that mainly contribute to the linear combinations on the independent orthogonal axis.

6.4 RESULTS

The main differences on P sorption capacity were verified between soils under natural vegetation, the control without P application and soils fertilized with P on the long-term (Figure 1a). In comparison to the natural vegetation Cerrado soil, which presented a pH (H_2O) of 4.5, the control treatment in the experiment, which was fertilized with all nutrients and soil conditioners (as lime and gypsum) necessary for crop development except with P, presented a significantly reduced P sorption capacity and a pH (H_2O) of 5.2. Fertilization during 16 years significantly reduced P sorption in comparison with the control (Figure 1a).

The effects of P fertilization period and P source on P sorption capacity are shown in Figure 1b. Soils fertilized with the soluble P source presented a lower capacity to adsorb P from solution than those with the sparingly soluble fertilizer, in both evaluation occasions. Similarly, for both P sources, the later evaluation occasion (after 16 crops) showed soils with reduced sorption capacities than those sampled after 8 crops. Therefore, irrespective of P source, a positive P balance in the soil resulted in decreased P sorption capacity. For the TSP fertilized treatment, the calculated P balance considering all P inputs as fertilizer minus outputs as harvested grains resulted in a P accumulation of 68 kg ha^{-1} between the end of 8th and 16th crops. In the RPR treatment, this accumulation was of 109 kg P ha^{-1}. On both occasions, TSP fertilized soil presented lower sorption capacity than those that received RPR (Figure 1b), but that happened only in the 0-5 cm soil layer (Figure 1c); sorption properties were not influenced by P source in the 5-10 cm soil layer (Figure 1c). TSP was more effective in reducing P sorption capacity in the soil despite the lower amounts of residual P derived from fertilizers in the soil in this treatment in both evaluation occasions. For instance, after the 8th crop, the TSP treatment soil shown in Figures 1b and 1c contained a P stock of 61.5 kg ha^{-1} less than that in the RPR treatment at that same time. After the 16th crop, that difference was of 102 kg P ha^{-1} less than the RPR treatment soil.

Regardless of P fertilizer placement, soil P sorption capacity was lower at the crop row sampling position than that observed at the crop interrow, considering the TSP fertilized treatment after the 16th crop and the 0-5 cm layer (Figure 1d). Although non statistically significant, sorption when fertilizer was band applied was visually lower than broadcast fertilization when soils were sampled at the crop row position (Figure 1d). Conversely, slightly higher sorption was observed in the interrows of the band application treatment when compared to the same sampling positions in the broadcast treatment.

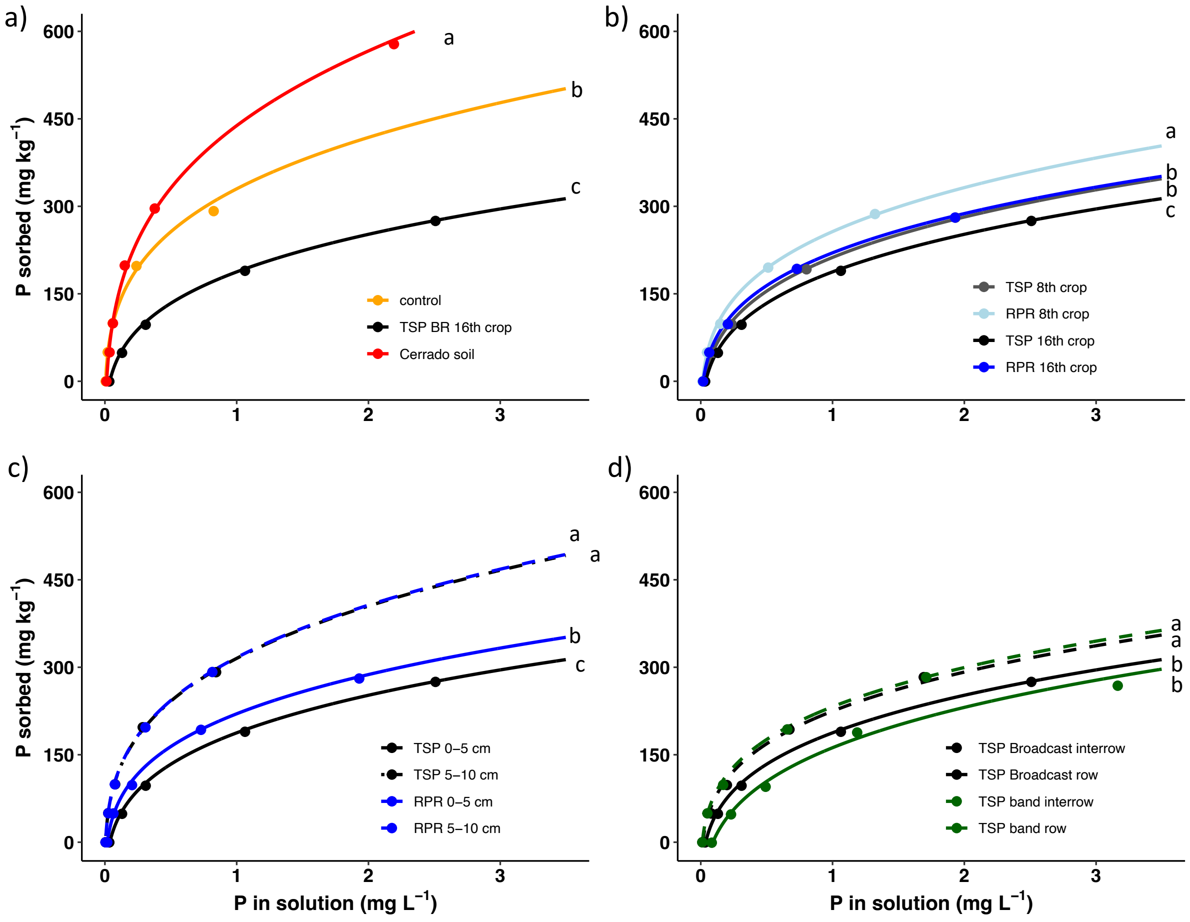

Figure 1: Sorption curves of natural vegetation Cerrado soil compared to P fertilized and unfertilized soils in the 0-5 cm layer (a); of two P sources and sampling occasions in BR treatments sampled at the crop row position in the 0-5 cm layer (b); of different P sources and soil layers under BR application sampled after the 16th crop at the crop row position (c); and of different P fertilizer application methods and sampling positions in soil samples taken from

TSP fertilized 0-5 cm soils after the 16th crop (d). The continuous curve in black is the same over all plots and represents soil from the TSP broadcast treatment sampled at the crop row in the 0-5 cm layer after the 16th crop. Lowercase letters compare sorption curves models according to the model identity test ($P<0.05$) (Regazzi and Silva, 2010).

In order to better illustrate the effects of a series of factors evaluated in the experiment (e.g, P source, application method, sampling position, soil layer), sorption capacity indexes were calculated for all specific combinations of these factors (all soils), but presented according to the different levels of the factors of interest considering the means of the other factors (Table 2). For example, the effects of application method were analyzed considering the two different sampling positions, on the average of the two soil layers, evaluation occasions and P sources. That way, broadcast treatments presented, on average, a low effect of sampling location, while band application treatment soils showed a 12.7% higher sorption index in the interrows of the crop lines (Table 2). Both application methods presented an average sorption index of 108 L kg^{-1} considering all other factors means.

Table 2: Adsorption indexes according to different factors (P application methods and sources), soil layers, sampling positions and soil references evaluated in the experiment.

Application method	**Sampling position**	**Adsorption index (L kg^{-1})**	**n=8**
broadcast	interrow	108.7	Soil layers (2), sampling occasions (2) and P source (2) means
broadcast	row	107.3	
band	interrow	114.7	
band	row	101.8	

Soil layer (cm)	**P source**	**Adsorption index (L kg^{-1})**	**n=8**
0-5	TSP	91.7	Sampling positions (2), sampling occasions (2) and application methods (2) means
0-5	RPR	92.3	
5-10	TSP	124.5	
5-10	RPR	127.4	

Reference soils	**Adsorption index (L kg^{-1})**	**n**
Unfertilized control	139.9	n=8 *
Cerrado soil	188.9	n=4 **

*sampling occasions (2), positions (2) and soil layers (2) means

**sampling occasions (2) and soil layers means (2)

The effects of P source, on the average of all samples evaluated, was small compared to the effects of soil layers on the sorption index (Table 2). The soil depth commonly used for banded P applications (5-10 cm) presented a sorption index capacity 37% greater than that found on the 0-5 cm layer. In relation to P source, although average sorption indexes were similar when comparing both alternatives, it must be taken into account that residual fertilizer P stocks in soils under RPR were on average 48% higher than in treatments fertilized with TSP. As a reference, unfertilized control showed a sorption index of 139.9 L kg^{-1}, while soil under the natural vegetation of the Cerrado showed an adsorption index of 188.9 L kg^{-1} (Table 2).

Although sorption indexes were not particularly sensitive to residual fertilizer P stocks in soils, especially according to the P source factor as commented above, this index was significantly and negatively correlated with total P contents in the soil as determined by acid digestion (Figure 2). Increasing total P contents quickly reduced P sorption in low total P soils, with diminishing effects with the increase in total P. Mehlich-1 P contents, represented by the size of the point observations, generally increased in accordance with total P, while Bray-1 P did not follow a clearly defined pattern. The amount of additional P required to reduce P sorption from 140 L kg^{-1}, a value similar to that found in the unfertilized control, to 100 L kg^{-1}, a value found in high yielding fertilized treatments, was estimated in 191 mg P kg^{-1} soil, or 191 kg P ha^{-1} in the 0-10 cm soil layer, considering a bulk soil density of 1.0 kg dm^{-3}.

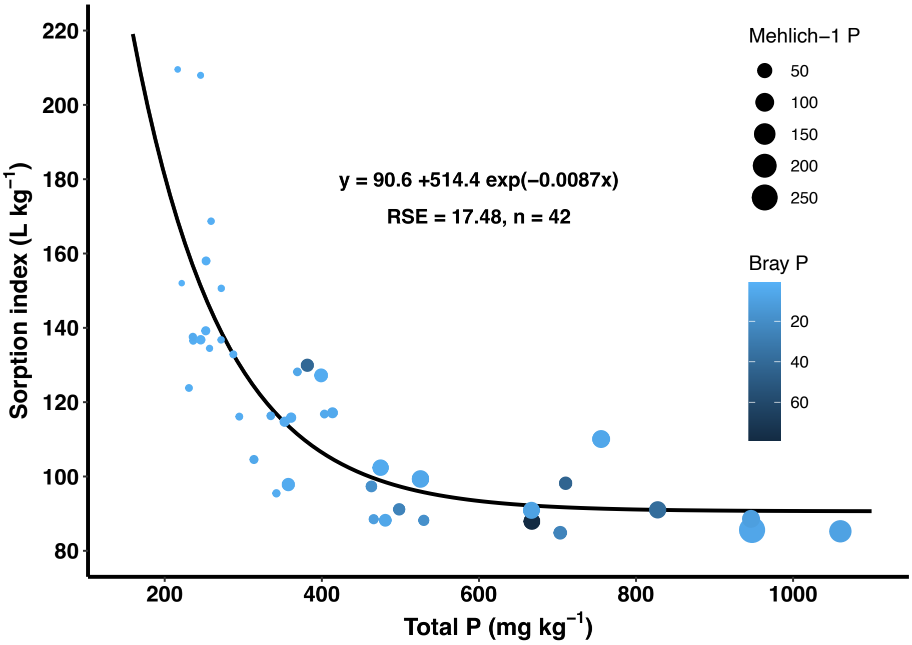

Figure 2: Sorption index (L kg^{-1}) as a function of total P contents in soil samples taken from the 0-5 cm and 5-10 cm layers. Circles size represent labile Mehlich-1 P contents (mg kg^{-1}) and circles colors indicate Bray-1 P (mg kg^{-1}) contents of the samples according to the legends. All model coefficients were significant in the F test (P<0.05). RSE: standard error of the residuals.

Corrective fertilization with P showed significant effects on crop yields even 16 years after application (Table 3). That was especially so for corrective fertilization with RPR, while when TSP was used in this initial application, corn yields were not significantly improved in relation to treatments exclusively under annual maintenance P fertilization. Under all P correction levels, maintenance P source did not affect yields. Yields in controls without maintenance P were severely compromised, though. Foliar P contents in this crop only showed significant differences when comparing treatments that received maintenance P applications with the controls, with reduced contents in these (Table 3). Although non statistically significant, foliar P under corrective fertilization plots generally presented higher nutrient concentrations, especially in the RPR corrective fertilization control.

The calculated residual fertilizer P stocks were able to reflect the initial corrective P fertilization strategies that were applied 16 crops before, similarly to what was observed with crop yields, i.e, increased stocks under TSP and RPR application in comparison to the control level of the P correction factor (Table 3). Phosphorus stocks were highest with RPR maintenance, followed by the TSP+RPR mix, TSP and the control. Remaining P in solution after mixing soil with a 60 mg P L^{-1} solution was especially low in the control treatment with no P applications, and significantly higher with RPR residual corrective P in the control level of maintenance P (Table 3).

Labile P contents evaluated by the Mehlich-1 procedure were mainly influenced by maintenance P source, but also by corrective fertilization, with the highest values in both cases with the use of RPR. Bray P was not sensitive to corrective fertilization, however, when evaluating the maintenance factor, values were highest with TSP. The TSP and RPR mix in equal P doses generally presented an intermediate behavior between the application of each source individually, for all variables evaluated (Table 3).

Figure 3 represents the relative contributions of crop response and soil attributes in a principal component analysis considering samples taken at the last experimental crop (16^{th}), involving all annual maintenance fertilized treatments (total of 18). The variable that was best linked to crop yield was foliar P, while both were inversely correlated with Mehlich-1 and residual P stocks. Band application treatments can be more predominantly found on the right side quadrants of the plot, better linked with labile P contents, residual and total inorganic P and total P. Broadcast application treatments, on the other hand, were found related to crop yields and foliar P contents.

Table 3: The effects of initial soil P correction and maintenance P fertilizer on yields and foliar P of the last crop cultivated in the experiment (corn, 16th crop); on the estimated fertilizer residual P present in the soil after the last crop harvest, according to the input – output P balance; and the soil attributes remaining P, Mehlich-1 P and Bray P after the last crop. Capital letters in the same row compare P correction strategies in a given P maintenance condition while lowercase letters in the same column compare P maintenance strategies in a given P correction strategy, according to Tukey's test (*P*<0.05). Values represent the means of application methods for maintenance fertilization treatments (n=6), while control treatments represent mean field replicate values (n=3).

	P correction						**P correction**					
P maintenance	**Control**		**TSP**		**RPR**		**Control**		**TSP**		**RPR**	
	Yield (kg ha^{-1})*						**Foliar P (mg kg^{-1})***					
Control	52.5	Bb	307.8	ABb	616.4	Ab	1.01	Ab	1.02	Ab	1.16	Ab
TSP	13,361.8	Ba	13,484.6	ABa	13,878.6	Aa	2.81	Aa	2.85	Aa	2.91	Aa
RPR	12,788.6	Ba	13,505.3	ABa	13,260.0	Aa	2.51	Aa	2.84	Aa	2.66	Aa
TSP+RPR	13,261.8	Ba	13,124.9	ABa	13,782.9	Aa	2.73	Aa	2.79	Aa	2.86	Aa
	Residual P (kg ha^{-1})*						**P rem (mg L^{-1})**					
Control	-8.1	Bd	27.7	Ad	19.3	Ad	21.6	Bb	23.2	ABb	24.9	Ab
TSP	186.8	Bc	251.2	Ac	247.1	Ac	25.7	Aa	27.4	Aa	25.9	Aab
RPR	276.8	Ba	300.8	Aa	301.1	Aa	27.4	Aa	27.6	Aa	27.5	Aa
TSP+RPR	226.9	Bb	270.0	Ab	283.6	Ab	27.3	Aa	27.6	Aa	27.4	Aab
	Mehlich-1 P (mg kg^{-1})*						**Bray P (mg kg^{-1})***					
Control	1.1	Bd	1.1	ABd	1.2	Ad	2.0	Ac	2.2	Ac	2.2	Ac
TSP	6.1	Bc	6.9	ABc	7.4	Ac	7.5	Aa	9.1	Aa	9.3	Aa
RPR	14.8	Ba	14.8	ABa	16.4	Aa	5.1	Ab	5.0	Ab	5.0	Ab
TSP+RPR	9.0	Bb	8.5	ABb	10.7	Ab	5.3	Ab	5.8	Ab	6.1	Ab

*only main factors effects were significant, i.e, the interaction was not significant

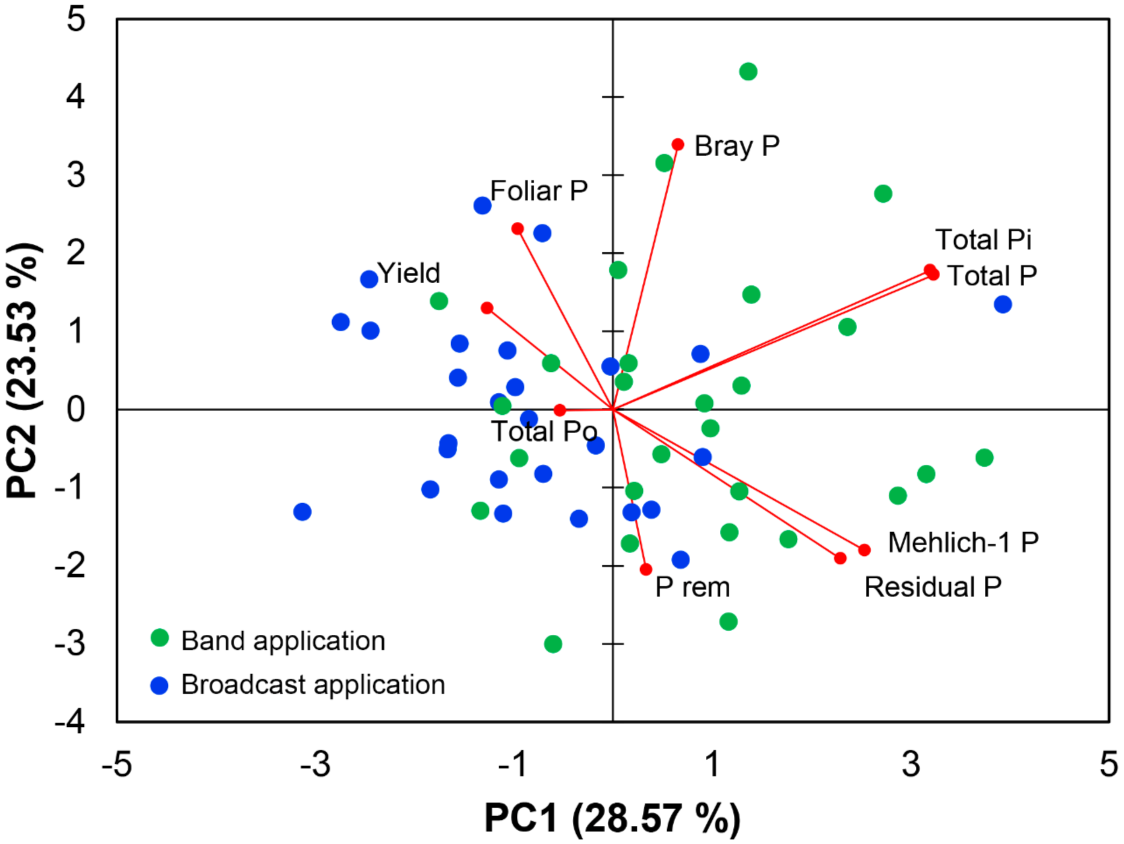

Figure 3: Principal components analysis of the variables yield and foliar P of the last (corn) crop, and soil attributes after that crop including: remaining P (P rem), Mehlich-1 P, Bray P, calculated residual P stock (residual P), total inorganic P (Pi), total organic P (Po) and total P (Pi+Po). Data from the 3 field replicates of the 18 fertilized treatments were considered, totaling n=54.

6.5 DISCUSSION

The great differences in P sorption capacity between natural vegetation Cerrado soil and the unfertilized control (Figure 1a) may be explained by the effects of liming on soil pH, as a result of applications performed before the first crop and occasionally in order to amend soil acidity. Although sorption is generally increased when soil pH is lowered (considering the scale frame generally found in soils), desorption also increases under low pH conditions (Barrow, 2017; Barrow et al., 2020a, 2021), what is consistent with the high *q* coefficients of the Freundlich equations of the Cerrado soils evaluated (data not shown). The *q* coefficient represents the amount of P that could theoretically be desorbed from the soil if solution concentration could be maintained at zero. The effects of P fertilization are also quite significant in terms of reducing P sorption capacity (Figure 1a), due to the negative charge conveyed to the interior of soil particles by diffusion of previously applied phosphate (Barrow, 2015, 2021), reducing the ability to sorb newly applied P from the P solutions reacted with the soil samples.

The long-term effects of P fertilizer management on P sorption capacity have not yet, to our knowledge, been analyzed elsewhere. It could be expected, though, that samples taken from soils with known high contents of total and labile P would present reduced sorption capacity due to the diminished affinity for P when compared to the natural or unfertilized soils, but the magnitude of that effects at field conditions was unknown. Indeed, P accumulation provoked by a positive P balance reduced P sorption capacity after the last 8 crops of the experiment (Figure 1b), with either P source. Samples taken at the crop row also presented reduced sorption capacity (Figure 1d), with especially low sorption indexes in samples taken at the crop row in band application treatments, which can be explained by the higher concentration of fertilizer P at that zone (Oliveira et al., 2022).

Although sorption index values for both P application methods were equal considering both sampling positions means (Table 2), the lowest value found in the interrows when P was broadcast may be substantially beneficial for crop P nutrition once the interrows comprise a larger area of soil at the field scale when compared to the region of influence of the rows in band applications (Oliveira et al., 2022). This could be expected, once successive P applications at the soil surface gradually saturate P sorption sites, leaving more labile P available for crop absorption (Oliveira et al., 2020a). The effects of no-tillage and surface application of phosphate fertilizers on increased contents of labile P extracted by a variety of methods in surface layers are well known (Fernández and Schaefer, 2012; Hansel et al., 2017; Nunes et al., 2020). However, how may that contribute to the efficiency of subsequent applications of phosphate fertilizer was still to be better understood, and can be further investigated within shallower soil layers than the 0-5 cm layer investigated in the current study.

The slightly higher sorption capacities of P under RPR fertilized treatments (Figure 1c; Table 2) is especially interesting when considering that these treatments presented significantly higher residual fertilizer P stocks in soil (Table 3). This fact is probably explained by the fact that residual P in RPR treatments was predominantly found in soil as unreacted, not yet solubilized fertilizer particles. This hypothesis is supported by the increased Mehlich-1 P contents in RPR treatments, once the acidic extraction solution solubilized these unreacted fertilizer granules, overestimating P contents (Menon and Chien, 1995; Schlindwein et al., 2011). Undissolved phosphate is not able to penetrate into the adsorbing soil colloids, what would cause a reduction in the P drain character of the soil (Kurihara et al., 2016; Barrow et al., 2021). Another consequence of the low phosphate release rate from RPR was observed as the long lasting positive effects of the initial P correction with this source on crop yields (Table 3). Analyzing soils from the same region as ours, Smyth and Sanchez (1982) noticed that soils that presented the largest amounts of clay and F_2O_3, and not necessarily the most acidic ones, were those where phosphate rocks solubilization was intensified. This was explained by the high sorption capacities of these soils, where the maintenance of low labile P levels promoted by the sink effect of the solid phase for P is a driving force for phosphate rock dissolution. Therefore, it can be implied that large residual amounts of RPR, as was the case in the maintenance fertilized treatments, limit the dissolution of each extra unit of phosphate rock fertilizer that is applied (Khasawneh and Doll, 1979), explaining the indications of the presence of unaltered RPR particles in these treatments despite the naturally highly adsorbing soil.

Despite the distinct dynamics of the P fertilizers studied in the soil, a significant negative correlation between total P and sorption index was observed. Unlike conclusions drawn from other studies that considered the sorption properties of Oxisols for P (Riskin et al., 2013; Roy et al., 2017), we observed that not much of this nutrient is required to reduce sorption capacity to levels able to sustain high yields (Figure 2). Although most Oxisols rich in oxyhydroxides of iron and aluminium can adsorb more than 1,000 mg P kg^{-1} soil (Roy et al., 2017; Gatiboni et al., 2020), a small fraction of that is able to reduce sorption capacity to levels capable of sustaining high yields. Nonetheless, it is widely believed that most of P that is added to Oxisols become associated to forms said as “unavailable” or “occluded” (Rodrigues et al., 2016). Although it is true that a “P tax” (Roy et al., 2016), i.e, a corrective P fertilization (Kurihara et al., 2016; Oliveira et al., 2020b; Rein et al., 2021), must be paid to soils in order to start crop cultivation in low P Oxisols, the residual effects of these initial applications are long-lasting (Yost et al., 1981; Oliveira et al., 2019) and the efficiency of subsequent applications, increased (Barrow and Debnath, 2014; Barrow, 2015). The actual amount of P estimated to reduce sorption to high yielding levels in our study was in accordance with P rates recommended for the region (Sousa et al., 2004; 2016).

The remaining P method (P rem), a simplified, single-point measure of P sorption capacity, was unresponsive to soil P status under different maintenance fertilization strategies (Table 3), but was able to detect the effects of corrective fertilization in control treatments without annual P inputs, even after 16 crop harvests and small amounts of residual fertilizer P (Table 3). This is consistent with the observations of Barrow (1978), who state that the evaluation of phosphate adsorbed (or left in solution, conversely) at a single given concentration is not a good measure of the P sorption capacity of a soil if a large amount of phosphate is already previously adsorbed.

The multivariate analysis of all fertilized treatments and all soil and plant variables together revealed a close relationship between yield and foliar P (Figure 3), what could be expected once P nutrition was the main object of study, and the driver of yield in the experiment and in the highly weathered soils in the region (Nunes et al., 2021); the amount of P that crops could actually absorb was therefore critical for plant development. The opposite behavior of residual P in relation to yield is in accordance with reduced P offtake by crops in lower-yielding conditions, while Mehlich-1 P contents were related with the high residual stocks observed in treatments with RPR maintenance. Bray P and P rem could not be considered good predictors of labile P contents in soil; in the first case due to the low affinity of extractant solution to calcium bound phosphate present in RPR (Oliveira et al., 2019), and in the latter due to the low sensitivity of the method in treatments with maintenance P fertilization (Table 3). The predominance of broadcast fertilization on the left quadrants of the PCA figure (Figure 3) is related to improved yields (Oliveira et al., 2020b) and P nutrition (Oliveira et al., 2022) with this application method, and also in line with reduced sorption (Figure 1; Table 2) and therefore probably better P use efficiency of new P fertilizer inputs to a low sorption capacity surface soil layer.

6.6 CONCLUSIONS

Long-term fertilizer management influenced P adsorption capacity according to phosphate source, application location and P content in the soil. Sorption capacity was negatively related to the amount of P previously placed at a given soil location. The water-soluble source TSP was able to decrease the retention of new additions of P to soil more effectively, probably due to older and inner adsorbed phosphate in soil clays reducing the electric potential of the surfaces and its affinity for P. In its turn, RPR fertilizer particles probably presented a longer residence time in soil, what prevented phosphate from this fertilizer being swiftly adsorbed by the soil, promoting a longer residual effect and possibly almost direct crop absorption of the slowly solubilizing phosphate. The positive effects of the application of corrective fertilization with RPR to a very low soil P status soil could still be observed even 16 years later. On the other hand, P rem, a kind of single-point measure of P sorption by soils, was not sensitive to different conditions of continuously fertilized soils. The variable more closely related to crop yields was foliar P, which represents the amount of P that is actually taken up by the crop, according to the real availability of this nutrient in the soil. Application method was the experimental factor that was best separated in the PCA, with broadcast fertilization linked with crop yields and foliar P contents, while band application was found associated with high levels of different P fractions in soils, what is probably related to slightly lower yields under this application method. The application of phosphate fertilizer to highly P adsorbing soils was found to greatly benefit crop yields for a long period, even with relatively low P doses.

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